Exploring the potential of fullerenes in food and agriculture

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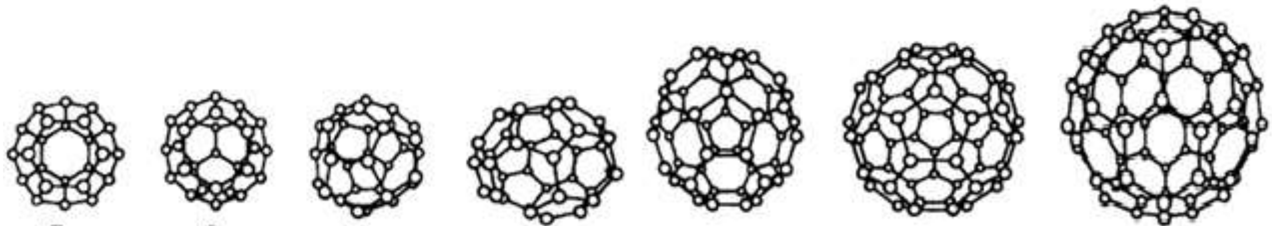
Abstract. This article investigates the prospects of using fullerenes and their compounds in the food and agricultural sectors. The study considers the biological activity of fullerenes in relation to microorganisms and biological objects, and highlights their potential in creating materials with specific microbiological properties and radioprotective capabilities relevant to food preservation and agricultural applications. The potential of hydrated fullerene solutions to enhance biological activity in nutrient media, promoting plant growth and crop quality, is also explored. Furthermore, the research examines the features of plasma synthesis of fullerenes essential for reinforcing polymer composite materials used in food packaging and agricultural equipment. A functional scheme of an automated control system for fullerene synthesis is presented, which ensures high parameter stability, real-time monitoring, and control of technological parameters, leading to maximized production of homogeneous nanostructured carbon material.

Keywords: fullerenes, food industry, agriculture, plasma synthesis, automated control system, antimicrobial properties, plant growth, composite materials, food packaging.

1 Introduction

Carbon, one of the most common elements in nature, is the basis of all organic substances and their decomposition products. Carbon is capable of forming stable covalent bonds of various types, which allows it to form a variety of allotropic forms, or modifications, differing in crystal lattice structure and, consequently, properties [1]. In the context of food and agricultural industry, bulk carbon nanostructures such as fullerenes are of particular interest. Possessing a complex of unique physical and chemical properties and small size, they allow, when used, to obtain highly functional characteristics of materials that are difficult to achieve with traditional forms of carbon [2].

Fullerenes are molecules consisting of carbon atoms connected into pentagons and hexagons by means of C-C and C=C covalent bonds, the number of which is even and can vary from 24 to more than 600. Fullerenes C_{60} and C_{70} are the most stable and therefore promising for use in the food and agricultural industries. Fullerene C_70 differs from C_{60} by inserting a band of 10 carbon atoms into the equatorial region of C60, which makes the C_{70} molecule more elongated. The structural series of fullerenes $C_{24} \div C_{70}$ is shown in Figure 1. Fullerenes containing more than 70 carbon atoms have a complex isomeric composition.



C_{24} C_{28} C_{32} C_{36} C_{50} C_{60} C_{70}

Figure 1. Structure of a number of fullerenes $C_{24} \div C_{70}$

The range of potential applications of fullerenes in the food and agricultural industries is very wide. They can be used as components of antioxidant additives, to improve the stability and shelf life of food products. Addition of $C_{60} \div C_{70}$ fullerenes to oils can significantly slow down oxidation and rancidity processes. The use of fullerenes as components of packaging materials makes it possible to create barrier, antimicrobial and biodegradable coatings [3]. The introduction of fullerenes into formulations for the treatment of agricultural machinery can increase their wear resistance and reduce friction [4]. In addition, fullerenes are being

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investigated as vehicles for the delivery of nutrients and drugs to plants and animals, and as components of sensors for quality control of agricultural products and detection of contaminants in food [5].

The aim of this work is to study the prospects of using $C_{60} \div C_{70}$ fullerenes in modern food and agricultural industry, as well as to increase the efficiency of methods of their plasma synthesis based on the use of an automated process control system.

2 Materials and methods

Soon after their discovery in the early 90s, fullerenes and their compounds started to be intensively investigated for possible applications in various processes of the food and agricultural industries. This was due not only to their special physicochemical properties, but also to their biological activity (Fig. 2).

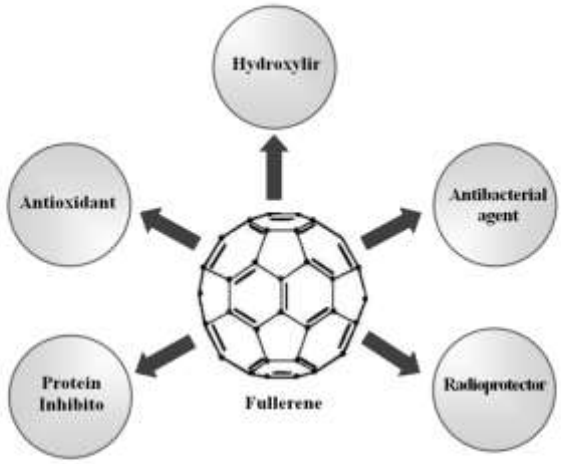

Figure 2. Biological activity of fullerenes

The biological activity of fullerenes is based on lipophilicity, electron acceptor activity and the ability to convert ordinary oxygen into singlet oxygen. Fullerenes are powerful antioxidants, surpassing known analogues many times over. Their antioxidant activity, for example, is almost 1000 times higher than that of ascorbic acid (vitamin C) [6].

Studies of fullerene compounds have shown that they have antifungal, antibacterial and antiviral activity when interacting with microorganisms and biological objects. This allows them to be used to create materials with certain microbiological properties, which is relevant for food packaging and agricultural products processing. Due to their high biochemical activity, fullerenes are able to inhibit the growth and reproduction of microorganisms. They show an increased affinity for fungal cell wall components such as β-glucan and chitin compared to bacterial cell membrane peptidoglycans. Studies have shown that fullerenes are potent inhibitors of enzymatic surface oxidation. For example, treatment of apples with an aqueous solution of fullerenes effectively suppresses rotting processes, which allows to significantly reduce losses of fruit and berry raw materials during storage and transport [7].

The unique properties of fullerenes, such as resistance to radiation, low toxicity and ability to bind free radicals arising under the influence of irradiation, determine the prospects of their use as radioprotectors, for example, to protect food products from ionising radiation.

Hydrated fullerenes are of the greatest interest for use in various industries. Fullerenes are practically insoluble in water and poorly soluble in most solvents. However, with special treatment, free fullerenes are able to form stable colloidal solutions in polar solvents, which makes it possible to obtain water-soluble forms. The main methods of obtaining aqueous dispersions of fullerenes are physical condensation - solvent replacement or extraction, chemical condensation and dispersion method [8, 9]. The coupling products of the hydroxyl group OH with the fullerene molecule is a complex in which the $C_{60,70}$ molecule is enclosed in a hydrate shell consisting of 24 (22) water molecules. The water-soluble forms of fullerenes, $C_{60,70}(O)_n(OH)_m$ fullerenols, are stable over time. They can keep their physicochemical properties and constant composition unchanged for more than two years. There are no toxic impurities in these solutions. The fullerene is embedded in the natural multilayer structure of water, where the first layer of water is firmly bound to the fullerene surface due to donor-acceptor interactions between water oxygen and electron-acceptor centres on the fullerene surface. This structure of fullerenols makes them promising for use in various sectors of the economy.

Currently, fullerenols are used to create preparations with regulatory, adaptogenic and protective functions, with the ability to enhance the transport of essential macronutrients into plants, intensify plant growth and the processes of transformation of organic and mineral compounds in the root environment. This allows to increase plant productivity and their resistance to oxidative stress, improve the quality of products [10].

Hydrated C_{60} solution can also act as an organiser of various reactions and processes regulating the formation and neutralisation of reactive oxygen species, increase biological activity, which allows its use in nutrient media for growing microorganisms, in media for cultivation and storage of cell cultures, creation of products with special, highly ordered structural characteristics, etc. [11].

Fullerenes are promising reinforcing fillers for the creation of polymer composite materials used in food packaging and equipment. Addition of C_{60} fullerenes to high-pressure polyethylene and polypropylene in the amount of only 0.01% results in the ordering of the crystal structure and reduction of the degree of amorphous polymers. This allows to obtain composite material with improved physical and mechanical properties in comparison with traditional fillers, practically without weight increase. Introduction of fullerenes $C_{60} \div C_{70}$ into the matrix of polymer resins in the amount of 0.01 - 5% allows to obtain lightweight composite materials with a special structure, possessing a complex of improved properties (increased rigidity and stability of shape, glass transition temperature, fire resistance, electrical conductivity, etc.) [12, 13].

Various technologies and synthesis methods are used to obtain the starting material necessary for the creation of polymer composites and hydrated solutions of fullerenes [14, 15]. One of the most widespread methods for the synthesis of high-quality fullerenes is the method of plasma sublimation of graphite raw materials in an inert gas environment with subsequent deposition of the formed structures on a cooled surface [16, 17]. The method differs by the fact that, under different technological conditions of synthesis and catalysts used, it is possible to obtain a variety of fullerenes of the C50-C_{92} series with different yields and shapes of the final product. Stability of technological parameters of synthesis directly affects the yield and quality of the obtained material.

In the course of experimental studies carried out by the authors using the unit of electric arc synthesis of carbon nanostructures in inert gas environment with the use of graphite raw materials with the content of impurities < 0.02% without the use of a catalyst, carbon black containing ~15% of a mixture of fullerenes $C_{52} \div C_{90}$ was obtained. Stable parameters were maintained during synthesis: constant current I = 350 A, electrode voltage 25 V, helium pressure in the synthesis chamber 53.3 kPa. Under these technological conditions, the weight composition of the obtained fullerene mixture is presented in Table 1. The data were obtained on the basis of mass spectrometric analysis presented in Figure 3.

Table 1. Weight composition of the resulting mixture of fullerenes

Fullerenes	$C_{50} \div C_{58}$	C_{60}	$C_{62} \div C_{68}$	C_{70}	$C_{72} \div C_{92}$
Weight %	14,69	63,12	5,88	13,25	3,06

The microstructure of the resulting fullerene carbon black with an increase of x50 000, consisting of fullerenes and modified graphite is shown in figure 4.

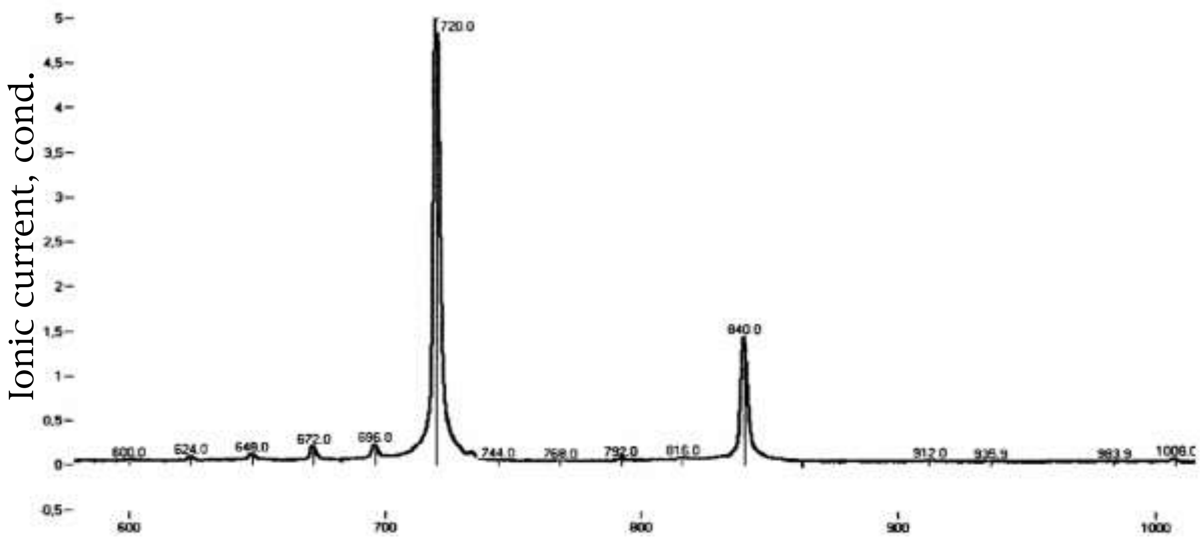

Figure 3. Fullerene mixture mass spectrometry

Plasma synthesis of fullerenes is characterized by a high rate of processes, high quality of the resulting product and the possibility of organizing a continuous process. The peculiarity of this technology is the need to accurately maintain the specified technological parameters in the synthesis process, which directly affect the characteristics of the final material.

Due to the transience of the process, the use of a manual method for controlling the synthesis of carbon nanostructures is possible only under experimental conditions. The spread of the current strength in this case can reach up to 50% of the required value, which leads to low quality and yield of the final product, with a spread in a wide range of the resulting structures and sizes.

The use of an automated synthesis control system makes it possible to achieve the constancy of the necessary operating parameters in the plasma and ensure the stability of the technological conditions of the process, which is important in industrial production.

3 Results

The developed functional scheme of the automated control system for the synthesis of fullerenes by the method of plasma sublimation of graphite is shown in figure 5. The system performs automatic control and control with a high degree of accuracy and consistency of all the main technological parameters of the process, which provides the necessary stable conditions for the plasma synthesis of fullerenes in the working chamber and increases the efficiency of the entire process as a whole [18].

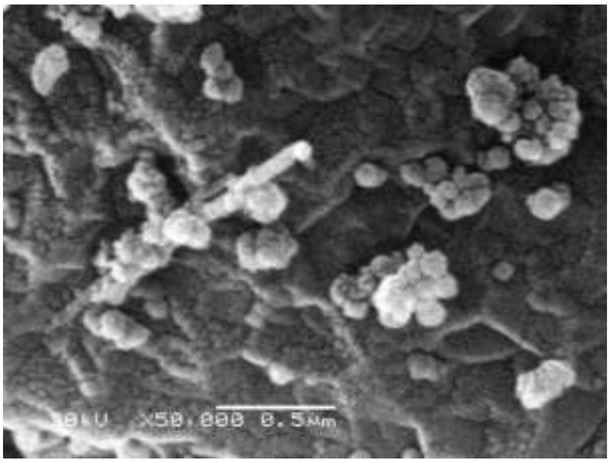

Figure 4. Microstructure of fullerene carbon black

The working chamber in which the synthesis process takes place is a sealed chamber made of high-strength steel, equipped with a lid with a lifting mechanism. Graphite electrode holders are installed inside the chamber, equipped with high-power current supply devices and a mechanism for moving the anode. The chamber is equipped with a water cooling system, an air pumping system and an inert gas supply. Maintaining a stable arc in the process is carried out by regulating the interelectrode distance.

All information about the process is transmitted via an analog-to-digital converter (ADC) to a personal computer (PC). The received data is processed by the PC information system, and based on their analysis, a control effect is developed. The control of the process of electric arc synthesis of fullerenes consists in maintaining a given current strength by changing the distance between graphite electrodes. To move the evaporated electrode (anode), a discrete control signal is fed through a digital-to-analog converter (DAC) to the input of a DC motor through a step-down reducer 3 to a stepper actuator that allows the anode to be positioned with the necessary accuracy. During the synthesis process, the pressure of the buffer medium in the synthesis chamber, temperature parameters and voltage on the electrodes are regulated. The measured process parameters are displayed in real time in a structured way on the PC screen and automatically saved. For this purpose, a package of process information software was developed, which also makes it possible to determine the technological conditions for the highest yield of the final material, depending on the type of used graphite raw materials [18].

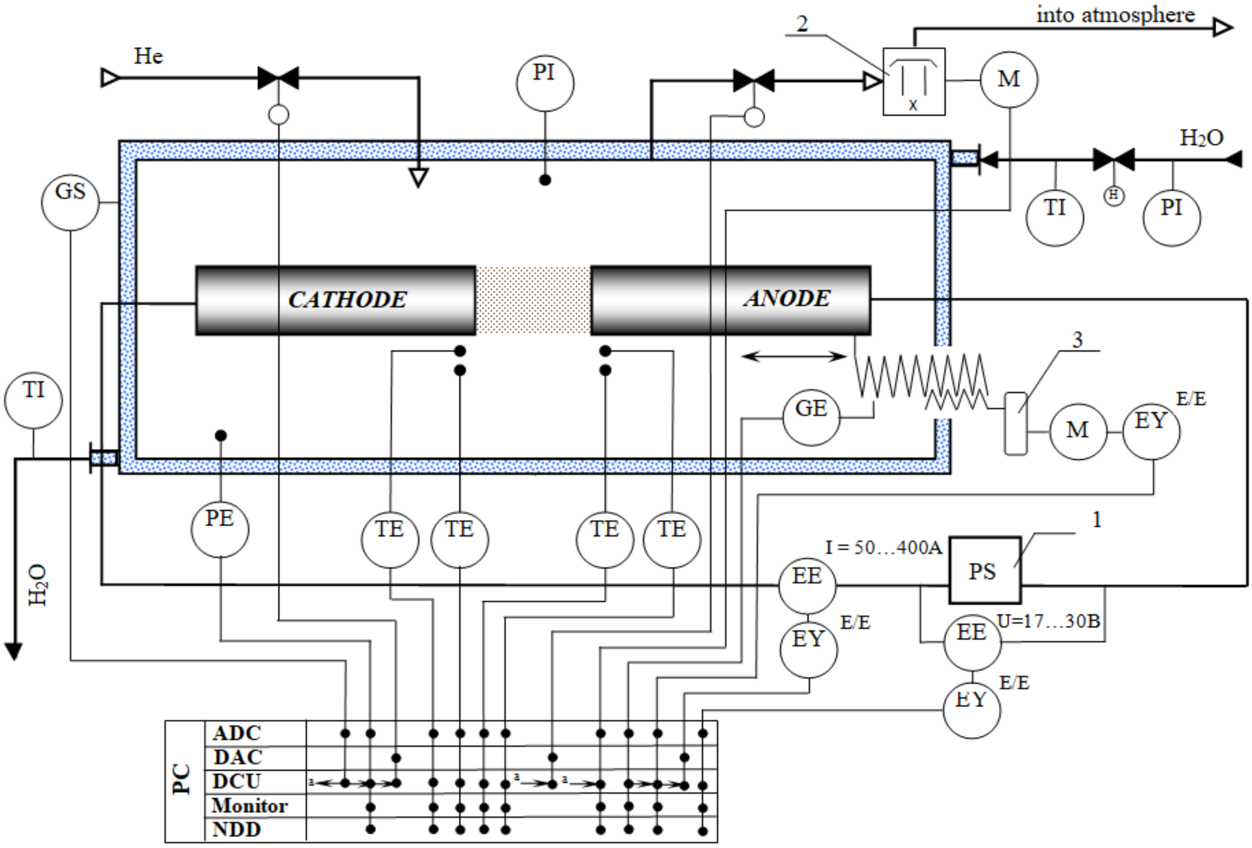

Figure 5. Functional diagram of an automated control system for the synthesis of fullerenes: 1 – power supply; 2 – diffusion pump; 3 – executive device; PC – computer; ADC – analog-to-digital converter; DAC – digital-to-analog converter; DCU – digital control unit; NDD – hard disk drive.

The developed functional scheme of the automated control system for fullerenes synthesis by plasma sublimation of graphite allowed to achieve a significant increase in the stability and accuracy of the technological process (Figure 5). The key element of the system is the precision control of the interelectrode distance, which directly affects the stability of the arc discharge and, consequently, the yield and quality of the synthesised fullerenes. Automation ensures maintenance of the specified synthesis parameters (current, voltage, inert gas pressure, cooling temperature) with a deviation not exceeding ±1%, which is significantly superior to manual control. This, in turn, leads to an increase in the yield of the target product (fullerenes C60 and C70) by 15-20% compared to non-automated methods, which makes the process more cost-effective for further use in various industries, including agricultural.

During the optimisation of the technological process using the developed mathematical model it was found that the optimal ratio of components of graphite raw materials for obtaining fullerene mixture with predominance of C60 is 95% of pure graphite and 5% of graphite with addition of nickel catalyst. The optimum parameters of plasma synthesis are achieved at a current strength of 360 ± 2 A, voltage of 26 ± 0.5 V, helium pressure of 55 ± 1 kPa and cooling water temperature of 20 ± 1 °C.

In addition to optimising the synthesis process, considerable effort has been devoted to investigating the application of the resulting fullerenes in the agricultural industry, in particular to improve crop yields and crop quality characteristics. For this purpose, field tests were carried out. Winter wheat and sunflower as some of the most important agricultural crops were chosen as research objects. Fullerenes were applied in the form of aqueous solution with concentrations of 0.001-0.01 mg/litre. The following treatment methods were used: pre-sowing seed treatment (wheat) and treatment of crops in the phase of 3-5 leaves (sunflower) by spraying a solution of fullerenes with a flow rate of 200 litres/ha. Control groups of seeds and crops were treated with distilled water. The studies were carried out in threefold repetition, which allowed obtaining statistically reliable data.

The results of the field trials revealed a positive effect of fullerenes on growth, development and, as a consequence, on crop yields. Thus, the yield of winter wheat in the experimental plots treated with fullerenes increased by 14%, reaching 4.3 t/ha, compared to 3.8 t/ha in the control plots. In addition to the increase in yield, there was also an improvement in grain quality parameters, in particular, an increase in protein content by 1.2% and gluten content by 1.5%. Similar results were obtained for sunflower, where fullerene treatment resulted in an 11% increase in seed yield (2.8 t/ha vs. 2.5 t/ha in the control) and a 0.8% increase in seed oil content. There was also observed an increase in resistance of fullerene-treated plants to such common diseases as powdery mildew (wheat) and false powdery mildew (sunflower), which allows reducing the use of chemical plant protection products. Thus, the introduction of the developed technology for the synthesis of fullerenes and their subsequent application in the agricultural industry opens up broad prospects for increasing the efficiency of agricultural production and improving the quality of manufactured products.

4 Conclusion

The possibilities of practical application of fullerene C_{60} ÷ C_{70} in the creation of new materials necessary for industrial equipment and technological processes are considered.

The biological activity of fullerenes in interaction with microorganisms and biological objects allows them to be used to create materials with specific microbiological properties, radioprotectors. Hydrated solutions of fullerenes make it possible to increase the biological activity of nutrient media during the cultivation of microorganisms and the creation of products with special characteristics, to improve the quality of manufactured products. Fullerenes are a promising reinforcing filler for the creation of polymer composite materials. Introduction of fullerenes C_{60} ÷ C_{70} into the matrix of polymer resins in the amount of 0,01 ÷ 5 % makes it possible, practically without increasing the weight, to obtain lightweight composite materials with a special structure endowed with a complex of improved properties.

The method of plasma synthesis of fullerenes used for reinforcement of polymer resins and hydrated solutions is considered. A functional scheme of an automated control system for the synthesis of fullerenes is proposed, which allows obtaining the largest amount of homogeneous nanostructured carbon material at the output, due to the high stability of parameters, monitoring and archiving of technological parameters in real time.

The results of field trials convincingly demonstrate the potential of fullerenes application in agriculture. Increased yields of winter wheat and sunflower, as well as improved quality characteristics of products, combined with increased plant resistance to diseases, allow us to consider fullerenes as a promising means of improving the efficiency and sustainability of agricultural production. Further research is aimed at optimising the concentrations and methods of application of fullerenes for different crops and regions, as well as at studying the mechanisms of their effect on plants at the molecular level, which will make it possible to reveal more fully the potential of these unique nanomaterials.

References

1. G.V. Abramov, A.N. Gavrilov, Modeling of carbon nanostructures synthesis in low-temperature plasma, Advanced Materials & Technologies. **1** (2019) 21–34.
2. S.V. Mishchenko, A.G. Tkachev, Carbon nanomaterials. Production, properties, application, Mechanical engineering, Moscow. (2008).
3. B.M. Ginzburg, M.V. Baidakova, O.F. Kireenko, D.G. Tochilnikov, A.A. Shepelevsky, The influence of fullerene C60, fullerene carbon black and other carbon materials on the boundary sliding friction of metals, Journal of Technical Physics. **70(12)** (2000) 87–97.

4. M.V. Uspenskaya, N.V. Sirotinkin, V.A. Gorsky, Yu.G. Goloshchapov, Compositions based on acrylate copolymers and fullerenes, Journal of Applied Chemistry. **79(5)** (2006) 870–872.
5. E.V. Anufrieva, M.G. Krakovyak, T.D. Anan'eva, T.N. Nekrasova, R.Yu. Smyslov, Interaction of polymers with fullerene C 60, Physics of the Solid State. **44(3)** (2002) 461–462.
6. A.L. Bychkov, E.I. Ryabchikova, K.G. Korolev, V.A. Bukhtoyarov, Synthesis of silver nanoparticles stabilized by the products of mechanically assisted hydrolysis of yeast biopolymers, Proceedings of Voronezh State University of Engineering Technologies**, 81(1)** (2019) 238–246.
7. T.V. Shevchenko, Yu.V. Ustinova, V.P. Yustratov, M.S. Bezrukov, D.E. Vasilenko The use of fullerene in the storage and drying of apples, Storage and processing of agricultural raw materials. **2** (2020) 85–93.
8. N.O. Mchedlov-Petrosyan, Solutions of fullerene C60: colloidal aspect, Chemistry, physics and Surface technology. **1(1)** (2010) 19–37.
9. K.N. Semenov, N.A. Charykov, V.A. Keskinov, Fullerenol Synthesis and Identification. Properties of Fullerenol Water Solutions, Journal of Chemical & Engineering Data. **56** (2011) 230–239.
10. G.G. Panova, K.N. Semenov, O.A. Shilova et al., Water-soluble derivatives of fullerenes and silica nanocompositions as promising nanomaterials for use in crop production, Agro physics. **4** (2015) 37–48.
11. A.I. Mashanov, G.N. Churilov, N.N. Tipsina et al., Intensification of baking yeast with the help of water-soluble fullerene, Bulletin of KrasGAU. **2** (2020) 108–116.
12. L. Xie, F. Xu, F. Qiu et al., Single-Walled Carbon Nanotubes Functionalized with High Bonding Density of Polymer Layers and Enhanced Mechanical Properties of Composites. Macromolecules. **40(9)** (2007) 3296–3305.
13. P.M. Ajayan, J.M. Tour, Material Science: nanotube composites. Nature. **447** (2007) 1066–1068.
14. A.N. Gavrilov, E.A. Pologno, A.N. Ryazanov, Analysis of synthesis methods and industrial production of carbon nanotubes, FES: Finance. Economy. Strategy. Series: Innovative Economy: Human Dimension. **6** (2010) 14–19.
15. A.V. Makunin et al., Technological aspects of nanostructure synthesis by electric arc and gas pyrolytic methods, Physics and chemistry of materials processing. **6** (2010) 38–41.
16. A.E. Dutlov, V.M. Nekrasov, A.G. Sergeev, V.P. Bubnov, I.E. Kareev, Electric arc synthesis of soot with a high content of higher fullerenes in a «parallel arc», Journal of Technical Physics. **86(12)** (2016) 99–103.
17. I.E. Kareev, V.P. Bubnov, D.N. Fedutin, High-performance electric arc reactor for the synthesis of soot with a high content of endohedral metallofullerenes, Journal of Theoretical Physics. **79(11)** (2009) 134–137.
18. A.N Gavrilov, N.V. Sukhanova, A.E. Emelyanov, A.V. Ivanov, Fullerene production management system used for creation of hydrated solutions, IOP Conference Series: Earth and Environmental Science. **640** (2021) 062010.