

SORPTION ACTIVITY OF SILVER NANOPARTICLES

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The absorption activity of silver nanoparticles (AgNPs) on the surface of fibers of natural and artificial origin is estimated. In addition, it is determined that the sorption activity of natural or artificial fibers with respect to silver nanoparticles depends on their size, fabrication method, and properties of the gelling agent. It is found that the highest absorption of silver nanoparticles is observed when using natural silk fibers, which possess a significantly higher activity as compared with an artificial fiber (fluoroex).

Keywords: silver nanoparticles, electron microscopy, fibers, sorption capacity.

INTRODUCTION

Silver nanoparticles (AgNPs) are increasingly used in modern science and technology, including for biomedical purposes, due to their special physicochemical properties caused by their size and biological functions, in particular, high antimicrobial activity and lack of toxicity for the macroorganisms. Nanomaterials based on AgNPs [1–3] are also an effective system for the drug delivery, increasing the microbicidal properties of the suture and dressing consumables, improving the viability of the decellularized matrix, and increasing the operation duration of special implant coatings. The wide range of antimicrobial activity exhibited by AgNPs is primarily associated with their size and a variety of other physicochemical parameters (shape, concentration, surface charge, and colloidal state) [4]. In addition, carriers (for example, fibers of natural and artificial origin) that adsorb AgNPs of a certain size, shape, and colloidal state and generally modify their overall effectiveness of action, have a significant impact on the biological activity of finished materials with nanoparticles. At the same time, the nanoparticles themselves provide additional mechanical, optical, chemical, and biological qualities to carrier materials, which acquire particular advantages when used in biomedical practice [5]. There is no doubt the relevance of use of AgNPs in combination with natural or artificial polymers, including N-isopropylacrylamide and cellulose [6]. In this case, incubation of AgNPs with gelatin had a pronounced stabilizing effect on their synthesis, which subsequently increased antimicrobial activity.

A number of literary sources have shown the feasibility of obtaining a food film based on synthetic polymers with immobilized silver nanoparticles [7]. The advantage of such a film is in the decreasing possibility of desorption of silver laponite immobilized on quaternized chitosan, which also makes it possible to reduce own toxicity of the food film. In addition, some methods are known for modifying natural wool fibers, the structural proteins of which act as the redox biomatrix, by assembling silver nanoparticles *in situ* [8], which in the long term will make it possible to produce clothing with antibacterial properties without loss of those during the washing process.

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In addition, the catalytic activity of silver nanoparticles with face-centered cubic geometry, sorbed on special carriers, can be used for the degradation of anthropogenic pollutants [9], which will allow them to be included in the drinking water purification filters to use the antioxidant and antibacterial properties of AgNPs. Therefore, the possibility of prolonged stabilization of nanoparticles on the surface of a carrier to limit their entry into the drinking water, is of particular importance. Such developments can potentially be applied in the composition of filters for wastewater treatment, if it is necessary to quickly inactivate high concentrations of the pollutant in a short time by catalytic degradation of the latter.

Given the above, the practical use of AgNPs in a natural way provides for the feasibility of assessing their sorption and desorption activity on the surface of both artificial polymeric fibers and fibers of natural origin. It should be noted that, depending on the storage duration, the properties of the nanoparticle preparations may vary depending on the storage conditions, duration, and dilution of the initial solution [10].

The purpose of this study was to assess the sorption activity of silver nanoparticles synthesized by cavitation-diffusion photochemical reduction with different exposure times in the gelatin gel compositions on fibers of natural and artificial origin.

EXPERIMENTAL

When performing the study, the equipment of the “Center for collective use of diagnostics of the structures and properties of nanomaterials” of the Kuban State University (Krasnodar) was used. We evaluated the sorption activity of AgNPs in a freshly prepared gel composition based on gelatin (gel composition 1), in the same gel composition, but after 36 months storage (gel composition 2), as well as of silver nanoparticles in the composition of the official reference drug Argogel (comparator drug A) for both natural fibers (silk) and artificial fibers (fluoroex suture material, which is a surgical synthetic polyester fibers coated with polyethylene terephthalate). The method of electron microscopy was used to estimate the sorption activity, size, and number of nanoparticles in each of the samples after 1 and 24 h exposure.

The comparator drug A was used in the concentration recommended by the manufacturer. Synthesis of an aqueous solution to obtain gel compositions 1 and 2 was carried out by the method of cavitation-diffusion photochemical reduction, involving the reduction of silver ions in the presence of a polyvinylpyrrolidone ligand under combined exposure to ultraviolet radiation with a wavelength of 280–400 nm and ultrasonic waves with a frequency of 1.7 MHz under continuous mixing conditions for 1 h [11]. Then, the resulting solution was diluted to an AgNPs concentration of 5 µg/ml and heated to 60°C. Then, gelatin was added up to 0.9% in the resulting solution. After preparation, gel composition 2 was additionally stored in the dark under the conditions of the air oxygen access at a temperature of 5°C for 36 months. The sorption activity was evaluated by exposing the 1 cm long fiber segments in the selected preparation for 1 and 24 hours followed by freeze drying of these fiber segments before the electron microscopy.

Electron microscopy study of the obtained samples was performed on a JEOL JSM-7500F scanning electron microscope in the detection mode of reflected and secondary electrons with an accelerating voltage up to 10 kV and magnification up to 30 000 times. When interpreting the obtained results, the size and number of silver nanoparticles on the sample surface were estimated. The AgNP size was estimated relative to a 100 nm long standard marker. The sorption activity was calculated as the ratio of the relative area of AgNPs to the total area of the image.

RESULTS OF THE EXPERIMENT

According to the data obtained as a result of the study, the following features of the nanoparticle interaction with artificial fibers were noted when assessing the sorption activity of AgNPs on the artificial fiber fluoroex. When this fiber was exposed in the comparator drug A for 1 hour, the degree of adsorption was 1%. The size distribution of AgNPs is shown in Fig. 1.

According to the presented micrograph (Fig. 1a), the degree of the sorption activity of the comparator drug A on the artificial fluoropolymer fiber is low (1%). It is noteworthy that most of AgNPs (69%) have a size in the range

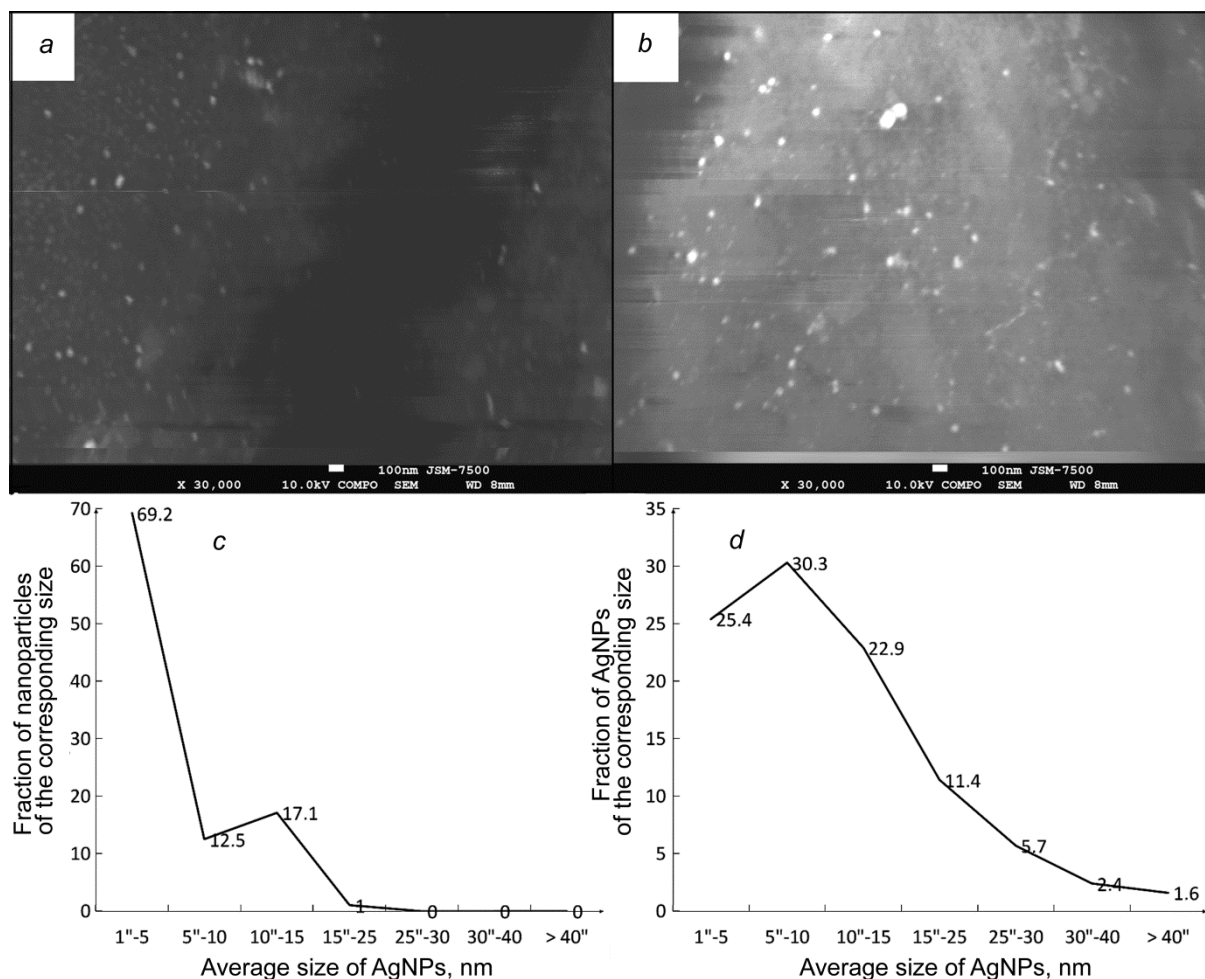


Fig. 1. Electron micrograph of the fluoroex fiber, exposure in the comparator drug A, magnification 30 000 times, COMPO mode, exposure for 1 hour (a) and 24 hours (b), and the AgNPs size distribution obtained during image analysis (c) and (d).

from 1 to 5 nm (Fig. 1c), which suggests their high catalytic and antibacterial activity due to the large specific surface area.

After 24 h of exposure of the fluoropolymer fiber in the comparator drug A, the degree of adsorption of AgNPs remained at the same level (Fig. 1b), however, changes in the sizes of AgNPs adsorbed on the fiber surface were noted. As can be seen from the presented micrograph, after 24 hours, the size of most of AgNPs was in the range from 1 to 10 nm (Fig. 1d). It should be noted that in addition to an increase in sizes of adsorbed AgNPs, a decrease in their total number by about 37% was recorded. The observed changes may indicate a rather active process of the nanoparticle aggregation with an increase in their size, which is inevitably accompanied by a decrease in their microbicidal and catalytic activity. At the same time, no pronounced desorption process of previously adsorbed AgNPs was established, since the ratio of their relative area to the total area of images of two samples, did not change over the next 23 hours of exposure.

Evaluation of the sorption activity of gel composition 1 on the fluoroex fiber after 1 h of exposure revealed a low sorption activity within 1% (Fig. 2).

As can be seen from the presented micrograph (Fig. 2a), almost half of AgNPs (44%) has a size in the range from 1 to 5 nm. The number of nanoparticles is also relatively large, amounting to 47% in comparison with the official reference drug A. This may indicate a significant activity of nanoparticles prepared by the method of cavitation-

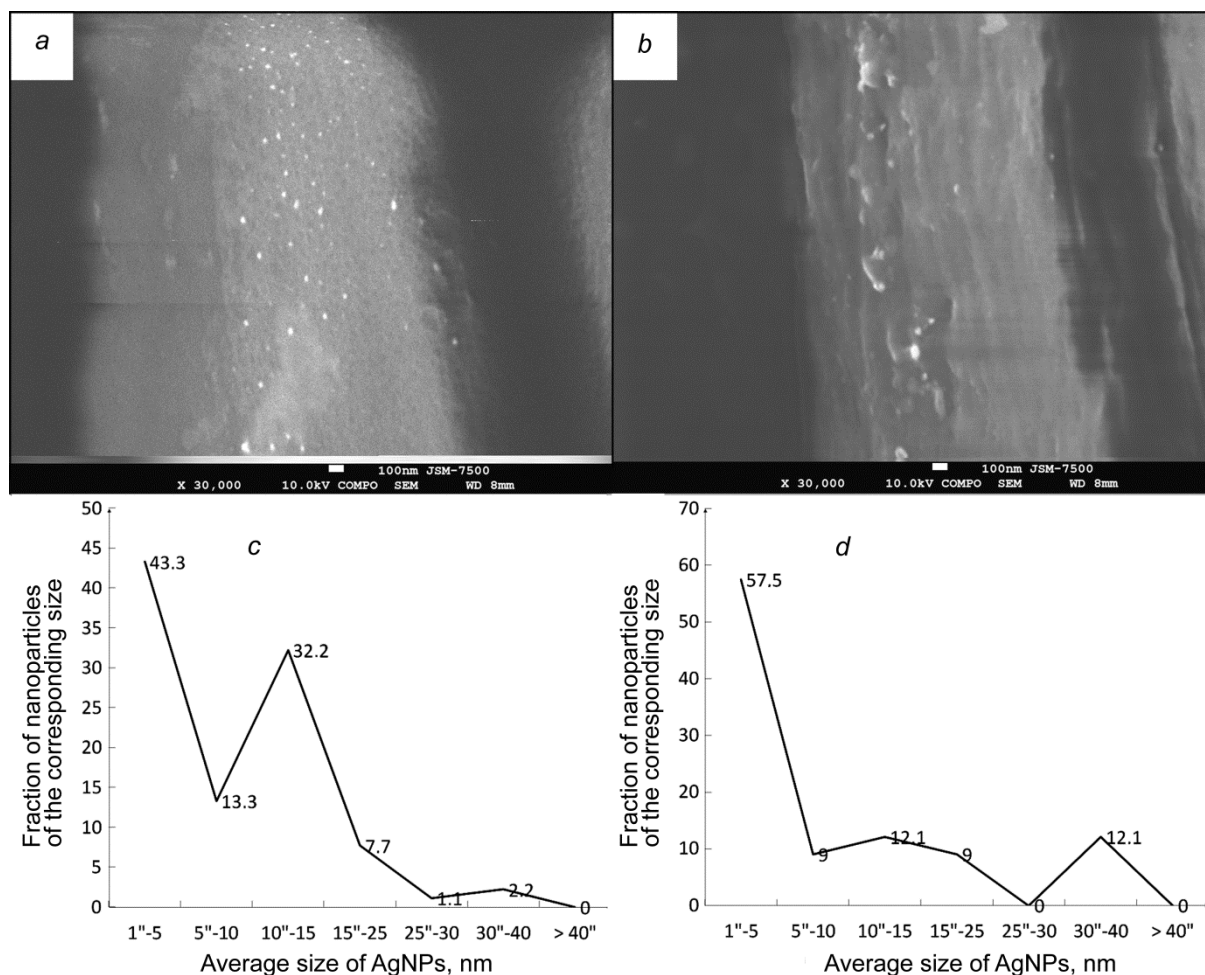


Fig. 2. Electron micrograph of the fluoroex fiber, exposure in gel composition 1, magnification 30 000 times, COMPO mode, exposure for 1 hour (a) and 24 hours (b), and the AgNPs size distribution obtained during image analysis (c) and (d).

diffusion photochemical reduction and sorbed on an artificial fiber with preliminary stabilization of AgNPs with gelatin. After exposing this gel composition for 24 hours, it was found that the degree of the sorption activity did not change, but it was revealed that on the surface of the artificial fiber, the number of AgNPs with sizes in the range from 5 to 30 nm decreased (Fig. 2c) and the size of AgNPs increased due to the increase in the number of AgNPs with sizes in the range from 30 to 40 nm. In addition, the number of AgNPs adsorbed on the artificial fiber decreased by almost 3 times. Such changes may indicate an active desorption process. This process is more pronounced within the size range from 5 to 30 nm, which is apparently due to higher surface energy of silver nanoparticles ranging in size from 1 to 5 nm compared to those in the range from 30 to 40 nm. This is of major importance for the processes of adsorption and desorption [12].

Evaluation of the sorption activity of AgNPs in gel composition 2 on the fluoroex artificial fiber for 1 h revealed an adsorption of 1%, which is shown in Fig. 3.

When assessing the nanoparticle size, it was determined that AgNPs with sizes from 1 to 5 nm are absent in the micrograph, and most of nanoparticles are in the ranges from 5 to 10 nm and from 15 to 25 nm (Fig. 3a). Such a distribution may indicate a lower, compared with previous preparations, catalytic and antibacterial activity of adsorbed AgNPs, which is also evidenced by the fact that the number of the sorbed nanoparticles is also much smaller (24% compared to the comparator A and 52% compared to the gel composition 1 ($p < 0.05$)). After 24 h, the degree of

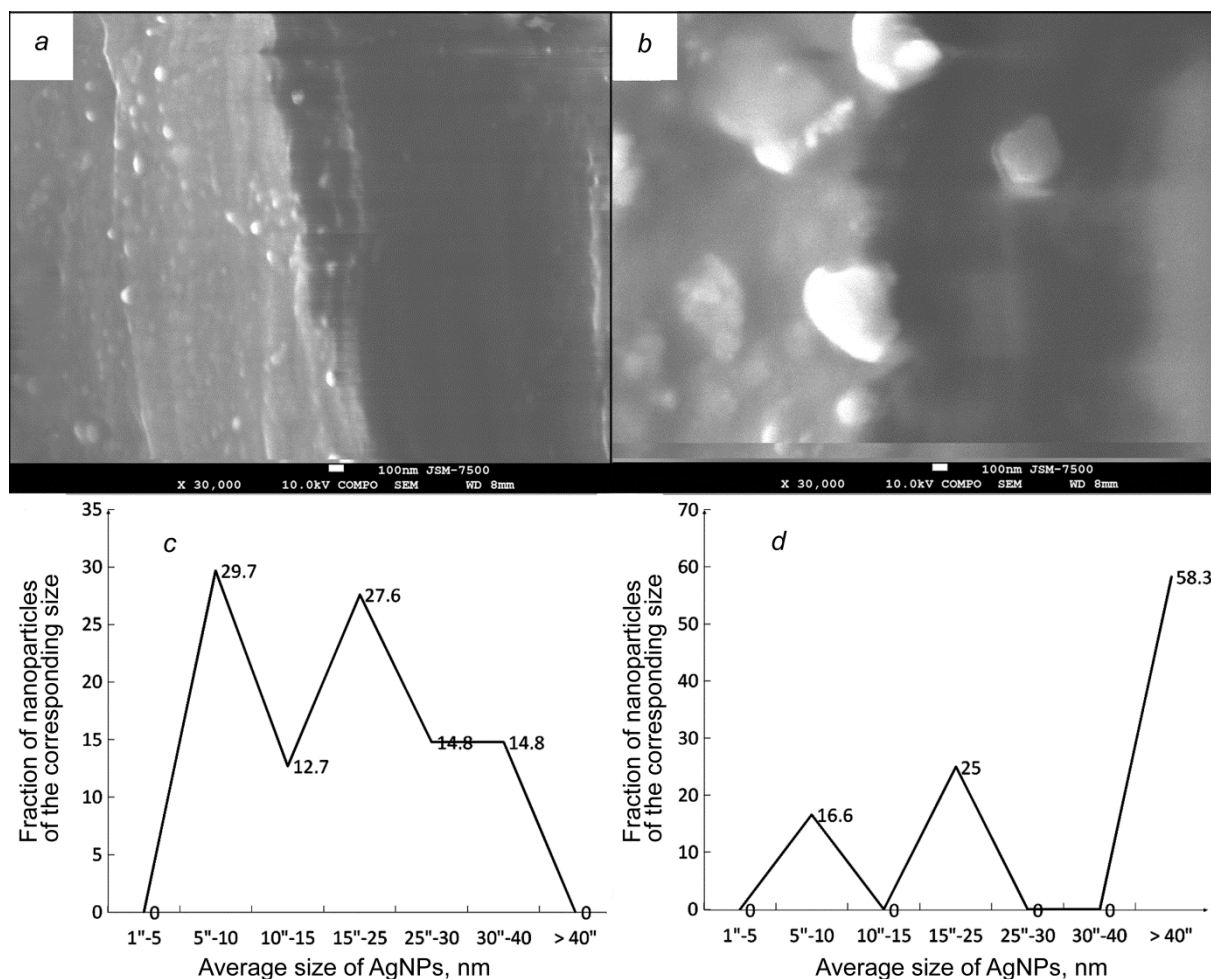


Fig. 3. Electron micrograph of the fluoroex fiber, exposure in gel composition 2, magnification 30 000 times, COMPO mode, exposure for 1 hour (a) and 24 hours (b), and the AgNPs size distribution obtained during image analysis (c) and (d).

adsorption of AgNPs increased significantly reaching 14% relative to the total area of the micrograph (Fig. 3c), while at the same time, a significant increase in the size of nanoparticles was observed (Fig. 3d). Within 24 hours, most of nanoparticles had sizes above 40 nm, although it should be noted that the previously noted peaks in the ranges from 5 to 10 nm and from 15 to 25 nm were preserved. The micrographs also showed an almost twofold decrease in the number of AgNPs (by 49%, Fig. 3c). Such changes indicate a high activity of the aggregation process of AgNPs accompanied, probably, by a general decrease in their functional activity due to a significant decrease in their specific surface area.

On the basis of the study, it is possible to speak on a low degree of the AgNP absorption on artificial fibers. Over time, there is a partial desorption of nanoparticles accompanied by their aggregation, largely dependent on the method of the AgNP preparation. All this generally reduces the efficiency of using artificial fibers for practical purposes in case of processes characterized by a high degree of external mechanical, physical, or chemical effects on the fibers with AgNPs, for example, when used as the components of cleaning devices.

When assessing the sorption activity of AgNPs on a fiber of natural origin (silk), the following results were obtained: upon exposure of this fiber to the comparator A for 1 h, the silver-nanoparticle absorption degree reached 3% (Fig. 4a).

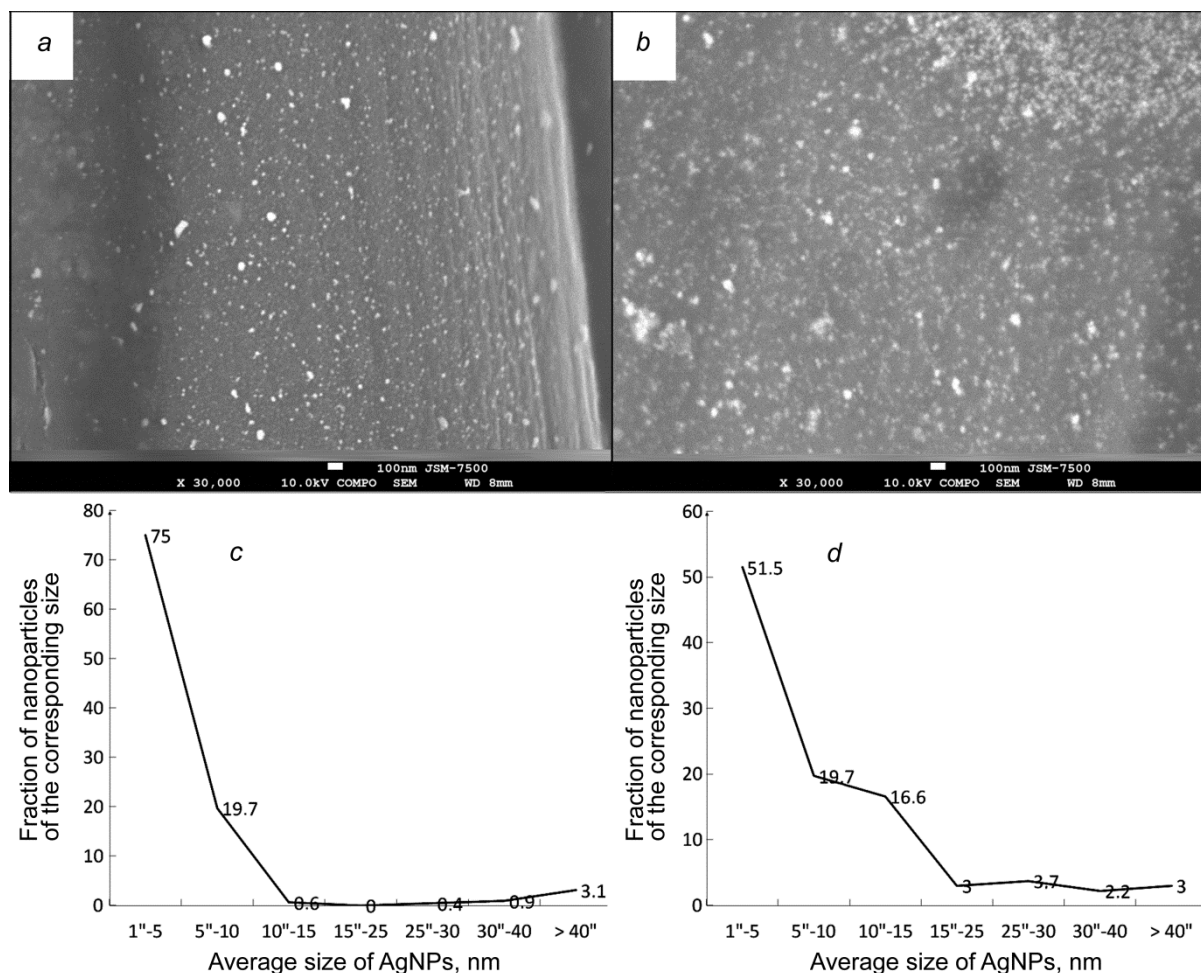


Fig. 4. Electron micrograph of the silk fiber, exposure in the comparator drug A, magnification 30 000 times, COMPO mode, exposure for 1 hour (a) and 24 hours (b), and the AgNPs size distribution obtained during image analysis (c) and (d).

In addition to the significant sorption activity compared with the artificial fiber, a large number of AgNPs ($n > 700$) and their significant fraction (up to 75%) with sizes in the range from 1 to 5 nm were observed (Fig. 4c), which suggests high catalytic and microbicidal activity of nanoparticles of this preparation on the fiber of natural origin.

After exposure for 24 hours, adsorption of AgNPs increased significantly, reaching 22% of the total micrograph area (Fig. 4b). A decrease in the total number of AgNPs (up to 132 in the micrograph) was also noted, which indicates a fairly active process of their desorption from the fiber surface and an increase in their size, obviously due to the aggregation. This is confirmed by an increase in the number of nanoparticles in the size range from 5 to 15 nm and a decrease in their number in the range from 1 to 5 nm (Fig. 4d). However, despite the observed changes, the number of nanoparticles of the most functionally active group from 1 to 5 nm remains relatively high (over 50% of their total number).

Evaluation of the nanoparticle adsorption degree on the silk fiber in gel composition 1 for 1 h revealed a low degree of absorption 1% (Fig. 5a). It is necessary to note a small number of absorbed AgNPs ($n = 40$), as well as a relatively large number of silver nanoparticles ranging in size from 1 to 5 nm (over 32%, Fig. 5c). Also attracts the attention a large number of nanoparticles with sizes in the range from 15 to 25 nm (30%). This distribution characterizes low sorption activity of these AgNPs on the silk fiber, although at the same time, it reflects a rather high potential functional activity of the sorbed silver nanoparticles.

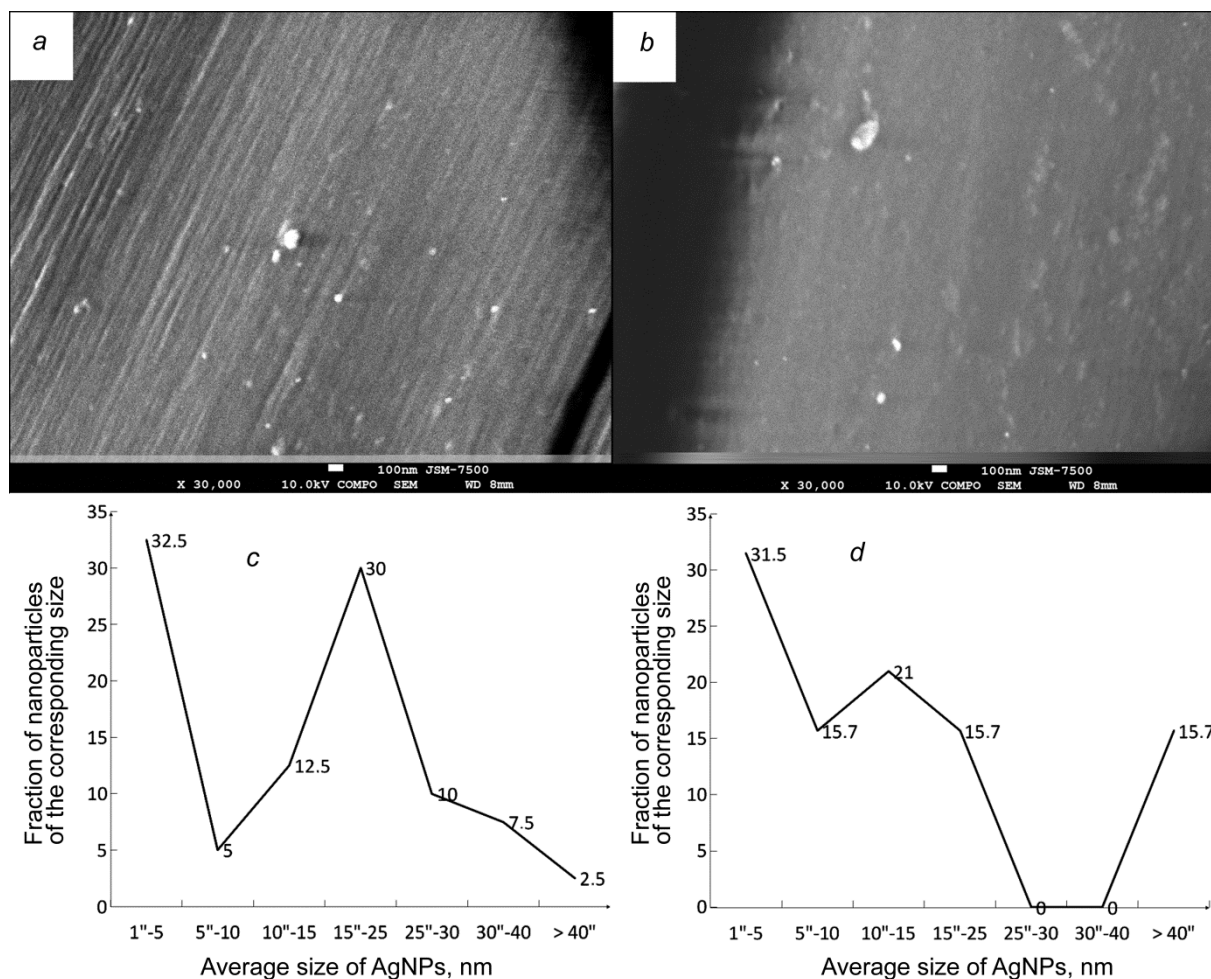


Fig. 5. Electron micrograph of the silk fiber, exposure in gel composition 1, magnification 30 000 times, COMPO mode, exposure for 1 hour (a) and 24 hours (b), and the AgNPs size distribution obtained during image analysis (c) and (d).

Figure 5b demonstrates an increase in the number of large nanoparticles over 40 nm, which indicates active aggregation processes. At the same time, the fraction of nanoparticles with sizes in the range from 1 to 5 nm decreases slightly (Fig. 5d), and the number of AgNPs with sizes in the range from 5 to 10 nm even increases by 10.7%. Together, this indicates, along with a decrease in the number of sorbed nanoparticles (from 40 to 19 in Fig. 5a and 5b), both the possible continued sorption of nanoparticles in the size range from 1 to 10 nm and the predominant desorption and aggregation of larger AgNPs. It is known that such processes as adsorption, desorption, and distribution of silver nanoparticles over the fiber surface are primarily affected by their surface energy, which is much higher for nanoparticles with sizes from 1 to 5 nm, compared to AgNPs with sizes from 5 to 30 nm [13].

When evaluating the results of the electron microscopy obtained after exposing the silk fiber in gel composition 2 for 1 hour, we found insignificant sorption activity within 1% (Fig. 6a).

The micrograph shows that most of the nanoparticles had sizes ranging from 5 to 10 nm and from 30 to 40 nm in an approximately equal amounts of 18.5 and 17.7%, respectively (Fig. 6c). All this indicates a smaller, compared with the comparator A, functional potential of these AgNPs, although the presence of nanoparticles in the size range from 1 to 5 nm in a sufficiently large amount (9.7%) indicates a much larger (by an order of magnitude, Fig. 3c) potential functional activity of these nanoparticles on the silk fiber, as compared with the use of the fluoropolymer-based artificial fibers.

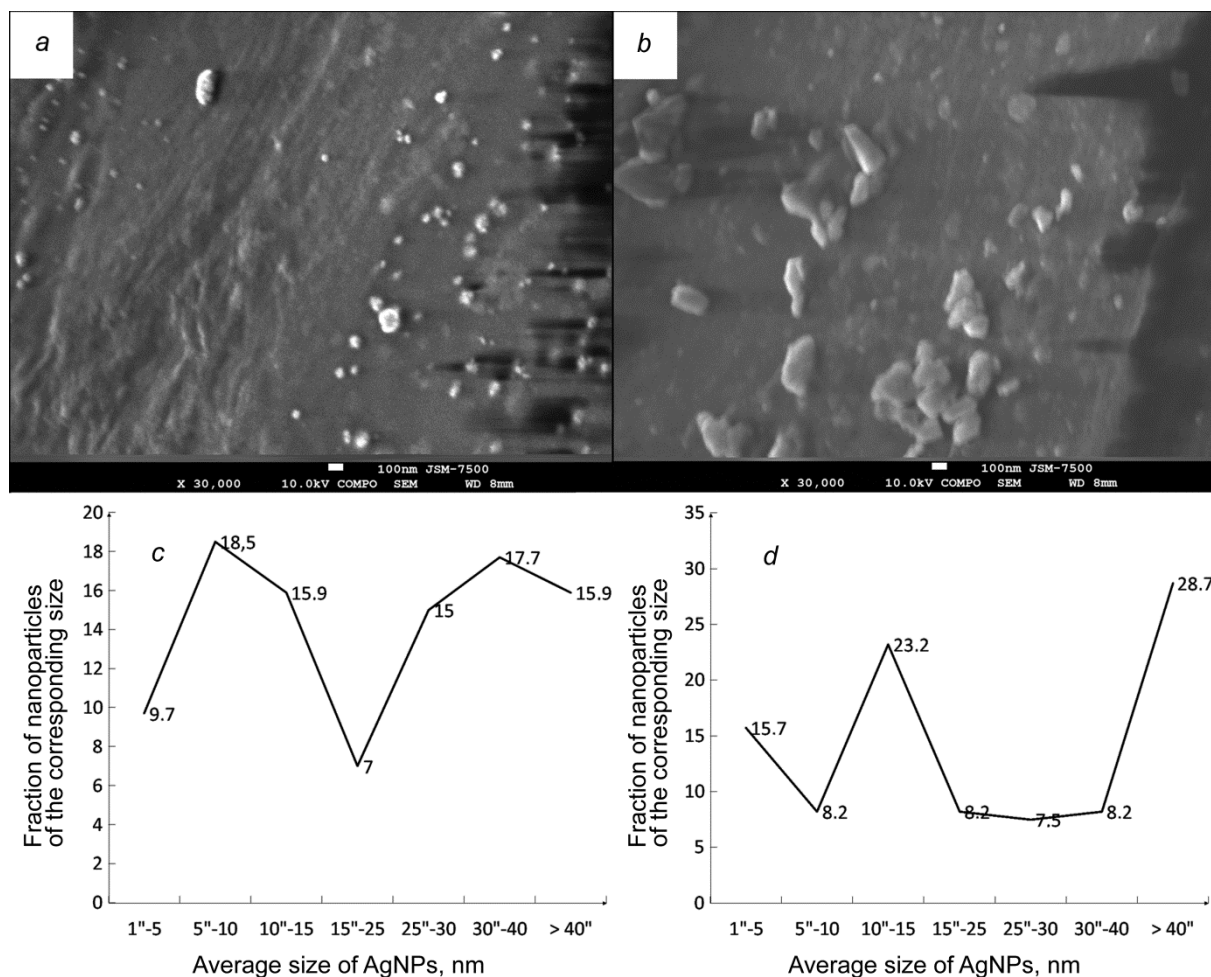


Fig. 6. Electron micrograph of the silk fiber, exposure in gel composition 2, magnification 30 000 times, COMPO mode, exposure for 1 hour (a) and 24 hours (b), and the AgNPs size distribution obtained during image analysis (c) and (d).

After 24 h of exposure of the silk fiber in gel composition 2, the sorption activity of nanoparticles increased up to 5% of the total micrograph area (Fig. 6b). Judging by the Fig. 6b, a high degree of activity of the aggregation process seems obvious, as evidenced by the increase in the fraction of AgNPs with sizes above 40 nm (up to 28.7%). At the same time, a thorough analysis also reveals an increase in the fraction of nanoparticles in the most functional size interval from 1 to 5 nm (up to 15.7%) and a significant increase (up to 23.2%) in the number of AgNPs in the size interval from 10 to 15 nm (Fig. 4d). In general, together with an increase in the number of adsorbed nanoparticles (from 113 after 1 h exposure to 146 after 24 h exposure), it can be assumed that, along with a rather active aggregation process, no desorption of silver nanoparticles characteristic of other compared fiber-AgNPs combinations was observed. On the contrary, the process of adsorption of these nanoparticles continued, as evidenced by the increase in the number of nanoparticles in the range from 1 to 5 nm, which may be due to higher surface energy of silver nanoparticles of this size.

CONCLUSIONS

All of the above suggests that there is a prospect of using these silver nanoparticles together with natural fibers, such as silk. The resulting AgNPs in combination with a gelatin gelling agent can be used in human or veterinary medicine to impart antibacterial properties to the suture material including silk fibers. For example, the authors of [14] proved the possibility of using silver nanoparticles in the composition of wound dressings, to suppress the vital activity of a wound infection, in the form of a composite film of sericin and agar, which, like gelatin, has high hydrophilicity providing preparation of a film with long-lasting antibacterial activity. In addition, the sorption activity of natural or artificial fibers with respect to silver nanoparticles depends on a number of factors, primarily on their size, the method of the AgNPs' preparation, and the properties of the gelling agent. Silk, which is a fiber of natural origin, has a significantly greater ability to sorb silver nanoparticles as compared with the artificial fiber (fluoroex). It should also be noted that during prolonged exposure of fibers in the studied compositions, along with the desorption of the relatively large (from 5 to 30 nm) silver nanoparticles, high activity of their aggregation process was revealed, which can reduce the microbicidal and catalytic activity of AgNPs.

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