

*Досліджено фізико-хімічні особливості синтезу наноматеріалів на основі монтморилоніту та органоментморилоніту модифікованих нанорозмірним залізом. Проведено дослідження реологічних властивостей дисперсій отриманих матеріалів. Показано можливість їх використання при очищенні підземних вод із застосуванням сучасних природоохоронних технологій*

*Ключові слова: стабілізоване нанодисперсне залізо, монтморилоніт, органоментморилоніт, сорбція, хром(VI), реологічні властивості*

*Исследованы физико-химические особенности синтеза наноматериалов на основе монтмориллонита и органоментморилонита модифицированных наноразмерным железом. Проведено исследование реологических свойств дисперсий полученных материалов. Показана возможность их использования при очистке подземных вод с применением современных природоохраных технологий*

*Ключевые слова: наноразмерное железо, монтмориллонит, органоментмориллонит, сорбция, хром(VI), реологические свойства*

# OBTAINING STABILIZED NANODISPERSED IRON BASED ON ORGANOFILIZED MONTMORILLONITE

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## 1. Introduction

The prospects of applying nanomaterials in a variety of fields including environmental protection have been attracting the attention of scientists lately [1, 2].

One of such materials is nanocomposites based on nanoiron, which display high characteristics when cleaning water environments from organic and inorganic toxicants [3].

The effectiveness of the use of such materials is connected with the small sizes of iron nanoparticles and, accordingly, their large specific surface and high chemical activity. Despite all the positive results, such systems have a number of disadvantages, the main of which is an essential tendency of particles to aggregation and a high speed of oxidation. One of the ways of slowing down these processes is immobilization of particles of nanoiron on the surface of the dispersed inorganic matrix [4]. Therefore, montmorillonite, which is characterized by relative cheapness and has high specific surface, was chosen in the study as a substrate for nano-dimension zero-valent iron.

On the other hand, it is known that the purposeful regulation of the hydrophobic and hydrophilic properties of the surface allows influencing the course of processes on it. The speed of nucleation and the number of primary nuclei on the surface defines dimensions and final properties of the obtained nanoparticles [1]. The possibility of regulation of sorption properties of iron-containing nanomaterials based on montmorillonite, as a result of surface organofilization, was studied.

Thus, the relevance of the work is predetermined by the need for improving modern highly effective sorbents and technological decisions regarding their application for the extraction of heavy metals and radionuclides from aquatic environment.

## 2. Literature review and problem statement

Synthesis of zero-valent iron for using in environmental protection technologies is conducted in different ways. Namely, the reduction of goethite or hematite particles by hydrogen at temperature of 200–600 °C or by decomposition of  $\text{Fe}(\text{CO})_5$  in the organic solvents or in argon medium. But the most common way is the reduction of  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  ions from the solutions of their salts using boron hydrides of alkali metals [4].

Zero-valent iron, obtained in this way, has a typical so-called "core-shell" structure, in which central part consists of zero-valent iron and the surface is covered with a thin layer of Fe(II) and Fe(III) oxides, which are formed as a result of oxidation processes [5]. These materials have large specific surface and high reactivity [6]. However, an essential drawback is the fact that zero-valent nanoiron has a tendency to aggregate and is easily oxidized with the formation of oxide layer on the surface of the particles. These factors reduce activity and effectiveness of zero-valent nanoiron [7].

The application of zero-valent nanoiron on the inorganic matrix allows significant slowing down the aggregation of

nanoparticles and their oxidation. The composite, in which activated carbon, a typical sorbent, was used as a substrate for nano-dimension zero-valent iron, was synthesized by authors [8]. Given that the cost of these composites is very high, there is a need to search for alternative materials for mineral substrate. To obtain stable nano-dimension iron on the mineral surface, some authors used silicate materials that are significantly cheaper than coal. So, in paper [9], the possibility of using materials based on  $\text{SiO}_2$  as the basis for  $\text{Fe}^0$  was shown. Porous silicon dioxide was obtained, and highly dispersed and active zero-valent iron covered with a layer of  $\text{FeOOH}$ , immobilized in mesoporous microspheres of  $\text{SiO}_2$ , was synthesized. In article [10], iron-containing sorbents, where natural silicate material kaolin was used as a material for substrate, were obtained. These composites were developed to remove contaminated ground waters and displayed higher sorption properties in comparison with natural kaolin. But given that specific surface of kaolin is not quite developed, and therefore the capacity for absorption is low, there was a need for studying other clay minerals with much higher sorption properties. So, zero-valent iron nanoparticles were successfully synthesized on the surface of montmorillonite [11]. The composites, obtained in this way, contained stable highly dispersed particles of  $\text{Fe}^0$ , which had “core-shell” structure, the shell thickness of which was 3 nm and remained virtually unchanged under conditions of the environment. The similar results were obtained in paper [12]. The synthesized material showed high sorption properties. Thus, montmorillonite as a mineral substrate deserves attention for further research. The disadvantage of this synthesis is that it is conducted in the inert atmosphere with the use of high surplus of  $\text{NaBH}_4$ . Articles [13, 14] describe the synthesis of nanomaterial based on montmorillonite, modified by the cation surface active substance (SAS) hexadecyltrimethylammonium bromide (HDTMA).

Given that the conditions of synthesis of stable nano-dimension iron on the surface of natural silicates have not been studied enough, there is a need for additional research in order to obtain iron-containing composites. The purposeful regulation of hydrophobic and hydrophilic balance of the matrix surface due to its organofilization with the help of SAS will give the opportunity to influence the course of processes of formation of iron nanoparticles, thus forming high sorption properties.

### 3. The aim and the tasks of the study

The aim of this work is synthesis of iron-containing nanocomposites based on organomontmorillonite for extracting ions of heavy metals from aqueous environment.

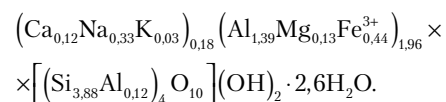
To achieve the set aim, it is necessary to solve the following problems:

- to explore physical and chemical features of the processes of synthesis of nanomaterials based on organofilized laminated silicates and nanodispersed iron;
- to explore special features of extraction of  $\text{Cr(VI)}$  ions from aqueous environment using the obtained nanomaterials;
- to investigate rheological properties of the obtained composite materials and to demonstrate possibility of using them for cleaning aqueous environment contaminated with ions of heavy metals in situ.

## 4. Materials and methods of the study

### 4.1. Synthesis of nanomaterials

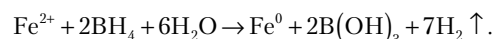
As the object of the study we took natural silicate with laminated structure of 2:1 and swelling structural packages – montmorillonite of the Cherkassky deposit, which has general structural formula



The following chemically pure reagents produced by the company (Merck):  $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ , hexadecyltrimethylammonium bromide (HDTMA) and sodium borohydride ( $\text{NaBH}_4$ ) were used in the experiments.

Montmorillonite (further MMT) was cleaned from impurities by the method of sedimentation of coarse dispersed phase. Organomontmorillonite (OMMT) was obtained by modifying the surface of MMT by the cation surface active substance HDTMA.

The synthesis of nano-dimension zero-valent iron (NZI) was carried out without the use of inert atmosphere by the techniques described earlier [14, 15] with some modifications. Reduction of iron is performed by reaction:



The solution  $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  of volume  $200 \text{ cm}^{-1}$  of certain concentration was put into a three-neck flask, and while stirring, the reducing agent  $\text{NaBH}_4$  of volume  $100 \text{ cm}^{-1}$  was slowly added for 1 hour with the use of a peristaltic pump. The excess of  $\text{BH}_4^-$  in the reaction amounted to 30 % of stoichiometric amount according to the equation of reaction. Once the entire volume of the reducing agent was used, the mixture was stirred for another 1 hour. The resulting nano-dimension iron was separated from the liquid phase by centrifugation, washed three times with alcohol and dried under vacuum at temperature of  $80^\circ \text{C}$ .

Similarly the iron-containing nanomaterials, where OMMT and MMT were used as substrates, were synthesized. Mass ratio between the components of the composite sorbent was 0,25 g  $\text{Fe}^0$  to 1 g montmorillonite ( $\text{Fe}^0$ -MMT (0,25:1)) or organomontmorillonite ( $\text{Fe}^0$ -OMMT (0,25:1)).

The samples for examining rheological properties of the materials were prepared by the technique described above with some modifications. The original suspension of montmorillonite was pretreated using the dispersant UZDN-2T by the ultrasound of frequency 22 kHz and radiation intensity of  $12 \text{ W/cm}^2$ . Duration of treatment was 10 minutes. After that the surface of montmorillonite was modified with HDTMA in the ratio  $\text{CEC/SAS}=0,1$  ( $\text{OMMT}_p$ ). The samples prepared in this way without cleaning with SAS were mixed with the solution of  $\text{FeSO}_4$  and reduced with the excess of  $\text{NaBH}_4$  at constant stirring. The samples with the different  $\text{Fe}^0$  content were synthesized, the ratio of  $\text{OMMT}_p/\text{Fe}^0$  by mass was: 1:0, 1:0.025, 1:0.1 and 1:0.2 (the samples are marked, respectively,  $\text{OMMT}_p/\text{Fe}^0$  (0,01),  $\text{OMMT}_p/\text{Fe}^0$  (0,025),  $\text{OMMT}_p/\text{Fe}^0$  (0,01) and the sample  $\text{OMMT}_p/\text{Fe}^0$  (0,2). The suspensions of 2% mass fraction of solid phase, obtained in this way, were used for rheological studies.

#### 4. 2. Physical and chemical methods of studying nano-materials

X-ray diffraction examination of the original and modified samples was carried out using the diffractometer DRON-4-07 in the range of 1–60° (2θ) using CuK of α-radiation. Diffractograms of the cleaned original samples of montmorillonite indicate their practical monominerality and existence of only minor quartz impurities in them.

Infrared spectroscopic study of the samples was carried out at the Fourier spectrometer Spectrum-One (Perkin-Elmer) in the range of 4000–450 cm<sup>-1</sup> at twenty-fold scanning.

The processes of Cr(VI) extraction from waters were studied using the sample solutions, which were prepared in distilled water using the salt K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and 1 M of the NaCl solution for creating necessary ionic strength (I=0.01). The pH value of the sample solutions were corrected with 0.1 M solutions of NaOH and HCl and controlled by the ionmeter I-160M.

Experiments of chromium extraction were conducted under static conditions at temperature of 25 °C. The weight portion of the mineral in the experiments amounted to 0.1 g, the volume of water phase was 50 cm<sup>3</sup>. After establishing adsorption equilibrium (within 1 hour), the aqueous phase was separated by centrifuging and equilibrium concentration of Cr(VI) was defined by the spectrophotometric method (UNICO 2100UV) using the reagent diphenylcarbazide with wavelength of 540 nm by standard technique.

The value of sorption of Cr(VI) (a) was calculated by formula:

$$a=(C_0-C_p)V/m, \text{ mg/g,}$$

where C<sub>0</sub> and C<sub>p</sub> are the initial and equilibrium concentration of metal, mg/dm<sup>3</sup>; V is the volume of solution, dm<sup>3</sup>; m is the mass of the weight portion of the sorbent, g.

Rheological properties of montmorillonite dispersions were determined using the rotational viscosity meter «Reo-test-2» (Germany) with the thermostatic control of the samples at 25 °C. Concentration of solid phase in the suspension amounted to 2 %.

#### 5. Results of research into physical and chemical features of the synthesis of stabilized nano-dimension iron

As can be seen from diffractogram (Fig. 1, a), the original MMT has clear reflex with the corresponding value of the interlayer distance of 1,235 nm, which is typical for air-dry mineral [16]. Basal reflex of the modified material (OMMT) is 2.872 nm, indicating the increase in the interlayer space of montmorillonite, compared with the natural samples, due to intercalation of SAS molecules among structural packages of the mineral. The reflex is not sufficiently expressed as there is irregular filling of the interlayer space of the mineral.

The infrared spectra of the original montmorillonite look typical for this mineral with the absorption bands at 680, 750 and 1030 cm<sup>-1</sup>, which are caused by fluctuating bonds of Si–O, and the bands at 530 and 850 cm<sup>-1</sup> are caused by the fluctuation of the Si–Al–O bond. A very intense band at 3625 cm<sup>-1</sup> refers to the valent fluctuations of groups O–H (Fig. 2). In IR spectra of organofilled montmorillonite, in addition to the basic characteristic bands of montmorillonite, new bands appear at 2921 cm<sup>-1</sup> and 2852 cm<sup>-1</sup>, which correspond to the groups (–CH<sub>2</sub>–) of alkali chains of HMDMA molecules, sorbed on the surface of particles [17].

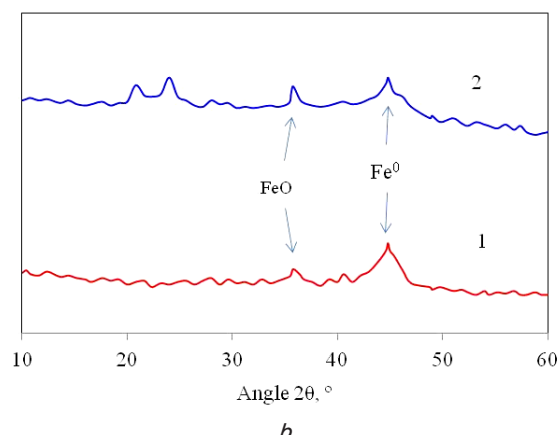
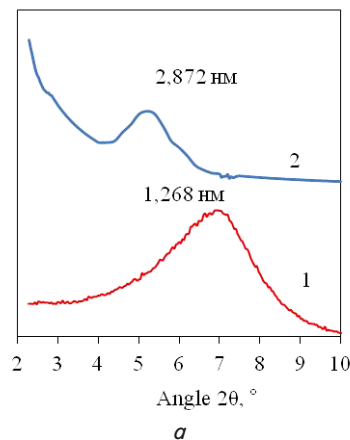


Fig. 1. Diffractograms of the studied samples: a – diffractograms of natural (1) and modified montmorillonite (2); b – diffractograms of the samples of NNI (1) and OMMT/NNI (2)

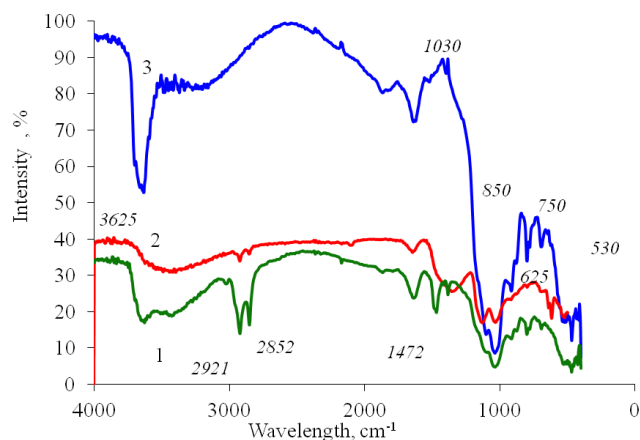


Fig. 2. IR spectra of materials: 1 – OMMT, 2 – OMMT/NNI, 3 – MMT

Diffractograms and IR-spectra of the montmorillonite samples undergo significant changes after formation of nano-dimension iron layer on the surface. Thus, the reflexes at 2θ from 44.8° and 35.8° are registered on the diffractograms of NNI and OMMT/NNI, presented in Fig. 1, indicating the presence of nanoparticles of zero-valent iron (α-Fe) in the samples as well as oxide (FeO) of iron hydroxide (FeOOH) at the lower values of 2θ [18]. In the infrared spectrum of iron-containing montmorillonite (OMMT/NNI), the weakening of bands 2921 and 2852 cm<sup>-1</sup>, which correspond to the groups (–CH<sub>2</sub>–) of alkali chains of SAS molecules,

is observed, and new bands appear at 625 cm<sup>-1</sup>, which is the characteristic for valence fluctuations of Fe–O.

The efficiency of cleaning water environment from pollution with metal anions using the obtained nanomaterials was studied on the example of Cr(VI).

Optimal conditions of carrying out the corresponding experiments were determined in the course of studying kinetics of the processes of extraction of Cr(VI) OMMT and OMMT/NVI (I=0, C=50 mg/dm<sup>3</sup>, pH=7). As can be seen from Fig. 3, the main quantity of ions of chromium (VI) is extracted within 1 hour. That is why this duration of experiments was chosen for further work.

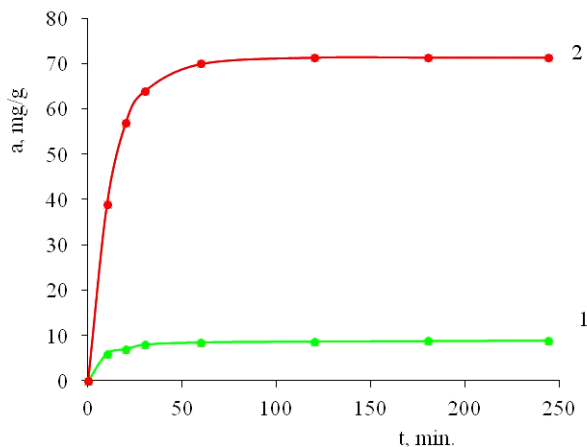


Fig. 3. Kinetics of Cr(VI) removal: 1 – OMMT, 2 – Fe<sup>0</sup> – OMMT (0.25:1)

Fig. 4 presents the curves of dependency of magnitudes of extracting Cr(VI) ions by composite materials (a, mg/g) on the equilibrium concentration of metal in the solution (C<sub>p</sub>, mg/dm<sup>3</sup>). For comparison, dependencies of magnitudes of extracting Cr(VI) ions by montmorillonite, organomontmorillonite and nano-dimension iron Fe<sup>0</sup> are presented as well.

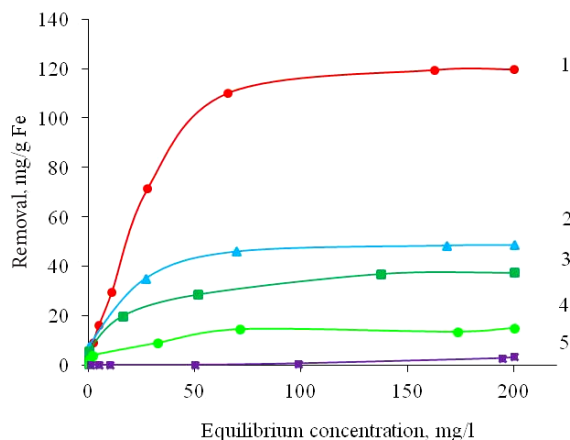


Fig. 4. Isotherms of Cr(VI) sorption at pH=7: 1 – MMT – OMMT, 2 – Fe<sup>0</sup> – OMMT (0.25:1), 3 – nano-dimension Fe, 4 – Fe – MMT (0.25:1), 5 – Fe – OMMT (0.25:1)

To compare the operating efficiency of the obtained samples, specific efficiency was calculated per 1 g of active component of composite material – nanodispersed iron. In conversion to iron, the highest indicators of Cr(VI) extraction were obtained with OMMT/NNI, followed by MMT/NNI

and NNI (Fig. 4). Both iron-containing sorbents MMT/NNI and OMMT/NNI appeared to be much more active compared with NNI. At the OMMT sample, insignificant magnitudes of extraction of Cr(VI) ions were observed compared with the synthesized iron-containing composite materials, while MMT does not practically remove the anions of chromium (VI).

While using the reagents in the powdered form in water protection technologies, rheological properties of their aqueous dispersions are their important characteristic.

Fig. 5 presents rheological curves of the flow of dispersions of organomontmorillonite and the obtained iron-containing nanomaterials based on it. As can be seen from the presented data, rheological curves look typical for clay dispersions with clearly defined boundary shear stresses and hysteresis loops.

For the analysis of obtained results, we used the Shvedov-Bingham rheological model, which is characterized by two parameters:  $\tau_0$  – boundary shear stress and plastic viscosity –  $\eta$ .

$$\tau = \tau_0 + \eta \cdot D, \tag{2}$$

where  $\tau$  is the shear stress, Pa; D is the shear speed, s<sup>-1</sup>.

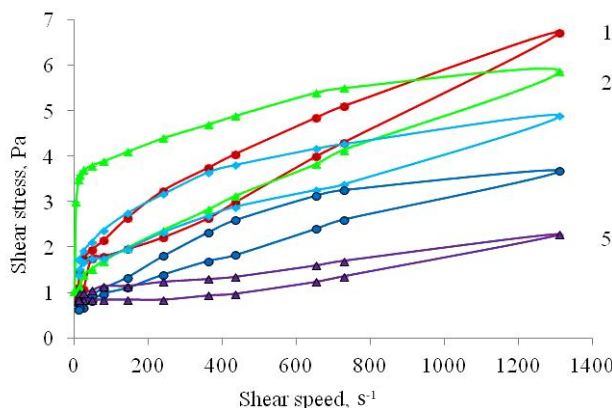


Fig. 5. Rheological curves of the flow of dispersions based on montmorillonite: 1 – OMMT<sub>p</sub>; 2 – OMMT<sub>p</sub>/Fe (0,01), 3 – OMMT<sub>p</sub>/Fe (0,025), 4 – OMMT<sub>p</sub>/Fe (0,1), 5 – OMMT<sub>p</sub>/Fe (0.2)

Parameters of the Shvedov-Bingham equation, obtained on the basis of rheological curves of the flow of the examined suspensions, are given in Table 1.

Table 1

Rheological parameters of montmorillonite suspensions

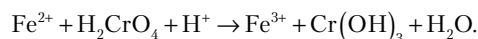
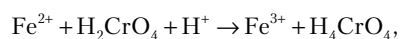
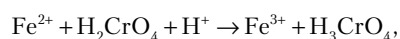
Sample	Boundary shear stress, $\tau_0$ , Pa	Plastic viscosity, $\eta$ , Pa·s
OMMT <sub>p</sub>	2,2	0,0051
OMMT <sub>p</sub> /Fe(0,01)	3,8	0,0045
OMMT <sub>p</sub> /Fe(0,025)	2,4	0,0037
OMMT <sub>p</sub> /Fe(0,1)	1,6	0,0032

Experimental data of rheological studies demonstrate that with the increase in iron content in samples, the boundary stress and plastic viscosity decrease.

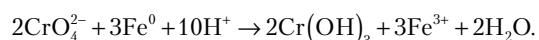
## 6. Discussion of results of research into physical and chemical characteristics of the obtained nanomaterials

In aqueous solutions, Cr(VI) ions, depending on pH and concentration, may exist in the following forms:  $\text{CrO}_4^{2-}$ ,  $\text{HCrO}_4^-$ ,  $\text{H}_2\text{CrO}_4$ ,  $\text{H}_2\text{Cr}_2\text{O}_7$  or  $\text{Cr}_2\text{O}_7^{2-}$ . Accordingly,  $\text{HCrO}_4^-$  is the dominant form of chromium hexavalent chromium in acidic medium, and  $\text{CrO}_4^{2-}$  and  $\text{Cr}_2\text{O}_7^{2-}$  prevail at the increase in pH [19].

The extraction of all forms of hexavalent chromium from aqueous solutions can occur by two parallel mechanisms: sorption and reduction. With the first one, the anionic form of chromium are sorbed by active centers of hydroxide film formed on the surface of iron nanoparticles due to their partial oxidation (so-called "core-shell" structure). With the second one, hexavalent chromium is reduced by nano-dispersed zero-valent iron to the trivalent state [20] by the following possible stages:



Summing up, these reactions can be written down as:



In this case, trivalent chromium ions can also be sorbed on the surface of iron nanoparticles with the formation of complex hydroxocomplexes or be found in the solution in the form of cations  $\text{Cr}^{3+}$ , non-toxic for humans. It should be emphasized that the method for determination of chromium in the solution with the use of the reagent diphenylcarbazide, applied in the work, captures only six-valent chromium and is insensitive to chromium in the trivalent state. That is why the results given in Fig. 3, 4 demonstrate integral extraction of toxic mutagenic hexavalent chromium from the solutions as a result of both its sorption in the form of complicated surface complexes and the reduction to non-toxic trivalent chromium.

All obtained nanocomposites display better sorption-reduction properties than pure nanoiron (Fig. 4). The maximum magnitudes of extraction of Cr(VI) ions are observed for iron-containing nanocomposites with organofilized surface of clay particles. So, for the sample of OMMT/NNI, the magnitude of extracting hexavalent chromium is 120 mg/g of  $\text{Fe}^0$ . MMT/NNI displays lower activity than OMMT/NNI, but larger activity than NNI, OMMT and MMT.

The increase in the activity of composite samples of OMMT/NNI compared with other samples is explained

by the greater dispersion of nanoiron particles, which are formed on hydrophobic surface of organomontmorillonite, compared with the ones on hydrophilic surface of particles of the original montmorillonite or simply in the solution. Nanodispersed state of substance in zero-valent iron, immobilized on the surface of composites, results in increased percentage of the most active surface atoms, which leads to intensification of all sorption-reduction reactions.

However, it is an essential drawback that nano-dimension zero-valent iron has tendency to aggregation and is easily oxidized with the formation of oxide layer on the surface of the particles. These factors decrease the activity and efficiency of nano-dimension zero-valent iron [7].

The application of zero-valent nano-dimension iron on inorganic matrix allows significant slowing down of the aggregation of nanoparticles and their oxidation.

Analysis of obtained rheological data shows that similar to the dispersions of original montmorillonite, in aqueous dispersions of OMMT/NNI, tixotropic coagulation-condensation structures are formed, which are characterized by rather high values of structural-mechanical characteristics.

This makes it appropriate to use them in innovative environmental technologies based on cleaning ground waters contaminated with dangerous organic and inorganic toxicants in situ, by way of pumping water dispersions of nanomaterial into contaminated soil layers [21].

In future, a study of application of the synthesized iron-containing composite materials for extracting U(VI) ions from aqueous environment is planned.

## 7. Conclusions

As a result of conducted studies, iron-containing materials were synthesized on the basis of organofilized montmorillonite. It was proved that a mono layer of SAS, formed on the surface between structural packages of montmorillonite, contributes to the formation of more dispersed particles of zero-valent iron.

It was established that the synthesized composite extracts up to 120 mg/g of Fe ions of Cr(VI), which is much more efficient in comparison with the iron-containing sorbents that do not contain SAS.

It was proved that aqueous dispersions of the obtained material remain resistant to aggregation and sedimentation at iron content in solid phase up to 0,146 %, which makes it possible to use them in innovative environmental technologies based on pumping aqueous dispersions of nanomaterial into contaminated layers of soil.

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