

Review

# Reviewing Advanced Treatment of Hydrocarbon-Contaminated Oilfield-Produced Water with Recovery of Lithium

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**Abstract:** The global demand for lithium, which is indispensable for electric cars and electrical devices, has increased. Lithium recovery from oilfield-produced water is necessary to meet the growing need for lithium-ion batteries, protect the environment, optimize resource utilization, and cut costs to ensure a successful energy transition. It is useful for keeping water supplies in good condition, adhering to legal requirements, and making the most of technological advances. Oil and gas companies might see an increase in revenue gained through the lithium extraction from generated water due to the recouping of energy costs. Therefore, this review focuses on contamination and treatment strategies for the oilfield-produced water. It includes a discussion of the global lithium trade, a financial analysis of lithium extraction, and a comparison of the various methods currently in use for lithium extraction. It was evaluated that economic considerations should be given priority when selecting environmentally friendly methods for lithium recovery from oilfield-produced water, and hybrid methods, such as adsorption–precipitation systems, may show promising results in this regard. Lastly, future prospects for the lithium industry were also discussed.

**Keywords:** global demand; lithium; oilfield-produced water; resource utilization; technological advances

## 1. Introduction

Lithium, a metal with a high electrochemical activity, is essential for energy storage, electric mobility, and cordless gadgets, and it has helped advance these fields [1]. Oilfields, particularly in the Middle East, extract oil and gas for various uses, including automotive fuel. However, this process generates wastewater with toxic substances, which threatens

ecosystems and food webs. Treatment of oilfield-produced water is crucial for ecosystem survival. Lithium in wastewater can cause health issues like skin disorders, heart and kidney problems, and contaminated drinking water [2]. Lithium pollution poses health and ecosystem risks. Measures are taken to raise the purity of wastewater, recover lithium, and improve the effectiveness of wastewater treatment to eliminate lithium compounds from water generated by oilfields.

One major factor propelling the growth of the lithium industry is the exponential increase in demand for lithium-ion batteries. The USGS estimates that global lithium output will reach an astounding 100,000 tons in 2021, up substantially from 2016's 82,500 tons [3]. Since this boost in production became apparent, the price of lithium has been on the rise. Lithium-ion batteries, in particular, are seeing tremendous growth, necessitating strategic measures to ensure a steady supply of lithium and the continued advancement of battery technology. The correlation between increasing lithium output, its subsequent price dynamics, and increasing demand within the lithium-ion battery industry exemplifies the complicated interplay between market demand, raw material availability, and technological innovation. This scenario emphasizes the critical need for a balanced and sustainable strategy for raw material extraction, battery production, and overall resource management in order to meet the expanding demands of energy storage and electric cars while still being environmentally responsible. Although Australia and Chile are the primary sources of raw lithium ore, China is the world's leading processor of lithium compounds such as lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) and lithium hydroxide monohydrate. Large quantities of enriched brines and igneous-rock mineral deposits are held by each of these countries. Concerns about the existing supply chain structure have prompted efforts to declare lithium an essential mineral. This categorization includes usage limits to protect national security, economic significance, and long-term energy self-sufficiency [4].

Since 2015, the quantity of lithium in storage has skyrocketed from roughly 39 million tons [5] to 86 million tons in 2020 [6], 89 million tons in 2022 [3], and 98 million tons in 2023 [7]. This expansion is due to increasing exploration efforts and the discovery of new resources. Both raw materials with high economic feasibility for production and those with low economic viability are included here. For instance, it is estimated that there are 52 million tons of elemental lithium reserves in the lithium triangle, which includes parts of Argentina, Bolivia, and northern Chile. Canada, Australia, and the USA all possess significant reserves of elemental lithium: 12 million tons, 7.9 million tons, and 2.9 million tons, respectively [7]. The geographic distribution of the world's lithium reserves is shown in Figure 1.

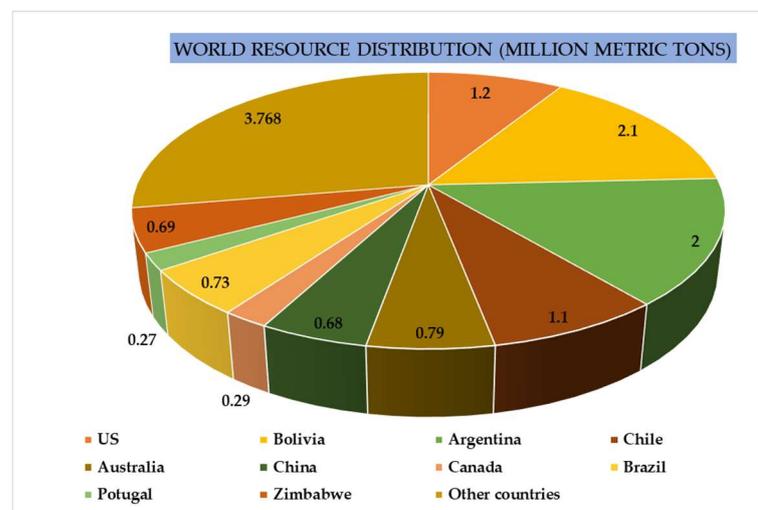


Figure 1. Country-wise Geographical distribution of Global Lithium Resources [7].

Lithium is, with a few notable exceptions, ubiquitous throughout the Earth's continental crust. However, insufficient lithium has been extracted due to a lack of technically or financially viable extraction technology. Despite its vast use, there are challenges associated with its extraction due to its geological complexity and the need for ecologically benign procedures. Technology has simplified the process, but environmental and financial factors must be considered. Maintaining this equilibrium is necessary for the responsible use of this resource [8]. Only two companies provide the majority of the world's lithium requirements. Lithium may be found in spodumene, a mineral that can be mined from ore deposits. Because of its importance, reliability, and low cost, this mineral is the best bet for meeting the rising demand for lithium [9]. Lithium is also found in continental brines in the Salars of South America and the Qinghai Tibet Plateau in China, which together make up the second largest source of lithium in the world [10]. Differentiating methods might lead to different total resource levels reported by different authorities. It has been speculated that brine deposits might contain far more lithium than all the mining ore resources in the world put together [11]. Brine deposits account for around 65% of global lithium reserves, with other mineral occurrences accounting for 35% [12]. Lithium may be reliably sourced from brine sources or mined from ore. However, turning these resources into products requires the creation of reliable extraction methods, adequate money and investment opportunities, and the maintenance of a sound regulatory framework. Some areas with abundant lithium reserves are now debating whether or not to begin mining due to exploratory or regulatory limitations. It is best shown by comparing Argentina and Chile, two countries that have highly similar climates and natural resources. One such country is Argentina, which has an annual output of 9200 tons and 19 million tons of lithium resources [3]. Figure 2 displays the worldwide lithium production reserves in 2020 and the lithium output by the nation in 2022. It can be seen in Figure 2a that the US made a significant discovery of lithium ore. In contrast, Figure 2b represents the share of other countries in the years 2020 and 2022, respectively.

Lithium recovery from brine sources employs diverse technologies, ranging from conventional methods to advanced breakthroughs, reflecting its importance in various sectors and applications. Lithium is extracted from brines through solvent extraction, precipitation, ion exchange, and membrane separation. These processes involve specialized chemical solvents, the measured addition of chemicals, the selective capture of ions using resin beads, and the selective filtering of ions like lithium. Lithium recovery technology is evolving, focusing on practical financial and ecological aspects through adsorption procedures, direct extraction from geothermal brines, and innovative techniques from wastewater and oilfield-produced water. The growing demand for lithium and the need for sustainable recovery techniques underscore its importance in various industries, particularly energy storage and electric car manufacturing. Table 1 presents a recent overview of the numerous technologies applied for lithium recovery. Among the researched approaches, solvent extraction stands out as the most promising method for extracting lithium from brine sources. It is essential to note that, as of now, no one technique has achieved a 100% lithium recovery rate, emphasizing the ongoing challenges in this sector. Interestingly, the oil and gas industry has also experimented with solvent extraction to recover lithium, largely at the laboratory scale. Nonetheless, the search for more effective and scalable solutions remains a top priority. It is necessary to close the gap between present lithium extraction technologies and industrial-scale extraction.

**Table 1.** Comparison of Lithium Recovery Technologies.

Year	Source	Technology	Performance	Ref.
2020	Industrially cleansed brine	Precipitation	>85.00% Li recovery	[13]
2020	Simulated shale gas produced water	Solvent extraction	83.00% Li recovery	[14]
2022	Shale gas produced water	Adsorption	13.27 mg/g adsorption capacity	[15]
2023	Salt Lake brine	Adsorption	11.90 mg/g adsorption capacity	[16]
2023	Lithium carbonate solution	Solvent extraction	>80.00% Li recovery	[17]
2023	Geothermal brine	Nanofiltration	Salt rejection: >99% Flux = 14–19 L/m <sup>2</sup> h Li concentration: >1100 ppm	[18]

Lithium is a vital component in lithium-ion batteries, which are used in energy storage applications. Lithium extraction is crucial for the transition to sustainable energy, the expansion of electric cars, technical improvements, employment creation, and resource efficiency. As the world pursues more sustainable and ecologically friendly energy and technological solutions, the ethical extraction and distribution of lithium are essential to achieving these objectives. Lithium extraction from brine sources utilizes numerous technologies, ranging from conventional procedures to cutting-edge advances, as a result of its significance in a variety of industries and applications. Reducing carbon emissions from the oil and gas industry is a crucial step in the transition to renewable energy. Lithium recovery from oilfield-produced water is essential due to increased lithium demand and environmental concerns over the usage of lithium-based batteries. The main purpose of the review is to explore technologies for recovering lithium from oil-field-produced water and present future directions for maximum recovery.

Oilfield brines could serve as an alternate source of lithium recovery. Produced water (PW) is the wastewater generated from the pumped water from the ocean floor for oil and gas recovery on offshore platforms, representing a significant byproduct of the oil and gas industry. Chemical and inorganic compounds with varying solubility are found in PW. Offshore oil and gas production significantly impacts marine ecology, necessitating the removal of oil and the treatment of PW for organic contaminants, particularly hydrocarbons. The oil industry and environmental groups face challenges in reducing freshwater requirements for hydraulic fracturing, for example, in North Dakota (US), which currently requires 75–84 million m<sup>3</sup> per year [19]. Moreover, 5% to 15% of total drilling expenditures can be attributed to water management, including PW treatment [20]. Produced water recycling reduces waste and freshwater use, but it poses environmental threats due to its presence of organic and inorganic minerals [21]. The cost of processing and recycling PW might be offset by the extraction of important inorganic elements, such as lithium. The lithium discovered in PW has the potential to meet the expanding demand for electric cars and energy storage systems [1]. The increasing demand for scarce resources (lithium) is prompting exploration of alternative sources, like saltwater and generated water, necessitating continuous technological advancements for extraction. Several reviews have investigated methods for cleaning up oil and gas waste [22–24], but very few have looked at how to safely recover lithium from the generated water [25,26]. Therefore, the objectives of the current review are: (1) to investigate current treatment options for extracting lithium from oilfield PW, (2) to review the international lithium market, and (3) to focus on the hybrid treatment approach for extracting lithium from oilfield PW.

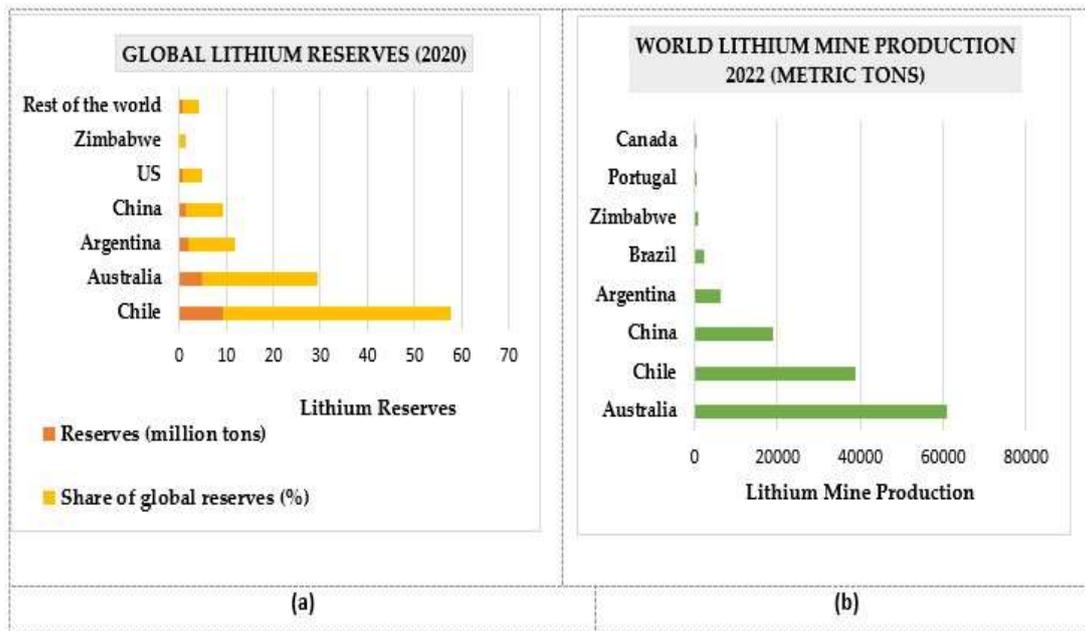


Figure 2. (a) Global Lithium Production Reserves 2020 [27]; (b) Country wise Lithium Production 2022 [28].

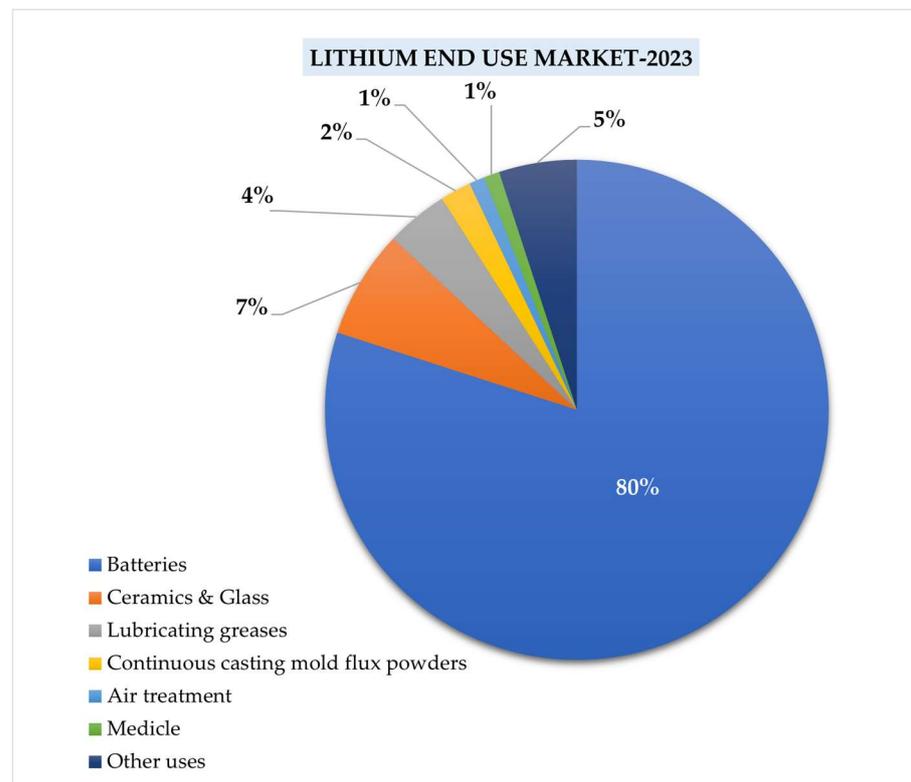
## 2. The Lithium Market

### 2.1. Market Overview

Four mineral operations in Australia primarily contributed to world lithium production, with other operations in Argentina, Chile, and China contributing both brine and minerals. Four mining operations in Chile were also involved in the creation of lithium. Several smaller-scale initiatives in nations including Zimbabwe, Brazil, China, Portugal, and the United States aided lithium production. The global COVID-19 epidemic in 2020 halted capacity expansion ambitions at production sites throughout the globe, but with the resurgence in demand and rise in lithium prices, these efforts have resumed [3]. Reserves are the economically viable component of a resource, such as lithium [29]. It was estimated that 2021 lithium reserves would reach 22 Mt, and 100,000 Mt would be produced [3].

In addition to lithium metal, lithium compounds derived from brine sources and lithium minerals mined from hard rock contribute to the lithium market [30]. Lithium, discovered in 1817 by Swedish scientist Johan Arfvedson, has shown promise in various fields ever since. Lithium's large specific heat capacity and remarkable redox potential set it apart from other solid elements [12]. In contrast to its use in batteries, ceramics, lubricants, polymers, medicines, and glass, lithium is also found in a wide variety of other items [31–33]. The market is broken down into several applications in Figure 3. The battery industry accounts for 80% of the lithium end-use sector, whereas glass and ceramics account for just 7%.

Potential lithium alternatives include many different compounds. While potassium and sodium are used as fluxes in the production of glass and ceramics, lithium may be used in place of these elements in battery applications [30]. Lithium is the best technology material because of its high power density and historically low cost. It is ideal for meeting energy storage needs, especially in the creation of hybrid and electric cars [34].



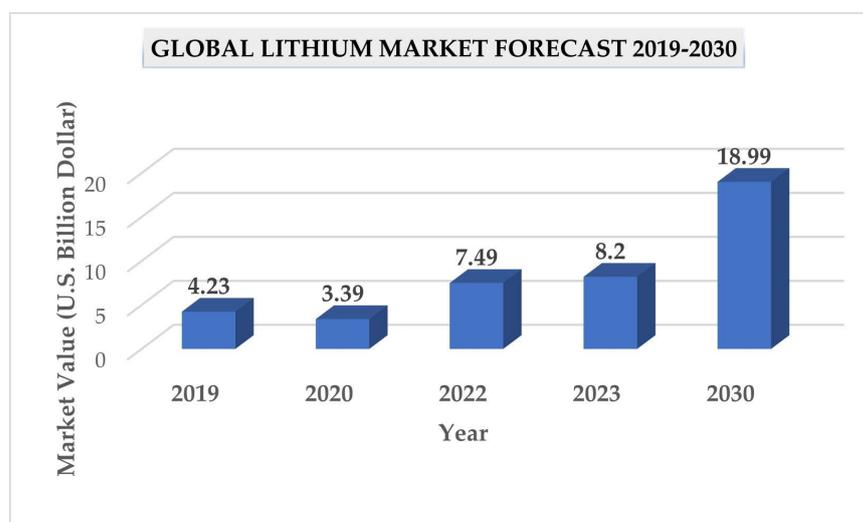
**Figure 3.** Commercial Lithium Use Around the World in 2023 [7].

#### 2.1.1. Price of Lithium

Lithium prices escalated by 485.8% in the third quarter of 2021, with high-quality battery-safe lithium carbonate (Ex Works, China) reaching USD 41,925 per ton. There was a yearly increase of 17.4% in the cash expenses of extracting lithium from hard-rock ores and brines, bringing the total to USD 2529 per ton of lithium carbonate equivalent (LCE). Rising costs associated with production and transport were cited as the primary driver of these price increases [35].

The fourth quarter of 2021 spike in the Chinese domestic market was the primary driver of the lithium price increase that persisted into 2022 [36]. Sales of electric vehicles (EVs) worldwide hit 4.2 million units in 2021, up 198% from 2019 and 108% from 2020, making EVs the principal trigger for the increased demand for lithium [37]. Even though the Russia–Ukraine war caused first-quarter market swings, it had a minor effect on the lithium supply chain [36].

Benchmark Mineral Intelligence data showed that, despite relatively constant pricing, lithium prices increased by almost 123% during the second quarter of 2022. Increased demand from the EV industry was the primary factor in 2017's lithium price increase. Warmer temperatures in the latter part of the second quarter boosted seasonal evaporation rates, increasing the supply of materials from Chinese domestic brine sources. The unexpected drop in the EV sector demand occurred in April due to COVID-19 lockdowns that affected numerous car production businesses, mainly in Shanghai [36]. As COVID-19 limits were relaxed in the third quarter, lithium prices in China rose sharply, reaching a new high by September due to increased demand ahead of the Golden Week vacation [36]. By 2030, the market value of lithium is expected to reach almost USD 19 billion because lithium is increasingly used in products like lithium-ion batteries. The global market value of lithium is anticipated to reach USD 8.2 billion by the end of 2023, as shown in Figure 4.



**Figure 4.** Global Lithium Market Forecast [38].

### 2.1.2. Demand and Supply

The demand for lithium is estimated to rise three times between 2020 and 2025, and sevenfold by 2031 as the world moves away from fossil fuels. The increased use of lithium-ion batteries in stationary power sources, such as energy storage systems, and the trend toward electric vehicles are two key drivers of this expansion [39]. This need may be addressed by developing more efficient extraction methods and identifying additional lithium deposits [40]. Benchmark Mineral Intelligence (London, UK) revised its prediction of a deficit in lithium supply of 60,000 metric tons of LCE in 2022 to an estimated deficiency of 80,000 metric tons of LCE. Lithium carbonate continued to be in high demand in China, and by the latter half of 2021, there was a noticeable price gap between carbonate and hydroxide. However, many Chinese converters started switching from carbonate to hydroxide because of the large pricing discrepancy, closing the gap. The strong demand for both commodities has resulted in almost identical prices on a global scale. After a brief slump in the wake of the Shanghai lockdowns, the Chinese EV market surged in Q2 2022, setting new records for both production and sales. Sales of electric vehicles are expected to more than triple to 6.4 million units in 2022. However, Goldman Sachs' study aroused worries among investors since it indicated a probable glut in the lithium supply and predicted a significant price decrease by the end of the year. According to Benchmark Mineral Intelligence, structural lithium shortages will persist until at least 2025. Lithium demand is still driven mainly by the ever-growing electric vehicle market. The number of electric vehicles sold more than doubled from 2 million in the fourth quarter of 2020 to 6.6 million in 2021. The IEA predicts that electric vehicles will capture 13% of the market by 2025. Hydroxide costs rose as manufacturers rushed to increase output before China's EV subsidies were eliminated on 1 January 2023 [36].

### 2.1.3. Economic Analysis of Lithium Extraction

According to projections provided by the World Bank, the production of graphite, lithium, and cobalt would need to increase by more than 450% between the years 2018 and 2050 in order to meet the need for devices that store energy [41]. Royalties for lithium carbonate and hydroxide were established in the 6.8% to 40% range when the Chilean government, via CORFO, signed new contracts with Rockwood (now Albemarle, Charlotte, NC, USA) and SQM (Santiago, Chile) in 2016 and 2018. Beyond the typical "chlorides" (potassium, magnesium, sodium, and boric), these agreements included various commodities. CORFO estimates that between 2018 and 2030, the new agreements will bring in a total of USD 12 billion for Chile, with USD 10.9 billion going to taxes and royalties for the state, USD 981 million going to the Antofagasta area, and USD 352 million going to R&D.

CORFO's projection, which factors in the Albemarle contract's incremental values from 2031 through 2043, comes to almost USD 16 billion [42].

Lithium carbonate is presently priced at USD 10,000 per metric ton, and the Chilean government takes home a 40% commission on the commodity. This high cost was eclipsed in 2022, when prices hit about USD 75,000 per metric ton. The price of lithium may fall between 2023 and 2024 if all the worldwide lithium production projects come to fruition, creating enough supply to satisfy the rising demand for the metal [43]. In Table 2, Warren et al. [42] outlines the financial considerations of direct lithium extraction (DLE) from oilfield, evaporite, geothermal, and Salar brines.

**Table 2.** Techno-Economic Analysis of few Lithium Extraction Technologies.

Company	Vulcan Energy Resources	Standard Lithium	E3 Metals Corp	Pure Energy Minerals	Lake Resources
Project	Upper Rine Valley	Lanxess Smackover	Clear Water	Clayton Valley	Kachi
Country	Germany	USA	Canada	USA	Argentina
Brine Type	Geo-thermal	Evaporite	Oilfield	Evaporite	Salar
Production (mt/yr)	40,000	20,900	20,000	11,500	25,500
Production (\$/mt)	3217	4319	3656	3217	4178
Capital Expenditure (\$1000)	1,287,600	437,162	602,000	358,601	544,000
Operating Expenditure (\$1000/yr)	128,688	90,259	73,200	36,516	106,539
Technology	Adsorption	Ion Exchange	Ion Exchange	Solvent Extraction	Ion Exchange
Lithium Recovery	90%	90%	>90%	90%	83.20%

Source: Adapted from Warren, I. Techno-Economic Analysis of Lithium Extraction from Geothermal Brines; National Renewable Energy Lab (NREL, USA), 2021 [42].

### 3. Produced Water

The transition to lithium extraction from oilfield-generated water suggests a significant shift in resource utilization. Reusing oilfield water for lithium extraction is a sustainable and ethical method that optimizes resource use, reduces waste, and combats climate change. This method reduces the carbon footprint of lithium manufacturing, diversifies supply sources, and ensures reliable supply. It also contributes to the global energy transition by meeting environmental regulations and reducing liabilities associated with incorrect water disposal.

The formation water that rises to the top contains a mixture of salty water and the injected fluids. Produced water (PW) is the outcome of this mixture. A large amount of water is pumped into the reservoir so the pressure can be maintained for longer, and the amount of oil that can be recovered may be increased. During drilling and production, separating the naturally occurring hydrocarbons from the by-products, such as injection water, formation water, and other compounds, is essential. Components of the aquifer, formation water from the reservoir, water injected to enhance oil recovery, and even chemicals used in drilling and production might all be part of the created water [44]. Forecasts indicate that by 2035, the world will be producing more than 605 million barrels of generated water from oilfields, up from the current 250 million barrels per day. For obvious reasons, it is the most significant contributor to wastewater from the industry [45,46]. The properties of the aquifer determine the best way to dispose of the produced water. Notably, 70% of the generated water is released as surface water, while around 30% is disposed of in a deep well [47]. Table 3 Ghafoori et al. [48] presents the compositional attributes of the produced water.

**Table 3.** Components of Produced Water.

Concentration Range (mg/L)			
Organic Components		Minerals	
Total oil and grease	2–560	Na	0–150,000
Total organic acids	0.001–10,000	Cl	0–250,000
Salinity	5000–300,000,000	Ba	0–850
Aliphatic hydrocarbons	17–30	Sr	0–6250
Phenols (primarily C0–C5-phenols)	0.4–23	K	24–4300
Ketones	1–2	SO <sub>3</sub> <sup>2-</sup>	10
Polycyclic aromatic hydrocarbons (PAH)	0.04–3	Mg	8–6000
Total BTEX	0.73–24.1	Fe	0.1–100
Benzene	0.032–14.97	Al	310–410
Toluene	0.058–5.86	B	5–95
Ethylbenzene	0.086–0.57	Cr	0.02–1.1
Naphthalene	0.194–0.841	Li	3–50

Source: Adapted from Ghafoori et al. “New Advancements, Challenges, and Future Needs on Treatment of Oilfield Produced Water: A state-of-the-Art Review. Separation and Purification Technology”, 2022 [48].

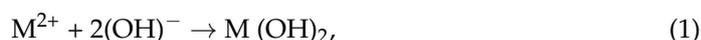
#### 4. Current Technologies for Oilfield Produced Water Management

Oilfield-produced water contains various harmful substances, and its improper disposal has significantly contributed to surface contamination, especially in water sources and soil [49,50]. Therefore, proper management is crucial for efficient environmental preservation. The inadequacy of traditional procedures for removing tiny suspended oil particles and dissolved organic matter from produced water necessitated the development of contemporary remedies to this problem. Furthermore, sludge is a known hazardous consequence of the traditional procedure [51]. Olajire et al. [52] proposed a three-stage treatment procedure, including primary, secondary, and tertiary treatment, before oilfield PW is discharged into the environment. Physical treatment of the produced water initially removes the larger particles and hydrocarbon compounds in the effluent [52,53]. After the sludge particles and the produced water have been separated by gravity separation, deoiling hydrocyclones are used to remove any remaining oil from the wastewater. Polymeric flocculants are added to the first process to help in the sedimentation and coalescence of particles before moving on to the secondary treatment step [52]. Subsequently, several methods are used in the secondary phase to extract the dissolved components. Flotation, biological treatment, membrane processes (such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis), and combinations thereof are all included here (known as a membrane bioreactor) [52]. Finally, in the tertiary treatment step, organics, turbidity, nitrogen, phosphorus, metals, and pathogens will be reduced in the generated water using oxidation and degrading processes [52,54].

#### 5. Lithium Extraction Technologies from Oilfield Brine

##### 5.1. Precipitation

Chemical precipitation is a process where a solid precipitate forms in a solution due to a chemical reaction. This precipitate, often insoluble, separates from the solution and sinks to the bottom. It is used in water treatment, analytical chemistry, and industrial processes. It is considered the most efficient technique for removing trace metals and rare earth elements from wastewater. This strategy is simple and cost-effective to apply. Adjusting the pH appropriately is a vital element of the precipitation process. Creating alkaline conditions, for instance, often results in the transformation of dissolved metals into solid metal hydroxides, which may then be separated by sedimentation or filtering [55]. The following formulation serves as a basic explanation of the hydroxide precipitation reaction [56]:



where,

$M^{2+}$  = Metal

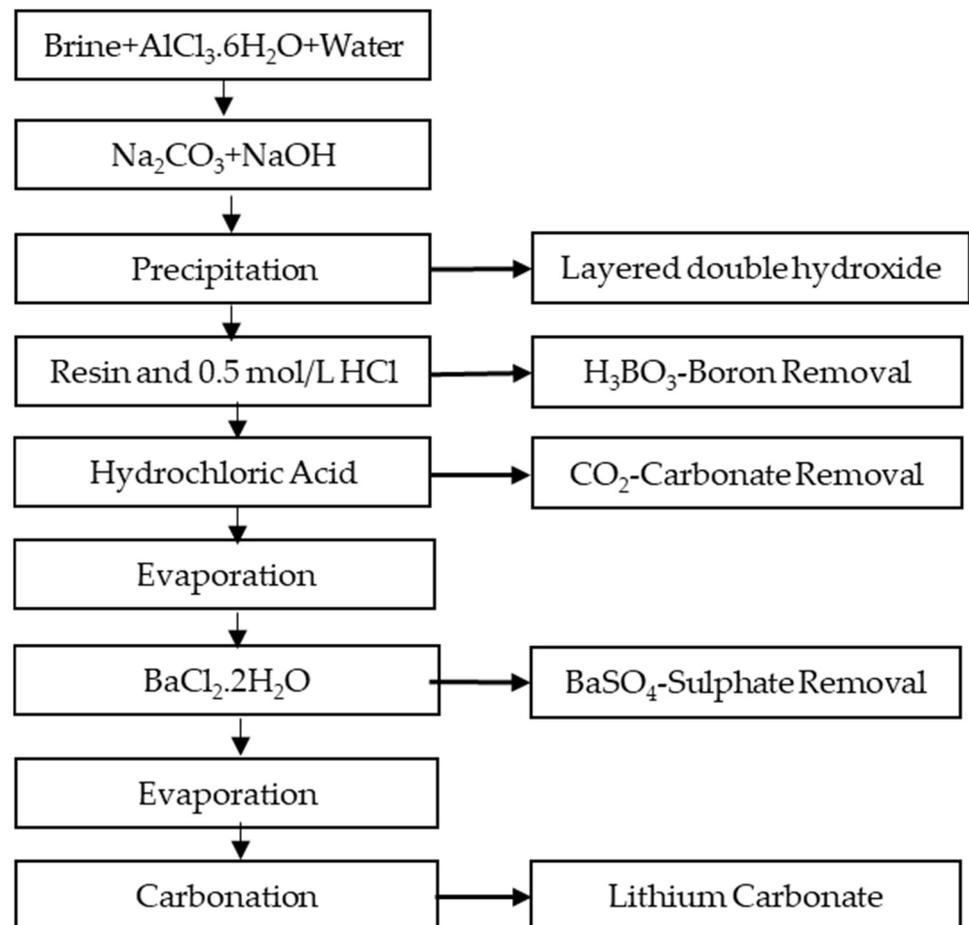
$M(OH)_2$  = Metal hydroxide in solid form.

The recycling process of lithium extraction from used lithium-ion batteries by precipitation involves disassembling old batteries, isolating the cathode material, and then using chemical precipitation to selectively recover lithium in solid form for reuse. A unique technique was developed by Yang et al. [57] to selectively precipitate metals from lithium-ion batteries. Several precipitation steps were used. At first, manganese was separated under specific conditions (molar ratio of ammonium sulphate to manganese = 3, pH = 5.5, and 80 °C for 90 min). Afterwards, nickel was selectively precipitated by dimethylglyoxime under certain conditions (molar ratio of dimethylglyoxime and nickel = 2 and 30 °C for 20 min). Cobalt was recovered by adjusting the pH to 10 as cobalt hydroxide. Lastly, lithium was precipitated by sodium carbonate at 90 °C. Surprisingly, the rates of precipitation were found to be manganese (99.5%), nickel (99.6%), cobalt (99.2%), and lithium (90%).

The precipitation technique of lithium recovery is frequently utilized because of its ease of use and scalability, particularly when working with solutions of lithium that are extremely pure and highly concentrated [58]. The extraction of lithium frequently involves the use of precipitation processes such as those using phosphate, carbonate, and aluminate. Aluminum chloride has been combined with brine from the Dead Sea in order to precipitate lithium in the forms of lithium aluminate [54–56] and lithium carbonate [59]. Co-precipitation of magnesium is the major challenge in the process of lithium precipitation; as a result, researchers have proposed alternate precipitation strategies based on the ratio of magnesium to lithium found within brine. The process known as “carbonate precipitation” is more likely to occur in brine that has low magnesium to lithium ratios (below six), since in this scenario the lithium is precipitated as lithium carbonate by infusing sodium carbonate after the magnesium has been precipitated using calcium oxide [60–62]. In order to produce lithium bicarbonate from the magnesium-deficient raw lithium carbonate found in brine reservoirs, the process of carbonation precipitation is used [63]. Carbonate and carbonation precipitation have been used to create ultra-pure lithium carbonate [64].

Natural brine sources often have a high magnesium-to-lithium ratio; therefore, “aluminate precipitation” or “Mg precipitation” procedures must be used to extract lithium. Aluminum hydroxide is produced by the precipitation of aluminate when sodium hydroxide and aluminum chloride are mixed. The produced aluminum hydroxide is then subjected to a selective precipitation process in which lithium precipitates as lithium aluminate [65]. The efficiency of lithium extraction from brine has been enhanced by the development of novel complexes and activated compounds. Li et al. [66] evaluated the effect of Al–Ca alloy and Al–Fe alloy on the precipitation of lithium by testing aluminum-based materials in a salt-lake brine. The results indicate that the Al–Ca alloy interacts well with brine and produces  $LiClAl(OH)_3 \cdot xH_2O$ , but the Al–Fe alloy reacts poorly with brine. The rate at which lithium crystallizes when brine is broken down with an Al–Ca alloy depends on the mole ratio of Al to Li, the concentration of Ca in the Al–Ca alloy, and the temperature of the reaction. The lithium precipitation rate from brine may reach 94.6% when the Al:Li ratio is 3.5:1, the Ca content is 35%, the starting  $Li^+$  concentration is 0.8 g/L, the reaction temperature is 70 °C, and the reaction duration is one hour. Liu et al. [67] on the extraction of lithium from brines with a high Mg/Li mass ratio found that aluminum-based materials were effective in achieving a 64.8% Li precipitation rate and a 0.8% Mg precipitation rate. Temperature also significantly impacted precipitation rates, with Li precipitation increasing from 18.14% at 20 °C to 65.83% at 80 °C. The precipitation rate increased from 34.8% to 62.8% between 60 and 180 min, but only slightly improved over 180 min. The researchers also found that the reaction performance of Al-based materials declines as precipitates grow at a fixed Li concentration. Moreover, Li aluminum layered double hydroxide chloride is an example of an engineered double hydroxide that can recover over 90% of lithium at a low cost and with no negative environmental effects [68]. Magnesium precipitation may also be used to lower the Mg/Li ratio and make lithium recovery easier. Under ideal reaction

conditions, ammonium oxalate and 2% sodium carbonate were shown to precipitate magnesium at a 98% efficiency rate [69]. Therefore, it is feasible to precipitate and extract 99% of Mg from brines with a higher Mg/Li ratio using integrated and multi-step procedures. Figure 5 shows that the approach proposed by Wang et al. (2018) [70] for selective recovery of Mg and Li involves several steps and molecules. After a lengthy procedure, 99.7% pure Li carbonate was obtained with a 91% yield.



**Figure 5.** A hybrid method for extraction of Li as Lithium Carbonate [70].

The co-precipitation method was developed to remove magnesium from brines rich in lithium (where the magnesium to lithium mass ratio is more than forty), such as those found in China's Taijinar Salt Lake. The procedure included a boron-lithium co-precipitation step. Sulfate precipitation occurred after the first evaporation of sodium and potassium salts inside the brine. After filtering, the solution's pH was adjusted with HCl or H<sub>2</sub>SO<sub>4</sub> to fall between two and four. Since making this change, the possibility of lithium and boron co-precipitation has increased. Using a boron wash may further separate the lithium. There was an 80–90% success rate in lithium recovery using this method [71].

Phosphate precipitation is a new technique that has the potential to replace the carbonation step in solar evaporation processes. Lithium phosphate is much more easily precipitated at ambient temperature than lithium carbonate, which has a solubility of 13.3 g/L. The solubility of lithium phosphate, on the other hand, is just 0.39 g/L. Although this method requires more steps in processing to convert Li phosphate into Li carbonate or hydroxide, it might cut down on processing time and costs [72]. Sodium phosphate salts, including di-sodium phosphate, tri-sodium phosphate, sodium pyrophosphate, and sodium tri-polyphosphate, have been utilized in various research studies [73–76]. The study conducted by Alsabbagh et al. [76] showed suitable salts for lithium-precipitating reagents,

with tri-sodium phosphate (TSP) recovering 40% of lithium in the Dead Sea evaporated end brine. It was found that the amount of precipitating reagent significantly impacted the Li extraction percentage, with 7 g yielding the best recovery. The stirring speed, ranging from 150 to 1000 rpm, significantly impacted the experiment, as indicated by an ANOVA test. The maximum yield of Li extraction was achieved at 450 revolutions per minute, and the procedure required no more than two hours of extraction rates. Temperature analysis showed 40 °C yielded a higher Li extraction percentage than 25 °C–70 °C, with over 40% recovered from the Dead Sea evaporated end brine using TSP under optimal conditions.

POSCO is currently developing programs to extract lithium from brine and recycle batteries [77]. Although phosphate precipitation still necessitates sun evaporation as a pre-concentration step, this is restricted to only targeted extraction of Li from a supersaturated brine (for example, greater than 500 mg/L) within an acceptable time frame, making the viability of this method for treating oil field effluent questionable.

Recent research on precipitation methods for brine-based lithium extraction is summarized in Table 4. Despite its antiquity, precipitation is still a popular technique for lithium extraction from brine sources because of its low cost and high efficiency. However, significant work is needed to improve energy efficiency and lessen the negative effects of chemical reagents on the environment. The Mg/Li ratios at oil and gas sites often exceed 20. The increased salinity of the generated water from these sources reduces the precipitator's selectivity for Li<sup>+</sup> ions [78]. Therefore, before using the traditional precipitation method to collect lithium from oil and gas fields, it is essential to change it by lowering both the Mg/Li ratio and salinity.

**Table 4.** Lithium extraction from brines via precipitation.

Year	Sources	Reagents	Operating Conditions	Li Recovery (%)	Ref
2018	Salt Lake brine	Aluminum based material	Temp = 90 °C, Reaction time = 3 h, Mg/Li = 0.02	78.30	[67]
2019	Simulated brine	Sodium Metasilicate Nonahydrate	Temp = 25 °C, Mg/Li = 0.022 Reaction Time = 5 min Agitation speed = 300 rpm	86.73	[79]
2020	Industrially cleansed brine	NaOH and Na <sub>2</sub> CO <sub>3</sub> solution	Temp = 60 °C Reaction time = 1 h	>85.00	[13]
2020	Refined Salt Lake brine	Na <sub>2</sub> HPO <sub>4</sub> solution	Temp = 40 °C, Reaction time = 0.5 h, Mg/Li > 40	93.20	[80]
2021	Chinese Dangxiang Co Salt Lake	Facet engineered Li <sub>3</sub> PO <sub>4</sub> Na <sub>3</sub> PO <sub>4</sub> ·12 H <sub>2</sub> O	Temp = 25 °C, Li/PO <sub>4</sub> = 3:1 Agitation speed = 450 rpm	51.62	[81]
2021	Dead Sea end brine	Tri sodium phosphate	Temp = 40 °C, Reaction time:0.5 h, Agitation speed = 450 rpm	>40.00	[76]
2022	Brine Water	Sodium Silicate	Temp = 25 °C Reaction Time = 5 min	84.00	[82]

## 5.2. Solvent Extraction

Lithium ions are selectively extracted from an aqueous solution via solvent extraction, which uses an organic solvent that contains an extractant. Following separation, the solvent is recovered together with the lithium, enabling the production of pure lithium compounds from materials like ores or battery parts. The recovery of lithium from brine by means of solvent extraction is a process that is not only efficient, but also very cost-effective and produces high yields. When using a solvent-based method to extract lithium from water, the distribution coefficient of the metal between the aqueous phase and the organic phase is often a critical consideration that must be taken into account. The extraction agent, the co-extraction agent, and the diluent are the three components that make up the solvent system. This technique allows for the dissolution of lithium chloride while preserving selectivity against ions that are not desirable [10]. Tributyl phosphate (TBP) is a powerful extractant that may be used to selectively recover lithium from magnesium-rich brines. This technique uses TBP, an uncharged organophosphorus extractant, and kerosene as the diluent. Lithium recovery is improved by using FeCl<sub>3</sub> in a co-extraction technique [83]. Li et al. [84] presented an easy and effective technique for extracting lithium from brine with a

high Mg/Li ratio at a regulated temperature.  $\text{Li}^+$  was extracted from brine containing a high magnesium-to-lithium ratio by means of liquid-liquid extraction. The extraction organic phase consisted of tributyl phosphate (TBP) and N-butylpyridinium tetrachloroferrate ( $[\text{BP}_y][\text{FeCl}_4]$ ), a temperature-responsive ionic liquid. The results revealed that  $[\text{BP}_y][\text{FeCl}_4]$  played an essential role in enhancing lithium selectivity, interacting with TBP, and aiding phase separation. At a Mg/Li ratio of 310 and an aqueous-to-organic phase ratio (A/O phase ratio) of 0.5, the  $\text{Li}^+$  extraction rate and lithium-magnesium separation coefficient ( $\beta_{\text{Li/Mg}}$ ) could reach 84.2 and 65.5%, respectively.

The TBP-NaBPh<sub>4</sub>-phenethyl isobutyrate extraction technique, combining classic extractant TBP with innovative co-extractant NaBPh<sub>4</sub>, ensures quick phase separation without creating a third phase, demonstrating cyclic stability under appropriate extraction, washing, and stripping phases. The single-stage lithium extraction efficiency was 85.73% utilizing these parameters: TBP volume proportion of 30%, phenethyl isobutyrate volume proportion of 70%, NaBPh<sub>4</sub>/ $\text{Li}^+$  molar ratio of 1.5, and phase ratio of 1. In contrast, the extraction efficiency for magnesium was only 0.44%. A remarkable washing efficiency for  $\text{Mg}^{2+}$  of 99.63% was achieved for the washing procedure using a solution of 2.0 mol/L NaCl and 0.25 mol/L LiCl with a phase ratio of 5, bringing the concentration of  $\text{Mg}^{2+}$  in the organic phase down to <3 mg/L. The washing efficiency for  $\text{K}^+$  was 90.27%, with no loss of  $\text{Li}^+$  and a  $\text{K}^+$  concentration in the organic phase of less than 1 mg/L. The method that used sodium bicarbonate instead of hydrochloric acid for lithium stripping achieved a 99.87% efficiency after five stages, demonstrating system stability and a consistent extraction efficiency of 84% for  $\text{Li}^+$  [85]. Moreover, Waengwan et al. [86] investigated the lithium-extracting efficacy of several extracting agents (n-butanol, tri octylamine (TOA), 4-methyl-2-pentanol (MIBC), bis(2-ethylhexyl) phosphate (DEHPA), and tri octyl phosphine oxide (TOPO) from synthetic battery solution. Distilled water and HCl were used to produce a 10 mg/L solution of lithium carbonate and cobalt carbonate in the synthetic battery solution, respectively. Kerosene was used as a diluent. Extraction was performed in a sanity test at 32 °C with a 1:1 aqueous-to-extractant ratio and a total extraction time of 2 h. Bis(2-ethylhexyl) phosphate (DEHPA) exhibited the most outstanding extraction efficiency of lithium ions from an aqueous solution, with 75% recovery. In this experiment, the effects of several extractants were investigated, and it was shown that the acidic extractant group provided more extraction efficiency than the solvating extractant group. Further analysis of relevant variables, including extraction time, pH of the aqueous solution, and initial concentration, was conducted. It was observed that 6 h of extraction achieve equilibrium, and a pH of 1.5 is best for extraction efficiency.

Lithium levels in Marcellus shale gas production water average 95 mg/L after 14 days of flowback [87]. The high concentration of organic compounds in the water used to produce shale gas indicates that organics significantly impact lithium recovery. Water used in Marcellus shale gas production has an average TOC concentration of 2348 mg/L [88].  $\text{Li}^+$  competes with other metal ions such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  in solvent extraction for interaction sites. Since a concentrated Li solution is required for the following extraction phase, it is critical to eliminate  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  beforehand. For instance, Lee et al. (2020) [89] examined how n-hexane, n-undecane, and n-hexadecane affect solvent extraction for lithium recovery from shale gas effluent. A two-way process was used due to the much-increased attraction between polyvalence cations and di-(2-ethylhexyl) phosphoric acid. Before attempting to extract the lithium resources, this process sought to remove multivalent cations like  $\text{Ca}^{2+}$ . Low  $\text{Li}^+$  concentration, interference from multivalent cations, and the presence of organic compounds are common issues that reduce the effectiveness of lithium recovery utilizing solvent extraction procedures [25,89]. The potential for lithium recovery from water used in shale gas production was studied using solvent extraction with a bifunctional ionic liquid [90]. The two-step procedure for lithium recovery from synthetic brine has been developed. In the first stage, divalent metals are removed from the repeated extraction cycles using DEHPA (1 mol/L) dissolved in dodecane. Step two included the use of the ionic liquid extracting agent [Aliquat-336] [DEHPA] to remove 83%

of Li in a single extraction cycle, which is better than the results of solvent extraction with conventional extracting molecules [14]. In contrast, there are limitations to using solvent extraction methods in the real world, such as the solution's acidity, equipment corrosion, increased chloride ion levels, and complicated operating setups [91]. Extracting Li from brine sources is presented in Table 5, along with a comparison of the various extraction methods.

**Table 5.** Lithium extraction from brines via solvent extraction.

Year	Sources	Extraction System	Li Recovery (%)	Ref
2017	Salt Lake brine	TBP, FeCl <sub>3</sub> , MIBK	>98.00	[92]
2017	Shale gas produced water	D2EHPA, Kerosene	30.80	[93]
2018	Salt Lake brine	N523, TBP, FeCl <sub>3</sub> , Kerosene	96.00	[94]
2019	Simulated brine	TBP, [Bmim] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> , Dimethyl phthalate	99.23	[95]
2020	Simulated shale gas produced water	D2EHPA, Kerosene	>20.00	[89]
2020	Simulated shale gas produced water	methyl tri(octyl)ammonium chloride, DEHPA, n-dodecane	83.00	[14]
2021	Simulated brine	TBP, [N1888][P507], FeCl <sub>3</sub> , Kerosene	>70.00	[96]
2022	Simulated brine	NBEHMOA, FeCl <sub>3</sub> , 6H <sub>2</sub> O and sulfonated kerosene	96.70	[97]
2023	Lithium carbonate solution	HTTA-TBP, HTTA-TOPO	>80.00	[17]

### 5.3. Ion Exchange/Adsorption

Ion exchange has been shown to be a successful commercial process for the recycling of high-value components derived from waste streams. It is possible to employ solutions with a low concentration as input and yet achieve a considerable improvement in concentration, thereby reducing the amount of surplus separation medium. However, its efficiency could be better when dealing with concentrated feed solutions due to slower kinetics and reduced selectivity. In many situations, the economic viability of ion exchange is determined by the concentration of dissolved salts in the brine sample that is utilized for the regeneration process. Ion exchange is a cost-effective method for treating brine water with a dissolved salt concentration of 1500 mg/L [98]. Ion exchange has a cheap initial cost, a relatively high rate of recovery (between 90 and 95%), and a relatively low amount of maintenance and repair needs. These features make it a desirable option regardless of the total dissolved solids (TDS) concentration [99]. The insufficient loading capacities of the used resins restrict the broad implementation of effective lithium extraction from brines by ion exchange [100].

Lithium may be selectively extracted from brine with a high Mg/Li ratio using adsorption techniques. The adsorbent material is crucial to this approach. First and foremost, it must be very stable, able to keep its shape in highly salinized brine and during the acid elution process. Additionally, it should be able to accommodate changing brine temperatures as well as the physical requirements of the adsorption process. Second, the lithium adsorbent substance must exhibit a strong predilection for lithium and have a high adsorption capacity to enable effective extraction from complicated, highly salinized brine deposits. Ion exchange resin [101], aluminum adsorbent [102], manganese adsorbent [103], and titanium adsorbent [104] are all exceptional adsorbents for lithium adsorption. Liu et al. [101] used granular titanium-type lithium ion-sieves (GTI) to extract lithium from brines using continuous-stirring tank adsorbers with three stages for constant Li<sup>+</sup> concentration. The researchers separated GTI ion-sieves and 335 resin using mesh cylinders, withdrawing them at 5 h intervals to improve Li<sup>+</sup> adsorption and maintaining a pH range of 7.8 to 8.1 in the brine. The study found that adding 50 g of wet GTI ion-sieves and 100 mL of 335 resins to a lithium-rich solution improved lithium recovery efficiency by an average of 2.0 times. Chen et al. [102] used magnetic lithium-aluminum layered double hydroxides (MLADHs) as adsorbents to extract lithium from brines with high Mg/Li ratios (284), using chemical coprecipitation and magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The Fe<sub>3</sub>O<sub>4</sub> nanoparticle suspension was adjusted to 4.5 by adding a 2:0.8 AlCl<sub>3</sub>·6H<sub>2</sub>O and LiCl·H<sub>2</sub>O solution, resulting in the formation of layered double hydroxides. The final MLADHs adsorbents were produced after ageing and washing with deionized water at 40 °C for 4 h, and their elemental composition was analyzed in nitric acid. MLADHs demonstrated exceptional adsorption efficacy

and structural stability in low-lithium content brines, with high selectivity for  $\text{Li}^+$  and an adsorption capacity of approximately 6 mg/g. Superparamagnetic  $\text{Fe}_3\text{O}_4$  facilitates rapid recovery of MLADHs from solution, maintaining their adsorption capabilities and crystal structure after eight cycles, demonstrating their superior recyclability. Moreover, Chen et al. [104] developed a titanium-based lithium-ion sieve (PTIS) using an agar-assisted approach to recover lithium from geothermal water. The porous structure facilitated  $\text{Li}^+$  ion passage, resulting in fast kinetics and a high adsorption capacity of 25.8 mg/g in 6 h. PTIS effectively removes  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  ions, with high separation factors for  $\text{Li}^+$ . Its convenient, easily eluted with HCl solution, and maintains consistent adsorption performance. PTIS enhances titanium-based lithium ion sieve post-separation performance, offering high capacity and rapid kinetics for lithium recovery from geothermal and saltwater. This environmentally friendly, porous granular material has potential for various industrial applications.

There needs to be more specificity for lithium within oil field brine when using the organic ion exchange resin technique to extract metals from solutions. Some group 1 and 2 metals have a greater propensity to interact with the cation exchange resin than lithium. Because of its complex production process and the use of potentially dangerous raw components, this resin has limited practical applications [105]. For lithium recovery, however, inorganic metal-centric adsorbents have emerged as a popular alternative to resins because of their superior selectivity, eco-friendly properties, increased lithium perpetuation capacity, and remarkable reusability performance [106].

### 5.3.1. Aluminum Derived Adsorbent

Li-Al layered double hydroxides (Li/Al-LDHs) are the most common type of aluminum-based adsorbent because they do not leach metal, have a high sorbent capacity, and are easy to make [107]. Hydrogen bonds, electrostatic interactions, and van der Waals forces all contribute to the cohesion of the layers of aluminum hydroxide that make up Li/Al-LDHs in their two-dimensional arrangement [108]. In addition, the hydroxide ions' octahedral gaps accommodate lithium ions. Li/Al-LDHs have a chemical formula of  $[\text{Li}_m\text{Al}_2(\text{OH})_6]\text{Cl}_m\text{nH}_2\text{O}$ , where  $m$  is an integer between 0 and 1 [108]. Adsorption is critical in lithium recovery because of the vacancies created when  $\text{Li}^+$  ions are removed from the substance. Li/Al-LDHs have a unique method for adsorbing and desorbing materials from trash, and the presented equation describes it.



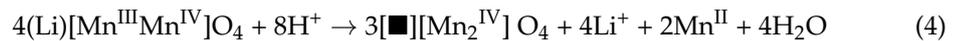
### 5.3.2. Manganese Derived Adsorbent

Much attention has been paid to lithium manganese oxide (LMO) because of its many desirable qualities. These features include high selectivity, excellent reusability, and a novel chemical arrangement [106]. Lithium recovery utilizing LMO precursors has a chemical feature that is unique to it due to its composition.  $\text{Li}_x\text{Mn}_{3-x}\text{O}_4$  ( $0 \leq x \leq 1.33$ ) is the typical composition for spinel phases that are chemically and electrically stable, spanning the range from  $\text{Mn}_3\text{O}_4$  to  $\text{Li}_4\text{Mn}_5\text{O}_{12}$  [109].

Lithium adsorption in LMO is generally thought to occur via either ion exchange or redox reactions [106]. Lithium is hypothesized to be traded for protons in the first scenario within the lattice structure. Experiments show that the adsorption is not pH-dependent since this process does not result in changes to the manganese trivalent and manganese tetravalent sites [110]. This model, however, does not account for the possibility of manganese breakdown, which leads to the unrealistic expectation that the spinel structure will continue to function and look the same even while it is being used. Shen et al. proposed  $\text{Li}^+$  extraction/insertion in  $\text{LiMnO}_4$  to follow an ion exchange mechanism [111].



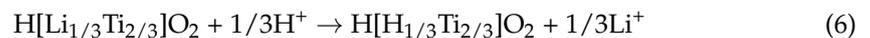
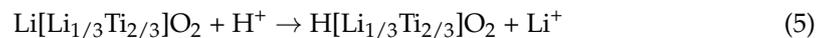
On the other hand, redox adsorption is caused by the uneven behavior of trivalent and tetravalent manganese in acidic conditions, which causes lithium to move between ions and back again. It is predicted that Mn(III) would migrate to the surface and dissolve in the aqueous solution, whereas Mn(IV) stay inside the crystal structure if this process were correct [112]. This explains the decrease in performance found when manganese dissolution was noted; however, it does not clarify the pH dependency. The following equation depicts the redox adsorption process, in which surface-localized  $\text{Mn}^{3+}$  ions undergo reduction to yield soluble  $\text{Mn}^{2+}$  ions. Despite this, the material's underlying structure has not changed.



where ( ), [ ], and  $\blacksquare$  represent the 8a tetrahedral sites, 16d octahedral sites, and vacancies, respectively.

### 5.3.3. Titanium Derived Adsorbent

Lithium titanium oxide and lithium manganese oxide are popular selective adsorbents, with titanium dioxide being a popular electrode in lithium-ion batteries and solar cells due to its unique features [110]. LTO has several advantages, including being environmentally safe, resistant to structural damage from acidic solutions, being very selective in its adsorption properties, and losing very little material during dissolution [113]. For these reasons, LTO is well suited for practical use. LTO, also known as  $\text{Li}_2\text{TiO}_3$ , has a layered crystalline structure that may be described by the chemical formula  $\text{Li}[\text{Li}_{1/3}\text{Ti}_{2/3}]\text{O}_2$  [114]. Different configurations of Li and Ti can be seen between the layers; one layer is entirely made of Li, while another is made of 1/3 Li and 2/3 Ti [115]. The extraction of lithium is shown in detail in Equations (5)–(7). For clarity, the memory effect of lithium is responsible for controlling the selectivity of the adsorption and desorption processes in LTO.



Some studies have attempted to create a single composite of mixed oxides by mixing LMO and LTO adsorbents. While each kind of adsorbent has its own set of benefits and drawbacks, the combined composite may have some distinct advantages. In order to extract lithium from a solution of 200 mg/L, Cui et al. [116] developed a hydrogel composite of  $\text{H}_4\text{Mn}_{3.5}\text{Ti}_{1.5}\text{O}_{12}$ /reduced graphene oxide/polyacrylamide (HMTO-rGO/PAM) with an adsorption capacity of 51.5 mg/g. Fumihiko Ohashi and Yutaka Tai were the first to produce surface-modified adsorbents, treating  $\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$  with transition metal oxide oligomers. This treatment and subsequent calcination created adsorbents with a thin metal oxide covering [117]. The current state of the art for brine Li recovery by adsorption is summarized in Table 6.

**Table 6.** Lithium extraction from brines via adsorption method.

Year	Sources	Adsorbent	Adsorbent Capacity (mg/g)	Ref
2019	Synthetic salt solution	Aluminum-doped Li manganese oxides	32.60	[118]
2020	Salt Lake brine	Granular $\text{H}_4\text{Mn}_3\text{O}_{12}$	17.20	[119]
2021	Salt Lake brine	Li-Al-LDHs	7.27	[107]
2021	Synthetic salt solution	Titanium-based Li-ion sieve powder	19.22	[120]
2022	Shale gas produced water	$\text{H}_{1.33}\text{Mn}_{1.67}\text{O}_4$	13.27	[15]
2023	Salt Lake brine	PVC, PAN	11.90	[16]

#### 5.4. Membrane Technology

Nanofiltration is a pressure-dependent separation technique that uses steric hindrance to selectively block divalent and multivalent ions in concert with the Donnan effect, which includes an unequal dispersion of permeant ions over the boundary [121]. NF membranes have traditionally found broad application in desalination operations as the last phase before reverse osmosis because of their molecular weight cut-off, which ranges from 200 to 1000 Da [122]. This method, which uses size exclusion in conjunction with electrostatic repulsion, has also been adopted for water treatment, where it successfully removes impurities and preserves pharmaceutical chemicals [123]. Recent studies have investigated the feasibility of using nanofiltration to increase lithium concentrations in aqueous solutions. Wen et al. (2006) reported on the first effort in this area [124]. NF membranes have been used to collect lithium from diluted brine and convert it to lithium chloride [124]. The NF90 membrane shows greater performance in lithium separation when used with a low-pressure RO membrane (LPRO), which is attributable to its increased hydraulic permeability and efficient separation of monovalent ions [125]. NF membranes retained divalent cations at a rate of 97%, but monovalent cations were retained at a far lower rate [126]. Significant importance is placed on mechanical characteristics like surface roughness and thickness in the context of nanofiltration (NF) membrane separation, which influences the relationship between outcomes and the efficacy of substance rejection. Successful use of NF in recovering lithium resources from oil and gas wastewater requires addressing the restrictions connected to trade-off effects, poor pollution resistance, and inferior mechanical strength [127]. Moreover, the selectivity of lithium may be affected due to its high salinity and low pH post treatment. Foo et al. [128] performed 750 tests on ion rejection across pH and feed salinity using brine solutions that were similar to the chemicals found in salt lake. The study shows that when the pH drops, the carboxyl and amino groups become charged. This makes the polyamide membrane 13 times more selective for  $\text{Li}^+$  and  $\text{Mg}^{2+}$ , but it also makes it 43% less selective for other charges. Li et al. [129] evaluated the performance of DK NF membranes in separating magnesium and lithium in salt lake brine. They found exceptional separation capabilities, with 81% magnesium retention and 69% lithium retention, resulting in 83% lithium extraction yield and a separation factor above 8.5. Separation efficacy and selectivity of the DK NF membrane decreased following prolonged usage due to fouling in salt lake brine. Surfaces showed elevated Mg, Si, Cl, and Ca, redshift in polyamide functional groups, and increased carboxyl group concentration. SEM revealed impurities, increasing surface roughness. Fouling NF membranes increases membrane flux but lowers hydrophilicity while increasing electronegativities, reducing separation performance but increasing membrane flow.

Membrane distillation (MD) and membrane crystallization (MC) are two ways to make a supersaturated solution by using a difference in vapor pressure across a microporous membrane that does not like water [130]. The primary difference between MD and MC is in the final product, whereas MD yields a supersaturated solution, MC causes the solution (derived from MD, if relevant) to crystallize. The theoretical ability of MC to achieve “zero-liquid” discharge makes it a promising candidate for seawater-related processes like desalination. It has also been evaluated for use in brine and seawater  $\text{Li}^+/\text{Mg}^{2+}$  separation tests [131].

In 2016, Quist-Jensen et al. [132] compared three different membrane distillation (MD) modes utilizing two different polypropylene membranes: direct contact membrane distillation, vacuum membrane distillation, and osmotic membrane distillation. Only vacuum membrane distillation resulted in sufficient supersaturation for LiCl crystallization, while the other methods failed to do so. Park et al. [133] have devised a method that includes a nanofiltration membrane and a membrane distillation phase as a contemporary replacement for conventional evaporation for lithium enrichment and undesirable ion removal. The membrane distillation process generally involves the crystallization of divalent ions. However, the presence of the NF phase effectively inhibited this. Combining them may increase brine’s lithium content dramatically, from 100 mg Li/L to 1200 mg Li/L

in as little as 140 h. Lithium manufacturing, which used to take between 12 and 24 months, can now be accomplished with much less time and chemical input.

Ion-selective recognition allows ion-imprinted membranes (IIMs) to separate and detect ions selectively. IIMs are the result of combining membrane separation technology and the ion-imprinting technique. In this scenario, highly selective adsorbents are produced by embedding functional monomers and target ions in the macroporous membrane, allowing for easy regeneration and low-energy processes. There is a considerable range in selecting membrane materials for any given membrane-based process. It is well recognized that graphene oxide (GO) membranes may be used in nanofiltration procedures, forward osmosis, and desalination to purify water [134–137]. In this context, GO can function as both the primary material and an addition. In the former, its porosity and layered structure make it an ideal ionic and molecular ion sieve, driving much of its application. As an addition, however, it is often employed to boost the matrix's antifouling, hydrophilic, and mechanical qualities [138]. Membranes are often made by combining GO with other polymers, such as PVDF, polyethersulfone, or PVA. Sun et al. [139] introduced polyvinylidene fluoride (PVDF) via carbodiimide esterification in dimethyl sulfoxide with 2-methylol-12-crown-4 ether into untreated GO flakes. The membrane was then tested in an H-model-tube configuration using a LiCl solution (50 mgLi/L), with the researchers finding a maximum adsorption capacity of 24.25 mgLi/g and satisfactory stability after 10 cycles. As Lu et al. [140] proposed, a multilayered polyether sulfone membrane is yet another kind of Li-IIM. Polyether sulfone's high porosity, structural integrity, and pressure resistance made it an ideal candidate for the support membrane. To finish things off, 12C4E was imprinted onto an adhesion layer of polydopamine (PDA) that had been operationalized with silica nanoparticles to increase the membrane's hydrophilicity and stability. Maximum adsorption of 27.55 mgLi/g was recorded when the membrane was tested in a 50 mgLi/L LiCl solution, and the membrane showed high regeneration capacity, maintaining rebinding capabilities around 90% after five cycles. On the other hand, Bai et al. [141] created 2-methylol-12C4E polymer brushes using UV-initiated surface polymerization, which they then adhered to a foam formed of a polymeric high internal-phase emulsion. This adsorbent's porous structure allowed it to reach equilibrium in about forty-five minutes, enhancing the bonding between the crown ethers. Its absorption, however, was significantly less than that of other foams. Instead, Cheng et al. [142] recommended functionalizing a chitosan nanofiltration membrane with crown ethers. The authors stated that their material was very selective when adsorbing 297 mgLi/g from a 1000 mgLi/L solution.

The use of electrodialysis (ED) as a technique for lithium extraction from different types of brine sources has increased in recent years. Cation and anion exchange membranes are stacked on top of one another to perform ED, and an electric field is applied. Correspondingly, ions are separated at the proper membrane and then transported to the correct electrodes [143]. Selective-electrodialysis (S-ED) uses a univalent selective ion exchange membrane to retain bivalent ions in the desalting compartment [144]. It is effective for recovering single ions like lithium but also considers sodium and potassium due to their similar radii. Strategies include ionic liquids and chemically modified membranes [145,146]. One of the main challenges in recovering the monovalent ions from brine solutions is the typically high Mg/Li ions (varying from 1 to 65, and even 400 to 7600), such as in the Mediterranean Sea [110]. In earlier research, the extraction of lithium from multi-ion electrolytes using ion exchange membranes selective for monovalent ions (S-ED) was examined. Nie et al. [147] found that 150 mgLi/L mixes and 10 to 60 g Mg/L worked well, recovering between 90 and 95% of lithium. S-ED was more practical and cost-effective than nanofiltration membranes. However, the presence of potassium affected efficiency. Higher voltages yielded better results, and brine from East Taijinar Lake in China effectively recovered 91% of lithium ions at 31 Wh mol/Li [145].

The bipolar (BP) arrangement of bipolar membranes has also been considered in the ED design. Layered ion exchange membranes are made of two polymers with opposing charges, as in BP membranes. When a suitable electric potential is present, water dis-

proportionation would occur at the hydrophilic junction, but no ions could penetrate the membrane [148]. Hydroxyl groups and protons develop in the various compartments because of a bipolar membrane in the ED configuration. Since lithium and boron are crucial to several industries, bipolar membranes have separated them from a standard stream. The lithium in this scenario might be extracted as LiOH. Boron would be extracted from seawater, where it exists as a borate ion, to produce boric acid. Because of how quickly they form borate complexes, divalent cations like magnesium and calcium must be removed from the feed solution before this process can begin [149]. Bunani et al. [150] proposed BP membranes for ion-exchange membranes, using  $\text{Li}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$  (approx. 850 mg B/L and 250 mg Li/L) as feed solution and  $3 \times 10^{-3}$  M HCl and NaOH as acid and base, respectively. Lithium recovery rates outpaced boron recovery, with boron recovery being more sensitive to sample volume and pH. Researchers altered the sodium chloride level in the feed solution to study ion transport. Sodium ions were transported to lithium ions, but sodium did not affect lithium-ion transport [151,152]. Higher acid and base concentrations improved ion transport, suggesting weaker acids/bases require higher concentrations [151]. The results also suggested that membrane ion retention could be responsible for the reduced recovery. Possible solutions to this issue include using other membranes or running the experiments for extended periods. With an applied electric field of 30 V and a concentration of  $50 \times 10^{-3}$  M HCl and NaOH, almost 50% of the boron and 62% of the lithium were effectively extracted at a specific power consumption of 7.9 kWh/m<sup>3</sup>. However, Jarma et al. [149] found that by decreasing the electrical potential to 20 V and continuing to use the same solutions ( $50 \times 10^{-3}$  M HCl and NaOH), they were able to recover around 57% of the boron and 89% of the lithium.

Strategically essential components of the solution may crystallize more easily using membrane enrichment techniques [153]. However, most of these lithium recovery techniques have only been tested in the lab. More research is needed to determine whether or not these techniques might be used to produce potable water from saltwater brines and to salvage valuable resources. Some difficulties that membrane technology must overcome include membrane fouling, scaling, and pore wetting, all of which may prevent its widespread commercial use [154,155]. Table 7 details current efforts in membrane technology for lithium recovery.

**Table 7.** Lithium extraction from brines via membrane technology.

Year	Sources	Operational Mode	Material of the Membrane	Performance	Ref
2020	Synthetic salt solution	Nanofiltration	BTESE coated TiO <sub>2</sub>	Mg <sup>2+</sup> rejection: 20.30% Li <sup>+</sup> rejection: 74.70% Flux: 57 LMH	[156]
2020	Synthetic salt solution	Electrodialysis	Mg doped Li manganese oxide	Li/Mg selectivity: 4.82	[157]
2021	Synthetic brine	Nanofiltration	Sulfonated PEEK	Li/K selectivity: 3 Li/Na selectivity: 2.17	[158]
2022	Synthetic salt solution	Nanofiltration	Cu modified polyamide membrane	16.20 ± 2.70 LMH/bar Li/Mg selectivity: 8 ± 1.00	[159]
			Quaternized bipyridine modified PEI	Flux: 96.60 ± 3 LMH Mg <sup>2+</sup> rejection: 92%	[159]
2023	Geothermal brine	Membrane distillation	Nanofibers with (3-Aminopropyl) triethoxysilane	Salt rejection: >99% Flux = 14–19 L/m <sup>2</sup> h Li concentration: >1100 ppm	[18]

LMH = Liters per square meter per hour.

### 5.5. Hybrid Technology for Lithium Recovery

The development of combination technology was driven by the need to improve the dismal efficiency of lithium resource recovery utilizing stand-alone methods. Divalent cations such as barium, calcium, and strontium were removed using a precipitation approach by Chung et al. [160]. The next step was effectively removing lithium from the produced water by employing HTO adsorbents. By combining H<sub>2</sub>TiO<sub>3</sub> adsorption and precipitation, Jang et al. [160] enhanced the highest lithium sorbent capacity (3.61 mmol/g) by 37.64% compared to the adsorption method. The technique presented by Kim et al. [161] allows organic contaminants to be lowered by 66% using lithium manganese oxide and an oxidant generation electrode from lithium solution with a 98.6 mol/L concentration. Therefore, decreasing the effect of organic matter in the oil and gas-produced water on the

manganese ion screen may improve lithium recovery rates. Using the coprecipitation technique, Gan et al. [162] extracted lithium from oilfield brine. The process involved extracting oil from a brine using  $\text{CCl}_4$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{AlCl}_3$ , and  $\text{HCl}$ . The solution was then filtered using oxalic acid and hydrogen chloride gas. The optimal molar ratio was 1:1, resulting in an 88% lithium recovery rate. Pan et al. [163] used freezing crystallization/Glauber nitrate and halogen to extract 96.73% lithium carbonate in an oil field brine with significant calcium content. They also recovered 15 metric tons of potassium-mixed salt with 15–20% potassium chloride and 40 kilos of lithium carbonate-mixed salt with 95.17% grade from Qinghai Oilfield oil and gas-generated water [164].

Density functional theory (DFT) has developed as a powerful tool for understanding chemical processes at the molecular level in recent years. Extraction techniques vary among solvent extraction procedures and often include complex chemical structures, thermodynamic factors, and a variety of interactions [165]. The synergistic impact of  $\lambda\text{-MnO}_2$  and graphene in the composite film for the adsorption of  $\text{Li}^+$  was comprehensively investigated by Zhang et al. [166] in terms of  $\text{Li}^+$  ion selectivity, ion conductivity, and electron conductivity. The results from the DFT simulations matched those from the experiments. DFT calculations suggested that the existence of graphene and the strong interaction between oxygen and manganese atoms inside  $\lambda\text{-MnO}_2$  were responsible for the film's exceptional electronic conductivity. The low diffusion energy barrier, the modest distance between manganese and oxygen (L Mn-O), and the higher average distance between lithium and oxygen (d Li-O) were also credited with contributing to the remarkable ion conductivity. Lithium-ion diffusion was preferred over sodium and magnesium ion diffusion because its energy barrier was substantially lower. In order to recover lithium from oil field brine, Zhao et al. [167] employed high-precision DFT computation to assess a synergistic system comprised of dibenzoylmethane (DBM) and trioctylphosphine oxide (TOPO). The organic phase was comprised of a specified mole ratio of DBM and TOPO dissolved in sulfonated kerosene, with a total DBM and TOPO concentration of 0.5 mol/L. The organic phase was then combined with a 2 M NaOH solution to create the saponified organic phase. After achieving phase equilibrium, the organic phase was removed and mixed with the aqueous phase in a ratio of two to one (organic to aqueous). The resultant mixture was then stirred for 30 min at 25 °C in order to achieve phase equilibrium. After 1 min of centrifugation at 5000 revolutions per minute, the loaded organic phase (LOF) and raffinate ( $R_f$ ) were removed from the centrifuge tube with a syringe fitted with a tube extender for further metal analysis. Analyzing the concentration of ions in the  $R_f$  phase allows one to estimate the effectiveness of ion extraction. Based on the McCabe Thiele diagram, the extraction conditions were determined as a three-stage countercurrent extraction with a 2:1 phase ratio after the study. After three phases of countercurrent extraction, the effectiveness of  $\text{Li}^+$  extraction reached 98.1%. This was accomplished with an organic phase containing 0.25 mol/L DBM and 0.25 mol/L TOPO, a saponification rate of 70%, and a phase ratio of 2:1. After selective stripping and scrubbing with different concentrations of  $\text{HCl}$ ,  $\text{Li}^+$  was separated from  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ . The mass ratios of  $\text{Mg}^{2+}/\text{Li}^+$  and  $\text{Na}^+/\text{Li}^+$  dropped by 49.7 and 102.4 times, respectively.

The global popularity and widespread use of computers and AI-driven approaches have significantly influenced various industries. Katterbauer et al. [168] developed an AI-driven optimization technique to enhance lithium recovery from reservoir operations while maintaining oil production objectives. The method uses AI technologies and genetic algorithms to optimize lithium recovery and oil production simultaneously. The AI component uses a deep learning LSTM algorithm to forecast oil, brine, and lithium recovery, fine-tuning water injection volume to maximize recovery while maintaining oil production schedules. A state-of-the-art AI optimization framework was successfully used in the Volve field to improve lithium recovery from brine in oil and gas reservoirs, demonstrating potential for increased brine usage and sustainability.

Oil and gas companies are exploring treatment techniques to extract lithium from oil fields. Canadian company MGX Minerals has used nanofiltration technology to recover

lithium from oil fields in Canada and America. Research and technology support for Nanyishan [169] in Qinghai Province includes a proposal to develop and use oil field water resources as part of an integrated pipeline with a 10,000 ton capacity. This state-of-the-art procedure incorporates both evaporation and freezing. Annual output targets have been set at 80,000 tons  $H_3BO_3$ , 1,000,000 tons KCl, and 20,000 tons  $Li_2CO_3$ . Silicon carbide ceramic membranes, induced gas oil float units, corrugated plate induction separators, and membranes are only some of the pretreatment instruments used by Ozone Tek [163]. These methods work in tandem to purge the environment of organic compounds and traces of metal. A pretreatment procedure incorporating membrane enrichment leads to the acquisition of high-purity lithium products.

## 6. Future Directions

The economic viability of the produced water treatment can be improved by using hybrid technological solutions. It is very important to use life cycle cost analysis when looking at new precipitants and adsorbents like facet-engineered  $Li_3PO_4$ , trisodium phosphate, sodium silicate, granular  $H_4Mn_3O_{12}$ , titanium-based Li-ion sieve powder, and  $H_{1.3}Mn_{1.67}O_4$ . By conducting exhaustive evaluations of these processes and materials, the way is set for commercially feasible lithium recovery from oil and gas wastewater, contributing to more sustainable and efficient wastewater management procedures. From a technological standpoint, future efforts to improve lithium recovery rates should focus on the following dimensions:

1. Increase the specificity of the adsorbent, extractant, and membrane materials, pollution resistance, and durability. It is vital to consider difficulties when attempting to improve adsorbents through modifications, including metal loss due to dissolution during acid treatment, uneven particle distribution and fragmentation, difficulties in recovering the adsorbent during regeneration, and the potential blockage of transfer pathways, which would result in reduced adsorption efficiency.

It is essential to reduce the divalent ion concentrations while working with extractants to improve the effectiveness of lithium recovery using solvents. In addition, problems like the considerable space needed for solvent extraction and the risk of equipment deterioration must be considered carefully.

Several approaches may be used to solve issues, including weak resistance to fouling and mechanical fragility. Improvements in the technology used to extract lithium from oil and gas production water include increasing the membrane's active water transport surface area, creating rapid water transport pathways, improving the film's water-attracting characteristics, refining surface charge dynamics, modifying surface chemical attributes, and adapting the membrane's pore distribution.

2. Improve the integration of existing lithium recovery methods. Lithium recovery with a single technology is not feasible due to the unique features of the produced water and the difficulties inherent in extracting lithium deposits. However, extracting lithium from oil and gas-produced water effectively requires different approaches. Integrating preprocessing and concentration improvement methods like adsorption/extraction with membrane separation and precipitation is a technically possible and potentially fruitful approach. Oxidation, aggregation, precipitation, and other preprocessing methods are used to reduce the number of disruptive materials such as organic compounds, suspended particles, total organic carbon, and ions like  $Ca^{2+}$  and  $Mg^{2+}$ . This order will improve the central processing unit's adsorption, concentration enrichment, and lithium extraction. The precipitation of lithium carbonate occurs when sodium carbonate is added.
3. In the framework of the oil and gas business, more research is needed in the area of density functional theory (DFT), with a particular emphasis on molecular modelling and the treatment process for lithium recovery.

4. Utilizing a life-cycle assessment of the treatment technology will be helpful in designing the economic process of extracting lithium from the produced water of oil and gas operations.
5. Tran et al. [170] recommended the utilization of biowaste to create Li-ion batteries in their review. In order to maximize the extraction of lithium from oil field-generated water, this idea suggests the possible synthesis of biobased precipitating or adsorbing compounds.
6. The cost is as significant as the technology in engineering applications. Because they need more expensive products and equipment, cutting-edge technologies for lithium recovery tend to have more significant upfront costs than conventional evaporation procedures. Commercially accessible non-evaporative solutions are limited when the lithium concentration in oil and gas-produced water is low. Most modern recovery methods for lithium extraction from brine still need to be economically viable for widespread use. The estimated cost of manufacturing lithium from seawater is roughly USD 80 per kilogram, whereas the cost of creating the same amount of lithium from brine from salt lakes is just USD 2. The cost of nanofiltration (NF) is between USD 5 and USD 7, and although it has shown promising results, it is still relatively high [78]. The total costs of a complete treatment for original oil and gas-produced water may be reduced by installing lithium recovery units and the money gained from selling lithium resources. This means that by adopting this technique, the oil field will be able to save money regarding the disposal of oil and gas wastewater.

## 7. Conclusions

This review examines in greater depth the complex link between oilfields and the oil and gas sector, concentrating on the production of wastewater and the presence of potentially harmful compounds. The inherent difficulty of treating lithium-containing chemicals and the crucial significance of treating produced water (PW) before its discharge into the environment are emphasized. In addition, the research analyzes the possibility of lithium recovery since this feature holds the key to optimizing the treatment procedure and overall value proposition.

Lithium extraction from the oil and gas industry could reduce treatment costs and develop new precious minerals. This aligns with the circular economy concept, enhancing energy costs and improving the financial outlook for oil and gas firms.

The applicability of various methods depends on wastewater characteristics and geographical conditions. Precipitation is cost-effective, but energy efficiency and chemical control are key priorities. Solvent extraction offers high yield potential. Ion exchange is eco-friendly but less effective with concentrated feeds. Adsorption is good but limited by adsorbent capacity. Membrane technology presents new channels but faces obstacles like fouling and pore wetting. Combining different treatment methods may thereby improve lithium recovery.

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### Abbreviations

PW	Produced Water
LDH	Layered double hydroxide
PEEK	Poly ether-ether ketone
PEI	Polyethylenimine
BTESE	1,2-bis(triethoxysilyl)ethane
TBP	Tri-butyl phosphate
MIBK	Methyl isobutyl ketone
N523	N, N-bi-(2-ethylhexyl) acetamide
[Bmim] <sub>3</sub> PW <sub>12</sub> O <sub>40</sub>	1-butyl-3-methylimidazolium phosphotungstate
D2EHPA	Di-(2-ethylhexyl) phosphoric acid
P507	2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester
[N1888][P507]	Trialkylmethylammonium di(2-ethylhexyl) orthophosphate
EDTA-Li	Lithium 2-carboxyhydrazine-1,1,2-tricarboxylate
HTTA-TBP	Thenoyltrifluoroacetone-tributyl phosphate
HTTA-TOPO	Thenoyltrifluoroacetone-trioctylphosphine
NBEHMOA	N,N-bis(2-ethylhexyl)-2-methoxyacetamide
PVC	Polyvinyl chloride
PVN	Polyacrylonitrile
CORFO	The Production Development Corporation (Chile)

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