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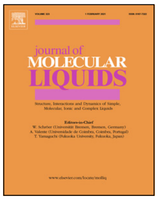

Review

Utilisation of adsorption as a resource recovery technique for lithium in geothermal water

Joshua O. Ighalo[a,b,*], James F. Amaku[c], Chijioke Olisah[d], Adedapo O. Adeola[e,f], Kingsley O. Iwuozor[g], Kovo G. Akpomie[h,i], Jeanet Conradie[h], Kayode A. Adegoke[f], Kabir O. Oyedotun[j]

[a] Department of Chemical Engineering, Nnamdi Azikiwe University, P. M. B. 5025, Awka, Nigeria
[b] Tim Taylor Department of Chemical Engineering, Kansas State University, Manhattan, KS, USA
[c] Department of Chemistry, Michael Okpara University of Agriculture, Umudike, Nigeria
[d] Department of Botany, Institute for Coastal and Marine Research, Nelson Mandela University, Port Elizabeth, South Africa
[e] Department of Chemical Sciences, Adekunle Ajasin University, Akungba-Akoko, Ondo State, Nigeria
[f] Department of Chemical Sciences, University of Johannesburg, Doornfontein 2028, South Africa
[g] Department of Pure & Industrial Chemistry, Nnamdi Azikiwe University, Awka, Nigeria
[h] Department of Chemistry, University of the Free State, Bloemfontein 9300, South Africa
[i] Department of Pure & Industrial Chemistry, University of Nigeria, Nsukka, Nigeria
[j] Department of Chemical Engineering, University of Pretoria, Hatfield, Pretoria 0028, South Africa

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ABSTRACT

Geothermal water is rich in lithium (Li) and it can be recovered by adsorption and other methods. Product recovery by adsorption is important for the achievement of a circular economy and the reduction of geogenic Li in the biosphere. This paper aims to review the performance of different adsorbents for the removal of Li from geothermal water. The reported adsorption capacity was between 6 and 69 mg/g for most materials and the optimal pH was about 12. Ion-exchange was the major mechanism of Li uptake onto nano-adsorbents of inorganic origin. Other important mechanisms observed were intercalation with associated hydrogen bonds, electrostatic attraction, intermolecular and intramolecular complexation. The Langmuir isotherm and pseudo-second-order model were best-fit to describe the Li uptake in most cases. Adsorption is observed to have some technical advantages over other processes. It is relatively cheaper, does not have chemical resistance observed in membranes, does not have the limited selectivity and difficulty of integration into industrial processes, and does not possess the high electrical requirement of electrochemical techniques. HCl is the most effective eluent for Li desorption and most adsorbents can be reused over 5 times with good retention of adsorption capacity. Future studies can look into column adsorption of Li, molecular modelling of Li interaction with sorbents, used adsorbent disposal and cost analysis.

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* Corresponding author at: Department of Chemical Engineering, Nnamdi Azikiwe University, P. M. B. 5025, Awka, Nigeria.
E-mail address: oshea.ighalo@yahoo.com (J.O. Ighalo).

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1. Introduction

Geothermal resources were developed and used early in the history of renewable energy as a member of the renewable energy family. In comparison to other renewable energy sources, geothermal sources have vast reserves, a wide distribution, strong stability, and a high usage efficiency; also, once established, they can be used for an extended length of time [1]. According to Zhu et al. [2], geothermal energy accounts for only 0.3 % of total power generation and 1.5 % of renewable energy generation. In the year 2020, the energy produced from global geothermal resources was estimated to be about 14,050 megawatts, a 1.18 % increase from that obtained in 2019 (Jaganmohan 2021).

Geothermal water is water sourced from geothermal wells which come at very high temperatures (in the form of steam), and can be used to drive turbines for electricity generation [3]. However, this can be saline and rich in dissolved minerals from source rocks [4]. Based on the nature of the rock, a wide assortment of metals is present in the water, such as lithium (Li), boron (B) and potassium (K) [5]. Li is an important component of batteries with high energy density [6], lubricants and metal alloys [7]. These are relevant in end-use electronics, electric vehicles, portable electronics and grid energy storage [8]. Based on the strong interest in Li for energy applications and storage, it is projected that global production will continue to increase across all continents (see Fig. 1) [9]. Demand by 2050 could be 56 times its current value [10]. Given that geothermal resources have the potential to be a green energy source, the lithium resources in lithium-rich geothermal fluid are gaining interest, with some experts claiming that lithium resources in geothermal water can reach 2 Metric tonnes [11].

Geothermal fluids are rich in valuable metals and various technologies have been used to extract these metals [12]. Lithium can be present in geothermal water to a concentration up to 10 mg/L [13]. The recovered amount of Li from geothermal water is about 2 % of the global production total [4]. Though this is comparatively low, it still represents a significant effort in the circular economy initiative where product recovery and reuse are paramount [14]. Meshram et al. [15] classified Li recovery from brines, minerals and seawater as a primary source whilst considering recovery from Li batteries as the only secondary source. Their classification was based on the obtainable production volumes. Geothermal water is also a secondary source of Li, due to its relatively lower volume, and because it is integrated in its application in electricity generation.

Table 1 summarises the technologies other than adsorption for the recovery of Li from geothermal water. This is done to provide proper context to readers to understand the place, relevance, and significance of adsorption compared to other competing processes. It also provides a good platform to compare process performance and other technical intricacies that would make each process unique under different application scenarios [16]. However, another excellent classification of the broad spectrum of the processes for Li recovery from geothermal water is presented by Stringfellow and Dobson [6,17], namely precipitation, organic sorbents, membrane separation, and electrochemical separation.

(a) Precipitation: Metals can be directly precipitated from the geothermal water as metal sulphides or hydroxides. However, this process is only suitable when (i) the concentration of metals is low and (ii) the variety of metals is not wide. If there is a wide variety of metals, the precipitate becomes a

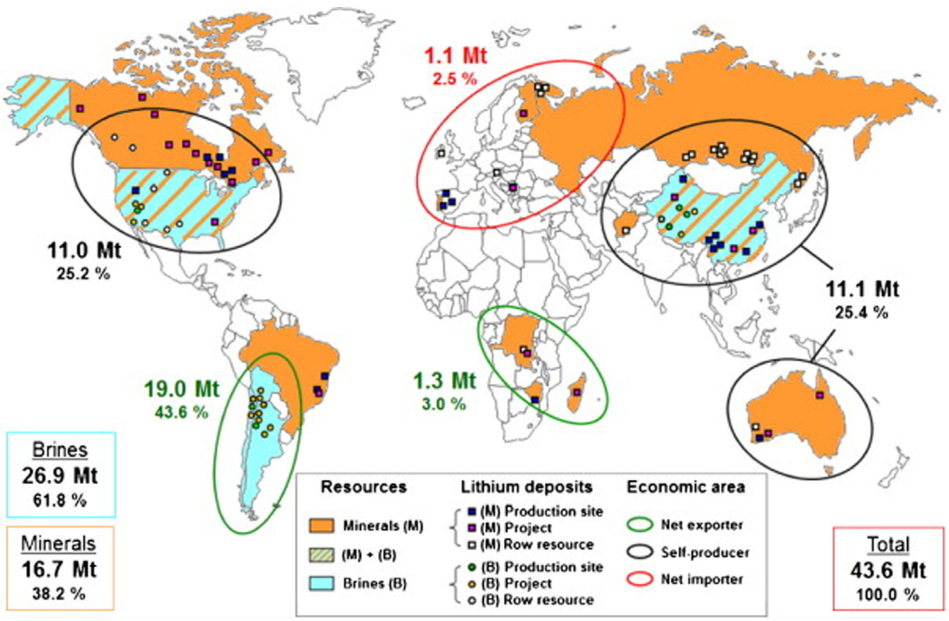

Fig. 1. Global projections of Li production based on mineral and brine sources. (Reprinted from Renewable and Sustainable Energy Reviews, Vol 16, Grosjean C, Miranda PH, Perrin M, Poggi P, Assessment of world lithium resources and consequences of their geographic distribution on the expected development of the electric vehicle industry, pg. 1735–1744, 2012 with permission from Elsevier).

Table 1
Other processes for the recovery of Li from geothermal water.

Process	Key findings	Existing challenges/Need for improvements	References
Electrochemical technique	Over 90 % Li recovery is achievable and developed electrodes could be regenerated and reused for up to 8 cycles. Good metal selectivity.	High energy consumption and the limitations of mass transfer	[22,23]
Bioaccumulation	Over > 80 % Li recovery is possible. Cellular uptake of metals drives the process.	The method is not robust as changes in process conditions could lead to the death of the microorganism and halt bio-recovery. The process takes a long time. Non-selective metal recovery.	[20,79]
Ion-exchange/ membrane hybrid process	Over 90 % Li recovery is achievable. The process was optimised to achieve best-condition parameters as 1.5 g resin/L solution, 6.0 mL/min replacement rates and a permeate flow rate of 5.0 mL/min.	Membrane fouling and associated cost remain a challenge. % Recovery (%) decreases with the presence of co-contaminants	[80]
Adsorption/ membrane hybrid process	100 % Li recovery was achieved, and regeneration was possible using 1 M HCl as eluent	Field or industrial application of the technique is a challenge as most wastewater treatment plants do not have the flexibility to accommodate hybrid techniques	[18,95]
Hybrid capacitive deionisation	The electrodes had very high selectivity and capacity for Li salts with up to 73 % recovery from the electrode captured	Electrode deactivation and process costs are challenges.	[81,82,83]

complex metal sulphide that would require further processing, thereby increasing production cost and time. If the concentration of the metal is above the maximum concentration for solubility [16], precipitation would also not be effective.

(b) Ion exchange: Li uptake by ion-exchange using resins or membranes (not adsorbents) can be a rather expensive and pH-sensitive process. The selectivity of the resin depends greatly on its hydrated radius, molecular configuration and electric charge. Membranes can also be effective for Li recovery. Besides their cost due to the use of higher pressures and observed chemical resistance [18], membranes preserve the chemical integrity of the dissolved salts and metals in the aqueous phase after separation, hence simplifying any required additional processing [19].

(c) Bioaccumulation: Bioaccumulation utilises biochemically-mediated reaction mechanisms in living cells to take up Li from geothermal water [20]. The key mechanism is redox reaction and sulphate reduction. It is quite different from biosorption which is a hybrid process of surface uptake and bulk absorption phenomena involving dead cells of plant and animal origin [21].

(d) Hybrid processes: These involve a combination of two or more processes for Li removal. Some of the key innovations in recent times (key findings summarised in Table 1) are the electrochemical techniques [22,23], bioaccumulation [20], and hybrid processes combining multiple techniques. Considering reusability, it was observed in the previous section that most nano-adsorbents of inorganic origin can be reused for Li uptake over 5 times with good retention of adsorption capacity. This is similar to most of the novel processes mentioned here. We believe that adsorption can compete as well as these processes (in the domain of reusability). This is not surprising because the ion-exchange mechanism for adsorption is similar to those observed in these systems.

(e) It can be summarised that adsorption possesses certain peculiarities that gives it a technical advantage over other processes. It is relatively cheaper, does not have chemical resistance observed in membranes, does not have the limited selectivity and difficulty of integration (into industrial processes) of solvent extraction, and the electrical requirements of electrochemical techniques.

Adsorption is a low-cost technology that can be used to recover various chemical species from the aqueous phase [24,25]. It is also very suitable for pollutant uptake at medium and low concentrations [26,27]. It has been used over the years as an important tool for pollutant recovery from geothermal water. This application bears two significance for two reasons; (i) product recovery for the circular economy and (ii) limitation of geogenic Li in the biosphere to mitigate its ecotoxicological effect.

Based on the authors' exhaustive search, there are no reviews examining the adsorption of Li from geothermal water. This paper aims to review the performance of different adsorbents for the removal of Li from geothermal water. The goal is to elucidate key reasons for effective Li uptake as identified by the key papers in the field, systematically organise the literature and discuss important innovations that could bear significance for future investigations on the subject. The review examined other aspects of the adsorptive process such as uptake mechanism, classical modelling (isotherm, kinetics and thermodynamics), desorption, and adsorbent reusability. The core literature analysis considered important research publications on the subject within the past 5 years.

2. Application of adsorption for Li removal

Adsorption in geothermal water is unique because it is unlike other systems with a single adsorbate. When experiments are done with the actual geothermal water (and not synthesised solutions of Li in water), there is the presence of competing ionic species such as boron (B) and potassium (K) [5]. The nature of the source rock can also influence the concentration and distribution of these ionic species in the aqueous phase. This means there is a constant competition between Li and other cations for active sites on the adsorbent. Based on the nature of the adsorbate, adsorbents that suit Li uptake have to be good cation exchangers or amphoteric exchangers. The adsorbent can have other unique features to improve uptake performance, impact specific capabilities (like reusability, affinity and stability) or introduce multiple uptake mechanisms in the process. However, the cation exchange ability of the adsorbent material is very important if significant performance for Li uptake will be achieved.

Various adsorbent materials have been investigated for the removal of Li from geothermal water. The key index used for the evaluation of the uptake performance is the monolayer adsorption capacity q_{max} (in mg/g) [28]. The q_{max} is an intrinsic property of the material for the specific chemical species albeit dependent on the solution chemistry (which are controlled by the pH and temperature) [29]. The pH and temperature at which the q_{max} was obtained

Table 2
Adsorbent performance for Li recovery from geothermal water.

Adsorbent	Adsorption mechanism	q_{max}(mg/g)	pH	Temp (°C)	Time (hrs)	SSA (m^2/g)	Average pore volume (cm^3/g)	Method of q_{max} determination	Ref.
$LiMn_2O_4$ nanoparticles	–	68.35	–	–	72.0	–	–	Experiments	[84]
Modified activated carbon (Mn0.1-CAC)	Ion-exchange	50.10	12	25	19.0	421.0	0.579	Experiments	[85]
$H_{1.6}Mn_{1.6}O_4$ Ion Sieve (HMO-1)	Ion-exchange, Langmuir	43.80	11	25	24.0	17.67	–	Experiments	[86]
$Li_4Ti_5O_{12}$ spinel ternary oxide nanotube	Ion-exchange, Freundlich	39.43	9.17	25	120	–	–	Experiments	[87]
Titanium-based sieve (PIS-4)	Ion-exchange, Freundlich	34.23	12	60	10.0	102.8	–	Langmuir	[34]
LIS-doped mixed matrix membrane (LIS-MMM)	Chemisorption, Langmuir	25.01	12	25	0.75	–	–	Experiments	[88]
H_2TiO_3 supported on Polysulfone fiber	Chemisorption, Langmuir	22.66	12	60	1.00	6.510	0.015	Experiments	[89]
Polyporous PVC – HTO	Chemisorption, Langmuir	12.84	12	55	12.0	–	–	Experiments	[90]
Granulated $H_4Mn_5O_{12}$/chitosan	Chemisorption, Langmuir	11.40	12	60	48.0	–	–	Experiments	[36]
Powdered λ-MnO_2	Intraparticle diffusion, Langmuir	10.17	8.4	25	24.0	68.00	–	Experiments	[91]
Crosslinked chitosan/LMO	Chemisorption, Langmuir	8.980	12	30	24.0	–	–	Experiments	[63]
Magnetic layered double hydroxides	Chemisorption, Langmuir	6.390	–	55	10.0	92.56	0.280	Langmuir	[62]
Magnetic layered double hydroxides (MLDH-1)	Chemisorption, Liu model	6.260	–	55	10.0	92.56	0.280	Liu	[32]
Phosphorylated hazelnut shell biosorbent	Freundlich	6.030	5.8	25	6 mins	0.8193	0.0006	Experiments	[43]
Hollow fiber membrane	–	18.10	9.2	30	24.0	–	–	Experiments	[92]
Inorganic nanofiber	Chemisorption, Freundlich	34.21	11.0	25	24.0	16.3191	–	Langmuir	[93]
poly(acrylonitrile) nanofibers-HMO composite	Chemisorption, Langmuir	10.3	11.0	25	48.0	–	–	Langmuir	Park et al. 2014

was therefore stated in Table 2. Furthermore, specific surface area (SSA) and average pore sizes of the adsorbent are also mentioned in the Table as these are key physico-chemical properties that determine the potentials of the adsorbent for the application [30]. q_{max} can either be determined by equilibrium isotherms or from direct observation of experimental values (noticeable in kinetics experiment results) [31]. This method of determination also determines the accuracy of the results hence it is specified in Table 2. q_{max} from equilibrium isotherm modelling is a theoretical prediction that is only accurate when the utilised model is a statistical fit to the experimental results. Due to the erroneous q_{max}, which could be vastly different from the actual results, it can be assumed that investigations on statistical validation of model accuracy is not thorough. Chen et al. [32] used iron oxide nanoparticles to modify layered double hydroxide for the selective uptake of Li from brine. Increasing the amount of the iron oxide nanoparticles reduced the available surface area for uptake and the eventual removal of Li. However, the adsorbent had preferential selectivity for Li in competition with Mg^{2+}, Na^+, K^+ and Ca^{2+}. The key highlight of this paper is that there can be a trade-off between performance and selectivity as the latter can be very important. If an adsorbent performs well but is more selective toward other competing species, then it is not of much use in a practical sense [33]. Further on selectivity, the titanium-based Li sieve developed by Chen et al. [34] achieved a higher uptake capacity for Li in an aqueous solution compared to that in geothermal water. This is due to the effect of the competition of other ionic species in the geothermal water, hence the reduced Li uptake in geothermal water. Selectivity can also be influenced by synthesis techniques, as λ-MnO_2 obtained from a hydrometallurgical method is superior to that from a pyrometallurgical method for Li uptake [35].

Besides the intrinsic properties like pH and temperature, there are other factors that affect the Li adsorption system. These are already well known, but a quick summary is presented. Contact time helps to increase Li uptake until equilibrium is achieved. Adsorption is a rate controlled process, and time is required for each step. At equilibrium, increasing contact time no longer has a positive effect on the process, as Li can even start desorbing into the aqueous phase. Smaller particle sizes favour adsorption because it results in higher SSA. Adsorption is a surface phenomenon, hence its direct relationship with SSA. The speed of agitation aids adsorption due to quicker sorbate-sorbent interactions. Looking at Table 2, it can be observed that most adsorbents can remove between 6 and 69 mg/g of Li. This is deceptively low when compared to other pollutants in many adsorption papers, but is actually a very high value for Li. Li is one of the lightest elements, and the quoted mass volumes correspond to relatively high molar volumes. Optimal pH is usually in the basic range, and most studies have observed a pH of 12 as optimum (especially using nano-adsorbents of inorganic origin).

3. Adsorption mechanism for Li

To be able to understand the uptake of Li properly, there is a need to evaluate the physical and chemical interaction mechanisms between itself and adsorbents. The key uptake mechanisms of Li adsorption from geothermal water as discussed in the literature is summarised in Table 3. From our analysis, it seems the nature of the adsorptive interaction is highly dependent on the nature of the adsorbent material.

Chen et al. [34] observed that ion-exchange was the key mechanism for the uptake of Li from aqueous media. H—O—Ti was changed to Li-O-Ti by exchange, due to the lower electronegativity of Li.

Table 3
Mechanism of Li adsorption from geothermal water.

Adsorbent	Optimum pH	Adsorption mechanism	Ref.
Titanium-based sieve (PIS-4)	12	Ion exchange	[34]
Granulated $H_4Mn_5O_{12}$/chitosan	12	Ion exchange	[36]
Polyporous PVC – HTO	12	Ion exchange	[90]
Li-Al layered double hydroxide	6	Intercalation	[41]
Li-Al layered double hydroxide	–	Intercalation, electrostatic interaction and hydrogen-bonds	[42]
$H_{1.6}Mn_{1.6}O_4$ Ion Sieve (HMO-1)	11	Ion exchange	[86]
Phosphorylated hazelnut shell biosorbent	5.8	Physisorption	[43]
Crosslinked chitosan/LMO	12	Ion exchange	[63]
Polymer modified zeolite	9	Intermolecular and intramolecular complexation	[44]
Polymer modified zeolite-sodalite	9	Intermolecular and intramolecular complexation	[45]

Ion exchange was also observed by Ding et al. [36] for granulated $H_4Mn_5O_{12}$/chitosan. The mechanism of ion exchange was confirmed by XPS as the authors noticed an unchanged Mn^{4+} in the material before and after adsorption. The same valency for Mn^{4+} suggests the direct exchange of H with Li during the uptake process. A similar mechanism has also been observed by many other studies shown in Table 3**,** especially for those with nano-adsorbents of inorganic origin. Even though the major mechanism was ion-exchange, other mechanisms like redox and redox-ion exchange recombination mechanisms were also observed [37,38,39,40]. We will propose a general expression of the mechanism for this ion exchange. Let us consider the general form of the oxide of manganese which always has associated hydrogen and is popularly used for the adsorption of Li. They can easily be lithiated into lithium manganese oxides (LMOs) by simple ion-exchange shown in **Eq. (1)**. LMOs themselves can also be used as adsorbents for Li again after delithiation by hydrogen enrichment by strong acids. **Eq. (1)** is reversible, and the reverse direction is Li desorption.

$$H_xMn_yO_z + Li^+ \leftrightarrow Li_xMn_yO_z + H^+ \tag{1}$$

For a layered adsorbent (layered double hydroxide), Luo et al. [41] observed that intercalation of the Li ions was the uptake mechanism. Intercalation is a process where chemical species are lodged within layers of a material [28]. The ions were observed to have lodged in the octahedral holes of $Al(OH)_3$. Besides intercalation, Zhong et al. [42] showed that the uptake can be associated with electrostatic interaction and hydrogen bonds. It should be noted that the ion exchange observed above was majorly for nano-adsorbents of inorganic origin. For biosorbents of plant origin with unique pore and morphological properties, the case was observed to be different. Based on deductions on the magnitude of chemical interactions from thermodynamic analysis, Recepoğlu and Yüksel [43] posed that the uptake of Li onto phosphorylated hazelnut shell biosorbent is by physisorption. Though specific interactions were not elucidated, this seems plausible as it complements the isotherm modelling observation of Freundlich as the best-fit. Under the physisorption regime, multi-layer Li uptake is possible. This is in contrast with most ion-exchange mechanisms that had the Langmuir isotherm as best-fit, suggesting monolayer uptake. For the case of poly(acrylic acid) modified zeolite, Wiśniewska et al. [44] observed the formation of polymer-metal coordination complexes in the intermolecular and intramolecular domain. The Li cations can interact with the dissociated $-COO^-$ ligands on the polymers. Similar observations were made by Wiśniewska et al. [45] for poly(acrylic acid) modified zeolite-sodalite. Furthermore, the Law of Matching Water Affinities has been used to describe the selective interactions/or binding/ or complexation of the cation with carboxylate groups in biological systems (i.e., protein) and in aqueous systems [46,6]. The principle states that similar hydration free energies facilitate the formation of stable insoluble carboxylic salts between cations (such as Li, Na, K) and the carboxylate group. Transitions from the atomic 1 s core levels to π^* carbonyl antibonding orbitals are seen in the carboxylate K-shell spectra, with the latter changing to a higher energy in response to a stronger contact with the cation [46]. Other selective lithium-complexing agents include crown ethers, Amic-Acid, beta-diketone, etc. [47,48,49,50].

In summary, ion exchange was the major mechanism for adsorption using nano-adsorbent of inorganic origin. Intercalation with hydrogen bonds and electrostatic attraction was layered with double hydroxides and physical adsorption for biosorbents, and intermolecular and intramolecular complexation for polymer-modified adsorbents (Fig. 2).

4. Equilibrium isotherm and kinetics modelling

Equilibrium isotherm modelling and kinetics modelling are classical techniques for modelling adsorption data that can help derive important information about the process based on model assumptions [51]. The obtained results are important in determining uptake performance, sorbent management, and key parameters for the potential upscaling of the process [52]. The results for best-fits for the equilibrium isotherm and kinetics modelling of Li adsorption from geothermal water are summarized in Table 4. The table also indicates whether the modelling was done via linear or non-linear techniques. The non-linear technique is more accurate, as it eliminates mathematical errors due to linearisation [53].

Chen et al. [32] observed that the Liu isotherm was the best-fit for describing the uptake of Li by magnetic layered double hydroxides. The obtained Liu equilibrium constant was also useful in thermodynamics modelling. Zhong et al. [42] observed that the Sips isotherm was the best-fit for Li by magnetic layered double

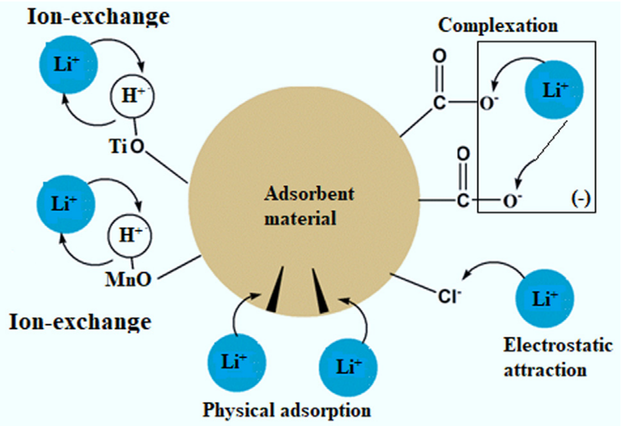

Fig. 2. Some important mechanisms of Li adsorption.

Table 4
Best-fit isotherm and kinetic models for Li uptake from geothermal water.

Adsorbent	Isotherm models Best fit	Technique	R^2	Kinetic models Best fit	Technique	R^2	Ref.
Magnetic layered double hydroxides (MLDH-1)	Liu	Non-linear	>0.984	PSO	Non-linear	0.992	[32]
Magnetic layered double hydroxides	Langmuir	Non-linear	>0.968	PSO	Non-linear	>0.979	[34]
Titanium-based sieve (PIS-4)	Langmuir	Non-linear	0.993	PSO	Non-linear	0.958	[34]
Modified activated carbon (Mn0.1-CAC)	–	–	–	PSO	Linear	0.985	[85]
Polyporous PVC – HTO	–	–	–	PSO	Linear	0.999	[90]
LIS-doped mixed matrix membrane (LIS-MMM)	Langmuir	Non-linear	0.9323	PSO	Non-linear	>0.995	[88]
$H_{1.6}Mn_{1.6}O_4$ Ion Sieve (HMO-1)	Langmuir	Non-linear	0.997	PSO	Non-linear	0.982	[86]
Powdered λ-MnO_2	Langmuir	Linear	0.966	PSO	Linear	0.99	[91]
Phosphorylated hazelnut shell biosorbent	Freundlich	Non-linear	0.999	–	–	-	[43]
H_2TiO_3 supported on Polysulfone fiber	Langmuir	Non-linear	0.997	PSO	Non-linear	0.994	[89]
Li-Al layered double hydroxide	Sips	Non-linear	>0.943	PSO	Linear	>0.997	[42]

hydroxides. The Sips isotherm model assumes either mono-layer or multilayer based on the values of the parameters [54]. Zhong et al. [42] proposed multi-layer adsorption based on the findings in their study. Besides these, the other studies had the Langmuir isotherm as the best-fit thereby suggesting mono-layer adsorption.

For kinetics modelling, the pseudo-second-order (PSO) model was observed as the best-fit. This suggests that both the available active sites in the adsorbent, and the Li concentration control the uptake rate [55,56]. There are sometimes erroneous deductions where the PSO has been pointed as a marker for chemisorption. Many recent papers have made efforts to debunk this [57,58]. It should be noted that the kinetics of Li uptake is very slow and can be between 24 and 72 h.

5. Modelling of thermodynamics

Modelling of thermodynamics is another classical adsorption modelling investigation that seeks to evaluate the temperature behaviour of the adsorption system and understand the related energies involved in the process [59]. The summary of thermodynamic parameters obtained in literature for the adsorption of Li from geothermal water is summarised in Table 5. Chen et al. [32] observed that the change in Gibbs free energy is negative for Li uptake by magnetic layered double hydroxides. This suggests a spontaneous process. The positive change in enthalpy suggests the process is endothermic and would be favoured at higher temperatures. This effect was experimentally verified in the study. In the context of industrial systems, endothermic adsorption is favourable because the water can be at an elevated temperature before treatment and would not require much cooling. From Table 5, it can be summarised that Li uptake from geothermal water is usually spontaneous and endothermic. This is due to the negative ΔG^0 values and the positive ΔH^0 values across all temperature regimes [60]. The positive ΔS^0 values suggest there is increased randomness at the solid–liquid interphase during the adsorption process [61].

6. Li desorption and adsorbent reusability

For an adsorbent material to be useful for Li recovery, it has to be reusable. Most competing technologies have reusability > 5 times especially for those related to ion-exchange resins and electrochemical techniques. It is thereby imperative that the reusability of the adsorbent be determined to give proper perspective to its potential in light of other competing technologies. Desorption is an important aspect of reusability hence the used eluent for desorption is also mentioned. The desorption and reusability of various adsorbents for Li from geothermal water is given in Table 6. Some studies choose to report removal efficiency while others choose to report adsorption capacity after n cycles.

For magnetic layered double hydroxide, Chen et al. [62] observed that the adsorbent is usable for up to 8 cycles with good retention of Li uptake capacity. Using Titanium-based Li sieve, Chen et al. [34] observed that about 90 % of the uptake capacity

Table 5
Thermodynamic parameters for Li uptake from geothermal water.

Adsorbent	Temp (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol. K)	Ref.
Magnetic layered double hydroxides (MLDH-1)	283	−16.25	4.69	42.87	[32]
	298	−18.15			
	313	−18.72			
	328	−18.04			
Magnetic layered double hydroxides	283	−15.21	13.81	101.83	[62]
	298	−16.12			
	313	−18.38			
	328	−19.57			
Titanium-based sieve (PIS-4)	298	−20.10	39.2	202.7	[34]
	308	−24.20			
	318	−28.30			
	323	-32.40			
Granulated $H_4Mn_5O_{12}$/chitosan	298	−20.60	10.17	103.51	[36]
	308	−21.81			
	318	-22.89			
	328	-23.67			
Polyporous PVC – HTO	298	−5.82	8.07	46.61	[90]
	308	−6.29			
	318	−6.75			
	328	−7.22			

Table 6
Desorption and reusability of various adsorbents for Li from geothermal water.

Adsorbent	Elution agent	Number of cycles (n)	Desorption efficiency at 1st cycle (%)	Removal efficiency at 1st cycle (%)	Removal efficiency at nth cycle (%)	Adsorption capacity at the nth cycle (mg/g)	Ref.
Magnetic layered double hydroxides	–	8	–	–	–	5.5 – 6	[62]
Titanium-based sieve (PIS-4)	HCl	5	95.8	91.3	~90	11 – 12	[34]
Granulated $H_4Mn_5O_{12}$/chitosan	HCl	6	–	–	–	10.44	[36]
Modified activated carbon (Mn0.1-CAC)	HCl	4	~99	99.88	–	43–7	[85]
Li_xAl_2-LDH@SiO_2	–	7	–	–	–	-	[94]
Polyporous PVC – HTO	HCl	5	–	~70	~70	~9	[90]
Li-Al layered double hydroxide	$CaCl_2$	5	–	–	–	~9	[41]
LIS-doped mixed matrix membrane (LIS-MMM)	HCl	5	–	–	–	23.6	[88]
$LiMn_2O_4$ Nanoparticles	HCl	1	1.20	42.8	–	68.35	[84]
$H_{1.6}Mn_{1.6}O_4$ Ion Sieve (HMO-1)	HCl	5	–	–	–	21	[86]
Phosphorylated hazelnut shell biosorbent	HCl	–	93.8	–	–	-	[43]
Crosslinked chitosan/LMO	HCl	5	–	–	–	~11.46	[63]
H_2TiO_3 supported on Polysulfone fiber	HCl	6	92.5	~97	~92	~23	[89]
Li-Al layered double hydroxide	–	12	–	–	–	~7	[42]

could be retained after 5 cycles. The desorption efficiency optimized by the appropriate use of HCl was also observed to be above 90 %. For crosslinked chitosan/LMO, the attenuation of Li uptake capacity did not go below 1.1 % of its initial value which can be considered to be relatively exceptional [63].

Generally, it is easy to achieve desorption of Li compared to other pollutants. All that is needed is a reduced pH and an acid to serve as an H^+ source for the replacement/ion exchange of Li in the adsorbent. This is why HCl is the most used eluent for Li desorption (see Table 6) as it is a strong acid that dissociates easily. It has been used beyond other strong acids due to its superior performance. It is the strongest chlorinated acid, and its suitability is further enhanced by the fact that Cl- is its anion (which already exists in brine) to form LiCl. Using other strong acids like H_2SO_4 and HNO_3 would introduce new anions into the system, thereby increasing complexity and cost of separation and isolation. The superiority of HCl has been proven experimentally as Recepoğlu and Yüksel [43] showed that HCl was a superior eluent to NaCl and H_2SO_4 albeit for Li uptake onto phosphorylated hazelnut shell biosorbent. We observe from Table 5 that most nano-adsorbents of inorganic origin can be reused over 5 times with good retention of adsorption capacity.

7. Lithium-related toxicological impact of untreated geothermal water

Besides the need for product recovery, adsorptive removal of Li from geothermal water is important because it reduces the amount of available geogenic Li in various facets of the biosphere. Areas with Li-battery disposal [64], Li-rich brines and minerals, and geothermal water, [65] can be susceptible to Li pollution. Research studies have shown that a high amount of Li in the ecosystem could have various adverse effects on the flora and fauna of the ecosystem (both in the aquatic and terrestrial domain) [65].

Though Li batteries have been shown to have negative environmental effects due to the metals it contains, the ecotoxicological contributions of Li in this domain are considered to be less [66]. Minerals, brines, and salts in pegmatite are rich in Li. These have formed an important source of Li pollution as they can be leached into major and minor water bodies [67]. The biomagnification of Li in the ecosystem has furthermore been established in a recent large-scale survey of living organisms from various habitats (demersal, benthic, and pelagic) and trophic groups (filter-feeders to *meso*-predators) [68].

It has been shown that Li can detrimentally affect embryogenesis, especially for sea urchins [69]. The activities of lactate dehydrogenase (LDH) and glucose mobilisation in American bullfrog tadpoles (Lithobates catesbeianus) can be affected by Li exposure at 2.5 mg/L [70]. For the same species at the same concentration, histopathological effects have also been observed as an endocrine response to Li toxicity [71]. In humans, Li toxicity can lead to neurological symptoms and renal insufficiency [72]. Using ramshorn snail (Marisa cornuarietis) to study the histopathological effects of Li, Sawasdee et al. [73] observed swelling of the digestive cells in the liver-pancreatic areas, irregularly shaped cilia, changes to the mucosal, and epithelial cells of the epidermis, alterations in the number of basophilic cells, and changes in the amount of mucus in the gills. A more detailed discussion on the spectrum of Li ecotoxicity is available in Aral and Vecchio-Sadus [65]. Having established the negative environmental consequence of Li, the need for efficient lithium decontamination in wastewaters cannot be over-emphasized.

8. Recommendations and future perspectives

Based on this review, several recommendations are discussed herein, and the authors also pose their thoughts for the future of the field. In an industrial setting, it will be easier to integrate a column adsorption system for Li recovery.

i. Considering that these systems are usually applied in geothermal energy generation facilities, most investigations have surprisingly taken up much interest in batch adsorption studies. Only a few studies like Can et al. [10] and Zhong et al. [42] have experimentally looked at aspects of the column adsorption systems for Li recovery. It would be more beneficial to conduct column-based investigations of adsorption systems as the parameters obtained would be more useful for understanding its industrial application potentials and for scale-up and costing purposes. Fixed-bed column adsorption experiments can be carried out to provide useful insight into parameters such as optimum flow rate, bed height, breakthrough time, and other operational conditions. This is the next essential step towards the field- or industrial-based application of the composite. Although fixed-bed column adsorption has its challenges (such as poor temperature control, pressure control requirements, difficulty in uniform packing, and regeneration of adsorbent, etc.), fixed-bed column experiments are relevant in understanding process variables between pilot- and industrial-scale applications of synthesized adsorbents.

ii. We also encourage that investigations on the cost of adsorption for the specific application be evaluated. This can help to quantitatively prove the cost superiority of adsorption over other techniques.
iii. Considering the need for environmental sustainability, there is a need for the careful disposal of spent adsorbents. Incineration is a popular technique that is not friendly to the environment [74,75]. Recent techniques being developed are immobilisation in cementitious binders and polymeric resins [21]. Other superior chemical techniques can be developed to modify or break down spent adsorbent for other applications (which would be advantageous to immobilisation).
iv. More information is required to understand the mechanism between lithium adsorbate and adsorbents for its recovery in geothermal water. Previous studies have engaged the use of XPS only, which has some limitations (such as its inability to determine hydrogen). Therefore, other techniques such as DFT (density functional theory) and XAFS (X-ray absorption fine structure) could be engaged for such studies.
v. It has been observed that lithium-based adsorbents containing manganese suffer from undesirable manganese loss during acid treatment. Such loss has been established to reduce the effectiveness and applicability of the absorbent. Various studies have explored the use of doping, electrochemical-ion separation, granulation, and surface coating to minimize the loss of Mn [76]. Therefore, future studies could utilize these techniques and discover other techniques to reduce Mn loss in Li-Mn based adsorbents for the recovery of Li in geothermal water.
vi. In recent times, interest in molecular modelling of adsorption systems via *in silico* platforms supported by theorems of statistical physics has grown [77,78]. The related energies of Li interaction with various adsorbent materials can be predicted using these tools. This could inform a suitable choice of adsorbent treatment and modification that could significantly improve different aspects of the adsorbent performance (such as uptake capacity and reusability).

9. Conclusion

The goal of this review was to elucidate key reasons for effective Li uptake as identified by the recent key papers in the field, systematically organise the literature, and discuss important innovations that could bear significance for future investigations on the subject. Based on these goals, several relevant conclusions were derived.

i. Most adsorbent materials can remove between 6 and 69 mg/g of Li. Optimal pH is usually in the basic range and most studies have observed a pH of 12 as optimum (especially using nano-adsorbents of inorganic origin).
ii. We observed that the nature of the adsorptive interaction is highly dependent on the nature of the adsorbent material. Ion exchange was the major mechanism for nano-adsorbent (nanoo-absorbance) of inorganic origin and intercalation with hydrogen bonds. Electrostatic attraction was for layered double hydroxides, physical adsorption for biosorbents, and intermolecular and intramolecular complexation for polymer-modified adsorbents.
iii. Most studies observed the Langmuir isotherm as the best-fit, thereby suggesting monolayer adsorption. The PSO model was also the best-fit to describe the Li uptake kinetics.
iv. Li uptake from geothermal water is usually spontaneous and endothermic across all temperature regimes.
v. HCl is the most effective eluent for Li desorption, and most nano-adsorbents of inorganic origin can be reused over 5 times with good retention of adsorption capacity. This is similar to most of the novel electrochemical processes because it is the ion-exchange mechanism in both scenarios.
vi. Based on the discussions, we propose that future studies should examine column adsorption since most of the experiments were carried out using batch adsorption experiments. We also propose molecular modelling, used adsorbent disposal, and cost analysis.

It can be concluded that adsorption is an effective technique for the recovery of Li from geothermal water. This will be very helpful in achieving environmental sustainability and the circular economy.

Disclosure statements

Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

Data availability

No data was used for the research described in the article.

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.

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