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ECOLOGICAL SORBENT BASED ON SAPONITE MINERAL FROM UKRAINIAN CLAY-FIELD

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Abstract. The physico-chemical, structural and adsorption characteristics of saponite mineral from Tashkivske clay-field and their changes under the influence of acid, thermal and ultrasonic activation were investigated. Stabilization mechanism of the colloidal system "saponite-water" under the influence of stabilizing agents was studied. Moreover, the effectiveness of saponite multipurpose usage was proved by experiments.

Keywords: saponite mineral, modifications of the surface, X-ray diffraction analysis, TGA, IR-spectra, electrokinetic potential.

1. Introduction

Nowadays, one the most important industrial problem in Ukraine is expanding a domestic material resource base. In our country rich deposits of natural raw materials, such as bentonite, kaolin, zeolite and others were discovered by geologists. Specifically, in many regions of Ukraine, namely Cherkasy, Khmelnytsky, Ternopil regions and the Crimea significant deposits of bentonite clays (generally more than 100 fields) were found [1]. However, many of them did not find industrial applications due to various reasons, for instance the lack of resources, complexity of mining and technical conditions of occurrence, relatively low content of basic species or poor quality, mainly caused by the high amount of quartz and carbonate inclusions. But, the main reason for the delay of using these clay materials in Ukraine is a lack of basic research in the area of physico-chemical characteristics and the methods of improving the quality and as a result expanding the range of their industrial applications.

It is well known that clay materials are widely used in industry and technology as an effective adsorbent, ion exchangers, filter material, *etc*. However, due to difficult ecological and economic situation in Ukraine, Belarus, Russia and other former Soviet countries, today one of the most important tasks for scientists and experts is to identify ways of sustainable using the cheap natural minerals for water and air treatment. For this reason in the number of research works scientists are looking for more effective methods in order to improve the quality characteristics of clay [2, 3], which offers the great possibilities for using natural sorbents for waste and pure water purification.

However, each clay-field is unique that is why geological and physico-chemical characteristics of the materials should be studied formerly which will help to make a list of possible applications of these materials in the near future. Therefore, this report concerns investigation of bentonite mineral from Tashkivske clay-field, which is situated in Khmelnytsky region.

1.1. Relevance of the Topic

The possibility of the surface modification of clays contributes to obtaining specific, selective, universal and high quality adsorbents. Immobilization of dispersed particles ligands on the surface, exchanged ions and the important analytical reagents, the ability to form mineral organic complexes provide the number of ways in which hybrid sorbents based on clay materials can be developed. The aim of this study was to establish the influence of chemical and physical methods of activation on the structural and physico-chemical characteristics of bentonite clay from Tashkivske clay-field, and as a result changes in its sorption and ion exchange ability in relation to different classes of pollutants.

1.2. Current State of the Problem

According to the literature information, a choice of method of clay activation depends not only on their qualitative and quantatative composition, but also depends dramatically on the main target of modification. One of the most important problems in the modern industrial chemistry is obtaining materials with the predetermined properties. Especially, a very important problem is the regulation of the surface properties for such materials as adsorbents, carriers, catalysts, effective participation of which in many manufacturing processes is conditioned by the surface properties, for instance the nature of active centers, porosity, specific surface area, *etc*.

Among a lot of natural dispersed materials a special place belongs to clay materials with the layered and band-layered structure, modification of which leads to the increasing of adsorption capacity. However, a complex crystalline structure and polydispersity of bentonite clay are the reason of that fact that only individual aspects of bentonite modification have been discovered.

2. Experimental

Nowadays there are several effective methods of chemical and geometrical modifications of the surface and porosity regulation, including the replacement of organic radicals instead of hydroxyl groups on the surface, cation exchange, thermal, hydrothermal, acid, alkaline, ultrasonic treatment, *etc*. Nevertheless that fact that some of these methods are applied to the clay materials and have been used by technologists for a long time, there is still just small quantity of information in the literature that provides data on the changes that are taking place on the surface and in the volume of clays during the activation process in different ways.

In order to obtain information on the effectiveness of activation process and to establish its optimum technological conditions, a chemical activation of saponite clay from Tashkivske clay-field with sulfate, hydrochloride, oxalic acid and with ammonium, potassium, sodium and lithium hydroxide solution was carried out. The parameters of the activation process, namely time of activation (from 1 to 4 h), the concentration of acid (10 and 20 %), and the combination of reagents were changed. The mass ratio of solid and liquid phases was maintained at 1:3. The activation process was carried out in a Teflon autoclave under a boiling temperature of the reaction mixture with a constant stirring. The scheme was equipped with a refrigerator and water reflux condenser to avoid reducing the concentration of acid due to its evaporation. The process of activation of oxalic acid was performed at the temperature that did not exceed 333–338 K to prevent the decomposition process of the organic compounds. The activated sorbent was filtered through a Buchner funnel, washed with deionized water to the moment of obtaining the neutral reaction of pH in the filtrate and, finally, dried at the temperature of 378 K over a span of 3 h. The obtained powder was treated with alkaline and bases solutions (NH_4OH, KOH, NaOH, LiOH) under the constant stirring over one-hour period at room temperature and then it was filtered, washed and dried.

The test samples of mineral sorbent were determined in order to investigate their main properties such as physical, chemical and adsorptive ones.

X-ray diffraction analysis of samples was carried out by X-ray diffractometer DRON-UM1 which has two Soller slits with $\mathrm{Co}K_a$-filtered radiation with 1° step size. The precision of measurements of the quantitative phase composition was estimated to be ± 5 %. According to ASTM card index, the mineral composition was identified.

The thermal gravimetric analyses (TGA) were recorded in the temperature interval from 298 to 1123 K with a heating rate of 10 K per minute.

Infrared spectra (IR) were recorded using a Specord M80 spectrometer. The studied wave number range was 450–4000 cm^{-1} with 2 s time of integration and 10 cm^{-1} step size. The samples for analysis were prepared by tableting with potassium bromide at a mass ratio of 1:100.

3. Results and Discussion

The first parameter that was fixed over a span of activation process was the weight loss of the solid minerals which is listed in Table 1.

Table 1

Weight loss of mineral material per 50 g of initial sample activated with acid

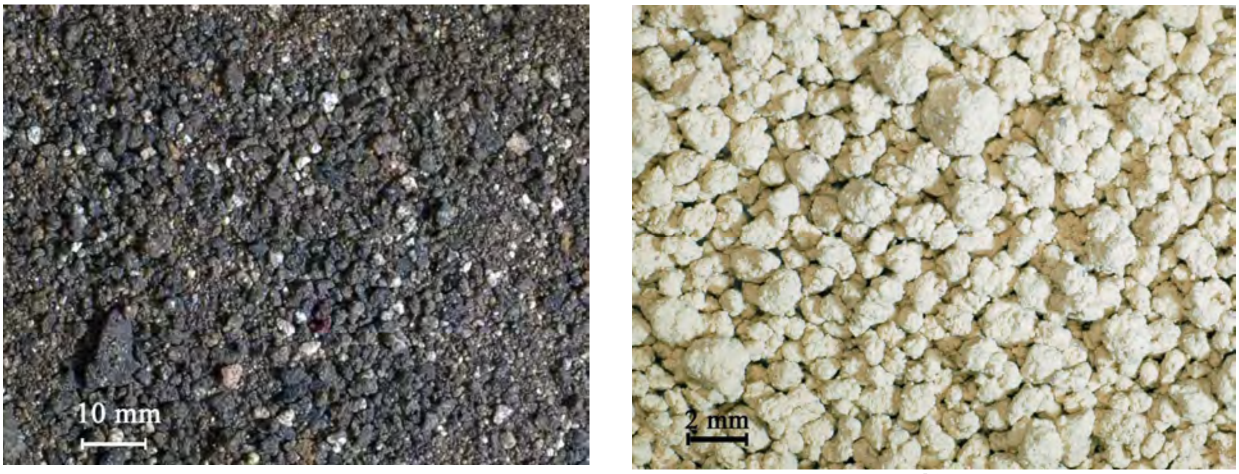
Activating acid	Activation length, h	Absolute weight loss, g	Percentage loss, %
HCl	1	20.75	41.50
	2	22.07	44.14
	3	22.69	45.38
	4	22.90	45.80
H_2SO_4	1	11.65	23.30
	2	10.65	21.30
	3	11.60	23.20
	4	12.05	24.10
$C_2H_2O_4$	1	2.07	4.14
	2	7.05	14.10
	3	4.17	8.34
	4	6.42	12.84

As can be seen from Table 1, the weight loss, which is associated with mineral dissolution, depends significantly on the activating agent and the length of activation. Obviously, the first stage of activation (1–2 h) is mainly associated with dissolution of iron, aluminum, alkaline earth metals oxides in a free state and a replacement of exchange cations such as calcium, magnesium, potassium in a crystal lattice of saponite on hydrogen ion from acid. Thus, the speed and depth of each stage of acid activation depend on the type of the compounds in the free state, their quantitative ratio, percentage, dispersion and reactivity.

The second stage of activation (3–4 h) is followed by deep changes in the crystal lattice which are associated with reducing of aluminum ions from the crystal lattice that sometimes can be resulted in its complete destruction.

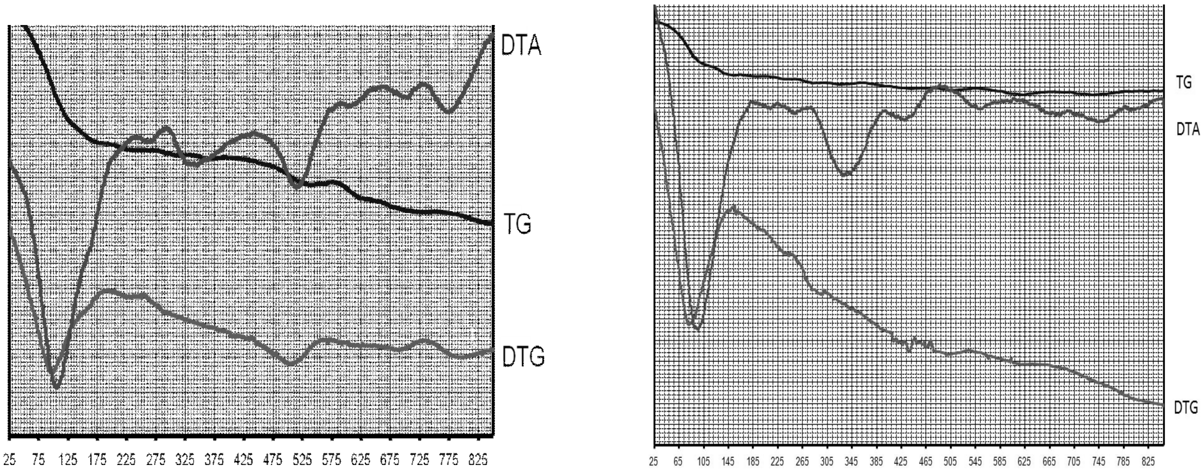
The most effective activator of bentonite clays is hydrochloric acid, which has a high level of selectively to Fe_2O_3 and Al_2O_3, whereas sulfate and oxalic acid are less selective to the compounds of clay that is why the ratio of Al_2O_3/ Fe_2O_3 remained almost constant over the time of the activation process. Taking into consideration the solubility of iron oxides, the efficiency of acid, which was used for activation, decreased gradually from HCl to H_2SO_4, while in the case of aluminum the situation has slightly changed and the efficiency decreased from HCl to $H_2C_2O_4$ [4].

To sum up, the first stage of saponite activation is followed by dissolution of iron and aluminum oxides presented in the mineral in the free state, which leads to the largest weight loss over the first hour of the process. The second hour of activation process is characterized by slight changes in the weight due to unbounded compounds which have already dissolved and the destruction of the crystal lattice has not started yet. The next stage is associated with the leaching of aluminum ions from the octahedron crystal structure and can continue to the weight loss which accounts for almost the mass of silicon oxide (IV). As a result, the amorphous silica gel could be formed.



a) b)

Fig. 1. Appearance of native (a) and saponite mineral activated by hydrochloric acid (b)



a) b)

Fig. 2. TG, DTG and DTA curve of natural (a) and saponite mineral activated by hydrochloric acid (b)

TGA of native and activated samples illustrate that the lowest endothermic effect at 393–473 K is due to the removal of adsorption water. The second endothermic effect at 523–573 K is associated with the cations exchange, ***i.e.*** with their transition to the octahedral positions or losing their hydration water, whereas the endothermic peak of 1033–1123 K is due to the removal of constitution water.

According to the X-ray analysis, native saponite samples have the same qualitative composition, for instance, quartz, anatase, calcite, hematite and clay minerals what was clearly identified with 001 refraction at 14.87 Å, 002 (7.32 Å), 003 (4.83 Å), 004 (3.63 Å), 005 (2.92 Å), and with two-dimensional diffraction: 4.58 Å (02, 11); 2.58 Å (13, 20); 1.53 Å (06, 33). In addition, combined with saponite the montmorillonite was identified. However, if the acid activation is implemented the clay fraction is partially (in the case of sulfate and oxalic acid) or completely (in the case of hydrochloric acid) destructed.

In the infrared (IR) spectra of initial samples, a valence (υOH at 3625 cm^{-1}) and a deformation (δAlAlOH at 915 cm^{-1} and δAlMgOH at 850 cm^{-1}) structural OH bonds vibration were observed (Fig.3).

An intense adsorption band at 1035 cm^{-1} is associated with Si–O stretching vibrations in the tetrahedral sheet, while 525 cm^{-1} – with their deformation vibrations. The absorption at 1630 cm^{-1} corresponds to the crystallization water deformation vibration in the interlayer space of saponite. The process of acid activation leads to a decrease in the intensity of this absorption band, which confirms the results of TGA and may indicate the closeness of tetrahedral and octahedral layers. A decline of band intensity at 1035 cm^{-1} for the activated samples indicates the partial destruction of tetrahedral sheets, however, Si–O vibrations are presented because the samples still have a lot of quartz and the amorphous silica gel. Fade vibrations at 3400 cm^{-1} suggest that due to the process of acid activation the number of OH groups on the surface of the mineral decreases dramatically, whereas a sharp peak of δAlMgOH deformation vibrations at 850 cm^{-1} in the spectra of activated samples provides information of OH groups increase in the octahedral sheet.

The process of acid activation also affects the physical and physico-chemical properties of clays, including the amount of specific surface area, porosity, hydrophilicity, electrokinetic properties of the colloid system, *etc*.

The amount of specific surface area was investigated by a N_2 gas adsorption-desorption process based on the well-known Brunauer, Emmet and Teller (BET) method. The results are listed in Table 2.

Thus, using different kinds of acids as the activators the amount of specific surface area could be increased more than 4–6 times compared to natural samples. In addition, the average pore radius also showed an upward trend. Specifically, 29–30 Å is the dominated pores radius for natural sorbent, however, if the hydrochloric acid is implemented, it increases approximately twofold and accounts for 62–65 Å. Whereas sulfate or oxalic acid are implemented, the effective radius of pores increases much less significantly.

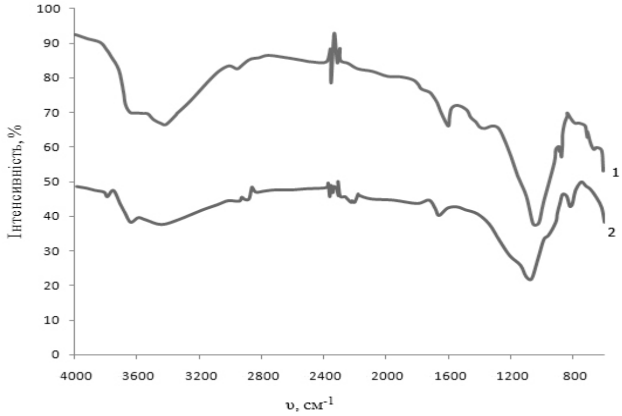


Fig. 3. Infrared spectra of natural (1) and saponite mineral activated by hydrochloric acid (2)

Table 2

Changes of the specific surface area of sponite as a result of activation

Activating acid	Activation length, h	S_{BET}, m^2/g
Natural sample	-	59.018
HCI	1	375.56
	2	351.70
	3	330.45
	4	329.61
H_2SO_4	1	286.10
	2	299.70
	3	305.80
	4	315.10
$C_2H_4O_2$	1	238.61
	2	238.85
	3	243.60
	4	212.68
HCI+NH_4OH	2+1	176.25

A heat of wetting and hydrophilicity of adsorbent are also important characteristics. In this case a wetting angle is a quantitative characteristic of the wettability for solids, but its measurement cannot be done if a powdered material is used and the heat of wetting, in this case, is the main quantitative characteristic of the wettability. A wetting coefficient β is the hydrophilicity characteristic of powdered sorbent, which is a heat ratio of wetting with water and nonpolar liquid, for instance, benzene. If the wetting coefficient represents the number that is less than one ($\beta > 1$), the material has hydrophilic characteristics; if $\beta < 1$ – the material has hydrophobic characteristics.

The heat of wetting was determined for different samples by calorimeter, which was represented as a tube fixed in Dewar flask and closed with a plug supplied with Beckmann thermometer and a stirrer. The heat of wetting was defined as:

$$Q = (V \cdot C \cdot r + H) \cdot \Delta T \tag{1}$$

where V is a volume of liquid, cm^3; C – specific heat capacity of liquid, J/(g·K); ρ – density of liquid, g/cm^3; H – heat capacity of the calorimeter, J (it was determined by heat of potassium chloride solution); ΔT – temperature change, K.

The results are listed in Table 3.

Table 3

Changes of the heat wetting and the wetting angle of sponite as a result of activation

Activating acid	Activation length, h	Heat of wetting with water (Q_1), J	Heat of wetting with benzene (Q_2), J	Wetting angle (β)
Natural sample	-	5.774	0.496	11.64
HCI	1	70.949	31.321	2.27
	2	72.626	50.908	1.43
	3	74.304	46.629	1.59
	4	74.975	28.233	2.66
H_2SO_4	1	84.026	54.155	1.55
	2	84.460	51.726	1.63
	3	85.357	52.220	1.63
	4	86.480	52.371	1.65
$C_2H_4O_2$	1	50.990	28.045	1.82
	2	50.147	26.640	1.88
	3	48.723	27.645	1.76
	4	45.807	26.217	1.75
HCI+NH_4OH	2+1	43.823	24.288	1.80

Table 4

Electrokinetic potential of the modified saponite clay

Activating acid	Natural sample	Modified agent		
		Li^+	Na^+	NH_4^+
Natural sample	0.81	5.59	2.15	0.94
HCI*	- *	-	-	-
$C_2H_4O_2$	-	0.43	-	-

Note: * suspension is unstable, the high speed of sedimentation prevents measurement of ζ-potential

Electrokinetic effects that are taking place on the verge of the solid and liquid phases (clay-water) are due to the presence of charge on the surface of saponite. Natural mineral particles are negatively charged and represented as a “macro-anions”. The distribution of ions on the surface of these particles determines the presence of elecrokinetic potential relevant to the thickness of the diffusion layer, whereas the thickness of the hydration cover is approximately characterized by electrokinetic potential ζ. Therefore, it is assumed that there is a define relationship between the amount of adsorption connected water and ζ-potential.

Electrokinetic speed of particles was determined by moving beyond method in Bertine apparatus which was slightly modified. It was represented as a U-shaped glass tube with the diameter which accounts for 5–6 cm and could be easily filled with 10 % suspension.

ζ-Potential was defined as:

$$\zeta = \frac{l \cdot \eta \cdot S}{E \cdot t \cdot \varepsilon \cdot \varepsilon_0} \tag{2}$$

where l is the distance between the electrodes, m; η – viscosity of the dispersion medium (for water η = 0.001 Pa·s at 293 K); S – distance (m) passed in time t (s);

E – potential difference of the external electric field, V; ε – dielectric constant of the dispersion medium (for water ε = 81); ε_0 – dielectric constant in vacuum ($\varepsilon_0 = 8.854\cdot 10^{-12}$).

As native samples do not form stable colloidal system in the water medium, that is illustrated by a low bentonite number, so various alkaline solutions, namely lithium, sodium and ammonium hydroxide with the concentration of 0.1 mol/ dm^3 were used in order to stabilize the suspension of saponite clay. The mass ratio of solid and liquid phases was maintained at 1:3. The results are listed in Table 4.

According to the data of sedementation analysis and the measurements of ζ-potential, if the alkaline solutions are implemented, the double electric layer becomes thicker and the solvation covers around the colloidal partiles of saponite are formed, which is one of the most powerful factor for obtaining stable colloidal system. However, other experimental studies show that the same effect can be achieved as a result of ultrasonic disintegration. Accoding to A. Ioffe, the process of microcracks formation on the surface of saponite clay is the main reason of a sharp decline of the solid strength.

All solids with different kinds of defects and microcracks are formed exactly in the weak areas of the crystal lattice. As the process of ultrasonic activation was carried out in the solution, once the microcracks were formed they were filled with the molecules of solvent which cause the effect of disjoining pressure and promote the process of disintegration. Along with the mechanical disintegration, the process of newly created particles solvation is presented and, consequently, clay particles confront the forces of adhesion.

After researching the basic physico-chemical properties of native and modified saponite with different methods identified above, various experiments were performed in order to establish the possibility of using saponite clay for the removal of different classes of pollutants from the contaminated water system, for instance, ions of heavy and transition metals, organic dye, phenolic substances, *etc*.

Adsorption treatment was carried out in a static mode. The amount of saponite accounted for approximately 4.5 ± 0.5 g per 1 dm^3 of waste water. As a result of previous studies, pH of water system was maintained at 7 ± 1. The duration of adsorption process was 90 min. The results of adsorption treatment illustrate that native and modified saponite clay could be used as an effective adsorbent for the waste and pure water purification.

For example, in the technology of wine production saponite mineral on the stage of lighting grape have to be activated by hydrochloric acid over a span of 90 min, washed with water and dried. Suspension, which was prepared by mixing powdered saponite and wine, was also modified by ultrasonic disintegration over 10-minute period at a frequency of 44 kHz. The obtained sorbent is a good alternative to the foreign sorbents which are currently used in the most wine producing plants in Ukraine.

Cationic dyes from waste water of textile manufactures can be removed by saponite activated by hydrochloric acid and stabilized by iron chloride and ultrasonic disintegration. The effectiveness of the purification accounts for 87–90 % in case of using the most popular industrial dyes – active bright red 5 SH [5, 6].

Industrial waste water contaminated with toxic organic, including phenolic compounds, can be effectively treated by native saponite clay stabilized with ultrasonic disintegration [7]. The same as waste water from electrochemical production plants contained a great amount of heavy and transition metals such as copper, nickel, manganese, cobalt, chromium, zinc, iron, *etc*. The effectiveness of the purification accounts for 70–95 %. However, this percentage increases significantly if sodium hydroxide solution is used as the stabilizing agent [8-10].

Sorption capacity of saponite material was investigated on the model solution of individual pollutants and on real waste water from the electroplating and textile productions, milk and butter manufacture "Dunaevetsky maslozavod" (Dunaevsky, Khmelnytsky region), wine manufacture "Kievsky zavod shampanskikh vin" (Kyiv) and "Tavria" (Kakhovka, Kherson region).

4. Conclusions

Thus, taking into consideration the results of thermogravimetric and X-ray analysis, IR-spectroscopy, determination of the specific surface area and pore size, heat of wetting and hydrophility, measurements of ζ-potentials of native as well as modified saponite samples under different conditions and stabilized by various alkaline solutions and ultrasonic disintegration it can be assumed that physical and chemical properties of minerals are regulated for different classes of adsorbate. Moreover, experimental data show that saponite can be effectively used in food industry and water treatment since this natural mineral is technologically efficient and safe for environment.

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References

[1] Sivij M.: Mineralni Resyrsu Podillja: Konstryktyvno-Geografichnyi Analiz i Sintez, Pidruchnyky i posibnyky, Ternopil 2004.
[2] Tarasevich Y.: Khimia i Techn. Vody, 1998, **1**, 42.
[3] Ozcan S. and Ozcan A.: J. Colloid Interface Sci., 2004, **276**, 39.
[4] Gates W., Anderson J., Raven M. and Churchman J.: Appl. Clay Sci., 2002, **20**, 189.
[5] Spivak V., Astrelin I., Tolstopalova N. and Stelmakh N.: Pat. Ukrainy 64424, MPK C02F 1/28 (2006.01), Publ. Nov. 11, 2011.
[6] Babchuk M., Alekseev O. and Astrelin I.: Shidno-Evrop. Zh. Providnykh Techn., 2009, **41**, 41.
[7] Spivak V. and Stelmakh O.: XIII Miznarodna Naykovo-Praktychna Konferencia Stydentiv, Aspirantiv ta Molodykh Vchenykh «Ecologia. Ljuduna. Syspilstvo», Ukraine, Kyiv 2010, 263.
[8] Spivak V.: Konferencia z Ekologii, Ukraine, Severodonetsk 2009, 86.
[9] Spivak V., Astrelin I. and Tolstopalova N.: Pat Ukrainy 45002, MPK C02F 1/28; B01J 20/02, Publ. Oct. 26, 2009.
[10] Spivak V., Astrelin I. and Tolstopalova N.: Visnyk Nats. Univ. «Kharkivsky Polytechnichnyi Instytut», 2010, **11,** 117.

ЕКОЛОГІЧНИЙ СОРБЕНТ НА ОСНОВІ САПОНІТУ УКРАЇНСЬКИХ РОДОВИЩ

Анотація. *Досліджено фізико-хімічні та структурно-адсорбційні характеристики сапонітового мінералу Ташківського родовища та їх зміну під впливом кислотного, термічного та ультразвукового активування. Вивчено механізм впливу стабілізуючих агентів на стійкість колоїдної системи “сапоніт-вода”. Експериментально доведено ефективність використання сапоніту для отримання сорбентів багатогалузевого призначення.*

Ключові слова: *сапоніт, модифікування поверхні, рентгено-структурний аналіз, ТГА, ІЧ-спектроскопія, електрокінетичний потенціал.*