ISSN 2181-8622

Manufacturing technology problems

Scientific and Technical Journal Namangan Institute of Engineering and Technology

INDEX COPERNICUS INTERNATIONAL

Volume 9
Issue 2
2024

Google Scholar Crossref doi SLIB.UZ Scientific library of Uzbekistan

STUDYING ISOTHERMS OF ADSORPTION AND DESORPTION OF NITROGEN ON A SORBENT SYNTHESIS FOR SELECTIVE EXTRACTION OF LITHIUM

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Abstract: The purpose of this work is to study the adsorption characteristics of a synthesized organoelement sorbent intended for the sorption of lithium from brines, based on the adsorption and desorption isotherm of nitrogen at 77.35°K. Determination of the main adsorption characteristics of sorbents such as specific surface area, monolayer capacity, specific volume, average pore width, etc. All calculations were performed based on the BET method. The specific surface area of the sorbent is determined in two ways, i.e. by mass and volume of adsorbate gas using linear forms of the BET equation. The results of the nitrogen desorption isotherm on the synthesized sorbent according to the BJH method are presented.

To achieve the goal of this study, the standard method for determining the specific surface area of adsorbents was used - the BET method and pore size distribution - the BJH method. To determine the specific surface area using the multipoint BET method, it is necessary to measure the equilibrium values of the mass of the adsorbed gas (in our case, nitrogen) per unit mass of the adsorbent for at least three different relative pressures.

The specific surface area of the sorbent, determined in two ways i.e. by mass and volume of adsorbate gas using the BET method was 4.99 m2/g. It was determined that the main capacity of the synthesized sorbent consists of pores with a width of 9 to 20 nm. The results of desorption based on the BJH method are presented.

The adsorption characteristics of the synthesized sorbent for the selective extraction of lithium from brines were determined, such as specific surface area, monolayer capacity, pore width, etc. The results were obtained with a nitrogen adsorption isotherm at 77.35 °K. Using the BET equations, the specific surface area of the synthesized sorbent was determined, which was 4.99 m2/g. The calculated results are compared with the results obtained by the specific surface area analyzer.

Keywords: adsorption, desorption, specific surface area, BET method, monolayer capacity, DHAL-Cl.

Introduction. Today, the most promising sorbents for extracting lithium from brines are compounds based on aluminum hydroxide. For the first time, the possibility of using a sorbent with the composition LiCl·2Al(OH)3·mH2O (abbreviated DHAL-Cl) when included in the pores of a macroporous ion-exchange resin to extract lithium from brines was shown in American patents back in the 70s of the last century [1].

Employees of the Tashkent Research Institute of Chemical Technology synthesized a selective sorbent based on DHAL-Cl and polyvinyl alcohol for the extraction of lithium from brines. There is a lot of data from different sources on the synthesis and application of this type of sorbent, but very little is known about the adsorption characteristics of this type of sorbent. Studying the adsorption of gases by solids can provide valuable information about their specific surface area and porous structure. The adsorption of

nitrogen at its boiling point of 77 K is currently most widely used for this purpose [2]. Therefore, studying the adsorption characteristics of sorbents based on DHAL-Cl is relevant due to the increasing demand for this type of sorbent. The BET method was chosen as a calculation method since the standard method for measuring the specific surface area of adsorbents, catalysts, powders and other materials is based on the BET theory [3].

Methods. *Determination of the specific surface area of the synthesized sorbent using the BET method and the pore size distribution using the BJH method.*

Currently, the standard method for determining the specific surface area is the BET method. To confirm the applicability of the BET equation and find its constants, it is convenient to use the linear form of the equation:

$$\frac{P/P_{\circ}}{A(1-P/P_{\circ})} = \frac{1}{A_{\circ} \cdot C} + \frac{C-1}{A_{\circ} \cdot C} \cdot \frac{P}{P_{\circ}} \qquad (1)$$

where: A is the adsorption value, mmol/g; P and P_o are the equilibrium pressure and the saturated vapor pressure of the adsorbate at the adsorption temperature; A_o - monolayer capacity, mmol/g; C is the BET constant, which characterizes the adsorption energy of the first adsorbed layer, i.e. interaction of adsorbate and adsorbent.

From the monolayer capacity A_o (expressed in moles of adsorbate, mmol/g) per gram of adsorbent, the specific surface area S as the surface area of 1 g of a solid is calculated using the simple equation:

$$S = A_o \cdot N \cdot \omega \qquad (2)$$

where N - Avogadro's number ($6{,}022 \cdot 10^{23}$ mol^{-1}); ω - the area occupied by one adsorbate molecule ($16{,}2 \cdot 10^{-20}$ m^2 for an N_2 molecule).

If the adsorbed amount is expressed in other units, the appropriate coefficient is entered. Thus, if adsorption is expressed in grams, then the basic equation of the BET theory relating the mass of adsorbate W per 1 g of adsorbent and the relative pressure of the adsorbate P/P_o can be written as follows:

$$\frac{1}{W(P_{\circ}/P-1)} = \frac{1}{W_{\circ}C} + \frac{C-1}{W_{\circ}C} \cdot \frac{P}{P_{\circ}} \qquad (3)$$

where W_o - the mass of the adsorbate monolayer on the surface of 1 g of adsorbent.

To determine the specific surface area using the multipoint BET method, it is necessary, for at least three different relative pressures P/P_o, to measure the equilibrium values of the mass of the adsorbed gas (in our case, nitrogen) per 1 g of adsorbent and calculate the values of $1/[W((P_o/P)-1)]$. Thus, we get a set of pairs of points in coordinates P/P_o and $1/[W((P_o/P)-1)]$. By approximating the obtained points with a straight line, we can obtain the slope of the straight line s and the point of its intersection with the ordinate axis i. Based on equation (3), they can be expressed as:

$$\frac{C-1}{W_{\circ}C} = s \qquad (4), \qquad \frac{1}{W_{\circ}C} = i \qquad (5)$$

By combining these two equations, we can determine the weight of the adsorbate monolayer per 1 g of adsorbent:

$$W_{\circ} = \frac{1}{s+i} \qquad (6)$$

from which the specific surface area of the sample can be calculated using the formula:

$$S = \frac{W_o \cdot N \cdot \omega}{M} \quad (7)$$

where M - the molecular weight of the adsorbate (28.013 g/mol for N_2).

If the monolayer capacity is expressed as gas volume at normal conditions (STP) and has the value V_o (ml/g), from the linear form of the equation:

$$\frac{P/P_o}{V(1-P/P_o)} = \frac{1}{V_o \cdot C} + \frac{C-1}{V_o \cdot C} \cdot \frac{P}{P_o} \quad (8)$$

where V is the volume of adsorbed adsorbate gas per gram of sample; V_o – specific capacity of the monolayer – the amount of adsorbate gas in sm^3 (in sm^3, reduced to normal conditions) per gram of sample, which would be absorbed by the sample if the entire surface was monolayered with adsorbate gas molecules;

From (8) we obtain the equation for calculating the specific surface area:

$$S = \frac{V_o \cdot N \cdot \omega}{22{,}414} \quad (9)$$

The specific surface area is usually calculated in m2/g. The accuracy of determining the specific surface area is usually 5–10%, which is due to both the approximations of the BET method itself and experimental measurement errors [4,5,6].

Results. The analysis of the specific surface area of the synthesized sorbent was carried out using a device – Quantachrome Autosorb iQ AG, USA. Analysis conditions: sample weight - 0.082 g, gas supply time - 1 hour, gas type - nitrogen, duration - 2 hours 27 minutes.

Table 1. N_2 adsorption-desorption isotherm data at 77.35 °K on the synthesized sorbent.

Relative pressure, P/P_o	Volume @ STP , sm^3/g	$1/[W((P_o/P)-1)]$, 1/g	Relative pressure, P/P_o	Volume @ STP , sm^3/g	$1/[W((P_o/P)-1)]$, 1/g
0,051	0,3025	142,28	0,8006	3,3713	952,94
0,1007	0,5484	163,54	0,8505	3,5662	1276,4
0,1509	0,7142	199,18	0,8999	4,1523	1733,6
0,2009	0,8979	224,12	0,9501	4,5102	3376,5
0,251	1,0221	262,42	0,993	5,1658	2204,9
0,3009	1,2041	286,05	0,8979	5,0054	1406,3
0,3509	1,3757	314,43	0,7983	4,7410	667,98
0,4008	1,5550	344,18	0,6984	4,4554	415,81
0,4509	1,6746	392,33	0,5981	4,1466	287,17
0,5006	1,9483	411,77	0,4995	3,6775	217,16
0,5505	2,2703	431,67	0,3989	3,0832	171,78
0,601	2,2328	539,81	0,2985	2,3692	143,72
0,6505	2,6230	567,62	0,1984	1,6512	119,98
0,7003	2,9973	623,74	0,9849	0,8164	107,08
0,7507	3,1851	756,41			

Using the data presented in **Table 1**, a graph of the linear dependence of the value $1/[W((P_o/P)-1)]$ on P/P_o was obtained according to equation (3) (**see Fig. 1**).

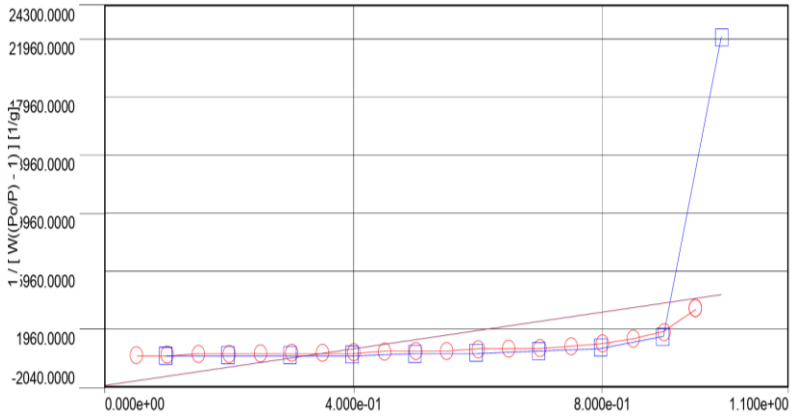

Figure 1. N_2 adsorption-desorption isotherm at 77.35 °K per 1 g of synthesized sorbent.

From a practical point of view, in the case of using nitrogen as an adsorbate, the linear portion of this dependence is observed in the region of relative pressures P/P_o from 0.05 to 0.35-0.4. (see **Fig. 2**)

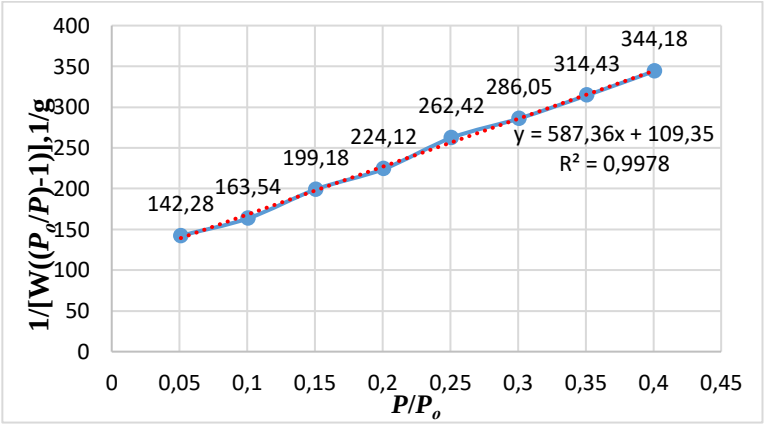

Figure 2. N_2 adsorption isotherm on the synthesized sorbent in coordinates of the linear form of the BET equation

From **Fig. 2** and equations (4), (5), and (6) we find the value W_o = 0.001435 g, then inserting the obtained value into equation (7) we find the specific surface of the synthesized sorbent:

$$S = 0{,}001435 \cdot 6{,}022 \cdot 10^{23} \cdot 16{,}2 \cdot 10^{-20} / 28{,}013 = 4{,}99 \text{ m}^2/\text{g}$$

To calculate the specific surface area based on the specific volume of the adsorbent (see **Table 1**), the linear form of the BET equation (8) can be represented as a linear dependence of the value $P/P_o/V\cdot(1- P/P_o)$ on P/P_o (**Fig.3**).

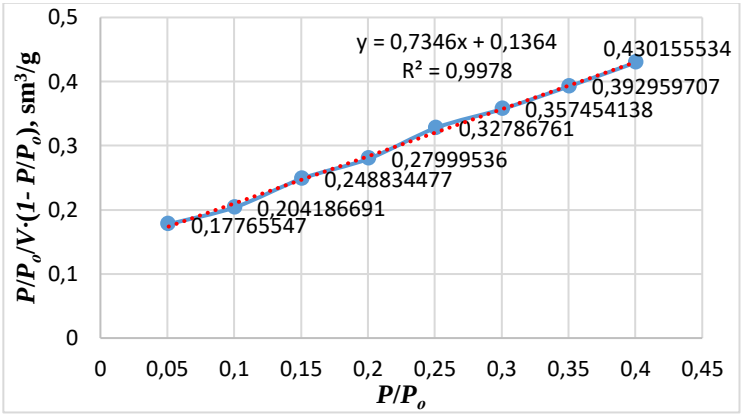

Figure 3. N_2 adsorption isotherm based on the specific volume of the adsorbent on the synthesized sorbent in the coordinates of the linear form of the BET equation

Using the data from **Fig. 3** and equation (8), we find V_o = 1.1481 and calculate the specific surface area using equation (9):

$$S = 1{,}1481 \cdot 6{,}022 \cdot 16{,}2 / 22{,}414 = 4{,}99 \text{ m}^2/\text{g}$$

The specific surface area of the synthesized sorbent, determined by the mass and volume of gas adsorbed in the monolayer, was 4,99 m^2/g

To check the correctness of the calculations, you can compare the results obtained with the data obtained using a specific surface area analyzer (see **Table 2** and **Fig. 5**).

Table 2. Results of the experiment data at the maximum value of P/P_o=1

Volume @ STP , sm^3/g	Surface area, m^2/g	$1/[W((P_o/P)-1)]$, 1/g	Volume @ STP , sm^3/g	Surface area, m^2/g	$1/[W((P_o/P)-1)]$, 1/g
0.3025	1.2493	142,28	3.3713	2.9258	952,94
0.5484	2.1463	163,54	3.5662	2.3206	1276,4
0.7142	2.6392	199,18	4.1523	1.8079	1733,6
0.8979	3.1227	224,12	4.5102	0.9801	3376,5
1.0221	3.3319	262,42	5.1658	0.1568	2204,9
1.2041	3.6637	286,05	5.0054	2.2236	1406,3
1.3757	3.8865	314,43	4.7410	4.1620	667,98
1.5550	4.0555	344,18	4.4554	5.8491	415,81
1.6746	4.0023	392,33	4.1466	7.2533	287,17
1.9483	4.2344	411,77	3.6775	8.0107	217,16
2.2703	4.4414	431,67	3.0832	8.0748	171,78
2.2328	3.8774	539,81	2.3692	7.2336	143,72
2.6230	3.9907	567,62	1.6512	5.7606	119,98
2.9973	3.9099	623,74	0.8164	3.2035	107,08
3.1851	3.4562	756,41			

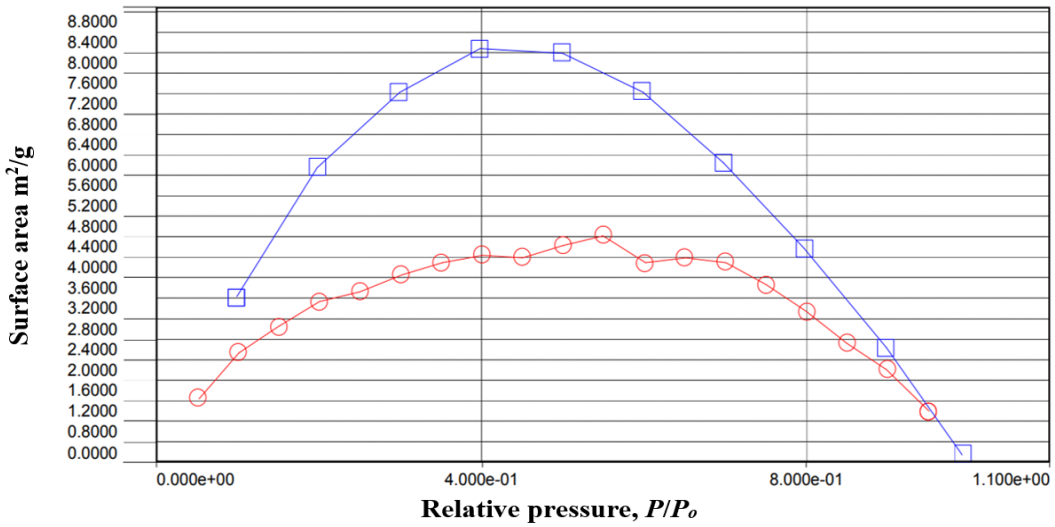

Figure 4. Graph of N2 adsorption-desorption isotherm on the synthesized sorbent at max. value P/P_o=1,

red line – adsorption, blue line – desorption

As can be seen, in Fig. 4 the specific surface area of the sample after analysis was 4.44 m²/g. Taking into account the 10% error of the method, we can safely say that the calculated data correspond to reality.

Table 3. Results of desorption using the BJH method (Barrett-Joyner-Halend)

Surface area, m²/g	Pore volume, sm³/g	Half pore width, nm
3,891	0,005	18,125

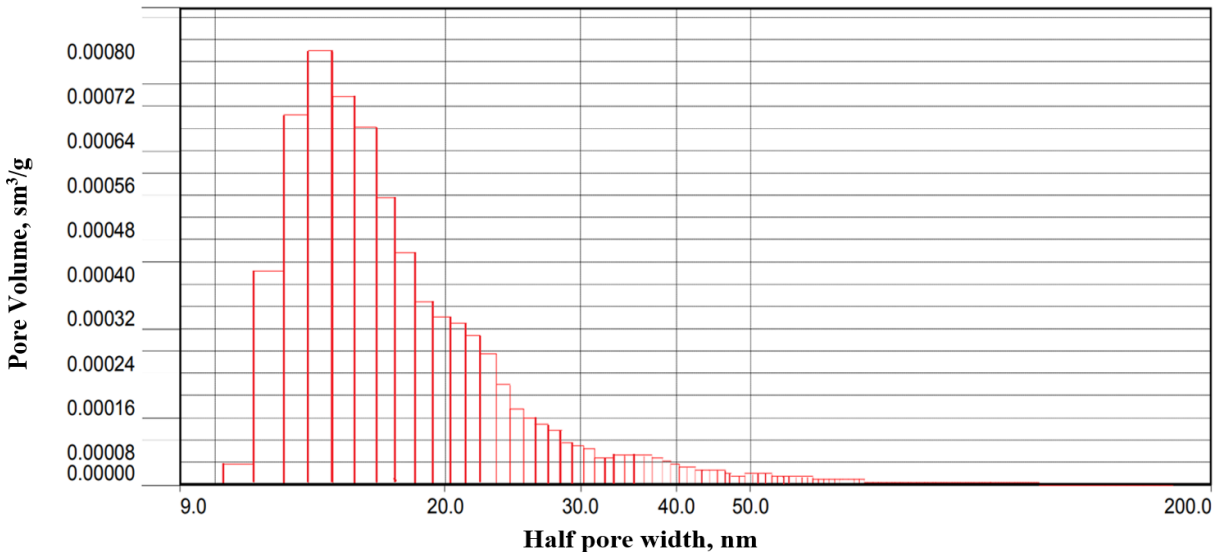

Figure 5. Histogram of pore volume distribution

From **Fig. 5** it can be seen that the main capacity of the synthesized sorbent consists of pores with a width of 9 to 20 nm. This also indicates that the sorbent consists mainly of mesopores (from 2 nm to 50 nm) [7]. The capacity of macropores (more than 50 nm) in the sorbent is very small.

Conclusion. The adsorption characteristics of the synthesized sorbent for the selective extraction of lithium from brines were determined, such as specific surface area, monolayer capacity, pore width, etc. The results were obtained with a nitrogen adsorption isotherm at 77.35 °K. The specific surface area of the sorbent, determined in two ways i.e. by mass and volume of adsorbate gas using the BET method was 4.99 m^2/g. The calculated results are compared with the results obtained by the specific surface area analyzer. The results of desorption based on the BJH method were studied. It was determined that the main capacity of the synthesized sorbent consists of pores with a width of 9 to 20 nm.

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