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PURIFICATION OF WATER-ALCOHOL MIXTURES BY MEANS OF NATURAL MATERIALS

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Abstract. The article presents the results of theoretical and experimental studies to improve the technology of purification of water-alcohol mixtures by means of modified natural minerals when manufacturing spirits. The methods and basic filter materials used in the technology of vodkas have been considered. A description is given of the methods that made it possible to determine the physicochemical parameters and cation-anion composition of the alcohol-water mixture, and to modify natural obsidian and a natural zeolite – clinoptilolite. It has been established that applying the modified minerals under study results in a decrease in the specific consumption of hydrochloric acid solution used to remove ash constituents and lime inclusions from the surface, of drinking water, and of prepared water to wash the material: by 1.3–1.9 times, 1.3–1.5 times, and 1.2–1.7 times respectively, compared with quartz sand. Besides, there is a 1.3 times decrease in consumption of the water-alcohol mixture before establishing the equilibrium value of alcohol strength to prevent dilution of the mixture. It has been shown how the modified natural materials effect on the physicochemical parameters and cation-anion content of the alcohol-water mixture prior to and after its purification with modified obsidian and clinoptilolite, in comparison with quartz sand. It has been proved that the technology of filtration with modified natural minerals allows improving the transparency of the water-alcohol mixture by 0.1–0.2 absorbance units, which has a positive effect. The expected stability of the alcohol-water mixture has been determined by the changes in its physicochemical parameters after its resting under critical conditions, as well as by the reference sample and by the array of the reserve of this parameter to the critical limit, and is equal to 26–28 months. It has been found that filtering the alcohol-water mixture with modified obsidian allows increasing the shelf life by two months, with modified clinoptilolite by four months. Modification of natural obsidian and clinoptilodite, with reduced specific consumption of hydrochloric acid and prepared water at the stage of preparation to the main cycle, increases the filtration effectiveness by 10–15% and allows obtaining vodka with improved microcomponent composition.

Keywords: alcohol-water mixture, vodka, purification, filtration, modification, mineral, obsidian, quartz sand, clinoptilolite.

Introduction. Formulation of the problem

For elite, ordinary, and special vodkas, the parameters of quality, safety, and shelf life, which are established by the forecasting method, are of special importance. Stability is the period during which a drink does not change its sensory and physicochemical properties. It depends on the quality of the prepared water used, variety of rectified ethanol, ingredients, filtering and sorption materials [1].

One of the priority areas of improving the technology of filtering and purifying water-alcohol mixtures is the search for new natural materials to replace quartz sand [2-6].

Analysis of recent research and publications

Alcoholic beverage enterprises use the dynamic method of processing alcohol-water mixtures in one or several series-connected carbon columns, where quartz sand is used for preliminary and final filtration [1,4-13].

Before entering the charcoal column, an alcohol-water mixture is filtered to protect activated carbon from mechanical and colloidal impurities. On leaving the column, the mixture is filtered to be cleared of activated carbon particles that have migrated from the charcoal columns, or to separate protein and other suspensions from the alcohol-water mixture during preparation of vodkas that involves processing with modified starch, protein, and milk powder [4,6,8].

The studies by domestic [1,4,6,14] and foreign scientists [8,9] have shown that quartz sand is not effective enough in modern conditions of alcoholic beverage production. In particular, the main reasons for this are [10-14]:

– significant consumption of water spent during preparation for the working cycle on regeneration by washing the filtering material;

– use of precursors, increased consumption of hydrochloric acid that, at the stage of preparing the material for work, is spent to remove lime deposits from the surface, which adversely affects the production environment and the workers' health.

Previously, high-quality quartz sand, with a low ash content, was brought to Ukrainian distilleries from the deposit at Gora Khrustalna (Russia). On the territory of Ukraine, the largest reserves of quartz sand are concentrated in the Hlukhivtsi and Vinnytsia fields [1,6,14].

Quartz sand is a granular material of mineral origin. The colour of its grains ranges from light yellow to reddish-brown and black. The structure is crystalline, the surface varies from rough to smooth. The shape of the particles is spherical or angular. Round grains contribute to the reduction of pores and the rapid formation of a filter film. Pure quartz sand has a milky colour and the minimum quantity of inert impurities: up to 99% of its composition is silica. The hardness by the Mohs scale is 7.0 [1,14]. However, when manufacturing alcoholic beverage, quartz sand from these fields cannot be used to filter water-alcohol mixtures without special long-term preliminary treatment using quite an amount of hydrochloric acid, nor is it applicable to purify drinking water and prepared water at the stage of their preparation and washing [1,6,14].

A number of researchers [3,15-20] purify water-alcohol mixtures and other products using natural carbon. It contains shungite, which has high adsorption properties, is mechanically stable and environmentally friendly. Shungite belongs to a large group of Precambrian rocks saturated with a special carbon (shungite) substance. Among the known forms of elemental carbon, this substance has the highest chemical activity in redox processes due to the presence of fullerene, a special modification of carbon, in its composition [15-20].

The efficiency of purifying water-alcohol mixtures with shungite is analysed at different durations of its interaction with the water-alcohol mixture. Although shungite is an effective material for removing harmful impurities from water, it is expensive, and its use in production of beverages is very limited [15,20]. As there are no shungite fields in Ukraine, but they are located mainly in Karelia (Russian Federation) and Kazakhstan [1,6], it is not economically practical to use this natural material.

The possibility of purification with shungite and clinoptilolite was determined by scientists under static conditions by adsorption of alcohol impurities, which can affect the quality of alcohol and water-alcohol mixtures both positively and negatively [3,16,17]. It was established that clinoptilolite was more practical for adsorption of the ethanol micro-impurities – aldehydes and esters [3,16]. The group of aldehydes contained in ethanol is determined mainly by acetaldehyde, acetals, propionaldehyde, and crotonaldehyde [27]. These compounds tell on the tasting properties of vodkas in different ways. For example, free acetaldehyde adds a burning flavour, bound acetaldehyde (acetals) makes the product taste softer, propionic and crotonic aldehydes are not allowed [3,16,19]. Nevertheless, this conclusion about the improvement of quality hardly applies to the technology of vodkas, because an alcohol-water mixture is purified not under static, but under dynamic conditions [3,16,19].

To process an alcohol-water mixture, it is recommended to use a microporous mineral – silicon-like silicide. It has a wide microporous structure, its hardness is 100%, and it can be repeatedly reactivated [26]. During the treatment of an alcohol-water mixture with this material, the content of esters, fusel oil, and unsaturated compounds decreases, and due to the absence of catalytic oxidation, the formation of aldehydes slows down, the organoleptic and physicochemical parameters of the finished product improve [25].

It is known that of a water-alcohol mixture can be purified more effectively by applying a small amount of colloidal dispersed silver on the surface of activated carbon. Silver is an active catalyst. Due to the electrochemical potential difference between activated carbon and silver, it effects on reactions of oxidation of alcohol to aldehydes and then to acetic acid, and on the formation of esters [13,19,21,25-28].

To purify alcohol-water mixtures by adsorption, the following natural dispersed minerals were tested: saponite, glauconite, montmorillonite, hydromica [2-5]. The most effective natural material was found to be glauconite. It shows a selective capacity for adsorption of aldehydes, ethyl butyrate, methanol, and n-pentanol. Besides, it improves the quality of alcohol-water mixtures by 0.2 points [2-5]. However, these materials need long-term preparation for a short filtering cycle, so they are not used at distilleries [1,6,23].

Natural zeolites have cation exchange, sorption, molecular sieve, and catalytic properties, and belong to the most promising materials, so their widespread introduction into the vodka technology is especially important [1,6,27-29].

One of the methods of vodka production is filtration through a natural zeolite, clinoptilolite [1]. This process is accompanied by a decrease in the mass concentration of ferrous ions of the alcohol-water mixture. Besides, a decrease was revealed in the content of a wide range of heavy metals due to an increase in the sorption processes characteristic of clinoptilolite as a natural mineral [1,3,34-37].

It was found that zeolite catalysts, including clinoptilolite, had high catalytic activity towards methanol, and the main directions of chemical reactions were established [34,36]. When choosing a filter material, special attention is paid to the technical characteristics and technological parameters: the optimal fractional composition, the homogeneity of the grains of the filter bed, the material's mechanical and chemical resistance to a water-alcohol mixture [1,4,6,35-37].

Natural clinoptilolite is a natural mineral of the zeolite group. Clinoptilolite, like all natural zeolites, has a variable chemical composition, which, of course, affects its sorption properties [1,34-35]. Zeolite, the natural material from the Sokyrnytsia field, contains about 80% of clinoptilolite. It is monochromatic blue-grey by its colour, and belongs to aluminosilicates by its composition, is resistant to strong alkalis, and is insoluble in water. Natural zeolite is characterised by granularity and dirt capacity allowing removal of particles as small as 5-10μm. Clinoptilolite has a large internal porosity (38–46%) and the surface area 19-23 m^2/g (the effective rough surface area available for the adhesion of colloidal particles is 1-2m^2/g, which is 10-15 times more than in quartz sand). This allows it to retain effectively not only suspended, but also colloidal particles [1,34]. Clinoptilolite from the Sokyrnytsia field (Transcarpathian Region) is one of the most common in Ukraine [1,33-35]. However, when it is used to filter water-alcohol mixtures, the transparency of the latter decreases. So, it is necessary to wash the material with drinking water, hydrochloric acid, and prepared water by filtration, softening, and demineralisation on a reverse osmosis plant [1]. The sorption and ion exchange potential of this mineral will be available if the process of activation and modification will take place according to a clearly defined mode [1,35].

Obsidian is a natural material of volcanic origin, a massive rock characterised by a conchoidal, cutting fracture, sometimes striped or spotted. The shape of the particles is spherical or rounded. There are a few types, namely obsidian of normal, subalkaline and alkaline series. Obsidian is formed by rapid solidification of viscous acid magma on the surface of lava or under subvolcanic conditions. The colour of the stone is usually black due to minute particles of magnetite, but there are also red, brown, grey, and other varieties, including alternating colours resembling decorative marble. Typical colours for minerals are black, brown, grey and grey-white, red, yellow with a silky, glassy sheen. The physical properties depend on the water content and the degree of crystallisation of the rock. The hardness of obsidian by the Mohs scale is 5.0–6.0 [1]. The problem of determining the specific consumption of washing materials at the stage of preparing the main filter cycle still needs solving.

Based on the analysis of materials used to filter and purify water-alcohol mixtures in the alcoholic beverage industry, it is important to find more efficient and economical filter-sorption materials to filter a water-alcohol mixture and establish whether they are applicable in the vodka technology as an alternative to quartz sand [1,4,6].

The purpose of the work is to study the effect of different modified natural materials on the physicochemical and sensory characteristics of the water-alcohol mixture in alcoholic beverage manufacture.

For this purpose, it is necessary to achieve the following **objectives**:

1. to determine the specific consumption of hydrochloric acid solution, drinking and prepared water, and the water-alcohol mixture at the stage of preparing modified materials for the main filter cycle;
2. to study the effect of modified filter materials on the physicochemical and sensory parameters of the water-alcohol mixture, on the efficiency of its purification, and on its expected stability.

Research materials and methods

During the research the following materials were used:

– a water-alcohol mixture having the strength 40% vol., which was prepared at "BRANDBAR" LLC by adding a calculated amount of prepared water to a calculated amount of rectified ethanol of the grade Lux. The prepared water was obtained by mechanical filtration with quartz sand, softening, sorption purification, and demineralisation by reverse osmosis. Rectified ethanol of the grade Lux should be used with the volume fraction of ethanol 96.5%, mass concentration of aldehydes, in terms of acetaldehyde in anhydrous alcohol, 1.8mg/dm^3, mass concentration of fusel oil, in terms of a mixture of isoamyl and isobutyl alcohols (1:1) in anhydrous alcohol, 0.5mg/dm^3, mass concentration of esters, in terms of acetic ethyl ester in anhydrous alcohol, 1.0mg/dm^3, volume fraction of methanol, in terms of anhydrous alcohol, 0.007%. Besides, it should stand a test for purity, and the result of an oxidation test should be 25 minutes;

– obsidian from the Rokosiv field (Ukraine), produced by "EKKOM" LLC with the fractional composition 1-5mm, humidity 5%, ash content 4%, and mechanical strength 98%;

– clinoptilolite from the Sokyrnytsia field (Ukraine), produced by "EKKOM" LLC with the fractional composition 1–5 mm, humidity 7%, ash content 7%, ion exchange capacity 1.5mmol/g, and mechanical strength 98%;

– quartz sand (reference sample) with the fractional composition 1–5mm, humidity 6%, ash content 7%, and mechanical strength 98%.

To obtain the starting material, obsidian was washed clean of dust first with drinking water, and then treated with 1.0% hydrochloric acid solution and washed with prepared water. The modified form of obsidian was obtained by thermal activation in a thermostat at 200–220°C for 4h, after which it was treated with electrolytic silver solution to the concentration 0.1–0.12% at 15–20°C.

To obtain the starting material, clinoptilolite was washed clean of dust first with drinking water, then treated with a 1.0% hydrochloric acid solution and washed with prepared water. The modified form of clinoptilolite was obtained by treatment with 10% sodium chloride solution and thermal activation in a thermostat at 150–200°C for 4h, followed by treatment with electrolytic silver solution to the concentration 0.1–0.12% at 15–20°C.

The electrolytic silver solution was prepared on the basis of distilled water using an ioniser with the cell volume 1.0 dm^3 and silver electrodes made of 999.9 grade silver. The time the installation needed to make electrolytic silver solution and achieve the saturation concentration of the two materials studied, obsidian and clinoptilolite, was calculated (in minutes) by the mass concentration (milligrams per cubic decimetre) of silver dissolved in the required volume of distilled water.

The filter materials were loaded separately into a filter with the diameter 100mm and height 500m: No. 1 – modified obsidian, No. 2 – modified clinoptilolite, No. 3 – quartz sand. The height of the layer of each filter material was 400mm.

Filtration of the alcohol-water mixture was performed in a filter, filled with one of these filter materials. The level of purity of the alcohol-water mixture before and after its purification with the modified natural materials was determined by the physicochemical parameters and cationic-anionic composition under dynamic conditions at the filtration rate 60dal/h [1,4,6].

The following methods of analysis were used:

– sensory studies were performed by tasting in accordance with DSTU 4165 and DSTU 4979;

– physicochemical determination of the mass concentration of aldehydes, in terms of acetaldehyde in anhydrous alcohol, mass concentration of fusel oil, in terms of a mixture of isoamyl and isobutyl alcohols (1:1) in anhydrous alcohol, mass concentration of esters, in terms of acetic ethyl ester in anhydrous alcohol was conducted by photocolourimetry using a photoelectric colourimeter KFK-2 in accordance with DSTU 4165;

– alkalinity (volume of hydrochloric acid c(HCI)=0.1mol/dm^3 spent to titrate 100cm^3 of vodka) was determined titrimetrically in accordance with DSTU 4165;

– strength was measured by the areometric method in accordance with DSTU 4165;

– volume fraction of methyl alcohol, in terms of anhydrous alcohol, and mass concentration of acetaldehyde, 2 propanol, 1 propanol, isobutanol, methyl acetate were determined by gas chromatography using a gas chromatograph Crystal-2000M according to DSTU 4222;

– effect of water-alcohol mixture purification and its transparency was determined spectrophotometrically using a spectrophotometer Specord UV in accordance with DSTU 5068;

– cation-anion composition was determined by capillary electrophoresis (using a capillary electrophoresis system KAPEL-105) in accordance with DSTU 4801 and DSTU 4932;

– transparency was measured spectrophotometrically in accordance with DSTU 5068;

– expected stability was found by testing the alcohol-water mixture before and after its purification, by establishing changes in the physicochemical parameters of the product after its resting under critical conditions, and by the reference sample and the array of the reserve of this parameter to the critical limit in accordance with DSTU 7397.

Results of the research and their discussion

The filter materials are used at the stage of filtering the alcohol-water mixture, so it is necessary to establish the unit volumes of:

- hydrochloric acid solution, which is necessary to remove ash constituents and lime inclusions from the surface;
- drinking water and prepared water to wash the material;
- water-alcohol mixture before establishing the equilibrium value of strength to prevent dilution of the mixture (Fig. 1).

It has been found that in comparison with the reference sample of quartz sand, modified obsidian requires less:

- drinking water at the stage of pre-washing – by 1.5 times;
- 1.0% hydrochloric acid solution to remove the residues of limestone, chalk, iron, and other inclusions – by 1.9 times;
- prepared water at the stage of washing after treating with hydrochloric acid solution – by 1.7 times;
- water-alcohol mixture until achieving a stable strength after filtration – by 1.3 times.

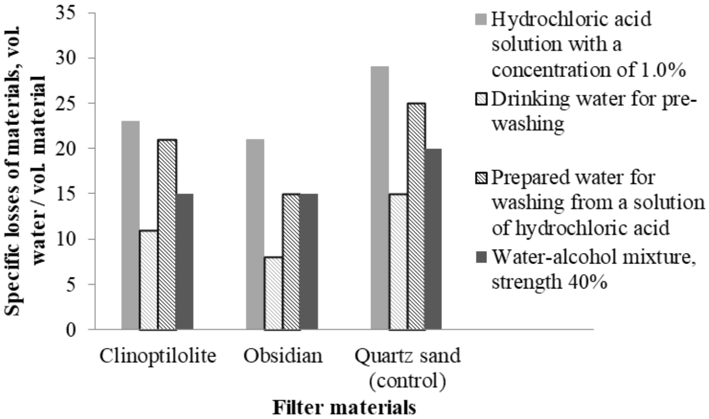

Fig. 1. Unit volume of the regenerated materials at the stage of preparation for the main cycle of alcohol-water mixture filtration

Modified clinoptilolite in comparison with quartz sand requires less:

- drinking water at the stage of pre-washing – by 1.3 times;
- 1.0% hydrochloric acid solution to remove the residues of limestone, chalk, iron, and other inclusions – by 1.36 times;
- prepared water at the stage of washing after treating with hydrochloric acid solution – by 1.19 times;
- water-alcohol mixture until achieving a stable strength after filtration – by 1.3 times.

Lower consumption of drinking water, prepared water, and hydrochloric acid solution will reduce wastewater and make the production environmentally friendly [1].

Filtration of the alcohol-water mixture is accompanied by oxidation and adsorption of such micro-impurities present in alcohol as aldehydes, fusel oils, unsaturated compounds, which affect the results of tasting the water-alcohol mixture [1,4,6]. That is why the physicochemical parameters, microcomponent composition (Table 1), and the cation-anion composition (Table 2, Fig. 2) of the alcohol-water mixture have been studied before and after its filtration with modified obsidian and clinoptilolite (as compared with quartz sand) at the filtration rate 60 dal/h which is standard for producing ordinary and high-quality vodkas [1].

The data in Table 1 confirm the other scientists' data that the electrochemical potential difference between silver and modified clinoptilolite intensifies the course of redox reactions and esterification reactions [6,22,33]. That is why after filtration, the alcohol-water mixture has better physicochemical parameters than the reference sample.

Clinoptilolite is a zeolite with ion exchange properties [26-32], and its modification makes sorption of micropurities from the aqueous-alcoholic solution more effective and selective [33,36-37]. This is accompanied by a decrease in the mass concentration of aldehydes by 0.5mg/dm^3, fusel oil by 0.3mg/dm^3, esters by 0.7mg/dm^3, acetaldehyde by 30%, 2-propanol by 2.5 times, as compared with quartz sand (Table 1), which is confirmed by the data [33].

The physicochemical and chromatographic findings on the content of the basic micro-impurities in the ethanol of the alcohol-water mixture (Table 1) confirm other scientists' conclusion [23]: the modified obsidian, due to its structure, actively adsorbs aldehydes, esters, higher alcohols, thus reducing their initial content by 0.3–0.5mg/dm^3 in comparison with quartz sand. This allows preventing an increase in recoverable spoilage, especially in the initial period of filtration, and is confirmed by the data [23].

The microelement composition significantly effects on the organoleptic characteristics and stability of the water-alcohol mixture [1,4,6]. Ash constituents (iron, magnesium, aluminium, potassium, calcium, silicon) play an important role in chemisorption, as metal oxides catalyse chemical reactions [1,4,6].

Analysis of the physicochemical parameters and of the microcomponent and cationic-anionic composition before and after filtering the alcohol-water mixture with modified obsidian indicate that they are practically invariable: there is no increase in harmful micro-impurities and no oxidation of the water-alcohol mixture. This is positive, because it does not lead to partial transition of impurities of the material into the solution, nor to the subsequent turbidity with formation of precipitate. The result obtained complies with the research data [1,6,23].

After filtration with modified clinoptilolite, as compared with modified obsidian, there is a decrease in the mass concentration of cations and anions: those of ammonium, nitrates, and phosphates decrease by 3 times, of nitrites by 4 times, of potassium and fluorides by 1.6 times, of sodium, chloride, and iron by 1.5 times, of magnesium and calcium by 2-2.5 times, of silicon by 20%. Reducing the content of cations and anions in the alcohol-water mixture allows increasing the filtration effect (Fig. 2), improves the transparency (Fig. 3), and increases the stability of the water-alcohol mixture. This is confirmed by the data presented in Fig. 4 and the studies [1,6,23].

Table 1 – Physicochemical parameters of the alcohol-water mixture before and after filtration with the materials studied (n=3; P≥0.95)

Parameters (according to regulatory documents) and units of measurement	Limit value for vodkas based on alcohol of the grade *Lux*	Results of testing the alcohol-water mixture			
		Initial values	after filtering		
			with quartz sand	with modified obsidian	with modified clinoptilolite
1	2	3	4	5	6
Strength, %	40±0.3	40.14±0.1	40.1±0.1	40.1±0.1	40.1±0.1
Alkalinity (volume of hydrochloric acid c(HCI)=0.1mol/dm^3 spent on titration of 100cm^3 of vodka), cm^3	not more than 3.5	0.9±0.05	1.1±0.05	0.9±0.05	0.7±0.05
Mass concentration of aldehydes, in terms of acetaldehyde in anhydrous alcohol, mg/dm^3	not more than 4.0	2.0±0.15	2.2±0.15	2.0±0.15	1.5±0.15
Mass concentration of fusel oil, in terms of a mixture of isoamyl and isobutyl alcohols (1:1), in anhydrous alcohol, mg/dm^3	not more than 2.0	0.50±0.15	0.50±0.15	0.50±0.15	0.20±0.15
Mass concentration of esters, in terms of acetic ethyl ester, in anhydrous alcohol, mg/dm^3	not more than 5.0	1.2±0.25	1.40±0.25	1.20±0.25	0.7±0.25
Volume fraction of methanol in terms of anhydrous alcohol, %	not more than 0.01	0.007±0.002	0.007±0.002	0.007±0.002	0.003±0.002
Mass concentration of acetaldehyde, mg/dm^3 anhydrous alcohol	not regulated	1.3±0.3	1.3±0.3	1.3±0.3	1.0±0.3
Mass concentration of 2-propanol, mg/dm^3 anhydrous alcohol	not regulated	0.5±0.1	0.5±0.3	0.5±0.3	0.2±0.3
Mass concentration of 1-propanol, mg/dm^3 anhydrous alcohol	not regulated	0.2±0.04	0.18±0.04	0.18±0.04	0.18±0.04
Mass concentration of isobutanol, mg/dm^3 anhydrous alcohol	not regulated	0.20±0.04	0.20±0.04	0.20±0.04	0.20±0.04
Mass concentration of methyl acetate, mg/dm^3 anhydrous alcohol	not regulated	0.20±0.04	0.20±0.04	0.20±0.04	0.20±0.04

Table 2 – Effect of the materials under study on the cation-anion composition of the alcohol-water mixture (n=3; P≥0.95)

Mass concentration, mg/dm^3	Results of testing the alcohol-water mixture			
	Initial values	after filtering		
		with quartz sand	with modified obsidian	with modified clinoptilolite
ammonium	0.05±0.025	0.05±0.025	0.03±0.025	0.01±0.025
aluminium	0.05±0.025	0.05±0.025	0.03±0.025	0.03±0.025
potassium	25±0.5	25±0.5	25±0.5	15±0.5
sodium	15±0.2	15±0.2	15±0.2	10±0.2
magnesium	0.5±0.025	0.7±0.025	0.5±0.025	0.2±0.025
calcium	0.4±0.02	0.6±0.02	0.4±0.02	0.2±0.02
silicon	1.2±0.05	1.7±0.05	1.2±0.05	1.0±0.05
chlorides	15±0.3	15±0.3	15±0.3	10±0.3
nitrites	0.01±0.002	0.01±0.002	0.008±0.002	0.002±0.002
sulphates	10±0.5	10±0.5	10±0.5	10±0.5
nitrates	0.09±0.03	0.09±0.03	0.06±0.03	0.02±0.03
fluorides	0.5±0.025	0.5±0.025	0.5±0.025	0.3±0.025
phosphates	0.02±0.0015	0.02±0.0015	0.015±0.0015	0.005±0.0015
iron	0.005±0.001	0.005±0.001	0.003±0.001	0.002±0.001

During the production of vodkas, it is necessary to monitor purification of water-alcohol mixtures. The process is controlled by the optical density in the near ultraviolet region of the spectrum [1,4,6,23], which indicates the presence of aldehydes, ketones, esters, carboxylic acids in the water-alcohol mixture [1,6,22,23]. The main result of filtering should be a positive purification effect (Fig. 2) and the improved transparency of the alcohol-water mixture (Fig. 3) [1,6,23].

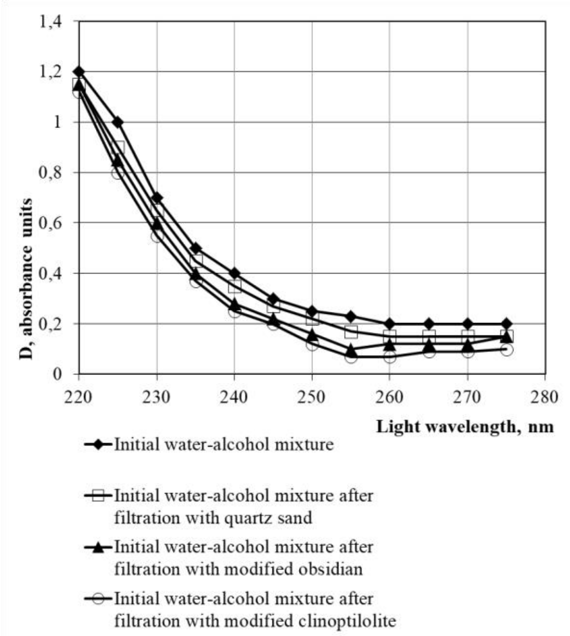

Fig. 2. UV absorption spectra of the alcohol-water mixture before and after filtration with natural materials (n=3; P≥0.95)

The optical density at the light wavelength λ=260nm characterises the degree of contamination with organic and mineral impurities [1,6,22]. It has been found that after filtration with obsidian, compared with quartz sand, the purification effect is higher by 10%, and after filtration with clinoptilolite, it is higher by 15%. This is also confirmed by the improvement of transparency, with the alcohol-water mixture acquiring a crystal shine (Fig. 3) [6,22]. Our studies are confirmed by the data [6,22] and indicate that the absorption of alcohol impurities of different nature depends on their bonds with the materials considered and on hydrogen bonds between water and ethanol. Thus, using mineral adsorbents results in more effective sorption of ethanol [6,33].

In the production of vodkas, the parameter of transparency is especially important. By their appearance, vodkas are characterised as "transparent as a tear," "crystal clear" [1,4,6]. Another estimation criterion is the absorbance unit – the degree of contamination of an alcohol-water mixture or vodka with impurities that come with water and alcohol [1,4,6]. After adsorption of impurities from the alcohol-water mixture with a filter material, its optical density decreases [1,4,6].

It has been found that due to its structural and microporous properties, the alcohol-water mixture, when filtered with modified natural obsidian and modified clinoptilolite, is more transparent by 0.1-0.2 absorbance units, then when filtered with quartz sand. This is confirmed by the data [23].

The expected stability has been established by the change of the physicochemical parameters of the alcohol-water mixture after its resting under critical conditions, as well as by the reference sample and by the array of the reserve of this parameter to the critical limit (Fig. 4).

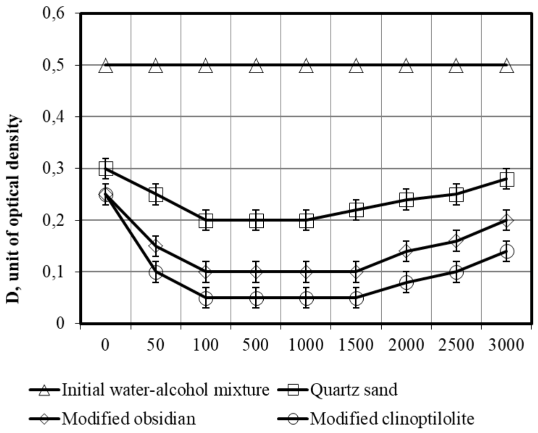

Fig. 3. Changes in the transparency of the alcohol-water mixture before and after filtration with the natural materials (n=3; P≥0.95)

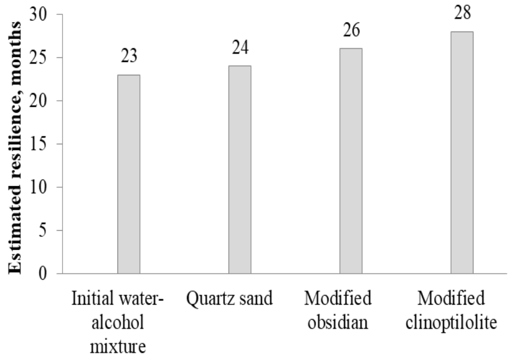

Fig. 4. Dependence of the expected stability of the alcohol-water mixture on the filter material (n=3; P≥0.95)

The shelf life of finished alcoholic beverages is one of the most important parameters. It characterises the quality of vodkas or their loss of stability [1,4,6]. Stability of beverages is the duration of their storage until turbidity or changes in the physicochemical or sensory parameters, which is characterised as non-compliance with DSTU 4256. When studying the materials used in the vodka technology and before launching a new product onto the consumer market, its shelf life is determined [1,4,6] by the method of expected stability based on the array of data obtained presented in Tables 1, 2. The results of studying the expected stability show (Fig. 4) that the two modified natural filter materials under consideration, if used in the technology of ordinary vodkas and special vodkas, increase their shelf life: obsidian by two months, clinoptilolite by four months.

Conclusion

It has been scientifically grounded and established that filtration of a water-alcohol mixture with obsidian and modified clinoptilolite allows increasing the purification effect by 10–15% and improving the transparency of the original alcohol-water mixture by 0.1–0.2 units, compared with the reference sample of quartz sand.

The use of the studied modified natural materials in a carbon purification battery increases the projected shelf life of the finished product by 2 months (using obysidian) and 4 months (using clinoptilolite), This indicates the prospects of using obsidian to filter water-alcohol mixtures.

It has been found that in comparison with the reference sample of quartz sand, the specific consumption of materials used at the stage of preparation for the main filter cycle with the use of obsidian and modified clinoptilolite is 1.2-1.9 times lower.

Analysis of the physicochemical parameters and of the microcomponent and cation-anion composition before and after filtering the alcohol-water mixture with obsidian indicates that they are practically invariable. This is positive, because it does not lead to an increase in harmful micro-impurities and oxidation of the water-alcohol mixture.

The studies presented show that due to the modification and ion exchange properties, clinoptilolite has a higher potential and is more effective in filtration than modified obsidian.

After filtration with modified clinoptilolite, as compared with modified obsidian, there is a decrease in the mass concentration of cations and anions by an average of 1.5 times, which is confirmed by a 5% more positive purification effect and increases the stability of the water-alcohol mixture by 2 months.

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ОЧИЩЕННЯ ВОДНО-СПИРТОВОЇ СУМІШІ МОДИФІКОВАНИМИ ПРИРОДНИМИ МАТЕРІАЛАМИ

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Анотація. У статті наведено результати теоретичних та експериментальних досліджень з удосконалення технології очищення водно-спиртової суміші природними модифікованими мінералами для виробництва горілчаної продукції. Розглянуто способи та основні фільтрувальні матеріали, які використовуються у технології горілок. Викладено методи визначання фізико-хімічних показників, катіонно-аніонного складу сортівки, спосіб модифікації природного обсидіану та природного цеоліту клиноптилоліту. Встановлено, що у порівнянні з кварцевим піском, для досліджуваних модифікованих мінералів змешуються основні одиничні питомі витрати розчину соляної кислоти для видалення з поверхні зольних елементів та вапнякових включень – в 1,3–1,9 рази, води питної – в 1,3–1,5 рази та підготовленої – у 1,2–1,7 рази для промивки матеріалу, водно-спиртової суміші до встановлення рівноважного значення міцності для запобігання розбавлення сортівки – в 1,3 рази. Показано вплив модифікованих природних матеріалів на фізико-хімічні показники і катіонно-аніонний склад сортівки до та після її очищення модифікованими обсидіаном та клиноптилолітом у порівнянні з кварцевим піском. Доведено досягнення позитивного ефекту покращення прозорості сортівки на 0,1–0,2 одиниці оптичної густини у технології фільтрування модифікованими природними мінералами. Визначено прогнозовану стійкість за зміною фізико-хімічних показників сортівки після її витримки в критичних умовах і контрольним зразком за масивом запасу параметра до критичної межі, яка становить 26–28 місяців. Встановлено, що фільтрування сортівки модифікованим обсидіаном дає змогу збільшити строк придатності до споживання на два місяці, модифікованим клиноптилолітом – на 4 місяці. Модифікування природних обсидіану та клиноптилодіту, за зменшених питомих витрат соляної кислоти та підготовленої води на стадії підготовки до основного циклу, сприяє підвищенню ефективності фільтрування на 10-15% та дозволяє отримати горілку з покращеним її мікрокомпонентним складом.

Ключові слова: сортівка, горілка, очищення, фільтрування, модифікування, мінерал, обсидіан, кварцевий пісок, клиноптилоліт.

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