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OBTAINING AND STUDYING PROPERTIES OF ORGANOSORBENT BASED ON MODIFIED KRANTAUSK BENTONITE CLAY WITH CHITOSAN

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Annotation:
The article investigates the modified Krantau clay (Na-CK) with chitosan and adsorption capacity of organobentonite based on. It was revealed that at low values of the equilibrium concentration there is a sharp increase in the amount of adsorption for the sample under study, the adsorption capacity for 2B reaches 100 mg / g and is 86% of its maximum amounts. A further increase in the concentration of the dye (reactive blue-2B) has almost no effect on the amount of 2B adsorption on ChS-Na-CK.

Keywords: Krantau bentonite, montmorillonite, chitosan, organobentonite, adsorption, Langmuir equation, specific surface area, monolayer capacity.

ПОЛУЧЕНИЕ И ИЗУЧЕНИЕ СВОЙСТВ ОРГАНОСОРБЕНТА НА ОСНОВЕ МОДИФИЦИРОВАННОГО КРАНТАУСКОЙ БЕНТОНИТОВОЙ ГЛИНЫ С ХИТОЗАНОМ

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Аннотация:
В статье указаны модификация бентонита Крантауского месторождения с хитозаном и исследованы адсорбционные способности органобентонита (Na-КР). Выявлено при низких значениях равновесной концентрации наблюдается резкое возрастание количества адсорбции для исследуемого образца, адсорбционная емкость по 2В достигает 100 мг/г и составляет 86% от его максимальных количеств. Дальнейшее увеличение концентрации красителя

(анионный активный -2В) почти не влияет на количество адсорбции 2В на ХЗ-Na-КР. .

Ключевые слова: бентониты Крантау, монтмориллонит, хитозан, органобентонит, адсорбция, уравнение Ленгмюра, удельная поверхность, емкость монослоя.

The rapid development of industries and the expansion of the scope of adsorption processes, obtaining effective relatively cheap adsorbents from local mineral bentonite clays is an urgent task that requires a timely solution. To obtain sorbents effective in various technological processes, it is necessary to study their structural characteristics and properties.

It is known that industrial enterprises pollute the air with various toxic gases, and wastewater with heavy metals, organic reagents, oil products, surfactants, dyes. The variety of pollutants and their nature requires polyfunctional and selective adsorbents with the ability to purify from frequently occurring polar and non-polar substances. Composite sorbents based on bentonite modified with organic molecules can have such characteristics. [1].

In the scientific and technical literature, methods for obtaining modified bentonites are widely covered [2]. However, despite this, the industrial production of organobentonites in our Republic for the purification of various media lags behind the production requirements [3-4]. The main reason for this is the lack of a scientifically based acceptable technology that ensures the production of organobentonites with high characteristics as adsorbents. Therefore, scientific experimental research in this direction is doubly relevant..

Research goal is the modification of Krantau bentonite with chitosan and the study of their physicochemical properties, as well as the sorption parameters of the organomineral in relation to the active dye in wastewater of the textile industry.

Clays from the lower horizon of the Krantau deposit (KP) of the Republic of Karakalpakstan, with a high content of montmorillonite, were chosen for research [5]. A reagent, chitosan Apis Mellifera (X3), was used as a clay modifier [6–7]. The synthesized organobentonite is conventionally named X3-Na-КР.

When modifying the minerals of the smectite group, which have an expanding structural cell, with relatively large organic cations, the introduction of organic molecules into almost the entire inner surface of the minerals is observed. As a result, the molecules of the medium, i.e. waters are adsorbed mainly on their outer surface [8]. However, as the results of the study show, adsorption of molecules of polar

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organic substances is possible not only on the outer, but also on the inner surface of bentonites with organic cations in the exchange complex [9]. From a scientific point of view, the replacement of inorganic exchangeable cations of clay minerals with organic ones should lead to a sharp change in their physicochemical and sorption characteristics. There is data confirming an increase in the adsorption capacity of modified montmorillonite with respect to petroleum products, aromatic and paraffinic hydrocarbons [10]. The increased interest in organo derivatives of clay minerals can be explained by the possibility of their use as selective sorbents.

Adsorption capacity in relation to the active dye produced in Turkey (reactive dye 2B) was measured by determining the optical density at a characteristic wavelength using a KFK-3M photoelectric calorimeter. Active anionic dye 2B, is a dark blue crystals with a luster.

In laboratory experiments to determine the adsorption capacity, solutions of 2B were prepared in water with a concentration of 1 to 200 mg/l, and the optical densities of these solutions were determined. To construct a calibration graph, data on the optical densities of solutions were used. In solutions with a volume of 100 ml, 0.1 g of adsorbents were added in the form of a powder. After the adsorption equilibrium was established (from 6 to 24 hours for individual samples), the optical densities of the solutions were measured and, using the data from the calibration curve, their concentrations mg/l were established. The amount of adsorbed dye was determined by the formula:

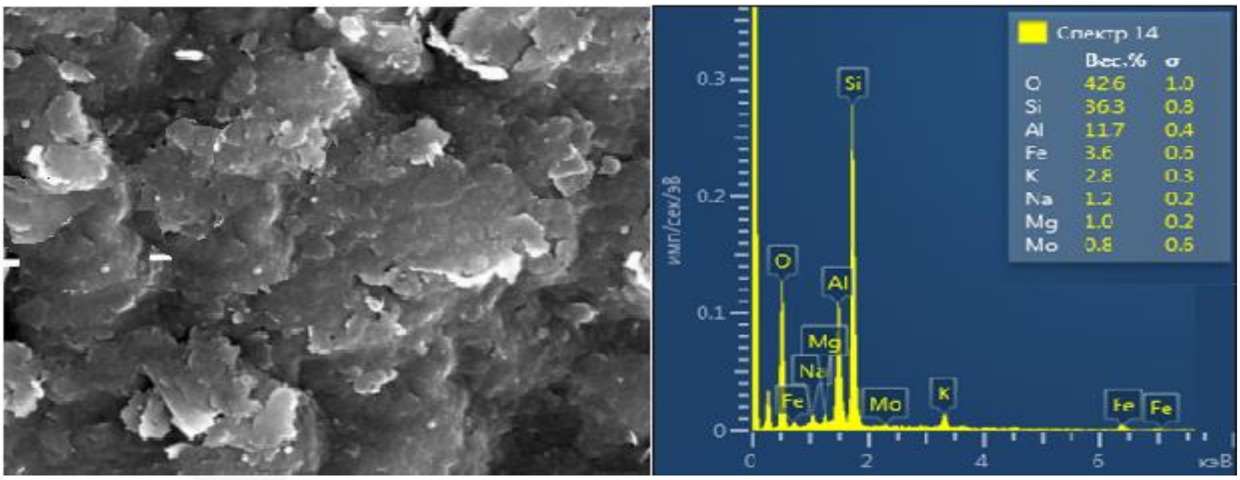
$$A = \frac{(C_0 - C_1) * V}{m}, \qquad (1)$$

where, A – amount of adsorbed dye mg/g; C_0 and C_1 – initial and equilibrium concentration of dye in solution, mg/l; V – solution volume, l; m – mass of adsorbent, g.

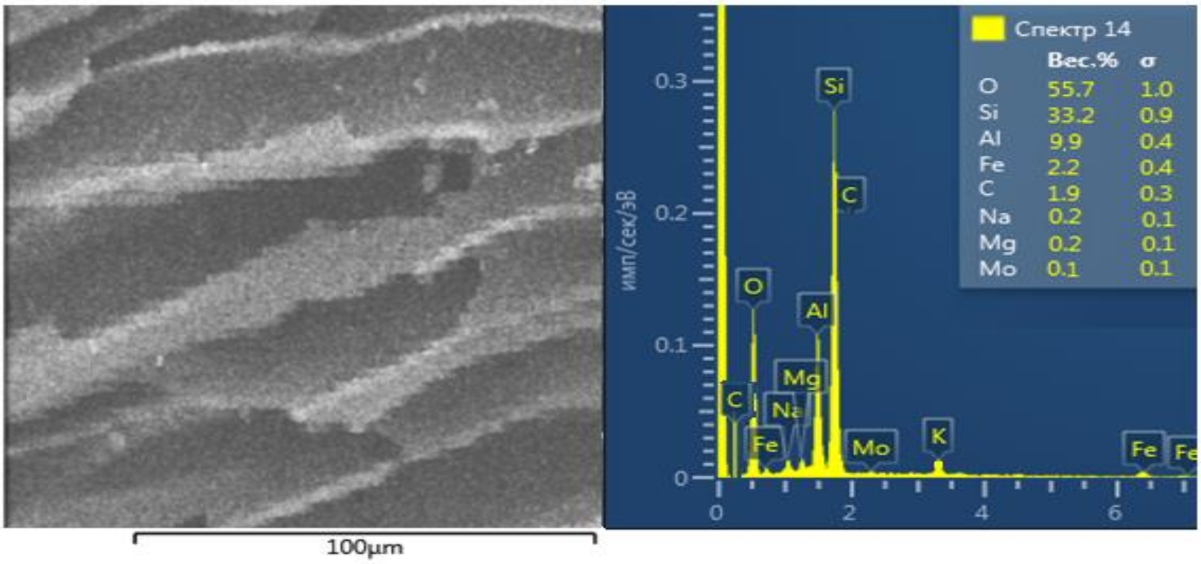
pH aqueous solutions were measured using an ion meter I160-M.

The main method for studying the crystal structure of orgonobentonites is X-ray diffraction analysis and electron microdiffraction. (pic.1).

In the case of chitosan, a polymeric modifier, the formation of associates with a thickness of one layer of modifier cations is observed, instead of hydrate-ionic layers of the outer surfaces of montmorillonite crystals. At the same time, an increase in the size of the modifier molecules contributes to an increase in the degree of three-dimensional order in the packing of silicate layers. Under an electron microscope, it can be seen that large X-KP particles are mainly rectangular in shape with a size of about 1 mkm These assumptions are fully consistent with the results of X-ray phase analysis. In order to determine the quantitative characteristics, thermogravimetric studies were carried out. Effects on thermograms at the temperature range of 350-450°C indicate the amount of absorbed organic modifier, i.e. entered the interlayer space, and not remaining on the surface of the packages. So, an important characteristic is the value of loss on ignition within the above-mentioned temperatures. Orgonoclays dried at a temperature of 95°C were taken for analysis, which contain minimal amounts of molecular water, and therefore the intensity of the first thermal effect should decrease as much as possible in relation to the intensity of the original clay.



A)



B) Pic. 1. Electron microscopic image of bentonite and orgonobentonite
A) Na-КР; B) X-КР;

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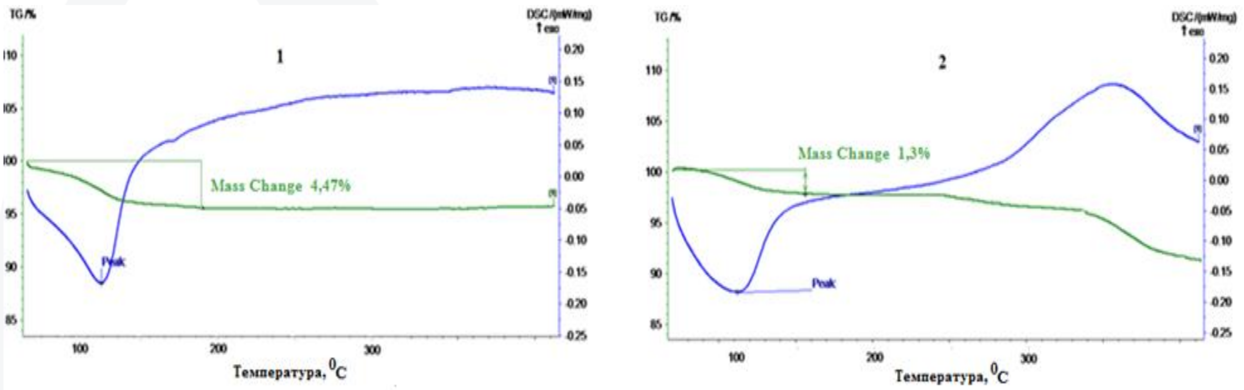
At the same time, the formation of a second thermal effect is observed at higher temperatures, the intensity of which characterizes the amount of chemically bound organic matter. The formation of the second thermal - exo effect at a temperature of about 400°C corresponds to the combustion of organic matter.

This effect, as can be seen from Fig. 2. absent in the natural sample of KR. In the X-KP sample, during heat treatment, a decrease in the intensity of the first endoeffect, which characterizes the expenditure of heat to break molecularly bound water, is observed. Thus, the mass loss of natural bentonite at temperatures of 100-150°C is about 4.4%, and that of its organic derivative X-KP is 1.30%, respectively. A further noticeable decrease in the mass of X-KR samples occurs at temperatures above 390°C and amounts to 4.02% of the mass of the original orgonophilic clay. The location of endo- and exo-effects, as well as the change in mass during heat treatment, prove early assumptions about the incorporation of surfactants into the interlayer space of clays.



Pic. 2. Thermal analysis results (simultaneous differential thermogravimetric analysis and scanning calorimetry): 1) KP; 2) X-KP;

It is known that the course of anionic dye sorption processes depends on the electrosurface properties of sorbents in various media. Based on these provisions, the adsorption of this dye was studied at various pH values of the solution (from 1 to 11). To describe the processes of adsorption of 2B on the synthesized organobentonite, the Langmuir model was used, which makes it possible to estimate the equilibrium characteristics of adsorption systems. The applicability of the Langmuir equation is related to the monomolecular nature and localization of adsorption, and another

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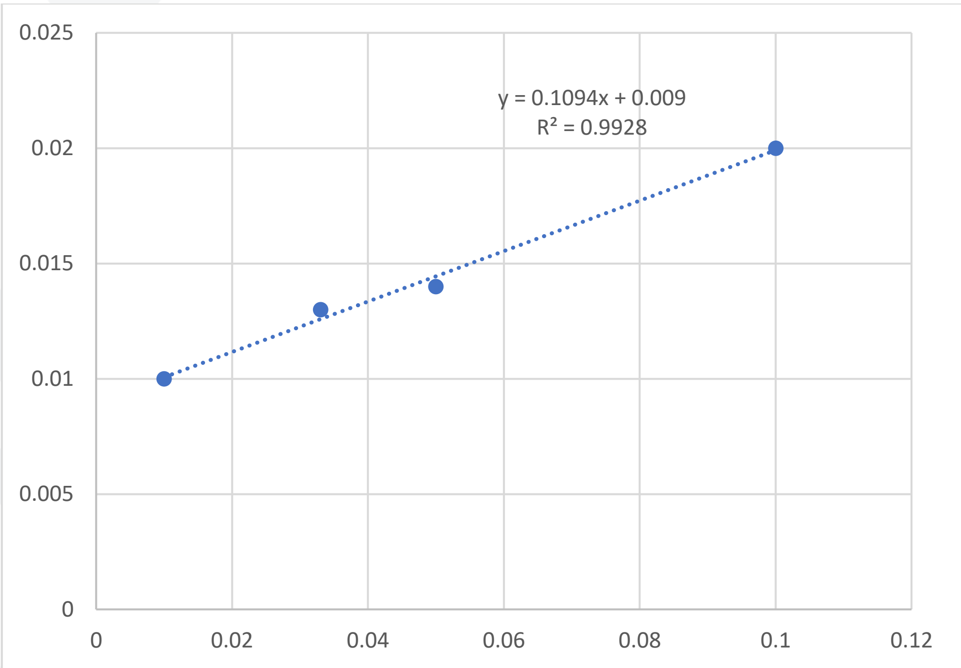
mandatory condition is the equipotentiality of the adsorbent surface, i.e. the presence of equal values of the interaction energy of the adsorbate with the adsorption center over the entire surface of the adsorbent and the absence of lateral interaction in the system [10]. The Langmuir adsorption model is expressed by the formula:

$$A = A_{\infty}\frac{K\frac{C}{C_0}}{1 + K\frac{C}{C_0}}, \qquad (2)$$

where A – adsorption value, mg/g; A_{∞} - capacity of the adsorption monolayer, mg/g; C_0 and C – initial and equilibrium concentration of absorbent, mg/l. K – Langmuir constant characterizing the energy of interaction of the adsorbate with the adsorbent. For the convenience of finding its constant, it is advisable to use the linear form of this equation [10]:

$$\frac{1}{A} = \frac{1}{A_{\infty}} + \frac{1}{A_{\infty}K} * \frac{1}{C}. \qquad (3)$$

As it was established, the equation of the Langmuir model satisfactorily describes the mechanism of adsorption of this sample (pic. 2), as evidenced by the high values of the correlation coefficient R2 (0.9928).



Pic. 3. 2B adsorption isotherms on X3-Na-KP in coordinates of the linear Langmuir equation.

Using the data from the diagram (the tangent of the slope of the straight line and the value of the segment cut off on the y-axis) corresponding to 1/A∞ and 1/A∞K, the values of K and A∞ were calculated.

As shown by the research results, lowering the pH of the medium to 2 in the adsorbent + 2B system greatly increases the amount of adsorption. A further decrease in the pH of the medium negatively affects the values of the adsorption capacity of X3-Na-KP, probably due to the adsorption of super high amounts of H+ on its surface, and as a result, even the destruction of the structure of the sorbents. An increase in the pH of the medium to 6 causes a decrease in the amount of adsorption at the same values of the initial concentration of the adsorbate, a further increase in pH to 10 does not cause a noticeable change in this indicator. Such a change in the adsorption capacity shows that the adsorption of the active anionic dye on X3-KP depends not only on the number of cation-exchange centers, but also on the size of its accessible surface.

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