The object of research is kaolin from the Hlukhovetsky deposit (Ukraine). On its basis, granulated sorbent materials were obtained with the addition of various amounts of cellulose as a pore former. After forming the samples, they were dried and fired at a temperature of 800 °C. The obtained granules with a size of 8–9 mm were modified with zero-valent iron. The physicochemical, including sorption properties of granular composites were studied. Using scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), the morphology of the obtained samples was investigated and the presence of zero-valent iron particles on the surface and in the pores of the sorbents was confirmed. Based on desorption experiments, it was determined by chemical analysis that the Fe⁰ content in modified samples with increased pore former content increases from 0.01 g/g of granules for a sample containing 1 % cellulose to 0.016 g/g for a carrier with 3 % pore former. The specific surface area and pore volume of the samples were determined by the method of low-temperature adsorption-desorption of nitrogen. Thus, with an increase in the surface of the pore former in the ceramic mass, the specific surface of both unmodified and modified samples slightly decreases. Thus, with a cellulose content of 1 %, it is 20 m²/g and 17 m²/g, respectively. When the pore former is increased to 3 %, these values are 15 m²/g and 12 m²/g. After applying a layer of zero-valent iron on porous granules, the volume of pores decreases, which is due to the formation of agglomerates of iron particles during synthesis. The study of the sorption capacity of the obtained sorbents with respect to Cr(VI) from model solutions containing a mixture of metal cations (copper, cadmium, cobalt, zinc) showed that granular materials exhibit sorption capacity for metal anions, even in the presence of cations. The amount of chromium sorption naturally increases for modified samples with an increase in the cellulose content in them. However, for model solutions that do not additionally contain metal cations, the sorption value is somewhat higher. Thus, for a sample with a 3 % pore former content, the sorption value is 0.7 mg/g and 0.9 mg/g, respectively, at an initial chromium(VI) concentration of 10 mg/g. The obtained experimental data indicate that the obtained porous granular sorbents based on kaolin can be used in the further treatment of wastewater from electroplating enterprises, which contain a mixture of pollutants in both anionic and cationic forms.

Keywords: granular sorbents, kaolin, pore former, cellulose, water purification, heavy metals, anionic toxicants.

1. Introduction

Obtaining sorption materials for water purification from heavy metal ion contamination based on available and cheap natural raw materials is an urgent environmental task today. For example, during electroplating processes (nickel-plating, chrome-plating, zinc-plating, copper-plating), washing water is generated, which, as a rule, is not regenerated separately, but is fed to general treatment facilities. Since up to 2 g of metal enters the waste to obtain 1 m² of galvanic coating, a significant amount of galvanic sludge is formed when using traditional methods of wastewater neutralization [1]. That is why, at galvanic enterprises, it is advisable to additionally use adsorption methods for cleaning washing waters. To ensure a continuous technological process, it is necessary to use adsorbents in granular forms, which will be reactive to both anionic and cationic forms of metals.

Granular sorbents are obtained on the basis of both natural and synthetic raw materials [2]. To clean large volumes of water contaminated with heavy metals in low concentrations, it is economically expedient to use sorbents based on cheap raw materials. Such materials can be, in particular, natural aluminosilicates, which are characterized by high chemical, thermal and mechanical strength [3, 4].

The process of obtaining granular sorbents based on clay raw materials can be carried out using plastic mass by the extrusion method. Molded granules must be dried and fired at high temperatures. After heat treatment, the sorption capacity of silicate sorption materials decreases due to the reduction of the specific surface as a result of sintering processes. One of the ways to increase the sorption capacity of such samples is to modify their surface with various inorganic and organic compounds [5, 6]. Another method of obtaining effective sorption materials...
based on clay is the formation of composites with cellulose, which have proven themselves well in the processes of water purification from metal ion contamination [7–9]. If such materials are subjected to heat treatment at high temperatures, porous ceramic sorbents can be obtained due to the burning of the organic component. In addition, the addition of such an additive to natural aluminosilicates, for example, kaolin, leads to an improvement in the forming properties of the ceramic mixture. Currently, the processes of structure formation in granular materials based on kaolin and cellulose fibers have not been sufficiently studied. In addition, it is interesting to investigate the possibility of using such porous media for obtaining sorption materials modified with zero-valent iron.

Therefore, the aim of this research is to study the physicochemical properties of porous granular sorbents based on kaolin. This will make it possible to evaluate the sorption properties of the modified samples in relation to aqueous solutions contaminated with heavy metal ions.

2. Materials and Methods

The object of research was kaolin from the HLukhovetsky deposit (Ukraine), which was previously cleaned of impurities by repeated washing with distilled water. Porous materials based on kaolin were obtained in the form of granules with dimensions of 8 × 2 ± 1 mm (∅ x w). Granulation of samples was carried out by the method of plastic molding. For this, two-component ceramic masses with a molding humidity of 26 % were used. In this study, sulfated cellulose bleached from hardwoods, fiber length 1.2–1.3 mm was used as a pore former. The mass ratio of the pore-forming additive to kaolin varied in the range of 1–3 %. Samples were fired in a muffle furnace at a temperature of 800 °C in an air atmosphere, exposure time at the maximum temperature was 2 hours.

The obtained granular materials were modified with a layer of zero-valent iron (Fe°) according to the general method described in the previous work [10]. In order to quantitatively determine the content of iron in the modified samples, their chemical analysis was carried out. To do this, a weight of granules was placed in a container with nitric acid and stirred for 1 hour.

The morphology of granular samples (before and after Fe° modification) was studied using scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) on a Tescan MIRAX LMU microscope (Czech Republic). Samples were previously metallized with gold-palladium sputtering. Analysis of the obtained images was carried out using ImageJ software. Point element analysis was performed at various points on the surface to minimize the effect of possible surface inhomogeneity.

The characteristics of the porous structure were determined by the method of low-temperature adsorption-desorption of nitrogen on the Quantachrome NOVA-2200e Surface Area and Pore Size Analyzer (USA). Processing of the obtained data was carried out using the ASIQuinTM V 3.0 software. The value of the specific surface area ($S_{\text{BET}}$, $\text{m}^2/\text{g}$) was calculated by the multipoint BET method (Brunauer, Emmett and Teller). The total pore volume ($V_T$, $\text{cm}^3/\text{g}$) was determined by the maximum adsorbed volume of nitrogen at a relative pressure ($p/p_0$) close to 1. The micropore volume ($V_{\text{mic}}$, $\text{cm}^3/\text{g}$) for iron-containing samples was estimated by t-plot method. The average pore size is calculated by Density Functional Theory (DFT).

The study of the adsorption properties of the obtained granular materials for the extraction of anionic forms of toxicants was carried out using model solutions containing Cr(VI) and a mixture of extraneous heavy metal cations with a concentration of 10 mg/dm$^3$. The model solution was prepared in distilled water using standard solutions of chromium, copper, cadmium, cobalt, and zinc (Sigma), the pH value is 6.2. The ionic strength value (0.005) was set with 1M KNO$_3$ solution. The adsorption experiment was carried out under static conditions for 2 hours at a temperature of 20 °C. After the adsorption equilibrium was established, the liquid phase was separated from the solid phase and the equilibrium concentration of Cr(VI) was determined in it by atomic emission spectrometry with inductively coupled plasma (Thermo Scientific iCAP 7400 ICP-OES, USA).

The value of the adsorption value was calculated according to the formula:

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

where $C_0$, $C_e$ – initial and equilibrium metal concentration, mg/dm$^3$; $V$ – solution volume, dm$^3$; $m$ – the weight of the sorbent, g.

3. Results and Discussion

Fig. 1 presents photographs of the obtained granular materials based on kaolin and cellulose before and after modification with zero-valent iron. After conducting a chemical analysis of the modified granules, it was established that the amount of the modifying layer increases with an increase in the cellulose content in the composition of the ceramic mass (Table 1).

![Photos of the obtained granular materials with cellulose: a – before modification; b – after modification](image)

**Table 1**

<table>
<thead>
<tr>
<th>Sample cipher</th>
<th>Cellulose content in ceramic mass, wt. %</th>
<th>The amount of applied iron, g (in relation to 1 g of clay)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KC1 %</td>
<td>1</td>
<td>–</td>
</tr>
<tr>
<td>KC2 %</td>
<td>2</td>
<td>–</td>
</tr>
<tr>
<td>KC3 %</td>
<td>3</td>
<td>–</td>
</tr>
<tr>
<td>KC1 %–Fe</td>
<td>1</td>
<td>0.01</td>
</tr>
<tr>
<td>KC2 %–Fe</td>
<td>2</td>
<td>0.013</td>
</tr>
<tr>
<td>KC3 %–Fe</td>
<td>3</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Firing the samples at a temperature of 800 °C allows for the complete removal of cellulose, as a result of
which pores of a characteristic size and shape are formed, which is confirmed by images of scanning electron microscopy (Fig. 2, a, b). In Fig. 2, c shows the SEM image of the modified granule. The presence of spherical agglomerates confirms the successful formation of Fe⁰ on the surface and the inner layer of granules close to the surface.

The formation of a layer of zero-valent iron is also confirmed by the results of point element analysis (Fig. 3). On the EMF spectrum of the modified sample, in comparison with the original granule, the intensity of Fe peaks is much higher; in addition, the total number of Fe peaks also increases. The presence of Cl peaks in the KC₃ %–Fe sample is explained by the use of a FeCl₃·6H₂O solution to modify the granules and, accordingly, insufficient complete washing of the obtained material at the final stage of synthesis. This does not affect the physical and chemical properties of the sample under study. The characteristic peaks of Au and Pd present in the two spectra are formed as a result of gold-palladium sputtering at the stage of sample preparation.

The parameters of the porous structure of the granular samples are given in the Table 3. When the content of the pore former increases, the average size of the pores formed as the result of its burning increases from 5.37 nm to 9.95 nm. This can be explained by the fact that the cellulose is unevenly distributed in the ceramic mass or during its burning, the walls between adjacent pores are destroyed and larger pores are formed. For comparison, the average pore size of a kaolin granule without the addition of pore formers is 1.39 nm.

For samples with Fe⁰, the opposite trend is observed, i.e., the average pore size decreases in the order KC₃ %–Fe > KC₂ %–Fe > KC1 %–Fe, which is due to the agglomeration of zero-valent iron, which was also described by SEM results. Also, such agglomeration can affect the value of the specific surface of the samples, reducing it in comparison with the values of the specific surface for similar samples without additional modification. If to compare the specific surface for similar samples, where polyvinyl alcohol was used as a pore former [10], the samples with cellulose have twice as high values.
The results of studying the adsorption properties of the obtained porous materials based on kaolin are presented in Fig. 4. When Cr(VI) ions are extracted from model solutions containing extraneous heavy metal ions, the sorption capacity of the samples increases with an increase in the amount of cellulose in the ceramic mass and, accordingly, with the amount of applied Fe⁰ layer (Fig. 4, a). So, for the KC3 %–Fe sample, the sorption value is 0.7 mg/g. At the same time, it should be noted that the efficiency of Cr(VI) removal for similar samples from model solutions containing only chromium ions does not differ significantly (Fig. 4, b).

Thus, the obtained porous materials can be used for further purification of washing water of electroplating enterprises, which are multicomponent systems.

It should be taken into account that the described adsorption properties are valid only for the interaction of granular samples with aqueous systems that correspond to the model solutions used in this study. With any change in the initial parameters, the amount of chromium(VI) adsorption, and, accordingly, the degree of its extraction may differ from those given above.

The conditions of martial law did not affect the obtained results in any way. However, hostilities on the territory of Ukraine and missile attacks cause significant damage to the environment. In particular, the destruction of critical infrastructure facilities and industrial enterprises leads to the ingress of heavy metals, fuels, lubricants into ground-water and significant pollution of surface water bodies.

In the following studies, it would be expedient to investigate how the methods of preparing the ceramic mass affect the physico-chemical and mechanical properties of the obtained samples.

### 4. Conclusions

Porous granular sorbents based on kaolin, modified with zero-valent iron, were obtained. The effect of the content of different amounts of pore former (cellulose) on the physical and chemical properties of sorption materials was studied. The morphology of porous samples was studied. It is shown that with an increase in the content of the organic component in the ceramic mass, the number of pores and applied iron on the carrier increases. The average pore size increases by 4–7 times, depending on the amount of added cellulose, compared to the sample without a pore former.

The presence of a modified iron layer on the surface was confirmed by scanning microscopy with energy dispersive X-ray spectroscopy and chemical analysis based on desorption experiments. The sorption capacity of the obtained materials in relation to metal anions (chromium) contained in an aqueous solution containing cations of copper, cadmium, nickel and zinc was established. The perspective of using synthesized granules for further purification of water contaminated with a complex mixture of metal ions is shown.

### Conflict of interest

The author declares that she has 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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### Data availability

The manuscript has no associated data.

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