Review Article

Adsorption Method and Adsorbents for the Recovery of Lithium Compounds from Water Sources

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Abstract - Lithium compounds (carbonate, chloride) are the most widely used materials in glass, ceramics, pharmaceuticals, and electric vehicle batteries. The production of vehicles runs on electricity, and some of the devices having electronic circuits gradually increased the Li demand for the derivatives. The material base is mainly focused on Li production and Li derivatives. Lithium reserves account for 70-80% of Salt Lake waters; marine and geothermal waters account for the total lithium reserves and can be used as the best raw material for Li extraction. Many ways of extracting Li have been investigated using water resources. The adsorption method is the most effective method among those. This article provides information about some sorbents which is used in the process of Li extraction by adsorption method, their merits and demerits, as well as their impact on the environment. The use of the efficient and most promising selective type of sorbents with higher functionality, lower energy consumption, and environmental safety ensures the achievement of high economic performance.

Keywords - Recovery of lithium, Ion exchange, Adsorption, Saline-like, Geothermal water, Brine.

1. Introduction

In the periodic table of chemical elements, lithium is an element that comes in third place after H and He. This has 6.939 ha atomic weight and 0.534 g/cm³ in the literature, such as the conventional method of evaporation precipitation, solvent extraction method [9-11], and adsorption method, new density [1]. It is the lightest metal among metals. Further, among all of the solid elements in the table, it has the highest specific heat capacity [2-4]. The properties of Li compounds ensure their wide application in various fields. Not limited to Lithium-Ion Batteries (LIB), metallurgy, pharmaceuticals, aerospace, ceramics, and glass industries [1].

Lithium is one of the rare and expensive elements; it amounts to 0.007% of the earth's crust [5-7]. The resources of Li are divided into solid and liquid. Seawater brines, lake salts and geothermal waters are categorized under liquid and mineral deposits, waste from Li-ion batteries, the secondary raw materials and the industries related to electronics are categorized under solid [4].

Lithium reserves account for 70-80% of Salt Lake waters, and marine and geothermal waters account for the total lithium

reserves. They can be used as the best raw material for Li extraction [5, 8].

The methods for extracting Li from water are available technologies such as electrochemical methods [12-16] and membrane technology [17-22]. There are key factors that adversely affect lithium recovery. These are the effects of polyvalent cations that pollute water and some of the elements that disrupt the extraction process (Na $^+$ and K $^+$) [23].

The precipitation method commonly used is limited due to the high amount of Li/Mg ions contents because of the time-consuming, complex and primary processes to remove elements present in the seawater [24-26].

Lithium from poly-ionic seawater exhibited some undesirable stability during the solvent extraction process since the organic solvents we use there can cause some corrosion in the experimental equipment and environmental pollution, too [27-28]. Systems of electrochemical extraction of Li, including capacitive deionization and electrodialysis based on electrochemical ion exchange based on an external electric field, lead to high-energy consumption [29-34].



Membrane technologies to extract lithium, including selective electrodialysis, membrane capacitive deionization, nanofiltration, trace ion membranes, and membrane distillation crystallization, are controlled by pressure, electric field and temperature gradient [35-47].

These types of technologies have greater potential for development within the future generation perspective, but their implementation is difficult due to problems associated with the consumption of energy, membrane durability and technology efficiency. The Li/Mg separation technology reaction to precipitate Al and Mg ions with a hydroxide solution is in its infancy up to now [48-49].

Compared with all the technologies discussed above, the adsorption method shows high lithium selectivity, simple and efficient operation, wide application in almost all saline water resources, high economic efficiency, and low environmental impact [50-51]. The adsorption method uses lithium-selective adsorbents to extract lithium from polyionic water sources and then desorb them with other solvents to extract lithium. The main adsorbent requirements include sufficient capacity for adsorption, adequate performance stability and high Li selectivity [52].

Adsorbents used to extract lithium from water sources can be divided into three main groups. They are divided into inorganic, organic, and composite adsorbents [53-57].

The use of organic adsorbents such as polymeric ion exchange resins is limited because it has hazardous feedstocks of organic compounds, and the synthesis processes are more complex. Their price and quantity are important when using inorganic and metal adsorbents, such as naturally available mineral and metal adsorbents. It is difficult to use saltwater sources in various fields. At present, metal-based adsorbents are becoming the main technology for the most massive studies of lithium extraction. The advantages of metal Li adsorbents are the highest Li retention capacity, low feedstock losses during the regeneration process, high percentage of efficiency, relatively low consumption of power, and excellent Li selectivity that make them promising environmentally friendly ways to recover Li from water sources [58-59].

Even if numerous adsorption techniques are used to extract Li from water sources, it is advisable to understand the benefits and drawbacks of each technique in order to choose the most effective one for Li extraction. However, we could not locate any pertinent analyses of the adsorption methods that explicitly stated the most effective technique for doing so. Therefore, there is a need to find the appropriate analysis to determine the efficient and effective adsorption method. We attempted to provide information about the many organic, inorganic, combined and other adsorbent types employed in

the process of using the adsorption method to extract Li from water sources in this review paper. Future researchers can choose an adsorption technique more effectively and spend less time looking for the right one.

2. Demand for Lithium and its Economic Prospects

According to the forecasts of world scientists, the global demand increases significantly in future for lithium, and the deficit is also expected to rise [5, 60]. By 2025, it will triple due to increased production of electric vehicles and electrical appliances, and it will be difficult to satisfy the need for lithium on Earth [61]. According to other estimates, the demand will exceed around 2,000,000 MT in 2030 [62].

As mentioned earlier, lithium has many end uses other than batteries. The metal consumption in the world is associated with the Li battery sector: thirty five percent of the production of Li is utilized for batteries. The production of ceramics and glass also requires resources of around 32%. Lubricants and greases accounted for around 9%, and air treatment and continuous casting accounted for 5%. Polymer production utilizes 4%. Sanitation, construction, organic synthesis, pharmaceuticals, alkyd resins and alloys account for around 9%, as shown in Fig. 1 [63, 64].

Without efficient technologies to produce this precious metal using water sources as raw material, it will be difficult to meet Li demand globally. An important factor is investing in research and innovation to obtain lithium and its compounds and new technology development, ensuring a stable supply of raw materials. Increased investment from automakers and electronics companies increases the demand for new offerings entering the market. Therefore, it is important and necessary to find an additional alternative to fulfil the demand for Li in all types of industries [65].

Conducted literature materials show that the adsorption method of extracting Li is the most promising and trusted method to obtain Li from water sources in terms of manufacturability, resource and energy savings, economic efficiency and environmental friendliness.

3. Lithium Recovery from Liquid Sources

The ocean will serve as a promising and important resource for Li to cater to global Li demand [66]. The world reserve in total of lithium in the oceans is 2.6 x 10¹¹ tons. [67]. In some countries, Li extraction from hydro-mineral sources was done in semi-industrial scale salt lakes in the USA [68-70] and geothermal waters in Japan and Israel [71, 72]. The extraction of Li from seawater has become an integral part of the chemical industry [73]. The Li extraction from water sources (geothermal and saline seawater) is explored with great interest in China, Bulgaria, Germany, and Korea [74].

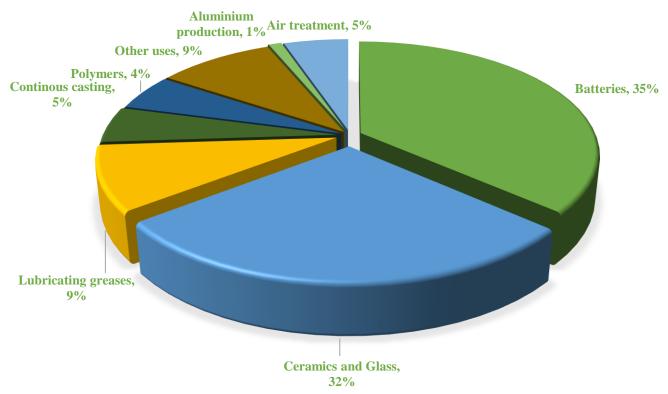


Fig. 1 Application of metallic lithium and lithium compounds throughout the world in percentage [63, 64]

Li extracted from the seawater is mainly through the chemical precipitation, adsorption ion exchange and extraction processes. In connection with the development of chemical technology, various methods are used to extract Li from seawater, including the L-L extraction method and the membrane method, which also belongs to.

However, among the above methods, the adsorption method is the most rapidly developing and widely used; a brief analytical summary is given in Table 1 [74].

The Li extraction from water sources (seawater) is the main potential resource available now to extract Li. It is advisable to consider the following when extracting Li from water sources for economic advantages.

Those are attention to the stability of the soil of ponds intended for the collection of seawater and their evaporation under the influence of sunlight, the Li concentration in seawater, alkaline earth elements, the alkali metals ratio, the complexity of chemical phases [84].

Table 1. Extraction of lithium from seawater with sorption flow mechanism [77]

Process	Chemical	Reference	
Adsorption method	λ-Manganese Oxide adsorbent	[75]	
	Aluminium Hydroxide layer	[76]	
	(HMnO) ion-sieve (microporous)	[77]	
	λ - Manganese Oxide	[78]	
	Manganese Oxide	[79]	
	HMnO	[80]	
	Nanostructure Manganese Oxide ion-sieve	[81]	
	Manganese Oxide adsorbent	[82]	
	$H_{1.6}Mn_{1.6}O_4$	[83]	

Table 2. Compositions of various global lithium brine [84]

Loodin		Composition (wt. %)							
Location	Na	K	Li	В	Cl	Mg	Ca	SO ₄	
Bonneville, USA	8.30	0.50	0.01	0.01	14.0	0.40	0.01	-	
Great Salt Lake, USA	7.00	0.40	0.01	0.01	14.0	0.80	1.50	-	
Clayton Valley, USA	4.69	0.40	0.02	0.05	7.26	0.02	0.05	0.34	
Hombre Muerto, Argentina	10.0	0.70	0.10	-	16.0	0.09	0.08	1.00	
Salar de Atacama, Chile	9.10	2.36	0.16	0.04	18.9	0.97	0.05	1.59	
Dead Sea, Israel	3.01	0.56	0.001	0.003	16.1	3.09	1.29	0.06	
Sua Pan, India	6.00	0.20	0.002	-	7.09	-	-	0.83	
Salar de Uyuni, Bolivia	7.06	1.17	0.03	0.07	5.0	0.65	0.03	-	
Taijinaier, China	5.63	0.44	0.31	-	13.4	2.02	0.02	3.41	
Zabuye, China	7.29	1.66	0.05	-	9.53	0.003	0.01	-	

Based on scientific research conducted by world scientists, it can be seen that lithium compounds mainly contain dissolved sulfates or chlorides salts, or carbonates and hydroxides of metals.

The concentration of Li in salt water in the world varies from 10-1500 ppm. B+, Na+, K+, Mg2+, and Ca2+ concentrations also vary. Based on the salt composition, the salt solution was prepared artificially, which contains Li in moderate concentrations, as shown in Table 1.

The salt concentration was taken into account and normalized according to the ratio with lithium [84].

It should be noted that the more complex the mineralogical composition of seawater, the more complicated way of Li extraction from it, which complicates the processing technology. Therefore, it is important and desirable to pre-evaporate seawater in the sun [59].

In addition, it should be taken into account that the compositional concentration of seawater may increase or decrease depending on the season. Studies show that the Li concentration in seawater is comparatively high, mainly in the summer months [22].

The Li extraction from the seawater is determined by the volume, concentration, and local brine processing technology [85].

4. The Adsorption Process of Li Extraction

Adsorption means the ability of an adsorbate to be absorbed by an adsorbent. It is a separation method well suited for the removal of dilute contaminants as well as some valuable metals recovery from the water sources. In this Li extraction process, the adsorbent's particle size is controlled by pressure drop, which is a hydrodynamic phenomenon [86].

Van der Waals force is one of the main parts of the adsorption related to the physical nature and the force. This kind of adsorption is comparatively weak and does not depend on the surface reactions because they are not strong enough to significantly affect the molecule's reactivity. The second part of adsorption is much stronger, called chemisorption. Adsorbed molecules are available on the surface, and the same type of attractive force occurs between the bonded atoms in the molecules. Ten to one hundred kcal/mole of heat is released, compared to physical adsorption, which is <5 kcal/mole [87].

So many adsorbents are used in Li extraction from salt lakes, seawater and geothermal water. Inorganic, organic, and other types of sorbents show very good selectivity during the Li extraction from seawater [53, 88-93].

5. Organic Sorbents

The use of strongly acidic cation exchange resins during the Li extraction from saltwater, geothermal, and Li source solutions has been studied since 1970 [94, 95-99]. Table 3. Materials used in Lithium-ion batteries and adsorbents [108]

Component	The weight Percentage of the Total Weight of the Battery	Material Name	Li Structure	Properties and Advantages
Cathode	39.1±1.1	LiCoO ₂	Layered	Higher structural stability, cycled >500 times with 80-90% capacity retention.
		LiNiO ₂	Layered	Having a high energy density (20% higher by weight and 15% higher by volume), it is cheap; however, it is less stable and organized than LiCoO ₂ .
		LiMn ₂ O ₄	Spinel	Ecological, attractive and economic reasons; discharges ~3 V
		LiCo _{1/3} Ni _{1/3} Mn _{1/3} O	Layered/Spinel	Safe, high capacity with thermal and structural stability.
		Li ₂ FePO ₄ F	Olivine	-
		LiFePO ₄	Olivine	Biomedical applications, cheap and safety
		Li(Li _a Ni _x Mn _y Co _z)O ₂	Layered/Spinel	-
Anode		С	Graphite	Availability and cheap. Reversibly absorb and release a significant amount of Li (Li:C = 1:6)
		Hard C	Microspheres	-

AmberSepTM G26 H, which is a resin with strong acid cation exchangeability, can be utilized to extract Li from water sources. Li has a much lower affinity for resins (ion exchange) than the cations; conventional resins are not suitable for the process of Li extraction [98, 99]. This resin type is effectively used in the selective extraction of Li only in combination with inorganic lithium-selective sorbents [100, 101-104].

Much research has been done to explore organic polymers' extraction and applications, specifically Li extraction over some metal ions. Introducing reagents into steric structures of a certain size by using an ion-imprinting process, which allows Li ions to enter rather than competing ions due to better metal selectivity.

A nanocomposite sorbent that consists of Li-containing polymer resins and molecular sieve nanoparticles for selective Li extraction from geothermal waters [105, 106]. However, such sorbents have not yet been used in practice due to their low selectivity [100].

6. Inorganic Ion Exchange Adsorbents

Inorganic solids such as aluminium hydroxide $Al(OH)_3$, crystalline aluminium oxide (AlO_x) , titanium oxide (TiO_x) and manganese oxide (MnO_x) show selectivity for Li [107].

Most Li sorbents are recommended to extract Li from brines and are applied in the Li batteries as cathode materials (Table 3) [108]. Dow Chemical was one of the first companies

to use microcrystalline Al(OH)₃ in the anion exchange resins during the Li extraction from salt water [95]. The use of sorbents MnO_x during the Li extraction from seawater was recommended by Ooi and others [77, 109].

Titanium oxides (TiO_x) are widely used in Li-ion batteries. Titanium oxides have also been proposed as sorbents for Li extraction from geothermal and saline waters [96, 110-113]. The properties of inorganic crystalline sorbents are being made to utilize these solid sorbents in technological systems to extract Li from industrial fluids and natural fluids, including geothermal waters [114].

When choosing sorbents to extract Li from water sources by applying the adsorption method, their metallic crystal structure is important. The main reason is that the exchange sites of cations are protected within the crystalline matrix and act as the molecular sieve for this process. Small Li ions can penetrate the internal ion exchange centres through the molecular sieve, while large cations cannot penetrate the internal centres. Feng and his colleagues showed that the main reaction of lithium MnO_x sorption is ion exchange rather than redox reactions [115-116].

As a result of the studies, it became known that the property of selective adsorption of MnO_x , Li ions are allowed to enter the crystal lattice, but it has a crystalline structure that acts as the molecular sieve, sterically preventing the penetration of other ions [79, 115-117].

Many scientists noted that the selective adsorption capacity of TiO_x and Al(OH)₃ crystals is very close and similar to the adsorption selectivity of MnO_x [96, 111-124].

7. Sorbents Based on Aluminium

The main reasons for the industrial interest in Al-based sorbents are that they are environmentally friendly, inexpensive, and very little secondary waste is generated during their use [125]. During the process of Li extraction, the counter-current alumina pellets are in contact with the brine. Precipitation of AlCl₃, LiOH and Al(OH)₃ requires precise and suitable mixing. Then, the adsorbed material is washed with the dilute LiCl solution and concentrated by solar evaporation [126].

Al-based sorbents [LiAl₂(OH)₆]⁺Cl⁻·nH₂O are called Li-Al layered with double hydroxide chlorides and have the hexagonal shape in which aluminium cations occupy 2/3 of octahedral positions, hydroxyl anions occupy between the layers, and lithium cations occupy the remaining octahedral positions [127].

In this structure, the Aluminium-based sorbent layer is separated by the balanced molecular charges; therefore, the gap between the layers is extremely small to penetrate any other ions except Li-ion. During the extraction process of Li, the Li ions are filled with free octahedral sites [124]:

$xLiCl\ (brine)+(1-x)$ $LiCl.mAl(OH)\cdot 3nH_2O \rightarrow LiCl.mAl(OH)_3\cdot nH_2O$

The concentration of Li ions in sea salt water can reach 360 mg/L where the sorbent is saturated, and it cannot additionally absorb any Li⁺. In the process of desorption, Li

ions are transported along the chloride cycle, where a low concentration of Cl⁻ in the sorbent interlayers leads to charge balance disturbance and a change in the direction of Li diffusion [124].

Unlike sorbents based on Ti and Mn, the sorbent regeneration based on aluminium does not lead to the formation of a secondary type of waste; perhaps the LiCl solvent is important to maintain chemical stability, prevent the formation of nonreactive gypsum, and allow the sorbent to be reused [124].

Despite recent interest in the use of double hydroxide chlorides with lithium and alumina layers, Li recovery focuses on recovery from brines by nucleation of double hydroxide chlorides with lithium and alumina layers, with little regard to reusability and chemical stability sorbent [124].

8. Sorbent Based on Manganese Oxides

MnO_x is used in Li extraction from liquid sources with spinel structures [115, 128]. In these structures, octahedral pores are larger than tetrahedral ones. Cavity MnO_x crystals can enclose octahedral MnO₆ units with common corners or edges [129]. In the process of obtaining porous MnO_x crystals, organic base ions and metal ions can be utilized as a template for constant control of the size of pores in the course of various types of syntheses [128].

Manganese oxides have an ion-filtering ability and belong to the spinel type with a pore radius of 0.7 Å, which makes them selective concerning Li adsorption [128]. Materials widely used as MnO_x templates for Li adsorption include Mg and Li. However, other types of metals also can be used here [111, 113, 116, 130, 131].

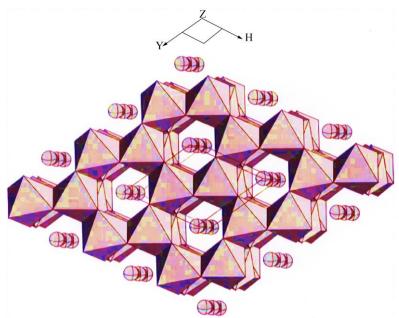


Fig. 2 Diagram of Al(OH)₃ layer with the octahedral holes through which Li can penetrate [118]

Some researchers studied HMnO(Mg) in adsorption properties to extract Li from brines [109]. HMnO(Mg) has a high selectivity for Li in monovalent and divalent cations, with the order of selectivity found to be Mg<Ca<Na=K<< Li at the pH of 8. This sorbent has HMnO(Sr), HMnO(Ca), and HMnO(Ba), which shows selectivity and limited capacity. The Li sorption rate increases with the increase in pH and adsorption temperature. The maximum level of adsorbed Li from seawater reaches 8.5 mg of Li/g of HMnO (Mg). The adsorption capacity of Li is decreasing gradually with repeated adsorption cycles, therefore, after 4 applications, the adsorption capacity of Li HMnO (Mg) drops to 60% of the initial value [77, 109].

Li adsorption in the geothermal water in the form of granular and powdered forms of the λ -MnO₂ is created from Li manganese dioxide with a spinel structure [132]. The MnO_x sorbent is a part of Li-extracting technology from geothermal water. Pre-treatment to remove divalent cations and silica was considered important to get rid of the MnO_x sorbent coating from affecting Li sorption [133].

Scientific studies have shown that MnO_x crystals exhibit the best lithium selectivity compared to monovalent and divalent cations prepared with magnesium or lithium [134-136]. Many varieties of manganese oxide have been synthesized and experimented with for Li adsorption in various conditions. Due to several modifications, the sorption capacity of lithium has been increased [79] and succeeded in synthesizing Li_{1.6}Mn_{1.6}O₄, dissolving Li⁺ in acid, and preparing a MnO₂·0.5H₂O ion-exchange sieve at the pH of 10 with 10 mg/g ion-exchange capacity. In the next steps, the sorption properties of lithium-antimony oxides are addedmanganese formed by the interaction of antimony (V) chlorides and the aqueous solution of manganese (II) with Li hydroxide; modifications increase the capacity of Li exchange to 38.9 mg/g [137].

In addition, at the pH of 7.2, the iron-doped manganese oxide with a capacity of sorption of 0.028 g/g was obtained from another research [138], and up to 28.2 mg/g Li absorption with a spinel structure was obtained from tartaric acid form nano-Li_{1.33}Mn_{1.67}O₄. This made it possible to use artificial seawater to extract lithium at least 5 times [139].

Manganese oxide sorbents found that the maximum capacity of $Li_{1.33}Mn_{1.67}O_4$ is around 55 mg/g; however, in most cases, this value ranges from 20-40 mg/g [96]. Another study has shown that with an increase in pH to the value of 10, the sorption of Li on MnO_x can be increased from about 6-25 mg [139]. The application of manganese oxide in complex solutions results in less than synthetic solutions. Some of the synthesized MnO_x include $Li_{1.66}Mn_{1.66}O_4$, $LiMn_2O_4$, and $Li_4Mn_5O_{12}$. They identified that the powdered form of $Li_4Mn_5O_{12}$ worked best at low Lithium concentrations. However, the maximum adsorption capacity of this

composition did not exceed 8.98 mg/g during the same study with real geothermal brines [140].

Manganese oxide ion sieves have high Li ion selectivity and also a high capacity of ion exchange in the Li extraction from various water sources, but they identified that the dissolution state of sorbent used in the experiment in acid regeneration deteriorates the capacity of ion exchange, which leads to process failure. The instability of manganese oxide in acidic conditions is the limiting factor to utilizing MnO_x as a sorbent, and research is currently underway on alternative elements that do not disturb the crystal structure of MnO_x [141]. The industrial use of manganese oxide sorbent is often aimed at increasing the stability of sorbents and using regenerating solutions that do not destroy their structure. Lilac Solutions is an active marketing form of sorbent to recover Li from brines [142] and is evaluated and tested for use in geothermal waters [114].

9. Sorbent Based on Titanium Oxides

Crystalline titanium oxides (TiO_x) are used in some batteries, which act as a molecular sieve or the ion exchange adsorbent for Li [110, 143]. Titanium oxide spinel structures operate on the same principle as MnO_x spinel pore in the crystal structure and were determined to find the specificity and efficiency of molecular sieve [113]. The synthesis of titanium oxide sorbents with 37 mg/g as the maximum capacity [121]. Scientific experiments show that the efficiency of titanium oxides in the Li-ion sorption from solutions is lower than that of manganese oxide [96, 111, 112, 143]. Spinel TiO_x has a relatively high level of acid resistance and exhibits energy efficiency when alternating sorption and desorption processes [96]. Titanium oxides have many advantages over MnO_x, which is an environmentally friendly sorbent, too [96, 113].

The Li-ion sorption from Salar de Uyuni salt water in Bolivia by the layered H_2TiO_3 obtained from the Li_2TiO_3 . The research found that the H_2TiO_3 has the highest Li selectivity (Li⁺, K⁺, Na⁺, Mg²⁺, Ca²⁺), (pH - 6.5) the capacity of adsorption was 0.0326 g/g when they applied molecular sieve method [112, 144, 145].

Titanium oxides are being studied at a fundamental level in laboratories. So many scientific articles have tested the effectiveness of titanium oxide in complex brines [96, 112, 113, 143]. However, TiOx sorbents' processes to extract lithium from water sources have been patented [146, 147].

In 1989, Onodera and his research group succeeded in developing the first method for obtaining lithium by acid treatment of Li₂TiO₃ using a titanium-based ion exchanger [148]. It can form a reaction of solid phase involving Li₂CO₃ and TiO₆ subsequent crystallization under high temperatures [149].

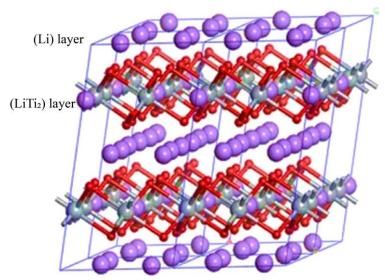


Fig. 3 Crystalline structure of Li₂TiO₃ (Li, Ti and O are shown in purple, grey and red spheres) [83]

In the monoclinic crystal structure of lithium and titanium, 2/3 of the lithium ions occupy octahedral positions between the octahedral TiO₆ layers, and the remaining 33% of the Li ions are located inside the octahedral TiO₆ layers (Fig. 3) [150 -152].

During Li desorption, when Hydrogen ions replaced the Li ions in an octahedral structure, the OH groups and TiO_6 groups located inside the octahedral layers form molecular hydrogen bonds [151, 152]. The preparation of sorbents from titanium oxides for Li extraction from water sources has been the main focus of researchers in the last decade. This is mainly because lithium is very convenient to extract from unconventional resources such as process fluids [153-157]. Titanium oxide sorbents have several advantages over other metal-based sorbents, where they give ease of manufacture and a low amount of loss in the weak acids condition.

10. Combination of Adsorptive Separation

When Asanic-containing geothermal water was fed into the MnO₂-containing column, suppression of Li⁺ adsorption and breakdown of MnO₂ were observed. Magnetite (Fe₃O₄) were used to remove Asanic from geothermal water; the breakdown of MnO₂ was considerably reduced during Li⁺ adsorption, while a minor quantity of Asanic remained [158].

11. Other Types of Metal Oxides as Sorbent

In addition to the sorbents studied above, oxides of other metals, for example, HSbO₃·12H₂O [159-160], H₈Nb₂₂O₅₉ 8H₂O [161], including HTaO₃ [162] and how these metal compounds will form an ion exchange when Li is a presence there. Their selectivity of Li is reduced due to K⁺ or Na⁺ presence and competing with ions; therefore, they cannot be compared with other metal-based sorbents [165]. Previous studies have shown that the above sorbents are reinforced with

Ti or Sn, which is a tetravalent metal that can be effectively prepared with sorbents with a crystal structure and used to increase the separation factor of Li [166-167]. Nevertheless, due to the complex synthesis process, the metal oxide dissolution and the high cost of reagents were the limiting factors for industrialization.

12. Conclusion

So many sorbents have the same type of defects. These include low lithium-ion absorption index, poor acid resistance, and loss of sorbents after several applications. Titanium oxides are the most effective sorbents, which have a 28 mg/g capacity compared to other sorbents. In addition, it is resistant to acids and shows energy savings when switching from the adsorption to the desorption process. It has several advantages over manganese oxides, including easier production, environmentally friendly and less wastage in use. Many types of research have been conducted to strengthen the sorbent's stability, increase the ability to absorb Li ions and selectivity and reduce the sorption time. However, not all of this allows the use of the lithium adsorption method on an industrial scale. For this reason, developing and improving Li extraction from water sources by adsorption method remains difficult.

Soon, lithium production by the adsorption method may become the most efficient and alternative option for meeting the demand for lithium, primarily due to energy stability, environmental friendliness, and closed-loop economy.

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