Lithium Recovery from Water Resources by Ion Exchange and Sorption Method

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(Received on 15th August 2020, accepted in revised form 28th April 2021)

Summary: Demand to lithium rising swiftly as increasing due to its rapidly increasing dosages diverse applications such as rechargeable batteries, light aircraft alloys, and nuclear fusion. Lithium demand is expected to triple by 2025 driven by battery applications, specifically electric vehicles. To ensure the growing consumption of lithium, it is necessary to increase the production of lithium from different resources. Natural lithium resources mainly associate within granite pegmatite type deposit (spodumene and petalite ores), salt lake brines, seawater, and geothermal water. Among them, the reserves of lithium resources in salt lake brine, seawater, and geothermal water are in 70–80% of the total, which are excellent raw materials for lithium extraction. Compared to the minerals, the extraction of lithium from water resources is promising because this aqueous lithium recovery is more abundant, more environmentally friendly, and cost-effective. There are many ways to recover lithium from water resources. Among existing methods, the adsorption method is more promising on the way of manufacture. Therefore, the important progress on ion-exchange adsorption methods for lithium recovery from water resources searched ways, were summarized in detail, and the new trends in the future were also carried out.

Key words: Lithium recovery, Adsorption, Ion exchange, Bittern.

Introduction

Lithium and its compounds are widely used in manufactured glass, batteries, ceramics, greases, refrigerants, chemical reagents, and other industries [1-4]. The lithium source in the earth's crust is very limited [2]. That is why the development of an effective method for extracting lithium from salt lakes, seawater, and geothermal waters is of great importance and interest. The reserve of lithium in the world is about 14 million tons (Mt) [4], from them 70%–80% is conserved in salt lake brine, geothermal water, and seawater. In recent years, more and more researches turn their attention to the seawater containing about 2600 billion tons of lithium, which is about 15,000 times the amount of land [1, 5-8].

Lithium is being the 25th more abundant element on the Earth [9]. Lithium is found in more than 150 minerals, in clays, in many continental brines, geothermal waters, and in seawater. The concentration of lithium in seawater is very low, averaging 0.17 ppm [10, 11]. Around the world concentrations of lithium in geothermal waters varying from 1 to 100 ppm [12, 13]. Although lithium deposits in all of the above forms are widespread throughout the world, very few are large and/or concentrated enough for potential exploitation. Several high-grade lithium minerals and brines are the only ongoing commercial lithium recovery operations [6, 10, 12].

Considerably accordingly to the source, lithium resources and reserves different, we can see that lithium resources in brine are much larger than those in hard rock [8, 12, 13, 14]. Estimated minimum and maximum resources for hard rock lithium at 12.8 Mt and 30.7 Mt respectively; while brine deposits were reported as 21.3 Mt and 65.3 Mt, respectively for minimum and maximum estimates [10].

The coming years expecting increased demand for lithium since different types of lithium batteries are the most promising candidates to power electric or hybrid vehicles [15, 16]. These batteries include both existing technologies, such as lithium-ion, as well as emerging battery technologies such as lithium-air or lithium-sulfur [17].

In the next 5 years, the demand for lithium is forecast to increase by ~60% from 102,000 t to 162,000 t of lithium carbonate equivalent, batteries application taking a large percentage (40,000 t) of this growth [18, 19]. The current resource of lithium in continental/salar brines is approximately 52.3 million tons of lithium equivalents, mostly in Chile, Argentina, and Bolivia, of which 23.2 million tons is recoverable [20]. On the other side, lithium from mineral resources is 8.8 million tons, where large deposits are located in the USA, Russia, and China.

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Lithium reserves and recoverable resources were estimated as 29.79 Mt of Li [21].

Currently, lithium is relatively inexpensive (about 15,000US$ for a ton of battery-grade Li_2CO_3), but its price increases with demand [22]. Lithium prices since 2016 have increased around 300% in China with contract prices for existing producers rising to over US$ 16,000/t.

In connection with the depletion of lithium ores, recent studies have highlighted the need to extract lithium from brine, geothermal water, and seawater. Lithium production from water resources has now become more important due to its extensive availability, ease of the process, and cost-effectiveness compared to its production from other resources [2].

Various methods for lithium recovery from brines, seawater and geothermal water have been reported [22]: including precipitation, solvent extraction, selective membrane separation, liquid-liquid extraction, ion exchange adsorption, electrodialysis and so on [23-29]. Among these strategies, the most attention was drawn to the methods of ion-exchange adsorption based on lithium-ion sieves due to their high selectivity for lithium-ion and good recycling properties [30-32]. In terms of cost and efficiency, ion exchange adsorption is an important method for extracting lithium ions from solutions [33].

Various Li adsorbent materials, including clay minerals, metal oxides, zirconium phosphate, and silicotitanates are all previously reported for lithium removal. The researchers were mainly focused on aluminum salt adsorbents [34-35], titanium lithium-ion sieves [36-40] and manganese lithium-ion sieves [41-50].

However, quantitative correlations for competing for ion extractions, which are crucial in industrial design, have not been reported.

This review focuses on the extraction of lithium from brine, bittern, sea, and geothermal waters by ion-exchange adsorption to extract lithium from water resources, making it possible to compare different sorbents that are different. Also, scientists around the world have a goal to find a way to extract lithium from water resources, which is highly selective, economical, environmentally friendly, easy to process, and time-saving.

Resources of Lithium

The average lithium content in the earth's crust is estimated at 0.007% [51]. Lithium is not found freely in nature but is found in combination with small amounts in almost all igneous rocks and the waters of many mineral springs, in seawater, and the ocean [51, 52]. Lithium is produced from a variety of natural sources, for example, minerals such as spodumene, clays such as hectorite, salt lakes, underground brine reservoirs, etc. Lithium is a minor component of igneous rocks, primarily granite. Of the approximately 20 minerals known to contain lithium, only four, i.e., Lepidolite ($KLi_{1.5}Al_{1.5}[Si_3O_{10}][E,O]_2$), Spodumene ($LiO_2 \cdot Al_2O_3 \cdot 4SiO_2$), Petalite ($LiO_2 \cdot Al_2O_3 \cdot 8SiO_2$), and Amblygonite ($LiAl[PO_4][OH,F]$) are known to occur in quantities sufficient for commercial interests, as well as industrial significance [51-55]. Mineral spodumene ($LiAlSi_2O_6$) is the most important industrial ore mineral of lithium [56-58]. Other minerals are lepidolite, amblygonite, and zinnwaldite and eucryptite. Zinnwaldite-an impure form of lepidolite with higher contents of FeO (up to 11.5% Fe as FeO) and MnO (3,2%) [59]. Pegmatites contain recoverable amounts of lithium, tin, tantalum, niobium, beryllium, and other elements. The theoretical lithium content of these minerals ranges from 3% to 5.53%, but most deposits have about 0.5-2% Li and pegmatite-containing ores, which are often exploited in <1% Li [60]. Spodumene is the main lithium mineral mined.

Mainly lithium is extracted from brine, or seawater has a high concentration of lithium carbonate. The brine found in the earth's crust is called continental brine/subsurface brines are the main source of lithium production (lithium carbonate). Lithium is found in significant amounts in geothermal waters as well as in petroleum brines. These sources are seawater and brine considered to be less expensive than the extraction from rocks such as lepidolite, spodumene, amblygonite, and tenorite lithium-containing minerals.

Seawater contains about 0.1-0.2 mg/L Li [61]. The total amount of lithium metal in seawater (worldwide) is estimated at ~230 Gt [3]. Sources of brine include lithium found in salt deposits of the lakes, salars, oil fields brine, and geothermal brines. Oil-field brines are underground brine tanks, which are located with oil. Geothermal brines are underground brines, heated by natural means, for example, in the California Salton Sea. Lithium containing brines make up 66% of the world's lithium resources, pegmatites-26%, sedimentary rocks-8% [12, 62].

Brines and high-grade lithium ores are current sources for all commercial lithium production. The distribution of lithium has spread over various resources. Continental brine is the largest resource (59%) for lithium deposits, and then hard rock shows 25%. Almost 70% of the world's lithium deposits are concentrated in the ABC region of South America (Argentina, Bolivia, and Chile), the largest known lithium deposits [2, 63]. Australia and Chile are the leading producers and exporters of lithium ore materials. China and Chile have significant resources of lithium ore. Canada, Congo (Kinshasa), Russia, and Serbia have lithium resources of about 1 million tons each, and the same reserve for Brazil is a total of 180,000 tons [64].

Table-1 provides detailed information on the geographical availability of different lithium resources compared to lithium and their location.

The concentration of lithium in the salars of Chile, Argentina, and Bolivia are in the range of 0.04–0.16%. According to [20] lithium resource is estimated at 64 Mt. Chile has the world's largest brine resource (7.5 Mt, 1500–2700 mg/L Li) containing lithium, followed by Bolivia (resource: 9.0 Mt with 532 mg/L Li) and Argentina (resource: 2.6 Mt, 400-700 mg/L Li), and these three countries account for almost 80% of the world's brine reserves [3, 63, 72].

Production of lithium rocks has begun with lithium minerals (1899) in the United States [73]. Since the first production of lithium from brines at Searles Lake, the USA in 1936, brines have been used mainly in South America and China. The largest lithium producer in the world is Chile, where lithium is extracted from salt brine in Atacama Salt Flat. Lithium is also produced from brines in salt lakes in Tibet and Qinghai in China and Nevada in the United States. Several new facilities (by 2013) are at different stages of exploration/exploitation of the brine source: one in China, six in Argentina, three in Chile, and one in Bolivia [74].

Currently, 8% of lithium is obtained from salt lake brines and the sea by sedimentation. A significant number of lithium compounds and ore concentrates are also produced in Australia, Zimbabwe, Canada, Portugal, and Russia. Australia currently produces lithium concentrate from spodumene in mines in Mt Catlin, Western Australia. At 160,000 t/year, concentrate produced in Western Australia is processed to 16,000 t/year of lithium carbonate in its Chinese plant. Lithium carbonate is mainly produced from ores and brines, and production rates are often expressed in the equivalent of lithium carbonate.

Lithium Extraction from Brines/Seawater/Bittern

To meet the growing demand for lithium, increasing attention is being paid to brines and bitterness. Table-2 prepare a summary of works recently carried out for the extraction of lithium from seawater/brine/bitterns. The process of production of brine lithium is 30-50% cheaper than that of mined ores [75]. As mentioned earlier, lithium carbonate is obtained from brines by evaporative concentration and refining. First, the brine is concentrated by solar evaporation during the year in a pond for the crystallization of sodium, potassium, and magnesium chlorides. In the refining process, calcium carbonate is fried and then added to the LiCl solution to remove $Mg(OH)_2$.

Table-1: World lithium resources and their lithium contents.

Resources	Li content % (w/w)	Location of the largest amount	References
Pegmatites			
Spodumene	1.9–3.3	Australia	[65]
Lepidolite	1.53–3.6	Zimbabwe	[66]
Zabuyelite	17–18.75	China	
Petalite	1.6–2.1	Zimbabwe	
Amblygonite	3.5–4.2%	Canada, Brazil, Surinam	
Eucryptite	2.34	Zimbabwe	
Sedimentary rocks			
Smectite (hectorite)	0.27–0.7	Hector, California. and Nevada, US	[67]
Lacustrine evaporites	1.8% lithium oxide	Jadar Valley, Serbia	
Brine			
Continental	<2700 mg/L (with K, B)	Chile	[68]
	~532 mg/L	Bolivia	[69]
Geothermal	<400 mg/L (with Mn and Zn)	United States	[70]
Oil field	<700 mg/L (with Br)	United States	[71]
Sea water	0.18 mg/L	Chile, Argentina, China and Tibet	
Secondary resource			
Spent LIBs	2–7%	–	[45]

Table-2: Lithium extraction from seawater, brines, and bitterns by adsorption process.

Source/Raw material	Adsorbent used	Conditions	Adsorption/Remarks	Product	Ref.
Seawater	$H_{1.6}Mn_{1.6}O_4$	Adsorbent: 200 mg, sea water: 50 L, 4 weeks; desorption by 0.5 M HCl, 1 day	Max. uptake: 40 mg Li/g adsorbent	–	[44]
Seawater (Li 0.17 mg/L)	Spinel type Mn-oxide	30 °C, 15 days	<90% Li, Li uptake: 10.6 mg/g adsorbent	LiCl	[77]
Seawater (Li 0.15 mg/L)	λ-MnO_2 (granulated)	150 days	Recovery-264 g LiCl in 791 g dried precipitated salt (816 m^3 seawater)	LiCl	[78]
Artificial seawater (Li 0.2 mg/L, 8.01 pH)	Ion-sieve type Mn-oxide spinels: $HMg_{0.5}Mn_{1.5}O_4$(I) $HZn_{0.5}Mn_{1.5}O_4$ (II)	Adsorption at 0.4 M HCl, 5 days	Adsorption: 88% Li by adsorbent I and 89% Li by adsorbent II. Equil. sorption: 30.3 mg/g (I) and 33.1 mg/g (II).	LiCl	[79]
Seawater (1 mmol/L Li)	HMn_2O_4	60 °C, 24 h	Loading capacity: 1.53 mmol/g sorbent	Li salt	[71]
Brine (Salars de Uyuni, Bolivia)	$LimMgxMn^{III}yMn^{IV}2O_4$ ($0 < x < 0.5$)	24 h, pH 6.5	Adsorption capacity: 23-25 mg/g adsorbent	Li_2CO_3	[80]
Seawater (Li 0.192 mg/L)	Surface deposition on corrosion product of Al	30 °C, 10 days	34% Li	–	[66]
Salt lake bitterns	Hydrated alumina: LiOH = 2 M ratio	pH 5.8	Adsorption: 0.6-0.9 mg/g sorbent	–	[81]
Egyptian bitterns (19.5, 5.5, 8.8 mg/L)	$Al(OH)_3$	30 °C, pH 9	Adsorption capacity: 123 mg/g adsorbent	$LiAlO_2$	[82]
Brine (Salar de Hombre Muerto, Argentina)	Hydrated alumina	LiCl solution-1% Li (20 times conc.) by solar evaporation.	Adsorbed Li eluted by acid and precipitated by sodium carbonate	Li_2CO_3	[74]

The main approaches to the extraction of mineral products (K, Mg, Na, Ca, Li) from seawater include flotation (using anionic collectors), sorption, ion exchange, solvent extraction, etc. as described [76]. The existing evaporation process for lithium recovery from brine lakes takes a long time and suffers from low recovery efficiency. Besides, a huge burden is placed on the environment due to waste generation and significant water consumption.

More promising is condition shows the adsorption method to recover lithium from water resources, which can avoid evaporation and crystallization processes.

Adsorption process

Different types of adsorbents have been used to selectively extract lithium from seawater and brines. In the adsorption method, some inorganic ion exchangers, such as spinel-type manganese oxide, demonstrate extremely high selectivity to lithium from seawater [77, 78, 83-86]. Such materials have high adsorption capacity in alkaline medium (seawater pH ~8) for Li^+ in the presence of alkali and alkaline earth metal ions. For example, [83] reported separation of Li^+ from a large amount of Na^+ by spinel-type λ-MnO_2, resulting in Li^+ concentrating 400 times, leaving most of the Na^+ in seawater. Lithium extraction/separation from brines and such resources are summarized in Table-2.

Manganese oxide ($H_{1.6}Mn_{1.6}O_4$), derived from the precursor $Li_{1.6}Mn_{1.6}O_4$ by hydrothermal and reflux methods showed the maximum absorption of 40 mg Li/g of adsorbent from seawater, the highest among inorganic adsorbents [45]. It was found that the very small size (nano-size range) of the synthesized manganese oxide is responsible for its high adsorption capacity concerning lithium compared to other adsorbents. Adsorption of lithium from seawater by spinel-type λ-MnO_2 resulted in the formation of low purity Li^+ ions (~33%) contaminated with Na^+ [78]. Nano-manganese oxide ($Li_{1.33}Mn_{1.67}O_4$) through the gel process [79]. After acidification, ion-sieve adsorbent containing magnesium was obtained which selectively adsorbed lithium (~30.3 mg/g adsorbent) from seawater. When using a polymer membrane tank containing an inorganic ion exchange adsorbent with zinc, lithium extraction from seawater was very effective and kinetically confirmed the adsorption of 33.1 mg Li/g of the sorbent [87]. This inorganic ion exchange adsorbent had excellent lithium adsorption of 89% of 400 mg Li per day; desorption efficiency was 92.88% when immersed in 4 liters of 0.5 M HCl solution per day. Chitrakar *et al.* (2013) also observed very rapid adsorption equilibrium (within 24 h) for the efficient extraction of lithium from salt brine using Mg-doped manganese oxide (Table-2) [80].

Wajima *et al.* (2012) obtained HMn_2O_4 by elution of spinel-type lithium di-manganese tetraoxide ($LiMn_2O_4$) and investigated the kinetics of lithium adsorption [71]. The intermediate, $LiMn_2O_4$, has also been synthesized by acid treatment from $LiOH{\cdot}H_2O$ and Mn_3O_4. By using both products, lithium recovery from seawater reached ~100% at 60 °C.

Aluminum foil immersed in seawater forms a corrosion product on its surface that selectively extracts lithium from seawater at an optimal temperature of ~ 30 °C [66]. Aluminum salt adsorbent using $Al(OH)_3$ and LiOH at pH 5.8 and molar ratio 2, and investigated the extraction of lithium from salt Lake bitterness by this adsorbent obtained by Dong *et al.* (2007). The sorbent showed high adsorption and absorption of 0.6-0.9 mg Li/g, rather than other alkali metals. The use of hydrated alumina for lithium adsorption has also been reported from Egyptian bitterns [82] and Salar brines of Argentina [74].

The Institute of Oceanic Energy at Saga University has launched the world's first but small laboratory aimed at the practical production of lithium from seawater and has managed to produce about 30 g of lithium chloride from 140,000 liters of seawater in one month. In early 2010, POSCO and the Korean Institute of Geology and mineral resources, Korea have joined forces to build a pilot plant for commercial production of lithium carbonate from seawater based on the adsorption process, the outcome of which is currently uncertain.

Recovery of lithium from brine by ion-exchange

Brine is one of the important potential recourse for lithium recovery. From an economic and scientific point of view, the following points are important for considering the extraction of lithium from brine: (i) the presence of pond soil and the suitability of the area for solar evaporation, (ii) the concentration of lithium in brine, (iii) the ratio of alkaline and alkali metals to lithium, and (iv) the complexity of phase chemistry [88].

By using specially prepared resin/aluminates composite/inorganic ion exchanger, lithium can be recovered efficiently from the brine. The release of pure LiCl from brines containing a higher content of $CaCl_2$ and $MgCl_2$ was reported in the process of carboxylation and ion exchange [89]. Three different ion exchange resins (MC50 resin, (Chemie AG Bitterfeld-Wolfen), TP207 resin (Bayer AG), Y80-N Chemie AG (Chemie AG Bitterfeld-Wolfen)) for lithium extraction from synthetic brine were studied. The study showed that the purification of LiCl solutions with Y 80 resin at room temperature and TP 207 resin at 50 °C is possible [89]. Synthesis of H_2TiO_3 ion exchanger and extraction of lithium from the brine of natural gas wells were reported [90]. H_2TiO_3 ion exchangers from TiO_2 and Li_2CO_3 or TiO_2 and LiOH were synthesized, followed by calcination at 400-800 °C. As a result of the H_2TiO_3 ion exchanger, the high selectivity of Li^+ with the exchange capacity of Li^+ was 25.34 mg/g in mixtures of alkali metal and alkaline earth metal. The H_2TiO_3 ion exchanger showed 97% of the exchange rate and 98% of the Li^+ elution from brine (local natural gas well) [90]. It was reported the salvation of the lithium from the brine of the Salt lake using the same ion exchanger H_2TiO_3. It is reported adsorption of lithium ions by the ion exchanger H_2TiO_3 to follow the model of Langmuir with the capacity of exchange for Li^+ 25.34-32.6 mg/g at pH 6.5 from the brine. The brine pH was controlled by $NaHCO_3$ [91].

Recovery of Lithium from Seawater by Ion Exchange and Sorption

The ocean is considered to be the most important and promising resource of lithium for the near future to meet the demand of the world community for lithium [54]. It is reported that the total volume of lithium reserves in the oceans is approximately 2.6×10^{11} tons [92]. Lithium is extracted from hydro-mineral sources on a semi-industrial and industrial scale in the United States of America from salt lakes [93-95], in Japan from thermal waters [96, 97], in Israel from the Dead Sea [54, 98]. The extraction of lithium metal from the hydro-mineral source (geothermal and brine) has also been studied in Russia, Bulgaria, Germany, Korea [98]. Usually, lithium is extracted from seawater by ion exchange and sorption.

The extraction of lithium from brine and synthetic brine by ion exchange and sorption processes is considered in Table-3.

Table-3: Recovery of lithium from seawater by ion-exchange and adsorption processes.

Process	Reagents	Mechanism	Reference
Ion-exchanger	Titanium(IV) antimonate cation exchanger (TiSbA)	Ion-exchange	[100]
Ion-exchanger	H_2TiO_3 ion exchanger	Ion-exchange	[90]
Adsorption	λ-MnO_2 adsorbent	Sorption	[65]
Adsorption	$Al(OH)_3$ layer	Sorption	[66]
Adsorption	(HMnO) ion-sieve (microporous)	Sorption	[101]
Adsorption	k-MnO_2	Sorption	[67]
Adsorption	MnO_2	Sorption	[68]
Adsorption	HMnO	Sorption	[69]
Adsorption	Nanostructure MnO_2 ion-sieve	Sorption	[70]
Adsorption	MnO_2 adsorbent	Sorption	[71]
Adsorption	$H_{1.6}Mn_{1.6}O_4$	Sorption	[45]

Although various mega-industries are interested in extracting lithium from seawater in the present decade, the extraction of lithium from seawater has become increasingly attractive to researchers over several years through ion exchange and sorption. Several alternative methods of lithium extraction from seawater using ion-exchange after solar evaporation and fractional crystallization of NaCl, $CaSO_4$, KCl are also proposed. According to this method, organic and inorganic sorbents are similar to compounds used to extract lithium. Reports explaining this method are discussed below. Lithium selective aluminum-containing resin obtained by treating a microporous anion exchanger of type Dowex-1 with a saturated solution of $AlCl_3$, ammonia and, finally, a solution of lithium halide before heating to produce a composite $LiX{\cdot}_2Al(OH)_3$ microcrystalline resin matrix are examples of such products that have been patented in the United States of America [54, 95, 102]. Sorbents based on tin, antimony, dioxides based on titanium and zirconium [103], mixed oxides of titanium, and iron, titanium and chromium, arsenate of titanium and magnesium and thorium with high selectivity for lithium extraction were synthesized [54]. In a wide range of lithium-selective ion exchange materials, only cation exchange based on manganese oxides shows effective results for the extraction of lithium from seawater. Obtained from Russia manganese oxides and mixed oxides of manganese and aluminum, known as ISM-1 and ISMA-1, respectively, are used for lithium recovery [54, 104]. The H_2TiO_3 ion exchanger resulted in high selectivity for Li^+ in mixtures of alkali metal and alkali metal ions. The exchange capacity for Li^+ was 25-34 mg/g.

It has been reported that synthetic inorganic ion exchange materials of titanium (IV) antimonate cationite exchanger (TiSbA) have high selectivity to lithium cations. It can be successfully applied to the recovery of lithium cations from hydrothermal water as well as seawater. The influence of K^+, Mg^{2+}, and Ca^{2+} cations on the adsorption of lithium cations on TiSbA by charge method was also investigated. They observed that lithium adsorption decreased significantly with increasing concentrations of K^+, Mg^{2+}, and Ca^{2+} cations [100].

Although the rate of lithium adsorption was relatively slow (one day was required to achieve equilibrium at room temperature), the capacity of Li^+ could reach 32.6 mg/g^{-1} (4.7 mmol g^{-1}) at pH 6.5, which is the highest value among the lithium adsorbents studied to date in acidic solution. Also, H_2TiO_3 can effectively adsorb lithium ions from brine containing competitive cations such as Na^+, K^+, Mg^{2+}, and Ca^{2+}. This is because exchange sites are so narrow that Na^+ (0.102 nm), K^+ (0.138 nm) and Ca^{2+} (0.100 nm), which have ionic radii larger than Li^+ (0.074 nm), cannot enter these sites [105].

Selective extraction of lithium from seawater using two successive ion exchange processes has been recorded [65]. Mainly lithium has been concentrated from seawater using activities bench-scale chromatography with an adsorbent of the k-MnO_2 (granule), which has an efficiency of 33% for recovery of lithium. Lithium purification from the concentrated liquor of the reference plant was then carried out by a combination of ion-exchange using a resin and a resin impregnated with a solvent. The purification process consists of the removal of bivalent metal ions by strong cation exchange resin followed by the removal of Na^+ and K^+ by a resin impregnated with b-diketone/TOPO; and finally, the reduction of Li^+ in the form of Li_2CO_3 precipitation using a saturated solution of $(NH_4)^{2-}CO_3$. The yield was 56% and the purity was 99.9% [65]. A new method of extracting lithium from seawater is also supported by Takeuchi [66]. This method is based on the high selectivity of the $Al(OH)_3$ layer for the lithium-ion at an effective temperature of 50 °C and nearly 70% reduction achieved in batch conditions. The selectivity coefficient Li^+, K^+, Ca^{2+} and Mg^+ is 990, 90, 45 and 11, respectively [66]. Lithium recovery from seawater by sorption/desorption is a fairly common process reported by several authors, which is discussed below [106]. Typically, the sorbate based on the manganese oxide is used for the sorption/desorption of extracting lithium from seawater. Sorbet based on hydrated c-oxides of manganese and mixed manganese and magnesium oxide was developed by Japanese scientists [67, 101]. Lithium extraction from seawater by ion-sieve (microporous) manganese oxide ion-sieve (HMnO) was investigated. Maximum (7.8 mg/g) absorption of lithium HMnO from seawater was achieved [101]. To improve the kinetic properties of manganese oxide sorbents, the Japanese researcher developed a composite material by including k-MnO_2, fine powder with a spinel structure in polyvinyl chloride [107]. The sorbents ISM and ISM-1 synthesized in Russia are also composite material obtained using polymer binder [54]. Lithium recovery from seawater using manganese oxide ion exchange adsorbent has also been reported in Korea. They are specially trained in the method were prepared by ion-exchange high-performance adsorbent for recovering lithium dissolved in seawater. By solid-state reaction, Li_2CO_3 and $MgCO_3$ synthesized adsorbate ion-exchange type of high performance. After the treatment of seawater with an adsorbate, an ion sieve is formed, which is restored by acid treatment. The Li-ion sieve was obtained by 3 cycles of 0.5 M HCl treatment cycles with stringing of 24 H/Cycle, which exhibits 25.7 mg/L of lithium absorption from artificial seawater [99]. Lithium extraction from seawater by manganese oxide ion-sieve has been reported. The most promising process of industrial application was considered to be the extraction of lithium from seawater by adsorption using manganese oxide ion sieves [68]. The sorption properties of lithium HMnO in seawater and wastewater were studied and it was shown that HMnO can be effectively used to extract lithium from seawater with good selectivity [69]. Lithium recovery from lake Urmia has been reported using MnO_2 ion-sieve (nanostructure), where more than 90% of lithium recovery can be achieved [70]. Adsorption behavior of lithium from seawater using manganese oxide adsorbent was studied [71]. Higher kinetics of adsorption of lithium cations in seawater was observed using a pseudo-second-order kinetic model [71]. Lithium extraction from seawater using manganese oxide adsorbent synthesized from the precursor $Li_{1.6}Mn_{1.6}O_4$ was investigated. Manganese oxide $LiMnO_2$ adsorbent is synthesized from $H_{1.6}Mn_{1.6}O_4$ at 400°C by hydrothermal and reflux method. $H_{1.6}Mn_{1.6}O_4$ was synthesized from precursor $Li_{1.6}Mn_{1.6}O_4$. The adsorbent can absorb lithium up to 40 mg/g from seawater, which has been quite an effective adsorbent [45].

In other words, the extraction of lithium from seawater in large-scale production using adsorption methods is the ultimate goal. Thus, scientists around the world are faced with the task of synthesis of stable and sorption-intensive sorbent and its use in the extraction of lithium from seawaters.

Conclusions

Lithium is one of the rarest metal with various applications and the demand for lithium will increase with the ever-increasing use of electric and electronic devices and hybrid electric vehicles.

Therefore, the search for ways to obtain lithium from water sources suitable for the production of lithium compounds is a serious and very important problem.

Various methods have been given in the literature for lithium recovery from brines, seawater, and geothermal water: including precipitation, solvent extraction, selective membrane separation, liquid-liquid extraction, ion exchange adsorption, electrodialysis and so on.

The recovery of lithium by the absorption method shows promising results for future production. In the adsorption method, evaporation and crystallization processes can be avoided. That is why it is necessary to develop and recommend a technically and economically feasible, environmentally friendly, and sustainable process.

Scientists and manufacturers are faced with the task to solve several problems: the ion sieve has a relatively low ion exchange capacity and weak stability; lithium absorption reaches from 16 to 26-28 mg/g, the theoretical adsorption capacity is 54 mg/g; dissolution of sorbents. Weight loss was observed in almost all compositions; low stability during recycling; the appearance of secondary waste in the regeneration of acids; the process takes a long time.

To solve this problem, scientists of the world have carried out many scientific works to improve the stability of sorbents, increase the absorption capacity, selectivity, acceleration of sorption time, for this purpose, many methods were used, including organic chemicals, synergies, binders, various composites. But none of them makes it possible to industrialize the method of lithium adsorption. That is why it is still a challenge to find ways to improve the method of adsorption of lithium. Lithium adsorption extraction can be an alternative option to meet future demand, energy sustainability, environment, and circular economy.

Acknowledgements

The authors gratefully acknowledge partial financial supports from the National Natural Science Foundation of China (U1607123 and 21773170), the Key Projects of Natural Science Foundation of Tianjin (18JCZDJC10040), the Major Special Projects of Tibet Autonomous Region (XZ201801-GB-01) and the Yangtze Scholars and Innovative Research Team of the Chinese University (IRT_17R81).

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