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PECULIARITIES OF SYNTHESIS AND BACTERICIDAL PROPERTIES OF NANOSILVER IN COLLOIDAL SOLUTIONS, SiO_2 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 SiO_2 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 $NaBH_4$ 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 SiO_2 with adsorbed benzophenone (SiO_2/BPh); by UV irradiation of Ag^+ ions in solution in the presence of the amino acid tryptophan (Trp); on silica surface when Ag/SiO_2 sol-gel films production via irradiation of adsorbed Ag^+ ions on SiO_2 film (Ag^+/SiO_2) in the BPh solution. It is shown that when Ag NPs are adsorbed on the surface of highly dispersed SiO_2, 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, SiO_2 films, SiO_2 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, bio-chemical 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, terpinoids, as well as non-toxic renewable biopolymers such as chitosan, alginate, starch are used. Most of them contain OH, COOH, $-NH_2$ 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:

$$6AgNO_3+3Na_3C_6H_5O_7\cdot\rightarrow$$
$$\rightarrow 3Na_2C_5H_4O_5+3CO_2+3NaNO_3+3HNO_3.$$

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]:

$$4Ag^{+}+nBH_4^{-}+3nH_2O \rightarrow 4Ag+nH_2BO_3^{-}+4nH^{+}+2nH_2,$$

$$8Ag^{+} + nBH_4^{-} + 3nH_2O \rightarrow 8Ag+ nH_2BO_3^{-} + 8nH^{+}.$$

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

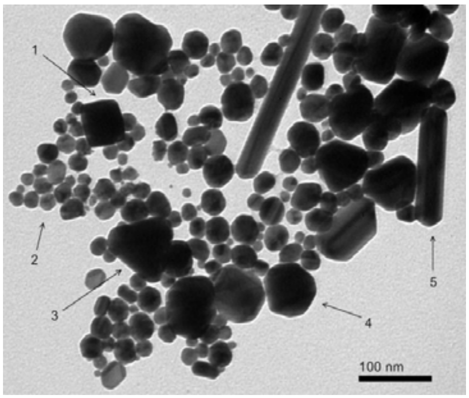


Fig. 1. TEM images of silver nanoparticles (magnification ×200000) of various shapes and sizes: (*1*) cubic, (*2*) spherical ~ 10 nm, (*3*) triangular, (*4*) spherical ~ 60 nm, (*5*) rods. TEM was performed using JEOL JEM 1400 TEM (Tokyo, Japan) [2]

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).

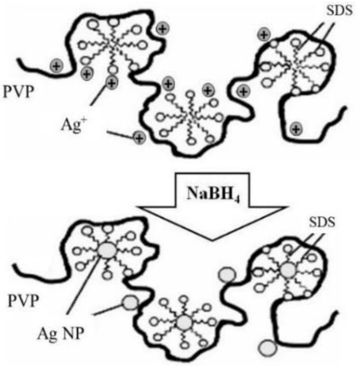
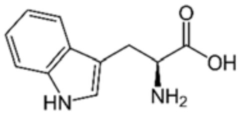


Fig. 2. Schematic representation of the interaction of the stabilizer SDS/ PVP with Ag $^{+}$ ions and NPs after reduction

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 $\lambda_{\max}$ = 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:



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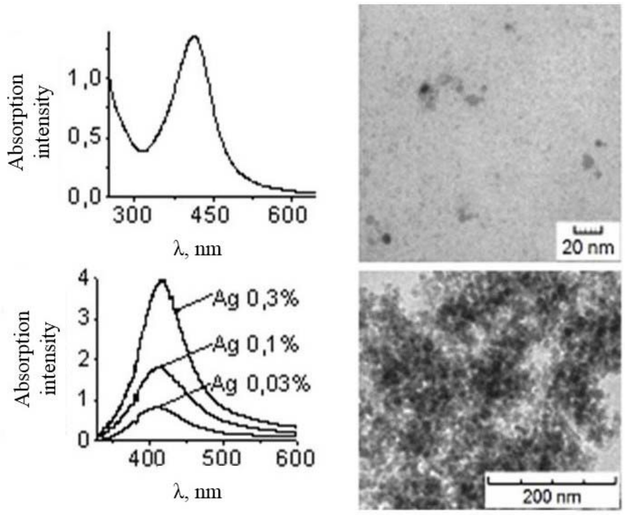


a *b*

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**		
		E. coli	***S. aureus***	***C. albicans***
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 –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*).

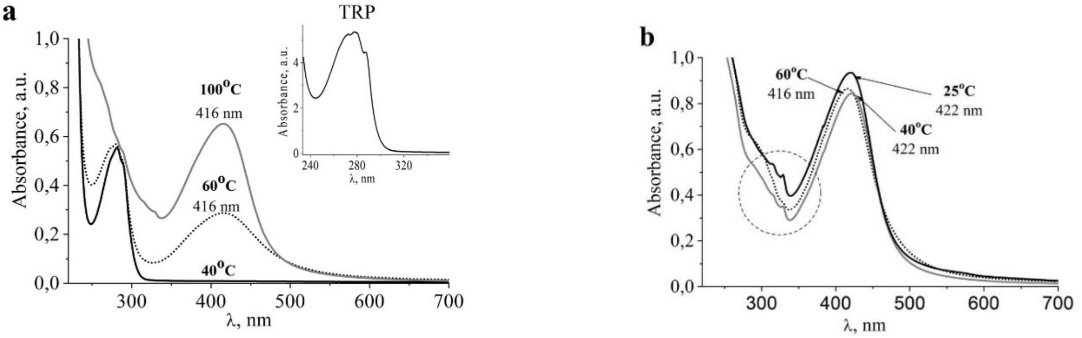
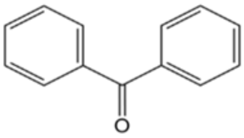


Fig. 4. *a* – Absorption spectra of Ag NPs in colloids obtained in the presence of Trp at different temperatures without UV-C irradiation; *b* – absorption spectra of colloids of Ag NPs at different temperatures with UV-C irradiation (λ = 278 nm, initial optical power density 1.0 mW/cm^2) after a week 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) – SiO_2/BPh_{ad}, for one-stage reduction of noble and transition metal ions in solution [46–53]:



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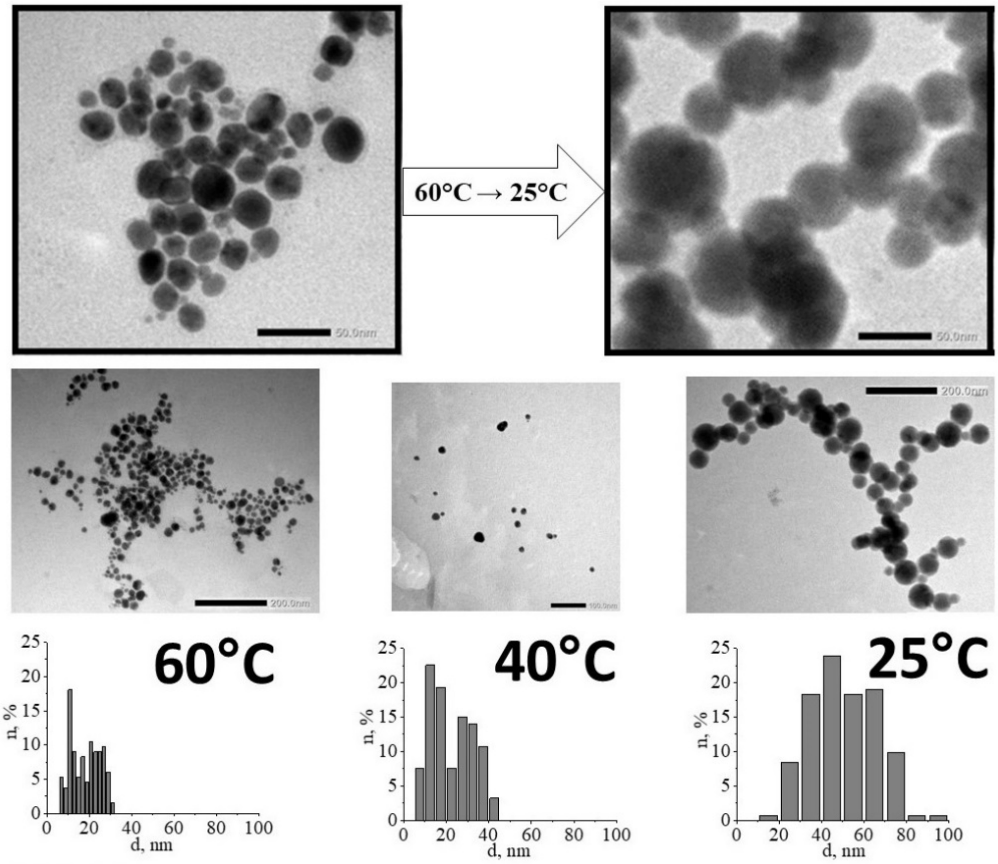

Fig. 5. TEM images of Ag NPs obtained under UV irradiation at 60, 40, and 25 °C and the corresponding size distributions calculated using ImageJ

Synthesis of mesoporous SiO_2-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 SiO_2-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:

$$R_2C^{\bullet}OH + Ag^{+} \rightarrow R_2C{=}O + Ag^{0} + H^{+} \quad (R = CH_3,\ C_6H_5)$$

$$R_2C^{\bullet}O^{-} + Ag^{+} \rightarrow R_2C{=}O + Ag^{0}.$$

Formation of primary clusters and growth of Ag NPs:

$$nAg^{0} \rightarrow (Ag)_n\ ,$$

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

$$R_2C^{\bullet}OH + (Ag^{0})_n \rightarrow R_2CO + (Ag^{0}) + H^{+}.$$

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 SiO_2-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 SiO_2. Here, on the contrary, BPh is in solution and silver ions are fixed in the SiO_2 film. The first stage of the synthesis is to add a solution of $AgNO_3$ to the precursor SiO_2 at the stage of sol-gel transition. After drawing the film on a glass substrate and appropriate heat treatment, the Ag^{+}/SiO_2 film was irradiated in aqueous-alcoholic BPh solution. Absorption spectra of SiO_2-Ag films 2 % before (1) and after 15 min irradiation (2) in $1.4 \cdot 10^{-3}$ M solution of BPh in isopropanol and SEM image of SiO_2-Ag film after 15 minutes of irradiation with distribution of Ag NPs by size are shown in Fig. 7 [54–56].

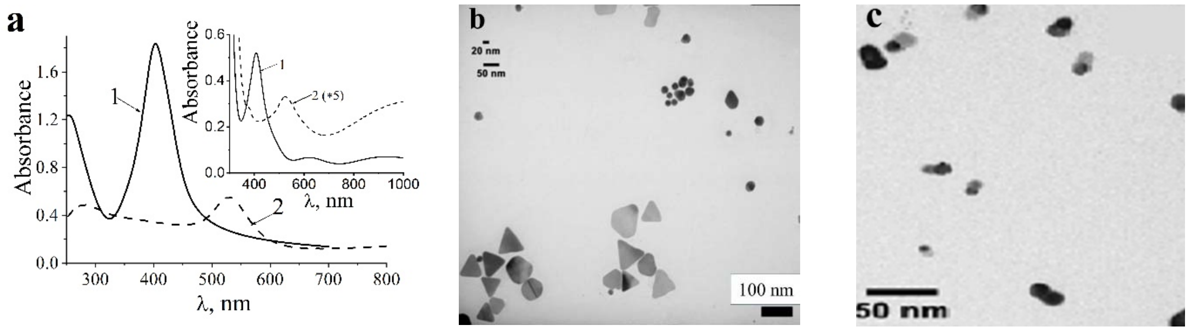

Fig. 6. *a* – Absorption spectra: *1* – colloidal solution of Ag NPs; *2* – colloidal solution of Au NPs; in the insert: absorption spectra: *1* – films SiO_2-Ag 10 %, and *2* – SiO_2-Au 10 %; *b* – TEM images of colloids Au NPs; *c* – TEM images of colloids Ag NPs

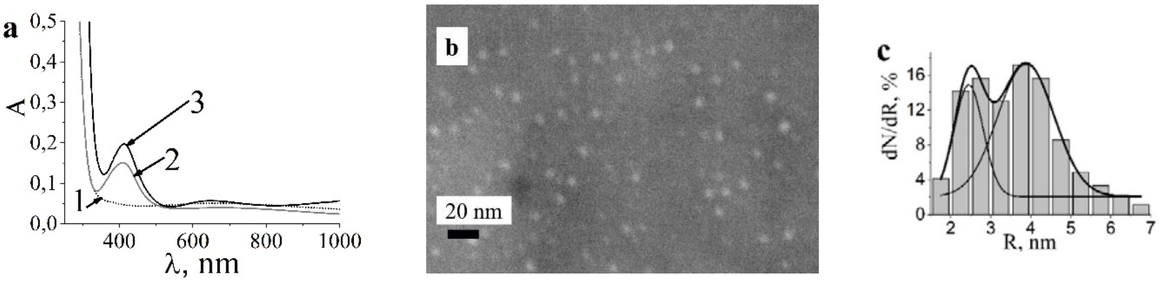

Fig. 7. *a* – absorption spectra of SiO_2-Ag 2 % films before (*1*) and after 15 min of irradiation (*2*) in a $1.4 \cdot 10^{-3}$ M solution of BPh in isopropanol (*3*) the spectrum of the SiO_2-Ag film after 6 hours of calcination at 500 °C; *b* – SEM image of SiO_2-Ag film after 15 min of irradiation; *c* – size distribution of photogenerated Ag NPs

Bactericidal activity of silver NPs in the colloidal state and in the presence of Ag/SiO$_2$ composite. Colloidal solutions of nanosized silver and Ag/SiO_2 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 $lgR = lgN_0 – lgN_a$, 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].

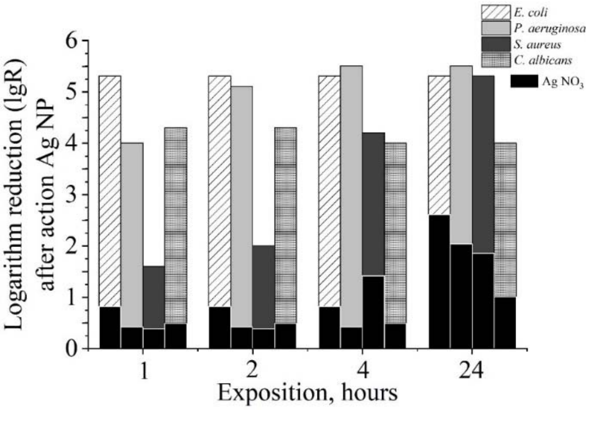

Fig. 8. Antimicrobial activity of colloidal Ag NPs (lgR)

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/SiO_2 (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 *lgN₀*
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/SiO_2 suspension, lg R

Sample	Time of exposition, h	Test strains		
		E. coli	*S. aureus*	*C. albicans*
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, *lgNo*		7.21	7.32	6.69

Bactericidal activity of AgNPs in suspensions of nanodisperse SiO₂. As mentioned above, Ag/SiO_2 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 m^2/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/SiO_2 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].

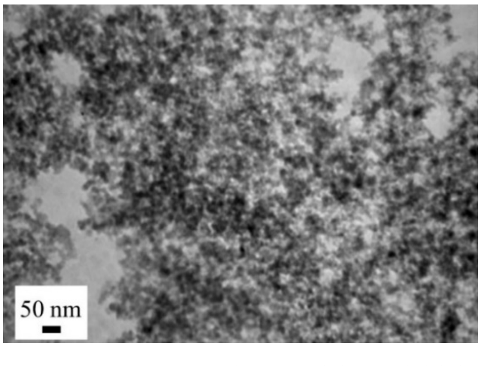

Fig. 9. TEM image of dispersed bactericidal silica Ag/SiO_2

It is interesting to note that in presence of both silver and gold NPs in the composite Ag(Au)/SiO_2 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 $Cu_2(SO_4)O$ and AgCuS are also fixed [80].

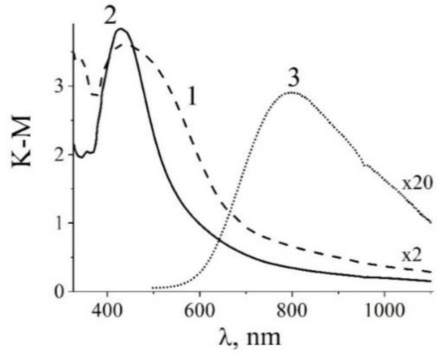

Fig. 10. Absorption spectra (as a function of Kubelka-Munk) of tissues modified with Ag/Cu (*1*), Ag (*2*), Cu (*3*) NPs

Fig. 11 shows a comparative activity of tissue samples with Ag and bimetallic NPs (BMNP) against a number of microorganisms (*Escherichia coli, Klebsiell apneumoniae, 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^+/Cu^{2+} binary ions from the surface of BMNP, and their combined interaction with bacterial membranes.

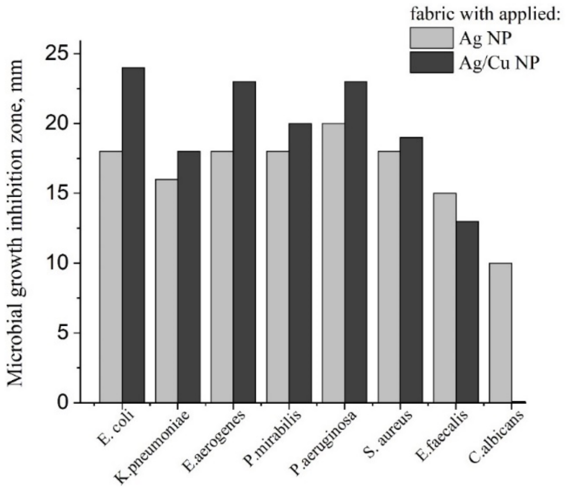

Fig. 11. Comparative activity of tissue samples with silver and bimetallic NPs in relation to different cultures of bacteria

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].

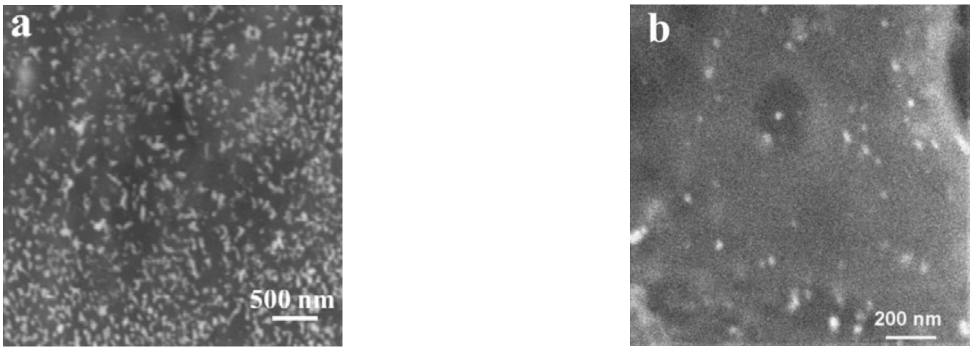

Fig. 12. Electron microscopic image of tissue impregnated with *a* – Ag and *b* – Ag/Cu NPs

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 Cu^{2+} ions show similar behavior (Fig. 13).

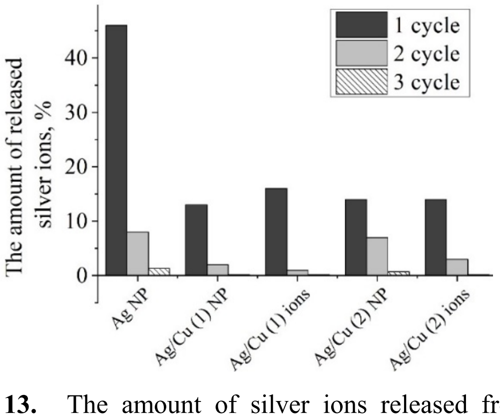

Fig. 13. The amount of silver ions released from modified tissues during three consecutive cycles of desorption

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 KNO_3) 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 KNO_3 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).

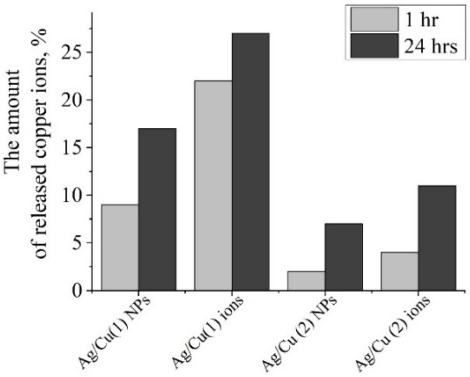

Fig. 14. The amount of released copper ions from modified tissues after desorption for 1 hour and 24 hours in water

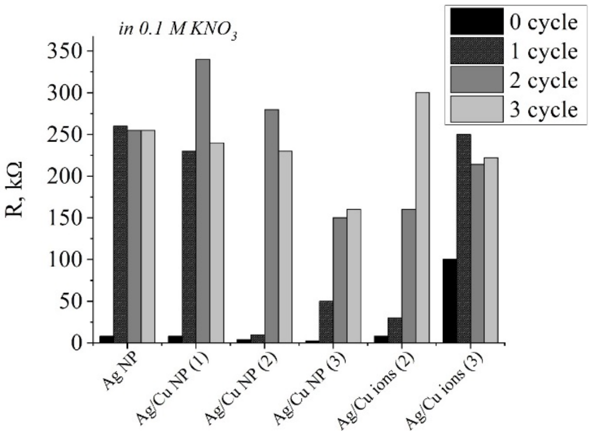

Fig. 15. Electrical resistance of tissues with nanoparticles and metal ions in 0.1 M KNO_3

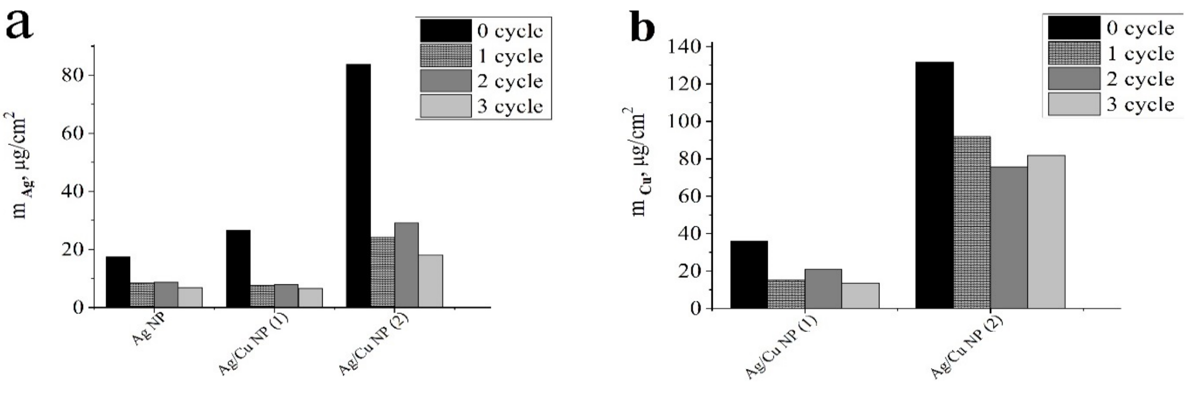

Fig. 16. The amount of silver (*a*) and copper (*b*) atoms on the surface of tissues before and after 0–3 cycles of desorption

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 $AgNO_3$ and $Cu(CH_3COO)_2{\cdot}2H_2O$ salts were used to obtain the Ag and Ag/Cu NPs samples indicated in the Table.

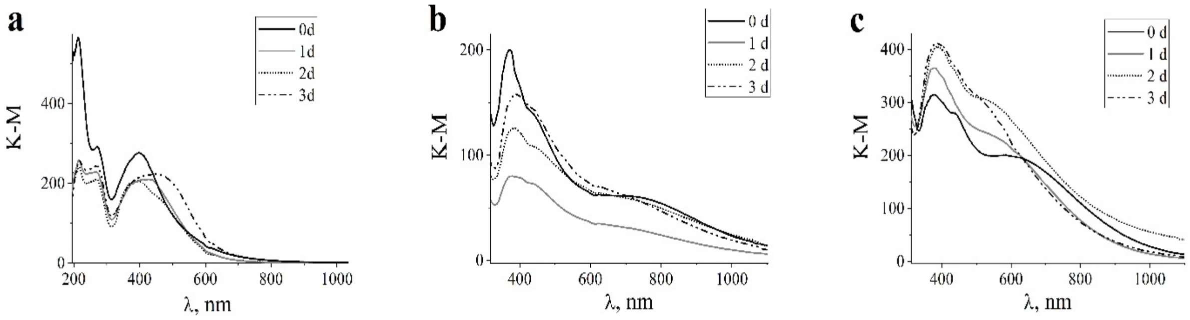

Fig. 17. DRS of tissues modified Ag (*a*), Ag/Cu (1) (*b*) and Ag/Cu (2) NPs (*c*) after three cycles of desorption

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**							
		E. coli	***K. pneumoniae***	***P. mirabilis***	***P.aeruginosa.***	***E. faecalis***	***S. aureus***	***C. albicans***	***C. non albicans***
Ag NP	0	19	13	17	24	12	17	Θ	11
	1	18	13	18	23	14	Θ	Θ	Θ
	2	18	12	17	22	Θ	Θ	Θ	Θ
	3	17	11	17	17	Θ	Θ	Θ	11
Ag ions	0	16	0	15	18	Θ	15	Θ	Θ
	1	16	Θ	17	20	Θ	Θ	Θ	Θ
	2	12	Θ	18	21	Θ	Θ	Θ	0
	3	17	Θ	15	19	Θ	Θ	12	0
Ag/Cu NP	0	20	12	17	18	15	19	12	0
	1	18	12	18	27	Θ	16	Θ	0
	2	17	12	20	26	12	18	11	0
	3	19	11	19	25	Θ	16	11	Θ
Ag/Cu ions	0	20	13	19	27	16	20	Θ	Θ
	1	20	12	20	25	16	18	Θ	Θ
	2	15	11	Θ	25	12	17	Θ	0
	3	19	11	18	22	Θ	16	Θ	0

Θ – 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 imprenation	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 SiO_2 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 SiO_2/BPh (adsorbed benzophenone) 2) formation and fixation of AgNPs on the surface of silica films when irradiated the ionic form of Ag^+/SiO_2 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/SiO_2 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 SiO_2 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 дисперсій SiO_2 та в складі текстильних тканин, в залежності від методу синтезу, на основі літературних даних та власних досліджень. Хімічне відновлення срібла (борогідридами, воднем, гідразином тощо) дозволяє регулювати і контролювати розмір і форму НЧ. Форма НП 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 $NaBH_4$ 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 SiO_2 з адсорбованим бензофеноном (SiO_2/BPh); шляхом УФ-опромінення іонів Ag^+ у розчині в присутності Trp; на поверхні кремнезему при золь-гель синтезі плівок Ag^+/SiO_2 шляхом опромінення адсорбованих іонів Ag^+ на плівці SiO_2 у розчині BPh. Показано, що при адсорбції НЧ Ag на поверхні високодисперсного SiO_2 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*

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