

## INFLUENCE OF PHYSICAL-CHEMICAL PROPERTIES OF ACTIVE CARBONS ON GALLIC ACID ADSORPTION

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**Abstract:** The adsorption of gallic acid on active carbons of different ranks with different pore structure and chemical state of the surface is investigated. The regularities and features of the adsorption process are established. It is revealed that the adsorption isotherm of gallic acid from the aqueous solution with activated carbon of AG-OB-1 rank refers to the L-type isotherms by Giles's classification, and AC adsorption isotherm of ABG and Purolat-Standard ranks – to the S-type isotherms. L-type isotherm gives evidence concerning the flow of physical adsorption. With S-type isotherm is the adsorption described, at which the strength of the interaction between the solute and the adsorbent is less than the force of interaction between the adsorbed molecules, which can be explained by the formation of hydrogen bonds. It was found that the maximum adsorption of gallic acid with carbon sorbents changes in the following sequence - "Purolat-standard" > ABG > AG-OV-1. The mechanism of adsorption of gallic acid on active carbons is offered. Proceeding from the structure, the chemical state and the main adsorption parameters of active carbon, we can assume that the adsorption of gallic acid has physical nature. It can take place in pores, both due to dispersion interaction (of van der Waals forces) and due to the interaction between the active carbon surface functional groups, containing oxygen with carboxyl and hydroxyl groups of gallic acid. The values of adsorptive capacity testify to the dependence of the adsorption efficiency on the structure and physical-chemical properties of the sorbent. It has been determined that by the absorption of gallic acid specific interaction makes greater contribution. It is shown that the results obtained can be applied to create adsorption technologies on removing gallic acid from the sewage containing individual components and from the mixture with other polyphenols, including beer wort.

**Keywords:** Gallic acid, carbon sorbents, adsorption

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### INTRODUCTION

Gallic acid (3,4,5-trihydroxybenzoic acid) is one of the most common plant acids. As a part of the plant usually in a bound form (esters, polymers) it is a precursor to a number of polyphenolic substances [1].

This acid is contained in the sewage of pharmaceutical factories, it is present as a component in the beer wort. Gallic acid and its derivatives have a pronounced astringent taste. When being boiled together with hops, they contribute to the formation of trub, reducing the colloidal stability and the quality of beer.

It has all the properties of hydroxycarbon acids. The most reactive is OH group in the position 4 (Fig. 1).

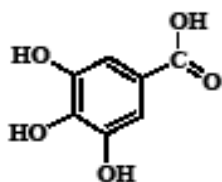


Fig. 1. Chemical structure of gallic acid.

Of the various reactions of gallic acid (oxidative coupling and esterification) there arise tannins. The tannins are divided into hydrolyzable tannins - carbohydrate and gallic acid esters (or its oligomers) and non-hydrolyzable condensed tannins.

Gallic acid forms oligomers of two types: with a carbon-carbon bond between the phenyl rings and with a complex ester linkage between the fragments. In this regard, gallic acids themselves are divided into non-hydrolyzable (diphenyl derivatives) and hydrolyzable (esters). Both these and those acids form hydrolyzable tannins with carbohydrates, because in an aqueous medium under conditions of enzymatic, alkaline or acid catalysis phenolic acids and carbohydrates are formed. These tannins are esters of monosaccharides with gallic or trigallic acids. Glucose esters with condensed gallic acid can be considered as tannins of dual nature, because they contain hydrolyzable fragments. These completely non-hydrolyzable tannins are derived from flavonols.

Under the influence of atmospheric oxygen tannins form stable black dyes [1].

Dimerization and polymerization of coniferyl alcohol compounds help to form such derivatives of phenolic acid or, to be more exact, phenolic alcohol

groups as lignans and lignins. Lignans are accumulated in all plant organs, they are present in dissolved form in resins and essential oils. Lignins in plants - important components of the cell wall of conducting and supporting tissues that act as tissue mechanical strengthening and cells protecting from biological, chemical and physical effects [1].

In practice, for the bleaching of natural water and food processing environments active carbons (AC) are used. In the production of beer to improve the properties of the final product active carbon of BAU-A, BAU-MF ranks is used [2]. For water treatment carbon AG-OB-1, with good performance is widely applied. Furthermore, in recent years the range of carbon materials has been expanded due to semi-cokes produced by the new technology. The difference of applied technology consists in replacing the traditional two-step process of carbonizing the raw material in an inert atmosphere, followed by activation for one-step process of air carbonization/activation. This reduces

the final price of the sorbent due to the reduction of energy consumption for its production [3]. The use of these adsorbents will reduce the cost of production of beer and soft drinks as well.

The aim of the study was to investigate the adsorption of gallic acid by active carbons different in their structure and nature, to identify the possibility of their use in the process of improving the quality of beer.

## OBJECTS AND METHODS OF RESEARCH

The objects of study are aqueous solutions of gallic acid, active carbons of the ranks: AG -OV-1 - granular AC (JSC "Sorbent", Perm) and semi-cokes ABG (PO "Carbonika F", Krasnoyarsk) and "Purolat-Standard" (JSC "Synthesis", Rostov-on-Don) [3]. General characteristics of carbon sorbents are shown in Table 2 [4]. All AC before study were washed with distilled water to remove dust particles. Then they were dried at room temperature ( $23 \pm 2^\circ\text{C}$ ) during the day.

**Table 2.** Characteristics of carbon sorbents

AC rank	AG -OV-1	ABG	Purolat-Standard
Raw material	the mixture of coals, wood-chemical and coke pitch	brown coal	anthracite
Graining (form)	Granular (cylinder)	crushed	crushed
Carbonization and activation	Two-step	One-step	One-step
Particle size, mm	0.5–2.8	1.0–5.0	0.1–3.0
Bulk density, g/cm <sup>3</sup>	0.52	0.49	0.68
Strength, %	70	70	70–80
Ash content, %	31	12	6
Mass fraction of Fe, %	0.62	0.13	0.02
Pore surface area, m <sup>2</sup> /g	700–800	500	800
Total volume of pores on water, cm <sup>3</sup> /g	0.76–0.84	0.50–0.57	0.24
Adsorptive activity on I <sub>2</sub> , %	65	60	60
Adsorptive activity on new methylene blue, mg/g	-	160	140
Time of the protective effect on benzene, min	-	41	60
pH of the aqueous extract	6.8	7.5	8–9

Adsorption of the aqueous solution of gallic acid was studied at room temperature ( $23 \pm 2^\circ\text{C}$ ) of limited volume under continuous stirring for 7–9 hours, in static conditions at concentrations ranging from 20 to 800 mg/dm<sup>3</sup> at the ratio of AC: an aqueous solution of gallic acid of 1 : 100.

Adsorption of gallic acid ( $\Gamma$ ) was estimated by the equation

$$\Gamma = \frac{C_0 - C_p}{m} V_p, \quad (1)$$

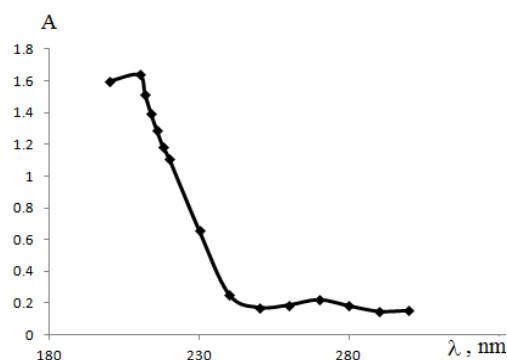
where  $C_0$  is the concentration of the initial solution, mole/dm<sup>3</sup>;  $C_p$  is the concentration of the equilibrium solution (after adsorption) mole/dm<sup>3</sup>;  $V_p$  is the volume of the solution, dm<sup>3</sup>;  $m$  is the mass of the adsorbent, g.

Determination of gallic acid in the solution was carried out by spectrophotometry at its own absorption.

For analysis, the wavelength was chosen according to the spectral curve registered on the instrument SF-46 for aqueous solution of individual substances (Fig. 2) [5].

The concentration of the solutions for the individual substances of gallic acid in the selection of optimum conditions of analysis was 20 mg/dm<sup>3</sup>, distilled water

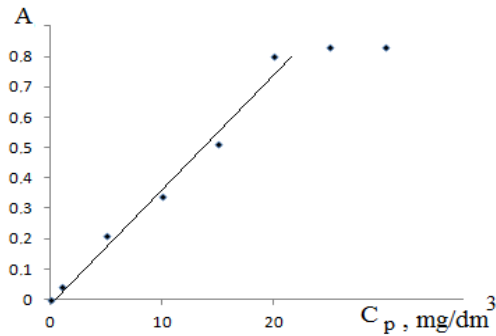
was used as a reference solution. According to the analysis, light absorbing layer thickness of 10 mm, and the wavelength of 230 nm were chosen.



**Fig. 2.** The spectral dependence of the optical density of the gallic acid aqueous solution at the concentration of 20 mg/dm<sup>3</sup>.

In a series of solutions with different concentrations there was determined the linear region for the construction of calibration curves. The dependence of

the optical density of the concentration is shown in Figure 3. The relative error in the determination of polyphenolic compounds is 4%.



**Fig. 3.** The calibration dependence of the optical density on the concentration of gallic acid in the solution.

In the gallic acid determining, the test solutions with the concentration of more than 25 mg/dm<sup>3</sup> were diluted, for each solution dilution factor was chosen individually. The content of gallic acid in the test solution was calculated as follows:

$$C = X \cdot \frac{V_{mf}}{V_{al}}, \quad (2)$$

where  $X$  is the concentration of gallic acid in mg/dm<sup>3</sup>, found from the graph;  $V_{al}$  is the aliquot of the test solution, cm<sup>3</sup>;  $V_{mf}$  is the volume of measuring flask, cm<sup>3</sup>.

The limiting value of the adsorptive capacity was calculated using the equation of Dubinin-Radushkevich:

$$\Gamma_0 = \frac{W_0}{V_m} \exp - \frac{RT \ln C_s C_p^2}{E\beta}, \quad (3)$$

where  $\Gamma_0$  is adsorbent maximum adsorptive capacity, mole/g;  $K$  is the universal gas constant, J/mole·K;  $T$  is temperature, K;  $E$  is characteristic adsorption energy, J/mole;  $\beta$  is coefficient of affinity;  $C_p$  is equilibrium concentration of the solution, mole/dm<sup>3</sup>;  $C_s$  is the concentration of saturated solution, mole/dm<sup>3</sup>;  $V_m$  is molar volume of the adsorbent, cm<sup>3</sup>/mole;  $W_0$  is the limiting volume of the adsorption space cm<sup>3</sup>/g.

Structural characteristics of the adsorbents were determined by the low-temperature nitrogen adsorption on the specific surface area analyzer "Sorbtometer M" (production of Inst. of catalysis, Sib. Branch of RA of Sci., Novosibirsk).

The chemical state of the active coal surface - the amount of functional groups containing oxygen was determined by Boehm titration procedure.

The values of characteristic energies ( $E$ ) and the size of the half-width slit-shaped pores ( $\gamma$ ) have been determined taking into account the coefficient of affinity [6, 7].

$$E = \beta E^0, \quad (4)$$

where  $E$  is the characteristic adsorption energy of dissolved organic compounds, kJ/mole;  $E^0$  is the

characteristic adsorption energy of benzene vapor, kJ/mole;  $\beta$  is the affinity factor.

The affinity factor was calculated using the formula:

$$\beta = P P_0 = 0.97, \quad (5)$$

where  $P$  and  $P_0$  is the parachors of the test substance and benzene, respectively [Tolmachev's hand-book].

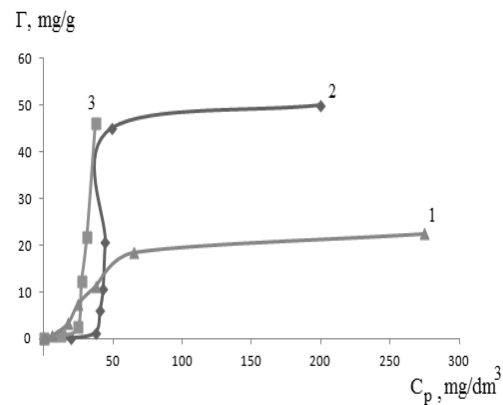
These parachors of organic matter were calculated by the formula [6, 8]:

$$P = \frac{M}{\rho} \sigma^{1.4}, \quad (6)$$

where  $M$  is the molar mass of the matter, g/mole;  $\rho$  is the density of the matter, g/cm<sup>3</sup>;  $\sigma$  is surface tension of the matter in the liquid state, N/m.

## RESULTS AND DISCUSSION

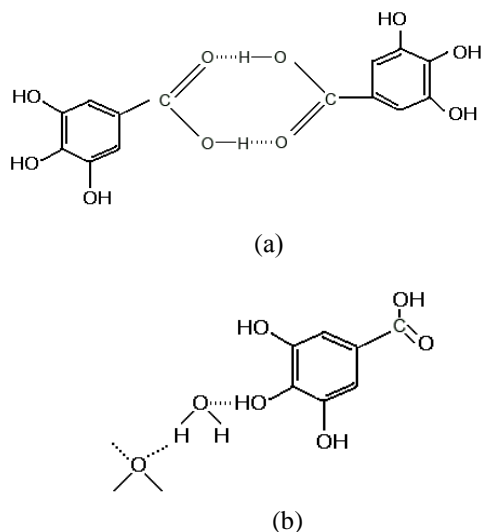
The experimental adsorption isotherms of gallic acid from the aqueous solution are given in Figure 4.



**Fig. 4.** Adsorption isotherms of gallic acid from the aqueous solution with adsorbents of (1)AG-OV-1, "Purolat-Standard" (2) and ABG (3) ranks.

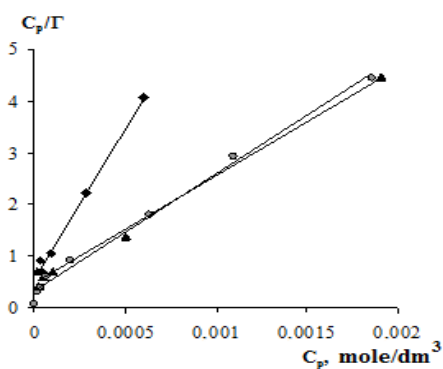
The adsorption isotherm of gallic acid from the aqueous solution by active carbon of AG-OV-1 rank refers to the isotherms of L-type according to the Giles's classification, which testifies to physical adsorption. AC adsorption isotherms of ABG and Purolat-Standard ranks refer to the S-type isotherms. By the S-type isotherm the adsorption is described, at which the strength of the interaction between the solute and the adsorbent is less than the force of interaction between the adsorbed molecules, which can explain the formation of hydrogen bonds [4, 6, 9]. Succeeding from the structure and properties of gallic acid there can form hydrogen bonds both between molecules of the acid itself and with water (Fig. 5 a, b). The presence of a plateau with increasing adsorption (Fig. 4, isotherm 2,3) makes it possible to assume presence of a monomolecular layer at the AC followed by polymolecular layer sorption. In this regard, the adsorption of carbon sorbents is likely to be characterized by both primary and secondary interactions. Adsorbed molecules of gallic acid can act as active sites for secondary adsorption. Both separate molecules of gallic acid and clusters of polyphenolic

compounds may be adsorbed. High values of the adsorption can be explained by the fact, that it is the molecular aggregates that pass onto the activated carbon surface, not isolated macromolecular balls. The degree of aggregation of the molecules increases with increasing concentration, however with low content of gallic acid, there is large adsorption of the solvent in which similar structures begin to form first. When the concentration being increased the interaction of the macromolecules and supramolecular structures with each other becomes stronger, resulting in the occurrence of a spatial solution net.

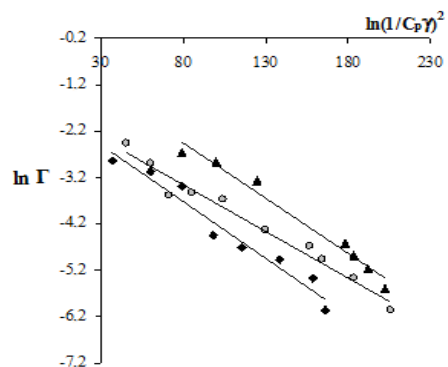


**Fig. 5.** Possible schemes of the interaction of agents in the gallic acid – water system: (a) between the molecules of gallic acid, (b) between the molecules of gallic acid and water.

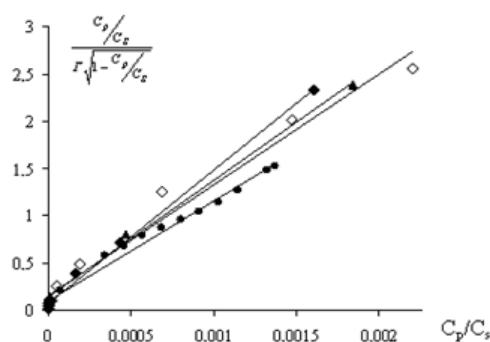
For a more complete characterization of carbon sorbents and calculation of adsorption parameters, the theories of monomolecular adsorption (Langmuir and Freundlich equations), polymolecular adsorption (equation of the Brunauer-Emmet-Teller (BET) type), the theory of volume filling of micropores (the equation of Dubinin-Radushkevich) were used [6, 9]. The adsorption isotherms in the corresponding linearization coordinates are shown in Fig. 6–8.



**Fig. 6.** The adsorption isotherms of gallic acid in the coordinates of Langmuir from the solutions on AC: ♦ - AG-OB-1; ▲ - ABG; ○ - Purolat-Standard.



**Fig. 7.** The adsorption isotherms of gallic acid in the coordinates of Dubinin- Radushkevich from the solutions on AC: ♦ - AG-OB-1; ▲ - ABG; ○ - Purolat-Standard.



**Fig. 8.** Adsorption isotherms of gallic acid in the coordinates of BET from the solutions on AC: ♦ - AG-OB-1; ▲ - ABG; ○ - Purolat-Standard.

The calculated values of adsorption parameters for all active carbons by monomolecular theory, generalized theory of BET and the theory of volume filling of micropores are shown in Table 3.4.

**Table 3.** Parametres of gallic acid adsorption by active carbons, calculated by the equations of Langmuir and Freundlich

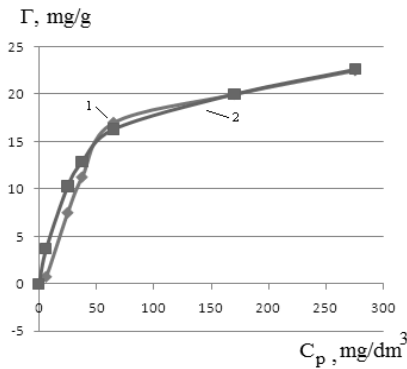
Carbon rank	Langmuir		Freundlich	
	-G, κJ/mole	Γ <sub>max</sub> , mole/g	1/n	b
AG-OB-1	30.72	0.00015	1.41	6.1·10 <sup>-5</sup>
Purolat-Standard	30.19	0.00016	8.08	6.6·10 <sup>-16</sup>
ABG	29.41	0.00012	4.27	8.8·10 <sup>-9</sup>

**Table 4.** Parameters of gallic acid adsorption by active carbons, calculated by the equations of Dubinin - Radushkevich and BET

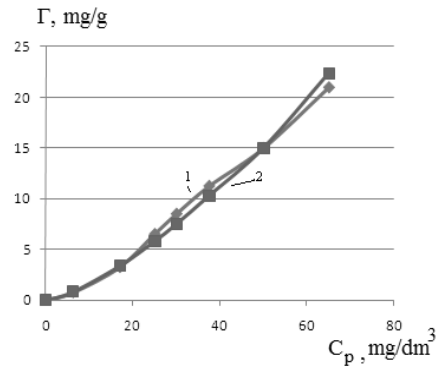
Carbon rank	Dubinin - Radushkevich		BET	
	Γ <sub>0</sub> , g/g	E <sub>0</sub> , κJ/mole	Q, κJ/mole	Γ <sub>max</sub> , mole/g
AG-OB-1	0.1225	8.54	13.00	1.5·10 <sup>-4</sup>
Purolat-Standard	0.0301	3.05	7.00	9·10 <sup>-5</sup>
ABG	0.0024	4.60	12.50	1.2·10 <sup>-4</sup>

Using obtained data, adsorption isotherms were calculated. Comparative analysis of experimental and theoretical adsorption isotherms showed that the BET, Langmuir, Freundlich and Dubinin-Radushkevich

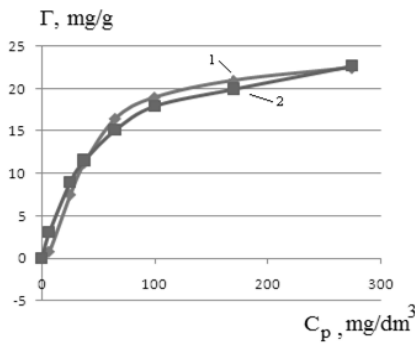
equations can be used to describe the adsorption process of gallic acid by active carbons from the aqueous solution (Fig. 9-12).



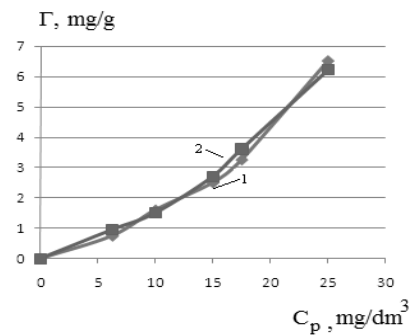
**Fig. 9.** The adsorption isotherms of gallic acid by of AC AG-OB-1 from the aqueous solution: (1) experimental; (2) calculated by the equation of Langmuir.



**Fig. 10.** Adsorption isotherms of gallic acid by AC of AG-OV-1 from the aqueous solution: (1) experimental; (2) calculated by the equation of Freundlich.



**Fig. 11.** Adsorption isotherms of gallic acid by AC of AG-OV-1 from the aqueous solution: (1) experimental; (2) calculated according to the BET theory.



**Fig. 12.** Adsorption isotherms of gallic acid by AC of AG-OV-1 from the aqueous solution: (1) experimental; (2) calculated by the equation of Dubinin-Radushkevich.

Theoretical calculations showed that the maximum adsorption of gallic acid by carbon sorbents changes in the following sequence - "Purolat-Standard" > ABG > AG-OV-1.

The energy of the hydrogen bond (8-40 kJ/mole) is comparable with the values obtained by the Gibbs energy (-G, Table 3) in the adsorption on all active carbons, suggesting the specific interaction between the adsorbate and the adsorbent due to the formation of hydrogen bonds [7].

The values of the adsorption heat (Q, Table 4) confirm the physical nature of adsorption.

The value of characteristic energy (E0, Table 4) equal to (3.05–8.54 kJ/mole) testify to the fact that the

adsorption of gallic acid takes place mainly in the meso- and macropores of the sorbent [6, 9].

The difference in the adsorption behavior of the studied sorbents is associated with their structural characteristics, and chemical state of the AC surface (Table 5, 6).

**Table 5.** Structural characteristics of active carbons

Active carbon rank	V <sub>micro</sub> , cm <sup>3</sup> /g	V <sub>meso</sub> , cm <sup>3</sup> /g	V <sub>macro</sub> , cm <sup>3</sup> /g	V <sub>p</sub> , cm <sup>3</sup> /g
AG-OB-1	0.22	0.24	0.57	1.03
Purolat-Standard	0.07	-	0.43	0.5
ABG	0.02	0.24	0.73	0.99

**Table 6.** The surface condition of active carbons

Sample	Content of elements*		N <sub>fgc</sub> , mmole-equ/g (mmole-equ/M <sup>2</sup> )			
	N+S+O	O <sub>act.</sub>	-OH	-COOH <sub>str.</sub>	-COO-	> C=O
AG-OB-1	2.71	2.28	0.213 (0.312)	0.032 (0.047)	0.078 (0.114)	2.08 (3.05)
ABG	7.05	2.76	0.130 (0.314)	0.020 (0.048)	0.040 (0.097)	3.70 (8.94)
Purolat-Standard	9.23	0.86	0.218 (0.700)	-	0.020 (0.064)	0.63 (2.02)

Note. \* Percentage on the carbon organic mass.

AC of ABG rank can be attributed to mesoporous and Purolat - Standard - to macroporous adsorbents [3], which is also confirmed by the value of the heat of adsorption (7–13 kJ/mole) [6, 7]. AC of AG-OB-1 rank can be attributed to the sorbent having pores of mixed type (volumes of its micro- and mesopores are almost equal).

The presence of micropores provides physical adsorption due to van der Waals forces, and the functional groups containing oxygen - specific adsorption due to the interaction between the surface of the AC with the carboxyl and hydroxyl groups of gallic acid.

AC AGOB-1 contains the largest number of micropores. The highest total content of oxygen and the concentration of the active oxygen functional groups on the surface area is observed for the carbon sorbent of ABG rank, which is associated with the

peculiarities of the production technology of the sorbent.

Adsorption is the result of the joint action of these factors. Obviously, in the case of gallic acid adsorption's greater contribution is made by specific interaction.

Analysis of experimental data has shown that the structure and physical-chemical properties of the sorbent have a significant impact on the adsorption of gallic acid.

Calculated from the experimental data the values of adsorption parameters for the studied carbon sorbents may be used in the data bank of sorption parameters of basic adsorbents at gallic acid adsorption.

The results can be used to make the adsorptive removal technologies of gallic acid from the sewage containing individual components and from the mixture with other polyphenols, including beer wort.

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