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DEVELOPMENT OF ANTIMICROBIAL PACKAGING MATERIALS FOR FOOD PRODUCTS BASED ON COPPER NANOPARTICLES

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In the process of storage and delivery, food products are subjected to physical changes, resulting in moisture exchange between the product and the environment, mechanical damage, chemical processes occurring in the product itself, as well as microbiological damage. The use of packaging materials on the basis of polyolefins, reduce the influencing factors leading to rapid corruption of food products. However, by their nature, polyethylene and polypropylene films do not have antimicrobial properties. Therefore, in order for the packaging based on them to protect the product from microbiological damage, various technological techniques are used for the processing of packaging, as well as the introduction of special antimicrobial agents into the composition of the film. The present study developed a method of synthesis of copper oxide nanoparticles stabilized with gelatin and pectin. The synthesis was carried out by direct chemical sedimentation. Copper chloride was used as a precursor to the synthesis of copper oxide. Gelatin and pectin were used as stabilizers. Gelatin and pectin were used as a stabilizer as an environmentally friendly component of the film. In addition, consumers are interested in innovative, economical, harmless and effective food packaging materials.

The results showed that CuO nanoparticles, stabilized with gelatin and pectin, have a high potential for use in food packaging - both as a stand-alone nanoplane and as part of other packaging materials.

Keywords: CuO nanoparticles, gelatin, pectin, polylactide, antimicrobial, packaging.

МИКРОБҚА ҚАРСЫ ТАҒАМДЫҚ ҚАПТАМА МАТЕРИАЛДАРЫН МЫС НАНОБӨЛШЕКТЕРІНІҢ НЕГІЗІНДЕ ӘЗІРЛЕУ

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Сақтау және сату процесінде тамақ өнімдері физикалық өзгерістерге ұшырайды, нәтижесінде өнім мен қоршаған орта арасында ылғал алмасу, механикалық зақымдану, өнімнің өзінде болатын химиялық процестер, сондай-ақ микробиологиялық бүліну пайда болады. Полиолефиндерге негізделген орау материалдарын қолдану әсер етуші факторларды азайтуға мүмкіндік береді, бұл тағамның тез бұзылуына әкеледі. Алайда, табиғаты бойынша полиэтилен және полипропилен пленкалары микробқа қарсы қасиеттерге ие емес. Сондықтан, олардың негізінде қаптама өнімді микробиологиялық бұзылудан қорғау үшін қаптаманы өңдеудің әртүрлі технологиялық әдістері, сондай-ақ пленкаға, арнайы микробқа қарсы агенттерге кіріспе қолданылады. Бұл зерттеуде желатин мен пектинмен тұрақтандырылған мыс оксидінің нанобөлшектерін синтездеу әдісі жасалды. Синтез тікелей химиялық тұндыру арқылы жүзеге асырылды. Мыс оксидін синтездеу үшін прекурсорлар ретінде мыс хлориді қолданылды. Тұрақтандырғыш ретінде желатин мен пектин қолданылды. Желатин мен пектин экологиялық тұрақтандырғыш өнім ретінде қолданылды. Сонымен қатар, тұтынушылар инновациялық, үнемді, экологиялық таза және тиімді азық-түлік қаптама материалдарына қызығушылық танытуда.

Нәтижелер желатин мен пектинмен тұрақтандырылған CuO нанобөлшектерінің азық - түлік қаптамасында-тәуелсіз нанопленка ретінде де, басқа орау материалдарының бөлігі ретінде де пайдалану мүмкіндігі жоғары екенін көрсетті.

Түйін сөздер: CuO нанобөлшектері, желатин, пектин, полилактид, микробқа қарсы, орау.

РАЗРАБОТКА АНТИМИКРОБНЫХ УПАКОВОЧНЫХ МАТЕРИАЛОВ ДЛЯ ПИЩЕВЫХ ПРОДУКТОВ НА ОСНОВЕ НАНОЧАСТИЦ МЕДИ

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В процессе хранения и реализации пищевые продукты, подвергаются физическим изменениям, в результате которых происходит влагообмен между продуктом и окружающей средой, механическим повреждениям, химическим процессам, протекающим в самом продукте, а также микробиологической порче. Применение упаковочных материалов на основе полиолефинов, позволяют снизить воздействующие факторы, приводящие к быстрой порче пищевых продуктов. Однако по своей природе полиэтиленовые и полипропиленовые пленки не обладают антимикробными свойствами. Поэтому для того, чтобы упаковка на их основе защищала продукт от микробиологической порчи, применяются различные технологические приемы по обработки упаковки, а также введение в состав пленки, специальных антимикробных агентов. В настоящем исследовании был разработан метод синтеза наночастиц оксида меди, стабилизированных желатином и пектином. Синтез осуществлялся путем прямого химического осаждения. В качестве предшественников для синтеза оксида меди использовались хлорид меди. В качестве стабилизатора использовался желатин и пектин. Как экологически продукт в качестве стабилизатора использовался желатин и пектин. Кроме того, потребители заинтересованы в инновационных, экономичных, экологически чистых и эффективных упаковочных материалах для пищевых продуктов.

Результаты показали, что наночастицы CuO, стабилизированные желатином и пектином, обладают высоким потенциалом для использования в упаковке пищевых продуктов - как в качестве самостоятельной нанопленки, так и в составе других упаковочных материалов.

Ключевые слова: наночастицы CuO, желатин, пектин, полилактид, антимикробная, упаковка.

Introduction. The issue of healthy and high-quality nutrition is global. In developing countries, this problem is linked to underdeveloped agriculture and processing.

The high rate of urbanization has forced the population of large cities to switch to industrial methods of food supply. Such methods require various measures aimed at significantly extending the shelf life of food. This constantly leads to a decrease in the nutritional value of foodstuffs. As the population continues to grow, these challenges will have an increasing impact on the global food distribution system, creating imbalances between regions with varying levels of economic development.

There are various ways to address the above challenges: agricultural development, improved food supply chains, sustainable production and consumption. An important factor in ensuring food security is the development of methods to increase the shelf life of food products without significantly reducing their quality. Such methods for extending shelf life include the use of antimicrobial packaging. Antimicrobial packaging is made by modifying traditional packaging to provide protection against the growth of pathogens during food storage.

Nanoparticles are often used in the food industry to create antibacterial films [1, 2]. Research is currently under way to develop antimicrobial packaging materials derived from various nanoparticles, including CuO [3-5]. Nanopackets can be applied to food products by wrapping, grinding, brushing or spraying to provide a selective barrier against the movement of gases, moisture and dissolved materials, as well as protection against mechanical damage [6, 7]. The main development is aimed at obtaining nanoparticles with subsequent surface treatment of finished packaging materials. According to Kamran Tahir, Dipranjan Laha, Arindam Pramanik, the activity of nanoparticles depends on the shape and their dispersion. The stabilization of nanoparticles is an important aspect in the design of food packaging with nanocomposites.The bactericidal activity and migration of nanoparticles into the product depends on the method of synthesis [8] and determines the stability of nanoparticles in the polymer composition of packaging materials. With high stability, migration of CuO nanoparticles into the product will be eliminated, which guarantees no toxicity of the packaging material. The safety of food products during their long-term storage is influenced by a wide range of factors: adverse influence of the external environment, processes of natural corruption due to natural biochemical and chemical reactions, development of microorganisms. Microbiological damage is one of the most significant factors affecting the preservation of the quality of foodstuffs, both of plant and animal origin.

Microbiological stability can be achieved in various ways: by adding preservatives to the product, using special storage technologies, use of special packaging, etc. Often many methods of preventing microbiological damage are associated with the influence on the biochemical processes of the life of living organisms. Along with the effects on microorganisms, these methods can have a significant effect on a person whose body functions according to similar biochemical patterns. Thus, the use of preservatives reduces the quality of the product, use of special technologies can also lead to a significant loss of nutritional value and significantly increase the cost of products. One of the most promising directions to increase the shelf life of foodstuffs is the use of special packaging materials that can protect the product from negative environmental factors, as well as reduce the rate of microbiological damage.

The aim of this work is to development of a method for the synthesis of CuO nanoparticles stabilised with gelatin and pectin, to study the possibility of their using in food packaging to protect against microbiological spoilage and increase the storage life.

Materials and methods. *CuO Nanoparticles Synthesis Method.*

Reagents: Copper (II) 2-water chloride (Sigma-Aldrich Pty Ltd, Merck KGaA branch, Darmstadt, Germany), gelatin (Segma-Aldrich Ptys Ltd, merck KGAA subsidiary, DARMSTAD, Germany); sodium hydroxide (Shandong Zhoushun International Trade Co., Ltd); ascorbic acid-L (SIGMA-ALDRICH PTY Ltd, MERCK KGA A branch, darmstad, Germany) and pectin (Jiaxing Renze Import & Export Co., Ltd.).

CuO nanoparticles, stabilized with gelatin and pectin, were polluted by direct chemical sedimentation. Copper chloride was used as a precursor to CuO nanoparticles (II). Pectin and gelatin acted as a stabilizer, as a restorative used ascorbic acid, sodium hydroxide - as a sediment. Distilled water was used as a reaction medium.

CuO nanoparticles stabilized with gelatin and pectin were obtained by the following procedure: 0.03 g of precursor (copper chloride), 0.03 g of gelatine and 0.1 g of ascarbic acid, dissolved in 90 ml of reaction medium (distilled water), a similar procedure was performed with pectine. The resulting solution was heated to boil with constant mixing and an additional 0.5% solution of NaOH was added to pH-10. The sample was mixed for 2-3 minutes, cooled to room temperature, mixed at room temperature for 20 minutes. As a result, copper oxide nanoparticles were produced. The phase of obtaining nanoparticles is an important component of the work on the creation of nanocomposite packaging materials, because it is the nanoparticle that gives the newly obtained packaging unique properties.

For the preparation of packaging material modified by CuO nanoparticles, polylactic film was used, which is often used in the production of eco-packages. As a test sample, ordinary polylactic film from ECO Prodacts Group (Astana) was taken.

As part of the development of nanoparticles preparations - visual evaluation, microphotography of samples of CuO nanoparticles and data on the elemental composition were obtained with the scanning electron microscope INTEGRA TERMA and integration of probe and optical microscopy and spectroscopy, ASM - Raman - SBOM - TERS [9]. The samples were dried for study. The samples were prepared as follows: a two-sided conductive carbon tape was glued to the standard toolboard. CuO powder was applied to the conductive carbon tape. They then applied a carbon coating about 10 nm thick. The pH was measured using the Testo 206 ph1 pH meter using a silver chloride combined electrode.

Microbiological analysis methods were used to study the antimicrobial effectiveness of polylactide films modified with CuO nanoparticles on bread shelf life.

The effects of polylactid films modified by CuO nanoparticles on the quality and shelf life of bread were studied.

For the experiment they took white wheat bread produced by ”Aksai nan” (Almaty). The shelf life at the time of purchase was 3 days. In order to study the initial parameters of the bread on the day of beginning of the experiment, slices weighing 50±0.2g corresponding to the number of experimental films were cut.

The bread samples were stored in the SCTC TS-1/80 SPU thermostat at 25 ± 1°C for 120 ± 3 hours of the experiment. After the time passed, microbiological analysis was carried out. The analysis was carried out according to GOST 10444.12-2013 Microbiology of food and animal feed. Methods of detection and counting of yeast and mold mushrooms [10].

Results and discussion. The color of nanoparticles is an important qualitative characteristic, because it can characterize the size of particles and their chemical composition. The reason for the difference in colour of colloid nanoparticles solutions is different: the nature of the dispersion phase and the disspersion medium, particle dispersiveness, shape and structure. All these factors affect not only the absorption of light in the solution, but also its dispersion. Even a slight change in the color of the solution may indicate a change in particle size and chemical composition. Figure - 1 shows solutions of silver nanoparticles obtained by different methods and having different sizes.

Fig. 1 - Appearance of copper nanoparticles solutions

The optical spectrum of nanoparticles and nanomaterials solutions is no less important qualitative characteristic than the color of the solution. The method of optical spectroscopy is based on the measurement of particle absorption of the electromagnetic radiation of the optical range. Figure 2, 3, 4 shows the optical spectra for the colloidal solutions studied.

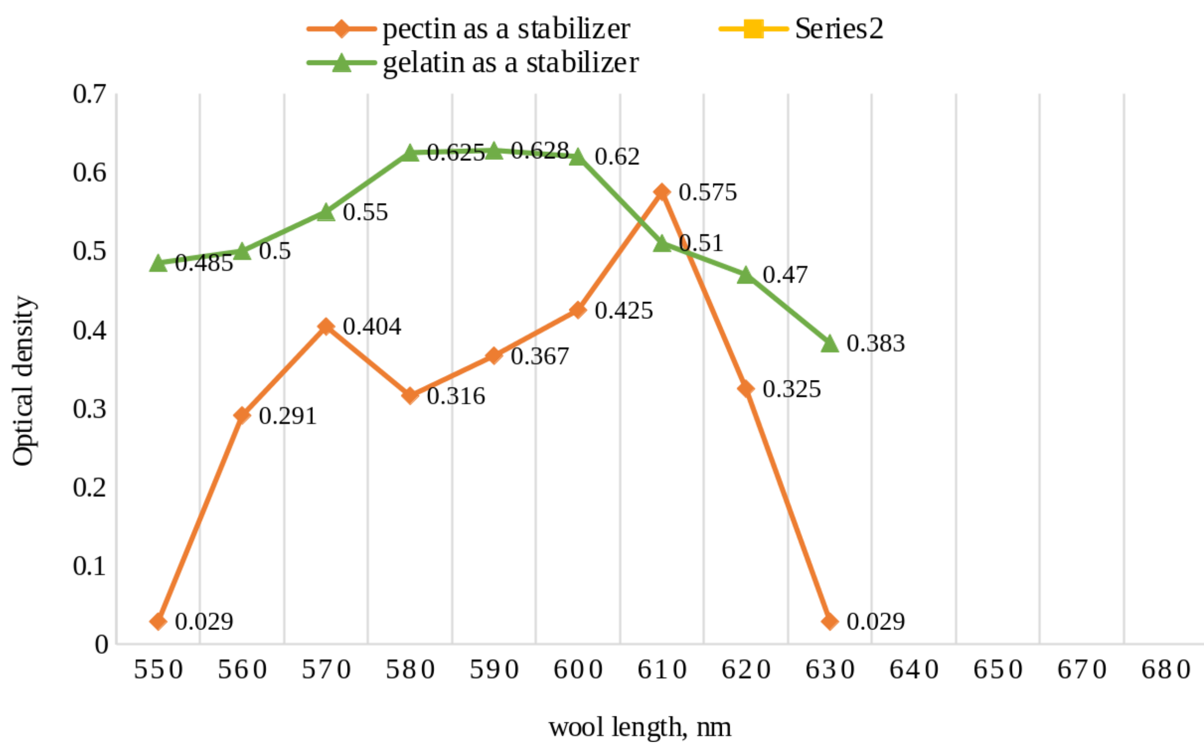


Fig. 2 - Graph of obtained data on spectroscopic photometer Jenway 6705

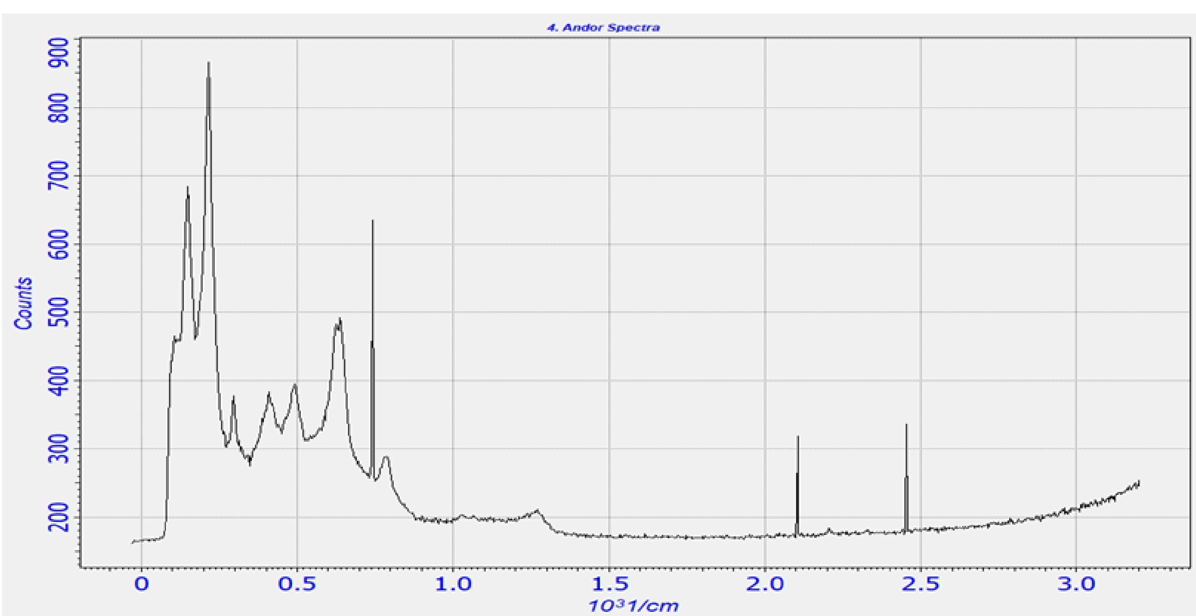


Fig. 3 - Optical spectrum of copper nanoparticles using gelatin as a stabilizer in exhaust solutions

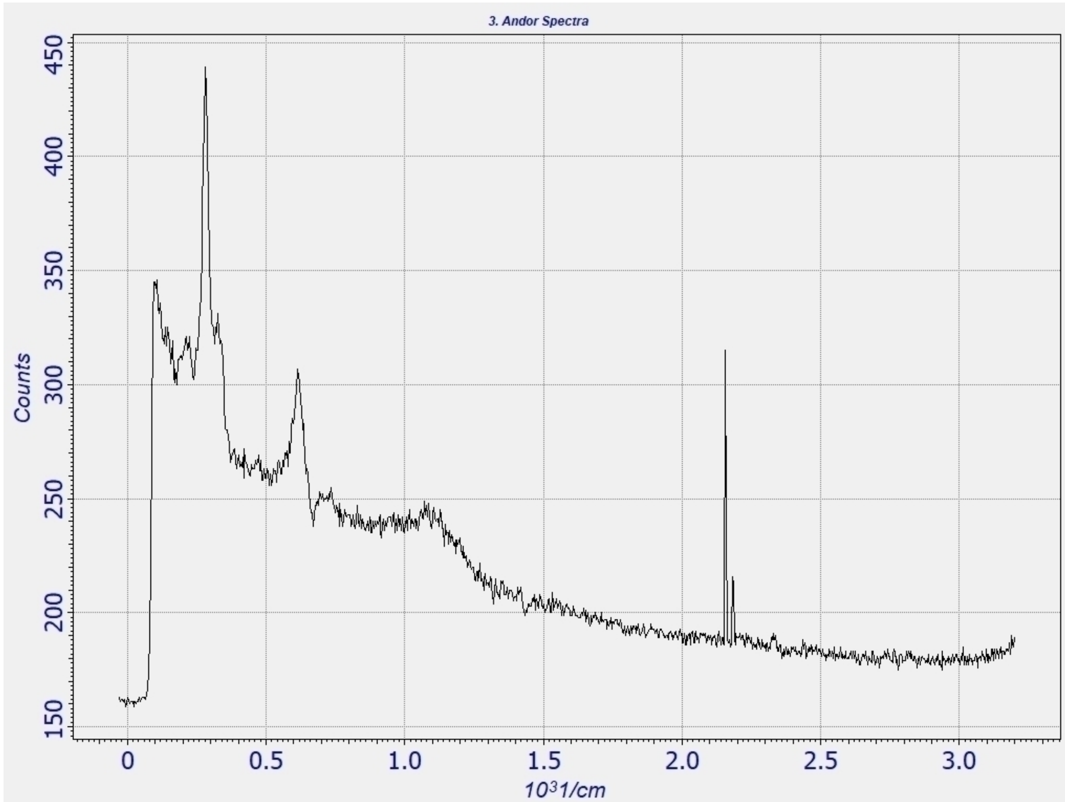


Fig. 4 - Optical spectrum of copper nanoparticles when pectin is used as a stabilizer in baseline solutions

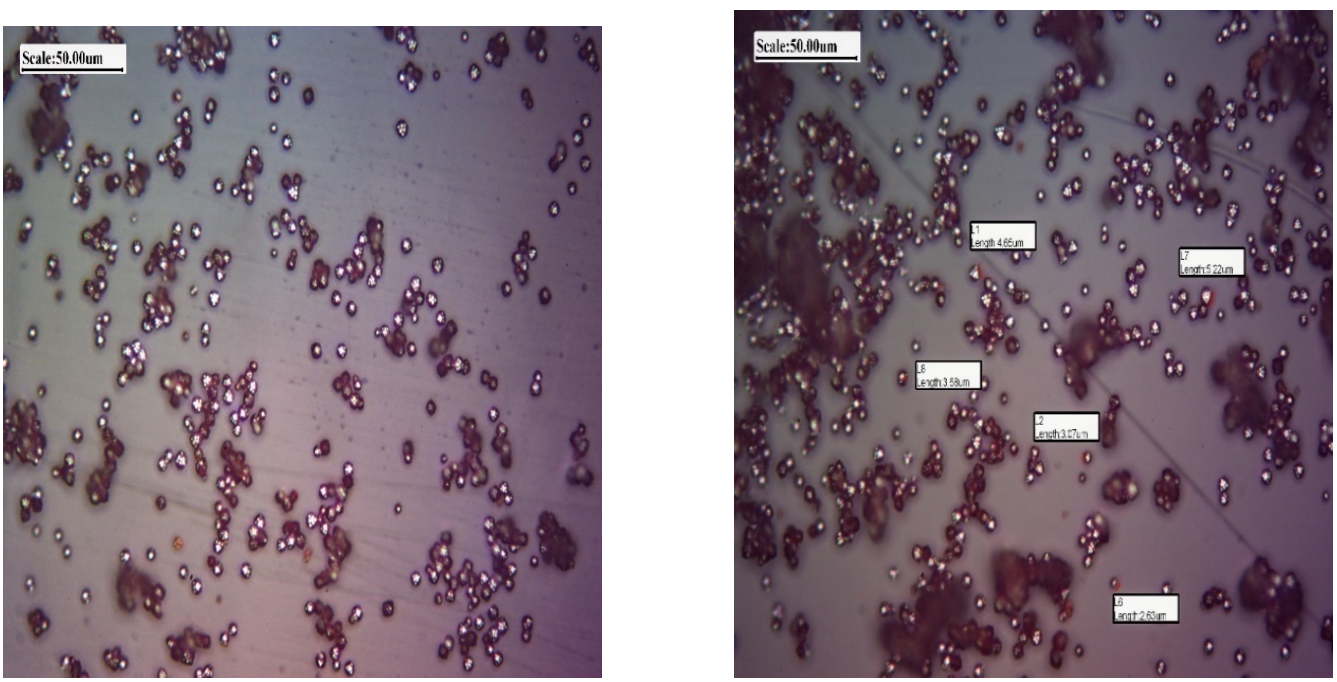


Fig. 5 - Optical imaging of copper nanoparticles in the 50 µm range

Dispersion phase particle size is one of the most important characteristics of colloidal solutions, determining their many properties. In particular, the stability of the solution and its biological properties may depend on the size of the nanoparticles [11]. The samples showed nanoparticles with sizes ranging from 136 to 995 nm. When pectin was used as a stabiliser, and when gelatin was used as a stabiliser, the particle sizes ranged from 62 to 313 nm. Photos of samples made by optical and scanning electron microscope are shown in Figures 5 - 7. Based on the results of scanning and transmission microscopy, nanoparticles as seen in Figure 7 have spherical shape like granules. Figure - 8 shows the surfaces of the films before and after treatment with copper nanoparticles. In the treated film the clusters of nanoparticles reached up to 500 nm in some places.

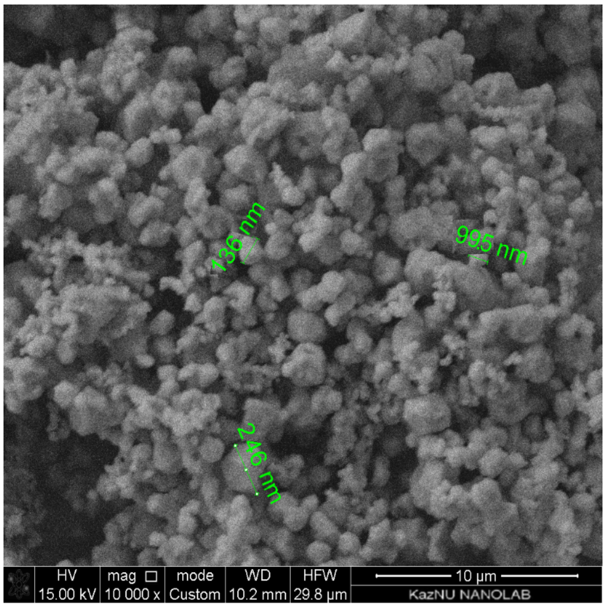


Fig. 6 - Dimensions of copper nanoparticles using pectin as a stabilizer

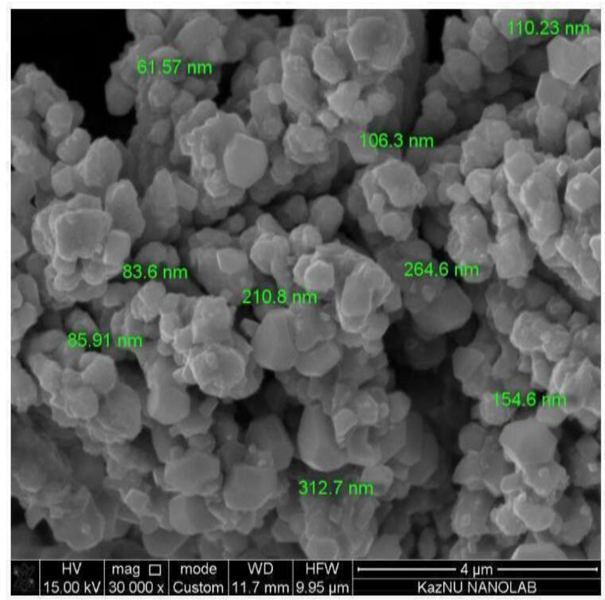
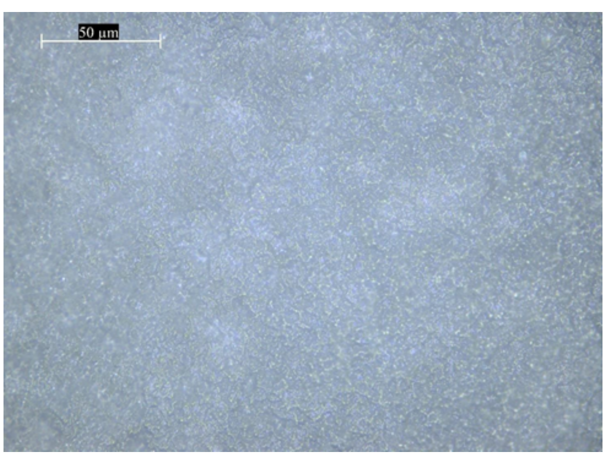


Fig. 7 - Dimensions of copper nanoparticles using gelatin as a stabilizer



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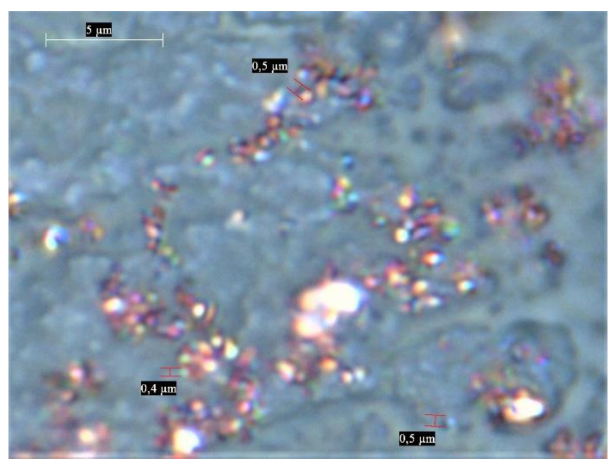

b

Fig. 8 - Polylactid film samples (a) before treatment and (b) after copper nanoparticles treatment

As a result of the study of the basic physico-chemical characteristics of nanoparticle solutions, it can be concluded that they differ strongly and as a consequence different effects when they are used to create composite packaging materials. Evaluation of the effectiveness of the application of a product is an important part of its development process. Since often not individual characteristics of a product are the reason for its purchase, but the ability of the product to solve a particular problem, it is important to determine the possibility of solving the problem. For nanopackaging, this problem is the extension of the shelf life of the products packaged in it. The benefits of use can be significant if such packaging is used as effectively as possible.

In order for the packaging to be used effectively, it is necessary to determine an extended shelf life compared to conventional packaging. It is known that the main cause of damage is the development of various microorganisms, so the use of packaging with antimicrobial agents is relevant. The shelf life can be determined in different ways, depending on the type of product.

The method of microbiological testing is most appropriate if the cause of damage is mainly the development of microorganisms in the product. In this case, both the total number of microorganisms (COE) can be measured and differentiated depending on the type of micro-organism. The advantage of this method is the ability to identify the main source causing the damage of the product.

The effects of CuO-modified polylactid films on changes in the microbiological purity of bread storage are further studied in Table 1 and Figure 9.

Table 1 - Dynamics of changes in microbiological parameters of bread samples during storage

№	Sample	Mold index, CFU/g						
		1 day	2 day	3 day	4 day	5 day	6 day	7 day
1	Bread without packaging	-	-	1	3	5	8	17
2	Bread with a control package without processing	-	-	1	2	3	4	10
3	Bread with processed packaging (using gelatin as a stabilizer)	-	-	-	-	1	2	4
4	Bread with processed packaging (using pectin as a stabilizer)	-	-	-	-	1	2	5

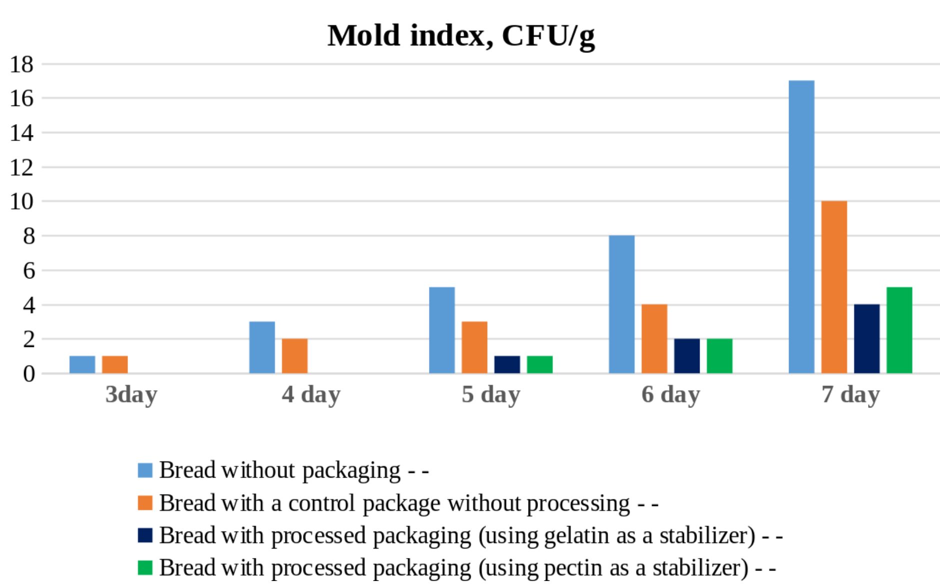

Fig. 9 - Effect of polylactide packages treated with copper nanoparticles on microbiological parameters

In accordance with the results presented in Table 1 and Figure 9, films modified with CuO nanoparticles were found to reduce mold growth and development in experimental bread samples compared to the control bread sample. The data obtained shows the activity of CuO nanoparticles stabilized with gelatin and pectin, and also coincides with the data of other authors [12, 13], who studied the antibacterial activity of CuO nanoparticles.

Conclusions. The problem of healthy and quality nutrition, along with the problem of adequacy of such nutrition is relevant for modern humanity. One way of addressing this problem, as discussed in this paper, is to keep products fresh and suitable for consumption for a considerable period of time. Fortunately, modern technologies allow to obtain and explore the latest materials that can be used to solve the above-mentioned problems. As a result of the studies carried out and presented in this paper, the following conclusions can be drawn:

1. A method of synthesis of CuO nanoparticles stabilized with gelatin and pectin has been developed, their colloidal stability in various dispersion media has been studied and their possibility of use in bread packaging has been explored.

2. The results showed that the use of copper chloride as a precursor allows to produce copper oxide (II). According to the data, copper oxide nanoparticles stabilized by gelatin and pectin in the aquatic environment had particles of the smallest diameter of 62 nm.

3. It has been found that CuO nanoparticles, stabilized with gelatin and pectin, have antimicrobial activity and can be used as a material for food nanopackets, providing an increase in the shelf life of products, as shown in the example of bread. The high level of stability of CuO nanoparticles stabilized with gelatin and pectin will also facilitate their use in the creation of active food packaging materials.

4. It was found that polylactic films modified by CuO nanoparticles inhibited mold growth and development in experimental bread samples.

5. The morphology of the surface is studied by electronic microscopy. The result showed that when using gelatin as a stabilizer, the maximum copper nanoparticles size was 313 nm, and when using pectin, the particle size was 246 nm.

Thus, the results of experiments show that CuO nanoparticles, stabilized with gelatin and pectin, have a high potential for use in food packaging - both as a self-propelled nanofilm and as part of other packaging materials, and can also be laid as a basis for food interaction studies, the environment and be useful for developers engaged in the creation of promising packaging material.

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