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The object of this study is granular adsorbents based on kaolinite and zero-valent iron. The ceramic mass for their preparation contained polyvinyl alcohol as a powder-forming additive. It was established that its addition in quantities of 1.8–3.3 % practically does not change the porosity of the granules but increases their strength. X-ray phase and chemical analyzes confirmed the presence of a layer of zero-valent iron on the surface of the granules. The structural and adsorption characteristics of adsorption materials have been studied and the calculations of the main parameters of their porous structure were carried out. It is shown that when modifying granules with zero-valent iron, there is a decrease in the specific surface area and micropores volume for samples without a powder-forming additive by almost 2 times compared to the original granules. Moreover, these values almost do not change for samples obtained with the addition of polyvinyl alcohol. It was found that the application of the reaction layer to the granules leads to a significant increase in their adsorption capacity with respect to heavy metal ions Cu(II), Cd(II), Co(II), Zn(II), and Cr(VI). It has been shown that the resulting adsorbents can be used for wastewater treatment containing a mixture of these toxicants. It was found that the values of maximum adsorption on modified samples are 10–20 times higher than those for the original granules. A feature of the obtained adsorbents is the ability to simultaneously remove metal ions, both in the form of cations and anions. A significant increase in the adsorption values of Cr(VI) anionic forms, which are difficult to remove from water by natural ion exchangers, has been established. It has been shown that granules based on kaolinite and zero-valent iron are effective adsorbents for water purification from heavy metal ions. The resulting materials can be used for wastewater treatment of electroplating industries and hydrometallurgical industry

Keywords: granular adsorbents, kaolinite, zero-valent iron, water purification, heavy metal mixture

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SYNTHESIS AND CHARACTERIZATION OF KAOLINITE-BASED GRANULAR ADSORBENTS FOR THE REMOVAL OF Cu(II), Cd(II), Co(II), Zn(II), AND Cr(VI) FROM CONTAMINATED WATER

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1. Introduction

An important scientific task is the development of adsorption materials to protect water bodies from contamination by heavy metal ions. Inorganic toxicants can enter the aquatic environment in various ways. For example, as a result of the processes of natural leaching of metal ions from soils and polymetallic ores. However, the main sources of their entry into the waters are the activities of non-ferrous metallurgy, radio engineering, electronic and electrochemical industries. Such toxic elements as Pb, Cd, Cr, As, Hg, etc., are practically not removed from the human body but accumulate in tissues and organs. Various technologies based on physical and chemical processes are used to purify water from heavy metal ions. Main ones among them are chemical precipitation, ion exchange, electrochemical treatment, coagulation followed by flocculation, ultra- and nanofiltration, reverse osmosis, flotation, photocatalysis, and adsorption. The choice of method for removing pollutants depends on the form of finding the metal in water, its concentration, the content of salt and organic matter in natural or waste water [2]. Effective in the purification of water from heavy metal ions are adsorption methods. This is due to the ability of adsorption materials to remove metal ions from water, which are in very low concentrations compared to other pollutants.

When cleaning large volumes of polluted water, the economic aspects of the proposed technologies play a special role. Water treatment technologies using materials based on cheap and affordable raw materials should have significant advantages. A promising direction in the processes of water purification from various inorganic contaminants, including heavy metal ions, is the use of natural silicates. They combine sufficiently high efficiency with low cost, availability, mechanical strength, and chemical resistance [3]. Layered silicates are one of the most important types of silicate raw materials, in terms of their use in water treatment processes. However, their widespread use is significantly limited due to the high dispersion in their natural state. This greatly complicates the creation of continuous technological processes. One of the ways to solve this issue is to granulate dispersed minerals. It can be implemented both with the use of various binding substances of inorganic and organic nature, and without the introduction of additives by subsequent heat treatment.

Scientific research on this topic is important because the processes of formation of a porous structure during heat treatment of dispersions of layered silicates to obtain granular adsorbents have not been studied enough. In addition, in the process of firing granules from powdered silicates, their adsorption characteristics decrease. Therefore, an important issue is to increase the adsorption capacity of granular adsorbents in relation to metal ions by modifying their surface. The results of such studies are needed to obtain effective adsorption materials and their wider application in water treatment technology.

2. Literature review and problem statement

To obtain adsorbents, materials are used both on the basis of artificial and natural raw materials (activated carbon, metal oxides, natural and synthetic silicates, waste from industrial and agricultural enterprises, biomass, etc.) [4]. Some of them are effective in removing organic contaminants from water, other materials are related only to inorganic compounds. Expansion of the raw material base for the synthesis of adsorbents makes it possible to obtain more efficient or economically feasible materials. For example, various adsorbents are used to remove heavy metal ions from wastewater [5]. Among them, materials based on graphene, carbon nanotubes, activated aluminum oxide and titanium modified with chitosan differ in their significant adsorption capacity with respect to cadmium, copper, and chromium ions. Despite their high efficiency, they require significant investments in their manufacture. In this regard, materials based on cheap raw materials, the so-called “low-cost” adsorbents , attract the attention of scientists. These include, in particular, natural clay minerals (halloysite, montmorillonite, vermiculite, attapulgite, etc.) [6]. The advantages of their use are availability and low cost. The disadvantages of natural silicates include the presence of various impurities and high dispersion. This requires additional equipment for pre-cleaning of clays and high-quality separation of the spent adsorbent after adsorption. In addition, the form in which heavy metals are found in water significantly affects the efficiency of using this kind of inorganic materials. To improve the adsorption characteristics of natural aluminosilicates, their surface is modified. For this purpose, various methods are used, in particular, chemical (treatment with acids, alkalis, organic and inorganic compounds) and physical (heat treatment and mechanoactivation) [7]. Depending on the task, one or another method of processing clay is applied. For example, chemical methods allow a goal-directed change in the nature of the surface of aluminosilicates, giving them specific properties. Along with powdered adsorption materials, granular ones are also obtained. They can be obtained from both natural and artificial raw materials. However, the use of synthetic materials is associated with additional costs for their production [8]. That is why interesting are the studies aimed at obtaining granular adsorbents based on cheap modified natural clays.

In water purification processes, adsorption materials based on nanoscale zero-valent iron are also used. This is due to its high reactivity, significant specific surface area, and the ability to remove a wide range of pollutants by a complex adsorption-reducing mechanism [9]. However, there are some limitations for its widespread use. Thus, the synthesized nanoscale Fe^0 is subject to aggregation and enlargement of particles, which leads to a decrease in the specific surface area of such materials. In addition, its storage is complicated due to the course of iron oxidation processes. To increase the stability of such powders, synthesis is carried out in the presence of various carriers. One of the most effective approaches is to use natural clay minerals that combine high specific surface area and reactivity with their low cost. The feasibility of using adsorbing materials based on layered silicates and nanoscale zero-valent iron for water purification from Ni(II), Zn(II), Pb(II) is shown in [10]. Most often, in the synthesis of oxidation-resistant iron-containing adsorbents, such available aluminosilicates as montmorillonite and kaolinite are used. With their help, wastewater is purified, both from cationic forms of metals and anions [11]. It should be noted that in the cited scientific works the authors investigated the effectiveness of composite adsorbents to remove inorganic toxicants from solutions that contained any one metal ion. In [12, 13], the results of the study of the adsorption capacity of powdered adsorbents based on montmorillonite and kaolinite on the removal of metals (Cu(II), Cd(II), Zn(II), Co(II), Cr(VI)) from complex wastewater content containing a mixture of these ions are presented. It was shown that powdered adsorbents based on nano-sized iron effectively remove heavy metal ions from complex solutions. However, the issues related to the difficulties of separating the dispersed solid phase from the liquid after adsorption remained unresolved. An option to overcome the corresponding difficulties may be the use of iron-containing granular adsorbents using clay dispersions. In this regard, research aimed at studying the physicochemical features of wastewater treatment with granulated adsorbents based on kaolinite with an applied layer of zero-valent iron should be considered expedient. This is especially important for electroplating industries and the hydrometallurgical industry containing a complex mixture of heavy metal ions (copper, cadmium, cobalt, zinc, chromium).

3. The aim and objectives of the study

The purpose of this study is to obtain granulated iron-containing adsorbents based on kaolinite. This will make it possible to use them for wastewater treatment from a complex mixture of heavy metals.

To accomplish the aim, the following tasks have been set:

– to determine the influence of the conditions for obtaining granular adsorbents based on kaolinite and zero-valent iron on the strength and parameters of the porous structure of samples in the process of granulation, heat treatment, and modification of their surface;

– to investigate the phase composition and structural and adsorption characteristics of the obtained composites;

– to establish the physicochemical features of the removal of heavy metals (Cu(II), Cd(II), Zn(II), Co(II), Cr(VI)) from complex wastewater containing a mixture of these ions, using the resulting adsorption materials.

4. The study materials and methods

The object of this study was kaolinite ($Al_4Si_4O_{10}(OH)_8$) from the Glukhovetsky deposit (Ukraine), which was previously cleaned of impurities by repeated laundering with distilled water. Granulated samples based on kaolinite were obtained by plastic molding using ceramic masses prepared with the addition of distilled water and polyvinyl alcohol (PVA) solutions (($C_4H_6O_2 \cdot C_2H_4O$)n, molecular weight approx. 70000, Merck) of different concentrations. The mass ratio of the pore-forming additive to kaolinite was 1.8–3.3 % (Table 1). The formative moisture content of ceramic masses was 26–28 %. After molding, the granules were dried at room temperature and then at 105 °C in a drying cabinet to a constant mass. The samples were burned in a muffle furnace at temperatures of 600–800 °C with exposure at a maximum temperature of 2 hours.

The mechanical strength of ceramic granules was estimated by modeling the adsorption process in the aquatic environment by changing the mass of granule samples before and after shaking the samples on the shaker for 3 hours.

The amount of water absorption of ceramic granules based on kaolinite was determined by the standard procedure described in [14, 15], and was calculated by the formula (1):

$$W = \frac{(m_1 - m_0)}{m_0} \cdot 100\ \%, \quad (1)$$

where m_0 is the mass of dry granules, g;

m_1 is the mass of a sample saturated with water, g.

The granules with the applied Fe^0 layer were obtained by impregnating annealed ceramic samples with 1 M solution of $FeCl_3 \cdot 6H_2O$ for 1 hour, followed by reduction of Fe^{3+} to Fe^0 ions in sodium borohydride solution $NaBH_4$. After that, the resulting granules were separated from the liquid phase and washed three times with ethyl alcohol. The resulting modified samples were dried under vacuum at a temperature of 60 °C and stored in an airtight container. The iron content in modified adsorbents after leaching with nitric acid according to chemical analysis was 0.012 g per 1 g of kaolinite.

The monomineralty of kaolinite and the qualitative composition of the obtained thermally processed and modified granules were controlled by X-ray phase analysis using the diffractometer DRON-3M. The interpretation and decryption of the obtained results was carried out using Match! software, into which the international database of diffractograms PDF-2 was integrated.

The sample surface was characterized using an optical microscope and the digital camera Delta Optical HCDE-50 (China) and ScopeTek View (China) software.

We determined the parameters of the porous structure by the method of low-temperature adsorption-desorption of nitrogen on the Quantachrome NOVA-2200e Surface Area and Pore Size Analyzer (USA) device. The calculations of specific surface specific values (BET method), micropores volume, and pore size distribution were carried out using ASiQwinTM V 3.0 software (USA).

To study the processes of adsorption, model solutions were used that contained a mixture of heavy metals ((Cu(II), Cd(II), Co(II), Zn(II), Cr(VI)) in the concentration range of 50–400 µmol/l. They were prepared in distilled water using potassium bichromate and copper nitrate salts, cadmium, zinc, cobalt. The ionic force was 0.005, which was set by 1M solution of KNO_3. The pH value of the model solutions was 5.9–6.1. The temperature of the adsorption experiments was 25±2 °C.

The duration of the adsorption process is 2 hours with continuous shaking, the ratio of the solid phase to the liquid phase is 1:500. To study the effect of pH on the adsorption value of heavy metal ions, solutions with concentrations of 100 µmol/l and 400 µmol/l were used for the initial granules and their modified samples, respectively. After establishing the adsorption equilibrium, the liquid phase from the solid was separated by centrifugation and the equilibrium concentrations of each of the metals were determined in it by atomic emission spectrometry with inductively coupled plasma (Thermo Scientific iCAP 7400 ICP-OES, USA).

The values of adsorption values for heavy metal ions (Cu(II), Cd(II), Co(II), Zn(II), Cr(VI)) a (µmol/g) were calculated from (2):

$$a = \frac{\left(C_{in} - C_{eq}\right) \cdot V}{m}, \quad (2)$$

where C_{in}, C_{eq} is the initial and equilibrium concentrations of metal, µmol/l;

V is the volume of solution, l;

m is the weight of the sample of the adsorbent, g.

5. The results of studies of the properties of granular adsorbents

5. 1. Determining the influence of conditions for obtaining granular adsorbents on their strength and parameters of the porous structure

The results of determining the water absorption of kaolinite-based granules, depending on the firing temperature and the content of polyvinyl alcohol in the ceramic mass, are given in Table 1.

It should be noted that the amount of water adsorption of the resulting granules is practically not affected either by the increase in the firing temperature from 600 °C to 800 °C, nor by the addition of polyvinyl alcohol in the preparation of ceramic masses in the studied range of mass ratios.

Fig. 1 shows photographs on the example of sample K-800, which depict the phased production of a granular adsorbent based on kaolinite.

Table 1

The dependence of water absorption of granular samples on the firing temperature and the content of polyvinyl alcohol in the mass

Sample	Firing temperature t, °C	Polyvinyl alcohol content in ceramic mass C, %	The amount of water absorption W, %
Kaolinite (granules)			
K-600	600	–	35.5
K-700	700	–	36.2
K-800	800	–	35.9
Kaolinite with polyvinyl alcohol (granules)			
M2-700	700	1.8	33.9
M3-700		2.4	34.1
M4-700		3.3	34.7
M2-800	800	1.8	34.8
M3-800		2.4	33.9
M4-800		3.3	34.9

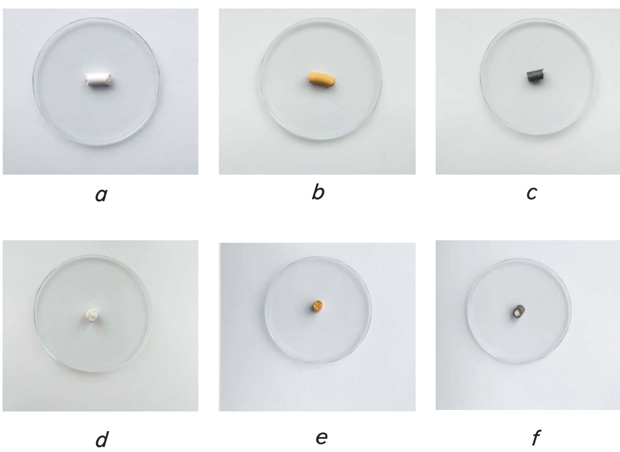


Fig. 1. Photographs of phased production of granulated adsorbent based on kaolinite: *a*, *d* – kaolin-based granule; *b*, *e* – the granule is impregnated with a solution of iron; *c*, *f* – granule after reduction of Fe^{3+} ions to Fe^0

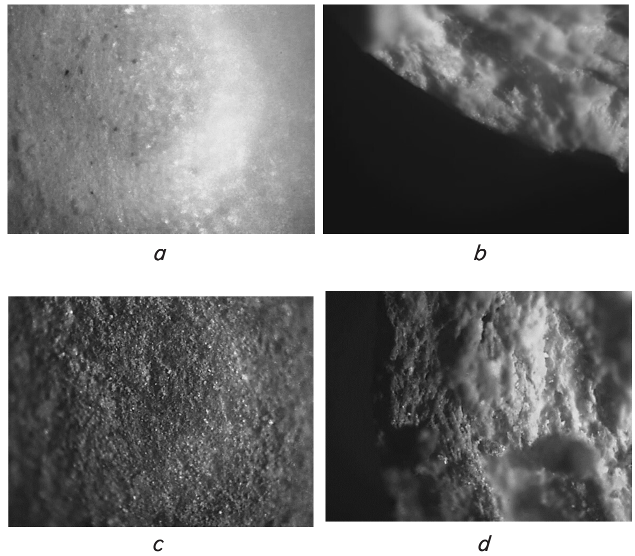


Fig. 2. Photographs of kaolinite granules taken using optical microscopy: *a*, *b* – K-800; *c*, *d* – K-800- Fe^0 (magnification 50 times)

Visually, there is a difference between the granules K-800 (Fig. 2, *a*, *b*) and K-800-Fe^0 (Fig. 2, *c*, *d*). In the photo of the latter, a layer of zero-valent iron of black color is clearly visible.

5. 2. The phase composition and structural and adsorption characteristics of the obtained composites

The results of X-ray phase analysis of granular adsorbents based on kaolinite and its modified forms are shown in Fig. 3. It should be noted that the processing of granules at a temperature of 800 °C (Fig. 3, *a*) and the application of a layer of iron to the granules K-800 and M4-800 (Fig. 3, *b*) leads to a decrease in the intensity of the characteristic peaks of kaolinite.

Fig. 4, 5 show the isotherms of adsorption-desorption of nitrogen on granular samples and the distribution of pores by radii, respectively; Table 2 gives parameters of the structure of adsorption materials.

Attention should be paid to the fact that in the process of synthesis there are qualitative changes with the material. Fig. 1, *a*, *d* demonstrate that the kaolin-based granule acquires a light brown color after impregnation with a solution of $FeCl_3 \cdot 6H_2O$ (Fig. 1, *b*, *e*). Then it turns black from the outside as a result of the reduction of Fe^{3+} ions to Fe^0 with sodium borohydrite (Fig. 1, *c*, *f*).

The photographs of samples taken using optical microscopy (Fig. 2) also confirm the presence of a modifying layer of zero-valent iron on the surface of kaolinite granules.

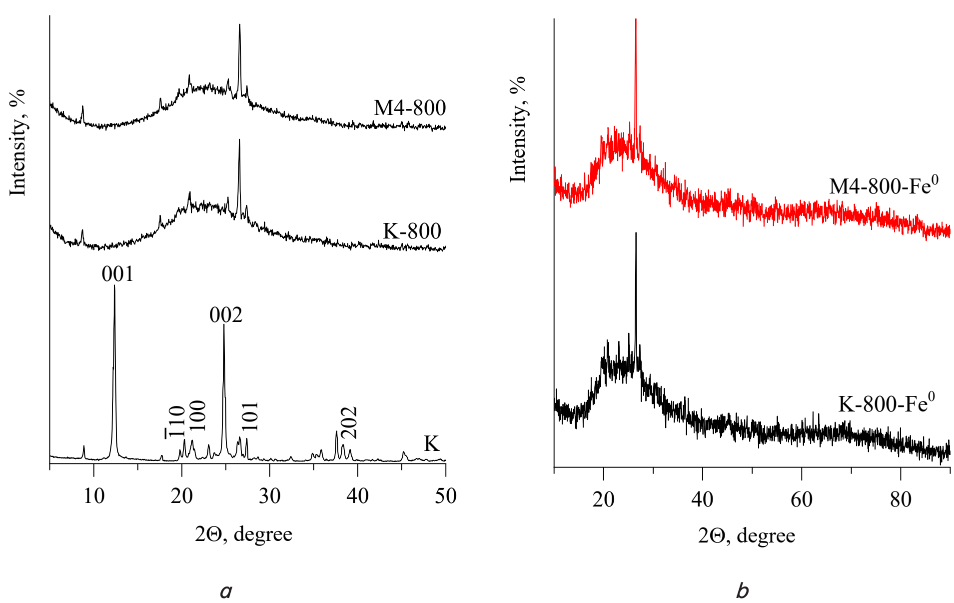
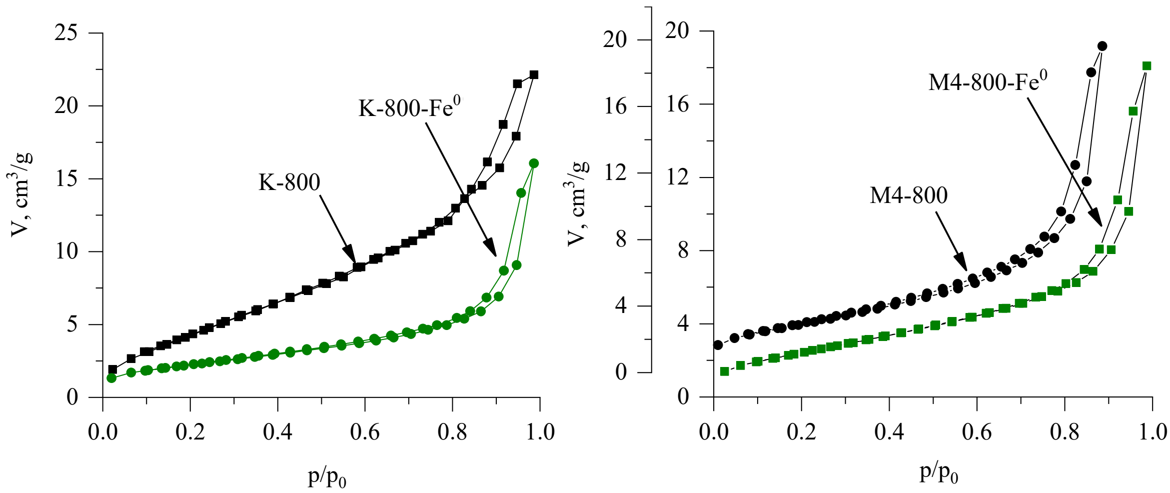


Fig. 3. Diffractograms of sorption materials: *a* – kaolinite (K) and granules (K-800 and M4-800); *b* – granules with applied zero-valent iron (K-800-Fe^0 and M4-800-Fe^0)



a *b*

Fig. 4. Isotherms of low-temperature adsorption/nitrogen desorption:
a – granular samples without polyvinyl alcohol;
b – granular samples with polyvinyl alcohol

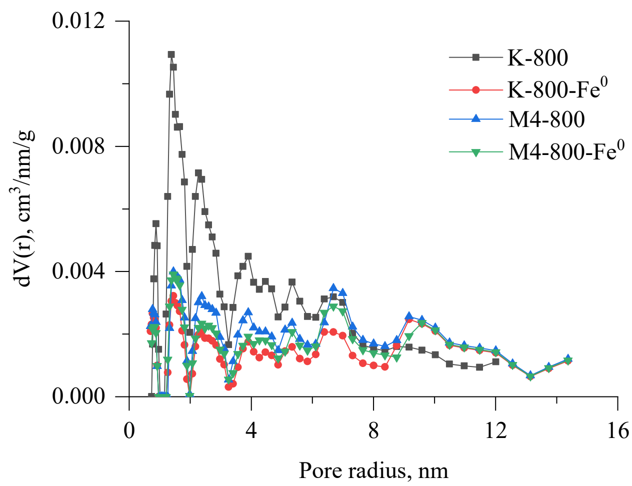


Fig. 5. Pore distribution by radius of granular samples

Table 2

Parameters of the porous structure of granular samples

Sample	S, m^2/g	V_{Σ}, cm^3/g	V_{μ}, cm^3/g	$V_{\mu\,\%}$, %
K-800	19	0.0342	0.0153	44.74
M800-4	10	0.0304	0.00890	29.27
K-800-Fe^0	8	0.0248	0.00677	27.29
M4-800-Fe^0	9	0.0279	0.00788	28.24

Note: S – specific surface area, m^2/g; V_{Σ} – total pore volume, cm^3/g; V_{μ} – micropores volume, cm^3/g

The obtained granular adsorbents have different structural and adsorption characteristics. However, the forms of nitrogen adsorption-desorption isotherms on the studied samples are of a similar nature (Fig. 4). The application of the modifying layer reduces the specific surface area and micropores for kaolinite-based granules (K-800-Fe^0) and almost does not change those for samples M4-800-Fe^0 (Fig. 5, Table 2).

5. 3. Physical-chemical features of the removal of heavy metals from water by the resulting adsorption materials

The results of the study of the effectiveness of the removal of heavy metals (Cu(II), Cd(II), Zn(II), Co(II), Cr(VI)) from a complex mixture containing these ions can be seen in Fig. 6.

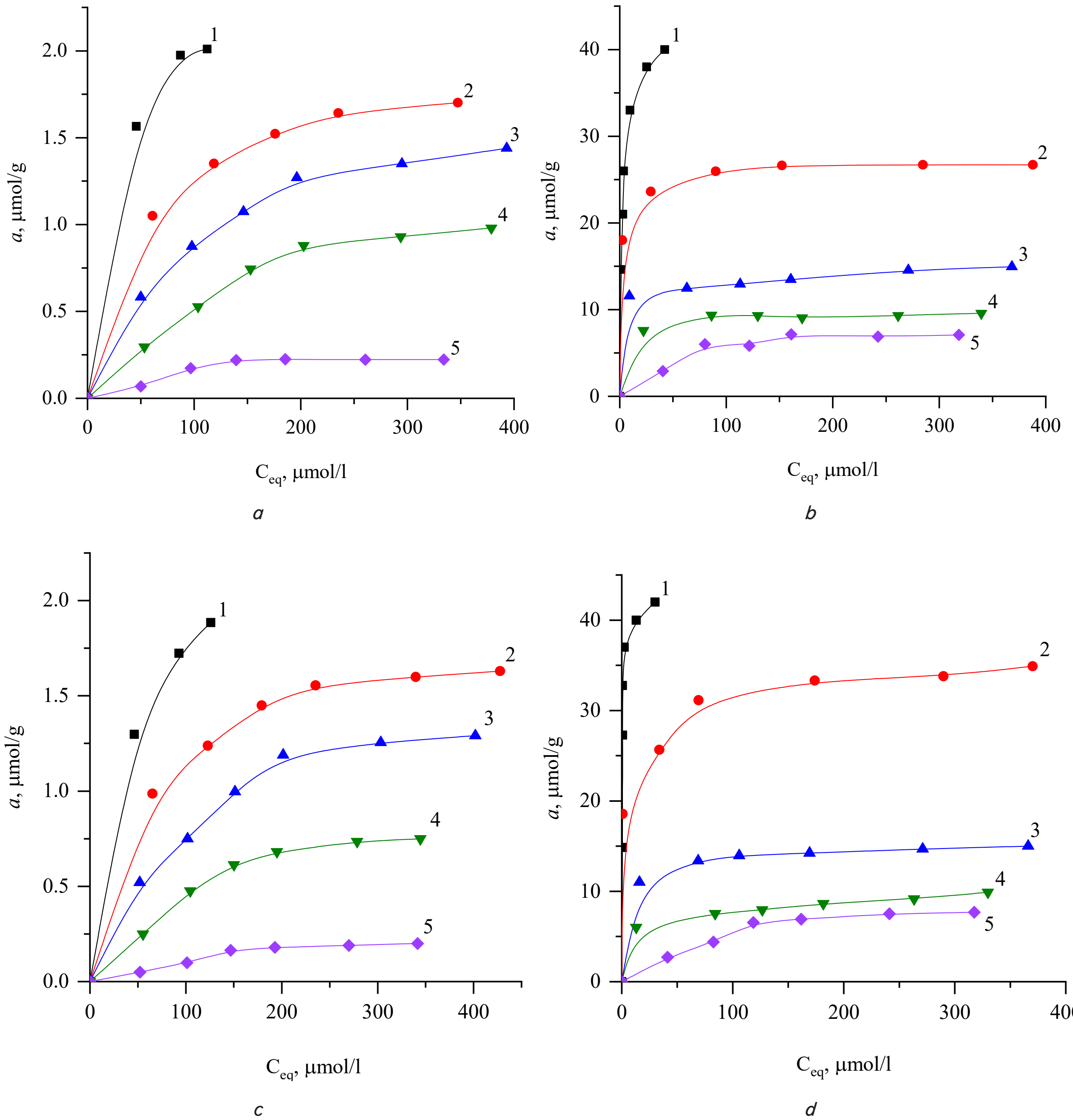


Fig. 6. Adsorption isotherms on granular samples: *a* – K-800; *b* – K-800-Fe^0; *c* – M800-4; *d* – M4-800-Fe^0; 1 – Cu, 2 – Zn, 3 – Co, 4 – Cd, 5 – Cr

It can be stated that the adsorption capacity of granules with an applied layer of zero-valent iron significantly exceeds that for the original samples. Moreover, modified granules prepared with the addition of polyvinyl alcohol show almost the same effectiveness in extracting heavy metals as samples without additive.

6. Discussion of results of studying the properties of granular adsorbents

For the effective use of granular adsorbents based on layered silicates in the purification of water from contaminants, the strength of the samples obtained is important. To do this, ceramic granules are subjected to mandatory heat treatment or special binding additives are introduced into the mass. In the studies, it was proposed to check the effect of adding a water-soluble polymer (polyvinyl alcohol) to kaolinite in the preparation of the masses from which the granules were formed. The obtained data (Table 1) indicate that the values of water absorption practically do not change either when the temperature rises from 600 °C to 800 °C, or when a pore-forming agent is added. However, the study of the stability of granules in the aquatic environment revealed that the most durable are the samples prepared on a solution of polyvinyl alcohol (M4-800). Therefore, for all further experiments, samples were selected that were fired at 800 °C.

Fig. 1, 2 clearly demonstrate the presence of a layer of zero-valent iron of black color after the reduction of Fe^{3+}ions to Fe^0 with sodium borohydrite. Moreover, this is also confirmed by chemical analysis of solutions for the presence of iron ions after leaching them with nitric acid from modified samples.

The X-ray diffraction analysis (Fig. 3) indicate the practical monomineralality of the initial kaolinite. Diffraction peaks at 2θ=12° (0.715 nm), 20° (0.434 nm), 25° (0.358 nm), and 38° (0.238 nm) correspond to PDF File No. 01-078-2110. The presence of a small amount of quartz as impurity at 2θ=21° (0.426 nm) and 27° (0.334 nm) (PDF File No. 01-083-2472) was detected. The diffractogram of thermally treated samples K-800 and M4-800 (Fig. 3, *a*) is characteristic of an amorphous structure, and the presence of weak peaks of aluminosilicate phases indicates incomplete conversion of kaolinite to meta-kaolinite under these conditions. The diffraction pattern of granules with an applied layer of Fe^0 (Fig. 3, *b*) is characterized by a weak reflection in the area of angles of 2θ~45°, 66°, 84 °, which corresponds to the phase of α-Fe^0 (PDF File No. 6-696).

By the nature of the nitrogen adsorption isotherm on thermally treated kaolinite granules (Fig. 4, *a*, sample K-800, and Fig. 4, *b*, sample M4-800), they belong to type II(b) according to the modified classification by de Boer [16, 17]. Their appearance is typical for non-porous adsorbents with a small macroporous component. A narrow hysteresis loop of the H3 type on the isotherms is formed as a result of capillary condensation. The calculated characteristics of the porous structure of the samples are given in Table 2. The application of zero-valent iron reduces the specific surface area by almost 2 times and the micropore content for samples prepared without a powder-forming additive (sample K-800-Fe^0) and practically does not change these values for the sample M4-800-Fe^0 .

For the studied samples, based on the theory of density functional, the distribution of pores by radii has been determined (Fig. 5). Due to the introduction of PVA into the composition of the ceramic mass and its burnout at a temperature of 800 °C, the number of mesopores in the range from 6 nm increases.

The study of the effectiveness of the removal of heavy metal ions ((Cu(II), Cd(II), Zn(II), Co(II), Cr(VI)) from wastewater containing their mixture, initial and modified granular samples is shown in Fig. 6. The obtained isotherms indicate that the adsorption values of both cations and anions by iron-containing adsorbents are several times higher than those for the starting materials. This is due to the fact that on thermally treated kaolinite granules (Fig. 6, *a*, *c*), the adsorption of metal ions can occur mainly on hydroxyl groups located on the side faces of the particles. Such adsorption centers, depending on the pH of the water, may have a different composition (>Si—OH, >Si—O–, >Al—OH^{2+}; Al—OH and >Al—OH— along the torn tetrahedral and octahedral meshes of kaolinite, respectively. Heavy metal ions, according to their ability to sorb on kaolinite, form a series of Cu>Zn>Co>Cd>Cr, which corresponds to the Irving-Williams series of stability of the corresponding complexes in solutions. This indicates the formation on the surface with the participation of heavy metal ions of strong intrasphere surface complexes [18]. The adsorption values of ions Cu(II), Zn(II), Co(II), Cd(II), and Cr(VI) by granular iron-containing samples are several times higher than those for the initial adsorbents (Fig. 6, *b, d*). This is due to the structure and properties of zero-valent iron, which is applied to the surface of the granules. It is known that iron obtained by the reaction of reduction of ions Fe^{3+} to Fe^0 has the so-called "core-shell" structure. It is characterized by the presence on the surface of particles of zero-valent iron of a thin oxide-hydroxide film of variable composition FeO(OH). It protects the inner core from oxidation and exhibits a high adsorption capacity for both cationic and anionic forms of metals [19]. It should be noted that the difference in adsorption values on samples obtained without the addition of polyvinyl alcohol and with the addition of this additive is insignificant.

The curves of dependence of the adsorption values of heavy metal ions on the pH of the aquatic environment have an S-shaped shape typical of adsorption on hydroxide surfaces with a sharp rise in adsorption values with increasing pH. This may be due to the formation in an alkaline medium of hydrated forms of metals, which are better absorbed on the functional groups of the sample surface [20]. Similar results are reported in the works on the extraction of heavy metal ions from their mixture on powdered silicate adsorbents with an applied layer of zero-valent iron [12, 13].

Thus, granular materials based on kaolinite and zero-valent iron are effective for treating wastewater from a mixture of heavy metals. Limitations to the successful use of the obtained adsorbents can be a high concentration of pollutants and a complex chemical composition of waters. The disadvantages of the study include the imperfect technology of applying a layer of iron to the surface of the granules. As a result of the proposed method of modification, the iron content does not exceed 1 % in relation to the mass of the carrier. To increase the efficiency of adsorption materials, it would be advisable to improve the method of modifying granules in order to increase the number of the reaction layer on their surface. In the future, it would be interesting to investigate the influence of various pore-forming agents on the production of highly porous granular ceramic matrices. This will make it possible to synthesize materials with improved physicochemical properties.

7. Conclusions

1. The influence of the conditions for obtaining granular adsorbents based on kaolinite and zero-valent iron on the strength and parameters of the porous structure of samples in the process of granulation, heat treatment, and modification of their surface has been determined. It has been shown that when adding polyvinyl alcohol to kaolinite in the amount of 3.3 % in relation to the mass of clay mineral and increasing the processing temperature to 800 °C, sufficiently strong granules can be obtained. Their treatment with a solution of iron (III) chloride followed by the reduction of Fe^{3+} ions to Fe^0 with sodium borohydrite leads to the production of composites with an active reaction layer.

2. The phase composition and basic structural and adsorption characteristics of samples were studied. The presence of a layer of zero-valent iron on the surface of kaolinite granules has been confirmed. It was found that the application of iron leads to a decrease in the specific surface area and micropores content for a sample prepared without a pore-forming additive and practically does not change these values for the adsorbent with the addition of polyvinyl alcohol.

3. Our studies have established that applying a layer of zero-valent iron to the surface of granular samples of kaolinite leads to a significant increase in their adsorption capacity. It was shown that the obtained iron-containing granular adsorbents can be successfully used for wastewater treatment containing a mixture of toxic heavy metals, in particular,

Cu(II), Cd(II), Co(II), Zn(II), and Cr(VI) ions. It was established that the adsorption capacity of modified forms of materials is 10–20 times higher than that of the original granules. A significant increase in the adsorption values of Cr(VI) anionic forms, which are difficult to remove from polluted waters by natural ion exchangers, has been confirmed.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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