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Physicochemical parameters of lithium sorption from hydromineral raw materials using synthesized inorganic sorbents

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ABSTRACT

This paper presents the results of a study on the physicochemical parameters of the lithium sorption process from hydromineral raw materials using synthesized sorbents. The physicochemical parameters of lithium sorption from brine, including the enthalpy change (ΔH, kJ/mol), entropy change (ΔS, kJ/mol·K), and Gibbs free energy (ΔG, kJ/mol), were investigated. The enthalpy value $\Delta H = -0.698$ kJ/mol indicates that the process is exothermic, as it is accompanied by heat release. The positive value of entropy $\Delta S = 0.0122$ kJ/(mol·K) indicates a low degree of order and increased randomness at the interface between the manganese dioxide-based sorbent and the brine during lithium absorption. The negative Gibbs free energy (ΔG) values, ranging from -4.401 to -4.769 kJ/mol at temperatures of 303–333 K, confirm that the lithium sorption process on the manganese oxide sorbent is spontaneous and can proceed without external influence. Additionally, the activation energy value $E_a = -0.592$ kJ/mol suggests a decrease in the sorption rate as the temperature increases. Using a modified Arrhenius-type equation, the adhesion probability S^* was determined to be 0.188. This value indicates the predominance of the chemisorption mechanism in the lithium sorption process.

Keywords: lithium, physicochemical parameters, chemisorption, lithium-ion sieves, hydromineral raw material.

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Introduction

Lithium is one of the key elements of modern energy, widely used in the manufacture of batteries, glass, ceramics, and pharmaceutical products [[1], [2], [3], [4], [5]]. However, the extraction of lithium from natural sources such as salt lakes, oil brines, and seawater presents significant technological challenges [6]. In recent years, lithium-ion sieves (LIS) have emerged as an innovative solution for the efficient extraction of lithium from liquid media [[7], [8]]. Li-ion sieves are characterized by high selectivity toward lithium ions as well as environmental safety, making them a promising tool for the sustainable development of the lithium industry [[9], [10]].

Lithium-ion sieves (LIS) are specialized adsorbents capable of selectively capturing lithium ions (Li^+) from aqueous solutions [[11], [12]]. Their structure is based on porous materials containing lithium, which is replaced by hydrogen ions (H^+) when interacting with the solution. The principle of operation of LIS is illustrated in Figure 1. The synthesis of LIS involves several steps: preparation of the precursor, its calcination, and acid treatment of the precursor to obtain the sorbent. The vacant sites in the crystal lattice formed during this process are able to retain ions whose radius does not exceed that of the target lithium ions.

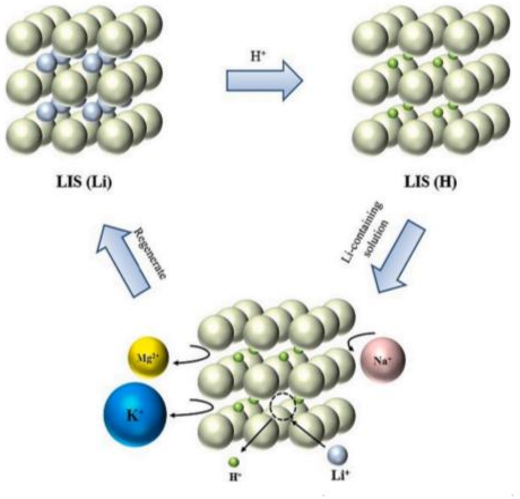

Figure 1 - Schematic representation of LISs process [13]

Among the many materials used in LIS, manganese-based oxides are the most widespread. From the precursors $LiMn_2O_4$, $Li_{1.33}Mn_{1.67}O_4$, and $Li_{1.6}Mn_{1.6}O_4$, scientists have developed manganese oxide-based sorbents such as λ-MnO_2, $MnO_2 \cdot 0.3H_2O$, and $MnO_2 \cdot 0.5H_2O$ [[14], [15]]. These sorbents exhibit excellent adsorption capacity. For example, precursor sorbents have sorption capacities of 39.9 mg/g for $LiMn_2O_4$, 59 mg/g for $Li_4Mn_5O_{12}$, and a high capacity of 72.3 mg/g for the $Li_{1.6}Mn_{1.6}O_4$ precursor sorbent [[16], [17]].

In previous papers, the results of studies on the synthesis of inorganic sorbents based on manganese oxide compounds were presented, along with the results of lithium sorption from formation brines of oil fields. Additionally, the kinetic model of lithium sorption from hydro-mineral raw materials on the synthesized sorbent was determined, and the synthesized manganese dioxide sorbent was studied after its saturation with lithium from brine [[18], [19]].

To gain a more detailed understanding of lithium sorption from brine and to increase the completeness of sorption extraction, it is particularly important to study the physicochemical parameters characterizing the process.

Research methods

Experimental methodology. Experiments on lithium sorption from brines were conducted in a thermostated reactor with a capacity of 0.5 dm^3, equipped with a mechanical stirrer (VELP Scientifica LS F201A0151, Italy) operating at a fixed number of revolutions. The temperature was maintained constant using a LOIP LT-100 circulation thermostat. A specific amount of brine was poured into the reactor and heated to the desired temperature. Once the target temperature was reached, the required amount of sorbent was added to the brine in the reactor, and stirring was initiated. The start of the process was then recorded. At the end of the experiment, the brine was separated from the sorbent, and the lithium content in the brine was analyzed.

Analysis methods. The quantitative content of lithium in the initial brine and filtrates after sorption was determined on an Optima 8300DV inductively coupled plasma atomic emission spectrometer and on a SHIMADZU AA-7000 atomic absorption spectrophotometer (Japan).

Results and Discussion

The study of the physicochemical characteristics of the sorption process provides important information regarding the Gibbs free energy of the system and other thermodynamic parameters during the sorption of lithium from brine. This information can be used to determine the type and mechanism of the process.

The physicochemical parameters of lithium sorption from brine such as enthalpy change (ΔH, kJ/mol), entropy change (ΔS, kJ/mol·K) and Gibbs free energy (ΔG, kJ/mol) are calculated using the following equations:

$$\Delta G = -2{,}303\ RT \log K_d \qquad (1)$$

$$\log K_d = \frac{\Delta S}{2{,}303R} - \frac{\Delta H}{2{,}303RT} \qquad (2)$$

$$\Delta G = \Delta H - T\Delta S \qquad (3)$$

where, K_d is the sorption equilibrium constant, dm^3/g; R is the universal gas constant, 8.314 J/(mol·K); T is the absolute temperature, K.

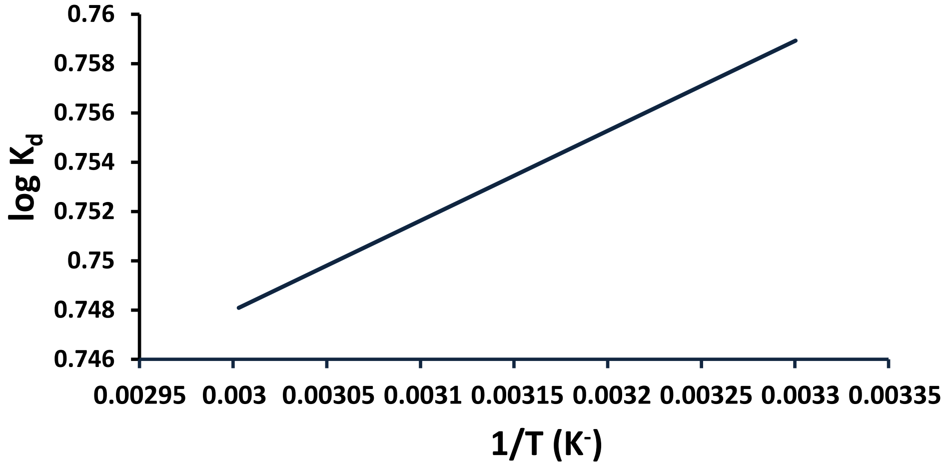

Figure 2 - Graph of dependence of the logarithm of the equilibrium constant of lithium sorption on manganese-oxide sorbent log K_d on the inverse temperature 1/T

By constructing a line graph in the coordinates log K_d versus 1/T, in accordance with equation (2), we can determine the values of the enthalpy change (ΔH) and the entropy change (ΔS) from the slope of the line and its intersection with the ordinate axis, respectively.

The process of lithium sorption from brines with initial lithium concentration of 5.477 mg/dm^3 under the following conditions was studied: temperature from 30 to 60 °C (step 10 °C); duration 24 h; ratio of sorbent mass to brine volume = 1: 1000. According to the obtained results, K_d values were calculated and a graph in log K_d - 1/T coordinates was plotted (Figure 2). The parameters calculated from the graph of Figure 2 are shown in Table 1. The negative value of Gibbs energy (ΔG) indicates that lithium sorption on manganese oxide sorbent under these conditions can proceed spontaneously, i.e. spontaneously. The negative value of the enthalpy change (ΔH) indicates that the sorption process proceeds with heat release. The positive value of entropy change (ΔS) indicates a low degree of order and indicates that randomness increases at the manganese dioxide sorbent/salt interface during lithium adsorption.

Table 1 - Physicochemical parameters for lithium sorption process on manganese oxide sorbent

Parameters	Temperature, K	Value
ΔG, kJ/mol	303	–4.401
	313	–4.528
	323	–4.645
	333	–4.769
ΔH, kJ/mol		–0.698
ΔS, kJ /(mol·K)		0.0122
E_a, kJ/mol		–0.592
S^*		0.188

The modified Arrhenius-type equation related to surface coverage (θ) is the sticking probability (S*), which is a function of the adsorbate/adsorbent system under consideration and depends on the temperature of the system. The value of S* is a measure of the ability of the adsorbate to remain on the adsorbent indefinitely [20]. The effect of temperature on the sticking probability is estimated by calculating the surface coverage at different temperatures and can be expressed as [21]:

$$S^* = (1-\theta)\exp-\left(\frac{E_a}{RT}\right) \quad (4)$$

$$\ln(1-\theta) = \ln S^* + \frac{E_a}{RT} \quad (5)$$

$$\theta = 1 - \frac{C_e}{C_0} \quad (6)$$

where, θ is the fraction of the sorbent surface occupied by adsorbed lithium; E_a is the apparent activation energy, kJ/mol; C_0 and C_e are initial and equilibrium concentrations of lithium in brine, respectively, mg/dm^3.

The probability of adhesion under optimal conditions of the sorption process was evaluated as a function of the degree of coverage of the sorbent surface and temperature in the range of 303–333 K. Based on the linear dependence plotted in the coordinates of ln(1-θ) versus 1/T, it is possible to determine ln S* and E_a/R (Figure 3).

The calculated values of apparent activation energy (E_a) and sticking probability (S*) are presented in Table 1. The sorption process in the studied temperature range of 303-333K is exothermic and proceeds with heat release. The

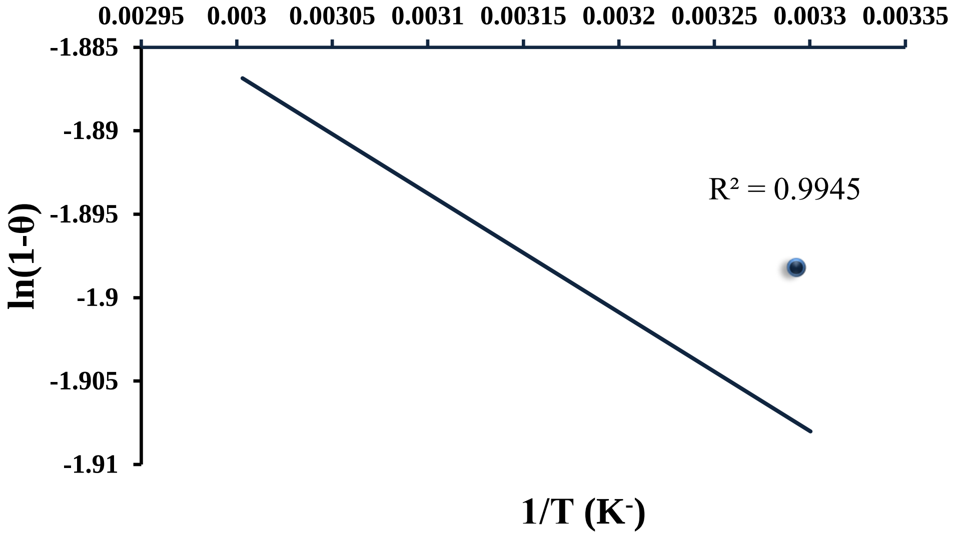

Figure 3 - Graph of ln(1-θ) versus 1/T for lithium sorption on manganese oxide sorbent

negative value of activation energy shows that sorption slows down with increasing temperature. The sticking probability should lie in the range 0 < S^*<1 [21].

The sticking probability S^* > 1 indicates the adhesion of adsorbate from adsorbent (no sorption), S^* = 1 implies a linear dependence of adhesion between adsorbate and adsorbent and a mixture of physical and chemisorption mechanisms is possible, S* = 0 means unlimited adhesion of adsorbate to adsorbent in which the chemisorption mechanism prevails.

Finally, in the region of values 0 < S*< 1 means favourable adhesion of adsorbate to adsorbent with predominance of physical sorption mechanism. The calculated value of S*, which is 0.188, is closer to 0 in the range of 0 to 1, indicating the predominance of the chemisorption mechanism [22].

Therefore, the physicochemical parameters derived from both calculations and experiments can be utilized for scientific research.

Conclusions

The study of the physicochemical parameters of the lithium sorption process from hydromineral raw materials was conducted. The physicochemical parameters of lithium sorption from brine, such as enthalpy change (ΔH, kJ/mol), entropy change (ΔS, kJ/mol·K), and Gibbs free energy (ΔG, kJ/mol), were calculated. The enthalpy change ΔH = -0.698 kJ/mol indicates that the lithium sorption process is exothermic, accompanied by heat release. The entropy changes ΔS = 0.0122 kJ/(mol·K) suggest a low degree of ordering and an increase in chaos at the manganese dioxide sorbent/salt interface during lithium adsorption. The negative values of Gibbs free energy (ΔG), ranging from -4.401 to -4.769 kJ/mol within the temperature range of 303–333 K, demonstrate that the sorption of lithium on the manganese oxide sorbent can proceed spontaneously. A negative activation energy E_a = -0.592 kJ/mol, was obtained, indicating that the sorption process slows down as the temperature increases. The sticking probability S* = 0.188 was calculated, which suggests the predominance of a chemisorption mechanism.

Conflicts of interest. On behalf of all authors, the corresponding author states that there is no conflict of interest.

CRediT author statement: **B. Kenzhaliyev**: Conceptualization, Validation, Visualization; **Z. Karshyga**: Supervision, Validation, Original draft preparation, Reviewing and Editing; **A. Yersaiynova**: Investigation, Methodology, Data curation, Writing draft preparation; **N. Muhammed**: Validation; **A. Yessengaziyev**: Investigation, Software.

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Синтезделген сорбенттер көмегімен гидроминералды шикізаттан литийді сорбциялау процесінің физика-химиялық көрсеткіштерін зерттеу

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ТҮЙІНДЕМЕ

Бұл жұмыста синтезделген сорбенттерді қолдана отырып, гидроминералды шикізаттан литийді сорбциялау процесінің физика-химиялық параметрлерін зерттеу нәтижелері келтірілген. Тұзды ерітіндіден литийді сорбциялаудың физика-химиялық параметрлері, мысалы, энтальпияның өзгеруі (ΔH кДж/моль), энтропияның өзгеруі (ΔS, кДж/моль) және Гиббстің бос энергиясы (ΔG, кДж/моль) есептелді. Энтальпия мәні $\Delta H = -0{,}698$ кДж / моль процестің жылу шығарумен бірге жүретінін растайды, бұл оның экзотермиялық сипатын көрсетеді. Энтропияның оң мәні $\Delta S = 0{,}0122$ кДж / (моль·К) марганец диоксиді негізіндегі сорбент пен литийді сіңіру кезінде тұзды ерітінді арасындағы фазалық интерфейсте реттіліктің төмен дәрежесін және ретсіздіктің жоғарылауын көрсетеді. 303-333 К температурада -4,401-ден -4,769 кДж/моль диапазонында алынған Гиббс бос энергиясының теріс мәндері (ΔG) марганец-оксид сорбентіндегі литий сорбциясы процесі өздігінен жүретінін және сыртқы әсерсіз жүруі мүмкін екенін растайды. $E_a = -0{,}592$ кДж/моль активтендіру энергиясының мәні температура жоғарылағанда сорбция жылдамдығының төмендейтінін көрсетеді. Модификацияланған Аррениус типті теңдеуді қолдана отырып, 0,188-ге тең S* жабысу ықтималдығы анықталды, бұл литийді сорбциялау процесінде хемосорбциялық механизмінің басым екендігін көрсетеді.

Түйін сөздер: литий, физика-химиялық параметрлер, хемосорбция, литий-ионды елек, гидроминералды шикізат.

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Физико-химические параметры процесса сорбции лития из гидроминерального сырья с использованием синтезированных сорбентов

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АННОТАЦИЯ

В данной работе представлена результаты изучения физико-химических параметров процесса сорбции лития из гидроминерального сырья с использованием синтезированных сорбентов. Рассчитаны термодинамические параметры сорбции лития из рассола, такие как изменение энтальпии (ΔH кДж/моль), изменение энтропии (ΔS, кДж/моль·К) и свободная энергия Гиббса (ΔG, кДж/моль). Значение энтальпии ΔH = –0,698 кДж/моль подтверждает, что процесс сопровождается выделением тепла, что указывает на его экзотермический характер. Положительное значение энтропии ΔS = 0,0122 кДж/(моль·К) свидетельствует о низкой степени упорядоченности и увеличении хаотичности на границе раздела фаз между сорбентом на основе диоксида марганца и рассолом при поглощении лития. Полученные отрицательные значения свободной энергии Гиббса (ΔG) в диапазоне от –4,401 до –4,769 кДж/моль при температурах 303–333 К подтверждают, что процесс сорбции лития на марганцево-оксидном сорбенте является спонтанным и может протекать без внешнего воздействия. Значение энергии активации E_a = –0,592 кДж/моль свидетельствует о снижении скорости сорбции с ростом температуры. С использованием модифицированного уравнения типа Аррениуса определена величина вероятности прилипания S^*, равная 0,188, которая указывает на преобладание хемосорбционного механизма процесса сорбции лития.

Ключевые слова: литий, физико-химические параметры, хемосорбция, литий-ионное сито, гидроминеральное сырье.

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