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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Study of Fractal Characteristics and Rheological Properties of Karbodon Combined Sorbent and Its Constituents

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Abstract—The structure-sorption properties of the bottom sediments and their compositions with the KAU carbon modified with K^+, Mg^{2+}, and Zn^{2+} cations, which were synthesized for the first time, were studied. The adsorption data were used to calculate the surface fractal dimension for composites under study and their constituents. The rheological curves of the composites synthesized in a wide range of the shear rates were obtained. The effect of their composition on the structure-mechanical properties (viscosity) of the sorbents was determined.

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The main goal of the study was the development of new application sorbents, cosmetic agents, and enterosorbents on the basis of mineral and biological complexes of sea bottom sediments and of a KAU carbon prepared from fruit kernel and modified with K^+, Mg^{2+}, and Zn^{2+} ions. In this study the physicochemical (rheological) properties of the initial components and combined preparations (Karbodon) obtained by them were analyzed by the modern methods.

The development of new competitive and efficient compositions, in which cheap and readily available natural raw materials such as bottom sediments, mud, and sludge are used as the basic component, is urgent and promising [1–4].

Previously, the mineral and chemical composition and the structure-sorption and bactericidal properties of the mineral bottom sediments taken from the Black sea were studied and the methods of sorption extraction of heavy metal ions and organic dyes by them were analyzed in comparison with activated carbons and clays. A conclusion was made that the bottom sediments in combination with KAU oxidized carbons specially modified with the ions of vital microelements can be used as medical preparations and bactericidal agents for purification of human body from organic pollutions and toxic metals and for the water purification [9].

Indeed, the first search tests [9] showed that the development of such composite materials is appropriate and necessary. Note, the synthesis of the above composites involves the same methods, which were used for Ul'trasorb [10] and Karboksikam [11], whose properties are known.

Preparations selectively binding radionuclides, heavy metals, and organic pollutants [10, 11] must contain modifiers to regulate overall mineral balance [12]. Therefore, for possible correction of the microelement composition of the salts in the human body, we used in this study KAU oxidized carbon containing certain amounts of the exchangeable cations, K^+, Mg^{2+}, and Zn^{2+} [13]. Their presence and the dosed introduction, using the ion-exchange method, into the body (i.e., under the conditions of the established cation-anion balance) is necessary to reach the best therapeutic effect in the sorption therapy of serious diseases, which are hardly treatable or cannot be treated at all by the traditional methods. The preparation of the ionic forms of KAU carbons, the mechanisms of therapeutic effect of the bottom sediments, and the factors responsible for their therapeutic and antimicrobial properties have been described in detail in [9].

Table 1. Characterization of the obtained samples

Sample (component ratio)	Designation	Composition
Peloid	P	Deep-sea bottom sediment
Modified carbon	KAU_m	K, Mg, Zn forms
Окисленный уголь	KAU_0	H form
KAU_m : P :		
1.5 : 1	KS-1	K, Mg, Zn, Cu form KAU_0 + P
2 : 1	KS-2	The same
1 : 1	KS-5	"
1 : 2	KS-6	"
1 : 500	KS-7	"
1 : 100	KS-8	"
KAU_0 : P :		
1 : 500	KS-9	KAU oxidized carbon
1 : 100	KS-13	the same
KAU_m : P:		
5% of carbon	KS-11	Modified, KAU_m+P
10% of carbon	KS-12	the same
30% of carbon	KS-14	"

EXPERIMENTAL

KAU carbon was oxidized in liquid phase with 25% nitric acid in boiling water for 4–6 h [13], till a necessary static exchange capacitance (SEC) in a 0.1 N NaOH was attained (1.7 mg-equiv g^{-1} in the given case). SEC was determined by chemical titration of the surface functional groups (SFGs) with bases of different strength [14] (KAUo carbon).

The modifying cations were incorporated, using the cation exchange method [13], into the surface of oxidized carbon (OC) in amounts providing a partial or complete neutralization (compensation) of its protogenic groups. The therapeutic effect may be obtained, if physiological cations are introduced in strictly fixed proportions [15]. The technology developed allows use of OC containing (wt %) 1.3–5.0 K^+, 0.2–1.0 Mg^{2+}, and 0.2–1.5 Zn^{2+}, which are bound to the surface functional groups (SFGs) by the ion-exchange mechanism.

The Karbodon composites KS-1–KS-13 (Table 1) were prepared from the mineral bottom sediment and carbon, taken at a mass ratio from 1:1 to 500:1, respectively. The constituents were carefully agitated at the chosen ratio, ground in a disperser, and passed through a 0.1-mm sieve.

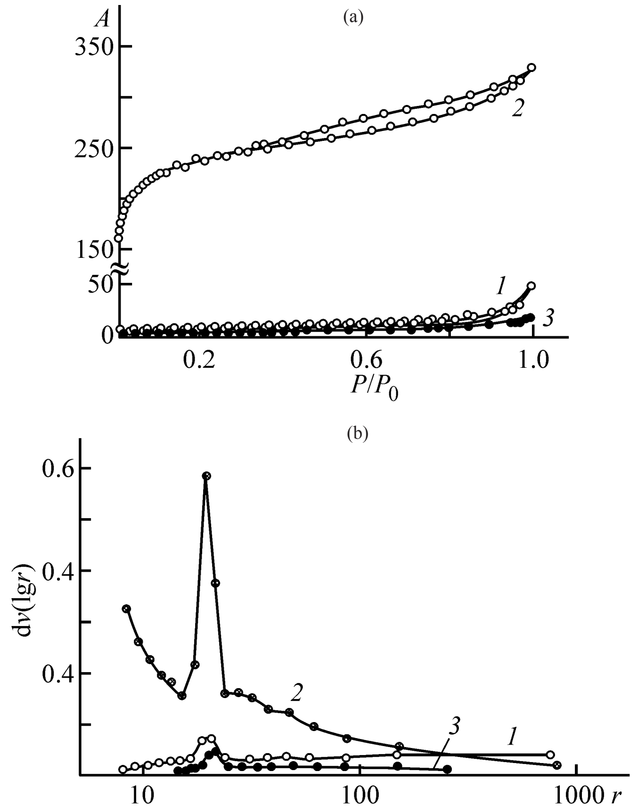

Fig. 1. (a) Sorption isotherms A (cm^3 g^{-1}) of nitrogen and (b) distribution of pores dV/d log r with respect to radii r (Å) on various sorbents. P/P_0 Relative pressure; the same for Fig. 2. (*1*) Peloid, (*2*) KAU_0, K, Mg, and Zn form, and (*3*) KS-9.

Since the pore structure characteristics allow predicting the performance of a sorbent under real conditions of a particular sorption technique, we examined, using the traditional methods [16], the structure-sorption characteristics of starting components (KAU, BS) and Karbodon composite material made of them.

Using a NOVA 2200E high-speed gas sorption analyzer, the isotherms of low-temperature (77K) nitrogen sorption-desorption by sorbents under examination were measured; the specific surface area S_{sp} was calculated by the BET method; the curves of distribution of the micropore volume V with respect to the pore radii r were obtained; the micropore volume V_{mi}, the micropore surface area S_{mi} and pore radius were determined by various calculation methods with the correlation factor of 0.999 (Table 2).

Table 2 and Figs. 1a, 1b show results obtained in studying the structure-sorption properties of the starting peloid, KAU_0, modified carbon, and KS-9 composite.

The data presented show that a peloid sample chosen for examination is a micropore sorbent possessing small

Table 2. Structure-sorption properties of peloid samples, KAU modified carbon, and composites of varied compositions based on them

Sample	Nitrogen specific sorption, cm^3 g^{-1}	S$_{sp}$, m^2 g^{-1}	V_{tot}, cm^3 g^{-1}	S_{mi}, m^2 g^{-1}	V_{mi}, cm^3 g^{-1}	r_{por}, Å	Fractal dimension, D
Peloid	49	19	0.077	0.0	0.0	20; 78; 1; 50	2.11
KAU$_0$ H form	280	866	0.438	605.7	0.242	10; 23	2.78
KAU$_0$, Zn form	240	739	0.378	547	0.220	10; 20	2.78
KAU$_0$, Mg form	260	798	0.410	527	0.214	10; 25	2.72
KAU$_0$, K, Mg, Zn form	325	881	0.509	519	0.212	11; 20	2.62
Composites							
KCS-1	255	648	0.390	351	0.144	12; 40	2.72
KS-5	165	455	0.254	316	0.128	11; 50	–
KS-2	265	668	0.397	345	0.141	12; 50	–
KS-6	200	573	0.309	430	0.175	11; 25	2.74
KS-8	20	22	0.005	10.9	0.03	28; 75	2.55
KS-9	18	14	0.027	1.54	0.001	5; 10; 20; TS	2.26
KS-13	18	26	0.287	5.88	0.003	22; 25	2.53

pore radius (R ~ 20 Å) and small surface area (S_{sp} ~19 m^2 g^{-1}). The micropore volume for this sample is V_{mi}= 0.077 cm^3 g^{-1}.

Note, in the presence of modified carbon, the structural characteristics of the prepared composite sorbents (CSs) were improved in comparison with peloid (P). For example, the micropore volume was increased from 0.0 to 0.175 cm^3 g^{-1}and the total pore surface area in nitrogen absorption, from 19 to 668 m^2 g^{-1}. The same is true for pore radii: alongside with samples with R ~10 Å, sorbents with r ~ 40 –75 Å were obtained. The sorption capacity of CSs by nitrogen, a_{N2}, also increased depending on carbon content (Table 2).

As seen from Fig. 1, the natural clay mineral, deep-sea peloid, has low specific adsorption at the small relative pressures, P/P_0 = 0–0.4, and its sorption isotherm exhibits weak hysteresis owing to capillary condensation. The sorption isotherms of the samples of KAU$_0$ carbon and its ionic forms rise steeper owing to large surface area. For these samples the values of the nitrogen specific sorption were also larger: ~50 cm^3 g^{-1} for peloid and 250–340 cm^3 g^{-1}for carbon-containing sorbent.

The structure-sorption characteristics of the prepared KS composites were better than those of the starting peloid (Fig. 1). For these samples, steeper rise of the sorption isotherms at the relative pressures P/P_0 = 0–0.4 and more readily developed hysteresis were observed. The nitrogen specific adsorption was reasonably high and reached a value of 170–270 cm^3 g^{-1}, depending on the carbon amount.

On the contrary, the samples with large peloid amount possess lesser specific sorption for nitrogen (~20 cm^3 g^{-1} for KS8, KS9, and KS13). Their specific surface area S_{sp} is high as 455–668 m^2 g^{-1} (Table 2). The micropore volume is also reasonably high (0.13–0.17 cm^3 g^{-1}) and the micropore surface area is S_{mi} = 316–430 m^2 g^{-1}.

On the one hand, the physicochemical and technological properties of clay minerals and other sorbents, for example, carbon, depend on crystalline structure. On the other hand, they depend on the degree of dispersion and presence of impurities. However, the surface heterogeneity of particles and other characteristics of these fractal objects have been studied little.

The fractal geometry approach [17, 18] to determination of surface characteristics describes topography of real surfaces in terms of surface heterogeneity, known as fractal dimension D. Ideal, relatively smooth, surfaces can be modeled in terms of the simple geometric concepts, such as for example, $6L^2$ for cubes and $4\pi R^2$ for spheres. For such surfaces $D = 2$, because surface area is proportional to X^2, where X is a characteristic parameter obtained for a specific sorbent by measurement (for example, $X = L$ for squares and $X = R$ for circles).

Real surfaces are rough at all. Depending on scale under consideration, various groups of atoms, defects, points, dislocations, and especially pores are observed. Most of real surfaces are a set of surface iirregularities, which seem similar in various scales. These surfaces are known as fractals, because their magnitude is proportional to X^D, where D is the fractal dimension accepting the values from $D = 2$ (for smooth surfaces) to $D = 3$ (for very rough surfaces occupying the whole accessible volume). The fractal dimension D can serve as a measure of the roughness of real surfaces.

The surface fractal properties of clay minerals and sea bottom sediments have been considered elsewhere [19 –23]. Clay particles may possess surfaces of different degree of irregularities and roughness. Therefore, the use of only one measured value, specific surface area, for their description is made difficult. The fractal approach to the particle surface allows characterization of the irregularity (disorder) by only one parameter, surface fractal dimension. In [9], the fractal geometry approach and the mechanisms of the physicochemical processes, which occur in aqueous smectite dispersions, were used to describe their physicochemical and rheological properties. This description is more complete than that, in which only rheological data are used. The fractal structure, whose dimension depends on the specificity of interaction between the particles of natural systems, was confirmed for the aggregates obtained in the course of formation of sea bottom sediments at the stage of coagulation in [21].

Clay minerals and sea bottom sediments are used in medicinal practice [21, 23]. At the same time, a little attention has been given in the literature to the properties of their surface in terms of the fractal geometry. Therefore, in this study we attempted for the first time to establish the values of the surface fractal dimension D for a deep-sea peloid, KAU carbon, its ionic forms, and composite sorbents based on them (KS, Table 2).

The D values were calculated from the sorption isotherms of nitrogen on samples under examination. In the calculation we used the best known FHH Frenkel–Hasley –Hill version of the polymolecular adsorption theory [16] and equation [19].

$$a/a_m \sim [RT\log (P/P_0)]^S,$$

where P is relative pressure, P_0 is saturation pressure; a and a_m is the adsorption at given pressure and upon filling a monolayer, respectively; S is the coefficient relating to the fractal dimension D [19].

At small pressure, when the interaction of adsorbed molecules with the surface is mainly determined by the Van der Waals forces,

$$S = D\,(3–1).$$

At high degree of filling, effects of capillary condensation become more significant, which leads to the validity of relation

$$S = D\ - 3.$$

To derive the necessary formula, we calculated the coefficient

$$\delta = 3(1 + S) - 2.$$

The formula (1) is used at $\delta > 0$, when capillary condensation is negligible, and the formula (2), at $\delta < 0$.

For estimation of D, the range of pressures corresponding to filling of a monomolecular layer is optimal [17]. In the study, δ at these relative pressures was always negative. Therefore, for estimating D we always used formula (3).

The log V_{ads} vs. log [log (P/P_0)] curves constructed from data on the sorption isotherm of nitrogen on KS-9 sample are shown in Fig. 2. Similar dependences were obtained for other composite sorbents and their constituents. The dependence for peloid was linear at the relative pressures P/P_0 = 0.02 –0.65. On mixing peloid with KAU_0 carbon and its salt forms, this pressure range changed to P/P_0 = 0.1 –0.5.0 and the surface fractal dimension D decreased from 2.78 to 2.26.

It was found that all samples exhibit surface fractal behavior in the different regions of relative pressure. Note, their fractal surface dimensions differ only slightly from those of natural clay minerals, glauconite and hydromica [24, 25].

In addition to fractal coefficients, the structure-mechanical properties of peloid composites were analyzed by rheological methods. We studied three specially synthesized samples (КС-11, КС-12, and КС-14) containing 5, 10, and 30% carbon, respectively.

The structure formation in free dispersion systems is a result of loss of their aggregation stability. As a rule, the

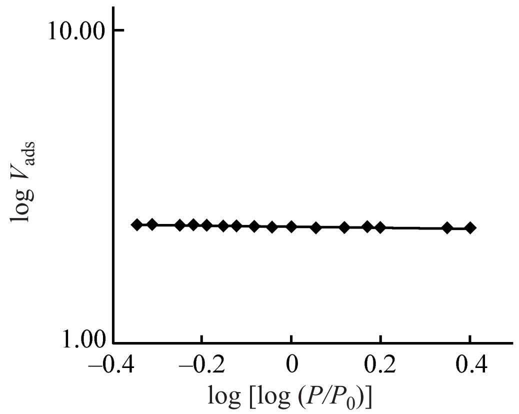

Fig. 2. log V_{ads} (cm^3 g^{-1}) vs. log [log (P/P_0)] dependence for composite KS-9.

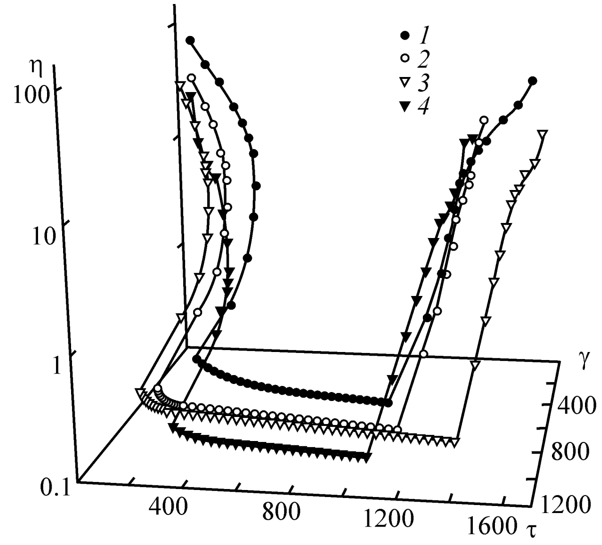

Fig. 3. Overall rheological curves for the peloid–carbon systems with varied content of carbon. (η) Viscosity (Pa s^{-1}), (γ) shear rate (s^{-1}), and (τ) time (s). Carbon content (wt %): (*1*) 0, (*2*) 5, (*3*) 10, and (*4*) 30.

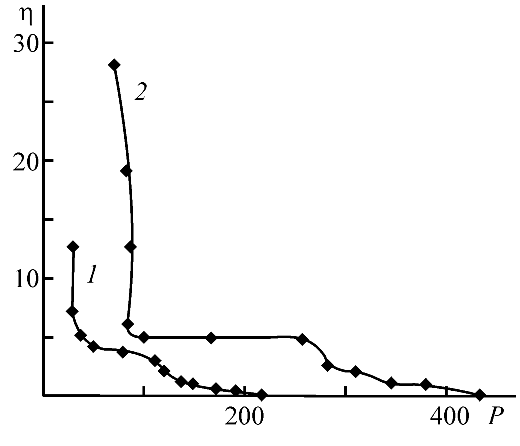

Fig. 4. Viscosity η (Pa s) vs. the shear stress *P* (Pa) for KS-14. Run: (*1*) reverse, and (*2*) direct.

formation and character of the structures are determined by the mechanical properties, of which viscosity, elasticity, plasticity, and strength are the most important. Because the properties of the systems directly relate to their structure, they are often referred to as structure-mechanical properties. Commonly, the above properties are studied by the shear rheology in the presence of the applied stress.

The rheological properties of dispersion systems have been described in detail [26–28]. Knowledge of the general regularities of the formation of systems possessing certain structure-mechanical properties helps to find methods of control of these properties for particular materials.

In this study, the effect exerted by composition of the composite materials on their structure-mechanical properties (viscosity) was studied.

The rheological properties of the synthesized samples and initial bottom sediment (Fig. 3) were analyzed on a Medingen GmbH Reotest-2 rotation viscometer (Germany) in cylindrical geometry.

The structural (effective) viscosity η was calculated from the ratio of the shear stress *P* (Pa) to the shear rate $\dot{\gamma}^2$ (s^{-1}):$\eta = P/\dot{\gamma}^2$. To study the rheological properties of chosen materials, we constructed graphs of viscosity η and deformation rate D_r on the shear stress *P* (Pa) and time τ (Fig. 3).

The rheological curves in a wide range of shear rates were described by the Hershel–Bukley equation $P = P_f + k\dot{\gamma}^n$, where *P* and P_f are shear stress and yield stress; *n* is the constant; *k,* the consistency index ($n = 1$ for Newtonian fluids, $n < 1$, for pseudoelastic fluids, and $n > 1$, for dilatant systems).

The yield stress at $\dot{\gamma} = 0$ was determined by the procedure described in [24]. The coefficients of the Hershel-Bukley equation for the systems studied are given in Table 3; the moisture amount and structure-

Table 3. Coefficients of the Hershel-Bukley equation

Content of carbon introduced into the solution, %	n	*k*	P_0
0	0.215	115.1	45.30
5	0.341	28.50	25.71
10	0.241	42.77	22.28
30	0.305	20.05	18.00

Table 4. The structure-sorption properties of the composite sorbents (KSs) of varied composition

Sample	Nitrogen adsorption, $cm^3\ g^{-1}$	S_{sp}, $m^2\ g^{-1}$	V_{tot}, $cm^3\ g^{-1}$	S_{mi}, $m^2\ g^{-1}$	V_{mi}, $cm^3\ g^{-1}$	r_0, Å	Moisture, %	Viscosity, η, Pa s
Peloid	49	19	0.077	0.0	0.000	20; 78; 150	64.8	0.257
KS-11	90	33	0.141	10.1	0.005	20; 86	69.6	0.117
KS-12	100	52	0.162	28.0	0.012	20; 63	68.1	0.094
KS-14	115	103	0.178	73.8	0.033	35	69.3	0.068

sorption characteristics of chosen samples are collected in Table 4. Results obtained in studying their viscosity η and moisture are plotted in Fig. 4. Figure 3 demonstrates viscosity vs. the shear stress typical dependences, the same at all carbon concentrations in the peloid.

The rheological curves (Fig. 3) and the data of Table 4 show that as the carbon concentration in the peloid composite is raised to 5%, the viscosity decreases from the highest value of 0.257 Pa s (initial peloid) to 0.117 Pa s, and then decreases further to 0.068 Pa s as the carbon concentration is raised to 30%.

These changes in viscosity correlate by the same manner with the moisture content in the samples (Table 4.). Note, for samples with close moisture contents (Table 4, samples with carbon concentration 5 and 30% and moisture content 69.6 and 69.3%, respectively), the viscosity decreases with increasing carbon concentration, which indicates that presence of carbon affects viscosity of the peloid samples.

Thus, the structural viscosity of the systems under examination depends on both carbon concentration and moisture content in the samples.

The peloid-carbon systems are thixotropic [27, 28]: their viscosity decreases as shear stress *P* is increased and this decrease is reversible (Fig. 4, direct and reverse run, respectively).

CONCLUSIONS

(1) Composite sorbents of varied composition based on peloid, deep-sea bottom sediment, and a KAU carbon prepared from fruit kernel and specially modified with metal cations (K^+, Mg^{2+}, and Zn^{2+}) were synthesized.

(2) All sorbents under examination are microporous (pore radius 20–70 Å, specific surface area 20–668 $m^2\ g^{-1}$). In comparison with peloid, the pore volume increased from 0.003 to 0.175 $cm^3\ g^{-1}$, surface area, from 6 to 430 $m^2\ g^{-1}$, and the nitrogen specific sorption, from 20 to 270 $cm^3\ g^{-1}$.

(3) It was established that composite samples exhibit surface fractality in the different regions of relative pressures, within 2.26–2.78 (±0.1), and this fractality differs only slightly from the fractal dimensions of natural clay minerals.

(4) As the concentration of the carbon constituent in the samples increases, the viscosity of the composite sorbents decreases from 0.257 Pa s (initial peloid) to 0.068 Pa s (sample containing 30% carbon). Variations of the moisture content with carbon concentration in the composite sorbents are similar.

(5) The peloid-carbon systems are thixotropic. Their viscosity decreases with increasing shear stress and this decrease is reversible.

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