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A PROSPECTIVE METHOD TO USE WASTE OF WALNUTS

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Abstract

One of the ways to solve ecological problems is rational use of natural resources and their complex processing. Involving the plant waste as a secondary raw material allows it to be converted into a valuable product with subsequent widespread use. The given scientific work is devoted to the way of processing of organic waste of a walnut, namely pericarp. The results of studies of ripe nuts pericarp in terms of harvesting are presented. It has been proven that pericarp has the highest content of biologically active substances (L-antiscorbutin, pectin substances, polyphenols), when it is not yet separated from its maternal base. It has been proven that pericarp is a biologically valuable raw material that is not used in food production. The method of its processing into an extract has been developed and analyzed. The dynamics of extraction of extractive substances of pericarp depending on the type of extractant are presented. Therefore, 70 % aqueous-alcoholic and 50 % aqueous-sugar solutions for both fresh raw material and after storage at low temperatures were selected as extractants for biologically valuable substances with high extractive ability and microbiological stability. The technology of aqueous-alcoholic and aqueous-sugar extracts and its description are presented. It has been proven that the developed technology will minimize organic waste, maximize the use of the nut raw materials, improve food technology, while increasing their biological value.

Keywords: organic waste; recyclables; walnuts; pericarp; technology; extract.

ПЕРСПЕКТИВНИЙ СПОСІБ ВИКОРИСТАННЯ ВІДХОДІВ ВОЛОСЬКОГО ГОРІХА

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Анотація

Одним із шляхів до вирішення екологічних проблем є раціональне використання природних ресурсів та їх комплексне перероблення. Залучення рослинних відходів як вторинної сировини дозволяє перетворювати їх у цінний продукт з наступним широким використанням. Дана наукова робота присвячена способу перероблення органічних відходів волоського горіха, а саме перикарпію. Наведено результати досліджень перикарпію стиглого горіха за термінами збирання. Доведено, що перикарпій має найбільший вміст біологічно-активних речовин (L-аскорбінова кислота, пектинові речовини, феноли) тоді, коли він ще не відділений від материнської основи. Доведено, що перикарпій є біологічно цінною сировиною, яка не використовується в харчовому виробництві. Розроблено та проаналізовано спосіб його перероблення у екстракт. Наведено динаміку вилучення екстрактивних речовин перикарпію залежно від типу екстрагента. Отже, в якості екстрагентів для біологічно-цінних речовин горіха, які мають високу екстрагуючу здатність і мікробіологічну стабільність, обрано 70 %-вий водно-спиртовий і 50 %-вий водно-цукровий розчини для сировини як свіжої, так і після зберігання за низьких температур. Представлено технологію екстракту на водно-спиртовій і водно-цукровій основах та її опис. Доведено, що розроблена технологія дозволить мінімізувати органічні відходи, максимально використати горіхову сировину, вдосконалити технології харчових продуктів, підвищуючи їх біологічну цінність.

Ключові слова: органічні відходи; вторинна сировина; волоський горіх; перикарпій; технологія; екстракт.

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ПЕРСПЕКТИВНЫЙ СПОСОБ ИСПОЛЬЗОВАНИЯ ОТХОДОВ ГРЕЦКОГО ОРЕХА

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Аннотация

Одним из путей решения экологических проблем является рациональное использование природных ресурсов и их комплексная переработка. Привлечение растительных отходов в качестве вторичного сырья позволяет превращать их в ценный продукт с последующим широким использованием. Данная научная работа посвящена вопросам использования органических отходов грецкого ореха, а именно перикарпия. Приведены результаты исследований перикарпия спелого ореха по срокам уборки. Доказано, что перикарпий имеет наибольшее содержание биологически-активных веществ (L-аскорбиновая кислота, пектиновые вещества, фенолы) тогда, когда он еще не отделен от материнской основы. Доказано, что перикарпий является биологически ценным сырьем, которое не используется в пищевом производстве. Разработан и проанализирован способ его переработки в экстракт. Приведена динамика извлечения экстрактивных веществ перикарпия в зависимости от типа экстрагента. В качестве экстрагентов для биологически-ценных веществ ореха, которые обладают высокой екстрагирующей способностью и микробиологической стабильностью, избран 70 %-й водно-спиртовой и 50 %-й водно-сахарный растворы для сырья как свежего, так и после хранения при низких температурах. Представлена технология экстракта на водно-спиртовой и водно-сахарной основах и ее описание. Доказано, что разработанная технология позволит минимизировать органические отходы, максимально использовать ореховое сырье, усовершенствовать технологии пищевых продуктов, повышая их биологическую ценность.

Ключевые слова: органические отходы; вторичное сырье; грецкий орех; перикарпий; технология; экстракт.

Introduction

Complex utilization of waste of food industry at all stages of the food chain from production to consumption is a progressive direction of ensuring resource conservation in the national economy. The market transformations that have taken place in the agricultural sector of Ukraine have contributed to the introduction into the process of manufacturing of the major achievements of scientific and technological progress and world experience on waste reuse [1].

The scientific and practical results of the research on the complex use of food industry waste allow to obtain significant savings of material and energy resources, provide an increase in the level of closed production and resource cycles in the industry, which contributes to the increase of economic efficiency of production, increase of its volumes and assortment. At the same time, the process of environmental pollution with production waste is minimized [2; 3].

The problem of rational use of raw materials is multifaceted and largely due to the specifics of the processing industry [4–6]. The use of agricultural and growing wild raw materials in the technological processes of the food industry does not reach 100 %. In most cases, in the manufacturing process of the main products raw materials are used by only 15–30 %. Virtually all waste is a secondary raw material that contains valuable substances – vitamins, minerals, phenolic and pectin compounds, etc. [7].

The introduction of eco-innovation in food industry is a priority, since its implementation depends on the competitiveness of domestic food products in the world and national food markets. Eco-innovations from food waste are new or improved technologies and new foods derived from them, which significantly improve the structure and quality of food and do not harm the environment and have a positive effect on the health of consumers [8]. Therefore, the development and implementation of an organizational and economic mechanism for the use of food waste will help to: their minimization, integrated use of raw materials and the creation of biologically valuable food products.

Walnut production in Ukraine is now a profitable type of business activity at the farm level, which in recent years has become a systematic type of business nationwide [9; 10]. Walnut is a unique plant, all parts of which have high biological value. Since ancient times, the leaves, amniotic fluid, green and ripe nuts have been used as medicinal raw materials. All parts of the plant contain a large number of biologically active substances (BAS): bark – triterpenoids, steroids, alkaloids, vitamin C, tannins, quinones (yuglons, etc.); leaves – aldehydes, essential oils, alkaloids, vitamins C, PP, carotene, phenolcarboxylic acids, tannins, coumarins, flavonoids, anthocyanins, quinones and high aromatic hydrocarbons; amniotic fluid – organic acids, vitamin C, carotene, phenolcarboxylic acids, tannins, coumarins and quinones [11].

Leaves, green fruits and the pericarp differ in the record, compared to other plants, concentration of vitamin C, P-active polyphenols and iodine. However, leaves and green fruits are widely used in folk medicine and pharmacology, green fruits are used in the food industry for the production of jam, tinctures, and pericarp of ripe nuts is considered a waste due to the lack of substantiation of its technological characteristics.

It is well known that pericarp of walnut is a valuable raw material containing: organic acids – malic, citric; vitamins – C, B_1, P and carotene; phenolcarboxylic acids – gallic; tannins – derivatives of pyrocatechin and pyrogalol; coumarins – ellagic acid; quinones – yuglon, α-hydroglone, β-hydroglone, 5-glucoside hydroglone [12–14].

The unique chemical composition and the presence of biologically active substances in it explains its wide use for medicinal purposes. Pericarp has antioxidant, antibacterial, antiparasitic and antitumor properties [13]. However, despite its widespread use in pharmacy and light industry, the nutritional properties of walnuts have not been sufficiently studied compared to Manchurian walnuts [15; 16]. Therefore, the search for optimal ways to use the chemically valuable pericarp of ripe walnut in food production is an urgent task.

Materials and methods

The fruits of the walnut of the variety "Ideal", which is widely spread in central Ukraine, were used for the research. Waste of a ripe walnut, namely, pericarp, and extracts based on it were used as research materials.

During the studies standardized methods were used. In raw materials, semi-finished products, extracts the key physical and chemical properties were defined.

Sampling and preparation of samples were carried out according to DSTU 7661:2014 [17]. In determining the parameters, the following documents were used:

- content of dry substances in the raw material - DSTU 7804:2015 [18];
- mass fraction of soluble solids - refractometric method of DSTU ISO 7661:2014 [19];
- active acidity (pH) - potentiometric method of DSTU EN 1132:2005 [20];
- mass fraction of titrated acids (in terms of malic acid) - volumetric titration method of DSTU 4957:2008 [21];
- the total content of phenolic compounds - by Folin-Chokalteu in terms of gallic acid per DSTU 3845-99 [22];
- vitamin C content – by iodometric method according to DSTU ISO 6557-1:2015 [23];
- content of pectin – titrimetric method according to DSTU 8069:2015 [24].

All determinations were carried out in two or three replications and for getting the final result arithmetic average was calculated. To obtain comparative data, analyses were carried out in all the same conditions.

Results and discussion

The formed ripe fruits of a walnut collected in August (technical stage) and October (consumer stage) were investigated. The ratio of the anatomical parts of the nut fruit to the stage of its ripeness has been experimentally established (Fig. 1).

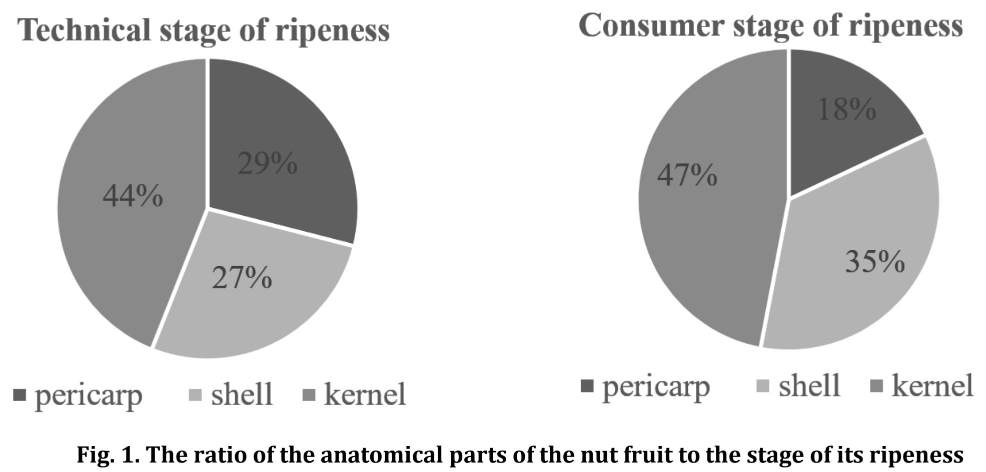

Fig. 1. The ratio of the anatomical parts of the nut fruit to the stage of its ripeness

It has been determined that at the technical and consumer stages of ripeness the share of pericarp is 29 and 18 %, respectively (Fig. 1). The shell and kernel of the nut at the technical stage of ripeness is 71 %, in the consumer – 82 %. Pericarp according to the stage of ripeness differed in consistency and color: at a technical it was juicy, hard, deep green, at a consumer stage it was dry, softer, green with dark spots.

One of the methods of extracting and preserving BAS of pericarp is to get extracts, which are convenient for enriching foods. For processing of pericarp into extracts the rational time of its preparation was investigated in Poltava region [25]. Pericarp harvesting was performed at the first signs of ripening of the nuts – a slight cracking of its surface, and continued until the nuts from the tree without pericarp fell. The harvesting period was from September 13 to October 3. Raw material research was conducted every four days and discontinued due to changing weather conditions. After a downpour (rain), the pericarp massively cracked, separated from the fruit and fell to the ground, which led to its massive decay and the impossibility of using it as prototypes.

In the samples suitable for testing, the main physicochemical parameters were determined according to generally accepted standardized methods (table 1).

Table 1

Physical and chemical indicators of pericarp of walnut

Sample number	Mass content, %				Content by weight, mg/100 g	
	dry substances	titrated acids	pectin substances	monosaccharides and disaccharides	polyphenols	L-antiscorbutic
1	7.1±0.2	0.2±0.01	0.4±0.01	1.75±0.05	4 500±150	249.2±4.0
2	8,0±0.2	0.3±0.01	–	1.23±0.05	4 275±150	242.5±4.0
3	8.0±0.2	0.5±0.01	0.5±0.01	0.85±0.05	4 200±150	204.2±4.0
4	11.0±0.2	0.4±0.01	–	0.82±0.05	4 114±150	197.1±4.0
5	11.1±0.2	0.4±0.01	0.8±0.01	0.37±0.05	3 073±150	112.6±4.0
6	11.6±0.2	0.4±0.01	–	0.25±0.05	2 649±150	91.52±4.0

It has been confirmed that pericarp has biologically valuable components: sugars, pectic substances, organic acids, vitamin C, phenolic substances (Table 1). The analysis of samples by the timing of raw material collection showed a sharp decrease in the sugar content (4.7 times), which indicates active metabolic processes in this raw material, even separated from the fruit and the maternal plant. The increase in solids content is explained solely by the evaporation of water from pericarp. It exfoliates from the wooden surface of the fruit. Pericarp dries up, especially when separated from the nut.

Fig. 2–3 presents changes in the concentration of ascorbic acid and polyphenols in pericarp, depending on the harvest period (13 September – 3 October) and the condition of the pericarp.

It has been proven that the content of vitamin C in pericarp decreases as the nut ripens, especially after its separation from the maternal base – almost 2.2 times. It is possible that the cracking of the fruit leads to the release of ascorbatoxidase, which in tandem with chlorophyll accelerates the oxidation of the vitamin [26]. But it should be noted that the final content of vitamin C is greater than its presence in most fruits and berries, including citrus (70–90 mg / 100 g) (Fig. 2) [27].

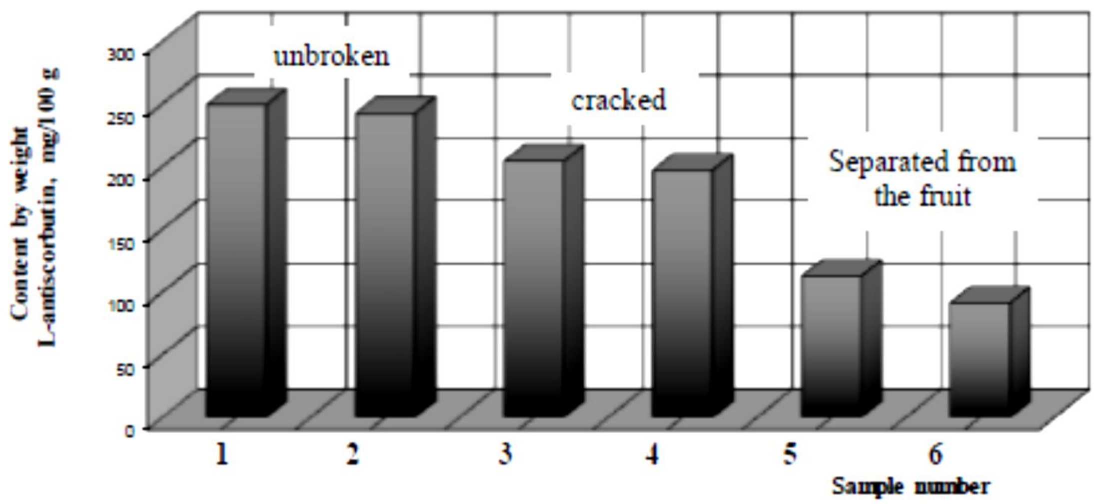

Fig. 2. Vitamin C concentration in pericarp of walnut since harvest time (mid-September to early October)

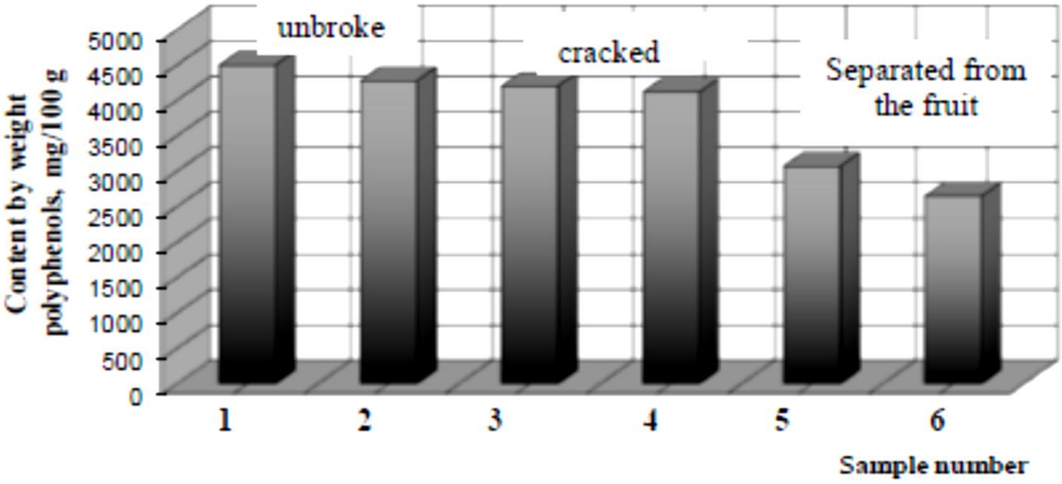

Fig. 3. Concentration of polyphenolic substances in pericarp of walnut since harvest time (mid-September to early October)

The presence of a significant content of polyphenols in pericarp after nuts fall was determined (Fig. 3). It is probable that the decay of polyphenolic substances occurred under the action of oxygen due to the action of polyphenoloxidase [28].

Thus, it has been proven that pericarp of ripe walnut has the highest content of BAS when it is not yet separated from its maternal base – September. The timing of pericarp harvesting depends on the natural climatic conditions. The longer the warm weather with slight precipitation persists, the longer is pericarp harvesting period. Nuts ripen not at the same time, so they can be harvested in several stages, or you can wait for the pericarp to crack in the vast majority of nuts.

Each type of plant raw material, which is characterized by rational parameters, regimes, conditions of extraction of biologically valuable substances have been established experimentally [29]. The target substances for extraction have been flavonoids and ascorbic acid, which are rich in walnut. Belonging of the selected target substances to hydrophilic compounds explains their high extractability with water, but short-term preservation of extracts. The effect of the concentration of aqueous-alcoholic mixture on the extraction of BAS from fresh pericarp has been studied [11]. The dependence of BAS extraction on the hydromodule and the duration of extraction for L-ascorbic acid and phenolic substances has been established [11]. The optimal technological parameters and modes of preparation of dietary supplements from walnut pericarp have been determined: hydromodule – 1: 1 for 70 % aqueous-alcoholic solution and 0.75 : 1 for 50 % aqueous-sugar solution; the particle size of the raw material is 10…25 mm, the extraction time is 20 days; re-extraction of the nut residue with 50 % aqueous-alcoholic solution – 7–10 days at ambient temperature of 18 ... 20 °C [30; 31].

To prolong the period of use of pericarp, it was stored at low temperatures. Raw materials collected at the end of September were frozen at a temperature of minus 18 °C and stored in a freezer for 6 months. Of course, the process of freezing and thawing of plant raw materials leads to mechanical damage to cells. It was assumed that this factor will improve the quality of extraction of valuable substances. As extractants for the removal of hydrophilic BAS we used water, 70 % aqueous-alcoholic solution (AAS) and 50 % aqueous-sugar solution (ASS), which were selected rationally according to previous studies [30; 31]. The raw material was thawed at room temperature 18…20 ° C. Adding of the components was performed in a ratio of 1 : 10 (pericarp:extractant).

It has been established that the degree of extraction of biologically valuable substances of pericarp is significantly dependent on the type of extractants. The dynamics of extraction of extractives depending on the type of extractant is shown in Fig. 4–5.

It was determined that extracts reached the maximum concentration of BAR during the fourth day, after which their gradual decrease was observed (Fig. 4–5).

It has been noted that the concentration of ascorbic acid in aqueous extract on the 10th day decreased by 10.3 % in comparison with the highest indicator, which proves its high extracting ability (Fig. 4).

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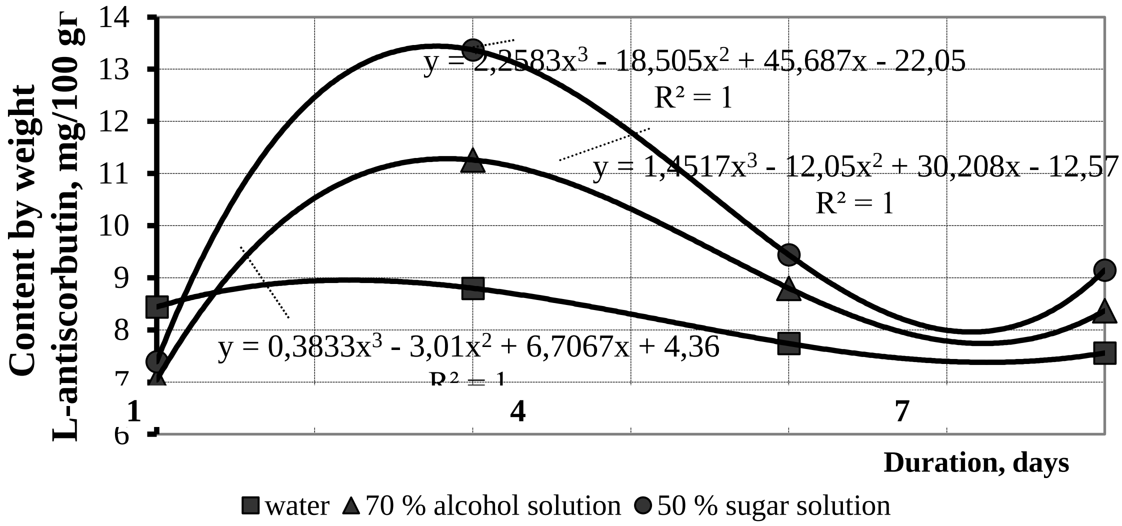


Fig. 4. Dynamics of extraction of ascorbic acid from the duration of extraction

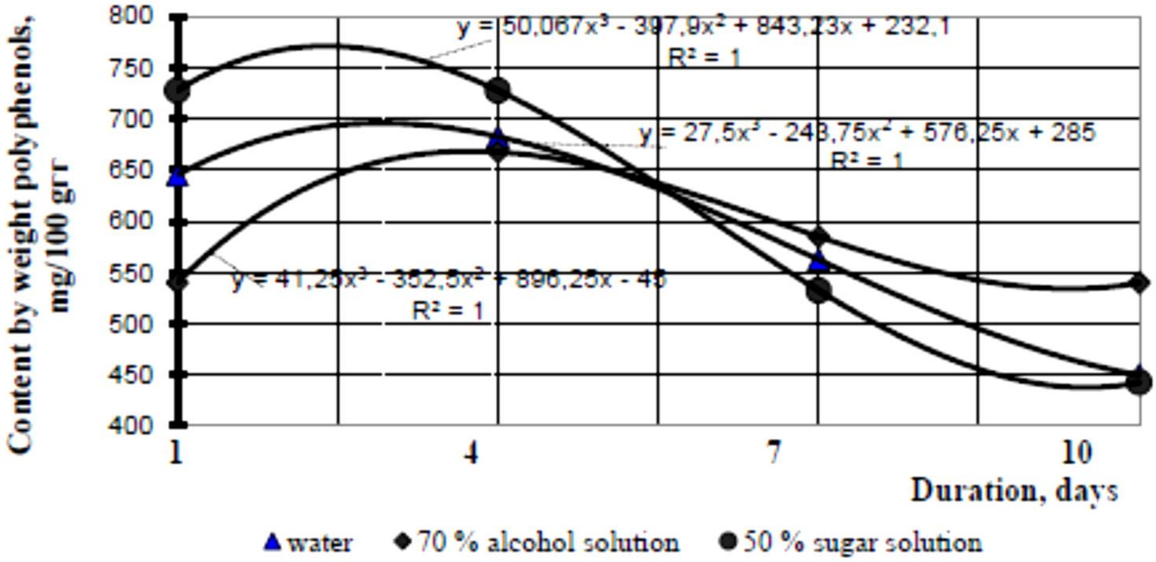
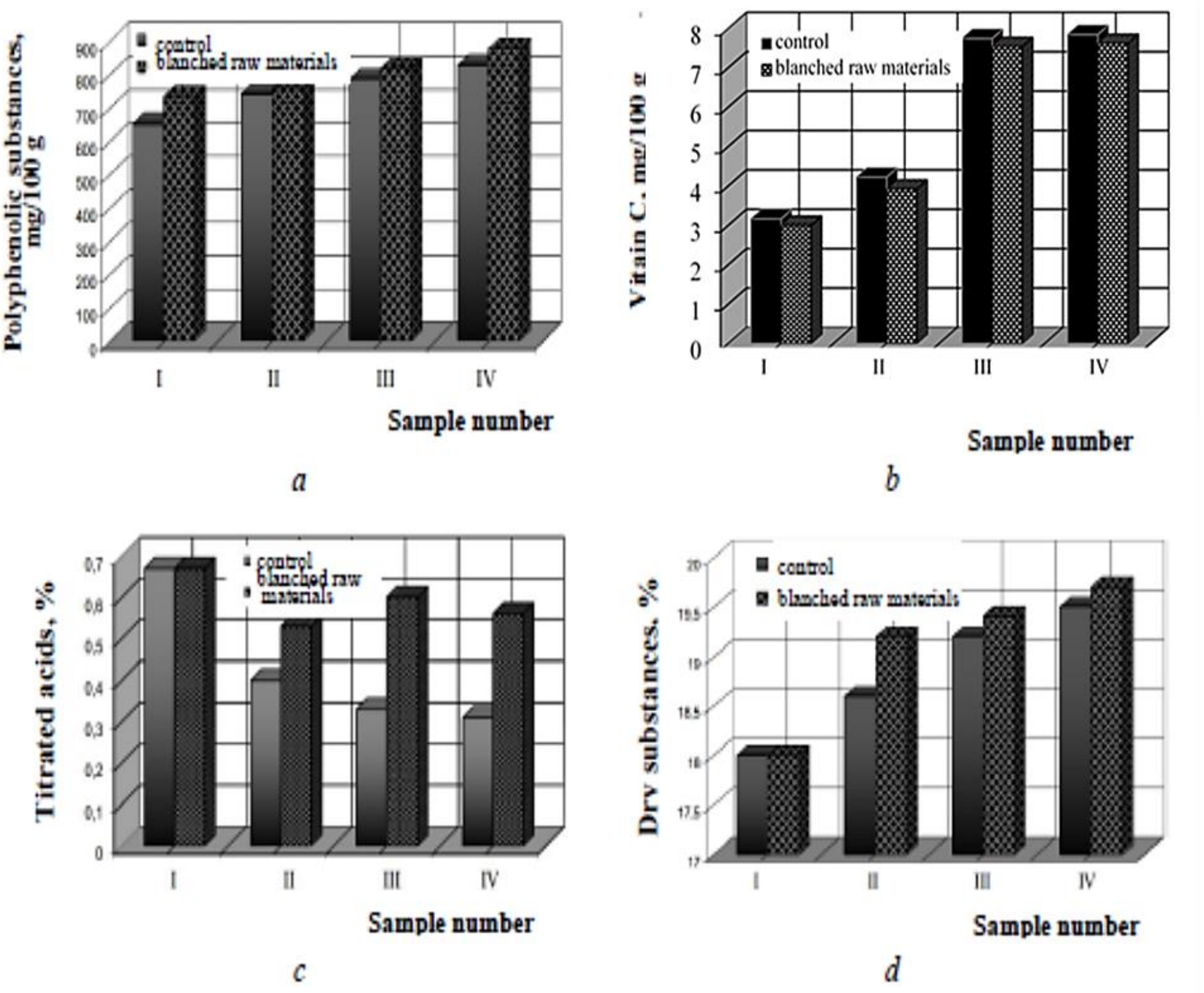


Fig. 5. Dynamics of extraction of phenolic substances from the duration of extraction

We can assume that degradation of ascorbic acid and polyphenols occurs under the action of oxygen due to the action of the enzymes – ascorbatoxidase and polyphenoloxidase, which are released from the destroyed pericarp cells. Therefore, 70 % AAS and 50 % ASS were selected as extractants for BAS of the nut, which have high extractive capacity and microbiological stability.

The influence of the heat pre-treatment of pericarp on the extraction process has been determined. Extracts from blanched pericarp of ripe nuts contained a higher concentration of phenolic substances by 5–15 %, soluble solids by 2–3 %, and titrated acids by 35–85 %, ascorbic acid decreased by 3–5 % (Fig. 6). In pericarp, the insoluble protopectin fraction, which strengthens the cell surfaces, prevails. This factor explains the need for temperature treatment of pericarp to hydrolyze pectic insoluble substances. Therefore, heat treatment for the pericarp at t = 80 °C, τ = 600 s has been selected.



Note: I–IV – Harvesting dates – mid-September – early October

Fig. 6. Influence of heat treatment of pericarp on the content of biologically valuable substances in the extracts: a - phenolic substances, b - L-ascorbic acid, c - titrated acids, d - soluble solids

On the basis of the conducted research, the technological scheme of production of walnut pericarp extracts has been developed (Fig. 7).

The received raw materials are washed with clean running water, and the rotting places are cut out. Pericarp is monitored by the main indicators, after which the fruits are cut by machines for cutting fruits and vegetables with a particle size of 10–25 mm. Prepared raw materials are blanched with hot steam at 80 °C for 600 s.

Extraction conditions: 70 % AAS or 50 % ASS in a ratio (raw material: extractant) of 1: 1 and 1: 0.75, respectively, in a container of non-corrosive material with stirrer, without access of light and air at ambient temperature 18… 20 °C, duration – up to 5 days.

The resulting extract was decanted from the precipitate and filtered through a tissue filter. The extracts are collected in special tanks of non-corrosive material, and then packed in a glass container made of dark glass, sealed and sent for storage in a dark place.

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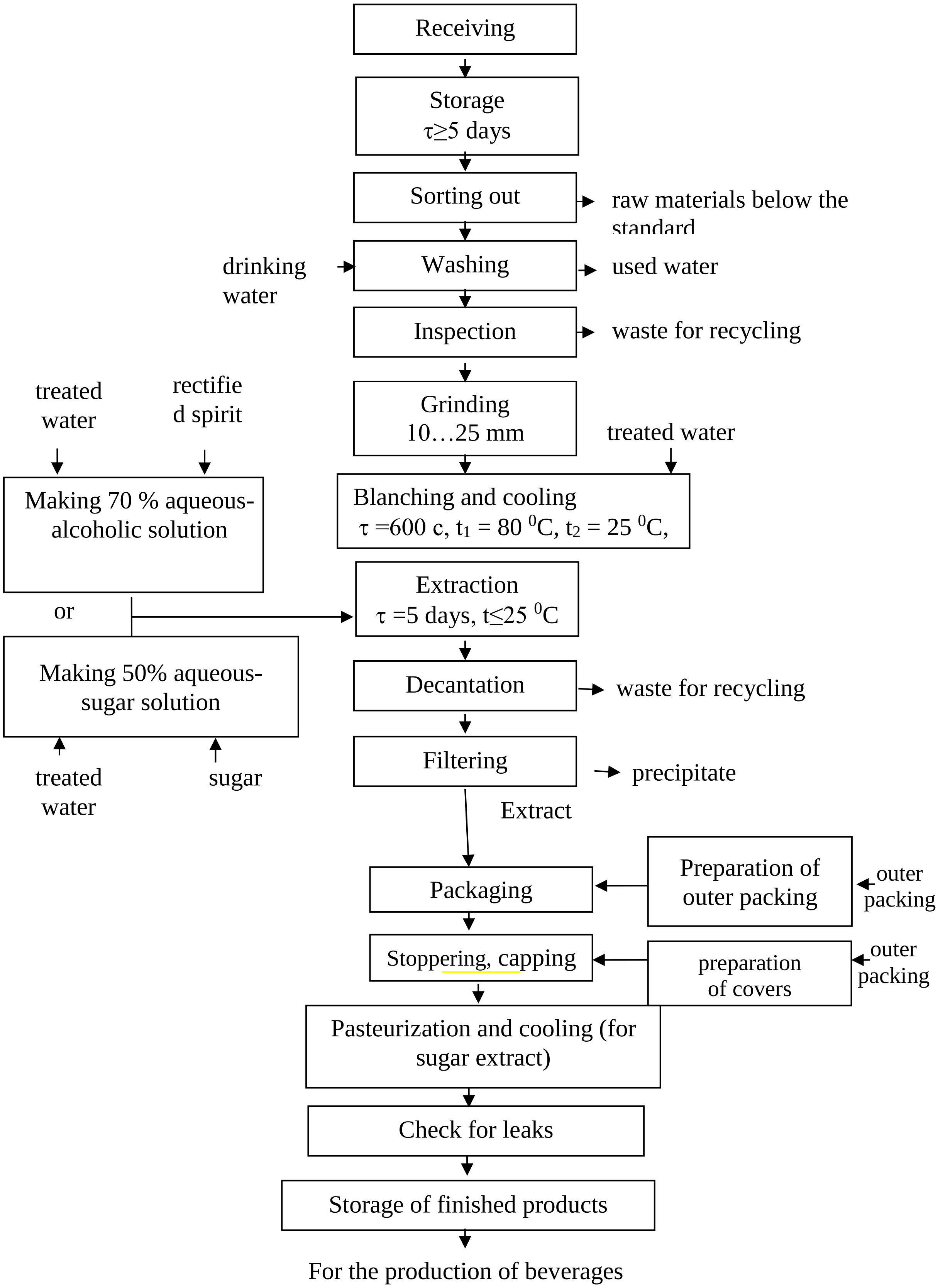

Fig. 7. Principal technological scheme of extracts production out of walnut pericarp

Sugar extract is pasteurized by the regime, which indicates the duration and temperature of processing in the sections of the device:

$$\frac{35}{60^0C}\bullet\frac{5}{55^oC}\bullet\frac{5}{45^oC}\bullet\frac{5}{20^oC}\bullet 5$$ (III-82-1000).

Shelf life of the finished product is not more than 1 year at temperatures of 16… 18 ºC and relative humidity of 70–75 %. Technology has been protected by a patent of Ukraine [32].

Physical and chemical analysis of fresh pericarp of walnut and its extracts are given in Table. 2.

Table 2

Physical and chemical parameters of pericarp and extracts on its basis

Name	Mass content, %			Content by weight, mg/100 g		pH
	dry substances	titrated acids	pectin substances	polyphenols	L-antiscorbutin	
Pericarp	21.0 ±0.3	0.50 ±0.02	0.50±0.02	2 870 ±250	140.0 ±10	4.2 ±0.2
Aqueous-alcoholic extract	11.0 ±0.3	0.60 ±0.02	0.15±0.01	1680 ±25	72.0 ±0.3	4.6 ±0.2
Aqueous-sugar extract	37.0 ±2.0	0.30 ±0.01	0.18±0.01	1630 ±25	91.0 ±0.3	4.1 ±0.2

The presented basic physical and chemical indicators of the samples (Table 2), confirm their nutritional and biological value. The developed parameters of the BAS extraction process for walnut waste – pericarp allows to extract a high content of antioxidants (up to 60% of phenolic substances and ascorbic acid, pectin compounds). The extracts have a distinctive taste, aroma and color inherent in the raw material.

Conclusion

The obtained experimental results prove the expediency of using walnut waste (pericarp) for the production of extracts by the developed technology, which allows to obtain high-quality extracts on water-alcohol and water-sugar bases with a high content of BAS. Extracts can be used for food purposes: as a basis and natural biologically valuable additives for a wide range of functional products (drinks, smoothies, jellies, mousses, puree soups, etc.) [33; 34].

Thus, the processing of pericarp is a promising area of use of walnut residues, which solves the problem of waste-free processing and rational use. The development of new food technologies with the integrated use of green walnuts will contribute to the health effects on the human body, prevention of food-dependent diseases, correction of the body's defense system and restoration of impaired functions of organs and systems.

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