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This paper considers ways of using walnut shells for food products. The study is based on three varieties of walnut as raw materials. Such physicochemical indicators as the shape, mass, thickness, kernel yield, fat, protein, ash, vitamins, minerals, amino acids, and bioflavonoids have been investigated. The results showed that the walnut shell has a large, rounded, and roundovoid shape. The weight of the shell ranges from 11.7 to 14.1 g, the thickness – from 1.5 to 1.6 mm, the kernel yield – from 45.7 to 48.8 %. The fat content ranges from 0.7 to 0.9 %, the protein content – 2.4 to 2.5 %, the ash content – from 1.6 to 1.7%. The study of vitamins in the walnut shell showed that vitamin A is absent in the shell of all varieties of walnut. The content of the vitamin E ranges from 8.59 mg to 9.53 mg, the content of the vitamin C - from 9.31 mg to 15.0 mg, and the content of β , carotene, – from 0.053 to 0.070 mg. The studies have also shown a fairly rich amino acid composition of walnut shells. The results demonstrated that the shell of walnut contains a sufficient amount of daily intake of vitamins. The results of investigating mineral substances showed that the iodine content ranges from $5.52 \,\mu g$ to 14.81 µg, iron - from 3.33 mg to 7.39 mg, and zinc – from 3.1 mg to 6.9 mg. The content of quercetin in the shell of a walnut ranges from 0.945 mg to 1.51 mg, catechin – from 2.46 mg to 12.07 mg, tannins - from 611.32 mg to 805.62 mg. Based on the results of the analysis, it is planned in the future to devise technology for obtaining an extract that could be used as a food additive in a soft drink, enriching it with the missing nutritional components Keywords: walnut shell, physicochemical

properties, phenolic acids, functional products, food additive, soft drink

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REVEALING THE FEATURES OF THE COMPOSITION OF THE WALNUT SHELL FROM THE POINT OF VIEW OF THE POSSIBILITY OF ITS USE IN THE FOOD INDUSTRY

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1. Introduction

The lack of immunostimulants and biologically active substances, as well as the need for the most complete utilization of the raw material base, is the main reason for conducting research on the applicability and introduction into secondary circulation of crop production waste. It is well known that plantbased raw materials, under appropriate technologies, can yield all the necessary biocomponents for the normal functioning of the body, rehabilitation, and prevention of human diseases. The main task of the food industry is to create a healthy food industry, which is based on the use of the latest technologies. That would make it possible to preserve a valuable set of biologically active substances in finished products.

Therefore, it is a relevant task of research to devise technology for using walnut shells in the food industry.

2. Literature review and problem statement

Currently, the world scientific and industrial community is very intensively developing an innovative direction in the field of environmental protection – the use of industrial and agricultural waste. Of particular interest are waste from the recycling of agricultural raw materials, as well as components and waste from the processing of wood biomass of coniferous and hardwood trees.

Work [1] shows that for the technology of food production, natural food additives based on plant-derived raw materials are relevant, which enrich food with natural biologically active substances. In this regard, it is necessary to devise new useful types of natural biologically active substances in order to enrich food products for functional purposes.

Paper [2] reports the results of walnut research. It is shown that walnut is a unique plant raw material. All its parts, for

example, ripe and immature fruits, shells and partitions, green pericarp and leaves, bark, wood, roots can also be widely used in various industries, including food.

The green pericarp of the walnut contains hydro juglones and tannins. In the kernels of walnut fruits, fatty oils, protein substances, vitamins K and P, amino acids are identified. Therefore, the use of walnut for cooking is promising.

Work [3] reports the results of studying walnut shells. Walnut shells have been shown to be rich in phenolic acids and related polyphenols, which, as the cited study suggests, have numerous health effects. In this regard, it is necessary to use not only the walnut kernel but also the shell, which is rich in vitamins and minerals, while ensuring waste-free production.

In [4], it is noted that anticarcinogenic, anti-allergic, anti-inflammatory, antimicrobial, vasodilator, antimutagenic, and cardioprotective effects and other beneficial effects obtained from phenolic compounds indicate a high antioxidant activity inherent in the shell of a walnut. Therefore, it is so important that antioxidants enter the body every day and help the body strengthen its natural defenses.

According to work [5], phenolic compounds are used in the food industry as a food stabilizers. They are also now considered more powerful antioxidants than vitamin C, vitamin E, and carotenoids.

The phenolic compound juglone is present in all parts of the walnut and is known for its antimicrobial action. At the same time, phenolic compounds extracted from walnut shells have greater antioxidant capacity than in any other product. All this, as well as the dynamic growth of the food industry's need for natural antioxidants, make walnut shells very promising. They are agricultural waste and an ideal raw material for the extraction of phenolic compounds.

According to [6], more and more research efforts are now focused on recycling low-cost waste from the food, forestry, and agricultural industries due to environmental and economic benefits. As natural compounds, flavonoids have many biological properties, such as antioxidant, antibacterial, anti-inflammatory, and anti-cancer. In this context, the flavonoids contained in walnut shells, as natural antioxidants, are attracting the attention of an increasing number of people.

Therefore, when using the shell in food, the antioxidant activity and beneficial properties of food products increase.

Analysis of the data [7] reveals that the tendency of consumers to avoid products prepared together with preservatives of chemical origin with increased resistance to antibiotics is promoting interest in the use of natural antimicrobial compounds, especially extracted from plants.

Thus, walnut by-products can be used as sources of natural antioxidants and antimicrobial agents.

The use of walnut shells is common in the pharmaceutical and cosmetic industries, in the manufacture of fuel briquettes, some companies even add them to tires as a replacement for spikes. At home, the shell is used in the garden and vegetable plots, in creativity and decor, medicinal settings, and home scrubs are made of it. The useful properties of walnut shells have been investigated.

For the prevention of various diseases, it is necessary to create therapeutic and prophylactic products using natural food raw materials and biologically active additives of plant or animal origin. Micronutrients and biologically active substances should be added, first of all, to consumer products available to all groups of children and adults and regularly used in everyday nutrition. These include, first of all, dairy products, bakery products, and beverages. Therefore, it is justified to conduct a study on the possibility of using walnut shells in the production of a soft drink.

3. The aim and objectives of the study

The purpose of this study is to assess the composition of walnut shells from the point of view of the possibility of using them for the preparation of prophylactic products that meet the needs of the population for high-quality and safe products with a functional focus. This will make it possible to enrich food products with useful substances and provide waste-free technology.

To accomplish the aim, the following tasks have been set:

- to investigate the physical properties of walnut shells;

- to explore the chemical properties of walnut shells.

4. The study materials and methods

Walnut shells are used in our work.

The hypothesis of the current study assumed that the shell of the walnut is considered a waste and the recycling of the walnut solves the problems of rational use of all parts of the nut.

The mass fraction of fat was determined according to GOST 8756.21-89 "Products of processing fruits and vegetables. Methods for determining fat". The mass fraction of proteins was determined according to GOST 26889-86 "Food and taste products. General guidelines for the determination of nitrogen by the Kjeldahl method".

Ash content was determined according to GOST R 55960-2014 "Standard method for determining ash content". Vitamin A was determined by STB EN 12823-1-2014 "Food. Determination of vitamin A content by high-performance liquid chromatography. Part 1. Measurement of the amount of total trans-retinol and 13-cis-retinol". Vitamin E was determined according to GOST EN 12822-2014 "Food products. Determination of the content of vitamin E ($\dot{\alpha}$ -, β -, γ - and δ -tocopherols) by high-performance liquid chromatography". Vitamin C was determined according to GOST 34151-2017 "Food products. Determination of vitamin C by high-performance liquid chromatography" [8,9]. β -carotene was determined according to GOST EN 12823-2-2014 "Food products. Determination of vitamin A content by high-performance liquid chromatography. Part 2. Measurement of beta-carotene content". Zinc was determined according to GOST 26934-86 "Raw materials and food products. Method for determining zinc". Iron was determined according to GOST 26928-86 "Food products. Method for determining iron". Iodine was determined according to GOST 31660-2012 "Food products. Inversion-voltammetry method for determining the mass concentration of iodine". Amino acids were determined using high-performance liquid chromatography by the MVI method MN 1363-2000 [10, 11].

Bioflavonoids such as quercetin and catechin, tannins, in terms of tannin were determined according to P 4.1.1672-2003 "4.1. Methods of control. Chemical factors. Guidelines for quality control and safety of dietary supplements".

Tannins, in terms of tannin, were determined according to OFS.1.5.3.0008.15 "Determination of the content of tannins in medicinal plant raw materials and medicinal herbal preparations" in the following way:

- about 2 g (precise batch) of the crushed raw material, sifted through a sieve with holes of 3 mm in size, are placed in a conical flask with a capacity of 500 ml. Then we pour 250 ml of water

heated to a boil and boil with a reverse refrigerator on an electric stove with a closed spiral for 30 minutes with periodic stirring. The resulting extraction is cooled to room temperature. It is filtered through cotton wool into a measuring flask with a capacity of 250 ml so that the particles of raw materials do not fall into the flask, we bring the volume of the solution with water to the mark and mix. 25.0 ml of the resulting aqueous extraction are placed in a conical flask with a capacity of 1,000 ml, 500 ml of water, 25 ml of indigo sulfonic acid solution are added. Then we titrate at the constant stirring of potassium permanganate with a solution of 0.02 M until golden-yellow staining;

- in parallel, a control experiment is carried out: 525 ml of water, 25 ml of a solution of indigo sulfonic acid are placed in a conical flask with a capacity of 1,000 ml. Then we titrate at the constant stirring of potassium permanganate with a solution of 0.02 M until golden-yellow staining.

1 ml of potassium permanganate solution of 0.02 M corresponds to 0.004157 g of tannins in terms of tannin. The content of the sum of tannins in terms of tannin in absolutely dry raw materials in percentage (*X*) is calculated from the formula:

$$X = \frac{(V - V_1) \cdot 0.004157 \cdot 250 \cdot 100 \cdot 100}{a \cdot 25 \cdot (100 - W)}$$

where V is the volume of potassium permanganate of the solution of 0.02 M spent on titration of aqueous extraction, ml;

 V_1 is the volume of potassium permanganate solution of 0.02 M spent on titration in the control experiment, ml;

0.004157 is the amount of tannins corresponding to 1 ml of potassium permanganate solution of 0.02 M (in terms of tannin), g;

a is the batch of raw materials, g;

W is the moisture content of raw materials, %; 250 is the total volume of water extraction, ml;

25 is the volume of aqueous extraction taken for titration, ml.

Quercetin and catechin were determined as follows: 2 g of crushed walnut shells are placed in

a chemical beaker with a capacity of 250 cm^3 ; 50 cm^3 of a 0.1% solution of phosphoric acid are added. Next, the extraction is carried out in an ultrasonic bath for 5 minutes. The resulting solution is filtered through a paper filter "blue tape" into a measuring flask with a capacity of 250 cm^3 or, if necessary, centrifuged at 3,000 rpm for 5 minutes. Then the supernatant is placed in a measuring flask of 250 cm^3 , brought to a mark with a 0.1% solution of phosphoric acid, and stirred. The solution is analyzed using high-performance liquid chromatography.

5. Results of studying walnut shells

5. 1. Investigating the physical properties of walnut shell Biologically active components of walnut are represented

by vitamins, trace elements, amino acids, and bioflavonoids. The introduction of a food additive based on walnut shells into the formulation of food products will enrich them with biologically active substances.

For our research, samples of the three most common walnut varieties in the Republic of Kazakhstan were selected: "Ak-Terek peaked", "Uygur", and "Kazakhstan". In the laboratory of the Astana branch of the Kazakh Research Institute of Food and Processing Industry LLP (AB LLP KazRIFPI), the physical composition of the shell was determined (Table 1).

The data in Table 1 show that the mass of the nut ranges from 11.7 to 14.1 g, the thickness of the shell is 1.5-1.6 mm, the kernel yield is from 45.7 to 48.8 %.

Table 1

Physical properties of walnut shell

Variety	Shape	Mass, g	Shell thick- ness, mm	Kernel yield, %
Kazakhstan	large, round	12.9	1.6	47.4
Uygur	large, round	14.1	1.5	48.8
Ak-Terek peaked	round-ovoid shape	11.7	1.5	45.7

5.2. Investigating the chemical properties of walnut shell

To study the beneficial properties of walnut shells, chemical indicators were determined.

Fig. 1 shows the chemical composition of the walnut shell.



Fig. 1. Chemical composition of walnut shells

Fig. 1 shows that the fat content in the shell is very small, from 0.7 to 0.9 %. But there is sufficient protein content; on average, 2.4 %; the ash content is on average 1.7 %.

The results of studying walnut shells reveal the presence in the chemical composition of the walnut shell of β -carotene, vitamins C, E, minerals such as zinc, iron, iodine, as well as tannins, amino acids, and bioflavonoids. The level of vitamin content is shown in Fig. 2.

Fig. 2 demonstrates that no vitamin A was detected in the shell of all varieties of walnuts. The content of vitamin E ranges from 8.59 mg to 9.53 mg, the content of vitamin C in the studied samples is in the range of 9.31–15.0 mg, and the content of β -carotene is from 0.053 to 0.070 mg. The results of studying walnut shells reveal that the walnut shell contains a sufficient amount of the daily norm of vitamins for the human body, specifically: vitamin E, 4-19 mg; vitamin C, 10–120 mg; β -carotene, 5–10 mg [12].

Our study of the parameters of the chemical properties of walnut shells in terms of the content of mineral substances has shown the following:

- iodine content ranges from 5.52 µg to 14.81 µg;
- iron content from 3.33 mg to 7.39 mg;

- zinc content - from 3.1 mg to 6.9 mg (Fig. 3).



Fig. 2. The content of vitamins in a walnut shell, mg



	Ak-Terek peaked	Uygur	Kazakhstan
Iodine, μg	14.81	9.81	5.52
Iron, mg	3.33	4.59	7.39
■Zinc, mg	6.9	3.1	6.2

Fig. 3. The content of minerals in walnut shells

Our studies have also shown a fairly rich amino acid composition of walnut shells. In this case, the parameter of the

amino acid composition indicates a high level of the nutritional value of the shell. At the same time, one can see (Fig. 4) that the Ak-Terek peaked variety contains a greater amount of amino acids in its composition, 55.53 mg, than the Uyghur and Kazakhstan varieties (49.55 mg and 53.65 mg, respectively).

The flavonoid composition of walnut shells is characterized by the content of quercetin, catechin, and tannins, the so-called P-vitamins – antioxidants that are very useful for the heart, helping to protect the brain functions. They also support connective tissue and improve blood circulation, having an antibacterial (antimicrobial) effect.

Our study of the content of bioflavonoids in the shell of walnut has revealed that the content of quercetin in the shell of a walnut ranges from 0.945 mg to 1.51 mg, catechin – from 2.46 mg to 12.07 mg, tannins – from 611.32 mg to 805.62 mg (Fig. 5). All antioxidants protect the body from damage by harmful free radicals, toxins, which come from the environment and damage healthy cells, leading to inflammatory processes. Therefore, it is necessary to note the significant role of the flavonoid composition of the walnut shell as one of the components in determining the further direction of research.

The physicochemical properties of the shell of the walnut of the Uygur variety are inferior in all respects to the other two varieties, namely, in the quantitative content of nutrients.

As shown by the results of the physical-chemical study, the shell of the Kazakhstan variety has an advantage in terms of the content of vitamins and flavonoids, and specifically, the content of catechins(up to 12.07 mg). Given that polyphenols contribute to the binding of various toxic substances and their excretion from the body, they take an active part in the metabolism of complex proteins, affect the activity of enzymes, in particular the enzyme telomerase. They also protect the genetic apparatus of the cell from the damaging effects of ionizing radiation, inhibit the development of diseases such as Alzheimer's and Parkinson's disease. The use of shells of this variety as an additional dietary supplement in the main products is of promising importance for further research

The rich mineral and amino acid composition of the shell of the Ak-Terek peaked walnut variety, in particular the content of iodine and zinc, also makes it attractive and promising for further research. It is recommended to use a shell-based dietary supplement as a raw material in the production of additives with an active immuno-

stimulant that reduces the risk of cancer, as well as containing elements for the normal functioning of the whole organism.







Fig. 5. The content of bioflavonoids in the shell of a walnut: a – quercetin; b – catechin; c – tannins

6. Discussion of results of studying yeast-free bakery products

This paper describes the shell of walnuts, gives indicators of the main substances that make up the shell. Analysis of the physicochemical studies, given in Table 1 and shown in Fig. 1–5, reveals that the shell of the walnut is rich in biologically active substances. The content of fat, protein, and ash is in very small quantities. The biologically active substances of the nut shell are recommended to be isolated by extraction. Based on the results of the analysis, a conclusion was made about the prospects of using walnut shells as a source of biologically active substances.

As a result of this study, it is recommended to use walnut shells in the production of a soft drink. The resulting products could be used for therapeutic and prophylactic products. The devises technology would expand the range of products, diversify the daily human diet, enrich the body with valuable substances, which could help increase its resistance to diseases and adverse environmental factors.

In turn, preparing new functional products from walnut waste makes it possible not only to save the main raw materials but also to create a new or enhance the existing positive biological effect of nutrition. The development of technology would make it possible to obtain waste-free production.

The introduction of an additive from walnut waste into food formulations could significantly increase the nutritional value of the finished product. Since the walnut shell is used for the treatment and prevention of various diseases, products that are obtained using the developed technology could be used in the production of dietary supplements, the market of which is increasing annually. Also, such products enjoy an increased demand by the end-users.

A comprehensive study of the quality indicators of walnut shells has shown that they have good physicochemical properties, increased nutritional value, and meet the safety requirements that are specified in Table 1 and Fig. 1-5.

The introduction of an additive from walnut shells to the recipe of various foods, including a soft drink, helps enrich them with macro-and micronutrients and also corrects the amino acid and fatty acid composition of the product.

The devised products could be successfully used for the nutrition of various groups of the population (children, the elderly, athletes working in extreme conditions), as well as for therapeutic and prophylactic purposes.

In the context of the modern development of food technologies, the optimal solution to the problem of nutrient deficiency of the population's diet is to expand the range of functional products and increase the share of their production in the total mass of food produced. Products prepared using walnut shells are not medicines but can prevent the occurrence of many diseases.

Conclusions regarding the results obtained are limited to the considered varieties of walnuts, therefore, further development of the study in terms of expanding the varieties is required. The implementation of the results could significantly expand the production of new generation products with specified quality characteristics, preventive, therapeutic, gerontological, and other products for different groups of the population.

7. Conclusions

1. The physical properties of walnut waste of such varieties as "Kazakhstan", "Uygur", and "Ak-Terek peaked" were investigated. The shape, mass, thickness of the shell, and yield of the kernel were determined. The color of the shell should be smooth, without dark spots, which may indicate damage to the core inside. The color of the kernel clearly indicates the quality of the walnut. A rancid or sour smell is a very clear sign of a spoiled nut. But usually, the shell (if its integrity is not violated) does not allow odors to pass through, and, therefore, this criterion is more relevant to the assessment of already cleaned kernels. The results showed that the shape, mass, thickness of the shell, and the kernel yield correspond to GOST 16832-71 "Walnuts. Specifications".

2. The chemical properties of walnut waste have been studied, the content of fat, protein, ash, vitamins A, E, C, β-carotene, non-essential and essential amino acids, iodine, iron, zinc, quercetin, catechin, and tannins has been determined. The results of our study showed that the shell of the walnut is rich in biologically active substances and is recommended for use in the preparation of food products for functional purposes. These data show that rich in elemental composition and vitamins, the walnut shell is a natural multi nutrient and can saturate the body with the necessary macro-and microelements, as well as vitamins. Using the data on the elemental composition of the ash of the walnut shell, it is possible to judge the goodness of the material for further use in the production of food products, in particular sausages. Thus, our analysis of the elemental and vitamin composition reveals that the shells of walnuts and Siberian pine nuts contain specific macro-and microelements, as well as vitamin, composition, which is considered useful and necessary for maintaining the health of the human body.

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