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Investigation of Oxidized and Modified Carbon Materials as Mercury Sorbents

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Abstract

An investigation of the oxidized and modified carbon materials and sorbents around them has been carried out by physicochemical methods (electron microscopy, thermoanalysis, X-ray diffraction, and IR spectroscopy). The processes of mercury sorption to the new modified carbon sorbents under static and dynamic conditions are studied with model solutions and processing media. It has been found that adsorption capacity for mercury depends on oxidation state of the carbon surface and on the properties of the introduced modifier.

INTRODUCTION

The widespread use of mercury in chemical industry, while obtaining alkali metals hydroxides and chlorine, leads to contamination of the recycled water and sewage wastes, together with air.

It is common knowledge that metallic mercury is highly toxic in respect to any form of life (MPC of mercury in the air of the work zone comprises 0.01 mg/m^3, 0.0003 mg/m^3 in the outer air, 0.0005 mg/l in the water of reservoirs, 2.1 mg/kg in ground; the 1st grade of danger is stipulated) [1]. Ecological consequences are most distinctly evidenced in aqueous medium where, due to ingress of toxicants, the life activity of single-celled seaweeds and fishes is suppressed, photosynthesis is disturbed, accumulation of nitrates, phosphates, ammonium compounds, *etc.* occurs, and water body pollution becomes so tangible that this results in destruction of water bodies and has an effect on the human health.

In this connection, all the manufactures based on application of a great deal of mercury in the technological processes use and develop treatment technologies for purification of sewage and processing media from mercury. One of the parts of the complex decontamination of processing media and sewage is adoption of adsorption processes [2].

Application of these processes requires creation of the mercury-selective sorbents characterized by the large saturation capacity, mechanical strength, readily available regeneration processes, and economic feasibility [3–9].

We have chosen synthetic carbon-carbon composites as a basis for creating the new sorbents, since they are relatively inexpensive, show high reagent resistance, mechanical strength, developed specific surface, and exchange capacity comparable with those for resins [10–12].

One of the first solid sorbents suggested for absorption of mercury vapours from air was absorbent carbon [13] capable to adsorb up to 5–7 mass % of mercury under static conditions. However, in dynamic conditions absorbent carbon is ineffective at anywhere near significant gas flow rates [14].

Saturation capacity of absorbent carbon can be increased through oxidation of carbon surface and by incorporation of various modifiers. For example, there are known methods to produce sorbents based on the absorbent carbon processed with oxidizers (with $KMnO_4$, chlorine, nitrogen oxides) [15–20], or by means of adding of ferric chloride [21–23], oligomers of vinyl chloride [24], chlorinated derivatives of diantipyrilmethane or antipyrine [25], sulphur and hydrogen sulphide [26].

In the process of treatment of active coals with various oxidizers (nitric acid, hydrogen peroxide, sodium hypochlorite), carbon surface fixes up to 15–25 % of oxygen with the formation of a variety of oxygen-containing functional groups, specifically, hydroxyl, carboxylic, phenolic, carbonyl, lactone ones, *etc.* [27]. Such oxidized coal containing coordinatively unsaturated oxygen atoms can fix rather strongly ions of metals, capable to complex formation, into superficial inner-complex compounds of chelate type. Binding strength in these superficial complexes is such that the oxidized coal can extract appropriate ions (first of all, ions of heavy metals) from complex mixtures, including the ones in which these elements are bound, for example, inside the less strong anionic complexes [8, 28].

Hence, besides the pattern and structure of carbon material (CM), the processes of modification (of oxidation, introduction of complexing agents) have significant effect upon its sorption value.

The purpose of the present work is to study these processes for creating the new mercury-selective carbon sorbents.

Studying the oxidized and modified carbon sorbents was conducted by methods of electronic microscopy, potentiometric titration, thermal analysis, X-ray phase analysis, Fourier IR spectroscopy.

Investigation of the process of mercury sorption by carbon sorbents with the model solutions and processing media was conducted under static and dynamic conditions.

The special attention was paid to IR spectroscopy method for studying the composition of functional groups, arising on the carbon surface during the oxidation, since carbon sorbents are poorly studied by this method because of an optical opaqueness of CM. The big loss of infrared radiation due to dispersion and continuous background absorption of sorbents results in that with usual technique of taking the spectrum, absorption IR spectra either cannot be got at all, or poor resolution spectra are obtained with the small intensity of bands [29], interpretation of which presents a problem. More encouraging results have been achieved last years when IR spectra were taken with the use of the new Fourier spectrometers. This has allowed absorption spectra to be obtained and functional groups of carbon materials to be interpreted with the samples of absorbent carbons [30–34].

EXPERIMENTAL

The CM used in this work represented synthetic carbon-carbon composite material of "Tekhnosorb" mark (TU (technical specifications) 3841514, manufactured by Omsk KTI-TU) with the following specifications: particle size of 0.5–0.7 mm, specific surface 440 m^2/g, volume weight of 0.5 g/cm^3, total volume of pores 0.7–1.1 cm^3/g, volume of mesopores 0.5 cm^3/g, content of impurities (mass %): Fe 0.125–0.15, Al 0.025–0.035, Si 0.005, K 0.06–0.075, Ca 0.125–0.15.

Oxidation of carbon material by nitric acid

The batch of CM (100 g) was brought into a heat-resistant glass or glassy-carbon beaker with the capacity of 1000 cm^3, then 200 cm^3 of nitric acid solution (1 : 1) were added progressively under stirring. Then heating of suspension on the hot plate was conducted for 1–4 h at a temperature of 100 °C. Heating occurred with release of nitrogen oxides. Then the reaction mixture was cooled up to ambient temperature, 200 cm^3 of distilled water were added, and filtration of CM suspension was performed through the "yellow ribbon" paper filter. A deposit was washed out with distilled water to neutral reaction of the filtrate, dried up at a temperature of 150 °C for 1.5–2 h, and then it was used as a starting material to yield calcium and sodium selective sorbents.

Oxidation of carbon material by hydrogen peroxide

A batch of CM (100 g) and 250 cm^3 of 10 % solution of hydrogen peroxide were brought into a glassy-carbon or glass beaker of capacity 1000 cm^3 under stirring. On hydrogen peroxide introduction, one could observe a warming up of the mixture with the release of gas. The suspension volume increased threefold. Upon termination of gassing, CM suspension was filtered through the “yellow ribbon” paper filter, washed out with distilled water, and dried up at a temperature of 150 °C for 2 h.

Likewise, CM was oxidized by sulphuric acid, by mixture of sulphuric and nitric, nitric and fluoric acids, by lithium hypochlorite. The highest oxidation state of carbon surface is observable on CM treatment with the mixture of nitric and sulphuric acids. Oxidation proceeds so vigorously that initial CM structure ruptures. The process of CM oxidation by hydrogen peroxide (10 %) and nitric acid (1 : 1) solutions turned out to be the most adaptable commercially and nondestructive one.

For oxidized CM, the total ion-exchange capacity with 0.1 M NaOH solution has been determined by means of potentiometric titration (Table 1). The process of oxidation by nitric acid for 240 min, which results in the greatest value of total exchange capacity of 4.32 mg-eq/g, was demonstrated to be a preferable one. With an increase in time of oxidation of carbon surface, an increase in CM exchange capacity is observed.

TABLE 1

Exchange capacity of oxidized CM

Oxidizer	Oxidation time, min	Exchange capacity, mg-eq/g
HNO_3	20	2.60±0.04
	60	3.50±0.05
	240	4.32±0.066
H_2O_2	20	0.43±0.007
	60	2.16±0.033
	240	1.08±0.02

Modification of carbon material

We used I_2, Cl_2, Br_2, 1 M HCl solution, and $CH_3COCH_2COCH_3$ as the modifiers to obtain the new modified carbon sorbents (NMCS), specifically, NMCS-I, NMCS-Cl, NMCS-Br, NMCS-IHCl, and NMCS-HAA, that are advantageous for mercury fixation in ionic and metallic states.

Obtaining of NMCS-I sorbent. The batch of CM (5 g) was put into a glass beaker, then was covered with 50 ml of 10 % alcohol–iodine solution and covered by a clock glass. After 24 h the remainder of alcohol-iodine solution was distilled off, the sorbent was air-dried. Iodine content was determined by titrimetric method with sodium thiosulphate and was equal to 9.96 %. NMCS-I sorbents were obtained with iodine content of 5, 10, 15, and 20 %.

Obtaining of NMCS-Cl sorbent. The batch of CM (20 g) was saturated with gaseous chlorine for 3 h. Chlorine content was 0.8 %.

Obtaining of NMCS-Br sorbent. The batch of CM (5 g) was soaked with 2 ml of liquid bromine, and air-dried for 24 h. Bromine content was 17 %.

Obtaining of NMCS-IHCl sorbent. The batch of CM (5 g) was covered with 1 M HCl solution, allowed to stand for 24 h, then filtered off and air-dried up.

Obtaining of NMCS-HAA sorbent. The batch of CM (5 g) was covered with acetylacetone and was conditioned in exiccator for 36 h, then an excess of acetylacetone was distilled off in the air atmosphere. Acetylacetone content was 15 %.

To determine the value of adsorption capacity of the obtained sorbents for mercury in static conditions (static capacity (SC), in mg/g), solutions of mercury (II) nitrate, chloride, and bromide with the concentration of 100–101 mg/l determined by the atomic absorption spectroscopy (AAS) method were applied. Solutions of mercury (II) nitrate and chloride were obtained by dissolving of mercury (II) oxide in the solutions of appropriate acids.

To determine dynamic capacity (DC, in mg/g) of the same sorbents, the processing media with mercury content of 0.2–1.5 mg/l, chloride ion content of 0.2–0.3 g/l, and lithium content of 0.15 g/l were used. The pH value of the solution varied from 3–4 to 11–12.

Analytical methods

Thermoanalytical study. The analysis was conducted with derivatographs of Setaram company and Q-1500D system of Paulik–Paulik–Erdey (MOM company, Budapest, Hungary).

A batch of a sorbent (50–100 mg) was pounded in the mortar until a fine homogeneous powder was obtained, and then put in the weighed platinum crucible. The covered crucible with the batch was weighed and placed on the holder of a working sample of derivatograph. A covered platinum crucible, approximately two-thirds full of aluminium oxide, was placed on the holder of sample of comparison. The holder of samples of the derivatograph was covered with a quartz beaker. The working space of the derivatograph was blown through with helium. Analysis conditions: heat rate of 5 °C/min, DTA channel sensitivity 0.5 mV, DTG 1 mV, balance sensitiveness 100 mg, temperature range 0–1000 °C, chart speed of 2.5 mm/min.

Positioning of zero lines was made individually for each channel (%): TG 90–95, DTA 30–35, DTG 75–80, T – according to ambient temperature. As the temperature of the beginning of thermal decomposition has been reached, the pattern of curves on the chart belt changed drastically. The sample loses weight, and a peak is being registered in the DTG curve. The termination of process is determined from flattening out of this curve.

X-ray phase study. The analysis of samples of sorbents was conducted on diffractometer Philips APD 1700. Analysis parameters: $Cu_\alpha = 1.54051$ Å, the range of angles $2\theta = 3.6$–110°, a step of 0.03°. The set of impulses for samples was: up to 26 100 for the most intensive reflex for initial CM; up to 35 800 for the CM oxidized by nitric acid, 7800 for NMCS-I (I_2), up to 6200 for mercury-bearing NMCS-I (I_2). For plotting the difference diffractogram, the diffractogram of CM (initial) was subtracted from the diffractogram of the sample under study, this diffractogram being previously normalized to the intensity corresponding to the initial CM:

$I(2\theta)^{III} = aI(2\theta)^{I} - bI(2\theta)^{II}$

where $I(2\theta)^{I}$ is the intensity in the corresponding point on the diffractogram of the sample under study; $I(2\theta)^{II}$ is the intensity in the corresponding point on the diffractogram of CM (initial); $I(2\theta)^{III}$ is the intensity in the corresponding point on the difference diffractogram; a and b are the associated normalizing constants, the values of which are given below:

Substance	a	b
CM oxidized with HNO_3	0.729	1.0
NMCS-I (I_2)	3.360	1.0
NMCS-I (I_2) + Hg	4.243	1.0

Electron microphotos were made with an electron microscope (SEM, type BS-350, Tesla, magnification 5000–50 000).

IR absorption spectra were obtained with IFS-66 Bruker Fourier spectrometer in the range 80–4000 cm^{-1}. The procedure of samples preparation was a standard one: the samples were pounded up to a fine-dispersed state, and then pressed into the KBr powders (detection range of IR spectra 400–4000 cm^{-1}) or into polyethylene powders (the range of 80–450 cm^{-1}). A ratio of weights (in mg) sample : matrix was 1(1.5) : 150 in the case of KBr and 5 : 50 in the case of polyethylene. Contrary to typical IR spectrometer (for example, Specord IR-75), the Fourier spectrometer makes available IR spectra of these samples by means of the computer programs, which allow performing the spectrum smoothing, correction relative to the base line, and accumulation (256–512 scans).

Investigation technique

Static conditions. All experiments were conducted at ambient temperature (20 ± 5) °C, batches of sorbents and solution volumes were constant and equal to (100 ± 2) mg and 100 ml. Sorption processes were performed with stirring on magnetic stirring machine MM2a at rotation speed of 300 min^{-1} (further increase in the speed of an agitator is undesirable because of the strong abrasion of sorbents) in 250 ml volumetric flasks, 75 mm in diameter; time of contact (with periodic stirring) was 1–3 days. Upon termination of the experiment, phase separation was performed by decantation of the solution into a funnel onto the “green ribbon” paper filter; the solution on the filter was acidified to pH 2 by several drops of nitric acid and then was filtered off. Mercury concentration inside the solutions before and after sorption was determined by the AAS method with gold sorbent applied.

Dynamic conditions. Dynamic experiments were conducted with the adsorption columns of diameter 11 mm, with the height of sorbent layer 5–50 cm. An eluating speed was set at 100–500 ml/h. Delivering of sewage into a column was performed at the top, from the gravity tank. The sampling for residual mercury content was made in 100–500 ml intervals of the sewage passed. Determination of mercury concentration in the processing media was made before and after sorption by the AAS method.

RESULTS AND DISCUSSION

Research of CM employing electron microscopy has suggested that the particles of CM have the size of the order of magnitude of 70 000 Å. Electron microphotos (Fig. 1) show the layered structure of CM. Lighter particles of modifiers (chlorine, iodine) of size 200–1000 Å are clearly visible on the layered surface. The surface of microparticles of the material is similar to asphalt, which is made from strongly bound porous formations of nearly ordered shape, 2000–5000 Å in size. There are small and large deep holes with diameters from 30–50 to 200 Å in these formations.

Data of thermoanalytic study (Fig. 2, *a)* of initial CM suggest that CM is stable in the air environment up to 534 °C; the weight loss is as little as 1.8 % that is due to sorbed moisture. The main loss of weight of a sample is caused by carbon oxidation and its transformation into gaseous products (CO or CO_2), which occurs with the intensive wide exoeffect that begins at the temperatures higher than 534 °C.

The thermogram of the CM oxidized by hydrogen peroxide suggests that oxidation process has an influence on the temperature of the maximum development of exoeffect, and lowers this temperature by 10 °C (see Fig. 2, *b*). Oxidation of CM by nitric acid (240 and 360 min) lowers the temperature of the maximum development of exoeffect to 483.7 and 415.4 °C, respectively (Fig. 3, *a*, *b*). Calculation of the weight loss in the thermogram of the CM oxidized by HNO_3 for 240 min shows that at 115 °C, ΔM amounts to 1.14 %, and up to 483.7 °C, does 2.59 %. As the time of oxidation is increased to 360 min, the weight loss increases to 5.375 % (the temperature interval 109.6–415.4 °C). Hence, in the process of oxidation, on the one hand, the accumulation of oxygen-containing superficial groups occurs on the carbon surface; on the other hand, thermal stability of CM decreases.

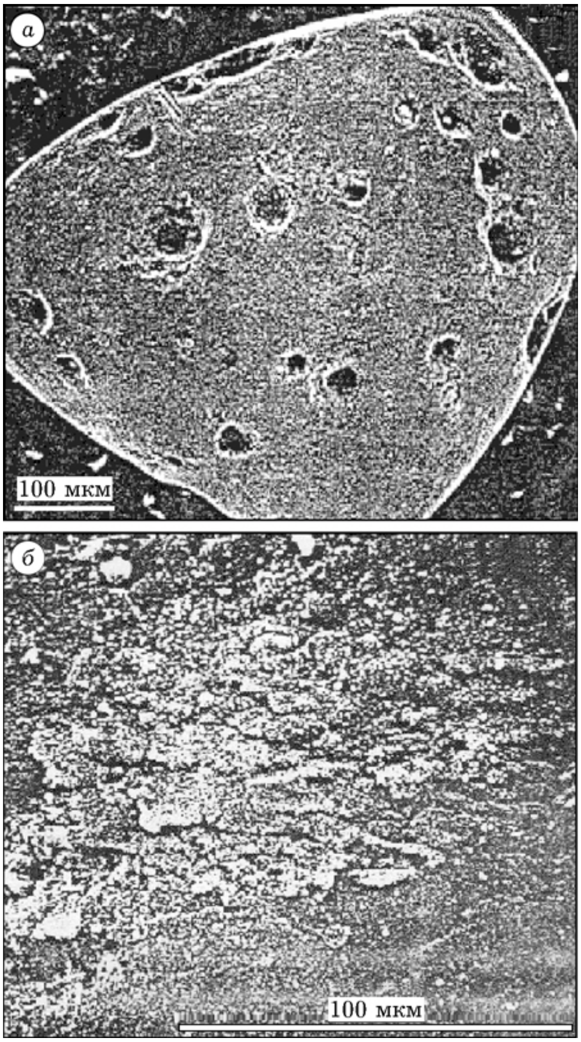


Fig. 1. Electron microphotos of particles of carbon material of the “Tekhnosorb” mark.

X-ray phase investigation of the initial CM oxidized by nitric acid, modified by iodine, and saturated with mercury, and investigation of NMCS sorbents have demonstrated the following: diffractograms (Fig. 4) show a wide diffraction maximum with (002) index, which can be associated with an orderly graphite-like phase available [35]. The interplane distance d_{002} varies within the limits of 3.559–3.574 Å. The strain degree in the packing of carbon assemblies was estimated according to [37] from the h/l ratio, where h is the height of (002) maximum, and l is the width at its half maximum. For initial CM and NMCS-I (I_2), the

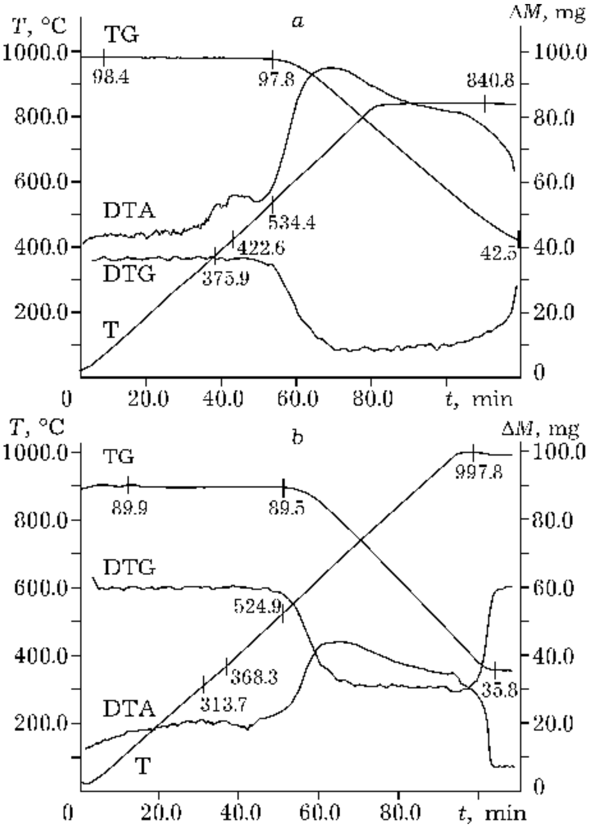


Fig. 2. Thermograms of initial carbon material of "Tekhnosorb" mark (*a*) and of the carbon material oxidized with hydrogen peroxide for 20 min (*b*). M_0 = 55.0 mg.

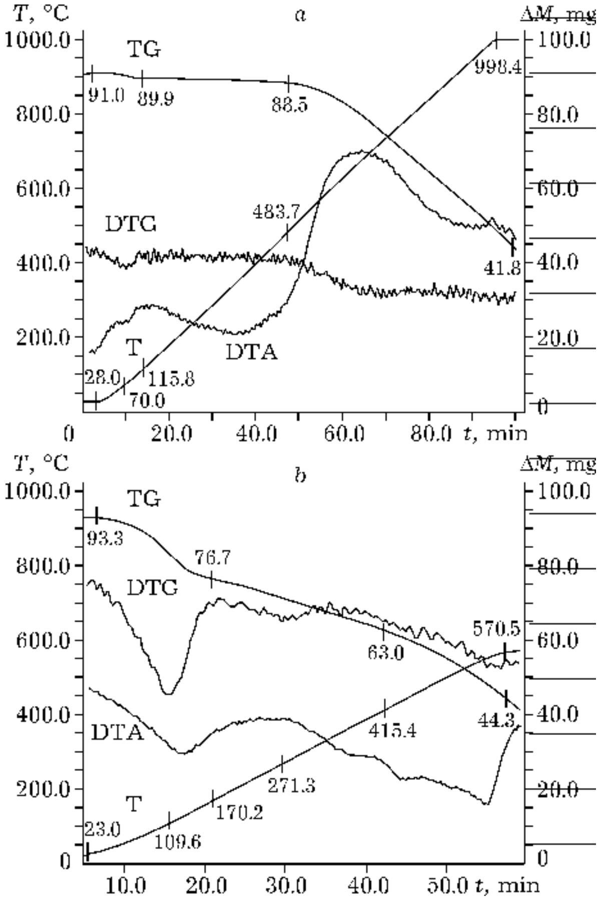


Fig. 3. Thermograms of CM oxidized with HNO_3 for 3 (*a*) and 6 h (*b*). M_0, mg: 96.4 (*a*), 563.7 (*b*).

strain degrees are equal and comprise 20.25; the strain degree increases to 26.67 in the case of CM oxidation by nitric acid; saturation of NMCS-I sorbent (I_2) by mercury results in ordering of structure and decreasing the strain degree up to 15.6. In addition, lowering of reflections intensity in going from initial CM to the one modified by iodine, and saturated with mercury (27 500, 7800, 6000 relative units) is registered in the diffractograms.

The performed analysis of difference diffractograms (Fig. 5) shows the presence of iodine in CM in the difference diffractogram of NMCS-I (I_2). In the case of mercury-containing sorbent NMCS-I (I_2 + Hg), the difference diffractogram is more complex, the head reflection is observed, which represents a superposition of, at least, three reflections at 38.5, 40.0, 47.7 – 2θ. Correlation with the reported diffractograms for Hg I_2 and Hg_2I_2 compounds suggests that mercury, with the big

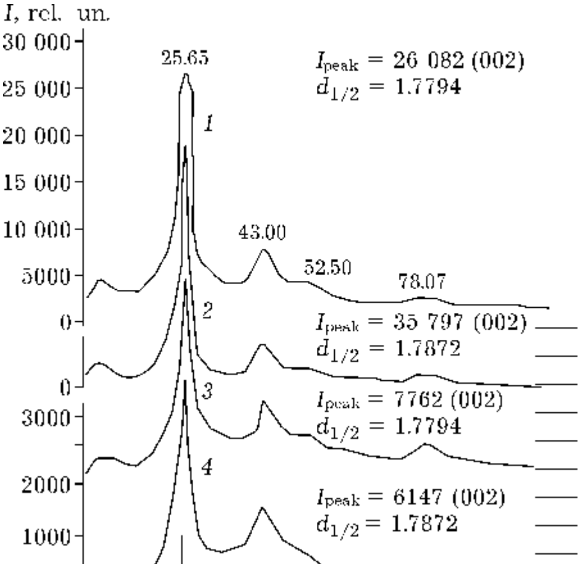


Fig. 4. Diffractograms: *1* – initial CM; *2* – CM oxidized by HNO_3; *3* – NMCS-I, 9.96 % iodine; *4* – the same, 9.96 % iodine, 15.2 % mercury; *5* – graphite.

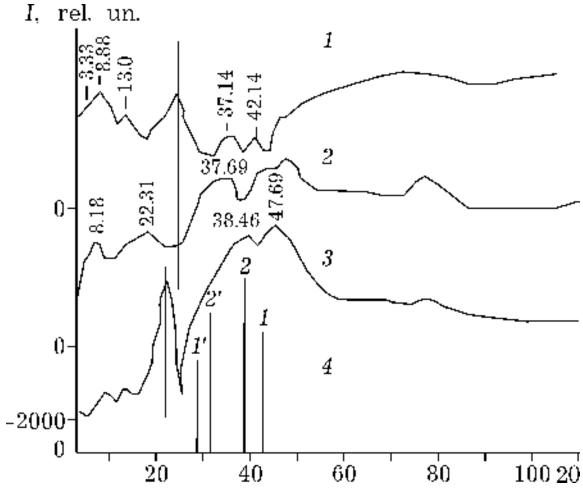


Fig. 5. Difference diffractograms: *1* – CM oxidized by HNO_3; *2* – NMCS-I, 9.96 % of iodine; *3* – the same, 9.96 % of iodine, 15.2 % of mercury; *4* – Hg_2I_2 (*1'*), HgI_2 (*2'*).

extent of probability, is present on the carbon surface in the form of these compounds.

Studying of initial, oxidized, and modified CM by Fourier IR spectroscopy method has shown the following: the IR spectrum of initial CM in the range 400–4000 cm^{-1} (Fig. 6) shows a very intensive 1582 cm^{-1} band (asymmetric stretching vibration) and a band of moderate intensity at 1443 cm^{-1} (symmetric stretching vibration of the ionized carboxylic group COO^- [33, 37, 38]). Splitting of these bands is indicative of inequivalence of these groups in the sorbent structure. In addition, the spectrum of initial CM contains intensive bands of stretching vibrations of hydroxyl groups OH: 3801, 3518 cm^{-1} [33].

Besides the most intensive 1583 cm^{-1} band of stretching vibration of carboxyl ion COO^-,

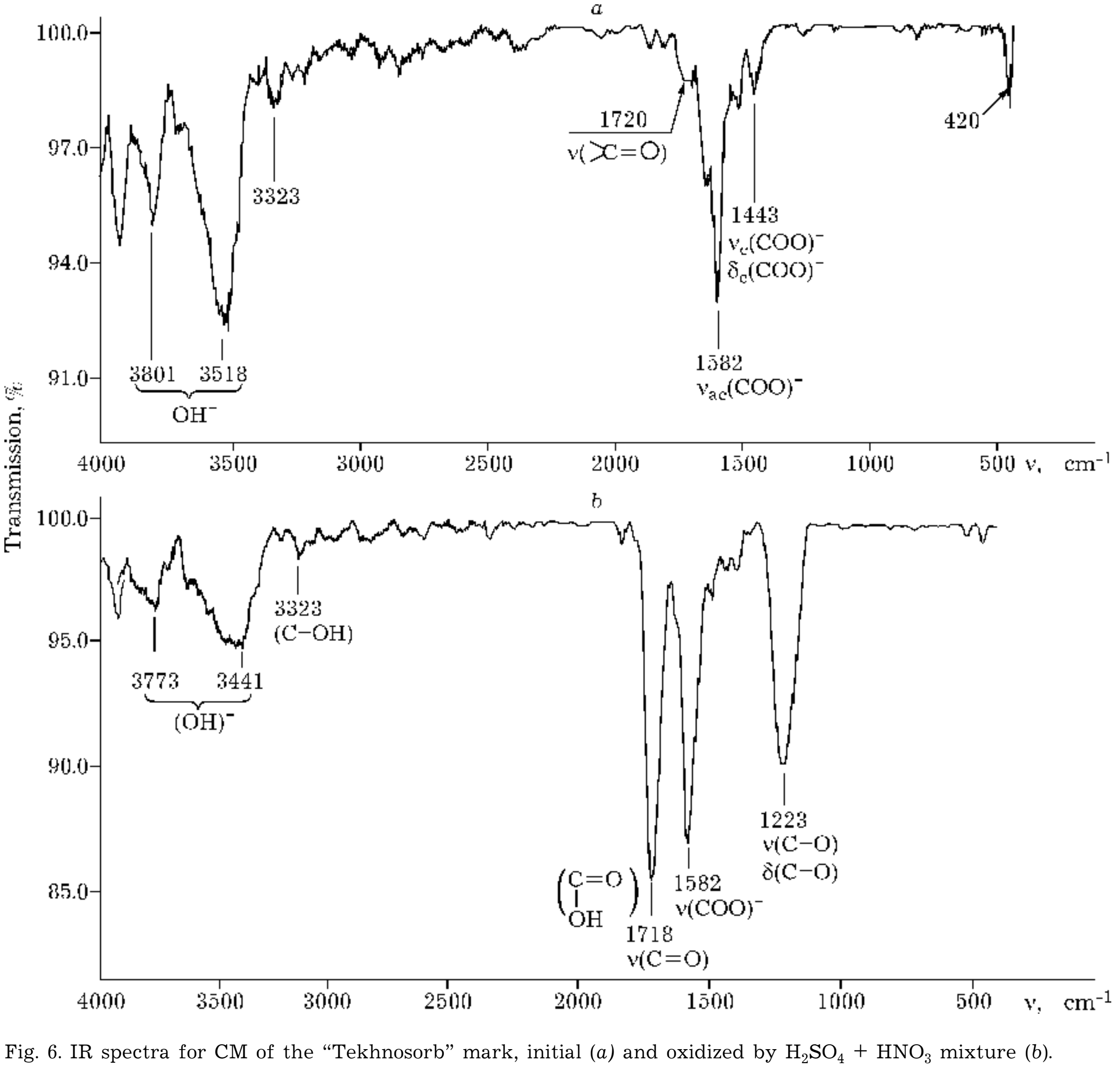


Fig. 6. IR spectra for CM of the "Tekhnosorb" mark, initial (*a*) and oxidized by H_2SO_4 + HNO_3 mixture (*b*).

the bands of carboxylic group CO(OH) in the region of 1718–1770 cm^{-1} (stretching vibrations of C=O bond) and 1223–1260 cm^{-1} (stretching vibrations of C–O bond and deformation vibrations of C–OH groups) [30, 33, 34, 38] appear in the IR spectra of initial and oxidized CM samples (by nitric, sulphuric, saline, fluoric acids with hydrogen peroxide and chlorine, bromine, iodine).

The bands of acidic group are most intensive in the IR spectrum of the CM oxidized by sulphuric acid (see Fig. 6, *b)*, and are the weakest ones in the spectrum of CM treated with 1 M HCl solution. Seemingly, carboxylic acids are formed in oxidation of the CM surface, in much the same manner as an oxidation process of coals [39, 40].

IR spectra of the carbon surface subjected to oxidation contain the bands of different intensity in the region of 3400–3800 cm^{-1} corresponding to the stretching vibrations of OH groups. According to [41], the presence of these bands provides an evidence for the existence of structural hydroxyl groups (in the case of carboxylic acids, C–OH groups) on the carbon surface in the absence of absorption bands of deformation vibrations of wa-

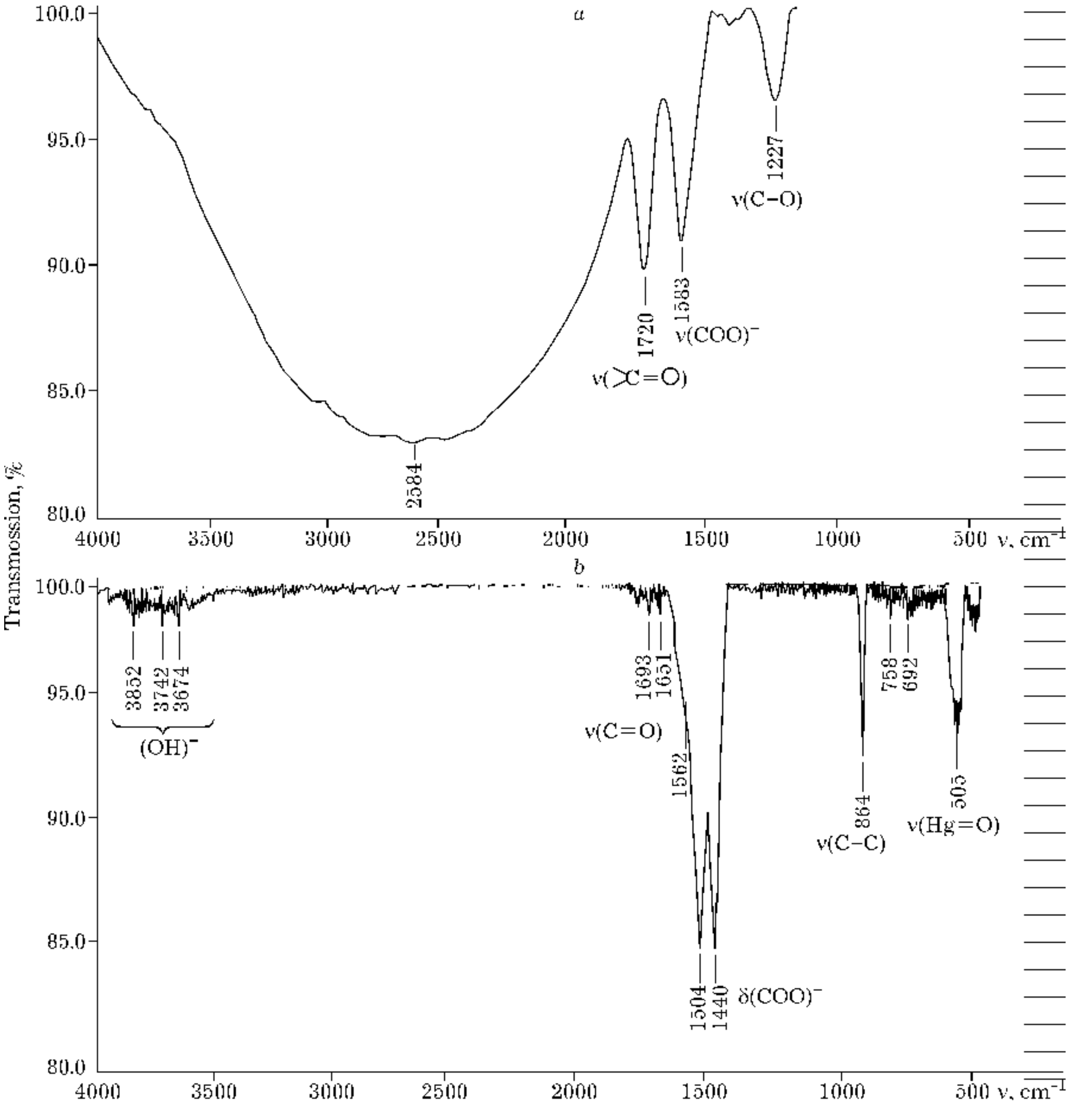


Fig. 7. IR spectra of NMCS-I (*a*) and NMCS-HAA (*b*) sorbents saturated with mercury.

TABLE 2

Experimental data for mercury sorption by the oxidized and modified carbon materials from nitrate and chloride solutions of mercury (II)

Sample No.	Batch m, mg	Oxidation and modification conditions	C_{Hg}^{eq}, mg/l, after sorption from the solution of		SC, mg/g	
			$Hg(NO_3)_2$[a]	$HgCl_2$[b]	$Hg(NO_3)_2$ (samples 1–12)	$HgCl_2$ (samples 1-1–12-12)
1	107.9	Initial CM	101.3±8.11	101.4±8.11	0.2±0.02	0.00
1-1	103.0					
2	100.8	HNO_3 (1 : 1), 20 min	92.6±7.41	74.6±5.97	8.8±0.71	25.7±2.05
2-2	100.1					
3	104.2	The same, 60 min	49.5±3.96	66.1±5.29	49.9±3.99	34.095±2.728
3-3	100.6					
4	99.5	The same, 240 min	55.3±4.42	80.3±7.25	46.4±3.72	20.0±1.60
4-4	100.5					
5	103.3	10 % H_2O_2, 20 min	88.8±7.10	73.3±5.86	12.3±0.98	27.2±2.17
5-5	99.8					
6	102.9	The same, 60 min	100.0±8.00	94.6±7.57	1.5±0.12	2.9±0.23
6-6	101.5					
7	100.5	The same, 240 min	100.0±8.00	92.7±7.42	1.5±0.12	7.7±0.62
7-7	100.1					
8	102.0	1 M HCl solution, 100 °C, 60 min	96.6±7.728	92.8±7.424	4.8±0.38	7.5±0.60
8-8	101.3					
9	100.0	Cl_2 (0.8 %)	96.8±7.744	82.6±6.608	4.7±0.38	17.8±1.42
9-9	100.0					
10	100.0	10 % H_2O_2+ Cl_2 (0.8 %)	100.0±8.00	93.2±7.46	1.5±0.12	7.2±0.58
10-10	100.0					
11	102.2	Br_2 (17 %)	55.6±4.45	45.2±3.62	44.9±3.59	56.3±4.51
11-11	98.0					
12	102.8	I_2 (9.96 %)	66.5±5.32	50.7±4.06	34.1±2.72	48.3±3.86
12-12	102.9					
13	103.8	10 % H_2O_2(20 min)+I_2(9.96 %)	66.4±5.312	14.3±1.144	33.8±2.71	84.5±6.76
13-13	101.9					

[a, b] Initial concentrations C_{Hg}^{eq} are equal to 101.5 and 100.4 mg/l, respectively.

ter (1640 cm^{-1}), as is observed in the IR spectra both for initial and oxidized CM.

It is pointed out that the bands of acidic group are most intensive in the IR spectrum of NMCS modified by iodine, and are the weakest ones in the spectrum of NMCS modified by 1 M HCl solution. The bands of acidic group are missing from the spectrum of the sorbent modified by acetylacetone (NMCS-HAA).

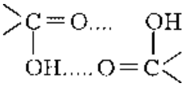
In addition, the bands of different intensity in the region of 3400–3800 cm^{-1} corresponding to stretching vibrations of OH groups are present in the IR spectra of all NMCS.

Upon mercury sorption by the modified sorbents, some changes in the IR spectra were to be expected, which were due to the presence of metal in the samples under investigation, as it is evidenced in the spectra of ion-exchange resins [34, 37, 38] and coals of the various surface nature [38].

In the region 80–450 cm^{-1}, there are no any absorption bands in the IR spectra of initial NMCS and NMCS saturated with mercury, although absorption bands for Hg-Hal (Cl, Br, I), $HgHal_2$, $HgHal_4^{2-}$ have been reported. Expressly prepared samples of sorbents with the greatest possible mercury content did not give rise to the new absorption bands in the IR spectra too. Possibly, this is attributable to polymeric mercury species formed on the carbon surface so that absorption bands of mercury-halogen bond cannot be observed in IR spectra.

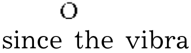
In the region 400–4000 $\mathrm{cm^{-1}}$, an intensive 1583 $\mathrm{cm^{-1}}$ band of carboxyl ion is present in the IR spectra (Fig. 7, *a*) of all samples after mercury sorption, as well as in the IR spectra for initial NMCS, and also the bands of group with an equal ratio of intensities.

However, after mercury sorption, the wide intensive bands with maxima in the region from 3600 $\mathrm{cm^{-1}}$ (for a sorbent modified by Cl_2) to 2500 $\mathrm{cm^{-1}}$ also arise in IR spectra (see Fig. 7, *a*). This bears witness to hydrogen bond formation, which becomes more intensive with the shifting of maximum of these bands in the low-frequency region, *i.e.* carboxylic groups can interconnect by means of the strong hydrogen bonds according to the pattern



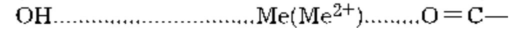
$$\begin{array}{l} >C=O\cdots\quad OH \\ \quad | \qquad\qquad | \\ OH\cdots O=C< \end{array}$$

As a consequence, one may assume the following: the mechanism of mercury sorption to modified (by chlorine, iodine, bromine, by 1 M HCl solution) NMCS is due to functional oxygen-containing superficial groups on the carbon surface. In the case of carboxyl COO^-, supposedly, K^+A^- cation-anion interaction occurs, *i.e.*, $Hg(COO)_2$ is formed. It is pointed out that ionization of carboxylic groups does not occur during mercury sorption; also does not form



$$\mathrm{Me{-}\underset{\underset{O}{\|}}{O}{-}C{-}R,}$$

since the vibration frequency of C–O bond in this case should change and the vibration frequency of Me–O bond should appear. It can be assumed that metal (ion of metal) is an agent for “crosslinking”, that is, dimerization or polymerisation of carboxylic groups according to hydrogen bond pattern and formation of “strongly cross-linked” film on the sorbent surface:



$$\begin{array}{l} -C=O\cdots\cdots Me(Me^{2+})\cdots\cdots HO \\ \quad | \qquad\qquad\qquad\qquad\qquad\qquad | \\ OH\cdots\cdots Me(Me^{2+})\cdots\cdots O=C- \end{array}$$

A completely different pattern is observed in the case of modification of a carbon substrate by acetylacetone (HAA): upon HAA incorporation (saturation) into the initial CM, the absorption bands of carboxylic group are missing from the IR spectrum. IR spectrum of NMCS-HAA saturated with mercury after decontamination of lithium hydroxide solution is presented in Fig. 7, *b*. It is common knowledge that acetylacetone $CH_3{-}CO{-}C{-}CH_2{-}CO{-}CH_3$ is a good complexing agent. It forms chelates of composition $Me(AA)_2$ or $Me(AA)_3$ with metals depending on oxidation state of metal, and is coordinated with metal by means of oxygen. IR spectra of HAA [40] and HAA complexes of the large number of metals are reported [41].

The IR spectrum shown in Fig. 7, *b* represents the spectrum of $Hg(AA)_2$ complex. The assignment of the main absorption bands is made on the basis of work [41]. The most intensive 1504 and 1440 $\mathrm{cm^{-1}}$ bands are asymmetric and symmetric stretching vibrations of C–O bond. Intensity of these bands is such, that they overlap the carbonyl band of sorbent, this band manifesting itself in the IR spectrum as an arm. A band of moderate intensity of 864 $\mathrm{cm^{-1}}$ is the stretching vibrations of C–C bond, and 505 $\mathrm{cm^{-1}}$ band is the vibrations of M–O bond. It should be noted that KAD-iodine coal saturated with acetylacetone has a similar IR spectrum.

Results of the experiments on studying the sorption capacity of oxidized and modified carbon materials from nitrate and chloride solutions of mercury (II) under static conditions are presented in Table 2. The static capacity (SC, mg/g) was calculated from the equation

$$\mathrm{SC} = (C_{\mathrm{Hg}}^{\mathrm{ini}} + C_{\mathrm{Hg}}^{\mathrm{eq}})V/1000/m \qquad (1)$$

where $C_{\mathrm{Hg}}^{\mathrm{ini}}$ is the mercury concentration in the initial solution, mg/l; $C_{\mathrm{Hg}}^{\mathrm{eq}}$ is an equilibrium mercury concentration in the solution after sorption (24 h), mg/l; V is the solution volume (100 ml); m is the batch of CM, g.

From data of Table 2 it follows that initial CM practically does not absorb mercury from nitrate and chloride solutions. Oxidation of the carbon surface involves a gain in sorption capacity for mercury. It has been demonstrated that CM oxidation by nitric acid solution (1 : 1)

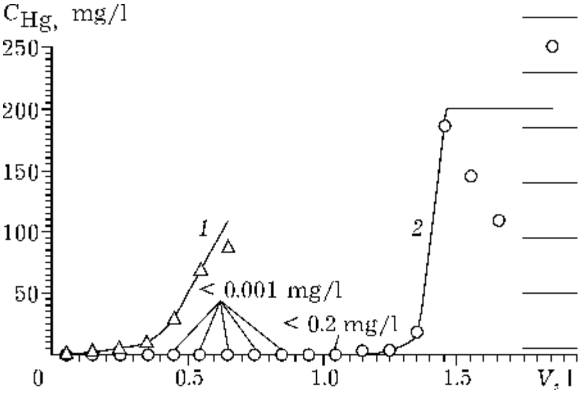


Fig. 8. Mercury absorption by NMCS-I sorbent *versus* its speciation in the solution: *1* – $HgBr_2$ solution, *2* – $Hg(NO_3)_2$ solution, pH 2.

for 60 min results in the maximum value of SC = 49.9 mg/g from mercury nitrate solution. A sharp difference in mercury sorption is noted with the CM oxidized by hydrogen peroxide, chlorine, bromine, and iodine: for $HgCl_2$ solution, the sorption of mercury is much more as compared to $Hg(NO_3)_2$. An increase in sorptive capacity for mercury is observed upon CM modification by chlorine, iodine, and bromine. Higher value of SC for mercury for the CM modified by bromine in comparison with modification by iodine is attributable to a greater content of bromine (17 %), since mercury sorption depends also on the quantity of the modifier. The maximum SC for mercury (from $HgCl_2$ solution) is observed for the CM previously oxidized by hydrogen peroxide and modified by iodine.

In addition, we performed the experiments to study mercury sorption by NMCS-I (the CM modified by iodine) from water solutions of $Hg(NO_3)_2$ and $HgBr_2$. Nitrate solution with mercury content of 200 mg/l was prepared with water acidified to pH 2 and was passed through a column of diameter 11 mm with 2.5 g NMCS-I iodinated by passing 3 l of iodine water solution with the concentration of 200 mg/l through this NMCS-I. Hence, iodine concentration in NMCS-I was 240 mg/g. Fresh $HgBr_2$ was dissolved in 0.001 M HBr solution so that mercury concentration was likewise 200 mg/l, and the solution was passed through an analogous column. Flow rate was 4 ml/min. Presented in Fig. 8 are the output curves of mercury sorption. Sharp distinction between the curves is related, conceivably, to that $Hg(NO_3)_2$ is the compound well dissociating in water in contrast to $HgBr_2$, in which mercury should exist almost entirely in the form of complex compound under the test conditions. Strong Hg–Br chemical bond in the solution hinders Hg–I bonding, and thereby retards mercury passing from solution to sorbent. The resulting is that

TABLE 3

Data on mercury sorption from the process water wastes by NMCS-IHCl sorbent

Sample No.	Volume of solution passed through *V*, l	C_{Hg} at the outlet, mg/l	Mercury mass, mg		Sample No.	Volume of solution passed through *V*, l	C_{Hg} at the outlet, mg/l	Mercury mass, mg	
			passed through the sornebt	on the sorbent				passed through the sorbent	on the sorbent
4-2	1.0	0.0033± 0.00017	0.845	0.836	4-13	6.5	0.0007± 0.00004	5.493	5.200
4-3	1.5	0.0027± 0.00014	1.268	1.253	4-14	7.0	0.0006± 0.00003	5.915	5.618
4-4	2.0	0.002± 0.0001	1.690	1.673	4-15	7.5	0.0007± 0.00004	6.340	6.037
4-5	2.5	0.002± 0.0001	2.113	2.091	4-16	8.0	0.0013± 0.00006	6.760	6.447
4-6	3.0	0.002± 0.0001	2.535	2.455	4-17	8.5	0.0025± 0.0002	7.183	6.849
4-7	3.5	0.003± 0.00011	2.958	2.770	4-18	9.0	0.0028± 0.0002	7.605	7.245
4-8	4.0	0.002± 0.0001	3.380	3.112	4-19	9.5	0.0033± 0.0002	8.028	7.637
4-9	4.5	0.0013± 0.00006	3.803	3.529	4-20	10.0	0.0042± 0.0002	8.450	8.017
4-10	5.0	0.001± 0.0001	4.225	3.946	4-21	10.5	0.0056± 0.0003	8.873	8.381
4-11	5.5	0.0009± 0.0001	4.648	4.364	4-22	11.0	0.061± 0.003	9.295	8.775
4-12	6.0	0.0008± 0.0001	5.070	4.781					

Note. MDC = 0.399 mg/g (the ratio of the total amount of mercury absorbed by the sorbent, 8.775 mg, to the sorbent batch of 22 g).

TABLE 4

Data on mercury sorption from sewage (pH 10) by NMCS-HAA sorbent
(h = 50 sm, m = 17 g, V = 500 ml/h, ∅ = 11 mm, Hg determination by the AAS method, S_r = 0.2)

Sample No.	C_{Hg}, mg/l	V, ml	C_{Hg} at the outlet, mg/l	Mercury mass in the filtrate, mg
5k-1	0.06	500	0.038±0.008	0.019
5k-2	0.06	1000	0.040±0.008	0.02
5k-3	0.06	1500	0.043±0.009	0.022
5k-4	0.06	2000	0.040±0.008	0.02
5k-5	0.06	2500	0.036±0.007	0.018
5k-6	0.06	3000	0.040±0.008	0.02
5k-7	0.06	3500	0.045±0.009	0.023
5k-8	0.06	4000	0.042±0.008	0.021
5k-9	0.06	4500	0.045±0.009	0.023
5k-10	0.06	5000	0.047±0.009	0.024
5k-13	0.06	6500	0.040±0.008	0.02
5k-14	0.06	7000	0.032±0.006	0.016
5k-15	0.06	7500	0.040±0.008	0.02
5k-16	0.06	8000	0.030±0.006	0.015
5k-17	0.06	8500	0.040±0.008	0.02
5k-18	0.915	9000	0.046±0.009	0.023
5k-19	0.915	9500	0.040±0.008	0.02
5k-20	0.915	10000	0.040±0.008	0.02
5k-21	0.915	10500	0.046±0.008	0.023
5k-22	0.915	11000	0.040±0.008	0.02
5k-23	0.915	11500	0.040±0.008	0.02
5k-24	0.915	12000	0.040±0.008	0.02
5k-25	0.915	12500	0.040±0.008	0.02
5k-26	0.915	13000	0.040±0.008	0.02
5k-27	0.915	13500	0.040±0.008	0.02
5k-28	0.915	14000	0.040±0.008	0.02
				Σ= 0.527

Note. Mercury content on the NMCS-HAA sorbent is defined as 0.06 mg/l · 8.5 l + 0.915 mg/l · 5.5 l − 0.527 mg = 5.033 mg. The effective capacity of NMCS-HAA sorbent under these conditions is equal to 0.3 mg/g.

TABLE 5

Decontamination of sewage (pH 3–4) from mercury by NMCS-Cl sorbent (C_{Hg}^{eq} = 0.06 mg/l, m = 21 g, h = 50 sm, V = 500 ml/h, ∅ 11 = mm)

Sample No.	V, ml	Mercury content at the column outlet C_{Hg}, mg/l
6k-2	1000	0.0023±0.0005
6k-3	1500	0.0034±0.0007
6k-4	2000	0.003±0.00071
6k-5	2500	0.003±0.0007
6k-6	3000	0.004±0.008
6k-7	3500	0.0035±0.0007
6k-8	4000	0.0023±0.0005
6k-9	4500	0.0022±0.0005
6k-10	5000	0.0022±0.0005
6k-11	5500	0.0022±0.0005
6k-12	6000	0.0025±0.0005
6k-13	6500	0.0037±0.0007
6k-14	7000	0.0037±0.0007
6k-15	7500	0.0039±0.0007
6k-16	8000	0.006±0.001
6k-17	8500	0.006±0.001
6k-18	9000	0.0098±0.001

Note. The dynamic capacity of NMCS-Cl sorbent for mercury (before the breakthrough of 0.01 mg/g) is defined as (0.06 · 9 − 0.0387 · 9) : 21 = 0.024 mg/g.

TABLE 6

Decontamination of sewage (pH 3–14) by NMCS-Br sorbent (C_{Hg} = 1.3 mg/l, h = 50 sm, ∅ = 11 mm, V = 500 ml/h, m = 20 g)

Sample No.	V, ml	Residual mercury content, mg/l
7k-1	500	0.0066±0.0003
7k-2	1000	0.0029±0.0001
7l-3	1500	0.0029±0.0001
7k-4	2000	0.0055±0.0003
7k-5	2500	0.0054±0.0003
7k-6	3000	0.0023±0.0001
7k-7	3500	0.0057±0.0003
7k-8	4000	0.003±0.0002
7k-9	4500	0.0025±0.0001
7k-10	5000	0.0025±0.0001
7k-11	5500	0.0031±0.0002
7k-12	6000	0.0025±0.0001
7k-13	6500	0.0025±0.0001
7k-14	7000	0.0027±0.0001
7k-15	7500	0.0027±0.0001
7k-16	8000	0.0027±0.0001
7k-17	8500	0.0049±0.0002
7k-18	9000	0.005±0.0003
7k-19	9500	0.0052±0.0003
7k-20	10 000	0.004±0.0002
7k-21	10 500	0.003±0.0002
7k-24	12 000	0.0018±0.0001
7k-25	12 500	0.0072±0.0004
7k-26	13 000	0.017±0.0009

Note. Mercury content on the sorbent: 1.3 mg/l · 12.5 l = 16.25 mg; dynamic capacity of NMCS-Br sorbent for mercury before the breakthrough (0.01 mg/g): 16.25 mg : 20 g = 0.8 mg/g.

TABLE 7

Decontamination of sewage (pH 3–4) from mercury by NMCS-I sorbent (C_{Hg} = 0.2 mg/l, m = 1061.32 g, h = 100 sm, ∅ = 52 mm)

Sample No.	V, l	Residual mercury content at the column outlet, mg/l
1	24	0.0005±0.00003
2	48	0.0005±0.00003
3	72	0.0005±0.00003
4	96	0.0005±0.00003
5	132	0.0005±0.00003
6	156	0.0005±0.00003
7	184	0.0005±0.00003
8	232	0.0006±0.00003
9	312	0.0005±0.00003
10	392	0.0005±0.00003
11	472	0.0005±0.00003
12	800	0.0005±0.00003
13	880	0.0005±0.00003
14	1360	0.0005±0.00003
15	1440	0.0005±0.00003
16	1860	0.0005±0.00003
17	1960	0.0005±0.00003
18	2060	0.0005±0.00003
19	2560	0.0005±0.00003
20	2660	0.0005±0.00003
21	2860	0.0005±0.00003
22	3300	0.0005±0.00003
23	3380	0.0005±0.00003
24	3460	0.0005±0.00003
25	3880	0.0005±0.00003
26	4000	0.0005±0.00003
27	4096	0.0005±0.00003
28	4590	0.0005±0.00003
29	4660	0.0005±0.00003
30	5092	0.0005±0.00003
31	5164	0.0005±0.00003
32	5524	0.0005±0.00003
33	5956	0.0005±0.00003
34	6388	0.0005±0.00003
35	6868	0.0005±0.00003
36	7028	0.03±0.0003
37	7428	0.038±0.0003

Note. DC = 1.37 mg/g (with the total mercury content on the sorbent of 1454.00 mg, sorbent weight of 1061.32 g, and initial mercury concentration in the sewage equal to 0.2 mg/l).

TABLE 8

Dynamic capacity of NMCS sorbents in decontamination of processing water wastes from mercury (pH 3–4 for the sorbents 2–5, and pH 10 for the sorbent 1)

Sorbent	Mercury content, mg/l		DC, mg/g
	at the inlet	residual	
NMCS-HAA	0.06	0.04	0.3
NMCS-Cl	0.06	0.002–0.006	0.024
NMCS-IHCl	0.845	0.0006–0.006	0.4
NMCS-Br	1.3	0.0025–0.006	0.8
NMCS-I (I_2)	0.2	0.0005	1.37

$[HgBr_2]^0$ complex, as distinct from $[Hg(NO_3)_2]^0$, is sorbed worse.

Studying the processes of mercury sorption from the processing media (lithium-containing) with pH 3–4, 11–12 under dynamic conditions has been made. The adsorption columns of diameter 11 mm were used in this work, the height of sorbent layer (it has been determined previously as an optimum one) was 50 cm, the rate of volume flow was 500 ml/h. Mercury concentration in the initial solution and at the column outlet was determined in every 500 ml by the AAS method.

Obtained data on mercury sorption from sewage water by the modified NMCS sorbents are listed in Tables 3–6.

Dynamic exchange capacities of sorbents were calculated before the mercury breakthrough of 0.01 mg/l (MDC) (Tables 7, 8). MDC increase is observed upon CM modification (by chlorine, bromine, and iodine). The greatest value of MDC is noted for NMCS-I (10 % of iodine).

CONCLUSIONS

An investigation of the oxidized and modified carbon materials and sorbents based on them has been carried out by various physicochemical methods (electron microscopy, thermoanalysis, X-ray diffraction, IR spectroscopy).

X-ray diffraction investigation has demonstrated that all carbon materials and sorbents based on them have amorphous structure with the wide diffraction maximum of graphite-like phase, the structure of the carbon material being invariable also upon the oxidation and introduction of various modifiers and mercury.

IR spectroscopic investigation has demonstrated that oxidation of the carbon surface gives rise to oxygen-containing functional superficial groups, the quantity of which is determined by the strength of the oxidizer and by an increase of CM reactivity, which allows the various chemical reactions to be run on the particle surface and allows the properties to be modified in the desired direction.

Studying the processes of mercury sorption to the oxidized and modified NMCS sorbents has suggested that the adsorption properties of sorbents depend on oxidation state of the surface, on the quantity of superficial functional groups and on the kind of modifier. It has been demonstrated that the initial carbon material practically does not absorb mercury from nitrate and chloride solutions. Oxidation of carbon surface causes sorption capacity for mercury to increase. An increase of sorptive capacity for mercury upon the modification of carbon material by chlorine, iodine, and bromine is observed. The NMCS-I sorbent previously oxidized and modified by iodine manifests the largest sorption properties (from $HgCl_2$ solution) for mercury.

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