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POTENTIAL OF SILVER NANOPARTICLES IN IMPARTING ANTIMICROBIAL PROPERTIES TO LEATHER

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To protect natural leather from microorganisms, substances with antimicrobial properties are used. The rapid adaptation of microorganisms to antimicrobial agents requires a constant search for fundamentally new materials. When choosing antimicrobials, attention should be paid to their safety. An increase in the antimicrobial activity of a drug leads to an increase in its toxicity. Traditional antimicrobial agents are based on cationic surfactants, guanidine or polyalkylene guanidine compounds. However, given the possibility of antimicrobial resistance, research should be aimed at finding new effective biocidal products. Today, one such product is metal nanoparticles, whose properties can be successfully used in leather technology. The aim of this work is to summarize antimicrobial properties of silver nanoparticles and to study the advantages of biosynthetic production of silver nanoparticles. Biosynthesis of silver nanoparticles involves the reduction of silver ions to form silver nanoparticles. This process is environmentally friendly, and silver nanoparticles have potential to be used to impart antimicrobial and antifungal properties to leathers and leather products.

Keywords: silver nanoparticles, antimicrobial properties, leather.

INTRODUCTION

Leather is a material of biogenic origin. Its production involves the multi-stage and sequential processing of raw hides and skins with chemicals to create the required set of quality indicators. Leather production is based on the processing of canned hides and skins during preparatory, tanning and finishing processes. This process affects the collagen structure of the dermis with salts, acids, alkalis, enzymes, tannings, surfactants, fats, etc.

Raw hide contains proteins, water, lipids, carbohydrates, etc., which makes it susceptible to microorganisms. The challenge in leather processing lies in achieving strong antimicrobial protection without compromising the natural properties of the material.

At different stages of leather production, the nature of biodamage and the development of microorganisms is different. Gram-positive (*Bacillus*, *Staphylococcus*, *Clostridium*) and gram-negative (*Pseudomonas*, *Proteus*, *E.coli*) bacteria and fungi (*Penicillium*, *Aspergillus*, *Mucor*) have been identified as microorganisms that can adversely affect the structure and properties of the dermis. In order to avoid bioinjury, technological measures have been developed, the use of which is aimed at not inhibiting the action of microorganisms and protecting dermal collagen from damage to preserve the integrity of the dermal structure and form the necessary set of functional properties of the genuine leather.

Aerobic bacteria are the most active at the stage of hide curing. Once the hide has been removed, the metabolic processes that were previously occurring cease and the hide begins to decay (Andreieva, 2012). Autolysis leads to an increase in the looseness of the leather and a decrease in its strength. Bacteria of the genus *Bacillus*, *Pseudomonas* and *Proteus* damage the proteins in the hide and the grain of the leather. With further decay, bacteria of the genus *Clostridium* multiply in the hide (Demkevych *et al.*, 2013). As a result of storage at high humidity in poorly ventilated rooms, hides may be affected by fungi of the genus *Penicillium*, *Aspergillus*, *Mucor*. The damage consists in the appearance of spots on the surface of the hide, which then spread to the hide. The effects of molds can lead to a loss of leather strength.

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That is why antiseptic materials of different nature are traditionally used for hide curing. Namely: formalin, sodium hexafluorosilicate, zinc chloride, etc.

At the preparatory stage of liming, non-spore-forming and spore-forming bacteria are active. The use of alkaline materials for dermis liming reduces the risk of bioinjury.

At the stage of tanning, bacteria of the *Bacillus mesenteticus* species, fungi *Aspergillus niger, Penicillium chrisogenum, P. ceclopium* can be agents of biodamage. Their effect on semi-finished products and leather is to damage the grain and reduce the strength of the leather structure. At the same time, the risk of biological damage to the dermis can be reduced by using mineral and organic tannins for tanning. The risk of biodamage occurs when the semi-finished leather product is stored or transported in a wet state under plastic wrap.

The use of synthetic dyes and tannins, as well as fat-liquoring materials, in the subsequent after-tanning processes of leather production further increases the biostability of leather. But despite this, genuine leather remains susceptible to biological damage.

If the proper storage conditions for leather and leather products are not met, for example, in humid conditions at a temperature of 22-25°C, or if leather products get wet or are not dried sufficiently, or if products are used in harsh climatic or living conditions, the occurrence of biological damage is quite likely.

Production must ensure the safety of genuine leather at different stages of the life cycle. The market offers a limited range of antimicrobial products to protect the structure of the leather dermis that would be environmentally tolerant, not pollute the environment, be technologically available and cost-effective, and have a wide range of antimicrobial effects on microorganisms of different groups (bacteria, fungi, etc.) with a long protective effect. To impart antimicrobial properties to natural leathers, the following are used: quaternary ammonium compound derivatives, phenol derivatives, chloroactive compound derivatives, aldehyde-based preparations, preparations based on high molecular weight cationic surfactants, polymeric guanidine or polyalkylene guanidine compounds (Kozar *et al*., 2017).

Currently, the most widely used and relatively safe drug is polyhexamethylene guanidine hydrochloride. This is a cationic polyelectrolyte, a biocide with a broad spectrum of antimicrobial activity against gram-positive and gram-negative bacteria, viruses, fungi, etc. When treated with this polyelectrolyte, a biostable film is formed on the surface of the material. After treatment, the materials can retain their bactericidal effect for 3 days to 8 months. The polyelectrolyte is classified as a class 3 moderately hazardous substance.

Therefore, to protect natural leather from microorganisms at various stages of animal hide processing, substances with broad-spectrum antimicrobial properties should be actively used. The goal of leather treatment is to provide powerful antimicrobial protection while maintaining the material's natural properties. However, given the possibility of antimicrobial resistance, research should be aimed at finding new effective biocidal products. Today, one such product is metal nanoparticles, whose properties can be successfully used in leather technology.

SUBSTANCES WITH ANTIMICROBIAL PROPERTIES AND REQUIREMENTS FOR THEM

Antimicrobial agents are used to prevent biodamage of various materials. From the point of view of use, these drugs must meet two main requirements: penetrate the surface or inside the microorganism's cell and, accumulating in it, disrupt at least one vital process of the microorganism.

Drugs with antimicrobial properties are called biocides. They should have a broad spectrum of antibacterial action against pathogenic microflora and be produced from available raw materials for industrial production. The range of such drugs is quite large. At the same time, the use of some drugs is limited due to the safety of their use.

The possibility of using biocidal products is regulated by the requirements of Regulation (EU) No. 528/2012 and a number of other EU legislative acts (Document 32012R0528, 2012). The Regulation stipulates the application of precautionary measures to protect against harmful effects of biocides on human or animal health or unacceptable environmental impact. The Regulation prohibits the use in a biocidal product of a substance that is classified as dangerous in accordance with Regulation (EC) No 1272/2008 or in a dangerous concentration (Document 32008R1272, 2008); a substance that meets the criteria for being a persistent organic pollutant or meets the criteria for being persistent, bioaccumulative and toxic or very persistent and very bioaccumulative in accordance with Regulation (EC) No 1907/2006 (Document 32006R1907, 2006).

Microorganisms often exhibit natural resistance or rapid adaptation to antimicrobial drugs. However, an increase in the antimicrobial activity of a drug often leads to an increase in its toxicity. Thus, every year dozens of drugs are discontinued due to their low antimicrobial activity, high toxicity, low environmental safety, and the ability to cause dermatitis or allergic reactions. These characteristics are unacceptable when using such products for natural leather. The active ingredient of a biocidal product may not contain carcinogens, mutagens, toxic substances that affect the reproductive or endocrine system of humans or animals, environmental pollutants, and substances with high bioaccumulation.

In order to improve the safety of biocides, alternative materials with antimicrobial properties are constantly being sought. Research is mainly focused on finding polyfunctional or hybrid materials. For example, the antimicrobial effectiveness of polyhexamethylene guanidine hydrochloride can be increased by combining it with natural silicates (Kozar *et al.*, 2017). Oil obtained from *Origanum vulgare* is also considered as a preparation with antimicrobial properties for the treatment of leather or leather materials (Bayramoglu, 2007; Bielak *et al.*, 2020). The ability of chitosan to impart antimicrobial properties to leather materials is being studied (Ocak *et al.*, 2015). The effectiveness of the use of hybrid organic-mineral nanomaterials based on essential oils is being investigated (Bacardit, 2016).

The development of nanotechnology and functional features of nanomaterials have opened up new opportunities for the production of drugs with antimicrobial properties. The synthesis of nanoparticles of various metals (copper, silver, titanium, zinc, etc.) and their use as biocides for the treatment of leather materials makes it possible to expand the range of safe materials with antimicrobial properties (Carvalho *et al.*, 2018; Maestre-Lopez *et al.*, 2015).

Metal nanoparticles are often used to combat multidrug resistance in microorganisms. Silver nanoparticles are most often considered because of their broad spectrum of action and reliable antimicrobial properties (Mijnendonckx *et al.*, 2013; Morones *et al.*, 2005). Moreover, researchers have noted (Dakal *et al.*, 2016; Skiba *et al.*, 2019) that the stability of nanoparticles, their size, shape, and surface chemistry play an important role in their antibacterial activity.

Thus, the prospects for the use of metal nanoparticles, especially silver, can be considered as a unified approach to solving the problems of bio-damage to the skin dermis structure at different stages of production.

ANTIMICROBIAL POTENTIAL OF SILVER NANOPARTICLES

Silver nanoparticles (AgNPs) are clusters of silver atoms. A cluster contains about 20-15000 silver atoms, and its size ranges from 1 to 100 nm. AgNPs are characterized by high surface sorption activity and are of great interest to researchers in various fields (Siddiqui *et al.*, 2023).

AgNPs are part of packaging materials, consumer products made of polymeric and composite materials, and mixtures designed to protect materials from external influences. AgNPs are used in the textile, electroplating, paper, perfumery, and food industries. Another area of application for AgNPs is water purification: the use of nanoparticles in filters and wastewater treatment plants.

The use of AgNPs as components of antimicrobial agents in the healthcare industry is considered effective. AgNPs are proposed to be used as carriers for the effective delivery of active pharmaceutical ingredients or to improve the solubility of drugs (Farjadian *et al.*, 2019). Dressings with silver nanoparticles significantly reduce wound healing time and increase the rate of cleaning of infected wounds (Ronavari *et al.*, 2021).

The effectiveness of AgNPs has been observed against a number of gram-positive and gram-negative bacteria, fungi, and viruses (Carvalho *et al.*, 2022; Gajbhiye *et al.*, 2009; Roy *et al.*, 2013; Skiba *et al.*, 2019). Numerous studies have proven the antimicrobial effect of AgNPs against *Escherichia coli, Salmonella typhimurium, Bacillus anthracis, B. cereus, Pseudomonas aeruginosa, Vibrio cholerae,* etc. AgNPs also have antifungal potential against A*spergillus niger, A. foetidus, A. flavus, A. oryzae, A. parasiticus, Phoma glomerata, P. herbarum, Fusarium semitectum, Trichoderma sp. Oxysporum,* etc.

Considering the tasks of tanning and after-tanning processes, it should be noted that AgNPs are also capable of interacting with lipids and proteins. AgNPs have a high affinity for sulfo-, amino-, and carbonyl groups, which are widely present on the membrane or proteins. AgNPs can bind to protein groups to form stable bonds that can change the three-dimensional structure of proteins and block their active sites (Klueh *et al.*, 2002).

The antibacterial activity of AgNPs is associated with the release of silver ions, which can be created and introduced by oxidative dissolution of AgNPs in the presence of oxygen (Reidy *et al.*, 2013). It is assumed that the antibacterial effect is also associated with the interaction of AgNPs with the bacterial cell walls. As a result of this interaction, the permeability of the cell membrane changes, which causes cell death (Ivask *et al.*, 2014).

The size of nanoparticles has a particular impact on their antibacterial activity. Studies have shown that for the formation of a bond between the membrane and AgNPs and further penetration into the membrane, the size of nanoparticles should be 1-10 nm (Morones *et al.*, 2005). Considering the wide range of antimicrobial activity of silver nanoparticles against microorganisms of different nature, it is possible to predict the effective effect of nanomaterials at different stages of leather production.

SYNTHESIS OF SILVER NANOPARTICLES

The main methods of synthesizing silver nanoparticles are chemical, physical, and biological (Almatroudi *et al*., 2024). Chemical and physical methods of nanoparticle synthesis are resource-intensive and involve the use of strong reducing agents or organic solvents, various types of irradiation, ultrasonic treatment, etc. The implementation of these technologies produces toxic emissions, pollutes industrial wastewater, and worsens the environmental aspect of production. The most promising is the method of producing metal nanoparticles through green biosynthesis, or “green” technology (Ahmad *et al.*, 2019; Bawskar *et al.*, 2015).

The “green” technology for producing AgNPs is based on the environmentally friendly synthesis of nanoparticles by using the ability of biological systems (yeast, fungi, bacteria, plants) to synthesize metal nanoparticles through the enzymatic reduction of metal ions (Peiris *et al.*, 2017; Murali Krishna *et al.*, 2016; Voloshyna *et al.*, 2023). “Green” biosynthesis of nanoparticles occurs in the absence of toxic chemical materials.

Biosynthesized AgNPs for the leather industry should exhibit strong antimicrobial properties and reduce biofilm formation or destruction. To ensure the diffusion of AgNPs into leather materials, a spherical or elliptical shape of the nanoparticles is desirable.

Nowadays, plant extracts are most often used to implement the technology of green biosynthesis of AgNPs. Extracts from various plant parts can be used for synthesis. Synthesis of AgNPs using plant extracts is interesting due to cheap raw materials and the possibility of obtaining stable nanoparticles (Akhter *et al.*, 2024; Rehman *et al.*, 2023; Mohanta *et al.*, 2020). The biological safety of the synthesis AgNPs is ensured by the absence of a biological agent cultivation stage.

In general, plant-based biosynthesis involves the extraction of plant material with water, alcohol or a mixture of both, the addition of argentium nitrate to the extract, the biosynthesis stage, centrifugation and drying.

Biosynthesis based on *Aloe vera* (Yadav *et al.,* 2016) allows to obtain spherical AgNPs with a size of 30-40 nm.

The biosynthesis based on *Coffea arabica* (Dhand *et al.,* 2016) allows to obtain AgNPs agglomerates of spherical and ellipsoidal shape with a size of 30-40 nm. The minimum inhibitory concentration of the synthesised AgNPs is 0.2675 mg/l against *E. coli and S. aureus*.

The biosynthesis based on *Murraya Koenigii* (Philip *et al.,* 2011) allows to obtain AgNPs agglomerates of spherical and ellipsoidal shape with a size of 10 nm.

The biosynthesis based on *Coriandrum sativum* (Ahmad *et al.*, 2024) allows to obtain cubes AgNPs with a size of 100 nm. The researchers found that the mechanism of antibacterial action is morphological damage, metabolic disruption and respiratory inhibition, leading to bacterial death.

Different classes of algae are used for the synthesis of AgNPs: *Cyanophyceae, Phaeophyceae, Chlorophyceae*, *Rhodophyceae* (Fawcett *et al.,* 2017). When using *Codium capitatum*, we obtain AgNPs with a size of 3-44 nm of mixed spherical and cubic shapes; when using *Spirogyra insignis*, spherical AgNPs with a size of 30 nm; when using *Padina tetrastromatica,* spherical AgNPs with a size of 5-35 nm.

Microbial biofilms are often resistant to various treatments, but biosynthesized AgNPs from biopolymers like chitosan have demonstrated significant potential in disrupting these biofilms (Regiel-Futyra *et al.,* 2017). The biosynthesis involves adding a chitosan solution to a solution of silver nitrate and ascorbic acid, subsequent stirring for 15 hours, evaporation, neutralisation, and drying. The technology allows the synthesis of spherical AgNPs with a size of less than 10 nm.

In the technology of "green" biosynthesis of AgNPs, bacterial cultures are most often used. Microbial biosynthesis of nanoparticles can occur intracellularly or extracellularly.

The biosynthesis of AgNPs includes a biological agent cultivation step, an argentum nitrate injection step, an inoculation step for 24 hours, a centrifugation step, and a drying step.

The first biosynthesis of metal nanoparticles using the bacterial culture *Pseudomonas stutzeri* was carried out in 2000. Another interesting area is the use of bacteria of the genus *Lactobacillus*, as they are inhabitants of normal human microflora. The green synthesis of AgNPs involves the reduction of silver ions to form silver nanoparticles under the action of bacterial cells and their metabolites. It is well known that silver nanoparticles are synthesized by the interaction of *Lactobacillus mindensis* biomass and their metabolites with silver ions. A safe and rapid method for the biosynthesis of AgNPs using *Lactobacillus acidophilus* in Mann-Rogosa-Sharp broth has been developed (De Man *et al.,* 1960). It has been proved that cultures of other microorganisms can also be used for the green biosynthesis of silver nanoparticles, namely: *Bacillus licheniformis, B. subtilis, Brevibacterium frigoritolerans, Aspergillus flavus, Pseudomonas aeruginosa, Pediococcus pentosaceus, Enterococcus faecium, Lactococcus garvieae*, *Citrobacter freundii* etc (Al-Asbahi *et al.*, 2024; Bharose *et al.*, 2024; Xia *et al.*, 2023; Shakhatreh *et al.*, 2021; Sulaiman *et al.*, 2015).

Lactobacillus sp. allows the synthesis of spherical AgNPs with a size of 7.97-14.3 nm, and *Bacillus sp.* – 11-22.8 nm (Al-Asbahi *et al*., 2024). The synthesised AgNPs showed high antibacterial activity against *Staphylococcus aureus* and *Pseudomonas aeruginosa.* Antifungal activity of spherical AgNPs produced by *Bacillus subtilis* against *Aspergillus flavus* was determined (Bharose *et al.*, 2024).

Citrobacter freundii can be used for biosynthesis to produce stable spherical AgNPs with a size of 15-30 nm (Shakhatreh *et al.*, 2021). The synthesised nanoparticles are characterised by antibiofilm activity against *Staphylococcus aureus* and high antibacterial activity against *S. aureus* and *Pseudomonas aeruginosa*.

AgNPs obtained by microbial biosynthesis can have different shapes and thus can exhibit high antimicrobial efficiency. The green biosynthesis technology is environmentally friendly, resource-efficient and has a wide range of applications.

Nanosynthesis technologies involve the production of AgNPs of various shapes: spherical, nanocubes, nanoplatelets, nanowires, etc. (Helmlinger *et al.*, 2005). The shape and size of nanoparticles affects the efficiency of surface binding to the cell membrane, cellular uptake, and effective bacterial killing. Researchers believe that the properties of AgNPs are directly related to the methods of their synthesis (de Souza *et al*., 2019; Kesharwani *et al*., 2018; Oves *et al.*, 2018; Saravanan *et al.,* 2018). The antibacterial activity of AgNPs also depends on their concentration in the drug.

Given the environmentally friendly nature of green biosynthesis and the antimicrobial properties of AgNPs, it would be beneficial to focus research on their potential in leather production, particularly during tanning and post-tanning processes, to improve both product durability and safety.

CONCLUSIONS

The prospect of using silver nanoparticles to impart antimicrobial properties to materials is growing. The safety and undisputed antimicrobial properties of silver nanoparticles can be a prerequisite for their successful use in the treatment of leather. The replacement of traditional biocidal agents with silver nanoparticles will contribute to resource efficiency of the technology, increase the safety of leather and leather products, and reduce the environmental impact. Future research should focus on optimizing the biosynthesis of silver nanoparticles to further reduce costs and environmental impacts, while expanding their application in various industries.

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