THE IMPROVEMENT OF THE WATER TREATMENT TECHNOLOGY FOR THE KVASS PRODUCTION

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Abstract. The composition of water significantly affect the flow of the process and the main indicators of the finished drink. The article presents the results of theoretical and experimental researches on improvement of the technology of preparation of drinking water for the production of non-alcoholic fermented beverages, in particular, bread kvass. The high efficiency of the application of natural minerals – clinoptilolite, rock crystal and activated carbon with combined treatment of water in the technology of bread kvass is proven. The quality and usefulness of the product depend on the content of its impurities. The integrated action of investigated materials with adsorption, ion exchange and redox properties provides water conditioning and achievement of the intensification of the technological process and high organoleptic qualities of the finished product. The work presents the physical-mechanical characteristics of the investigated materials, technological parameters of treatment, the influence of filter materials on the organoleptic and physical and chemical parameters of water and finished product. The article also gives a taste-aroma profile of bread kvass, made from the use of prepared water. The materials of the conducted research testify to the expediency of water treatment for the production of bread kvass in the sequence of clinoptilolite, active coal, rock crystal with a filtration rate of 8–15 m/h. In this case, the total iron content is reduced by 5 times, the total stiffness decreases by 75%, permanganate oxidation is 9 times. It has been established that such processing allows for high organoleptic qualities of prepared water and end product and increases the tasting score of bread kvass by 7 times, with no unpleasant taste and aroma that is characteristic of chlorinated water and decreases the turbidity of the beverage as a result of a decrease in the overall rigidity of water.

Key words: bread kvass, water, water preparation, mechanical filtration.

УДОСКОНАЛЕННЯ ТЕХНОЛОГІЇ ПІДГОТОВУВАННЯ ВОДИ ДЛЯ ВИРОБНИЦТВА КВАСУ

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Анотація. На перешкоді технологічного процесу та основні показники готового напою суттєво впливає склад води. У статті наведені результати теоретичних та експериментальних досліджень з усунення корисних водних породин від сировини для виробництва хлібного квасу – найбільш поширений безалкогольний ферментований напій. Комплексна дія досліджуваних матеріалів з адсорбційними, іонобмінними та окисно-відновними властивостями забезпечує кондиціонування води та інтенсифікацію технологічного процесу, досягнення високих органолептичних якостей готового продукту. Від вмісту домішок води залежить якість та корисність готового продукту. Доведено високу ефективність застосування природних мінералів – клиноптилоліту та гірського криштала, а також, активного вугілля при комбінованій обробці води в технології хлібного квасу. У роботі наведено фізико-механічні характеристики досліджуваних матеріалів, технологічні параметри обробки, вплив фільтрувальних матеріалів на фізико-хімічні та органолептичні показники води та готового продукту. У статті, також, наведено смако-ароматичний профіль хлібного квасу, виготовленого з використанням підготовленої води. Матеріали проведених досліджень свідчать про доцільність обробки води для виробництва хлібного квасу у послідовності клиноптилоліту, активне вугілля, гірський криштал із швидкістю фільтрування 8–15 м/год. При цьому вміст загального заліза зменшується у 5 разів, загальна жорсткість знижується на 75%, перманий залісність зменшується у 9 разів. Встановлено, що така обробка дозволяє надати високі органолептичні якості підготовлені воді та кінцевому продукту і збільшує дегустаційна оцінка хлібного квасу на 7 балів, при цьому відсутній неприємний смак та аромат, якій характерний для хлорованої води та зменшується міцність навпаки внаслідок зниження загальної жорсткості води.

Ключові слова: хлібний квас, вода, водопідготовка, механічне фільтрування.

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Introduction. Formulation of the problem

The health and longevity of a human depends on his or her diet, in particular the consumption of drinking water and beverages. Water is the main component of non-alcoholic beverages (85–96%), therefore the quality, stability and usefulness of a beverage depend on its macro- and micro-element composition. The annual increase of the population, as well as rapid development of industry leads to a significant increase in water consumption and drainage. The consequence of these phenomena is the change in the chemical and microbiological composition of drinking water, the doubtfulness of its safety. So, the preparation of water for beverages is becoming increasingly important.

Analysis of recent research and publications

Bread kvass, which is prepared based on rye raw materials, is a traditional Slavic beverage. It contains a wide range of biologically active substances. Bread kvass has always been one of the most popular fermented non-alcoholic drinks, but during the last two decades, many domestic producers became bankrupt, so the production of kvass significantly decreased. Today, kvass returns its popularity; its production takes in an increasing part in the market of non-alcoholic beverages [1].

According to the organoleptic characteristics, bread kvass is a fermented non-alcoholic beverage of dark brown color with a pleasant sweet-sour taste and characteristic flavor of rye bread. The beverage is obtained through the unfinished combined alcoholic and lactic fermentation. However, in most enterprises, with the purpose to simplify the technology only the alcoholic fermentation is used, and the necessary acidity of the beverage is achieved by addition of lactic acid.

The presence of insignificant content of ethyl alcohol (0.4–0.5% vol.) in the bread kvass does not reduce the physiological significance of this drink for a person. Its usefulness is characterized by the content of vitamins, organic acids, amino acids, macro- and micro-elements [1, 2].

Water takes the main place in the mix formulation of any non-alcoholic drink. Enterprises of the food industry use the water of centralized water supply systems or artesian wells in production technology. In the first case, the water is already brought to the drinking-water condition, and in the second, which is used more often, it may not meet such requirements. Moreover, there are additional requirements for technological water in non-alcoholic production [1, 2], at the same time there are no special requirements for water for the production of kvass. In many cases, water is softened by nitro-cation filters, but this purification is not enough. Therefore, it is urgent to improve the technology of water preparation with the effective and convenient for the practical use natural minerals of various types during mechanical filtration.

There are various types of water purification, including the use of mechanical filters with fillings of natural minerals (quartz sand, gravel) [3]. When conditioning water for the production of fermentative beverages, the use of such filtering is obligatory. As a result, water should be released from mechanical impurities, colloidal gravity and sediment. However, such treatment does not fully ensure the quality of the prepared water by organoleptic, physico-chemical and toxicological indicators. Therefore, it is important to improve the method of mechanical water filtration using new effective natural materials, especially minerals. Thanks to the strictly determined pore and inner hollow sizes, they appear effective sorbents of organic and inorganic substances. Such materials are able to improve the organoleptic and physico-chemical parameters of water, provide its structuring, which increases the health-giving effect of the finished beverage [3,4].

Modern technologies of water purification envisage the use of natural and artificial minerals for solving various problems. Sorption processes are realized by the use of activated carbon and its analogues (graphite mineral sorbents). For these purposes, and also as a filter material, zeolites are used [3].

Zeolites haven’t been of practical importance for a long time. Before much longer, it was found that their unique properties can be used in many industries. In our time, more than forty structural types of zeolites are known, the most common of which are clinoptilolite, heulandite, phillipsite, limonite, mordenite, erionite, chabazite, analcime [3,5].

Ukraine has one of the world's largest deposits of zeolites, which is located in the village Sokrymsytia, Khust district, Transcarpathian region. Clinoptilolite from this deposit contains 85–90% of the main component. The formula of Transcarpathian clinoptilolite in the oxide version has the following form, %: SiO₂ – 67.29; TiO₂ – 0.26; Al₂O₃ – 12.32; Fe₂O₃ – 1.26; FeO – 0.25; MgO – 0.99; CaO – 3.01; Na₂O – 0.66; K₂O – 2.76; H₂O – 10.90 [6]. Low prime cost, unique, and useful technological properties of zeolites – selective (cation-exchange, molecular-sieve), sorption (first of all, adsorption) and catalytic, are conditioned by special features of crystal lattice and chemical composition. These aquatic aluminum silicate minerals have a frame structure, which enables to use them as an effective filtering material for water purification [5,6].

In addition to natural zeolites, artificial zeolites are also produced. However, according to some properties (resistance to high temperatures, acid influence, etc.), these materials considerably compromise on the natural ones, but despite of this, their cost is significantly higher. Simultaneously, natural dehydrated zeolites are
able to absorb molecules of different substances, as well as gases, liquids and solids [7]. The intensity of adsorption is provided by the large internal surface of the mineral, which reaches 47%, while in artificial zeolites this figure is 50% at a higher prime cost.

The benefits of natural zeolites include their ability of regeneration, and as a consequence, the opportunity of using in a multi-cycle mode. The artificial zeolites are not suitable for water purification because they do not meet the requirements of sanitary norms for organoleptic parameters and acidity. In turn, the natural zeolites of the Transcarpathian deposit are acceptable from the point of view of ecological requirements, and are close to artificial ones in terms of purity [3,5-7].

Activated carbon is a highly porous carbon sorbent material. The activated carbon, used in water preparation: powdered, grainy (crushed or granulated), and also fibrous. Now, in the sorbent purification of water, the grainy activated carbon from coconut, coal or bituminous raw materials is applied [8,9].

In modern water purification systems the most widespread method for the removal of chlorine and its derivatives, as well as organic matters and gases, is the activated carbon, in particular Silcarbon K835. This activated carbon is extracted from the shell of coconut by means of pyrolysis, therefore, it has a high density and mechanical strength that enables to carry out the multiple regeneration in carbon filters [8,10-15] with improved organoleptic characteristics of water, in particular its transparency, color, smell, flavor and taste.

The rock crystal, rauchtopaz, morion, smoky diamond, smoky crystal, Cairngorm, Scottish stone are natural variations of the quartz mineral, which belongs to the class of oxides and hydroxides, has a SiO₂ composition (silicon oxide). Nowadays, the rock crystal is used in the distilled beverages production for the final filtration of the water-alcohol mixture and improvement of its tasting evaluation, but it is not used in the production of other drinks [3].

The Carpathian region is well known for the presence of a significant number of healing natural waters, which obtained their properties through natural filtration and ion exchange, when passing through the terrestrial and underground horizons of minerals with the original adsorption properties (clay, aluminosilicates, and zeolites). Therefore, the application of investigated in the work natural mineral adsorbents, in particular zeolites, in the treatment of natural waters will not only eliminate hazardous and toxic substances, but also preserve the necessary salt water balance without use of chemical reagents. This creates the conditions for a significant impact on the flow of technological processes in the beverage technology.

The aim of the work is to study the physico-mechanical characteristics of various materials of different types; their influence on physico-chemical and organoleptic parameters of prepared water and bread kvass.

To achieve the stated aim, the following tasks must be solved:
1. to determine the physico-mechanical characteristics of sorption and filtration materials,
2. to determine the technological parameters of water treatment by the investigated materials,
3. to study the influence of filtration materials on the physico-chemical and organoleptic parameters of water and bread kvass and its flavor-aromatic profile.

### Research materials and methods

As objects of study were used: drinking water from centralized water supply of Lviv city, according to approved governmental standards (DSanPiN) 2.2.4-171-10, activated carbon Silcarbon K835, rock crystal and clinoptilolite of Sokynzyskii deposit in accordance with current normative documentation, ready-made bread kvass according to DSTU 4069.

Water treatment was carried out on the laboratory assembly, which included a 10 dm³ pressure scoop, a 1.0 dm³ filter with appropriate activated carbon and filtration materials, and a 10 dm³ intake scoop.

During the production of kvass, it is necessary to take into account the following indicators of water, such as hardness, dry residue, the amount of organic impurities and heavy metals, organoleptic parameters, redox potential. The value of the above-mentioned indicators of water quality affects the technological process of kvass preparation, as well as the quality and usefulness of the finished product.

*Fig. 1. Laboratory assembly for water purification with natural materials*

1 – pressure dumpster with a capacity of 10 dm³, 2 – filter with a capacity of 1.0 dm³, 3 – filtration materials, 4 – drainage, 5 – receiver with a capacity of 10 dm³

To reduce water hardness and remove heavy metals we used clinoptilolite, which allows in addition to adjusting calcium and magnesium content to reduce ammonium content and alkalinity significantly [7]. This is due to the peculiarities of the clinoptilolite structure (framework structure of the mineral). The framework of clinoptilolite is a tetrahedron, the tops of which form
Eight-membered rings, creating channels in the structure of matter. Inside the channels, there are water molecules ("zeolite water"), as well as ions of alkaline (Na	extsuperscript{+}, K	extsuperscript{+}) and alkaline-earth metals (Ca	extsuperscript{2+}, Mg	extsuperscript{2+}). With a large quantity of input windows on the surface, the structure penetrated with channels, and complex of cations inside appears the possibility of using clinoptilolite as a «molecular sieve» and replacing cations that can penetrate through the molecular window (the size of the input windows 3.5–4.8 Å) through structural cations of the mineral [6,7].

To reduce the content of organic matters and improve the organoleptic parameters of water, it was used the sorption purification with activated carbon, which contains micropores.

In order to structure the water, adjust the redox potential and remove the foreign microflora it was used the rock crystal, which has bactericidal properties [3].

For the cooking of kvass, we used drinking water, treated in different sequences of the use of activated carbon and natural minerals at the rate of 8–15 m/h. The source drinking water was used as a control. The process of water preparation was cyclic and consisted of the following consecutive stages:

- preparation of sorption and filtration materials;
- filtration of water until achieving the limit values of indicators through the material layer: clinoptilolite according to the hardness index; rock crystal in terms of transparency; activated carbon for transparency, color and permanganate oxidation;
- fluffing up a layer of materials with the source water stream to prevent the soiling and remove the dirt from their surface and control the transparency and color indexes;
- regeneration of clinoptilolite.

The preparation of water was carried out by treatment with natural minerals and activated carbon: sample Nr.1 – source drinking water (control); sample Nr.2 – water, sequentially treated with clinoptilolite, activated carbon, and rock crystal; sample Nr.3 – water, sequentially treated with activated carbon, clinoptilolite, and rock crystal; sample Nr.4 – water, consistently treated with rock crystal, clinoptilolite, and activated carbon.

The mash was made by introduction the concentrate of kvass mash into the water, appropriately prepared according to the above-mentioned treatment, to the concentration of dry matter of 2.2–2.3%. After that, the content of dry matter was adjusted to 3.2–3.5% by means of sugar syrup. Into the finished mash, it was added a pure culture of yeast Saccharomyces cerevisiae MP-10 in the amount of 2–5% of the volume at a concentration of cells in the culture liquid of 50–70 ml/cm	extsuperscript{3}. The fermentation time is 15 hours. After fermentation, the kvass was cooled, the yeast residue removed and the beverage mixed with sugar syrup to a dry matter content of 5.6%.

**Results of the research and their discussion**

In order to improve the technology, the method of water filtration with activated carbon and natural minerals (rock crystal and clinoptilolite) was developed, laboratory studies of water preparation were carried out, and the effect of prepared water on the physico-chemical and organoleptic parameters of bread kvass was determined.

To define the possibility of application of the investigated materials, it were designated their physico-mechanical properties which influence the degree of water purification while preventing an increase in the content of silicates in the filtrate and increasing the permanganate oxidation. The results of the studies are shown in Table 1.

The mechanical strength of the studied samples of materials was more than 95 %, which contributed to an increase of the period of their operation and the quantity of regenerations, reduction of the starting period, decrease of water consumption and washing reagents [8]. The average particle size of clinoptilolite is 3.3 times greater than that of rock crystal and activated carbon. The bulk weight of rock crystal is 15 % higher than of the other materials studied.

Technological parameters of water treatment with the investigated materials are given in Table 2.

**Table 1 – Physical-mechanical characteristics of sorption and filtration materials**

| Parameter                  | Material          | Rock crystal | Clinoptilolite | Activated carbon |
|----------------------------|-------------------|--------------|----------------|------------------|
| Bulk weight, g/dm	extsuperscript{3} |                  | 1300         | 1100           | 1100             |
| Humidity, %                |                   | 7            | 4              | 5                |
| Mechanical strength, %     |                   | 98           | 96             | 96               |
| Grain size composition, mm |                   | 0.5–2.5      | 3–7            | 0.5–2.5          |

**Table 2 – Technological parameters of water treatment**

| Technological operation          | Linear speed, m/h | Relative volume, vol./vol. of filtration materials |
|----------------------------------|-------------------|-----------------------------------------------|
| Preparation (rinsing) of materials | 10–20             | Rock crystal (5–7) Clinoptilolite (10–20) Activated carbon (5–8) |
| Duration of filtration cycle     | 8–15              | 1200–1500 Clinoptilolite (1500–1800) Activated carbon (1500–2200) |
| Regeneration of materials:       |                   |                                               |
| – fluffing up with source water  | 12–16             | Rock crystal (5–7) Clinoptilolite (8–15) Activated carbon (5–10) |
| – rapid rinsing                  | 15                | Rock crystal (5–7) Clinoptilolite (10–15) Activated carbon (5–7) |
It was established that at the stage of preparation for work, in comparison with the rock crystal, the use of clinoptilolite and activated carbon contributed to a decrease of relative volume of rinsing water to the volume of material by 2.5 times, an increase in the duration of the filtration cycle by 2.2–2.5 times, and clinoptilolite – by 1.8 times. During regeneration of the investigated filtration materials, while fluffing up and rapid rinsing, water consumption reduced by 1.5–2 times.

Tables 3, 4 show the organoleptic and physico-chemical parameters of water before and after treatment with the materials studied.

### Table 3 – Influence of filtration materials on the organoleptic parameters of water

| Number of sample | Color intensity, grad. | Turbidity, mg/dm³ | Smell by 20°C | Flavor by 20°C | Transparency, D, units of opt. density |
|------------------|------------------------|-------------------|--------------|---------------|-------------------------------------|
| 1                | 10.0                   | 0.6               | 1.0          | 1.5           | 0.11                                |
| 2                | 0                      | 0                 | 0            | 0             | 0                                   |
| 3                | 0                      | 0                 | 0            | 0             | 0                                   |
| 4                | 0.5                    | 0.04              | 0            | 0.5           | 0.03                                |

### Table 4 – Influence of filtration materials on the physico-chemical parameters of water

| Sample number | Dry residue, mg/dm³ | Total hardness, mmol/dm³ | Iron total, mg/dm³ | Cl, mg/dm³ | NO₃, mg/dm³ | SO₄²⁻, mg/dm³ | pH | Oxidation permanganate, mg O₂/dm³ |
|---------------|---------------------|--------------------------|--------------------|------------|-------------|---------------|----|-------------------------------|
| 1             | 251.0               | 4.5                      | 0.05               | 34         | 4.6         | 37            | 7.39 | 4.0                           |
| 2             | 205                 | 1.1                      | less than 0.01     | 15         | less than 0.05 | 15            | 8.10 | 0.5                           |
| 3             | 219                 | 1.5                      | less than 0.01     | 15         | 0.4         | 18            | 7.51 | 0.5                           |
| 4             | 234                 | 1.8                      | less than 0.01     | 15         | 0.6         | 19            | 7.56 | 0.9                           |

Active acidity is one of the most important indicators of water quality, which essentially determines the nature and speed of chemical and biological processes, identifies the acidity or alkalinity of water. With neutral pH, acids and alkalis are present in water in an equal amount or altogether absent. Such an environment is the most balanced and optimal for biochemical reactions in the human body.

Salts of calcium and magnesium, which are characterized by the hardness index, interact with organic acids, reducing their content in the finished drink, and besides they form the complex compounds that cause turbidity of drinks, and at the stage of mixing lead to an excess consumption of acid.

The content of iron significantly influences the biological value of kvass. Reduction of the iron content in water has a positive impact on the amino acid composition of mash and kvass, because it happens the increase of balanced nitrogen nutrition for yeasts, reduction of fermentation time, and the finished beverage becomes more useful to the consumer.

It was established that water treated with investigated materials in the sequence of clinoptilolite, activated carbon, and rock crystal had the highest organoleptic and best physico-chemical values. At the same time, the water acquired a pleasant taste of spring water without undesirable smells; it was clean and transparent. Simultaneously, the total iron content decreased by 5 times, total hardness for 75 %, permanganate oxidation was 9 times lower.

The organoleptic parameters and the taste-aroma profile of kvass obtain ed by use of the studied water samples are given in Table 5 and on Figure 2.

### Table 5 – Organoleptic parameters of kvass

| Sample number | Color, appearance | Organooleptic values (evaluation) | Total evaluation |
|---------------|-------------------|----------------------------------|------------------|
| 1             | Brown, turbid     | Sweet and sour taste; Flavor of rye bread with unpleasant shade, characteristic for chlorinated water (7 grades) | 11 grades “Sufficient” |
| 2             | Brown, without turbidity | Sweet and sour taste, balanced, without foreign odors, fresh. Vivid aroma of rye bread (11 grades) | 18 grades “Excellent” |
| 3             | Brown, without turbidity | Sweet and sour taste, without foreign odors. Aroma of rye bread, characteristic for brad kvass (9 grades) | 16 grades “Good” |
| 4             | Brown, without turbidity | Sweet and sour taste, without foreign odors. Aroma of rye bread (9 grades) | 15 grades “Good” |
It was established that the proposed method of water treatment significantly increases the organoleptic qualities of kvass. In terms of appearance, aroma and taste, the sample number 2 received a 7-grades higher evaluation. The lowest grades had the control sample number 1, which was conditioned by the excess turbidity of the drink and an unpleasant shade in taste and aroma. The rest of samples were transparent, with characteristic kvass brown color, and without foreign inclusions. All samples had sour and sweet taste, characteristic for bread kvass.

During the analysis of physico-chemical parameters of kvass, it was found that all samples met the normative requirements (content of dry matters was 5.4–5.8%, total acidity 2.0–4.0 cm$^3$ of NaOH concentration of 1 mol/dm$^3$ per 100 cm$^3$ of kvass).

Therefore, the obtained results of experimental studies demonstrate the expediency of using the natural minerals clinoptilolite, rock crystal and activated carbon for water preparation for making kvass.

**Fig. 2. Taste-aroma profile of kvass**

| Sample | Intensity of aroma | Aroma of rye bread | Fullness of taste | Sweetness | Acidity |
|--------|--------------------|--------------------|------------------|-----------|---------|
| Sample 1 | 4                  | 5                  | 7                | 6         | 4       |
| Sample 2 | 5                  | 6                  | 8                | 7         | 5       |
| Sample 3 | 6                  | 7                  | 9                | 8         | 6       |
| Sample 4 | 7                  | 8                  | 10               | 9         | 7       |

**Conclusion**

1. It was established that the use of rock crystal, clinoptilolite and activated carbon in preparation of technological water can increase the filtration cycle by 1.8–2.5 times while reducing the water consumption for regeneration by 1.5–2 times.

2. It was determined that water treatment in the sequence of clinoptilolite, activated carbon, and rock crystal with a linear speed of 8–15 m/h enables to decrease the total iron content by 5 times, total hardness by 75%, permanganate oxidation by 9 times, and provide high water organoleptic properties.

3. The use of water prepared by clinoptilolite, activated carbon and rock crystal is advisable in the technology of bread kvass and allows obtaining the finished product with high organoleptic and normative physico-chemical values.

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