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REVIEW ARTICLE

Methods and recent developments in the field of lithium extraction from water resources

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ABSTRACT

With rapid development in car electronics, hybrid, and electric vehicles, there is an emerging demand for Lithium and its products, such as the carbonate, lithium hydroxide, and mineral concentrates, which capture 80% of the world's demand. The demand for lithium will rise by 60% over the next few years due to electric vehicle use. This requires quick and effective methods of discovery and exploration for new deposits and low-cost, high-resolution technologies for exploration. You can quickly map minerals and obtain information on the quantity and spatial distribution of ore and fossil minerals with hyperspectral imagery. The lithium resource deposit within Salt Lake water, sea, and geothermal water consists of 70-80% of the total and is a superior raw material for lithium extraction. In this respect, there is increasingly more research on joining the industrial extraction of Lithium from water bodies. Recycling lithium-ion batteries is also a means of increasing lithium extraction with a different method. Lithium levels in geothermal waters are confined compared with brines, and not all the methods are effective. The extraction procedures for Lithium from liquid media involve evaporation, extraction with solvents, and the use of membranes, nanofiltration, and adsorption. The most efficient and plausible application of highly functional selective adsorbents with minimal energy usage and safety for the environment. The most investigated are ionic sieves based on manganese LMO. The most chemically stable lithium-ion sieves based on titanium LTO are also considered.

Keywords: lithium recovery; adsorption; ion exchange; geothermal water; bittern

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1. Introduction

Lithium, because of its extremely high theoretical specific capacity (3860 mAh g^{-1}), lower weight (6.94 g mol^{-1}), and lowest redox potential (-3.04 V vs. standard hydrogen electrode) [1-4], is a highly sought-after anode battery material, which has prompted extensive usage across industries. Besides battery usage, lithium and lithium compounds have been used for ceramics, refrigerants, glass, aluminum, rubber catalysts, air conditioning, drugs, and drainage system usage [5]. Lithium has a crustal abundance of about 0.007% [5-7], world deposits of which amount to 14-15 million tons [8, 9]. Deposits of lithium have predominantly been categorized as liquid (salt lake brines, geothermal waters, seawater) or solid, like lithium-ion battery wastage, electronic industries' wastage, etc. [4, 8]. Significant deposits of lithium compounds exist in Chile, Russia, China, Congo, Canada, Afghanistan, and Serbia [10, 11]. Lithium, which does not exist independently, is found in more than 150 minerals and clays [12]. Seas, salt lakes, and geothermal waters together form 70-80% of the world's lithium deposits [5, 10].

Although there is lithium in seawater and ocean water, their concentrations, between 0.1 and 0.2 ppm, respectively, render them commercially unviable for lithium extraction [13-18]. Geothermal waters, with concentrations between 1 and 100 ppm [9, 19], are problematic for lithium processing and manufacturing due to the presence of numerous contaminants along with high concentrations of other metals [20]. Concentrations of lithium in saline lakes are much higher, between 100 and 1000 ppm, yet the high salinity, particularly of magnesium, renders brine treatment highly difficult [21]. Lithium extraction from natural fluids is also problematic due to high concentrations of alkaline and alkaline earth metals [22].

Presently, the world lithium market is based on mineral concentrates, lithium carbonate, and lithium hydroxide, which hold a market share of about 80% [23]. Lithium carbonate is obtained from spodumene ores and salt lake brine treatment [24]. Pegmatite, a characteristic igneous rock, is one of the prominent sources of lithium, which has lithium between 1-4%, out of which about 60-70% of lithium is recovered [24]. Apart from spodumene, some of the lithium-containing available ores based on pegmatite could be utilized for lithium carbonate synthesis [24].

Prior to lithium-containing water solutions being amenable to commercial processing, lithium must first be extracted from ores. Potential lithium-rich water sources would be hydrothermal fluids, salt lake brines, or sea/ocean waters. This review article examines processes for lithium extraction from water solutions with a focus on environmentally friendly processes, high selectivity, low cost of product, and easy technological schemes.

2. Mineralogy and geosciences

World demand for lithium skyrocketed as it has numerous applications for battery technologies and hybrid electric vehicles (EVs). It is one of the cleanest and greenest types of energy sources when it is recovered from mineral ores. As a result, lithium and, by extension, other related minerals for these ores, have garnered tremendous scientific and industrial interest [25].

In order to keep pace with expanding demand, there is also a related demand for exploration methods that are not just effective and accurate, but also for their capacity to rapidly pinpoint new lithium-bearing mineralization sources. Mineral deposit mapping requires efficient exploration techniques, and large regional surveys are feasible nowadays by utilizing satellite and airborne imagery [26].

One of the most encouraging technologies here is hyperspectral imaging (HSI), a young technique that facilitates comprehensive mineral mapping and Earth surface analysis across a variety of space scales [27]. Hyperspectral sensors acquire information across a broad spectrum of wavelengths, providing high-resolution information at a millimeter to a centimeter scale into core samples, hand samples, and surface exposures about the composition and areal distribution of ores and fossil minerals.

Table 1. Lithium resources and reserves in Europe.

Country	Resource Tonnage (t)	Resource Li_2O (t)	Resource Li metal (t)
Czech Republic	695900000.00	2921631.77	1355.637
Germany	35510000.00	124959.69	57.981
Spain	112000000.00	683200.00	317.005
Portugal	10300000.00	103000.00	47.792
Finland	4429000.00	50047.70	23.222

Country	Resource Tonnage (t)	Resource Li_2O (t)	Resource Li metal (t)
France	8500000.00	66300.00	30.763
Austria	10980000.00	109800.00	50.947
England	26666666700.00	16000000.02	7424.000

Table 1. (*Continued*)

It is still a significant challenge to achieve precise geological localization, particularly for inaccessible places or remote areas. A solution to overcome this challenge is by introducing a real-time 3D surface scanning system for characterizing lithium-bearing mineral deposits and revealing compositional heterogeneities of pegmatites [27]. It shows how hyperspectral imagery helps scan, characterize, and discriminate lithium-bearing substances accurately. Besides, hyperspectral photography also holds bright prospects for expanding and adjusting multiple steps of lithium and its compounds product development and production procedures [28].

3. Availability of lithium compounds, their economic importance, and world demand patterns

Over the past decade, market demand for lithium-ion (Li-ion) batteries, automobile battery technologies, and lithium and its various compounds has increased substantially, leading to lithium being nicknamed “new gold” and “white oil” [29]. This is mainly due to lithium’s extensive applications across various industrial sectors [30]. Today, lithium is being utilized in batteries 87%, 4% of ceramic products and glasses, 2% of greases for lubrication, 1% of air purifiers, 1% of casting mold flux powders, 1% of medical, and 4% of other industrial applications [31,32] (Fig. 1). In 2019 alone, global lithium demand reached 58,000 tons a notable 18% increase compared to 2017 levels [33]. Looking ahead, lithium consumption is projected to rise significantly, potentially accounting for up to 60% of total usage in the near future [34-36]. Regarding its sources, approximately 38% of lithium is extracted from mineral ores, while 62% is derived from aqueous brines [24].

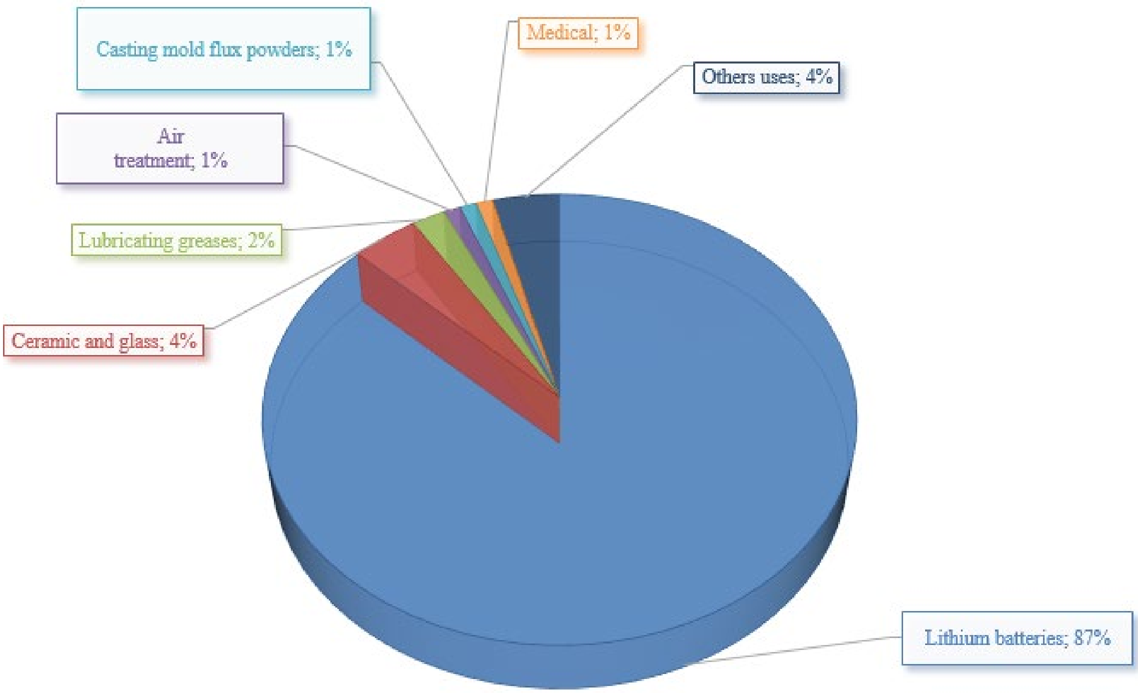

Figure 1. Main uses of lithium are classified according to the lithium metal-related equivalent consumption

Currently, lithium is primarily recovered by two large sources, i.e., brine pools and spodumene-bearing hard rock deposits. There is, however, increasing scientific interest regarding how geothermal waters can act as a complementary source of lithium, potentially contributing around 4-8% of global lithium production [37].

It is intriguing to note that lithium production for hard rock sources is projected to nearly double the output of lithium sourced by deposits of brine [38].

To meet growing demand for lithium globally, researchers are actively developing new, innovative, and green technologies of lithium separation, both for common and recovered feedstocks. One of the brightest prospective replacements is lithium-ion battery recycling. However, some serious challenges are inhibiting its potential, stemming primarily from high production costs, complex separation processes, and relatively low efficiency of the recycling process, only around 5% today [37]. To address both production limitations and environmental concerns regarding lithium mining, a multi-layered approach of conservation is necessary. It would involve, not just more responsibly operated mining, but also the adoption of advanced, effective systems of recycling to optimize resource capture and decrease dependence upon virgin material [7].

4. Extraction of lithium from natural sources

The lithium deposits contain 25% lithium minerals and 65% brines, which are easily found [39]. According to the method of evaporation, lithium production from the brines constitutes the calculation as 30-50%, which is cheaper compared to lithium production from the minerals [4]. It is the process fueled by solar and wind energy until the optimal concentration is achieved in artificial pools [40]. Due to the capability of the brines to provide lithium, the production facility output is restrained by the process that takes one to two years through the evaporation of the brines [1]. According to the project by the EU Commission, the lithium demand is predicted to be multiplied by 18 times by the year 2030 and 60 times by the year 2050 [41].

5. Lithium recovery by the membrane method

The fractionation of lithium by membrane technology is the subject of recent active work. Pressure-driven operations, and especially nanofiltration, have been considered one viable avenue through which lithium can be isolated from intricate aqueous matrices [42-47]. Nanofiltration membranes have been capable of rejecting approximately 26% of lithium, along with more than 85% of magnesium cations, from samples of seawater [48]. In a manner that would yield the ultimate permeate adequately diluted and appropriate for further processing, however, a specific concentration step is generally needed in advance before nanofiltrating [42].

Membrane distillation has also been attempted at lithium production from brine, efficiently differentiating salts found in these liquids [48]. However, the method on its own has had low efficiency in lithium enrichment on separation [42-43]. At the moment, there is a substantial knowledge gap regarding integrated approaches that can produce purified water and recover lithium at the same time. To deal with this, a hybrid process that integrates nanofiltration and membrane distillation is under consideration for the controlled separation of the multivalent cations (e.g., Mg^{2+}, Ca^{2+}) from lithium ions [49]. Several investigations have considered the viability of applying the integrated method towards decreasing the magnesium concentrations in natural brines, like the ones in the salt lakes, in the hope that lithium production can be enhanced. It is common for these brines to have more than 90% divalent cations such as Mg^{2+} and Ca^{2+}, as well as between 42-60% monovalent cations such as K^+, Na^+, and Li^+. By making use of the process that starts with nanofiltration followed by membrane distillation, the Mg/Li ratio can be lowered to under 6, making lithium production from these feedstocks considerably better.

6. Nanofiltration methods

Membrane processes are the most widely used approaches for extracting lithium from seawater and other saline feedstocks [50-51]. Of these, nanofiltration (NF) and electro dialysis are the most common methods, both providing continuous flow and high selectivity toward ions. Electro dialysis works through the use of an electrical field, causing the transportation of ions under the effect of a selective membrane, whereas nanofiltration separates the ions via a size- and charge-based process under the effect of a pressure gradient.

The one-stage nanofiltration process was able to concentrate the lithium in brines yielded through the desalination of seawater by roughly three times, up to as high as 1.5 ppm lithium while rejecting a high number of the divalent impurities such as Ca^{2+} and Mg^{2+} [52-53]. This differential separation is invaluable, as the magnesium and calcium ions tend to create problems in the final lithium recovery process.

Recent studies by Wang et al. [54] have cited nanofiltration as the best lithium recovery process from brines due to the high water flux, high accuracy in ion separation, and high Li^{+}/Mg^{2+} selectivity that the process presents. Much of the success is owing to the polyamide-based commercial nanofiltration membranes that have been designed to have a high preference in retaining the divalent ions, with the monovalent lithium ions passing through. This selectivity is the key factor that ensures the efficiency and quality of lithium recovery from intricate matrices of the brines is enhanced.

7. Solvent Extraction

Solvent extraction is also a popular method of lithium extraction with high-purity products and relatively simple operation procedures [55-56]. Regardless of these merits, the process faces a number of significant challenges. Generation of nuisance emissions is one of the key issues associated with the process, leading to the degradation of equipment as well as environmental hazards. Solvent extraction also demands the use of high amounts of organic solvents and longer periods to carry out the separation effectively. Use of the solvents consequently translates into high amounts of wastewaters, providing disposal and environmental handling challenges. Environmental effects of spent organic solvents remain one of the key detriments, leading to the need for the production of greener, more environmentally friendly alternatives or more efficient waste handling methods.

8. Lithium extraction using lithium-ion sieve adsorbents

Adsorption is one very efficient and selective process that can be utilized for the recovery of lithium from low-concentration aqueous streams. Lithium-ion sieves (LIS) with high ion selectivity and easy applicability have been found as a very promising group of adsorbents that can be utilized for lithium recovery from rich complex brine or wastewater streams [57-59]. Based on manganese oxide (LMO) and titanium oxide (LTO) with high lithium capture capacities and low energy inputs, these sieves are characterized as very environmentally favorable [60-61].

Different lithium manganese oxides (LMOs), like $MnO_2 \cdot 0.3H_2O$, $MnO_2 \cdot 0.5H_2O$, and MnO_2, have shown high lithium adsorption, the highest among them being that of $MnO_2 \cdot 0.5H_2O$ in terms of the Li:Mn molar ratio [62-63]. They have a spinel structure, as, for example, $LiMn_2O_4$, following the stoichiometry of 1:2 Li:Mn, although the stoichiometry is sometimes exceeded by synthesis conditions [64]. But structural integrity is often undermined in spinel LMOs by lithium loss upon regeneration and dissolution of the manganese under process conditions [61].

Adsorption efficiency is largely determined by the morphology, porosity, and crystalline framework of the adsorbent material [57-65]. For example, single-crystal LMO nanotubes treated with $(NH_4)_2S_2O_8$ as the eluent have low solubility of Mn with high lithium recovery efficiency when undergoing the cycles of adsorption-desorption [66]. In one such work conducted with pure LiCl solutions, the lithium extraction efficiency was found to be 89.73%, compared to the adsorbent capacity [67].

Despite their high selectivity, the industrial application of LMO-based sieves is limited by separation challenges and reduced adsorption capacity due to manganese leaching [68]. To improve material stability and performance, the effects of calcination time, temperature, iron doping, and solution parameters (e.g., pH, initial lithium concentration) have been systematically investigated. Iron alloying proved to be particularly effective in reducing manganese dissolution losses to 0.51% compared to 2.48% in unalloyed materials by suppressing disproportionation reactions and strengthening the manganese framework. After four adsorption cycles, undoped sieves exhibited a 50% reduction in capacity, whereas Fe-doped sieves showed only a ~32% decline, indicating superior cyclic stability.

LTO-based lithium-ion sieves are more chemically stable compared to the manganese-based variety [69]. Their ultrafine particulate morphology, however, translates into low fluidity and separation efficiency on industrial scales. Immobilization of LTO powders is possible via polymeric binders like polyvinyl chloride (PVC), polyvinyl alcohol (PVA), polyacrylonitrile (PAN), and chitosan [70-75]. Recent literature by Zhao et al. [76] documented a new porous fiber adsorbent material that was derived with the active phase as H_2TiO_3 (HTO) and structural binder as polysulfone (PSF). High efficiency in powder sorption and structural integrity, as seen with powdered sorbents, was possessed by this polymeric sorption fiber, and this has the potential to be useful in lithium recovery from geothermal water, as well as other aqueous streams.

Despite enhanced mechanical and chemical stability through coating with polymers like polystyrene, PAN, PVC, and PSF [77], the composite adsorbents continue to have low capacities of adsorption as opposed to the powdered versions. Polymer-based filamentous material with high surface area, however, holds high promise, especially when high-affinity polymers are coating the surface, giving an enhanced increase in the adsorption performance as well as structural stability [58, 78]. In the absence of the polymeric coating, however, the stability of the adsorbents in the long run is still inadequate for commercialization.

9. Liquid-liquid extraction

Numerous studies have investigated traditional liquid-liquid extraction processes, including IL-based processes, for the extraction of lithium from brine deposits. Gabra et al. established a laboratory-scale process for the extraction of lithium chloride (LiCl) from model solutions of n-butanol with variable lithium, potassium, calcium, and sodium chloride concentrations. Their approach placed forward a lithium separation process with LiCl purification from distribution coefficients, separation factors, and calculation of the McCabe-Thiele diagram. The process was capable of extracting LiCl up to 99.6% pure [79].

Related work by Bukowski et al. purported the recovery of lithium from brine by alcohols such as isoamyl alcohol and n-butanol, with posterior precipitation of lithium as a lithium-aluminum complex. The extractability efficiency of LiCl from brine by varied alcohols was reported to follow the order 2-ethyl-1,3-hexanediol > isoamyl alcohol > diisopropyl ether > diethyl ether below pH 5.4 by extracting Li rates of 32.8%, 25.2%, 11.4%, and 9.1%, respectively, with co-extraction of Na, Mg, and calcium ions. Binary combinations comprising the above extractants in an equal 1:1 volume ratio were also examined under the above pH. The composition, comprised of 2-ethyl-1,3-hexanediol supplemented by isoamyl alcohol, was found to be extremely effective, achieving up to 90% decrease of the LiCl concentration level with simultaneous reduction of the other present metal ions' co-extraction [80-82].

Extraction of lithium from brine by tributyl phosphate (TBP), the extractant, was investigated by Zhou et al. under three diluent systems, namely, methyl isobutyl ketone (MIBK), kerosene, and 2-octanol [83]. The study also examined the role of $ZnCl_2$, $FeCl_3$, and $CrCl_3$ as the co-extractants to achieve the maximum separation for lithium. The equilibrium studies determined that lithium extraction efficiency was given below: TBP/2-octanol < TBP/kerosene < TBP/MIBK. Strikingly, the efficiency for the TBP/MIBK system was optimal for lithium recovery under the chosen $FeCl_3$ co-extractant [83].

In addition, Baldwin and Seeley also patented the process of lithium recovery from neutral brines through the extractant consisting of β-diketone and trioctylphosphine oxide (TOPO) in benzene [84-85]. The extraction process that followed was also rendered clearer by combined discussion studies by other experts [86].

10. Conclusion

Lithium is a very popular as well as fairly scarce element, found worldwide in more than 150 documented mineral species. Although lithium is prevalent in many raw materials, the element is never found naturally in its elemental form. Due to the growing need for electric cars, the worldwide lithium market has seen very high annual growth that has been very fast-paced. Today, over 60% of the world is found in aqueous environments like seawater, geothermal fluids, and brines, which have become the chief targets in lithium production.

Out of the multiple extraction methods, the application of ionic sieves through the process of selective adsorption has gained significant importance. This process is especially useful in dealing with intricately composed solutions containing low concentrations of lithium but high concentrations of competing cations. This method is characterized by high environmental compatibility as well as high energy efficiency. The lithium-ion sieves act as specific sorbents whose capability is that of preferential uptake of lithium cations. Many factors, however, limit their practical use, including structural instability, low ion exchange capability, and sorbent material losses upon operation.

Current efforts focus on the resolution of these issues through the enhancement of the chemical and physical character of the sorbents. Methods involve increasing the stability of the sorbent, the sorbent selectivity, as well as the sorption volume, and the time of processing. All these are being attempted through several methods, including organ chemical modifications, synergistic effects, the mechanism of binding, and the synthesis of hybrid composite sorbents.

Even with these progressions, none of the existing methods has reached the needed level of performance for widespread commercial use. For this reason, the optimization of lithium adsorption technology is still one major scientific and engineering challenge. Despite this, the viable adaptation of lithium recovery through the process of adsorption can provide a sustainable alternative in accommodating future demand, aiding in the transition towards clean energy, safeguarding the environment, as well as promoting the creation of a circular economy.

Conflict of interest

The authors declare no conflict of interest

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