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PROPERTIES, STRUCTURE OF ENVIRONMENTALLY FRIENDLY SORBENTS BASED ON NATURAL RAW MATERIALS

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The article presents data on the selection of natural raw materials corresponding to the structural material in the preparation of effective sorbents. It is noted that clay minerals in composition and physicochemical properties fully meet the requirements for the development of effective sorbents and have important scientific and practical significance for industry. It is noted that wastewater from a number of industries, in some cases, is contaminated with cations of various heavy metals, such as Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{3+}, Co^{2+}, Pb^{2+}, Mn^{2+}, Cd^{2+} etc. It has been established that modification of natural aluminosilicates improves their sorption properties. It has been shown that the modified Na-form of natural bentonites in weakly acidic and alkaline environments exhibits better colloidal properties and is capable of rapidly absorbing heavy metal ions.

Key words: *structural properties, sorbents, aluminosilicates, toxic elements*

INTRODUCTION

The intensive development of a number of industries has created environmental problems due to the increased anthropogenic impact on the biosphere, and in the last quarter of the outgoing century, humanity has entered an era of deep ecological and economic crisis, despite the fact that from the beginning of the 17th century until the end of the 17th century, environmental pollution was local in nature [1]. The environment has become so polluted that the ecological crisis in local areas threatens the life of living organisms, and in recent years this process has accelerated even more. If such a situation in the biosphere continues, serious threats to the life of living beings and humans may arise in the future [2]. This is due to the fact that high concentration of production leads to the release of waste considered harmful to the environment. and leads to a rapid increase in environmental tension in industrial centers. In ancient times, measures were taken to protect water sources, caves of ancient settlements, valuable trees and territories rich in wildlife in Central Asia, the Mediterranean countries, and the Caucasus. So, beginning in the 11th and 12th centuries, a number of practical measures were taken to prevent environmental pollution in Western European countries[3-4]. Currently, the degradation of the biological world as a result of anthropogenic and technogenic impacts annually leads to the destruction of a large number of plant and animal species. Currently, the influence of the human factor on the ecosystem has increased dramatically, since technogenic technologies used as a means of influencing nature have become practically uncontrollable and anarchic, acquiring a status practically independent of man. As a result, global problems have arisen that worry humanity and are becoming increasingly difficult to solve, and it is difficult to say that they will not continue in the future. It should be noted that the main sources of chemical pollution are various industries, energy, motor transport and agricultural production, the accumulation of industrial and household waste in the lithosphere, the release of pollutants and compounds into the atmosphere and hydrosphere, etc [5-7]. Violation of the energy, including thermal, balance has led to the creation of a "greenhouse" (greenhouse) effect as a result of an increase in the concentration of carbon dioxide (CO_2) in the atmosphere, global warming, the opening of holes due to the degradation of the ozone layer, etc [8]. The lack of improvement of modern technology does not ensure full processing and use The United Nations (UN) system actively works on international cooperation in the field of environmental protection [9-11]. From the very beginning of the United Nations, environmental protection has been one of the practical tasks of the organization. mineral raw materials. According to the results of the study, it should be noted that it is better to prevent the occurrence of environmental problems with the help of preventive measures than to think about solving environmental problems caused by any anthropogenic activity in the field of environmental protection and rational use of natural resources [12-14].

EXPERIMENTAL PART

At present, various industries, such as oil production, oil refining, metallurgy and many others, occupy a leading position among enterprises that cause environmental damage. Chemical, metalworking, oil, metallurgy and some other industries pollute the biosphere with gas emissions, solid waste and wastewater. Also, during the period of intensive operation of a number of industries, including nuclear and thermal energy, industrial and rural construction, transport, etc., there is one or another negative impact on the ecobalance of the environment [15]. Thus, galvanic production, which applies protective or decorative coatings to metal and non-metal products (galvanizing, nickel plating, oxidation), can be classified as an enterprise that heavily pollutes the environment with wastewater [16]. It should be noted that at present galvanic coatings are used in almost all branches of industry: mechanical engineering, instrument making, printed circuit board production, etc., however, despite the various methods of surface treatment of products, when all the standards for the technological process are observed, some amount of waste water of complex composition is still formed. With an insufficient degree of purification, they are one of the sources of pollution of aquatic environments. The main toxic components polluting this type of wastewater are heavy metals: chromium (VI), cadmium, lead and other toxic substances [17]. Thus, various types of toxic wastewater are formed at such enterprises. Accordingly, chromium-containing wastewater contains cadmium - 0.3-0.5 mg / l chromium (III) - 0.2-0.5 mg / l copper - 0.5-1.0 mg / l iron - 0.1-0.5 mg / l nickel 0.2-0.5 mg / l and zinc 0.2-1.0 mg / l, such indicators do not comply with the MAC standards according to GOST 9.314.90 and are subject to neutralization [18]. At this stage of development, with the tightening of environmental legislation, stricter standards are established for the discharge of industrial wastewater and penalties for exceeding the established MAC are increased - the introduction of closed water management systems is of great importance. The implementation of closed water management systems is possible only if the water fully complies with the requirements of galvanic production - GOST 9.314-90 "Water for galvanic production and galvanic washings" [19]. Various treatment methods are used to remove them: settling, filtration, neutralization, chemical precipitation, coagulation, sorption, etc.

MATERIAL AND METHODS

Also, when cleaning wastewater and liquid waste from heavy metal ions and various toxic substances in sorption processes, clay minerals are widely used as promising and relevant raw materials due to their low cost and inexhaustible reserves. Porous materials with a crystalline structure are represented by non-stoichiometric compounds of the aluminosilicate class with the general formula $(MeO)n(AlO_2)x(SiO_2)y\cdot mH_2O$.

In this aspect, the development of methods for the preparation of new effective sorbents based on natural bentonites is of great practical importance. Wastewater from metallurgical and galvanic industries is contaminated with cations of various heavy metals, such as Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{3+}, Co^{2+}, Cd^{2+}, etc. Since clay minerals differ from each other in their structural composition, a careful selection of rational raw materials corresponding to the structure of effective sorbent materials was carried out in the studies. Clay minerals from a number of deposits were studied. The largest among the deposits we studied were clays: Khanlarsky district with a total reserve of 5 million tons, Khirdalansky - 3.5 million tons, Khizi and Dash-Salakhlinsky districts with a total reserve.

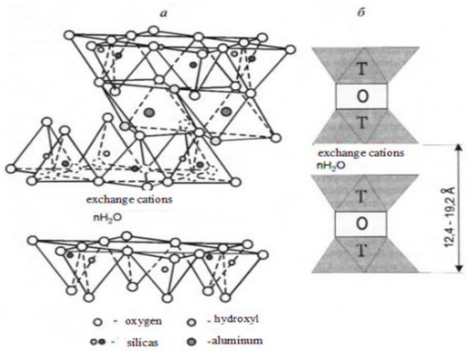

Fig. 1. Structure of montmorillonite:
a-atomic; b-schematic (T- tetrahedron; O- octahedron)

The chemical and mineralogical composition of a number of mineral clays was studied, which are presented in Tables 1-4.

When comparing the obtained analysis results, bentonites of the Dash-Salakhlinskoye deposit found real application as an alternative raw material in the synthesis of sorbents.

Preliminary preparation of clay minerals was carried out before conducting physicochemical analyses of the samples, since the success of studying clay minerals largely depends on the correctness of sample preparation. Parts of the clay mineral dried in air were freed from brown veins of iron oxide, dark grains of manganese oxide, lenticular accumulations of carbonates, in bentonite clays the latter are quite easily recognized by their white color and granular texture, as well as other impurities and inclusions noticeable to the naked eye. Further purification of the bentonite mineral was carried out by elutriation. An approximately 3-5% aqueous suspension of clay was prepared, thoroughly mixed with a mechanical mixer until the lumps disappeared, left alone for two hours, and the finest fraction was decanted using a siphon. Then, its Na-form was obtained by the ion exchange method [20]. Since it is the Na-form of bentonite clays that exhibits the best colloidal properties in weakly acidic and alkaline environments and is capable of rapidly absorbing heavy metal ions.

RESULTS AND DISCUSSION

Table 1.

Chemical composition of bentonite clays of the Khizi deposit

№	Name of the deposit	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3
1	Ag-Dere-1	3.17	3.71	13.64	55.17	0.024	0.031	1.19	2.66	0.590	0.286	4.57
2	Ag-Dere-2	2.28	3.42	13.35	51.08	0.021	0.033	0.85	2,08	0.587	0.270	4.15

Modification of natural bentonite to obtain its Na-form was carried out according to the following scheme: a saline solution of NaCl was added to natural aluminosilicate in a ratio of 1:10 and mixed intensively for six hours . Then, after filtering the solid mass, the reaction product was separated from undesirable impurities. As a final result, the solid mass was calcined in a drying cabinet at 110^{0}C. The purity (monomineralality) of the obtained samples, natural and modified, was checked using IR spectroscopy, X-ray diffraction and thermogravimetry, which are shown in Figures 2-8.

Table 2.

Chemical composition of bentonite clays of the Gazakh deposit

№	Name of the deposit	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3
1	Dash-Salahly-1	3.17	4,62	13.04	57.97	0.024	0.98	1.39	2.66	0.590	0.286	4.57
2	Dash-Salahly-2	2.28	4,58	12.85	57.55	0.021	0.93	1.25	2,4.8	0.587	0.205	4.15

Table 3.

Mineralogical composition of bentonite clays of the Gazakh deposit

Name of the deposit	Feldspar	SiO_2 (crucibolite)	Montmorillonite	Illite	Kaolinite	$CaCO_3$ calcite
Dash-Salahly-1	9,1	15,0	76,6	-	-	2,0
Dash-Salahly-2	9,7	15,1	75,6	-	-	2,1

It is known that clays, in addition to the main mineral of one or another crystalline type, often contain admixtures of other clay minerals. In kaolinite and montmorillonite clays, although in small quantities, there may be traces of hydromica, and in hydromica clays, on the contrary, montmorillonite or kaolinite. In addition, clay minerals often include various amounts of so-called non-clay minerals - quartz, cristobalite, tridymite, calcite, dolomite, gypsum, pyrite, feldspar phosphates, etc. [21].

Table 4.

Mineralogical composition of bentonite clays of the Khizinsky deposit

Name of the deposit	Feldspar	SiO_2 (crucibolite)	Montmorillonite	Illite	Kaolinite	$CaCO_3$ calcite
Ag-Dere -1	7,2	14,7	75,2	-	-	2,9
Ag-Dere -2	7,0	14,5	74,8	-	-	2,8

When conducting a series of physicochemical analyses of the structural characteristics of layered aluminosilicates, it was established that the main chemical components are silicon dioxide SiO_2 (30–70%), aluminum oxide Al_2O_3 (10–40%) and water H_2O (5–10%). When comparing the results of Tables 1–2, it can be established that the chemical composition of the Gazakh and Khizinsky deposits is identical in their elemental composition, but the differences in both cases are manifested in the compositions of different samples of the same deposits.

Regarding the mineralogical composition of bentonites presented in Tables 3-4, it can be noted that they differ only in terms of content: crestbolite SiO_2 - 15.0% for the Gazakh and 14.7% for the Khizin deposits and feldspar - 9.1 for the Gazakh and 7.2% for the Khizin deposits. In terms of the content of montmorillonite, the main component of clay minerals, it can be said that they are close to each other - 76.6- 75.2%. Fig. 2 shows the structure of the Na- form of bentonite from the Dash-Salakhly deposit. Analysis of the structure of the Na- form of bentonite from the Dash-Salakhly deposit modified by us showed that it is similar to the natural analogue of bentonite clay from the Dash-Salakhly deposit. Bentonite clays, related to the class of aluminosilicates, have an elementary structural layer of the 2:1 type and consist of an octahedral oxygen-hydroxyl network $Al(O,OH)_6$, enclosed between two SiO_4 tetrahedral networks (Fig. 1). The size of aluminosilicate microcrystals does not exceed several micrometers, so they are classified as nanosized materials, and determine the high physicochemical activity of clay minerals [21]. The expansion of the structural cell of montmorillonite when interacting with water makes aluminosilicate clay materials indispensable as adsorbents of heavy metal cations and a moisture-retaining component in the process of soil improvement.

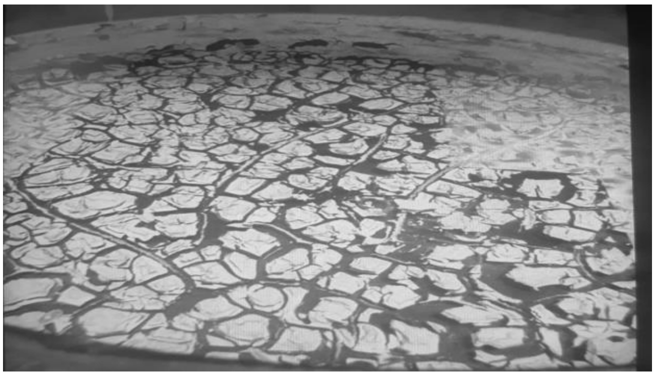

Fig. 2. Structure of the modified Na-form of bentonite from the Dash-Salakhlinskoye deposit

Clay minerals contain free iron and aluminum oxides of varying crystallization. They are found on clay particles in the form of veins, point grains or films. Organic carbonaceous (phyosen), bituminous, and humic substances are also found in clay minerals. Thus, clay minerals are complex multicomponent systems consisting of associations of clay and non-clay minerals, amorphous, inorganic, and organic substances.

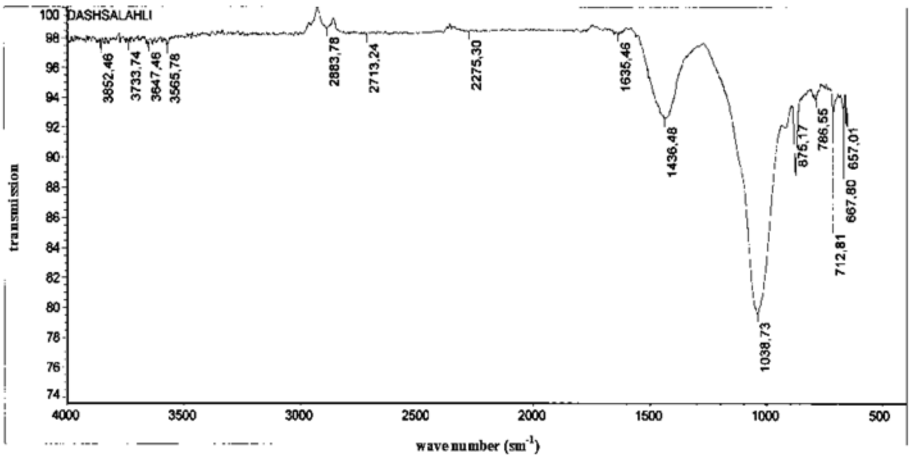

Fig. 3. IR spectra of bentonite clay from the Dash-Salakhlinskoye deposit

When studying the nature of the interaction of cation-substituted forms of modifiers with the surface of natural aluminosilicates, IR absorption spectra of bentonite clay from the Dash-Salakhlinsky and Khizinsky deposits were recorded (Fig. 3-4).

When comparing the IR absorption spectra of bentonite clay from the Dasch-Salakhlinskoye and Khizinskoye deposits, a coincidence is observed in the 1000 cm^{-1} region, corresponding to the absorption bands of montmorillonite.

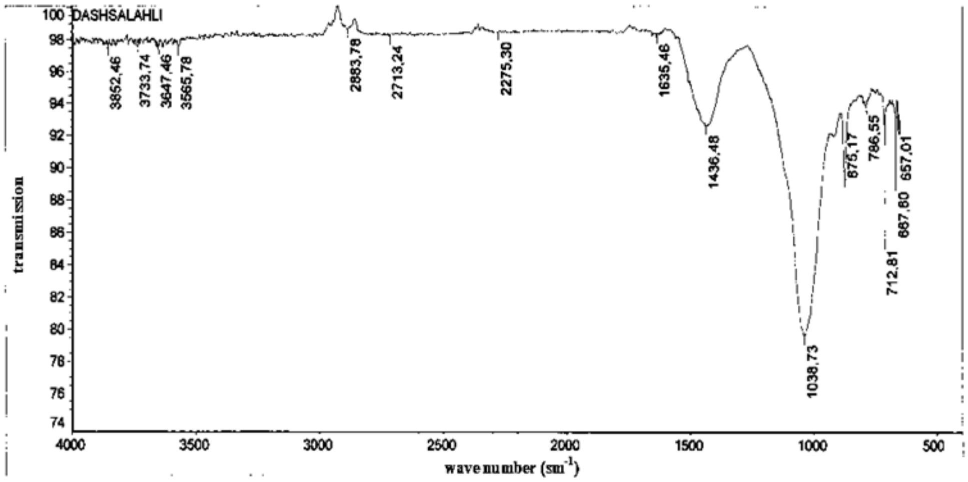

Fig.4. IR spectra of the modified Na- form of bentonite clay from the Dash-Salakhlinskoye deposit

New IR absorption spectra were also revealed within the range of 1052.03 -1060.75 cm^{-1}, corresponding to the C–H bond, and 3625.57 and 3702.58 cm^{-1}, corresponding to the absorption band of the OH group. The structure of the bentonite clay of the Dash-Salakhlinskoye deposit and its modified Na- form were confirmed by X-ray phase analysis (Fig. 6-7).

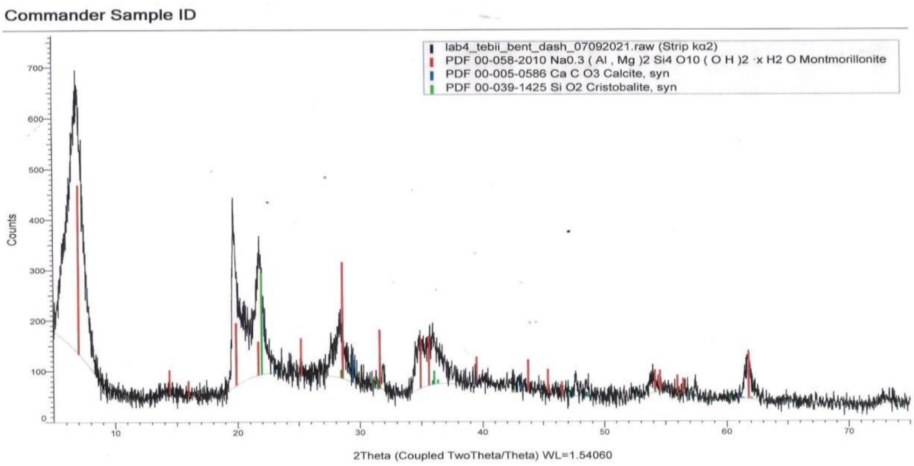

Fig. 5. X-ray diffraction pattern of bentonite clay from the Dash-Salakhlinskoye deposit

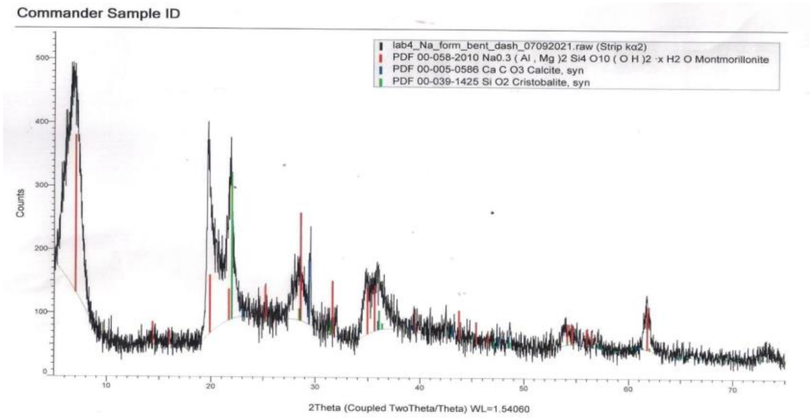

Fig. 6. X-ray diffraction pattern of modified Na- form of bentonite clay from the Dash-Salakhlinskoye deposit

With the help of a justified derivatographic analysis, the mechanisms of the ongoing processes were substantiated.

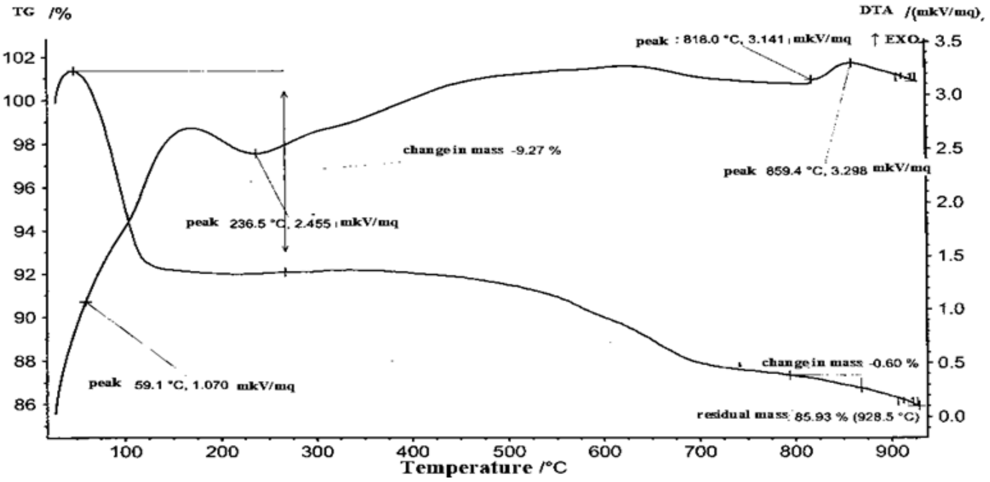

Fig. 7. Derivatogram of bentonite clay of the Dash-Salakhlinskoye deposit

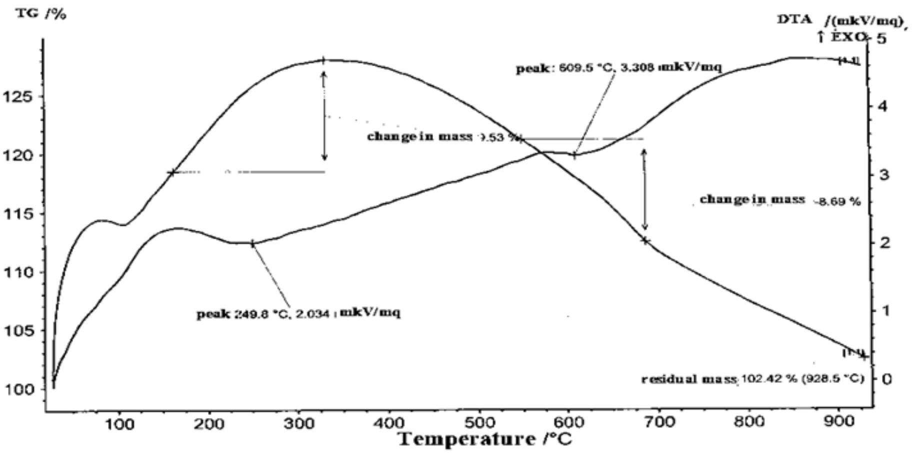

Fig.8. Derivative diagram of the modified Na- form of bentonite clay from the Dash-Salakhlinskoye deposit

When comparing the obtained derivatograms (Fig 8, it can be established that active centers were observed on the Na-form of natural bentonite at 248.6^{0}C - 2.034 μV/mg and at 609.5^{0}C - 1.308 μV/mg. And for natural bentonite, active centers were observed at 206.5^{0}C - 3.308 μV/mg and at 249.8^{0}C - 2.034 μV\mg), the total change in mass loss was -8.69 and 0.60%, respectively. It was established that a characteristic increase in pore volume was observed for the Na-form of bentonite samples. Based on the obtained data, it can be assumed that modification of bentonite with Na salts leads to an increase in the specific surface area of the pore volume and a decrease in the average pore size. The content of Na cations in the interlayer space of bentonite leads to an increase in the interlayer space and an increase in the sizes of macro and mesopores in the internal structure of the adsorbents. This contributes to the fact that mainly both heavy metal ions and other toxic substances are sorbed on the surface of bentonite [22], which interact with partially hydrolyzed metal cations that form the lining of the double electric layer, exchange with particles of the double electric layer or counterions that create the double electric layer.

CONCLUSION

Based on the conducted studies, it was established that aluminosilicate raw materials are suitable for the synthesis of effective sorbents. It was also established that the modification of bentonite clays contributes to the improvement of adsorption-structural characteristics in relation to toxic elements. The main conclusion of this study was that nanoparticles of natural and modified forms of bentonite clays are a reliable material for neutralizing unwanted compounds in the ecosphere.

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TƏBİİ XAMMAL ƏSASINDA ALINMIŞ EKOLOJİ TƏMİZ SORBENTLƏRİN STRUKTURU VƏ XASSƏLƏRİ

V.Ə. İsmayılova, S.S. Bayramova, E. Kazımova, G.R. Əzimova, Z.R. Ağayeva

Məqalədə effektiv sorbentlərin hazırlanmasında struktur materiallara uyğun təbii xammalın seçilməsi ilə bağlı məlumatlar təqdim olunur. Qeyd olunur ki, tərkibinə və fiziki-kimyəvi xassələrinə görə effektiv sorbentlərin işlənib hazırlanması üçün gil mineralları tələblərə tam cavab verir və sənaye üçün böyük elmi və praktik əhəmiyyətə malikdir. Qeyd edilmişdir ki, bir sıra sənaye müəssisələrinin tullantı suları bəzi hallarda Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{3+}, $Co2^{+}$, Pb^{2+}, Mn^{2+}, Cd^{2+} və s. kimi müxtəlif ağır metalların kationları ilə çirklənir. Müəyyən edilmişdir ki, təbii alüminosilikatların modifikasiyası onların sorbsiya xüsusiyyətlərini yaxşılaşdırır. Təbii bentonitlərin modifikasiya olunmuş Na-formasının zəif turşu və qələvi mühitlərdə daha yaxşı kolloid xassə nümayiş etdirdiyi və ağır metal ionlarını sürətlə udmaq qabiliyyətinə malik olduğu göstərilmişdir.

Açar sözlər: *struktur xassələri, sorbentlər, alümosilikatlar, zəhərli elementlər.*

СВОЙСТВА, СТРУКТУРА ЭКОЛОГИЧЕСКИ ЧИСТЫХ СОРБЕНТОВ НА ОСНОВЕ ПРИРОДНОГО СЫРЬЯ

В.А. Исмаилова, С.С. Байрамова, Э. Кязимова, Г.Р. Азимова, З.Р. Агаева

В статье приведены данные по подбору природного сырья соответствуюший структурным материалом при приготовлении эффективных сорбентов. Отмечено, что глинистые минералы по составу и физико-химическим свойствам вполне отвечают требованиям разработки эффективных сорбентов и имеют важное научно-практическое значение для промышленности. Отмечено, что сточные воды ряда производств, в некоторых случаях, загрязнены катионами различных тяжелых металлов, таких как Cu^{2+}, Zn^{2+}, Ni^{2+}, Cr^{3+}, Co^{2+}, Pb^{2+}, Mn^{2+}, Cd^{2+} и др. Установлено, что модифицирование природных алюмосиликатов улучшает их сорбционные свойства. Показано, что модифицированная Na-форма природных бентонитов в слабокислой и щелочных средах проявляет лучшие коллоидальные свойства и способна стремительно поглощать ионы тяжелых металлов.

Ключевые слова: *структурные свойства, сорбенты, алюмосиликаты, токсичные элементы*