Original Article

INVESTIGATION OF SORPTION CHARACTERISTICS OF CARBON MATERIALS AND THEIR APPLICATION IN MEDICINE

A.M. Nuraly[1,2], S.H. Aknazarov[1,2]
[1]Al-Farabi Kazakh National University, Almaty, Kazakhstan
[2]Scientific Production and Technical Center "Zhalyn", Almaty, Kazakhstan
[3]Anadolu University, Dept.of Chemical Engineering, Eskisehir/Turkey
DOI: 10.47750/pnr.2023.14.03.067

Abstract

The article shows the results of obtaining a hemosorbent of carbon material. Samples of a hemosorbent of a multichannel cellular structure were prepared, obtained under various modes of processing the mass and the ratio of components. Data on adsorption activity for methylene blue were obtained. A preclinical study was conducted on animals according to the indicators of the general blood test.

Keywords: carbon materials, hemosorbent, adsorption activity.

INTRODUCTION

Carbon does not belong to the most common elements in nature – out of the total number of atoms of the earth's crust, it accounts for only 0, 14%. However, this element is the basis of the structure of the entire animal and plant world. Therefore, carbon occupies a special position among the chemical elements. Carbon underlies the synthesis of polymer materials, artificial fibers, etc. Finally, carbon has taken a special position in the development of new composite materials. In the beginning, as the basis of matrix polymer materials, then discrete fillers – graphite, soot, pyrocarbon. A sharp increase in the role of composite materials occurred with the appearance of reinforcing filler, carbon and graphite fibers, then carbon-carbon composites, multifunctional and finally nanocomposites. Currently, carbon is known as crystalline, amorphous and partially crystalline transition carbon substances. The crystalline forms of carbon include diamond, graphite, carbine, and fuplerene. Amorphous and partially crystalline transitional forms of carbon include: pyrocarbon, pyrographite, glass-carbon, soot, coke, fibers, films, etc. As V.I. Kasatochkin notes, here we meet with a rare case of continuous changes in the physical and physicochemical properties of a single-component system that depends only on the structure, and not on the composition, as is usually observed for multicomponent systems [1]. Graphite is a common natural mineral, occurring in the form of granular, scaly or lamellar masses, sometimes containing up to 20% of mineral impurities.

The origin of all of them in nature is associated with the effect of high temperatures and pressures on rocks such as coal and bitumen. Graphite has a hexagonal structure. A hexagonal graphite cell belongs to a spatial group with four atoms per unit cell.

Along with crystalline, a large number of amorphous and partially crystalline transition carbon substances are known. These include soot, coke, pyrocarbon, glass carbon, products of thermal decomposition of polymers, fibers, coals of varying degrees of metamorphism. Due to the high kinetic barriers, carbon in the state of transition forms is extremely stable and can exist indefinitely under normal conditions. Structural transformations of carbon occur only under the influence of high temperatures.

Carbon of transitional forms has valuable properties and is of great practical importance. A wide range of changes in properties is associated with the possibility of a set and combination of various hybrid forms and features of the carbon structure. The main elements of its structure include basic tapes, turbostratic packages, amorphous carbon consisting of a set of various hybrid forms, and superatomic formations of the highest order. The structural organization and properties depend significantly on the nature of the feedstock used to produce carbon and the conditions of heat treatment.

The turbostrate structure of carbon is similar and different from that of graphite. Its basis is the basic planes, the structure of which is similar to graphite planes. A certain number of interconnected planes form turbostratic crystals (packets). Unlike graphite, there is no mutual orientation of the planes in the direction perpendicular to the basic planes in the packages, i.e. they are located at different angles to each other [2]. In a strictly crystallographic sense, packages by structure cannot be attributed to crystals, since there is no three-dimensional ordering in them. In each plane of the package, the carbon atoms are arranged in a strict order, so the packages are like two-dimensional crystals [3].

The Franklin diagram of the structure of nongraphitating carbon matter is shown in Figure 1. Only under the influence of high temperatures do structural transformations of carbon occur. Figure 1 shows a diagram of the structure of carbon substances - non-carbonized carbon (a) and artificial graphite (b).

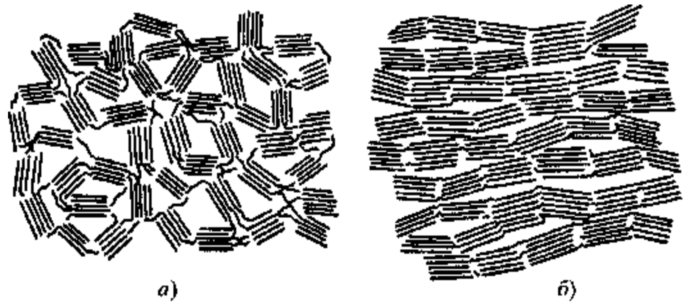

Figure 1 - Diagram of the structure of carbon substances: a - nongraphitating carbon; b - artificial graphite

Under the influence of high temperatures, a carbon material is obtained. Depending on the feedstock, it is possible to obtain a carbon material and a carbon composite material. One of the important properties of carbon composite material is the possibility of application in medicine.

MATERIAL AND METHODS.

To obtain samples, as the raw material vegetable raw material was used - rice husk, which was washed with water and then dried at a temperature of 85-100 ° C for 24 hours.

The chemical composition of the husk indicates the presence of a number of substances useful to humans (Table 1).

Table 1 - Composition of rice husk (Rice)%:

Component	Content, % (wt)
Water	3,75 – 24,08
Ash	11,86 – 31,78
Pentosan	4,52 – 37,0
Cellulose	34,32 – 43,12
Lignin	19,2 – 46,97
Protein	1,21 – 8,75
Fats	0,38 – 6,62

To create a carbon composite material, rice husks were subjected to high-temperature treatment. The process of converting rice husks into carbon composite material was carried out in one stage – carbonation, in which a turbostratic structure is formed (up to 200 ° C - 800 ° C). Carbonation of rice husks has a number of advantages: there is no need for additional mechanical action on raw materials, such as grinding, classification. Carbonation of the feedstock was carried out at various temperatures from 200 ° C-800 ° C. The process was carried out as follows: the activator gas (CO2) was supplied, starting from 200 ° C, up to the selected activation temperature (800 ° C), at which the carbon composite material was kept for 5 hours. For the samples obtained under various temperature conditions, the carbon content was measured on a Quanta 200i 3D scanning electron microscope at the Al-Farabi Kazakh National University, in the "National Open-type Nanotechnology Laboratory".

Carbonized carbon composite material was demineralized. The demineralization process was carried out in the Soxlet apparatus at the Scientific Production and Technical Center "Zhalyn". Demineralization is carried out with 5% nitric acid, with a ratio of rice husk: 5% nitric acid = 1:(3-7); then boiled for 2-3 hours; after boiling, the mixture was left overnight for more complete demineralization.

After that, the spent nitric acid is drained by decantation, the sorbent is transferred to another container and washed several times with distilled water by boiling to establish a neutral medium.

Carbonation of rice husks produced a carbon composite material consisting of carbon and silica. During the temperature rise, volatile carbonation products are released (CO, CO2). The bonds that close on carbon are released and a turbostratic structure is formed. During carbonization, an increase in the average size is observed Lc reducing the interlayer distance d002 in bundles of parallel carbon layers up to 0.343 nm and an increase in density.

Specific surface area was measured for CCM samples obtained at different temperature conditions. The specific surface area was measured by gas adsorption: the sample is cooled by liquid nitrogen when a certain amount of adsorption gas (nitrogen, etc.) of a certain density is supplied to helium. To calculate the surface area of the adsorbent, the volume of gas relative to the monomolecular layer and the cross-sectional area of the adsorbed gas molecule were determined.

When desorption equilibrium is reached, the detector signal returns to the baseline. The desorption peak is usually used for calculations, as it has a sharp shape and is suitable for accurate integration.

The resulting CCM was used to create a carbon monolith of a hemosorbent. A plastic mass was prepared for 5 samples of hemosorbent.

The preparation of the base mass of a carbon monolith involves mixing UKM with binding components - carboxymethylcellulose (CMC) and dextrin. Mixing of 3 dry components is carried out for 20-30 minutes - until a homogeneous mass. An alcohol solution was added to the mixture of dry components. With careful mixing, a homogeneous plastic mass is obtained for 20-30 minutes. The mass is placed in a sealed plastic container for interoperative storage. A carbon monolith of direct flow with a multi-channel structure is made from the resulting mass (Figure 2).

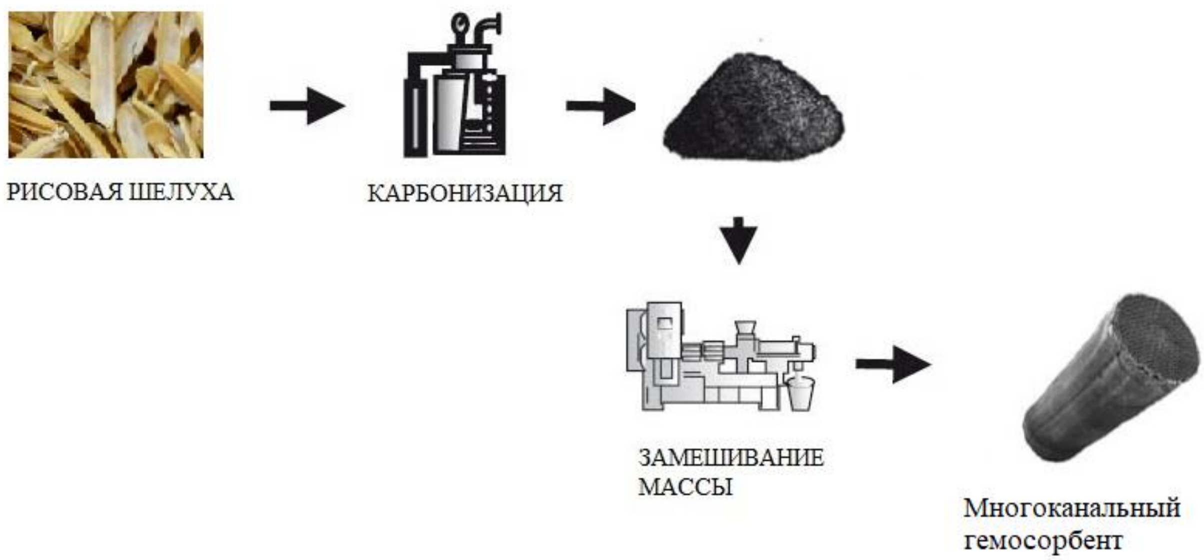

Figure 2 – technological operations for obtaining a carbon monolith of direct flow with a multi-channel structure

Samples were obtained: No.1, No.2, No.3 (MgCitr, without washing HNO3), No.4 (desilicated),No.5 (desilicated, sugar, magnesium citrate, with washing with nitric acid). For 5 samples, the base composition was modified according to the following ratio:

Sample No. 1 - desilicated carbonized carbon composite; binder composition - carboxymethylcellulose, dextrin, alcohol solution;

Sample No. 4 - desilicated;

Sample No. 5 - desilicated carbonized carbon composite, sugar, magnesium citrate, washed with nitric acid).

For the samples, the dynamics of sorption of a methylene blue solution was observed depending on time.

Preclinical animal tests were carried out for sample 1. Sample 1 was washed with 1 liter of 0.9% saline solution for 40 minutes. Washing was carried out until complete dust removal.

When washing, ash content is not observed in the washing solutions (ash content - destruction of channels, dustiness). At speeds of 100 and 200 ml /min, ash content was practically absent.

The experiment was carried out in a sterile operating unit in vivo conditions at the RSE on the REM at the Institute of Human and Animal Physiology of the SC of the Ministry of Education and Science of the Republic of Kazakhstan. Blood sampling was performed before hemosorption, at 25 minutes, at 45 minutes of hemosorption. A general clinical blood test was performed for three blood samples.

Results and discussions.

The study of the properties and production of a carbon composite material based on rice husk showed the following results: Samples carbonized at different temperatures differed significantly in appearance. Thus, samples carbonized at low temperatures (300-500 °C) visually differed from samples carbonized at higher temperatures, having a dark brown rather than black color. From this it can be concluded that the carbonization process to a temperature of 500 ° C did not take place completely, but only partially. To obtain a carbon composite material with positive properties, it is advantageous to use a temperature of 700oC (Figure 3).

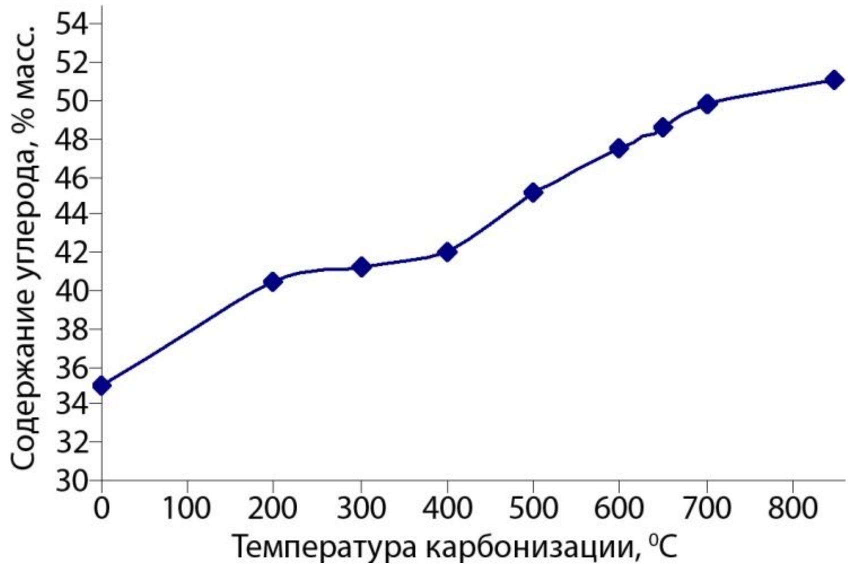

Figure 3 – Dependence of carbon content (% by weight) from the carbonation temperature of the sample

To increase the specific surface area, the method of vapor-gas activation was used.

The specific surface of UKM during carbonization reaches ≈ 210 m2/g at 700 ° C (Figure 4). This shows that an increase in the carbonation temperature increases the specific surface area and creates a developed porous structure.

Porosity is a property of the CCM, which characterizes the presence of voids (pores) between the layers of the structure. CCM has an open porosity consisting of voids in the structure that communicate with each other and with the outer surface of the body and are accessible to replacement media molecules. The pores that are located in the structure of the CCM absorb various medium-molecular toxins, which confirms the possibility of using a carbon monolith as a hemosorbent.

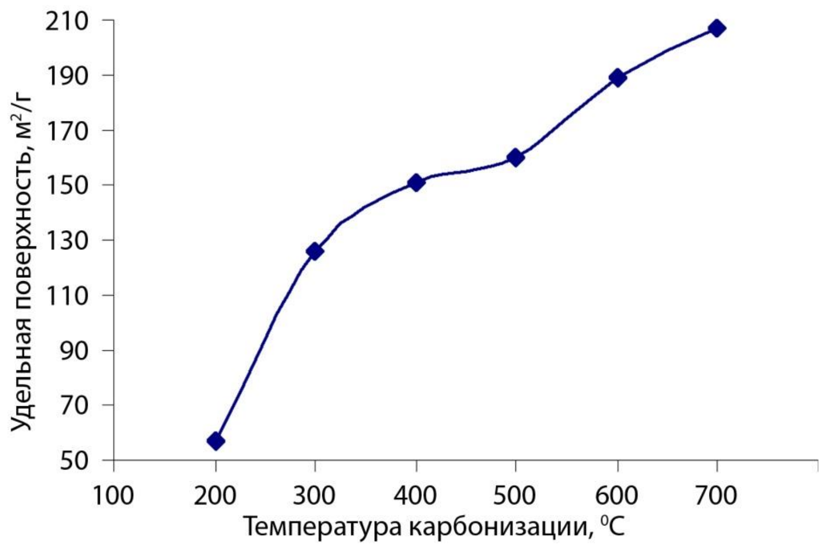

Figure 4 - Dependence of the specific surface of rice husks on the temperature of the process using steam activation

The measurement of the sorption dynamics of the methylene blue solution as a function of time is shown in Figure 5.

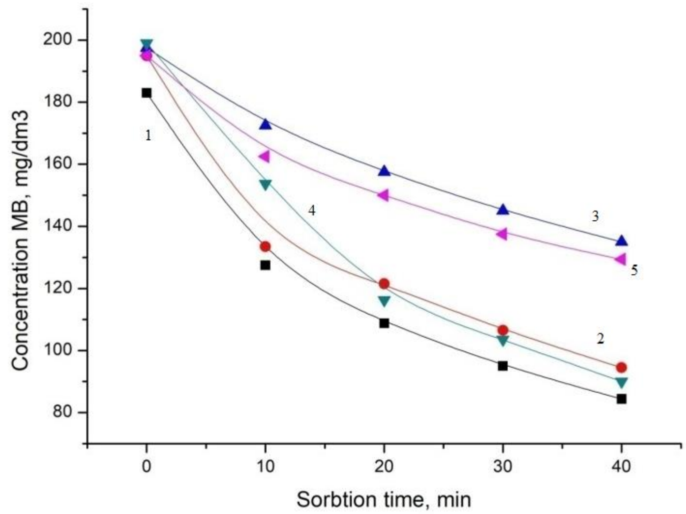

Figure 5 – change in the concentration of the solution depending on time

The initial concentration of methylene blue was 200 mg/m3 at the initial minute. After 3rd minute, the concentration for sample No.1 was 183 mg/m3, at 11th minute the concentration was 123 mg/m3, for sample No.5 (desilicated, sugar + MgCitr, HNO3) at 11th minute the concentration was 162 mg/m3. For samples No.4 (desilicated) and sample No.1 at 21st minute the concentration was equal to 107 mg/m3 and 103 mg/m3, respectively. And for sample No.3 (MgCitr, without HNO3), the concentration was equal to 161 mg/m3.

На 40 минуте концентрация образца №1 была равна 83 мг/м3, образца 32 - 100 мг/м3, образца 32* (MgCitr, без HNO3) - 142 мг/м3, образца 32 Д

(десилицированный) - 87 мг/м3, образца 32Д (десилицированный, сахар + MgCitr, HNO3) - 138 мг/м3.

At 40th minute, the concentration of sample No.1 was 83 mg/m3, sample 32 - 100 mg/m3, sample 32* (MgCitr, without HNO3) - 142 mg/m3, sample 32 D

(desilicated) - 87 mg/m3, sample 32D (desilicated, sugar + MgCitr, HNO3) - 138 mg/m3.

As shown in the graph, sample No. 1 has an effective sorption capacity. Sample No. 1 is made of carbon composite material and binder, not modified.

It is shown that modification of the initial composition of the carbon monolith does not increase the sorption efficiency in relation to toxins.

The use of 5% nitric acid for hydrolysis is due to availability and safety.

The composition and qualitative characteristics of carbonized rice husks and ingredients make it possible to create a plastic mass of carbon hemosorbent with high adsorption activity, tuned to extract pathological toxic substances [7].

Thus, the structural transformations of homogeneous graphitized carbon during the heat treatment of plant raw materials makes it possible to create a carbon monolith of a hemosorbent with an effective sorption capacity.

As a result of preclinical studies, the following general analysis results were obtained (Table 1):

Table 2 – results of a general blood test

Indicators	Hematological Analyzer	Dog	Result	Result	Result
white blood cells	WBC $*10^5$/L	6,0-17,0	15,9	5,8	2.4
	Lymphocytes	0,8-5.1	0,9	0,6	0.7
	Monocytes	0,0-1,8	0,7	0,4	0.3
	Granulocytes	4,0-12.6	14,3	4,8	1.4
red blood cells	RBC $*10^{12}$/L	5,5-8,5	9,60	9,9	8.60
	HGB	110-190	139	124	122
	HCT %	66,0	66	58,1	58.7
	MCV fL	68,8	68,8	68,3	68.3

As can be seen in Table 1, the process of hemosorption by carbon monolith affected granulocytes. The initial blood sample contained granulocytes above the norm – 14.3. Then, after 30 minutes of sorption, the sample was equal to 4.8, after sorption for 45 minutes, granulocytes were equal to 1.4 (Figure 6).

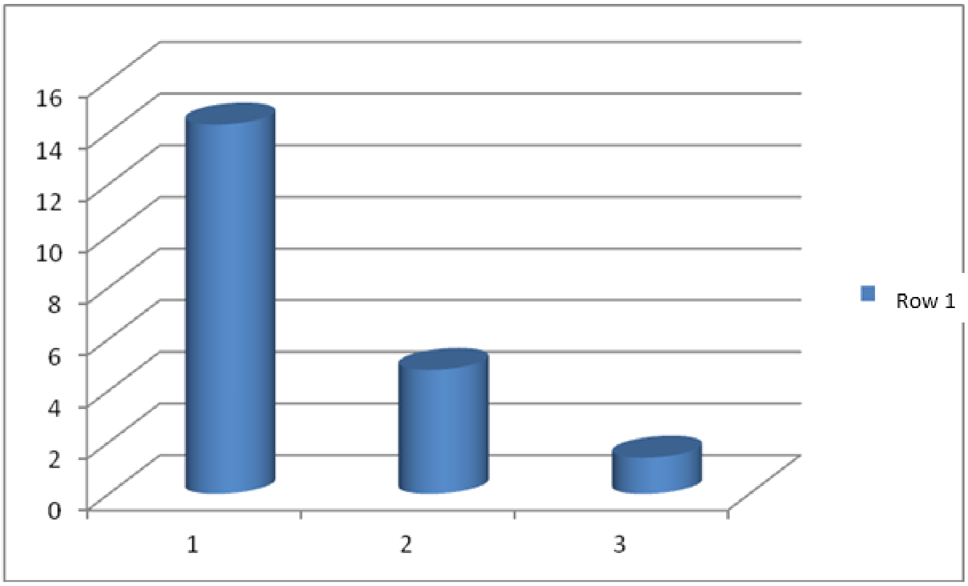

Figure 6 - Diagram of the reduction of granulocytes in the blood of animals

Conclusion.

Granulocytes are usually elevated in the presence of inflammation in the body. A decrease in the level of granulocytes occurs with aplastic anemia (loss of the ability of the bone marrow to produce blood cells), after taking certain medications, as well as with systemic lupus erythematosus (connective tissue disease), etc.

Viruses multiply at a high rate. Everyone throws out into the blood the products of their vital activity - toxins. When there are few toxins, the immune system copes with their detection and elimination easily. But when there are too many of them (for example, with food poisoning) or they occur faster than they are excreted (as with the flu), then a person gets sick. If the toxins are too strong or there are too many of them, then the organs and systems of the body will begin to fail [8]. Perhaps hemosorption with a carbon monolith will allow timely sorption of toxins in the body, preventing poisoning of the whole organism.

Thus, the effect of hemosorption by a carbon hemosorbent of a multichannel structure possibly sorbs viral foci in the body. However, this area requires additional research.

The preclinical animal study was conducted with the approval of the Local Ethics Committee of the Faculty of Medicine and Healthcare of Al-Farabi Kazakh National University IRB00010790.

The research was carried out within the framework of project No. 0097-17–GC: "Creation of the first production of domestic laminar flow hemosorbents" (JSC "Science Foundation" RK).

Conclusions. Thus, it was shown that:

- carbon composite material makes it possible to manufacture a carbon monolith with a multi-channel structure;
- the resulting carbon monolith has high sorption characteristics and specific surface area;
- it is possible to use carbon monolith as a hemosorbent for intoxication of the body;
- hemosorption on animals has shown that carbon monolith can possibly sorb viral foci in the body. However, this area requires additional research.

References

1. Nuraly A.M., Bekseytova K.S., Biysenbayev M.A., Nuraliev M.A., Panov S.A., Myrzagaliev A.K. (2017). Comparison of adsorption properties of dietary fiber obtained from vegetable raw materials. Journal "Biomedicine". Vol. 4 (56). pp. 35-39.
2. Yuyao Li, Biisembaev M.A., Qianming Gong, Aknazarov S.KH , Fangping Lu, Yilun Huang. (2019) Preparation of Lotus Root-Type Monolithic-Activated Carbons with an Hiearchical Pore Structure from Rice Husks and Their Adsorption of Vitamin B 12. - ACS Omega. Vol. 4, No.20. pp. 18930-18935.
3. Kostyuk G. P. (2007). Differentiated assessment and correction of the mental state of military sailors during screening psychoprophylactic examinations. Bulletin of Psychotherapy. No.22 (27). pp. 80-86.
4. Nuraly A.M., Aknazarov S.H., Varol E.A., etc. (2019). Investigation of the effect of carbon hemosorbent of the microcell structure on the absorption of ethanol.- Internauka. Collection of articles based on the materials of the XXIX International scientific and practical conference. Section. Chemistry, Physics, Biology. No. 11 (20). Moscow: 2019. pp.54-59
5. Iticenter study of the naturalistic outcomes of patients with treatment resistant depression. (2006). J. Clin. Psychiatry. Vol. 67. p. 688-695. 13.
6. Fava M. (2003). Diagnosis and definition of treatment-resistant depression // Biol. Psychiatry. Vol. 53. – p. 649-659.

7. Anikhovskaya I. A., Oparina O. N., Yakovleva M. M. (2006). Intestinal endotoxin as a universal factor of adaptation and pathogenesis of the general adaptation syndrome. Human Physiology 2006; 32 (2); 87-91.
8. Medical Toxicology. (2012). National leadership. Edited by Academician of the Russian Academy of Medical Sciences E.A., Luzhnikov. M., Publishing Group "GEOTAR-Media", pp. 725 - 810.