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## MULTIFUNCTIONAL NANOCOMPOSITES AS HIGHLY EFFICIENT SORBENTS FOR PURIFICATION OF TECHNOGENICALLY POLLUTED WATERS

*The article is devoted to the development of nanosized sorbents for the removal of cesium and strontium, as well as heavy metal ions simultaneously present in a multicomponent two-phase solution containing complexing agents and surfactants. Magnetically sensitive nanosorbents are currently considered promising since the influence of external fields can improve the performance of the developed sorbents. To create magnetically sensitive nanoparticles and composites based on them, we used carbon-coated nanoparticles of metals in a composition with montmorillonite. The scanning electron microscopy revealed that the use of electric hydraulic discharge to increase the efficiency of sorbents had not led to a positive result because the high voltage electric pulse passage through the aqueous dispersion causes the carbon shell disintegration, while the metal nanoparticles form aggregates as a result of the partial melting. The use of the pulsed magnetic field in the synthesis of a nanosized composite based on montmorillonite and magnetite is explained by the influence of the magnetic field on the particle size. It has been ascertained that the size of the nanoparticles changes depending on the duration of the magnetic field interaction with the aqueous dispersion. At the beginning the particle size slightly decreases, and then it increases. The obtained nanosized composite allows to remove cesium – 80%, strontium – 90%, iron – 99%, cobalt – 97%, and manganese – 98% from a multicomponent two-phase solution containing simultaneously cesium, strontium, cobalt, manganese, iron and organic substances, including surfactants and complexing agents. The results of the research allow us to recommend using nanosized magnetically sensitive composite based on magnetite and montmorillonite for the purification of multicomponent technogenically polluted waters.*

**Keywords:** nanocomposite, magnetically sensitive sorbent, sorption, montmorillonite, technogenically polluted waters, radionuclides, heavy metals.

**Introduction.** In recent years as a result of development of new materials, improvement of research methods and progress in technology, nanomaterials have attracted considerable attention from researchers [1, 2]. Creation of nanocomposite materials allowing solving the problem of stabilization of nanoparticles and having good performance and chemical-analytical characteristics seems promising from the scientific viewpoint.

Nanometer size and the transition from a massive solid body with a zonal structure to individual electronic levels cause the emergence of new physical properties: optical, electronic, magnetic, mechanical, and thermal [1, 3]. Nanoparticles show the so-called dimensional effects in the reactions involving them, if the parameters of their structural elements are proportionate to the correlation radius of a chemical or physical phenomenon in one direction at least [4]. Nanoparticles have excess

energy compared to homogeneous materials because a significant number of atoms is on the surface [5]. The development of nanoparticle-based composite materials contribute not only to the increase of chemical activity but also to the emergence of multifunctionality in comparison with their components.

Nanocomposites are used to increase the properties of nanoparticles. The nature of the nanoparticle influence on the properties of composite nanomaterials and their use depends significantly on the medium where the nanoparticles disperse (the type of matrix).

Irrespective of their origin the composite materials are the result of a three-dimensional combination of heterogeneous components. One of the components forms a matrix (binder), the other (filler) has high strength and/or certain functional properties. At the

same time, the composite materials have properties that are not inherent for the individual components.

The best results were achieved in obtaining nanocomposites by using sol-gel technology [6]. This technology is based on the reaction of hydrolysis of molecular chemical precursor materials, forming nanosized particles dispersed in the dispersion medium ("sol"). Polycondensation of the sol particles results in formation of nanoparticle clusters that generate a three-dimensional matrix which is called a "gel" and contains dispersion medium molecules in its pores. Further evaporation of the solvent allows obtaining a light solid with a developed inner surface, the so-called "aerogel" or "xerogel". Sol-gel synthesis is carried out at relatively low temperatures and allows obtaining materials that are homogeneous in structure and properties, and also makes it possible to include composition particles of different nature. To increase the efficiency of the extraction of heavy metals and radionuclides in the presence of organic and inorganic compounds, various methods of natural and synthetic material modification are used. Earlier we proposed a method for the synthesis of a nanocomposite sorbent for the removal of heavy metals and radionuclides from technogenically contaminated water [7, 8]. Natural highly dispersed layered aluminosilicates (smectites and hydromicas), frame aluminosilicates, natural and synthetic zeolites are widely used to develop such composite sorbents.

The principal mechanism of the sorption of radionuclides and heavy metals from aqueous solutions by clay minerals is the ion exchange between the dispersion medium and the surface of the sorbents [9, 10].

The composites based on humic substances and clay minerals are proposed to increase the adsorption capacity of clay mineral nanoparticles [11, 12]. The disadvantage of these composites is a high sensitivity to the composition and acidity of the treated water. So, they are not effective enough as sorbents for purification of technogenically contaminated water.

Nowadays the development of nanosorbents based on magnetically sensitive materials is a challenging problem [13]. The properties and fields of application of metal-containing nanocomposites which include metal-carbon sorbents and sorbents based on metal oxides are widely studied in many countries [14, 15]. This interest in nanostructured materials, which include nanoparticles of ferromagnetic metals and alloys, is caused by their specific magnetic properties.

The effect of metal-carbon nanocomposites on different media and composite materials is determined by the properties of the metal-carbon nanocomposite. The main properties of nanocomposites depend on the following parameters [14]:

1) the chemical composition and structure of nanocomposite;

2) the size and shape of the particles;

3) the presence and number of electrons in the metal-containing phase and the carbon shell.

In a metal-carbon nanocomposite, the metal particle interacts with the carbon component, while the metal-containing clusters do not interact chemically with carbon and do not form valence bonds. As a result of the association of the metallic and carbon components, the charges are redistributed in the nanostructure [14].

In addition to iron and its alloys, magnetite-based sorbents have become widespread as a magnetic matrix [15]. The use of magnetites is determined by the relative simplicity of their synthesis, the ability to control the size of nanoparticles by varying the physicochemical conditions of the synthesis, and the influence of different fields [16].

### The aim of the study

The aim of the work was the development of a highly efficient multifunctional montmorillonite-based nanocomposite for heavy metal and radionuclide extraction from aqueous solutions.

### Materials and methods

In our experiments, we used montmorillonite isolated by the standard sedimentation method from the bentonite clay of the Cherkasy deposit of bentonite and palygorskite clays (Ukraine). The chemical composition of montmorillonite (according to the results of classical chemical silicate analysis) is the following (in percent):  $\text{SiO}_2$  – 59.92;  $\text{Al}_2\text{O}_3$  – 14.78;  $\text{TiO}_2$  – 0.75,  $\text{Fe}_2\text{O}_3$  – 6.95,  $\text{FeO}$  – 0.07,  $\text{MnO}$  – 0.08,  $\text{MgO}$  – 2.26,  $\text{CaO}$  – 1.73;  $\text{Na}_2\text{O}$  – 0.35,  $\text{K}_2\text{O}$  – 0.23;  $\text{SO}_3$  – 0.15,  $\text{P}_2\text{O}_5$  – 0.05, losses during calcination – 8.42, total – 100, adsorption water – 10.67. The monominerality of the sample was confirmed by X-ray diffractometry and IR spectroscopy [17].

A laser sedimentgraph Mastersizer 2000 with a liquid dispersion module HydroS (Malvern Instruments, UK) was used for a detailed analysis of the particle size distribution of the montmorillonite samples.

We also used a metal-carbon nanosorbent (manufactured in Zaporizhzhia). Studies of the metal-carbon nanosorbent were performed by thermography and scanning electron microscopy (SEM) – by a JEOL JSM-6490LV scanning electron microscope (JEOL Ltd., Japan).

In our studies, we used an aqueous dispersion of magnetite nanoparticles obtained by the Massart method [18].  $\text{Fe}_3\text{O}_4$  was precipitated in an aqueous medium by adding ammonia to the solution of ferrous and ferric chloride mixture in a ratio of 1: 2.

To study the sorption capacity of sorbents, the following model solutions were prepared: P-1 – aqueous solution of salts containing cesium, strontium, cobalt,

copper, manganese cations (the concentration of each cation – 10 mg/dm<sup>3</sup>) and P-2 containing cesium – 10 mg/dm<sup>3</sup>, strontium – 10 mg/dm<sup>3</sup>, cobalt – 5 mg/dm<sup>3</sup>, copper, manganese, and iron – 2.5 mg/dm<sup>3</sup>, the organic substances (including complexing agents and surfactants (nonionic and anionic) amounted to 0.64 g/dm<sup>3</sup> and inorganic substances – 2.89 g/dm<sup>3</sup>.

The sorption was performed according to standard methods. A calculated amount of purified liquid was poured in a container equipped with a stirrer, and a temperature and pH control system (pH 8.5 – 9.5), then a sorbent was added under rapid agitation. After sorption being completed, the solid and liquid phases were separated. The content of pollutants was determined in the liquid phase.

The cesium, strontium, cobalt, copper, manganese, iron cation content was determination by the atomic absorption spectrophotometer, model AA-8500 (Nippon Jarrell-Ash Co., Ltd., Kyoto, Japan).

Plasma-chemical equipment was used to increase the activity of sorbents [19]. During the operation of the equipment, a high-voltage discharge (10–70 kV) is formed. It generates a discharge wave in water, causing an electro hydraulic effect (electric hydraulic discharge) characterized by 10<sup>4</sup>–10<sup>5</sup> kg/cm<sup>2</sup> and medium elastic oscillations (~ 100 Hz).

We used the setup to generate a pulsed magnetic field (PMF) scheme, the parameters of which are given in [20].

To study the PMF effect on the particle size, we used ferric hydroxide colloid obtained by hydrolysis of ferric (III) chloride in hot water.

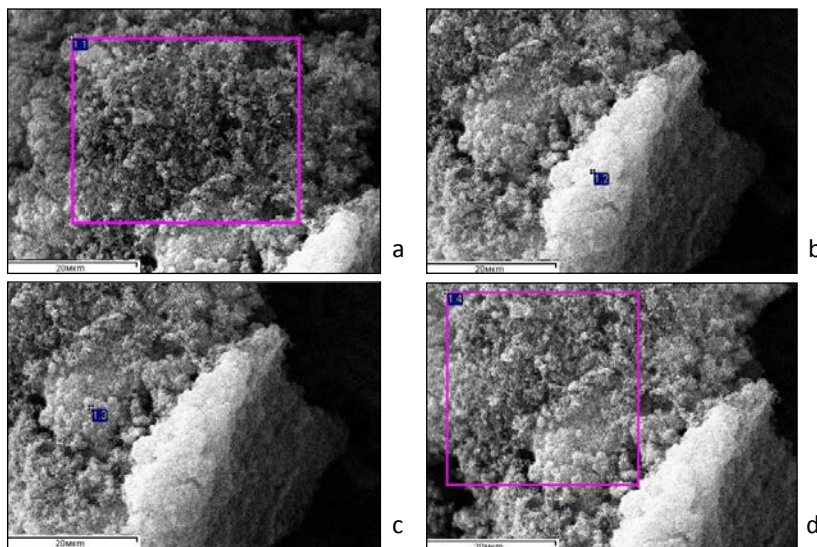
## Results and discussion

The study of the physicochemical properties of the metal-carbon nanosorbent showed the presence of a magnetic core consisting of an alloy of metals and metal oxides covered with a carbon layer. According to the results of thermographic studies, the carbon content in the initial nanosorbent sample was 70 – 75%, that of iron 9 – 20%, and oxides 5 – 21%.

The results of metal-carbon nanosorbent study by scanning electron microscopy are presented in Fig. 1 (a – d).

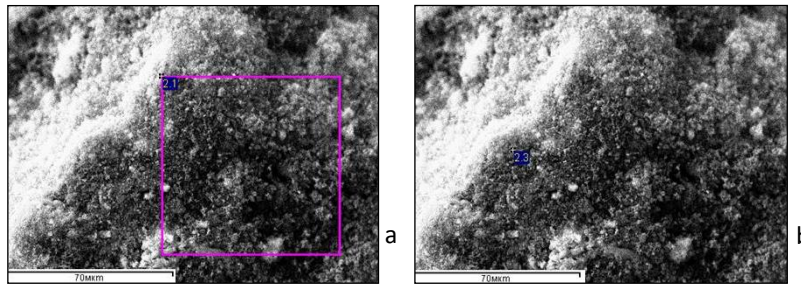
It was found that the magnetically sensitive core of the nanosorbent consists of metallic iron doped with manganese, cobalt, nickel (less than 2% in total), and iron oxide. Analysis of the SEM data suggests that the size of individual particles (non-aggregated) is 1.5 μm for the metal phase and 1.4 μm for the oxide form.

To activate the sorbent, we used electric hydraulic discharge in an aqueous medium [19]. The studies have shown that after electric hydraulic discharge there was a phenomenon of aggregation due to the melting of individual nanoparticles as a result of electric hydraulic pulse: for the metal phase, the particle size increases to 3.3 μm, and for the oxidized form — up to 2.6 μm, however, there is the partial disintegration of carbon shell and carbon release in a separate phase (Fig. 2 (a – b)).



**Fig. 1.** Electron microscopic images of the surface of the initial sample of metal-carbon nanosorbent (a – d)

**Рис. 1.** Електронно-мікроскопічні зображення поверхні вихідного зразку метало-вуглецевого наносорбенту (a – d)



**Fig. 2.** Electron microscopic images of the surface of the sample of metal-carbon nanosorbent after electric hydraulic discharge (a – b)

**Рис. 2.** Електронно-мікроскопічні зображення поверхні зразку метало-вуглецевого наносорбенту після електрогідророзрядної обробки (a – b)

Plasma chemical treatment of the aqueous dispersion of the sorbent is accompanied by a change in the chemical composition of the metal phase, a decrease in the amount of metallic iron, and an increase in the amount of oxides. The passage of the electric pulse through a layer of water is accompanied by electric hydraulic discharge and increase in local temperature that led to the redox process, resulting in the formation of free radicals  $\text{OH}\cdot$  and  $\text{H}\cdot$ , as well as molecules of oxygen and ozone.

To study the sorption of cesium, strontium, copper, cobalt and manganese simultaneously present in the solution P-1, the initial metal-carbon nanosorbent was added to the model solution, stirred for one hour and kept for 24 hours at a temperature of  $20 \pm 2$  °C. The effect of electric hydraulic discharge on the sorption process in the mixture of model solution (P-1) and nanosorbent was studied. The results are shown in Fig. 3.

The analysis of the obtained data shows that electric hydraulic discharge has almost no effect on the sorption of copper, improves slightly the sorption of cesium, reduces the sorption of cobalt by half, while manganese and strontium are almost not sorbed under these condi-

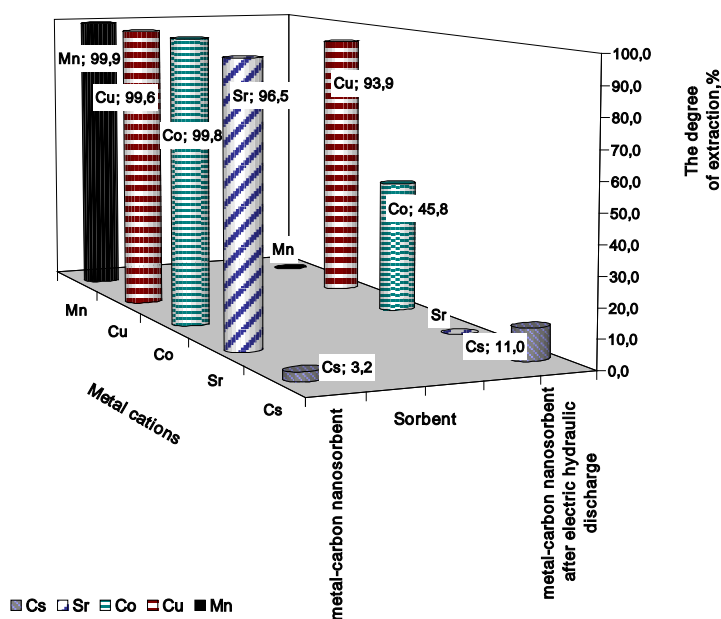
tions. We believe that the decrease in the sorption activity of the sorbent is due to the inactivation of its surface as a result of electro-discharge treatment. It is associated with the disintegration of the carbon component and the melting of individual microparticles into aggregates.

We investigated the effect of electric hydraulic discharge on the physicochemical and sorption properties of montmorillonite.

The particle size distribution of the samples is presented in the Table 1.

The above data suggest that the share of highly dispersed fraction increases due to the disintegration of aggregates (size 0.1 mm or more) under the electric hydraulic discharge effect. Long-term influence of the electric hydraulic discharge (more than 60 min) decreases the proportion of highly dispersed nanoparticles (fraction less than 0.001 mm) due to their aggregation.

Fig. 4 shows the changes in the distribution of particles by volume depending on the duration of electric hydraulic discharge.



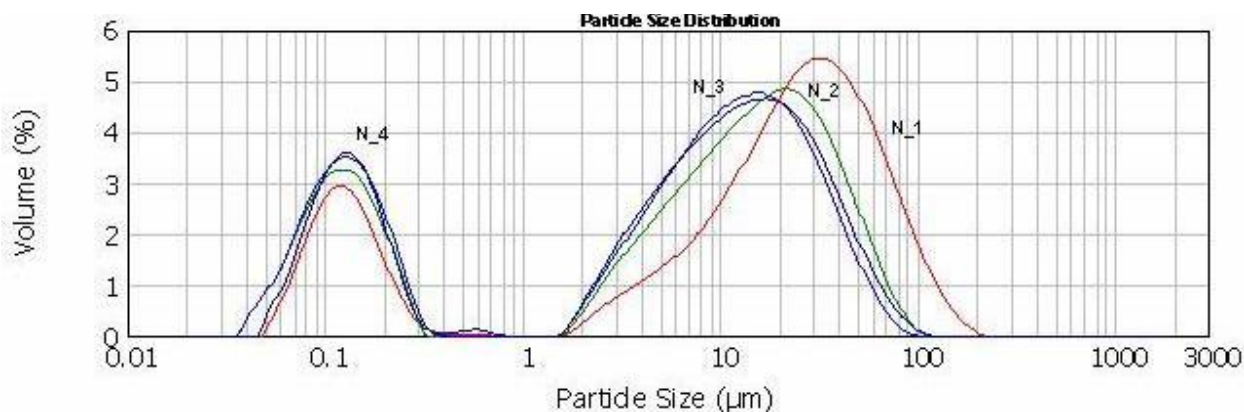
**Fig. 3.** The results of the sorption of metal ions by metal-carbon nanosorbent after electric hydraulic discharge in comparison with the initial sample

**Рис. 3.** Результати сорбції іонів металів метало-вуглецевим наносорбентом після електрогідророзрядної обробки у порівнянні з вихідним зразком



**Table 1.** The particle size distribution of montmorillonite samples before and after electric hydraulic discharge  
**Табл. 1.** Гранулометричний склад зразків монтморилоніту до і після електрогідророзрядної обробки

№	Sample	Fractions, mm			
		< 0.001	0.001 – 0.01	0.01 – 0.1	> 0.1
1.	N_1 (initial sample)	20.26	13.46	62.70	3.58
2.	N_2 (30 minute treatment)	26.71	23.44	49.80	0.05
3.	N_3 (60 minute treatment)	28.90	27.74	43.36	0.00
4.	N_4 (90 minute treatment)	26.18	28.21	45.55	0.06



**Fig. 4.** Differential curves of particle distribution

N\_1 (initial sample); N\_2 (30 minute treatment); N\_3 (60 minute treatment); N\_4 (90 minute treatment)

**Рис. 4.** Диференційні криві розподілу частинок

N\_1 (вихідний зразок); N\_2 (обробка 30 хв.); N\_3 (обробка 60 хв.); N\_4 (обробка 90 хв.)

The analysis of the obtained data showed that the increase in the sample dispersion was due to the disintegration of the aggregates within 30 – 60 minutes.

The sorption of cesium, strontium, cobalt, copper and manganese cations from the P-1 solution by activated and nonactivated montmorillonite was performed according to the above method. The results are presented in Fig. 5. The analysis of the given data indicates that the application of electric hydraulic discharge practically does not improve the sorption properties of montmorillonite.

Considering the positive and negative properties of metal-carbon nanosorbent and montmorillonite, it is reasonable to recommend the montmorillonite-based sorbent with the metal-carbon nanosorbent additive (5: 1) to purify contaminated water.

Our experiments showed that this sorbent removes cesium – 77.9%, strontium – 95.2, cobalt, manganese, copper – more than 99% from the solution P-1 (Fig. 6).

The presence of metal-carbon nanosorbent in the mixture with montmorillonite is seen to increase significantly the sorption of cations of strontium (almost twice), manganese (one third) and cobalt (17%) by montmorillonite. However, we failed to increase the

degree of cesium removal, which remained at the same level (about 80%).

The treated water is usually multicomponent and, as a rule, two-phase. In such cases, the use of the proposed sorbent is not effective enough because the colloidal phase is present. The precipitation of the colloidal phase in such multicomponent systems should be carried out by heterocoagulation that is achieved by adding nanoparticles with a charge opposite to the charge of the colloid in the technogenically contaminated water to the system.

The presence of surfactants and complexing agents in the nuclear power plants' drains causes the formation of complex colloidal particles with a negative zeta potential. For their precipitation, we recommend to use the process of heterocoagulation by positively charged nanoparticles [8].

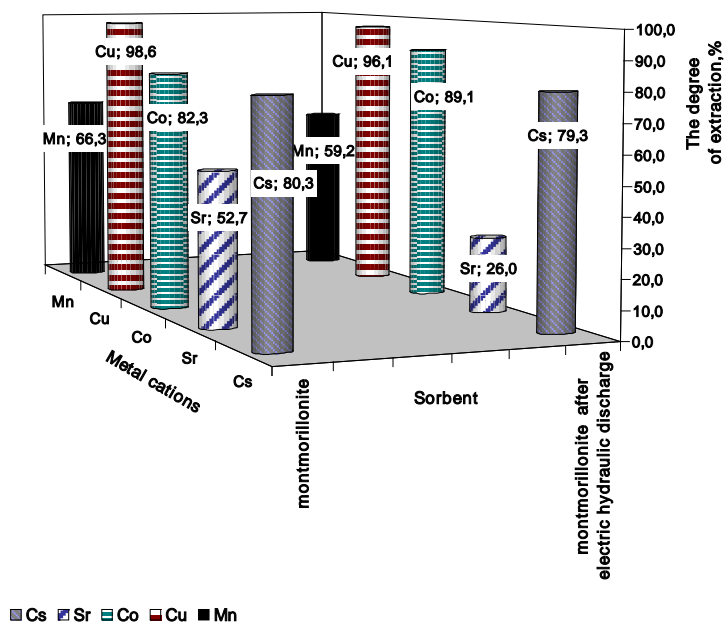
Aqueous dispersions containing iron oxides and hydroxides or their complexes (nanocomposites) with dispersed clay mineral particles (montmorillonite, hydromica) can be recommended as the precipitators [8].

To increase the degree of the extraction of toxic pollutants, the synthesis of such nanocomposites should be carried out in a pulsed magnetic field.

A magnetic field was found to enhance the particle aggregation processes in the aqueous dispersion. The particles lose kinetic stability and precipitate [21]. Our studies of the PMF effect on iron hydroxide colloid showed that under the PMF influence the particle size (Table 2) and the kinetic stability of the colloidal solution change.

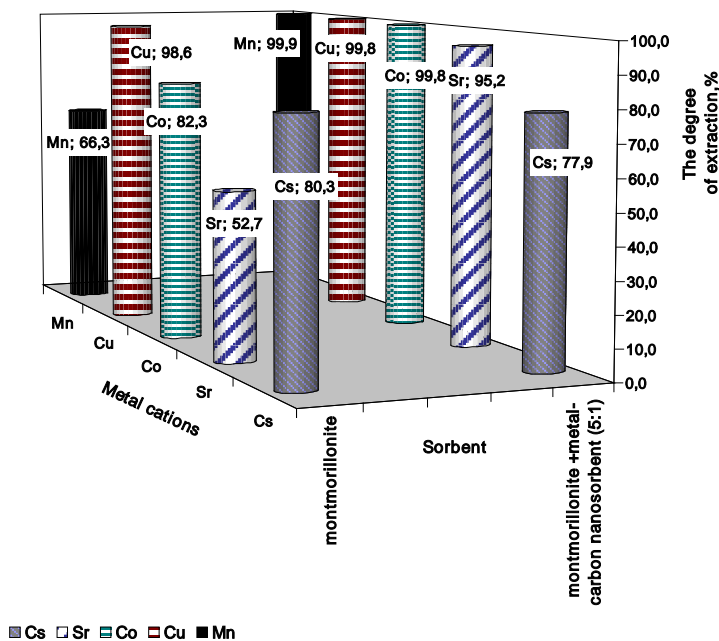
The size of the colloidal particles increases slightly under the PMF influence during 1 min. An increase in the duration of the PMF effect on the solution up to 2-3 minutes leads to a decrease in the colloidal particle

size. This is associated with the self-organization processes in a diffuse ionic atmosphere. The colloid treatment with PMF for 5 minutes and more leads to an increase in the size of colloidal particles due to an increase in field energy and, accordingly, the diffuse ionic atmosphere loosening. Additionally, PMF promotes the dispersion of clay particle aggregates to smaller particles and increase in their hydrophilicity [20].



**Fig. 5.** The results of the sorption of metal ions by montmorillonite after electric hydraulic discharge compared to the initial sample

**Рис. 5.** Результати сорбції іонів металів монтморилонітом після електрогідророзрядної обробки у порівнянні з вихідним зразком



**Fig. 6.** The results of the sorption of metal ions by the mixture of montmorillonite with metal-carbon nanosorbent (5: 1) in comparison with montmorillonite

**Рис. 6.** Результати сорбції іонів металів сумішшю монтморилоніту з металовуглецевим наносорбентом (5:1) у порівнянні з монтморилонітом

**Table 2.** Dependence of the particle radius of the dispersed phase of iron hydroxide colloid on the duration of the pulsed magnetic field effect**Табл. 2.** Залежність радіуса частинки дисперсної фази колоїду гідроксиду заліза від тривалості впливу імпульсного магнітного поля

Duration of PMF effect, min.	Initial colloid Fe(OH) <sub>3</sub> (0 min.)	Minutes			
		1	2	3	5
Radius, nm	11.55±0.06	11.96±0.07	11.85±0.04	11.58±0.04	11.94±0.05

The dispersion of clay microaggregates on a nanocrystal promotes the opening of new hydrophilic adsorption centers, and, as a consequence, increases the affinity of such nanocrystals to positively charged particles. To obtain a magnetosensitive biminerall nanocomposite, the magnetite nanocolloid with zero or positive surface charge can be used, which is synthesized in a clay dispersion medium from the solution of ferrous and ferric salts at a ratio of 2:3 and at pH ~ 9. Ammonium hydroxide solution is used to adjust the pH. The obtained magnetite nanoparticles interact with negatively charged nanocrystals of clay minerals resulting in a silicate-magnetite nanocomposite formation.

The study of the sorption properties of the obtained nanocomposite showed that cesium, strontium, iron, cobalt, manganese ions are removed from aqueous solutions effectively.

We suggest the following method of the nanocomposite synthesis and the extraction of pollutants from technogenically contaminated solutions:

The P-2 solution and montmorillonite are introduced into the working area (volume V = 1000 ml) of a specially designed reactor equipped with a thermostat, stirrer, glass, silver chloride electrodes and a set of induction coils. After being mixed for 30 minutes the mixture is left to swell for 5 - 10 hours, after that the mixture is stirred and subjected to PMF for 5 minutes. Then the pH of the solution is adjusted to ~ 9 with ammonium hydroxide solution. The calculated amount of 10% solution of the ferrous and ferric salt mixture in a ratio of 2:3 is added slowly to obtain a stable biminerall nanocomposite. In the precipitation process, additional activation is performed to reduce the size of magnetite particles that precipitate on the surface of nanocrystals of silicates.

The analysis of the purified solution after the separation of the solid phase showed that cesium – 80%, strontium – 90%, iron – 99%, cobalt – 97%, manganese (II) – 98% were removed from the P-2 solution.

The method can also be used for the treatment of domestic wastewater containing, in addition to heavy metals, a large amount of organic matter, both in the colloidal and aqueous phases.

The use of the above method for cleaning the Kyiv landfill filtrates showed that the treatment of the filtrate with biminerall nanocomposite allowed to reduce the chemical oxygen demand (COD) from 2500 – 2700 mgO/dm<sup>3</sup> to below 500 mgO/dm<sup>3</sup>.

### Conclusions

1. The method for obtaining a complex nanosized composite based on montmorillonite and magnetically sensitive sorbents is proposed, which allows us to remove cesium, strontium, and heavy metals (iron, nickel, cobalt, manganese, copper, etc.) from a multi-component two-phase aqueous solution in the presence of surface substances and complexing agents.

2. The activation of metal-carbon sorbents and montmorillonite by electric hydraulic discharge does not improve their sorption properties. It is shown that under the influence of electric hydraulic discharge the carbon shell is disintegrated and metal nanoparticles form aggregates due to partial melting.

3. The use of a pulsed magnetic field in the synthesis of an iron-montmorillonite composite, due to the influence of a pulsed magnetic field on both montmorillonite aggregates and the size of colloidal particles, allows obtaining a nanocomposite with improved sorption properties.

Taking into consideration that the main dose-forming radionuclides are radiostrontium and radiocesium, it is reasonable to conduct further research to develop sorbents with improved sorption characteristics for cesium and strontium.

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#### БАГАТОФУНКЦІОНАЛЬНІ НАНОКОМПОЗИТИ ЯК ВИСОКОЕФЕКТИВНІ СОРБЕНТИ ДЛЯ ОЧИЩЕННЯ ТЕХНОГЕННО ЗАБРУДНЕНИХ ВОД

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*Стаття присвячена розробці нанорозмірних сорбентів для видалення цезію і стронцію, а також іонів важких металів при їх одночасній присутності в багатокомпонентному двофазному розчині, що містить комплексоутворювачі і поверхнево-активні речовини. Перспективними в даний час є магніточутливі наносорбенти, зважаючи на те, що вплив зовнішніх полів може поліпшити експлуатаційні властивості розроблюваних сорбентів. Для створення магніточутливих наночастинок і композитів на їх основі нами використано наночастинок металів, поверхня яких вкрита вуглецевою оболонкою, в композиції з монтморилонітом. За даними скануючої електронної мікроскопії встановлено, що застосування електрогідродару для підвищення ефективності сорбентів не привело до позитивного результату, оскільки при проходженні електричного імпульсу високої напруги через водну дисперсію відбувається руйнування вуглецевої оболонки, а наночастинок металу внаслідок часткового оплавлення утворюють агрегати. Використання імпульсного магнітного поля в процесі синтезу нанорозмірного композиту на основі монтморилоніту і магнетиту обумовлено впливом магнітного поля на розмір частинок. Встановлено, що розмір наночастинок змінюється в залежності від тривалості взаємодії магнітного поля з водною дисперсією. Спочатку розмір частинок децю зменшується, а потім збільшується. Отриманий нанорозмірний композит дозволяє з багатокомпонентного двофазного розчину, що містить одночасно цезій, стронцій, кобальт, манган, залізо в присутності органічних речовин, в тому числі поверхнево-активних речовин і комплексоутворювачів, вилучити цезій – 80 %, стронцій – 90 %, заліза – 99 %, кобальту – 97 %, мангану – 98 %. Результати досліджень дозволяють рекомендувати використання нанорозмірного магніточутливого композиту на основі монтморилоніту і магнетиту для очищення багатокомпонентних техногенно забруднених вод.*

**Ключові слова:** наноккомпозит, магніточутливий сорбент, сорбція, монтморилоніт, техногенно забруднені води, радіонукліди, важкі метали.