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The potential of non-traditional walnut shells waste for the production of antioxidant reach extracts intended for the food industry

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ABSTRACT

Phenolic compounds extracted from walnut shells are potentially good natural sources of antioxidants for the food industry and have numerous health benefits. Walnuts have more antioxidant capacity than any other nut because the shell is primarily composed of lignin, a strong source of phenols. Studies demonstrated that lignin characterizes the shell strength level and is a source of antioxidants due to its chemical composition. In the current study, an extract obtained by extraction with a hydroalcoholic solvent of various concentrations from a walnut shell was investigated. The results of this study have proven that walnut shell extract contains the main sources of mineral elements and vitamins, which are of great importance. According to the biological value, this extract contains essential amino acids for the body. The high content of quercetin and catechin shows the antioxidant activity of the extract. In the present article, the authors disclose methods for obtaining an experimental batch of a prophylactic product based on walnut shells and give the product a technological characteristic. Consequently, a product was developed for prophylactic usage of 10 ml per 100 ml of water and must be taken 1-2 times a day for 21 days. The required product amount was calculated from the daily intake of vitamins, minerals, and flavonoids.

Keywords: walnut shell, vitamin, mineral, antioxidant, phenolic compound

INTRODUCTION

Currently, in the development of food production technology, natural food additives based on plant raw materials are of particular importance, enhancing the organoleptic characteristics of food products and enriching them with valuable biologically active components **[1]**, **[2]**. Nutrition optimization, as it is known, promotes the introduction of biologically active food supplements and specialized products enriched with biologically active substances into the diet. A special place among them is occupied by supplements enriched with components with high antioxidant activity. The usage of such additives is most relevant in conditions of a significant spread of cardiovascular and oncological diseases caused by the action of free radicals on the cells and tissues of the human body **[3]**. The characterization of polyphenol content and evaluation of the antioxidant activity of diverse plant materials have received much interest recently because frequent consumption of these foods is linked to a lower risk of certain diseases, such as cancer and cardiovascular disorders. They are also relevant for raising immunity **[4]**. The walnut is recognized as a rich source of various valuable chemicals because the kernel, fresh green fruit, husk, shell, peel, bark, leaves, and root have been extensively studied for use in the food, cosmetic, and pharmaceutical industries. In this regard, all parts of the walnut tree can be utilized as an excellent source of various compounds expressing antioxidant and antimicrobial potential, as well as an antihistamine, antiulcer, antiasthma, antidiabetic, immunomodulatory, hepatoprotective, central nervous system stimulant, anti-

inflammatory, wound healing, lipolytic, and many other properties that have positive effects on human health **[5]**. The walnut is classified as a strategic species for human nutrition, as the Food and Agriculture Organization (FAO) has included it in the group of priority plants **[6]**. Meanwhile, inedible parts, including leaves, shells, rinds, green shells, and bark, have been used in traditional medicine for treating various ailments. For instance, walnut leaf infusion is used in some countries for its antioxidant and antimicrobial properties. Moreover, green peel extract has been utilized for treating skin conditions and inflammation **[7]**. The population of those regions where it grows has been using its therapeutic and prophylactic properties for a long time (Moldova, the North Caucasus, Romania, Tibet, Greece, Japan, China, France, etc.). The composition of plant raw materials, extracts, and preparations based on walnut comprises essential oils, organic acids, alkaloids, glycosides, saponins, coumarins, carotenoids, water-soluble vitamins, phytoncides, phenolic compounds, tannins, microelements. Such natural unique complexes determine both the therapeutic and prophylactic effect and the possibility of using raw walnut materials as technological food additives since they have various flavouring, tannic, antioxidant, antimicrobial, and other properties. The chemical composition of all walnut parts is based on the variety, place, and environmental conditions of growth **[8]**. The industrialization of fruits leads to the formation of many plant residues. In this regard, 70% of walnut fruits are estimated to turn into residues, mainly peel, bagasse, green peel, peel, and leaves (Figure 1), containing many biologically active compounds valuable for their use and exploitation. These residues are usually thrown into landfills, incinerated, or used for composting. However, the most effective use of this waste would be a circular economy strategy that would reduce the environmental impact and, at the same time, stimulate the economic sector. In this sense, the agricultural remains of the walnut have been extensively researched in search of natural products. Evidence shows that all parts of the walnut tree can be utilized as a source of compounds with major antioxidant, antimicrobial, antidiabetic, immunomodulatory, hepatoprotective, and anti-inflammatory potential **[9]**.

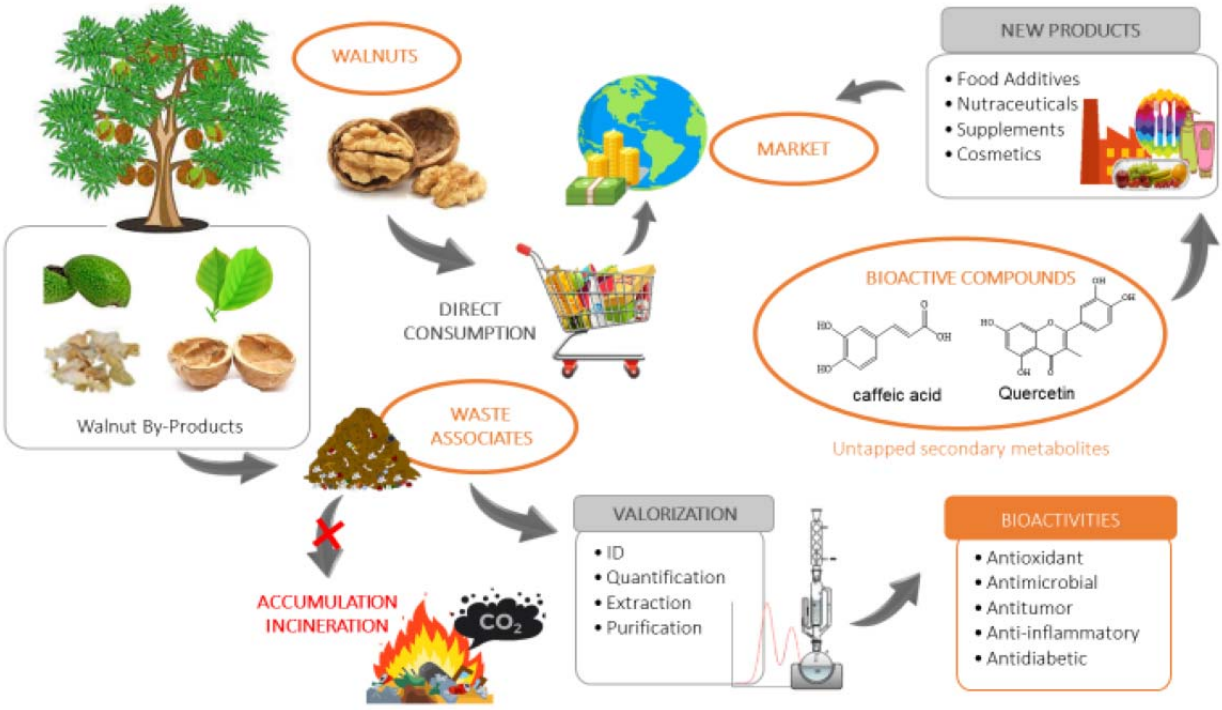

Figure 1 Evaporation of by-products from walnuts according to circular economy approaches and extraction of compounds with biological properties for bio-based products in various industries **[9]**.

The collection of fruits is conducted at a time when they are rich in biologically active healing substances. The most valuable is the walnut fruit, the core of which has not yet hardened and is in a gelatinous state, and the shell is still soft, juicy, and easily cut with a knife; that is, a strong shell has not formed. If such fruit is pierced, the blade easily passes through, and milky juice flows abundantly from the incision. In this state, the fruits of wax ripeness are a natural vitamin concentrate, and it is advisable to use them for processing during this period **[10]**. The walnut has more antioxidant capacity than any other nut because the shell is mainly composed of lignin, a strong source of phenol. Natural antioxidants such as phenolic compounds are gaining importance due to their positive effects on human health, such as reducing the risk of degenerative diseases by reducing oxidative stress and inhibiting macromolecular oxidation **[11]**. In Russia, walnut leaves are utilized only in traditional medicine, and when used in homeopathic practice, reference is made to the regulatory documents of foreign countries. In

order to standardize the quantity of tannins (measured in terms of gallic acid), flavonoids (measured in terms of hyperoside), and naphthoquinones (measured in terms of juglone), researchers have produced a homeopathic matrix tincture from dried and fresh walnut leaves **[12]**. Information about the study of the composition of the walnut leaves (*Juglans regia* L.) growing in the vicinity of the Caucasian Mineral Waters and the development of a dry extract based on it is given. It has been established that the dry extract from the leaves of this plant has antioxidant activity and is classified as a practically non-toxic substance **[13]**. The green peel of nuts includes pentacyclic triterpenes, sesquiterpenes, tetralones, naphthoquinones, phenolic acids, diarylheptanoid, neo-lignans, flavonoids, phenylethanoids, and tannin. The walnut pericarp is superior to rose hips in vitamin C content **[14]**. The walnut is recognized as a crop that produces more waste containing heavy materials. ~70% of the fruit weight is estimated to be made up of shells and husks, low-value waste products rich in different chemicals, mainly phenolic compounds **[15]**. As agricultural waste from walnut processing, walnut shells are available in large quantities. Walnut shells are also beneficial due to their availability as renewable resources. They are utilized as an abrasive for cleaning and polishing soft metals, stone, fibreglass, plastics, and wood. Walnut shell provides an effective way to grind and polish jewellery, gun cases, metal parts, and ink pens. In recent years, some studies have described the production of antioxidant and antimicrobial pyroacids from walnut shells **[16]**, **[17]**. The walnut shell contains antioxidant compounds, including flavonoids, isolated by extraction. Solvent extraction is often utilized for isolating plant antioxidant compounds. However, due to the chemical properties of the extracts and their solubility in a particular solvent, the yields of the extracts and their antioxidant activity vary greatly. Methanol **[18]**, ethanol **[19]**, chloroform **[20]**, water **[21]**, N-butanol **[22]**, and ethyl acetate **[23]** are often utilized for extracting antioxidant compounds from plant matrix.

Scientific hypothesis

Improving a functional product's quality depends on the walnut's quality, the mode, and the production technology. The quality and composition of the extract significantly affect the content of flavonoids and polyphenols (antioxidants).

MATERIAL AND METHODOLOGY

Samples

Walnut shells were taken for research. Walnuts collected in the fall of 2023 were provided for research by a farm (Turkestan region, Zhetysay, Kazakhstan).

Chemicals

All reagents were of analytical grade and were purchased from Laborfarm (Kazakhstan) and Sigma Aldrich (USA).

Instruments

Extraction was performed on a semi-automatic Soxhlet apparatus Vilitek "ASV-6" (Vilitek, Russia), while grinding was carried out on a laboratory mill "MShL-1P" (OJSC Promstroymash, Russia).

Laboratory Methods

The following methods and GOSTs were utilized to achieve the goals and objectives: GOST 32874-2014 “Walnuts. Specifications"; GOST 5962-2013. Ethyl alcohol is rectified from food raw materials. Specifications. GOST EN 12822-2014 Food products. Determination of vitamin E by high-performance liquid chromatography. MUK 4.1.1090-02 "Method for determining the mass concentration of iodine." GOST 26573-2014 "Method for the determination of iron". GOST 26573.2-2014 "Method for determination of zinc". MVI MN 1363-2000 "Method for determining amino acids using high-performance liquid chromatography". GOST R 57990-2017 "Method for determination of quercetin". GOST ISO 14502-2-2015 "Method for determining the content of catechins" **[24]**, **[25]**, **[26]**.

Total phenols were estimated using the Folin-Ciocalteu colourimetric method, and the results were expressed in milligrams of gallic acid equivalents (mg GAE/extract).

The antioxidant activity of nutshell extracts was determined by using the procedures detailed in a study by Sartori et al. The determination using 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH) was expressed as the amount of extract. Walnut shell extracts were added to 1.5 ml of DPPH solution (4.02 mg/100 ml in ethanol), and the mixture was kept in the dark for 30 minutes at room temperature. The absorbance at 517 nm was utilized for determining the concentration of the remaining DPPH through a UV-VIS spectrophotometer. The assay was performed three times, and the radical scavenging activity of DPPH was expressed as percent (%) inhibition using the following equation:

$$\text{DPPH scavenging effect \%} = \frac{AD-AS}{AD} * 100 \quad (1)$$

Where: AD is the absorption value at 517 nm of the control type DPPH and AS is the absorption value at 517 nm for the sample.

Description of the Experiment

Sample preparation: The walnut shell was washed and dried, then it was crushed in a Novital Magnum 4V crusher, then the crushed shell was crushed with steel balls in a MSHL-1P mill. The crushed shell was extracted on a semi-automatic Soxhlet extraction apparatus "ASV-6"

Grinding and Laboratory Mill "MShL-1P": Mill "MShL-1P" is a batch device equipped with steel balls. After preparing raw materials, wetting and drying, before feeding to the mill, the walnut shell is crushed using the crusher "Novital Magnum 4V." Then, the shell is crushed using steel balls on the mill "MShL-1P." When the drum rotates, the material is crushed due to the abrasive and impact action of the balls. Grinding time depends on the fineness of grinding and varies from 1 to 3 hours.

Extraction on a Semi-Automatic Soxhlet Extraction Apparatus "ASV-6": Samples are prepared for extraction to start the analysis. Sleeves are made from filter paper, where crushed walnut shells are placed in 5 g. 45 ml of a solvent (water, ethanol) is poured into the extraction flask and placed in a water bath, raising the appropriate glass refrigerator and the sample installed. After reaching the set temperature, the sample is transferred to the solvent, where the sample is processed for 30 min. After that, the sample is transferred to the position for washing with pure solvent. The process of washing with a pure solvent is the main extraction stage, which takes 60-180 minutes. After the extraction end, within 30 minutes, the solvent passes to the top of the refrigerator, and the extracted substance remains in the extraction flask. The extraction method is most often used to isolate antioxidant substances. In order to obtain a prophylactic product and identify antioxidant substances, a technology has been developed for obtaining an extract from walnut shells. To obtain an extract from the walnut shell, certain technological operations are utilized as follows: preparation of raw materials, washing of the sorted batch of the shell and drying it. Only after this is the main technological process of extraction carried out. The resulting extract is filtered, dried, and packaged. The flow diagram of the process is shown in Figure 2.

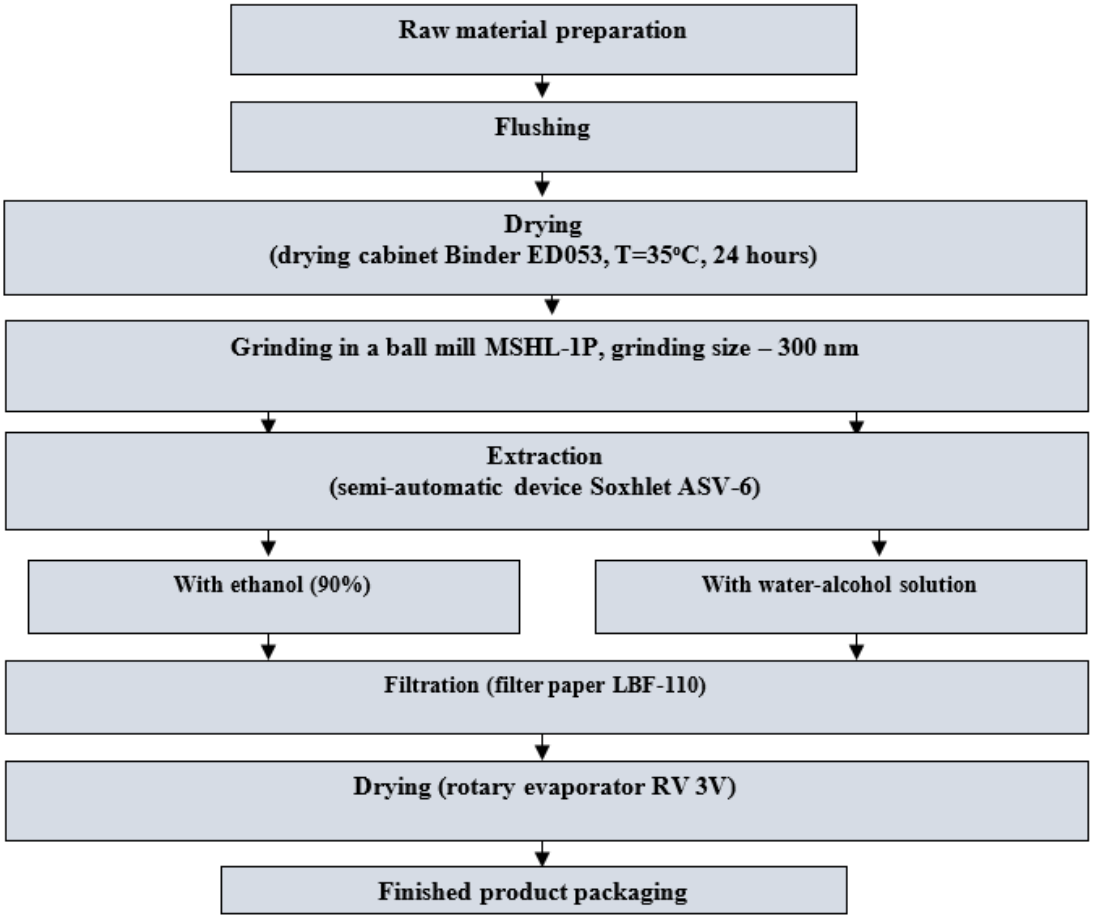

Figure 2 Scheme of the technological process for obtaining an extract from the walnut shell.

To determine the complete extraction of the antioxidant properties from the walnut shell, the walnut shell extraction was conducted in 3 different modes, as shown in Table 1.

Table 1 Modes for obtaining an extract from walnut waste.

Used raw materials	Mass of raw materials, g	Water, %	Ethanol, %	Size, microns	Extraction time, min
Chopped walnut shell	5	30	70	300	120
	5	20	80	300	120
	5	-	90	300	150

According to the relevant regimes, an experimental batch of walnut shell extract was obtained in 100 mg of each sample (Figure 3).

a b c

Figure 3 An experimental batch of walnut shell extract was obtained a) with an alcohol concentration of 70%; b) with an alcohol concentration of 80%; c) with an alcohol concentration of 90%.

Number of samples analyzed: Two samples were analyzed.
Number of repeated analyses: All tests were performed in triplicate.
Number of experiment replication: Replications were conducted 2 times.
Design of the experiment: First, sample preparation was carried out: by washing, drying, and grinding the walnut shell. Next, an extract was obtained using solvents (water, ethanol) on a semi-automatic Soxhlet apparatus ASV-6. Thirdly, the obtained extract was filtered and dried on a rotary evaporator. Next, the packaging of the resulting product was carried out.

Statistical Analysis

The data obtained during the experiments were processed using the mathematical method of variation statistics using the Statistica 10.0 developer: StatSoft, USA. Also, the data were analyzed using MS Excel for Windows version 10 Pro, 2010. One-way analysis of variance ANOVA was used to analyze the data and determine if there were significant differences between samples. The data collected during the study were subjected to independent testing. The analysis used absolute and relative statistical indicators and tabular and graphical methods to present the results. Values were estimated using mean and standard deviations.

RESULTS AND DISCUSSION

The antioxidant activity of the walnut extract was compared with that of three commonly used synthetic antioxidants, BHT, BHA, and TBHQ, as presented in Figure 4. Since DPPH is a stable organic nitrogen-free radical, its scavenging capacity has been widely utilized for evaluating the antioxidant capacity of the extracts from vegetable matter **[27]**, **[28]**, **[29]**, **[30]**.

The uptake activity was the same at lower concentrations of walnut shell extract. In the concentration range from 100 to 500 µg/ml, the absorbing activity of walnut shell extracts was higher than that of TBHQ, BHA, and BHT. These data proved that walnut shell extract could be utilized as a natural replacement for synthetic antioxidants, negatively affecting human health **[31]**, **[32]**, **[33]**.

Furthermore, in the samples of walnut shell extract, the flavonoid composition was investigated, comprising quercetin and catechin, antioxidants that are very useful for the heart, help protect brain functions, support connective tissue, enhance blood circulation, and have an antibacterial effect. Dietary intake of flavonoids ranges from 50 to 800 mg/day, depending on the consumption of food sources containing various flavonoids **[34]**, **[35]**.

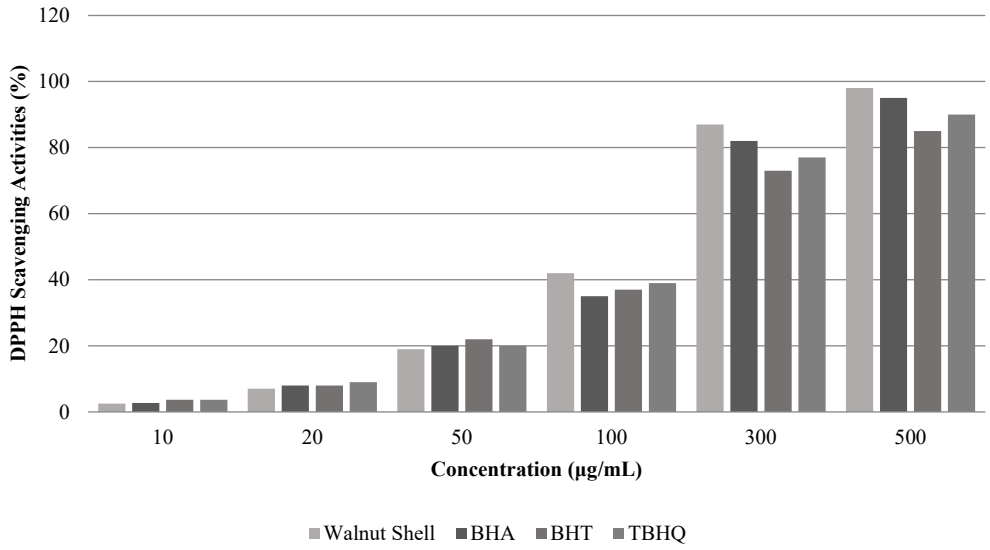

Figure 4 Comparison of antioxidant activities of walnut shell extract with BHA, BHT, and TBHQ by DPPH analysis.

The level of quercetin and catechin is displayed in Figure 5.

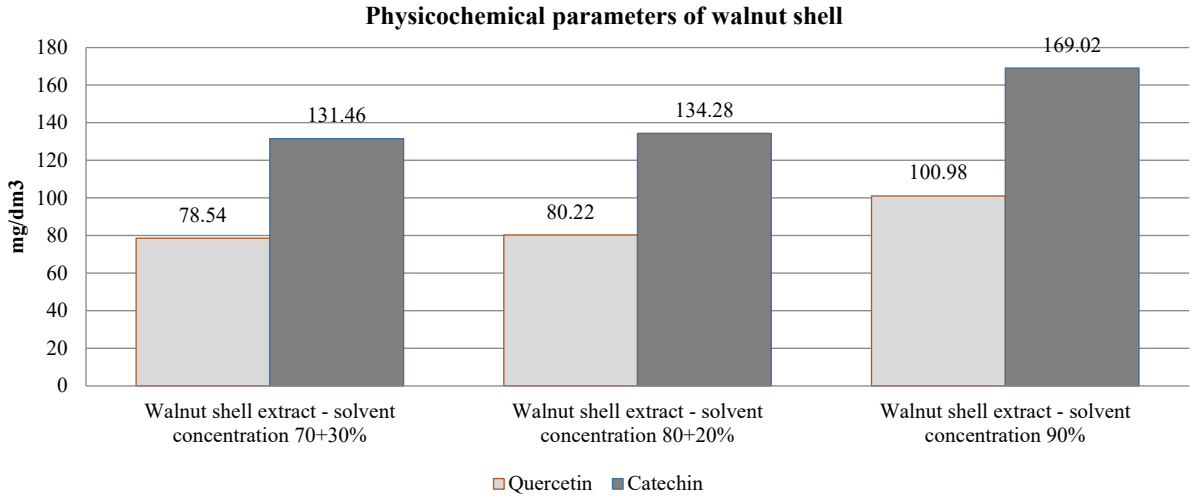

Figure 5 Content of catechin and quercetin in walnut shell extract, mg/dm^3.

As illustrated in Figure 5, as the solvent concentration increases, the quercetin and catechin content increases. The maximum value was in the extract obtained with 90% solvent. According to the maximum value, the catechin content is 169.92 mg/dm^{3,} and that of quercetin is 100.98 mg/dm^3. Given that all antioxidants protect the body from damage by harmful free radicals – toxins that enter from the environment and damage healthy cells, leading to inflammatory processes, it is worth noting the significant role of the flavonoid composition of the walnut shell as one of the components **[36]**, **[37]** in identifying the further direction of research.

The analysis in Figure 6 displays the content of vitamins in the extract obtained with various concentrations of solvent from the walnut shell.

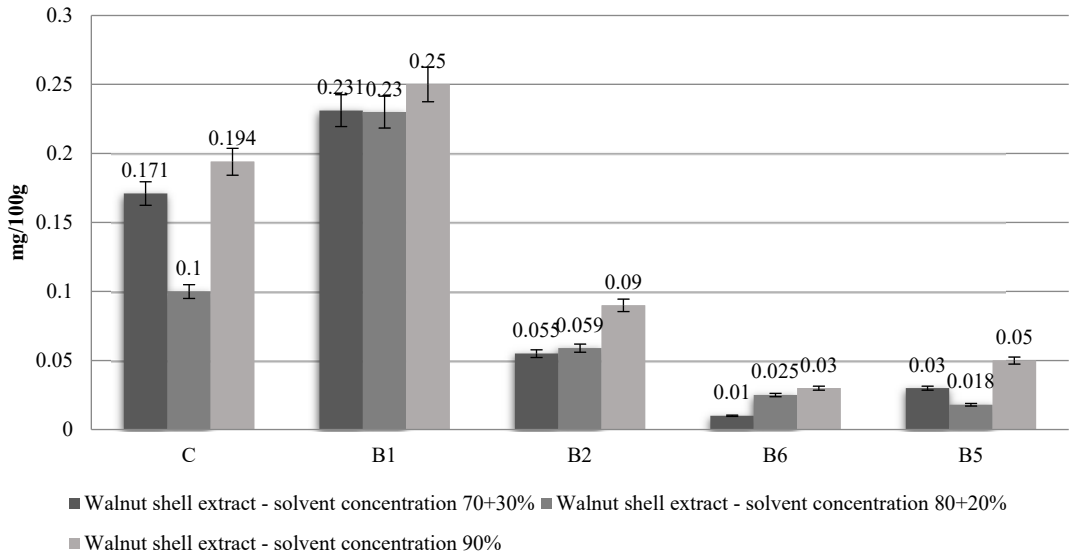

Figure 6 The vitamin content in the walnut shell extract (mg/100g).

Based on this analysis, the amount of vitamins increases as the solvent concentration increases. The content of vitamin C ranges from 0.1 mg/100g to 0.171 mg/100g. Vitamin B1 is stabilized within 0.25 ±0.05mg/100g. Vitamin B2 is found in the range of 0.05-0.09 mg/100g, B6 is 0.03 mg/100g, and B5 is 0.05 mg/100g.

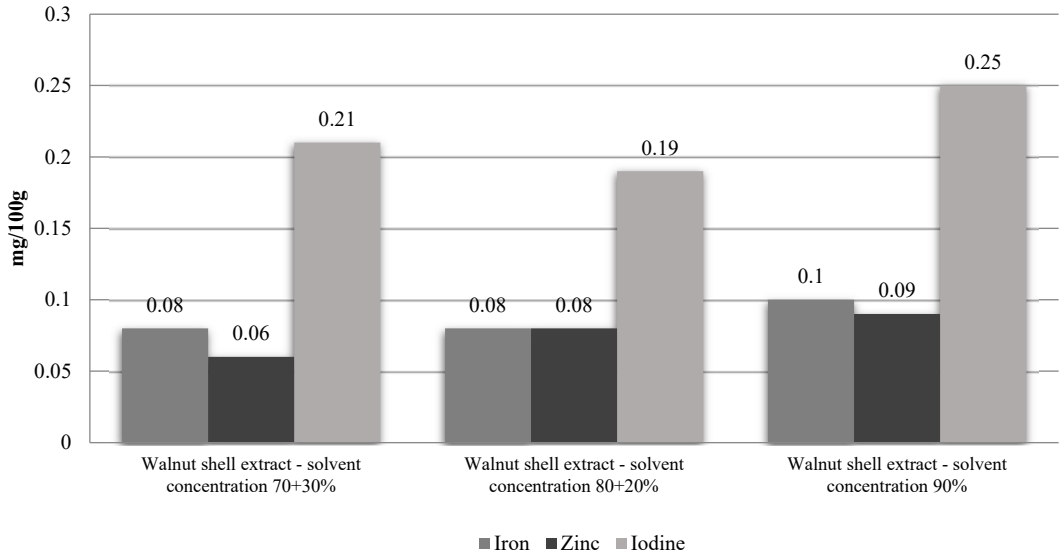

Figure 7 The content of mineral substances in the extract from the walnut shell.

The study of the parameters of the physicochemical properties of the extract obtained from the walnut shell (Figure 7) with various extractants indicated the following:

- iodine content up to 0.1-0.25 mg/100g;
- iron content up to 0.08-0.1 mg/100g;
- zinc content up to 0.06-0.09 mg/100g.

The study results proved that the most optimal extraction mode was the one in which the antioxidant properties were maximally extracted from the walnut shell, where the ethanol content was 90% and the extraction time was 120 minutes.

Studies have also demonstrated the walnut shell extract's rather rich amino acid composition (Figure 8). In this case, the amino acid composition parameter indicates a high level of the nutritional value of the extract **[38]**, **[39]**. One of the most important functions of amino acids is their participation in the synthesis of proteins that perform catalytic, regulatory, reserve, structural, transport, protective and other functions **[40]**, **[41]**, **[42]**.

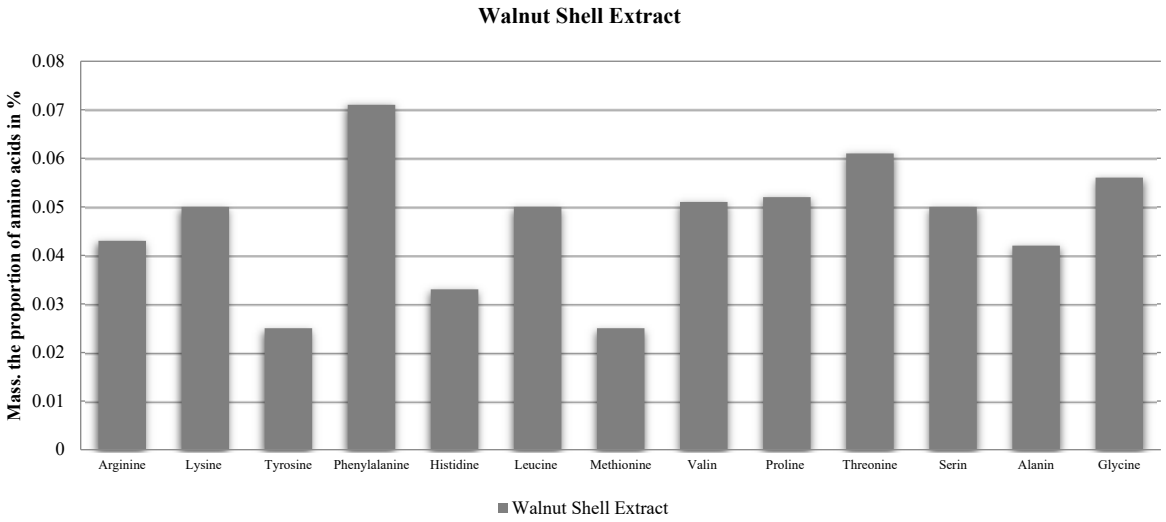

Figure 8 The content of amino acids in the walnut shell extract.

As can be noticed from the diagram, walnut shell extract shows a high proportion of amino acids, indicating their importance in food production. They are rich in essential amino acids not synthesized in the human body **[43]**, **[44]**, **[45]**. The proportion of fat-soluble and water-soluble antioxidants in the walnut shell extract was tested (Figure 9).

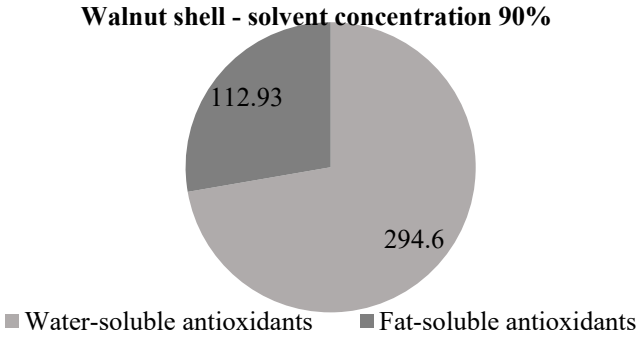

Figure 9 The content of water-soluble and fat-soluble antioxidants.

In terms of the proportion of fat-soluble and water-soluble antioxidants in the walnut shell extract, it was found that it contains 2 times more water-soluble antioxidants. Regarding the fat-soluble antioxidants, our extract contains a small amount of vitamin E.

The walnut shell extract contains vitamins C and E, minerals like iodine, iron, zinc, amino acids, flavonoids, catechin and quercetin **[46]**, **[47]**, **[48]**.

Table 2 presents the recipe for preparing a prophylactic product using walnut extract.

Table 2 Recipe for the preparation of a prophylactic product using walnut shell extract.

Compound	Weight, g
Active substances	
Walnut shell extract	77
Vitamin A	0.225
Iodine	0.005
Fructose (syrup)	20
Excipients	
Lemon acid	2.5
Preservative (sodium benzoate)	0.27
Total	100

The developed prophylactic product is a plant antioxidant whose components increase the body's immunity and defences, protect against the dangerous effects of environmental pollution, give strength, cleanse the body of cholesterol, and prolong youth. This is primarily due to its high content of flavonoids and polyphenols (antioxidants), which, when applied, immediately begin to actively neutralize free radicals, the number of which can be very large in the human body. Even at the initial application stage, the liver begins to be cleansed of toxins and poisons. In this case, the immune system is strongly affected, as if shaken up, allowing you to turn on the body's defences to the maximum.

In alternative medicine, it can be utilized to strengthen the immune system and treat various viral, allergic, and inflammatory diseases. The extract is essential for liver detoxification, strengthening blood vessels, atherosclerosis, and lowering cholesterol. It reduces the risk of developing malignant tumours and stops the reproduction of bacteria harmful to the body **[49]**, **[50]**.

Thus, the active use of the developed complex contributes to the following:

- prevention and replenishment of deficiency of vitamins and macro- and microelements;
- increased immunity and body defences;
- stimulation of the body's resistance to harmful environmental influences and infections;
- reduction of the fragility of capillaries;
- stimulation of the regenerating activity of the body **[51]**, **[52]**.

Organoleptic properties and tasting tests were evaluated following a 6-point system. They demonstrated that the resulting product has a balanced mild taste, a pleasant aroma characteristic of raw materials, and astringency. The bright brown colour is due to the content of catechins and quercetin in the raw material (Figure 10).

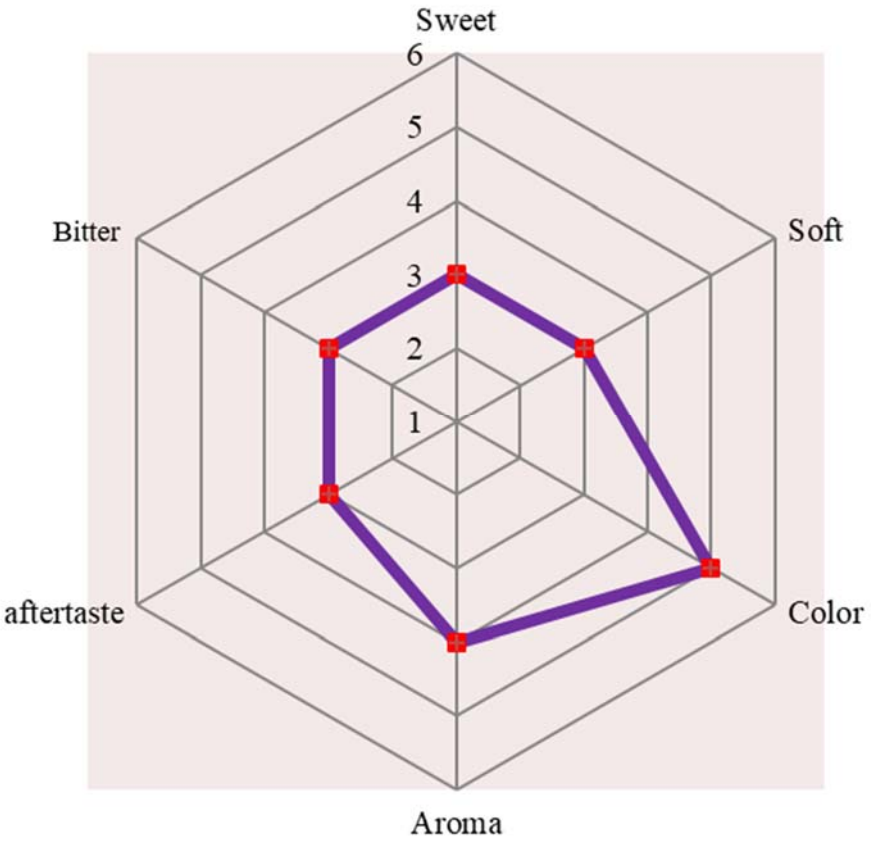

Figure 10 Profilogram of organoleptic and tasting properties of the product.

It is recommended to take the developed product for prophylactic purposes orally in the following amount: 10 ml of the product per 100 ml of water, 1-2 times a day for 21 days. The required product amount was calculated from the daily intake of vitamins, minerals, and flavonoids.

CONCLUSION

As a result of the work, an extract was obtained by extraction with a water-alcohol solvent of various concentrations from a walnut shell. The synthetic antioxidants at concentrations ranging from 100 to 500 μg/ml. Specifically, at a concentration of 100 μg/ml, the walnut shell extract exhibited an antioxidant activity of 75.3%, while the synthetic antioxidants had an activity of 58.2%. At a concentration of 500 μg/ml, the walnut shell extract had an antioxidant activity of 90.1%, while the synthetic antioxidants had an activity of 72.5%. Walnut shell extract has been proven to contain major sources of minerals, vitamins, essential amino acids, quercetin and catechins beneficial to the human body. The resulting product for prophylactic use in the ratio: 10 ml per 100 ml of water and must be taken 1-2 times a day for 21 days. The developed prophylactic product is a plant antioxidant whose components increase the body's immunity and defences, protect against the dangerous effects of environmental pollution, give strength, cleanse the body of cholesterol, and prolong youth. The obtained results demonstrated the potential of walnut shell extract as an economical source of antioxidant agents for the food industry.

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