

# STRUCTURE FORMATION OF IRON-CONTAINING DISPERSIONS OF ORGANOMONTMORILLONITE

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*The aim of the work is to study the processes of structure formation of organomontmorillonite in iron-containing dispersions by studying the rheological and colloid-chemical properties of such systems. To modify the surface of montmorillonite, a cationic surface-active substance, a quaternary ammonium salt, hexadecyltrimmonium bromide, was used. With the help of X-ray diffraction analysis, we confirmed the penetration of molecules of surface-active substances into the interlayer space of the mineral and its increase to 1.86 nm during the modification mineral surfactant/ cation exchange capacity (S/CEC)=1. The analysis of the results of rheological studies showed that the changes in the characteristics of montmorillonite dispersions depending on the concentration of surfactants are extreme and reach a maximum (6.7 Pa) at the degree of modification of the mineral S/CEC=0.3. The high values of ultimate shear stress confirm the formation of a continuous network between the mineral particles with an "edge-face" orientation. When the surfactant content in the system increases, the ultimate shear stress of the suspension gradually decreases and reaches practically zero values. These results lay the foundation for determining the optimal parameters for the synthesis of iron-containing dispersions based on organomontmorillonite. nZVI was obtained by its reduction on the solid surface of organomodified montmorillonite from a solution of iron(II) sulfate salt. X-ray diffraction data confirmed the fixation of nZVI on the surface of organophilized montmorillonite. Analysis of the results of rheological studies showed that changes in the characteristics of dispersions of iron-containing material based on organomontmorillonite depending on the content of nZVI are extreme and reach a maximum at (6.8 Pa) when the iron content in the sorbent is 0.01 mass fraction in the solid phase of the sorbent. When the content of nZVI is increased to 0.05 mass fraction of the solid phase of the sorbent, it is possible to obtain dispersions with high values of ultimate shear stress (3.3 Pa) and clearly expressed hysteresis loops, which indicates the formation of thixotropic structures and confirms the possibility of its use in permeable reaction barriers. Experimental data confirm that with an increase in the content of nZVI above 0.1 mass fraction in the samples, the ultimate stress and plastic viscosity decrease, which leads to the failure of the suspensions. These results lay foundation for determining the optimal parameters of sorbents synthesis and regulation of their properties by changing the hydrophilic-hydrophobic balance of source systems.*

**Keywords:** bentonite suspensions, chromium(VI), nZVI, organomontmorillonite, rheological properties, sorption

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## 1. Introduction

Introduction provides information on the relevance, purpose and objectives of the study. In addition, montmorillonite has the highest specific surface area among silicates

and is characterized by a high cation exchange capacity. Such properties of the mineral ensure its wide use as a sorbent for the removal of cations of heavy metals, but montmorillonite practically does not remove anions (Zhdanyuk et al., 2016). One of the

effective ways to increase the sorption properties of natural silicates is to modify their surface with surfactants.

The essence of this method is cation exchange reactions. Interlayer cations of clay minerals are replaced by quaternary ammonium cations (Guo et al., 2020). The use of quaternary amine salts with the number of hydrocarbon atoms in nonpolar aliphatic groups more than 12 contributes to more effective displacement of interlayer cations

Surface modification of montmorillonite with hexadecyltrimmonium bromide (HDTMA) allows changing the hydrophilic-hydrophobic balance of the mineral surface. This process is accompanied by a change in surface charge from negative to positive, which determines the maximum sorption of  $\text{CrO}_4^{2-}$  anions at neutral and alkaline pH values. In addition, the application of surfactant on the surface of the mineral can improve the rheological properties of its suspensions (Zheng et al., 2019).

Additional application of nZVI on the organo-modified surface of montmorillonite makes it possible to obtain a highly selective sorbent capable of removing cations and anions of heavy metals due to sorption and reduction mechanisms. Such sorbents are characterized by a unique ability to remove both cations and anions of heavy metals and radionuclides from water environments (Pang et al., 2014; Yin et al., 2020; Yin et al., 2021).

When low doses of nZVI are introduced into the composite based on organomontmorillonite, it is possible to obtain stable suspensions with clearly defined ultimate shear stresses and hysteresis loops, but when the content of nZVI increases, the suspension loses stability and collapses. Thus, the study of the processes of structure

formation in dispersions of iron-containing sorbents based on organomontmorillonite is of a rather limited nature. Therefore, the use of rheological methods to study the processes of structure formation in montmorillonite dispersions in the presence of cationic surfactants and nZVI is undoubtedly an urgent task (Wu et al., 2019). In addition, to confirm the possibility of using such dispersions for the extraction of heavy metal ions, it is advisable to study their sorption properties (Wu et al., 2012).

The purpose of the work is to study the effect of HDTMA and nZVI on structure formation in montmorillonite suspensions by studying the rheological properties and the possibility of using the obtained sorbents in permeable reaction barriers for the purification of groundwater from heavy metal ions and radionuclides. It is also necessary to evaluate the sorption properties of the obtained dispersions.

## 2. Materials and Methods

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Montmorillonite (Cherkasy deposit, Ukraine), pre-cleaned from quartz impurities by the sedimentation method, was taken as the starting material. Montmorillonite is a natural silicate with a 2:1 layered structure, high dispersion and swelling ability. The general structural formula of montmorillonite is  $(\text{Ca}, \text{Na})_{0,2}(\text{Al}, \text{Mg}, \text{Fe})_2[(\text{Si}, \text{Al})_4\text{O}_{10}](\text{OH})_2 \cdot n\text{H}_2\text{O}$ . Chemical composition of the mineral:  $\text{SiO}_2$  – 51,9 %,  $\text{Al}_2\text{O}_3$  – 17,10 %,  $\text{Fe}_2\text{O}_3$  – 7,92 %,  $\text{MgO}$  – 1,18 %,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{CaO}$  to 2 %,  $\text{H}_2\text{O}$  – 8,78 %. For further experiments, the Na-form of the mineral was used, which was obtained by treating purified natural samples three times with a 1M solution of NaCl, followed by repeated washing (the sample is labeled MT).

The following chemically pure reagents produced by the company (Merck) were used in the experiments: hexadecyltrimethylammonium bromide ((C<sub>16</sub>H<sub>33</sub>)N(CH<sub>3</sub>)<sub>3</sub>Br), heptahydrate of ferrum(II) sulfate Fe<sub>2</sub>SO<sub>4</sub>·7H<sub>2</sub>O and sodium borohydride (NaBH<sub>4</sub>).

Organophilized samples of the mineral were obtained according to known methods with some changes. The initial suspension of montmorillonite was pretreated using a UZDN-2T disperser (Ukraine) with ultrasound at a frequency of 22 kHz and a radiation intensity of 12 W/cm<sup>2</sup> for 10 minutes. After that, the surface of the montmorillonite was modified with hexadecyltrimethylammonium bromide (HDTMA) in a defined ratio of surfactants/CEC (marked as OMT).

To obtain iron-containing samples based on organomontmorillonite, a FeSO<sub>4</sub> salt solution was added to the organomontmorillonite dispersion and nZVI was reduced with an excess of NaBH<sub>4</sub> on the surface of the organomodified mineral with constant stirring without the use of an inert atmosphere according to known methods with some differences. Samples are labeled as nZVI-OMT.

X-ray studies of the original and modified samples were carried out using a DRON-4-07 (RF) diffractometer in the range 1 – 60° (2θ) using CuK of α-radiation.

The study of the sedimentation stability of dispersions was carried out with samples of organomontmorillonite at the degree of modification of their surface S/CEC=0.1-1. The height of the sediment was measured 24 hours after the preparation of the dispersions. The concentration of the solid phase in the studied suspensions was 2 %.

The rheological properties of the dispersions were determined using a rotary viscometer "Reotest-2" (Germany) with temperature control of the samples at 25 °C. For rheological studies of organomontmorillonite suspensions, samples with a degree of surface modification of the mineral S/CEC=0-0.4 were used.

For the study of rheological studies of iron-containing suspensions of organomontmorillonite, samples with a degree of modification of the surface of the mineral were used, where S/CEC=0.2. The nZVI content in the samples ranged from 0.01 to 0.2. The concentration of the solid phase in the suspensions was 2 %. To analyze the obtained results, the Shvedov-Bingham rheological model was used, characterized by two parameters: τ<sub>0</sub> – ultimate shear stress and plastic viscosity – η.

$$\tau = \tau_0 + \eta \cdot D,$$

where τ is the shear stress, Pa; D is the shear rate, c<sup>-1</sup>.

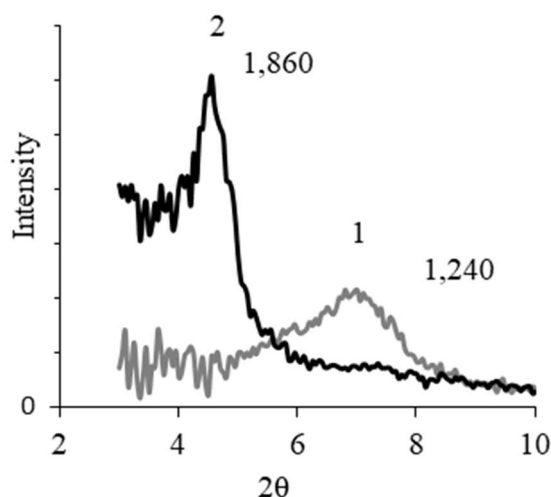
Experiments on the removal of Cr (VI) were carried out under static conditions at a temperature of 25°C. The ratio of solid and liquid phases was 0.1 g per 0.05 L. After establishing the adsorption equilibrium (within 1 hour), the aqueous phase was separated by centrifugation and the equilibrium concentration of Cr(VI) was determined in it by the spectrophotometric method on the UNICO 2100UV device (USA) using the diphenylcarbazide reagent at a wavelength of 540 nm according to the standard method. The initial concentration of Cr(VI) anions was 10 mg/L. The value of sorption of Cr(VI) (a) was calculated by formula:

$$a = \frac{(C_0 - C_p) \cdot V}{m},$$

where  $a$  – adsorption, mg/g;  $C_0$  and  $C_p$  – initial and equilibrium concentration of the metal, mg/L;  $V$  is the volume of solution, L;  $m$  is the mass of the weight portion of the sorbent, g.

### 3. Results and Discussion

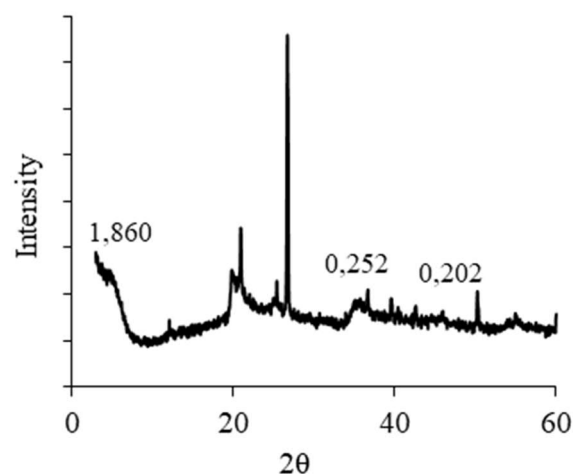
The layered structure of montmorillonite is capable of swelling and increasing the interlayer space due to the penetration of surfactant molecules into it. Thus, the diffractograms of the original montmorillonite and modified HDTMA at  $S/CEC=1$  showed that the interlayer space of the mineral increases from 1.24 nm to 1.86 nm (Fig. 1).



**Fig. 1.** Diffractograms of the studied samples: 1 – MMT; 2 – OMMT

The value of the interlayer space indicates a close to parallel orientation of HDTMA molecules relative to the basal surfaces of the mineral particles (Zhdanyuk & Chudinovych, 2019). X-ray data of an iron-containing sample confirmed the fixation of crystalline phases of nZVI and iron oxides on the surface of organophilized montmorillonite, which is confirmed by peaks

at 44.88 and 35.76 degrees, respectively (Fig. 2), and also, at lower values, goethite.



**Fig. 2.** Diffractogram of the nZVI-OMMT sample

In order to obtain stable suspensions of organomontmorillonite with their subsequent use for obtaining iron-containing suspensions, flocculation of HDTMA-MT systems was studied. The study of the sedimentation height of montmorillonite suspensions modified by HDTMA showed that with an increase in the surfactant content in the suspension, its gradual delamination is observed already at a ratio of  $S/CEC = 0.2$ . When the surfactant content in the dispersion is increased, we observe the flocculation of the system due to the compensation of the charge of the particles. The lowest height of the sediment was recorded for the sample at  $S/CEC = 1$ .

This is due to the gradual lyophobicization of the surface of the particles and a decrease in the thermodynamic stability of the colloidal system (Zhdanyuk & Chudinovych, 2019). Table 1 shows data for organomontmorillonite suspension with a solid phase concentration of 2 %. The value of the interlayer space indicates a close to parallel orientation of HDTMA molecules

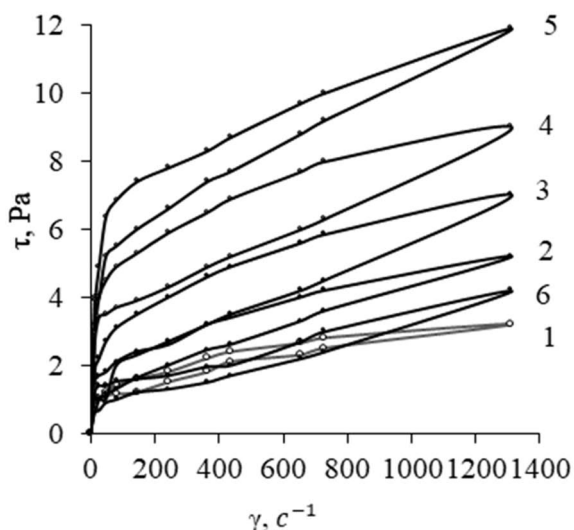
relative to the basal surfaces of the mineral particles.

**Table 1.** The degree of delamination of organomontmorillonite suspensions depending on the S/CEC

S/CEC	0	0.05	0.1	0.2	0.4	0.8	1.0
Suspension eight, %	99	99	99	98	83	53	41

Based on the results of the sediment height in the HDTMA-MT system, dispersions with a degree of mineral modification of S/CEC=0-0.4 were selected for conducting rheological studies.

Analysis of the rheological flow curves of suspensions of the original montmorillonite and in the presence of cationic surfactants confirm the significant influence of surfactants on the structural and mechanical properties of dispersions (Fig. 3).



**Fig. 3.** Rheological curves of the flow of dispersions of the organomontmorillonite from the surface modification degree of S/CEC: 1 – 0; 2 – 0.05; 3 – 0.1; 4 – 0.2; 5 – 0.3; 6 – 0.4

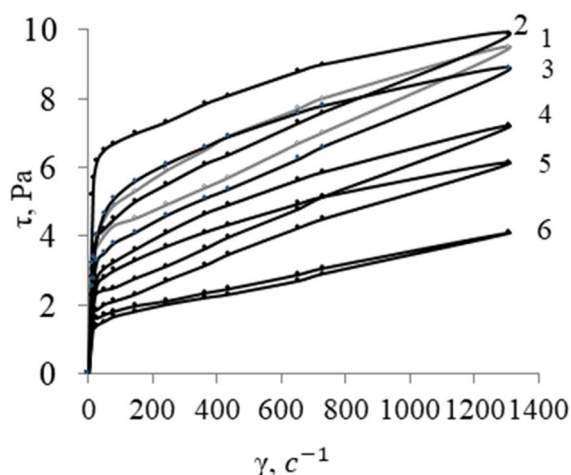
As it can be seen from the presented data, the rheological curves have a typical form for clay dispersions with clearly defined ultimate shear stresses and hysteresis loops, which indicates the formation of thixotropic structures (Gamal et al., 2019). Based on the study of the processes of structure formation in montmorillonite dispersions, the extreme nature of the dependence of structural and mechanical characteristics on the concentration of cationic surfactants was established. The maxima on the curves of the dependence of the ultimate shear stress on the surfactant concentration correspond to the formation of a continuous mesh between particles of the "edge-face" type.

The obtained results are the basis for determining the optimal parameters for the synthesis of porous heterostructures and regulating their properties by changing the hydrophilic-hydrophobic balance of the initial systems. The obtained data show that the area of hysteresis and shear stress gradually increase when the surface of the mineral is modified up to 0.2. At S/CEC=0.3, we observe an increase in shear stress, which confirms the strength of the system, and a decrease in the area of hysteresis, which indicates a decrease in the degree of its thixotropy. With an increase in the surfactant content in the system up to 0.4, we observe a sharp decrease in the ultimate shear stress and hysteresis area.

The continuous structural network is destroyed, the system loses its aggregative stability, which leads to the formation of a dense sediment. This is explained by the hydrophobic interaction of the alkyl parts of surfactant ions adsorbed on different montmorillonite particles. Thus, the initial system is a pseudo-plastic non-Newtonian

fluid, but with an increase in S/CEC, such a system turns into a Newtonian one.

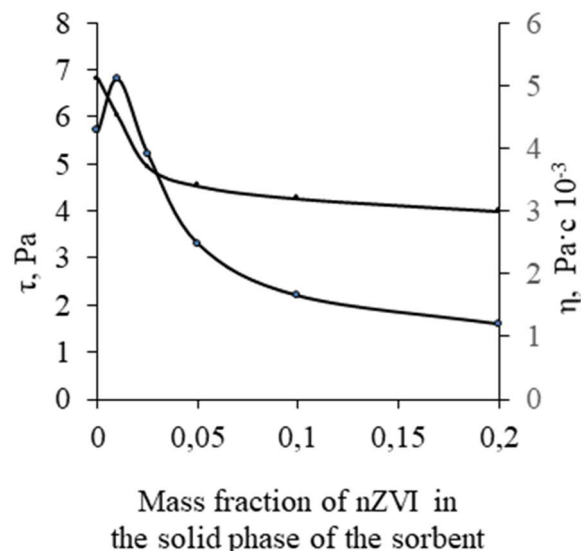
The obtained results are the basis for determining the optimal parameters for the synthesis of sedimentation-resistant iron-containing dispersions based on organomontmorillonite. To obtain iron-containing suspensions, we used montmorillonite, modified by HDTMA at S/CEC = 0.2. nZVI was introduced in quantities sufficient to carry out the technological process of cleaning polluted waters. As can be seen from the presented data, the rheological curves of iron-containing suspensions with clearly defined ultimate shear stresses and hysteresis loops (Fig. 4).



**Fig. 4.** Complete flow curves of suspensions of organomontmorillonite S/CEC=0.2 and iron-containing composites with nZVI content: 1 – 0; 2 – 0.01; 3 – 0.025; 4 – 0.05; 5 – 0.1; 6 – 0.2

Rheological studies of dispersions of organomontmorillonite and its modified forms confirm the significant influence of nZVI on the rheological properties of the dispersion. Shear stress and plastic viscosity were calculated based on the flow curves of the suspensions (Fig. 5).

Experimental data of rheological studies show that with an increase in the iron content in the samples, the ultimate stress and plastic viscosity decrease. The decrease in ultimate shear stress is due to the fact that nZVI iron particles are located in the contact points of colloidal montmorillonite particles in the thin residual layers of the dispersion medium.



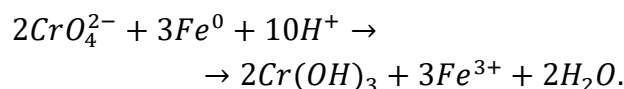
**Fig. 5.** Rheological parameters of montmorillonite suspensions: 1 – ultimate shear stress; 2 – plastic viscosity

This leads to a decrease in van der Waals forces, due to which the coagulation structure of the montmorillonite suspension is formed, and, as a result, to a decrease in the strength of the structure and the beginning of its destruction under the action of lower shear stresses. The plastic viscosity decreases with an increase in the content of nZVI, which affects the flow of the dispersion medium (Zhdanyuk et al., 2016).

The iron-containing sorbent removes Cr(VI) ions from aqueous solutions by two parallel mechanisms: sorption and reduction. According to the first, anionic forms of chromium are sorbed by the active centers of the hydroxide film formed on the surface of iron nanoparticles as a result of their partial

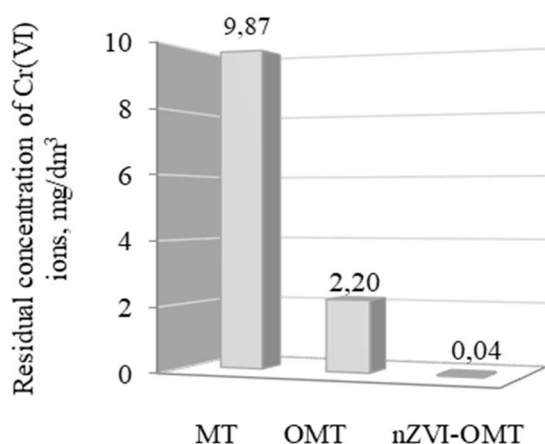
oxidation (the so-called "core-shell" structure) (Pang et al., 2014; Zhdanyuk et al., 2016; Wu et al., 2012, Yin et al., 2020; Yin et al., 2021).

According to the second, hexavalent chromium is reduced by nanodispersed zero-valent iron to the trivalent state according to the following reaction:



At the same time, trivalent chromium ions can also be sorbed on the surface of nZVI with the formation of complex hydroxocomplexes or be in solution in the form of non-toxic  $Cr^{3+}$  cations.

The results of testing the effectiveness of the developed sorbent on model waters with a Cr(VI) ion content of 10 mg/dm<sup>3</sup> at pH=7 are presented in Fig. 6.



**Fig. 6.** Residual concentration of Cr(VI) ions

Sorption studies confirm that the residual concentration of Cr(VI) anions was 0.03 mg/L. Thus, the purification of aquatic environments by the synthesized iron-containing composite from Cr(VI) ions reached the maximum permissible concentration (MPC) level of 0.05 mg/L.

The conducted studies provide a broader vision of the synthesis of sorbents based on natural silicates for the extraction of heavy metal anions and radionuclides, namely, the possibility of extracting Cr(VI), U(VI) directly from soil layers.

#### 4. Conclusions

The analysis of rheological studies showed that the studied systems are pseudoplastic non-Newtonian fluids characterized by sufficiently high values of structural and mechanical characteristics. In dispersions of original montmorillonite, organomontmorillonite and in aqueous dispersions of nZVI-OMT, thixotropic coagulation-condensation structures are formed, which are characterized by sufficiently high values of structural and mechanical characteristics.

It has been proven that nZVI-OMT aqueous dispersions remain aggregatively and sedimentationally stable when the surface of montmorillonite is modified using HDTMA with S/CEC=0.2 and nZVI content in the solid phase up to 0.1 mass fraction. This makes it expedient to use them in the latest environmental protection technologies, by injecting aqueous dispersions of nanomaterials into contaminated soil layers.

It was figured out that the synthesized composite is characterized by high sorption properties in relation to Cr(VI) anions. Sorption studies confirm that the residual concentration of Cr(VI) anions was 0.03 mg/L at the initial concentration of 10 mg/L. Thus, the use of iron-containing dispersions based on organomontmorillonite makes it possible to remove Cr(VI) anions from water environments up to the maximum permissible concentration level of 0.05 mg/L.

This makes it expedient to use iron-containing sorbents based on

organomontmorillonite in the latest environmental protection technologies based on in situ decontamination of groundwater contaminated with dangerous organic and inorganic toxicants.

## Acknowledgments

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# СТРУКТУРОУТВОРЕННЯ В ДИСПЕРСІЯХ ЗАЛІЗОВМІСНИХ ДИСПЕРСІЙ ОРГАНОМОНТМОРИЛОНІТУ

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*Метою роботи є вивчення процесів структуроутворення в залізовмісних дисперсіях органоментморилоніту шляхом вивчення реологічних та колоїдно-хімічних властивостей таких систем. Для модифікації поверхні монтморилоніту використано катіонну поверхнево-активну речовину, сіль четвертинного амонію — гексадецилтриамоній бромід. За допомогою рентгенівського дифракційного аналізу ми підтвердили проникнення молекул поверхнево-активних речовин у міжшаровий простір мінералу та збільшення його до 1,86 нм при модифікації мінералу ПАР/КОС=1. Аналіз результатів реологічних досліджень показав, що зміни характеристик дисперсій монтморилоніту в залежності від концентрації ПАР носять екстремальний характер і досягають максимуму (6,7 Па) при ступені модифікації мінералу ПАР/КОС=0,3. Високі значення граничного напруження зсуву підтверджують утворення безперервної сітки між частинками мінералу з орієнтацією «ребро-грань». При збільшенні вмісту ПАР у системі граничне напруження зсуву суспензії поступово знижується і досягає практично нульових значень. Ці результати закладають основу для визначення оптимальних параметрів синтезу залізовмісних дисперсій на основі органоментморилоніту. Наночастинки заліза отримували шляхом його відновлення на твердій поверхні органономодифікованого монтморилоніту з розчину солі ферум(II) сульфату. Дані рентгенофазового аналізу підтвердили закріплення наночастинок заліза на поверхні органофілізованого монтморилоніту. Аналіз результатів реологічних досліджень показав, що зміни характеристик дисперсій залізовмісного матеріалу на основі органоментморилоніту в залежності від вмісту наночастинок заліза мають екстремальний характер і досягає максимуму при (6,8 Па) при вмісті заліза у сорбенті 0,01 масових частки у твердої фази сорбенту. При підвищенні вмісту наночастинок заліза до 0,05 масової частки твердої фази сорбенту дозволяє отримати дисперсії з високими значеннями граничного напруження зсуву (3,3 Па) та чітко вираженими петлями гістерезису, що вказує на формування тиксотропних структур та підтверджує можливість її використання у проникних реакційних бар'єрах. Експериментальні дані підтверджують, що із збільшенням вмісту наночастинок заліза понад 0,1 масової частки в зразках, граничне напруження та пластична в'язкість зменшуються, що призводить до руйнування суспензій. Отримані результати створюють основу для визначення оптимальних параметрів синтезу сорбентів та регулювання їх властивостей шляхом зміни гідрофільно-гідрофобного балансу вихідних систем.*

**Ключові слова:** наночастинки заліза, органоментморилоніт, реологічні властивості, сорбція, суспензії бентоніту, хром(VI)