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Adsorption Properties of Carbon Enterosorbents Modified with Biologically Active Substances

L. G. P'YANOVA[1,2], V. A. LIKHOLOBOV[1,2,3], L. K. GERUNOVA[4], A. V. SEDANOVA[1], and A. V. LAVRENOV[1]

[1]*Institute of Hydrocarbons Processing, Siberian Branch, Russian Academy of Sciences, Omsk, Russia*

E-mail: medugli@ihcp.ru

[2]*Omsk State Technical University, Omsk, Russia*

[3]*Omsk Scientific Center, Siberian Branch, Russian Academy of Sciences, Omsk, Russia*

[4]*Omsk State Agrarian University, Omsk, Russia*

Abstract

To improve biospecific properties of carbon enterosorbents for veterinary purposes methods for chemical modification of their surface were proposed. Modified samples of carbon sorbent were synthesized: carbon sorbent containing polyarginine and the betuline preparation impregnated into a porous matrix. Adsorption properties of the tested samples in relation to substances modelling low and average molecular mass toxins (vitamin B12, methylene blue) were studied. The assessment of adsorption properties in relation to proinflammatory cytokines at the example of a sorbent modified with polyarginine was carried out. It was found that adsorption properties of carbon sorbents were influenced by localized application of modifiers to carbon sorbent samples and elevated contents of oxygen- and nitrogen-containing groups on their surface.

Key words: carbon sorbent, arginine, polyalanine, betuline, modification, adsorption properties, vitamin B_{12}, methylene blue, proinflammatory cytokines, interleukin 8, interleukin 6, TNF-alpha

INTRODUCTION

The development of carbon materials with elevated adsorption activities in relation to certain toxic substances with detoxification and corrective properties by regulating the chemical nature of their surface (chemical modification) is of significant interest, since it allows broadening the range of biospecific action sorbents.

The major action mechanism of sorptive preparations is based on binding toxic substances in the gastrointestinal tract by adsorption, absorption, ion exchange, complexation [1–3].

At sorption of toxic substances by the carbon sorbent surface, hydrophobic by nature, the major interaction mechanism is adsorption driven by the effect of dispersion forces. At physical adsorption, the determining factor is molecule proportionality of toxic substances and pores of the sorbent; therefore, well-known carbon sorbents have different activities [1, 4].

Table 1 presents characteristic dimensions of microorganisms and various compounds. The selection of sorbents with the specific surface structure allows extracting from an organism a wide range of toxic properties.

To improve biospecific properties of carbon sorbents two directions are used in the work:

TABLE 1
Effective sizes of small particles, molecules and ions

Particles	Size range, diameter, nm
Yeast and fungi	1000–10 000
Bacteria	300–10 000
Oil emulsions	100–10 000
Solid colloidal particles	100–1 000
Viruses	30–300
Proteins and polysaccharides (M = 10^4–10^6 g/mol)	2–10
Enzymes (M = 10^4–10^5 g/mol)	2–5
Antiparasitic preparations (M = 300–1000 g/mol)	1–3
Antibiotics (M = 300–1000 g/mol)	0.6–1.2
Organic molecules (M = 30–500 g/mol)	0.3–0.8
Inorganic ions (M = 10–100 g/mol)	0.2–0.4
Water (M = 18 g/mol)	0.2

1) chemical surface modification by polycondensation of arginine and in situ polymer formation (directly on the surface of carbon sorbents); 2) impregnation into a porous matrix of carbon carrier nanodispersed betulin in a water-soluble form into a porous matrix of a water-soluble form. Currently, similar processes almost have not been studied.

Earlier [5], we studied physicochemical characteristics of the synthesized veterinary preparations. The present work studies adsorption properties of samples in relation to substances modelling low and average-molecular mass toxins. Adsorption properties are one of the major characteristics to assess sorbents efficiency.

EXPERIMENTAL

A research object is mesoporous carbon enterosorbent Zoocarb. The carbon sorbent sample corresponded to the TU 9318-003-71069834–2006 specifications and represented shiny spherical granules with from 0.1 to 1.0 mm in diameter, black or silver in colour, odourless. The carbon mass fraction in the sample was no less than 99.5 %; mass loss at drying was no more than 0.10 %; the residue after calcination – no more than 0.5 %; The adsorption activity for methylene blue is not less than 30 μg/mg; according to sieve analysis results, the residue on the sieve with a hole diameter of 1.0 mm and passed through a sieve with a hole diameter of 0.1 mm did not exceed 0.5 %.

Methylene blue (M = 319.8 g/mol, average diameter of 1.26 nm), Shostka Chemical Reagents Plant JSC (Ukraine); vitamin B_{12} (M = 1355 g/mol; average pore diameter of 6 nm) Semashko Moskhimfarmpreparaty JSC (Russia) were selected as models of toxic compounds.

The study of adsorption properties of carbon sorbent samples in relation to marker substances was carried out by the spectrophotometric method [6–11].

Concentrations of adsorbates subject to possible concentrations of toxins in blood, the model of which was represented by methylene blue dye and vitamin B_{12}, were selected to undertake a study. Adsorption was studied under static conditions at a temperature of (25±2) °C. Studying the dependence of adsorption of substances on sorbent samples on contact time was carried out as follows: to a sample weight of the sorbent (0.1800±0.0002) g 1.8 mL of a solution of a dye or a vitamin with a concentration of (0.50±0.02) mg/mL was added, and the amount of adsorbate in solution was measured after a certain contact time (2, 4, 6, 24, 48 h). The concentration of substances in the solution was assessed before and after adsorption at appropriate wave lengths (wave length for methylene blue is 660 nm, vitamin B_{12} is 360 nm), the cuvette thickness is 10 mm.

The static exchange capacity of the sample was calculated according to the formula

$$a = (C_{ini} - C_{eq})V/m \quad (1)$$

where C_{ini} and C_{eq} are initial and equilibrium concentrations of the marker in the solution, respectively, mg/mL; V is the solution volume, mL; m is the sample weight of the sorbent, g.

After studies, a graph $f(x) = y$ the contact time versus the amount of adsorbed substance from the solution was constructed.

The dependence of adsorption on the investigated sorbents of marker substances on their concentration in the solution was investigated at the specified equilibrium time.

Static exchange capacity values were calculated, and the specific adsorption curve on the investigated sorbents of marker substances on their concentration in the solution was constructed.

Calibration curves of solutions of the dye and vitamin B_{12} had a linear dependence (correlation coefficient $R^2 = 1$) and were described by the following equations:

1) for solutions of methylene blue, in a concentration range of 0.005–0.010 mg/mL:

$y = 212.41x + 0.0509$;

2) for solutions of vitamin B_{12}, in a concentration range of 0.010–0.500 mg/mL:

$y = 16.945x + 0.0029$.

The assessment of adsorption properties in relation to anti-inflammatory cytokines was carried out on the example of a sorbent modified with polyarginine according to the techniques developed based on the Central Research Laboratory of the Omsk State Medical University. The study of adsorption properties of samples was studied in relation to cytokines (interleukin 6 (IL-6)), interleukin 8 (IL-8), tumor necrosis factor (TNF)). Testing was carried out using blood plasma of laboratory animals (rats) with experimental peritonitis. The concentration of proinflammatory cytokines in blood plasma of laboratory animals was determined before and after its contact with enterosorbents samples. Levels of interleukins were determined by enzyme-linked immunosorbent assay (ELISA) using a Multiscan EX tablet photometer (Finland) using kits Pro Con IL-6, Pro Con IL-8 (Protein Contour JSC, St. Petersburg) by the method of solid-phase ELISA.

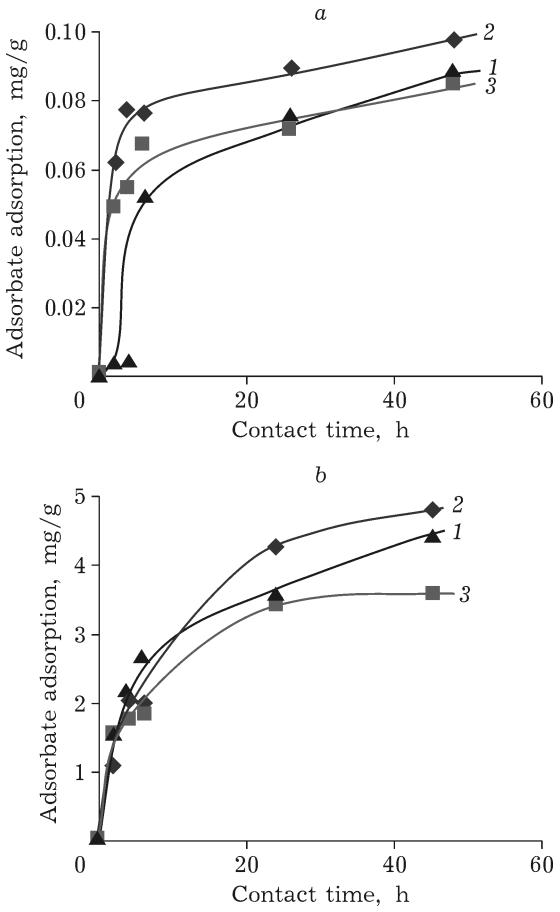

Fig. 1. Adsorption value of methylene blue (*a*) and vitamin B_{12} (*b*) *vs* contact time for the samples under study: *1* – initial sample; *2* and *3* – samples modified with betuline and polyalanine, respectively.

RESULTS AND DISCUSSION

Research results of adsorption of methylene blue and vitamin B12 on sorbent samples are presented in Fig. 1.

Equilibrium occurs faster at adsorption of methylene blue and vitamin on modified samples than on the initial sample. This can be explained by smaller values of the specific surface area of modified samples due to pores closed by the modifier. By occurring the equilibrium in the system, the amount of the adsorbed dye is almost identical for all samples and is 0.087–0.098 mg/g (see Fig. 1, *a*). Thus, to study the adsorption process the contact time equal to 24 h was selected.

The study of adsorption of methylene blue and vitamin B_{12} on sorbent samples on their

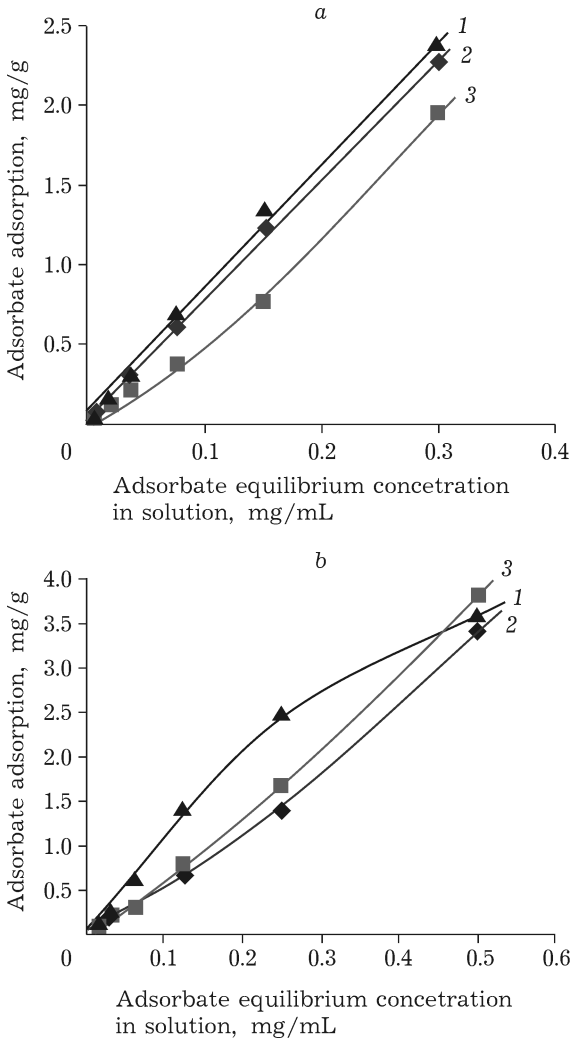

Fig. 2. Adsorption isotherms of methylene blue (*a*) and vitamin B_{12} (*b*) from a solution in the studied samples of the carbon sorbent at contact time of 24 h: *1* – initial sample; *2* and *3* – samples modified with betuline and polyalanine, respectively.

concentration in solutions allowed finding that adsorption values of the samples under study allowed finding that adsorption values did not differ from each other and were (2.17±0.22) mg/g (Fig. 2, *a*). Herewith, the adsorption curve for the sample modified with betulin nearly coincided with the curve found for the initial sorbent. The type of adsorption typical for microporous sorbents is observed for the sample modified with polyarginine. This is more likely due to a peculiarity of the modifier distribution in the porous structure of the carbon sorbent. The type of isotherms typical for mesoporous sorbents is observed in the initial sorbent.

It was found that the value of adsorption of vitamin B_{12} was higher for the sample modified with polyarginine and reached a value of (3.64±0.20) mg/g (see Fig. 2, *b*). It must be noted that adsorption isotherms of two adsorbates on the samples under study did not come out on the plateau, which indicates *the possibility of further saturation* of sorption materials. Thus, it was demonstrated that modified samples had the high adsorption capacity.

The assessment of adsorption properties in relation to proinflammatory cytokines was carried out on the example of the sorbent modified with polyarginine based on the OmSMU factor alpha (TNF-α), proinflammatory cytokines IL-6, IL-8 in blood plasma of rats (Table 2). Most likely, higher adsorption properties of the modified samples in relation to IL-8 are explained by the structure and molar mass, isoelectric point in aqueous solutions of the latter, sorbent pore sizes. Localized deposition of polymer films of amino acids on the carbon carrier surface with appropriate changes of its textural and acid-base properties exerted the main effect on the interaction of cytokines molecules with the modified surface of sorbents.

Thus, modification of carbon enterosorbent with polyarginine leads to the synthesis of a prep-

TABLE 2

Adsorption properties of samples with respect to proteins (n = 30), (M±m)

Blood plasma proteins	Level of cytokines, pg/mL	
	before sorption	after sorption*
IL-6 (M = 21 000, pI 6.2)	26.40±1.20 (11.2, 39.9)	22.20±0.50 (5.68, 27.2)
IL-8 (M = 8500, pI 9.9)	3.10±0.20 (1.03, 5.32)	0.95±0.06 (0.575, 2.250)
TNF-α (M = 26 000, pI 5.3)	2.25±0.75 (0.875, 4.550)	1.2±0.03 (0.1, 3.1)

Note. M is molar mass of protein molecules, g/mol; pI is protein isoelectric point.

* Statistically significant differences relatively to animal indicators before carrying out sorption ($p < 0.05$).

aration that allows extracting from biological liquids proinflammatory cytokines including IL-8.

CONCLUSION

Modification of the carbon enterosorbent surface with betuline and polyarginine leads to the improvement of their adsorption properties in respect to markers of toxic substances (methylene blue and vitamin B_{12}). The adsorption values of methylene blue and vitamin B_{12} depend on the specific surface value of sorbents and decrease with an increase in the amount of the applied modifier, which testifies that mostly physical adsorption occurs. The adsorption value of vitamin B_{12} for the sample modified with betulin is higher than that for the sample modified with polyarginine. Adsorption values of modified samples in relation to methylene blue almost do not differ from each other.

The carbon sorbent modified with polyarginine reduces the content of proinflammatory cytokines (interleukin 6, interleukin 8, tumor necrosis factor) in the blood plasma of rats with acute experimental peritonitis.

The usable concentrations of biologically active components (betuline, arginine) ensure incomplete pore closure of the material (localized surface modification). The free surface of the preparation not filled with particles determines effective sorption of substances that are models for toxins. The emergence of new functional groups on the surface of modified sorbents ensures their high adsorption properties in relation to proinflammatory cytokines.

The use of biospecific action sorbents developed will broaden the range of sorption materials used in veterinary medicine practice for the prevention and integrated treatment of a full range of diseases.

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