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PREPARATION TERMOSTABLE ADSORBENT USING BENTONITE CLAY

Abstract. Preparation inorganic adsorbents using modifying bentonite clay with iron zol is considered. The samples of clay which undergoes acid treatment increase specific surface areas but do not thermostable, and loose their porosity above the temperature 160^0C. For prevent from unthermostability bentonite clays treated by sol solution of iron hydroxide which give them pillar structural form. The charge of colloidial particles of sols hydroxide iron plays important role in formation of pillar structural form. Colloidial particles having positive charge were changed with ions containing between layers of montmorillonite mineral of bentonite clay. After modifying bentonite it shows thermostability until 500^0C.

Key words: adsorbent, bentonite clay, pillar structure, specific surface, zol, termostability.

Introduction. It is known that natural clays with a greater adsorption capacity are widely used as an adsorbent and for the preparation of supported catalysts. One of the kind natural clay is bentonite having layered structure of aluminosilicate and usually was used for clearing and clarification of oil distillates [1, 2]. Origine bentonite clay consist of montmorillonite mineral at calcinating above the temperature 140-160°C lose their porosity and due to the thermal instability not found wide application as adsorbent or catalyst in oil refining [1-3].

One of the possible ways to preserve the porosity at heating of this clay, is making them pillar structural form. It is possible including supports between layer spaces of montmorillonite mineral, from wich basically content the bentonite clay [2-5]. Thus, it is created new type adsorbents named "Layered silicates with support". It was an incitement to develope the methods of their synthesis and research colloidal and chemical properties of modified clays. For obtaining pillar s tructural clays often used to polyhydrocomlexes of aluminium, transitive metals or organometallic compounds [3-9]. Pillared clays have significant potential for application in industry and in petrochemistry, but relatively few studies of these types of materials have been carried out. However, methods of obtaining, pillar-structural system using colloidal aqueous of compounds aluminium or transitive metals in the scientific literature are in an insufficient degree. In this respect character of formation pillar structures, preservation of porosity at influence of heats, changes their acid centers on a surface are subjects of the profound studying.

In this work is considered condition and structure of the bentonite clay from the South-Kazakhstan area of the Republic Kazakhstan which was treated by sols of iron compounds.

EXPERIMENT

The clay used as the raw material was a montmorillonite from the South Kazakhstan region of the Repuplic Kazakhstan. It was sifted to fractions with the certain sizes of particles **and the fraction less 0.2 mm being collected.** A compositon of bentonite clay was defined by physicochemical methods. For changing any properties of bentonite clay it was treated by various concentration of HCl acid. Concentration acid is varied from 0.5 mol/L up to 2.0 mol/L.

For preparation modifying bentonite is prepared its suspension in water. Suspension bentonite (~1,0 mass. %) received by intensive hashing it in water during 3 h, pH-water extract of clay makes about 8. The obtaining colloidal solutions of iron hydroxides were relised by peptization. After cooling the firm mass was pounded to a powder, it was sifted in fractions with the certain sizes of particles.

Natural bentonite clay at first was treated for 4 hour by hydrochloric acid at temperature 80^0C. After that the suspension of clay was separated from liquid phase and dense mass was washed by aqua distillate until the Cl^- concentrations decreased to the point where the conductivity of the aqueous phase was less 30 µS. The obtained mass was dried at room temperature during 24 h, then its heated gradually increasing the temperature up to 120^0C(4h) and 160^0C(4h).

Sol of iron prepared by peptization of their hydroxide in hot water. Concentration of hydroxide in sols was paid off proceeding from calculation 5-30 mmole Fe^{3+} per gram clay. Transformation hydroxide of iron to sol is realized by adding a few droppers of 0.1M $FeCl_3$ and subsequent dilution with conductivity water . .In avoidance coagulation of sol the powder of bentonite clay was added into sol at stirring about pH 4. Acidity of aqueous medium supervised by means of digital pH meter OP-208/1.After endurance processed suspensions of clay during 24 h, a deposit was washed by water and condensed. The sample, after separate from a liquid phase, dried at first at the room temperature(24h), and then heated at a rate of 5^0/min up to 120°C ; 160°C and 500^0C kept in eash case during the 4 hour. Then, the samples of modifying bentonite were cooled to room temperature in the same flow of air and were undergoed to determine physical-chemical characteristics.

The textural properties of the bentonite clays were evaluated from the nitrogen adsorption-desorption isotherms obtained at 77K over the whole range of relative pressures, using a Micromeritics ASAP-2000 apparattus, for samples previously outgassed at 413K for 18h. BET surface areas were calculated from these isothermes using the BET method. In all cases, correlation coefficients above 0.999 were obtained. The scanning electron microscope (SEM) uses for obtaining the signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture) was carried out on Carl Zeiss EVO MA15. X-rayograms of the studied samples were taken on a DRON-3 using $Cu_{K\alpha}$-radiation. Thermogravimetric study was performed on derivatograph Paulik-Paulik-Erdei. Thermograms was taken under dynamic conditions.

RESULTS AND DISCUSSION

Results of experiment chemical analysis natural samples of bentonite clay in recalculation on oxides are represented in table 1.

Table 1 – Composition of bentonite clay in recalculation on oxides

Type of oxides	Composition of bentonite clay depending of the layer depth (% mass.)			
	I (depth-1m.)		II (depth-2m.)	
	test 1	test 2	test 3	test 4
Al_2O_3	16,0	15,6	15,0	15,0
SiO_2	57,0	56,0	56.7	55,0
Fe_2O_3	4,0	4,6	4,2	4,3
CaO	2,9	3,0	2,8	2,7
MgO	2,0	2,4	2,2	2,4
K_2O	1,0	1,1	1,6	1,7
Na_2O	2,0	2,0	1,9	1,9
CO_2	0,6	0,6	0,5	0,6
SO_3	0,7	0,8	1,0	1,0
P_2O_5	0,5	0,4	0,2	0,1
H_2O	10,0	11,0	11,0	13,0
The rest	3.3	2.5	2,9	2.3
SiO_2/Al_2O_3	3.56	3.58	3,8	3.66

Thermograms of the samples studied with three endothermic effects observed at 120-180, 560-580 and 820-850 °C are characteristic of bentonite clays containing mainly montmorillonite mineral (figure 1). The first endothermic effect (120-180 °C) corresponds to the release of adsorbed water, and the second endothermic effect (560-580 °C) relates to the separation of chemically bound water from montmorillonite lattice [1, 3]. Endothermic effect observed at 820-890 °C can be attributed to the destruction of the crystal lattice of montmorillonite [4].

At calcinating the samples of bentonite loose their porosity and decreased specific surface area from 90 to 20 m^2/g above the temperature 120^oC. In order to keep porosity and specific surface area the samples were treated by mineral acid HCl. In Table 2 represented physicochemical characteristics of bentonite clay which undergoes acidic treatment where total volume of pore is changed from 0.08 to 0.34 cm^3/g, and total porosity from 14.0% to 23.0%. Increase concentration of HCl above But the samples activated by acid at heating above the

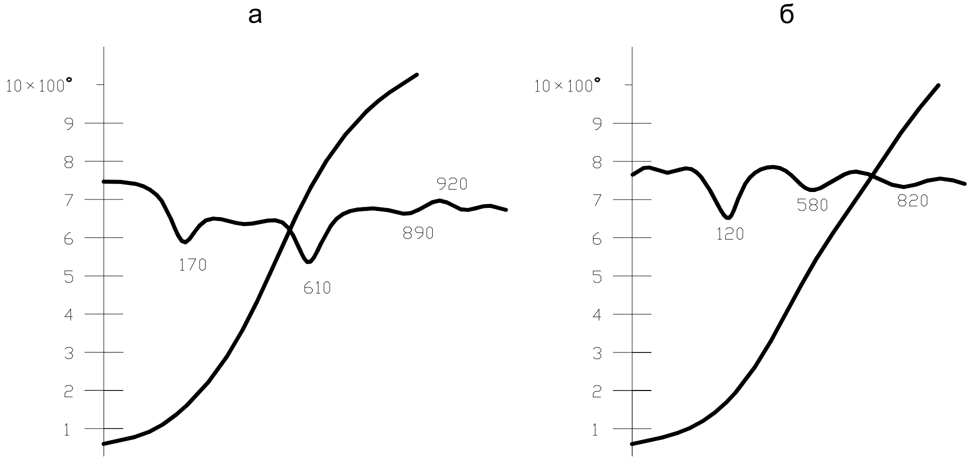


Figure 1 – Thermograms of bentonite clay:
a – clay (depth-1m.); b – clay (depth-2m.)

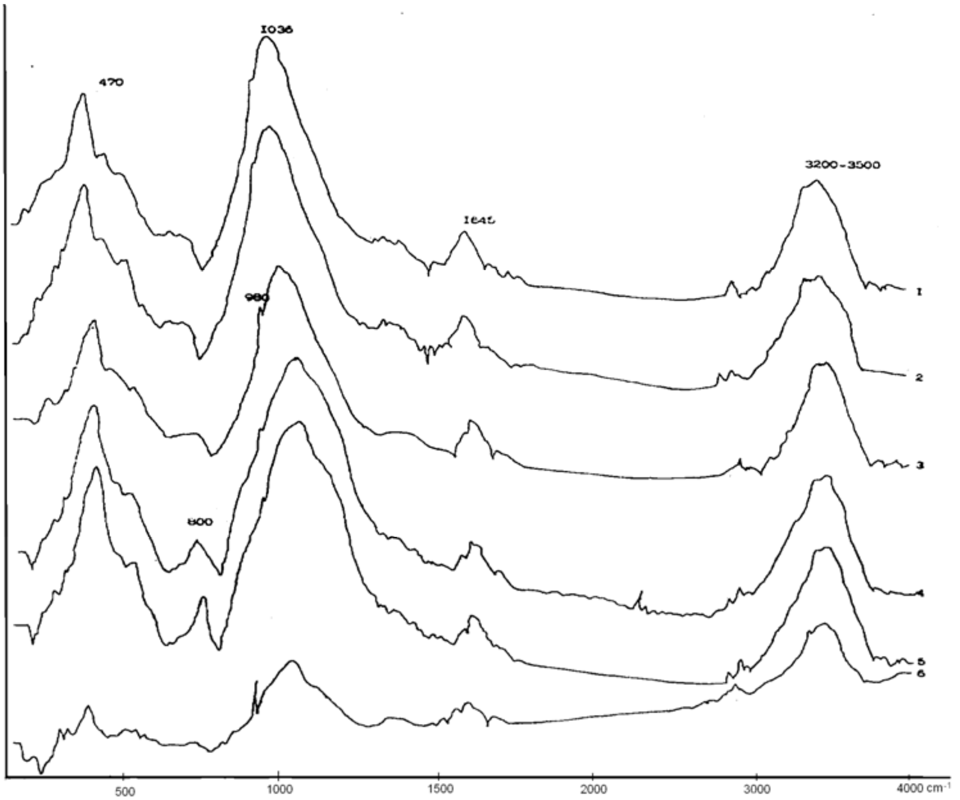
Table 2 – Data of some characteristics of bentonite clay after treating HCl

C(HCl), mol/L	Dencity, g/cm^3		Total porosity, %	Total volume of pore, cm^3/g
	original	after treating by acid.		
–	2,76		14.0	0,08
0.25	2,66	2,00	19.0	0,14
0.50	2,74	1,86	20.0	0,20
0.75	2,75	1,60	21.0	0,26
1.00	2,75	1,56	22.4	0,28
1.25	2,76	1,50	22.6	0.29
1.50	2,77	1,48	22.8	0,29
1.75	2.75	1.44	22.8	0.33
2.00	2.74	1.40	23.0	0.34
2.50	2.75	1.38	22.4	0.31
2.75	2.76	1.40	21,0	0.29
3.0	2.76	1.44	20.0	0.28

temperature 160^{o}C lose their porosity and type of sample is shown in scanning electron microscope (figure 2).

At treatment bentonite by hydrochloric acid (2,0 mol/L) the relation SiO_2/Al_2O_3 is changed from 3.5 up to 14,0. Above 2.0 mol/L the density of examples is increased. It means transformation aluminum from lattice montmorrilonite or destruction the mineral and changes in lattice are shown in figure 2.

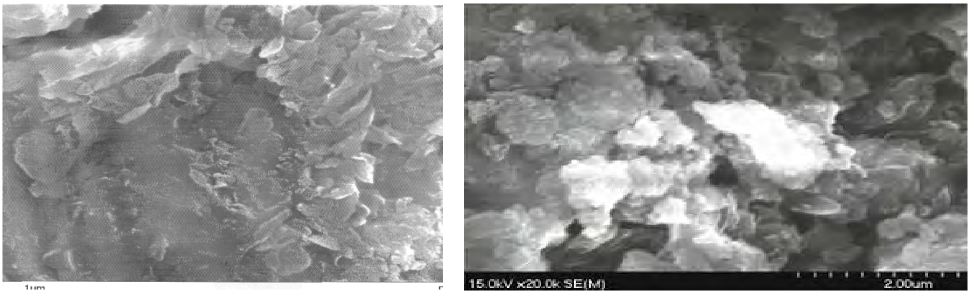
Analysing IR spectrogram showed characteristic value of spectral wavenumber at 400-1200 cm^{-1} according to -Al-O- bands in lattice of bentonite. Wavenumber 400-500 sm^{-1} are related to lattice deformatic vibration and frequency 900-1200 cm^{-1} are corrospending valence vibrations of the Al–O–Si and Si–O–Si



Frequency, cm^{-1}

Figure 2 – IR Spectra of bentonite clay treating by hydrochloric acid:
1 – natural bentonite; 2 – bentonite was treated 0,5M HCl; 3 – the same- 1,0M HCl;
4 – the same-1,5M HCl; 5 – the same 2,0M HCl; 6 – the same 3,0M HCl

of lattice. After aciding treatment is approached frequency at 800sm^{-1} which is related to forming new bonds as Si–O–Si and release the Al from tetracoordinate position at destruction of bonds Al–O–Si in lattice (figure 2).



a b

Figure 3 – Electron microscopy of bentonite clay was treated by acid:
a – 1.0 M HCl; b – 2.0 M HCl

The effect of the time of hydrothermal treatment on the crystallization and structure also can be clearly observed from the images of scanning electron microscopy as shown in figure 3.

Calculation of X-ray studied bentonite sample shows the presence of characteristic lines of montmorillonite as well as the chemical composition is consistent with the data in [1, 4].

Table 3 – Structural and adsorption characteristics of modifying bentonite clay

Content type of modifier	$S_{spec.}$*, m^2/g	d_{001}, nm	Total pore volume, cm^3/g	The loss of thermal stability	
				°C	$S_{spec.}$, m^2/g
Clay without modification	60	0.90	0.08	140	20
$\{[Fe(OH)_3]_m \cdot nFe^{3+} 3(n-x)Cl^-\}3xCl^-$	260	1.98	0.34	500	180
$\{[Fe(OH)_3]_m \cdot n(OH)^- \cdot (n-x)Na^+\}xNa^+$	100	1.06	0.18	160	60

Processing bentonite sols hydroxide leads to the distance between planes of moving apart, as evidenced by the value of d_{001}, which for a natural montmorillonite is 0.9 nm, and the modified clay sol hydroxides of iron are significant 1.98 and 1.06 nm, respectively. Here, it should be noted the role of the sign of the charge of the colloidal particles has the result of modification. It is shown that the most effective influence colloidal particles with positive charges, where the specific surface area varies from 60 to 260 m^2/g and a total pore volume from 0.08 to 0.34 cm^3/g. A particle with negative charges have almost no influence on the formation of the columnar structure of montmorillonite. Pillar structural bentonite were used for the preparation support catalysts and in chemical processes [1-3, 8-11]. In our opinion, this is due to the nature of the exchangeable cations of the mineral, which give way to a more massive cation sol in their swelling. When using such sols as $\{[Fe(OH)_3]_m \cdot nFe^{3+} 3(n-x)Cl^-\}3xCl^-$ colloidal particles with a positive charge displace exchangeable cations $K^{+,}$ Na^+, Mg^{2+}, Ca^{2+}, and others located in the interplanar space. Reduce the content of these cations in the pillar-structural samples clearly indicates the occurrence of ion exchange with positively charged colloidal micelles. The original sample of bentonite clay accordingly consist the sodium, magnesium and iron components about 2.0, 2.0-2.4 and 4.0-4.6%weight, and the modified samples by iron sols with positively charged colloidal particles they are reduced to 0.6; 0.8 and 1.4% weight. (calculated as oxide) respectively.

When the sample of bentonite modified by iron hydroxide sol is heated to 500 °C is a weight loss of about 17% and a further increase temperature does not lead to a significant loss of weight. The observed exothermic endothermic effect at 700-750 °C, probably due to the change in the crystal lattice of montmorillonite.

Dependence on a volume pore via from the effective diameter of modifying bentonite is represented in figure 4. At the change effective diemeter from 5.0 nm up to 30nm the volume pore is changed from $4.8 \cdot 10^{-2}$ cm^3/g to $10.0 \cdot 10^{-2}$ cm^3/g.

The maximum on the pore volume distribution curve corresponds to d = $50A^0$. The total pore volume of the adsorbents was determined as the product of the amount of a substance adsorbed upon saturation of the adsorbent with

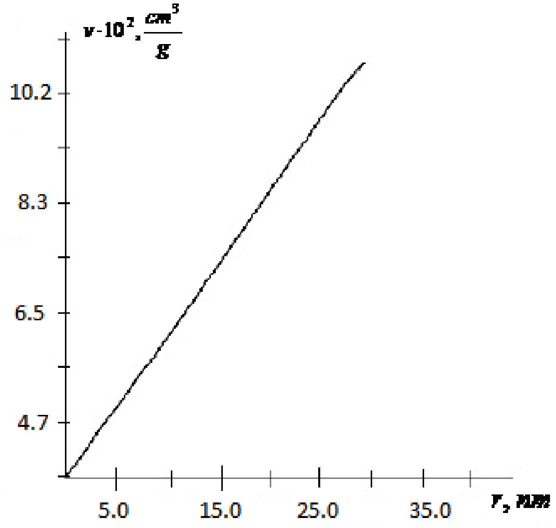


Figure 4 – Dependence on a volume pore via from the effective diameter of modifying bentonite

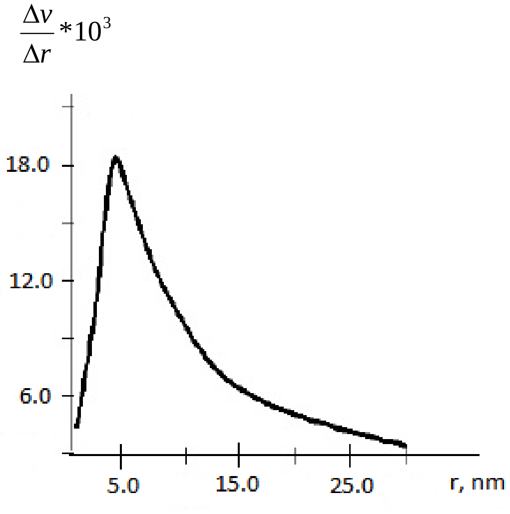


Figure 5 – Pore volume distribution curve along their radii

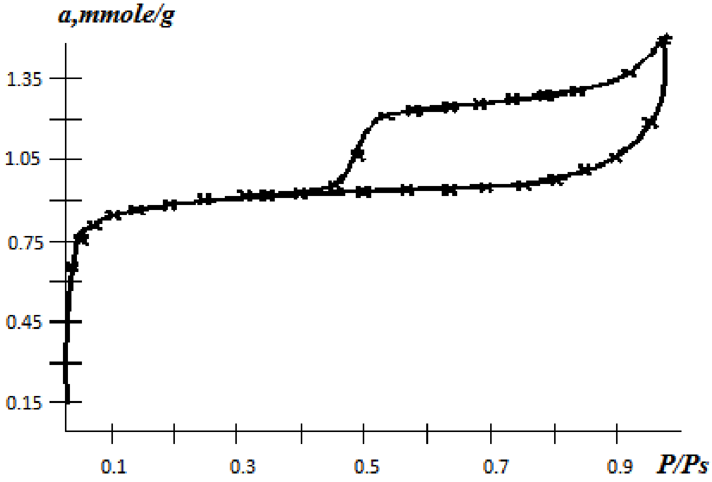


Figure 6 – Adsorption-desorption isotherms obtained by the BET method modified bentonite by sols hydroxides of iron (pre-drying for 4 hours at 500 °C. The Ssp. = 180 m^2/g)

liquid vapors, with P/Ps = 1 per mole volume. Preservation of the porous structure of the modified bentonite indirectly shows the adsorption-desorption hysteresis of nitrogen obtained using samples subjected to calcination at 500 °C with a surface area of 180 m^2/g (figure 6). By the nature of the hysteresis can be concluded that the pores are cylindrical or tapered.

Conclusion. Thus, on the basis of experimental data it can be concluded that the effect of massive ions sols of metal hydroxides, also contributes to the formation of columnar-porous structural systems developed specific surface. Thermal stability is due to the introduction of colloidal particles in the sol interplanar space layered clay. These results extend the range of data in the synthesis of pillar-structure of adsorbents used in refining and catalytic chemistry for catalysts.

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Резюме

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БЕНТОНИТ САЗЫНАН ТЕРМИЯЛЫҚ ТҰРАҚТЫ АДСОРБЕНТ АЛУ

Бентонит сазын темір золымен өңдеу арқылы, термиялық тұрақты бейорганикалық адсорбент алу жолы қарастырылған. Қышқылдармен өңделген бентонит сазының меншікті аудан беті артқанымен, термиялық тұрақтылық көрсетпейді және 160^0С температурадан жоғары, кеуектілігін жоғалтады. Ыстыққа төзімділік пен кеуектілігін сақтау үшін, бентонит сазы темір гидрооксиді золымен өңделді. Алынған золь бөлшектерінің заряд таңбасының маңызы зор. Коллоидты бөлшектердің ірі бөлшектері бентонит құрамындағы монтмориллонит минералының араларына кіріп, кеуекті құрылым түзеді. Зольмен өңделген бентонит 500^0С температурасына қыздырғанда өз кеуектілігін сақтайды.

Түйін сөздер: адсорбент, бентонит сазы, кеуекті құрылым, меншікті аудан беті, золь, термотұрақтылық.

Резюме

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ПРИГОТОВЛЕНИЕ ТЕРМОСТАБИЛЬНОГО АДСОРБЕНТА ИЗ БЕНТОНИТА

Рассмотрено приготовление термостабильного адсорбента модифицированием бентонитовых глин. Бентонитовые глины, обработанные соляной кислотой, хотя и приобретают достаточную пористость, однако не проявляют термостабильности и выше 160^0С теряют пористость. Для придания термостабильности бентонитовая глина обрабатывается золями гидрооксида железа, где знак заряда коллоидной частицы имеет важное значение. Коллоидные частицы, располагаясь между слоями монтмориллонитового минерала, придают столбчато-структурную форму бентонитовой глине. Полученные образцы не теряют пористости при температуре 500^0С.

Ключевые слова: адсорбент, бентонит, столбчато-структурное строение, удельная поверхность, золь, термостабильность.