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STUDY OF THE STRUCTURE OF ORGANO-MODIFIED PALYGORSKITE

Досліджено властивості палигорськіта, модифікованого катіонною поверхнево-активною речовиною гексадецилтриметиламоній бромідом з метою отримання сорбентів для очищення водних середовищ від йонів важких металів та радіонуклідів. Вивчено структуру палигорськітів за допомогою рентгенофазового та термічного аналізу. Виявлено температурні інтервали, в яких відбувається зміна структури вихідного матеріалу та синтезованих композитів, що супроводжується зміною їх фізико-хімічних властивостей.

Ключові слова: *палигорськіт, гексадецилтриметиламоній бромід, катіонна поверхнево-активна речовина, адсорбція Cr(VI).*

1. Introduction

In the technology of water purification, next to activated carbon and synthetic ion exchangers, mineral sorbents of natural origin become increasingly important [1]. Palygorskite is a natural silicate with a layered tape structure. It has a wide range of industrial applications due to its special adsorption, colloid-rheological and catalytic properties, which are the basis of many technological processes. Palygorskite is used as a cheap, ecological sorbent for extracting cationic contaminants from aqueous media. The change in the surface of palygorskite from hydrophilic to hydrophobic allows the use of organomodified mineral to extract anions of heavy metals and radionuclides. This determines the relevance of scientific and technical developments for solving the problem of directed synthesis of effective sorbents based on natural silicates with the studied properties and structure.

2. The object of research and its technological audit

The object of research is a natural silicate with a stratified ribbon structure – palygorskite of the Cherkasy deposit (Ukraine), with a cation exchange capacity (CEC) of 0.25 mmol/g [2]. This mineral, in its structure, occupies an intermediate type between banded and layered silicates. Palygorskite is characterized by the presence of primary and secondary porosity. Zeolite channels in the mineral form a primary porosity, which is a small part of the adsorption surface. The secondary porosity of the mineral is formed by ribbons of crystals that are densely packed together and exhibit high adsorption properties with respect to cationic forms of substances.

One of the problematic areas in the technology of sorption purification of aqueous media using palygorskite is the absence of kinship of the mineral in anionic forms of pollution. Therefore, its use as a sorbent to extract ions Cr(VI), U(VI), As(V), which are in aqueous media in anionic forms, is ineffective.

The subject of research is the structure of Na-palygorskite and synthesized organo-palygorskite, as well as their sorption properties.

3. The aim and objectives of research

The aim of research is obtaining sorbents based on natural silicates for the extraction of heavy metal ions.

To achieve this aim, it is necessary perform the following objectives:

1. To investigate the structures of palygorskite and modified samples by means of X-ray diffraction analysis (XRD).
2. To study the thermal properties of palygorskite and the resulting composites.
3. To compare the sorption properties of Na-palygorskite and synthesized sorbents on its basis.

4. Research of existing solutions of the problem

Clay minerals are widely used in environmental practice as cheap sorbents for the extraction of cationic forms of inorganic toxicants from aqueous solutions. However, they practically do not remove anionic forms of contaminants. To increase the sorption properties of natural silicates, acid activation, hydrothermal treatment, and modification with surfactants are used. A change in the surface of silicates with cationic surfactants makes it possible to obtain efficient and economical composites for the recovery of dangerous anions, such as As(V), Cr(VI), U(VI), etc. [3].

During the modification of the surface of natural silicates by cationic surfactants, not only the primary filling of the monolayer on the active centers of the mineral occurs, but also the formation of a bilayer or mosaic coating [4]. In this case, the ammonium groups of the cationic surfactant are electrostatically attracted to the negatively charged surface of the clay mineral, and the alkyl chains are oriented from the surface [5]. The formation of these structures is possible due to the interaction between hydrocarbon radicals of surfactant molecules [6]. As a result of the modification, it is possible to obtain partially a charge or a completely positively charged surface, which has a high affinity for anionic contaminants.

Research of literature sources shows that the study of the sorption of cationic surfactants on clay minerals was concentrated on layered silicates [7]. On their basis, organoclays with high sorption properties with respect to anions of heavy metals and radionuclides were synthesized.

Organosilicates obtained on the basis of palygorskite, sepiolite, and chabazite have been little studied. There are several works where the processes of synthesis of organoclays based on these minerals are described. Thus, Na-chabazite modified with hexadecyltrimethylammonium bromide (GDTMA) showed high indices and proved to be an economic sorbent for elimination of chromates [8]. The authors of [9] synthesized organo-palygorskite and organo-sepiolite, for the modification of which GDTMA was used and the ability of the obtained composites to remove the anionic forms of inorganic compounds was confirmed. The authors explain the increase in sorption properties in organoclays by the formation of complex admixture of GDTMA participating in adsorption processes.

In [10], the structure of the organo-palygorskites of various degrees of surface modification by cationic surfactants was studied using XRD. The authors confirmed that the structure of the palygorskite lattice varies little with the degree of surface modification of the mineral. Although the sorption properties of the obtained organo-palygorskite significantly increased in comparison with Na-palygorskite, which can be explained by the complex mechanism of GDTMA sorption on the surface of the mineral, which in turn participates in the binding of anions of heavy metals and radionuclides.

In [8], the authors used thermal analysis as a supplementary method for studying the structure of organo-chabazite. This allowed to explain the mechanism of GDTMA sorption on the mineral and anions on the modified surface.

This method was also used by the authors [11, 12] to refine the organo-bentonite structure.

Taking into account that in the examined publications the structure of the surface of organo-palygorskites has not been systematized and complexly studied so far, as well as their thermal properties, it has been decided to conduct thermal studies of synthesized materials. The given researches will allow to spend the directed synthesis organo-modified palygorskite on the basis palygorskite of the Cherkasy deposit with the set properties.

Thus, the results of the analysis of this problem indicate that there is a need to study the thermal and structural properties of composites based on natural palygorskite, as well as the comparative sorption properties of the resulting composites with Na-PG.

5. Methods of research

To achieve the aim of research work, XRD methods, thermal analysis and a spectrophotometric method for studying the sorption properties of synthesized materials are used.

To modify the palygorskite surface, the salt of tetrasubstituted ammonium GDTMA – $(C_{16}H_{33})N(CH_3)_3Br$ (Merck) was taken. Natural palygorskite was previously transferred to the Na-form by the method described in [10].

Modifications of palygorskite to Na-form were carried out according to the method described in [13].

Na-palygorskite (Na-PPG) and mineral samples were chosen for sorption experiments, they were modified at a ratio of CEC/surfactant equal to 1:1 and 1:2 and named OPG-1 and OPG-2, respectively.

The X-ray analysis was carried out using a ДРОН-3М diffractometer (Russian Federation), with a computer-based scanning and diffraction pattern recording system. Filtered Cu-K_α radiation was also used.

A solution of potassium dichromate $K_2Cr_2O_7$ and a sample of synthesized composites was used in sorption experiments. Sorption was carried out under static conditions with a continuous shaking of the samples for 1 h (the volume of the aqueous phase was 50 ml, the sample of the mineral was 0.1 g, the concentration of Cr(VI) in the sorption experiments was 50 and 100 mg/l) according to the procedure [13]. The ionic strength (0.01 M) of the solutions was established with the aid of NaCl. After the adsorption equilibrium was established, the aqueous phase was separated by centrifugation (5000 rpm) and the equilibrium concentration of the metal was determined by spectrophotometric method (UNICO 2100UV) (UNICO, USA) using a diphenylcarbazide reagent at a wavelength of 540 nm for chromium. Sorption of chromium ions was studied at pH=7 and chromium concentration 10 mg/dm^3. For such neutral pH, the dominant form Cr(VI) in aqueous solutions is CrO_4^{2-}, in the presence of significantly lower amounts of ions $HCrO_4^-$ and ions $Cr_2O_7^{2-}$ in trace concentrations.

Thermogravimetric studies of sorbents were carried out on the device Derivatograph Q-1500 (Hungary) of the «Paulik-Paulik-Erdei» system. Samples were analyzed in a dynamic mode at a heating rate of 10 °C/min to 1000 °C in an air atmosphere. The mass of the samples was 1500 mg. Reference substance was Al_2O_3. In the experiments, a platinum crucible was used. The sensitivity on the TG scale is 50 mg, on the DTA scale – 250 μV.

6. Research results

For the palygorskite sample, the interplanar distance *d* (hkl) for the (110) plane is 10.7 Å (Fig. 1). After treatment with Na-PG, changes in its crystal structure are observed. There is a shift of the peaks toward large angles 2θ. Significantly increases the intensity of the line (110). Other reflections also change their relative intensity $I_{(hkl)}/I_{(110)}$. Significantly decreases the intensity of the peaks (121) and (231). Comparison of the diffractograms OPG-1 and OPG-2 allows to conclude that the reflection with the same indices is not relatively displaced, but their intensity is different. An intensity of most peaks in OPG-2 is higher.

To carry out structural studies and determine the nature of the interaction of the applied modifier with the surface of the clay mineral as an additional method that will help to concretize the XRD results, a thermal analysis is chosen. The results of thermographic (TG), differential thermographic (DTG) and differential thermal analysis (DTA) for samples of Na-PG, OPG-1 and OPG-2 are presented in Fig. 2–4.

According to the thermal analysis of the Na-PG sample (Fig. 2), at a temperature range of 40–200 °C, let's observe a clear endothermic effect on the DTA curve with a maximum at 116 °C. Adsorption water is released in this temperature range. According to the data of the thermogravimetric analysis, the mass loss in this area is about 11.8 %.

Dehydration of the material takes place in the temperature range 200–280 °C. This process is accompanied by the appearance of a fuzzy endothermic effect on the DTA curve. According to the TG data, the mass loss in this area is 1.9 %. In the temperature range 380–580 °C, according to TG, the mass loss of a sample of natural clay in the region and the appearance of an index on the DTA curve with a maximum at 492.5 °C. These changes in the curves can be associated with the separation process of the third portion of water. The mass loss at this stage is 5.9 %. At temperatures above 700 °C, the crystalline lattice of palygorskite is destroyed and only some ordering remains in the ion distribution. In the temperature range 790–850 °C, let's observe a clear endothermic effect on the DTA curve, the removal of structural water, about 1.8 %, and complete destruction of the mineral structure. In the temperature range 850–960 °C let's observe an exothermic effect, which follows the previous endothermic effect. The size of the exothermic peak depends on the Mg content in the mineral. This effect corresponds to the onset of crystallization of new phases. When the temperature is raised to 1100–1200 °C, α-tridymite and clinoenstatite are formed [14].

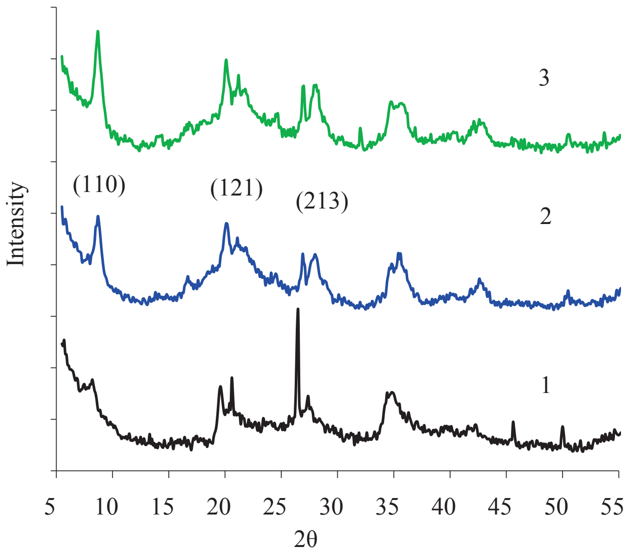

Fig. 1. Fragment of diffraction patterns of samples: 1 – Na-PG; 2 – OPG-1; 3 – OPG-2

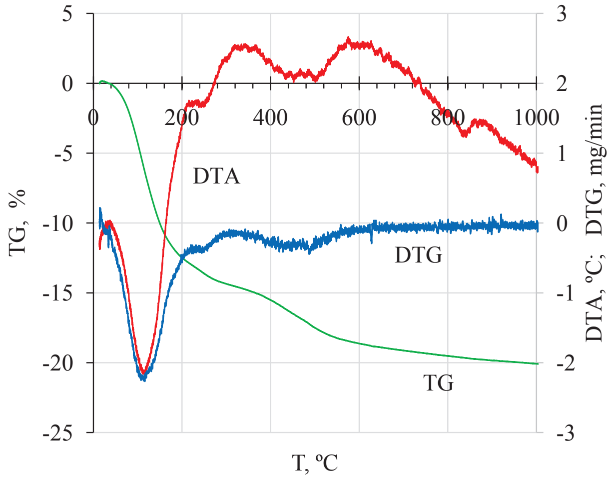

Fig. 2. Derivatogram of Na-PG sample

For samples of OPG-1 and OPG-2 composites based on DTA data (Fig. 3, 4), in the temperature range 80–150 °C, clear endothermic effects are observed. In this temperature range, physically bound water is removed. According to the thermogravimetric analysis, the mass loss in this area is 6.5 % and 5.4 % for the samples of OPG-1 and OPG-2, respectively. In the temperature range 220–300 °C, a part of the organic component of the composite ignites. This process is accompanied by the appearance of an exothermic effect on the DTA curve.

According to the TG data, the mass loss is 2.2 % and 4.2 % for OPG-1 and OPG-2, respectively. In the temperature range 360–580 °C, let's observe the loss of mass and the appearance of the beta-effect on the DTA curve with a maximum at 470.5 °C and 475 °C for OPG-1 and OPG-2, respectively. Such thermal behavior of the samples can be explained by the GDTMA pyrolysis, which is adsorbed on palygorskite and is firmly bound to the surface of the mineral.

The diagrams show wide peaks, as a result of the presence of various forms of surfactant introduced into the composite: monomers, micelles and other substances that are formed as a result of the GDTMA thermal decomposition.

For OPG-2, let's observe a much broader peak than the similar temperature range, due to the presence of a much larger number of surfactant in the composite.

Also on this site, it is possible to remove water.

The total weight loss is 3.9 % and 5.8 % for OPG-1 and OPG-2, respectively.

Thus, it can be argued that the surfactant molecules that are bound to the palygorskite surface burn out gradually. A proof of this fact can be the increase in the temperature of the organic burn-up from the OPG-1 and OPG-2 samples compared to the melting point and the burn-up of pure GDTMA equal to 250 ˚C. And also the absence of an acute endothermic peak resulting from the melting of the hydrocarbon chain in the organo-palygorskite samples. This is explained by the strong interaction of the GDTMA cations with palygorskite through electrostatic and van der Waals forces.

Between the GDTMA cations and the palygorskite surface, bonds are formed that make melting and light pyrolysis of GDTMA impossible [15].

At a temperature of 520 ˚C for the samples of OPG-1 and OPG-2, let's observe insignificant endothermic effects without loss of mass that can be explained by the structural phase transition without changing the chemical composition.

Already at a temperature above 670 ˚C for the samples of composites OPG-1 and OPG-2 according to DTA, the palygorskite lattice is destroyed and only some ordering in the ion arrangement remains. The organic component in the composite is absent. In the temperature range 790–840 °C let's observe the endothermic effect on the DTA curve – removal of water residues, about 0.5 % and complete destruction of the mineral structure. With a further increase in the temperature of the OPG-1 and OPG-2 samples, let's observe similar changes as for Na-PG.

The results of studies of the adsorption of Cr(VI) on Na-PG, OPG-1, and OPG-2 are shown in Fig. 5.

Modification of the palygorskite surface by GDTMA makes it possible to increase the adsorption of Cr(VI) with 0.45 mg/g and 9.2 mg/g, respectively. And for the initial concentration of the solution 100 mg/l to 4.2 and 12.3 mg/l, respectively.

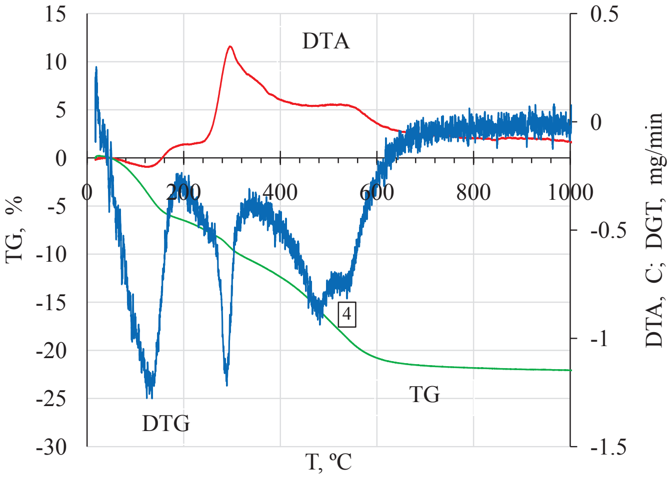

Fig. 3. Derivatogram of OPG-1 sample

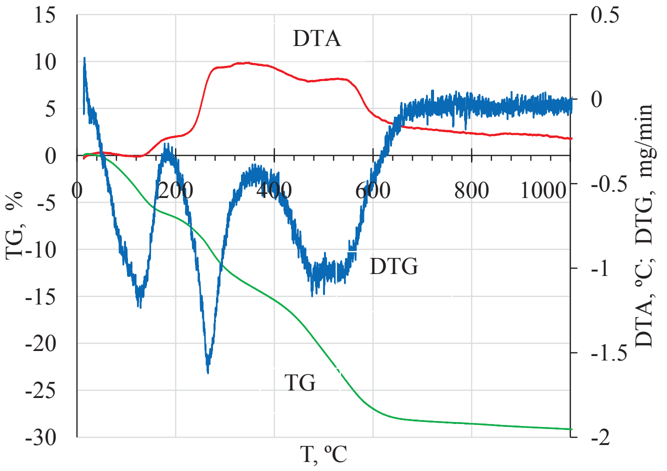

Fig. 4. Derivatogram of OPG-2 sample

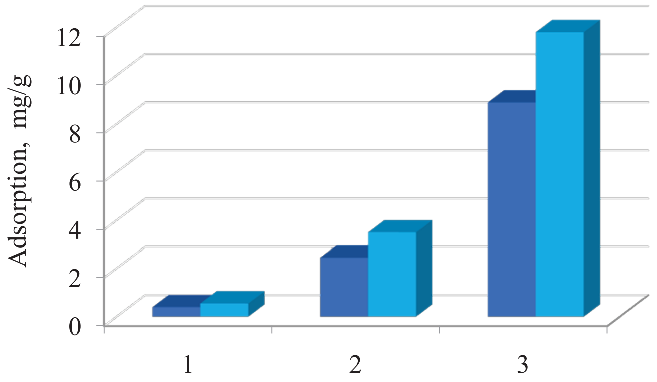

Fig. 5. Adsorption of Cr(VI) ions by samples: 1 – Na-PG; 2 – OPG-1; 3 – OPG-2

7. SWOT analysis of research results

Strengths. Among the strengths of this research, it is worth noting the obtained results determine the thermal properties of the organo-palygorskites. This provides a comprehensive solution to issues of improvement:

- technologies for obtaining sorbents, ecology (the possibility of directed synthesis of sorbents based on natural raw materials for the extraction of heavy metal ions from aqueous media);
- resource saving (due to the replacement of expensive sorbents based on activated carbon and ion exchange resins for cheap natural raw materials).

Weaknesses. The weaknesses of this research are related to the fact that the developments are based on the study of palygorskite and organo-palygorskites with certain degrees of modification. This raises the need for additional studies of materials with other degrees of modification.

Opportunities. Additional opportunities to achieve the aim of research may be associated with the features of the use of XRD data and thermal analysis for the synthesis of sorbents with specified properties. At the same time, depending on the parameters of palygorskite processing, it is possible to vary the degree of palygorskite modification and the use of such composites to extract heavy metal ions.

Modification of the palygorskite surface by GDTMA will make it possible to use cheap natural material as a sorbent for the recovery of heavy metal anions. The use of palygorskite is much more economical in comparison with ion-exchange resins. The cost of natural silicates is 550 times lower than the cost of cation-exchange resins.

Threats. Threats to the introduction of research results are related to the additional costs of the enterprise associated with the GDTMA acquisition and the synthesis of organo-palygorskites and also with the fact that analogs of synthesized sorbents are used to extract anionic dyes.

8. Conclusions

1. The structures of palygorskite and modified samples are studied using-ray diffraction analysis (XRD). After treatment with Na-PG, changes in its crystal structure are observed. There is a shift of the peaks toward large angles 2θ. Comparison of the diffractograms OPG-1 and OPG-2 allows to conclude that the reflection with the same indices is not relatively displaced, but their intensity is different. In OPG-2, the intensity of most peaks is higher.

2. Study of the thermal properties of organo-palygorskites allowed to clarify the data of the XRD and confirmed the formation of stable bonds between the cations of surfactant and the surface of the palygorskite.

3. According to the results of sorption studies, it was found that synthesized organopalygroskite can remove up to 97.8 % of Cr(VI) ions, which is 16.2 times more than in comparison with natural palygorskite. These materials can be used as sorbent for the removal of heavy metal anions.

Increasing the volume of practical use of natural silicate materials contributes to a comprehensive solution of environmental issues, resource saving and technology for the production of sorbents for the extraction of anionic forms of Cr(VI) and U(VI) from aqueous solutions.

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ИЗУЧЕНИЕ СТРОЕНИЯ ОРГАНОМОДИФИЦИРОВАНОГО ПАЛИГОРСКИТА

Исследованы свойства палыгорскита, модифицированного катионным поверхностно-активным веществом гексадецилтриметиламоний бромидом с целью получения сорбентов для очистки водных сред от ионов тяжелых металлов и радионуклидов. Изучена структура палыгорскит с помощью рентгенофазового и термического анализа. Выявлены температурные интервалы, в которых происходит изменение структуры исходного материала и синтезированных композитов, сопровождающееся изменением их физико-химических свойств.

Ключевые слова: палыгорскит, гексадецилтриметиламоний бромид, катионное поверхностно-активное вещество, адсорбция Cr(VI).

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