

Effect of particle size on adsorption kinetics of water vapor on porous aluminium oxide material

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Abstract. Influence of the grain size of aluminium oxide material, being a product of centrifugal thermal activation of hydrargillite, on adsorption kinetics of water vapors was studied. The material was characterized by the BET method and X-ray phase analysis (XRD). Influence of gas flow rate on adsorption dynamics was studied on a laboratory installation using McBain-Bakr quartz balance. It was shown that with the fraction size greater than 0.5-1.0 mm, the rate of water vapor adsorption on this adsorbent decreased, which was connected with the influence of internal diffusion resistance. On the base of the first-order kinetic equation for the water adsorption mathematical modeling was carried out. The kinetic parameters of the equation for the various grain size samples (0.25-0.5 mm and 0.5-1.0 mm and 3.7 x 6 mm granule) were determined.

1. Introduction

Porous materials based on aluminium oxide are widely used as catalysts for alcohol dehydration, in Claus process, in cracking and hydrocracking processes of petroleum products [1-4], as well as adsorbents for purification of industrial emissions [5, 6]. In particular, adsorbents based on aluminium oxide are used to extract water vapors when drying natural and associated petroleum gases [7, 8]. Gas transportation makes special demands on its degree of dewatering and cleaning. Since the presence of moisture at low temperature leads to formation of hydrocarbon hydrates, which, accumulating in a gas pipeline, can cause its partial or complete blockage, thereby disrupt normal operation of the pipeline. In this regard, the search for new more effective adsorbents is still relevant. 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 [9, 10]. High activity of porous materials based on aluminium oxide when interacting with polar adsorbates (primarily water vapors) ensures deep gas drying. 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 [11].

Adsorption dehydration of hydrocarbon gases is usually carried out in stationary granular layers of the adsorbent. The main parameters of the equilibrium process are commonly thought to be the maximum adsorption capacity of the sorbent, which serves as a basis for determining its necessary



volume for charging in the adsorber. The adsorption equilibrium of water vapor has been studied widely on different materials, such as activated carbon [12], cellulose fiber based materials [13], silica gel [14, 15], hypercrosslinked polymeric adsorbents [16], zeolite and activated alumina [17, 18]. It is commonly accepted that the adsorption of water vapor begins at specific active sites due to formation of hydrogen bonds between water molecules and the functional groups, and then water clusters develop with increasing relative pressure, followed by micropore filling [19]. Along with the equilibrium characteristics of the adsorbent, an important role belongs to adsorption kinetics, which considers the issues of dynamics of adsorbate's adsorption and diffusion in individual adsorbent's granules as well as the rate of filling the capacity of these granules. Since the adsorbent granules used in industrial conditions have as a rule a shape of cylinders and spheres of various sizes, an investigation on the influence of the grain size on the adsorption kinetics is important. Few works reported experimental results on the adsorption kinetics of water vapor on activated alumina [20, 21].

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.

2. Experimental part

A porous material, which was a product of centrifugal thermal activation of hydrargillite, was chosen as an object of research. The conditions for producing this material are given in [11, 22]. 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 McBain-Bakr quartz balance according to the procedure described in [22]. The balance sensitivity was $2.9 \cdot 10^{-3}$ g/mm. The optimal amount of adsorbent ($0.02 \div 0.03$ g) was selected, which allows placing an adsorbent fraction of $0.5 \div 1.0$ mm in size in a one-layer cup from aluminum foil. Before carrying out adsorption tests, each sample was trained (regenerated) at a temperature of 200 °C in argon current (Ar of special purity with an impurity content of no more than 10 ppm) fed at a rate of 5 l/h during an hour. To carry out the process of water vapor adsorption with 100 % moisture, argon, infiltrated through two Drexel bottles filled with distilled water, was supplied to the sample. The gas flow rate was 30 l/h.

X-ray phase analysis (XRD) was performed on a Rigaku Miniflex 600 diffractometer with the following shooting parameters: the measurement range was $2\theta=10-90$ with Cu K α radiation; voltage was 40 kV; current was 15 mA; shooting rate was 2 deg./min. Diffraction pattern deciphering was carried out using the ICDD database, version PDF2.

The contents of impurities – alkali metal cations in the samples – were determined by the method of mass spectrometry with inductively coupled plasma (ICP-MS) using device Agilent 7500cx. The textural characteristics were determined by nitrogen adsorption isotherms at 77 K. The mesopore volume was calculated by analyzing the integral curve of pore volume distribution depending on their radius (along the adsorption branch) [23].

3. Results and discussion

3.1. 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 - $(\gamma+\chi)\text{-Al}_2\text{O}_3$. The content of impurities of alkali metal cations of sodium and potassium in the sample was insignificant - hundredths of a percent.

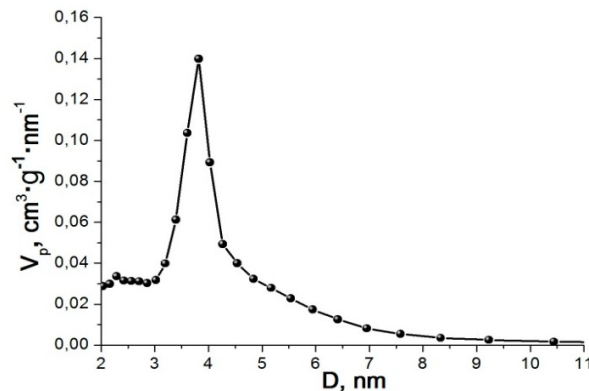


Figure 1. Pore size (D) distribution for the adsorbent (V_p -pore volume).

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 $\sim 305 \pm 30 \text{ m}^2/\text{g}$. Data on pore size distribution of the investigated samples, shown in figure 1, 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).

3.2. Effect of flow rate

To exclude the influence of the carrier's gas supply rate on water vapor adsorption on the outer surface of granules, series of experiments were carried out preliminary at different flow rates in the wide range of 3.6-36 l/h. The results are shown in figure 2.

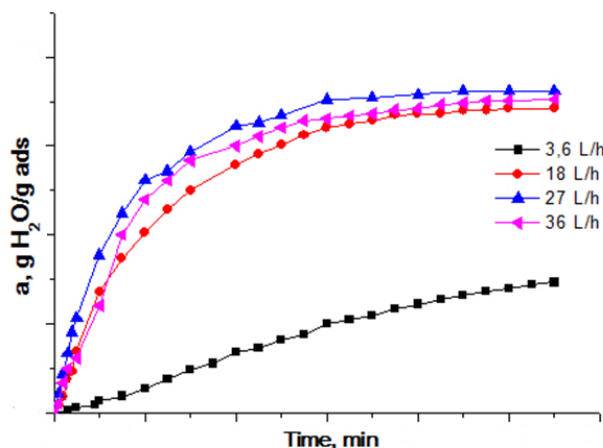


Figure 2. Influence of gas flow rate on adsorption dynamics.

At the carrier's gas flow rate of 36 l/h, rather slow velocity of increase of the sample weight was observed, which is due to the influence of external diffusion on the water vapor adsorption process. It was established that at the carrier's gas velocity over 27 l/h, the adsorption kinetics of water vapors

does not depend on the carrier's gas feed rate. Later on, all the experiments were carried out at the carrier's gas velocity of 30 l/h.

3.3. Effect of granules size on adsorption kinetics

Along with the equilibrium characteristics of the adsorbents (adsorbent capacities), an important role belongs to adsorption kinetics, which considers the matters of dynamics of water vapor adsorption and diffusion in individual adsorbent granules and the filling rate of the capacity of these granules. As a rule, adsorbent granules that are used in industrial conditions are shaped as cylinders and spheres of various sizes. To study the influence of the granule size on the dynamics of water vapor adsorption, the following fractions of the investigated aluminium oxide sample were taken: 0.25-0.5 mm and 0.5-1.0 mm and a 3.7 x 6 mm granule. The results of experimental studies (symbols) are shown in figure 3. 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:

$$a(t) \approx \frac{\iiint_V C(r,t) dv}{V}.$$

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 [24].

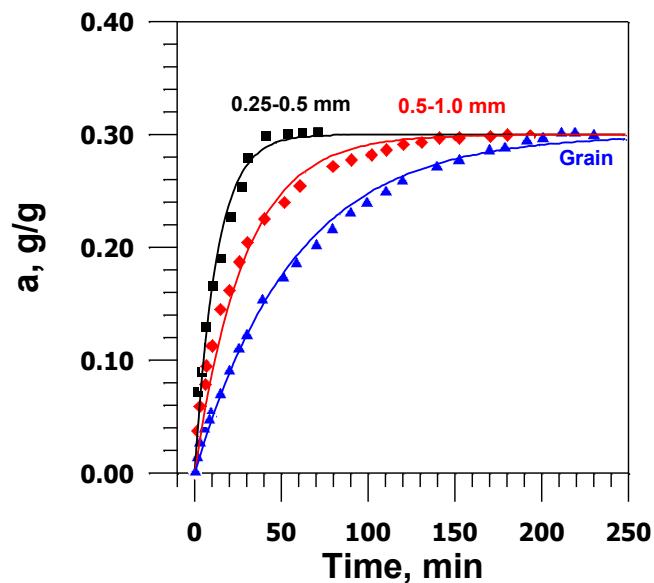


Figure 3. Kinetic curves of water vapor adsorption on a sample of aluminium oxide adsorbent of different fractions: 0.25-0.5 mm and 0.5-1.0 mm and a 3.7 x 6 mm granule. Symbols - experiment, lines, calculation by the model (4).

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. 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 (C_A) in the adsorbent grain:

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

- change in the concentration of adsorption sites on the adsorbent surface occupied by adsorbate molecules:

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

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.

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. These parameters are necessary for predicting the adsorption-desorption time for grains of various sizes. 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. 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:	$\theta + \theta_A = 1.$
$[] + [A] = N_a$	
$\theta_A = [A]/N_a$	

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:

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

$$t = 0: \theta_{H_2O} = 0, C_{H_2O} = C^0.$$

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 [25] and its value equalled 3.06%.

Equation (4) was solved by the method of numerical integration - by Runge-Kutta method. 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.

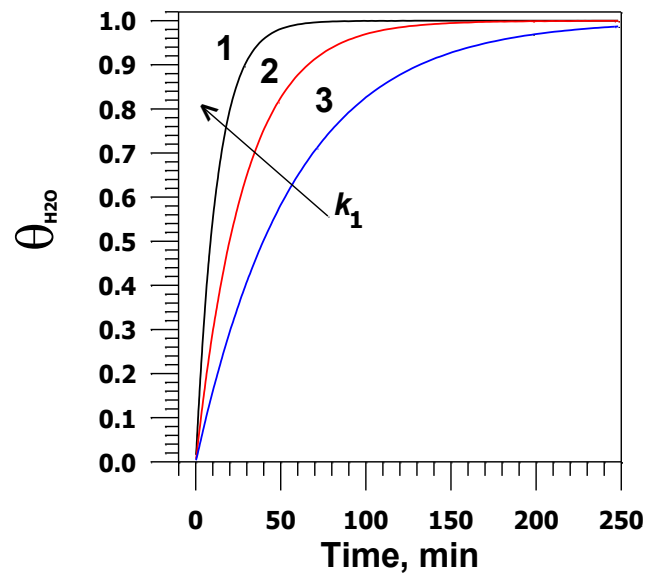


Figure 4. Influence of adsorption constant k_1 (1, 2, 3) on the concentration of centers on the adsorbent surface occupied by water molecules.

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.

4. Conclusion

An experimental study of the adsorption kinetics of water vapors on a porous material – active aluminium oxide, which was a product of centrifugal thermal activation of hydrargillite, was carried out. According to the data obtained by the mass spectrometry method with inductively coupled plasma, the content of impurities of alkali metal cations of sodium and potassium in the sample was insignificant - hundredths of a percent. According to the XRD results, the porous material under study was a mixture of low-temperature modifications of aluminium oxide - $(\gamma+\chi)$ -Al₂O₃. The influence of the adsorbent granule size on the adsorption dynamics of water vapors on fractions of 0.25-0.5 mm, 0.5-1.0 mm and 3.7 x 6 mm granule was investigated. The experiments were carried out on the adsorption plant using McBain-Bakr quartz balance. 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.

Acknowledgments

The study was financially supported by project RFMEFI57517X0139 of the Ministry of Education and Science.

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