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(Research Article)

New sorbents based on carbonized bentonite - Askan Clay

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Abstract

The paper presents the results of obtaining medical sorbents, studying their physical and chemical characteristics and conducting clinical trials. Carbonized modifications of “Askan clay” (montmorillonite clay from the village of Askana) were obtained by heat treatment of a mixture of “Askan clay” and carbohydrates (glucose, molasses). Carbonization is accompanied by a sharp increase in the overall porosity of “Askan clay”. Samples of carbonized “Askan clay” are characterized by high exchange and sorption capacity. Sorption of cations and anions for carbonized samples occurs in the following sequence: Ba2+ > K+ > Mn2+ > Ca2+ > Mg2+; PO43− > SO42− > Cl−. The possibility of using the carbonized form of "Askan clay" as a sorbent used in medicine has been investigated.

Keywords: Montmorillonite Clay; Carbonization Sorbent; Organophilization; Medical application

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1. Introduction

To improve the physical and chemical properties and operational characteristics of petroleum products, the adsorption purification method is mainly used. This method ensures the removal of unsaturated and aromatic hydrocarbons and their derivatives, resinous and asphaltene substances, sulfur-, nitrogen- and oxygen-containing compounds. As a result, petroleum products of a given group composition are obtained.

Both natural products (bleaching clays, bauxites, opoka, bentonites, activated clays, zeolites) and synthetic ones (silica gels, aluminosilicate gels, synthetic zeolites, active carbons) are used as adsorbents. Of the natural materials, the most effective adsorbent is bentonite - montmorillonite clay. The economic benefit obtained by using cheap natural raw materials is accompanied by the problem of recycling production waste (clay with adsorbed organic matter). Since the regeneration of clay sorbents by various solvents is economically inexpedient, and direct disposal of production waste leads to environmental pollution. Based on this, the possibility of obtaining new materials, from waste from the process of adsorption purification of petroleum products has been studied [1-3].

The studies were conducted on a model system of a mixture of montmorillonite clay from the Askana village deposit (Georgia) and the solar fraction of oil from the Norio village deposit (Georgia). After thermal treatment of Askan clay with different contents (5 ÷ 30%) of solar fraction, at different temperatures (100 ÷ 300 °C), the surface of the clay is covered with a product of thermal destruction of petroleum products - hydrogen-depleted resinous, partially coke substances. Optimal conditions for carbonization of organomineral composition were determined. Carbon-containing materials obtained under these conditions were tested as rubber fillers and drilling fluids [4-6].

Conditions for carbonization of organic matter adsorbed on montmorillonite “Askan clay” have been developed. New carbon-mineral materials have been obtained by changing the organic component in the clay-organic system. The obtained materials have high sorption capacity and polymerophilicity [7].

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This work demonstrates the possibility of obtaining high-quality sorbents for medical use using the carbonization method of carbohydrates adsorbed on “Askan clay”.

1.1. Experimental part

Carbonized samples were obtained by heat treatment of “Askan clay” with adsorbed calculated amount of carbohydrates – glucose and molasses. Molasses (waste of sugar production) contains 50% sucrose, 4% raffinose and various nitrogen-free and nitrogen-containing impurities.

A mixture of different proportions of “Askan clay” and carbohydrates, after thorough mixing, was placed in porcelain crucibles and subjected to heat treatment until a constant weight was achieved. The carbonization effect appears from a temperature of 250 °C. The duration of the process depends on the temperature. In particular, at a temperature of 250 °C it is 10-12 hours, and at 500 °C – 5 hours [8, 9].

In table 1 and table 2 shows the results of the study of the physical-chemical properties of carbohydrate-containing Askan clay, carbonized at 250 °C.

Table 1 Colloidal-chemical properties of carbohydrate-containing Askan clay, carbonized at 250 °C.

Sample	**pH 1% suspension, at 20^0C**	**Electrokinetic potential, mV**	**Total exchange capacity, g-eq/100 g of adsorbent**	**Composition**	
				C, %	H, %
Glucose modifier (40%)	5.75	106.0	82.62		
Glucose modifier (60%)	5.75	82.0	73.45		
Molasses modifier (40%)	6.00	98.0	78.00	9.86	0.64
Ascanian clay (control)	9.50	127.0	93.72	-	0.25

Table 2 Adsorption of electrolytes on carbon-containing Ascan clay carbonized at 250°C.

Sample	**Electrolyte adsorption. %**							
	Anions			**Cations**				
	Cl^-	**SO_4^{2-}**	**PO_4^{3-}**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**Mn^{2+}**	**Ba^{2+}**
Glucose modifier (40%)	2.76	3.15	5.21	-	-	-	-	-
Glucose modifier (60%)	5.47	9.55	11.52	39.00	8.50	5.00	34.45	43.00
Molasses modifier (40%)	3.74	6.47	7.93	38.00	15.00	4.50	28.00	38.00
Ascanian clay (control)	2.10	3.00	4.70	-	-	-	-	-

The exchange capacity of the initial and carbonized samples was studied using the classical Gedroits method [10]. The sorption capacity of the electrolytes was measured using analytical and potentiometric methods. The electrokinetic potential of the aqueous suspension (1%) of the studied samples was calculated using the Helmholtz-Smoluchowski formula by the cataphoretic method using the Rabinovich-Fodiman device. The degree of carbonization was characterized by quantitative determination of hydrogen and carbon on the surface of carbonized “Askan clay”. The studies were carried out on a CNH analyzer of Czech manufacture.

In carbonized samples, the mineral surface is covered with products of organic compound destruction. The average elemental formula of the C:H ratio is C:H 1.22 – C:H 1.68 and corresponds to a carbon content of 11.82-8.82%, which is within the limits of the coke composition formula. During the carbonization process, the highly hydrophobic properties of bentonite clay change to hydrophobic. When heated, the ion-exchange capacity of carbonized samples decreases, which is associated with the partial disintegration of active centers. This is explained by non-stoichiometric, isomorphic substitution in the crystal lattice of the mineral, as well as the blocking of active centers, presumably hydroxyl groups (van der Waals forces) on the carbonized surface of the mineral.

All this is confirmed by X-ray and electronographic studies. No changes in the intracrystalline structure are observed. The distance between the layers of the mineral crystal lattice remains unchanged. Thus, the process of carbonization on the clay surface is physical in nature. IR spectral analysis data showed that the ability to adsorb organic compounds on the clay surface is determined by the nature of the active centers.

According to IR spectral analysis, carbonization (heat treatment of clay mineral with organics) leads to the appearance of new absorption bands corresponding to organic radicals. Judging by all appearances, no processes of chemisorption of organic compounds occur on the surface of the mineral. The IR spectrum lacks absorption bands characteristic of Si-C and Si-O-C chemical bonds. It should be noted here that organic compounds are closely bound to the mineral surface, which is confirmed by the nature of their extraction with organic solvents (hexane, benzole, benzol-alcohole).

The IR spectrum lacks absorption bands characteristic of Si-C and Si-O-C chemical bonds. It should be noted here that organic compounds are closely bound to the mineral surface, which is confirmed by the nature of their extraction with organic solvents (hexane, benzole, benzol-alcohole). Extraction of organic matter from the surface of the mineral does not occur, since the distance between the layers of the crystal lattice of the mineral does not change, therefore, the molecules of thermal destruction products cannot reach them. Thus, this process is of a physical nature, since it was not possible to detect absorption bands corresponding to chemical bonds between the clay surface and organic radicals. In the spectrum of carbonized “Askan clay”, new absorption bands corresponding to organic radicals were identified [11].

The porosity of natural, enriched and carbonized samples of “Askan clay” was studied by the mercury porosimetric method on a PA-ZM-1 porometer, which consists of low-pressure (0.101 MPa) and high-pressure (253 MPa) porometers, which makes it possible to study equivalent pore radii in the range from 3.1 to 20,000 nm (Table 3 and Table 4) [12].

Table 3 Distribution of pore volume (V, cm3/g) of “Askan clay” samples by intervals of equivalent radii.

Equivalent radius range, nm	**Natural**	**Enriched**	**Carbonization at glucose content t= 250⁰C**
20000-500	0.003	0.004	0.134
500-80	0.065	0.052	0.071
80-20	0.027	0.041	0.037
20-10	0.018	0.019	0.042
10-301	0.056	0.046	0.055
V, см^3/г	0.169	0.162	0.339

Table 4 Distribution of specific pore surfaces (S, m2/g) of “Askan clay” samples by intervals of equivalent radii.

Equivalent radius range, nm	**Natural**	**Enriched**	**Carbonization at glucose content t= 250⁰C**
20000-1230	0.00	0.00	0.07
1230-123	0.49	0.31	0.51
123-12,3	3.77	4.14	6.03
12,3-4,9	9.19	8.98	8.98
4,9-3,1	10.00	8.00	12.50
S м^2/г	23.44	21.70	28.03

It is known that the thermogram of the clay mineral montmorillonite is characterized by three endothermic effects at 70-300°C (loss of adsorbed water and water of hydration of exchange cations), 600-700°C (dehydroxylation of the octahedral layer) and 800-900°C (destruction of the crystal lattice of the mineral).

On thermograms of organophilic samples of “Askan clay” show a shift of the first endothermic effect (70-210°C) towards lower temperatures (40-190°C), which indicates a weakening of the bond between water molecules and the surface of the mineral and its possible displacement by molecules of organic substances, variously associated with “Askan clay”. The thermo grams of organophilic samples of “Askan clay” do not show the second endoeffect, which is obviously due to the overlap of this area by an intense exoeffect (temperature range 220-700°C). The manifestation of the exoeffect on thermo grams of organophilic samples of “Askan clay” can be explained by oxidation and subsequent burnout of the organic component.

The surface of carbonized clay is so heavily covered with products of thermal decomposition of organic matter that its active centers are inaccessible to molecules of water and other solvents (hexane, benzene), since they are blocked in the mouths of micropores. The clay surface acquires a rigid structure against adsorption, which is manifested by the limited number of hydrophilic centers. This opinion is confirmed by X-ray and electron-graphic studies. In X-ray images and electrograms do not record any changes in the internal crystal structure. According to the IR spectra, it is evident that the original structure differs from the sample carbonized with modified organic “Askan clay”. In particular, in the spectrum of carbonized “Askan clay” modified with glucose, new absorption bands appear with lower intensity in the new bands at 475 and 427 cm^{-1}. The absorption bands at 580 and 630 cm^{-1} are practically not visible, and the absorption bands related to intertetrahedral layers at 845 cm^{-1} have completely disappeared. The intensity of the bands in the region at 800-920 cm^{-1} and 1640 cm^{-1}, related to deformation vibrations of water molecules, is reduced.

Carbonization of the mineral by modified organic matter is accompanied by the appearance of new absorption bands corresponding to organic radicals. It seems that there is no place for the processes of supersorption of organic compounds on the surface of the mineral. The IR spectrum does not contain absorption bands characteristic of the chemical bonds Si-C and Si-O-C. It should be noted here that organic compounds are closely connected with the surface of the mineral, which is confirmed by the result of extraction with organic solvents (hexane, benzole, benzol-alcohole). Extraction of organic matter from the surface of the mineral does not occur. The distance between the layers of the crystal lattice of the clay mineral does not change, since the molecules of the thermal destruction products cannot reach them.

Thus, this process is of a physical nature, since it was not possible to detect absorption bands corresponding to chemical bonds between the clay surface and organic radicals. In the spectrum of carbonized “Ascan clay”, new absorption bands corresponding to organic radicals were identified. The spectra can be used to judge the change in the structure of carbonized clay in relation to the original structure of the mineral. IR spectral analysis established that the ability to adsorb organic compounds on the clay surface is determined by the nature of the active centers.

1.2. Discussion of the obtained results

Analysis of the colloidal-chemical properties of carbonized samples of “Askan clay” modified with carbohydrates (Table 1) shows that during the carbonization process the exchange capacity of the carbonized samples decreases somewhat (compared to the original clay), however, the carbonized samples retain a fairly high ion-exchange capacity. As expected, the electrokinetic potential decreased from 127 mV to 106 mV, which can apparently be explained by the compression of the diffuse layer at the phase boundary. Data on the sorption capacity of the studied samples show that carbonized samples are characterized by high sorption capacity for electrolytes. The adsorption value of anions on the surface of carbonized samples decreases in the following order: PO_4^{3-} >SO_4^{2-} >Cl^- , and the adsorption of cations – in the order: Ba^{2+} >K^+ > Mn^{2+} > Ca2+ > Mg^{2+}. The high adsorption value of such a heavy metal as barium deserves special attention.

The results of mercury-porosimetric studies showed that the process of carbonization of “Askan clay” modified with glucose is accompanied by significant changes in the porous structure of the clay mineral surface (Tables 2 and 3). Carbonized “Askan clay” is characterized by a more developed pore system than the original sample. The total porosity of natural “Askan clay” is 0.169 cm^3/g, enriched – 0.162 cm^3/g, carbonized – 0.339 cm^3/g.

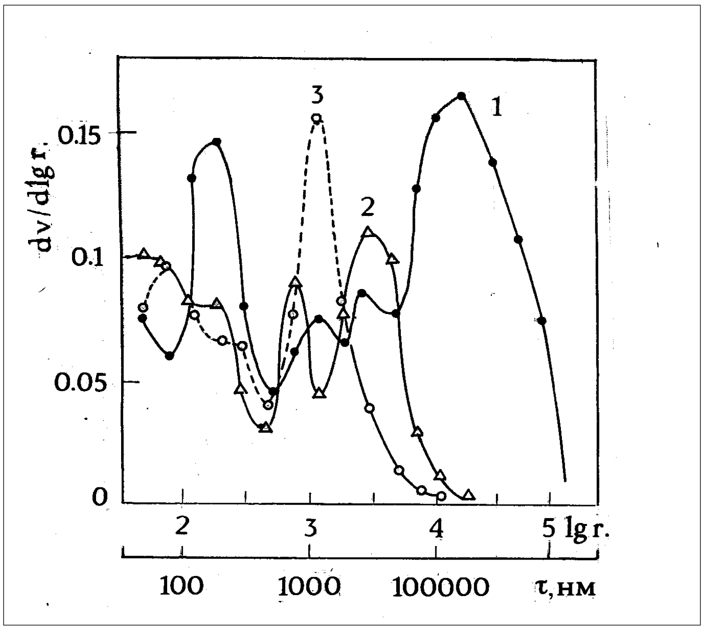

Figure 1 Differential curves of pore volume distribution by effective radii of “Askan clay” samples

1.3. 1 – carbonated, 2 – natural, 3 – enriche

Differential curves of pore volume distribution by effective radii showed that the carbonized sample is characterized by the widest range in the area of macropores – from 1000 to 10000 nm, with a maximum of 1500 nm and mesopores – from 4.0 to 30 nm, with a maximum of 16 nm (Figure 1).

In order to test carbonized “Askan clay” as an adsorbent in clinical conditions, samples in the form of small granules were prepared. Carbonization was carried out at 400-500 ° C. High temperature ensures mechanical strength and resistance to swelling of the granules of carbonized “Askan clay” [13-16].

Samples of carbonized “Ascan clay” were tested in the nephrology department of the A. Tsulukidze Institute of Urology. The patient's ascitic fluid was examined. Table 5 shows data on the content of residual nitrogen, creatinine, sodium and potassium in ascitic fluid before and after passing the fluid through carbonated “Ascan clay” [17].

Table 5 Contents of residual nitrogen, creatinine, sodium and potassium in ascitic fluid before and after passing the fluid through carbonized “Askan clay”.

Adsorbed substance	Initial concentration mmol/l	Final concentration mmol/l
Residual nitrogen	120.00	114.00
Creatinine	1.20	0.60
Na+	142.30	142.00
K^+	5.50	2.50

Clinical trials have shown that creatinine and K ions are well sorbet on the surface of carbonized “Askan clay”, the content of which decreases by half after passing liquid through this sorbent.

2. Conclusion

For the targeted regulation of the physical and chemical properties of “Askan clay”, a method of hydrophobization of the surfaces of clay particles by their thermal carbonization has been developed. During carbonization, the surface of “Askan clay” particles is covered with a product of thermal destruction of hydrocarbons. The structure of this product is soot-like and contains 9.8-4.4% carbon.

Carbonized samples retain a fairly high ion exchange and sorption (in relation to electrolytes) ability.

It has been established that during carbonization of enriched “Askan clay”, the volume of secondary pores increases significantly, with an increase in transitional pores, especially macropores.

The results of clinical trials indicate the feasibility of obtaining new adsorbents from carbonized “Askan clay” for their possible use in medical practice.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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