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Carbon-Mineral Sapropel Sorbent for Comprehensive Waste Water Purification

G. A. KOVALENKO and L. N. ADEEVA

Dostoevsky Omsk State University,
Pr. Mira 55A, Omsk 644077 (Russia)

E-mail: kovalenko_85@list.ru

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Abstract

It is demonstrated that carbonization of sapropel at the temperature of 700–800 °C may be used in order to obtain carbon-mineral sorbent for wastewater comprehensive purification either from polar substances or from nonpolar ones. Composition and structure for the material obtained were established using X-ray fluorescence and IR spectroscopy, XRD phase analysis, thermal and chemical analyses, low-temperature nitrogen adsorption, mercury porosimetry. Sorption characteristics of the sorbent were determined with respect to a wide range of substances (iodine, methylene blue, heavy metal ions, oil products, phenol, surfactants).

Key words: carbon-mineral sapropel sorbent, chemical composition, sorption of organic substances and heavy metals

INTRODUCTION

Wastewaters, as a rule, contain a great variety of pollutants: heavy metals, mineral oil, surface-active substances, and dyes. Sorbents are commonly known, for example activated carbon, those remove efficiently non-polar compounds being inefficient for purifying water from heavy metals. At the same time, the sorbents those are efficient for water purifying from heavy metals, are not efficient with respect to non-polar compounds (for example, mineral oil). In order to provide comprehensive wastewater treatment one as a rule uses obtaining sorbents via artificial mixing different components, for example activated coal, carbon-containing raw material and aluminosilicates, silica gels, *etc.* [1, 2]. Carbon-mineral sorbents those exhibit bifunctional properties, could be obtained from sapropel as a natural organomineral raw material.

The organic substance of sapropels represents a product of the biochemical processing of phytogenous and animal remains under anaerobic conditions. The inorganic part of sapropel is presented mainly by silicon, aluminium, iron, calcium compounds and contains aluminosilicates, quartz, amorphous silica [3]. In this connection, using the carbonization of sapropel in an inert medium one could obtain a bifunctional carbon-mineral sorbent that exhibits sorption properties simultaneously with respect to both polar and non-polar substances.

The present work is devoted to the studies concerning the chemical composition, physicochemical parameters and sorptive power of carbon-mineral sorbents obtained via the carbonization of sapropel, with respect to a great variety of substances (iodine, methylene blue, heavy metal ions, mineral oil, phenol, surfactants).

EXPERIMENTAL

As a subject of inquiry, we chose two kinds of sorbent made of silica-containing sapropel

(Gorkoye Lake) and organic sapropel (Molodavskoye Lake) of the Omsk Region. The mentioned deposits are of interest from the standpoint of developing them. We investigated carbon-mineral sorbents obtained via the carbonization of sapropel within the temperature range of 500–1000 °C. The carbonization is carried out in a flow of argon (140 L/h) at the rate of temperature rise equal to 10 °C/min during 2 h. At the additional stage of activation, the reactor was fed with steam with the consumption level amounting to 0.8 kg of steam per 1 kg of the carbonized material; the sorbent was kept at a preset temperature value within 20 min.

The chemical analysis of the mineral part was carried out using a gravimetric method according to the technique used for the analysis of silicate rocks [4]. The elemental structure was studied by means of X-ray fluorescent spectroscopy technique using an ARL OPTIM'X XRF spectrometer. The elemental CHN analysis was carried out using a Carlo Erba model 1106 elemental analyzer. The mineralogical composition of the samples was studied with on a DRON-3 stationary X-ray diffractometer. The thermal analysis of the samples was carried out using platinum crucibles by means of a Netzsch STA 449 Jupiter thermal analyzer. The measurement range was within 40–950 °C, the rate of heating was equal to 1 °C/min. The decomposition was carried out in a flow of argon (15 mL/min). IR spectra were registered using a Perkin-Elmer Spectrum One FT-IR spectrometer within the wave number range of 4000–400 cm^{-1} with the resolution of 4 cm^{-1}, the number of scans being equal to 32. Samples were triturated together with KBr using an agate mortar and the pressed to obtain tablets. The investigation of the textural characteristics of the samples according to nitrogen adsorption data was carried out on a Carlo Erba Sorptomatic 1900 device intended for obtaining adsorption–desorption isotherms. The adsorption isotherms were measured at the temperature of 77.4 K within the range of relative nitrogen pressure values $p/p_0 = 8 \cdot 10^{-3}$–0.99. The surface texture was also established using the method of mercury porosimetry by means of a Carlo Erba Porosimeter, series 2000. The crushing strength value for the samples of sorbents was measured using a MP-9C device. The essence of the mentioned method for determining the mechanical strength under static conditions consists in the measuring the destruction force concerning the particles of a sample located between two parallel plates.

Determining the adsorptive activity with respect methylene blue was carried out in accordance with the State Standard GOST 4453–74, that with respect to iodine was performed according to the GOST 6217–74.

When studying the laws of adsorption depending on different factors, the samples of adsorbents with the certain mass (0.5 g for the adsorption of metal ions, 0.1 g for the adsorption of organic substances) were placed into 20 mL of an aqueous solution containing an adsorptive, under a periodic stirring. After a preset time interval the aqueous solution was separated *via* decantation or centrifuging, and then we determined a residual content of the adsorptive by means of known techniques [5]. The total dynamic capacity was determined *via* passing the solution containing the adsorptive with known concentration through a column of 1 cm in diameter packed with 2 g of the sorbent sample. The rate of the solution filtering amounted to (0.4±0.02) mL/min. The experiment was carried out till obtaining equal values of the adsorptive concentration in the initial and treated solutions.

TABLE 1

Composition of sapropels and solid products of their carbonization at 700 °C

Initial sapropel	Composition of initial sapropel, mass %		Composition of carbonized product, mass %				
	Organic substances	Mineral substances	Carbon	Mineral substances			
				SiO_2	Al_2O_3	Fe_2O_3	CaO
Silica-containing	36.0	64.0	6.3	54.1	8.6	3.4	6.8
Organic	73.2	26.8	46.8	23.4	4.7	2.0	8.6

RESULTS AND DISCUSSION

Investigation of the chemical composition of sorbents

The samples of sorbents were synthesized from sapropels with different content of organic and mineral substances belonging to organic and silica-containing classification types presented in [3]. The content of main substances in the initial sapropels and the products of their carbonization at 700 °C are presented in Table 1. According to the elemental CHN analysis of the sorbents, the content of carbon changes depending on the type of sapropel which serves as a raw material for the synthesis, varying within the range of 6.3–46.8 mass %. The chemical composition of the mineral part of sorbents includes predominantly the compounds of silicon, aluminium, iron and calcium. The X-ray fluorescence analysis of the samples of sorbents reliably revealed the presence of the following elements: silicon, aluminium, potassium, calcium, titanium, manganese, iron, zirconium, strontium, rubidium, and zinc. As far as non-metals are concerned, phosphorus, sulphur, chlorine were revealed therein.

Using the XRD phase analysis of the samples of various sorbents, we established mineralogical forms of main elements present in the mineral part. Figure 1 displays the XRD profile of the carbon-mineral sorbent obtained by the carbonization of silica-containing sapropel at 700 °C. The XRD profiles of other samples are of a similar shape. The composition of sorbents includes quartz, aluminosilicates (feldspars anorthoclase and sanidine), and amorphous silica. The presence of amorphous silica is revealed *via* XRD profile repeated registration after double processing the samples by 5 % sodium carbonate solution of by a technique described in [3, p. 61]. Amorphous silica, to all appearance, is of an authigenic origin being accumulated in a biogenic way from the valves of diatoms.

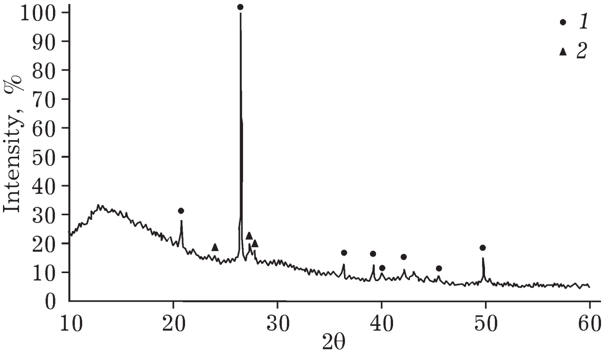

Fig. 1. XRD profile of carbon-mineral sorbent resulting from silica-containing sapropel (T_{carb} = 700 °C): *1* – quartz, *2* – aluminosilicates.

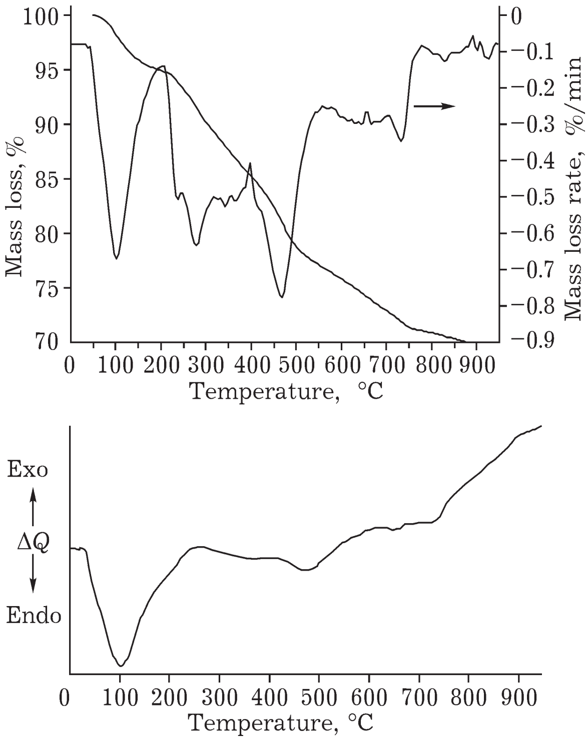

Fig. 2. Thermal analysis curves for the sample of native silica-containing sapropel.

Using thermal analysis, we investigated the samples of native sapropels those served as a raw material for synthesis (Fig. 2). Within the range of 200 °C we registered a low-temperature endothermic effect (with the maximum at 101 °C) corresponding to the removal of adsorbed water. On the DTG curve this period is characterized by an abrupt material mass loss. As the temperature further increases, an intensive process of organic substance decomposition begins to occur (for hemicelluloses at 230–265 °C, for cellulose at 300–320 °C, for humic acids and non-hydrolyzed residue at 340–380 °C). Within the range of 400–550 °C, the DTA curves demonstrate an endothermic effect (a peak on the DTG curve corresponds to

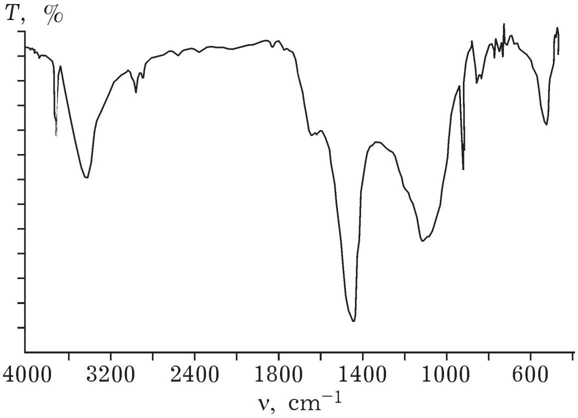

Fig. 3. IR spectrum of the carbonization product resulting from organic type sapropel (T_{carb} = 700 °C).

this phenomenon) responsible for thermal decomposition of organic, organomineral and mineral components. Thermal transformations of bitumens and other substances with the formation of resins most intensively occur within this temperature range; in addition, humate transformations occur, and the process of clay substance dehydration reaches a maximum at these temperature values. Within the temperature range of 550–700 °C the DTA curves exhibit an exothermic the effect caused by the carbonization of organic substance with the formation of aromatic structures. The mentioned effect, to all appearance, masks the endothermic effect of quartz polymorphic transformation expected at 573 °C. The endothermic effect at 740 °C accompanied with mass loss could be caused by the decomposition of calcium humates and partly of free fine dispersed calcium and magnesium carbonates. The exothermic the effect at the temperature of 800–950 °C corresponds to the decomposition of clay minerals [6]. The total mass loss for the sample of silica-containing sapropel amounts to 30.6 %, being equal to 85.6 % for organic sapropel.

The IR spectra (Fig. 3) of sapropel carbonization products exhibit absorption bands those could be attributed to carbonates (1430, 870 cm^{-1}), to sulphates (1100–1000, 670 cm^{-1}), phosphates (1100–1000, 500 cm^{-1}), and C–O–C, C–H, C–OH groups. There are also C=O bonds (1700 cm^{-1}), which allows us to assume the presence carboxylic, lacton-like, ketone groups. Carboxylic and lacton groups were quantitatively determined using the method of selective neutralization [7]. The region of the IR spectrum ranging within 3700–3100 cm^{-1} is inherent in stretching vibrations of various types of hydroxyl groups. Presumably, the band centred at 3650 cm^{-1} could be attributed either to isolated C–O–H groups, or to silanol groups Si–O–H [8, 9] those can efficiently bind heavy metals like ion exchange.

Determining the physicochemical characteristics of sorbents

The adsorption isotherm characterizes the porous material structure and allows one to determine a number of its properties. The sorbent obtained *via* the carbonization of silica-containing sapropel 700 °C exhibits the adsorption isotherm for nitrogen with a capillary condensation hysteresis loop (Fig. 4). This fact indicates that the adsorption occurs like capillary condensation and, hence, that there is a significant fraction of mesopores in the structure of the sample under investigation. Besides the mesopores, micro pores have been determined in a small amount, their volume being equal to less than $1 \cdot 10^{-3}$ cm^3/g. The volume of micropores on the sorbent obtained by carbonization of organic sapropel at 700 °C, amounts to $4 \cdot 10^{-3}$ cm^3/g.

Using the method of mercury porosimetry we established the specific surface area, total pore volume, pore size distribution, average pore radius for carbon-mineral sorbents synthesized at 700 °C (Table 2). One can see that the carbonization products of silica-containing

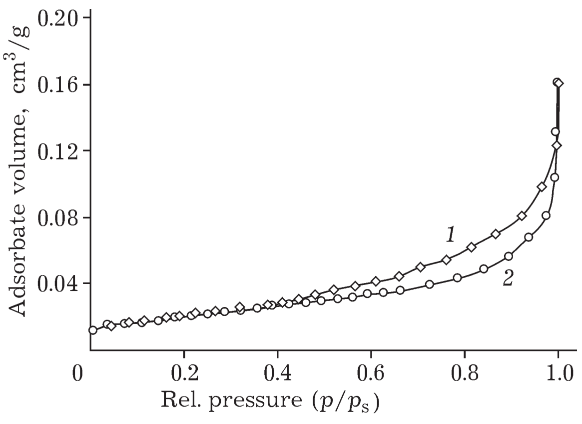

Fig. 4. Isotherms of nitrogen desorption (*1*), adsorptions (*2*) for carbon-mineral material obtained *via* silica-containing sapropel carbonization (T_{carb} = 700 °C).

TABLE 2

Textural characteristics of carbon-mineral sorbents synthesized at 700 °C

Initial sapropel	Stage of sorbent synthesis	S_{sp}, m^2/g	Total pore volume, cm^3/g	Average pore radius, nm	Pore size distribution, %	
					Mesopores	Macropores
Silica-containing	Carbonization	50	0.25	100	40	60
Organic	Carbonization	100	0.75	1000	0	100
Organic	Carbonization and activation	170	0.83	700	25	75

sapropels are meso/macroporous, whereas the carbonization products of organic sapropels are macroporous. Carrying the reacting substances within materials with large pores occurs due to molecular diffusion that facilitates the reagents' penetration deep into a grain and makes the rate of the reaction to increase as compared to microporous sorbents (for example, activated coal). An additional activation of carbonized organic sapropel by steam at 700 °C (up to the burn level of 17 %) results in increasing the total volume of pores up to 0.83 cm^3/g as well as in changing the pore size distribution function.

It is established that the sorbents obtained via carbonization of silica-containing sapropel exhibit a greater packed density value (810 kg/m^3) than the sorbents resulted from organic sapropel (305 kg/m^3) due to the fact that mineral components prevail therein as compared to carbon components. Due to this fact the strength level for the sorbents resulted from silica-containing sapropel is higher than for the analogues made of organic sapropels (65 and 59 kg/cm^2, respectively).

Studies on the sorptive power of sorbents

The sorbents obtained at various temperatures were investigated for adsorption capacity with respect to methylene blue and iodine (Fig. 5). With the increase in the carbonization temperature from 500 to 800 °C for the sorbents resulted from organic sapropels we observed an increase in the adsorption capacity (for methylene blue up to 18 mg/g, for iodine up to 75 mg/g), which could be explained by an increase in the specific surface area from 14 to 176 m^2/g. For the sorbents obtained from silica-containing sapropel, the adsorption the capacity with respect to methylene blue almost does not change with changing the temperature of carbonization being equal to 20 mg/g, whereas this value for iodine reaches a maximum (45 mg/g) at 800 °C. Thus, the optimum temperature value for the carbonization of organic and silica-containing sapropels, determined according to the adsorption data, amounts to 700–800 °C. An additional activation of carbonized products up to burn level equal to 3–17 % (depending on the type of initial material) results in increasing the adsorption capacity value with respect to methylene blue from 18.0 to 18.9 mg/g, and with respect to iodine from 74.5 to 85.6 mg/g, *i.e.* only by 5–15 %. In this connection, it is worthwhile to use for wastewater treatment a more accessible and cheap carbonized sorbent instead of an activated sorbent.

The sorptive power of the sorbents obtained from silica-containing and organic sapropels was determined with respect to organic substances by the example of mineral oil (diesel fuel of "Letneye" trademark, Sibneft Co.), phenol,

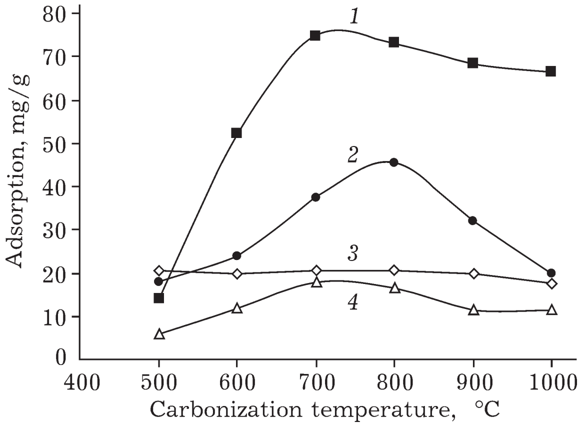

Fig. 5. Adsorption of iodine (*1*, *2*) and methylene blue (*3*, *4*) depending on the temperature of carbonization on the sorbents: *1*, *4* – resulting from organic sapropel; *2*, *3* – resulting from silica-containing sapropel.

TABLE 3

Adsorption of metal ions and organic substances onto the sorbents obtained by sapropel carbonization

Initial sapropel	T, °C	Adsorption, mg/g					
		Cu^{2+}	Ni^{2+}	Cr^{3+}	Mineral oil	Surfactants	Phenols
Silica-containing	700	24.0	20.0	34.0	45.1	31.0	4.5
	800	17.7	20.7	32.2	45.3	30.5	4.0
Organic	700	9.5	8.8	10.2	43.5	25.0	1.0
	800	9.5	7.0	10.5	42.7	25.3	1.3

anion-active surfactant (sodium dodecyl sulphate) and of heavy metal ions (Cu^{2+}, Ni^{2+}, Cr^{3+}). The sorbents obtained *via* the carbonization of silica-containing of sapropels are characterized by a higher capacity, both with respect to organic substances, and heavy metals (Table 3). A good adsorption with respect to large molecules and polar compounds onto a carbon-mineral adsorbent made of silica-containing sapropel could be caused by a great volume of mesopores and a great number of polar groups on the surface. For the further experiments, we used a sample of the sorbent obtained by the carbonization of silica-containing of sapropel at 700 °C.

The capacity of the mentioned sapropel sorbent with respect to heavy metals and organic substances was investigated depending on the solution pH (Fig. 6). One can see within the range of pH 1–6 the adsorption level of organic substances remains constant, the adsorption level of heavy metals grows up to pH 4 and with the further growing pH (from 4 up to 6) almost does not change. Figure 7 demonstrates the adsorption isotherms for copper, nickel, chromium, mineral oil, surfactants, phenol onto the sorbent chosen. The analysis of the data within the framework of known models demonstrated that the adsorption of heavy metal ions, phenol and surfactants is well described by the Langmuir equation, whereas that for mineral oil is described by the Freundlich equation. The limiting capacity of the sorbent with respect to surfactants amounted to 31.0 mg/g, being of 4.5 mg/g for phenol, and 20.0, 24.0, 34 mg/g with respect to nickel, copper and chromium (III) ions, respectively.

The results of kinetic studies have demonstrated that the adsorption equilibrium is es-

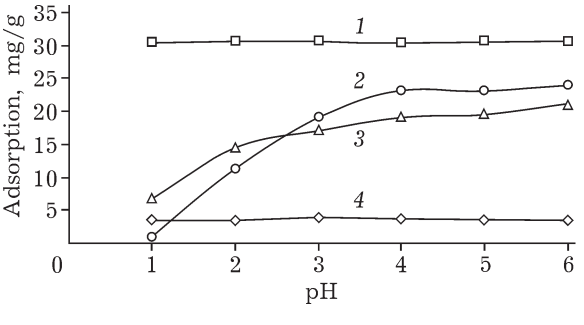

Fig. 6. Dependence adsorption of heavy metals and organic substances on the sorbent resulting from silica-containing sapropel (T_{carb} = 700 °C) depending on the solution pH: *1* – surfactants, *2* – copper, *3* – nickel, *4* – phenol.

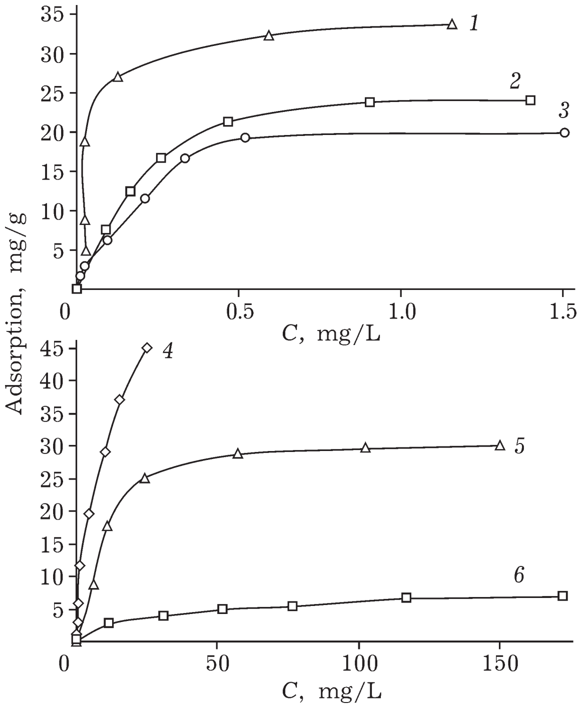

Fig. 7. Adsorption isotherms for chromium (*1*), copper (*2*), nickel (*3*), mineral oil (*4*), surfactants (*5*) and phenol (*6*) on the sorbent resulting from silica-containing sapropel (T_{carb} = 700 °C).

tablished for 10 h under the sorption of heavy metals, being established under the sorption of organic substances during 1–2 h.

The sorption of mineral oil and copper ions was performed from individual solutions onto the sapropel sorbent obtained *via* the carbonization of silica-containing sapropel at 700 °C, under dynamic conditions with a static layer of the sorbent. The initial solution contained 0.10 mg/mL of copper, at pH 4. The operation capacity (up to breakthrough) of the sorbent with respect to copper ions was equal to 4.0 mg/g; the total dynamic capacity amounted to 24 mg/g. The analysis of the data obtained in the course of dynamic capacity determination demonstrate that the first 80 mL of the solution output from the adsorption column, were additionally purified up to the MPC value. The minimum concentration of copper determined by means of the used photometric technique under use amounts to 0.03 mg/L, which is lower than the MPC for copper ions (1.0 mg/L) in water reservoirs for drinking and household water use. The determination of the dynamic capacity with respect to mineral oil was carried out under similar conditions; the initial solution contained 100 mg/L of dissolved mineral oil. According to the results of the experiment we calculated the operation capacity of the sorbent to be equal to 8.5 mg/g. The first 140 mL of the solution at the outlet from the adsorption column were purified up to the mineral oil MPC level recommended for fish industry reservoirs (0.050.1 mg/L).

Basing on the data obtained one can conclude that there is a possibility of using the sorbent resulted from carbonized silica-containing sapropel for wastewater purification both from organic substances, and from heavy metals. Due to the presence of mineral substances and carbon, the sorbent made of sapropel exhibits bifunctional properties to provide comprehensive purifying from pollutants of different nature. The sapropel represents one of few reproduced kinds of minerals spread almost everywhere over the territory of Russia [10]. The extraction and use of sapropel could prevent the progressing processes of bogging and would promote restoring the hydrological regime of lakes.

CONCLUSION

1. The carbonization of sapropel at the temperature of 700–800 °C can be resulted in obtaining a carbon-mineral sorbent for comprehensive wastewater treatment from a great variety of substances.

2. Using the methods of XRD phase analysis, IR spectroscopy, thermal analysis it is established that sapropel sorbents besides carbon are composed of quartz, feldspars, clay, amorphous silica. On the surface of the sorbent there are functional oxygen-containing group identified; they are silanol, hydroxyl, carboxyl, lacton groups.

3. It is demonstrated that a carbon-mineral material obtained via the carbonization of silica-containing sapropel in an inert medium, is meso/macroporous (R_{av} = 100 nm), whereas the carbonization of organic sapropel results in forming a macroporous material (R_{av} = 1000 nm), with insignificant amount of micro pores in both types of sorbents. The mechanical strength of sorbents with respect to crushing amounts to 59–65 kg/cm^2.

4. It is demonstrated, that for sapropel sorbents the adsorption of methylene blue amounts up to 20 mg/g, and that of iodine is equal to 76 mg/g.

5. The sorbents obtained *via* the carbonization of silica-containing sapropels, are characterized by a higher adsorptive power, both with respect to organic substances, and with respect to heavy metal ions. The limiting capacity of sorbents made of silica-containing sapropels amounts to 31.0 mg/g for surfactants, 4.5 mg/g for phenol, 20.0 mg/g for nickel ions, 24.0 mg/g for copper ions, 34 mg/g for chromium (III) ions.

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