

STATICS AND KINETICS OF ALBUMIN ADSORPTION
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Abstract. The statics and 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 external diffusion and the molecular diffusion constant for the pore diffusion are determined.

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

1. Introduction

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 have been widely used [2]. The basis of natural zeolites is aluminum and silicon oxides. Apart from the main components, in the zeolites structure there are metal oxides, alkaline and alkaline earth metals (Ca^{2+} , Mg^{2+} , Na^+ , K^+). Depending on the chemical composition and structure, various modifications of natural zeolites are distinguished, among which the most common are clinoptilolite, chabazite, heulandite.

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 an 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. These processes are important for purifying wastewater from heavy metals. However, natural zeolite has the ability to absorb anionic groups as well. 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].

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

The study of sorption processes on natural zeolites is associated with the determination of static parameters: the dependence of zeolite sorption capacity on the component concentration in a liquid, the establishment of an equation describing the isotherm of adsorption, determination of isotherm constants. The Langmuir equation, according to which the monomolecular adsorption or ion exchange occurs on the sorbent surface, describes most often the isotherm of adsorption. The Langmuir equation allows a linear interpretation of experimental data and the determination of the constants of the equation [1]. Among other models the Freundlich, Redlich-Peterson, Dubinin-Radushkevich isotherms and others are used [11]. When investigating the adsorption kinetics, a mathematical description based on the kinetic equations is used in the literature. This concept involves the absence of components transport to the external surface of the sorbent and the diffusion of this component inside the pores and channels of the sorbent [12]. There are no sufficient data in the literature regarding the mathematical modeling of adsorption dynamics in a fixed layer of adsorbent.

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The purpose of this work is to study the static and kinetic regularities of albumin adsorption, which is one of the protein compounds, by natural zeolite. This problem occurs during the treatment of milk processing factories wastewater. The main contaminants of wastewater are: lactic acid (α -oxipropionic acid), milk proteins (albumin), melissa, serum, fats, lactose, phosphorus compounds.

2. Experimental

The scanning electron microscope Nova 200 NanoSEM was used for investigation of the zeolite surface morphology and X-ray spectral analysis. 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.

To determine the albumen concentration in the test solution we used a photometric method based on the ability

of peptide bonds $\left[\begin{array}{c} \text{---C---N---} \\ || \quad | \\ \text{O} \quad \text{H} \end{array} \right]$ to form with copper

sulfate in alkaline medium the complex compounds of purple color, the intensity of which depends on the length of the polypeptide chain. Biuret reaction makes it possible to identify compounds having two or more peptide bonds.

Such compounds in the alkaline medium form a copper sulfate complex of pink-purple color. Peptide bonds in the enolium form are involved in the formation of this complex. In a strongly alkaline medium, the enol form of the polypeptide has a negative charge. Oxygen with copper forms a covalent bond. As a result of copper reaction with nitrogen the coordination bonds are formed. This reaction is provided by all proteins and peptides containing at least two peptide bonds.

To determine the albumin concentration we prepared a comparative solution (0.1 ml of water and 5 ml of biuret reagent). 0.1 ml of a standard solution containing 90 g/l of albumin was introduced in the control test-tube; all other tubes were filled by 0.1 ml of the appropriate test solutions. 5 ml of the reagent was added to each test solution. Samples were stirred and after 30 min they were analyzed using a photocolormeter KFK-2. A blue filter (440 nm) and 10 mm thick cuvettes were used. The appearance of a purple color (biuret reaction) indicates the presence of albumin or polypeptide in the solution. The color intensity varies depending on the albumin concentration in the solution according to the reaction (Fig. 1).

To determine the adsorption capacity of the zeolite relative to albumin, an albumin solution in a distilled water was placed in glass flasks with different initial concentrations. The concentration range corresponds to the albumin concentration in the real wastewater of food industry enterprises. 5 g of zeolite and 200 ml of albumin solution within the concentrations range of 1–17 g/dm^3 was added to five numbered conical flasks. The flasks were corked and left for 48 h. From time to time the flasks were thoroughly shaken in order the zeolite does not remain on the flask walls. After the adsorption, the solution pH was measured and the amount of absorbed albumin was calculated.

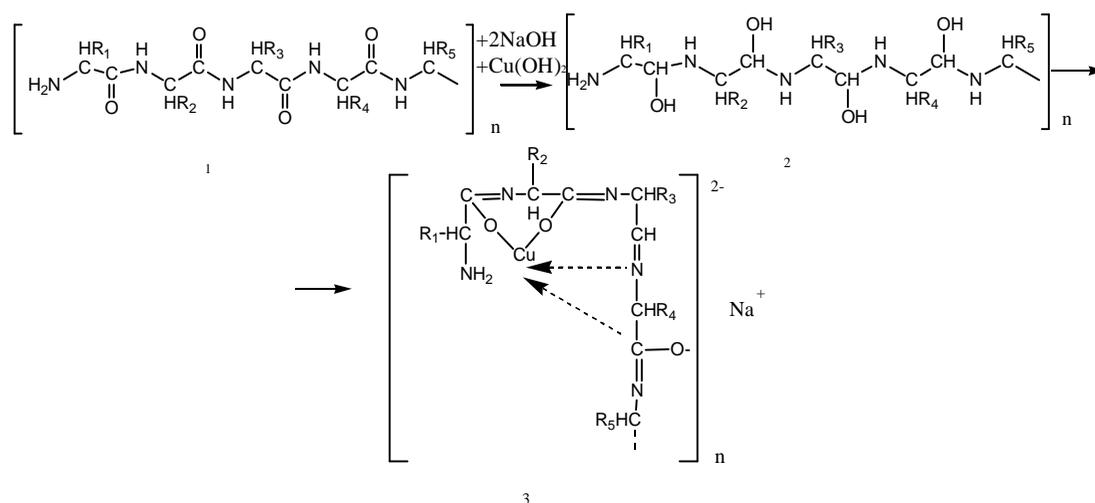


Fig. 1. Scheme of albumin determination by biuret method: polypeptide (1); enol form of polypeptide (2) and a biuret copper complex of violet color (3)

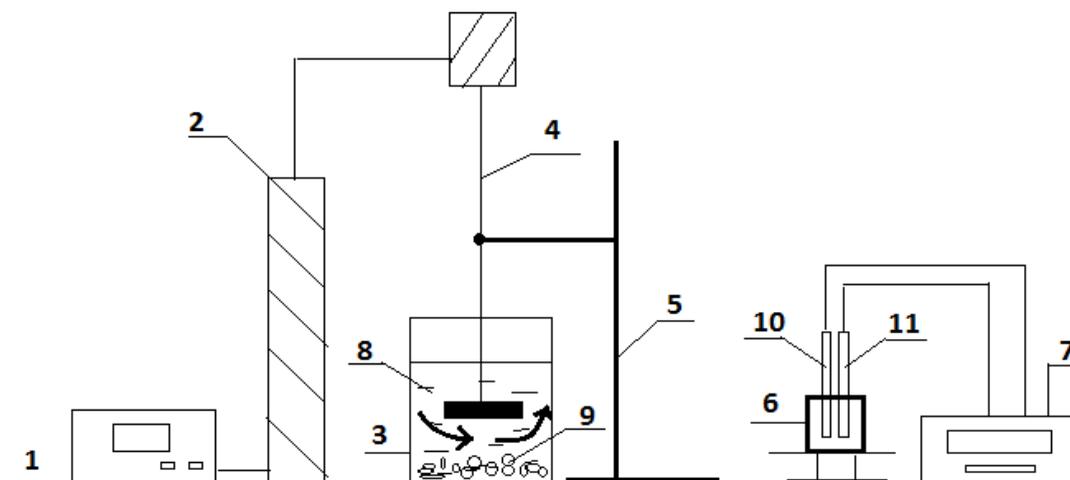


Fig. 2. Experimental setup for studying the kinetics of the adsorption process: digital controller (1); electric motor (2); vessel with albumin solution and zeolite (3); blade-type stirrer (4); support (5); vessel for selected samples (6); I160-M ionometer (7); albumin solution (8); zeolite (9); indicator electrodes (10, 11)

The static activity of the adsorbent a determines the equilibrium values of the component absorbed from the solution in the solid (adsorption) phase and the liquid medium:

$$a = f(c) \quad (1)$$

where a – adsorption activity in the solid phase, g substance/g adsorbent]; c – substance concentration in the liquid phase, g substance/dm³ solution.

The dependence (1) is defined by the properties of a solid adsorbent, and the properties of the absorbed substance as well. It is determined experimentally, and then its mathematical and physical substantiation is given. In this case, the type of dependence indicates the most probable character of the function (1), which corresponds to the Langmuir equation:

$$a^* = a_{\infty}^* \frac{b \cdot C}{1 + b \cdot C} \quad (2)$$

To determine the Langmuir equation constants, we present the experimental results as Eq. (3), which corresponds to a straight line in the coordinates

$$\frac{C}{a^*} = f(C):$$

$$\frac{C}{a^*} = \frac{1}{a_{\infty}^*} C + \frac{1}{a_{\infty}^* \cdot b} \quad (3)$$

To investigate the kinetics of the albumin sorption process under mechanical stirring (Fig. 2), the experiment was carried out in a vessel 3 with a blade-type stirrer 4 with a speed of 200–500 rpm. The number of revolutions was controlled by the device 1. Samples were withdrawn at certain intervals and analyzed for albumin content by ionometer 7 using electrodes 10, 11.

3. Results and Discussion

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. 3.

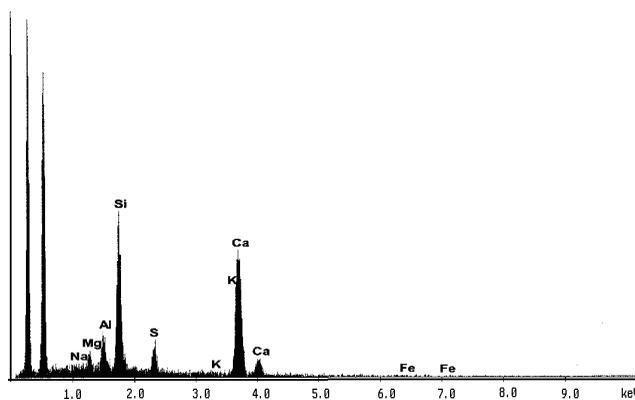


Fig. 3. X-ray spectrum of the zeolite

From the crystallochemical point of view the zeolite is a silicon- and aluminum-containing spatial structure with a certain porosity which is characterized by a corresponding size. Since the clinoptilolite lattice has a negative charge, the hydrated Na⁺, K⁺, Ca²⁺, and Mg²⁺ 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 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 porosimetry are presented in Table 1.

Static activity of the zeolite relative to albumin is represented in Fig. 4 and isotherm which was linearized according to Eq. (3) – in Fig. 5.

In accordance with the slope angle and the ordinate axis segment we determined the constants in the Langmuir equation. The isotherm of albumin adsorption on the zeolite can be described by Eq. (4):

$$a^* = 14.1 \cdot \frac{0.2 \cdot C}{1 + 0.2 \cdot C} \quad (4)$$

Experimental data on the kinetics of albumin adsorption on natural zeolite during mechanical stirring are shown in Fig. 6. 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.

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. (5) [1]:

$$b = \frac{\Delta M}{\sum F(C_0 - C_n)\Delta t} \quad (5)$$

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:

$$\Delta M = V \cdot (C_0 - C_1) \quad (6)$$

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

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

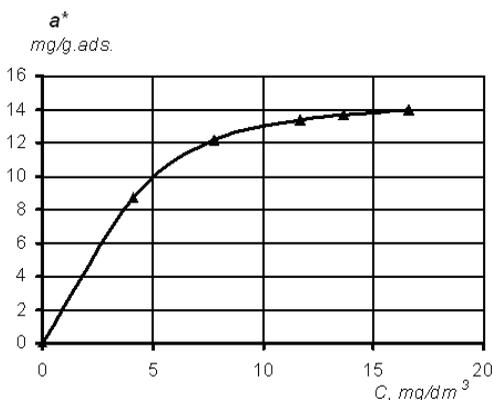


Fig. 4. Isotherm of albumin adsorption on the zeolite

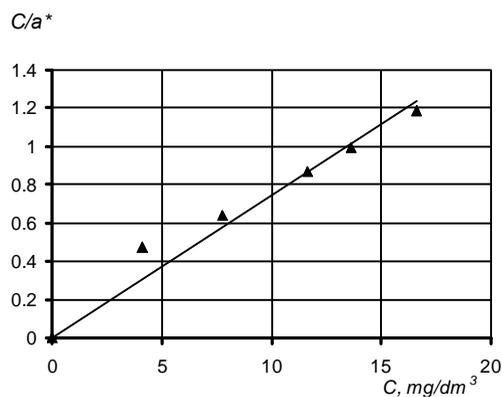


Fig. 5. Linear interpretation of isotherm of albumin adsorption on the zeolite

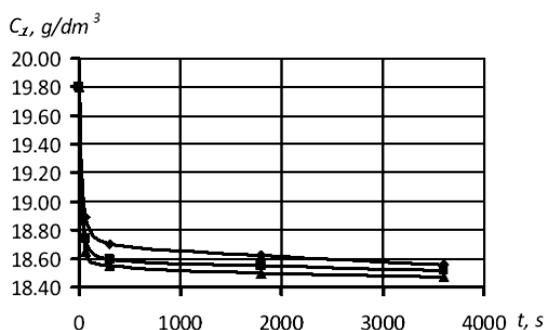


Fig. 6. Change in the albumin concentration during the study of the kinetics of its sorption by natural zeolite in the apparatus with mechanical stirring for different numbers of revolutions (rpm): 500 (◆); 300 (■) and 200 (▲)

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

$$\Sigma F = N \cdot p \cdot d^2 \quad (7)$$

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 has the following values, depending on the number of revolutions of the stirrer n :

n , rpm	β , m/s
200	$9.26 \cdot 10^{-5}$
300	$9.24 \cdot 10^{-4}$
500	$9.25 \cdot 10^{-4}$

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 a 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 the 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. 6).

$$\frac{C_n - C}{C_n - C_p} = 1 - \sum_{n=1}^{\infty} \frac{6}{p^2 n^2} \exp\left(-p^2 n^2 \frac{D^* t}{R^2}\right) \quad (8)$$

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 $D^*_{200} = 3.95 \cdot 10^{-9}$ m²/s, $D^*_{300} = 5.36 \cdot 10^{-9}$ m²/s and $D^*_{500} = 6.55 \cdot 10^{-9}$ m²/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.

Albumins under the influence of physical (temperature, ultrasound, ionizing radiation, stirring, etc.), chemical (mineral and organic acids, alkalis, organic solvents, heavy metals, alkaloids, etc.) 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 (hydrogen, disulphide, ether, van der Waals, etc.), 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.

4. Conclusions

We investigated albumin adsorption by natural zeolite and demonstrated the possibility of adsorption of organic substances of complex spatial forms. The determination methods of static and kinetic regularities are described. The static activity of natural zeolite was determined and described by the Langmuir isotherm.

The kinetics of albumin adsorption by natural zeolite was studied. We registered the presence of external and pore diffusion mechanism. The mass transfer coefficients for external diffusion and the coefficient of pore molecular diffusion were determined. We established the dependence of pore molecular diffusion coefficient of albumin on the stirring intensity, which is explained by the changes in the spatial structure of albumin.

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СТАТИКА ТА КІНЕТИКА АДСОРБЦІЇ АЛЬБУМІНУ ПРИРОДНИМ ЦЕОЛІТОМ

Анотація. Досліджено статичу та кінетику адсорбції альбуміну на природному цеоліті структури кліноптілоліту. Визначено основні характеристики цеоліту. Подано методику аналізу альбуміну у розчині. Графічно представлено ізотерму адсорбції альбуміну та наведено рівняння Ленгмюра, яке описує дану ізотерму. Експериментально встановлено наявність зовнішньодифузійного та внутрішньодифузійного механізму адсорбції під час дослідження кінетики в апараті з механічним перемішуванням. Визначено коефіцієнт масовіддачі для зовнішньої дифузії та коефіцієнт молекулярної дифузії для внутрішньодифузійної області.

Ключові слова: адсорбція, цеоліт, альбумін, ізотерма адсорбції, кінетика, кінетичні коефіцієнти.