Active coals as an important factor in improving the efficiency of the production of alcoholic beverages

N E Golovacheva¹, S S Morozova¹, I M Abramova¹ and V M Mukhin²

¹All-Russian Scientific-Research Institute of Food Biotechnology - Branch of the Federal Research Center for Nutrition, Biotechnology and Food Safety, 4B, Samokatnaya str., 111033, Moscow, Russia
²Joint-Stock Company «Elektrostal Scientific and Production Association" Neogranika», 4, Karl Marx str., Elektrostal, 144001, Moscow Region, Russia

E-mail: golovacheva.otlvp@mail.ru

Abstract. Active and activated carbons are adsorbents, which are used to solve a wide range of tasks to improve the quality of drinking water, alcoholic beverages, including vodka. The traditional active coal used in distilleries in Russia is BAU-A coal, which has recently been obtained of poor quality due to the fact that not only dense wood species (birch, oak, beech) are used in the production, but also soft tree species. The study of new adsorbents showed that the best indicators for abrasion strength, micropore volume and adsorption activity are activated carbon MEX and crushed anthracite sorbent (CAS). MEX activated carbon and pine nut shell activated carbon contain less ash impurities. After filtering through the studied adsorbents in water-alcohol solutions, the mass concentration of acetic aldehyde increased (which confirms their catalytic activity); the hardness determined by calcium and magnesium cations increased to acceptable limits, which allowed to soften the taste; the optical density decreased, the oxidability increased, and the organoleptic parameters improved, which indicates the effectiveness of cleaning with the studied adsorbents. The best results were noted for water-alcohol solutions treated with activated carbon MEX and CAS.

1. Introduction

Due to their physical and chemical properties, carbon adsorbents (active and activated carbons) are unique and ideal sorption materials that allow solving a wide range of issues related to ensuring chemical and biological safety of humans, the environment and infrastructure [1].

Active and activated carbons are highly porous solid substances obtained on the basis of carbon-containing raw materials, which have a developed internal surface, reaching 2500 m²/g, and have high absorption characteristics for impurities in the media to be cleaned. In the porous structure of coals (the volume of micropores and mesopores), any types of organic micro-impurities are absorbed due to adsorption forces (surface interaction forces). At the same time, these adsorbents solve a wide range of tasks to improve the quality of drinking water, alcoholic beverages, including vodka [2].

Active coal BAU-A is traditionally used in distilleries in Russia [3] and is made from charcoal obtained by pyrolysis of dense wood species (birch, oak, beech) [4]. However, as studies have shown, over the past 10-15 years, wood chemical plants use not only birch, and especially beech or oak, but also soft tree species for the production of raw charcoal. As a result, activated carbon is obtained of poor quality – it is not strong enough and has an underdeveloped microporous structure.
This is explained by the fact that when activated charcoal obtained from soft (loose) wood, a "ballast porosity" is formed - a large number of macropores of coal, which are "transport arteries", but do not take part in the processes of adsorption, while, as is known, the determining role in the purification of water-alcohol solutions belongs to micropores of activated carbon.

As a result, the resulting activated carbon has:

- low mechanical strength at abrasion, which significantly increases the time of washing (maintenance) of coal and, of course, the consumption of rectified water for washing coal from ash impurities;
- a small bulk density, which leads to a significant increase in the height of the coal layer in the column for the production of vodkas with high organoleptic characteristics;
- a small volume of sorbing micropores per unit volume, which reduces the efficiency of processing water-alcohol solutions.

In this regard, the Institute systematically conducts research on new modern adsorbents in order to intensify the production technology of alcoholic beverages and improve the quality of finished products.

The paper [5] presents the results of treatment of water-alcohol solutions with medical activated carbon MEX (Bulgaria), obtained by steam-gas activation of apricot and peach seeds. It is shown that in water-alcohol solutions, after filtering through coal, the optical density decreased, the oxidability increased, and the organoleptic parameters improved, which indicated the effectiveness of their use.

Production tests of VSK brand coal made from carbonized coconut shell (the volume of micropores in which is 1.44 times greater than in BAU-A coal, the abrasion strength is 2.3 times greater, and the ash content is 2.7 times less) showed the effectiveness of its use in the technology of vodka preparation, which was confirmed by an increase in the oxidizability of vodka, a decrease in optical density and an improvement in its organoleptic parameters.

Studies on the treatment of water-alcohol solutions with active carbons Norit GCN 830 PLUS and Norit RC 1-3 (the Netherlands), made from special varieties of coconut shells, have shown a number of advantages compared to active charcoal BAU-A [6]. The studied coals had higher indicators of adsorption activity, bulk density and abrasion strength. After filtering through the studied coals in water-alcohol solutions, the oxidability increased, the optical density decreased, and the organoleptic parameters improved, which confirms the effectiveness of purification.

The work [7] presents studies on the treatment of water-alcohol solutions with activated carbon «Lidercarbon-E», produced from fruit seeds, active carbon SKT-2, obtained from peat, coal «White Maple», experimental samples of coals obtained from the straw of grain crops (wheat, rye, barley and oats). The best adsorption activity of coal was noted for the coals «White Maple», «Lidercarbon-E» and coal from wheat straw.

In all cases, after treatment, the oxidability increased, the optical density decreased, and the organoleptic evaluation improved, which indicates the possibility of using the studied adsorbents in the preparation of vodka using various technological schemes (periodic coal treatment or column filtration).

The purpose of this work is to study new high-strength adsorbents with a developed microporous structure and a large number of sorbing micropores per unit volume (Vmi, cm³/cm³).

2. Material and methods

For treatment with adsorbents, water-alcohol solutions with a strength of 40 % were prepared from ethyl alcohol rectified from food raw materials of the Lux grade and specially prepared demineralized water.

The samples were treated with the following adsorbents:

- activated carbon MEX, which is produced from the seeds of peaches of the Krasnodar Territory, by carbonation in the atmosphere of carbon dioxide in a rotating electric furnace with a temperature rise rate of 5-8°C/min and exposure at a temperature of 450°C. After crushing and scattering into fractions of 1.7-3.4 mm, the carbonizate is sent for steam-gas activation to a
rotating electric furnace at a temperature of 870-900 °C until the total pore volume develops 0.50-0.75 cm³/g;

- activated carbon from the shell of pine nuts (based on raw materials from the Novosibirsk region), which is obtained in a reactor with external heating with wet water vapor, heated to a temperature of 600-700°C for 1-3 hours, after which the heating is stopped, the temperature in the reactor is gradually reduced to 200°C and the steam supply is completed;
- crushed anthracite sorbent (CAS), based on anthracite of the Gorlovsky deposit of Kuzbass, after its crushing into fractions of 1-3 mm, followed by activation in a rotating electric furnace in a medium of carbon dioxide and water vapor in a ratio of 1:3 at a temperature of 870°C to the value of the burnout of 15%;
- active coal UPK-1, obtained on the basis of a mixture of 95 % coal and 5 % coal pitch after crushing them, grinding the mixture, forming the coal-pitch composition into briquettes, crushing the briquettes with subsequent sieving, carbonization of crushed particles at 450°C, activation of carbonizate in a water vapor medium in a retort furnace at a temperature of 860 °C with a temperature rise rate of 10 °C/min and a duration of isothermal exposure of 5-6 hours.

Before testing, each sample of the adsorbent was filled with a 40% water-alcohol solution prepared with Lux alcohol and specially prepared demineralized water, kept for 12 hours, dried on a filter board to a humidity of 60 %, and loaded into a U-shaped tube-column with a filter layer height of 48 cm and a diameter of 1.5 cm. In the column loaded with adsorbent, water-alcohol solutions were fed by gravity from the bottom up at a rate of 3-4 ml/min (which corresponded to the optimal filtration rate of vodkas of 30-40 dal/h in production conditions).

In the samples of water-alcohol solutions before and after filtration, the following parameters were determined:

The content of toxic micro-impurities (methyl alcohol, fusel oil components, acetic aldehyde, esters), the presence of which is characteristic of vodka made from ethyl rectified alcohol from food raw materials, was determined by the gas chromatographic express method on a Hewlett Packard HP 6890 gas chromatograph using a capillary column [8];

Mass concentrations (iron, sulfates, chlorides, and silicates) by spectrophotometric methods on a Shimadzu UV-2501PC6 spectrophotometer:

- iron by reaction with ortho-phenanthroline hydrochloride with divalent iron ions in the pH range 3-3.5 to form a complex compound colored orange-red. The color intensity is proportional to the concentration of ferrous iron. The reduction of iron to divalent is carried out by hydroxylamine hydrochloride;
- silicates by the reaction of silicon ions in an acidic medium in the form of a reduced form of silicoxybdenic acid, colored blue. The color intensity is proportional to the concentration of silicon ions;
- on the measurement of the turbidity intensity of an aqueous alcohol solution containing sulfate ions when interacting in a hydrochloric acid medium with barium chloride in the presence of ethyl alcohol added to the reaction mixture during the precipitation of barium sulfate to stabilize the resulting suspension and increase the sensitivity of the method;
- measurement of the turbidity intensity of a sample of an aqueous-alcohol solution containing chloride ions when interacting in a nitric acid medium with silver nitric acid [9];

Alkalinity - by a method based on the determination of the volume of a hydrochloric acid solution with a molar concentration of 0.1 mol/dm³, spent on titration of 100 cm³ of vodka, in cm³[10];

The hydrogen index (pH value) was measured on the "Microprocessor pH Meter HI 9321" ionometer.

Sensory analysis. Organoleptic evaluation of samples of water-alcohol solutions before and after treatment with adsorbents was carried out by a commission of 15 tasters who are part of the «Tasting Commission for Assessing the quality of ethyl alcohol from food raw materials, vodka and alcoholic
beverages». Quantitative assessment, expressed in points on a 10-point scale, which provides for the characteristic of the quality of products in appearance (transparency and color) - 2 points, aroma-4 points; taste-4 points [11].

Statistical analysis. All samples were prepared and analyzed in three replicates. The statistical analysis was performed using the STATISTICA 10 software (Statsoft, USA).

3. Results and discussion
The technical characteristics of the studied adsorbents are given in table 1.

**Table 1.** Technical characteristics of adsorbents.

| Indicators                        | CAS   | MEX   | From the shell of a pine nut | UPK-1  | BAU-A  |
|----------------------------------|-------|-------|-----------------------------|--------|--------|
| Bulk density, g/cm³              | 820   | 545   | 193                         | 760    | 208    |
| Abrasion resistance, %           | 87.7  | 91.3  | 87.0                        | 92.6   | 48.5   |
| Mass fraction of total ash, %    | 9.6   | 4.0   | 4.3                         | 27.8   | 6.0    |
| Mass fraction of water, %        | 1.6   | -     | 5.0                         | 1.76   | -      |
| Total pore volume, cm³/g         | 0.23  | 0.52  | 1.29                        | 0.28   | 2.0    |
| Micropore volume, cm³/g          | 0.21  | 0.32  | 0.18                        | 0.15   | 0.24   |
| Micropore volume, cm³/g/cm³      | 0.22  | 0.17  | 0.04                        | 0.11   | 0.05   |
| Iodine adsorption activity, %    | 71    | 115   | 51                          | 42     | 70     |

The best indicators of abrasion strength, micropore volume, and adsorption activity were noted for MEX activated carbon and crushed anthracite sorbent (CAS). MEX coals and pine nut shells contain a smaller amount of ash impurities, which are able to pass into water-alcohol solutions during filtration.

The results of gas chromatographic analysis of water-alcohol solutions before and after treatment on the studied adsorbents and BAU-A coal, which is most often used in the production of vodka, are presented in table 2.

**Table 2.** Results of gas chromatographic analysis of water-alcohol solutions.

| Indicators                        | Initial sample | After filtration on adsorbents |
|----------------------------------|----------------|--------------------------------|
|                                   | CAS            | MEX                          | From the shell of a pine nut | UPK-1 | BAU-A |
| Mass concentration, mg in 1 dm³ of anhydrous alcohol: |                 |                               |                               |       |       |
| acetic aldehyde                   | 0.55±0.02      | 1.5±0.06                     | 2.25±0.09                     | 1.47±0.06 | 2.87±0.10 | 1.17±0.05 |
| ethyl acetate                     | -              | <0.5                         | -                            | -      | 1.19±0.04 | 1.19±0.05 |
| isoamylene                        | -              | <0.5                         | -                            | -      | -        | -        |
| 2-propanol                        | 1.01±0.04      | 1.5±0.04                     | 1.2±0.03                      | 1.04±0.04 | 1.02±0.04 | 1.02±0.04 |
| 1-propanol                        | 0.55±0.02      | <0.5                         | <0.5                          | <0.5   | <0.5     | <0.5     |
| 1-butanol                         | <0.5           | <0.5                         | <0.5                          | <0.5   | <0.5     | <0.5     |
| Volume fraction of methyl alcohol in terms of anhydrous alcohol, % | 0.00359± | 0.00348± | 0.00349± | 0.00346± | 0.00352± | 0.00353 ± |

The mass concentration of acetic aldehyde increased in all the vodka samples filtered through the studied coal samples: to a greater extent for the adsorbents UPK-1 and MEX, to a lesser extent for the crushed anthracite sorbent and activated carbon from the pine nut shell. At the same time, its value did not exceed the maximum permissible value for high-grade vodkas prepared with Lux alcohol (3.0 mg per 1 dm³ of anhydrous alcohol), established by the requirements of the current GOST [12]. A slight decrease in 1-propanol was observed in all samples after filtration. In vodkas after BAU-A coal, ethyl
acetate was found in small amounts, and traces of fusel oil (1-butanol and isooamyline) were found in CAS and UPK–1 coals. It should be noted that the content of methyl alcohol met the requirements of Regulation EC no. 110/2008 [13].

The results of physico-chemical and spectrophotometric analyses for determining the trace element composition of water-alcohol solutions before and after filtration on the studied adsorbents are presented in tables 3 and 4.

Table 3. Physico-chemical and microelement parameters of water-alcohol solutions before and after filtration.

| Indicators               | Initial sample | After filtration on adsorbents |
|--------------------------|----------------|---------------------------------|
|                          |                | CAS | MEX | From the shell of a pine nut | UPK-1 | BAU-A |
| Hardness, °H             | 0.23±0.01      | 0.32±0.01 | 0.26±0.01 | 0.24±0.01 | 0.32±0.01 | 0.30±0.01 |
| pH                       | 7.6±0.1        | 7.7±0.1 | 9.5±0.1 | 9.9±0.1 | 7.7±0.1 | 8.0±0.1 |
| Alkalinity, cm³          | 0.08±0.01      | 0.12±0.01 | 0.80±0.01 | 1.20±0.01 | 0.12±0.01 | 0.2±0.01 |
| Oxidizability test, min  | 10.5±0.1       | 12.0±0.1 | 16.0±0.1 | 13.5±0.1 | 13.3±0.1 | 11.5±0.1 |
| Mass concentration, mg/dm³ | 1.60±0.07    | 2.16±0.10 | 1.61±0.07 | 1.63±0.07 | 2.3±0.10 | 4.00±0.18 |
| SO₂²⁻                   | 0.75±0.03      | 0.75±0.03 | 0.70±0.03 | 1.00±0.04 | 1.00±0.04 | 1.20±0.05 |
| Si⁴⁺                    | 0.2±0.01       | 0.3±0.01 | 0.7±0.02 | 0.4±0.01 | 0.6±0.02 | 0.3±0.01 |

After filtration, the hydrogen index and alkalinity increased, to a greater extent after treatment with activated carbon MEX and activated carbon from the shell of pine nuts, which indicates the presence of alkaline oxides in them, which are also present in the active carbon of BAU-A. The increase in hardness noted for all adsorbents, with the exception of activated carbon MEX and activated carbon from the shell of pine nuts, indicates the presence of a significant amount of ash impurities in them, which is confirmed by the data given in table 1 (the mass fraction of total ash is 6.0-27.8 %). At the same time, it should be noted that the hardness value did not exceed the maximum permissible value of vodka, established by the requirements of the technological regulations. The indicator of the mass concentration of iron did not change and was 0.020±0.002 mg/dm³.

Table 4. Spectrophotometric and organoleptic quality indicators of water-alcohol solutions before and after filtration.

| Indicators                     | Initial sample | After filtration on adsorbents |
|-------------------------------|----------------|---------------------------------|
|                               |                | CAS | MEX | From the shell of a pine nut | UPK-1 | BAU-A |
| Optical density at wavelength, nm |                |     |     |                                |       |       |
| 220                           | 0.23±0.01      | 0.12±0.001 | 0.125±0.001 | 0.170±0.001 | 0.160±0.001 | 0.150±0.001 |
| 240                           | 0.075±0.001   | 0.015±0.001 | 0.025±0.001 | 0.040±0.001 | 0.050±0.001 | 0.050±0.001 |
| Cleaning efficiency, %        | -              | 47.0 | 45.6 | 26.0 | 30.0 | 35.0 |
| Tasting score, score          | 9.00±0.01     | 9.35±0.03 | 9.37±0.03 | 9.25±0.03 | 9.25±0.03 | 9.36±0.03 |

After treatment with adsorbents, the oxidability increased, the organoleptic parameters improved, and the optical density decreased, which confirms the cleaning efficiency estimated in accordance with the patent for evaluating the efficiency of coal [14]. The best results were noted for samples treated with activated carbon MEX and crushed anthracite sorbent (CAS), despite the fact that the latter showed a greater increase in hardness.
The obtained data allow us to conclude that the increase in the hardness determined by calcium and magnesium cations softens their taste to certain limits, thereby improving the organoleptic characteristics of vodkas.

4. Conclusion
MEX and CAS adsorbents have the highest abrasion resistance, which can ensure a minimum consumption of reclaimed water for their pre-washing before loading into the coal column. Activated carbon MEX and crushed anthracite sorbent have a high volume microporosity and the highest adsorption activity (table 1), showed the best cleaning efficiency (45.6-47.0%), tasting ratings of vodkas after treatment improved by 0.35-0.37 points.

Raw materials for the production of MEX activated carbon are quite limited due to the difficulty of collecting it, at the same time, the raw material base of crushed anthracite sorbent is measured in billions of tons, which is why, in our opinion, it is the most promising in the technology of preparing high-grade vodkas.

References
[1] Mukhin V M and Klushin V N 2012 Production and application of carbon adsorbents (Moscow: D. I. Mendeleev Russian State Technical University) p 308
[2] Mukhin V M, Tarasov A V and Klushin V N 2000 Active coals of Russia (Moscow: Metallurgy) p 352
[3] GOST 6217-74 Crushed active wood coal. Technical specifications Retrieved from: https://docs.cntd.ru/document/1200017213
[4] GOST 7657-84 Charcoal. Technical specifications Retrieved from: https://docs.cntd.ru/document/1200017215
[5] Polyakov V A, Burachevsky I I, Morozova S S, Ustinova E V, Shubina N A, Martirosyan A S and Mukhin V M 2012 New active coals in the technology of vodka preparation Food industry 5 40-3
[6] Polyakov V A, Abramova I M, Morozova S S and Ustinova E V 2015 Perspective coals in vodka technology Production of alcohol and alcoholic beverages 2 17-20
[7] Abramova I M, Morozova S S, Golovacheva N E and Shubina N A 2017 On the possibility of using new active coals in the technology of vodka preparation Modern biotechnological processes, equipment and methods for controlling alcohol and alcoholic beverages (Moscow: Federal State Budgetary Institution of Science Federal Research Center for Nutrition, Biotechnology and Food Safety) pp 149-55
[8] GOST 30536-2013 Vodka and ethyl alcohol from food raw materials. Gas chromatographic express method for determining the content of toxic micro-impurities Retrieved from: https://docs.cntd.ru/document/1200104836
[9] STO 00334586-3-02-2014 Special vodka and vodka and process water for their preparation. Methods for determining the mass concentration of iron and anions Retrieved from: https://cyberleninka.ru/article/n/vliyanie-kompleksnyh-pischevyh-dobavok-na-ironnyy-sostav-vodok-i-ih-organolepticheskie-pokazateli
[10] GOST 32035-2013 Vodka and special vodka. Acceptance rules and analysis methods Retrieved from: https://docs.cntd.ru/document/1200103858
[11] GOST 33817-2014 Ethyl alcohol from food raw materials, alcoholic beverages. Methods of organoleptic analysis Retrieved from: https://docs.cntd.ru/document/1200138864
[12] GOST 12712-2013 Vodka and special vodka. General technical conditions Retrieved from: https://docs.cntd.ru/document/1200105674
[13] Regulation 110/2008 of the European Parliament and of the Council of 15 January 2008 concerning the definition, description, presentation, labelling and protection of geographical indications of alcoholic beverages, repealing Council Regulation 1576/89 Retrieved from: https://eur-lex.europa.eu/legal-content/EN/LSU/?uri=CELEX%3A3A32008R0110
[14] Abramova I M, Morozova S S, Polyakov V A and Shubina N A 2015 Method for determining the efficiency of purification of a water-alcohol mixture with active carbons used in the production of vodkas Pat. № 2624521 (Moscow: Rospatent)