The definitive publisher version is available online at 10.1016/j.desal.2022.115951

Metal-based adsorbents for lithium recovery from aqueous resources

Hanwei Yu[1], Gayathri Naidu[1], Chunyao Zhang[2], Chen Wang[1], Amir Razmjou[3,1], Dong Suk Han[4], Tao He[2], Hokyong Shon[1,*]

[1]School of Civil and Environmental Engineering, University of Technology Sydney (UTS), City Campus, Broadway, NSW 2007, Australia

[2]Laboratory for Membrane Materials and Separation Technologies, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China

[3]School of Engineering, Edith Cowan University, Joondalup, Perth, WA 6027, Australia

[4]Center for Advanced Materials & Department of Chemical Engineering, Qatar University, P.O. Box 2713, Doha, Qatar

[*]Corresponding author email: Hokyong.Shon-1@uts.edu.au

Abstract

The continuous increase of demand for lithium (Li) chemicals in industrial applications calls for exploring affordable Li production and sustainable options beyond land mining. Thus, aqueous resources, such as geothermal brine, salt lake brine, and seawater, play an essential role in continuous Li supply due to abundant storage and low cost. Adsorption technology is promising in Li recovery with the advantages of attaining high selectivity for Li over other major ions present in aqueous resources at low cost and low energy demand with facile synthesis processes that enable practical large-scale production. Metal-based adsorbents are conspicuous among various adsorbents for presenting the visible prospect closest to industrial applications. This review presents a comprehensive summary and critical analysis of the synthesis methods for metal-based adsorbents, the mechanisms for Li selective recovery, and the performance of Li adsorption. The

advantages and challenges are discussed for different adsorbents and preparation methods. A specific focused case study on an industrial application of Al-based adsorbent production and Li recovery processes and operations on an engineering and economic scale is discussed in detail to provide a comprehensive overview of the practical industrial application of metal-based adsorbent.

Keywords

Lithium recovery; Metal-based adsorbents; Adsorption performances; Synthesis methods; Industrial case study

Table of Content

1. Introduction

Lithium (Li) has become one of the most crucial elements in this century in various industries because of its electrochemically active property and high specific heat capacity [1, 2]. **Fig. 1** shows diverse applications and distribution of identified Li resources on land. **Fig. 2** presents annual Li consumption from 2010 to 2020 and the distribution of extractable Li reserves with existing technologies [3-9]. The applications cover batteries, ceramics, lubricating greases, air treatment, catalysis, etc. Notably, in recent five years, the expansion of batteries for electric vehicles and other electric devices has been accelerated rapidly by the concept and policies of replacing traditional fuel energy to clean renewable energy in many countries [9-11]. The boom of global Li consumption, from 24.5 kt in 2010 to 93.0 kt in 2021 [4], challenges the supply of Li from conventional ore resources. On that note, recovering Li from aqueous sources exhibits significant advantages as an alternative Li resources, as about 75% of Li on land is stored in geothermal brines, oilfield brines, and the salt lakes in South America, China, and Australia [12], and the reserve in the ocean is even over 16 thousand times than that on land [9].

The main approaches to extracting Li from brines include conventional evaporation precipitation [13], solvent extraction [14-16], and adsorption [17], and emerging technologies such as electrochemical methods [18-22], membrane-based technologies [14, 23-27], and reaction-coupled separation [28]. The predominant factors that influence selecting a method for Li extraction are the practical applicability of the method, the co-existing contaminant multivalent coions (namely the Mg/Li mass ratio), and the effects of other competing co-existing ions, such as Na^+, K^+ [29-32]. The widely used evaporation precipitation method is limited to applying in the high Mg/Li ratio brines due to the complex and time-consuming pre-processes of removing co-existing ions [12, 33, 34]. The solvent extraction method for extracting Li from multi-ion-existing

brines shows undesirable sustainability since the organic solvents can corrode the process equipment and the solvent leakage pollutes the environment [35, 36]. Electrochemical Li capture systems [37], including capacitive deionization (CDI) [38-40] and electrodialysis (ED) [41-44] based on electrochemically switchable ion exchange (ESIX) rely on the external electric field, thus being limited by problems of high cost and energy consumption. Membrane-based technologies for Li recovery contain capacitive deionization (MCDI) [45-47], selective electrodialysis (SED) [21, 26, 32, 44], nanofiltration (NF) [24, 48], ion-imprinted membrane (IIM) [49, 50], and membrane distillation crystallization (MDC) [51, 52], driven by external stimuli such as thermal gradient, pressure, and electric field [53-57]. These technologies have vast potential to develop in the next generation roadmap, yet the difficulties of energy consumption, separation efficiency, and membrane durability limit their industrialization. Reaction-coupled separation technology for the separation of Mg/Li by co-precipitating Mg-ions and foreign Al-ions with an alkali solution is still at the start-up stage [28, 29].

Compared to the above technologies, the adsorption method shows an excellent balance of high Li selectivity, simple and efficient operation process, good applicability to most brine resources, high economical advantage, and less environmental impact [58, 59]. It utilizes Li-selective adsorbents to uptake Li from a multi-ion aqueous environment and then desorbs them with some solvents, thus extracting Li. The principle requirements for proper adsorption materials cover high Li selectivity, adequate adsorption capacity, and suitable operation stability [60]. As shown in **Fig. 3**, the mainly studied Li adsorbents involve inorganic, organic, and composite adsorbents. Organic adsorbents, such as crown ether and polymer ion-exchange resin, are limited for applications due to the hazardous organic raw materials and the complex synthesis processes. Inorganic adsorbents include metal-based adsorbents and natural mineral-based adsorbents. The

selection of the latter ones strongly depends on cost and resource quantity, impeding promoted applications in different brine source areas. Nowadays, metal-based adsorbents have become the hotspot and keystone of the research on Li adsorbents. The merits of metal-based Li adsorbents, including high Li capture capacity, low regeneration loss of raw materials, excellent Li selectivity, robust cycle performance, and relatively less energy consumption, qualify them as promising environmentally-friendly candidates for Li extraction from aqueous solutions containing different ions [61]. The pilot- and commercial-scale applications have been developed in Li recovery cases from the Qarhan Salt Lake by Qinghai Lakelithium Co., LTD. The related case study is developed in Section 3.

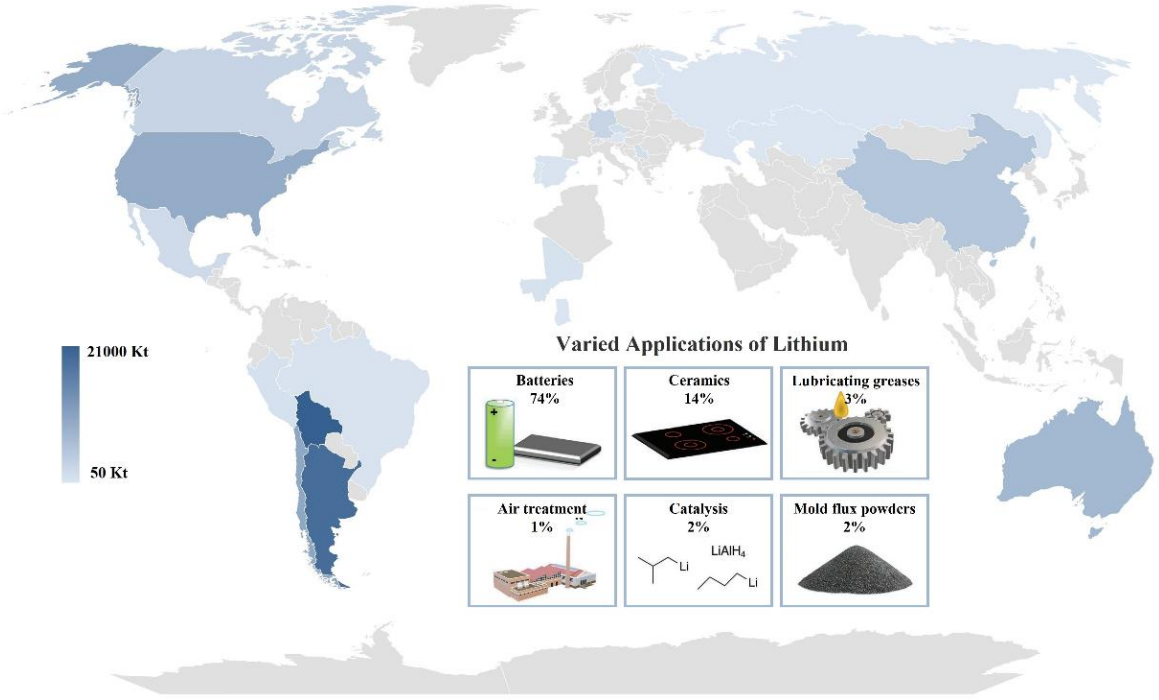


Figure 1. Diverse applications of Li and distribution of identified Li resources on land, including exploitable and unexploitable with existing technologies. Figure partly modified from [8] with copyright permission from John Wiley and Sons.

Previous review papers on Li recovery focused on 1) membrane-based [14], manganese-based [62], and MOF-based [8] Li extraction materials, 2) electrochemical methods [18, 41, 63],

and other industry production methods [64, 65] from one specific brine source [13, 66] or region [67], 3) brine and mineral management perspectives [68, 69]; however, thus far, almost no comprehensive reviews concerning the developments of all metal-based adsorbents for Li recovery from sorts of brines. This review emphasizes the synthesis methods and Li adsorption performances of the current and the emerging metal-based Li adsorbents. Simultaneously, the techno-economic analysis is studied based on the application case of Al-based adsorbent in Li recovery from the Qarhan Salt Lake. The challenges and potential opportunities to implement on the future engineering scale are also discussed.

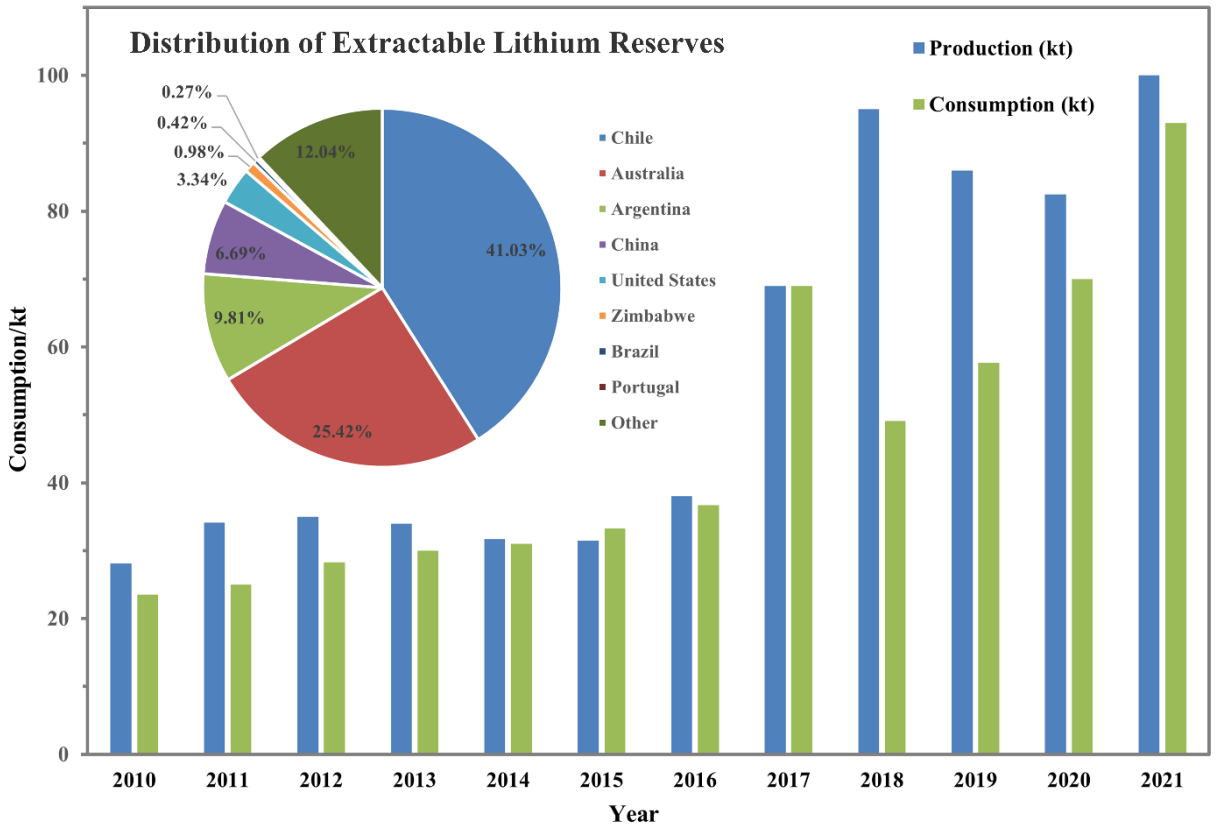


Figure 2. Global consumption of Li content from 2010 to 2020 and distribution of extractable Li reserves with existing technologies.

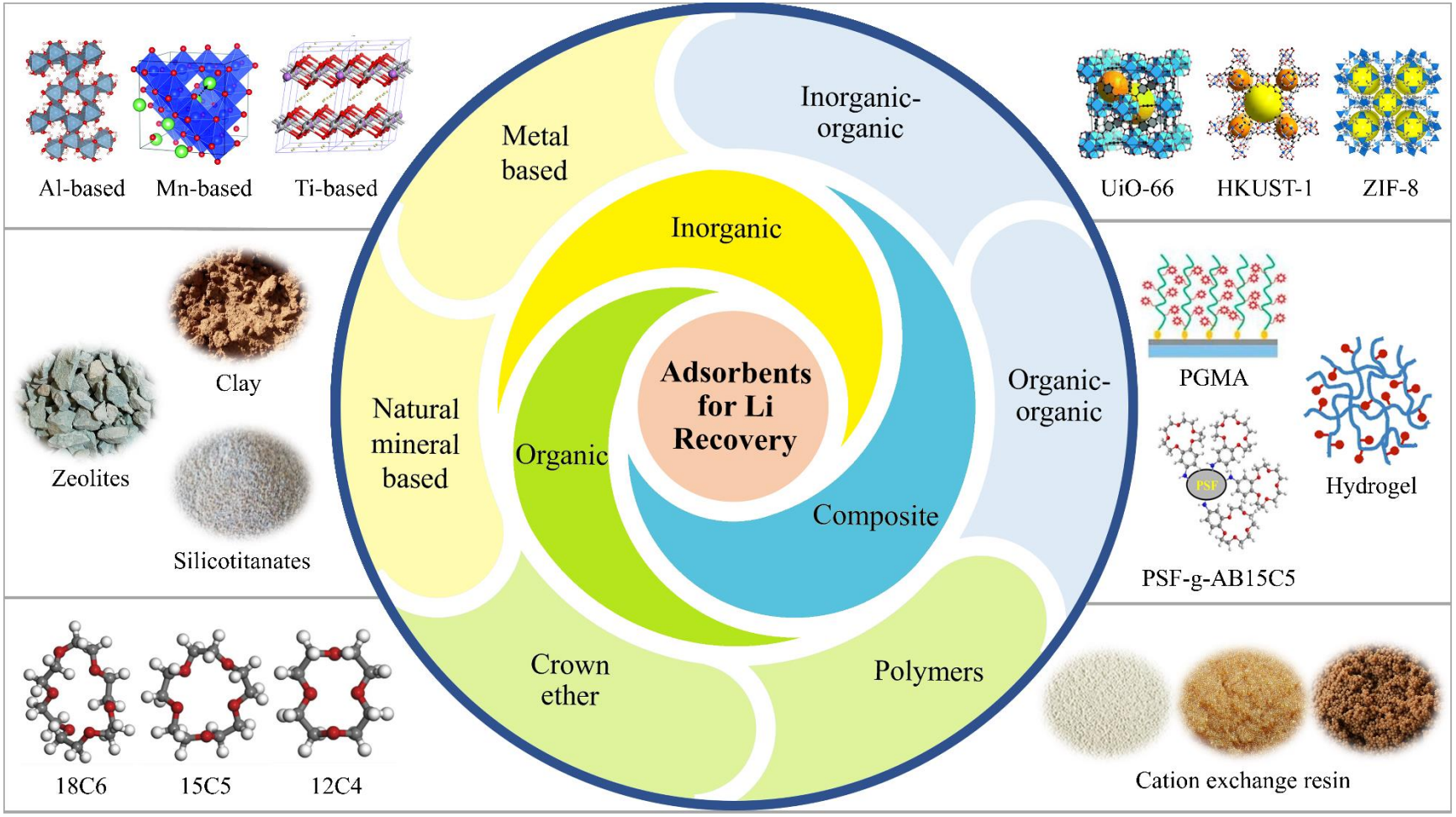


Figure 3. Classification of adsorbents for Li recovery.

2. Metal-based Li adsorbents

Metal-based Li adsorbents for Li recovery are basically comprised of aluminum (Al)-based, manganese (Mn)-based, and titanium (Ti)-based adsorbents. The overarching principle governing Li sorption by metal adsorbents is based on the structural memory effect of Li-ion sieves (LIS): Li tends to occupy the vacancies generated in the adsorbent preparation process by removing the original Li from the pristine structure [70-72]. For now, Al-based adsorbents exhibit the most potential in industrial application owing to the high technology maturity, yet the Li selective uptake performance is not ideal; Mn-based ones present excellent Li adsorption performances, but the Mn dissolution impairs its long-term stable application; Ti-based ones is a more recent entry but have shown promising prospects as it does not exhibit the similar disadvantages of the Al-based and Mn-based adsorbents.

2.1 Al-based adsorbents

2.1.1 Structure and adsorption mechanism

Al-based adsorbents, especially Li-Al layered double hydroxides (LiAl-LDHs), are widely studied inorganic adsorbents and the most applicable ones for industrial Li recovery from brines owing to the advantages of negligible elution damage, stable adsorption performance, and ease of production [71, 73]. LiAl-LDHs show a structure of a two-dimensional aluminum hydroxide layered plate linked by hydrogen bonds, electrostatic interaction, and van der Waals with Li filled in octahedral voids of the packing hydroxide ions (**Fig. 4**), and the chemical formula could be expressed as $[Li_mAl_2(OH)_6]Cl_m \cdot nH_2O$ (m=0-1) [70, 74-76]. Based on the mechanism of the structural memory effect, the process of Li adsorption-desorption can be described as the following formula [73]:

$$xLiCl + [Li_{(m-x)}Al_2(OH)_6]Cl_{(m-x)} + (n+1)H_2O \rightleftharpoons [Li_mAl_2(OH)_6]Cl_m \cdot nH_2O + H_2O$$

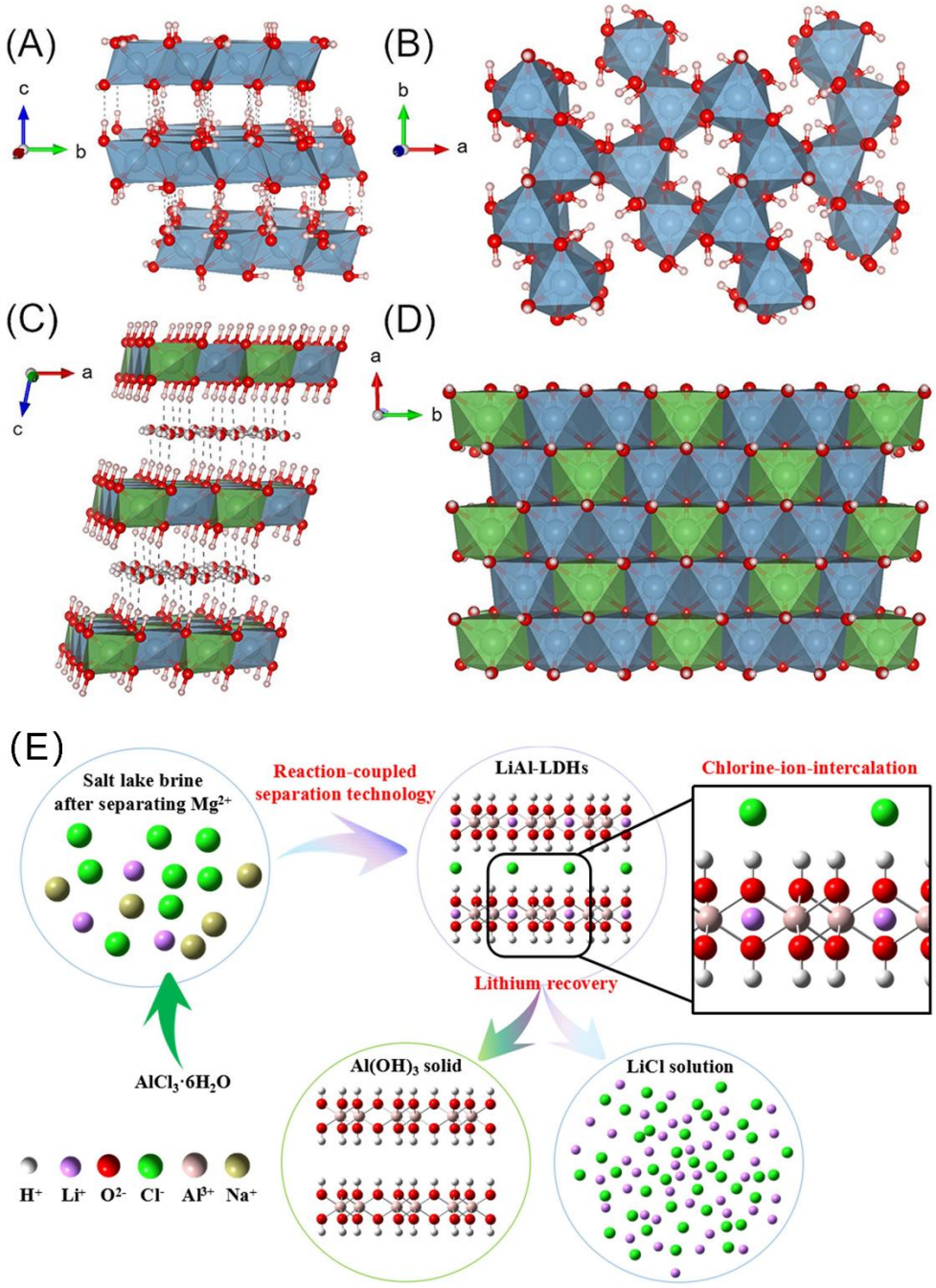


Figure 4. Crystal structures of gibbsite (A, B) and LiAl-LDH (C, D); the blue, red, green, and white dots represent Al, O, Li, and H atoms, respectively. (E) Flowchart for Li recovery from LiAl-LDHs via a mild solution chemistry process. Figure (A-D) obtained from [77] with copyright permission from ACS Publications. Figure (E) obtained from [78] (copyright 2019 MDPI).

2.1.2 Synthesis methods and Li recovery performances

The synthesis of LiAl-LDHs has a more extended history than the application studies in Li recovery. The Li intercalation method was reported to modify aluminum hydroxide by Frenkel et al. in 1980 [79]. The preparation method of lithium dialuminate using solid lithium hydroxide, polycrystalline aluminum trihydroxide (bayerite), and water vapor at room temperature was described by Poeppelmeier and Hwu in 1987 [80]. The mechanochemical process of LiAl-LDHs production was developed by combining grinding followed by hydrothermal crystallization [81-83]. Isupov et al. proposed using LiAl-LDH as a selective sorbent of Li salts from brines in 1998 [84], yet few studies emphasized the application of Li recovery until recent years. Liu et al. produced $LiCl{\cdot}2Al(OH)_3{\cdot}xH_2O$ and investigated the Li/Mg separation performance of LiAl-LDH in brine, revealing the ability of LiAl-LDHs to extract Li from the salt lake brine [85]. Zhong et al. prepared two-dimensional hexagonal flat Li/Al-LDHs with high Li selectivity via the coprecipitation method and developed a granulation method to adsorb Li from the Qarhan Salt Lake old brine at room temperature [73, 86]. Lee et al. synthesized silicon oxide-coated LiAl-LDH nanocrystals with stable regeneration cycles and high Li selectivity by oxidation of aluminum foil substrate under a urea and Li solution to extract Li from simulated solution resources [87]. Sun et al. exploited the hybrid technology of reaction-coupled separation and LiAl-LDHs to extract Li from the salt lake brine in the Chinese Qaidam Basin, achieving as low as 3.93% Li loss [88]. Lee et al. proposed a project to separate Li from urea solution using LiAl-LDH coated aluminum metal foils [89] and fabricated polyacrylonitrile hybrid membranes coated with aluminum hydroxide for separating Li [90].

For optimal application condition study and large-scale process design, Jiang et al. tested Li adsorption performances of LiAl-LDHs from simulated brine with various initial Li concentrations in different feed flow rates at 303 K in fixed-bed columns with varying heights of bed. Their results

indicate that the breakthrough time (the life span of adsorbents in a single adsorption operation) and capacity positively correlate with bed height but negatively with the initial Li concentration and feed flow rate [91], and the optimal pH condition is ascertained to 7 [92, 93]. Paranthaman et al. designed an economic three-stage bench-scale column extraction process, presenting the merits of low cost, easy preparation, and environmentally friendly nature for Li recovery from geothermal brine using LDHs [94]. The competitive and synergic effects of co-existing ions on Li adsorption are concerned in multi-salt feed solutions. Jiang et al. verified the promotion effect of anions and the competition effect of other cations on the Li adsorption through adsorption tests in the Li-$MgCl_2$, Li-NaCl, and Li-Na-$MgCl_2$ multicomponent system [17]. Similar investigations were also studied by Chen et al. [71], and Hu et al. [95]. The selectivity factor can be used to compare the Li adsorption ability in the multi-cation environment.

Despite the significant advantages in Li extraction from low-grade brines, the drawback of using LiAl-LDHs is that its sensitivity towards transforming to gibbsite in the desorption process reduces its adsorption capacity, which is a major challenge for application scale expansion [93, 95]. Prolonging the application life of LiAl-LDHs is also vital to reducing environmental impact [96]. Introducing magnetic materials is a strategy to reduce the sharp loss in the industrial application of adsorption capacity due to granulation as an external magnetic field can be employed after adsorption to recycle adsorbents [97, 98]. Fe_3O_4-doped magnetic LiAl-LDHs are proved not harmful to the physicochemical properties of the effective adsorption component and can achieve rapid recovery and long-term recycling potential [71, 99]. Additionally, except for solid-state intercalation, the dissolution-reprecipitation pathway was also discovered in the transformation from gibbsite to LiAl-LDHs, hinting at another potential study direction on the structural adjustment for reducing effective content loss [77].

Except for LiAl-LDHs, other Al-based adsorbents are also reported. Pauwels et al. investigated Li adsorption of polymeric aluminum hydroxide for geothermal water treatment in 1995 [100]. Wang et al. synthesized magnesium-aluminum-carbonate-layered double hydroxide adsorbent ($MgAlCO_3$-LDHs) and developed an integrated process to separate and recover both Mg and Li from brines [101]. Heidari and Momeni utilized $AlCl_3 \cdot 6H_2O$ as an adsorbent to recover Li from Urmia Lake and identified the optimal pH and temperature conditions [102]. In summary, the synthesis methods and performances of Al-based adsorbents are presented in **Table 1**.

Table 1. Synthesis methods and performances of Al-based adsorbents

Adsorbents	Sources	Preparation	Li adsorption performance	Ref.
$Al(OH)_3$	$AlCl_3 \cdot 6H_2O$, NaOH, brine	Coprecipitation	Li recovery rate of 76.4% when T=30°C, pH= 7.5	[102]
$Al(OH)_3$	$AlCl_3 \cdot 6H_2O$, KOH, LiCl	Coprecipitation	Li recovery rate of 95% when T=80°C and Al/Li molar ratio ~2.5	[100]
Li/Al-LDHs	LiCl, $AlCl_3$, NaOH	Coprecipitation	Li capacity of 7.27 mg/g in Qarhan old brine	[73]
Li/Al-LDHs	$AlCl_3 \cdot 6H_2O$, NaOH, brine	Coprecipitation	Li recovery rate of 89.7% when T=30°C and Al/Li =5	[103]
Li/Al-LDHs	LiCl, NaOH, $AlCl_3 \cdot 6H_2O$	Coprecipitation	Li capacity of 6 mg/g	[71]
Li/Al-LDHs	$Al(OH)_3$, $LiOH \cdot H_2O$, HCl	Hydrothermal method	Li recovery rate of 91%	[94]
Li/Al-LDHs	LiCl, $AlCl_3$, NaOH		Li capacity is about 3 mg/g	[104]
Li/Al-LDHs	$AlCl_3 \cdot 6H_2O$, NaOH, Na_2CO_3		3.93% Li loss under optimal separation conditions	[88]
Li/Al-LDHs	$AlCl_3 \cdot 6H_2O$, $LiOH \cdot H_2O$, NaOH	Coprecipitation	Li capacity of 9.33 mg/g	[93]
Commercial adsorbent	/	/	Li capacity range of 5.02 to 5.69 mg/g from 200 to 350 mg/L initial LiCl solution	[17]

2.2 Mn-based adsorbents

2.2.1 Type, structure, and adsorption mechanism

Mn-based adsorbents (LMO) are broadly emphasized in research due to their unique chemical structure, sufficient adsorption capacity, excellent Li selectivity, and outstanding regeneration performance [61]. For now, the precursors of LMOs can be divided into three types according to the different ratios of Li/Mn and crystal structures: $LiMn_2O_4$, $Li_{1.33}Mn_{1.67}O_4$ ($Li_4Mn_5O_{12}$), and

$Li_{1.6}Mn_{1.6}O_4$ ($Li_2Mn_2O_5$), with theoretical maximum adsorption capacities of 39.9 mg/g, 59.5 mg/g and 72.8 mg/g, respectively [105-108]. The crystal structures of $Li_xMn_{3-x}O_4$ spinels are determined by stoichiometry, applied pressure, and temperature in the solid-phase reaction by heating a mixture of Mn and Li compounds [109]. As **Fig. 5** shows, spinel-based $LiMn_2O_4$ and $Li_4Mn_5O_{12}$ exhibit cubic crystal structures. Li and Mn occupy tetrahedral and octahedral sites of $LiMn_2O_4$ crystal, respectively [110]. On the basis of $LiMn_2O_4$, the excessive amount of Li at octahedral sites compensate for the increase of Mn(IV) in $Li_4Mn_5O_{12}$ [111]. The structural model of $Li_2Mn_2O_5$ has not been explicitly reported, but the advantage of its superior theoretical exchange capacity appeals to researchers as a candidate precursor for an ideal Li-selective adsorbent.

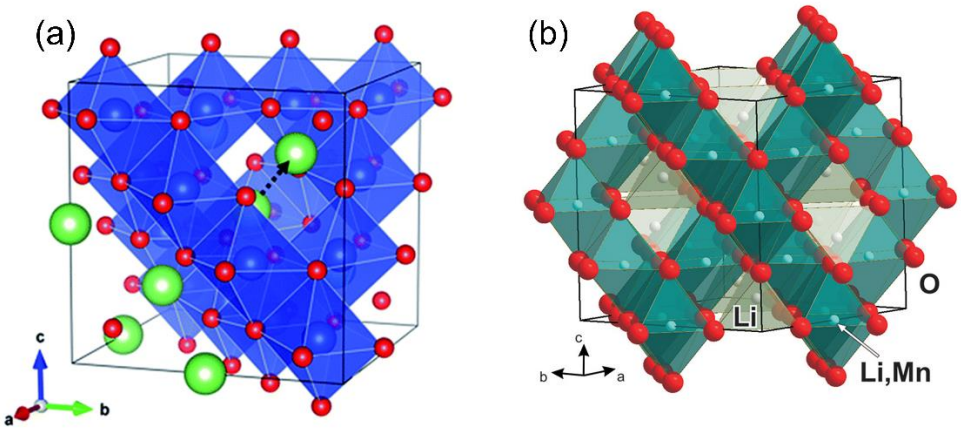


Figure 5. Crystal structure of spinel (a) $LiMn_2O_4$ and (b) $Li_4Mn_5O_{12}$, Mn ions reside in octahedrons formed by O ions. Figure (a) obtained from [112] with copyright permission from Royal Society of Chemistry and figure (b) obtained from [110] with copyright permission from ACS Publications.

A number of different mechanism theories of Li intercalation-deintercalation have been reported. In 1981, Hunter et al. proposed that Mn(III) in $LiMn_2O_4$ converted to Mn(II) and Mn(IV) through redox reaction under acidic conditions, only leaving Mn(IV) in λ-MnO_2 and providing

vacancies for Li intercalation [113]. The dissolution of Mn(II) can reduce the stability of the spinel, so adsorption capacity decreases with regeneration. But this theory was unable to explain the phenomenon of the positive influence of the adsorption capacity with pH. A follow-up study by Shen and Clearfield in 1986 stated that ion exchange between H and Li provided Li vacancies rather than the disproportionation reaction of Mn ions [114, 115]. Ooi et al. and Feng et al. concluded the two theories and investigated the Li intercalation process in different types of Mn-based ion-sieves, discovering that Mn(III) in the precursors deliver redox sites and Mn(IV) grant ion-exchange sites (shown in **Fig. 6**) [116, 117].

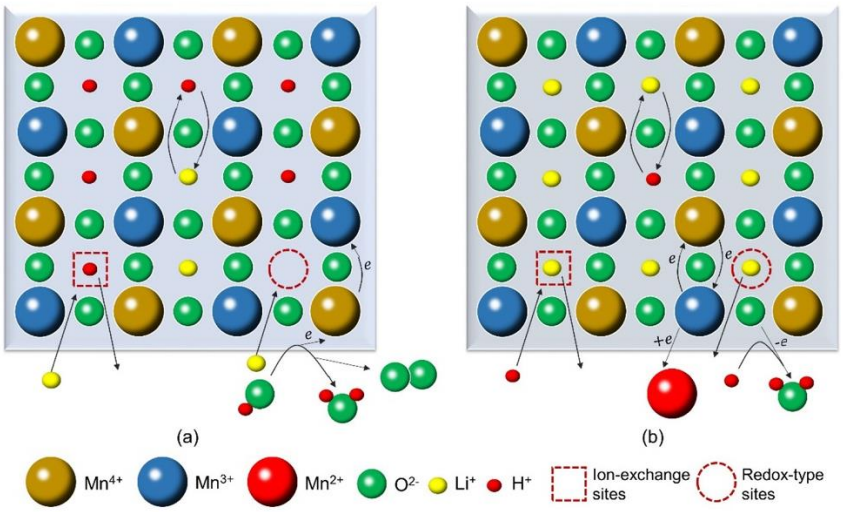


Figure 6. Schematic representation of the Li intercalation (a) and deintercalation (b) mechanisms in spinel LMO adsorbents. Figure obtained from [66] with copyright permission from Elsevier.

2.2.2 Synthesis methods and Li recovery performance

Traditional methods for synthesizing LMO precursors focus on redox precipitation and solid-phase calcination that Li and Mn compounds are mixed according to a certain stoichiometric ratio and calcined at more than 400℃ [118]. Sun et al. prepared a spinel $Li_{1.6}Mn_{1.6}O_4$ by a combination of controlled redox precipitation and solid-phase reaction, and the Li adsorption capacity from Qarhan Salt Lake brine was 3.88 mmol/g [119]. However, since this strategy exhibits the

disadvantages of coarse and uneven sizes and distributions of the product powders, prolonged reaction time, and high reaction temperature, the mechanochemical method [120] and rheological-phase-assisted microwave method [121] were proposed to improve the synthesis processes and products. The mechanochemical method is a mechanical activation method for preparing highly dispersed compounds at room temperature or relatively low temperatures. The rheological-phase-assisted microwave method is a combination of microwave treatment and rheological phase method, an approach to facilitate the uniformity of reactants from a solid-liquid rheological mixture. Then the sol-gel method was introduced to optimize the crystallization process [122]. Sun et al. synthesized spinel $LiMn_2O_4$ powders using metal acetates containing poly(acrylic acid) (PAA) as a chelating agent [123]. To further simplify the synthesis operation and decrease the cost, the hydrothermal and microwave hydrothermal methods were utilized in LMO precursor production. Different morphologies, including nanorods, nanowire, nanocubes, and nanospheres, can be achieved by controlling hydrothermal conditions [107, 108, 124, 125]. Chitrakar et al. employed monoclinic type γ-MnOOH reacting with LiOH solution at 120°C for 24 hours, giving orthorhombic $LiMnO_2$, and then heated to higher than 400°C to form cubic $Li_{1.6}Mn_{1.6}O_4$ [126]. Then they exploited microwave irradiation on the materials above, realizing a rapid formation of semicrystalline orthorhombic $LiMnO_2$ (*o*-$LiMnO_2$) within 30 minutes [127]. The maximum Li uptake of their adsorbent from seawater was 40 mg/g [128]. Shi et al. examined Li adsorption capacity and stability of $Li_{1.6}Mn_{1.6}O_4$ prepared by a hydrothermal reaction, showing a maximum Li uptake of 27.15 mg/g from brine at 50°C and 20 mg/g after 10 cycles [129]. The cross-linking strategy was employed by Wang et al., who produced ethylene glycol diglycidyl ether (EGDE) cross-linked spherical chitosan-$Li_4Mn_5O_{12}$ with 8.98 mg/g of Li adsorption capacity in geothermal brine [130]. In summary, the synthesis methods and performances of LMO are

concluded in **Table 2**.

Table 2. Synthesis methods and performances of Mn-based adsorbents

Adsorbents	Sources	Preparation	Li adsorption performance	Ref.
$Li_{1+x}Mn_{2-x}O_4$	LiOH, Li_2CO_3, $MnCO_3$	Solid-phase method	23.5 mg/g in mixed solution within 24 h	[131]
$Li_{1.6}Mn_{1.6}O_4$	γ-MnOOH, LiOH	Hydrothermal method	40 mg/g in seawater	[128]
$Li_{1.6}Mn_{1.6}O_4$	$KMnO_4$, LiOH, $MnCl_2$	Hydrothermal method and solid-phase method	28.32 mg/g in Qarhan Salt Lake Li adsorption 3.62 mmol/g after reusing for six cycles.	[108]
$Li_{1.6}Mn_{1.6}O_4$	LiOH, $Mn(NO_3)_2$	Hydrothermal method	26.93 mg/g in Qarhan Salt Lake brine	[119]
$Li_{1.6}Mn_{1.6}O_4$	LiOH, Mn_2O_3	Hydrothermal method	27.15 mg/g in brine, Mn loss <2.5%, capacity >20 mg/g after 10 cycles	[129]
$Li_{1.353}Mn_{1.626}O_4$	$Mn(NO_3)_2·4H_2O$ $Na_2S_2O_8$, $LiNO_3$	Hydrothermal method	Li recovery rate reaches 90% in Urmia Lake	[132]
$Li_4Mn_5O_{12}$	$LiNO_3$, β-MnO_2	Hydrothermal method and solid-phase method	45.95 mg/g in the solution with c(Li) =5.0 mol/L	[107]
$Li_4Mn_5O_{12}$	EDTA, $LiNO_3$ $Mn(NO_3)_2·4H_2O$	EDTA-citrate complexing method	43.1 mg/g in 0.5g/L LiCl solution	[133]
$HZn_{0.5}Mn_{1.5}O_4$	Li_2CO_3, $MnCO_3$ $Zn(CH_3COO)_2•4H_2O$	Solid-phase method	33.1 mg/g in artificial seawater	[134]
$LiAl_xMn_{2-x}O_4$	$Mn(NO_3)_2$, $AlCl_3·6H_2O$, $LiOH·H_2O$, H_2O_2	Hydrothermal method	27.66 mg/g in 50mg/L LiOH solution 19.5 mg/g after repeating 5 cycles	[135]
$Li_{1.6}Mn_{1.6-x}Cr_xO_4$	$LiOH·H_2O$, $Cr(NO)_3·6H_2O$	Hydrothermal method	25.5 mg/g in Lop Nor Salt Lake	[136]

For improving the feasibility of the practical application, the strategies of doping and coating are explored to reduce Mn dissolution in an acidic surrounding and enhance the structural stability of LMO adsorbents [137, 138]. In Qian et al.'s study, the maximum Li uptake capacity of $Li_{1.6}Mn_{1.6}O_4$ increased from 32.3 to 35.3, 35.4, and 40.9 mg/g, and Mn dissolution reduced from 5.4% to 3.95%, 4.42%, and 2.1% after tracing surface doping Fe^{3+}, Co^{2+}, and Al^{3+}, respectively [139, 140]. They also asserted that by doping F^-, S^{2-}, the capacity of $Li_{1.6}Mn_{1.6}O_4$ increased from 26.1 to 33.4 and 27.9 mg/g [141]. Their K-gradient doping experiment results reported that Mn dissolution reduced from 5.4% to 4% [142]. Xue et al. enhanced the Li adsorption capacity to 29.33 mg/g with 6.22% Mn loss by doping Fe_3O_4 via a hydrothermal process [143]. Cao et al. and Su et al. revealed the influence of Cr-doping content on Mn dissolution and Li adsorption capacity

[144]. By doping 1% Cr, the LMO-Cr shows an initial Li adsorption capacity of 31.67 mg/g and Mn dissolution ratio of 2.1%, yet Li adsorption capacity of 25.5 mg/g and Mn dissolution ratio of 0.35% after 20 cycles [136]. Bajestani et al. reported a high adsorption capacity of 53.52 mg/g via doping Co^{2+} in $LiMn_2O_4$ [145], and Chen et al. stated 27.66 mg/g via doping Al^{3+} [135]. Compared to doping studies, coating strategy currently lacks attention. Luo et al. coated Al_2O_3-ZrO_2 on $LiMn_2O_4$ to enhance chemical stability and utilized it as an electrode to capture Li in an electrochemical way, achieving a Li extraction capacity of 49.92 mg/g and Mn dissolution of 0.1% after 30 cycles [146].

Process investigations for practical Li recovery applications, such as granulation methods development and adsorption column design, are also studied by many research groups. Hong et al. immobilized spinel HMO on the alpha-Al bead and induced macropores by adding hydrogel beads before calcination, resulting in similar Li adsorption performance to powdery adsorbents from high Li concentration feed solutions and improving the performance from diluted feed solutions [147-149]. Han et al. prepared millimeter-sized spherical LMO foams with a Li adsorption capacity in natural seawater of 3.4 mg/g via foaming, drop-in-oil, and agar gelatin [150]. Ryu et al. designed a continuous flow adsorption column for efficient Li recovery from seawater with LMO, showing a maximum adsorption capacity of 54.65 mg/g [151]. Multi-ion feed solutions, including simulated and real brines, were also employed to test the selectivity of the adsorptions of Li and other cations. Sun et al. synthesized β-MnO_2, spinel-type $LiMn_2O_4$, and $Li_4Mn_5O_{12}$ via hydrothermal synthesis and solid-state reaction, then utilized these LMO adsorbents to uptake Li from a solution containing Li, Na, K, Mg, Ca ions, indicating that the MnO_2 nanorod had the best Li selectivity [106]. Similar studies were also researched by Wang et al. [152], Ryu et al. [153], Recepoglu et al. [154], Chaban et al. [155], Roobavannan [52], and Xiao et al. [156].

Besides directly adsorbing Li from the Li-rich solution, LMO adsorbents are also combined with electrochemical Li recovery methods [45, 46, 157-159]. Mu et al. coated λ-MnO_2 and $LiMn_2O_4$ on 3D-graphite felt electrodes to produce a novel flow-type electrochemical Li recovery system that extracts Li 75 mg/h per gram $LiMn_2O_4$ [160]. Siekierka built a negatively polarized electrode with LMO for the CDI system, realizing 32 mg/g LiCl adsorption [47]. Liu et al. developed a new device using the ESIX technique based on λ-MnO_2/$LiMn_2O_4$ structures, attaining 3.5 mmol/g of Li adsorption capacity and lower than 0.05% Mn loss [105].

2.3 Ti-based adsorbents

Ti-based adsorbents (LTO) applications for Li recovery have gained momentum in the recent ten years especially due to their stability in acidic solutions. They are considered to be eco-friendly due to their non-reactive leaching propensity to the water environment and easy removal from aqueous solutions [61]. Compared with LMOs, the relatively stable structures of LTOs provide less dissolved loss, high adsorption capacity, excellent selectivity, and recyclability [161, 162].

2.3.1 Type, structure, and adsorption mechanism

The procedure for Li extraction using a Ti-based ion exchanger H_2TiO_3 (HTO) dates from 1989, first outlined by Onoderaet et al., prepared via the acid treatment of HTO [163]. The HTO adsorbent presents a layer crystal structure designated by the $Li[Li_{1/3}Ti_{2/3}]O_2$. The cell structure, as illustrated in **Fig. 7a**, is a cubic close packing of oxygen atoms accompanied by metal atoms placed in octahedral voids [61, 164, 165]. The exchange of Li and H occurs during the adsorbent preparation, adsorption, and desorption processes. Explicitly speaking, Li is replaced by H in the HTO preparation process by pickling Li_2TiO_3 into hydrochloric acid. Then in the Li extraction process, the memory effect dominates the particular selectivity for accepting Li preferentially because narrow exchange sites left during the preparation reject the occupation of other ions with dissimilar ionic radius or dehydration energy due to steric effects [166]. In a recent study, Marthi

et al. proposed a new perspective to the generally accepted ion-exchange mechanism without chemical bond breakage theory. They proposed a new explanation that O–H bonds break and the O–Li bonds form after thermogravimetric analysis, Raman spectroscopy and Fourier transform infrared spectroscopy studies [167]. Except for layer crystal Li_2TiO_3, spinel $Li_4Ti_5O_{12}$ (**Fig. 7d**), a star candidate of large-scale Li-ion batteries [168], is considered another LTO adsorbent. The mechanisms of Li intercalation and deintercalation are similar to LMO adsorbents, i.e., the redox, ion exchange, and composite mechanisms [61].

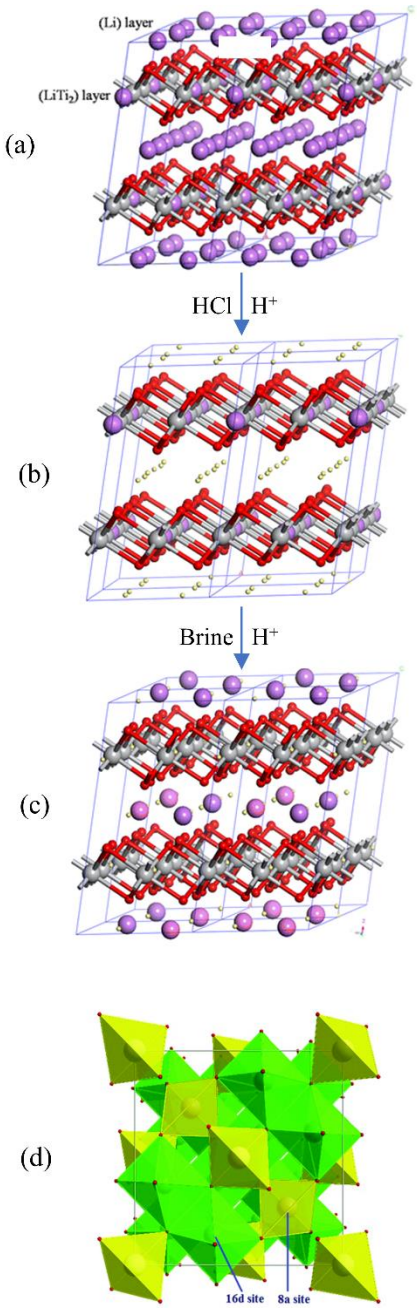


Figure 7. Crystal structure of (a) layered Li_2TiO_3, (b) H_2TiO_3, (c) H_2TiO_3 upon Li exchange, and (d) spinel $Li_4Ti_5O_{12}$. (a), (b), and (c) obtained from [166] with copyright permission from Springer Nature. (d) from [169] with copyright permission from Royal Society of Chemistry.

2.3.2 Synthesis methods and Li recovery performance

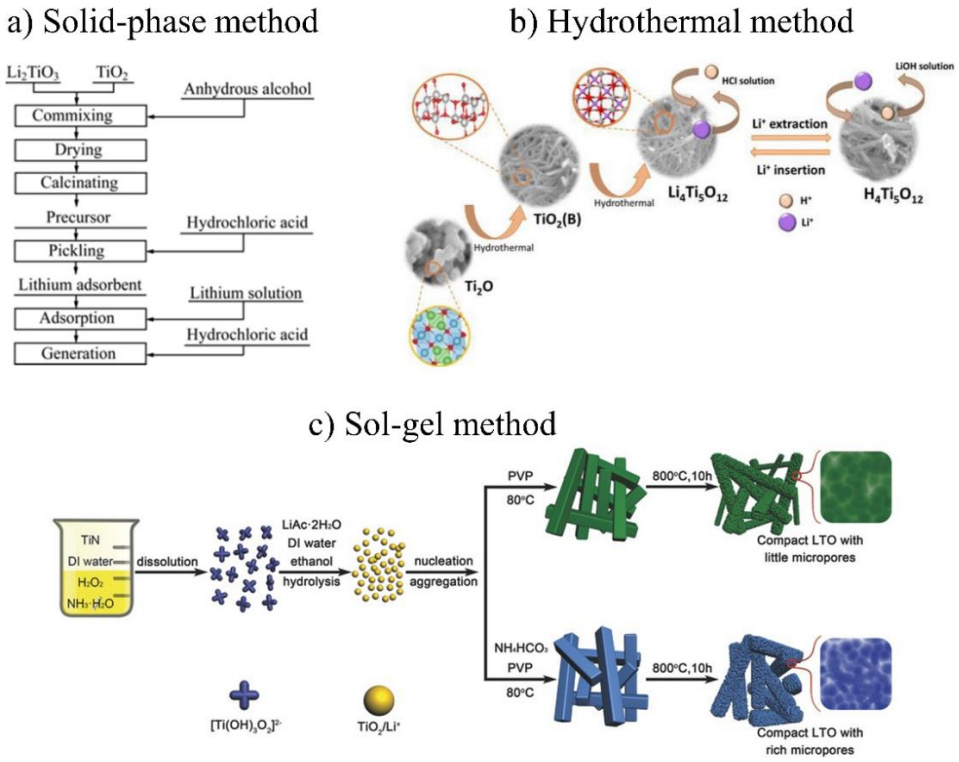
The synthesis strategies of LTO adsorbent highlight solid-phase [161, 164], sol-gel [170], and hydrothermal methods [171, 172] for precursor preparation (concluded in **Table 3** and **Fig. 8**) and

359 acid treatment for ion-sieve fabrication. The conventional solid-phase process requires the
360 calcination of the ground mixture of TiO_2 and Li_2CO_3 at around 700°C and then cooling down to
361 room temperature, presenting the merits of high capacity and selectivity for Li uptake and the
362 drawbacks of high reaction temperature and large grain sizes with low Li adsorption rate [164].
363 Shi et al. utilized mixed crystal titanium dioxide (TiO_2) to compound single crystal phase of HTO
364 through the solid-phase and hydrochloric solution immerging methods [161]. Hossain et al.
365 prepared HTO from sludge-generated TiO_2 via 4-h calcination in air at 750°C, and the Ti loss was
366 less than 3% after 72-h acid treatment [173]. Gu et al. applied the Li adsorbent derived via the
367 solid-state method from $C_2H_3LiO_2 \cdot 2H_2O$ and TiO_2 to separate Li and Mg in West Taijinar Lake.
368 The separation factor α (Li/Mg) of 5441.17 and the adsorption capacity of 24.5 mg/g after five
369 cycles demonstrated the feasibility of practical use [174]. Zhang et al. observed that calcination of
370 metatitanic acid produced different crystal phases of TiO_2 at various temperatures and that the
371 anatase structure reacted with $LiOH \cdot H_2O$ benefited the extraction of Li [175]. The sol-gel process
372 produces smaller particle sizes using multiple raw materials at a lower reaction temperature than
373 the solid-phase method. Zhang et al. synthesized Li_2TiO_3 with CH_3COOLi and $Ti(OC_4H_9)_4$ by the
374 sol-gel process, of which the Li adsorption capacity reached 21.0 mg/g [176]. The hydrothermal
375 method, widely utilized in the controllable synthesis of non-agglomerative nanomaterials, is also
376 a typical approach in LTO synthesis. Moazeni et al. synthesized monoclinic $Li_4Ti_5O_{12}$ nanotube
377 ion sieves with 50-70 nm in diameter and 1-2 micrometers in length via a soft hydrothermal
378 method, which presented outstanding Li selective adsorption capacity [171]. Zhao et al. fabricated
379 a $Li_4Ti_5O_{12}$ adsorbent with 5 μm length along the [100] direction by two hydrothermal processes
380 followed by a calcination process and HCl treatment [177]. The $H_4Ti_5O_{12}$ nanotubes synthesized
381 by Shoghi et al. via the hydrothermal method and acid treatment using TiO_2(B) nanotubes as a

precursor demonstrated a considerable high ion-exchange capacity (160.6 mg/g) for Li since the particular surface area was large (115.4 m^2/g) [178]. Wang et al. composited a Li-enriched β-Li_2TiO_3 by hydrothermal treatment with the TBA addition. It initially validated the enhancement of the Li adsorption capacity of the free hydrogen formation of β-Li_2TiO_3 and excessive HTi_2 layer exposure of HTO [172]. To overcome the difficulty that the adsorption capacity of LTO-LIS adsorbent is only about 40% of the theoretical value [58], doping strategy was induced in the synthesis process to improve the stability and practical capacity through flexible modification of the band structure of the materials [178, 179]. Wang et al. prepared a Fe-Ti-0.15(H) Li-ion sieve via solid-state reactions and acid treatment and a Mo-Ti-0.15(H) Li-ion sieve with a high O_2-content (61.58%) using a facile calcination method and acid pickling, which showed good stability, capacity and excellent selectivity [180, 181].

Composite strategy is also introduced in LTO adsorbent synthesis to produce composite materials [182]. Lawagon et al. selected hydrophilic polyacrylonitrile (PAN) from various polymers as the HTO matrix and fabricated nanofibers (NFs) by electrospun technology. The NFs showed excellent Li selectivity, capacity, durability, recyclability, and suitability for various aqueous Li sources [183]. Lin et al. employed acid-alkali resistant polyvinyl chloride (PVC) as a binder to granulate polyporous PVC-HTO adsorbents, exhibiting high separation factors between Li and Na, K, Ca of 297.55, 521.28, 273.58, respectively, in geothermal brine [184]. Limjuco et al. prepared a HTO/polyvinyl alcohol (PVA) (200 wt% HTO loading) composite foam, which exhibited consistent adsorption-desorption performance and mechanical stability in reusability experiments [185]. Marthi et al. adopted titania slag and diatomaceous earth as raw materials to synthesize HTO-DE composite adsorbent for extracting Li from the Great Salt Lake. They perceived that the Li uptake rate and the adsorption capacity in brine solution were influenced by

405 the competition of ions and the accumulation of protons and that adsorption sites were lost due to
406 the hydrolysis of metastable HTO at higher temperatures [186]. Zhang et al. coalesced
407 HTO powders prepared by solid-phase reaction of TiO_2 and Li_2CO_3 in LiCl molten-salt with the
408 forming agent polyvinyl butyral (PVB), obtaining chemically stable spherical adsorbent particles.
409 This synthesis method had a lower cost than the traditional solid-phase reaction approach, while
410 the adsorption capacity and microstructure stability remained, displaying a promising industrial
411 outlook [187]. Chen et al. developed a novel and easily reused granular and porous Ti-based Li-
412 ion sieve with the agar-assisted approach for recovering Li from geothermal water [188]. Wei et
413 al. prepared porous Ti-based nanofiber adsorbents with Li adsorption capacity of 59.1 mg/g and
414 high selectivity and stability from brine water via a combination strategy of electrospinning and
415 calcination [189]. Qian et al. prepared a series of HTO/cellulose aerogels with a porous network
416 for recovering Li from seawater rapidly and efficiently [190].



417

418 **Figure 8.** Schematic illustration of synthesis of LTO with a) solid-phase method, b) hydrothermal

method, and c) sol-gel method. (a) obtained from [161] and (b) from [178] with copyright permission from Elsevier. (c) obtained from [191] (copyright 2017 John Wiley and Sons).

For improving the performances of the adsorbents, optimal operation conditions are investigated. Zhu et al. reported that the shaping process did not impact the phase and pore structure of LTO adsorbents, while higher pH was beneficial to strengthening adsorption strength and increasing Li adsorption capacity notably [192]. Li et al. discovered that the adsorption process is mainly single-layer chemical adsorption by modeling the adsorption kinetics process of the LTO adsorbent, prepared by acid elution of a pure monoclinic spinel precursor [193]. Shi et al. found that the Li adsorption process conformed to the Langmuir equation with monolayer adsorption and pseudo-second-order rate model and that the optimal situation should be in the alkaline solution [161]. Lawagon et al. identified the Li adsorption process as endothermic and spontaneous and detected that a low ratio of its loading with the feed volume (i.e., low S/L ratio) could promote the performances of the HTO adsorbent [194]. Ooi et al. calculated the experimental Li elution curves by modeling and proposed conditions of having the eluate of high Li concentration in a short time [195]. Li et al. investigated the influence of the different crystal phases of TiO_2 precursors (amorphous, anatase, and rutile) on the adsorption performances of the terminated LTO and discovered a positive correlation between hydrophilicity and the adsorption performance of HTO based on contact angle experiments [196]. As for the influence of co-existing ions, Ji et al. noticed a slight influence of co-existing metal ions in the aqueous solution on Li recovery when searching the optimal synthesis conditions of their monoclinic crystal HTO [197]. Chitrakar et al. found that the size effect contributed to the HTO efficiently adsorbing Li from the salt lake brine collected from Salar de Uyuni, Bolivia, which contained competitive cations such as sodium, potassium, magnesium, and calcium in considerable excess [164].

Table 3. Synthesis methods and performances of Ti-based adsorbents

Precursors	Sources	Preparation	Li uptake capacity	Ref.
Li_2TiO_3	TiO_2, Li_2TiO_3	Solid-phase method	32.6 mg/g in brine containing $NaHCO_3$	[164]
Li_2TiO_3	CH_3COOLi, $Ti(OC_4H_9)_4$	Sol-gel method	21.0 mg/g after a treatment 24 h	[176]
Li_2TiO_3	TiO_2, $LiOH·H_2O$	Hydrothermal method	76.7 mg/g in LiOH solution (2g/L of Li) at 30℃ for 24h	[172]
Li_2TiO_3	Titania slag NaOH	Hydrothermal method	27.4 mg/g in LiCl buffered solution(pH=9.5)	[186]
Li_2TiO_3	Li_2TiO_3, TiO_2, ethanol	Liquid-solid phase method	34.2 mg/g in Li-containing solution	[196]
Li_2TiO_3	$Ti_2(SO_4)_3$, LiCOOH, $NH_3·H_2O$, H_2O_2	Precipitation-peptization method	33.35 mg/g within 8h	[198]
Li_2TiO_3	$C_2H_3LiO_2·2H_2O$, TiO_2	Liquid-solid phase method	24.5 mg/g after 5 adsorption-desorption cycles	[174]
Li_2TiO_3	TiO_2, $LiOH·H_2O$	Solid-phase method	52 mg/g in LiOH solutions (1.8 g/L of Li, pH=12)	[199]
Mo-doped Li_2TiO_3	TiO_2, $LiOH·H_2O$, MoO_2	Solid-phase method	78 mg/g in LiOH solution (1.8g/L of Li at room temperature)	[180]
Fe-doped Li_2TiO_3	TiO_2, $LiOH·H_2O$, Fe_2O_3	Solid-phase method	34.8 mg/g in adjusted brine with 1560 mg/L of Li	[200]
$Li_4Ti_5O_{12}$	TiO_2, NaOH, LiOH	Two-step hydrothermal method	39.43 mg/g in 120 mg/L of Li solution	[171]
$Li_4Ti_5O_{12}$	TiO_2, NaOH, LiOH	Hydrothermal method	160.6 mg/g in the LiCl solution with 2000 mg/L of Li	[178]

2.4 Comparison of three types of metal-based Li adsorbents

Table 4 compared the Li adsorption capacities, selectivity, technology maturity, stability and regeneration ability, operation condition requirement, environmental safety, and preparation cost of three types of metal-based Li adsorbents in their optimal operation conditions. Capacities reflect the Li adsorption ability; selectivity presents Li adsorption advantages in the competition with other co-existing ions; technology maturity, stability, regeneration ability, operation condition requirement, environmental safety, and preparation cost are the most significant factors in industrial scale-up and commercial applications. Al-based adsorbents have the highest technology maturity but lowest capacity. Mn-based adsorbents show good selectivity, yet the Mn loss during desorption can be harmful to the water environment. Ti-based adsorbents present remarkable capacity, but further investigations on fabrication for scale-up applications are required since the performances decrease dramatically after granulating the powdery adsorbents.

Table 4. Comparison of three types of metal-based adsorbents

Performance	Al-based	Mn-based	Ti-based
Li Adsorption Capacity	★☆☆	★★☆	★★★
Li Selectivity	★☆☆	★★★	★★☆
Technology Maturity	★★★	★★☆	★☆☆
Stability and Regeneration Ability	★★★	★☆☆	★★☆
Facile Operation Condition	★★★	★☆☆	★★☆
Environmental Safety	★★★	★☆☆	★★☆
Low Preparation Cost	★★★	★☆☆	★★☆

Due to the Li-H ion-exchange adsorption mechanism, pH is a critical condition to influence the capacities of metal-based Li adsorbents. Al-based adsorbents show the best performance in neutral solutions, while Mn-based and Ti-based adsorbents have the highest capacities in basic conditions [94, 141, 144, 192, 201-207]. **Fig. 9** compared the influence of pH on each type of metal-based Li adsorbents.

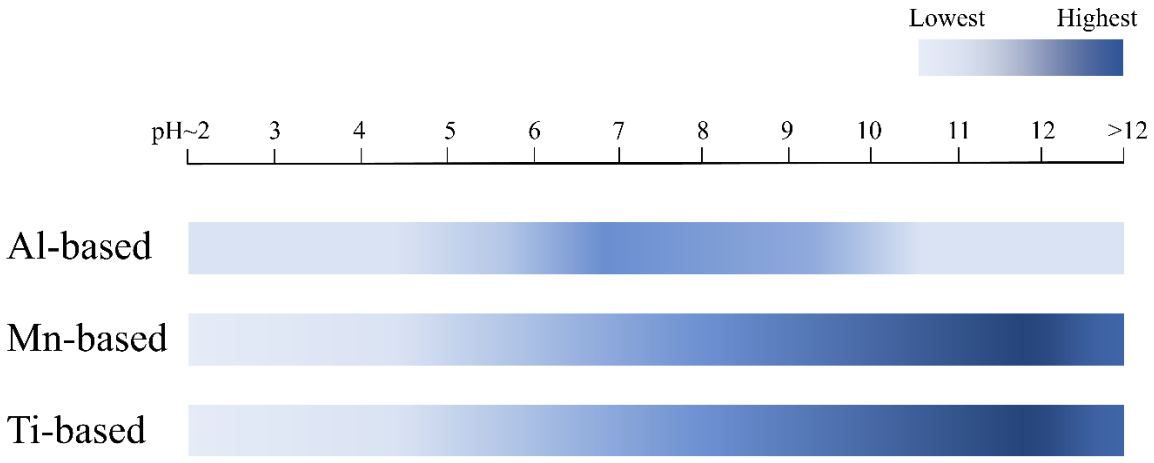


Figure 9. The capacity performances of metal-based Li adsorbents under different pH conditions.

3. Case study - Application of metal-based adsorbent for Li recovery in an actual industrial site

The Qarhan Salt Lake located in Qinghai Province is the largest salt lake with the highest Li reserves in China, with an estimated 10.49 million tons of lithium carbonate equivalents (LCE) reserves [208]. **Table 5** lists the ion compositions of the Qarhan Salt Lake brine. The primary interfering ion is Mg, and the Mg/Li ratio is approximately around 365. The current Li mining right of the Qarhan Salt Lake is held by Qinghai Lakelithium Co., LTD and Golmud Zangge Lithium Co., LTD. In 2021, a 20000-tonne-scale plant with adsorption technology was built at Qarhan Salt Lake by Qinghai Lakelithium Co., LTD, and a trial run was successfully completed.

Table 5. Ion Compositions of the Qarhan Salt Lake brine [67]

Li	Na	Mg	Ca	B	Cl	SO_4	Mg/Li
0.35	1.866	127.9	0.04	0.39	334.8	11.6	365.43

3.1 Adsorbent production and regeneration technologies

The production process of the Al-based adsorbent [$LiCl{\cdot}(2.2{\sim}2.8)Al(OH)_3{\cdot}(2.7{\sim}3.9)H_2O$] for Li recovery from the Qarhan Salt Lake is shown in **Fig. 10**. Firstly, $AlCl_3$ solution and Li compound ($LiOH/Li_2CO_3/LiCl$) are mixed thoroughly in a preparing tank, forming an intermediate product S0. The ratio of Al and Li should be 1.8-2.2:1. For example, 148 g Li_2CO_3 or 2 L LiOH solution (60 g/L) is added in 8 L $AlCl_3$ solution (120 g/L). Then, S0 and NaOH solution react in a reactor, generating an intermediate product S1. Next, S1 is separated, washed, dried, and ground to powder S2, and S3 is granulated by adding adhesive and liquid chlorine into S2. Finally, S3 is crushed and screened to produce Li adsorbents. The granular size of the final product is 0.5-1.8 mm, and the specific surface area is 2.9 m^2/g. The adsorption equivalent is 1.8-2.7 g/kg, and the loss rate in washing is 12-30% [209].

The adsorption performance of the adsorbent will decrease after the long-term operation in

the adsorption chamber because hydroxide precipitates caused by hydrolysis reaction gradually adhere to the surface of the Li adsorbent and block the inner pores. Thus, a regeneration process is necessary to reduce adsorbent loss and control the cost. The ammonium salt solution with a concentration of 0.6-2.0 kg/m^3 prepared in the mixing chamber using concentrated ammonium salt solution and salt-free water is infused into the adsorption chamber to meet with saturated adsorbents for a residence time (around 3 hours). In this process, during Li desorbing, the obstruction in adsorbents reacts with ammonium salt and dissolves in solution, and adsorbents regenerate. Finally, the desorbed LiCl solution and dissolved obstruction flow to the desorption solution tank [210].

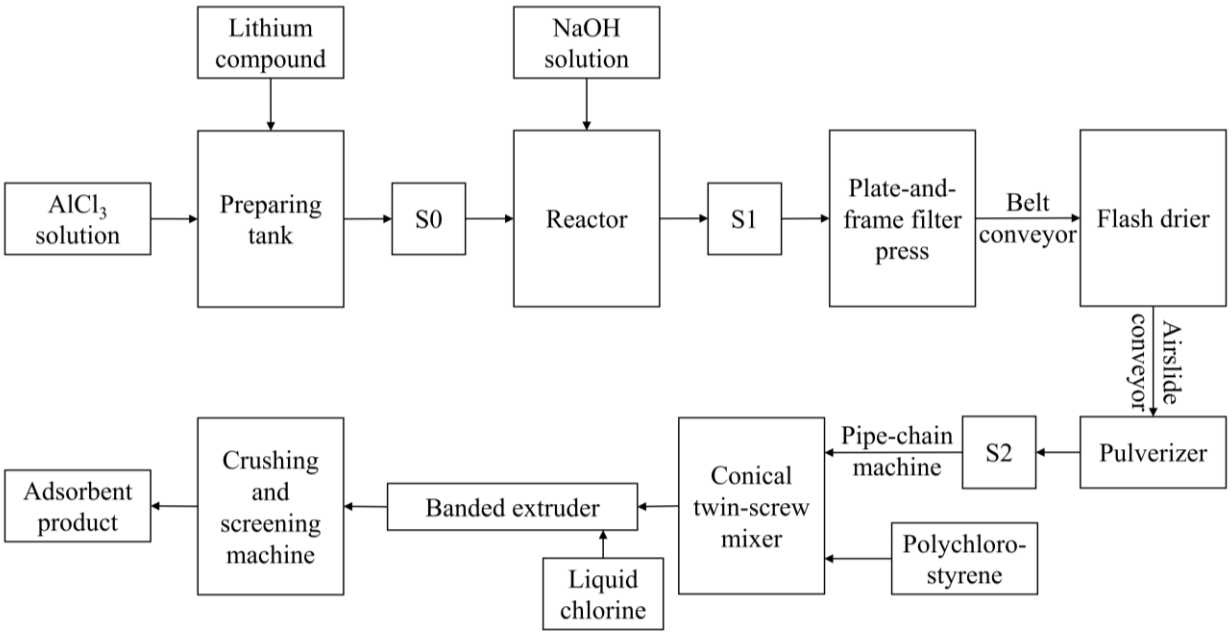


Figure 10. Flow sheet of adsorbent production. S0, S1, S2 represent intermediate products 1, 2, 3, respectively.

3.2 Li recovery process and operation

Li production on a commercial scale typically adopts integrated processes in terms of the compositions of different brine sources. **Fig. 11** presents the overall process of Li recovery in this

case. The path starts from adsorption in a full chamber bed. In specific scenarios, based on the Li concentration in the desorbed LiCl solution, nanofiltration is sometimes employed prior to electrodialysis as a pretreatment. Upon electrodialysis pretreatment, the main train of processes involves, firstly, ion exchange, reverse osmosis, and secondly ion exchange, followed by electrodialysis, and crystallization, to finally obtain LiCl product with high purity (LiCl > 99.1%) [211, 212].

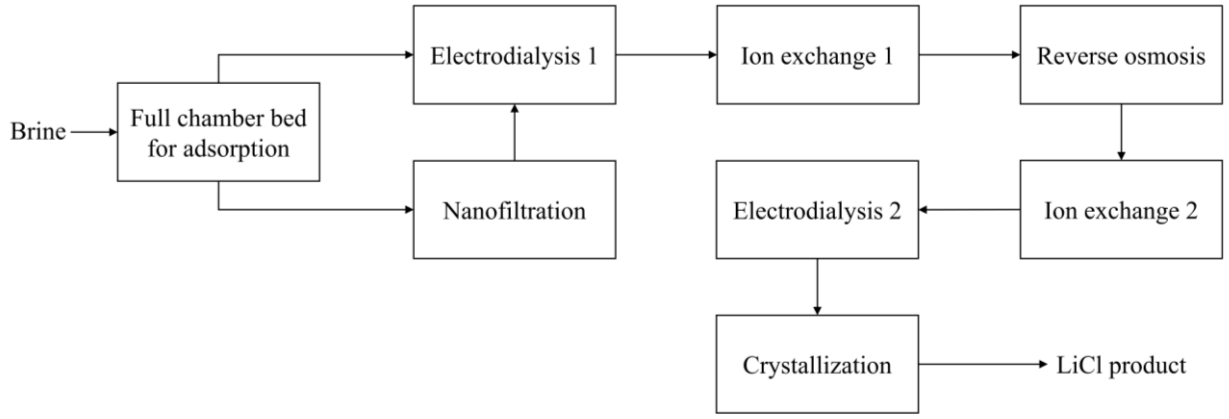


Figure 11. Li recovery process. Adsorption using a full chamber bed is the first step for concentrating LiCl solution from the brine.

The operation conditions in the adsorption process are listed in **Table 6**. The brine is injected into the adsorption tower loaded with low-Li-state adsorbents. After an adsorption process, the adsorbents become adsorbed-state, and the adsorption tail solution is discharged out of the adsorption unit. Next, the rinse solution is injected into the adsorption tower, and then the rinse tail solution is discharged out of the adsorption unit. Finally, the desorption solution is injected into the adsorption tower. After a desorption process, the adsorbents return to a low-Li state, and a high-Li mother solution is obtained and transferred to the next process unit. The discharged adsorption tail solution and rinse tail solution are mixed and injected back into the adsorption tower. The above step is repeated several times to produce concentrated LiCl solution continuously. The

desorption tail solution is left in the adsorption tower. The desorbed solution (high-Li mother solution) comprises of 0.4-0.9 g/L Li, 0.5-8.0 g/L Mg, 0.01-0.2 g/L Na, 2-20 g/L Cl. The recovery rate of LiCl reaches 40-60% [211-213].

Table 6. Operation conditions in the adsorption process [211].

Adsorption flow velocity	Adsorption temperature	Rinse flow velocity	Rinse temperature	Desorption flow velocity	Desorption temperature
5-8 m/h	10-25℃	10-20 m/h	10-25℃	10-20 m/h	20-40℃

3.3 Cost, benefit, and economic evaluation

The novel production lines with the adsorption method win the attention of Lakelithium Co. LTD from the Li market, even stimulating the share price of its parent companies to surge. In the past years, the Chinese market has shown unprecedented confidence in Li recovery from brines since new technologies can reduce the cost of production. The unit profits, productions, and costs of Li carbonate products from 2013 to 2021 are exhibited in **Fig. 12**. According to the financial reports and market survey reports [214, 215], the current cost of Li recovery can be controlled within 34000 RMB/ton (around 5340 USD/ton). Compared with membrane and electrodialysis processes, the overall capital expenditure on adsorption technology is higher. Thus, the future production expansion can further reduce the unit cost and increase the profit margin.

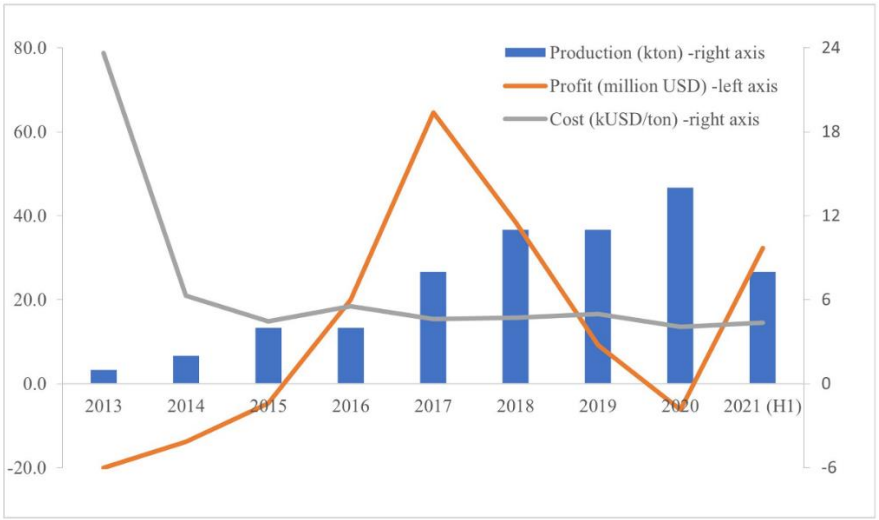


Figure 12. The unit profits, productions, and costs of Li_2CO_3 from 2013 to 2021 (data from [208]).

The US National Renewable Energy Laboratory investigated seven Li extraction projects from geothermal brines in various companies to compare Li recovery costs through different methods. The survey and modeled data of productions, production costs, capital expenses (CAPEX), operating expenses (OPEX), product prices, and Li recovery are listed in **Table 7**. Although direct cost comparison of different locations requires a number of assumptions and, therefore, to some degree, is unfair, the data is able to provide a broad visualization of economic indicators based on different approaches. The pilot plant project of Vulcan Energy Resources using commercial adsorbents performs outstandingly with the low production cost and high Li recovery rate.

Table 7. Summary of Li recovery project economics. Table obtained from [216] (copyright National Renewable Energy Laboratory).

Company	Production (mt/y)	Production cost (USD/mt)	CAPEX (kUSD)	OPEX (kUSD/y)	Product price (USD/mt)	Technology	Li recovery rate
SRI International	20000	3845	52300	76900	12000	Li-imprinted polymer	90%
Vulcan Energy Resources	40000	3217	1287600	128688	14925	Commercial adsorbents	90%
Standard Lithium	20900	4319	437162	90259	13550	Ceramic adsorbent and crystallization	90%
E3 Metals Corp	20000	3656	602000	73200	15160	Ion exchange	>90%
Anson Resources	15000	4545	120000	68180	13000	Ion exchange	75%
Pure Energy Minerals	11500	3217	358601	36516	12267	Solvent extraction	90%
Lake Resources	25500	4178	544000	106539	11000	Ion exchange	83.2%

4. Outlook and Conclusions

Li extraction from aqueous resources by Al, Mn, and Ti-based metal adsorbents, is comprehensively reviewed in terms of synthesis methods, Li uptake mechanisms, and Li recovery performances. Al-based adsorbents have been employed as commercial adsorbents in the industry due to the relatively mature preparation technology, low-cost price, and stability, although their Li adsorption capacity is lower than Mn-based and Ti-based adsorbents. A number of different types

of Mn-based adsorbents can be developed based on Li/Mn ratio in precursors, and the formations of the crystals rely on the control of synthesis conditions. Although Mn-based adsorbents present promising potential in Li adsorption capacity, the Mn loss problem still prevents further scale-up applications, requiring more investigations on stability improvements such as doping and coating. Ti-based adsorbents exhibit good stability in acidic surroundings with low leaching issues, yet practical adsorption capacity is inferior to theoretical capacity. Besides, an industrial case study is introduced to analyze the operation process and economic behavior, giving an example and benchmark for the application developments for commercial adsorbents.

The substantial Li demand promotes the rapid transition of lab-state research to engineering projects. Overall, the adsorbent productions and Li recovery processes show advantages of simple operation, high maturity, and strong reliability. The metal-based adsorbent presents good Li selectivity, high adsorption efficiency, and environmental-friendly property. Nevertheless, major limitations such as poor versatility, low reuse frequency, and dissolution loss hinder industrial applications. Scaling up to a large-scale plant is the ultimate goal for all kinds of adsorbents. Therefore, the study on metal-based adsorbents in Li recovery should be focused on 1) stability improvement to achieve the long-term operation goal, 2) adsorbent explorations for different application conditions, such as resources with different pH, Li contents, and temperatures, 3) economical process design to reduce operating cost, 4) hybrid process optimization to produce valuable net-worth products with high Li purity.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

We thank financial support from the Qatar National Research Fund under its National Priorities Research Program (NPRP 12S-0227-190166), Australian Research Council (ARC, IH210100001), Australian Indian Strategic Research Funding (Round 12 AIRXII000019), and Australian Research Council Discovery Early Career Research Award (DE200100661).

References

1. Choubey, P.K., et al., *Advance review on the exploitation of the prominent energy-storage element: Lithium. Part I: From mineral and brine resources.* Minerals Engineering, 2016. **89**: p. 119-137.
2. Martin, G., et al., *Lithium market research – global supply, future demand and price development.* Energy Storage Materials, 2017. **6**: p. 171-179.
3. USGS, *Mineral Commodity Summaries 2021*, in *Mineral Commodity Summaries*. 2021.
4. USGS, *Mineral Commodity Summaries 2022*, in *Mineral Commodity Summaries*. 2022.
5. USGS, *Mineral Commodity Summaries 2021*. 2021.
6. USGS, *Mineral Commodity Summaries 2020*, in *Mineral Commodity Summaries*. 2020.
7. USGS, *Mineral Commodity Summaries 2019*, in *Mineral Commodity Summaries*. 2019.
8. Hou, J., et al., *Lithium Extraction by Emerging Metal-Organic Framework-Based Membranes.* Advanced Functional Materials, 2021. **31**(2105991).
9. Yang, S., et al., *Lithium Metal Extraction from Seawater.* Joule, 2018. **2**(9): p. 1648-1651.
10. Vikström, H., S. Davidsson, and M. Höök, *Lithium availability and future production outlooks.* Applied Energy, 2013. **110**: p. 252-266.
11. Grosjean, C., et al., *Assessment of world lithium resources and consequences of their geographic distribution on the expected development of the electric vehicle industry.* Renewable and Sustainable Energy Reviews, 2012. **16**(3): p. 1735-1744.
12. Swain, B., *Recovery and recycling of lithium: A review.* Separation and Purification Technology, 2017. **172**: p. 388-403.
13. Zhang, Y., et al., *Systematic review of lithium extraction from salt-lake brines via precipitation approaches.* Minerals Engineering, 2019. **139**(105868).
14. Li, X., et al., *Membrane-based technologies for lithium recovery from water lithium resources: A review.* Journal of Membrane Science, 2019. **591**(117317).
15. Coterillo, R., et al., *Selective extraction of lithium from seawater desalination concentrates: Study of thermodynamic and equilibrium properties using Density Functional Theory (DFT).* Desalination, 2022. **532**(115704).
16. Shi, D., et al., *Removal of calcium and magnesium from lithium concentrated solution by solvent extraction method using D2EHPA.* Desalination, 2020. **479**(114306).
17. Jiang, H., et al., *Synergic and competitive adsorption of Li-Na-$MgCl_2$ onto lithium-aluminum hydroxides.* Adsorption, 2020. **26**(7): p. 1039-1049.
18. Battistel, A., et al., *Electrochemical Methods for Lithium Recovery: A Comprehensive and Critical Review.* Adv Mater, 2020. **32**(1905440).
19. Liu, D., et al., *A closed-loop process for selective lithium recovery from brines via electrochemical and precipitation.* Desalination, 2021. **519**(115302).

20. Palagonia, M.S., D. Brogioli, and F. La Mantia, *Lithium recovery from diluted brine by means of electrochemical ion exchange in a flow-through-electrodes cell.* Desalination, 2020. **475**(114192).
21. Bazrgar Bajestani, M., A. Moheb, and M. Dinari, *Preparation of lithium ion-selective cation exchange membrane for lithium recovery from sodium contaminated lithium bromide solution by electrodialysis process.* Desalination, 2020. **486**(114476).
22. Perez-Antolin, D., et al., *Regenerative electrochemical ion pumping cell based on semi-solid electrodes for sustainable Li recovery.* Desalination, 2022. **533**(115764).
23. Xu, Y., et al., *High performance Mg^{2+}/Li^{+} separation membranes modified by a bis-quaternary ammonium salt.* Desalination, 2022. **526**(115519).
24. He, R., et al., *Unprecedented Mg^{2+}/Li^{+} separation using layer-by-layer based nanofiltration hollow fiber membranes.* Desalination, 2022. **525**(115492).
25. Zhang, C., et al., *Lithium extraction from synthetic brine with high Mg^{2+}/Li^{+} ratio using the polymer inclusion membrane.* Desalination, 2020. **496**(114710).
26. İpekçi, D., et al., *Application of heterogeneous ion exchange membranes for simultaneous separation and recovery of lithium and boron from aqueous solution with bipolar membrane electrodialysis (EDBM).* Desalination, 2020. **479**(114313).
27. Paredes, C. and E. Rodríguez de San Miguel, *Selective lithium extraction and concentration from diluted alkaline aqueous media by a polymer inclusion membrane and application to seawater.* Desalination, 2020. **487**(114500).
28. Guo, X., et al., *Highly Efficient Separation of Magnesium and Lithium and High-Valued Utilization of Magnesium from Salt Lake Brine by a Reaction-Coupled Separation Technology.* Industrial & Engineering Chemistry Research, 2018. **57**(19): p. 6618-6626.
29. Sun, Y., et al., *Recent advances in magnesium/lithium separation and lithium extraction technologies from salt lake brine.* Separation and Purification Technology, 2021. **256**(117807).
30. Khalil, A., et al., *Lithium recovery from brine: Recent developments and challenges.* Desalination, 2022. **528**(115611).
31. Zhao, Y., et al., *An integrated membrane process for preparation of lithium hydroxide from high Mg/Li ratio salt lake brine.* Desalination, 2020. **493**(114620).
32. Ying, J., et al., *Selective separation of lithium from high Mg/Li ratio brine using single-stage and multi-stage selective electrodialysis processes.* Desalination, 2020. **492**(114621).
33. Flexer, V., C.F. Baspineiro, and C.I. Galli, *Lithium recovery from brines: A vital raw material for green energies with a potential environmental impact in its mining and processing.* Sci Total Environ, 2018. **639**: p. 1188-1204.
34. An, J.W., et al., *Recovery of lithium from Uyuni salar brine.* Hydrometallurgy, 2012. **117-118**: p. 64-70.
35. Kenta Onishi, T.N., Syouhei Nishihama, and Kazuharu Yoshizuka, *Synergistic Solvent Impregnated Resin for Adsorptive Separation of Lithium Ion.* Industrial & Engineering Chemistry Research, 2010. **49**(14): p. 6554-6558.
36. Masmoudi, A., et al., *Solvent extraction of lithium ions using benzoyltrifluoroacetone in new solvents.* Separation and Purification Technology, 2021. **255**(117653).
37. Hong, Z., et al., *Dependence of concentration polarization on discharge profile in electrochemical lithium extraction.* Desalination, 2022. **527**(115567).
38. M. Bryjak, A.S., J. Kujawski, K. Smolinska-Kempisty, W. Kujawski, *Capacitive deionization for selective extraction of lithium from aqueous solutions.* Journal of Membrane and Separation Technology, 2015. **4**: p. 110-115.
39. Sahin, S., et al., *Enhanced monovalent over divalent cation selectivity with polyelectrolyte multilayers in membrane capacitive deionization via optimization of operational conditions.* Desalination, 2022. **522**(115391).
40. Chen, Z., et al., *Ultra-durable and highly-efficient hybrid capacitive deionization by MXene confined MoS_2 heterostructure.* Desalination, 2022. **528**(115616).

41. Zavahir, S., et al., *A review on lithium recovery using electrochemical capturing systems.* Desalination, 2021. **500**(114883).
42. Zhao, W.-Y., et al., *Waste Conversion and Resource Recovery from Wastewater by Ion Exchange Membranes: State-of-the-Art and Perspective.* Industrial & Engineering Chemistry Research, 2018. **57**(18): p. 6025-6039.
43. Liu, G., Z. Zhao, and L. He, *Highly selective lithium recovery from high Mg/Li ratio brines.* Desalination, 2020. **474**(114185).
44. Sharma, P.P., et al., *Sulfonated poly (ether ether ketone) composite cation exchange membrane for selective recovery of lithium by electrodialysis.* Desalination, 2020. **496**(114755).
45. Siekierka, A., *Lithium and magnesium separation from brines by hybrid capacitive deionization.* Desalination, 2022. **527**(115569).
46. Siekierka, A. and M. Bryjak, *Selective sorbents for recovery of lithium ions by hybrid capacitive deionization.* Desalination, 2021. **520**(115324).
47. Siekierka, A., *Lithium iron manganese oxide as an adsorbent for capturing lithium ions in hybrid capacitive deionization with different electrical modes.* Separation and Purification Technology, 2020. **236**(116234).
48. Gong, L., et al., *Direct numerical simulation of continuous lithium extraction from high Mg^{2+}/Li^{+} ratio brines using microfluidic channels with ion concentration polarization.* J Memb Sci, 2018. **556**: p. 34-41.
49. Limjuco, L.A., et al., *Aerosol Cross-Linked Crown Ether Diols Melded with Poly(vinyl alcohol) as Specialized Microfibrous Li^{+} Adsorbents.* ACS Appl Mater Interfaces, 2017. **9**(49): p. 42862-42874.
50. Liu, W., et al., *Extraction of lithium ions from acidic solution using electrochemically imprinted membrane.* Desalination, 2020. **496**(114751).
51. Pramanik, B.K., et al., *A critical review of membrane crystallization for the purification of water and recovery of minerals.* Reviews in Environmental Science and Bio/Technology, 2016. **15**(3): p. 411-439.
52. Roobavannan, S., S. Vigneswaran, and G. Naidu, *Enhancing the performance of membrane distillation and ion-exchange manganese oxide for recovery of water and lithium from seawater.* Chemical Engineering Journal, 2020. **396**(125386).
53. Ryu, T., et al., *Recovery of Lithium by an Electrostatic Field-Assisted Desorption Process.* Industrial & Engineering Chemistry Research, 2013. **52**(38): p. 13738-13742.
54. Choi, J., H. Lee, and S. Hong, *Capacitive deionization (CDI) integrated with monovalent cation selective membrane for producing divalent cation-rich solution.* Desalination, 2016. **400**: p. 38-46.
55. Shi, W., et al., *Efficient lithium extraction by membrane capacitive deionization incorporated with monovalent selective cation exchange membrane.* Separation and Purification Technology, 2019. **210**: p. 885-890.
56. Zhang, Y., et al., *Selectrodialysis: Fractionation of divalent ions from monovalent ions in a novel electrodialysis stack.* Separation and Purification Technology, 2012. **88**: p. 191-201.
57. Ge, L., et al., *Electrodialysis with nanofiltration membrane (EDNF) for high-efficiency cations fractionation.* Journal of Membrane Science, 2016. **498**: p. 192-200.
58. Luo, Q., et al., *Extraction of lithium from salt lake brines by granulated adsorbents.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2021. **628**(127256).
59. Orooji, Y., et al., *Recent advances in nanomaterial development for lithium ion-sieving technologies.* Desalination, 2022. **529**(115624).
60. Xu, P., et al., *Materials for lithium recovery from salt lake brine.* Journal of Materials Science, 2020. **56**(1): p. 16-63.
61. Xu, X., et al., *Extraction of lithium with functionalized lithium ion-sieves.* Progress in Materials Science, 2016. **84**: p. 276-313.

62. Weng, D., et al., *Introduction of manganese based lithium-ion Sieve-A review.* Progress in Natural Science-Materials International, 2020. **30**(2): p. 139-152.
63. Zhao, X., et al., *Review on the electrochemical extraction of lithium from seawater/brine.* Journal of Electroanalytical Chemistry, 2019. **850**(113389).
64. Zhang, X., A. Han, and Y. Yang, *Review on the production of high-purity lithium metal.* Journal of Materials Chemistry A, 2020. **8**(43): p. 22455-22466.
65. Meshram, P., B.D. Pandey, and T.R. Mankhand, *Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: A comprehensive review.* Hydrometallurgy, 2014. **150**: p. 192-208.
66. Liu, G., Z. Zhao, and A. Ghahreman, *Novel approaches for lithium extraction from salt-lake brines: A review.* Hydrometallurgy, 2019. **187**: p. 81-100.
67. Shanshan Xu, J.S., Qiuyan Bi, Qing Chen, Wei-Ming Zhang, Zexin Qian, Lei Zhang, Shiai Xu, Na Tang, Tao He, *Extraction of lithium from Chinese salt-lake brines by membranes: Design and practice.* Journal of Membrane Science, 2021. **635**(119441).
68. Taghvaie Nakhjiri, A., et al., *Recovery of precious metals from industrial wastewater towards resource recovery and environmental sustainability: A critical review.* Desalination, 2022. **527**(115510).
69. Ogunbiyi, O., et al., *Sustainable brine management from the perspectives of water, energy and mineral recovery: A comprehensive review.* Desalination, 2021. **513**(115055).
70. Goh, K.-H., T.-T. Lim, and Z. Dong, *Application of layered double hydroxides for removal of oxyanions: A review.* Water Research, 2008. **42**(6-7): p. 1343-1368.
71. Chen, J., S. Lin, and J. Yu, *High-selective cyclic adsorption and magnetic recovery performance of magnetic lithium-aluminum layered double hydroxides (MLDHs) in extracting Li^+ from ultrahigh Mg/Li ratio brines.* Separation and Purification Technology, 2021. **255**(117710).
72. Kotsupalo, N.P., et al., *Effect of structure on the sorption properties of chlorine-containing form of double aluminum lithium hydroxide.* Russian Journal of Applied Chemistry, 2013. **86**(4): p. 482-487.
73. Zhong, J., S. Lin, and J. Yu, *Li^+ adsorption performance and mechanism using lithium/aluminum layered double hydroxides in low grade brines.* Desalination, 2021. **505**(114983).
74. S. G. Kozlova, S.P.G., V. P. Isupov & L.É. Chupakhina, *Using NMR in Structural Studies of Aluminum Hydroxide Intercalation Compounds with Lithium Salts.* Journal of Structural Chemistry, 2003. **44**(2): p. 198–205.
75. Hou, X.-J., et al., *Structural and electronic analysis of Li/Al layered double hydroxides and their adsorption for CO_2.* Applied Surface Science, 2017. **416**: p. 411-423.
76. Britto, S. and P.V. Kamath, *Structure of bayerite-based lithium-aluminum layered double hydroxides (LDHs): observation of monoclinic symmetry.* Inorg Chem, 2009. **48**(24): p. 11646-54.
77. Graham, T.R., et al., *Unraveling Gibbsite Transformation Pathways into LiAl-LDH in Concentrated Lithium Hydroxide.* Inorganic Chemistry, 2019. **58**(18): p. 12385-12394.
78. Sun, Y., et al., *Highly Efficient Lithium Recovery from Pre-Synthesized Chlorine-Ion-Intercalated LiAl-Layered Double Hydroxides via a Mild Solution Chemistry Process.* Materials (Basel), 2019. **12**(1968).
79. M Frenkel, A.G., S Sarig, *Crystal Modification of Freshly Precipitated Aluminum Hydroxide by Lithium Ion.* The Journal of Physical Chemistry, 1980. **84**: p. 507-510.
80. K. R. Poeppelmeier, S.-J.H., *Synthesis of Lithium Dialuminate by Salt Imbibition.* Inorganic Chemistry, 1987. **26**: p. 3297-3302.
81. Qu, J., et al., *Synthesis of Li–Al layered double hydroxides via a mechanochemical route.* Applied Clay Science, 2016. **120**: p. 24-27.
82. Qu, J., et al., *Mechanochemical approaches to synthesize layered double hydroxides: a review.* Applied Clay Science, 2016. **119**: p. 185-192.

83. Stepanova, L.N., et al., *The study of structural, textural and basic properties of MgAl- and LiAl-LDH prepared by mechanochemical method.* Catalysis Today, 2020. **357**: p. 638-645.
84. Isupov, V.P., et al., *Aluminium hydroxide as selective sorbent of lithium salts from brines and technical solutions.* Adsorption and Its Applications in Industry and Environmental Protection, Vol I: Applications in Industry, 1998. **120**: p. 621-652.
85. Xuheng Liua, M.Z., Xingyu Chena,b, Zhongwei Zhao, *Separating lithium and magnesium in brine by aluminum-based materials.* Hydrometallurgy, 2018. **176**: p. 73-77.
86. Zhong, J., S. Lin, and J. Yu, *Lithium recovery from ultrahigh Mg^{2+}/Li^{+} ratio brine using a novel granulated Li/Al-LDHs adsorbent.* Separation and Purification Technology, 2021. **256**(117780).
87. Lee, Y., J.H. Cha, and D.Y. Jung, *Selective Lithium Adsorption of Silicon Oxide Coated Lithium Aluminum Layered Double Hydroxide Nanocrystals and Their Regeneration.* Chem Asian J, 2021. **16**(8): p. 974-980.
88. Sun, Y., et al., *Highly efficient extraction of lithium from salt lake brine by LiAl-layered double hydroxides as lithium-ion-selective capturing material.* Journal of Energy Chemistry, 2019. **34**: p. 80-87.
89. Lee, Y., J.-H. Cha, and D.-Y. Jung, *Lithium separation by growth of lithium aluminum layered double hydroxides on aluminum metal substrates.* Solid State Sciences, 2020. **110**(106488).
90. Lee, Y. and D.-Y. Jung, *Polyacrylonitrile hybrid membrane coated with aluminum hydroxide for separating lithium.* Journal of Physics and Chemistry of Solids, 2022. **162**(110509).
91. Jiang, H., Y. Yang, and J. Yu, *Application of concentration-dependent HSDM to the lithium adsorption from brine in fixed bed columns.* Separation and Purification Technology, 2020. **241**(116682).
92. Jiang, H., et al., *Adsorption of lithium ions on lithium-aluminum hydroxides: Equilibrium and kinetics.* The Canadian Journal of Chemical Engineering, 2019. **98**(2): p. 544-555.
93. Zhong, J., S. Lin, and J. Yu, *Effects of excessive lithium deintercalation on Li(+) adsorption performance and structural stability of lithium/aluminum layered double hydroxides.* J Colloid Interface Sci, 2020. **572**: p. 107-113.
94. Paranthaman, M.P., et al., *Recovery of Lithium from Geothermal Brine with Lithium-Aluminum Layered Double Hydroxide Chloride Sorbents.* Environmental Science & Technology, 2017. **51**(22).
95. Hu, F.P., et al., *Quantitative Effects of Desorption Intensity on Structural Stability and Readsorption Performance of Lithium/Aluminum Layered Double Hydroxides in Cyclic Li^{+} Extraction from Brines with Ultrahigh Mg/Li Ratio.* Industrial & Engineering Chemistry Research, 2020. **59**(30): p. 13539-13548.
96. Huang, T.-Y., et al., *Life Cycle Assessment and Techno-Economic Assessment of Lithium Recovery from Geothermal Brine.* ACS Sustainable Chemistry & Engineering, 2021. **9**(19): p. 6551-6560.
97. Wu, L.L., et al., *Lithium aluminum-layered double hydroxide chlorides (LDH): Formation enthalpies and energetics for lithium ion capture.* Journal of the American Ceramic Society, 2019. **102**(5): p. 2398-2404.
98. Mak Yu, T., et al., *Exploring the surface reactivity of the magnetic layered double hydroxide lithium-aluminum: An alternative material for sorption and catalytic purposes.* Applied Surface Science, 2019. **467-468**: p. 1195-1203.
99. Chen, J., S. Lin, and J. Yu, *Quantitative effects of Fe_3O_4 nanoparticle content on Li^{+} adsorption and magnetic recovery performances of magnetic lithium-aluminum layered double hydroxides in ultrahigh Mg/Li ratio brines.* J Hazard Mater, 2020. **388**(122101).
100. Pauwels, H., M. Brach, and C. Fouillac, *Study of Li^{+} adsorption onto polymeric aluminium (III) hydroxide for application in the treatment of geothermal waters.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 1995. **100**: p. 73-82.
101. Wang, H., et al., *Recovery of both magnesium and lithium from high Mg/Li ratio brines using a novel process.* Hydrometallurgy, 2018. **175**: p. 102-108.

102. Heidari, N. and P. Momeni, *Selective adsorption of lithium ions from Urmia Lake onto aluminum hydroxide.* Environmental Earth Sciences, 2017. **76**(16).
103. Hawash, S., E.A. El Kader, and G. El Diwani, *Methodology for selective adsorption of lithium ions onto polymeric aluminium (III) hydroxide.* Journal of American Science, 2010. **6**(11): p. 301-309.
104. Menzheres, L.T., A.D. Ryabtsev, and E.V. Mamylova, *Synthesis of Selective Sorbent $LiCl{\cdot}2Al(OH)_3{\cdot}nH_2O$.* Theoretical Foundations of Chemical Engineering, 2019. **53**(5): p. 821-826.
105. Liu, D.-F., S.-Y. Sun, and J.-G. Yu, *A new high-efficiency process for Li^+ recovery from solutions based on $LiMn_2O_4/\lambda$-MnO_2 materials.* Chemical Engineering Journal, 2019. **377**(119825).
106. Sun, S.Y., et al., *Lithium extraction/insertion process on cubic Li-Mn-O precursors with different Li/Mn ratio and morphology.* Adsorption-Journal of the International Adsorption Society, 2011. **17**(5): p. 881-887.
107. Zhang, Q.-H., et al., *Lithium selective adsorption on 1-D MnO_2 nanostructure ion-sieve.* Advanced Powder Technology, 2009. **20**(5): p. 432-437.
108. Xiao, J.-L., et al., *Synthesis and Adsorption Properties of $Li_{1.6}Mn_{1.6}O_4$ Spinel.* Industrial & Engineering Chemistry Research, 2013. **52**(34): p. 11967-11973.
109. Kazunari Yamaura, Q.H., Lianqi Zhang, Kazunori Takada, Yuji Baba, Takuro Nagai, Yoshio Matsui, Kosuke Kosuda, and Eiji Takayama-Muromachi, *Spinel-to-$CaFe_2O_4$-Type Structural Transformation in $LiMn_2O_4$ under High Pressure.* Journal of the American Chemical Society, 2006. **128**(29): p. 9448-9456.
110. Darul, J., W. Nowicki, and P. Piszora, *Unusual Compressional Behavior of Lithium–Manganese Oxides: A Case Study of $Li_4Mn_5O_{12}$.* The Journal of Physical Chemistry C, 2012. **116**(33): p. 17872-17879.
111. Toshimi Takada, E.A., *Structure Refinement of $Li_4Mn_5O_{12}$ with Neutron and X-Ray Powder Diffraction Data.* Journal of Solid State Chemistry, 1997. **130**: p. 74-80.
112. Xiao, W., et al., *Insight into fast Li diffusion in Li-excess spinel lithium manganese oxide.* Journal of Materials Chemistry A, 2018. **6**(21): p. 9893-9898.
113. HUNTER, J.C., *Preparation of a new crystal form of manganese dioxide λ-MnO_2.* Journal of Solid State Chemistry, 1981. **39**: p. 142-147.
114. Xiang-MuShen, A., *Phase transitions and ion exchange behavior of electrolytically prepared manganese dioxide.* Journal of Solid State Chemistry, 1986. **64**(3): p. 270-282.
115. Koyanaka, H., et al., *Quantitative correlation between Li absorption and H content in manganese oxide spinel λ-MnO_2.* Journal of Electroanalytical Chemistry, 2003. **559**: p. 77-81.
116. Kenta Ooi, Y.M., Jitsuo Sakakihara, *Mechanism of Li^+ Insertion in Spinel-Type Manganese Oxide. Redox and Ion-Exchange Reactions.* Langmuir, 1991. **7**(6): p. 1167-1171.
117. Qi Feng, Y.M., Hirofumi Kanoh, and Kenta Ooi, *Li^+ Extraction/insertion with Spinel-Type Lithium Manganese Oxides. Characterization of Redox-Type and Ion-Exchange-Type Sites.* Langmuir, 1992. **8**(7): p. 1861-1867.
118. Yang, X., et al., *Synthesis of $Li_{1.33}Mn_{1.67}O_4$ spinels with different morphologies and their ion adsorptivities after delithiation.* Journal of Materials Chemistry, 2000. **10**(8): p. 1903-1909.
119. Sun, S.Y., et al., *Synthesis and Adsorption Properties of $Li_{1.6}Mn_{1.6}O_4$ by a Combination of Redox Precipitation and Solid-Phase Reaction.* Industrial & Engineering Chemistry Research, 2014. **53**(40): p. 15517-15521.
120. N.V. Kosova, N.F.U., E.T. Devyatkina, E.G. Avvakumov, *Mechanochemical synthesis of $LiMn_2O_4$ cathode material for lithium batteries.* Solid State Ionics, 2000. **135**: p. 107-114.
121. Cui, T., et al., *Preparation and electrochemical properties of $LiMn_2O_4$ by a rheological-phase-assisted microwave synthesis method.* Inorganic Materials, 2008. **44**(5): p. 542-548.
122. Chu, H.Y., et al., *Study of electrochemical properties and the charge/discharge mechanism for $Li_4Mn_5O_{12}/MnO_2$-AC hybrid supercapacitor.* Journal of Applied Electrochemistry, 2009. **39**(10): p. 2007-2013.

123. Yang-Kook Sun, I.-H.O., and Kwang Yul Kim, *Synthesis of Spinel $LiMn_2O_4$ by the Sol-Gel Method for a Cathode-Active Material in Lithium Secondary Batteries.* Industrial & Engineering Chemistry Research, 1997. **36**(11): p. 4839-4846.
124. Thanh, N.T., N. Maclean, and S. Mahiddine, *Mechanisms of nucleation and growth of nanoparticles in solution.* Chem Rev, 2014. **114**(15): p. 7610-7630.
125. YongCai Zhang, H.W., Bo Wang, Hui Yan, Anwar Ahniyaz, Masahiro Yoshimura, *Low temperature synthesis of nanocrystalline $Li_4Mn_5O_{12}$ by a hydrothermal method.* Materials Research Bulletin, 2002. **37**(8): p. 1411-1417.
126. Ramesh Chitrakar, H.K., Yoshitaka Miyai, and Kenta Ooi, *A New Type of Manganese Oxide ($MnO_2{\cdot}0.5H_2O$) Derived from $Li_{1.6}Mn_{1.6}O_4$ and Its Lithium Ion-Sieve Properties.* Chemistry of Materials, 2000. **12**(10): p. 3151-3157.
127. Chitrakar, R., et al., *Synthesis of o-$LiMnO_2$ by Microwave Irradiation and StudyIts Heat Treatment and Lithium Exchange.* Journal of Solid State Chemistry, 2002. **163**(1): p. 1-4.
128. Chitrakar, R., et al., *Recovery of lithium from seawater using manganese oxide adsorbent ($H_{1.6}Mn_{1.6}O_4$) derived from $Li_{1.6}Mn_{1.6}O_4$.* Industrial & Engineering Chemistry Research, 2001. **40**(9): p. 2054-2058.
129. Shi, X.C., et al., *Synthesis and properties of $Li_{1.6}Mn_{1.6}O_4$ and its adsorption application.* Hydrometallurgy, 2011. **110**(1-4): p. 99-106.
130. Wang, H.S., et al., *Selective recovery of lithium from geothermal water by EGDE cross-linked spherical CTS/LMO.* Chemical Engineering Journal, 2020. **389**(124410).
131. Wang, L., et al., *Correlation between Li^+ adsorption capacity and the preparation conditions of spinel lithium manganese precursor.* Solid State Ionics, 2006. **177**(17-18): p. 1421-1428.
132. Zandevakili, S., M. Ranjbar, and M. Ehteshamzadeh, *Synthesis of a nanostructure ion sieve with improved lithium adsorption capacity.* Micro & Nano Letters, 2014. **9**(7): p. 455-459.
133. Xu, H., C.-G. Chen, and Y.-H. Song, *Synthesis and Properties of Lithium Ion-sieve Precursor $Li_4Mn_5O_{12}$.* Journal of Inorganic Materials, 2013. **28**(7): p. 720-726.
134. Chung, K.S., et al., *Preparation of ion-sieve type (H) $[M_{0.5}Mn_{1.5}]O_4$ (M=Mg, Zn) and their lithium adsorption properties in seawater.* Solid State Phenomena, 2007. **124-126**: p. 739-742.
135. Chen, M., et al., *Improved performance of Al-doped $LiMn_2O_4$ ion-sieves for Li^+ adsorption.* Microporous and Mesoporous Materials, 2018. **261**: p. 29-34.
136. Cao, G.F., et al., *Synthesis, Adsorption Properties and Stability of Cr-Doped Lithium Ion Sieve in Salt Lake Brine.* Bulletin of the Chemical Society of Japan, 2019. **92**(7): p. 1205-1210.
137. Qiu, Z., et al., *$Li_4Mn_5O_{12}$ doped cellulose acetate membrane with low Mn loss and high stability for enhancing lithium extraction from seawater.* Desalination, 2021. **506**(115003).
138. Kamran, U. and S.-J. Park, *Hybrid biochar supported transition metal doped MnO_2 composites: Efficient contenders for lithium adsorption and recovery from aqueous solutions.* Desalination, 2022. **522**(115387).
139. Qian, F., et al., *Enabling highly structure stability and adsorption performances of $Li_{1.6}Mn_{1.6}O_4$ by Al-gradient surface doping.* Separation and Purification Technology, 2021. **264**(118433).
140. Qian, F., et al., *Enhancing the Li^+ adsorption and anti-dissolution properties of $Li_{1.6}Mn_{1.6}O_4$ with Fe, Co doped.* Hydrometallurgy, 2020. **193**(105291).
141. Qian, F., et al., *Trace doping by fluoride and sulfur to enhance adsorption capacity of manganese oxides for lithium recovery.* Materials & Design, 2020. **194**(108867).
142. Qian, F., et al., *K-gradient doping to stabilize the spinel structure of $Li_{1.6}Mn_{1.6}O_4$ for Li^+ recovery.* Dalton Trans, 2020. **49**(31): p. 10939-10948.
143. Xue, F., et al., *Fe_3O_4-doped lithium ion-sieves for lithium adsorption and magnetic separation.* Separation and Purification Technology, 2019. **228**(115750).
144. Su, Y., F. Qian, and Z. Qian, *Enhancing adsorption capacity and structural stability of $Li_{1.6}Mn_{1.6}O_4$ adsorbents by anion/cation Co-doping.* RSC Advances, 2022. **12**(4): p. 2150-2159.
145. Bajestani, M.B., A. Moheb, and M. Masigol, *Simultaneous Optimization of Adsorption Capacity and Stability of Hydrothermally Synthesized Spinel Ion Sieve Composite Adsorbents for Selective*

Removal of Lithium from Aqueous Solutions. Industrial & Engineering Chemistry Research, 2019. **58**(27): p. 12207-12215.
146. Luo, G., et al., *Electrochemical lithium ions pump for lithium recovery from brine by using a surface stability Al_2O_3-ZrO_2 coated $LiMn_2O_4$ electrode.* Journal of Energy Chemistry, 2022. **69**: p. 244-252.
147. Hong, H.-J., et al., *Macroporous Hydrogen Manganese Oxide/Al_2O_3 for Effective Lithium Recovery from Seawater: Effects of the Macropores vs Mesopores.* Industrial & Engineering Chemistry Research, 2019. **58**(19): p. 8342-8348.
148. Hong, H.-J., et al., *Highly porous and surface-expanded spinel hydrogen manganese oxide (HMO)/Al_2O_3 composite for effective lithium (Li) recovery from seawater.* Chemical Engineering Journal, 2018. **337**: p. 455-461.
149. Hong, H.-J., et al., *Immobilization of hydrogen manganese oxide (HMO) on alpha-alumina bead (AAB) to effective recovery of Li^+ from seawater.* Chemical Engineering Journal, 2015. **271**: p. 71-78.
150. Han, Y., H. Kim, and J. Park, *Millimeter-sized spherical ion-sieve foams with hierarchical pore structure for recovery of lithium from seawater.* Chemical Engineering Journal, 2012. **210**: p. 482-489.
151. Ryu, T., et al., *Recovery of Lithium Ions from Seawater Using a Continuous Flow Adsorption Column Packed with Granulated Chitosan–Lithium Manganese Oxide.* Industrial & Engineering Chemistry Research, 2016. **55**(26): p. 7218-7225.
152. Wang, Y., et al., *Mesoporous hollow silicon spheres modified with manganese ion sieve: Preparation and its application for adsorption of lithium and rubidium ions.* Applied Organometallic Chemistry, 2017. **32**(3): p. 4182-4193.
153. Ryu, T., et al., *Mechanochemical synthesis of silica-lithium manganese oxide composite for the efficient recovery of lithium ions from seawater.* Solid State Ionics, 2017. **308**: p. 77-83.
154. Recepoglu, Y.K., et al., *Equilibrium and Kinetic Studies on Lithium Adsorption from Geothermal Water by lambda-MnO_2.* Solvent Extraction and Ion Exchange, 2017. **35**(3): p. 221-231.
155. Chaban, M.A., et al., *Selectivity of new inorganic ion–exchangers based on oxides of titanum and manganese at sorpion of lithium from aqueous media.* Journal of Water Chemistry and Technology, 2016. **38**(1): p. 8-13.
156. Xiao, J., et al., *Lithium ion adsorption-desorption properties on spinel $Li_4Mn_5O_{12}$ and pH-dependent ion-exchange model.* Advanced Powder Technology, 2015. **26**(2): p. 589-594.
157. Guo, Z.-Y., et al., *Electrochemical lithium extraction based on "rocking-chair" electrode system with high energy-efficient: The driving mode of constant current-constant voltage.* Desalination, 2022. **533**(115767).
158. Jung, S.Y., et al., *Electrode design and performance of flow-type electrochemical lithium recovery (ELR) systems.* Desalination, 2022. **532**(115732).
159. Xu, W., L. He, and Z. Zhao, *Lithium extraction from high Mg/Li brine via electrochemical intercalation/de-intercalation system using $LiMn_2O_4$ materials.* Desalination, 2021. **503**(114935).
160. Mu, Y., et al., *Electrochemical lithium recovery from brine with high Mg^{2+}/Li^+ ratio using mesoporous λ-MnO_2/$LiMn_2O_4$ modified 3D graphite felt electrodes.* Desalination, 2021. **511**(115112).
161. Shi, X.-c., et al., *Synthesis of Li^+ adsorbent (H_2TiO_3) and its adsorption properties.* Transactions of Nonferrous Metals Society of China, 2013. **23**(1): p. 253-259.
162. Wang, S., et al., *Selective adsorption of lithium from high Mg-containing brines using H_xTiO_3 ion sieve.* Hydrometallurgy, 2017. **174**: p. 21-28.
163. Safari, S., B.G. Lottermoser, and D.S. Alessi, *Metal oxide sorbents for the sustainable recovery of lithium from unconventional resources.* Applied Materials Today, 2020. **19**(100638).
164. Chitrakar, R., et al., *Lithium recovery from salt lake brine by H_2TiO_3.* Dalton Trans, 2014. **43**(23): p. 8933-8939.

165. Kataoka, K., et al., *Crystal growth and structure refinement of monoclinic Li_2TiO_3.* Materials Research Bulletin, 2009. **44**(1): p. 168-172.
166. He, G., et al., *The optimal condition for H_2TiO_3-lithium adsorbent preparation and Li^+ adsorption confirmed by an orthogonal test design.* Ionics, 2015. **21**(8): p. 2219-2226.
167. Marthi, R., et al., *On the Structure and Lithium Adsorption Mechanism of Layered H_2TiO_3.* ACS Appl Mater Interfaces, 2021. **13**(7): p. 8361-8369.
168. Yi, T.-F., S.-Y. Yang, and Y. Xie, *Recent advances of $Li_4Ti_5O_{12}$ as a promising next generation anode material for high power lithium-ion batteries.* Journal of Materials Chemistry A, 2015. **3**(11): p. 5750-5777.
169. Sun, X., P.V. Radovanovic, and B. Cui, *Advances in spinel $Li_4Ti_5O_{12}$ anode materials for lithium-ion batteries.* New Journal of Chemistry, 2015. **39**(1): p. 38-63.
170. Zhang, L., et al., *Preparation of H_2TiO_3-lithium adsorbent by the sol-gel process and its adsorption performance.* Applied Surface Science, 2016. **368**: p. 82-87.
171. Moazeni, M., et al., *Hydrothermal synthesis and characterization of titanium dioxide nanotubes as novel lithium adsorbents.* Materials Research Bulletin, 2015. **61**: p. 70-75.
172. Wang, S., et al., *Hydrothermal synthesis of lithium-enriched β-Li_2TiO_3 with an ion-sieve application: excellent lithium adsorption.* RSC Advances, 2016. **6**(104): p. 102608-102616.
173. Hossain, S.M., et al., *Preparation of effective lithium-ion sieve from sludge-generated TiO_2.* Desalination, 2022. **525**(115491).
174. Gu, D., et al., *Lithium ion sieve synthesized via an improved solid state method and adsorption performance for West Taijinar Salt Lake brine.* Chemical Engineering Journal, 2018. **350**: p. 474-483.
175. Zhang, L., et al., *Effect of crystal phases of titanium dioxide on adsorption performance of H_2TiO_3-lithium adsorbent.* Materials Letters, 2014. **135**: p. 206-209.
176. Zhang, L., et al., *Synthesis of H_2TiO_3-lithium adsorbent loaded on ceramic foams.* Materials Letters, 2015. **145**: p. 351-354.
177. Zhao, B., et al., *Hydrothermal synthesis and adsorption behavior of $H_4Ti_5O_{12}$ nanorods along [100] as lithium ion-sieves.* RSC Advances, 2020. **10**(58): p. 35153-35163.
178. Shoghi, A., et al., *Spinel $H_4Ti_5O_{12}$ nanotubes for Li recovery from aqueous solutions: Thermodynamics and kinetics study.* Journal of Environmental Chemical Engineering, 2021. **9**(104679).
179. Zhang, L.-Y., et al., *Preparation of Ni-Doped Li2TiO3 Using an Inorganic Precipitation–Peptization Method.* Coatings, 2019. **9**(11).
180. Wang, S., et al., *High adsorption performance of the Mo-doped titanium oxide sieve for lithium ions.* Hydrometallurgy, 2019. **187**: p. 30-37.
181. Wang, S., et al., *Superior lithium adsorption and required magnetic separation behavior of iron-doped lithium ion-sieves.* Chemical Engineering Journal, 2018. **332**: p. 160-168.
182. Miao, J., et al., *Novel LIS-doped mixed matrix membrane absorbent with high structural stability for sustainable lithium recovery from geothermal water.* Desalination, 2022. **527**(115570).
183. Lawagon, C.P., et al., *Development of high capacity Li^+ adsorbents from H_2TiO_3/polymer nanofiber composites: Systematic polymer screening, characterization and evaluation.* Journal of Industrial and Engineering Chemistry, 2019. **70**: p. 124-135.
184. Lin, H., et al., *Synthesis of Polyporous Ion-Sieve and Its Application for Selective Recovery of Lithium from Geothermal Water.* ACS Appl Mater Interfaces, 2019. **11**(29): p. 26364-26372.
185. Limjuco, L.A., et al., *H_2TiO_3 composite adsorbent foam for efficient and continuous recovery of Li^+ from liquid resources.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2016. **504**: p. 267-279.
186. Marthi, R. and Y.R. Smith, *Application and limitations of a H_2TiO_3 – Diatomaceous earth composite synthesized from titania slag as a selective lithium adsorbent.* Separation and Purification Technology, 2021. **254**(117580).

187. Zhang, Y., et al., *Preparation of granular titanium-type lithium-ion sieves and recyclability assessment for lithium recovery from brines with different pH value.* Separation and Purification Technology, 2021. **267**(118613).
188. Chen, S., et al., *Titanium-based ion sieve with enhanced post-separation ability for high performance lithium recovery from geothermal water.* Chemical Engineering Journal, 2021. **410**(128320).
189. Wei, S., et al., *Porous lithium ion sieves nanofibers: General synthesis strategy and highly selective recovery of lithium from brine water.* Chemical Engineering Journal, 2020. **379**(122407).
190. Qian, H., et al., *HTO/Cellulose Aerogel for Rapid and Highly Selective Li^+ Recovery from Seawater.* Molecules, 2021. **26**(4054).
191. Tang, L., et al., *High-Density Microporous $Li_4Ti_5O_{12}$ Microbars with Superior Rate Performance for Lithium-Ion Batteries.* Adv. Sci., 2017. **4**(5): p. 1600311.
192. Zhu, X., et al., *Study on adsorption extraction process of lithium ion from West Taijinar brine by shaped titanium-based lithium ion sieves.* Separation and Purification Technology, 2021. **274**(119099).
193. Li, X., et al., *Amorphous TiO_2-Derived Large-Capacity Lithium Ion Sieve for Lithium Recovery.* Chemical Engineering & Technology, 2020. **43**(9): p. 1784-1791.
194. Lawagon, C.P., et al., *Adsorptive Li^+ mining from liquid resources by H_2TiO_3: Equilibrium, kinetics, thermodynamics, and mechanisms.* Journal of industrial and engineering chemistry, 2016. **35**: p. 347-356.
195. Ooi, K., et al., *Modelling of column lithium desorption from Li^+-loaded adsorbent obtained by adsorption from salt brine.* Hydrometallurgy, 2017. **169**: p. 31-40.
196. Li, X., et al., *Taming wettability of lithium ion sieve via different TiO_2 precursors for effective Li recovery from aqueous lithium resources.* Chemical Engineering Journal, 2020. **392**(123731).
197. Ji, Z.-Y., et al., *Preparation of titanium-base lithium ionic sieve with sodium persulfate as eluent and its performance.* Chemical Engineering Journal, 2017. **328**: p. 768-775.
198. Zhang, L.-Y., et al., *A novel study on preparation of H_2TiO_3-lithium adsorbent with titanyl sulfate as titanium source by inorganic precipitation–peptization method.* RSC Advances, 2018. **8**(3): p. 1385-1391.
199. Wang, S., et al., *Application of citric acid as eluting medium for titanium type lithium ion sieve.* Hydrometallurgy, 2019. **183**: p. 166-174.
200. Wang, S., et al., *Lithium adsorption from brine by iron-doped titanium lithium ion sieves.* Particuology, 2018. **41**: p. 40-47.
201. Jang, Y. and E. Chung, *Adsorption of Lithium from Shale Gas Produced Water Using Titanium Based Adsorbent.* Industrial & Engineering Chemistry Research, 2018. **57**(25): p. 8381-8387.
202. Liu, J., et al., *Alkaline Resins Enhancing Li^+/H^+ Ion Exchange for Lithium Recovery from Brines Using Granular Titanium-Type Lithium Ion-Sieves.* Industrial & Engineering Chemistry Research, 2021. **60**(45): p. 16457-16468.
203. Li, N., et al., *Yolk-shell structured composite for fast and selective lithium ion sieving.* J Colloid Interface Sci, 2018. **520**: p. 33-40.
204. Tian, L., W. Ma, and M. Han, *Adsorption behavior of Li^+ onto nano-lithium ion sieve from hybrid magnesium/lithium manganese oxide.* Chemical Engineering Journal, 2010. **156**(1): p. 134-140.
205. Liu, D.-F., S.-Y. Sun, and J.-G. Yu, *Li4Mn5O12 Desorption Process with Acetic Acid and Mn Dissolution Mechanism.* Journal of Chemical Engineering of Japan, 2019. **52**(3): p. 274-279.
206. Ooi, K., et al., *Modelling of column lithium adsorption from pH-buffered brine using surface Li^+/H^+ ion exchange reaction.* Chemical Engineering Journal, 2016. **288**: p. 137-145.
207. Chitrakar, R., et al., *Synthesis of Iron-Doped Manganese Oxides with an Ion-Sieve Property: Lithium Adsorption from Bolivian Brine.* Industrial & Engineering Chemistry Research, 2014. **53**(9): p. 3682-3688.

208. Jun Ge, J.S., Shuang Wu, *Lithium extraction from Salt lakes in China towards maturity*. 2021, Minerals Securities Co. LTD: Nonferrous metals.
209. HE Yongping, Y.X., WANG Wenhai, Xing Hong, Jin Shengjun, WANG Shijiao, ZHANG Rongzi, MAO Xinyu, CHEN Caixia, ZHANG Guicheng, *The preparation method and lithium adsorbent of a kind of lithium adsorbent*, C. Patent, Editor. 2017, Qinghai Salt Lake Industry Co Ltd: China.
210. WANG Wenhai, X.H., ZHU Hongwei, MAO Xinyu, ZHANG Chengsheng, YANG Jianyu, ZHANG Zhanwei, ZHANG Shengshun, DING Zhihai, JIN Caiying, *Method for restoring property of lithium adsorbent*, C. Patent, Editor. 2014, Qinghai Salt Lake Industry Co Ltd: China.
211. HE Yongping, X.H., ZHANG Zhanwei, WANG Wenhai, WANG Xingfu, XIE Kangmin, WANG Shijun, MAO Xinyu, YANG Jianyu, QI Wei, SUN Yonglong, MA Cunbiao, ZHANG Rongzi, SONG Shengzhong, CHEN Caixia, ZHANG Chengsheng, *A kind of new process of salt lake bittern production high-purity lithium chloride*, C. Patent, Editor. 2017, Qinghai Salt Lake Industry Co Ltd: China.
212. HE Yongping, X.H., SUN Yonglong, WANG Wenhai, ZHANG Chengsheng, YANG Jianyu, ZHANG Rongzi, SONG Shengzhong, ZHANG Zhanwei, HE Xiaojun, ZHU Xujia, DENG Yuxing, ZHANG Junxian, ZHANG Chengyong, CHEN Caixia, *Method and device for preparing high-lithium mother liquor by using old brine through adsorption method*, C. Patent, Editor. 2021, Qinghai Salt Lake Fozhao Lanke Lithium Industry Co ltd Qinghai Salt Lake Industry Co Ltd: China.
213. HE Yongping, X.H., YANF Jianyu, WANG Wenhai, MAO Xinyu, YAN Xiongzhong, ZHANG Zhanwei, MA Cunbiao, ZHANG Rongzi, ZHANG Chengsheng, QI Wei, SUN Yonglong, HE Xiaojun, ZHAO Yonggui, JIN Caiying, HAN Sheng, *A kind of new process and equipment of salt lake bittern production lithium chloride*, C. Patent, Editor. 2017, Qinghai Salt Lake Industry Co Ltd: China.
214. Shun Li, Z.X., Dalin Liu, Chengyong Zhang, *Record sheet of Investor Relations activities of Qinghai Salt Lake Industry Co.,Ltd in Jul. 2021*, G.W. Huayu Wu, Hong Wang, Zhenwei Zhang, Wenjie Zhang, Hao Li, Teng Zhang, Qi Zhang, Xin Jin, Xin Wan, Editor. 2021, * ST Saltlake.
215. Shun Li, Z.X., Jianyu Yang, Dalin Liu, *Record sheet of Investor Relations activities of Qinghai Salt Lake Industry Co.,Ltd in Sep. 2021*, J.C. Guomeng Sun, Feng Zhang, Chongxin Zhang, Ke Yang, Qian Wang, MIngsong Jiang, Editor. 2021, Saltlake shares.
216. Patrick, W., *Techno-Economic Analysis of Lithium Extraction from Geothermal Brines*. 2021, Golden, CO: National Renewable Energy Laboratory. NREL/TP-5700-79178.