Adsorption Activity of Logon Bentonite And its Pillar Forms in Relation to Dyes from Aqueous Solutions

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ABSTRACT: The article presents the results of adsorption of organic dyes of different nature, using the example of rhodamine B, carmoisine, Congo red and methylene blue samples of the original and pillared Logon bentonite. For experiments, solutions were prepared with concentrations of 0.01–1 mmol/L. By plotting the adsorption kinetic curve, the duration of the process was determined until adsorption equilibrium was established. The kinetics of the process is practically independent of the concentration of dyes in the solution. Therefore, the kinetics was studied for one concentration. However, the amount of pillar material and the duration of the Cr-pillar interaction process of the samples affect the final result, probably due to the catalytic effect of the active components of the pillar on the dyes under study.

KEYWORDS: montmorillonite, adsorption, methylene blue, congo red, intercalation, pillaring.

I. INTRODUCTION

Layous minerals are considered effective and profitable adsorbents when cleaning water drains from impurities of organic substances, in particular dyes [1].

The synthesis of columnar clay led to the development of a new class of microporous materials that are of potential interest as catalysts and adsorbents. Their pore structures can be characterized by distances between silicate layers (interglane distance) and distances between the pillars (the lateral distance between the pillars). The preparation of pyllars includes the exchange of cations located in the inter -layer space of clays with oligomeric hydroxycations of metals. Therefore, the amount of phase on is associated with the capacity of cationic exchange (CEC) of the clay of the host. The controlled heat treatment of several cationic forms of Montmorillonite (MM), for example, Li, CO, Ni, allows you to synthesize the family of solids with a of some in the range from the value of the native mineral (1.07-0.75 mekv/g) to almost zero [2]. Using these materials for the synthesis, the authors [3] obtained columns Al-clays with different columns density. These materials have a homogeneous distribution of the interculated phase and differ in the values of surface and acidity.

Organic dyes are a large group of pollutants in wastewater from the textile, paper, plastic, food and other industries. It is estimated that around the world, about 1-15% of the total amount (70 thousand tons) of dyes are lost as waste during dyeing [4]. Organic dyes are widely used because of their ease of application, durability, and do not wear out easily, however, the adverse effects are also very large. Cationic dyes are recognized as carcinogenic, mutagenic and have high coloring effects throughout the ecosystem when disposed of as waste into the environment, even at low concentrations. Therefore, reducing the concentration of dyes in wastewater, before being discharged into the environment, becomes a serious problem, therefore, the development of appropriate neutralization processes is required [3; 4].

II. SIGNIFICANCE OF THE SYSTEM

The adsorption activity of Logon bentonite (LB) and its pillar forms (Cr-LB and Cr/Al-LB) with respect to stable organic dyes from aqueous solutions was studied. The study of methodology is explained in section III, section IV covers the experimental results of the study, and section V discusses the future study and conclusion.

III. METHODOLOGY

Model dye solutions were used to determine the adsorption activity of Cr- and Cr/Al-pillar montmorillonites. Stable organic structures such as methylene blue (MB) and Congo red (CR) were studied as model dyes.

The concentration of adsorbents in the solution varied from 1 to 500 mg/l, and the consumption of the oxidizing agent was taken from the stoichiometric ratio with the adsorbent in the solution.

The activity of pillarar montmorillonite as a catalyst was determined by the rate and completeness of bleaching of dye solutions and the decrease in optical density.

The qualitative change in the catalysis process was determined using a UV/V-5100 spectrophotometer (Shanghai Metash Instruments Co.) in the wavelength range of 190-1100 nm.

Calculations of the change were carried out according to known methods [5] based on the absorption spectra of their solutions. The Langmuir, Freindlich, and Dubinin-Radushkevich equations were used to describe the adsorption equilibrium in the dye:LB system.

Using the Dubinin-Radushkevich model, the values of the average free energy of adsorption can be calculated[6; 7]:

$$E = (-2K)^{-0,5} \qquad (4.7)$$

IV. EXPERIMENTAL RESULTS
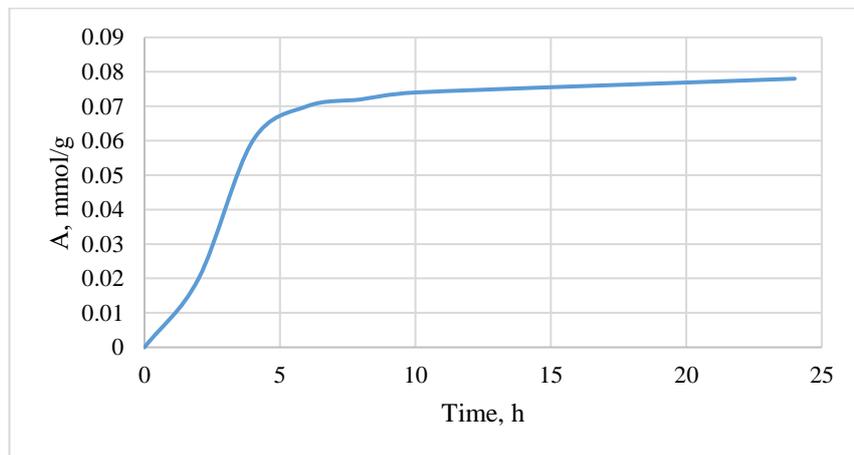
Fig. 1. Kinetics of MB adsorption on LB.

As the curves of the figure show, the adsorption equilibrium in the system with LB sets in after 10 hours of interaction. For the first time 5 hours the process speed is maximum, and then the process stabilizes and the process speed decreases to 0.0016 mmol/h.
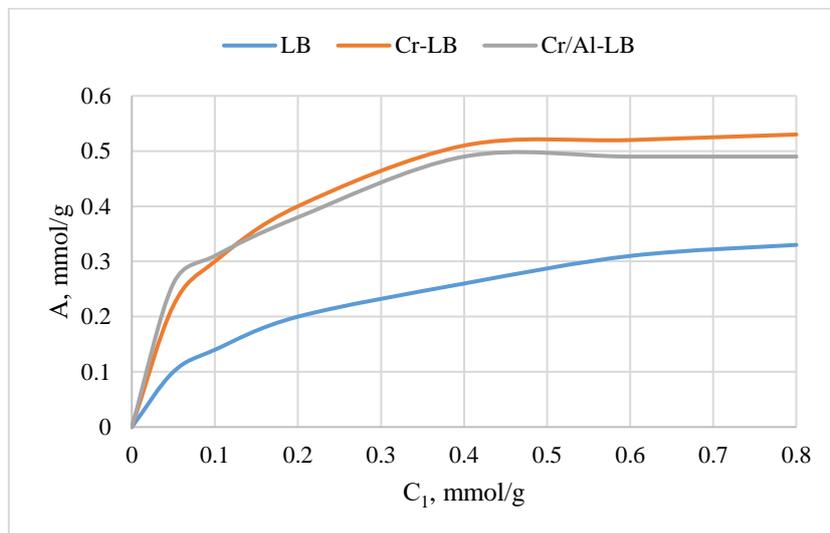
Fig. 2. Isotherms of MB adsorption on the studied samples.

Obviously, in terms of the amount of adsorption on the surface, MMs should be superior to cationic dyes. Of course, the adsorption activity of enriched LB with respect to cationic MB is higher than that of anionic carmoisine at their equal concentrations in the initial solution.

The values of the amounts of adsorption of LB by MB are significantly behind those of the characteristics of Cr-pillar LB. The adsorption of MB in dilute solutions proceeded almost completely, since the limiting adsorption capacity of MM for this dye can reach 250–400 mg/g [8]. The experimentally established amounts of the maximum adsorption of MB on LB are about 150–110 mg/g, while for Cr-LB and Cr/Al-LB at an equilibrium concentration of 0.8 mmol/L, the maximum amount of adsorption was about 156.8 and 169, 6 mg/g, respectively
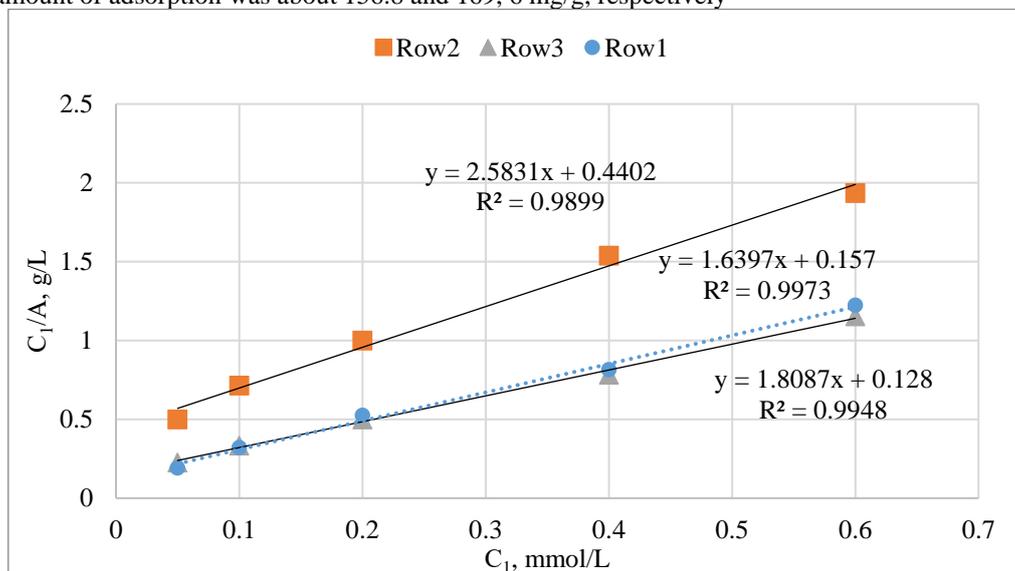
Fig. 3. Isotherms of MB adsorption on samples: 1) Cr/Al-LB; 2) Cr-LB; 3) LB in coordinates of the linear Langmuir equation.

It can be seen from Figure 3 that the experimental points of MB adsorption on all the studied samples literally exactly coincide on a straight line, which indicates the possibility of using this adsorption model to describe adsorption

equilibrium in a system with an equilibrium dye concentration of up to 0.6 mmol/L. Based on the data in the figure, the parameters of the Langmuir equation are calculated, which are given in Table. 1.

Table 1.
Indicators of surface characteristics of the studied samples

Sample	A_0, mmol/g	K	surface area, m^2/g.	G, Dj	V, sm^3/g	r, nm
LB	0,387	5,868	244,706	-4310,54	0,106	8,631
Cr-LB	0,610	10,444	385,497	-5714,91	0,170	8,799
Cr/Al-LB	0,553	14,13	349,478	-6451,34	0,157	8,973

The specific surface of Cr and Cr/Al-pillar MM for water vapor is about 70 and 82 m2/g, and for methylene blue 385.8 and 349.5. The adsorption interaction of methylene blue with Cr-LB is stronger than with Cr/Al-LB. Higher cationic dye adsorption rates for pillar materials are likely to be achieved by denser packing of dye particles. However, despite the similar dimensions of rhodamine B, the specific surface area for this dye lags far behind the values of the former and is only 112.3 and 137.6 m2/g. Probably, the decrease in the surface is caused by the achievement of loose packing due to the steric hindrance of the carboxyl group in the adsorbate molecule.
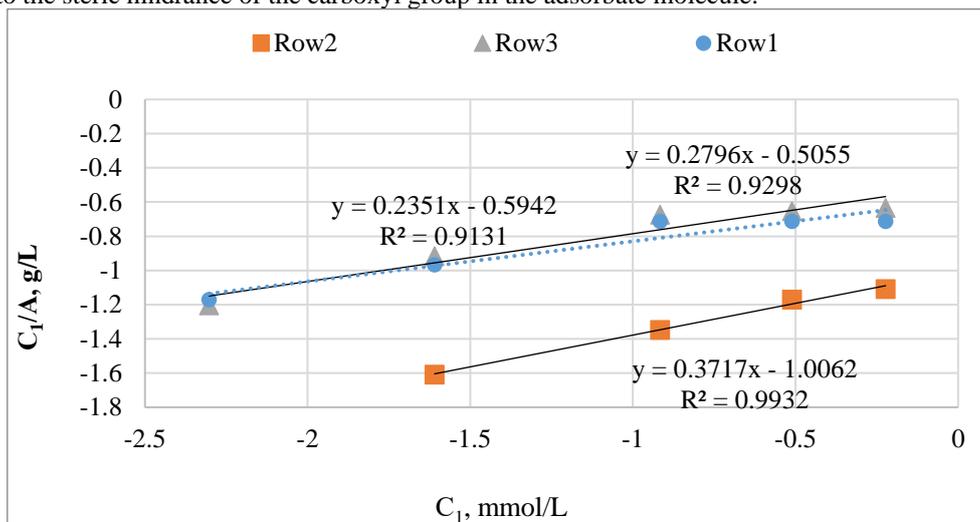
Fig. 4. Isotherms of MB adsorption on samples: 1) Cr/Al-LB; 2) Cr-LB; 3) LB in coordinates of the linear Freindlich equation.

Table 2.
Parameters of the Freundlich equation

n	1/n	K
2,690	0,372	0,3656
3,577	0,280	0,6032
4,254	0,235	0,5520

As the data in Fig. 4., the Freundlich equation completely describes the adsorption equilibrium in the LB + MB system at relatively high values of the equilibrium concentration of the dye. However, for pillar materials, the degree of application of this model is noticeably reduced, as evidenced by the values of the correlation coefficient. Somewhat underestimated coefficients compared to their values when using the Langmuir equation proves a more uniform energy surface of the pillar materials, compared to the original LB. Therefore, pillaring contributes to an increase in the energy

equipotentiality of active adsorption sites with respect to the cationic dye. The data obtained show that at low equilibrium concentrations (up to 0.3 mmol/l), adsorption on the initial bentonite can be characterized using the Langmuir equation, while for concentrations above 0.5 mmol/l, the Freundlich model is better applicable, which shows that at concentrations above 0.3 mmol/l, the filling of the most active centers ends, a further increase in concentration probably occurs at centers with lower energy values. The inflection in the adsorption isotherms at different concentrations (0.05-0.1) is associated with the reorientation of the adsorbate on the corresponding pores of the adsorbents.

All the studied processes are characterized by favorable adsorption, as evidenced by the values of n≥1, and in the LB<Cr-LB<Cr/Al-LB series, the values of n increase, and the value of the Freundlich constant (K) passes through a maximum.

It is known that the adsorption activity of montmorillonite with respect to anionic particles is determined mainly by the surface charge rather than by their specific surface area. If we take into account that pillaring noticeably affects the total negative charge of the surface, then, of course, their activity with respect to various anionic adsorbates increases. In this case, the particle size of the adsorbate should not strongly affect the amount of adsorption. However, the amount of adsorption of anionic azurubine and Congo red, as well as the form of adsorption, differ from each other. The isotherm of the first is characterized by a stepped shape, and for the second, the stepping is less pronounced. The stepped part of the isotherm is associated with the reorientation of carmoisine molecules and, due to this, the formation of new adsorption centers on the surface is possible. As a result, an increase in adsorption is observed. However, the obtained isotherm in the system with Congo red, although almost identical in values at low equilibrium concentrations, however, the maximum of the isotherm is more shifted to the region of low concentrations. The differences in the maxima of the curves are related to the particle size of the adsorbate; landing pad values (Fig. 5-6, Table 3).

Calculation of specific surface area values for LB by adsorption CR is 22.314 m2/g, and for pillar materials Cr-LB and Cr/Al-LB they are 108.2 and 118.4 m2/g. As in the case of this adsorbate, the adsorption of azurubin increases with an increase in the equilibrium concentration and reaches its maximum value at a concentration of 0.03 mmol/l for LB and 0.18–0.20 mmol/l for Cr-LB and Cr/Al-LB samples, respectively. The calculated landing area for azurubin is about 123 Å for LB, and no more than 98 Å for adsorption on pillar materials. However, the true values of this indicator for azurubin are more than 150 Å, which indicates the dense packing of this adsorbate and the possible occurrence of polymolecular adsorption..

Comparison of the results of adsorption of anionic dyes on the initial LB, its intercalated and calcined forms showed similarity with the results of earlier adsorption processes. Heat-treated LB exhibits an underestimated adsorption activity due to the loss of initial porosity and active adsorption centers. As it turned out, pillaring of Cr and Cr/Al polycations leads to a multiple increase in the surface activity of anions (Fig. 6).
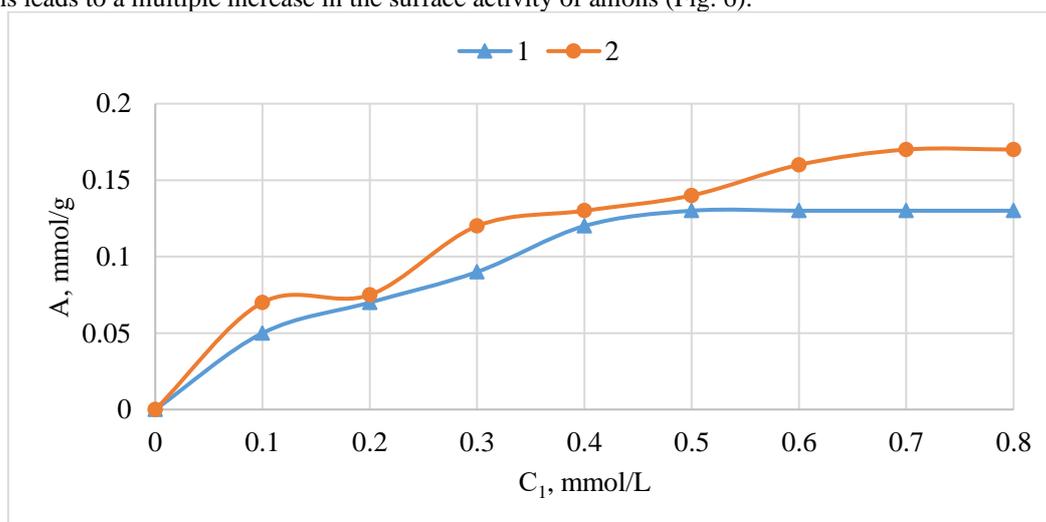
Fig. 5. Adsorption isotherms of anionic dyes on Cr-LB: 1) Congo red; 2) azorubine.
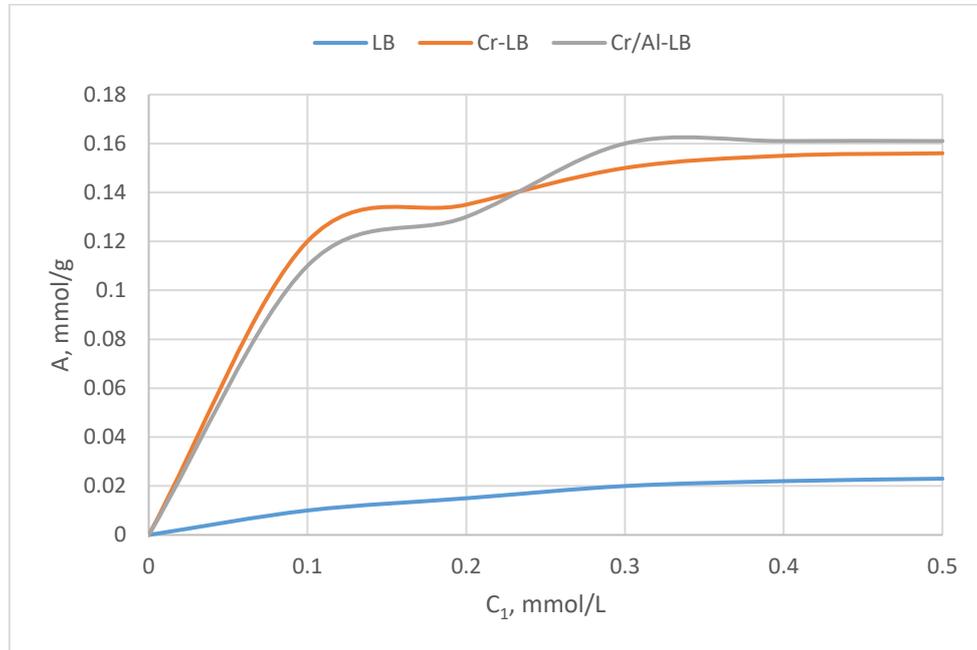
Fig. 6. Isotherms of CR adsorption on the studied samples.
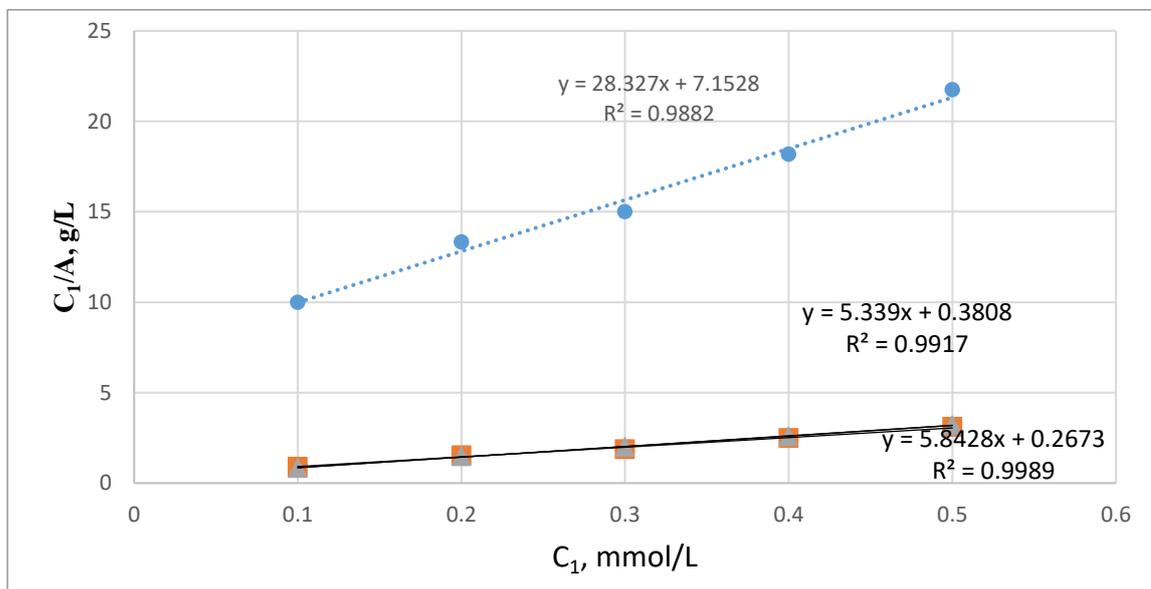
Fig. 7. Adsorption isotherms of CR on the samples under study in the coordinates of the linear Langmuir equation (from top to bottom): 1) LB; 2) Cr-LB; 3) Cr/Al-LB.

Table 3.
Textural characteristics of MM samples

Sample	A_0, mmol/g	K	Surface area, m²/g	G, Dj	V, sm³/g	r, nm
LB	0,035	3,960	22,314	-3352,698	0,007	14,537
Cr-LB	0,171	21,859	108,184	-7514,077	0,050	9,229
Cr/Al-LB	0,187	14,020	118,393	-6432,310	0,052	8,703

Table 3 shows a noticeable change in the specific surface area and adsorption volume. The values of the adsorption interaction of the adsorbate and the adsorbent passes through a maximum, the values of the Gibbs energy decrease in the series LB<Cr-LB<Cr/Al-LB. As in the case of methylene blue, the adsorption equilibrium in the system is well described by the Langmuir equation, which is proved by the regression coefficient of this equation. The Freundlich equation for describing equilibrium is less suitable both at low and at elevated equilibrium concentrations of CR in solution, which proves the energy equipotentiality of the surface of pillar materials with respect to a given adsorbate.

It is known that a change in pH affects the degree of dissociation of the surface groups of montmorillonite, and the number of such ions increases significantly after intercalation, and these surface unlike ions and a change in the degree of their dissociation affect the amount of adsorption of various dyes. A contribution to the change in the course of adsorption processes with a change in pH will also be made by adsorbates - dyes, which, being also electrolytes, greatly change their characteristics in this process.

Table 4.
Maximum values of adsorption capacity for dyes at various pH values

Samlpe	A_{Max} mmol/g			
	pH=2±0,5	pH=6,5±0,5	pH=10±0,5	optimal pH values*
MB				
LB	0,33	0,42	0,39	0,44
Cr-LB	0,28	0,68	0,51	0,72
Cr/Al-LB	0,21	0,63	0,53	0,65
CR				
LB	0,018	0,019	0,010	0,041
Cr-LB	0,172	0,159	0,101	0,181
Cr/Al-LB	0,174	0,165	0,132	0,192

pH values during MB adsorption for LB; Cr-LB and Cr/Al-LB is 6; 5.1 and 5.3;

Using the Dubinin-Radushkevich model, the average free energy of adsorption of dyes on the studied samples was calculated. The value of free energy is necessary for understanding the nature of the mechanism of this process, i.e. indicates the occurrence of physical (E<8 kJ/mol) or chemical adsorption (E>8 kJ/mol), due to ion exchange or the formation of new bonds. The values of the characteristic free energy of adsorption calculated using the values of the constant of the Dubinin-Radushkevich equation are given in Table. 5.

Table 5.
The value of the free energy of the process of adsorption of dyes on samples

Adsorbate	Sample		
	LB	Cr-LB	Cr/Al-LB
MB	13,3	18,9	20,2
CR	10,1	34,2	26,5

As can be seen from the data in Table 5, the calculated free energy values are greater than 8 kJ/mol, therefore, the adsorption of dyes on the surface of both the original bentonite and its pillared forms is responsible for the formation of new bonds or an ion exchange process due to existing surface chemical bonds.

V. CONCLUSION AND FUTURE WORK

It has been established that the adsorption equilibrium in the system with LB and MG sets in after 10 hours of interaction. For the first time for 5 hours, the process speed is maximum, and then the process stabilizes and the process speed decreases to 0.0016 mmol/h. The experimentally established amounts of maximum adsorption of MB on LB are about 150–110 mg/g, while for Cr-LB and Cr/Al-LB at an equilibrium concentration of 0.8 mmol/L, the maximum amount of adsorption was 156.8 and 169, 6 mg/g, respectively.

The data obtained show that at low values of the equilibrium concentration (up to 0.3 mmol/l), the adsorption of MB on the initial bentonite can be characterized using the Langmuir equation, while for concentrations above 0.5 mmol/l, the Freundlich model is better applicable, which shows at concentrations above 0.3 mmol/l ends with the filling of the most active centers, a further increase in concentration probably occurs at centers with lower energy values. The inflection

on the adsorption isotherms at different concentrations (0.05-0.1) is associated with the reorientation of the adsorbate on the corresponding pores of the adsorbents.

The calculated values of the specific surface area for LB according to CR adsorption are 22.314, and for pillar materials Cr-LB and Cr/Al-LB 108.2 and 118.4 m2/g. As in the case of this adsorbate, the adsorption of azurubin increases with an increase in the equilibrium concentration and reaches its maximum value at a concentration of 0.03 mmol/l for LB and 0.18–0.20 mmol/l for Cr-LB and Cr/Al-LB samples, respectively. The calculated landing area for azurubin is about 123 Å for LB, and no more than 98 Å for adsorption on pillar materials. However, the true values of this indicator for azurubin are more than 150 Å, which indicates the dense packing of this adsorbate and the possible occurrence of polymolecular adsorption.

The values of the adsorption interaction of the adsorbate and the adsorbent pass through a maximum and in the series LB<Cr-LB<Cr/Al-LB the values of the Gibbs energy decrease.

REFERENCES

[1] . Khankhasaeva S.Ts. Synthesis and physicochemical properties of intercalated systems based on polyoxo compounds of metals and montmorillonite. Abstract dis. … doc. tech. Sciences (02.00.04). - Ulan-Ude. 2010. 39 p.

[2]. Prost R. Sate and Location of Water Adsorbed on Clay Minerals: Consequences of the Hydration and Swelling-Shrinkage Phenomena // Clays and Clay Minerals. 1998. № 2(46). p. 117–131.

[3]. Horio M., Suzuki K., Masuda H., Mori T. Alkylation of toluene with methanol on alumina-pillared montmorillonite Suppression of deactivation by control of the lateral spacings of pillars // Applied Catalysis. 1991. № 1(72). p. 109–118.

[4]. Elmoubarki R., Mahjoubi F.Z., Tounsadi H., Moustadraf J., Abdennouri M., Zouhri A., El Albani A., Barka N. Adsorption of textile dyes on raw and decanted Moroccan clays: Kinetics, equilibrium and thermodynamics // Water Resources and Industry. 2015. (9). C. 16–29.

[5]. Seytnazarova O.M., Mamataliev N., Abdikamalova A.B., Ikhtiyarova G.A. Adsorption Activity of Organobentonite Based on Krantau Clay. IJARSET. Vol. 7, Issue 12 , December 2020. pp. 16164-16167.

[6]. Dubinin M.M. Physical Adsorption of Gases and Vapors in Micropores // Progress in Surface and Membrane ScienceElsevier, 1975. p. 1–70.

[7]. Ibhadon A., Fitzpatrick P. Heterogeneous Photocatalysis: Recent Advances and Applications // Catalysts. 2013. № 1(3). p. 189–218.

[8]. Konkova, T.V. Preparation and modification of porous nanostructured materials based on aluminum and silicon oxides with functional properties of sorbents and catalysts: Cand. ... doc. tech. Sciences: 02.00.04 / T.V. Konkova. - M., 2017. - 362 p.