Texture Characteristics of Modified and Activated Bentonite

¹Khamroev J.X., ²Fayzullaev N.I., ²Haydarov G'.Sh., ¹Temirov F.N., ¹Jalilov M.X.,

¹Samarkand Medical Institute, Uzbekistan ²Samarkand State University, Uzbekistan E-mail: <u>fayzullayev72@inbox.ru</u>

ABSTRACT

The method of modification and activation of bentonite of Navbahor district of the Republic of Uzbekistan is considered in the work. To obtain Fe-modified bentonite by the Zol-gel method, an aqueous suspension of bentonite (ratio of solid and liquid phases 1:10, aqueous extract of the suspension pH i 8) was left to swell at room temperature for one day, then bentonite particles were left for 3 minutes and was treated with ultrasound at a frequency of 22 Gts for good dispersion. The intercalating solution was prepared by mixing 1.0 M solutions of iron (III) chloride and sodium hydroxide ([OH -] / [Fe3 +] = 2.0) and left at room temperature for one day. After aging, the resulting ash was added dropwise to a 10% aqueous suspension of bentonite. The resulting modified bentonite was separated from the liquid phase in a Büchner funnel using a vacuum pump after 24 h, washed with distilled water until a negative reaction to chloride ions, and dried at room temperature. It was then thermally treated at 500 °C for 2 h. The method of obtaining Al-modified bentonite is carried out according to a similar method of obtaining Femodified samples.

Differential thermal analysis was performed using a NETZSCH STA 409 PC / PG derivatography (sample weight ~ 50 mg) in the temperature range 20 to 800 ° C (heating rate 10 ° / min). X-ray phase analysis of the catalyst was performed on an Advanced D8 diffractometer (Brucker, Germany) at an angle of reflection of 2TH at 20 to 80 ° in CuKa-monochromatic radiation. Phase identification of crystalline compounds was performed using the JCPDS PDF2 X-ray powder standards database. The adsorption and texture properties of the obtained samples were evaluated by volumetric method from physical adsorption-desorption of low temperature (77 K) nitrogen in ASAP 2020 MR surface area and porosity analyzer (Micromeritics, United States). The surface morphology of the catalyst was studied using JSM-5610 LV scanning electron microscope, JEOL (Japan). On the basis of the obtained data the technological schemes of activation of natural mineral sorbents are developed.

The purpose of the work is to modify and activate Navbahor bentonite and study the texture characteristics.

INTRODUCTION

The study of the structure and properties of minerals in the class of layered bent on ites derived from existing and widely used natural raw materials

clayrocksisanimportantscientifictaskaimedatcreatingnewmultifunctionalmaterials [1,2]. This is mainly explained by the specificity of the physicochemical properties of layered bentonites, the ability of active centers of different nature, adsorption and ion exchange. This opens up a wide range of possibilities for their use, for example in the creation of new effective materials for water treatment and wastewater treatment, sorbents in pharmacology, anti-migration and filtration barriers for long-term storage of hazardous waste. [3-8].

Layered silicates are common minerals in nature. They make up to 75% of the earth's crust. The most well-known representatives of layered silicates are clays. Clays have long been used in various fields of human activity. Their field of application is very wide: the production of ceramics and construction products, oil extraction and refining, metallurgy, chemistry, paper, pharmaceuticals, food and other industries [9].

They are also known as natural sorbents, ion exchangers, catalysts, and catalyst carriers [10 - 13]. The development of new methods for changing the structure of layered silicates and changing their physicochemical properties is constantly expanding the areas of their use.Recently, intensive research has been conducted on the creation and study of multifunctional inorganic 2D-nanomaterials belonging to intercalated layered substrates. Among them are pillar (or columnar) materials, which are distinguished by their unique texture and physicochemical properties. They are distinguished by a specific surface area, regular distribution of micro and mesopores, thermal stability and the presence of active centers of different nature. Therefore, efficient sorbents, molecular sieves, catalyst carriers, etc. are obtained from them.

At present, a large number of (pillar) superior materials based on bentonite matrices with unknown layered chemical formulas cross-linked with hydrolytic products of different metals are known [11].

Among the modification methods, pillaring is of great interest to researchers, this technological method opens wide prospects for the functional application of natural clays in various fields of science and technology. Pillaring is the process of maintaining a layered system while at the same time turning it into a heat-resistant micro- or meso-porous material. The basic concepts of the structure of elephant clays were formed in the research of Pinnavay [12-13], Sterte [14-16] and other scientists.

Regardless of its specific properties, this process can be described in three main stages: 1) hydrolysis of polyhydroxy complexes of the metal, 2) ion exchange (intercalation) of interlayer cations of layered bentonite, 3) heat treatment (firing) of layered bentonite.

It should be noted that intercalation is the main stage in the preparation of clays. Intercalation is a process based on changing the structure of sludge by expanding the interlayer space by introducing large inorganic complexes. This method was discovered in 1977 by scientists at the Brindlia Sample [17]. During the intercalation of layered silicates, an advanced micro-porous structure is formed, the specific surface area increases, and access to active centers located on the inner surface becomes possible. The most popular major molecule of aluminum hydroxide is the Al₁₃ ion, which was initially separated in the form of sulfate and selenite salts [18, 19]. The crystal formula is as follows: $[Al_{13}O_4(OH)_{24} (H_2O)_{12}]^{7+}$, this structure is called the Kegging ion. The structure can be thought of as a group of four trimeric Al₃O*(OH)₆(H₂O) with many facets connected around a central Al (O*) ₄ block. An asterisk represents a three-coordinate oxygen atom attached to a central aluminum atom. The Kegging-type cation Al₁₃ contains five different isomers (a, b, b, and g) belonging to the Baker-Figgis-Keggin structural class [20].] (Figure 1).



Figure 1. [Al₁₃O₄ (OH)₂₄ (H₂O)₁₂] Structure of 7⁺ (Al₁₃) [21] polyhydroxycomplex isomers EXPERIMENTAL PART

Activation of bentonite was carried out after purification of local mud in the following order: 100 g of natural clay was dissolved in 1 liter of distilled water, the resulting suspension was poured into a hydro cyclone battery system and cleaned of impurities for 1 hour. The purified suspension was left for one day and the fine fraction was separated in a centrifuge. The resulting fine bentonite powder was first dried in air, then in vacuum at 70 ° C for 4-5 hours. In a two-liter flask equipped with a mixer and refrigerator, 100 g of finely dispersed powder purified bentonite was placed and dissolved in 1 liter of distilled water, then the suspension was heated to 60–70 ° C and a 10% hydrochloric acid solution was added dropwise, stirring for 2 h. The resulting reaction solution was then cooled to room temperature. After cooling, the solution was repeatedly mixed with 500 ml of distilled water, centrifuged to separate the activated bentonite, and the resulting product was dried in a vacuum oven at 65 ° C for 12 h. Navbahor bentonite has the following structure:



Method of modification of bentonite with sodium hydroxide. To obtain bentonite modified with sodium cations, we used a pre-activated H-form (hereinafter bentonite) of bentonite separated from the Navbahor deposit mud [22-27]. The previously prepared H-form of bentonite was modified with sodium hydroxide. 2 liter flask was charged with 100 g of bentonite and 1 liter of distilled water was added to it. The calculated amount of pre-prepared NaOH solution was poured into the prepared 10% suspension solution. The prepared mixture was stirred at 85 ° C for 30 min. The sodium hydroxide solution was then added dropwise. After all of the sodium hydroxide solution had been added, the mixture was stirred for another hour. After modification with sodium hydroxide, the resulting solution was washed several times with distilled water and filtered, dried in a vacuum oven at 70 ° C for 48 h.

Acid activation and modification of bentonite.Prior to activation and modification, the original form of the sludge is enriched, i.e. a finely dispersed fraction of less than 1 micron in size is separated. To do this, the sludge is passed through an accumulator of hydrocyclones, where the sludge suspension passes several times through an injector tube, where the layered silicate clay particles are broken and the best part of the bentonite is separated after enrichment.

The best way to increase the catalytic properties of bentonite is cation exchange (activation), which is carried out with the possibility of further modification in solutions of mineral acids with the formation of the H-form of aluminosilicate. The mud activation process includes the following basic operations:

- enrichment and selection of fine fractions;
- activation with hydrochloric acid;
- centrifugation of the resulting suspension;
- washing of activated sludge;
- filtering;
- drying.



Acid activation of bentonite is a necessary step in the chemical modification of layered silicate. As a result of this activation, some changes occur in the bentonite composition associated with the exchange of positively charged exchangeable cations with hydrogen ions, leading to the formation of the hydrogen form of bentonite. It should be noted that, depending on the activator concentration, the maximum leaching of the exchangeable cations can be achieved. Thus, as a result of activation of bentonite with hydrochloric acid, complete replacement of Na⁺, Ca₂⁺, Mg₂⁺ cations with H⁺ ions can be achieved, as a result of which the surface of bentonite increases both

the radius and volume of pores. This is necessary for further modification and enrichment with the most optimal alkali metal cations. Bentonite was activated with 10% hydrochloric acid and modified with sodium hydroxide.

It is known that the limited use of bentonites as an adsorbent is due to their relatively low cation exchange capacity in the natural state. Alkaline activation is performed to increase this figure.

Zeolites obtained after acid activation and modification of Navbahor bentonite have the following appearance:



Production of Fe-modified bentonite by Zol-gel method. The aqueous suspension of bentonite (ratio of solid and liquid phases 1:10, aqueous extract of the suspension pH i 8) was left to swell at room temperature for one day, then treated with ultrasound at 22 Gts for good dispersion of bentonite particles for 3 minutes. The intercalating solution was prepared by mixing 1.0 M solutions of iron (III) chloride and sodium hydroxide ($[OH^-]/[Fe^{3+}]=2,0$) and left at room temperature for one day. The sol obtained after aging was added dropwise to a 10% aqueous suspension of bentonite. The resulting modified bentonite was separated from the liquid phase in a Büchner funnel using a vacuum pump after 24 h, washed with distilled water until a negative reaction to the chloride ions, and dried at room temperature. It was then thermally treated at 500⁰ C for 2 h.

Production of Al-modified bentonite by Zol-gel method. The aqueous suspension of bentonite (ratio of solid and liquid phases 1:10, aqueous extract of the suspension pH i 8) was left to swell at room temperature for one day, then treated with ultrasound at 22 Gts for good dispersion of bentonite particles for 3 minutes. A hand-held bentonite was prepared by hydrolysis of 0.2 M solutions of aluminum (III) chloride and sodium hydroxide at room temperature to obtain an intercalar solution ($[OH^{-1}]/[Al^{3+}]=2,0$). The solution was aged at 50°C for 24 h. Under these conditions, polyhydroxycation $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ complex ions were formed. This solution was then added dropwise to the intercalating solution suspension. and postponed for a day. Separation, washing, drying and firing of samples are carried out according to a similar method of obtaining Fe-modified samples.

Differential thermal analysis was performed using a NETZSCH STA 409 PC / PG derivatography (sample weight ~ 50 mg) in the temperature range 20 to 800° C (heating rate 10° / min). X-ray phase analysis of the catalyst was performed on an Advanced D8 diffractometer (Brucker, Germany) at an angle of reflection of 2TH at 20 to 80 ° in CuK_{α}-monochromatic radiation. Phase identification of crystalline compounds was performed using the JCPDS PDF2

X-ray powder standards database. The adsorption and texture properties of the obtained samples were evaluated by volumetric method from physical adsorption-desorption of low temperature (77 K) nitrogen in ASAP 2020 MR surface area and porosity analyzer (Micromeritics, United States). The surface morphology of the catalyst was studied using JSM-5610 LV scanning electron microscope, JEOL (Japan).

Qualitative and quantitative analysis of the element composition of sorbents was carried out on the energy-dispersion X-ray fluorescent spectrometer by the method of fundamental parameters EDX-720 (SHIMADZU, Japan).

The principle of operation of the spectrometer is based on the measurement of the intensity of fluorescent radiation by detectable atoms, which are stored in the test under the influence of X-rays. A semiconductor detector cooled with liquid nitrogen was used to record X-ray radiation quanta in an energy dissipation spectrometer.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Figure 5 shows the scattering spectrum of the sample particle size. The measurement results show that 95% of the clay fraction is represented by mineral particles of 0.04 - 0.7 μ m, which indicates the suitability of the samples taken for further mineralogical studies.





A study of the morphological and microporous properties performed using a scanning electron microscope showed that the mineral particles separated from the studied clay sample had an anisometric shape. In this case, Figure 5 shows that clay minerals are a combination of particles that make contact along the base planes, leading to the formation of microaggregates (globules). The boundary between micro aggregates is less defined and one micro aggregate gradually shifts to another. This shape of the particles is peculiar to the minerals of the smectite group (Fig. 5).



X-ray examination of the mud fraction was performed on an X-ray diffractometer DRON-7.0. The experiment was performed under normal conditions using CuK_{α} -radiation. Studies were performed on three drugs with the same suspension density and thickness on the substrate. The first diffraction sample was heated at 600° C for 1 h, the second from a sample saturated with methyltertbutyl ether, and the third from a natural sample (Fig. 6).

The specific surface area of the BET (Brunauer-Emmett-Telller) (S_{BET}), the volume of the micro-pores (V_{mp}), the volume of the meshes (V_{mzp}), the total volume of the pores ($\sum V_{pore}$) and the average diameter of the pores (D_{av}) are given in Table 1.

Texture characteristics of samples					
Sample	$S_{BET} M^2 / \Gamma$	V _{mp} sm ³ /g	V _{mzp} sm ³ /g	$\Sigma V_{por} sm^3/g$	C _{sr} nm
MM	96	0,010	0,160	0,170	7,00
Al ₁₃ -PMM	108	0,029	0,137	0,166	8,42
Al ₃₀ -PMM	125	0,035	0,138	0,173	8,04

Table 1Texture characteristics of samples

Peeling of layered bentonites.Pillaring is a special case of intercalation in which the introduction of inorganic compounds into the interlayer space takes place. Regardless of the properties, the modification process can be reduced to three main stages: 1) hydrolysis of multinucleated metal ions hydroxy complexes (PHC) -pillar solution, 2) ion exchange, 3) heat treatment of the modified material.Figure 7 shows a diagram of the stacking process of layered bentonites. In aqueous solutions, monmorillonite swells as the distance between the bentonite layers increases. Aluminosilicate is placed in a pill solution containing multinucleated metal hydroxides, while ion exchange of interlayer clay cations is performed for larger multinucleated hydroxy complexes. Polyhydroxo complexes are usually obtained by hydrolysis of cations with a NaOH solution.



Figure 7. Layering scheme of layered bentonites

After ion exchange, the modified material is washed, dried, and heated. Heat treatment is accompanied by dehydration and dehydroxylation of the introduced polyhydroxides, resulting in the formation of metal oxide clusters (columns, columns) in the interlayer space of bentonite, which is firmly bonded to the bentonite layers of bentonite and steel bridges. These clusters prevent the layers from converging, forming a stable two-dimensional micro-porous structure, in which the distance between the layers is significantly increased relative to the original material.

Layered bentonites modified by this method are called columnar, columnar, or layered silicates. In addition to the formation of micro-pores, due to delamination (stratification) of bentonite layers, additional formation of meso-pores occurs during the peeling process, as a result of which the specific surface area of the resulting materials can reach 200-300 m² / g.

The mesopores in the clays are mainly intercellular spaces. As for the formation of polyhydroxo complexes, the most studied metal ion is aluminum. Hydrolysis of aluminum salts is a multi-step process that results in the formation of aluminum hydroxide. According to modern concepts of the mechanism of formation of aluminum hydroxide, the first stage of its formation is the emergence and enlargement of multinuclear aluminum hydroxide complexes.

Almost immediately after the dissociation of the salt, aluminum hexahydrate Al (H₂O) $_{6}^{3+}$ is formed in solution, an octahedron with aluminum molecules at the center and water molecules at the top. These types of ions can exist in the free state only in sufficiently acidic solutions (pH <3). When the pH is higher than 3, assuming the coordination of the six water molecules as the first, the hydrolysis process, more precisely, its next stage, begins. In the process of layered bentonite plating, the researchers tried to solve two main problems: to maximize the textural properties of the starting material, as well as the introduction and detection of a catalytic active element in the bentonite composition.

Influence of heating temperature on the parameters of porous structure of columnar bentonites.The heating temperature of the samples under the influence of the solution, after rinsing and drying is an important factor determining the textural properties of the modified clay.

 Table 2

 Textural characteristics of Navbahor bentonite modified depending on the heating temperature

temperature					
Nº	Heating temperature	Texture characteristics			
		${S_{ud}\over m^2/g}$	Vs sm ² /g	$V_{mn} \ sm^2/g$	
1	$400 {}^{0}\mathrm{C}$	204	0,11	0,08	
2	500 ⁰ C	156	0,08	0,07	
3	$600 {}^{0}\mathrm{C}$	144	0,08	0,06	

Obtaining conditions: hydrolyzing agent - NaOH, OH-: $Me^{n+} = 2$: 1, T_{Hydrolysis} = $60^{\circ}C$, T_{ion} exchange = $60^{\circ}C$.

As can be seen from the Navbahor modified bentonite example (Tables 2 and 4), as the heating temperature of the specimens rises from 400 to 600 °C, their specific surface area and porosity decrease by about 30% mainly due to thermal adhesion of the micropores. Heat treatment of the original clay at temperatures above 100 °C leads to irreversible adhesion of the layers and deterioration of texture parameters, along with the removal of interlayer water. However, as can be seen from the images (Figures 5 and 6), no significant changes were observed in the porous structure parameters of the initial sludge samples in the heating temperature range of 70–500 °C.

 Table 3

 Texture characteristics of unpeeled Navbahor bentonite depending on the heating tomporature

temperature					
$T^{0}C$	S _{ud}	Vs	$W_0 sm^2/g$	E ₀ , kDj/mol	
	m²/g	sm ² /g			
70	65	0,062	0,031	12,74	
100	64	0,064	0,031	13,38	
150	72	0,061	0,034	13,09	
400	74	0,072	0,035	12,44	
500	66	0,063	0,032	11,72	

Table 4

Texture characteristics depending on the heating temperature of the modified sample of Navbahor bentonite

Т ⁰ С	S _{ud}	Vs	$W_0 sm^2/g$	E ₀ , kDj/mol
	m²/g	sm ² /g		
150	128	0,082	0,064	15,63
250	173	0,098	0,089	16,58
350	183	0,100	0,094	16,79
400	187	0,116	0,095	16,49
450	168	0,110	0,086	16,28
500	144	0,096	0,076	17,18
550	108	0,075	0,058	15,60
600	101	0,070	0,052	15,94



Figure 8. The effect of heating temperature on the surface of bentonite





Regardless of the composition and modification conditions of natural bentonites, the mean mesocyte diameter of all samples remains constant and varies in the range of 4.0–4.1 nm (Fig. 10). It should be noted that as a result of tabletting, the size of the mesentery is reduced.



Figure 10. Dependence of the distribution curve of the diameter of the pores on the size of unmodified bentonite on the ratio ON⁻ : Meⁿ⁺

For samples of initial and modified bentonite heated to 400 $^{\circ}$ C, the highest values of specific surface area and porosity were observed. For a modified sample, the dependence of the specific surface area and the volume of the pores on the heating temperature is very high, at a maximum temperature of 400 $^{\circ}$ C.

In the process of polishing natural clay, all modified specimens showed significant changes in the properties of their textures relative to the original specimens and to the previous ones.

It should be noted that natural mud contains micro-pores, but their volume is 30-40% of the absorption volume of the pores.

Modified specimens have mainly a micro-porous structure; the proportion of microporous volume is 70–80% of the total pore volume (Fig. 11). For natural and modified bentonite, the isotherms of nitrogen adsorption at 77 K are shown in linear coordinates of the Dubinin-Radushkevich equation, which satisfactorily describe the experimental data; mainly used in the calculation of the volume of E_0 micropores.

The specific energy of nitrogen adsorption in the modified samples increased 1.3-1.5 times compared to the original samples, which indicates an increase in the adsorption capacity of the obtained materials.



Figure 11. Isotherms of nitrogen adsorption at 77 K on linear coordinates of natural and modified bentonite Dubinin-Radush-Kevich equation

On the basis of the obtained data the technological schemes of activation of natural mineral sorbents are developed. Sorbent activation technology is simple and well reproducible. Processing of natural sorbents in real production conditions is divided into two main stages: 1) primary processing of natural mineral sorbents, including operations of extraction, transportation, crushing and classification of raw materials; 2) secondary processing of natural sorbents, consisting of their chemical and thermal activation, followed by classification, packaging and production of modified products. These operations are possible only in the production of appropriate chemicals, equipped with a number of necessary capacity devices that connect the pipes and pumps, provided that appropriate treatment facilities are available.

In figure 12-13 show technological schemes of acid and complex (acid-base) activation of natural mineral sorbents.



Fig. 12. Technological scheme of acid activation of natural mineral raw materials: 1-container with concentrated acid; 2-telpher; 3-unit for preparation of solutions; 4 - reactor; 5 - washing unit; 6 - unit for neutralizing acidic effluents; 7 - heater; 8 - pump; 9 - thermocouple; 10 -caps.

The unit is a technological line consisting of a reactor with an enamel coating for aggressive media, heated by heaters, a tank for storing and preparing acid solutions, a unit for washing and neutralizing acidic effluents. The activation of the zeolite is carried out with a 10% solution of hydrochloric acid for two hours at a mass ratio of S: L = 1:2 in boiling mode. The process of zeolite activation occurs according to the ion-exchange mechanism as a result of the replacement by the H⁺ ion (proton) of a part of the cations of the exchange complex (Na⁺, K⁺, Ca²⁺, Mg²⁺). Due to activation, the zeolite is partially converted into hydrogen (H-form). In this case, the specific costs of the activator of hydrochloric acid (HCl) per unit mass of the sorbent are determined by a decrease in the sum of the content of cations of the exchange

complex.According to experimental data, the residual concentration of hydrochloric acid in the solution after the completion of activation is 4.24%, and the specific consumption of hydrochloric acid for the activation process itself is 6.04 g / 100 g of zeolite. After activation, the activator solution is filtered (separated) from the sorbent. In this case, a part of the activator solution that saturates the sorbent enters the washing stage. Taking into account the water absorption parameter of the activated sorbent (37.15%), the specific amount of hydrochloric acid brought to the washing stage will be 1.628 g / 100 g of the sorbent. The total cost of HCl is4,135 g / 100 g of sorbent, or 41.35 kg / t.



Fig. 13. Technological scheme of complex activation of natural mineral raw materials: 1 - containers with concentrated acid and alkali; 2 - telpher; 3 - units for preparation of solutions; 4- reactors;. 5- washing units; 6 - unit for neutralizing acidic effluents; 7 - heaters; 8 - pumps; 9 - thermocouples; 10 - taps

Specific losses of hydrochloric acid with washing and water will amount to 1.615 g / 100 g of sorbent, or 0.443 mol / 100 g of sorbent. The technological scheme of the alkaline activation of natural sorbents is similar to the acid one. The flask is activated with a 5.5% sodium hydroxide solution for 2.75 h at a mass ratio of S: L = 1: 2 in boiling mode. NaOH, interacting with flask, is spent mainly on dissolving amorphous silica, the content of which in the initial sample O1 is 61.18%, in the activated sample - 53.04%. Thus, the residual concentration of sodium hydroxide is 0.0825%. Taking into account the fact that the water absorption of the activated flask is 129.75%, and also taking into account the low concentration of the activator, the separation of the activator for reuse does not make sense.

Consequently, the specific consumption of NaOH is 11 g / 100 g of sorbent, or 110 kg / t. Specific losses of sodium hydroxide with wash water will be 0.165 g / 100 g of sorbent. In addition, the wash water contains sodium silicate 0.135 mol / 100 g of sorbent. The sodium silicate formed as a result of alkaline activation can be used as a raw material for the production of water glass. To reduce the cost of producing activated sorbents, it is recommended to carry out simultaneously acid and alkaline activation. Mixing of rinsing waters of the processes of

flask and zeolite activation (with the ratio of the amount of flushing waters obtained from the activation of 163 mass parts of flask and 100 mass parts of zeolite) will lead to their complete neutralization, and after the separation of silica gel (H_2SiO_3) to the possibility of reuse or to discharge into the sewage system. Sorbents are processed directly at the field.

CONCLUSION

Thus, the methods of modification and activation of Navbahor bentonite were considered and the textural characteristics of the obtained sample were studied. Regardless of the composition and modification conditions of natural bentonites, the mean mesocyte diameter of all samples remains constant and varies in the range of 4.0–4.1 nm. It should be noted that as a result of tabletting, the size of the mesentery is reduced.In the process of polishing natural clay, all modified specimens showed significant changes in the properties of their textures relative to the original specimens and to the previous ones. Modified specimens have mainly a micro-porous structure; the share of microporous volume is 70-80% of the total pore volume. The specific energy of nitrogen adsorption in the modified samples increased 1.3-1.5 times compared to the original samples, which indicates an increase in the adsorption capacity of the obtained materials.

REFERENCES

1. Gil, A. Progress and perspectives on pillared clays appliyed in yenergetic and yenviron-mental remediation procyesses / A. Gil, A. Vicyente // Curr. Opin. Greyen Sustain. Chem. -2019. - Vol. 1. - P. 1-25.

2. Murray, H.H. Traditional and new applications for kaolin, smectite, and palygorskite: a general overviyew / H.H. Murray // Appl. Clay Sci. – 2000. – Vol. 17. – P. 207-211.

Hui, L. High performancye photocatalyss: Бентоните supported-nano TiO₂ composites / L.
 Hui, W. Zaiqin, L. Lingmin, C. Liang, L. Zhyen, F. Jing // Optic. – 2017. – Vol. 136. – P. 44-51.
 Belver, C. Titania-clay hysterostructures with solar photocatalytic applications / C. Belver, J.
 Bedia, J.J. Rodriguyez // Appl. Catal. B – 2015. – Vol. 176. – P. 278-287.

5. Hadjltaiyef, H.B. Photocatalytic degradation of methyl greyen de in aquyeous solution over natural clay-supported ZnO-TiO₂ catalyss / H.B. Hadjltaiyef, M.B. Zina, M.Ye. Gal-vez, P.D. Costa // J. Photochem. Photobiol. A. -2016. - Vol. 315. - No 15. - P. 25-33.

6. Zuo, Q. Investigation on thye thyermal activation of бентоните and is application for thye removal of U(VI) in aquyeous solution / Q. Zuo, X. Gao, J. Yang, P. Zhang, G. Chen, Y. Li, K. Shi, W. Wu // J. Taiwan Inst. Chem. Ye. – 2017. – Vol. 80. – P. 754-760.

7. Barrer, B.R. Activation of bentonite by ion exchange and sorption complexes of tetra-alkyl ammonium bentonites / B.R. Barrer, D.M. MacLeod // Trans. Fara-day Soc. –1955. –Vol. 51. –P. 1290-1300.

8. Gil, A. Preparation and Characterization of Microporosityand Acidity of Silica-Alumina Pillared Clays / A. Gil, G. Guiu, P. Grange. M. Montes // J. Phys. Chem. –1995. –Vol. 99. –P. 301-312.

9. Kloprogge, J.T. Synthesis of Smectites and PorousPillared Clay Catalysts: A Re-view / J.T. Kloprogge // J. Porous Mater. –1998. –Vol. 5. –P. 5-41.

10. Kloprogge, J.T. Thermal stability of basic aluminum sulfate / J.T. Kloprogge, J.W. Geus, J.B.H. Jansen, D. Seykens // Thermochimic. Acta. –1992. –Vol.209. –P. 265-276.

11. Kloprogge, J.T. The effect of thermal treatment on the properties of hydroxyl-Al and Hydroxy-Ga pillared бентоните and beidellite / J.T. Kloprogge, E. Booy, J.B.H. Jansen, J.W. Geus // Clay Miner. –1994. –Vol. 29. –P. 153-167.

12. Pinnavaia, T.J. On the pillaring and delamination of smectite clay catalysts by pol-yoxo cations of aluminum / T.J. Pinnavaia, M.-S. Tzou, S.D. Landau, R.H. Raythatha // J. Mol. Catal. –1984. –Vol. 37. –P. 195-212.

13. Pinnavaia, T.J. Layer Cross-Linking in Pillared Clays / T.J. Pinnavaia, S.D. Landau, M.-S. Tzou, I.D. Johnson // J. Am. Chem. Soc. –1985. –Vol. 107 –P. 7222-7224.

14. Sterte, J. Synthesis and properties of titanium oxide cross-linked бентоните / J. Sterte // Clays Clay Miner. –1986. –Vol. 34. –P. 658-664.

15. Sterte, J. Preparation and properties of pillared interstratified illite/smectite / J. Ster-te // Clays Clay Miner. –1990. –Vol. 38. –P. 609-616.

16. Sterte, J. Preparation and properties of large-pore La-Al-pillared бентоните / J. Sterte // Clays Clay Miner. –1991. –Vol. 39. –P. 167-173.

17. Brindley, G.W. Preparation and properties of some hydroxylaluminum beidellites / G.W. Brindley, R.E. Sempels // Clays Clay Miner. -1977. –Vol. 25. -P. 229-236.

18. Johansson, G. On the Crystal Structures of Some Basic Aluminium Salts / G. Jo-hansson // Acta Chem. Scand. –1960. –Vol. 14. –P. 771-773.

19. Johansson, G. On the Crystal Structure of a Basic Aluminium Sulfate and the Cor-responding Selenate / G. Johansson, G. Lundgren, L.G. Sillen, R. Soderquist // Acta Chem. Scand. –1960. – Vol. 14. –P. 769-771.

20. Baker, L.C. A New Fundamental Type of Inorganic Complex: Hybrid between Heteropoly and Conventional Coordination Complexes. Possibilities for Geometrical Isomerisms in 11-, 12-, 17-, and 18-Heteropoly Derivatives / L.C. Baker, J.S. Figgis // J. Am. Chem. Soc. –1970. –Vol. 92. –P. 3794-3797.

21. Keggin, J.F. The Structure and Formula of 12-Phosphotungstic Acid / J.F. Keggin // Proc. Roy. Soc. Ser. –1934. –Vol. 144. –P. 75-100.

22. Bobomurodova, S.Y., Fayzullaev, N.I., Usmanova, K.A.Catalytic aromatization of oil satellite gases//International Journal of Advanced Science and Technology, 2020, 29(5), crp. 3031–3039.

23. Fayzullaev, N.I., Bobomurodova, S.Y., Avalboev, G.A.Catalytic change of C_1 - C_4 - alkanes//International Journal of Control and Automation, 2020, 13(2), crp. 827–835.

24. Mamadoliev, I.I., Fayzullaev, N.I., Khalikov, K.M.Synthesis of high silicon of zeolites and their sorption properties//International Journal of Control and Automation, 2020, 13(2), crp. 703–709.

25. Mamadoliev, I.I., Fayzullaev, N.I.Optimization of the activation conditions of high silicon zeolite//International Journal of Advanced Science and Technology, 2020, 29(3), crp. 6807–6813.

26. Omanov, B.S., Fayzullaev, N.I., Musulmonov, N.K., Xatamova, M.S., Asrorov, D.A.Optimization of vinyl acetate synthesis process//International Journal of Control and Automation, 2020, 13(1), ctp. 231–238.

27. Fayzullaev, N.I, Bobomurodova, S.Y, Xolmuminova, D.A.//Physico-chemical and texture characteristics of Zn-Zr/VKTS catalyst. Journal of Critical Reviews, 2020, 7(7), crp. 917–920.