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Study of Sorbents Obtained from Sapropel of Lakes Kachkulnya and Barchin (Novosibirsk Region)

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Abstract

Porous materials from sapropels of lakes of the Novosibirsk Region of the organic (Lake Kachkulnya) and organomineral (Lake Barchin) types, as well as from solid residues of their thermal dissolution in ethanol were obtained by thermochemical activation methods with potassium hydroxide and one-step carbonization-activation by water vapour. Textural and adsorption properties of porous materials were studied. It was established that porous materials with the specific surface up to 618 m²/g, total volume of pores of 0.26 cm³/g (according to BET), sorption activity on iodine and methylene blue of 58.9 % and 189.1 mg/g, respectively, could be obtained by the thermochemical activation of sapropels of the organic type. It was shown that these materials could be used as organomineral sorbents in technologies of the sewage treatment from ions of heavy metals and air from vapours of low molecular mass hydrocarbons.

Key words: lacustrine sapropel, thermo-alkaline activation, carbonization-activation by water vapour, porous materials, sorbents

INTRODUCTION

Sapropels are bottom sediments of water bodies that are formed from the remains of dead plants and animal organisms, as well as from mineral substances of the biochemical and geochemical origin. The lower borderline of the content of organic substances in them is 15 % calculated per the absolutely dry mass of a sapropel. According to [1], the identified reserves of sapropels in Russia exceed 250 billion m³,

and inferred resources of sapropels of South-west Siberia are 17 billion tons [2].

Sapropels are used in agriculture, medicine, cosmetics, construction, etc. Extracts of sapropels obtained using organic solvents and supercritical carbon oxide contain vitamins B, C, D, amino acids and a number of other biologically active substances [3–7]. It was established that liquid products of pyrolysis of sapropels possessed antioxygenic properties [5].

Thermal and thermochemical methods of the preparation of liquid products from sapropels that can potentially be used as raw materials for the production of chemical substances are being developed. Thus, when thermal dissolution of sapropels from water objects of the Omsk Region in organic solvents, the maximal conversion degree in decalin is 83 mass % (at 450 °C), in anthracene oil – 77 mass % (at 450 °C) [8], in the petroleum residue – 72 mass % (at 430 °C) [9]. It was shown that products of thermal dissolution contained up to 68 mass % of phenols, up to 22 mass % of organic bases and up to 20 mass % of organic acids.

Combined methods of the processing of sapropels into in-demand products were proposed [8]. More than 20 % of liquid products (calculated per the dry substance) that include a wide variety of organic substances are formed in the course of the process of pyrolysis of sapropels in the inert atmosphere. In this case, organomineral sorbents were obtained from solid residues of the destruction of sapropels by calcination at 500–900 °C in the inert atmosphere. The specific surface of the resulting solid products from high-ash sapropels reaches 40–50 m²/g, from sapropels of the organic type – 150–190 m²/g. The additional activation by water vapour leads to the increase of the specific surface up to 500–600 m²/g, herewith, the specific pore volume reached the values of 1.5–1.7 cm³/g [8].

Organomineral sorbents from sapropels can be used for the integrated wastewater treatment from heavy metals ions and organic substances. Comparative tests of sorbents obtained from sapropels of the Omsk Region showed that the ability of the material from high-ash sapropels to sorb organic substances and heavy metals from water is higher, in comparison with a sorbent from low-ash sapropels of the organic type [10].

It was earlier established that the efficient method of the preparation of liquid products from sapropels was their thermal dissolution in ethanol. It was found that the process temperature had a significant impact on the degree of conversion of organic substance (OS) sapropels and yield of the extracted products. With an increase of the temperature from 200 to 400 °C the conversion degree of the OS of sapropels of the organic type increases in 1.8 times and reaches 69.7 mass %, and the yield

of the extracted products decreases in 1.5 times and is 27.4 mass % [11].

The goal of this work was to study sorption properties of porous materials obtained by methods of carbonization-activation by water vapour and thermochemical alkaline activation of sapropels of lakes of the Novosibirsk Region of the organic (Lake Kachkulnya) and organomineral (Lake Barchin) types, as well as from solid products of their thermal dissolution in ethanol.

EXPERIMENTAL

Samples of air-dry sapropels of Lakes Kachkulnya (S-1) and Barchin (S-2) of the Novosibirsk Region (fraction of less than 0.2 mm), as well as solid products of the thermal dissolution of sapropels in ethanol were used for the preparation of porous materials. It was carried out in a rotary boiler with the capacity of 0.25 L at the temperatures of 200–400 °C [11]. After the experiment, liquid products of the transformation of sapropels were isolated by the extraction by ethanol. The residue on the filter was dried up to the constant mass and used as the raw material for the preparation of porous materials. The following samples were selected: the remains of the thermal dissolution of sapropel S-1 at 200 °C (OT200-1), 300 °C (OT300-1), 400 °C (OT400-1), as well as sapropel S-2 at 300 °C (OT300-2).

Experiments on the one-step carbonization-activation with water vapour of sapropels and products of their thermal dissolution were carried out in the fluidized bed in the metallic stainless steel reactor with the length of 500 mm and diameter of 43 mm. The uploading of samples of sapropels and products of their thermal dissolution was 50 g. The rise of the reactor temperature was conducted out with the rate of 30 °C/min. When the temperature reaches 350 °C, the supply of water vapour into the reactor was started. When increasing the reactor temperature up to 800 °C the isothermal exposure for 0.5 h was produced. Further, feeding water vapour was stopped, the reactor was cooled to the room temperature, after which the sample of the porous material was retrieved from the reactor. The consumption of water on the activation was 100 mL/h.

The thermochemical alkaline activation of samples of sapropels was carried out by potassium hydroxide at the mass ratio of raw materials/alkali = 1 : 3 with the rate of the temperature rise of 10 °C/min up to 800 °C, according to the methodology described in [12] and subsequent isothermal exposure for 1 h in the atmosphere of argon.

The elemental composition of starting sapropels was determined using an analyser C,H,N,S,O Vario EL Cube (Elementar Analysensysteme GmbH, Germany). The chemical composition of the mineral part of sapropels was analysed by X-ray fluorescent method using a Bruker EDS XFS Ranger X-ray fluorescent spectrometer. The X-ray phase analysis was performed using a diffractometer ARL X“TRA in the diapason of angles $2\theta = 5-65^\circ$.

The specific surface (S_{BET}) and pore volume (V_{por}) of samples were determined according to the standard methodology based on the measurement of the equilibrium adsorption of nitrogen at 77 K and $P/P_0 = 0.2$. Measurements were carried out using an analyser of the specific surface “Sorbometr-M”.

The adsorption activity of samples by iodine (I2) and methylene blue (MB) was determined according to State Standards GOST 6217-74 and GOST 4453-74, respectively.

The activity of porous materials in sorption of low molecular mass hydrocarbons was evaluated according to their ability to absorb pairs of benzene under stationary conditions of equilibrium filling pores. To conduct the analysis, a sample weight of 0.5 g was selected, dried to the constant mass at the temperature of 102–110 °C. The dried sample in a glass weighing bottle with the lid open was placed on the grille of the desiccator, at the bottom of which benzene was poured and aged at the temperature of 25 °C during 1, 3, 5, 7 and 24 h. At the end of the sorption process, the sample was closed with a lid and weighted with the precision up to 0.0001 g. The amount of benzene sorbed was determined according to the change of the sample mass.

In order to determine the sorption of heavy metals on porous materials, a sample mass (0.5 g) was dried for 2 h at 110 °C in weighing bottles. After cooling in a desiccator, samples were weighted with the accuracy up to 0.2 mg and placed into flasks with friction lids of the capac-

ity of 150 mL. Then, by 50 mL of the starting solution containing ions of Cd^{2+} (125 mg/L), Pb^{2+} (132.5 mg/L) and Cu^{2+} (75 mg/L) was poured into the flasks. The samples were shaken continuously during 44 h at $(20 \pm 2)^\circ\text{C}$. After the completion of the sorption process, porous materials were filtered off, and filtered water was analysed on the content of ions of heavy metals.

The analysis of the content of ions of heavy metals in the starting solution and filters after the sorption was conducted by the method of mass spectrometry on a quadrupole inductively coupled plasma spectrometer (ICP-MS Agilent 7500A). The sample was sprayed in the chamber in the form of a dry aerosol, injected into a plasma flare. The time of the signal accumulation on one mass is 0.1 s, scanning step is 0.1 c. u. (carbon units). The calibration of the mass scale was carried out according to branded tuning solutions (Agilent Technologies 31-oct-2010). The results processing was carried out using the program ChemStation in the mode Semi Q according to five points per a peak.

RESULTS AND DISCUSSION

The studies conducted showed that the selected samples of sapropels differed substantially in their composition. The sapropel of the organic type S-1 (lake Kachkulnya) is characterized by an increased content of carbon and oxygen and relatively low content of mineral substances (Table 1). Its ash content is 16.3 mass %, which is much smaller, in comparison with the ash content of the sapropel of the organomineral type of the Lake Barchin (S-2), that is more than 42 mass %.

According to the X-ray fluorescence analysis, calcium (more than 51 mass % calculated per CaO) prevails in the composition of the

TABLE 1

Ash content and the elemental composition of sapropels from Lake Kachkulnya (S-1) and Lake Barchin (S-2)

Samples	Content, mass %				
	C	H	S	O	N
S-1	43.3	5.1	4.6	32.2	3.0
S-2	22.8	3.3	3.2	18.6	2.0

Note. Counting on absolutely dry mass of sapropel.

TABLE 2
Chemical content of the mineral part
of samples of sapropels S-1 and S-2, mass %

Components	Content in samples	
	S-1	S-2
Na ₂ O	1.83	0.34
MgO	12.0	4.69
Al ₂ O ₃	6.32	3.83
SiO ₂	29.10	27.4
P ₂ O ₅	1.21	0.38
SO ₃	23.50	7.57
Cl	0.23	0.47
K ₂ O	1.36	0.63
CaO	17.80	51.40
TiO ₂	0.59	0.20
MnO	–	0.12
Fe ₂ O ₃	5.30	2.52
SrO	0.31	0.37

mineral part of the sapropel S-2. The main elements of the mineral part of sapropel S-1 are silicon, calcium and magnesium (Table 2). Additionally, the mineral part of sapropel S-1 is characterized by a high content of sulphur (23.5 mass % calculated per SO₃). According to

the results of XRFA, mineral components of sapropel S-1 are mainly presented by quartz with a small admixture of pyrite, plagioclase, and mica. Low-magnesium calcite (~80 % of the weight of the mineral part) dominates in the mineral part of sapropel S-2.

In the course of the carbonisation-activation by vapour and thermochemical alkaline activation of the selected samples, the content of mineral substances in them increases significantly. It is obvious that the observed changes are due to thermal transformations of the organic mass of samples into volatile products. Porous materials (PM) obtained from high-ash sapropel S-2 contain more mineral substances, approximately on 30 mass %, in comparison with materials from sapropel S-1 (Table 3). The preliminary treatment of sapropel S-1 by the method of thermal dissolution in ethanol at 200 °C does not affect considerably the content of mineral components in the PM obtained from it. The increase of the temperature of the thermal dissolution up to 300 and 400 °C is accompanied by the increase of the content of mineral components in PM on 10–12 % (see Table 3).

Table 3 also gives results of the study of textural and adsorption properties of PM obtained by various methods from sapropels and

TABLE 3
Content of mineral substances, textural and adsorption properties of porous materials from sapropels and solid products of their extraction by ethanol

Samples	Content of mineral substances, mass %	S_{BET} , m ² /g	Volume of pores (V_{por}), cm ³ /g	Sorption	
				I ₂ , %	MB, mg/g
<i>Carbonization-activation by water vapour</i>					
PM from S-1	63.5	236	0.10	39.1	88.3
PM from S-2	92.8	7	0.01	5.9	3.3
<i>Thermochemical alkaline activation</i>					
PM from S-1	58.2	618	0.26	58.9	189.1
PM from S-2	89.7	64	0.03	2.6	14.2
<i>Carbonization-activation by water vapour</i>					
PM OT200-1	65.1	261	0.11	44.6	105.3
PM OT300-1	75.5	234	0.10	39.4	28.5
PM OT400-1	77.2	158	0.01	42.6	10.0
PM OT300-2	92.2	11	0.01	47.0	4.2
BAU-A [13]	–	>500	1.6*	60.0	77.0
DAK [13]	–	700–800	1.4*	30.0	53.0

* Total volume of pores on water.

solid residues of their thermal dissolution. For matching, appropriate characteristics of a number of industrial carbon sorbents obtained on the basis of the wood raw materials (BAU-A, DAK) are listed here. It can be seen that samples based on the sapropels of the organic type S-1 are characterized by a more developed specific surface and greater pore volume. The highest values of these indicators were obtained when using the method of the alkaline activation: $618 \text{ m}^2/\text{g}$ and $0.26 \text{ cm}^3/\text{g}$ for the specific surface and volume of pores, respectively. The highest values of the sorption activity on iodine (58.9 %) and MB (189.1 mg/g) were obtained for the same samples.

The temperature of the thermal dissolution of sapropels in ethanol has a significant influence on textural and sorption properties of PM obtained when steam and gas activating the formed solid residues. The sample of PM based on the residue of the thermal dissolution of sapropel S-1 at the temperature of 200°C demonstrates elevated indicators of the total pore volume ($0.11 \text{ cm}^3/\text{g}$) and specific surface ($261 \text{ m}^2/\text{g}$). At this, its sorption activity on iodine (44.6 %) and MB (105.3 mg/g) was higher, in comparison with the PM obtained at the activation of the starting sapropel. The increase of the temperature of thermal dissolution of sapropel S-1 in ethanol is accompanied by the decrease of values S_{BET} , V_{por} and, as a consequence, the sorption activity of the resulting PM. The sample obtained from the residue of extraction by ethanol of organomineral sapropel S-2 at 300°C is characterized by minimal values of the porous structure and sorption properties.

It follows from the data of Table 3 that PM obtained by methods of carbonization-activation by vapour and alkaline activation of the sapropel of the organic type S-1, as well as the method of carbonization-activation by vapour of the residue of its extraction of S-1 by ethanol at 200°C exhibited the sorption activity on iodine and MB, comparable with industrial samples of sorbents.

The sorption activity of PM from the high-ash sapropel S-2 on iodine and MB is much lower, in comparison with the PM from the sapropel S-1, which corresponds to the data of the test of the sorption activity of PM based on

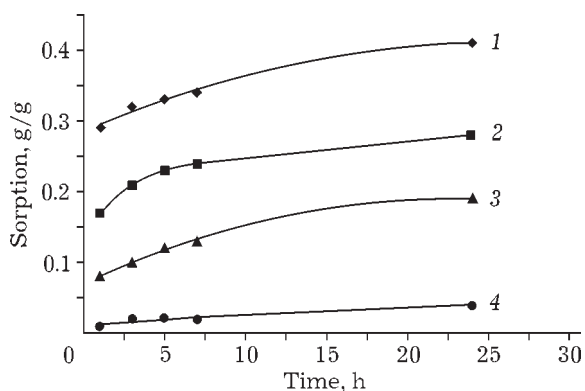


Fig. 1. Dynamics of sorption of benzene on porous materials obtained at activation by sapropels: 1 – alkaline activation S-1; 2 – carbonization-activation by vapour S-1; 3 – alkaline activation S-2; 4 – carbonization-activation by vapour S-2.

sapropels of lakes of the Omsk Region of the organic and high-ash organomineral types [8].

Results of the study of the activity of PM on sorption of benzene vapours are given in Figs. 1 and 2. It can be seen that samples obtained from the sapropel of the organic type S-1 exhibit a higher activity in this process. The sample obtained from sapropel S-1 by the method of the thermochemical alkaline activation is characterized by the maximal sorption value (up to 0.41 g/g). In the row of PM based on the remains of thermal dissolution of sapropels, the sample obtained from the residue at 200°C demonstrates the maximal activity (0.31 g/g).

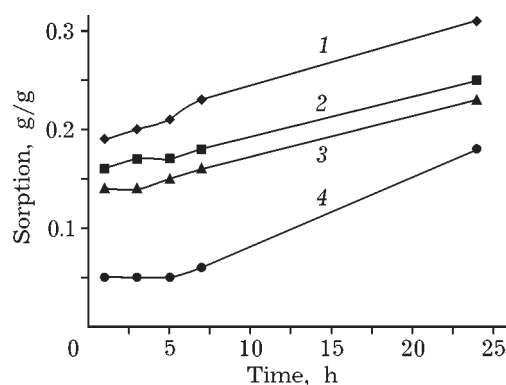


Fig. 2. Dynamics of sorption of benzene on porous materials obtained by the method of carbonization-activation by vapour of solid residues of the thermal dissolution of sapropels in ethanol: 1–3 – of the organic type S-1 at 200°C (1), 300°C (2) and 400°C (3); 4 – of the organomineral type S-2 at the temperature of 300°C .

TABLE 4

Content of ions of heavy metals in a solution after the sorption on porous materials obtained from sapropels and solid residues of their thermal dissolution in ethanol

Samples	Content, mg/L		
	Cu ²⁺	Cd ²⁺	Pb ²⁺
<i>Thermochemical alkaline activation</i>			
PM from S-1	n/d	n/d	n/d
PM from S-2	0.1	n/d	n/d
<i>Carbonization-activation by water vapour</i>			
PM from S-1	0.3	n/d	24
PM from S-2	0.1	n/d	22.3
<i>Carbonization-activation by water vapour</i>			
PM OT200-1	0.1	n/d	0.2
PM OT300-1	0.6	0.3	0.4
PM OT400-1	0.3	n/d	0.4
PM OT300-2	0.1	n/d	n/d

Note. n/d – not detected (detection limit is 0.1 mg/L).

It should be noted that porous carbon materials used broadly abroad in industrial filtering processes have the sorption capacity for benzene of 0.3–0.4 g/g [14]. The sorption activity for benzene for domestic activated carbons of the brands SKT-3 and SKT-10 is equal 0.26 and 0.22 g/g, respectively [15, 16].

Results of the test of samples of PM in sorption from aqueous solutions of the ions Cu²⁺, Vd²⁺, Pb²⁺ showed that the sample obtained by the method of the thermochemical alkaline activation of the sapropel of the organic type S-1 was characterized by the highest activity. Other samples excluding OT300-1 (from the residue of the thermal dissolution in ethanol of sapropel S-1 at 300 °C) exhibited a good activity in sorption of cadmium ions. In relation to Pb²⁺ ions, the sorption activity is demonstrated by products of the alkaline activation of sapropel of the organic (S-1) and organomineral (S-2) types, as well as PM obtained by the activation by vapour of a solid residue of the thermal dissolution of the sapropel of organomineral type (S-2). It is known that its mineral part is mainly presented by calcite (Table 4). An increased activity in the sorption of heavy metals of PM obtained from a high-ash sapropel with a high content of silicon was noted by the authors of the work [10].

CONCLUSION

1. Methods of the thermochemical activation by potassium hydroxide and one-step carbonization-activation by water vapour can be used for the preparation of porous materials from sapropels of lakes of the Novosibirsk Region of the organic and organomineral types, as well as from solid residues of their thermal dissolution in ethanol. PM with the specific surface of 618 m²/g and total pore volume of 0.26 cm³/g (according to BET), sorption activity for iodine of 58.9 % and methylene blue of 189.1 mg/g can be obtained by the way of thermochemical activation of sapropels of the organic type.

2. Porous materials obtained from a sapropel of the organic type, as well as from the residue of its thermal dissolution in ethanol at 200 °C on the sorption capacity of benzene vapours under the stationary conditions of equilibrium filling pores (up to 0.41 g/g) are comparable with foreign and domestic industrial carbon sorbents.

3. The porous materials obtained in the work can be used in technologies of the purification of wastewater from ions of heavy metals and air from vapours of low molecular mass hydrocarbons.

4. Complex processing of sapropels including the preliminary extraction of active components with ethanol and subsequent carbonization-activation by water vapour of the solid residue may become the basis for creating the non-waste production of chemical substances and PM having bi-functional properties in processes of the purification of wastewater from ions of heavy metals and of gases from hydrocarbons.

REFERENCES

- 1 Kosov V. I., Sapropel. Resursy, Tekhnologii, Geoekologiya, Nauka, St. Petersburg, 2007.
- 2 URL: <http://www.copah.info/articles/opinion/mif-obesplodnykh-nedrakh/>
- 3 Vysokogorskii V. E., Nozdrunova A. A., Plaksin G. V., Krivonos O. I., Mkrтчan O. Z., Petrosyan L. Yu., *Pharm. Chem. J.*, 43, 4 (2009) 191.
- 4 Krivonos O. I., Plaksin G. V., *Rus. J. Phys. Chem. B*, 4, 8 (2010) 1171.
- 5 Nozdrunova A. A., Krivonos O. I., Vysokogorskii V. E., Plaksin G. V., Chernyshov A. K., *Khim. Rast. Syrya*, 4 (2008) 141.
- 6 RU No. 2139710, 1999.
- 7 Yudina N. V., Pisareva S. I., Pynchenkov V. I., Loskutova Yu. V., *Khim. Rast. Syrya*, 4 (1998) 33.
- 8 Plaksin G. V., Krivonos O. I., *Ros. Khim. Zh.*, 4 (2007) 140.

- 9 Kuznetsov B. N., Tarabanko V. E., Chernyak M. Yu., Beregovtsova N. G., Sharypov V. I., Milishenko T. P., Plaksin G. V., *Khim. Rast. Syrya*, 1 (2004) 35.
- 10 Kovalenko G. A., Adeeva L. N., *Chem. Sust. Dev.*, 18, 2 (2010) 181.
URL: <http://www.sibran.ru/en/journals/KhUR>
- 11 Sharypov V. I., Beregovtsova N. G., Baryshnikov S. V., Taran O. P., Kuznetsov B. N., in: IV Mezhdunar. Nauch.-Tekhn. Konf. "Alternativnye Istochniki Syrya i Topliva AIST-2013" (Theses), Minsk, 2013, p. 71.
- 12 Mikova N. M., Kuznetsov B. N., Chesnokov N. V., *J. Sib. Fed. Univ. Chem.*, 1 (2009) 3.
- 13 GOST 6217-74. Ugol' Aktivny, Drevesny, Droblyeny, Tekhn. Usloviya, Moscow, 1974.
- 14 Lillo-Rydenas M. A., Cazorla-Amorys D., Linares-Solano A., *Adsorption*, 17 (2011) 473.
- 15 TU 6-16-2727-84. Ugol' Aktivny SKTZ, 1984.
- 16 TU 6-16-2266-78. Ugol' Aktivny SKT10, 1978.