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SORPTION OF CHROMIUM (VI) IONS BY NANOSTRUCTURED COMPLEX SORBENT BASED ON BENTONITE CLAY AND WASTE FROM MINERAL WOOL PRODUCTION

Abstract: In the present work, highly effective, accessible nanostructured complex sorbents (NSCS) possessing microporosity, high dispersity and high sorption ability and a low-waste method for their production using bentonite clay of Taganskoye deposit and wastes of mineral wool production are proposed. It has been experimentally established that mechanoactivation makes it possible to obtain a complex sorbent with nanoscale particles and a highly developed surface. At the same time, favorable conditions for mechanical dispersion are created in the presence of water and milling intensifier - waste products of mineral wool. Based on the results of a study of the sorption of chromium (VI) ions from model solutions (C (Cr (VI)) = 0.5-1.5 mg/dm^3), the NSCC provides a high degree of purification from chromium (VI) ions. Already in the first 30 minutes, sorption under static conditions proceeds at a high rate. The equilibrium value of the sorption for chromium (VI) ions on the complex sorbent averages 96-99 % of its limiting value for ~ 0.5 h. From the sorption isotherm characterizing the dependence of the sorption capacity on the concentration of the sorbed component at a constant temperature for the liquid phase, Basic information is obtained on the sorption properties of NSCC based on bentonite clay and wastes of mineral wool production and on the character of the adsorption of chromium (VI) ions on it. Nanostructured complex sorbent can be used to solve the problem of wastewater treatment of industrial enterprises from chromium (VI) ions.

Keywords: nanostructured complex sorbent, bentonite clay, wastes of mineral wool production, sorption, mechanical activation, chromium ions

Introduction. Wastewater treatment from heavy metal ions is currently a topical problem on a global scale. In the practice of industrial wastewater treatment, membrane technologies, electrochemical treatment, reagent and biochemical methods are currently used. Ions of zinc, chromium, copper, nickel, mercury are extracted efficiently from water by sorption cleaning methods [1].

The merits of the sorption method of wastewater treatment include the following: 1) cleaning up to MPC standards; 2) it is possible to jointly remove various impurities of a nature; 3) there is no secondary pollution of the treated waters; 4) the possibility of recovering sorbed substances; 5) the possibility of creating recycling water use. Disadvantages of this method of cleaning are the high cost and scarcity of many adsorbents, the emergence of secondary waste, which require additional purification.

When studying natural bentonite clays of East Kazakhstan deposits, the following advantages were revealed: high sorption properties; availability (deposits are located near consumers); low cost (compared to reagents used in wastewater treatment technology); resistance to temperatures and climatic conditions during transport, storage and operation.

In this regard, the priority area of research is the synthesis of a new highly effective sorbent based on bentonite clay of the Tagan deposit of the East Kazakhstan region that meets the specified requirements.

Experimental part. *Materials, apparatus and methods of investigation*. To carry out experiments on the purification of model solutions containing Cr (VI) ions, the nanostructured complex sorbent obtained by us in the laboratory was used. The composition of this sorbent is a waste of production of mineral wool - basalt fiber, which is a microfibrous material consisting of ultrathin fibers, obtained from the melt of basalt rocks. In pure form, basalt fibers can not be used to remove heavy metal ions from water, since the minerals that make up them do not have spatial voids in the crystal lattice [2-3].

In a nanostructured complex sorbent, basalt fiber was used as a sorption matrix, represented as chaotically crossing fibers with a diameter of 0.3-0.5 μm (Figure 1). To impart ion-exchange capacity to the material, it was treated with bentonite clay of the Taganskoye deposit (Figure 2).

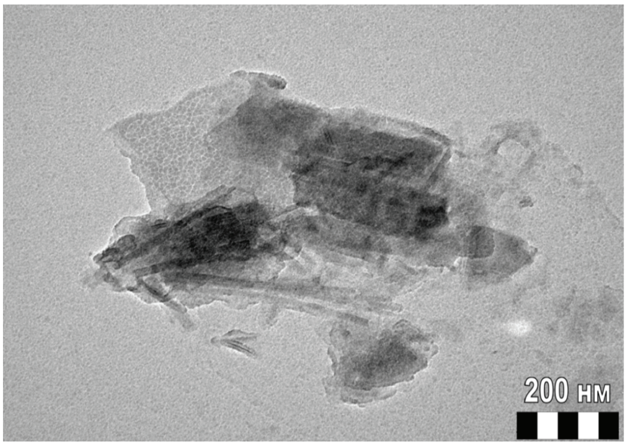

Figure 1 – Photo of microstructure of fragments of ground basalt fiber as a result of mechanoactivation

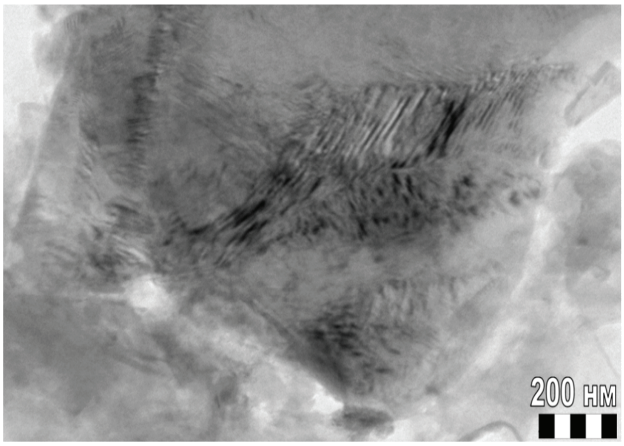

Figure 2 – Photo of microstructure of layers of flat crystals of montmorillonite

The processing of waste products of mineral wool - basalt fiber was produced by bentonite solution by mechanoactivation. For the mechanical activation of the components, a VZU-2 vibratory mill of periodic action by VIBROMASH UK LLP designed by Kovshik AV was used, in which the material is crushed by impact and abrasion. As grinding bodies are used steel rollers. The capacity of the grinding chamber is 1 liter. The grain size of the material of the load is up to 5 mm. The grinding cycle time is 10-30 minutes. The grinding cycle time depends on the initial characteristics of the materials to be crushed. The construction of the vibrating mill makes it possible to carry out the process of wet grinding [4-5]. Mechanical activation of materials in the process of grinding allows to achieve an increase in the overall activity of particles due to a reduction in their size, an increase in the total surface, the achievement of a more compact shape by the particles, and deep transformations in the crystal structure of the material. Mechanoactivation makes it possible to reduce the powder particle sizes on the average from 60 to 0.250 μm with the presence of a significant fraction of particles with sizes up to 50 nm.

The determination of the content of small amounts of chromium (VI) was carried out by photometric method according to the standard procedure [6]. Diphenylcarbazide reacts with bichromate ions in the acidic medium in the wavelength range from 540 to 550 nm to form a colored (red-violet) complex compound, the optical density of which determines the chromium (VI) content in the treated sample. The method is very sensitive: at $\lambda = 540$ nm the molar absorption coefficient is $4.2 \cdot 10^4$.

Method of obtaining the sorbent. According to the developed technology, the sorbent is prepared first as a paste-like product and then as a suspension. A sorbent with a ratio of bentonite clay and technogenic wastes of mineral wool production equal to 2: 1 was prepared for the studies.

The method for obtaining a nanostructured complex sorbent in the form of a paste is carried out as follows. Bentonite clay is preliminarily ground on a jaw crusher to particle sizes of 1-5 mm. Technogenic waste and bentonite clay in the above proportions are dried to constant weight at a temperature of 100 °C and are loaded into the grinding chambers of the vibrating mill with grinding bodies, and distilled water (temperature 18-20 °C) is also fed there. The grinding time was varied within 5-30 minutes. As a result of the experiments, the optimum time for mechanoactivation of the initial components of the NSCS, equal to 15 minutes, was established. Basalt fibers in the process of mechanoactivation are covered with layered nanoparticles of bentonite clay. The resulting paste is a uniform, ductile, well-moldable mass that was left for 24 hours during the process of adhesion of bentonite to basalt fiber (Figure 3).

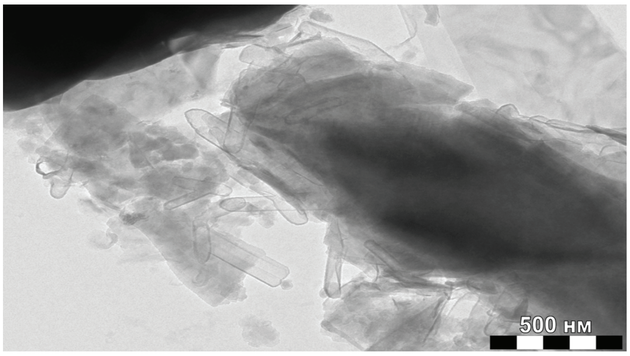

Figure 3 - Photos of microstructure of adhesion of bentonite on the sorption matrix of basalt fiber

Properties and conditions of use of NSC sorbent. The resulting nanostructured complex sorbent-paste (suspension) possesses aggregative stability, that is, it retains its spatial structure unchanged in time. Recommended moisture content of the resulting paste is 50-60 %, density is 1580 - 1640 kg/m^3. To obtain a suspension, the humidity should be 120 – 200 %, density - 1300 - 1400 kg/m^3.

As a result of the studies, it was found that the most technological solution is the dosing of NSCC into the water to be purified in the form of a suspension. It should be noted that when preparing the sorbent in the form of a suspension while mixing pasty sorbent with water, clay particles actively pass into a highly dispersed state. In addition, it was noted that the presence of fibers of mineral wool in the sorbent greatly accelerates the process of dispersing the sorbent suspension in the water being purified, thereby reducing the sorption time [4, 7].

An important factor determining the conditions for studying and practical use of the obtained NSCS is the rate of establishment of sorption-desorption equilibrium in the system under study. In order to determine the optimum contact time of the sorbent with the solution being purified, the kinetic dependences of the sorption of Cr (VI) ions from model solutions with a concentration of 0.5, 1 and 1.5 mg/dm^3 at a ratio of T : H = 1 : 100. The sorption time varied from 0.5 to 6 hours.

Investigation of sorption from model solutions of chromium (VI) was carried out in a static mode with constant shaking, for which a sample of NSCS, a solution with a certain concentration of sorbate, was introduced into the conical flask and held for a predetermined time and temperature.

After purification, all samples of the analyzed model solutions containing the visible precipitate of the sorbent were filtered through a “white tape” filter. During filtration, the first portions of the filtrate (20-25 cm^3) were discarded. Subsequently, a solution of sulfuric acid (1 mol/dm^3) was added dropwise to the filtrates obtained until a pH of 4 (control of the universal indicator paper) was reached. If after the pH of the test solutions was determined, a precipitate formed, then the samples were filtered through the defused “white tape” filter for a second time.

In a volumetric flask with a capacity of 100 cm^3 aliquots (25, 50 cm^3) of the filtrates of the test samples were added, 1 cm^3 of sulfuric acid solution (50 %), 0.3 cm^3 of orthophosphoric acid (concentrated), 2 cm^3 of a solution of 1,5-diphenylcarbazide 5 g/dm^3, brought to the mark with distilled water and stirred. The samples of the test solutions and the blank sample prepared for measurement were held for 15 minutes after their preparation, after which the optical density values were measured at least three times and the residual concentration of chromium (VI) ions was determined.

On the basis of the obtained experimental data, the extraction ratio (α, %) is determined, showing the fraction of the absolute amount of matter that is captured by the sorbent and gives a fairly complete picture of the nature of the process. This indicator is an important criterion in determining the optimal conditions for the sorption process and is calculated by the following formula:

$$\alpha = \frac{C_0 - C}{C_0} \cdot 100\%, \qquad (1)$$

where C_0 – initial concentration of chromium (VI), mg/dm^3; C – residual concentration of chromium (VI), mg/dm^3.

From the dependences of the degree of sorption of chromium (VI) ions on the NSCS versus time (Figure 4), it can be seen that sorption under static conditions with high velocity proceeds already in the first minutes and reaches a maximum value after 30 minutes.

To find the optimal sorption parameters, as well as to determine the sorption properties, the effect of the mass of NSCS on the sorption of chromium (VI) ions was studied, the results of which are presented in the table.

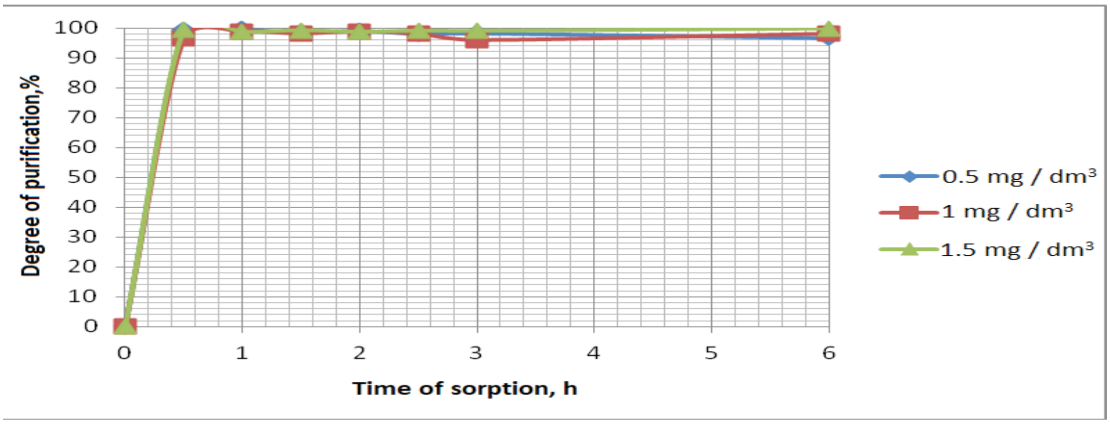

Figure 4 - Dependence of the degree of purification from chromium (VI) ions on the NSCS versus time at different initial chromium concentrations

Table - Effect of mass of NSCS on sorption of chromium (VI) ions at τ = 30 min

Mass of sorbent, g			
Sorbent NSCS	1	1,25	1,43
The concentration of chromium (VI) ions, mg/dm^3			
Initial C_o	0,534499	0,522653	0,522653
Residual C	0,003230	0,002510	0,002025
Extraction rate, %			
α	99,40	99,52	99,61

It has been established that an increase in the mass of the nanostructured sorbent does not have a significant effect on the sorption process, therefore, in order to determine the kinetics of the sorption of chromium (VI) ions, the optimum sorbent mass 1 g was chosen at the ratio L:S = 1 : 100 for the sorbent studied. The results of the studies are presented by the kinetic curve of sorption (Figure 5).

Figure 5, which reflects the dependence of the sorption of chromium (VI) ions on time, shows that for the system studied at different initial concentrations of chromium (VI) in model solutions (0.5, 1.5 mg/dm^3), the kinetic The curves have the same form. In the first section of the stepwise kinetic curves, the active sorption of chromium (VI) ions continues for the first 30 min after the onset of phase contact, the sorption values reach practically constant values. In the second section, during the next 0.5-6.0 hours,

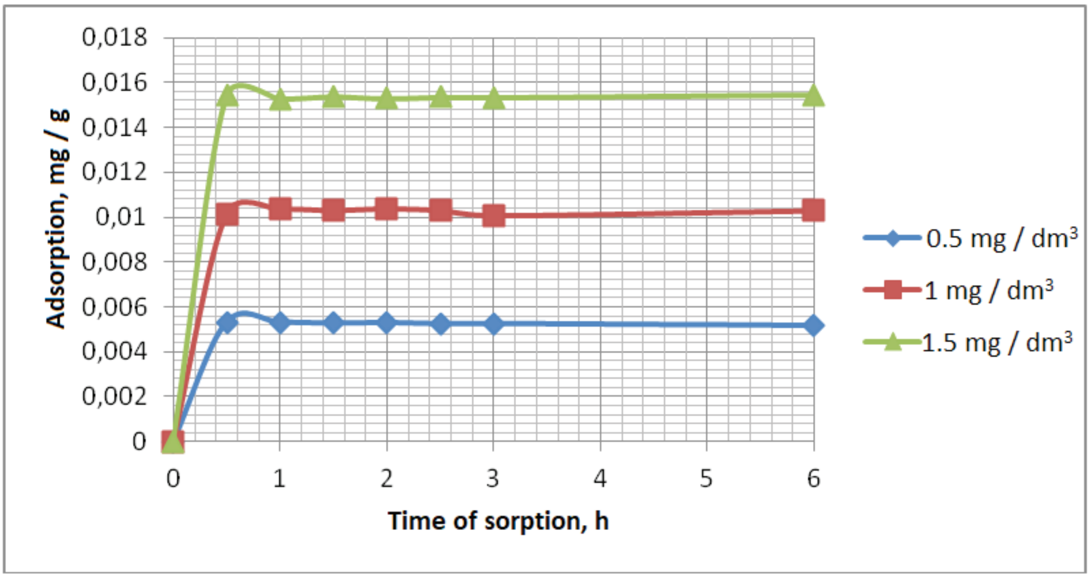

Figure 5 - Kinetic curves of the adsorption of chromium (VI) ions on the NSCR at various initial chromium concentrations

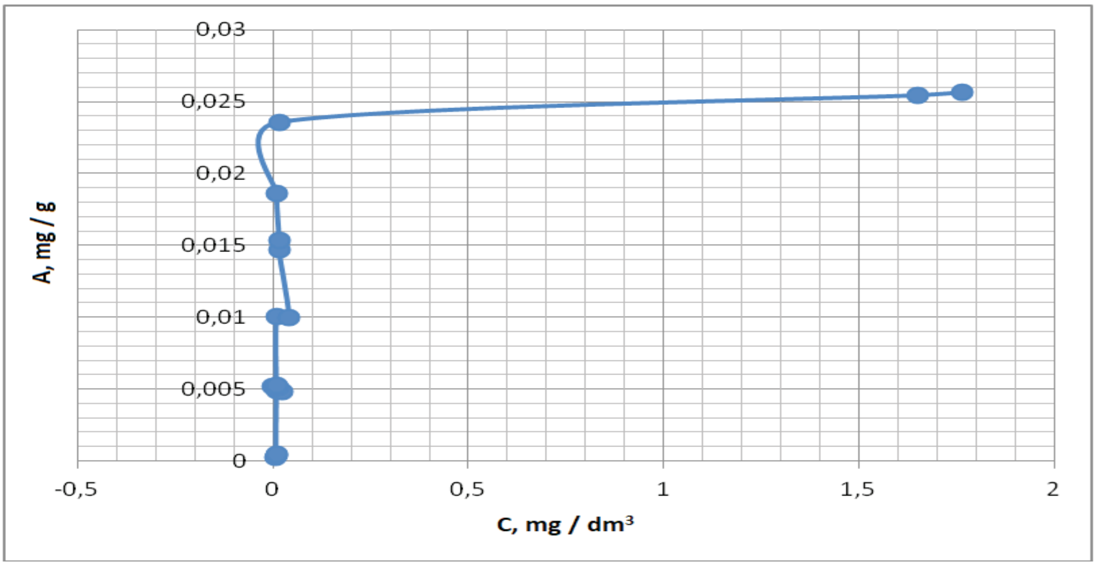

Figure 6 - Isotherm of adsorption of chromium ions (VI)

the amount of sorption changes insignificantly. Complete sorption of chromium (VI) ions occurs after 3 hours of interaction, sorption equilibrium sets in. Further increase in the contact time is not advisable.

To drawing an isotherm for the sorption of chromium (VI) ions (Figure 6), the following experimental steps were performed: preparation of model solutions of chromium (VI) (0.03-5 mg/dm^3) and determination of their concentration (C_0, mg/dm^3) by the photocolorimetric method; carrying out adsorption from model solutions of chromium (VI) NSCS on the basis of bentonite clay and waste products of mineral wool - basalt fiber; determination of the equilibrium concentration (C, mg/dm^3) of chromium (VI) solutions filtered after adsorption

Then, on the analytical scales, samples of nanostructured complex sorbent pastes based on bentonite clay and waste products of basalt fiber were selected. The obtained samples were transferred to conical calibrated flasks with a capacity of 300 cm^3 and dissolved in a certain volume of the model solution with a glass rod. During the research, the following conditions were observed: the ratio of S:L = 1: 100 (1 g paste (in terms of dry matter) per 100 cm^3 model solution); time of sorption for 3 hours with constant stirring; three experiments were conducted for each experiment. The optical density of the samples of the analyzed solutions and the blank sample was measured at 540 nm in cuvettes with an absorbing layer thickness of 30 mm. The obtained data were used to calculate the absolute adsorption and the degree of extraction of chromium (VI) ions from model solutions on the NSCS. Sorption (A, mg/g) of chromium (VI) ions was calculated by the following formula:

$$A = \frac{(C_0 - C)\cdot V}{m}, \qquad (2)$$

where C_0 – initial concentration, mg/dm^3; C – equilibrium (residual) concentration, mg/dm^3; m – weight of the sample of sorbent, g; V – volume of the solution, dm^3.

The shape of the isotherm provides qualitative information on the nature of the interaction of chromium (VI) ions with the surface of the adsorbent. The initial section of the sorption curve (Figure 6), rising upwards, shows that the adsorption is almost directly proportional to the concentration value. This corresponds to a significant degree of still free surface of the adsorbent. The final section of the curve, close to horizontal, characterizes the surface of the adsorbent, which is completely saturated with adsorbent.

Discussion of results. The obtained results of the studies showed the high adsorption ability of NSCC based on bentonite clay and waste products of basalt fiber production in relation to chromium (VI) ions. A study of the sorption kinetics has shown that in all cases (Figure 5) the initial region of relatively rapid sorption of Cr (VI) ions is separated with subsequent slowing down of the process. Thus, the equilibrium value of sorption on a nanostructured complex sorbent in all the experiments reaches on the average 96-99 % of its limiting value for ~ 0.5 h.

In accordance with the five main types of sorption isotherms identified by Brunauer, Emmett and Teller [7], the isotherm (Figure 6) is of type I. The isotherm, which has the appearance of a convex curve steeply rising upwards, suggests the presence of a chemical interaction (along with a physical one) between the adsorbate and the adsorbent.

The isotherm has a convex character with respect to the axis of equilibrium concentrations of sorbate in solution, which indicates a high affinity of chromium to the sorbent. The absence of kinks on the isotherm of the sorption of chromium (VI) ions by the sorbent confirms the assumption that under the experimental conditions the sorbed substance is in the water phase in a completely dissociated state.

The convex portion of the isotherm (Langmuir adsorption) indicates the presence of micropores in the sorbent, and the slope of the isotherm represents the ultra-microporous size of the sorbent under study. The cooler the isotherm, the smaller the micropores. The absence of concave sections on the isotherm indicates the absence of macropores.

Thus, the isotherm shown in Figure 6 corresponds to monomolecular adsorption on a microporous sorbent. This curve has two rectilinear sections - for small (the adsorption increases linearly with increasing concentration) and large (the whole surface of the adsorbent is occupied by adsorbate molecules) values of the equilibrium concentration of the adsorbate. Moreover, the isotherm curve has no rise in the region of high concentrations, which indicates the absence of the formation of a new adsorbed layer.

Comparison of the literature and data obtained allows us to draw the following conclusion: the stepwise character of the kinetic sorption curves is a consequence of the fact that the adsorption of chromium (VI) ions occurs on a microporous nanostructured complex sorbent. At the first stage of sorption, mass transfer at the interface between phases and the interaction of chromium (VI) ions with the sorbent surface play an important role; in the second stage, the internal diffusion of chromium (VI) ions into the accessible pores of the sorbent allows the chromium (VI) ions to be sorbed again on the external surface of the sorbent.

Conclusions. Thus, the results of studies have shown that the nanostructured complex sorbent has several advantages over other: a highly developed specific surface with catalytically active centers, high adsorption capacity for chromium (VI) ions and low cost.

The obtained results on the synthesis and study of a new sorption material show the promise of its use for solving urgent environmental and technological problems.

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ТҮЙІНДЕМЕ

Өндірістік кәсіпорындарда хром (VI) иондарынан ағынды сулардың мәселесін шешу үшін микрокеуектілікке, жоғары дисперсиялыққа және үлкен сорбциялық сыйымдылыққа ие Таған кен орнының бентонит саз балшықтары мен минералды талшықтар өндірісінің қалдықтарының негізінде жаңа наноқұрылымды комлексті сорбентті (НҚКС) қолданудың тиімділігі жоғары, аз қалдықты және қолжетімді сорбциялық технологиясы ұсынылады. Механикалық белсендіру жоғары дамыған бет және наноқұрылымды бөлшектері бар комплексті сорбентті алуға мүмкіндік беретінін эксперименталды түрде анықталды. Мұнда механикалық диспергация үшін қолайлы жағдайлар су және ұнтақтаудың интенсификаторы - минералды талшықтар өндірісінің қалдықтарының болуымен жасалады. Модельді ертітінділерден хром (VI) иондарының (C(Cr(VI))=0,5-1,5 мг/дм^3) сорбциясын зерттеудің нәтижелері бойынша наноқұрылымды комлексті сорбент хром (VI) иондарынан жоғары тиімділікті қамтамасыз етеді; статикалық жағдайдағы сорбция үлкен жылдамдықпен бастапқы 30 минутта өтеді, комплексті сорбентте хром (VI) иондары үшін сорбцияның тепе-теңдік мәні ~ 0,5 сағат ішінде оның шекті шамасынан орта есеппен 96–99% құрайды. Сұйық фаза үшін тұрақты температурада сорбциялық көрсеткіштің сорбцияланатын компоненттің концентрациясынан тәуелділігін сипаттайтын сорбцияның изотермасынан бентонит саз балшықтары мен минералды талшықтар өндірісінің қалдықтарының негізіндегі жаңа наноқұрылымды комлексті сорбенттің сорбциялық қасиеттері және ондағы хром (VI) иондарының адсорбциялық сипаты туралы негізгі мәліметтер алынған. Наноқұрылымды комлексті сорбент өндірістік кәсіпорындарпдың ағынды суларын хром (VI) иондарынан тазалаудың мәселелерін шешу үшін қолданылуы мүмкін.

Түйін сөздер: наноқұрылымды комлексті сорбент, бентонит саз балшықтары, минералды талшықтар өндірісінің қалдықтары, сорбция, хром иондары

РЕЗЮМЕ

В настоящей работе предложены высокоэффективные, доступные наноструктурированные комплексные сорбенты (НСКС), обладающие микропористостью, высокой дисперсностью и большой сорбционной способностью и малоотходный способ их получения с использованием бентонитовой глины Таганского месторождения и отходов производства минеральной ваты. Экспериментально установлено, что механоактивация позволяет получить комплексный сорбент с наноразмерными частицами и высокоразвитой поверхностью. При этом благоприятные условия для механического диспергирования создаются в присутствии воды и интенсификатора помола – отходов производства минеральной ваты. По результатам исследования сорбции ионов хрома(VI) из модельных растворов (C(Cr(VI)=0,5-1,5 мг/дм^3) установлено, что НСКС обеспечивает высокую степень очистки от ионов хрома (VI). Уже в первые 30 мин сорбция в статических условиях протекает с высокой скоростью. Равновесная величина сорбции для ионов хрома (VI) на комплексном сорбенте достигает в среднем 96–99 % от ее предельного значения в течение ~0,5 ч. Из изотермы сорбции, характеризующей зависимость сорбционной способности от концентрации сорбируемого компонента при постоянной температуре для жидкой фазы, получены основные сведения о сорбционных свойствах НСКС и характере адсорбции на нем ионов хрома (VI). Наноструктурированный комплексный сорбент может быть использован для решения проблемы очистки сточных вод промышленных предприятий от ионов хрома (VI).

Ключевые слова: наноструктурированный комплексный сорбент, бентонитовая глина, отходы производства минеральной ваты, сорбция, механоактивация, ионы хрома

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