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## Preparation and Light Stabilization of Natural Anthocyanin Dyes in the Presence of Fullerene for Food Products

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### Abstract

The paper presents the results of experiments on the selection of initial plant raw materials for the isolation of natural anthocyanin dyes by water extraction from berry press cake with water, which had previously been treated with shungite gravel containing fullerene, a molecular compound representing convex closed polyhedra composed of three-coordinated carbon atoms. The intensifying effect of shungite water on the degree of anthocyanin extraction has been established. The authors propose a mechanism of dye extraction from black currant berry press cake. For the light stabilization of anthocyanin dyes isolated during extraction, they were absorbed into powdered materials consisting of carbohydrates and proteins. The resulting colored powders had high light resistance. The authors propose a mechanism of dye light stabilization and ways of using light-stabilized dyes. Natural food dyes can be used to increase the range of bakery products, creating a healthy and delicious product.

**Keywords:** anthocyanin dyes, light stability, fullerene, shungite, extraction, carbohydrates, proteins, food additives.

### 1. Introduction

The results of the study of food dyes indicate a lack of research in the field of natural, light-resistant dyes, which, when added, can provide coloring to food products. The suitability of food dyes is currently being discussed since the impact of these compounds on human health is important [1]. Among the technical, functional products in various industries, a special place is occupied by dyes, the number of which is more than 10 thousand individual substances of various classes, for example, azo dyes, anthraquinone, xanthene, thiazine, acridine, and other types of dyes [2]. For practical purposes, bright, light-resistant, and harmless dyes of natural and synthetic origin are in demand. The available number of types of such dyes is not enough to meet the needs of various industries [3]. Therefore, at present, the development of new types of light-resistant dyes and their production technologies is very relevant.

Dyes constitute a group of complex organic substances that give a stable color in visible light (in solutions), depending on the selective absorption of a certain part of the rays of the visible spectrum. The observed substance color in transmitted light is always complementary to the color of the rays absorbed by this substance. Thus, the red dye absorbs high-energy rays of the short-wave blue-violet part of the optical spectrum [4]. The chromaticity of the compound, according to the existing theory, is due to the presence in the dye molecule of groupings containing double bonds of various types ( $>C=C<$ ,  $-N=N-$ ,  $>C=O$ ,  $-NO<$ ,  $-N=N-$ ,  $>_2$ , etc.), called chromophores. In the presence of additional groups,  $-NH_2$ ,  $-NR_2$ ,  $-OH$ ,  $-OR$ , called auxochromes, in a molecule containing chromophores, there was an increase in the intensity of coloring and deepening of the color of the colored substance [5]. From an energy point of view, the color of the dyes and their

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depth depends on the energy of the light quanta required for photoexcitation, which in the optical range is in the range of 158-300 kJ/mol. It depends on the length of the conjugation chains in aromatic and heterocyclic compounds with closed systems of conjugated double and single bonds. The wavelength ( $\lambda_{\max}$ ) at which maximum absorption (resonance effect) is observed can serve as a qualitative characteristic of the color of matter and the nature of the phenomenon of interaction between matter and light can be [6]. Anthocyanin dye molecules have a similar structure (Fig. 1) [7].

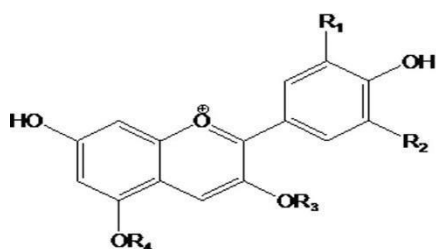


Fig. 1. General formula of the anthocyanin chemical structure

It follows that chromophores in anthocyanins are aromatic systems, and auxochromes are substituents in benzene rings (OH-, OR-) [8]. Auxochromic groups usually determine the affinity of the colored substance to plant or animal fibers [9]. The coupling chains and the light fastness of the dyes can be increased by increasing the length of the substituents (OR-). Thus, black currant (*Ribes nigrum*) contains more than 10 different types of anthocyanins, the main of which are cyanidin-3-glycoside, cyanidin-3-diglycoside delphinidin-3-glucoside, cyanidin-3-rutinoside, delphinidin-3-rutinoside [10]. One of them is shown in Fig. 2.

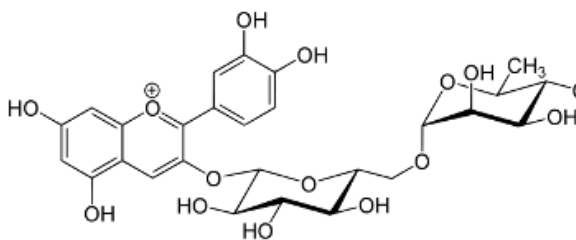


Fig. 2. Structure of anthocyanin dye with diglycoside (delphinidin)

During the study of Russian and foreign publications, we found no publications on the production of natural dyes that would have

antioxidant and light-resistant properties. This study was carried out as part of the isolation of red anthocyanin dyes from natural berry raw materials by water extraction in the presence of modern carbon antioxidant nanomaterials (fullerenes), followed by their application to powdered carbohydrate or protein products. In this regard, the issues of natural food dye isolation and the determination of dye content in food products are relevant.

## 2. Methods

In our study, we used the method of spectrophotometry based on the absorption of electromagnetic wave energy by the analyzed substances. Methods based on the absorption of electromagnetic radiation constitute a group of adsorption optical methods.

Of the optical methods of analysis and investigation of substances, the most widely used spectrophotometric methods are based on the measurement of absorption spectra in the optical region of electromagnetic radiation. The spectrophotometric study of the spectra of molecules in the visible and UV regions allows us to determine the type of electronic transitions and the structure of molecules. These methods of analysis are based on a comparison of the light absorption intensities of the test solution and the solvent [11]. Experimental data were processed using the basic law of light absorption (the Booger-Lambert-Beer law) expressed by the equation:

$$I = I_0 \cdot 10^{-\epsilon c l} \quad (1)$$

where  $I$  is the intensity of the transmitted light;  
 $I_0$  is the intensity of incident light;  
 $\epsilon$  is the light absorption coefficient;  
 $c$  is the concentration, mol/dm<sup>3</sup>;  
 $l$  is the thickness of the cuvette, cm.

The molar absorption coefficient is the absorption index of a solution containing 1 mol/dm<sup>3</sup> of a substance with a layer thickness equal to 1 cm. The  $\epsilon$  value depends on the wavelength of the transmitted light, the temperature of the solution, and the nature of the substance under study, but does not depend on the thickness of the absorbing layer and the concentration of the solution. According to the Booger — Lambert — Beer law, the intensity of the outgoing light is exponentially dependent on the thickness of the absorbing layer and the concentration

of the substance in the solution [12].

If we take the logarithm of the equation of the Booger-Lambert-Behr law and reverse the signs, then the equation will take the form:

$$\lg \frac{I_0}{I} = \varepsilon cl.$$

(2)

The value  $\left(\lg \frac{I_0}{I}\right)$  is a very important characteristic of the solution; it is called the optical density of the solution and is denoted by the letter  $D$ :

$$D = \lg \frac{I_0}{I} = \varepsilon cl. \quad (3)$$

The optical density (or absorptivity) was measured on a photoelectric concentration calorimeter KFK — 2.

To obtain titration curves, potentiometric acid-base titration was used, which is possible due to the presence of acid (carboxyl) and basic (amine) groups in the macromolecule of polyacrylamide.

Potentiometric titration is based on the determination of the equivalence point based on the results of potentiometric measurements. Near the equivalence point, there is a sharp change (jump) in the potential of the indicator electrode. This is observed only when at least one of the participants in the titration reaction is a participant in the electrode process [13].

For potentiometric titration, a chain was assembled from an indicator electrode in the analyzed solution and a reference electrode. A calomel or silver chloride electrode was used as reference electrodes.

Potentiometric titration of polyelectrolyte solutions with hydrochloric acid (HCl) and alkali (KOH) solutions with a concentration of 0.01 mol/dm<sup>3</sup> was carried out on a pH-meter-millivoltmeter pH-150M device, which had the following electrodes: a measuring laboratory-grade electrode ESL-15-11 and an auxiliary grade electrode EVL-1.M.4.

According to the obtained titration curves, the equivalent or endpoint of titration was graphically determined by determining the midpoint of the section corresponding to the vertical rise of the curve.

The oxidation-reduction potential (ORP) was measured using the pH meter-ionomer Ecotest-120.

To measure the pH, an ion-selective glass electrode with a solid contact ECOM-pH was used, pre-calibrated using three HANNA buffer solutions

with pH values of 4.01; 7.01, and 10.01. ORP was measured using platinum electrodes EPV-1sr, ETP-02, and glass redox electrode EO-01. The registration of ORP solutions was carried out automatically simultaneously on several indicator electrodes using the Ecotest program. The measurement time was from 10 to 40 minutes. To control the correctness of the readings of the redox electrodes, a standard HANNA solution with an ORP value of 240 mV was used. The potentials of all used electrodes in the standard solution did not deviate from the passport value by more than 3 mV [14].

### 3. Results and discussion

Numerous methods are known for producing anthocyanin dyes, the main methods of which are stages 1: extraction, dissolution using various solvents (water, ethanol, glycerin, mixtures thereof), 2: adsorption on adsorbents (clay, talc, synthetic products — Styrosorb — MHDE-100), and 3: evaporation under normal conditions or vacuum. However, in all the natural dyes, including anthocyanin dyes, the light resistance is not high enough [15].

Fullerene, also called buckminsterfullerene, is formed from a series of carbon molecules forming either a closed cell ("buckyballs") or a cylinder (carbon "nanotubes") [16].

It is a modern carbon nanomaterial and the fourth allotropic modification of carbon. From the main structures of the known fullerenes presented in (Fig. 3), fullerene C<sub>60</sub> was selected for experiments [17].

Fullerene C<sub>60</sub> is the most studied molecule of the fullerene class, which is a closed sphere consisting of sixty carbon atoms. The Nobel Prize (1996) was awarded for the discovery of a new allotropic modification of carbon (1985). Fullerenes are one of the forms of carbon existence in the form of a simple substance, which has become the "signature substance" of nanotechnology and nanochemistry [18]. Fullerenes are conjugated carbon structures with a high electron density, in which the C=C bond, which is a common side for two hexagons, is 1.39 Å, and the C-C bond, common for a six- and pentagon, is longer and equal to about 1.44 Å. [19]. In natural conditions, fullerene is part of a mineral called shungite (found in Karelia) [20].

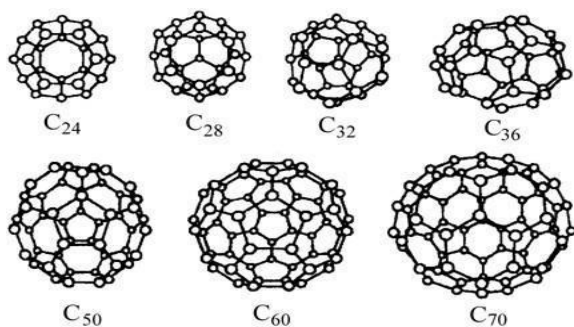


Fig. 3. Models of the structure of fullerene molecules  $C_{24}$ - $C_{70}$

Carbon in the shungite rock forms a matrix in which highly dispersed silicates with a particle size of 0.5-microns are distributed (Fig. 4).

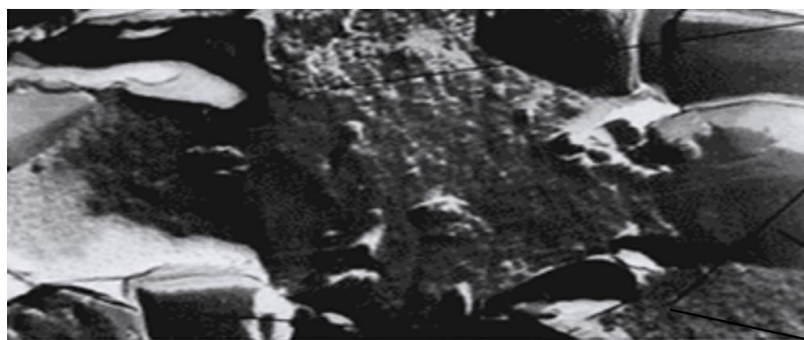


Fig. 4. Structure of a shungite rock

Due to its fundamental and technological significance, works on the effect of microwaves on the properties of water are of particular interest [24]. As a result of microwave exposure (MWE) to water, ionization of water molecules is possible, thus an atom can gain or lose an electron by changing the structure of water [25].

In experimental studies on the selection of raw materials for the isolation of natural food dyes (anthocyanins), the selection of berry raw materials was determined based on the spectral characteristics of their juice, shown in Fig. 5. It follows from Fig. 5 that solutions of anthocyanins isolated from black currant had the greatest spectral activity and intensity of light absorption (at a wavelength of 510-525 nm).

Following the objectives of the presented work, further research consisted of several stages: 1: preparation of the selected berry raw materials; 2: preparation of shungite water for extraction with an assessment of its physicochemical properties; 2:

The composition of the shungite of the Zazhoginsky deposit is represented by the following minerals: carbon (30%); quartz (45%); complex silicates (micas, chlorides) (20%), sulfites (3%) [21].

Light stabilization is a special process in the production of resistant dyes, which is complex, multi-stage, and expensive. Therefore, the study of the patterns and mechanism of phototransformation of dyes in different media and under different conditions is a difficult task and belongs to fundamental research [22]. Basic principles of light stabilization: 1: the deactivation of active particles (radicals) formed during photochemical transformations of dyes; 2: light shielding (UV adsorbers); 3: extinguishing of photoexcited states of dyes [23].

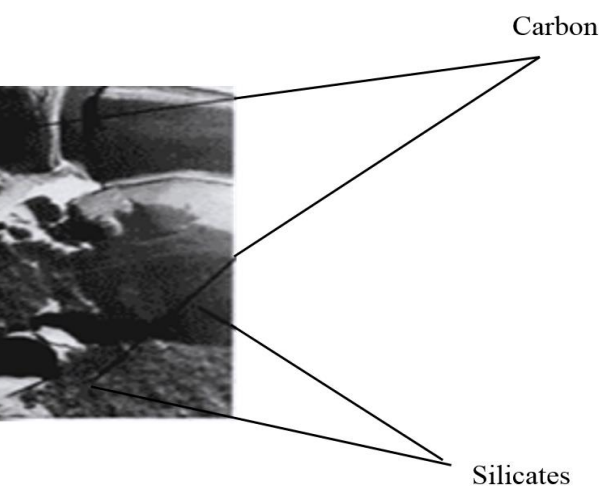
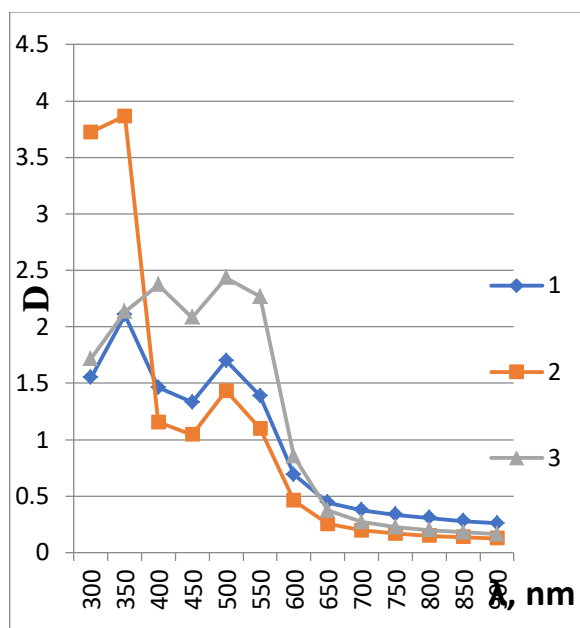


Fig. 5. Spectra of solutions of natural anthocyanins

Preparation of raw materials. The necessity of preliminary preparation of the initial crushed berry raw materials by methods of its pre-freezing and microwave (MW) processing has been proved.

The results of the selection of individual factors for the preliminary preparation of crushed raw materials (black currant) are shown in Fig. 6.

It follows from Fig. 6 that, based on a comparison of the D-optical density of solutions (at  $\lambda = 525 \text{ nm}$ ), pre-freezing of raw materials increases the yield of anthocyanin dye into the water by 1.2 times, and when exposed to MW in a household microwave oven for 5 seconds (frequency 2.45 GHz) by 1.7 times. It is noted that due to the preliminary preparation of berry raw materials by the proposed methods, additional separation of individual components of anthocyanin dye is observed. These facts indicate a weakening of the strong chemical bond between the dye and the solid phase of the raw materials [10].



Preparation of water for extraction. Water for extraction was treated for a day with crushed solid material (crushed stone fraction) of the natural mineral shungite (Zazhoginskoye deposit, Karelia), prepared according to TU 5714-007-12862296-01 and containing an allotropic modification of carbon-fullerene ( $C_{60}$ ). Water treated with shungite (shungite water), according to scientific publications, has special properties. Its medicinal properties concerning allergies, oncology, viral diseases, skin diseases, etc. have been noted and proven. We tested the possibility of its use in industrial technologies.

Determination of the properties of shungite water. Some properties of water infused with shungite have been determined, such as specific electrical conductivity, pH, ORP, bactericidal activity (Table 1).

Some acidification of such water with a simultaneous increase in electrical conductivity was established. Its antimicrobial activity, anti-spore activity concerning spores of gray, white, and black mold was proven microbiologically.

Fig. 6. The effect of preliminary preparation of raw materials on the degree of staining of aqueous extracts (1: freezing, 2: without preparation, 3: MW processing)

Table 1. Properties of treated distilled water samples

Shungite water properties	Time, sec				
	0	5	10	15	20
Electrical conductivity, Ohms <sup>-1</sup> cm <sup>-1</sup>	210 x 10 <sup>-6</sup>	330 x 10 <sup>-6</sup>	510 x 10 <sup>-6</sup>	520 x 10 <sup>-6</sup>	520 x 10 <sup>-6</sup>
pH	6.6	6	4.5	3.3	3.3
ORP, mV	158.1	170.5	189.1	189.2	158.1
Properties of water processed with MWE	Time, sec				
	0	5	10	15	20
Electrical conductivity, Ohms <sup>-1</sup> cm <sup>-1</sup>	210 x 10 <sup>-6</sup>	330 x 10 <sup>-6</sup>	510 x 10 <sup>-6</sup>	520 x 10 <sup>-6</sup>	520 x 10 <sup>-6</sup>
pH	6.6	6	4.5	3.3	3.3
ORP, mV	92.5	143.2	160.3	187.4	187.4

Extraction of dyes. Anthocyanin dye was extracted from pre-prepared crushed and processed with microwaves frozen berry raw materials with shungite water that had been treated with shungite during a day in an Aquashungite household water

filter (Novosibirsk, according to TU2627-002-0123432105-2013). The extraction time was 30 minutes. The results of the experiments are shown in Fig.7.

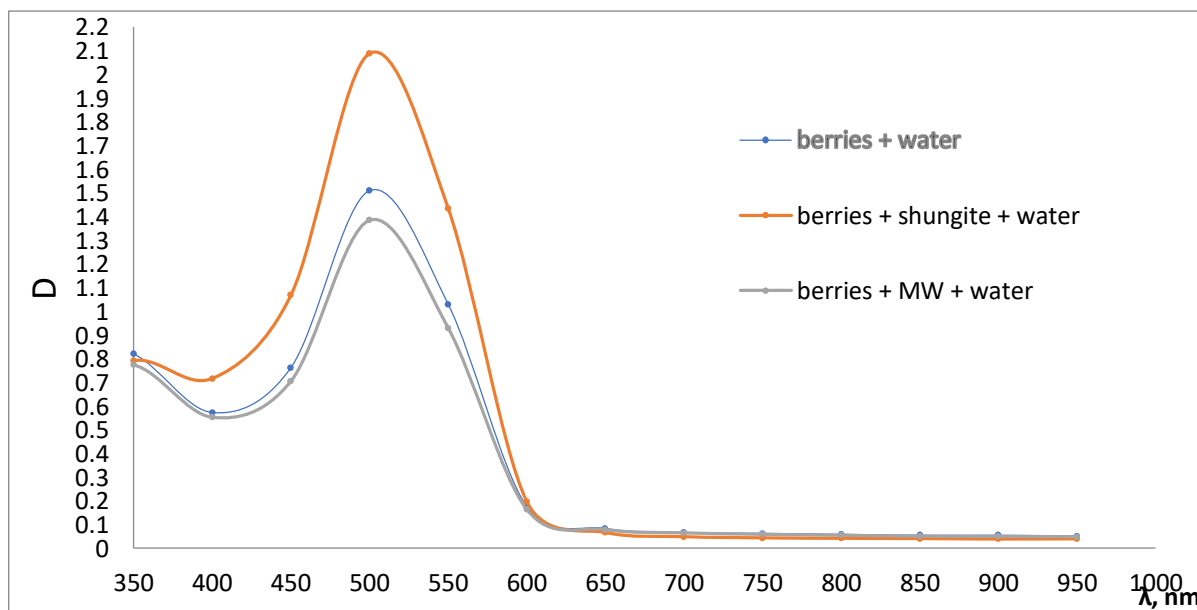


Fig. 7. Absorption spectra of berry extracts

It follows from the obtained spectra that the proposed methods of aqueous extraction of anthocyanins in the presence of fullerene contribute to increasing its effectiveness. The main extraction results are presented in Table 2.

From Table 2 it follows that the most effective is the aqueous extraction of anthocyanin dyes from

crushed frozen material with MW processed shungite water.

Adsorption of dyes. The dyes were isolated on powdered products (carbohydrates and proteins) from previously obtained extracts. The choice of such natural polymers is not accidental, because they can adsorb dyes on their surface due to heteroatoms (analogy with berry press cake as the place of the

highest concentration of dyes due to their connection with pectin, cellulose, starch).

Table 2. Influence of anthocyanin dye extraction conditions on its effectiveness

Experiment No. (item No.)	Extraction conditions	Optical density, D	The degree of increase in the dye content, %
1	Crushed frozen berry press cake, extraction on distilled water	1.40	100
2	Crushed frozen berry press cake + shungite water	2.10	150
3	Crushed frozen berry press cake + MW processed water	2.20	157

The results of the selection of the optimal adsorption time are shown in Fig. 8., from which it follows that the most rational adsorption time (an estimate for reducing the optical density of the colored solution) is 60 minutes (the lower curve). At the same time, the optical density of the extract decreased by 2 times, which corresponds to a 50% degree of separation of dyes from the raw material on potato starch. An increase in the extraction time to 90 minutes led to the phenomenon of desorption or destruction of the dye (the set of upper curves 2, 3, 1\*). Repeated extractions with fresh portions of starch from the same extract showed a slight increase in the degree of dye release (5-10%).

D

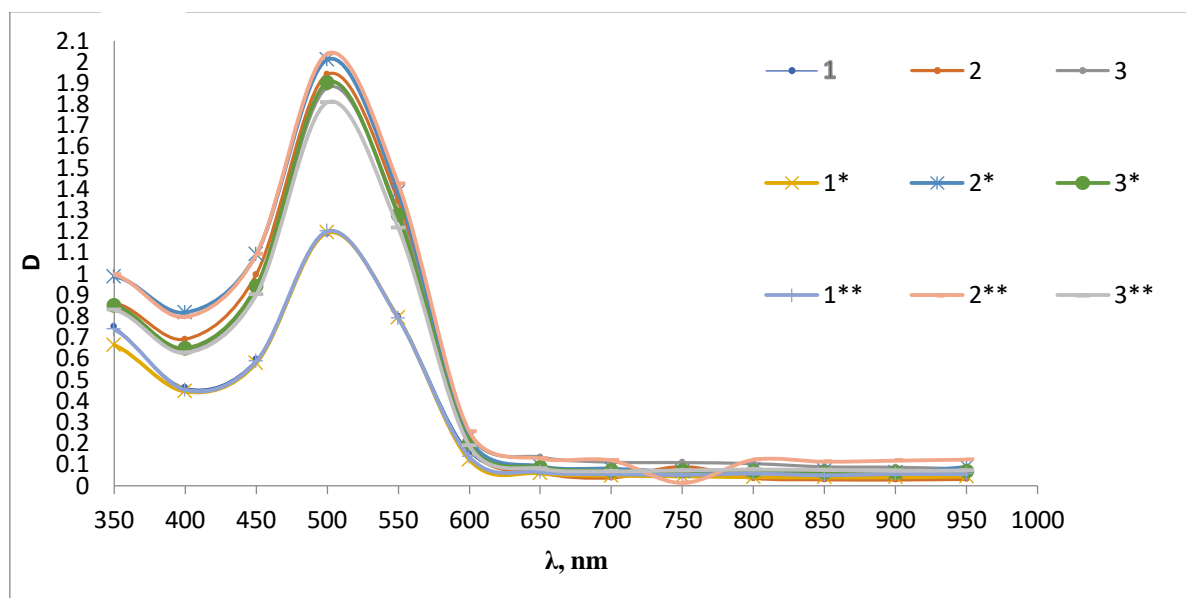


Fig. 8. Adsorption of dyes on starch at an adsorption time of 30-90 minutes

The resulting colored starch is shown in Fig. 9.



Fig. 9. Dry starch stained with anthocyanins

It follows from Fig. 9 that the colored starch is colored intensely red and the color doesn't fade for more than 12 months.

Starch dyed without fullerene retained its color for 2 months.

In addition to colored starch, other anthocyanin-colored solid powder products were obtained, namely carbohydrates (microcellulose (MCC), pectin, chitosan) and a representative of proteins (gelatin), which are presented for comparison in Fig. 10.

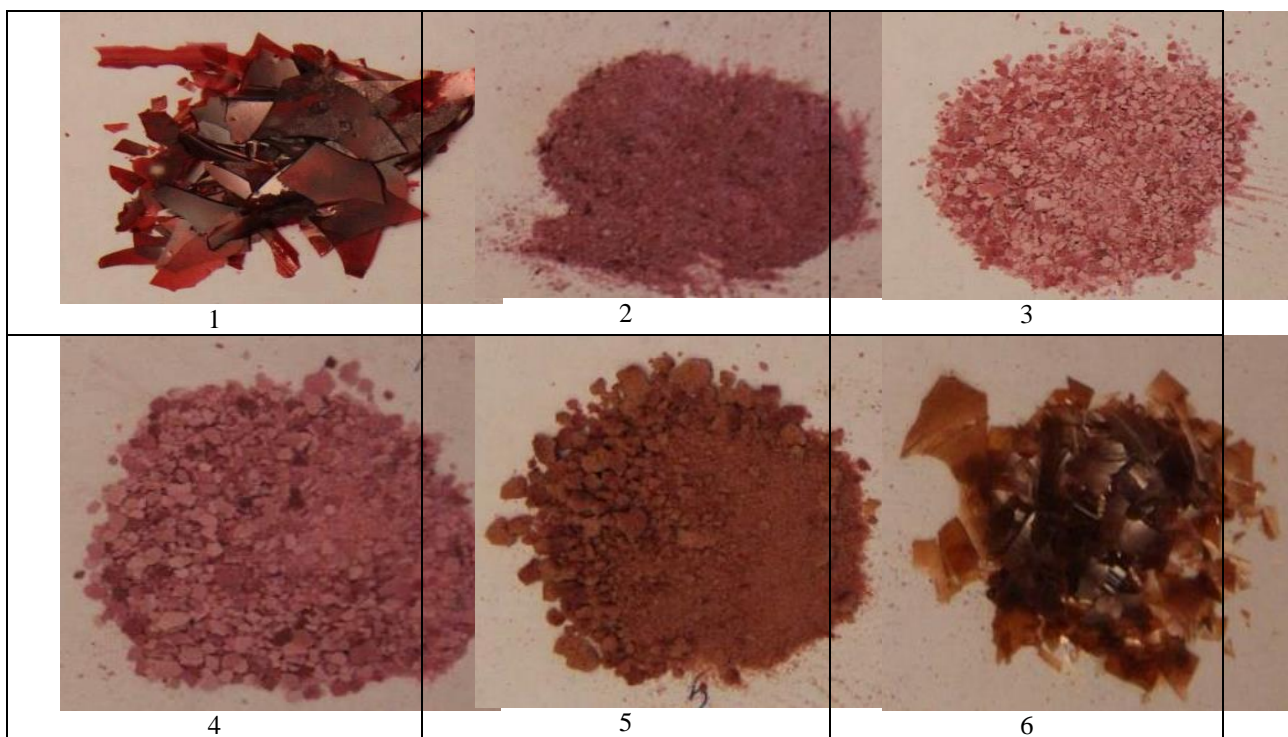


Fig. 10. Colored products: 1, 6: gelatin of different quality, 2: chitosan, 3: pectin, 4: starch, 5: MCC

The use of carbohydrates and then proteins as adsorbents is an important technique for the light stabilization of dyes.

The dye molecule is held by adsorption forces by a carbohydrate macromolecule (a model of the skin of a black currant berry). It is noted that in the case of using gelatin as an adsorbent, the brightness of its color is higher than that of carbohydrates (Fig. 13), which is explained by the special chemical structure of its macromolecules.

The resulting dry colored products were stored in the light for more than 12 months. Therefore, the found method of stable staining of carbohydrates and proteins in the presence of fullerene can be used in the food, textile, pharmaceutical industry, etc. Based on the regularities of photochemical reactions, a mechanism for photo stabilization of unstable dyes in the presence of fullerene can be proposed [26].

Based on theoretical and practical studies, a possible variant of the mechanism of adsorption of anthocyanin on starch in the presence of fullerene is proposed (Fig. 11-13), consisting of three stages: fullerene hydration (stage 1), fullerene adsorption (stage 2), and anthocyanin adsorption on starch (stage 3).

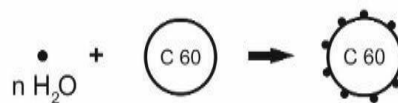


Fig. 11. Fullerene hydration stage (Stage 1)

It follows from Fig. 11 that due to its chemical structure (generalized active electron cloud), fullerene ( $C_{60}$ ) easily interacts with water molecules due to an unshared electron pair in oxygen.

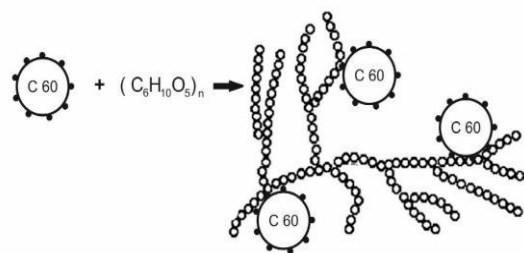


Fig. 12. Fullerene adsorption on starch (stage 2)

Further, at stage 2 (Fig. 12), hydrated fullerene is adsorbed on starch macromolecules due to hydrogen and donor-acceptor bonds.



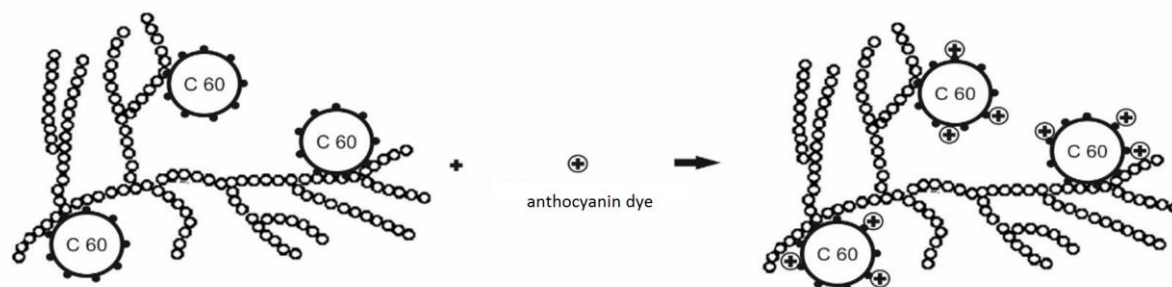


Fig. 13. Anthocyanin dye adsorption on starch (stage 3)

At the third stage (Fig. 13) of the adsorption process, positively charged anthocyanin dye molecules easily interact with fullerene molecules with increased electron density.

The photo destruction of dyes (D) can take place by three mechanisms:

Mechanism 1 begins with the absorption of daylight quanta with the formation of their activated form ( $D^*$ ), which, with further absorption of the oxygen molecule, passes into destruction products ( $DOO^*$ );

Mechanism 2 happens through the formation of hydrogen peroxide followed by oxidation of dyes;

Mechanism 3 happens through the formation of radicals with subsequent destruction of dyes:

1.  $D + \text{light quanta} = D^* + O_2 = D\ OO^*$ -destruction products

2.  $O_2 + 2\ N_2O + \text{light quanta} = 2H_2O_2; N_2O_2 + D =$  destruction products

3.  $D + HOH + \text{light quanta} = D + OH.; D\ H + OH =$  destruction products

In photochemical processes, the third mechanism of radical destruction of organic compounds is most often realized in the presence of radicals formed under the action of light quanta. Therefore, using an antiradical preparation (in this case, it is shungite water with an admixture of fullerene), the light resistance of the dye can be significantly increased.

Therefore, it can be concluded that fullerene is a new effective inhibitor of the destruction of dyes. Fullerene can deactivate the formed radicals of various structures.

#### 4. Conclusion

Based on the conducted analytical review, the most rational direction of isolation of anthocyanin dyes from available natural raw materials in the presence of an innovative nanomaterial, fullerene, which has antioxidant and antiradical properties, has been determined. To increase the efficiency of water

extraction, studies have been conducted to evaluate the methods of preliminary preparation of raw materials necessary to increase the degree of isolation of red natural dyes. A new method has been developed for the isolation and long-term preservation of anthocyanin dyes by applying them to solid forms of carbohydrates and proteins of various chemical structures in the presence of fullerene. An antiradical mechanism for increasing the light resistance of anthocyanin and betalain dyes is proposed. The resulting natural food dyes can be used to increase the range of bakery products, creating a healthy and delicious product.

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