Like all raw materials of plant origin, persimmon fruits are considered a material rich in carbohydrates. This subtropical plant grows almost throughout the entire territory of the Republic of Azerbaijan. Despite the widespread distribution of this plant in the republic, very few types of products are produced from it. The main reason why persimmon fruits are not used effectively from a production point of view is that they have astringent properties. Since fruit carbohydrates play an important role in eliminating the tart taste of persimmons, the study of the carbohydrate complex was considered as a basic condition.

After fractionation of carbohydrates with a water-alcohol mixture, certain stresses arise in the filter residue, which consists of cellulose-lignin. These stresses are analyzed using tensors. It has been established that the size of the filter pores is about 0.005÷0.05 microns, and the volume of these pores is 0.062÷0.195 cm^3/g. The clearance coefficient averaged 19.97 %.

It is known that the outer layer of a plant cell consists of cellulose and other structural compounds. These substances determine the porosity of the material. The mass fraction of the final product of the fractional residue, more precisely cellulose, averaged 0.63 %.

The use of the resulting filter membrane in the clarification of fruit juices has shown its usefulness in industry. It has been established that the selectivity of these membranes for various amino acids is 5÷18 %, and for minerals 1÷30 %. The lipid resistance of the membranes was high. It should be noted that cellulose has the ability to restore its structure and at the last stage acts only as a filter membrane. This explains the usefulness of the cellulose-lignin mixture as a membrane material

Keywords: cellulose, carbohydrate fractionation, stress tensor, node problem, percolation transition, fractal structure

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ASSESSMENT OF THE POSSIBILITY OF USING THE FRUITS OF THE ORIENTAL PERSIMO (DİOSPYROS KAKI L.) AS A SOURCE OF FILTER MEMBRANES BASED ON THE TENSOR APPROACH

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1. Introduction

The use of plant extracts is widespread in various areas of the food industry. Therefore, the process is being improved both in terms of the use of improved technological equipment and new filter membranes. The solution to the problem is to increase the efficiency of use of raw materials and energy resources. The production of juices, drinks and wine products is largely associated with extraction, filtration and percolation operations, therefore there is a great need for various types of raw materials [1].

As is known, the transition of chemical components of plant raw materials into the extractant is a mass transfer process. As mentioned earlier, the residue resulting from the fractionation of persimmon fruit carbohydrates consists mainly of cellulose.

High molecular weight organic compounds, including cellulose, have a complex surface structure. It was found that the corner and central chains of cellulose form a two-dimensional sheet structure in which the molecular chains are connected to each other by hydrogen bonds. Thus, the corner and central sheets, alternating, form a three-dimensional structure. It should be noted that the connection between the sheets is due to weak dispersion forces and weak hydrogen bonds. Therefore, it can be assumed that such compounds can be formed in several polymorphic modifications in the case of a crystalline structure. The reason for this is the intermolecular interaction that occurs during the formation of such a structure, and the hydrogen bonds formed in this case affect both the conformational state of cellulose and the mutual formation of its molecular chains.

In general, percolation in esterified cellulose is caused by its anisotropy [2].

In membrane filtration, the pressure generated by the membrane is the main driving force. The filtrate (permeate) flows perpendicular to the membrane surface. According to their structure, membranes can be porous or non-porous (solid). Examples of porous membranes include extruded metal, ceramics, glass powder, cellulose, and specially processed polymers [3]. Non-porous membranes include metal, glass and polymer coatings, pipes, hollow structures, etc. Not only membranes are used in food production, but also porous materials are used in processes such as cleaning, maceration, sorption, etc. Since such technological operations are associated with materials with a porous structure, it is possible to construct a mathematical model of the process based on the theory of percolation and tensors. In general, liquids passing through the lacunar layer have the property of percolation. Also, the formation of polymer gels, ferromagnetism, the passage of electric current through semiconductors, and the penetration of the liquid phase into polycrystals have this property. Porosity is the ratio of the volume fraction of pores in a material to the total volume. This feature is the main quality indicator for sorbents, catalysts, membranes, building materials, etc. The use of membrane technology in the production of various products is very common [4], so the main requirement is to find new sources of cheap raw materials. This makes relevant scientific research relevant.

2. Literature review and problem statement

Persimmon fruits are common in tropical and subtropical regions of the globe. This plant is perennial with a productivity cycle of 50÷60 years. Due to its high calorie content [5], it belongs to the group of industrial fruits. Persimmon belongs to the genus Diospyros and has 200 species. However, only four of its species – *D. kaki L.*, *D. lotus L.*, *D. virginiana L.* and *D. oleifed cheng* are used for food production.

Studying the carbohydrate content of persimmon fruits grown in the Republic of Azerbaijan using the fractionation method was supposed to reveal how rich it is in essential sugars. Also, the main goal was to determine the effectiveness of using fruits as a natural filter material. As shown in [6], methods of fractionation of various organic compounds – lipids, polyphenols, carbohydrates, acids, etc. differ from each other in the variety of extraction reagents. And this is due to the chemical properties of organic compounds. The use of various innovative technologies in the food industry is very relevant for the modern world and is gaining momentum. One such technology is membrane technology. Membrane technology can be considered a new principle for separating liquid and gas components. This technology differs from other technologies in its low energy consumption and environmental friendliness. The areas of application of membrane technologies are very wide. In the food industry, this technology is used to thicken juices, obtain high-quality proteins in milk production, prepare sugars, etc. But it should be noted that the purpose of work [6] was only to study the method of separating the carbohydrate composition, and the usefulness of the final product has not been studied.

Despite the widespread use of cellulose in various industrial fields, it is still not used to its fullest extent. Every time research is carried out, new properties of cellulose are discovered. The anisotropic nature of cellulose allows it to exhibit positive properties in electric fields. The macromolecular structure of cellulose makes it mandatory to use it as a natural filter material. The remainder of the mixture of cellulose and lignin, after fractionation of carbohydrates of persimmon fruits, is a natural filter material. There are also various ways to increase the porosity of such a cellulose material, in which case cellulose is considered as a substance with a micro- or monocrystalline structure. Cellulose is known to be difficult to process conventionally. But, despite these properties, it was shown in [7] that cellulose in pure or functionalized form [8] or as part of a composite is one of the most important natural polymers due to its good biocompatibility, biodegradability and renewability. Despite the fact that the above works noted the usefulness of cellulose, all these studies used different additives. The presented work was also based on this approach to the problem of waste-free technology. However, it is environmentally friendly technologies that require renewable resources. Therefore, the regeneration of cellulose residues is part of such technologies. Works [9, 10] devoted to the study of the dissolution and precipitation of cellulose show that this changes the crystal structure of the polysaccharide. The use of ionic liquids to dissolve cellulose can also be used for the preparation of membranes [11, 12]. As a natural membrane, cellulose residue meets all the requirements for natural resources.

As mentioned above, anisotropy is a characteristic feature of crystal structures, but this feature appears only in single crystals. The ordered arrangement of cellulose molecules is also the reason for its anisotropy. Therefore, cellulose should be considered as a molecular crystal. In such crystals, molecules are connected to each other due to van der Waals forces, and hydrogen bonds predominate inside. It is possible to say that any directed effect on cellulose has different effects on its properties.

When using cellulose residue as a filter membrane, it would be necessary to predict their behavior after deformation. Mathematical modeling would serve to achieve this goal. It was shown in [13] that the evolution of degradation components is associated with the deformed state. And when the load direction coincides with the global coordinate system, some components are related to the normal and shear strains, while others represent the relationship between any two strain components. It is also found that a tensor defined in a global coordinate system can correctly track changes in the deformed state locally and thus correctly develop the components of the tensor. Based on these data, it is possible to say that a tensor approach to the study of the cellulose-lignin residue of persimmon fruits will allow to analyze the elastic properties of this residue. The effect of plant materials on the deformation properties of the product was noted in [14].

The theory of percolation is closer to statistical physics, and states such as phase transitions, critical indices, etc., similar concepts are applied here. Percolation processes lead to self-organization and the formation of fractal structures. This theory is more useful for studying critical phenomena, such as sol-gel and insulator-metal transitions, the spread of forest fires, the development of viral epidemics, the likelihood of gases and liquids passing through porous materials, the transition from paramagnetic to ferromagnetic, etc. processes. The transformation of the carbohydrate fractionation residue into a porous structure is a critical phenomenon, which is explained by the theory of percolation [15].

Summarizing the above, it can be noted that the carbohydrate residue was not considered as a membrane material. This attitude towards the residue will allow the use of persimmon fruits as membrane raw materials.

3. The aim and objectives of the study

The aim of the study is to substantiate the use of persimmon fruits as a source of filter membranes. This will make it possible to use such membranes in various industries, for example, in the production of clarified juice, in the concentration and purification of liquid materials, for air sterilization, etc.

To achieve the aim, the following objectives were set:

– evaluate persimmon fruits as a source of pentoses, hexoses and oligo- and polysaccharides;

– study porous material based on tensor stresses arising due to the anisotropy of cellulose;

– determine the conditions for the formation of a porous structure in the fractional residue.

4. Materials and methods of the study

The object of the study is persimmon fruits.

The subject of the study is the carbohydrate composition of persimmon fruits, since after the extraction of these and other polymer chemical compounds, the final residue is a cellulose-lignin substance, which has a porous structure.

The hypothesis of the study is the feasibility of using carbohydrate residue as a useful filter material for various industries. To deeply study the filtering ability of fractional residues of these fruits, it is necessary to analyze and model changes in their membrane properties based on tensors, since long-term exposure to various extractants affects the physical and chemical characteristics of the residue.

To study the carbohydrate fractional composition, four varieties of oriental persimmon were used – *Diospyros kaki L*, the most common in the Republic of Azerbaijan: Hiakume, Khachia, Zenji-Maru and Emon. The average weight of the fruit is approximately 100±300 g. For analysis, persimmon fruits were taken from 10 trees and an average sample of 50 fruits was prepared.

Dry substances of persimmon fruits (14÷24 %) are mainly represented by carbohydrates. Persimmon is characterized by a large amount of polysaccharides, such as pectin (more than 0.7 %) and cellulose (0.58÷0.70 %). The color of persimmon fruits is due to the presence of a sufficient amount of carotenoid pigments. It is a low-acid raw material, so its sugar-acid index is very high.

A characteristic feature of persimmon fruits is their tart taste, which is the main obstacle to its technological processing. Research has shown that polyphenols are the cause of this astringent taste. When persimmon fruits ripen, a decrease in astringency is associated with the transition of monomeric forms of polyphenols to polymeric forms. This occurs due to their binding to high molecular weight compounds (proteins, polysaccharides, etc.). Polyphenols are also affected by carbohydrate breakdown products, with ketoses showing the greatest activity, aldoses showing less activity, and pentoses being more active than hexoses.

To increase the efficiency of using persimmon fruits, it is also advisable to use them as a filter membrane. Thus, the solution to this issue opens up wide possibilities for the use of fruits from an industrial point of view.

Experiments to study the fractional composition of persimmon fruits were carried out in late October and November, taking into account their technical and physiological maturity. During the ripening process, dry matter accumulates in the fruits, and acidity decreases. At the technical stage of maturity, these fruits contain approximately twice as much fructose as glucose. But this difference gradually disappears during the maturation process.

Fractionation of persimmon fruit carbohydrates was carried out according to the given sequence (Fig. 1). The fruits were peeled, crushed, pitted and degreased. 100 g of raw material with a humidity of 85 % after degreasing was processed for 30 minutes. 82 % ethyl alcohol at 80 °C. The use of alcohol is also convenient because the material can be stored in alcohol for some time without spoiling. The end of fractionation was determined by the anthrone reagent (0.2 g of anthrone is dissolved in 100 cm^3 of H_2SO_4 solution), since when hexoses are heated in an acidic medium, they turn into furfural derivatives, forming blue compounds with anthrone.

After a heating period, the extract was filtered. The residue was returned to the previous flask and this extraction was repeated 3 times. Each time the extract was filtered and the filtrates were collected in the same flask.

To remove alcohol from the filtrate, this filtrate is condensed in a rotary evaporator at 40÷45 °C. After removing the alcohol in an evaporation flask, a syrupy solution is obtained. This solution was mixed 4 times with 15÷20 cm^3 of distilled water and transferred to a 200 cm^3 volumetric flask, and the flask was filled with water to the mark. The extract was clarified with a mixture of reagents intended for carbohydrates, and the amount of sugars in the resulting filtrate after filtration was determined. For this, 3 cases are considered:

1) using the Bertrand method, the amount of reducing sugars in 20 cm^3 of filtrate was found;

2) after hydrolysis of 20 cm^3 of filtrate with 2 % HCl solution, the amount of reducing sugars was determined;

3) after hydrolysis of 20 cm^3 of filtrate with a 25 % HCl solution for 3 hours in a hot water bath (neutralization with soda), sucrose, maltose, and monosaccharides were determined. The remaining filtrate is used in the chromatographic determination method.

After isolating alcohol-soluble carbohydrates (ASC) from the sample, the residue was dried in an oven at a temperature of 40÷50 °C and the alcohol was removed. Then the residue, together with filter paper, was added to a pre-cleaned flask and extraction was carried out 3÷4 times with 200 cm^3 of water at a temperature of 45÷50 °C (20 min.). Water-soluble carbohydrates (WSC) go into solution. The extract was filtered each time and the filtrate was concentrated to 200 cm^3.

Let's take 100 cm^3 of the condensed filtrate and poured (with stirring) 50 cm^3 of 96 % ethanol into a beaker along with 2.5 cm^3 of solid acetic acid. The active acidity (pH) of the solution should be 4.5. Polysaccharides will settle to the bottom of the glass. The liquid above the precipitate was separated, and the residue was centrifuged. The resulting precipitate was washed 2÷3 times with 50 cm^3 of 96 % ethanol and transferred into bottles with the participation of ether. The resulting precipitate was completely purified from ether using an air pump in a cabinet, and the dry mass was weighed.

For chromatography, a certain amount was taken from the dry residue and 2 % HCl (weighed portion×100 cm^3) was added to it and hydrolyzed using a reflux condenser. After removing water-soluble carbohydrates from the sample, the residue was extracted 3 times with 100 cm^3 of 0.5 % ammonium oxalate at a temperature of 70 °C for 2 hours each time. This salt extracts water-insoluble carbohydrates (WINC) – protopectin and other polysaccharides. The extract was filtered and its volume was brought to 400 cm^3 with the same salt. 200 cm^3 of the filtrate was taken and precipitated with

acetic acid and ethanol as described above. Hydrolysis of the resulting precipitate was carried out as described above.

To separate hemicellulose A from the sample, 100 cm^3 of a 5 % NaOH solution was added to the residue. Extraction was carried out for 2 hours at room temperature with continuous stirring. The alkaline extract was filtered, and 50 cm^3 of 5 % NaOH and 50 cm^3 of water were added to the residue. The extract was centrifuged. The main extract and washes were combined. The flask was filled with water to the mark. Precipitation and hydrolysis of hemicellulose A were carried out as described above.

After extraction of hemicellulose A, the residue was returned to the flask and this time hemicellulose B was extracted with 100 cm^3 of 18 % NaOH at 20 °C for 2 hours. Then the extract was filtered, 25 cm^3 of 18 % NaOH and 50 cm^3 of water were added to the residue. The extract was centrifuged. The main extract and washes were combined and the flask was filled to the mark with water. Precipitation and hydrolysis of hemicellulose B was carried out as described above.

After extraction of hemicellulose B, β-cellulose present in the residual material was determined. To do this, the residue was dried at a temperature not exceeding 50 °C. Then this dried material was transferred to the previous extraction flask, 10 volume parts (by weight of the residue) of an 80 % H_2SO_4 solution were added to it and kept in this state for 2.5 hours at room temperature. After this period, a certain amount of water was added to the flask (1 part acid to 15 parts water) and the cellulose was hydrolyzed in a boiling water bath for 5 hours. Cellulose is broken down into glucose. The resulting hydrolyzate was passed through a glass filter, and the residue was washed 3–4 times with water. The filtrate was evaporated to a certain volume and neutralized with soda. Then, using Bertrand's method, the amount of glucose in it was found. The found value is multiplied by the conversion factor to glucose (0.9).

The residue remaining in the glass filter consists of lignin and mineral matter. It was weighed and the total mass was found.

The hydrolysis products of each fraction were analyzed by chromatography. The best results are obtained by the method of descending paper chromatography. This process is carried out in special closed chambers.

A mixture of various solutions was used as a solvent. One such system is a mixture of n-butanol, acetic acid and water (4:1:5). More accurate separation of carbohydrates can be achieved in the ethyl acetate-pyridine-water system (8:2:1). Chromatograms were stored in the chamber for 24 hours. The separation of carbohydrates generally works well at low temperatures. The chromatogram was then removed from the chamber and dried in a fume hood. Again, this chromatogram was stored for 24 hours. The chromatogram was then completely dried. Drying is completed at a temperature of 60÷80 °C.

For example, to detect aldoses, a mixture of aniphthalate is used (1.66 g of phthalic acid is dissolved in 95 cm^3 of n-butanol, 0.76 cm^3 of purified aniline is added and the volume is adjusted to 100 cm^3); for ketosis – urea solution (5 g of urea is dissolved in 100 cm^3 of 96 % ethanol, 20 cm^3 of HCl solution is added to it [c(HCl)=2 mol/dm^3]).

After treating each chromatogram strip with the selected indicator (using a spray bottle), they were dried at 100÷120 °C for 5÷10 minutes. and sugars were determined from the resulting spots. Aldohexoses give a brown color, and aldopentoses give a reddish color. Uronic acids mainly accumulate near the starting line. Sugars are arranged in this order (starting from the starting line): galactose, glucose, mannose, arabinose, xylose, rhamnose, etc.

To identify sugars, mixtures of different reagents are used.

To quantify sugars, a small section of the chromatogram strip corresponding to the detected spot was cut off and eluted with alcohol by heating in a water bath. The amount of sugar in this solution was then determined using red blood salt.

In another method, the stain detected by anilinphthalate was eluted with 5 cm^3 of acetic acid. This process was carried out in a boiling water bath for 10 minutes. Another strip corresponding to the detected spot was also cut out and eluted with acetic acid. Both eluates were photoelectrocolorimetrically measured.

To quantify the detected ketoses, part of the corresponding chromatogram bands was cut and eluted with alcohol in a hot water bath. They were determined by one of the methods applied to them (resorcinol, Kolthoff, etc.) [6].

Fractional analysis revealed that the quantitative ratio of glucose-fructose is greater in the direction of glucose. This can be explained by the ketoenol tautomerization of fructose and its conversion into glucose during prolonged alcohol extraction.

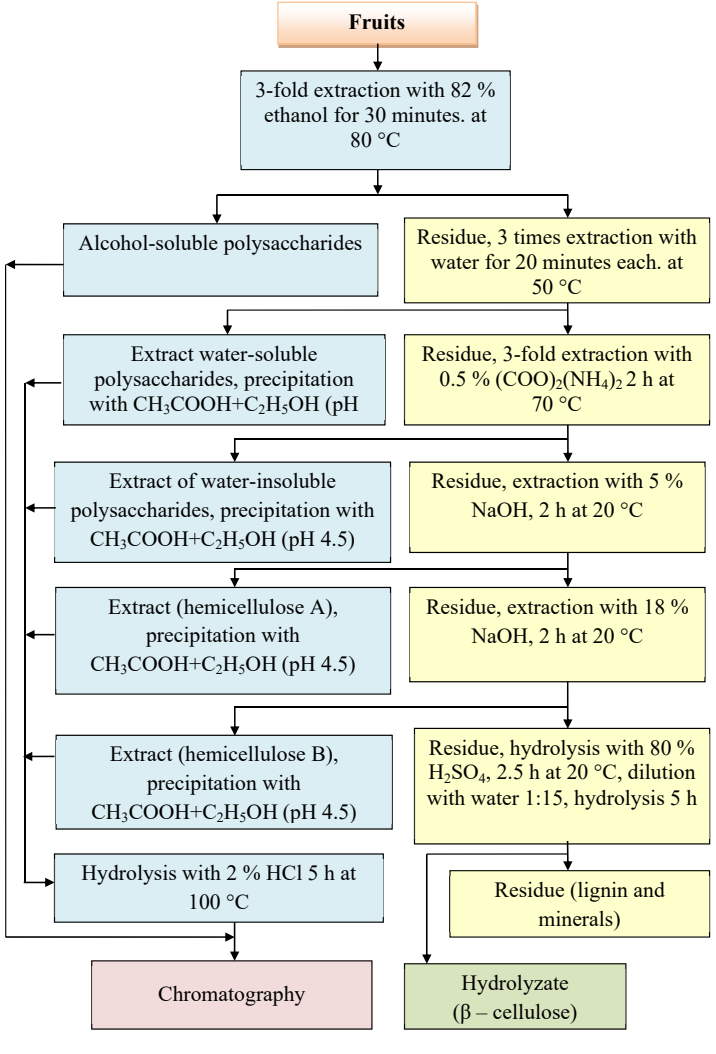


Fig. 1. Scheme for the separation of carbohydrates of persimmon fruits

With such fractionation, naturally, polyphenols and some lipids are also included in the extract, and their quantitative analysis is carried out with other extractants. In general, small amounts of these compounds do not affect the membrane properties of cellulose.

5. Results of a study of the fractional composition of carbohydrates in persimmon fruits

5. 1. Evaluation of persimmon fruits as a source of mono- and polysaccharides

The carbohydrate content in individual fractions is shown in Table 1. Table 1 shows that uronic acids are present in all fractions. Galactose, arabinose, xylose and furfural were found in hemicellulose fractions A and B. Galactose and rhamnose are found in the water-soluble fractions of carbohydrates, and glucose, fructose, ribose, and rhamnose are found in the alcohol-soluble fractions.

Determination of cellulose at different stages of persimmon fruit maturity showed that during ripening its content decreases due to the transition to lower molecular weight carbohydrates. This is reflected in the taste and rheological properties of the fruit. The pectin content of fruits is also subject to great fluctuations. At the technical stage of maturity, insoluble protopectin predominates in them. As the fruits ripen, the quantitative ratio of protopectin-pectin changes towards an increase in soluble pectin.

The production of cellulose in the carbohydrate fractionation residue as the final product involves the use of persimmon fruits as a source of this organic compound. As said earlier, persimmon fruits do not lend themselves very well to technological processing. Therefore, by using these fruits as a cheap source of membrane filters, it is possible to expand their use and at the same time provide waste-free technology.

As shown in Table 2, the final product of the fractional composition of carbohydrates of persimmon fruits consists of cellulose, lignin and minerals.

Table 2

The final product of the fractional composition of carbohydrates of persimmon fruits

Variety	Residue, mass fraction, %	
	Cellulose	Lignin and minerals
Khachia	0.58	0.68
Khiakume	0.70	0.76
Zenji Maru	0.63	0.46
Emon	0.60	0.50

These substances determine the porosity of the residue. All physical and chemical characteristics of the filter membrane are due to residual chemical compounds.

In order to study the properties of the resulting filter membrane, lemon juice was clarified. The results of the analyzes are presented in Table 3. As can be seen from table. 3, the active and total acidity of the juice, as well as the content of sugars, total nitrogen and ascorbic acid, change little compared to the original juice. Pectin and cellulose, which are biopolymers, remain in the membrane.

It has been established that the selectivity of filter membranes for various amino acids is 5÷18 %, and for mineral substances 1÷30 %. The lipid resistance of the membranes was high.

To assess the quality of the resulting filter membrane, lemon juice was clarified. As can be seen from the results of Table 3, such membranes are suitable for use in both clarification and concentration of fruit juices.

Table 1

Carbohydrates of persimmon fruits (mass fraction, %)

Fractions	Variety	Carbohydrates								
		Uronic acids	Galactose	Glucose	Fructose	Arabinose	Xylose	Ribose	Rhamnose	Furfural
Alcohol-soluble polysaccharides	Khachia	0.7	–	5.8	4.8	–	–	2.6	1.9	–
	Khiakume	0.4	–	6.1	5.1	–	–	2.5	2.3	–
	Zenji Maru	0.3	–	6.2	5.9	–	–	2.3	1.8	–
	Emon	0.2	–	3.0	5.6	–	–	2.1	1.7	–
Water-soluble polysaccharides	Khachia	0.14	0.38	–	–	–	–	–	0.06	–
	Khiakume	0.16	0.34	–	–	–	–	–	0.04	–
	Zenji Maru	0.19	0.30	–	–	–	–	–	0.04	–
	Emon	0.15	0.16	–	–	–	–	–	0.05	–
Oxalate-ammonium fraction	Khachia	0.19	0.29	–	–	–	–	–	trace	–
	Khiakume	0.14	0.36	–	–	–	–	–	trace	–
	Zenji Maru	0.12	0.32	–	–	–	–	–	trace	–
	Emon	0.18	0.38	–	–	–	–	–	trace	–
Hemicellulose A	Khachia	0.47	0.15	–	–	0.24	trace	–	–	0.03
	Khiakume	0.45	0.14	–	–	0.25	trace	–	–	0.04
	Zenji Maru	0.41	0.16	–	–	0.26	trace	–	–	0.06
	Emon	0.46	0.15	–	–	0.21	trace	–	–	0.06
Hemicellulose B	Khachia	0.39	–	–	–	0.23	0.14	–	–	0.04
	Khiakume	0.45	–	–	–	0.20	0.12	–	–	0.06
	Zenji Maru	0.41	–	–	–	0.28	0.13	–	–	0.03
	Emon	0.46	–	–	–	0.20	0.12	–	–	0.08

Table 3

Comparative evaluation of lemon juice and filtrate

Indicators	Lemon	
	Juice	Filtrate
Dry substances, %	7.05	6.89
Reducing sugars, %	1.9	1.75
Sucrose, %	0.30	0.27
Pectin, %	0.25	0.10
Cellulose, %	0.15	0
Ascorbic acid, mg/gg	39.5	38.2
Flavonols, mg/gg	129	95
Carotenoids, mg/gg	100	87
Total nitrogen, %	0.61	0.58
Total acidity, %	4.5	4.3
Active acidity	2.2	2.2

5. 2. Tensor stresses arising in the cellulose-lignin residue

The difference between diffusion and percolation is that diffusion is the chaotic movement of a particle in an ordered environment, and percolation is the ordered movement of a fluid in a chaotic environment. Percolation is a model of a disordered medium, and this modeling method is carried out on random lattices. This topological model is compatible with any geometric figure that is a porous structure. In randomized lattices and in percolation theory in general, two types of problems are studied - connections and nodes. In the case of bonds, an extended cluster is studied, or more precisely, the bonds that form a cluster connecting opposite sides of the lattice. In the case of nodes, in the study carried out, the pores are closed and in this case the formation of an infinite cluster is considered [16]. Closing a pore or removing a node from the process means cutting the connections connecting the nodes. The forming cluster can be considered as a random graph.

If to consider the porous cellulose residue as a two-dimensional lattice, then the distribution of the extractant can be explained by the laws of fluid flow in the Hele-Shaw channel. Such flows are called invasive percolation. The structural arrangement formed in the Hele-Shaw canal is called "viscous fingers" or "tongue". This phenomenon is also called Saffman-Taylor instability. Such phenomena can also occur in biological systems. The Hele-Shaw channel serves as a physical model of invasive percolation.

In general, the properties of liquids or gases passing through a filter are explained by Darcy's law, according to which the flow velocity is directly proportional to the pressure gradient [15]. In accordance with this law, the speed of fluid passing through a pore is determined by the expression obtained from the Navier-Stokes formula and is expressed as follows (the minus sign indicates that the speed is opposite to the increase in pressure):

$$u=-\frac{k_{ij}}{\eta}\nabla(\rho gz+p)=-M\nabla f, \quad (1)$$

where M – expresses fluid mobility $M=\frac{k_{ij}}{\eta}$, where k_{ij} –the fluid permeability coefficient or permeability tensor and is defined as $k_{ij}=\frac{b^2}{12}$; 12 – Darcy area of the intermediate channel, $1D=1.02\cdot10^{-12}$ m^2; b – distance between plates; η – dynamic viscosity. It should be noted that the attitude $\frac{k_{ij}}{\eta}$ expresses interactive force, i. e. force between the extractant and the filter frame [17]; ρ – fluid density; g – free fall acceleration; z – vertical coordinates; p – external pressure; f – fluid flow potential, $f=\rho gz+P$ – Hamilton operator.

From equation (6) it is possible to obtain the Laplace equation for an incompressible fluid, since at a constant permeability the flow velocity field has a scalar potential:

$$\nabla\cdot u=-\nabla^2(\rho gz+p)=\nabla^2 f=0. \quad (2)$$

Flows that are explained by Laplace's formula (8) are potential flows.

Filtration of liquid in an anisotropic medium, more precisely in a cellulose-lignin residue, is considered in the general case. It has been established that absolute permeability can be represented as a second-rank tensor, which is determined by nine components:

$$u_i=\frac{k_{ij}}{\mu}\frac{\partial p}{\partial x_i} \text{ or } \nabla_i p=-\mu r_{ij}u_j, \quad (3)$$

$$k_{ij}=k\delta_{ij}=\begin{pmatrix}k_i & 0 & 0\\ 0 & k_i & 0\\ 0 & 0 & k_j\end{pmatrix}, \quad (4)$$

where k_{ij} – permeability coefficient tensor; r_{ij} – filter resistance tensor; δ_{ij} –Kronecker symbol [18].

Taking into account the continuity equation for a liquid in a porous medium, let's obtain:

$$\frac{\partial(\rho m)}{\partial t}-\frac{\partial}{\partial x_i}\left(\rho\frac{k_{ij}}{\mu}\frac{\partial p}{\partial x_i}\right)=u, \quad (5)$$

where p – pressure; $m=m(p)$ – porosity; $\rho=\rho(p)$ – liquid density; u is a distributed source of mass.

To explain the filtration process occurring in anisotropic porous materials, such as cellulose, the porous medium is usually represented as a system of capillaries. In such a model, the radius of common parallel capillaries is found as follows [19]:

$$F(r)=\int_0^r f(r)\,\mathrm{d}r, \quad (6)$$

where $f(r)$ –the density of pore radius distribution; $f(r)\mathrm{d}r$ – the proportion of pore space with capillaries, the radius of which lies in the range from r to $r+\mathrm{d}r$.

To determine permeability, let's use the formula:

$$k=\frac{m}{8}\int_0^\infty r^2 f(r)\,\mathrm{d}r. \quad (7)$$

The values of the effective pore diameter and the permeability coefficient along an arbitrary direction are determined as a tensor property in a given direction according to the formula:

$$k(n)=k_{ij}n_i n_j=\frac{1}{8}\int_0^\infty r^2 S_{ik}f_{kj}(r)n_i n_j\,\mathrm{d}r. \quad (8)$$

In formula (8), S_{ij} is the tensor of the transmission coefficients. The porosity of the filter membrane was determined

using a mercury porosometer. It was found that the size of the pores under study is about 0.005÷0.05 microns, and the volume of these pores is 0.062÷0.195 cm^3/g. It is noticeable that as the pore size increases, their volume also increases. Formula (3) determines the transmission coefficient, which averaged 19.97 %.

Table 4

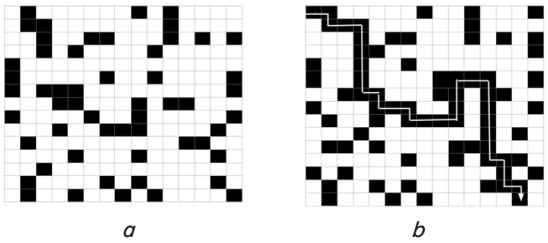
Distribution of pore volume by size

Pore diameter, μm	Pore volume, cm^3/g
0.005	0.062
0.016	0.143
0.029	0.166
0.048	0.181
0.056	0.200
0.093	0.215
0.195	0.298

Permeable porosity is divided into channel (more than 5 μm wide) and non-channel (less than 5 μm wide) forms. As porosity and size increase, the permeability of membranes or filters increases, but the tensile strength decreases. Therefore, as the amount of solid phase decreases and the pore size increases, the hydraulic resistance to gas and liquid becomes smaller [19].

5. 3. Conditions for the formation of a porous structure in the fractional residue

Either water or alcohol was added to the membrane as an extractant, and under such conditions the possibility of the extractant flowing through the membrane pores in the opposite direction was studied. The porosity problem was studied in a square lattice with dimensions 15×15 (Fig. 2).



a *b*

Fig. 2. Model of the percolation process: *a* – when percolation does not occur, p<ph; *b* – when percolation occurs p>ph

The cage was colored randomly. Black squares represent pores and white squares represent solid matrix elements. In some cases, the pores are also presented in the form of nodes, and these nodes can have different geometric shapes. It was assumed that the probability of coloring the squares, in other words, the presence of pores, is equal to the probability p, and the probability of the presence of elements of the solid part, that is, non-porosity, is equal to $1-p$. If the number of black squares is 56 $p=\frac{56}{100}=0.56$. The sum of elements in which percolation or flow occurs are called clusters. The percolation threshold p_h expresses the occurrence of flow at a minimum value of pores or nodes in the lattice. The percolation limit shows a lower value in the case of links than in the case of nodes. With dimensions in the lattice $L\to\infty$ (L is the number of squares in the lattice) at $p<p_h$, flow through the pores does not occur and the cluster is finite, but in the case of $p>p_h$, flow always occurs in the lattice, where an infinite cluster is formed. And when the condition $p=p_h$ is satisfied, this is called a percolation transition, and the clusters have fractal properties. Such critical transitions cause fluctuations, and it becomes necessary to explain the percolation process using the theory of scale invariance. For square lattices, the percolation limit is taken to be $p_h=0.59275\pm0.0003$. For the Bethe lattice, the calculation is carried out as $p_h=1/(z_{\text{number of nodes}}-1)$ [20].

The strength of an infinite cluster formed by the percolation process is an order parameter denoted by P∞, and this quantity determines the probability that a node or link belongs to the resulting infinite cluster. At $p<p_h$, $P_\infty=0$, it is possible to talk about the existence of finite clusters, and in the case of $p>p_h$, the cluster power increases according to a power law:

$$P_\infty \sim (p-p_h)^{\beta}, \tag{9}$$

where β – the index of the order parameter and for a two-dimensional flow it is equal to 5/36, for a three-dimensional flow it is approximately equal to ~0.417, and for higher-dimensional flows it is equal to one. This characterizes the change that occurs during a phase transition. In the ordered phase, the order parameter differs from zero [21].

The linear sizes of clusters are characterized by the correlation length ξ, and this value is defined as the average value of the distance between the nodes of one cluster, and their commonality arises from random fluctuations. As the flow approaches the percolation limit, the correlation length increases and is defined as:

$$\xi \sim (p-p_h)^{-\nu}, \tag{10}$$

where ν – the correlation radius index and for a two-dimensional flow it is equal to 4/3, for a three-dimensional flow it is approximately equal to ~0.875, and for higher-dimensional flows it is equal to 0.5. Using these indices, the fractal size of the cluster can be determined [18]:

$$D=d-\frac{\beta}{\nu}. \tag{11}$$

It should be noted that the porous nature of a cluster does not necessarily mean that it has a fractal property, but it is only considered fractal when its density decreases as its size increases. The fact that an infinite cluster is fractal allows it to play a decisive role in various physical processes.

6. Discussion of results on issues of fractionation and filtration

It should be noted that the results obtained (Tables 2, 3) confirm the usefulness of conducting research in the direction of identifying the membrane properties of the fractional residue of persimmon fruits (Fig. 2). Despite the fact that these fruits are a source of the necessary chemical components (Table 1), they are difficult to process. Therefore, identifying the beneficial properties of persimmon fruits as a source of membrane raw materials expands their use in various industries.

In the works [9–11] there are only studies of cellulose as a membrane material, but its use as filter membrane materials from the fractional residue of carbohydrates is not found.

When water and alcohol are used sequentially as an extractant, the cellulose residue remaining at the final stage first undergoes swelling, and in subsequent fractions only deforms [1]. Severe deformation can also be observed when the residual layer is compressed at the end of the process. As a result, the remaining solvent and dissolved substances are quickly removed. However, in this case, the porosity of the material decreases, and this negatively affects the membrane properties of the residue. Such restrictions prevent the residue from being used for a relatively long time. It should be said that cellulose has the ability to restore its structure and at the last stage acts only as a filter membrane.

Although there are some similarities between filtration processes and membrane separation processes, there are also major differences between them. This is due to the fact that during filtration, at least one of the components of the gas or liquid mixture remains inside the filter, as a result of which this filter layer is filled with the component and prevents further continuation of the process. The separation of components in all different filter media is accomplished by gravity.

Membrane filters have fine and controlled pores. In general, a membrane is understood as a layer separating two or more phases, because the Latin meaning of the word "membrane" means "skin", "film". They have specific selectivity towards inhomogeneous liquid and gas components. In this case, the membrane residue of persimmon fruits may lose its filtering ability during subsequent technological applications, which is a disadvantage for such membranes. But this loss may come quickly or late. Therefore, carbohydrate fractionation must be carried out based on compliance with membrane requirements. This depends on a limited set of extractants and on environmental parameters. In table 4 there is a dependence of the pore volume on their size, since as the pore diameter increases, their occupied volume also increases.

A further development of this research is to increase and control the porosity of the residual material, and this depends on the selective choice of extractants for fractionation and subsequent functionalization. Crystal lattice percolation allows the process to be approached using graph theory. This approach will make it possible to determine the leakage limit in advance.

7. Conclusions

1. The study of carbohydrates in various varieties of persimmon fruits using the fractionation method made it possible to demonstrate their beneficial properties. It has been established that fruits contain more glucose than fructose. Uronic acids were found in all fractions. According to the fractional composition, hemicelluloses A and B consist of galactose, arabinose, xylose and furfural. Galactose and rhamnose are found in water-soluble carbohydrate fractions, and glucose, fructose, ribose, and rhamnose are found in alcohol-soluble fractions.

2. Consideration of cellulose as a filter membrane allows to explain the process using tensor analysis. This is due to the fact that extractants used in the fractionation of carbohydrates have a certain effect on the residual material and, consequently, certain stresses and deformations arise in the material. These changes can be studied using a tensor approach. It was found that the size of the pores under study is about 0.005÷0.05 microns, and the volume of these pores is 0.062÷0.195 cm^3/g. The clearance coefficient averaged 19.97 %.

3. Cellulose filtration, considered on the basis of percolation theory, allows to simulate the process. According to this theory, the limit for the occurrence of percolation was indicated and a crystal lattice was constructed for it. The formation of the resulting clusters with a fractal structure makes it possible to study them using topological geometry, and due to the formed nodes in the crystal lattice, the cluster manifests itself as a random graph. For square lattices, the percolation limit is taken to be p_h=0.59275±0.0003. For the Bethe lattice, the calculation is carried out as $p_h=1/(z_{\text{number of nodes}}-1)$.

Conflict of interest

The authors declare that there are no conflicts of interest regarding this study, including financial, personal, authorship or other nature, which could affect the research and its results presented in this article.

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Data Availability

The manuscript has associated data in a data warehouse.

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