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Synthesis of Carbon Sorbents with Antibacterial Properties

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Abstract

A method for the synthesis of the application material for medical purposes based on the carbon hemosorbent is described. The chemical modification of a carbon material was performed *via* impregnation by azobisisobutyric acid dinitrile (DINIZ) in monomer N-vinylpyrrolidone (VP) with the subsequent polymerization. Selecting the optimal parameters of the modification that allow applying up to 8–15 mass % of poly-N-vinylpyrrolidone (PVP) onto the carbon sorbent is described in detail. As the general analysis we used a thermal method that provides monitoring the VP polymerization process on the carbon material. The proposed method for the synthesis of PVP on the surface of the carbon sorbent was compared with alternative methods of PVP preparation on the surface of different nature carriers. The analysis of the physicochemical properties of the studied sorbents is presented. The reported results of microbiological studies have demonstrated the possibility of using carbon sorbents for the vulnerosorption.

Key words: carbon sorbent, polymerization of N-vinylpyrrolidone, poly-N-vinylpyrrolidone, thermogravimetry, antibacterial properties

INTRODUCTION

Currently, in Russia there is increasing the number of infectious diseases associated with wound infections. As a rule, the matter concerns nosocomial (hospital-acquired) infections. Every year the infections of this kind (purulent-septic infection after surgery, infection in newborns, women in childbirth, *etc*.) affect about 2–2.5 million people in Russia [1–5].

Approximately 90 % of all nosocomial wound infections are of bacterial origin. Viral, fungal pathogens and protozoa are much rarer. The main part wound infection pathogens (67 %) represent Gram-positive bacteria, including staphylococci and streptococci.

The main method of treating the infectious diseases consists in antibiotic therapy [1–7]. However, the traditional approach has some serious disadvantages:

1) antibacterial drugs have an effect only after 3–4 h;

2) an organism absorbs about 50 % of the pharmaceutical preparation;

3) the widespread use of antibacterial therapy, including antibiotics leads to appearing and spreading numerous antibiotic-resistant strains of microorganisms;

4) a long and expensive course of treatment;

5) antibiotics affect negatively microbiocenosis, causing dysbacteriosis, they disrupt the assimilation and absorption of different nutrients, and reduce the immunity;

6) the greatest part of the antimicrobial pharmaceutical drugs exhibit side and other undesirable effects on an organism.

In this regard, the prevention and treatment of mixed infections, infectious complex diseases of bacterial origin requires for new approaches and novel pharmaceutical preparations with a different mechanism of action than that inherent in antibiotics. They should have a high antibacterial activity to exert a general-revitalizing effect on an organism as a whole.

Currently, among the methods of sorption therapy, a method of vulnerosorption (application sorption) is the most actively developing one [8–11]. The method consists in the removal of toxic components (residues of tissue destruction of microbial cells, bacterial toxins *etc*.) through the wound surface or through the area of inflammation. Upon the application of a sorbent there occurs cleaning the wound contents, or purulent cavity, the transport of certain substances from the blood and the subsequent sorption thereof is accelerated. The sorption of wound contents promotes the normalization of the biological response of an organism as a whole, which allows quickly reducing the inflammatory or traumatic edema of soft tissues, improving the microcirculation and reducing the number of microorganisms in average by 100–1000 times as compared with conventional bandaging materials.

The application sorption exerts a positive effect on the outcome of treating the traumatic, septic, burn wounds, trophic ulcers, *etc*. The intracavitary sorption is widely used in the case of purulent processes: peritonitis, the abscesses of the lungs, liver, and other organs.

Thus, the development of carbon adsorbents with antibacterial properties for the treatment of infectious diseases is of urgency.

Sorbents for application medicine

In case of developing application materials contacting with organism's biological fluids, there are special requirements to the quality thereof: a high level of chemical purity, minimal content of impurities, low toxicity, high mechanical strength and a smooth surface topography of granules, no dust formation (formation of ultrafine particles), high sorption capacity with respect to the substances under removing, blood compatibility and the inertness with respect to blood corpuscles.

The porosity of the carbon sorbents determines the direction of using them in the sorption medicine. So, using microporous carbon sorbents result in efficiently removing the products with a low molecular mass from biological fluids, for example creatinine, aliphatic hydroxy acids, amino acids, uric acid, *etc*.

The developed mesoporous structure of sorbents satisfies the most part of the tasks of the sorption therapy. In the course of removing toxic substances by a carbon sorbent with the hydrophobic surface, the main sorption mechanism is presented by physical adsorption, caused by the influence of dispersion forces. The efficiency of adsorption is determined by the commensurability of adsorbate molecules and the pores (mesopores) of a sorbent.

At the Institute of Hydrocarbon Processing (IHP) of the SB RAS (Omsk) there are technological approaches developed concerning the targeted synthesis of a new class of porous carbon–carbon materials on the base of globular nanosized carbon and of sorbents for medical purposes based on them: sterile carbon hemosorbent in physiologic saline VNIITU-1 and carbon enterosorbent Activated Charcoal (VNIITU-2) [12].

In the course of studying the mechanism and kinetics of the thermal decomposition of hydrocarbons on the surface of particles of dispersed carbon with the formation pyrocarbon performed at the IHP of the SB RAS the concept of the matrix synthesis of porous carbon materials has been established. The starting raw materials are presented by natural gas and petroleum refinery gases, as well as petroleum and coal resins. The synthesis is based on a two-stage transition of carbon into nanodispersed carbon particles and pyrocarbon [12].

The developing new direction in the synthesis of carbon sorbents allows making medical sorbents that meet the demands of medicine.

The technological process of the preparation of the medical sorbent from the matrix of porous carbon material with certain porosity comprises the operations aimed at imparting the compatibility with the blood, sterility and pyrogen-free properties to the sorbent. The principal operation the among them is presented by pneumo-hydromechanical processing the porous carbon material in the fluidized bed mode, whereby, one could remove pulverized carbonaceous particles from the surface and from the pores of the sorbent, adjust the sorbent pH to physiological standards, improve the average strength of the granules *via* the destruction of "weak" granules and eliminate possible surface irregularities ("polishing" the granules) [12].

The carbon hemosorbent differs from many well-known sorbents in a number of properties. It is characterized by the following parameters:

– high level of chemical purity;

– mesoporous structure;

– minimum content of impurities;

– mechanical strength and a smooth surface topography of granules;

– the absence of dust (no formation of ultrafine particles);

– a high absorption capacity with respect to toxins with a low and medium molecular mass, trapped in an organism from the environment or formed in the course of life;

– low toxicity;

– blood-compatibility and inertness with respect to the blood corpuscles (Table 1).

This hemosorbent seems a promising material as a basis for the development of sorbents for vulnerosorption.

At the present time in Russia, and abroad there are several developments based on sorbents of different nature used for purposes of application medicine. Among them, of particular interest are the developments based on carbon sorbents, because the latter are characterized by high sorption capacity with respect to bacteria and bacterial toxins. So, the sorption capacity of activated carbon with respect to the staphylococcal toxin was determined in a number of studies [13–16].

Polymers of medical and biological purposes with antibacterial properties

In order to increase the efficiency of antibacterial properties inherent in carbon sorbents there should be used a modifier, *i. e.*, the pharmaceutical preparation that exhibits the activity against a wide variety of pathogenic microorganisms, and exerts no negative effect on an organism. Such substances comprise polymers of medical and biological purposes, having their own antibacterial properties.

The choice of a modifier in the course of developing an application material for vulnerosorption is primarily determined by its conformity with the essential health requirements such as low toxicity and the presence of biologically active highly reactive functional groups.

It is known that polymers based on N-vinylpyrrolidone (VP) are widely used in medicine and biology as a non-toxic hydrophilic material. They are allowed for using in contact with the biological fluids of a living organism, and for performing various functions in the structure of materials intended for medical purposes [17, 18]. The VP based polymers are

TABLE 1

Physicochemical and biomedical characteristics of carbon hemosorbent in the physiological solution of sterile VNIITU-1

Parameters	Values
Mass fraction ash, %, no more than	0.15
Mass fraction of total sulphur, %, no more than	0.30
Specific surface on nitrogen adsorption, m^2/g	300–400
Specific surface on CTAB adsorption, m^2/g	65–125
Iodine number, mg/g	175–245
Number of granules with the diameter of 0.5–1.0 mm, %, no less than	90
Number of granules with the diameter less than 0.5 mm, %, no more than	10
Granule strength at abrasion, %/min, no more than	0.30
Concentration of NaCl solution, in equilibrium with hemosorbents, mol/dm^3	0.14–0.15
pH of NaCl solution, in equilibrium with hemosorbent	6.0–7.8
Impact on the blood corpuscles at the blood flow equal to 80–120 mm/min to 350 cm^3 of the sorbent:	
decreasing the number of white blood cells, %, no more than	10
decreasing the number of thrombocytes, %, no more than	15
increment of free hemoglobin, %, no more than	6

used for modifying anionic surfactants having a high bactericidal activity [17–21]. Several VP copolymers with ionic comonomers exhibit their own antimicrobial, immunostimulatory and immunomodulatory activities. For the excretion of toxic substances from an organism, one usually uses polyvinylpyrrolidone (PVP) having the molecular mass ranging within 10 000–15 000 g/mol.

It is known concerning the use of PVP in the ointments for the treatment of infected wounds with the content thereof amounting up to 5.5 %. According the authors of [21], the substance begins to exhibit antimicrobial properties at the concentrations equal to about 1.0 %.

The application of PVP onto the surface of the carbon sorbent could allow increasing the detoxifying properties thereof owing to the migration of PVP macromolecules to the biological fluid. An additional positive effect consists in improving the wettability of the carbon material caused the lyophilization of by its surface and lowering the surface energy.

EXPERIMENTAL

As the sample, we chose a sorbent, obtained by hydromechanical treating a porous carbon material [12]. The sample of the carbon sorbent represented a mesoporous sorbent with grain size (mm): ≥1.25 (2 %), 1.00 (54 %), 0.63 (43 %), ≤0.50 (1 %). The specific surface area of the sorbent BET (S_{BET}) was equal to 394 m^2/g; the pore volume, cm^3/g was as it follows: the total pore volume 0.630, the volume of micropores 0.013, the volume of mesopores 0.604, and the volume of macropores 0.013.

For modifying the surface of the carbon sorbent we used: N-vinylpyrrolidone C_6H_9NO as a modifier (Merck, Germany), azobisisobutyric acid dinitrile $C_8H_{12}N_4$ (DINIZ) (Merck, Germany) as a radical polymerization initiator.

The thermal analysis of the samples under investigation (TG, DTG, and DTA) was performed using a Shimadzu DTG-60H unit. The accuracy of determining the temperature was equal to 1 °C, the accuracy in mass changing amounted to 0.1 %. The measurements were carried out in atmospheric air within the temperature range from a room temperature to 1000 °C; the weighed sample portion being equal to 10 mg, the temperature rise rate amounting to 10 °C/min.

The morphology and relief of the carbon sorbent samples was studied by means of scanning electron microscopy with the help of a Jeol JSM-6460LV electron microscope. The technique of sorbent sample preparation consisted in the vacuum deposition of a gold film 10–15 nm thick onto the sample under investigation. We studied 6–10 granules for each sample of the sorbent. In order to obtain contrast electron microscopy images the investigation of the surface was performed under the following conditions: voltage 20 kV, current strength 10–30 mA.

The textural characteristics of the carbon sorbents were studied by the low-temperature nitrogen adsorption method. The isotherms of nitrogen adsorption–desorption (T_{ads} = 77.4 K) were obtained on a Micromeritics Gemini 2380 device. The value of S_{BET} was determined from the adsorption isotherms within the range of relative equilibrium nitrogen vapour pressure P/P_0 = 0.05–0.3. Additionally, the specific pore volume was determined for the samples under investigation. Before the adsorption measurements, the samples were trained under vacuum at a temperature of 300 °C (initial sample) and 60 °C (modified samples) during 6–8 h.

The elemental analysis was performed using a Vario EL Cube Elementar CHNOS elemental analyzer. When carrying out the elemental analysis, the samples under investigation were automatically fed to the combustion zone using an autosampler equipped with a ball cock. The content of the elements was determined using a thermal conductivity detector (katharometer).

The parameters of the C, H, N, S analysis were as follows: the temperature of the oxidizing tube was 1150 °C, the temperature of the reducing tube was 850 °C, the temperature of the sulphuric adsorption column in the course of the adsorption was 120 °C, helium flow rate amounting to 230 mL/min, oxygen flow rate amounting to 35–38 mL/min. The catalytic oxidation of the sample was performed at 1150 °C in a quartz reactor filled with a catalyst. The calculation of the concentration of elements was carried out according to a calibration curve for the standard substance sulphonamide (Art-No.: 15.00-0062).

The determination of oxygen was carried out by means of the pyrolysis of the sample

in a quartz tube filled with carbon black at the temperature of 1170 °C. In the course of the pyrolysis, oxygen transforms quantitatively into carbon monoxide, further, its desorption and the detection of CO using a katharometer occur.

The parameters conducting of the analysis for determining the oxygen content were as follows: the temperature of the pyrolysis tube was 1170 °C, the temperature of the CO adsorption column in the course of the adsorption was 40 °C, the temperature of the CO adsorption column in the course of CO desorption was 260 °C, the consumption of helium was 230 mL/min. The calculation of the concentration of oxygen was carried out according to the calibration curve for the standard substance, *viz.,* benzoic acid (Cas-No.: 65-85-0).

Using the X-ray microanalysis, the elemental composition at certain sites of the granules of the samples under investigation was determined. The analysis was performed using a Jeol JSM-6460LV electron microscope. We studied 6–10 granules of samples of the sorbent.

The qualitative composition of the functional groups of the samples obtained was determined by means of infrared spectroscopy. The IR spectra of the transmission were registered using a Thermo Fisher Scientific Nicolet 5700 spectrometer with the resolution of 4 cm^{-1} and spectra accumulation number equal to 32. The methods of the investigation consisted in preparing a sample in the form a very thin uniform layer obtained *via* the sedimentation of fine particles in a glass cylinder with the height of 25 cm onto an optical IR transparent plate BaF_2. Then, the IR spectra were registered. The spectra were processed in the software package Origin for correcting the baseline and smoothing the background fluctuations.

The possibility of the removal (desorption, migration) of the polymer from the sorbent surface was evaluated on changing the specific surface area and content of total nitrogen in the samples held in the physiological solution (0.9 % NaCl solution) during 1 day. The total nitrogen content in the samples before and after the modification was determined using a chemical method according to Kjeldahl [22].

The adsorption properties of the studied samples of the carbon sorbent and the reversibility of the mentioned process (desorption) were determined under model conditions. As the substances modelling the toxins of microorganisms, methylene blue dye $C_{16}H_{18}ClN_3S$ and vitamin B12 $C_{63}H_{88}CoN_{14}O_{14}$ were selected. The absorption capacity of the original and modified samples with respect to methylene blue and vitamin B12 was studied for several days prior to establishing the equilibrium in the systems under investigation.

The evaluation of the microbiological purity and antimicrobial properties of carbon sorbents with respect to the pathogenic microflora was carried out at the Central Research Laboratory of the Omsk State Medical Academy (the Central Scientific Research Laboratory of the OmSMA).

RESULTS AND DISCUSSION

The size of PVP polymeric globules with the molecular mass ranging within 8000–10 000 g/mol is higher than the pore size of the carbon sorbent, so in the course of the modification, it is difficult to introduce the modifier uniformly over the entire volume of the porous material. In this case, the modifying polymer is distributed predominantly over the outer surface of the granules in a small amount. As a consequence, the concentration of PVP is low, and the pharmaceutical preparation cannot completely exert any efficient effect on the bacterial cells (pathogenic microflora).

For this reason, as a modifying agent, VP monomer, sizes of molecules of which allow filling the pores of the sorbent (estimated average diameter of the sorbent pores is 6–9 nm, of VP molecule is 0.4–0.8 nm) was selected. N-vinylpyrrolidone is colourless liquid with a faint characteristic odour, miscible with water and organic solvents.

In practice, as a rule, the polymerization of VP is most often carried out in the environment of the monomer (bulk polymerization) or in the presence of a solvent of the monomer (in solution). The molecular mass of forming PVP depends on the selected parameters of polymerization (the presence of a solvent, the solvent type, the type of initiator, the temperature of the process and *etc.*).

One of the major tasks when developing a method for the polymerization of the VP on a

carbon sorbent is the selection of the optimal parameters of the modification process (the temperature, duration of the process, type and concentration of the initiator, *etc.*) that allow obtaining of PVP with a linear structure and the molecular mass of 8000–10 000 g/mol, without impurities of toxic initial VP monomer and its low molecular mass derivatives on a sorbent.

The impregnation of granules of the carbon hemosorbent was carried out in a round-bottom flask with 0.2–1.0 % solution of the initiator DINIS in VP at pH 7.0–7.5, the residual pressure was 15–20 mmHg, ratio of sorbent/VP solution (1.0 : 1.4)–(1.0 : 2.0), duration of the impregnation was 40–60 min (Fig. 1).

The polymerization process of VP is determined to a considerable extent by the temperature and its duration [29, 30]. The temperature of the reaction medium was changed up to 65–70 °C; the dwell time in the inert atmosphere was to 2–9 h. The modified sorbent was dried at room temperature for 18–24 h.

In order to select optimal conditions for modifying, a number of samples were synthesized at various parameters. As the main method for monitoring VP polymerization process on the carbon sorbents, the thermal analysis was used. This method allows monitoring the progress of the polymerization process, determining the temperature range, in which the process occurs, its endothermic or exothermic character. Furthermore, alongside with the thermal analysis one could measure and register the mass loss of the sample, determine the amount of the modifier deposited.

The dynamic thermal analysis allows identifying chemical phases and mixtures thereof according to the effects observed when changing the temperature. The polymerization process was studied using the thermogravimetric (TG) and differential thermogravimetric (DTG) analyses. As the temperature function, either the change of the sample mass (TG), or rate of this change (DTG) was registered.

Figure 1 demonstrates the TG curves for the samples synthesized at different VP polymerization parameters including the sample of the carbon sorbent modified by a solution of commercial PVP with the molecular mass of 10 000 g/mol (Sigma-Aldrich).

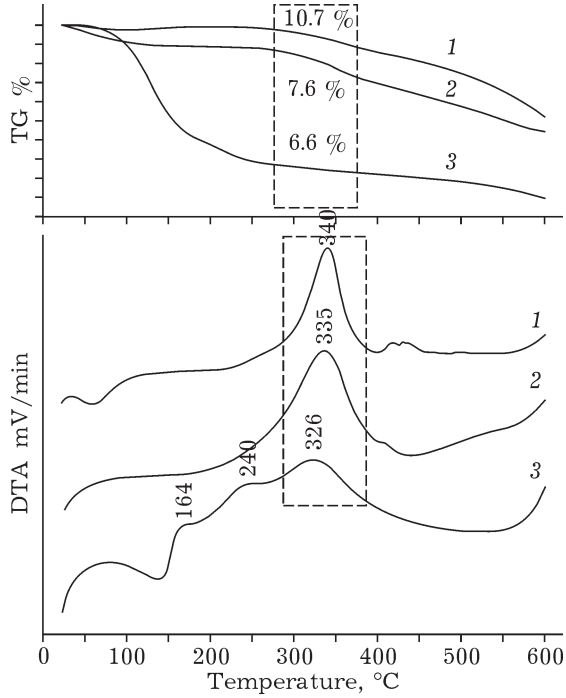

Fig. 1. Thermograms of modified carbon sorbents: *1* – sorbent coated with commercial PVP (30 % solution); *2, 3* – sorbent coated with VP and its further polymerization under optimal and non-optimal conditions, respectively.

According to the literature and experimental data, PVP of the linear structure with the molecular weight of 8 000–10 000 g/mol is decomposed within the temperature range of 300–400 °C [23–28]. The analysis of the resulting thermal profiles for the synthesized samples allowed to determine the conditions of the synthesis of modified the carbon sorbent: the temperature is 68–70 °C; the duration of VP polymerization on the carbon sorbent is 9 h.

Figure 1 demonstrates that the DTA curve of the sample modified under non-optimal conditions (curve *3*) has a low-temperature endothermic peak at 100–110 °C,, associated with the sample mass loss due to removing water from its pores. Appearing the peaks in a low-temperature region at 164 and 240 °C could be explained by the decomposition of VP and its derivatives formed in the course of the polymerization. At the temperature of 326 °C an exothermal peak characterizing the applied modifier appears the DTA curve. In this case, the loss of the sample mass amounts to 6.6 %.

The DTA curve for the sorbent coated with VP followed by its polymerization under opti-

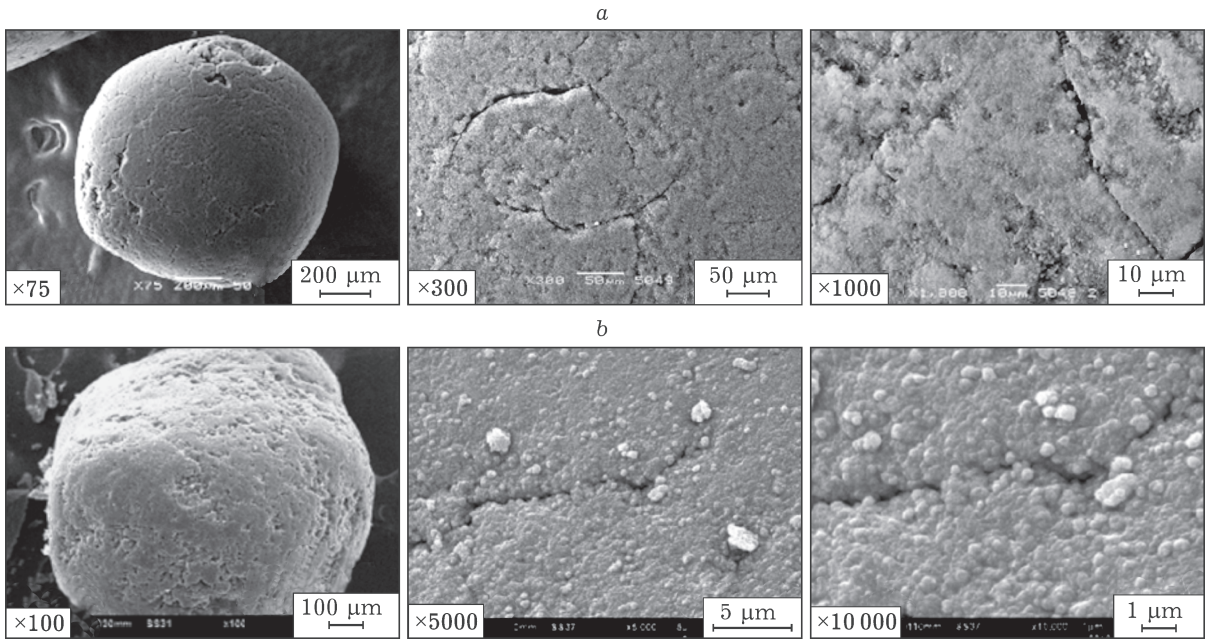

Fig. 2. Electron micrographs of the granules and of the carbon surface of the original (*a*) and modified (*b*) sorbents.

mum conditions, demonstrate only one exothermic peak at a temperature of 340 °C (see Fig. 1, curve *2*). The mass loss for the sample is 7.6 %. This curve is comparable by the form with the curve *1* (see Fig. 1) that corresponds to the sample coated by commercial PVP from the 30 % solution (mass loss is 10.7 %).

It follows from the analysis of thermograms that the polymer synthesized on the carbon sorbent is apparently, PVP (see Fig. 1, TG curve *2*), and the character of thermograms corresponds to the polymer degradation. Consequently, the conditions of the synthesis of this modified carbon sorbent are optimal.

Figure 2 demonstrates changes on the surface of the samples before and after the modification. It can be seen that the entire surface of the carbon sorbent is formed by a polymer film in the form of tightly contiguous polymeric particles with the size up to 1 μm.

It follows from data of Table 2 where the effect of modifying the carbon sorbent on its textural characteristics is shown that when polymerizing VP on the surface of the carbon sorbent pores are closed almost completely.

The distribution of elements on the surface of the carbon sorbent samples before and after the modification was investigated by the method X-ray microanalysis. It was found that after the modification, the carbon content on the surface was reduced from 100 to 75 mass %, due to the presence of oxygen here (15.6 mass %) and nitrogen (11.4 mass %).

Table 3 demonstrates the results of the elemental analysis of the samples. It can be seen that the VP polymerization on the carbon sorbent affects the elemental composition of the latter. After the modification, the total carbon content in the carbon sorbent decreases, however, the content of hydrogen and oxygen in-

TABLE 2

Textural characteristics of carbon sorbents

Samples	S_{BET}, m^2/g	Specific pore volume, cm^2/g			
		Total	macro-	meso-	micro-
Original	394	0.630	0.014	0.0603	0.013
Modified	7.6	0.052	–	0.050	0.002

TABLE 3

Results of the elemental analysis for the samples under study

Elements	Content of the elements in the sample, %	
	Original	Modified
C	98.46±0.26	85.31±0.41
H	0.28±0.08	2.77±0.07
N	–	3.80±0.10
S	0.22±0.08	0.11±0.08
O	0.96±0.07	6.65±0.07
Σ	99.90±0.17	98.64±0.65

creases. Furthermore, nitrogen appears in the modified sample. That is what serves the indicator of the fact that the modifier is present on the surface of the carbon sorbent.

The qualitative composition of the functional groups of the samples obtained was determined by means of IR-spectroscopy. Figure 3, *a* demonstrates the IR spectra of the modifying agents, *viz.*, VP and PVP.

The presence of the modifier on the surface of the carbon sorbent affects the composition of the functional groups. In the spectrum of the modified carbon sorbent there are no vibration of the carbonyl groups typical for the original carbon sample, however, characteristic absorption bands of the polymer PVP appear (see Fig. 3).

The main differences of the IR spectra of the samples studied are the appearance of new absorption bands at 1660 and 1561 cm^{-1} corresponding to the stretching vibrations of the C=O (amide I).These vibrations could also correspond to the composite frequencies of the deformation vibrations of the N–H bonds and stretching vibrations of the C–N bonds (amide II) of the amide group. In addition, one should note the absorption bands observed for the nitrogen groups at 1420 and 1460 cm^{-1} that are characteristic for the deformation vibrations of CH_2 groups bound with the atoms of nitrogen and/or carbon.

Via comparing the IR spectra of the monomer VP, of the commercial PVP solution and of the carbon sorbent before and after the modification some ideas concerning the process of the VP polymerization on the surface of the carbon sorbent have been obtained. It has been demonstrated this method allows controlling the VP polymerization process on the carbon sorbent.

The investigation of the migration of the polymer from the surface of the modified sample upon contacting with aqueous solutions allows assessing the "prolonged" action of the resulting preparation. The term the "drug of the

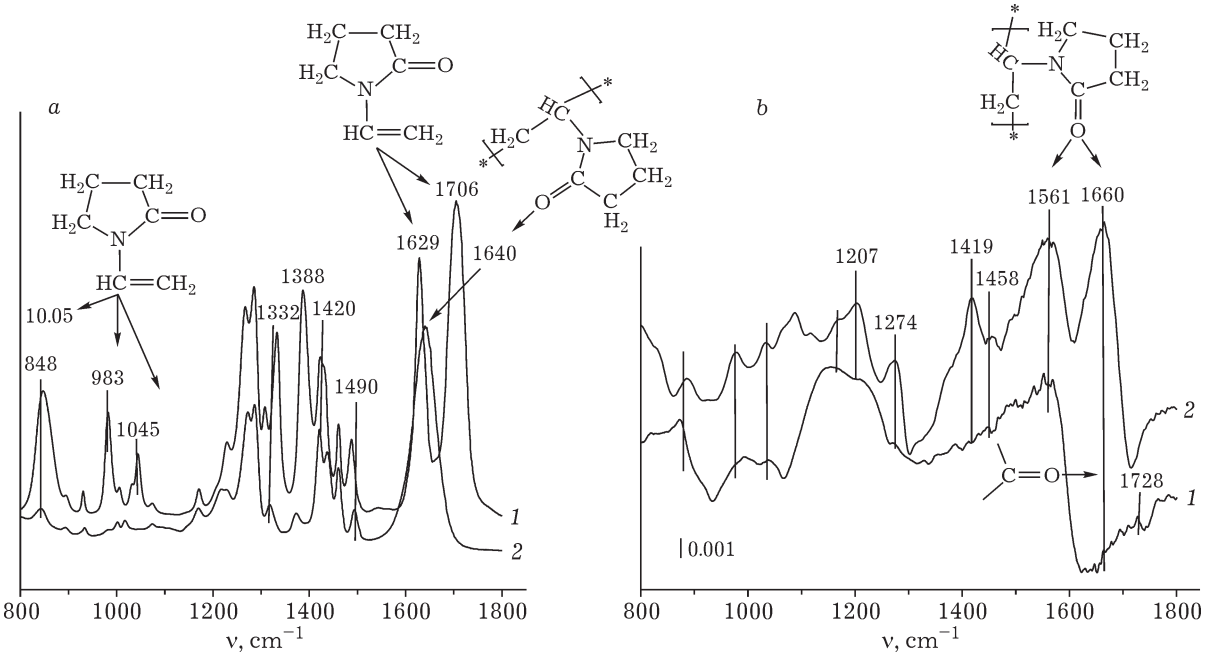

Fig. 3. IR spectra of the samples under study: *a* – VP (*1*) and PVP aqueous solution (*2*); *b* – original (*1*) and modified (*2*) sorbents.

prolonged action" is used for the characteristic of such drugs that provide a longer period of the therapeutic action of an active substance (medicinal) entrapped in them, in comparison with conventional drugs of the same agent. A drug of the prolonged action should release a dose of an active (medicinal) agent continuously over a certain period of time to provide the constant optimal level of this substance in the organism. In this case, the PVP modifier deposited acts as a biologically active component.

It has been found that under the model conditions of the experiment the major amount of the modifier migrates into the solution from the surface of the sorbent within the first hour after the contact. In this case, from the polymeric film, up to 40 % (160 m^2/g) of carbon surface is released, whereas the total nitrogen content decreases in 2.8 times (Table 4). Thus, upon the transition of the modifier into solution, the surface is released and the content thereof in the sorbent decreases.

As already established, the migration of the modifier to the solution is accompanied by the liberation of a considerable part of the surface of the sorbent. It could be assumed that the modified sorbent will exhibit detoxification properties, *i. e.* adsorb toxins secreted by microorganisms onto the accessible surface. It is known that the main toxic effect of microorganisms is caused by microbial toxins is produced by them [1–6].

The evaluation of the adsorption properties of the samples studied of the carbon sorbent and of the reversibility of this process (desorption) was performed under model conditions. As the substances modelling toxins of microorganisms, methylene blue dye (the molecular mass MM = 319.85 g/mol, the molecular diameter is about 2.0 nm^2) and vitamin B12 (MW = 1355.38 g/mol, molecular diameter is 6–8 nm^2) were selected (Fig. 4).

It has been found that the adsorption equilibrium on the modified sorbent is established for a considerably longer time than that on the original sample. So, for the system original sorbent – methylene blue the equilibrium is established after 50 h (~2 days), whereas for the system modified sorbent–methylene blue the equilibration is 4 times slower, so, the equilibrium is established after 200 h (about 8 days). In case of the adsorption of vitamin B12 the equilibrium in the system original sorbent–vitamin is established after 120 h (~5 days), whereas for the system sorbent modified–vitamin the process duration is 3 times longer, and the equilibrium is established only after 400 h (~17 days).

TABLE 4

Polymer desorption from the surface of the modified sample as a drug of the "prolonged" action

Samples	S_{sp}, m^2/g	N_{total}, %
Original	394	absent
Modified	8	5.2
The same after contacting the physiological solution, during, h:		
1	88	2.5
3	125	2.0
6	148	1.5
24	161	0.9

The differences observed could be explained by textural characteristics of the samples: the surface and pore volume of the original sorbent is much greater, in comparison with the modified sorbent (see Table 2).

It is interesting that upon establishing the equilibrium in the systems sorbent–adsorbate under investigation, the amount of the model

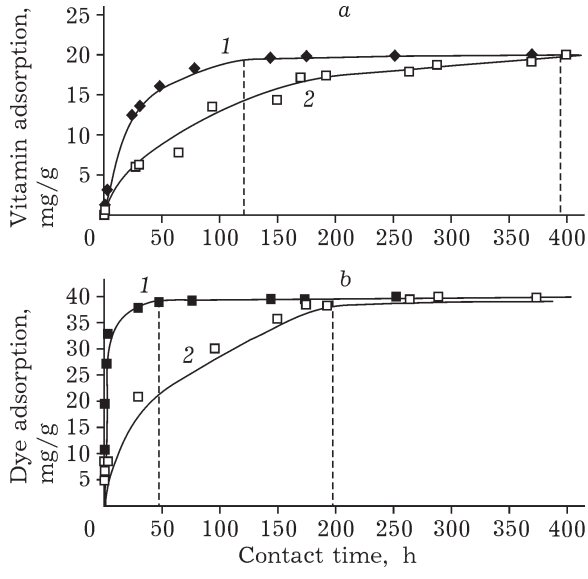

Fig. 4. Adsorption isotherms for vitamin B12 (*a*) and methylene blue dye (*b*) on the carbon sorbent samples under study.

compounds adsorbed on the original carbon sorbents almost coincides with the adsorption level of the substances on the modified sample. So, the adsorption on the samples under study with respect to methylene blue reaches (38±2) mg/g, whereas that for vitamin B12 does (19±2) mg/g.

The adsorption of the dye and vitamin on the modified sample with a low surface area, to all appearance, is caused by the fact that the two processes occur simultaneously: the process of the migration of PVP polymer the pores of the modified sorbent resulting in increasing the surface and pore volume of the sorbent, as well as the process of filling gradually "vacating" pores ("vacant sites") by the adsorbate molecules. Thus, the polymer molecules in the pores of the carbon sorbent are gradually replaced by molecules of the dye or vitamin.

It has been found that the adsorption of methylene blue and vitamin B12 is reversible (the desorption proceeds in an ethanolic solution). Therefore, the absorption of adsorbates onto the modified carbon sorbent is realized via the mechanism of the physical sorption and it is caused by the manifestation of a "sieve effect".

The results of the investigations have demonstrated that the modified carbon sorbent is able to exhibit bifunctional properties.

According to the results of microbiological testing, the original carbon sorbent exhibits antimicrobial properties with respect to gram-positive, Gram-negative bacteria and a mixture of cultures after 24 h. The modified carbon sorbent after 6 h inhibits the growth of gram-positive and gram-negative bacteria, whereas after 24 h it exhibits an antibacterial activity with respect to a mixture of pathogenic cultures. The modified sorbent has the efficient antibacterial activity with respect to bacterial cells of Gram-negative bacteria in the order of *Klebsiella pneumonia* > *Pseudomonas aeruginosa* > *Escherichia coli*, and against Gram-positive bacteria in the order of *Streptococcus agalactiae* > *Staphylococcus aureus*.

Particularly remarkable is the action of the modified carbon sorbent with respect to the bacteria *Pseudomonas aeruginosae*, whose growth cannot be efficiently inhibited by the antibiotics available nowadays.

The manifestation of the antibacterial properties of modified sorbents with respect to Gram-positive bacteria could be caused by the antibacterial properties of the original sorbent. It is known that solutions of PVP decrease the toxicity of *Escherichia* coli and *Proteus*, as well as exhibit the agglutinating effect on microbial cells [18].

Antibacterial properties of the modified sorbent with respect to gram-negative bacteria could be explained by the manifestation of antibacterial properties in the modifier, *viz*., poly-N-vinyl pyrrolidone that has its own antimicrobial activity. Antibacterial properties of PVP are determined by its structure and the presence of the lactam ring in the structure: the main interaction of bacterial cells occurs with the nitrogen atoms of PVP pyrrolidone cycles. Owing to the presence of a hydrophobic polymeric chain and hydrophilic carbonyl groups in the structure of PVP, physical binding between the bacterial cells with the polymer matrix (adhesion) is possible. The binding, to all appearance, could also be caused by the Coulomb interaction of the negatively charged cell membrane and positively charged protonated nitrogen atom in a macromolecule of the polymer.

Thus, the modified carbon sorbent developed represents a promising material with antibacterial properties.

CONCLUSION

A method of the synthesis of modified carbon sorbents has been developed. The selected optimal conditions of modifying carbon material VP allowed obtaining PVP on the surface of the carbon sorbent without impurities of the toxic monomer and its low molecular mass polymerization products.

The porous structure, elemental composition and structure of functional groups inherent in carbon sorbents were studied by a complex of physicochemical methods. The possibility of the migration of the polymer from the modified carbon sorbent over time has been established.

Antibacterial properties of the sorbent have been studied. It has been shown that using the modification of carbon material PVP the modified carbon sorbent with antibacterial properties can be obtained.

The mechanism of the antibacterial action of the modified sorbent has been proposed. It

consists in a gradual removal of the polymer (PVP) from the porous structure of the sorbent to a solution for interacting with the cells of pathogenic microorganisms and suppressing their growth and vital activity.

The carbon sorbents obtained are of interest as the application material for the prophylaxis and treatment of various diseases.

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