Sorption of petrochemicals from aqueous solutions on thermally activated schungite rock

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Thermal oxidative treatment enhances the activity of a schungite rock in the sorption of petrochemicals from aqueous solutions. The effect of the thermal oxidative activation on the content and distribution of carbon in the rock and the dependence of the sorption activity on the texture of sorbents were studied.

Key words: schungite rock, thermal oxidative activation, sorption, aqueous solutions, petrochemicals, pore structure.

Carbonaceous schungite rock (SR) of the Zazhoginsk deposit, Karelia, containing nearly 30% carbon is one of promising natural sorbents that are used for waste water purification from organic compounds.[1—3] It was shown earlier[4] that an increase in the specific surface area and pore volume of the material can be achieved by partial burning a schungite carbon off the rock after thermal oxidative activation of SR at various temperatures. This work is aimed at the study of the effect of the SR thermal oxidative activation on the sorption of petrochemicals from aqueous solutions.

Experimental

Samples of schungite sorbents (SS) were prepared by grinding SR of the Zazhoginsk deposit to obtain a fraction from 0.5 to 2 mm. The sorbents were activated in a muffle in air at 410, 530, and 750 °C. The activated sorbents were designated as SS 410-4, SS 530-1, SS 750-2, *etc.*, where by the first three figures stand for the temperature and the fourth figure means the activation time in hours. According to XRD data, the main phases in both initial and all activated sorbents are low-temperature quartz and amorphous to X-rays carbonaceous substance.[5]

The sorption of petrochemicals (PC) was carried out at 20 °C on laboratory setups with the use of model PC solutions. To produce the latter, a solution of a spent motor oil in gasoline ROC-92 was prepared. Then the solution was stirred with water for 1 h in a 20 L reactor equipped with agitators. The PC aqueous solution thus obtained was stored for 24 h in the same reactor for stratification of a water-oil emulsion and then transferred to a storage container. High-concentrated solutions containing up to 70 mg dm^{-3} PC were diluted with water to specified concentrations.

The sorption properties of SS were studied under both static and dynamic conditions. Experiments under the static conditions were carried out in a 1 dm^3 vessel with 1 g of a sorbent, and the duration of run was specified based on the time needed to attain adsorption equilibration. A shaker with a frequency of 100 min^{-1} and an amplitude of 50 mm was used for mixing. Reference measurements with the use of a blade mixer at a rotation frequency of 400 min^{-1} showed the same results. In a dynamic regime, a column setup was used: a 12 mm-diameter column, a sorbent loading height of 260 mm, and a solution flowing with a rate of 2—5 m h^{-1}. The amount adsorbed (A) was found from a difference between the initial and final PC concentrations in solutions. The adsorption capacity was estimated with an accuracy of ±10 rel.%. The PC concentration in solutions was measured by fluorometry on a Fluorate-02 instrument.

The specific surface areas of sorbents (S_{sp}) were measured by the Brunauer—Emmett—Teller method from the thermal desorption of argon adsorbed at the liquid nitrogen temperature.[4] The contents of carbon and silicas in the samples were determined in the Analytical Certification Testing Center of the All-Russian Institute of Mineral Resources by the methods of the chemical and elemental analyses. The pore volume and structure were measured in the Institute of Physical Chemistry, Russian Academy of Sciences using adsorption of benzene vapor and in the M. V. Lomonosov Moscow State University with a mercury porosimeter 2000 Macropore Unit Model 120.[4,5] The adsorption isotherms of benzene vapor were measured by a gravimetric method on a vacuum adsorption setup at 293 K in the range of relative pressures from 10^{-6} to 1.0.

Results and Discussion

The kinetic curves of PC sorption from the model aqueous solution with a PC concentration of 60 mg dm^{-3} at a small amount of the sorbent and a great excess of the

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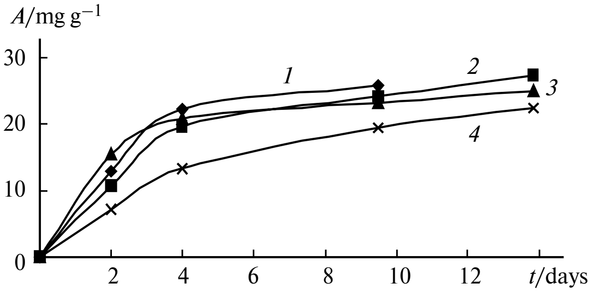

Fig. 1. Kinetic curves of the sorption of petrochemicals on sorbents SS (*1*), SS 410-4 (*2*), SS 530-1 (*3*), and SS 750-2 (*4*) (here and in Figs 2, 4, 6 *A* is adsorption).

solution (sorbent : solution = 1 : 1000) are presented in Fig. 1.

The curves show that PC sorption proceeds slowly and more than 14 days is needed to attain equilibration. When the initial concentrations are lowered to 50 mg dm^{-3}, ~9 days are required for equilibration. At low initial concentrations (<0.3 mg dm^{-3}), the sorption equilibration on SS is achieved in 2 days and on the activated samples it is achieved in 5—6 days.

The PC sorption isotherms from aqueous solutions are shown in Fig. 2. The isotherms of the activated samples lie above the isotherms of SS at all the equilibrium concentrations. Comparison of the slope of the initial regions of the isotherms (Fig. 2, *b*) observed in the range of low equilibrium concentrations of the solutions (C < 0.3 mg dm^{-3}) indicates that the order of decreasing adsorption capacity for the SS series is SS 530-1 > > SS 410-4 ≈ SS 750-2 >> SS (Table 1, data for C = 0.1 mg dm^{-3}). It is clear that the most efficient sorbents in the region of low-concentration solutions are those activated at moderate temperatures.

Table 1. Specific surface area (S_{sp}) and adsorption (A) on schungite sorbents in solutions of various concentrations

Sample	S_{sp} /m^2 g^{-1}	A/mg g^{-1} at C/mg dm^{-3}			
		0.1	0.3	0.5	12
SS	9[4]	1	2.5	4.4	29
SS 410-4	28[4]	6	13.5	16.5	72
SS 530-1	29[4]	11.5	13	13.5	42
SS 750-2	6	6	13.5	17.2	80

In the region of higher concentrations of solutions (C > 0.3 mg dm^{-3}), the sorbents activated at the highest and lowest temperatures possess the greatest adsorption capacity, whereas the activation at moderate temperatures (SS 530-1) is less efficient.

The specific surface areas and the adsorption capacities are presented in Table 1. The ability of the sorbents of consuming PC from solutions with different concentrations is independent of the S_{sp} value. At low concentrations of the solutions, the sorbents with high and low S_{sp} values (SS 410-4 and SS 750-2) are equally active. At higher concentrations, SS 750-2 with the lowest S_{sp} value possesses the highest adsorption ability.

To examine the degree of uniformity of the adsorption sites,[6] the Langmuir and Freundlich model adsorption isotherms were used. The isotherms were processed with the Origin 4.1 computer program. The Langmuir model implies that adsorption sites are energetically uniform, whereas the Freundlich model corresponds to adsorption on the non-uniform surface with an exponential distribu-

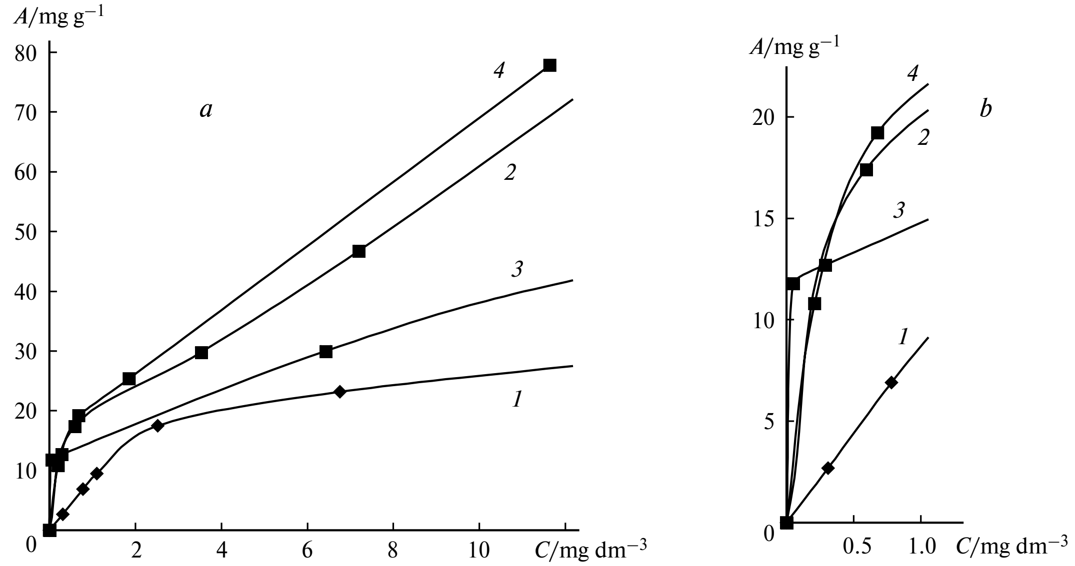

Fig. 2. Sorption isotherms of petrochemicals (*a*) and their initial sections (*b*) on sorbents SS (*1*), SS 410-4 (*2*), SS 530-1 (*3*), and SS 750-2 (*4*).

Table 2. Parameters of the adsorption isotherms of petrochemicals

Sorbent	Langmuir isotherm				Freundlich isotherm			
	A_m/mg g^{-1}	K_L/L mg^{-1}	R	SD	K_F/mg$^{1-(1/n)}$ L$^{1/n}$ g^{-1}	$1/n$	R	SD
SS	55.2	0.169	0.998	0.0093	7.45	0.575	0.972	0.0246
SS 410-4	54.6	0.772	0.943	0.0079	20.2	0.458	0.969	0.1926
SS 530-1	39.81	1.625	0.946	0.0111	17.8	0.297	0.977	0.1778
SS 750-2	36.8	1.95	0.981	0.0071	20.8	0.440	0.995	0.0766

Note. A_m, K_L and K_F, $1/n$ are the constants of the Langmuir and Freundlich equations, respectively; R is the correlation coefficient; SD is the mean-square error.

tion of adsorption heats among the adsorption sites. The constants calculated with the Langmuir and Freundlich equations along with the correlation coefficients R and the mean-square errors SD are shown in Table 2.

Comparison of the correlation coefficients allows the conclusion that the sorption isotherm on the nonactivated sample is better described by the Langmuir equation. The found monolayer capacity A_m = 55.2 mg g^{-1} makes it possible to evaluate the coverages of the surface with the SS, which are ~50% of the monolayer (28 mg g^{-1}) at C = 12 mg dm^{-3} and ~75% (41.2 mg g^{-1}) at C = 22.8 mg dm^{-3}.

The Freundlich model is more suitable for description of the isotherms of the activated samples. This allows us to conclude that the thermal oxidative activation converts an initially uniform surface into the surface with a considerable degree of heterogeneity.

The contents of the main components in the SS are shown in Fig. 3. The diagram shows that after the thermal oxidative activation, the carbon content decreases by 10, 30 and ~90 rel.% for SS 410-4, SS 530-1 and SS 750-2, respectively, whereas the relative content of the silica compounds increases. Note that substantial amounts of alumina (5—6 wt.%) and iron compounds (up to 2 wt.%) were found in the sorbents.

Comparison of the adsorption ability (see Table 1) and the carbon content in the samples (see Fig. 3) makes it possible to conclude that a decrease in the carbon content in the thermally activated samples leads to a growth in their adsorption ability at any PC concentrations in solutions, whereas no noticeable correlation between these parameters is obseved.

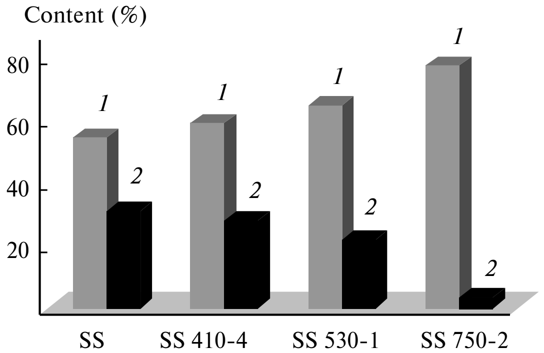

Fig. 3. Contents of main components SiO_2 (*1*) and C (*2*) in the samples of schungite sorbents.

The high sorption activity in low-concentration solutions is usually ascribed to the filling of micropores.[7] The effect of activation on the pore structure of SS can be found by analysis of the adsorption isotherms of benzene vapor (Fig. 4).

Comparison of the isotherms shows that SS 530-1 adsorbs the highest amount of benzene and SS 750-2 adsorbs the lowest amount of benzene. The micropore structure parameters in the range of relative pressures 10^{-5}—0.2 were calculated according to the Dubinin—Radushkevich equation derived from the theory of volume filling of micropores.[5] The limiting adsorption volume (V_s), total micropore volume ($W_0{}^0$), micropore half-width (x_0), and characteristic adsorption energy in micropores (E_0) were estimated from the adsorption isotherms (Table 3). The mesopore volume (V_{me}) was determined by the γ-method and the Kiselev—Kelvin method. Since the samples have the non-uniform micropore structure, their parameters can be described by the Dubinin—Stoeckli equation. Table 3 includes the dispersion parameter δ, which characterizes the spread of size distribution of micropores.

Comparison of the parameters (see Table 3) shows the same limiting volumes of the adsorption space for SS, SS 410-4 and SS 530-1 and somewhat lesser V_s value for SS 750-2. Sample SS 530-1 is characterized by the highest total micropore volume, whereas SS 750-2 contains no micropores. The differences in the mesopore volume of sorbents are negligible.

Table 3. Parameters of the micropore structure of schungite sorbents

Sorbent	V_s	$W_0{}^0$	x_0 /nm	E_0 /kJ mol^{-1}	δ /nm	V_{me} /cm^3 g^{-1}
	cm^3 g^{-1}					
SS	0.04	0.014	0.41	24.34	1.26	0.026
SS 410-4	0.04	0.013	1.18	8.45	0.82	0.027
SS 530-1	0.04	0.017	0.25	39.47	0.56	0.023
SS 750-2	0.03	—	—	—	—	0.03

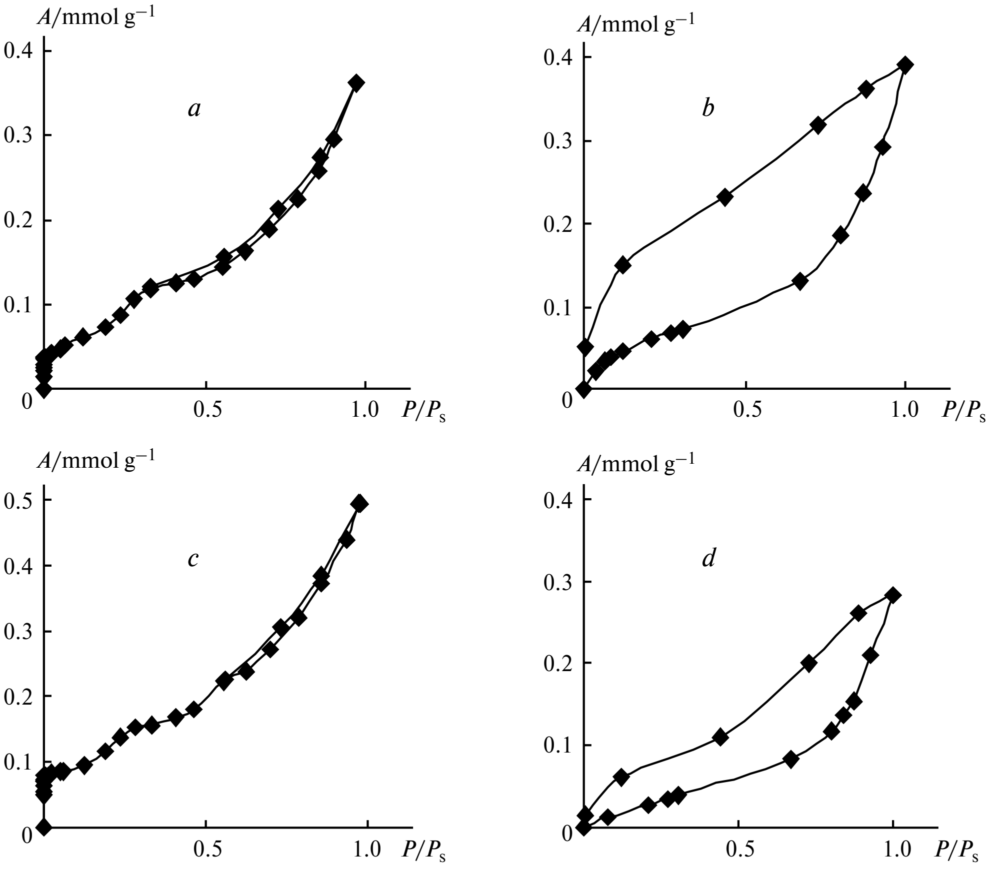

Fig. 4. Adsorption isotherms of benzene vapor on sorbents SS (*a*), SS 410-8 (*b*), SS 530-1 (*c*), and SS 750-1 (*d*) (P/P_s is the relative pressure of benzene vapor).

An increase in the micropore half-width for SS 410-4 compared to SS is likely due to the burning carbon off the sample and the destruction of walls between neighboring pores during activation, and a small value of x_0 for SS 530-1 may indicate the formation in this sample of a new micropore structure with the high characteristic adsorption energy in micropores (see Table 3). It has been shown earlier[8] by the computer-aided tomography that carbon diffuses from the bulk to the subsurface layers of grains during thermal activation of the schungite sorbents. This carbon is likely responsible for the formation of the new micropore structure.

Noteworthy, the developed micropore structure and specific surface area are observed for sorbents containing more than 20% carbon and disappear when the carbon content in the sample decreases to 3.5 wt.%. This allows a conclusion that a developed surface and microporosity of sorbents are likely due to a high concentration of the schungite carbon. As the sorbent with the most developed microporosity and specific surface area (SS 530-1) possesses the highest adsorption power in low-concentration solutions, the conclusion can be drawn that sorption occurs in the carbon micropores under these conditions.

Table 4. Total volume of large mesopores and macropores (V_m) as studied by mercury porosimetry

Sorbent	V_m /cm^3 g^{-1}	R* /nm
SS[4]	0.025	13
SS 410-4	0.193	596
SS 530-1	0.058	106
SS 750-2	0.234	596

* R is the prevailing pore radius.

The total volume of large mesopores and macropores (V_m) and the prevailing radius of the sorbent pores (R) as studied by mercury porosimetry are shown in Table 4 with the size pore volume distributions presented in Fig. 5.

Activation at the lowest (410 °C) and highest (750 °C) temperatures produces a similar increase in V_m (almost by the order of magnitude) and in the prevailing pore size (by several tens times), whereas at the average activation temperature (530 °C) an increase in V_m and R is much lesser.

To explain the dependence obtained, one can suggest that at an activation temperature of 410 °C, burning a

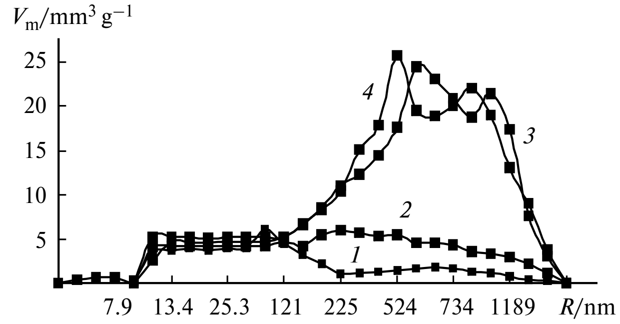

Fig. 5. Curves of the pore volume radius (R) distribution for meso- and macropores (V_m) in sorbents SS (*1*), SS 530-1 (*2*), SS 410-4 (*3*), and SS 750-2 (*4*) (as studied by mercury porosimetry).

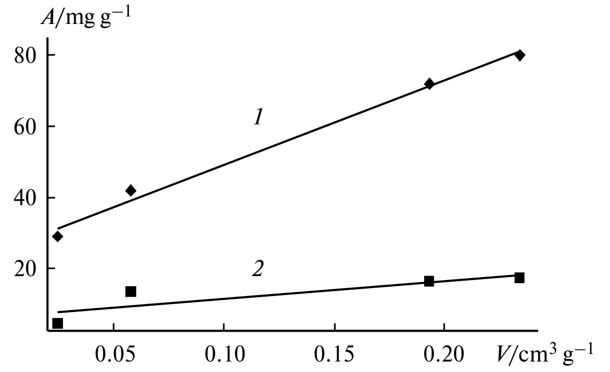

Fig. 6. Equilibrium capacity of schungite sorbents *vs.* total pore volume (V) at concentrations of petrochemicals of 12 (*1*) and 0.5 mg dm^{-3} (*2*).

portion of carbon off the sample and opening the closed pores makes the quartz fraction of the rock, which contains a significant number of macropores, available for adsorption and most of them retain a layer of microporous carbon at the surface. The macropore volume decreases at 530 °C because of the formation of the layer of porous carbon upon diffusion from the bulk of grains.

The activation at 750 °C results in burning a greater portion of carbon off the sample, and the macropores of the quartz fraction can again be reached by sorbate molecules; thin non-porous carbon layer either disappears or remains on their surface. Thus, a developed macroporous structure likely characterizes the surface of the quartz fraction of the schungite sorbents. This suggestion corresponds to the observed pore radii distribution shown in Fig. 5.

According to the distribution curves, all the sorbents are characterized by a nonuniform pore structure and an uniform distribution of the volumes of meso- and macropores with the size lesser than 120 nm. The main difference between the samples manifests itself in the region of macropores with the size greater than 120 nm. The activation at 410 and 750 °C results in the development of nearly the same macropore structure with a poorly pronounced bidispersion. At the average activation temperature (530 °C), the pore distribution is characterized by a higher uniformity and a small amount of the widest pores.

The adsorption power of the schungite sorbents in the PC solutions with high and average concentrations as the function of the total pore volume as studied by mercury porosimetry is presented in Fig. 6.

Comparison of the curves shows that the adsorption ability increases with the increasing pore volume and this dependence is more pronounced at high concentrations of solutions. The obtained correlations allow the conclusion to be made that the PC sorption on the schungite sorbents in the region of high concentrations occurs on the highly active, more probably quartz surface of macropores covered by a thin film of carbon. The adsorption mechanism changes in the region of low concentrations, and SS 530-1 with the highest micropore volume becomes the most active, whereas sorption occurs to a substantial extent *via* the mechanism of volume filling of micropores formed by activated schungite carbon.

Figure 7 presents the breakthrough curves obtained by the dynamic method for sorbents under study, which reflect the extent of purification of the model solution with the PC concentration of 30 mg dm^{-3}, at the linear flow velocity of 5 m h^{-1} as the function of the time of passing the solution through the column.

The microporous sample SS 530-1 that exhibits the time of protective action ~8 h is characterized by the best dynamic activity. On other sorbents under the chosen conditions (column height 260 mm) the breakthrough of PC is observed after few minutes of the run, *i.e.*, the height of the protective layer is greater than 260 mm. A typical feature of all the schungite sorbents is reaching in time a constant level, 50—30%, of the solution purification.

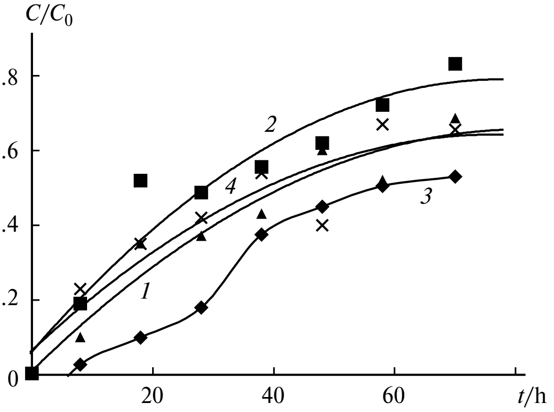

Fig. 7. Breakthrough curves for adsorption of petrochemicals on sorbents SS (*1*), SS 410-8 (*2*), SS 530-1 (*3*), and SS 750-2 (*4*).

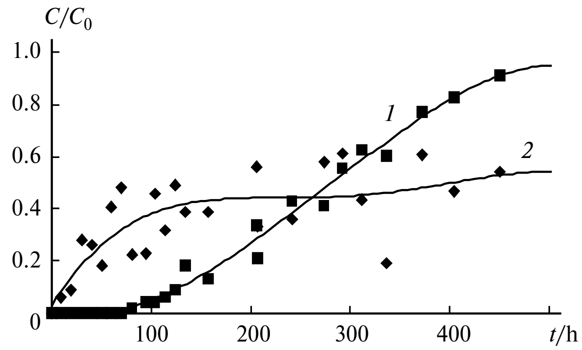

Fig. 8. Resource breakthrough curves for adsorption of petrochemicals on sorbents AG-3 (*1*) and SS (*2*).

The findings of prolonged comparative testing of SS and activated carbon AG-3 under milder conditions of the run (flow velocity 3.7 m h^{-1}, PC concentration 20 mg dm^{-3}) are presented in Fig. 8. The period of protective action for AG-3 is ~70 h, and then the activity decreases; after 250 h the extent of the solution purification on AG-3 becomes lesser than that on SS and after 400 h the adsorption ability of carbon virtually disappears.

Curve *2* (see Fig. 8) shows that SS continues to purify the solution to a high and constant extent (~50%) without decrease in activity during the first 250 h and additional 150 h, *i.e.*, it exhibits the properties of the sorbent-catalyst, in spite of its time of protective action is several minutes and its initial adsorption activity is lower than that of AG-3.

The previously reported data on the SS catalytic activity in the oxidation of organic microadmixtures in aqueous solutions at room temperature are available.[9] The activity of the rock in gas-phase oxidation reactions arises or markedly enhances upon the thermal oxidative activation. Depending on the reaction type, the activity is treated to be due to schungite carbon or admixtures of transition metal oxides, particularly, to the presence of iron-containing mineral phase.[10,11] The data on sorbate catalytic transformations in the volume of micropores of activated carbon were obtained in works on the sorption of organic substances on carbon sorbents.[12]

According to the mineral composition, SR is retained as a base in the samples activated at 410 and 530 °C; but at 530 °C its transformation is observed, particularly many fragments covered by iron hydroxides are seen. At 750 °C, ~75% of the material activated for 1 h represents a finely dispersed quartz with an admixture of iron oxides.

Based on the data obtained one can conclude that the carbon layer in the peripheral zone and hence on the surface of pellets is responsible for the adsorption power of the sorbents SS, SS 410-4, and SS 530-1.

The reason for the observed redistribution and variation of the properties of the schungite carbon during the thermal oxidative activation is likely due to partial burning carbon from the surface and diffusion of the carbon remained in bulk to the surface of pellets.

A growth of the adsorption capacity of the activated schungite sorbents in the region of low and high concentrations of the PC aqueous solutions is due to the development of the pore structure of a specified type.[4] Correlations between the adsorption capacity and pore structure indicate different sorption mechanisms in the low- and high-concentration PC solutions. In the region of low concentrations, sorption on the schungite carbon occurs rapidly via the mechanism of micropore filling. Note that the model low-concentration PC solutions well correspond to the compositions of real waste waters of petrol filling stations, washbaies, storm flows from highways, *etc.*, preliminarily treated on standard waste disposal plants, which often, because of design objectives, cannot approach the PC content that fit the requirements for water discharge to the earth surface or fisheries waters. In the high-concentration solutions, when the sorbent has no micropores, sorption occurs on the highly active surface of the quartz macropores likely covered by the carbon film.

The study performed shows the promising use of thermally activated schungite sorbents in purification of waste water from petrochemicals. Variation of the activation procedures provides a way for producing the schungite materials with specified properties for purification and aftertreatment of waste water by the filtration methods as well as under stationary conditions in settling tanks and natural basins.

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