

Kinetics of albumin adsorption by natural zeolite

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Abstract - The kinetics of albumin adsorption on natural zeolite of clinoptilolite structure have been investigated. The basic characteristics of zeolite have been determined. The method of albumin in a solution analysis was given. An isotherm of albumin adsorption was plotted and the Langmuir equation describing this isotherm was given. The presence of an external and pore diffusion adsorption mechanism has been experimentally established during the study of kinetics in a machine with mechanical stirring. The mass-transfer coefficient for.

Keywords – adsorption, zeolite, albumin, adsorption isotherm, kinetics, kinetic coefficient.

Introduction (use Times New Roman, 12, bold, center)

Adsorption processes are widely used in chemical, food, pharmaceutical and especially in environmental technologies. These processes are among the most effective methods of water purification from contaminants. An important advantage of these methods is the possibility of sorbents regeneration and their reuse [1]. Solid sorbents are applicable for various processes that differ by certain regularities. Such processes include physical adsorption, chemisorption, ion exchange, chromatography, *etc.* Various synthetic and natural solid sorbents are used for the adsorption processes. The choice of sorbent is determined by its sorption ability, selectivity, and cost. Recently, natural aluminosilicates – zeolites are widely used [2].

The industrial application of sorbents requires the study of their properties, namely sorption ability, kinetic and dynamic regularities, the possibility of regeneration or the zeolites use with adsorbed component.

The structure of natural zeolite is investigated by different physical and chemical methods (electron microscopic, X-ray, IR-spectroscopy), by means of which physical characteristics, porosity, specific surface, pore sizes and other properties are determined [3, 4]. The most of the investigations is devoted to the sorption of inorganic substances, mainly metals [5-8]. The researchers show that there is an ion exchange between metal cations and alkaline/alkaline earth metals. The adsorption of phosphates was investigated and satisfactory adsorption of the anionic phosphate group P_2O_5 was found, which is adsorbed only by physical adsorption and chemisorption [9].

Natural zeolites are capable of absorbing the substances of organic origin [10, 11].

Page Setup

For investigation of the zeolite surface morphology and X-ray spectral analysis the scanning electron microscope Nova 200 NanoSEM was used. The chemical and oxide composition of the material was determined by X-ray spectrometer ARL 9800 XP. Spectrometric studies were performed using the spectrophotometer SPECORD-75 IR. The material porosity was determined using the Autopore 9500 IV (mercury porometer) in the range of mercury pressure 0.036–413 MPa, which allows to determine the pore radius within 0.0015–47 μm . Before the test, the zeolite was dried in a drying oven at 373 K and degassed in vacuo under a

residual pressure of 6.67 Pa at 293 K. The Washburn equation was used to determine the pore radius.

The zeolite adsorption capacity was investigated using a natural zeolite of the clinoptilolite structure, and its characteristics were determined. X-ray spectral analysis of the chemical composition of zeolite is presented in Fig. 1.

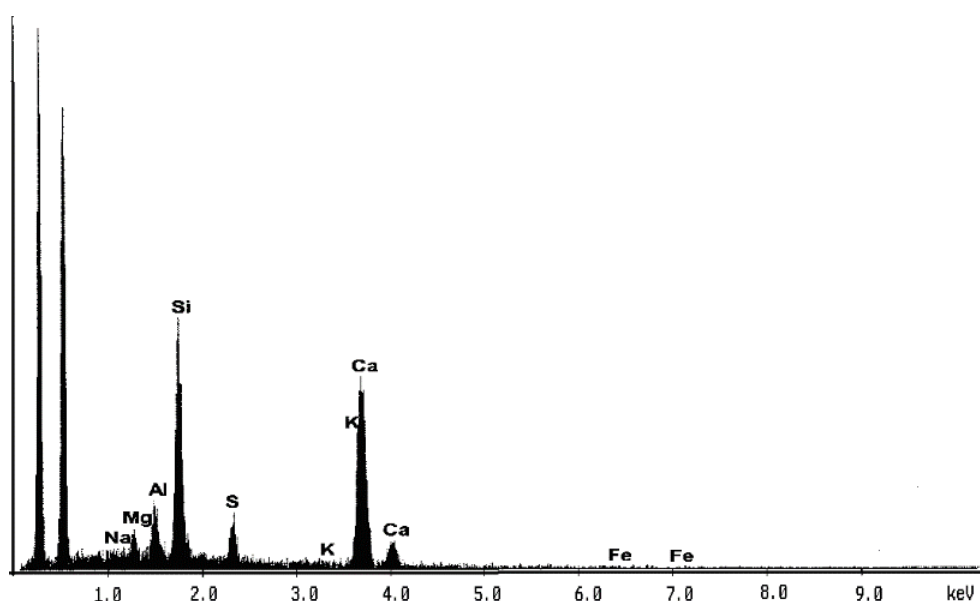


Fig. 1. X-ray spectrum of the zeolite

From the crystallochemical point of view the zeolite is a silicon- and aluminum-containing spatial structure with a certain porosity which is characterized by corresponding size. Since the clinoptilolite lattice has a negative charge, the hydrated Na^+ , K^+ , Ca^{2+} , and Mg^{2+} ions in the pores can participate in ion exchange processes, that is very important for adsorption processes. In this case, these hydrated ions occupy certain positions in the structure which creates micropores of corresponding size and spatial orientation, namely: I – Na- and Ca-ions localized in 10-fold ring by size of 0.44×0.72 nm; II – Na- and Ca-ions in 8-fold structural ring by size of 0.41×0.47 nm; III – K-ions in 8-fold vertical structural ring by size of 0.40×0.55 nm; IV – Mg-ions in 10-fold structural ring which are located in the center of the channel.

Parameters of the studied samples, obtained by the method of mercury porometry are presented in Table 1.

Table 1

Adsorbent characteristics

Zeolite	Total area of pores, m^2/g	Average radius of pores, μm	Density, g/cm^3	Porosity, %
Clinoptilolite	14.077	0.027	1.534	28.2

To investigate the kinetics of the albumin sorption process under mechanical stirring, the experiment was carried out in a vessel 3 with a blade-type stirrer 4 with a speed of 200–500 rpm.

Experimental data on the kinetics of albumin adsorption on natural zeolite during mechanical stirring are shown in Fig. 2. The sharp change in the nature of the curves indicates two mechanisms of adsorption: external diffusion and pore diffusion. Exit to the plateau at $\tau > 200$ s and a sharp change in the sorption rate indicate the transition of the adsorption process from the external diffusion region to the pore diffusion one.

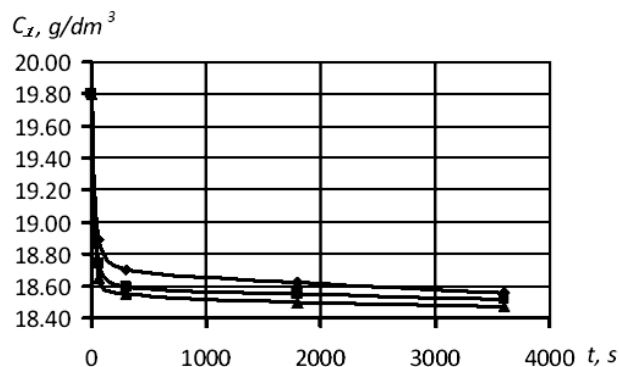


Fig. 2. Change in the albumin concentration during the study of the kinetics of its sorption by natural zeolite in the apparatus with mechanical stirring for different numbers of revolutions (rpm): 500 (♦); 300 (■) and 200 (▲)

The process in its pure form takes place only at initial intervals of time, when albumin concentration is equal to 0 on the adsorbent surface, and to the initial concentration – in solution. For these conditions, we determine the coefficient of mass transfer according to Eq. (1) [1]:

$$b = \frac{\Delta M}{\sum F(C_0 - C_n)\Delta t} \quad (1)$$

where C_0 – albumin concentration in solution, kg/m^3 ; C_n – albumin concentration on the zeolite surface, kg/m^3 ; $\sum F$ – total area of the external surface of zeolite particles, m^2 ; Δt – time, s.

The mass of the absorbed albumin was determined according to the equation of the material balance:

$$\Delta M = V \cdot (C_0 - C_1) \quad (2)$$

where V – volume of solution, m^3 ; C_1 – current concentration of albumin in solution, kg/m^3 .

The total external surface of the particles was determined by their average diameter and the number of particles N :

$$\sum F = N \cdot \pi \cdot d^2 \quad (3)$$

For the given granulometric composition, the average diameter of the zeolite particles is $d = 1.8 \cdot 10^{-3}$ m.

The defined mass transfer coefficient β have the following values, depending on the number of revolutions of the stirrer n :

Table 2

The number of revolutions of the stirrer n			
n , rpm	200	300	500
b , m/s	$9.26 \cdot 10^{-5}$	$9.24 \cdot 10^{-4}$	$9.25 \cdot 10^{-4}$

Thus, the stirring significantly influences the mass transfer coefficient, increasing it by an order of magnitude. At $n = 300$ rpm and higher values the mass transfer coefficient is maximum, which indicates the transition to the pore diffusion region.

Pore diffusion kinetics investigates the processes of mass transfer in pores and channels of the zeolite grains. The transport of components is due to molecular diffusion, because there is no effect of the hydrodynamic parameters inside the particles. Mathematically, the problem of pore diffusion is described by the differential equation of molecular diffusion with initial and boundary conditions [1, 9]. The analytical solution of this equation allows us to determine the change in albumin concentrations within the zeolite grains. The equation of material balance of

the system allows to establish a connection between the concentration in solution C and the volume average concentration in grain \bar{C}_A .

Having determined \bar{C}_A , the analytical equation will be written in a form that allows the use of experimentally determined data (Fig. 4).

$$\frac{C_n - C}{C_n - C_p} = 1 - \sum_{n=1}^{\infty} \frac{6}{p^2 n^2} \exp\left(-p^2 n^2 \frac{D^* t}{R^2}\right) \quad (4)$$

where R – the radius of zeolite grain; D^* – pore diffusion coefficient; C_p – equilibrium concentration.

Introducing Eq. (7) in the logarithmic form for the first term of the sum, this dependence in the coordinate system $\ln\left(1 - \frac{C_n - C}{C_n - C_p}\right) = f(t)$ gives a straight line, the slope angle of which determines the effective coefficient of pore diffusion D^* . For different numbers of mechanical stirring $D^*_{200} = 3.95 \cdot 10^{-9} \text{ m}^2/\text{s}$, $D^*_{300} = 5.36 \cdot 10^{-9} \text{ m}^2/\text{s}$ and $D^*_{500} = 6.55 \cdot 10^{-9} \text{ m}^2/\text{s}$. So, the D^* value depends on the number of revolutions. For the substances, *e.g.* metals, the structure of which does not change under the influence of external factors, this dependence should not be observed.

Conclusion

Albumins under the influence of physical, chemical and biological factors undergo profound changes related to the imperfection of quaternary, tertiary and secondary structure, which leads to changes in the physical, chemical and biological properties of albumin. During the albumin denaturation there is a rupture of secondary bonds, which “cement” albumin molecule. In many cases, this leads to the change in spatial structure, the decrease in the molecular weight of the dissolved albumin and deterioration of its hydrophilic properties. The mechanical stirring is also accompanied by the decrease in the viscosity of the studied non-Newtonian solution. Thus, the increase in the number of stirrer revolutions will increase the pore diffusion coefficient, and thus the intensification of albumin adsorption by natural zeolite.

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