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Adsorption Activity of Organobentonite Based on Krantau Clay

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ABSTRACT. The adsorption capacity of organobentonite based on Krantau clay modified with dodecyl tri methyl ammonium bromide was investigated. It turned out 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 MG reaches 100 mg/g and is 86% of its maximum amount. A further increase in the MG concentration will hardly affect the amount of MG adsorption on HDTMA-CR. As shown by the research results, lowering the pH of the medium to 2 in the adsorbent + MG system significantly increases the amount of adsorption. A further decrease in the pH of the medium negatively affects the values of the adsorption capacity of HDTMA-KR, probably due to the adsorption on its surface of super high amounts of H⁺, and as a result, even leading to 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 adsorbate in the solution, 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 MG dye on HDTMA-CR depends not only on the number of cation exchange centers, but also on the size of its accessible surface.

KEYWORDS: Bentonite, montmorillonite, organobentonite, dodecyltrimethylammonium bromide, adsorption, Langmuir equation, specific surface area, monolayer capacity.

I. INTRODUCTION

The rapid development of industries and the expansion of the scope of adsorption processes, the production of effective relatively cheap adsorbents from local mineral bentonite clays is an urgent task that requires a timely solution. To obtain sorbents that are 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 poisonous gases, and waste water with heavy metals, organic reagents, oil products, surfactants, dyes. The variety of pollutants and their nature requires polyfunctional and selective adsorbents that have the ability to cleanse from common 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 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 absence of a scientifically grounded acceptable technology that ensures the production of organobentonites with high characteristics as adsorbents. Therefore, scientific experimental research in this direction is doubly relevant.

II. SIGNIFICANCE OF THE SYSTEM

The aim of the research is to study the adsorption characteristics of the synthesized organobentonite dye methylene blue (MG). The study of literature survey is presented in section III, methodology is explained in section IV, section V covers the experimental results of the study, and section VI discusses the future study and conclusion.

III. METHODOLOGY

Clays of the lower horizon of the Krantau deposit (KR), with high contents of montmorillonite, were selected for research [5]. The reagent hexadecyltrimethylammonium bromide (HDTMABr) was used as a clay modifier. The method of obtaining organobentonites is given in the early works of the authors [6]. The synthesized organobentonites conventionally named GDTMA-KR. The paper also presents studies of some properties of bentonites of the Navbakhord deposit enriched and modified with sodium containing reagents [7]. The adsorption capacity in relation to methylene blue (MG) was measured by determining the optical density at a characteristic wavelength (660 nm) using a KFK-3M photoelectric calorimeter. Methylene blue basic dye chemical formula $C_{16}H_{18}NSCl$ molecular weight 320 g/mol. It is a dark green crystal with a bronze sheen. In laboratory experiments to determine the adsorption capacity, solutions of MG in water with a concentration from 1 to 200 mg/L were prepared and the values of the optical densities of these solutions were determined. To construct a calibration graph, we used data on the optical densities of solutions. 0,1 g of adsorbents in the form of a powder were added to solutions with a volume of 100 ml. 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 of the calibration graph their concentrations were established in mg/L. The amount of adsorbed dye was determined by the formula:

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

where, A is the amount of adsorbed dye mg/g; C_0 and C_1 - initial and equilibrium concentration of the dye in solution, mg/l; V is the volume of the solution, l; m is the mass of the adsorbent, g. The pH of aqueous solutions was measured using an I160-M ionomer. It is known that the course of the sorption processes of a cationic dye depends on the electro-surface properties of sorbents in various media. Based on these positions, the adsorption of this dye was studied at various pH values of the solution (from 1 to 11). When modifying 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. water is adsorbed mainly on their outer surface [8]. However, as the results of the study show, the adsorption of molecules of polar 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 are data confirming an increase in the adsorption capacity of modified montmorillonite in relation to petroleum products, aromatic and paraffinic hydrocarbons [10]. The increased interest in organic derivatives of clay minerals can be explained by the possibility of their use as selective sorbents.

IV. EXPERIMENTAL RESULTS

The adsorption isotherm describes the correlation between the amount (mg) of adsorbate and adsorptive (Fig. 1). Equilibrium adsorption isotherms were used to calculate the values of the equilibrium constant of adsorption and adsorption capacity.

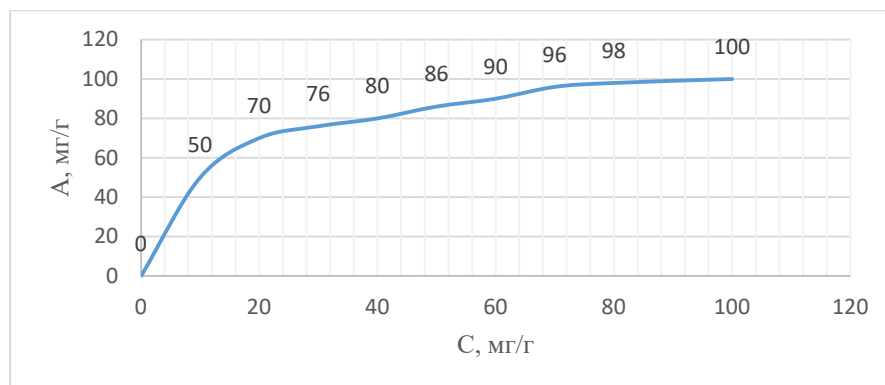


Figure: 1. Isotherms of MG adsorption on the GDTMA-KR sample at 20 °C and pH = 7, the adsorbent dose is 1 g/L, the initial solution concentration MG 1-200 mg/l

As seen from Fig. 1, at low values of the equilibrium concentration, a sharp increase in the amount of adsorption for the sample under study is observed, the adsorption capacity for MG reaches 100 mg / g or more, which is 86% of its maximum values. A further increase in the concentration of MG will have almost no effect on the amount of MG adsorption on DTMABr-Na-KR. The isotherm curve according to the shape of the initial section refers to H-type isotherms, which are characterized by strong adsorption at low concentrations of adsorbate, which is explained by the high affinity of organobentonite for MG. To describe the processes of MB adsorption 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 associated with the monomolecularity and localization of adsorption, and also one more 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 [11]. The Langmuir adsorption model is expressed by the formula:

$$A = A_{\infty} \frac{K \frac{C}{C_0}}{1 + K \frac{C}{C_0}} \tag{2}$$

where A is the value of adsorption, mg/g; A_{∞} - capacity of the adsorption monolayer, mg/g; C_0 and C - initial and equilibrium concentration of adsorbent, mg/l. K is the Langmuir constant characterizing the interaction energy of the adsorbate with the adsorbent. For the convenience of finding its constant, it is advisable to use the linear form of this equation [8]:

$$\frac{1}{A} = \frac{1}{A_{\infty}} + \frac{1}{A_{\infty}K} * \frac{1}{C} \tag{3}$$

As it was established, the equation of the Langmuir model satisfactorily describes the mechanism of adsorption of this sample (Fig. 2), as evidenced by the high values of the correlation coefficient R_2 (0.9928).

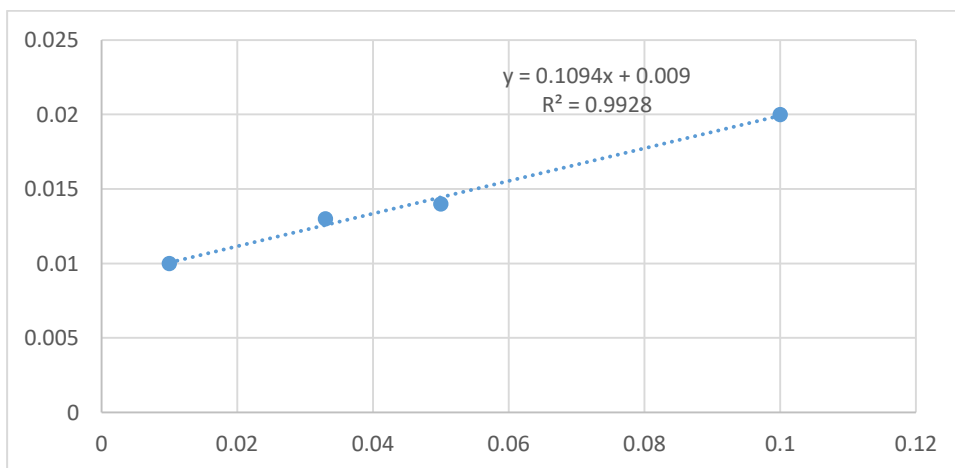


Figure: 2. Isotherms of MG adsorption on GDTMA-KR in the coordinates of the linear Langmuir equation. Using the data from the diagram (the tangent of the slope of the straight line and the size of the segment cut off on the ordinate) corresponding to $1/A_{\infty}$ and $1/A_{\infty} * K$, the values of K and A_{∞} were calculated.

VI. CONCLUSION AND FUTURE WORK

As shown by the research results, a decrease in the pH of the medium to 2 in the adsorbent + MG 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 HDTMA-KR, probably due to the adsorption on its surface of extremely high amounts of H^+ , and as a result, evens 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



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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 MG dye on HDTMA-CR depends not only on the number of cation exchange centers, but also on the size of its accessible surface.

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