



EFFECT OF PARTICLE SIZE ON ADSORPTION OF WATER VAPOR ON POROUS ALUMINIUM OXIDE MATERIALS: EXPERIMENT AND KINETIC MODELING

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- Adsorbents based on aluminium oxide have been widely used namely owing to the high efficiency when dewatering gases with a relative humidity of up to 100 % and significant mechanical strength. Advantages of aluminium oxide, providing its wide application along with such adsorbents as zeolites and silica gels, are thermodynamic stability, relative ease of production, as well as availability of raw materials. Nowadays, effective adsorbents, based on low-temperature forms of aluminium oxide (η -, γ - and χ -), obtained by calcination of alkaline hydration products of thermally-activated aluminium hydroxide with a bayerite phase content of 50 % and more, are being actively studied .
- In this paper, an experimental study on adsorption kinetics of water vapors on a porous material – active aluminium oxide, which was a product of centrifugal thermal activation of hydrargillite, was performed. Mathematical modeling of the data obtained for adsorbent grains of various sizes was carried out; kinetic parameters were determined.



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To conduct the experiment, the following fractions of this sample were taken: 0.25-0.5 mm and 0.5-1.0 mm and a 3.7 x 6 mm granule. The experiments on the study of kinetics on the aluminium oxide sample of the mentioned fractions were carried out on a laboratory installation using Mac-Ben-Bakr quartz balance according to the procedure described in [1]. The balance sensitivity was $2.9 \cdot 10^{-3}$ g/mm.

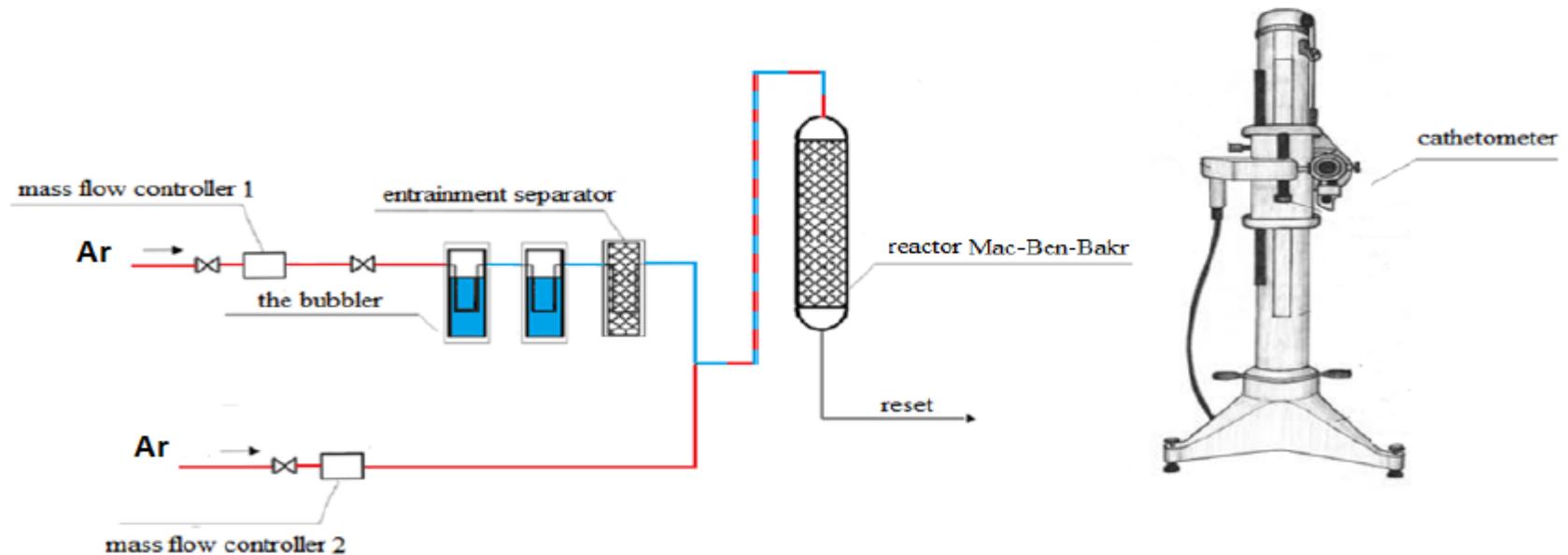


Figure 1. Scheme of a laboratory installation



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• Material characterization

The adsorbent sample was characterized by physicochemical research techniques. According to the XRD results, the porous material under study represented a mixture of low-temperature modifications of aluminium oxide - $(\gamma+\chi)\text{-Al}_2\text{O}_3$. Using the isotherms of low-temperature adsorption and desorption of nitrogen, the following parameters were determined: specific surface area, porosity and pore size distribution. Adsorption isotherms at relative pressures of 0.05-0.3 were described by the BET equation allowed calculating the specific surface size, which was $305\pm 30\text{ m}^2/\text{g}$. Data on pore size distribution of the investigated samples, shown in figure 2, are evidence of presence of fine mesopores in the adsorbent under study ($3\div 7\text{ nm}$) with a size of $\sim 4\text{ nm}$. Such pore distribution indicates that the adsorption process can be influenced by internal diffusion of water vapors in the porous material grain. Therefore, it is important to determine the influence of the grain size of adsorbent particles on adsorption dynamics (kinetics).

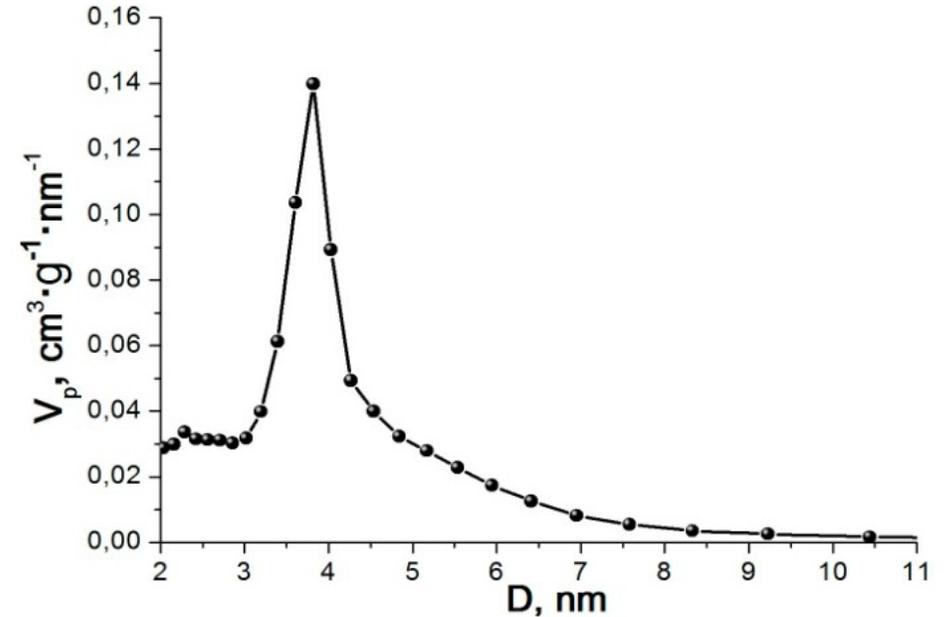


Figure 2. Pore size (D) distribution for the adsorbent (V_p -pore volume)



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- Effect of granules size on adsorption kinetics

The results of experimental studies (symbols) are shown in figure 3.

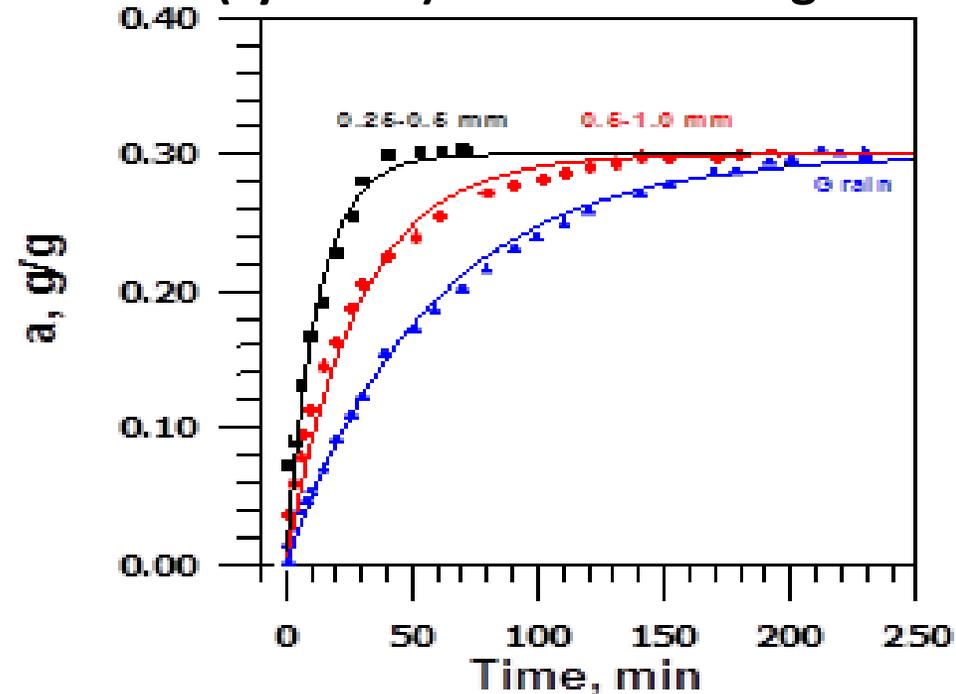


Figure 3. Kinetic curves of water vapor adsorption on a sample of aluminium oxide adsorbent of different fractions: 0.25-0.5 mm and 0.5-1.0 mm and a 3.7 x 6 mm granule. Symbols - experiment, lines, calculation by model (4).



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The graph shows the dynamics of the medium-integral in terms of granule volume (V) amount of water vapors (a) depending on their concentration in the gas phase inside the grain:

$$a(t) = \frac{\iiint C(r,t) dv}{V}$$

It was established that the time for achieving an equilibrium filling of adsorbent granules depended essentially on the grain size of the adsorbent. Thus, for a 3.7 x 6 mm granule, the time necessary for the equilibrium filling of adsorbent pores (a^* , g/g) makes ~250 minutes, and for a grain size of 0.25-0.5 mm - ~ 30 min. Further reduction of the granule size to a fraction of 0.125-0.25 mm does not influence the adsorption time [2].

The use of a mathematical modeling apparatus allows obtaining quantitative assessments of kinetic parameters, such as diffusion rate constants, adsorption equilibrium constant, an effective diffusion coefficient of the adsorbate inside the grain, and etc.



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A widely known quasi-homogeneous model, considering the adsorbent as a homogeneous absorbing medium, is used most commonly. The mathematical model includes the following equations:

- change in the concentration of the substance (CA) in the adsorbent grain:

$$\varepsilon_c \frac{\partial C_A}{\partial t} = D_e \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_A}{\partial r} \right) - R_A(C_A, \theta), \quad (1)$$

$$\frac{\partial \theta_A}{\partial t} = R_\theta(C_A, \theta). \quad (2)$$

Initial and boundary conditions: $t=0: C_A(0, r) = C_A^0, \theta_A=0. \quad (3)$

$$r=0: \frac{\partial C_A(t, r)}{\partial r} = 0, \quad r=R: C_A(t, r) = C_A^0.$$

In this case, C_A – molar fraction of the adsorbate; t - time, s; D_e – effective diffusion coefficient of the adsorbate in the adsorbent granule, m^2/s ; ε_c – grain porosity; r - grain radius coordinate, m; R – the adsorption rate, s^{-1} ; θ_A – concentration of sites on the adsorbent surface occupied by the adsorbate.



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Mathematical model (1) - (3), representing partial differential equations, describes the process of substance adsorption, taking into account the effect of its diffusion in the grain in the spherical approximation of its geometric shape. Having solved model (1) - (3) numerically, the kinetic constant of adsorption rate and the diffusion coefficient can be obtained from the description of the experimental data. In the framework of the obtained experimental data on adsorption dynamics as a result of mathematical modeling, it is possible to obtain an estimate of values of total (diffusion) constants, included in equation $R_{\theta}(C_A, \theta)$.

The adsorption-desorption process of water vapor on the surface of the aluminium oxide adsorbent can be represented by a scheme of Langmuir type.



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The scheme and kinetic functions are given in Table 1.

Table 1. Water adsorption model and kinetic functions.

Adsorption model	Kinetic functions
$A + [] \rightarrow [A]$	$W_1 = k_1 C_A (1 - \theta_A),$
$[A] \rightarrow A + []$	$W_2 = k_2 \theta_A,$
Normalisation:	$\theta + \theta_A = 1.$
$[] + [A] = N_a$	
$\theta_A = [A]/N_a$	



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Then the equation for the change of the adsorption sites concentration on the adsorbent surface, occupied by water vapor molecules, can be written in the following form:

$$\frac{\partial \theta_{H_2O}}{\partial t} = R_1 - R_2 = k_1 \cdot C_{H_2O} \cdot (1 - \theta_A) - k_2 \cdot \theta_{H_2O},$$
$$t = 0: \theta_{H_2O} = 0, C_{H_2O} = C^0. \quad (4)$$

In this case, k_1 , k_2 – constants of adsorption/desorption rate of water vapors; C^0 – molar concentration of water vapors in the gas flow. To conduct the experiment of water vapor adsorption, argon, infiltrated through two Drexel bottles filled with distilled water, was fed on the sample and the water vapor concentration corresponded to 100% moisture at 25 °C. The value of C^0 was determined by Antoine equation [3] and its value equaled 3.06%. Equation (4) was solved by the method of numerical integration - by Runge-Kutta method.



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Figure 4 shows the dependence of influence of adsorption constant k_1 on the concentration of centers on the adsorbent surface occupied by water molecules. As the rate constant increases, the value of adsorbed substance reaches quicker its value, equilibrium with the water vapor concentration surrounding the grain.

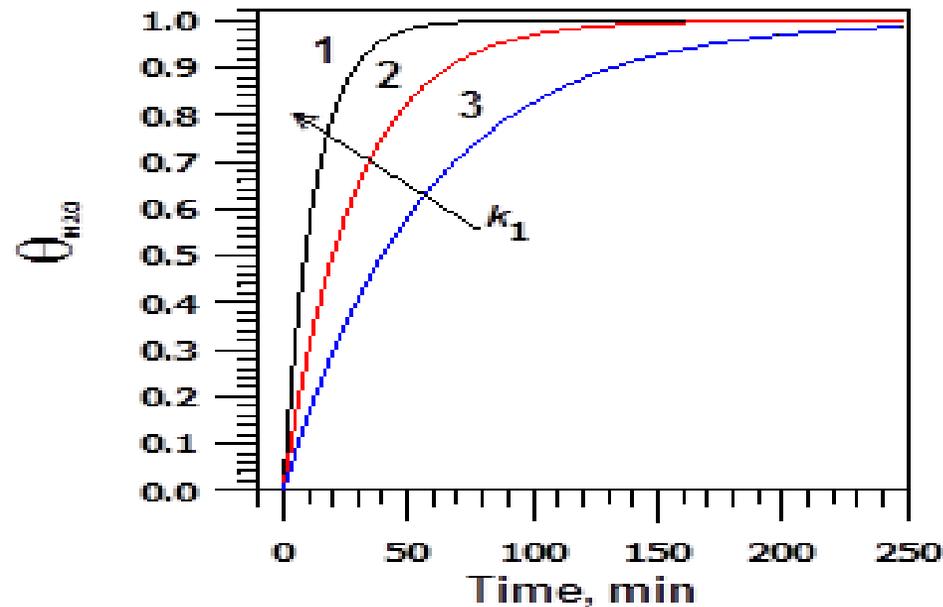


Figure 4. Influence of adsorption constant k_1 (1,2,3) on the concentration of centers on the adsorbent surface occupied by water molecules.



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Table 2. Value of kinetic parameters of model (4).

Adsorbent grain, mm	a^* , g/g _{ads}	k_1 , min ⁻¹
0.25-0.5	0.3	2.61
0.5-1.0	0.3	1.14
3.7 x 6	0.3	0.57

Values of the adsorption constant (table 2) were selected from the description of the experimental data presented in figure 2, where $a=a^*\cdot\theta$. Model (4) describes quite well the experimental data on the adsorption kinetics of water vapor on the aluminium oxide adsorbent.



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Conclusion

- It was shown that when the fraction size was greater than 0.5-1.0 mm, the water vapor adsorption rate on this adsorbent decreased, which was connected with the influence of internal diffusion. That happened due to the presence of fine mesopores (3÷7 nm), which was evidenced by the data obtained by the BET method.
- Mathematical treatment of the obtained data was carried out. The basis was the kinetic equation of adsorption, proceeding by the first order relatively the water vapor concentration. The model fits well with the experimental data on the adsorption kinetics of water vapors on the aluminium oxide adsorbent. The kinetic parameters included in the equation were determined. These parameters are necessary for predicting the adsorption-desorption time for grains of various sizes.

Acknowledgments

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