BEER QUALITY ASSURANCE BY CONTROLLING WORT POLYPHENOLIC CONTENT WITH ADSORPTION METHOD

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Abstract: This research explores feasibility of adsorption method used for regulating polypenols content in wort with a view of improving beer quality. It examines adsorption of polyphenols (quercetin, gallic acid, rutin) from pure substance solutions, their mixtures and beer wort treated by sorbents that differ by origin, making, structure and surface chemical composition. The work determines patterns and specific features of polyphenols adsorption with activated carbons. To describe adsorption mechanism more precisely, we specified structure, surface chemical condition, and calculated adsorption parameters using equations of Langmuir, Freundlich and Dubinin-Radushkevich, and the multilayer adsorption theory (BET model). It is demonstrated that polyphenols adsorption mechanism depends on carbon characteristics and is of physical nature that reveals itself in dispersion interaction in micropores and in specific one with oxygen-containing functional group (OFG) on carbon surface. Polyphenol competitive adsorption in mixture and wort recognized. At polyphenols adsorption from model solutions and wort, carbon sorbents are identified to share sufficiently close sorption characteristics. We performed comparative evaluation of quality characteristics of beer produced from activated carbons treated and untreated worts. It is shown that beer samples produced from unhopped wort filtered through semi-coke adsorption, meet regulatory standards requirements of safety by organoleptic, physical and chemical indicators. Moreover, beer obtained from semi-coke treated wort exceeds control sample in terms of organoleptic and stability ensuring indicators.

Keywords: gallic acid, rutin, quercetin, wort, carbon sorbents, adsorption

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INTRODUCTION

Breweries particularly focus on quality of their product. Lately, there has been observed an increase in demand for beer of higher quality and nontrivial formulation [1]. Polyphenolic compounds are an important component in chemical composition of hop and barley that have a substantial effect on intensity of beer making processes and its quality. They negatively affect stability of aroma, flavor, foam properties, color and colloidal stability; therefore, regulating their content appears to be pertinent problem [2, 3].

In 1950s beer polyphenols became an active area of research all over the world. Emergence of the substances specific adsorbents facilitated a removal of significant amount of polyphenolic compounds substantially improving beer stability. Intensive research revealed polyphenols distinctive properties and structure. In Russia polyphenolic compounds in domestic beers and brewery ingredients became a subject of research in the end of 1970s [4].

To remove polyphenols from beer, activated carbons of the grades BAU-A and BAU-MF are used in production [5].

However, due to the fact that the finished product is largely affected by polyphenolic compounds contained in malt rather than hop, it seems more practical to remove polyphenol through adsorption from wort.

One of the effective means of lowering polyphenol levels might be unhopped wort treatment by activated carbons. There is no reference to such studies in scientific literature.

In the last years the assortment of carbon materials has been expanded by introduction of semi-cokes produced using a new technology. The given technology distinction lies in substitution of traditional two-stage carbonization of source material in inert medium followed by activation, for one-stage process of carbonization/activation by air. It lowers a final cost of sorbent by reducing energy consumption for the production. Use of such adsorbents enhances cost-effectiveness of the beer and non-alchoholic beverages manufacturing process.

In order to study patterns and specific features of polyfphenolic compounds adsorption, main polyphenol components of wort have been selected (quercetin, gallic acid, rutin). Quercetin and rutin represent flavonoids, a large group of natural polyphenols that have significant impact on beer stability during storage; gallic acid being a predecessor of a series of polyphenolic substances. The studied compounds are

characterized by acid-base properties, hydrophobicity and presence of substituents on an aromatic ring [6, 7].

The purpose of this study was to explore adsorption of polyphenols for adjustment of polyphenol component in wort with a view of beer quality improvement.

OBJECTS AND METHODS OF STUDY

The objects of research are the following: water solutions of polyphenols (gallic acid, quercetin, rutin) and wort; activated carbon of the grade AG-OV-1 – granular AC (OJSC "Sorbent", Perm); and semi-coke ABG (OJSCO "Karbonika F", Krasnoyarsk) and "Purolat-Standart" (OJSC "Sintez", Rostov-na-Donu). Prior to the research all activated carbons were rinsed with distilled water to remove the dust particles and dried at room temperature (23 ± 2°C) for 24 hours.

Adsorption from water solutions of polyphenols and wort was studied at room temperature (23 ± 2°C) from limited quantity continuously stirring for 7–9 hours in static conditions within concentration range from 20 to 700 mg/dm^3. Ratio of activated carbon : phenolic components solution was 1 : 100. Ratio of the studied polyphenols in the solution was 1 : 1 : 1 close to their actual ratio in wort. Sorption of polyphenolic compounds from wort was observed in static conditions using activated carbon "Purolat-Standart", phenolic components concentration ranging from 8 to 160 mg/dm^3.

Polyphenols adsorption (Γ, mg/g) was estimated using the equation:

$$\Gamma = \frac{C_0 - C_{eq}}{m} \cdot V_{solut}\ , \qquad (1)$$

where C is the initial solution concentration, mg/dm^3; C_{eq} is the equilibrium solution concentration (following the adsorption), mg/dm^3; V_{solut} is the volume of the solution, dm^3; m is the adsorbent mass, g.

The amount of gallic acid, quercetin and rutin in the solution was measured by spectrophotometric method of bandgap absorption.

To perform the analysis we selected a wavelength based on spectral curve registered by a device SF-46 for a pure substances water solution.

Concentration of pure substances solutions for examined polyphenols under optimal conditions was 20 mg/dm^3, to reference a solution distilled water was used. Based on the results obtained through analysis we have selected the thickness of light absorbing layer to be 10 mm, and wavelength 230 nm for gallic acid, 340 mm for quercetin and 380 nm for rutin.

The relative error in polyphenolic compounds measurement was 4%.

To determine polypenols, the studied solutions where concentration was above 25 mg/dm^3 were diluted, a dilution coefficient selected for each solution individually. Gallic acid content in the studied solution was calculated from the formula:

$$C = X \cdot \frac{V_{mc}}{V_{al}}, \qquad (2)$$

where X is the gallic acid concentration in mg/dm^3, determined from graph; V_{al} is the aliquot of the studied sample, cm^3; V_{mc} is the measuring cup, cm^3.

Structural characteristics of adsorbents were found based on low temperature adsorption of nitrogen with specific surface area analyzer "Sorbtometer M" (Institute of Catalysis SB RAS, Novosibirsk).

We evaluated chemical condition of activated carbon surface that is a number oxygen-containing functional group using Bem titration method

Characteristic energy values (E) and half-width size of slit-like pores (χ) were calculated taking into account the affinity coefficient:

$$E = \beta \cdot E^0, \qquad (3)$$

where E is the characteristic energy of dissolved organic compound adsorption, kJ/mol; E^0 is the characteristic energy of benzene vapors adsorption, kJ/mol; β is the affinity coefficient.

We identified the total number of polyphenolic components in wort and beer using the the Erumanis method. The method implies treatment of samples with the solution containing trilon b and carboxymethyl cellulose (CMC), which if present in alkaline solutions makes polyphenolic compounds to react with iron ions. Then, we calculated the optical density at 600 nm of test solution versus blank.

Polyphenols concentration is determined using the formula:

$$X = A820 \cdot F, \qquad (4)$$

where X is the polyphenols concentration , mg/dm^3, A is the optical density; F is the dilution coefficient [8].

RESULTS AND DISCUSSION

To reveal the patterns, specific features and mechanisms of polyphenols removal with activated carbons, it appeared to be necessary to specify the activated carbons structure (Table 1) and to determine sorbents surface composition (Table 2). The adsorption of polyphenolic compounds was examined.

Based on experimental data produced by adsorbing polyphenols with activated carbons from pure substance solutions, we drew the adsorption isotherm shown in Fig. 1.

Table 1. Structural characteristics of activated carbons

Grade of activated carbon	V_{micro}, cm^3/g	V_{meso}, cm^3/g	V_{macro}, cm^3/g	V_s, cm^3/g
AG-OV-1	0.22	0.24	0.57	1.03
ABG	0.02	0.24	0.73	0.99
"Purolat-Standart"	0.07	-	0.43	0.5

Table 2. Surface composition of activated carbons

Sample	Elements content*		N_{OFG}, mmol(eq)/g (mcmol(eq)/m^2)			
	N+S+O	O_{act}	*-OH*	$-COOH_{strong}$	*-COO-*	*>C=O*
AG-OV-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-Standart"	9.23	0.86	0.218 (0.700)	-	0.020 (0.064)	0.63 (2.02)

Note. * Percents per organic matter.

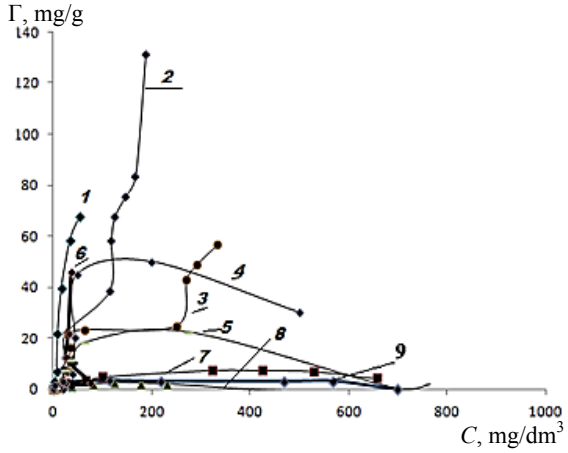

Fig. 1. Isotherm of polyphenols adsorption from pure substance solutions: quercetin with the sorbents grades ABG (1), "Purolat-Standart" (2) and AG-OV-1 (3); gallic acid with the sorbents grades "Purolat-Standart" (4), AG-OV-1 (5) and ABG (6); rutin with the sorbents grades ABG (7), AG-OV-1 (8) and "Purolat-Standart" (9).

Patterns of the studied organic components removal vary and depend on the grade of the sorbent used.

The shapes of quercetin adsorption isotherm drawn based on removal of the studied flavonoid from standard test solutions with carbon sorbents grades ABG and "Purolat-Standart", belong to S-type isotherms according to Giles classification. Curve knee and further rise of the isotherm is observed, which is typical of the sorption in meso- and macropores [9]. The shape of adsorption isotherm exhibiting quercetin removal with microporous activated carbon AG-OV-1, can be described as L-type according to Giles classification. The isotherm curves at higher concentrations and becomes flat. Drawing upon the graphs of adsorption isotherms it can be suggested that adsorption has a physical nature, which with activated carbon grade AG-OV-1 largely reveals itself in dispersion interaction; and with sorbents ABG and "Purolat-Standart" – in specific interaction.

When removing quercetin with semi-cokes, monomolecular adsorption of the studied organic component prevails on the surface of carbon sorbent at the initial stages of the process; then followed by removal at the expense of the formed secondary adsorption centers due to adsorbate-adsorbate interaction, which explains the isotherms inflections. Adsorbed molecules inter-molecular forces promote further removal revealing cooperation where separate molecules loose their individuality in complexes [10]. Probably, the complexes formation occurs due to hydrogen bond between quercetin molecules (Fig. 2).

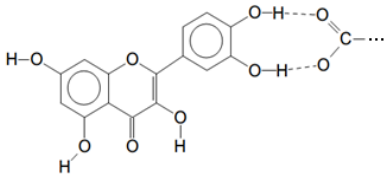

Fig. 2. Suggested bonding structure of quercetin and oxygen-containing surface groups of carbon sorbent.

Isotherm of gallic acid adsorption with activated carbon AG-OV-1 is of a classical shape and belongs to L-type isotherms according to Giles classification, which may indicate physical nature of adsorption. Isotherms of adsorption with sorbents grades "Purolat-Standart" and ABG belong to the S-type. It can be concluded from the sorption isotherms that interaction forces between solute and adsorbent are less than adsorbed molecules interaction forces, which might be explained by a formation of hydrogen bonds. Based on gallic acid properties and structure hydrogen bonds can form both with water and between the molecules of gallic acid itself (Fig. 3 a, b).

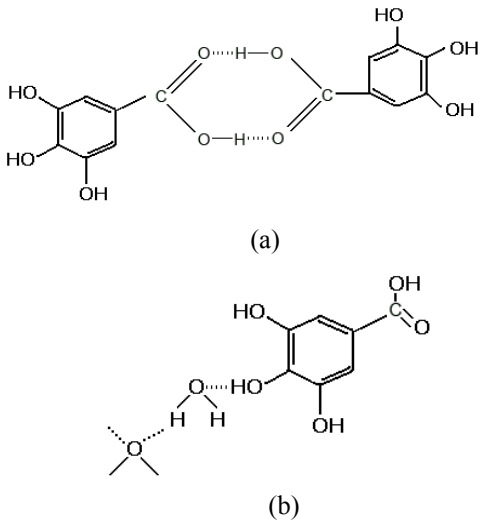

Fig. 3. Suggested hydrogen bonds formation schemes in gallic acid – water system: (a) between gallic acid molecules; (b) between molecules of gallic acid and water.

The shape of initial part of experimental isotherm of rutin adsorption with the sorbens grade ABG and AG-OV-1 (Fig. 1) belongs to the L-type, and with the

sorbents grade "Purolat-Standart" it can be classified as H-type by Giles. Isotherms of the given types describe the adsorption where removed molecules practically fail to interact between each other. Besides, L-type adsorption isotherms suggest physical adsorption. Chemically, adsorbed particles maintain their molecular nature and remain unchanged. The H-type isotherm of the sorbent grade "Purolat-Standart" suggests that the removal occurs by chemical bonding between oxygen-containing functional groups (OFG) from carbon sorbent surface and adsorbed molecules. Steep rise of the adsorption isotherm illustrates a high rate of removal from low concentration solutions when rutin is adsorbed with semi-coke "Purolat-Standart", which can be attributed to the interaction of adsorbents active centers with flavonoid molecule.

Table 3 shows the adsorption parameters calculated values.

Table 3. The parameter of polyphenol adsorption from pure substance solutions with the studied carbon sorbents in static conditions Langmuir, Freundlich and Dubinin-Radushkevich, and the multilayer adsorption theory (BET model)

Carbon grade	Equation type							
	Langmuir		Freundlich		BET model		Dubinin-Radushkevich	
	-G, kJ/mol	Γ_{max}, mmol/g	1/n	b	Q, kJ/mol	Γ_{max}, mmol/g	Γ_0, g/g	E_0, kJ/mol
Quercetin								
AG-OV-1	29.36	0.16	0.88	$3.6 \cdot 10^{-4}$	2.47	0.15	0.115	7.17
ABG	27.33	0.59	1.51	$4.6 \cdot 10^{-5}$	2.48	0.56	0.940	4.86
"Purolat-Standart"	27.59	0.58	1.30	$1.3 \cdot 10^{-4}$	2.49	0.55	0.699	4.57
Gallic acid								
AG-OV-1	30.72	0.15	1.41	$6.1 \cdot 10^{-5}$	13.00	0.15	0.023	8.54
ABG	29.41	0.12	4.27	$8.8 \cdot 10^{-9}$	12.50	0.12	0.024	4.60
"Purolat-Standart"	30.19	0.16	8.08	$6.6 \cdot 10^{-16}$	7.00	0.19	0.030	3.05
Rutin								
AG-OV-1	29.08	0.04	0.53	$1.8 \cdot 10^{-4}$	9.92	0.038	0.006	11.23
ABG	32.35	0.01	0.53	$3.2 \cdot 10^{-4}$	11.86	0.014	0.004	10.55
"Purolat-Standart"	41.54	0.05	0.12	$1.7 \cdot 10^{-3}$	16.96	0.051	0.004	25.35

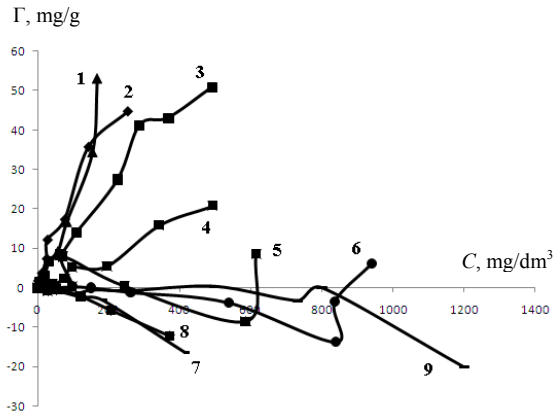

Fig. 4. Isotherms of polyphenols adsorption from mixture: quercetin with sorbents grade ABG (1), "Purolat-Standart" (2) and AG-OV-1 (3); gallic acid with sorbents grade "Purolat-Standart" (4), ABG (5) and AG-OV-1 (6); rutin with sorbents grade ABG (7), "Purolat-Standart" (8) and AG-OV-1(9).

We examined adsorption from mixtures of polyphenols in order to specify the components mutual influence. Fig. 4 displays equilibrium study results-based isotherms of polyphenols mixture adsorption. The isotherm shapes at the origin for quercetin with carbon sorbents grades ABG and "Purolat-Standart" belong to the L-type isotherms by Giles classification which is evident of physical adsorption.

During the studied process interaction is insignificant between adsorbed molecules; and surface filling degree has no impact on activation energy. Quercetin adsorption isotherms with activated carbon grade AG-OV-1 belongs to C-type. The initial linear portion characterizes ongoing distribution of solute between solution and adsorbent, which is typical for removal with microporous sorbents (the given activated carbon incl.). At lower concentration adsorption occurs in micropores, and at higher concentration – on carbon sorbent surface. The obtained results suggest that as the active centers fill and provoke the emergence of new secondary adsorption centers, the surface available for adsorption grows in proportion to the amount of removed from solution substance.

We observed negative adsorption (Fig. 4) for gallic acid sorption with activated carbons grades AG-OV-1 and ABG. However, with the concentration increase, isotherm climb and transition to positive area become noticeable, the reason for this probably being a concurrent interaction of quercetin with OFG and secondary activation centers formation, gallic acid included. Reasoning from the polyphenols molecules structure it appears possible that removed at their high concentration flavonoid molecules promote gallic acid sorption by forming complexes where specific interaction between hydroxyl groups of quercetin and those of gallic acid tend to change molecules individuality. When gallic acid is removed with semi-coke "Purolat-Standart", the shape of the initial section is concave relative to isotherm concentration axis belongning to L-type (Fig. 4). The acid removal pattern

differs due to structural characteristics of activated carbons.

Negative adsorption of rutin is indicative of mutual effect polyphenols mixture components have on each other, and results from the specific structure and the size of phenolic compounds molecules.

The comparative evaluation of isotherms of phenolic compounds adsorption from pure substance solutions and their mixture provides evidence that at polyphenols removal from pure substance solutions rate of adsorption is higher than at polyphenols removal from solutions containing phenolic compounds mixture. This is consistent with a Freundlich and Mazius mutual exclusion rule at organic components mixtures adsorption removal. At this, the phenolic compound to be adsorbed at a higher rate is the one that is better absorbed from a pure substance solution. The isotherms describing gallic acid adsorption with activated carbons ABG and "Purolat-Standart" clearly shows that pure substance solutions removal rate is 5 times higher than removal rate for mixtures. Experiments proved that quercetin removal rates values with carbon sorbents are higher both for mixtures AND pure substance solution when compared to other studied compounds. Quercetin is adsorbed stronger than gallic acid, the latter having a higher solubility value. Rutin sorption removal from pure substance solution was lower compared with other polyphenols, on account that their molecules are too large for sorption in micropores. Rutin negative adsorption from mixture might be explained by phenolic compounds competing for adsorption centers. Rutin and quercetin compounds are structurally related both containing bulky disaccharides substituents.

Calculated adsorption parameters values are shown in Table 4.

Table 4. Parameters of polyphenols adsorption from mixture with the studied carbon sorbents in static conditions

Carbon grade	Type of equation							
	Langmuir		Freundlich		BET		Dubinin-Radushkevich	
	-G, kJ/mol	Γ_{max}, mmol/g	1/n	b	Q, kJ/mol	Γ_{max}, Mmol/g	Γ_0, g/g	E_0, kJ/mol
Quercetin								
AG-OV-1	27.28	0.00026	0.86	0.00027	2.48	0.00036	0.064	7.64
ABG	27.99	0.00026	0.66	0.0011	2.48	0.00029	0.087	7.93
"Purolat-Standart"	31.61	0.000056	0.92	0.010	2.482	0.000055	0.073	8.09
Rutin								
"Purolat-Standart"	33.8	0.000051	0.685	0.00019	6.11	0.00014	0.078	6.62

Isotherm shape and calculated parameters indicate physical nature of adsorption. Phenolic compounds are sorbed due to Van der Waals forces in micropores and specific interactions resulting in formation of hydrogen bonds with surface OFG, this being supported Gibbs energy values (-G, Table 4).

Coefficient b values obtained using Freundlich equation, relate to the nature of carbon sorbent. Increase in its value at adsorption with activated carbon grade ABG may be attributed to intermolecular interaction increase.

Based on the research carried out with model solution we chose semi-coke "Purolat-Standart" to further study polyphenols behavior under static conditions in wort.

Polyphenols adsorption from wort was studied under static conditions with activated carbons within concentration range from 8 to 160 mg/dm^3. It is worth noting that apart from the studied polyphenols there are other polyphenolic compounds groups present in wort.

With a view to examine impact of substances of different nature we conducted correlation of experimental data obtained from polyphenols adsorption from the model solutions and wort.

As it may be seen from Fig. 5 the isotherm of polyphenols mixture adsorption from water solution belongs to L-type according to Giles classification, whereas the isotherm of polyphenolic compounds adsorption from wort is S-shaped.

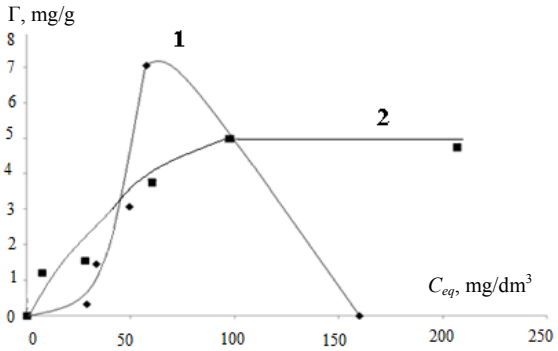

Fig. 5. Isotherms of polyphenolic compounds adsorption from wort (1) and their mixture in the model solution (2) with carbon sorbent grade "Purolat-Standart".

Isotherm 1 (Fig. 5) as opposed to isotherm 2 has an obvious maximum point which may be attributed to the presence of wide range of polyphelic compounds and substances of a different nature in wort.

Low polyphenolic content promotes individual molecules to be sorbed. Increase in polyphenols concentration causes molecular aggregation. It is a transition of molecular aggregations into carbon surface that can explain the significant increase in adsorption. Macromolecular and supermolecular structures interaction in the solution becomes stronger leading to the emergence of continued three-

dimensional mesh in solution, which blocks macromolecules from transiting to the carbon surface. Consequently, having passed its maximum adsorption falls to zero.

Sorption parameters were found from Langmuir, Freundlich and Dubinin-Radushkevich equations (Table 5).

Table 5. Polyphenols adsorption parameters with carbon sorbent "Purolat-Standart"

Langmuir	Dubinin-Radushkevich		Freundlich	
-G, kJ/mol	Γ_0, mg/g	E_0, kJ/mol	1/n	b
mixture				
27.85	5.1	7.3	0.54	$9 \cdot 10^{-4}$
wort				
27.18	7.8	6.14	0.55	$1.9 \cdot 10^{-4}$

When comparing parameters of polyphenols adsorption from model solutions and wort, sorption characteristics of carbon sorbent were found to be sufficiently close (Tables 3, 4). Maximum adsorption capacity value for polyphenols removal from wort is higher, which may be explained by its components interaction with each other and activated carbon.

Comprehensive studies of polyphenols adsorption from pure substance solutions, their mixture and wort revealed that polyphenols adsorption behavior in pure substance solutions and mixtures have varying characteristics. When the studied compounds being removed from mixture the isotherm shape and steepness change is observed, which may be attributed to change in interaction nature between components in the solution and carbon adsorbent surface. Polyphenols adsorption from wort (taking into account its more complex composition compared with the studied polyphenols mixture) will proceed somewhat differently. Experimental data indicate that the process of association of molecules of various nature actively proceed in the solution during polyphenols adsorption from wort; and it is molecular aggregates and not individual molecules that are sorbed on activated carbons further transforming into the active adsorption centers and thus, polyphenols adsorption amount increases.

To reveal semi-cokes application potential in the process of improving beer quality, we compared quality properties of beer produced from semi-coke treated and untreated worts. To make beer we selected samples of untreated wort (control sample) and the wort treated by adsorption on pilot unit with a capacity of 0.8 m^3/h using semi-cokes ABG and "Purolat-Standart" (Table 6).

Table 6. Physical and chemical indicators of unhopped wort

Indicators	Wort control sample	Wort treated by sorbent	
		Sorbent grade ABG	Sorbent grade "Purolat-Standart"
Color, color units	1.2 ± 0.02	0.93 ± 0.02	0.85 ± 0.01
Polyphenols content, mg/dm^3	224 ± 1.50	180.40 ± 1.20	175.89 ± 1.25
pH	4.87 ± 0.02	4.93 ± 0.03	4.9 ± 0.02

After that the obtained wort samples boiled for an hour with addition of granulated hops and suspended solids were removed. Characteristics of the obtained hopped wort are shown in Table 7.

Table 7. Physical and chemical indicators of hopped wort

Indicators	Wort control sample	Sorbent-treated wort	
		Sorbent grade ABG	Sorbent grade "Purolat-Standart"
Color, color units	1.7 ± 0.02	1.6 ± 0.02	1.4 ± 0.02
Polyphenols content, mg/dm^3	271 ± 1.20	225.5 ± 1.25	221.4 ± 1.20
pH	4.92 ± 0.02	4.99 ± 0.03	4.96 ± 0.02
Dry solids mass fraction, %	12 ± 0.01	12 ± 0.01	12 ± 0.01

Hopped wort fermentation took place in laboratory environment at temperature 10 ± 1°C. Laboratory samples underwent secondary fermentation for 21 days at temperature 2°C followed by tasting and analysis of the drink.

Tables 8, 9 display main indicators of the beer control sample, and the beer produced with semi-cokes grades ABG and "Purolat-Standart".

Table 8. Physical and chemical indicators of light beer

Indicators	Beer control sample	Beer produced from sorbent-treated wort		GOST (State Standard) 31711-2012
		Sorbent grade ABG	Sorbent grade "Purolat-Standart"	
Color, color units	1.55 ± 0.02	1.45 ± 0.03	1.15 ± 0.02	0.20–2.50
pH	4.64 ± 0.02	4.72 ± 0.02	4.70 ± 0.02	3.80–4.80
Acidity, acid. units	3.00 ± 0.01	2.60 ± 0.01	2.70 ± 0.01	lesser than 3.20
Dry solids mass fraction, %	5.00 ± 0.02	4.60 ± 0.03	4.50 ± 0.03	lesser than 5.00
Alcohol by volume, %	4.50 ± 0.02	4.81 ± 0.03	4.85 ± 0.03	more than 4.50
Foam head, mm	40.0 ± 2.0	50.0 ± 2.5	60.0 ± 2.0	more than 40.0
Foam stability, min	4.00 ± 0.15	7.00 ± 0.15	8.00 ± 0.20	more than 3.00
Carbohydrates, g in 100 g of beer	4.4 ± 0.02	4.10 ± 0.02	4.05 ± 0.02	lesser than 4.70

Table 9. Controllable physical and chemical indicators

Indicators	Beer control sample	Beer made from sorbent treated wort		Recommended values [4, 10]
		Sorbent grade ABG	Sorbent grade "Purolat-Standart"	
Polyphenols content, mg/dm^3	256.08 ± 1.00	207.51 ± 1.15	201.36 ± 1.20	180–220
Sedimentation limit	13.00 ± 0.05	14.00 ± 0.04	15.00 ± 0.04	more than 15.00
A protein fraction, mg/100cm^3	10.00 ± 0.02	9.55 ± 0.02	9.20 ± 0.02	lesser then 14.00

Table 10. Comparative organoleptic indicators of wort treated by adsorption with semi-cokes ABG and "Purolat-Standart" and untreated wort

Indicators	Control beer	Beer made from sorbent-treated wort	
		Grade ABG	Grade "Purolat-Standart"
Clarity	Clear, no brilliance	Clear with brilliance, no haze particles	Clear with brilliance, no haze particles
Color	Matches beer type, at mid level	Matches beer type, at mid level	Matches beer type, at mid level
Aroma	Fresh, pronounced, fermented, malty, hop, matches given type of beer, no off-odors	Fresh, pronounced, fermented, malty, hop, matches given type of beer, no off-odors	Fresh, pronounced, fermented, malty, hop, matches given type of beer, no off-ordors
Flavor	Clean, pronounced, fermented, malty, hop, matches given type of beer	Excellent flavor, full, clean, well-balanced, fermented, malty, hop bitter, soft, matches given type of beer, no off- flavors	Excellent flavor, full, clean, well-balanced, fermented, malty, hop bitter, soft, matches given type of beer, no off- flavors
Head (foam) and carbon dioxide saturation	Rich, stable, compact, adhesive, 40 mm depth and 4 min retention with slow and abundant bubbling	Rich, stable, compact, adhesive, 50 mm depth and 6–8 min retention with slow and abundant bubbling	Rich, stable, compact, adhesive, 60 mm depth and 7–10 min retention with slow and abundant bubbling

As compared with beer control sample, alcohol volume fraction increases in beers produced from semi-cokes treated wort, and is associated with yeast life function intensification due to reduction in polyphenolic compounds content. The obtained data show that samples of beer made from wort filtered by sorption with semi-cokes contain less polyphenolic compounds and have a higher sedimentation threshold limit value of subsidence compared to control sample. Beer made from wort treated by sorbent grade "Purolat-Standart", has indicators of higher quality.

Loss in value of A protein fraction content (Table 9) in comparison with control sample may be explained by its removal due to interaction with adsorbed polyphenolic compounds. Beer sample from wort treated with activated carbon grade "Purolat-Standart" has the smallest A protein fraction in agreement with its higher adsorption capacity towards polyphenolic compounds.

Tasting analysis of samples was undertaken; organoleptic indicators determined for compliance with GOST (State Standard) requirements 31711-2012 "Beer. General technological conditions" (Table 10) [11] In addition, evaluation was performed quantitatively on a scale system from 1 to 25 (Table 11).

As it may be seen from the tasting analysis result, beer containing smaller amount of polyphenolic compounds is soft flavored, light with brilliance, and has stable and deep head.

Table 11. Organoleptic estimate of beer samples

Indicators	Beer control sample	Beer made from sorbent-treated wort	
		Sorbent grade ABG	Sorbent grade "Purolat-Standart"
Clarity	4.5 ± 0.2	4.9 ± 0.1	4.9 ± 0.1
Color	3.5 ± 0.2	3.5 ± 0.2	4.0 ± 0.1
Aroma	4.9 ± 0.1	4.9 ± 0.1	4.9 ± 0.1
Flavor	4.0 ± 0.2	4.5 ± 0.1	4.5 ± 0.2
Head (foam) carbon dioxide saturation	4.0 ± 0.2	4.5 ± 0.1	4.5 ± 0.1
Total	21.0 ± 0.1	22.5 ± 0.1	23.0 ± 0.1

Beer samples were studied for compliance with Technical Regulations of Customs Union 021/2011 "On food safety" in terms of toxic elements content and safety microbiological indicators (Tables 12, 13) [12].

The obtained experimental data prove that the beer complies with the technical regulations of Customs union in terms of toxic elements content (Table 13).

As it is evident from Table 12 by the 11th day beer samples exhibit growth in number of mesophilic aerobic and facultative anaerobic microorganisms in control sample to a greater degree; however their quantity is below minimum standards.

Table 12. Microbiological indicators of beer safety

Indicators	Beer control sample		Beer made from sorbent-treated wort				TR CU requirement 021/2011
			Sorbent grade ABG		Sorbent grade "Purolat-Standart"		
	1 day	11 days	1 day	11 days	1 day	11 days	
QMAFAnM, CFU/cm^3	10	440	10	400	10	320	lesser than 500
Product volume, cm^3, containing:							
Coliform bacteria	—*	—	—	—	—	—	not allowed in 10 cm^3 of product
Pathogenic (salmonella incl.)	—	—	—	—	—	—	not allowed in 25 cm^3 of product

Note. * not found.

Table 13. Toxic elements contained in beer

Indicators, mg/kg	Beer control sample	Beer made from sorbent-treated wort		Technical regulations requirement, lesser than
		Sorbent grade ABG	Sorbent grade "Purolat-Standart"	
Lead, Pb	0.02 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.3
Arsenium, As	0.04 ± 0.001	0.04 ± 0.001	0.04 ± 0.001	0.2
Cadmium, Cd	0.01 ± 0.001	0.01 ± 0.001	0.01 ± 0.001	0.03
Mercury, Hg	less than 0.001	less than 0.001	less than 0.001	0.005
Nitrosamines	less than 0.001	less than 0.001	less than 0.001	0.003

Thus, control beer complies with the GOST (State Standard) requirements 31711-2012 and TR CU (Technical regulations of Customs union) TP TC 021/2011 in microbiological indicators for unpasteurized beer.

It may be concluded from the analysis that beer from wort treated with semi-coke "Purolat-Standart" exceeds other samples both in organoleptic and colloidal stability predictive indicators.

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