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PECULIARITIES OF SYNTHESIS AND BACTERICIDAL PROPERTIES OF NANOSILVER IN COLLOIDAL SOLUTIONS, SiO₂ FILMS AND IN THE TEXTILE STRUCTURE: A REVIEW

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The aim of this work is a comparative analysis of the biocidal efficiency of Ag nanoparticles (NPs) in the colloidal state, in the structure of films and dispersions of SiO₂ and in the composition of textile fabrics, dependent on the method of synthesis, based on literature data and on own researches. Chemical reduction of silver (with borohydrides, hydrogen, hydrazine, etc.) allows one to adjust and control the size and shape of NPs. The shape of the NPs is mostly spherical, what is confirmed by the presence of a band of surface plasmon resonance in absorption spectra and by electron microscopy measurements. To prevent aggregation of NPs obtained by the method of chemical reduction in solution, the optimal ratio of two stabilizers based on surfactants and polymer at their minimum concentration was found, namely NaBH₄ as a reductant and polyvinylpyrrolidone + sodium dodecyl sulfate as binary stabilizer of Ag NPs, with bactericidal activity of 99 % and stability for more than 3 years. Chemical reduction of silver ions was carried out also by the amino acid tryptophan (Trp) which has a dual function – a biocompatible reducing agent and stabilizer of silver NPs while maintaining their shape, size and stability for long-term use.

Effective methods of photochemical synthesis of Ag NPs have been developed in different ways: by UV irradiation of Ag⁺ ions in solution in the presence of solid-state photosensitizer SiO₂ with adsorbed benzophenone (SiO₂/BPh); by UV irradiation of Ag⁺ ions in solution in the presence of the amino acid tryptophan (Trp); on silica surface when Ag/SiO₂ sol-gel films production via irradiation of adsorbed Ag⁺ ions on SiO₂ film (Ag⁺/SiO₂) in the BPh solution. It is shown that when Ag NPs are adsorbed on the surface of highly dispersed SiO₂, the logarithm of the reduction of microorganisms reduces and the time of their deactivation increases.

A cheap and convenient way to modify of cotton textiles with Ag NPs by soft heat treatment of Ag⁺/cotton samples with high (90–95 %) efficiency of destruction of bacteria *E. coli*, *K. pneumoniae*, *E. aerogenes*, *P. vulgaris*, *S. aureus*, *C. albicans*, etc., with saving of biocidal activity after 5 cycles of washing has been developed. The dynamics of silver ions release from the surface of NPs in the structure of textile upon their contact with water for 72 hours and the number of irreversibly bound particles have been studied. The electrical resistance of the tissue is proportional to the quantity of NPs. That is NPs in the structure are in different degrees of binding, a certain part of them is retained (adsorbed) irreversibly, saving bactericidal properties after repeated contacts with water. On the basis of literature analysis it is shown that ecologically safe “green synthesis” is a promising way to silver NPs produce with pronounced bactericidal efficiency, which is becoming more common due to the large resource of cheap plant raw materials.

Keywords: silver ions, silver nanoparticles, chemical reduction, photochemical reduction, stabilization, colloids, SiO₂ films, SiO₂ dispersions, textile, bactericidal activity

INTRODUCTION

Over the past 20 years, pathogenic bacteria have developed resistance to almost all known and available antibiotics. Currently, hundreds articles published on the development of bactericidal materials with antimicrobial properties based on nanosized particles (NPs) of metals, in particular silver, gold and copper. In this paper, the dependence of the biocidal efficiency of nanosized silver particles in the colloidal state and introduced into the structure of various bactericidal materials - dispersed oxides,

textile fabrics, as well as in colloid state have been analyzed on the basis of literature data and our investigations in recent years dependent on the method of their production – chemical, photochemical, soft heat treatment etc.

Quite comprehensive reviews of the literature on this topic are made [1–4]. There is a relationship between the size of NPs, their concentration and antimicrobial activity, which allows one to optimize the biocidal action and functionality of NPs in colloids, in the structure of oxides of silicon, titanium, biomedical textiles

have been studied. The antibacterial properties of nanoparticles are influenced by various factors, such as size, charge, zeta potential and surface morphology.

AgNPs have proven, among others, to be the most effective against bacteria, viruses and fungal microorganisms for use in medical practice with relatively low toxicity to human cells. The mechanism of action of silver on the microbial cell is that silver ions are adsorbed by the cell membrane, which performs a protective function. The interaction of silver with bacteria and viruses is to block the capability of peptidoglycans to carry oxygen inside the bacterial cell, which leads to the death of microorganism.

Silver penetrates into the cell, interacts with enzymes, enters into redox reactions with phosphorus-containing molecules, resulting in cell death. Silver ions inhibit phosphate uptake, inhibit DNA function and transmembrane transport of organic and inorganic substances. As mammalian cells do not contain peptidoglycans, silver does not affect them [5–8]. However, there are many publications that claim the toxic effects of silver ions on living organisms in excess of the MPC-50-150 µg/l [9–13]. In the review article [14] there is a reference to the paper [15] that the lethal dose of colloidal solution of silver and silver nitrate in experiments on mice was 2820 and 125 µg/kg, respectively. That is, silver nitrate was significantly more toxic than nanosized silver particles. According to other studies, nanosized silver particles (average size 10 nm), volume Ag concentration 0.27 µg/ml, stabilized with surfactants, with a single intragastric route of entry are low-toxic substances (lethal dose 5000 µg/kg) [16].

The authors [17] discuss the delayed mechanism of toxic action of nanoparticles, probably mediated by perturbation of mitochondrial function of cells. The potential risk of toxic effects of NPs is determined by their properties and dosage (narrow therapeutic window), so it is necessary to obtain their detailed physicochemical characteristics. In general, the mechanism of toxicity is associated with oxidative stress, mitochondrial dysfunction and increased membrane permeability. Also high stability of silver NPs in the environment and the capability to retain toxic properties for a long time are elucidated. That is, an increasing duration of the introduction of silver NPs increases its danger. Therefore, there is a problem of uncontrolled

release of NPs into wastewater and their impact on human health and the environment.

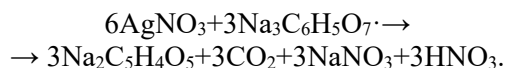
Investigations which are published over the last decade have shown that bacteria can indeed develop stable resistance mechanisms under permanent exposure to bactericidal metal NPs. Bacteria use methods of individual (coded mechanisms) and collective (formation of microbial aggregates and biofilm) security, or the production of substances that immobilize or modify the NPs [18–20].

Individual strategies involve reducing the adsorption of the NPs by squeezing metal ions out of the cell. Microbial aggregates with other microorganisms provide an aggregate matrix that acts as a physical barrier that prevents the penetration of NPs. Authors [21] argued that NPs of colloidal silver in concentrations up to 100 mg/l do not show antimicrobial action, and ionic silver inhibits the growth of bacteria not specifically, but in synergism with nitrate anion.

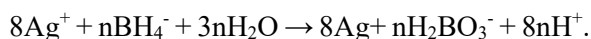
Currently, many physical (vacuum evaporation, pulsed lasers, microwave radiation), chemical, photochemical, biochemical and mixed methods of obtaining colloidal nanosized silver particles have been proposed. Among them recently popular is the “green synthesis”, wherein the reducing agents extracts of most plants, which contain polysaccharides, proteins, polynucleic acids, flavonoids, amino acids, terpenoids, as well as non-toxic renewable biopolymers such as chitosan, alginate, starch are used. Most of them contain OH, COOH, -NH₂ groups, which exhibit chelating properties, i.e. the capability to bind metal cations in the complex [22–29]. Some bacteria are also capable to produce Ag NPs. The efficiency of silver NPs obtained by green chemistry methods is estimated in the size of the inhibition zone, close to or slightly less than that of NPs obtained by chemical methods (10–15 mm), and is, dependent on the dose (between 2–15 mg) of silver, 50–80 % destruction of bacteria (with no antimicrobial action for some strains) [30]. In general, green synthesis can be considered as a promising cost-effective energy-saving method for the synthesis of silver NPs with pronounced bactericidal efficiency.

Colloidal Ag NPs obtained by chemical reduction of silver nitrate by the widely used citrate method of Turkevich, usually have high biocidal activity [4, 31]. The citrate anion acts simultaneously as a reducing agent and stabilizer

of NPs. Therefore, it is the concentration of citrate ions that determines both the rate of reduction and the growth processes of metal nanoparticles. The citrate reduction reaction of silver can be expressed by the following equation:



When the critical size (50–100 silver atoms or cluster diameter 1–1.5 nm) is reached, their growth takes place not through the condensation mechanism, but through the reduction of silver ions on the cluster surface [32]. Sodium borohydride (as well as hydrogen, hydrazine, *etc.*) in the presence of surfactants, such as sodium dodecyl sulfate and others, also were used successfully for the synthesis of resistant Ag NPs with high bactericidal activity [1, 33–36]:



Typical forms of Ag NPs in colloidal solution (cubic, spherical, triangular, rods) presented in Fig. 1, are taken from [2].

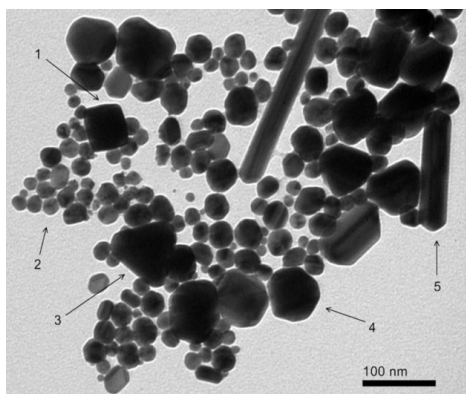


Fig. 1. TEM images of silver nanoparticles (magnification $\times 200000$) of various shapes and sizes: (1) cubic, (2) spherical ~ 10 nm, (3) triangular, (4) spherical ~ 60 nm, (5) rods. TEM was performed using JEOL JEM 1400 TEM (Tokyo, Japan) [2]

We performed the chemical reduction of silver ions with the formation of Ag NPs colloids using NaBH_4 , in the presence of a polymer of polyvinylpyrrolidone (PVP) and a surfactant – cetyltrimethylammonium bromide (CTAB) or sodium dodecyl sulfate (SDS). The mechanism of the process is the association of silver ions with the active groups of dodecyl sulphate by

electrostatic interaction, following a recovery process [41, 52, 60] (Fig. 2).

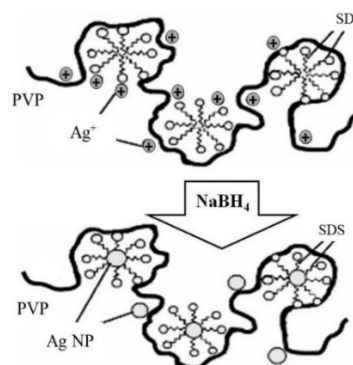
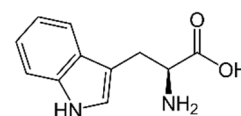


Fig. 2. Schematic representation of the interaction of the stabilizer SDS/ PVP with Ag^+ ions and NPs after reduction

Ag NPs are located in the center of the hydrophobic part of the SDS micelle, and along the polymer chain (Fig. 2). Increasing the amount of reducing agent in a number of molar ratios of NaBH_4 : Ag from 1 : 1 to 25 : 1 contributes to reduce the size of NPs from 20 to 1 nm, respectively, due to the competition of nucleation processes and particle growth. Ag NPs in colloidal solutions are stable and retain the dimension and characteristic band of surface plasmon resonance (SPR) in the absorption spectra at $\lambda_{\text{max}} = 420$ nm for more than 2 years (Fig. 3). The effect of NPs was tested in the colloidal state (Table 1), also after adsorption on the surface of high dispersed silica (HDS) (Fig. 3). The quantity of adsorbed NPs on the surface of HDS was 0.05 %. According to DTA-DTG, organic components from the obtained material are removed at a temperature of about 300 °C.

For the synthesis of NPs by chemical reduction of noble metal ions, the most environmentally friendly and biocompatible reagent for the formation and stabilization of Ag NPs, (as well as gold and copper NPs) the essential amino acid Tryptophan (Trp) has been used. Trp contains an indole ring and three different electron donor groups, which are potential centers of coordination of the amino acid with the metal ion: the oxygen of the carboxyl group, the nitrogen atom of the amino group and the nitrogen atom of the indole ring:



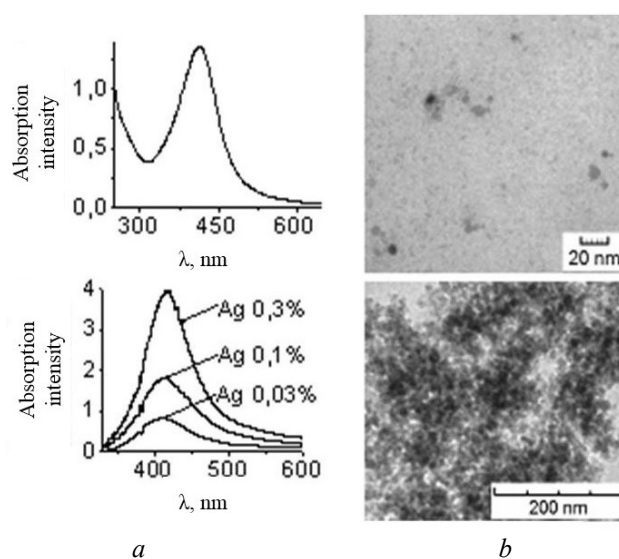


Fig. 3. Absorption spectra (a) and TEM images (b) of silver nanoparticles stabilized with SDS/PVP in colloidal solutions (top) and on silica surface (bottom)

Table 1. Antimicrobial action of synthesized colloidal solutions of Ag NPs, stabilized with SDS and PVP (lg R)

Sample	Exposition (h)	Pathogens of in-hospital infections		
		<i>E. coli</i>	<i>S. aureus</i>	<i>C. albicans</i>
AgNPs (0.0016 %) + PVP	1	< 0.39	< 0.43	< 0.57
	2	< 0.39	< 0.43	< 0.57
	4	< 1.08	< 0.43	< 0.57
	24	> 5.06	< 0.43	< 0.57
Ag NPs (0.0016 %) + SDS	1	> 5.06	2.73	> 4.19
	2	> 5.06	5.01	> 4.19
	4	> 5.06	> 5.18	> 4.19
	24	> 5.06	> 5.18	> 4.19
AgNPs (0.0016 %) +PVP@SDS	1	> 5.06	1.57	> 4.19
	2	> 5.06	2.07	> 4.19
	4	> 5.06	4.35	> 4.19
	24	> 5.06	> 5.18	> 4.19
Initial amount of microorganisms lg*R		7.45	7.17	6.68

The interaction of Trp with silver ions was studied in [37, 38], with conclusions about the mechanism of reduction through the formation of coordination complexes of Ag-Trp. The author [39] considers the reduction of silver ions in the presence of Trp solution and PVP and CTAB stabilizers due to the formation of Trp zwitter-ion through the protonated amino group and the deprotonated carboxyl group, when indole interacts with silver ions and AgNPs. The functional groups of Trp, which are involved in the formation of coordination compounds with

the silver ion, cannot be unambiguously determined by conventional spectrophotometry.

The amino group of Trp participates at all ratios of Ag:Trp, while at ratios of 1:1 and 2:1, along with amino group the carboxyl group also interacts. At two and more excess of silver content, probably, and indole group is involved in the reaction also, that is a consequence of simultaneous presence in solution of coordination compounds of different composition. In the papers of Iu. Mukha and co-authors [40–45] it is shown that the formation of the complex

competes with the process of metal reduction via the indole ring.

The reduction process occurs with the rupture of the C–C bond of the indole ring and proceeds through the substitution reaction and the formation of a complex with the silver cation Ag^+ , the formation of silver NPs with a size of 20 nm and a characteristic absorption band with a maximum at 437 nm at pH close to physiological value. The formation of stable silver nanoparticles occurs in the presence of the anionic form of tryptophan, which exists at high pH of the solution and partly at neutral (due to the existence of the zwitter ion).

In this case, the stabilization of NPs occurs due to the transfer of the electron density of the deprotonated carboxyl group $-\text{COO}^-$ and the unshared electron pair on the nitrogen atom of the amino group to the d -sublevel of the metal. The formation of NPs is accompanied by the appearance of a characteristic yellow color of the solutions.

It is shown that photochemical reduction of silver ion in solution also occurs efficiently in the

presence of Trp under UV light irradiation from a semiconductor LED with a wavelength of 280 nm, which corresponds to the maximum absorption of the indole fragment of Trp and is a promising way of synthesizing Ag NPs with specified properties.

Activation of the redox reaction between the metal ion and the amino acid 2–10 times accelerates the formation of NPs and allows one to obtain stable colloidal NPs of silver with a certain size (25–50 nm). The oxidation of Trp proceeds through the cleavage of the indole ring, as shown in [40]. Decreasing the temperature of the chemical reaction in the Ag/Trp system significantly slows down the process of metal reduction and, in turn, the formation of particles. Compared with the chemical reaction that took place at 100 °C, the SPR band has a low intensity after the reaction at 60 °C after 120 min, and is not observed at 25–40 °C (Fig. 4 *a*). Irradiation of Ag/Trp at 278 nm leads to the appearance of intensive SPR of Ag NPs at the temperatures of 60, 40 and 25 °C (Fig. 4 *b*).

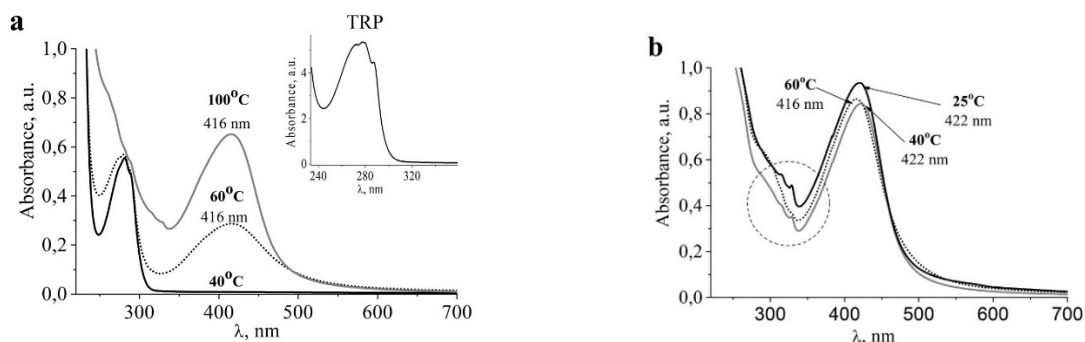
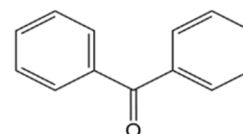


Fig. 4. *a* – Absorption spectra of Ag NPs in colloids obtained in the presence of Trp at different temperatures without UV-C irradiation; *b* – absorption spectra of colloids of Ag NPs at different temperatures with UV-C irradiation ($\lambda = 278$ nm, initial optical power density 1.0 mW/cm^2) after a week of storage. Insert, the spectrum of Trp

Thus, the photochemical oxidation of Trp passes through the kynurenine pathway via the cleavage of the indole ring. As can be seen from the TEM images (Fig. 5), a decrease in the reaction temperature from 60 to 25 °C causes an approximately 2.5-fold increase in the average size of Ag NPs from 20 to 50 nm and their heterogeneity. The increase in the intensity of the absorption bands in the range of 300–350 nm is associated with the formation of elongated structures at 25 °C, composed of spherical nanoparticles.

Photochemical reduction of silver nitrate with diphenylketone is also used to obtain Ag NPs with an average size of 7–30 nm. We have developed a solid-state photocatalyst based on silica films modified with benzophenone (BPh) – $\text{SiO}_2/\text{BPh}_{\text{ad}}$, for one-stage reduction of noble and transition metal ions in solution [46–53]:



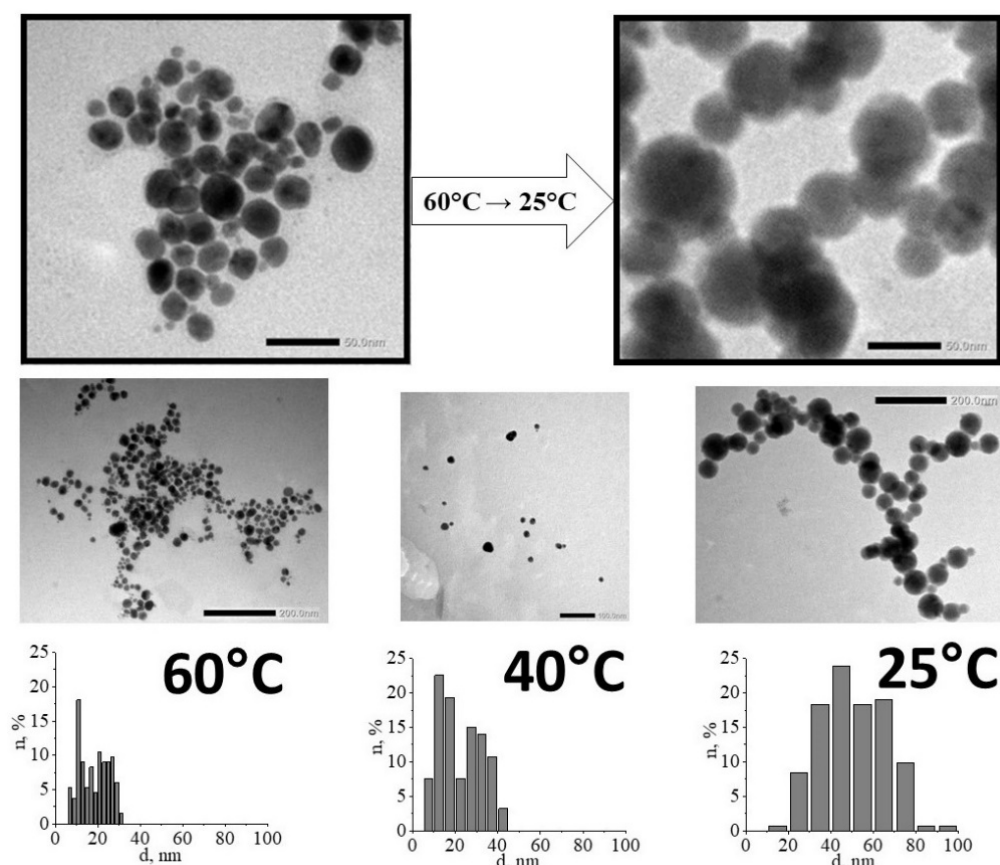
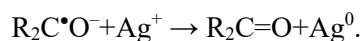
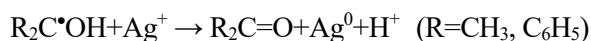
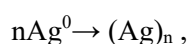


Fig. 5. TEM images of Ag NPs obtained under UV irradiation at 60, 40, and 25 °C and the corresponding size distributions calculated using ImageJ

Synthesis of mesoporous SiO₂-BPh_{ad} films (8.4 % of BPh) with a hexagonal pore structure with an adsorbed sensitizer bound to the surface irreversibly was performed by the sol-gel method in the presence of Pluronic P123. The mechanism of photosensitized reduction of silver ions in the presence of SiO₂-BPh_{ad} is as follows: 1) Excitation of adsorbed BPh molecules to the triplet state; 2) Separation of the BPh(T1) of the hydrogen atom from isopropanol and the formation of ketyl radicals; 3) Protolytic dissociation of ketyl radicals; 4) Reduction of silver ions by ketyl radicals and anion radicals:



Formation of primary clusters and growth of Ag NPs:



Negative charge on Ag NPs occurs due to the peptizing effect of BPh ketyl radicals and isopropanol

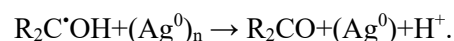


Fig. 6 *a* demonstrates the absorption spectra of NPs solutions of silver (and gold) obtained by photochemical reduction of ions in the presence of a photocatalyst SiO₂-BPh_{ad} and their electron microscopic images (Fig. 6 *b, c*).

We have also developed a photochemical method for silica films producing with silver fixed on the surface of SiO₂. Here, on the contrary, BPh is in solution and silver ions are fixed in the SiO₂ film. The first stage of the synthesis is to add a solution of AgNO₃ to the precursor SiO₂ at the stage of sol-gel transition. After drawing the film on a glass substrate and appropriate heat treatment, the Ag⁺/SiO₂ film was irradiated in aqueous-alcoholic BPh solution. Absorption spectra of SiO₂-Ag films 2 % before (1) and after 15 min irradiation (2) in 1.4·10⁻³ M solution of BPh in isopropanol and SEM image of SiO₂-Ag film after 15 minutes of irradiation with distribution of Ag NPs by size are shown in Fig. 7 [54–56].

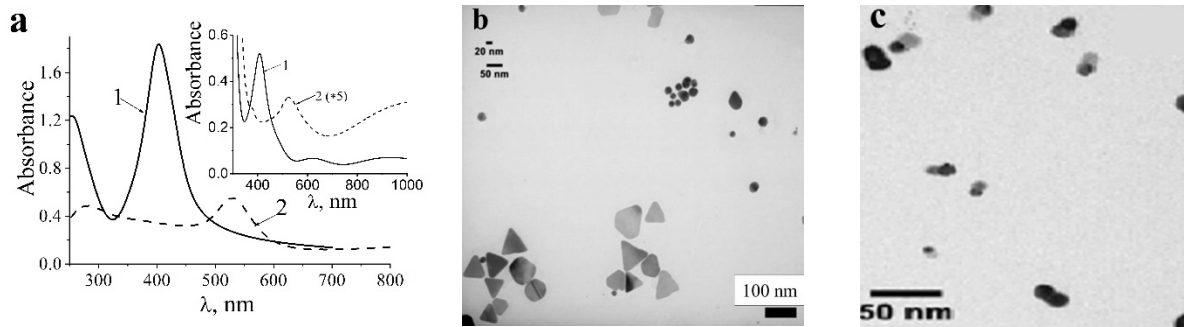


Fig. 6. *a* – Absorption spectra: 1 – colloidal solution of Ag NPs; 2 – colloidal solution of Au NPs; in the insert: absorption spectra: 1 – films SiO₂-Ag 10 %, and 2 – SiO₂-Au 10 %; *b* – TEM images of colloids Au NPs; *c* – TEM images of colloids Ag NPs

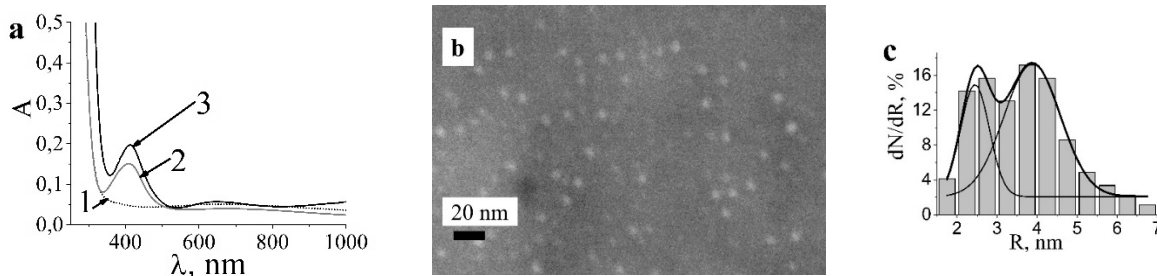


Fig. 7. *a* – absorption spectra of SiO₂-Ag 2 % films before (1) and after 15 min of irradiation (2) in a $1.4 \cdot 10^{-3}$ M solution of BPh in isopropanol (3) the spectrum of the SiO₂-Ag film after 6 hours of calcination at 500 °C; *b* – SEM image of SiO₂-Ag film after 15 min of irradiation; *c* – size distribution of photogenerated Ag NPs

Bactericidal activity of silver NPs in the colloidal state and in the presence of Ag/SiO₂ composite. Colloidal solutions of nanosized silver and Ag/SiO₂ films are antimicrobial materials with a broad spectrum of action against a number of pathogenic microorganisms *S. aureus*, *E. coli*, *P. aeruginosa*, *C. albicans*, etc., which according to European standards is expressed as a logarithm reducing the number of viable microorganisms after exposure to the test sample compared to their initial number $\lg R = \lg N_0 - \lg N_a$, where R is the reduction factor.

Yeast-like fungi *C. albicans* are most sensitive to the Ag NPs; the value of the required reduction of 4.0 lgR was achieved in the first hour of contact with colonies of microorganisms. Gram-negative group of microorganisms (*E. coli*, *P. aeruginosa*) have an intermediate position. The most resistant were the bacteria of the gram-positive group *S. aureus* - the required reduction of 5.0 lg R occurred after 4 h of exposure, which is associated with less pronounced inactivation of

sulfhydryl groups located in the cytoplasmic membrane of cells under a thick layer of peptidoglycan, compared with more vulnerable membranes of bacteria of gram-negative group and *C. albicans* fungi (Fig. 8) [47, 57, 58].

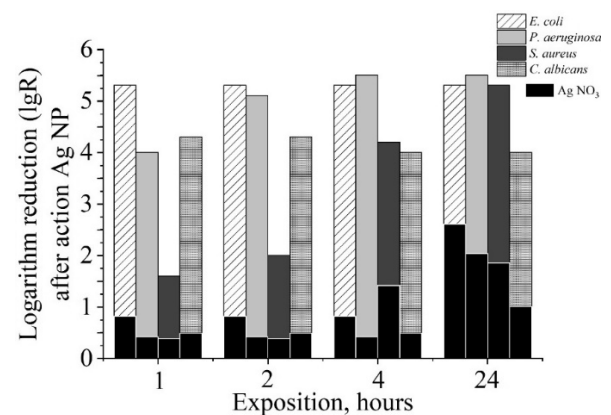


Fig. 8. Antimicrobial activity of colloidal Ag NPs (lgR)

Materials based on Ag NPs with a reduced content of stabilizer SDS to the level of the maximum allowable concentration can be used as antimicrobial drugs (patents of Ukraine [59, 60]).

High antimicrobial activity (99 %) of colloidal solutions of silver nanoparticles at ultralow concentration of silver ($1.5 \cdot 10^{-4}$ M

(Table 2) and composite systems Ag/SiO₂ (Table 3) against microorganisms *E. coli*, *P. aeruginosa*, *S. aureus* and *C. Albicans* is shown. Biocidal effect remains constant for more than two years, which allows us to recommend them for use.

Table 2. Antimicrobial properties of Ag NPs in a colloidal solution of Ag NPs after 2 years of preparation on the example of a test strain of *E. coli*

Storage time, years	Time of contact, hours	lgR	Logarithm of the initial number of microorganisms lgN ₀
1	1	> 5.29	7.44
	2	> 5.29	
	4	> 5.29	
	24	> 5.29	
2	1	2.9	7.12
	2	3.76	
	4	> 4.97	
	24	> 4.97	

Table 3. Antimicrobial properties of the Ag/SiO₂ suspension, lg R

Sample	Time of exposition, h	Test strains		
		<i>E. coli</i>	<i>S. aureus</i>	<i>C. albicans</i>
Ag NPs (0.0016 %)/ SiO ₂ (3.13 %)	1	< 1.39	3.89	> 4.54
	2	1.48	5.14	> 4.54
	4	3.58	> 5.17	> 4.54
	24	> 5.06	> 5.17	> 4.54
SiO ₂ (3.13 %) (blank)	1	< 1.39	< 1.5	< 0.87
	2	< 1.39	< 1.5	< 0.87
	4	< 1.39	< 1.5	< 0.87
	24	< 1.39	< 1.5	< 0.87
The initial number of microorganisms, lgN ₀		7.21	7.32	6.69

Bactericidal activity of AgNPs in suspensions of nanodisperse SiO₂. As mentioned above, Ag/SiO₂ was also synthesized by adsorption of pre-prepared stabilized colloidal solutions of nanosized silver on the surface of dispersed silica with a specific surface area of 300 m²/g for comparison with photochemically stimulated samples of similar composition. The image of the TEM is shown in Fig. 9.

The introduction of Ag NPs in the suspension of silica Ag/SiO₂ leads to the increase of time to achieve the required reduction compared with their action in solution (up to 4 hours) (Table 3) because of the change of the nature of the interaction of NPs with cells of microorganisms,

which include the adsorption of strains on the surface of the dispersed silica [61–64].

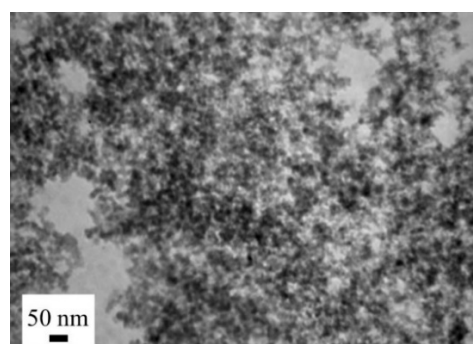


Fig. 9. TEM image of dispersed bactericidal silica Ag/SiO₂

It is interesting to note that in presence of both silver and gold NPs in the composite Ag(Au)/SiO₂ the bactericidal activity significantly increases under the action of light, probably due to the synergetic activation of the processes underlying the destruction of bacteria [57].

Preparation and properties of bactericidal textiles. Nanotechnology is now a leader in the production of smart textiles by providing it with antimicrobial and antiviral properties, self-cleaning capability, electrical conductivity, controlled hydrophilicity, protection against UV radiation and more. Antimicrobial treatment of textiles for biomedical and clinical purposes is an important direction of research. The method of tissue modification using metal NPs fundamentally affects their size, shape and crystal structure, and thus the toxicological effect on microorganisms. The toxicity of the NPs in the tissue is much lower compared to colloids due to the strong interaction with the structure of the fabrics, while maintaining the availability of NPs for bacteria.

Thus, today a very important task is to develop methods of manufacturing cost-effective, safe and effective biocidal fabrics.

Impregnation of wool, viscose, nylon, polyamide, cotton fabrics, application of Ag NPs on fabrics by plasma or thermal spraying, electrochemical method, laser ablation and others are widely represented in the literature [65–73]. Ag NPs in the form of crystallites interact with the tissue surface and inhibit the spread of resistant bacteria. The depth of penetration of nanoparticles into the cotton is approximately 30 Å [74–77].

We have proposed an original method of obtaining of Ag NPs and bimetallic Ag/Cu NPs in the cotton by impregnation with aqueous solutions of salts under a soft heat treatment (200–210 °C), which does not require significant energy consumption and special equipment. The absorption spectra of samples of cotton, modified with silver, copper and their bimetallic composite, contain bands of corresponding SPR (Fig. 10) [78, 79]. It is important to emphasize that nanooxides of these metals, in particular CuO, which also has bactericidal activity, are formed on the surface of biomedical textiles along with Ag and Cu NPs. In the case of textile modification by both Ag and Cu NPs, traces of Cu₂(SO₄)O and AgCuS are also fixed [80].

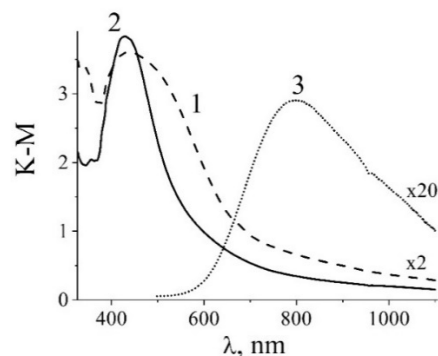


Fig. 10. Absorption spectra (as a function of Kubelka-Munk) of tissues modified with Ag/Cu (1), Ag (2), Cu (3) NPs

Fig. 11 shows a comparative activity of tissue samples with Ag and bimetallic NPs (BMNP) against a number of microorganisms (*Escherichia coli*, *Klebsiella pneumoniae*, *Enterobacter aerogenes*, *Proteus mirabilis*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*). The activity of the samples with BMNP exceeds that of the silver NPs against a series of bacteria due to the synergistic effect. The increased antimicrobial action of silver-copper/fabric compounds is the result of the release of biologically active Ag⁺/Cu²⁺ binary ions from the surface of BMNP, and their combined interaction with bacterial membranes.

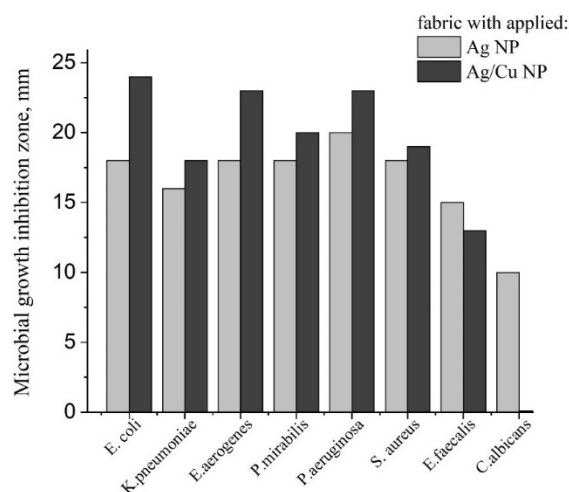


Fig. 11. Comparative activity of tissue samples with silver and bimetallic NPs in relation to different cultures of bacteria

SEM – image of the surface of cotton, modified Ag and Ag/Cu NPs is shown in Fig. 12.

Measurements of electrical resistance (mobility of the NPs in the fabric) show that dry fabrics with applied NPs are insulators, which

indicates the absence of contact between the NPs in the fabric structure [81]. A sharp decrease in the electrical resistance of the tissue when soaked in water or electrolyte solution indicates the diffusion of ions and/or metal atoms in the tissue,

which is a strong argument in favor of the mechanism of action of NPs in the tissue structure in contact with biological fluids containing bacteria [82].

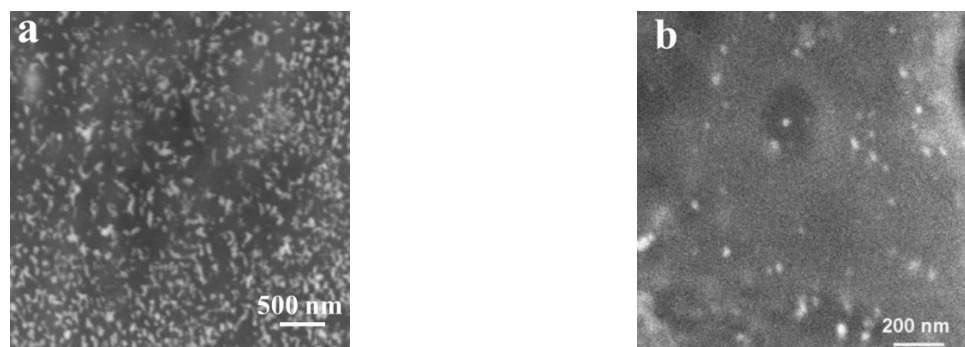


Fig. 12. Electron microscopic image of tissue impregnated with *a* – Ag and *b* – Ag/Cu NPs

To verify the assumption of ion migration from the NPs surface upon contact with water or biological tissue fluids, three 24-hour cycles of desorption in water were performed, after which the amount of released ions was determined. Fig. 13 shows the % of silver ions that are washed from the respective tissue samples after 3 cycles of desorption. The largest amount of silver ions is released from the tissue surface in the first cycle of desorption in water, after the second and third cycles of desorption, the release of silver decreases almost 4.5 times. Interestingly, the presence of copper in samples Ag/Cu (1) and Ag/Cu (2) (made by soft heat treatment of various starting salts of copper (sulfate (1) or nitrate(2) and silver nitrate) significantly contributes to the retention of silver inside the fabric. Tissue samples containing Ag⁺ and Cu²⁺ ions show similar behavior (Fig. 13).

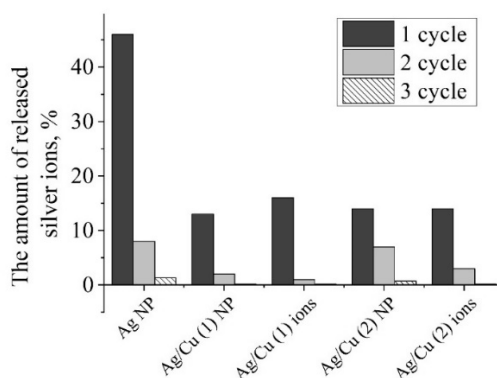


Fig. 13. The amount of silver ions released from modified tissues during three consecutive cycles of desorption

The amount of copper ions detected in water after the cycles of desorption from tissues containing Ag/Cu (1) and Ag/Cu (2) after 1 and 24 hours of desorption is much less than the amount of desorbed silver ions (Fig. 14). Cu presents on the surface of the tissue mainly in the form of oxide, protoxide, and dolerophanite, from the surface of which the release of copper ions is complicated, compared with Cu NPs. It is possible that Ag NPs are tightly held on the surface of copper oxides, with the formation of an alloy-like structure. The second and third desorption cycles (48 and 72 hours) do not lead to the release of copper ions from Ag/Cu (1) and Ag/Cu (2) tissues. The same trends were observed for tissues containing only copper ions: approximately 30 % of ions are washed out after 24 hours of contact with water.

The concentration of NPs in the tissue correlates with the electrical resistance (ER) of the samples before and after desorption, which was carried out in several cycles, as described above. For the dry tissue impregnated with silver and copper ions, the ER is 1000 kOhm, and after contact with the electrolyte solution (0.1 M KNO₃) it decreases to 10 kOhm. After three cycles of desorption (24, 48 and 72 hours of contact with water), its resistance in the presence of KNO₃ solution increases (and the conductivity decreases) and is 620, 1800 and 2000 kOhm, respectively (Fig. 15). The decrease in the metal content on the tissue surface before and after several cycles of desorption was confirmed by atomic absorption spectroscopy (Fig. 16).

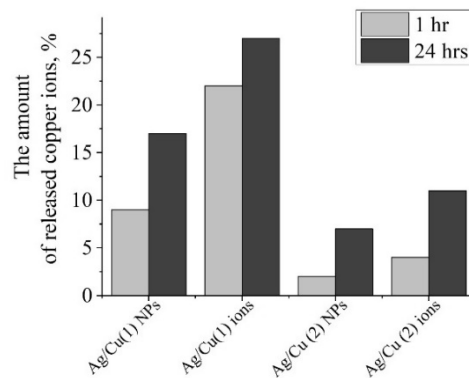


Fig. 14. The amount of released copper ions from modified tissues after desorption for 1 hour and 24 hours in water

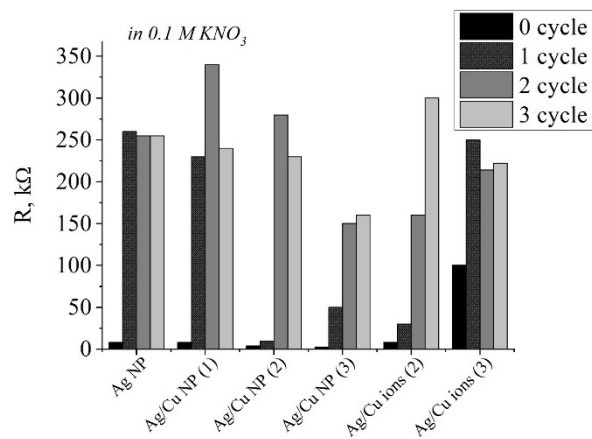


Fig. 15. Electrical resistance of tissues with nanoparticles and metal ions in 0.1 M KNO₃

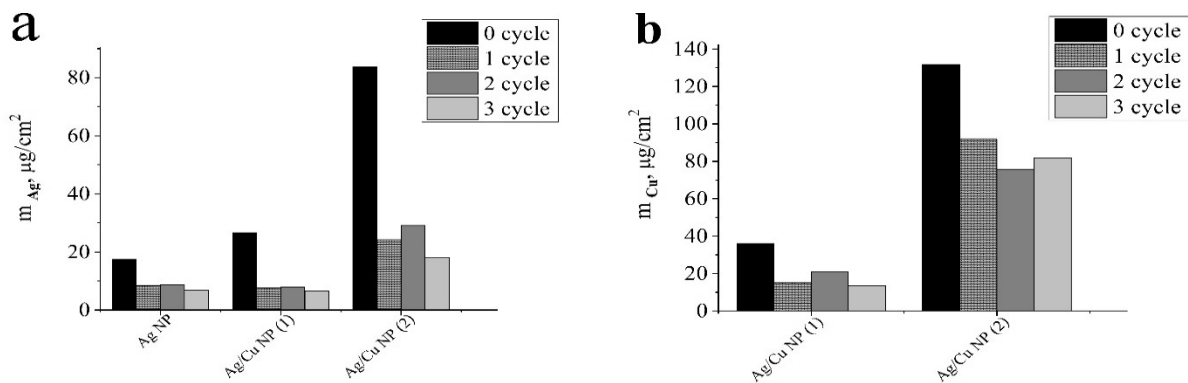


Fig. 16. The amount of silver (a) and copper (b) atoms on the surface of tissues before and after 0–3 cycles of desorption

Thus, the NPs in the tissue structure are in different degrees of binding, a certain part of them is adsorbed irreversibly, retaining bactericidal properties after repeated contact with water or bioliquids.

The decrease in the NPs content on the tissue surface after contact with water can be traced in the evolution of the spectra of diffuse reflection (Fig. 17). A band of surface plasmon resonance of the Ag NPs is observed for all samples. The

maximum spectra are shifted after the loss of some ions. In Ag/Cu (1) the intensity of Ag SPR decreases, after the second and third cycles of desorption it increases. We believe that silver is reduced and new Ag NPs are formed from silver ions with the participation of tissue glucoside residues.

The bactericidal properties of mono- and BMNC-modified tissues after three soaking cycles are shown in Table 4. The corresponding AgNO₃ and Cu(CH₃COO)₂·2H₂O salts were used to obtain the Ag and Ag/Cu NPs samples indicated in the Table.

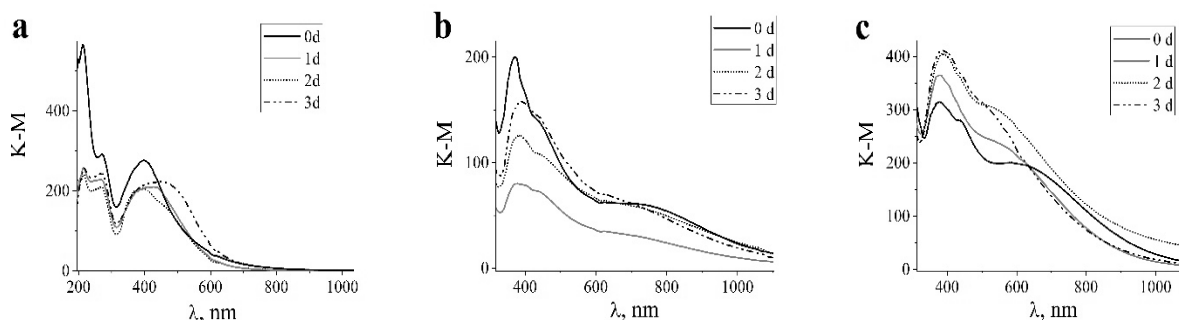


Fig. 17. DRS of tissues modified Ag (a), Ag/Cu (1) (b) and Ag/Cu (2) NPs (c) after three cycles of desorption

Table 4. Bactericidal properties of tissues modified with mono- and BMNPs after three desorption cycles of metal ions (24, 48 and 72 hours)

Composition	Desorption cycle	Bacterial growth inhibition zone, mm							
		<i>E. coli</i>	<i>K. pneumoniae</i>	<i>P. mirabilis</i>	<i>P. aeruginosa</i>	<i>E. faecalis</i>	<i>S. aureus</i>	<i>C. albicans</i>	<i>C. non albicans</i>
Ag NP	0	19	13	17	24	12	17	⊖	11
	1	18	13	18	23	14	⊖	⊖	⊖
	2	18	12	17	22	⊖	⊖	⊖	⊖
	3	17	11	17	17	⊖	⊖	⊖	11
Ag ions	0	16	0	15	18	⊖	15	⊖	⊖
	1	16	⊖	17	20	⊖	⊖	⊖	⊖
	2	12	⊖	18	21	⊖	⊖	⊖	0
	3	17	⊖	15	19	⊖	⊖	12	0
Ag/Cu NP	0	20	12	17	18	15	19	12	0
	1	18	12	18	27	⊖	16	⊖	0
	2	17	12	20	26	12	18	11	0
	3	19	11	19	25	⊖	16	11	⊖
Ag/Cu ions	0	20	13	19	27	16	20	⊖	⊖
	1	20	12	20	25	16	18	⊖	⊖
	2	15	11	⊖	25	12	17	⊖	0
	3	19	11	18	22	⊖	16	⊖	0

⊖ – No growth under the disc, no growth of inhibition zone

However, as noted in [83], the results of studies presented in numerous publications have certain limitations that make it difficult to compare antibacterial activity, such as different properties of NPs, use of different bacterial strains, lack of standardization of duration of work and so on.

Table 5 shows some literature data on the bactericidal activity of silver NPs on different types of tissues, taken from the article Zille *et al.*

([2] and references therein) (this is approximately 20 % of the data given in [2] having the relevant references). From the list of substances used for the manufacture and modification of fabrics, it should be noted that the production and use of biomedical textiles has recently focused on the widespread use of non-toxic biopolymers, such as chitosan, alginate, starch and others, combined with textile.

Table 5. Bactericidal properties of different types of tissues with Ag NPs [2]

Textile	Bactericidal Activity, %	Bactericidal activity after washing, %
Acrylic with starch NPs	20	0.5–1
Bamboo with starch NPs	98.7	84.9
Cellulose acetate (electrospinning)	99	0
Cotton with alginate, impregnation with colloidal Ag NPs after microwave treatment	99.9	99.9
Chitosan with impregnated Ag NPs	99.9	65
Cotton with polyester + Ag/SiO ₂ and drying	100	0
Polyamide + polyester + Ag NPs, electrospinning	99.9	0
Polyester + colloid Ag NPs	99.7	15.3
Chitosan + colloid LF Ag, impregnation	90	50
SiO ₂ /Ag/CuO	100	20
Ag/TiO ₂ spinning	99	0
Chitosan + colloid Ag NPs electrospinning	99.9	0
colloid Ag NPs + silk impregnation	99 at high Ag content	98
SiO ₂ + Ag NPs colloid impregnation	71	0
Alginate on trypton-soy agar, impregnated on the fabric [84]	99	99

Main trends of innovative fabric processing technologies according to the analysis of literature data and the needs of today will be aimed at the production of textiles with new functionalities, such as protection against biological, chemical, mechanical, thermal attacks, protection against UV radiation, long-term use *etc.*

CONCLUSIONS

1. The biocidal efficiency of Ag NPs depends on the method of synthesis and the environment: the highest in the colloidal state (99%), slightly reduced in the structure of SiO₂ and in the composition of textile fabrics. The shape of the NPs is mostly spherical, the distribution is

uniform, the nanoscale of silver is spectrally confirmed by the presence of a band of surface plasmon resonance. To prevent aggregation of NPs obtained by the method of chemical reduction in solution, the optimal ratio of two stabilizers based on surfactants and polymer at their minimum concentration was found, which prevents aggregation while maintaining bactericidal activity and stability for more than 3 years.

The amino acid tryptophan has a dual function – a biocompatible reducing agent and stabilizer of silver NPs while maintaining their shape, size and stability for long-term use.

2. Effective methods for photochemical synthesis of Ag are developed: 1) irradiation of

silver ions in the presence of solid-state photosensitizer SiO₂/BPh (adsorbed benzophenone) 2) formation and fixation of AgNPs on the surface of silica films when irradiated the ionic form of Ag⁺/SiO₂ in a solution of benzophenone and 3) UV activation of the synthesis of Ag NPs with a given size in the presence of the amino acid tryptophan. The Ag/SiO₂ system has a slightly increased microbial deactivation time.

3. The dynamics of silver ions release from the surface of NPs in the structure of textile upon their contact with water for 72 hours and the number of irreversibly bound particles have been studied.

4. An original cheap and convenient way to modify cotton/NPs by soft heat treatment with

high (90–95 %) efficiency of destruction of bacteria *E. coli*, *K. pneumoniae*, *E. aerogenes*, *P. vulgaris*, *S. aureus*, *C. albicans et al.*, with saved biocidal activity after 5 cycles of washing has been developed.

5. The concentration of NPs in the tissue correlates with electrical resistance of the tissue. That is NPs in the structure are in different degrees of binding, a certain part of them is retained (adsorbed) irreversibly, saving bactericidal properties after repeated contacts with water.

6. Ecologically safe “green synthesis” is a promising way to produce silver NPs with pronounced bactericidal efficiency, which is becoming more common due to the large resource of cheap plant raw materials.

Особливості синтезу та бактерицидні властивості наносрібла в колоїдних розчинах, плівках SiO₂ та в структурі текстилю: огляд

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Метою даної роботи є порівняльний аналіз біоцидної ефективності наночастинок Ag (НЧ) у колоїдному стані, структурі плівок і дисперсії SiO₂ та в складі текстильних тканин, в залежності від методу синтезу, на основі літературних даних та власних досліджень. Хімічне відновлення срібла (борогідрідами, воднем, гідразином тощо) дозволяє регулювати і контролювати розмір і форму НЧ. Форма НЧ переважно сферична, що підтверджується наявністю смуги поверхневого плазмонного резонансу в спектрах поглинання та електронно-мікроскопічними дослідженнями. Для запобігання агрегації НЧ, отриманих методом хімічного відновлення в розчині, було встановлено оптимальне співвідношення двох стабілізаторів на основі ПАР та полімера полівінілпіролідон + додецилсульфат натрію як бінарний стабілізатор Ag НЧ при їх мінімальній концентрації, та NaBH₄ як відновника, з бактерицидною активністю 99 % та стабільністю НЧ понад 3 роки. Хімічне відновлення іонів срібла здійснювалось також амінокислотою триптофан (Trp), яка виконує подвійну функцію - біосумісний відновник та стабілізатор НЧ срібла, при збереженні їхньої форми, розміру та високої стабільності.

Ефективні методи фотохімічного синтезу НЧ Ag розроблені різними способами: шляхом УФ-опромінення іонів Ag⁺ у розчині в присутності твердого фотосенсибілізатора SiO₂ з адсорбованим бензофеноном (SiO₂/BPh); шляхом УФ-опромінення іонів Ag⁺ у розчині в присутності Trp; на поверхні кремнезему при золь-гель синтезі плівок Ag⁺/SiO₂ шляхом опромінення адсорбованих іонів Ag⁺ на плівці SiO₂ у розчині BPh. Показано, що при адсорбції НЧ Ag на поверхні високодисперсного SiO₂ логарифм ступеня відновлення мікроорганізмів зменшується, а час їхньої дезактивації збільшується.

*Розроблено дешевий і зручний спосіб модифікації бавовняного текстилю за допомогою НЧ Ag шляхом м'якої термічної обробки зразків бавовни, просоченої іонами срібла, з високою (90–95 %) ефективністю знищення бактерій *E. coli*, *K. pneumoniae*, *E. aerogenes*, *P. vulgaris*, *S. aureus*, *C. albicans* та ін., із збереженням біоцидної активності після 5 циклів прання. Вивчено динаміку вимивання (десорбції) іонів срібла з поверхні НЧ у структурі текстилю при їхньому контакті з водою протягом 72 годин та вивчено кількість необоротно зв'язаних частинок. Електричний опір тканини пропорційний кількості НЧ, тобто НЧ у структурі*

знаходяться в різному ступені зв'язування, певна їх частина адсорбується необоротно, зберігаючи бактерицидні властивості після багаторазових контактів з водою. На основі аналізу літератури показано, що екологічно безпечний "зелений синтез" є перспективним способом отримання НЧ срібла з вираженою бактерицидною ефективністю, який стає все більш поширеним завдяки великому ресурсу дешевої рослинної сировини.

Ключові слова: іони срібла, наночастинки срібла, хімічне відновлення, фотохімічне відновлення, стабілізація, колоїди, SiO_2 плівки, дисперсії SiO_2 , текстиль, бактерицидна активність

REFERENCES

1. Edwards B. *Silver nanoparticles. Advances in research and application*. (New York: Nova Science Publishers, 2017).
2. Zille A., Almeida L., Amorim T., Carneiro N., Esteves M.F., Silva C.J., Souto A.P. Application of nanotechnology in antimicrobial finishing of biomedical textiles. *Mater. Res. Express*. 2014. **1**(3): 32003.
3. Marambio-Jones C., Hoek E.M.V. A review of the antibacterial effects of silver nanomaterials and potential implications for human health and the environment. *J. Nanopart. Res.* 2010. **12**: 1531.
4. Sánchez-López E., Gomes D., Esteruelas G., Bonilla L., Lopez-Machado A.L., Galindo R., Cano A., Espina M., Ettcheto M., Camins A., Silva A.M., Durazzo A., Santini A., Garcia M.L., Souto E.B. Metal-Based Nanoparticles as Antimicrobial Agents: An Overview. *Nanomaterials*. 2020. **10**(2): 292.
5. Bukina Yu.A., Sergeeva E.A. Antibacterial properties and mechanism of bactericidal action of silver nanoparticles and ions. *Bulletin of the Kazan Technological University*. 2012. **14**:170. [in Russian].
6. Holler J.S., Nordberg G.F., Fowler B.A. *Handbook on the Toxicology of Metals*. (Amsterdam: Elsevier Sci. Pub., 1986).
7. Scherbakov A.B. Silver preparations. *Pharmaceutical Journal*. 2006. **5**: 45. [in Russian].
8. Savadyan E.S., Melnikova V.M., Belikova G.P. Current trends in the use of silver-containing antiseptics. *Antibiotics and Chemotherapy*. 1989. **11**: 874. [in Russian].
9. Ivask A., Juganson K., Bondarenko O., Mortimer M., Aruoja V., Kasemets K., Kahru A. Mechanisms of toxic action of Ag, ZnO and CuO nanoparticles to selected ecotoxicological test organisms and mammalian cells in vitro: a comparative review. *Nanotoxicology*. 2014. **1**: 57.
10. Schrand A.M., Rahman M.F., Hussain S.M., Schlager J.J., Smith D.A., SyedA. F. Metal-based nanoparticles and their toxicity assessment. *Wiley Interdiscip. Rev. Nanomed. Nanobiotechnol.* 2010. **2**(5): 544.
11. Hsiao T.-C. Allergenicity and toxicology of inhaled silver nanoparticles in allergen-provocation mice models. *Int. J. Nanomedicine*. 2013. **8**: 4495.
12. Amaro F., Moron A., Diaz S., Martin-Gonzalez A., Gutierrez J.C. Metallic Nanoparticles—Friends or Foes in the Battle against Antibiotic-Resistant Bacteria? *Microorganisms*. 2021. **9**(2): 364.
13. Beer C., Foldbjerg R., Hayashi Y., Sutherland D.S., Autrup H. Toxicity of silver nanoparticles - nanoparticle or silver ion? *Toxicol. Lett.* 2012. **208**(3): 286.
14. Leonenko N.S. Comparative analysis of toxicity and danger of chemical compounds of various dimensions. *Ukrainian Journal Modern Problems of Toxicology, Modern Problems of Toxicology, Food and Chemical Safety*. 2016. **2**: 48.
15. Ji J.H. Twenty-eight-day inhalation toxicity study of silver nanoparticles in Sprague-Dawley rats. *Inhal. Toxicol.* 2007. **19**(10): 857.
16. Kim Y.S., Kim J.S., Cho H.S., Rha D.S., Kim J.M., Park J.D., Choi B.S., Lim R., Chang H.K., Chung Y.H., Kwon I.H., Jeong J., Han B.S., Yu I.J. Twenty-eight-day oral toxicity, genotoxicity, and gender-related tissue distribution of silver nanoparticles in Sprague-Dawley rats. *Inhal. Toxicol.* 2008. **20**(6): 575.
17. Kaba S.I., Ignashkova T.I., Rybakov A.S., Meshchersky M.E., Sokolovskaya A.A., Yurkiv V.A., Moskovtsev A.A., Egorova E.M., Kubatiev A.A. Cytotoxic and stress-inducing effect of silver nanoparticles on cells of HeLa and U937 lines. *Pathogenesis*. 2013. **11**(2): 46.
18. Panacek A., Kvitek L., Smekalova M., Vecerova R., Kolar M., Roderova M., Dycka F., Sebela M., Prucek R., Tomanec O., Radek Z. Bacterial resistance to silver nanoparticles and how to overcome it. *Nat. Nanotechnol.* 2018. **13**: 65.
19. Tang J., Wu Y., Esquivel-Elizondo S., Sorensen S.J., Rittmann B.E. How Microbial Aggregates Protect against Nanoparticle, Toxicity. *Trends Biotechnol.* 2018. **36**(11): 1171.

20. Ellis D.H., Maurer-Gardner E.I., Sulentic C.E.W., Hussain S.M. Silver nanoparticle antibacterial efficacy and resistance, development in key bacterial species. *Biomed. Phys. Eng. Express*. 2018. **5**(1): 015013.
21. Petritskaya E.N., Rogatkin D.A., Rusanova E.V. Comparative characteristics of the antibacterial action of silver and nanophase silver in vitro. *Almanac of Clinical Medicine*. 2016. **44**(2): 221. [in Russian].
22. Park Y., Hong Y.N., Weyers A., Kim Y.S., Linhardt R.J. Polysaccharides and phytochemicals: a natural reservoir for the green synthesis of gold and silver nanoparticles. *IET Nanobiotechnol.* 2011. **5**(3): 69.
23. Sperling R.A., Parak W.J. Surface Modification, Functionalization and Bioconjugation of Colloidal Inorganic Nanoparticles. *Philosophical Transactions of the Royal Society A*. 2010. **368**(1915): 1333.
24. Roy S., Das T.K. Plant Mediated Green Synthesis of Silver Nanoparticles-A Review. *Int. J. Plant Biol. Res.* 2015. **3**(3): 1044.
25. Laguta I., Stavinskaya O., Kazakova O., Fesenko T., Brychka S. Green synthesis of silver nanoparticles using *Stevia* leaves extracts. *Appl. Nanosci.* 2019. **9**(2): 755.
26. Stavinskaya O., Laguta I., Fesenko T., Krumova M. Effect of Temperature on Green Synthesis of Silver Nanoparticles Using *Vitex Agnus-castus* Extract. *Chemistry Journal of Moldova*. 2019. **14**(2): 1857.
27. Laguta I., Fesenko T., Stavinskaya O., Dzijuba O., Shpak L. Antioxidant and antimicrobial properties of *Stevia* leaves extracts and silver nanoparticles colloids. *Chemistry Journal of Moldova*. 2016. **11**(2): 46.
28. Okafor F., Janen A., Kukhtareva T., Edwards V., Curley M. Green Synthesis of Silver Nanoparticles, Their Characterization, Application and Antibacterial Activity. *Int. J. Environ. Res. Public Health*. 2013. **10**(10): 5221.
29. Abdelghany T.M., Al-Rajhi A.M.H., Al Abboud M.A., Alawlaqi M.M., Magdah A.G., Helmy E.A.M., Mabrouk A.S. Recent Advances in Green Synthesis of Silver Nanoparticles and Their Applications: About Future Directions. A Review. *BioNanoScience*. 2018. **8**: 5.
30. Shankar K.G., Pradhan N., Masilamani K., Fleming A.T. Silver Nanoparticles from *Trianthema Portulacastrum*: Green Synthesis, Characterization, Antibacterial and Anticancer Properties. *Asian. J. Pharm. Clin. Res.* 2017. **10**(3): 308.
31. Turkevich J., Stevenson P.C., Hillier J. A study of the nucleation and growth processes in the synthesis of colloidal gold. *Spec. Discuss. Faraday Soc. Special*. 1951. **11**: 55.
32. Zhang Q., Li N., Goebel J., Lu Z., Yin Y. A Systematic Study of the Synthesis of Silver Nanoplates: Is Citrate a "Magic" Reagent? *J. Am. Chem. Soc.* 2011. **133**(46): 18931.
33. Kim B.H., Lee J.S. One-pot photochemical synthesis of silver nanodisks using a conventional metal-halide lamp. *Mater. Chem. Phys.* 2015. **149–150**: 678.
34. Zhang J., Langille M.R., Mirkin C.A. Synthesis of silver nanorods by low energy excitation of spherical plasmonic seeds. *Nano Lett.* 2011. **11**(6): 2495.
35. Henglein A., Mulvaney P., Linnert T. Chemistry of Ag_n aggregates in aqueous solution: non-metallic oligomeric clusters and metallic particles. *Faraday Discuss.* 1991. **92**: 31.
36. Pal S., Tak Y.K., Song J.M. Does the antibacterial activity of silver nanoparticles depend on the shape of the nanoparticle? A study of the gram-negative bacterium *Escherichia coli*. *Appl. Environ. Microbiol.* 2007. **73**(6): 1712.
37. Bobiev G.M., Sufiev T.D., Shakhmatov A.N. Antibacterial activity of coordination compounds of silver and tryptophan. *Pharm. Chem. J.* 2008. **42**(11): 10. [in Russian].
38. Bobiev G.M., Sufiev T.D., Shakhmatov A.N., Abdulov Kh.Sh. Synthesis and characterization of coordination compounds of silver and tryptophan. *Pharm. Chem. J.* 2008. **42**(12): 36. [in Russian].
39. Zaheer Z., Malik M.A., Al-Nowaiser F.M., Khan Z.Z. Preparation of silver nanoparticles using tryptophan and its formation mechanism. *Colloids Surf. B*. 2010. **81**(2): 587.
40. Mukha Iu., Vityuk N., Severynovska O., Eremenko A., Smirnova N. The pH-Dependent Structure and Properties of Au and Ag Nanoparticles Produced by Tryptophan Reduction. *Nanoscale Res. Lett.* 2016. **11**: 101.
41. Vityuk N.V., Mukha Iu.P., Makhno S.M., Eremenko A.M., Smirnova N.P. Stabilization of silver nanoparticles in the presence of tryptophan. *Surface*. 2015. **7**(22): 222. [in Ukrainian].
42. Mukha Iu., Vityuk N., Khodko A., Kachalova N., Fedyshyn O., Malysheva M., Eremenko A. Photo- and temperature-dependent formation of tryptophan/silver nanoparticles. *Res. Chem. Intermed.* 2019. **45**(8): 4053.
43. Naumovets A.G. *Nanosized systems and nanomaterials: research in Ukraine*. (Kyiv: Akadempriodyka, 2014). [in Russian].
44. Shmarakov I.O., Mukha Iu.P., Karavan V.V., Chunikhin O.Yu., Marchenko M.M., Smirnova N.P., Eremenko A.M. Tryptophan assisted synthesis reduces bimetallic gold/silver nanoparticle cytotoxicity and improves biological activity. *Nanobiomedicine*. 2014. **1**: 01.
45. Mukha Iu., Vityuk N., Grodzyuk G., Shcherbakov S., Lyberopoulou A., Efsthathopoulos E.P., Gazouli M. Anticancer effect of Ag, Au, and Ag/Au bimetallic nanoparticles prepared in the presence of tryptophan. *J. Nanosci. Nanotechnol.* 2017. **17**(12):8987.

46. Krylova G., Eremenko A., Smirnova N. Photochemical production of stable gold nanoparticles in aqueous solutions and in silicate matrix. In: *All-Ukrainian Conference of Young Scientists "Nanomaterials in Chemistry, Biology and Medicine"*. (Kyiv, 2006). P. 68. [in Ukrainian].
47. Yashan H., Krylova G., Eremenko A., Smirnova N., Huang W., Tabor Ch. Optical Spectra and Morphology of Photochemically Produced Ag/Au Bimetallic Clusters. In: *Springer Book of NATO Science Series, Sol-Gel Methods for Materials Processing*. Proc. of the NATO Advanced Research Workshop on Sol-Gel Approaches to Materials for Pollutin Control, Water Purification and Soil Remediation. (2008, Kyiv, Ukraine). P. 473.
48. Eustis S., Krylova G., Eremenko A., Smirnova N., Schill A.W., El-Sayed M. Growth and Fragmentation of Silver Nanoparticles in their Synthesis with femtosecond Laser and CW Light by Photo-Sensitization with Benzophenone. *Photochem. Photobiol. Sci.* 2005. **4**(1): 154.
49. Krylova G., Eremenko A., Smirnova N., Eustis S. Photochemical formation of Ag nanoparticles in water-alcohol solutions and on the surface of mesoporous silica. *Theor. Exp. Chem.* 2005. **41**(2):105.
50. Krylova G., Eremenko A., Smirnova N., Eustis S. Structure and spectra of photochemically obtained nanosized silver particles in presence of modified porous silica. *Int. J. Photoenergy.* 2005. **7**(4): 193.
51. Krylova G., Smirnova N., Eremenko A., Eustis S., Huang W., El-Sayed M.A. Photocatalytic production of silver nanoparticles with benzophenone modified silica films. *J. Photochem. Photobiol. A.* 2006. **181**: 385.
52. Mukha Y.P., Eremenko A.M., Smirnova N.P., Mikhienkova A.I., Korchak G.I., Gorchev V.F., Chunikhin A.Yu. Antimicrobial activity of stable silver nanoparticles of a certain size. *Prikladnaia biokhimiia i mikrobiologiya.* 2013. **49**(2): 215.
53. Grechko L.G., Eremenko A.M., Krylova G.V., Smirnova N.P. Optical properties of small silver particles in colloidal solutions. *Visn. Kyiv. University, Ser: Phys.-Math. Science.* 2004. **4**: 450. [in Ukrainian].
54. Eremenko A.M., Yashan H.R., Krylova G.V., Smirnova N.P., Suzer S., Tabor Ch. Photochemical/thermal production, optical spectra and scanning electron microscopy of Ag/Au BMNP in silica sol-gel films. *Theor. Exp. Chem.* 2008. **44**(6): 348.
55. Krylova G., Eremenko A., Smirnova N. Photochemical generation of nanosized silver particles in mesoporous SiO₂ films. *Physics and Chemistry of Solid State.* 2006. **7**: 50.
56. Bugla-Ploskonska G., Leszkiewicz A. Bactericidal properties of silica particles with silver islands located on the surface. *Int. J. Antimicrob. Agents.* 2007. **29**: 738.
57. Yashan G.R., Krylova G.V., Eremenko A.M., Smirnova N.P., Jalko-Titarenko V.P., Marievsky V.F., Chekman I.S. Bactericidal properties of gold and silver nanoparticles in solutions and on the surface of highly dispersed silica. *Chemistry, Physics and Technology of Surface.* 2008. **14**: 524. [in Russian].
58. Shmarakov I.O., Marchenko M.M., Mukha Yu.P., Yashan G.R., Smirnova N.P., Eremenko G.M. Cyto- and genotoxic effect of colloidal nanopreparations based on Ag and Au on primary cell cultures. *Biological systems.* 2010. **2**(4): 13.
59. Patent UA 67484. Korchak G.I., Surmasheva O.V., Mikhienkova A.I., Yeremenko A.M., Mukha Yu.P., Smirnova N.P. Process for Preparation of Solutions of Nano-sized silver. 2012.
60. Patent UA 67536. Yeremenko A.M., Mukha Yu.P., Smirnova N.P., Surmasheva O.V., Mikhienkova A.I. Antibacterial Composite. 2012.
61. Mukha I., Eremenko A., Smirnova N., Korchak G, Mikhienkova A., Chekman I. Formation, physical – chemical and bactericidal properties of stabilized silver nanostructure on the surface of disperse silica. *Chemistry, Physics and Technology of Surface.* 2009. **15**: 255. [in Russian].
62. Mukha I., Eremenko A., Korchak G., Mikhienkova A. Antibacterial Action and Physicochemical Properties of Stabilized Silver and Gold Nanostructures on the Surface of Disperse Silica. *Journal of Water Resource and Protection.* 2010. **2**(2): 131.
63. Eremenko A.M., Smirnova N.P., Mukha Yu.P., Yashan G.R. Nanoparticles of silver and gold in silica matrices: synthesis, properties and application. *Theor. Exp. Chem.* 2010. **46**(2): 67.
64. Eremenko A., Smirnova N., Gnatiuk I., Linnik O., Vityuk N., Mukha I., Korduban A. Silver and Gold Nanoparticles on Sol-Gel TiO₂, ZrO₂, SiO₂ Surfaces: Optical Spectra, Photocatalytic Activity, Bactericide Properties. In: *Nanocomposites and Polymers with Analytical Methods.* (InTech, Rijeka, Croatia, 2011). P.51–82.
65. Mura S., Greppi G., Malfatti L., Lasio B., Sanna V., Mura M., Marceddu S., Lugli A. Multifunctionalization of wool fabrics through nanoparticles: A chemical route towards smart textiles. *J. Colloid Interface Sci.* 2015. **456**: 85.
66. Jasiorski M., Leszkiewicz A., Brzezinski S., Bugla-Ploskonska G., Malinowska G., Borak B., Karbownik I., Baszczuk A. Textile with silver silica spheres: it's antimicrobial activity against *Escherichiacoliand Staphylococcus aureus*. *J. Sol-Gel Sci. Technol.* 2009. **51**: 330.
67. Bianco C., Kezic S., Svetlicic M.C.V., Adami G. et al. In vitro percutaneous penetration and characterization of silver from silver - containing textiles. *Int. J. Nanomed.* 2015. **10**: 1899.
68. Cao H., Liu X., Meng F., Chu P.K. Biological actions of silver nanoparticles embedded in titanium controlled by micro-galvanic effects. *Biomaterials.* 2011. **32**(3): 693.

69. Agarwal A., Weis T., Schurr M., Faith N., Czuprynski C., McAnulty J., Murphy C., Abbott N. Surfaces modified with nanometer-thick silver-impregnated polymeric films that kill bacteria but support growth of mammalian cells. *Biomaterials*. 2010. **31**: 680.
70. Barcikowski S., Menendez-Manjon A., Chichkov B., Brikas M., Raciukaitis G. Generation of nanoparticle colloids by picosecond and femtosecond laser ablations in liquid flow. *Appl. Phys. Lett.* 2007. **91**: 083113.
71. Stelzig S., Menneking C., Hoffmann M., Eisele K., Barcikowski S., Klapper M., Mullen K. Compatibilization of laser generated antibacterial Ag- and Cu-nanoparticles for perfluorinated implant materials. *Eur. Polym. J.* 2011. **47**: 662.
72. Lohrer S., Schneider O., Maienfisch T., Bokorny S., Stark W. Micro-organism-triggered release of silver nanoparticles from biodegradable oxide carriers allows preparation of self-sterilizing polymer surfaces. *Small*. 2008. **4**(6): 824.
73. Khaydarov R., Khaydarov R., Gapurova O., Estrin Y., Scheper T. Electrochemical method of synthesis of silver nanoparticles. *J. Nanopart. Res.* 2009. **11**(5): 1193.
74. Yuranova T., Rincon A., Pulgarin C., Laub D., Xantopoulos N., Mathieu H.-J., Kiwi J. Performance and characterization of Ag-cotton and Ag/TiO₂ -loaded textiles during the abatement of *E. coli*. *J. Photochem. Photobiol. A*. 2006. **181**: 363.
75. Lee H., Yeo S., Jeong S. Antibacterial effect of nanosizes silver colloidal solution on textile fabrics. *J. Mater. Sci.* 2003. **38**: 2199.
76. Giannossa L.C., Longano D., Ditaranto N., Nitti M.A., Paladini F., Pollini M., Rai M., Sannino A., Valentini A., Cioffi N. Metal nanoantimicrobials for textile applications. *Nanotechnol. Rev.* 2013. **2**(3).
77. Timoshina Yu.A., Sergeeva E.A. Obtaining antibacterial textile materials based on silver nanoparticles by modifying the textile surface with nonequilibrium low-temperature plasma. *Bulletin of the Kazan Technological University*. 2012. **7**: 125. [in Russian].
78. Petrik I., Eremenko A., Rudenko A. Enhanced Bactericidal Activity of Cotton Fabrics Modified by Binary Ag/Cu Nanoparticle. *Am Journal of Biochemistry and Molecular Biology*. 2018. **3**(1): 1.
79. Eremenko A., Petrik I., Rudenko A., Tananaiko O., Lelyushok S., Ishchenko N. The peculiarities of Ag and Cu ions release from bactericidal textiles in water and their influence on spectral, electrical and biocide properties of textile. *J. Nanosci. Nanomed.* 2018. **2**(1): 20.
80. Petrik I.S., Eremenko A.M., Smirnova N.P., Rudenko A.V., Marikvas Y.S. Structural and optical properties of antibacterial materials based on Ag and Ag/Cu nanoparticles. In: *Ukrainian conference with international participation "Chemistry, Physics and Technology of Surface" devoted to the 30th anniversary of the founding of Chuiko Institute of Surface Chemistry of NAS of Ukraine and Workshop "Nanostructured Biocompatible/Bioactive Materials"*. (Kyiv, 2016). P. 131.
81. Eremenko A., Petrik I., Smirnova N., Rudenko A., Marikvas Y. Antibacterial and Antimycotic Activity of Cotton Fabrics, Impregnated with Silver and Binary Silver/Copper Nanoparticles. *Nanoscale Res. Lett.* 2016. **11**(28): 28.
82. Eremenko A., Petrik I., Smirnova N., Romanenko L., Surmasheva E., Korchak G., Tananaiko O., Ishchenko M. Bactericidal cotton fabrics modified by silver and copper nanoparticles: optical spectra, structures, electrical resistance. *Journal of Analytical, Bioanalytical and Separation Techniques*. 2016. **1**(1): 1.
83. Saddat Ghaderi R., Kazemi M., Soleimanpour S. Nanoparticles are More Successful Competitor than Antibiotics in Treating Bacterial Infections: A Review of the Literature. *Iran J. Med. Microbiol.* 2021. **15**(1): 18.
84. Kim H.W., Kim B.R., Rhee Y.H. Imparting durable antimicrobial properties to cotton fabrics using alginate-quaternary ammonium complex nanoparticles. *Carbohydr. Polym.* 2010. **79**: 1057.

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