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DETERMINATION OF ADSORPTION AND DESORPTION ISOTHERMS OF ZEOLITE LTA(4A) USING THE GRAVIMETRIC METHOD

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Abstract

The moisture adsorption and desorption behavior of porous materials is significantly influenced by the size and shape of their pore structure. A sorption isotherm graphically represents the equilibrium moisture content of a material as a function of the equilibrium relative humidity of the surrounding air (or water activity in the case of food materials) at a constant temperature.

In this study, the adsorption and desorption isotherms of Zeolite LTA (4A) granular material were determined at 30°C, 40°C, 50°C, and 60°C using a gravimetric measurement system. The obtained sorption isotherms exhibited S-shaped (sigmoidal) curves, characteristic of multilayer sorption mechanisms. The minor hysteresis loop indicates that the adsorption and desorption processes are governed by different physicochemical mechanisms, which can be attributed to the heterogeneity of the pore structure. Various model equations, including modified BET, mod. Chung-Pfost, mod. GAB, mod. Halsey, mod. Henderson, and mod. Oswin models, were fitted to the experimental data using non-linear regression analysis. The mod. GAB model demonstrated the best fit to the measured data, while all models, except for the mod. BET, provided satisfactory correlations ($R^2 > 0.85$).

Furthermore, the isosteric heat of adsorption and desorption of the investigated material was determined, quantifying the heat absorbed during adsorption equilibrium and the heat released during desorption equilibrium.

Our findings contribute to the optimization of zeolite applications in industrial moisture control and drying processes.

Keywords: *zeolite, sorption isotherm, gravimetric method, GAB model*

1. Introduction

One of the fundamental properties of materials is their moisture adsorption capacity (Johannesson and Janz 2002), which can be described by an equilibrium sorption isotherm. Sorption isotherms play a key role in modeling moisture transport processes and in studying the microstructure of materials. The structure of a material has a significant effect on its ability to adsorption and desorption moisture, and therefore many mathematical models have been developed to describe isotherms. *Table 1* presents the most commonly used equations that simultaneously take into account water activity and equilibrium temperature.

Based on the sorption isotherms determined at different temperatures, the isosteric sorption heat, which characterizes the binding energy between the adsorbent and the adsorbed component, can be calculated (Yang, Zhu, and Zhu 2012). Knowledge of this value is essential for estimating the energy requirements of sorption technologies and optimizing industrial processes.

The aim of this research is to experimentally determine the adsorption and desorption isotherms of granular zeolite for water vapor using the gravimetric method. The obtained data sets were analyzed using literature sorption isotherm models and the best-fitting model was selected using statistical method. Furthermore, the values of the isosteric sorption heat characteristic of

adsorption and desorption were determined, which allow a more detailed understanding of the sorption properties of zeolite.

Table 1. Sorption isotherm model equation

Model	Ref.	Equation
Mod. Chung-Pfost	(Raji and Ojediran 2011)	$X_{eq} = -\frac{1}{C}\ln\left[\frac{(T+B)}{A}\ln a_w\right]$
Mod. GAB	(Raji and Ojediran 2011)	$X_{eq} = \frac{AB\left(\frac{C}{T}\right)a_w}{(1-Ba_w)\left(1-Ba_w+\left(\frac{C}{T}\right)Ba_w\right)}$
Mod. Halsey	(Raji and Ojediran 2011)	$X_{eq} = \left[\frac{-\ln a_w}{e^{A+BT}}\right]^{-\frac{1}{C}}$
Mod. Henderson	(Nazreen et al. 2020)	$X_{eq} = \left[\frac{-\ln(1-a_w)}{A(B+T)}\right]^{\frac{1}{C}}$
Mod. Oswin	(Nazreen et al. 2020)	$X_{eq} = (A+BT)\left[\frac{a_w}{1-a_w}\right]^{\frac{1}{C}}$

X_{eq} – material's equilibrium moisture content $[kg_{H2O}/kg_{dry\ material}]$, T – equilibrium temperature of the material $[°C]$, a_w – water activity [1], $A;\ B;\ C$ – constants, Mod. – modified.

2. Materials and Methods

During the study, adsorption and desorption isotherms of zeolite particles with a diameter of 1.7-2.4 mm were determined using a measuring device based on the gravimetric method.

2.1 Material

Zeolite has a significant surface activity due to its porous structure. Due to its high energy storage density and excellent sorption capacity, it is widely used in detergent production, gas separation technology as a filler, and as a catalyst. It is used as an adsorbent in the petrochemical industry in drying and cleaning processes. However, its disadvantage is that its regeneration requires high temperatures.
The tested material belongs to the group of LTA-type zeolites, whose chemical formula is $Na_{12}(Al_{12}Si_{12}O_{48})\cdot 27H_2O$. Before starting the sorption isotherm measurements, the damaged parts and impurities present in the zeolite grains were separated using an air classifier.

2.2 Measuring equipment

During the measurements, the determination of the sorption isotherms was carried out using a measuring equipment based on the gravimetric measurement method, which is shown in *Fig. 1/a.* The measuring equipment consists of a Julabo Tw20 type water bath, which ensures the maintenance of a constant temperature for the samples in the solution bottles. The tank contains a stainless-steel positioning plate, which allows for the even arrangement and stable fixation of 15 solution bottles. The water bath is filled with filtered, softened water, into which the solution bottles shown in *Fig. 1/b* were placed. In order for the solution bottle to be completely immersed in the water, a steel disc was attached to the bottom of the bottle. The lower third part of the solution bottle was filled with the appropriate type of saturated salt solution. A stainless-steel holding basket is used to place the samples, which fits onto the rim of the solution bottle. The holding basket contains a glass sample bottle with a capacity of 30 ml. The holding basket has

cutouts on the side, thus ensuring adequate air flow around the sample. To ensure a hermetic seal of the system, the solution bottles are equipped with a threaded cap and a silicone seal that prevents water from entering the inside of the solution bottle.
The water temperature can be controlled between ambient temperature and 99.9℃ with an accuracy of ± 0.15℃, thus ensuring a constant temperature in the sample environment. During the measurement, the solution bottles must be completely covered by water, and the water bath is equipped with a lockable lid to reduce evaporation losses.

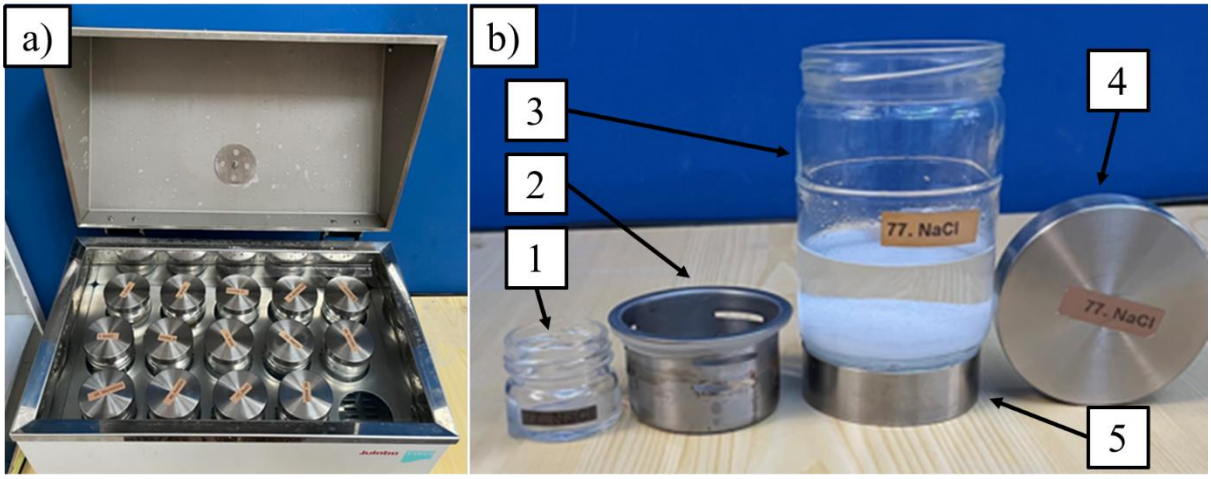

Fig. 1. a) Gravimetric sorption isotherm device
b) Solution bottle and its parts
(1-sample bottle, 2-holding basket, 3-solution bottle, 4- threaded cap, 5-steel disc weight)

During sorption measurements, it is essential to repeatedly determine the moisture content of the sample. To this end, the drying process was carried out in a Memmert VO400 type vacuum drying cabinet, which allows for precise adjustment of temperature and vacuum pressure. In order to remove the entire water content of the sample, the material must be dried in a vacuum dryer for at least 24 hours at 70 ± 2℃ and a vacuum pressure of $10\ mbar$. The moisture content was determined by knowing the dry mass after drying and the wet mass before drying. For mass measurements, a Sartorius LA1200 S type analytical balance was used, which has a weighing range of $1200\ g$ and an accuracy of $0.001\ g$.

2.3 Measuring method

Before starting adsorption measurements, sample preparation is essential: in case of adsorption measurement, the sample must be completely dried, while for desorption measurements, preliminary moistening is required to achieve the appropriate moisture content. Drying was carried out in a vacuum dryer, while moistening was achieved by adding water.
After that, the properly prepared zeolite samples were placed into the sample bottles. The weight of the sample bottle with the cap had to be measured both empty and filled with the sample, thus determining the actual sample weight. The lower one-third part of the solution bottles was filled with distilled water, to which enough salt/compound was added to make the solution saturated. The solution was considered saturated when no more crystals dissolved at the given temperature. The sample bottles without the cap were placed in the holding basket, which was then inserted into the solution bottle. The hermetic closure of the solution bottles was ensured by a cap with a seal, and then the prepared solution bottles were placed in the water bath tub with filtered, softened water at a given temperature.

During the measurements, 14 solution bottles were used, in which identical solutions in pairs were used. This allowed the simultaneous, parallel determination of adsorption and desorption isotherms at a given equilibrium temperature. The compounds/salts used were the following: KOH (potassium hydroxide), $MgCl_2$ (magnesium chloride), K_2CO_3 (potassium carbonate), $Mg(NO_3)_2$ (magnesium nitrate), $NaNO_3$ (sodium nitrate), $NaCl$ (sodium chloride) and KNO_3 (potassium nitrate).
The mass measurements required for the determination of the sorption isotherms were made at 24-hour intervals. During the measurement process, after removing the solution bottles from the water bath, the threaded cap was removed. The mass measurement was carried out after closing the sample bottle with its own cap. After the mass measurement, the sample bottle had to be placed back into the solution bottle without the cap, then closed with a threaded cap and placed in the water bath. This process had to be repeated for each sample, making sure that the samples were exposed to the ambient air for as short a time as possible, thus minimizing unwanted changes in moisture content.
Mass measurements were performed on a given sample until the mass difference remained below 0.1% in three consecutive measurements, assuming that the sample had reached equilibrium. The final samples were then dried in a vacuum oven for 24 hours, and the equilibrium moisture content was calculated by determining the dry mass.

2.4 Evaluation method

Water activity, which is the equilibrium relative humidity above the saturated salt solution in the solution bottle, was calculated using the equation developed by Lewis Greenspan (Greenspan 1977).
To determine the equation of the sorption isotherm, a curve fitting was performed on the obtained measurement points using the MagicPlot Pro ('MagicPlot' 2025) program, which uses the least squares method. For the fitting, sorption isotherm model equations from the literature were used, which are listed in *Table 1*. During the fitting procedure, the program determined the values of the constants in the model equations, and then the best-fitting model was selected based on various statistical indicators: SST – total sum of squares, SSE – error sum of squares, SSR – regression sum of squares, R^2 – coefficient of determination, $RMSE$ – root mean square error.
The isosteric sorption heat ($q_{st}, [J/kg]$) was determined using the Clausius-Clapeyron equation, which takes into account the heat of vaporization of water ($\Delta h_{H_2O}, [J/kg]$) and the net isosteric sorption heat ($q_{st,n}, [J/kg]$) (Tsami 1991):

$$q_{st} = \Delta h_{H_2O} + q_{st,n}\,. \tag{1}$$

The net isosteric heat can be calculated from the differential form using the following equation (Tsami 1991):

$$q_{st,n} = R_{H_2O}\frac{T_l T_h}{T_h - T_l}\ln\frac{a_{wh}}{a_{wl}}\,, \tag{2}$$

where R_{H_2O} is the specific gas constant of water vapor $\left[R_{H_2O} = 0.4615\ kJ/kgK\right]$, T_l is the lower and T_h is the higher equilibrium temperature $[K]$, a_{wl} is the lower and a_{wh} is the water activity obtained at the higher temperatures [1]. The latent heat of water was calculated using the equation reported by (Perry and Chilton 1973).

3. Results and discussion

The adsorption and desorption measurements were performed at different temperatures. The measurement results are given in *Table 2*, which shows the equilibrium moisture content values for the following four equilibrium temperatures: $T = 30℃;\ 40℃;\ 50℃$ and $60℃$. The table

contains both the adsorption $(X_{eq,ad})$ and desorption $(X_{eq,de})$ values, as well as the water activity values induced by each solution.
Various sorption isotherm model equations were fitted to the obtained measurement results, which allowed the parameters in the given models to be determined. During the fitting process, the goodness of fit was evaluated based on statistical indicators, the results of which can be found in *Table 3*.
Based on the tests, the determination coefficient value proved to be technically adequate for each measurement series ($R^2 > 0{,}85$). In some cases, the value $R^2 = 0{,}99$ was also achieved, indicating an excellent fit between the measurement points and the model. However, the results showed that the values of the individual determination coefficients are relatively close to each other, therefore this indicator alone is not sufficient to decide on the application of a given model. Additional statistical indicators are also needed to select the appropriate model equation.

Table 2. Equilibrium moisture contents and water activities measured at different equilibrium temperatures

$30°C$			$40°C$			$50°C$			$60°C$		
a_w [1]	$X_{eq,ad}$ $[g_{H2O}/kg_{dP}]$	$X_{eq,de}$	a_w [1]	$X_{eq,ad}$ $[g_{H2O}/kg_{dP}]$	$X_{eq,de}$	a_w [1]	$X_{eq,ad}$ $[g_{H2O}/kg_{dP}]$	$X_{eq,de}$	a_w [1]	$X_{eq,ad}$ $[g_{H2O}/kg_{dP}]$	$X_{eq,de}$
0.074	4.9	5.6	0.063	4.2	4.5	0.057	3.2	3.7	0.055	2.5	2.6
0.324	13.5	14.1	0.316	12.4	13.2	0.305	11.1	11.9	0.293	10.4	10.6
0.432	18.4	19.3	0.432	16.6	16.7	0.432	13.9	14.6	0.425	12.2	13.7
0.514	20.9	22.0	0.484	17.4	17.9	0.454	16.6	16.8	0.432	13.1	14.5
0.731	26.8	27.5	0.710	25.2	26.5	0.690	22.3	25.0	0.674	20.4	21.1
0.751	27.7	28.3	0.747	26.8	27.3	0.744	24.8	26.0	0.745	23.6	24.8
0.923	34.8	36.2	0.890	31.5	32.4	0.848	28.2	29.1	0.796	23.9	25.3

When examining the fit of sorption isotherm models, the values of the statistical indicators play a decisive role in selecting the appropriate model. The suitability of the fit was determined based on the SSE, SSR, R^2 and $RMSE$ values. The selection of the appropriate model is based on the fact that the values of these statistical indicators should be as small as possible, since their low values indicate a good match between the measurement points and the applied model equation. Based on the examined statistical indicators, it can be stated that the model providing the best fit among the examined sorption isotherm equations was the modified GAB equation at all temperatures. On the other hand, the least suitable fit was provided by the modified Halsey model in all cases.
Since the modified GAB model fitted the measured points best, the sorption isotherms of zeolite are shown in *Fig. 2* only for this model equation. The shape of the adsorption and desorption isotherms typically shows a sigmoidal (S-shaped) curve, which is especially characteristic of the moisture uptake and release processes of porous and surface-active materials, where multilayer sorption takes place. It can be seen that the curves become lower and lower with increasing temperature, which proves that the material is able to bind or desorb less and less moisture with increasing temperature.

Table 3. Statistical indicators of the fitted sorption isotherm model equations for adsorption and desorption

T	Models (modified)	Adsorption				Desorption			
		SSE	SSR	R^2	$RMSE$	SSE	SSR	R^2	$RMSE$
		[g/kg]	[g/kg]	[1]	[g/kg]	[g/kg]	[g/kg]	[1]	[g/kg]
$30°C$	Henderson	0.094	9.50	0.99	1.38	0.073	8.63	0.99	1.31
	Chung-Pfost	1.272	34.56	0.96	2.63	1.032	32.05	0.97	2.53
	Halsey	18.600	125.58	0.87	5.01	18.172	127.90	0.88	5.06
	Oswin	1.944	42.54	0.96	2.92	1.627	40.10	0.96	2.83
	GAB	0.005	2.16	0.99	0.66	0.013	3.59	0.99	0.85
$40°C$	Henderson	0.039	5.74	0.99	1.07	0.039	5.88	0.99	1.08
	Chung-Pfost	1.328	32.89	0.96	2.56	1.292	33.34	0.96	2.58
	Halsey	9.255	84.04	0.90	4.10	9.672	88.22	0.90	4.20
	Oswin	0.890	27.01	0.97	2.32	0.893	27.82	0.97	2.36
	GAB	0.003	1.62	0.99	0.57	0.005	2.05	0.99	0.64
$50°C$	Henderson	0.027	4.39	0.99	0.94	0.059	6.76	0.99	1.16
	Chung-Pfost	1.800	34.78	0.95	2.64	2.043	38.90	0.95	2.79
	Halsey	3.845	50.23	0.93	3.17	5.225	61.26	0.92	3.50
	Oswin	0.337	15.26	0.98	1.75	0.562	20.63	0.97	2.03
	GAB	0.010	2.66	0.99	0.73	0.020	3.99	0.99	0.89
$60°C$	Henderson	0.021	3.47	0.99	0.83	0.011	2.67	0.99	0.73
	Chung-Pfost	2.536	36.85	0.94	2.71	2.358	37.48	0.94	2.74
	Halsey	1.367	27.30	0.95	2.34	1.679	31.76	0.95	2.52
	Oswin	0.122	8.28	0.99	1.29	0.124	8.80	0.99	1.33
	GAB	0.014	2.83	0.99	0.75	0.003	1.45	0.99	0.54

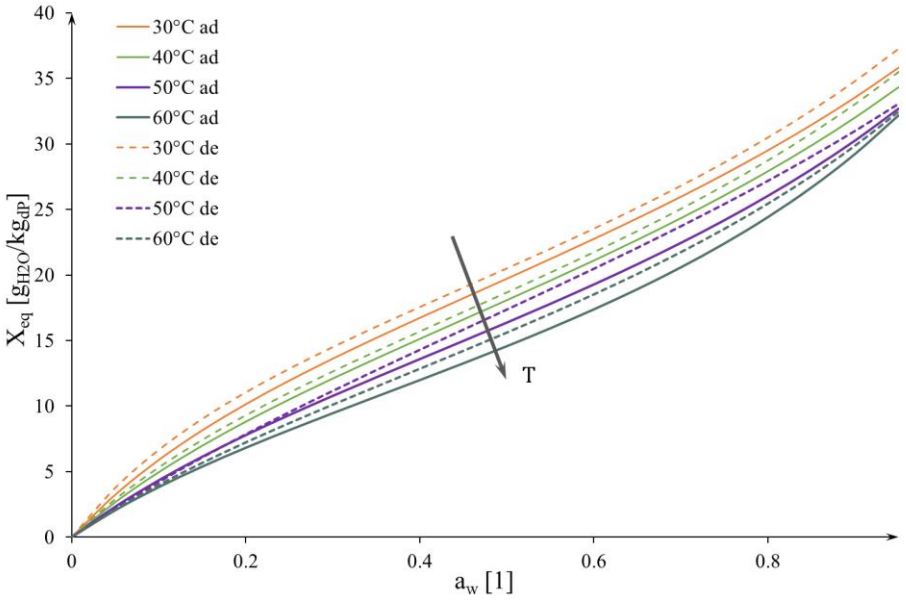

Fig. 2. Adsorption and desorption isotherms of zeolite at different temperatures based on the mod. GAB model

Based on the obtained data, hysteresis developed in the diagram between the adsorption and desorption isotherm pairs at the same temperature. The size of the hysteresis loop characterizes the degree of difference between the adsorption-desorption processes, which indirectly indicates the porous structure of the zeolite. The larger the area of the hysteresis loop, the greater the difference between the adsorption and desorption states. This indicates a pore structure where the exit of the liquid is hindered by constrictions in the pore network. So the water molecules are partially trapped within the structure of the material.
The numerical values of the parameters included in the equations of the modified GAB model are shown in *Table 4* for adsorption and desorption at the equilibrium temperatures examined.

Table 4. Parameter values of the modified GAB model equation for zeolite at different temperatures

T	Adsorption			Desorption		
[°C]	A	B	C	A	B	C
30	20.67	0.524	2026.271	19.67	0.553	2435.987
40	19.90	0.534	1715.238	19.52	0.551	1866.858
50	17.60	0.568	1625.372	23.87	0.470	1323.440
60	14.11	0.644	1638.698	16.72	0.589	1536.846

Fig. 3 shows the evolution of the isosteric heat in the case of adsorption and desorption for the tested measurement conditions ($T = 30 - 40°C$ and $X_{eq} = 2.5 - 34.8\ g/kg$). It can be seen from the diagram that the isosteric heat value is higher in the case of desorption than in the case of adsorption. This phenomenon is a consequence of the fact that during desorption more energy is needed to remove the moisture bound in the zeolite, i.e. to break the bonds of water molecules. The isosteric sorption heat is higher in the case of low moisture contents and gradually decreases with increasing moisture content and approaches the latent heat of water taken at average temperature. This can be explained by the fact that at low moisture content a large number of active binding sites are available, which are able to bind water molecules with high energy. As the moisture content increases, the binding sites gradually fill up, so fewer binding sites remain free, and the value of the isosteric sorption heat decreases as a result. The hysteresis loop is still visible at lower moisture contents but disappears at higher moisture contents.

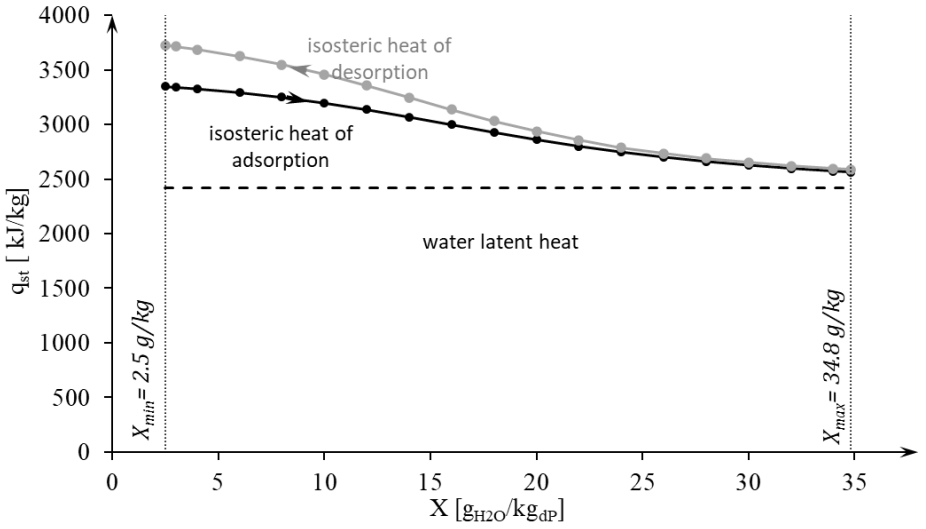

Fig. 3. The isosteric heat for LTA type zeolite is between 30°C and 40°C, depending on the moisture content of the material

4. Conclusions

During the research, adsorption and desorption isotherms were determined using the gravimetric method to characterize the water vapor sorption properties of LTA (4A) type zeolite particles at four different temperatures ($T = 30°C$; $40°C$; $50°C$ and 60℃). Different sorption model equations known in the literature were fitted to the measurement points. Based on the statistical indicators ($SSE, SSR, R^2, RMSE$), all examined models showed a good fit ($R^2 > 0.85$), however, the modified GAB model clearly proved to be the most suitable. Based on the fit, the values of the constants included in the model were determined for different temperatures. The isosteric sorption heat values calculated from the equilibrium moisture content values showed that the binding energies are significantly higher at lower moisture content and gradually decrease with increasing moisture content. This phenomenon can be explained by the change in the number of free surface sites available during sorption. According to the studied data, the isosteric heat during desorption is higher than during adsorption, which suggests that the removal of bound water molecules is an energetically more demanding process than their binding. Based on the results, the modified GAB model proved to be highly suitable for describing the adsorption and desorption processes of the studied LTA (4A) type zeolite particles, which may contribute to the optimal design of practical applications and sorption technologies, as well as to a more efficient estimation of the energy demand.

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