

Description Of The Adsorption Equilibrium In The Fe^{+3} System Of Intercalated Clay And Methylene Blue

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Abstract: *The results of adsorption of methylene blue from an aqueous solution on various samples of Fe^{+3} intercalated clays of the Navbakhor Deposit are presented. Comparative studies of the applicability of the Langmuir, Freundlich, and Dubinin-Radushkevich models for describing experimental adsorption isotherms of modified clays and their heat-treated forms at different pH values of the medium are presented. The Dubinin-Radushkevich isotherm model was used to calculate the free energy of methylene blue adsorption on intercalated systems.*

Key words: *intercalation, montmorillonite, adsorption isotherm, Langmuir, Freundlich, Dubinin-Gorodkevich model, free energy of adsorption.*

1. INTRODUCTION

Currently, research is widely conducted in the field of directed synthesis of new effective nanostructured materials for various purposes, as sorbents, catalysts, catalyst carriers, medicinal substances, membranes, various fillers, etc. Materials used in catalytic and adsorption processes must necessarily have a developed nanoporous structure. The current level of development of science and technology provides huge opportunities for creating such materials. One of the ways to obtain these is intercalation – the reversible inclusion of molecules (atoms, ions) or their groups between other layered groups [1]. Intercalates are substances obtained by introducing foreign compounds into matrices with a layered structure, which are currently not only widely used in practice, but are also of interest as an object of fundamental physical and chemical research. The easily tunable interlayer structure of layered materials allows us to develop a wide range of unique materials for effective use as potential sorbents, catalysts, anion exchangers, polymer composites, catalyst carriers, medicinal substances, bioactive materials, etc. Adsorbents take special attention among these substances [2-5].

Scientific and technical literature widely covers data on the possibility of regulating micro- and mesoporous structure, compositions and physical and chemical properties in the synthesis

and modification of amorphous and crystalline aluminosilicates, which make them very promising as the basis for intercalation processes [6-8].

Recently, numerous methods have been developed for the synthesis of intercalated systems based on montmorillonite, vermiculite, zeolites, etc. [9-17]. The list of intercalated agents whose compositions and sizes vary widely has been expanded. In most cases, polyvalent metal ions, such as aluminum, iron, zirconium, titanium, chromium, lanthanum, etc., enter the bases of the intercalating ion [8, 18, 19]. There are no fundamental differences in the intercalation process involving one and two cations. However, the situation is more complicated with the mechanism of formation and composition of hydroxy cations formed in solution during the joint hydrolysis of several metals [20]. As the authors note [7, 8], columnar montmorillonites synthesized by intercalation have high selective adsorption capabilities.

However, to date, the production of new highly efficient and regenerable sorbents and catalytic materials based on natural and synthetic aluminosilicates remains an unsolved urgent task. It should also be noted that the scientific basis for changes in the stability of their porous structure and functional properties (adsorption and catalytic) depending on the conditions of synthesis, modification and use is not sufficiently developed.

The aim of the research is the study of adsorptive abilities of intercalated systems Fe^{+3} synthesized on the basis of montmorillonite-containing clays Navbakhor Deposit on the example of adsorption of methylene blue and to evaluate the role of key parameters of the adsorption process and the choice of model that best describes the adsorption processes.

2. EXPERIMENTS

Bentonite clay was purchased from «Bentonite» LLC, whose physico-chemical and adsorption properties were previously well studied [21, 22]. For use in the synthesis process, natural montmorillonite-containing clays were enriched by the elutriation followed by modification of the enriched form of clays with soda ash in an amount of 1 % of its mass.

The method of synthesis of Fe^{+3} intercalated montmorillonites proceeds in the following stages: nitrate or iron chloride is embedded in a suspension of an enriched form of clay, where the mass ratio of the solid and liquid phases is from 1:10 to 1:20. the pH of the aqueous extract of suspensions was 7.5-7.8. the Number of iron cations was 3; 5 and 10 mmol per gram of clay. Then the suspension was treated with ultrasound at a frequency of 20 Hz for 3 minutes. Then the calculated amounts of 0.2 M sodium hydroxide solutions ($[\text{OH}^-]/[\text{Fe}^{3+}] = 1,5-2,5$) were added to the prepared suspension and left alone at room temperature for a day. After 22-26 hours, the resulting modified bentonite was separated from the liquid phase by centrifugation at a speed of 6000 rpm for 5-7 minutes, then the thick residue was washed with distilled water until a negative reaction to chloride ions. Then it was dried at a temperature of 80°C. The dried samples were subjected to heat treatment at 250°C for two hours. These conditions allow us to obtain clays of intercalated iron cations, which is proved as a result of complex physical and chemical analyses of research.

The adsorption capacity with respect to methylene blue (MG) was measured by determining the optical density at a characteristic wavelength (660) nm using a photoelectric calorimeter KFK-3M. Methylene blue is the main dye, its chemical formula is $\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}$ and molecular weight is 320 g/mol. It is a dark green crystal with a bronze luster.

Experiments for determining the adsorption capacity were performed in the following order: first, MG solutions were prepared in water with a concentration of 0.1 to 1 mmol/l and the values of the optical densities of these solutions were determined. A standard calibration graph was built based on the data obtained. 0.05-0.1 g of intercalated clays in powder form were added to 50 ml solutions with 7 different concentrations. After establishing the adsorption equilibrium, the optical densities of the solutions were measured and their concentrations were calculated using the calibration graph data. The amount of adsorbed dye was determined by the formula:

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

where, A is the number of adsorbed dye in mol/g; C_0 and C_1 – initial and equilibrium concentration of dye in solution, mg/l; V – volume of solution, l; m – mass of adsorbent, g. The pH of aqueous solutions was measured using ionomer I160-M.

3. RESULTS AND DISCUSSION

Adsorbents based on pillared clays are conventionally designated: 3.1-Fe; 5.1-Fe and 10.1-Fe-bentonites modified with iron polyhydroxo-cations(III) in the amount of 3; 5 and 10 mmol $[\text{Fe}^{3+}]$ / g of bentonite, respectively, and their annealed forms at a temperature of 250 ° C for 2 hours in an inert atmosphere of argon-3.2-Fe; 5.2-Fe and 10.2-Fe, respectively.

The processes of sorption of cationic dye depend on the electrical surface properties of sorbents in solutions. Therefore, the adsorption of these dyes was studied at different pH values of the solution (from 1 to 11).

The correlation between the amount (mol or g) of adsorbate and adsorbent is described by the adsorption isotherms (Fig. 1). Using the equilibrium adsorption isotherms, it is possible to calculate the adsorption equilibrium constant and the value of the adsorption capacity, using known models of the adsorption isotherms equation

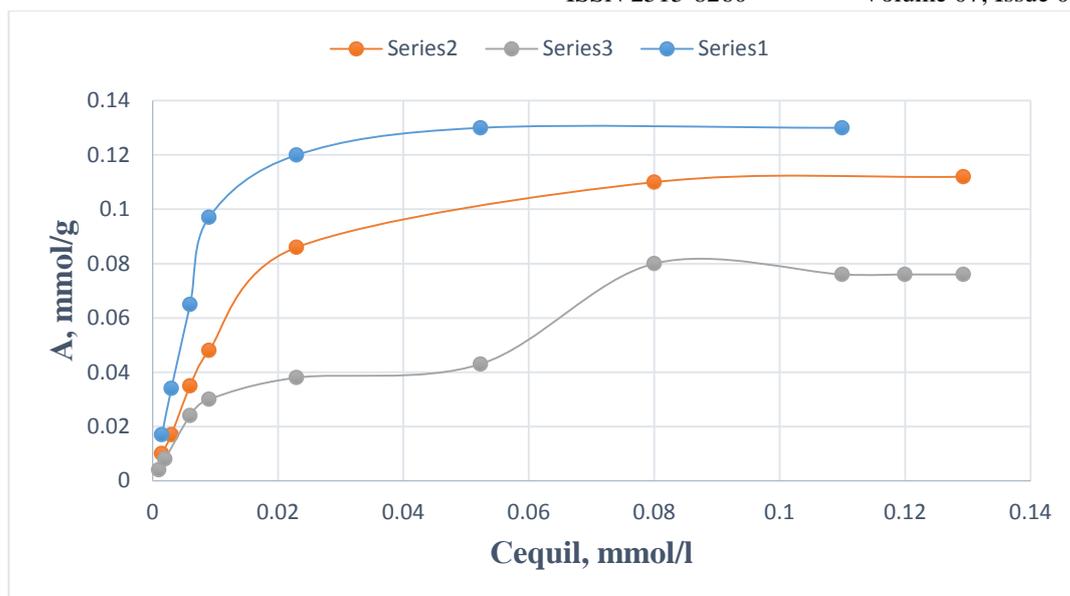


Fig. 1. Isotherms of MG adsorption on adsorbents at 20°C and pH=7, the adsorbent dose is 1 g/l, the initial concentration of the MG solution is 0.01-0.25 mmol/l: 1) 5.1-Fe; 2) 10.1-Fe; 3) 3.1-Fe.

As seen in Fig.1 at low values of the equilibrium concentration, there is a sharp increase in the amount of adsorption for the 5.1-Fe sample, the adsorption capacity for MG reaches 0.12 mmol/g and is 85.6% of its maximum values. A further increase in the concentration of MG (10-14 mmol / l) will have almost no effect on the amount of adsorption of this intercalated system. The values of the adsorption capacity of 10.1-Fe and 3.1-Fe are 0.098 and 0.07 mmol/g, respectively. Comparison of the adsorption isotherms for 5.1-Fe and 10.1-Fe samples shows that the isotherms of the former are located higher, indicating a greater affinity for the dye than 10.1-Fe. The curves of the isotherms of these samples in the form of the initial section belong to the H-type isotherms, which are characterized by strong adsorption at low concentrations of adsorbate, which is explained by the high affinity of the sorbents to MG. The shape of the curve of the isotherm for 3.1-Fe differs from the isotherms of the other two adsorbents, which indicates the distinctive structural features of this object of study. At MG's equilibrium concentration range of 0.05-0.08 mmol/l, an abrupt increase in the adsorption capacity of this adsorbent is observed. According to literature sources, it is known that the S-shape of the isotherm indicates the course of multilayer adsorption in macro and mesoporous sorbents [23-25].

Using the Langmuir model to describe the processes of adsorption from solutions allows us to evaluate the equilibrium characteristics of adsorption systems. Application of the Langmuir equation assumes that the adsorption is monomolecular and localized, the surface of the adsorbent is equipotential, i.e. the interaction energy of the adsorbate with the adsorption center over the entire surface of the adsorbent has the same values and there is no lateral interaction in the system [26]. The Langmuir adsorption model is expressed by the formula:

$$A = A_{\infty} \frac{K \frac{c}{c_0}}{1 + K \frac{c}{c_0}}, \quad (2)$$

where A – the amount of adsorption, mmol/g; A_{∞} - the capacity of the adsorption monolayer, mmol/g; C_0 and C –the initial and equilibrium concentration of the adsorbent, mmol/l. K is the Langmuir constant, which characterizes the interaction energy of an adsorbate with an adsorbent. Using the linear form of this equation is convenient for finding its constants:

$$\frac{1}{A} = \frac{1}{A_{\infty}} + \frac{1}{A_{\infty}K} * \frac{C}{C_0} \quad (3)$$

As it was established, the equation of the Langmuir model satisfactorily describes the mechanism of adsorption of these samples (Fig. 2).

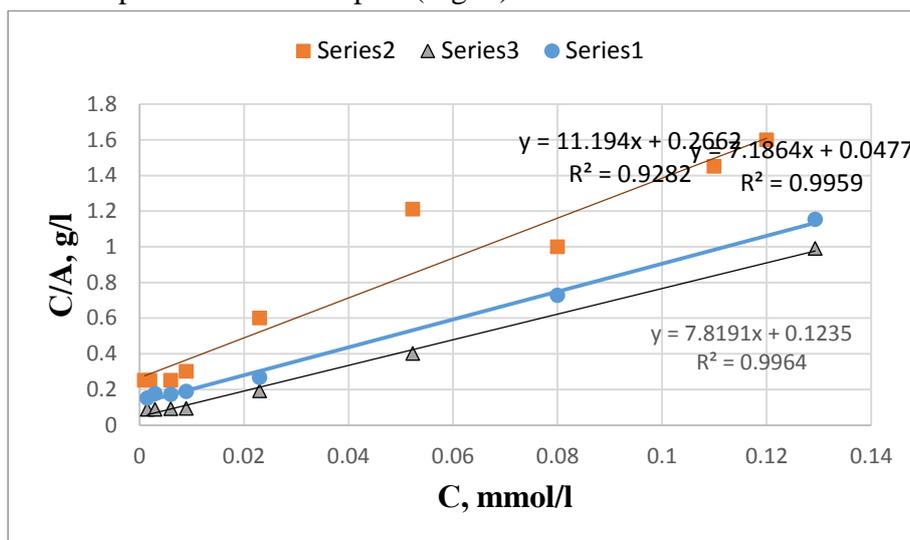


Fig. 2. MG adsorption Isotherms on intercalated samples: 1) 5.1-Fe; 2) 3.1-Fe; 3) 10.1-Fe in the coordinates of the linear Langmuir equation.

Experimental data on MG adsorption on 5.1-Fe and 10.1-Fe adsorbents have shown that they can be described by the Langmuir equation to the equilibrium concentration, which is proved by high values of the correlation coefficient R^2 . On the contrary, an increase in the values of the equilibrium concentration of 3.1-Fe contributes to a deviation from the linear Langmuir form, which leads to a decrease in the value of R^2 . Fig. 2 illustrates the isotherms of MG adsorption on samples in the coordinates of the Langmuir equation in linear form. Using data from the diagram (the tangent of the inclination angle of the straight line and the value of the segment cut off on the ordinate axis) the corresponding $1/A_{\infty}$ and $1/A_{\infty} * K$ values were calculated for K and A_{∞} . Table 1 shows the parameters of the Langmuir isotherm for these adsorbents.

Table 1.

Parameters of Langmuir isotherms for the studied samples by linear regression method

Parameter	Sample		
	3.1-Fe	5.1-Fe	10.1-Fe
A_{∞} exper., mmol/g	30,3	47,3	40,2
A_{∞} calc., mmol/g	31,2	49,2	41,3
K	0,185	0,214	0,256
R^2	99,6	92,8	99,6

Meanwhile, the Freundlich isotherm describes the adsorption equilibrium on an inhomogeneous surface with an exponential distribution of the adsorption centers, as a result of which the amount of the adsorbed substance often increases not in proportion to its concentration in the solution, but much slower, in proportion to the root of the n th degree of the solution concentration ($n^{-1}=0,1 \leq 0,7$) [27]:

$$A = K_F C^{1/n}, \tag{4}$$

where A is the adsorption value, mmol/g; C is the equilibrium concentration, mmol/l; K_F is the Freundlich constant; n is the constant that characterizes the distribution of adsorption centers by energy.

The parameter $1/n$ characterizes the degree of deviation of the adsorption isotherm from linearity. Values equal to $n=1$ indicate the linearity of adsorption with equipotential adsorption centers, and values of $n>1$ indicate the availability of adsorption centers and the possibility of continuing the adsorption process. Therefore, $n<1$ indicates a weak adsorption bond. The logarithmic form of the equation is more often used in calculations:

$$\ln A = \ln K_F + \frac{1}{n} \ln C. \tag{5}$$

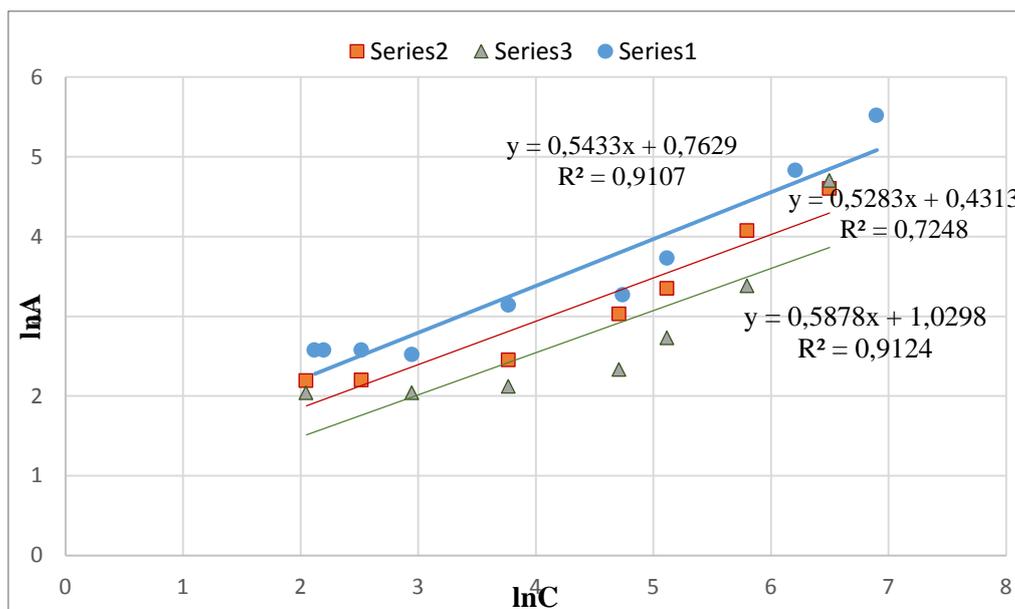


Fig. 3. MG adsorption Isotherms on intercalated samples: 1) 3.1-Fe; 2) 5.1-Fe; 3) 10.1-Fe in the coordinates of the linear Freundlich equation.

High values of the correlation coefficient can be the basis for successful application of the Freundlich model to describe the mechanism of MG adsorption on the studied intercalated systems. The values of K_F and $1/n$ were determined from the slope of the curve and the intersection of the $\ln A$ graph from $\ln C$.

Table 2.

Parameters of the Freundlich isotherm for the studied samples by linear regression method

Parameter	Sample		
	3.1-Fe	5.1-Fe	10.1-Fe
A_{∞} exper., mmol/g	27,6	40,1	39,4

A_{∞} calc., mmol/g	28,6	45,1	40,4
K_F , l/mg	21,1	28,2	25,1
R^2	91,1	72,4	91,2

Linear forms of isotherms (Eqs. 3 and 5) express the smallest deviations between the theoretical calculated equilibrium adsorption data and their experimentally determined values. It should be noted that the data on the amount of MG adsorption on Fe-intercalated adsorbents is suitable for straight lines, which indicates that the Langmuir and Freundlich models can be used to describe the process of MG sorption on these samples. The parameters of the Langmuir and Freundlich equations calculated graphically are shown in tables 1 and 2. From the comparison of data, it can be seen that the Langmuir model is better suited for describing the sorption of MG by the 5.1-Fe sample. The Langmuir and Freundlich models are also suitable for describing MG sorption isotherms on samples 3.1-Fe and 10.1-Fe, but the latter correlates better with experimentally determined adsorption data. According to the statements, MG adsorption occurs on a heterogeneous surface, since active adsorption centers have different values of adsorption energy.

It is well known that the above models do not provide information about the mechanism of the adsorption process. The Dubinin-Radushkevich isotherm is usually used to express the adsorption mechanism on microporous materials with Gaussian energy distribution over a heterogeneous surface [23, 28] and the isotherm equation has the following form:

$$A = A_0 \exp \left[- \left(\frac{\varepsilon}{E} \right)^n \right], \quad (6)$$

where ε is the differential free energy; E is the characteristic free energy. The linear form of the equation has the following form:

$$\ln A = \ln A_0 - K \left(RT \ln \frac{C_1}{C_2} \right), \quad (7)$$

Or it can be written as^

$$\lg A = \lg A_0 - 2,303 \frac{R^2 T^2}{E^2} \left(\lg \frac{C_1}{C_2} \right), \quad (8)$$

where R is the gas constant, 8,314 j/mol·K; T is the absolute temperature, K; C_1 and C_2 are the concentration of the saturated solution and the equilibrium concentration of the solution (mmol/l), respectively.

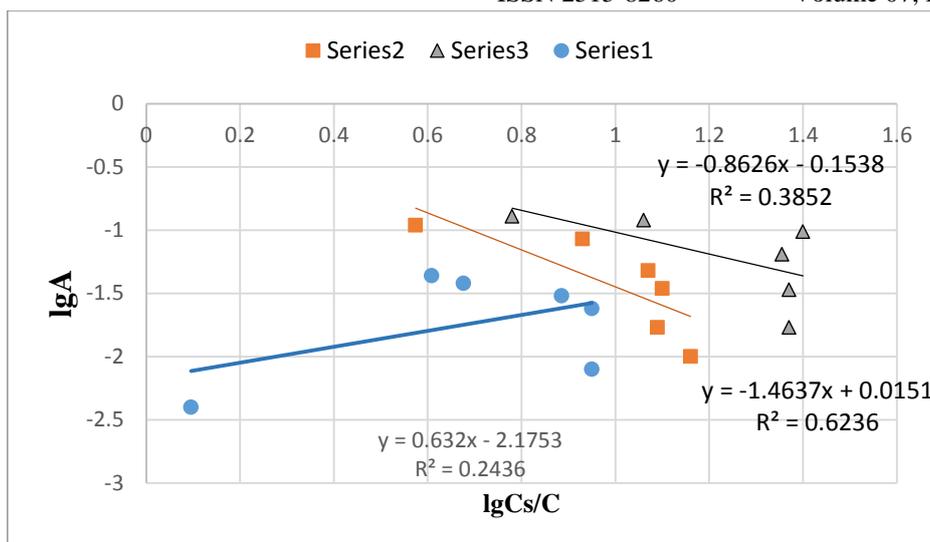


Fig 4. MG adsorption Isotherms on intercalated samples: 1) 3.1-Fe; 2) 5.1-Fe; 3) 10.1-Fe in the coordinates of the linear Dubinin-Radushkevich equation

The apparent adsorption energy for samples can be calculated from the Dubinin-Radushkevich isotherm, which is necessary to distinguish physical and chemical adsorption on the surface of adsorbents. However, as shown in Fig. 3, the MG adsorption isotherms on all the samples under study do not sufficiently correspond to the equation of the pore volume filling theory, therefore, this model is the least successful for describing the adsorption equilibrium and mechanism, especially for samples 3.1-Fe and 10.1-Fe. The calculations have determined the possibility of using this isotherm model to describe the adsorption processes of the 5.1-Fe sample in the range of relatively low values of the equilibrium concentration ($C < 0.2$).

The adsorption of various substances from solutions at the boundary of phase separation between solid surface and water depends on the electrical characteristics of the surface. It is known that an important electrochemical characteristic of the surface is the point of zero charge (PZC). The values of this indicator for the studied samples are 6.02; 5.84 and 5.71 for samples 3.1-Fe; 5.1-Fe and 10.1-Fe, respectively. Heat treatment of samples at temperatures over 200 °C leads to a change in these values towards lower values (pH=4.3 for 10.1-Fe). This is probably due to partial dehydration and dehydroxylation, which leads to changes in the structure of intercalated systems, as well as changes in the number of hydroxyl groups on their surface. Consequently, the surface of the studied objects in the entire range of studied pH has a negative charge, which is favorable for the processes of adsorption of MG.

Study the influence of pH on the adsorption process showed that all the investigated objects have their own characteristic pH, however at pH values over 10 occur the chemical processes that destroy the structure of intercalated clays, therefore, under these conditions, there is no value to specify about the distinctive characteristics of adsorption equilibrium in the system of intercalated clays.

It is known that at low pH values MG will also be protonated, as well as protons from an acidic solution, so in this system, positively charged particles will compete for adsorption centers. The ionic nature of the adsorbate can have a key effect on their retention, both on the surface and inter-surface layers of intercalated systems. Fig. 5 shows curves illustrating the effect of the pH solution on the values of MG adsorption on the samples under study.

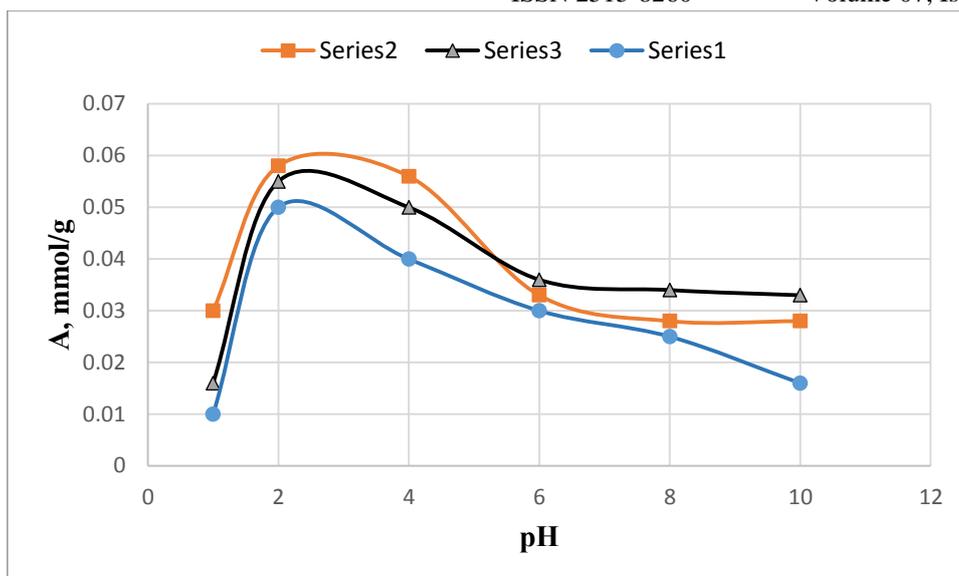


Fig. 5. Influence of pH medium on values of MG adsorption on samples: 1) 3.1-Fe; 2) 10.1-Fe; 3) 5.1-Fe (initial concentration of MG is 0.1 mmol/l, system temperature 20°C, adsorbent consumption 2 g/l).

As shown by research results, reducing the pH of the medium to 2 in the adsorbent + MG system significantly increases the amount of adsorption. Therefore, these systems, whose adsorption isotherms are shown in Fig. 6, were subjected to further research.

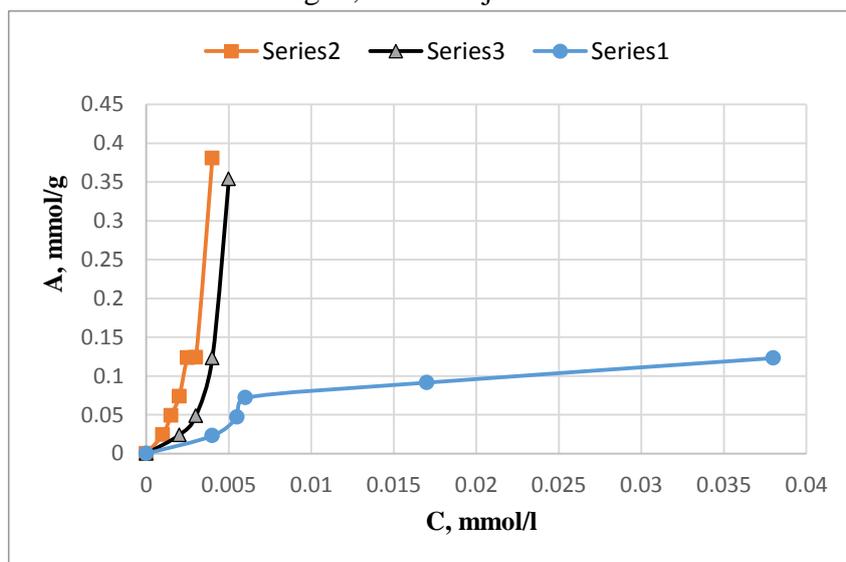


Fig. 6. Isotherms of MG adsorption on adsorbents at 20°C and pH=2, the adsorbent dose is 1 g/l, the initial concentration of the MG solution is 0.01-0.25 mmol/l: 1) 3.1-Fe; 2) 5.1-Fe; 3) 10.1-Fe.

As the curves of these diagrams show, under these conditions, the 10.1-Fe sample has higher sorption characteristics. At low values of the equilibrium concentration, the adsorption capacity for MG reaches 0.381 mmol/g and is 99.5% of its maximum values. With similar values of equilibrium concentrations, the values of the adsorption capacity of 5.1-Fe and 3.1-Fe samples are 0.35 and 0.1231 mmol/g, and are 99.2 and 86.1%, respectively. A further increase in the equilibrium concentration leads to an increase in the amount of adsorption for 5.1-Fe and 10.1-Fe samples, while for 3.1-Fe samples these values remain unchanged. Table

3 shows the parameters of the Langmuir, Freundlich, and Dubinin-Radushkevich equations calculated by the graphical method.

Table 3.

Parameters of Langmuir, Freundlich and Dubinin-Radushkevich isotherms for intercalated systems calculated by the graphical method

Parameter	Sample		
	3.1-Fe	5.1-Fe	10.1-Fe
TheLangmuirmodel			
K, l/mmol	0,26	0,31	0,34
A mmol/g	42,31	56,2	53,4
R ²	99,28	82,11	76,50
TheFreundlichmodel			
K, l/mgr ^{1/n}	21,2	24,6	23,4
1/n	0,131	0,101	0,118
R ²	84,3	99,71	98,26
TheDubinin-Radushkevichmodel			
K _{PD} , l/mmol	9,6*10 ⁻³	5,1*10 ⁻⁴	4,9*10 ⁻⁴
A mmol/g	21,2	25,4	27,9
R ²	55,1	96,5	99,6

The average free energy of adsorption is calculated using the Dubinin-Radushkevich model [29, 30]:

$$E = (-2K)^{-0,5} \quad (9)$$

The value of this energy determines the nature of the adsorption process, i.e. it answers the question about the course of physical ($E < 8$ kJ/mol) or chemical adsorption ($E > 8$ kJ/mol). The values of the characteristic free energy of adsorption calculated using the K_{DP} values for 3.1-Fe; 5.1-Fe and 10.1-Fe are 7.33; 31.31 and 32.96 kJ/mol, respectively. High values of the adsorption energy indicate the chemical nature of the interaction of the adsorbate with the adsorbent. As found, the relatively low values of the correlation coefficient calculated for the 3.1-Fe sample indicate against the applicability of the Dubinin-Radushkevich model to describe the adsorption mechanism for this sample.

The adsorption of MG dye on the studied sorbents depends not only on the number of cation exchange centers, but also on the values of their available surface. Heat treatment of sample data up to 250 °C leads to a change in the structure, as evidenced by changes in the values of PZC. The amount of adsorption of heat-treated intercalated adsorbents 3.2-Fe, 5.2 and 10.2-Fe differs significantly from the previous samples studied, at the corresponding pH values.

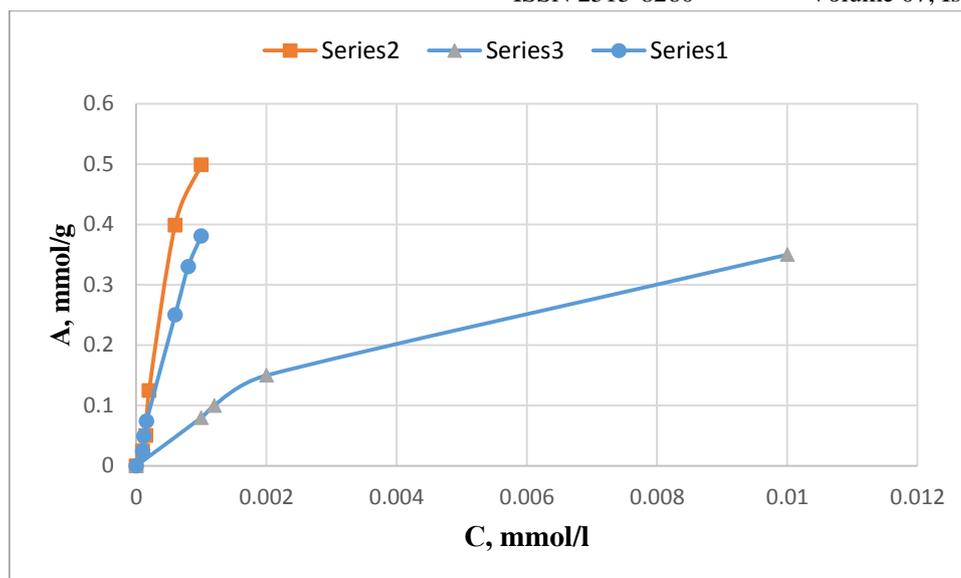


Fig. 7. isotherms of MG adsorption on adsorbents at 20 °C and pH=2, the adsorbent dose is 1 g/l, the initial concentration of the MG solution is 0.01-0.25 mmol/l: 1) 3.2-Fe; 2) 5.2-Fe; 3) 10.3-Fe.

As the curves show, heat treatment of intercalated adsorbents leads to an increase in the adsorption capacity relative to mg by 133; 32 and 8.6% for samples 3.2-Fe; 5.2-Fe and 10.2-Fe, respectively. The MG adsorption data on these samples is compatible with the straight lines of the Langmuir and Freundlich models, and it is important to note that the degree of correlation of the latter exceeds the values of the former for all the studied objects. The free energy values E were calculated from the corresponding K_{DP} values, which are 45; 57 and 51 kJ/mol for 3.2-Fe; 5.2-Fe and 10.2-Fe, respectively, which indicates the chemical nature of the interaction of MG and intercalated adsorbents.

4. CONCLUSIONS

The adsorption of organic dye of methylene blue on three samples of Fe^{+3} intercalated clays of the Navbakhor Deposit was studied. The dependence of adsorption mechanisms on the structure of adsorbents and on the pH values of the system is established. To determine the mechanism of MG adsorption, the data were processed using the Langmuir and Freundlich isotherm equations and constants of these equations were determined. The Langmuir model is better suited to describe the sorption of MG by a 5.1-Fe sample under neutral conditions. Both the Langmuir and Freundlich models are suitable for describing MG sorption isotherms on 3.1-Fe and 10.1-Fe samples, but the second model correlates better with experimentally determined adsorption data. According to which MG adsorption occurs on a heterogeneous surface, since active adsorption centers have different values of adsorption energy.

Heat treatment of sample data up to 250°C leads to a change in the structure, as evidenced by changes in the values of tnz and an increase in the adsorption capacity relative to mg by 133; 32 and 8.6 % for samples 3.2-Fe; 5.2-Fe and 10.2-Fe, respectively. The calculated values of free energy E indicate the chemical nature of the interaction of MG and intercalated adsorbents.

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