

# REVIEW

# **Recent Developments in the Extraction of Lithium from Water Resources**

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An increasing number of electric vehicles, hybrids, and synergistic types are adding electronic components, driving up demand for lithium and its derivatives. These chemicals comprise 80% of the worldwide market and come in forms such as carbonate, lithium hydroxide and mineral concentrates. The use of lithium is predicted to surge by 60% in the coming years due to the proliferation of electric vehicles. This demands efficient and rapid deposit detection methods as well as economical and high-resolution exploration equipment. The quantity and geographical distribution of fossil and ore mineral deposits can be easily mapped using hyperspectral photography. Since salt lakes, oceans, and geothermal water hold the majority of the world's lithium reserves ranging from 70% to 80%, these areas are ideal for the lithium extraction process. In this regard, there is an increase in research targeted at industrial lithium production from water resources. Recycling lithium-ion batteries is an alternative method that can be utilized to increase the production of lithium. Geothermal waters have lower lithium contents than brines and some of the processes are not suitable. Evaporation methods, solvent extraction, membrane technology, nanofiltration and adsorption can all be used to extract lithium from liquid media. Thus, lithium extraction from aqueous solutions was the focus of this review article, which aimed to provide straightforward technical solutions, low costs, decreased environmental impact and excellent selectivity for the lithium industry.

Keywords: Lithium, Recovery, Ion exchange, Adsorption, Geothermal water.

#### **INTRODUCTION**

The exceptional theoretical specific capacity (3860 mAh g<sup>-1</sup>), low weight (6.94 g mol<sup>-1</sup>) and lowest redox potential (-3.04 V *versus* standard hydrogen electrode) of lithium metal have made it the most attractive material for battery anodes [1-4]. The presence of these characteristics makes lithium and its compounds interesting in a variety of industries. In addition to being used to make ceramics, batteries, refrigerants, glass, *etc.* lithium and its compounds are also produced during aluminum manufacturing process, used as a catalysts for rubber industries, air conditioning systems, pharmaceutical and drainage systems [5].

The earth's crust contains 0.007% of the uncommon metal lithium [5-7] and its' deposits are thought to be about 14-15 million tons worldwide [8,9]. In terms of deposits, the two primary types are liquid lithium and solid lithium and majorly found in seawater, salt lake brines and geothermal waters and secondary raw materials deposits, such as lithium-ion battery trash and electronics industry waste [4,8]. The main lithium compound mineral reserves can be found in Chile, Russia, China, the Congo, Canada, Afghanistan and Serbia [10,11]. There are over 150 different minerals and clays that contain lithium, which does not naturally occur in a free state [12]. The sea, salt lakes, geothermal and ocean water represent 70-80% of the global lithium deposits [5,10]. However, sea

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and ocean waters are not suitable for commercial lithium production due to their low concentration of 0.1-0.2 ppm [13-18].

Lithium concentrations in geothermal waters can range anywhere from 1 to 100 ppm [9,19], whereas lithium processing and manufacturing face obstacles by the presence of several pollutants in geothermal fluids, along with significant levels of other metals [20]. In saline lakes, lithium concentrations range from 100-1000 ppm and due to the high concentration of salts, particularly magnesium, makes the treatment of brines difficult [21]. Thus, the presence of high concentrations of alkaline and alkaline earth elements significantly complicates the process of extracting lithium from natural fluids [22]. Currently, the industry is predominantly composed of mineral concentrates, lithium carbonate and lithium hydroxide, which collectively account for 80% of the market [23]. Lithium carbonate is obtained by extracting and processing spodumene ores and brines from salt lakes [24]. Pegmatite, a type of rock, is a source from which this mineral can be extracted and contain a lithium concentration of 1-4% and around 60-70% of lithium can be recovered [24]. In addition to spodumene, various ores contained in pegmatite rock can also be used to extract lithium carbonate [24]. To treat aqueous lithium solutions in an industrial process, lithium ores must first be extracted. Hydrothermal water, brine from salt lakes and ocean and seawater are all potential sources of lithium containing water. The review article explored lithium extraction from aqueous solutions as a means of advancing the lithium industry, which is distinguished by its goal of minimizing environmental impact, achieving high selectivity, maintaining low-cost cost and employing simple technical solutions.

Mineralogy and geosciences: The demand for lithium has increased dramatically due to its widespread use in battery devices and hybrid electric vehicle (EV) models. One of the most important and eco-friendly energy sources is the process of extracting lithium from ores. Lithium and other mineral resources linked to this specific ore are hence the subject of extensive research [25]. Therefore, efficient, effective and quick procedures should be required for the investigation and discovery of new resources. When mapping mineral resources, it is necessary to have exploration tools that are efficient. Using satellite and aerial images, the large-scale regional quartering can be obtained [26]. The preferable solution for this is hyperspectral imaging (HIS), a fast expanding technique that quickly map the minerals and examine earth surface at various sizes [27]. Data can be gathered across a broad spectrum with the help of sensors, which allows the collection of data with precision ranging from millimeters to centimeters regarding the quantity and spatial distribution of ore and fossil minerals found in the core samples, hand samples and deposits.

Precise placement in geology is a difficult challenge, especially difficult-to-reach areas. A continuous 3D map was developed to detect lithium-containing minerals and variations in pegmatite rock composition [27], showing the ability to accurately process and scan the lithium-bearing materials. This demonstration will illustrate the application of hyperspectral photography in the analysis and enhancement of diverse product manufacturing processes [28]. **Resources, economies and demand of compounds of lithium:** The demand for Li-ion batteries, automotive batteries, and lithium and its compounds has significantly increased in the last decade, leading to it being referred to as the "new gold" and "white oil" [29]. The global use of lithium has shown substantial growth in recent times, owing to its widespread utilization across several industries [30]. Lithium is present in 39% of batteries, 30% of ceramics and glass, 8% of greases, 5% of polymer goods, 3% of air treatment products, and 10% of other materials [31,32] (Fig. 1). In year 2019, the demand for lithium has reached 58 thousand tons, representing an increase of 18% compared to year 2017 [33]. In future, the consumption of lithium is anticipated to reach 60% in the coming years [34-36]. At the same time, about 38% of mineral rocks and 62% of aqueous brines are used to extract lithium [24].

45%



Fig. 1. Primary uses of lithium in relation to the amount of Li metal equivalent used

Presently, brine and spodumene ores are utilized to extract lithium; however, there is a growing research interest into the potential use of geothermal waters to extract lithium and may contribute for 4-8% of lithium supply [37]. Lithium extraction from the rocks is expected to nearly twice than extraction from the brines [38]. In order to satisfy the anticipated lithium demand, this drives researchers to look for novel and innovative ways to separate lithium from well-known and recycled feedstocks.

Recycling lithium-ion batteries is another technique for obtaining lithium. Unfortunately, there are a lot of obstacles for recovering lithium from rechargeable batteries, including the high cost, the difficulty of isolation and the poor recycling rate (approx. > 5%) [37]. An strategy to lithium resource conservation should be proposed as a partial solution to the production and resource problem, which include substantial mining and a more effective recycling system [7].

**Lithium isolation:** The lithium resources consist of 25% lithium minerals and 65% brines, which are readily available

[39]. Based on evaporation technique, lithium extraction from brines is accounted as 30-50%, which is less expensive than lithium extraction from the minerals [4]. Solar and wind energy drive the process in artificial ponds until the ideal concentration is reached [40]. Evaporation of brines, which takes place over a period of one to two years, limits the output capacity of production facilities due to the brines' ability to supply lithium [1]. According to the EU Commission's project, the demand for lithium is expected to increase by 18 times by 2030 and 60 times by 2050 [41].

Lithium membrane storage compartment: Lithium separations by the use of membrane technology are currently the subject of investigation. Numerous studies have been conducted on lithium separation under pressure methods, particularly nanofiltration [42-47]. It is known that 26% of lithium and more than 85% of magnesium in saltwater are rejected by nanofiltration [48]. In order to ensure that the solutions that can be generated by this process are sufficiently diluted, it is necessary for them to first go through an additional concentration phase [42]. Furthermore, membrane distillation can be utilized for extracting lithium from brines and salts present in brines are extracted using this technique [48]. It can be said that this method did not result in any enrichment at all [42,43]. Presently, there is a lack of study on the methods for simultaneously obtaining clean water and extracting lithium. A combination of nanofiltration and membrane distillation technologies is being investigated for the separation of multivalent cations and lithium [49]. Many studies have been conducted on the feasibility of employing membrane distillation and initial nanofiltration techniques to reduce the concentration of magnesium in brine present in lakes, with the goal of extracting sufficient quantities of lithium. There are more than 90% calcium and magnesium cations present as well as 42-60% of K, Na and Li cations. The Mg to Li ratio can be brought down to less than 6 using the nano-distillation technique.

**Solvent extraction:** The solvent extraction method for lithium extraction has the benefits of high purity and a simple procedure [50,51]. Nevertheless, the emissions it generates are highly adverse and they will actively contribute to the damage of equipment. However, this technique requires a substantial quantity of solvent and extended extraction periods. Organic solvents produce a substantial quantity of waste solvents, which has a detrimental impact on the environment.

**Nanofiltration methods:** Membrane technologies are the most common for the lithium extraction for seawater feeds [52,53]. The most prevalent are nanofiltration (NF) and electrodialysis, which operate continuously with good selectivity. Electrodialysis uses an electric field to drive ion mobility, while nanofiltration uses a pressure gradient. By employing a single nanofiltration stage, the concentration of lithium in saltwater desalination brine can be enhanced by approximately three times, resulting in lithium concentrations of up to 1.5 ppm, while simultaneously eliminating a substantial portion of contaminating Ca<sup>2+</sup> and Mg<sup>2+</sup> [54,55]. Recently, Wang *et al.* [56] reported the ideal method for recovering lithium brine is by the use of nanofiltration (NF), which offers high water flux, precise separation and good selectivity for Li<sup>+</sup>/Mg<sup>2+</sup> ions. The success of lithium recovery approaches is attributed to the Li<sup>+</sup>/Mg<sup>2+</sup> selectivity of polyamide-based commercial NF membranes.

Lithium extraction using Li-ion sieve adsorbents: Adsorption is also an effective process for extracting lithium from low-lithium solutions and known for its excellent selectivity and its ease of applications. Lithium is absorbed and extracted from the complicated aqueous solutions using Liion sieves, which are high-ion filtering selective adsorbents [57-59]. Lithium-ion sieves (LMO and LTO) based on manganese oxide and titanium oxide are distinguished due to their high adsorption capacity [60] and regarded as better promising technologies for lithium extraction from solutions due to the less power consumption and environmental safety [61].

Using MnO<sub>2</sub>·0.3H<sub>2</sub>O, MnO<sub>2</sub>·0.5H<sub>2</sub>O and MnO<sub>2</sub>, numerous LMOs with significant lithium adsorption capacities have been reported [62,63]. The molar ratio of Li:Mn shows that MnO<sub>2</sub>. 0.5H<sub>2</sub>O has the maximum adsorption capacity and these lithium ion adsorbents consist of spinel structure. The spinel LiMn<sub>2</sub>O<sub>4</sub> has a 1:2 ratio of Li to Mn cations but this ratio can occasionally be exceeded [64]. However, lithium adsorption during recycling and manganese dissolution during processing both affect the stability structure of spinel [61]. The efficiency of substance absorption is greatly influenced by the shape, porosity and crystal structure of adsorbent material [57,65]. Single crystal LMO nanotubes can be retained by having  $(NH_4)_2S_2O_8$  as the eluent, lowers the Mn solubility while retaining the capacity during adsorption and the desorption processes [66]. Using only pure LiCl solutions, the study achieved an extraction rate of lithium equal to 89.73% of adsorbent capacity of the material [67].

Although LMO lithium-ion sieves are having effective and selective for lithium ions in aqueous solutions, their industrial use is constrained by challenging separation and a decreased adsorption capacity as a result of manganese dissolution [68]. The impacts of period of calcination, temperature and the alloying iron quantity were investigated in addition to the phase composition, losses during dissolving and the adsorption properties, also pH of the solution, lithium concentration at initial stage and temperature. It has been demonstrated that lithiumion sieves have an adsorption capacity of up to 34.8 mg.

Manganese dissolving loss is substantially lower at 0.51% than for undoped Li-ion sieves, which is 2.48%. This is due to the fact that the disproportionation reaction was inhibited while the amount of manganese in the skeleton increased. Upon comparing the adsorption capacities of undoped and Fe-doped sieves, it was found that the adsorption capacity of undoped sieves decreases by 50% after the fourth cycle, which is significantly greater than the approximate 32% decrease in alloyed sieves.

Similarly, lithium-titanium-based lithium ion sieves (LTO) have greater chemical stability than manganese based sieves [69]. Due to its low liquidity, permeability and processing effectiveness, the ultrafine morphology causes serious post-separation issues in commercial settings. Thus, Ti-LiS powders can be immobilized using binding agents such chitosan, polyvinyl alcohol, polyacrylonitrile, polyvinyl chloride, *etc.* to effectively address these issues [70-75]. Recently, Zhao *et al.* [76] developed an novel porous fiber that makes use of H<sub>2</sub>TiO<sub>3</sub>

(HTO) as core material for the recovery of lithium from geothermal water. In this work, polysulfone (PSF) was used as an auxiliary material in the fiber composite adsorbent, which demonstrated strong performance on adsorption and the stability near to powder. Because of the better properties of the PSF/HTO fiber, Li extraction from geothermal waters and other aqueous solutions offers a wide variety of applications. Moreover, the good coating materials polystyrene binder, polyacrylonitrile, polyvinyl chloride and polysulfone have high chemical and mechanical stability [77]. However, compared to powder sieves, the adsorption rates and capacities of these composite materials are far lower. The high specific surface area, filamentous materials made of polymer fibers show significant potential in this respect and, as a result, increased adsorption capacity [58,78]. However, without coating with high adsorption polymeric materials, binders, their stability proved to be inadequate.

#### Conclusion

Lithium is a desirable and rare element which is abundantly available in raw materials and present in more than 150 minerals but does not occur naturally in a free state. The growing demand for electric vehicles is fueling the annual growth of the lithium market. The majority of the world's lithium reserves, over 60%, are now found in brines, seawater and geothermal waters, which are also the primary sites for lithium mining. The most favourable method is the utilization of ionic sieves for adsorption, enabling the extraction of lithium from solutions with elevated levels of various components but low lithium concentrations. The process is characterized by its eco-friendly nature and high energy efficiency. Lithium-ion sieves are highly effective adsorbents that selectively adsorb ions. Ion sieves, however, exhibit instability, possess a restricted ion exchange capacity and experience sorbent loss. Numerous research endeavors are underway to tackle this issue, including enhancing the stability of sorbents, augmenting their selectivity and capacity, and reducing the time required for sorption. This is achieved by the utilization of multiple methods, including organo-chemical, synergistic, binding and diverse composites. However, none of these permit the commercialization of lithium adsorption method. Consequently, efforts are underway to devise methods for enhancing lithium adsorption. However, none of them allows for the commercialization of the lithium adsorption technology. Therefore, the task of improving the lithium adsorption process remains a difficult endeavor. Utilizing lithium adsorption recovery could present an alternative method to address future demand, achieve sustainable energy production, safeguard the environment and foster a circular economy.

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#### **CONFLICT OF INTEREST**

The authors declare that there is no conflict of interests regarding the publication of this article.

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