Copper-containing non-woven materials from silk waste

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Abstract. A rational approach to the problem of recycling natural silk processing waste is proposed. Cocooning wastes are processed into needle-punched non-woven material onto which copper nanoparticles are deposited by chemical reduction methods with ascorbic acid from alkaline solutions of copper sulfate. It was shown that, depending on the time of impregnation of the nonwoven material with an alkaline copper solution, sericin, wax and fatty substances are removed from the material, and when impregnated for more than 15 minutes, the amorphous part of fibroin. The amount of copper on the fibrous material can be varied by the conditions of impregnation and washing. The size distribution of copper nanoparticles on the finished material was studied.

1. Introduction
Silkworm breeding for the industrial production of silk fiber for the textile industry is widely developed in China, Japan, Italy, Turkmenistan, Uzbekistan and several other countries. Silk fiber is a valuable natural raw material, which has high strength and consumer properties. Unfortunately, the processing of silk raw materials generates a lot of waste of various quality, still not widely used. They are very limitedly used as a filler for blankets and pillows, but most of the waste simply rots in the dumps. Meanwhile, this waste can be effectively used to obtain fibroin protein solutions for medicine and biotechnology [1–2], as well as to create non-woven materials with special properties. Silky neck, optimal hydrophobic-hydrophilic properties allow you to process silk waste into a fibrous webs and then into glued, needle-punched or other type of non-woven materials.

The use of non-woven materials from silk waste for medical and hygienic purposes may be more appropriate in comparison with cotton, as fungi, bacteria and viruses slowly develop on them. If, to increase the bacteriostatic properties, the canvas is additionally treated with silver or copper nanoparticles, such materials can find very wide application, from antibacterial wipes and masks to disinfection and water purification. Silver, gold, platinum and copper are widely known for their bactericidal properties and are actively used in the creation of fibrous nanocomposites for medicine, sports and hygiene products. Of these metals, copper is most preferred for processing non-woven material from waste due to its low cost and biological activity. Numerous results of biological studies [3] confirm the ability of copper to destroy many bacteria within 2 hours of contact with an efficiency of more than 99.9%.

Nanocomposites can be obtained by applying a prepared suspension or colloidal solution of nanoparticles to the fibrous material, or directly in the structure of the fibrous material by impregnating it with a solution of copper ions and subsequent chemical or physical reduction to a nullivalent metal.
At the same time, the sizes of nanoparticles significantly depend on the conditions of preparation and the reducing agent, but porous fibrous materials serve as good matrices for stabilization of copper particles in the nanoscale range that most effectively provides the required properties. The chemical reduction method is inexpensive and environmentally friendly using natural reducing agents, for example, glucose or ascorbic acid [4]. Safety distinguishes these drugs from reducing agents such as borohydrides, hydrazines, hypophosphites, sodium formaldehyde sulfoxylate, which are unsafe for the environment and humans. Cellulose or cotton material is most often used as fibrous carriers for producing bactericidal materials [5–7]. In fibrous materials, copper is present in the form of nanoparticles bound to fragments of macromolecules, as well as in the form of nanoparticles and their conglomerates on the surface of fibers or filaments.

Unlike cellulose, silk fibers have increased smoothness, since silk has no cellular structure. Earlier in our work, the possibility of obtaining a bactericidal fibrous product by applying silver nanoparticles to silk fibers was shown. But the treatment of waste with silver solutions is economically feasible; therefore, alkaline copper solutions were used to obtain a fibrous nanocomposite based on silk waste by the chemical reduction method, since alkaline treatment is known to contribute to the destruction of intra- and intermolecular bonds in the silk structure, up to complete dissolution. “Loosening” the surface of the silk fiber and the release of active groups contributes to the fixation of copper on the fiber. An extremely important factor is the processing time of the fibrous silk material to prevent significant weight loss.

2. Materials and methods

To obtain a nonwoven needle-punched material, cocooning wastes of silk raw materials from Uzbekistan enterprises (cotton wool tear category) were used with the following indicators: tensile strength 4–7 g/fiber, tensile strength 40–50 kgf/mm², tensile elongation 18–22%, specific gravity 1.42 g/m³, hygroscopicity under normal conditions 11%. Silk fibrous waste was previously shredded, partially freed from mechanical impurities, and combed twice on a laboratory cap combing machine with a rigid headset. After that, the fibrous canvas was applied for preliminary needle piercing on the IS-400 needle-punched stand, then the resulting material was doubled to reduce unevenness and served for final piercing at the same stand. The surface density of the nonwoven material was 185 g/m², and the thickness was ~ 4 mm.

In-Situ synthesis of copper nanoparticles on a fibrous material was carried out as follows. They prepared 15% of the mass. an aqueous solution of copper sulfate (all reagents from Sigma Aldrich), to which a 4% sodium hydroxide solution was added (volume ratio 1:1). A turquoise-colored jelly-like copper hydroxide was obtained, to which a five-fold volume of 40% sodium hydroxide was added. A solution of deep blue was received. Samples of 5x5 cm non-woven material were immersed in this solution for a fixed time, after which the blue-colored material was removed, squeezed to a weight gain of 200% and washed in excess of distilled water. After extraction, the material was placed in freshly prepared 10% of the mass. an aqueous solution of ascorbic acid and kept for a predetermined time. The color of the material changed to brown-green, then brownish due to the oxidation of copper nanoparticles. The material was dried in air at room temperature to constant weight.

The study of the dynamics of copper recovery with ascorbic acid over time was carried out by studying the spectral properties of solutions before and after the addition of ascorbic acid on an SP-56 spectrophotometer. Ultraviolet and visible light with a wavelength of up to 500 nm was transmitted through a quartz cuvette with an optical path length of 10 mm with background correlation; bidistilled water was poured into the comparison cuvette. The absorption spectra of the studied solutions were recorded several times - immediately after receiving the colloidal solution, and then after 5, 10, 30 minutes. A comparison of the spectra of the solution over time gives information about the change in its spectral properties with as a result of agglomeration, precipitation, and chemical transformations.

The copper content in the samples was determined by atomic absorption spectrometry using a spectrometer ContrAA 300 Analytik Jena.
The particle sizes of copper on the fibrous material were determined using an electron microscope JSM-35 CF.

The study of the surface of the material in visible and near light was carried out using a Varian Cary 500 spectrophotometer in the region of 400-800 nm.

3. Results and discussion

Since for silk materials, prolonged exposure to an alkaline solution can lead to partial or complete dissolution, we studied the effect of the duration of impregnation of the material with the prepared copper-alkaline solution on the material properties and the dynamics of the recovery process. Table 1 shows the data reflecting the influence of the time of impregnation of silk material with an alkaline solution (before washing and adding a reducing agent) on the mass loss of the fibrous material as a result of exposure to alkali, as well as the amount of copper on the fibrous material.

| Impregnation Time of Sample, min | Wash before the Chemical Reduction | Mass Loss, % | Copper Content, mg/kg |
|---------------------------------|-----------------------------------|--------------|---------------------|
| 0.5                             | +                                 | 26           | 575                 |
| 3                               | +                                 | 34           | 953                 |
| 4                               | +                                 | 40           | 1120                |
| 5                               | +                                 | 45           | 1230                |
| 15                              | +                                 | 71           | 1246                |
| 0.5                             | -                                 | 28           | 4530                |
| control sample                  |                                   |              | 10.4                |

From the above data it can be concluded that an increase in the time of impregnation of silk material with an alkaline copper solution before reduction from 0.5 to 15 minutes leads to an increase in weight loss. It should be borne in mind that up to 30% of the mass of silk fiber is sericin, which is easily washed out during water-alkaline treatments, up to 10% fatty and waxy substances are also present. These substances are removed from the fiber in 4-5 minutes of processing. With a longer contact of the silk material with an alkaline copper solution (15 min), partial dissolution and removal of, possibly, the amorphous part of the main fibroin polymer also occurs.

The copper content in the finished material is mainly affected not by the impregnation time, but by the presence or absence of washing. A sample with a minimum impregnation time of 0.5 min, for which washing was not carried out before the addition of the reducing agent, has almost 9 times more copper in finished form compared to that with washing before reduction.

A study of the optical properties of solutions after adding a reducing agent (without fibrous material) showed that exhaustive reduction of copper occurs 5 minutes after adding a solution of excess reducing agent (figure 1). The peak of about 280 nm is present in the spectra of the initial alkaline copper solution of copper (upper curve), which, when ascorbic acid is added in parallel with the color change of the solution, disappears with the appearance of two new peaks of about 360 and 420 nm. The areas of these peaks gradually increase over time, reaching a maximum in 5 minutes and then remain unchanged for 30 minutes.
Thus, the study of the synthesis of copper nanoparticles in time allows us to optimize the time for preliminary impregnation of the nonwoven material with an alkaline copper solution, the need for washing after impregnation, and the contact time with the reducing agent solution, depending on the desired properties of the finished material.

Examination of the surface of the material using an electron microscope showed that copper nanoparticles have sizes up to 100 nm, their distribution is reflected in the diagram in figure 2. You can see that all particles have a size of up to 100 nm, while most particles have sizes in the range of 20–50 nm. Particle size is essential to maintain a balance between the amount of metal deposited on the material and its bactericidal properties. When the copper content on the material is up to 1%, the nanoscale particle range provides the material with bacteriostatic and bactericidal properties by increasing the surface area of contact with the metal.

Examination of the surface of the material in visible and dipped light showed the presence of a peak of the so-called plasmon resonance of copper at about 620 nm (figure 3). This peak is characteristic of stabilized nanoparticles and is associated with the collective character of the displacement of the electrons of the surface atoms of the metal lattice as a result of interaction with electromagnetic radiation. Since the size of copper nanoparticles is less than the wavelength of the incident light, the movement of electrons leads to the appearance of a dipole and the appearance of a force of return to equilibrium. When the eigenfrequency of the collective oscillations of the electrons near the surface of the particle coincides with the frequency of the incident light, there is a sharp increase in the amplitude of the “electron plasma”.

Figure 1. UV and visible spectra of alkaline copper solutions, from top to bottom: before adding ascorbic acid solution, 1 min after adding, 5 and 30 min after adding.
For copper particles with a size of the order of 10–100 nm, the position and intensity of the plasmon resonance peak in the visible spectral region and in the near infrared range substantially depends on the size, shape, and aggregation of nanoparticles, as well as on the dielectric properties of the solution. In particular, nanoparticles of copper and its oxides can give a peak in the region of ~ 560–640 nm. In work [8], such a peak was observed during the reduction of copper sulfate with ascorbic acid in an aqueous solution at 566–620 nm, depending on the concentration of the stabilizer; in work [9], the peak shifted depending on the type of reducing agent from 560 to 620 nm. The authors [10], when studying cotton materials with copper nanoparticles, observed such a peak at about 625 nm. Such a shift in the position of the plasmon resonance peak of copper nanoparticles in a solid material in comparison with solutions can be explained by the difference in the conditions of formation and growth / stabilization of nanoparticles and their dielectric environment.

4. Conclusion
During the research, the optimal parameters of the process of obtaining fibrous nanocomposites based on silk waste by chemical reduction were found. A needle-punched non-woven material with copper nanoparticles was obtained from silk waste. The presented results allow us to conclude that the rational use of waste from processing silk raw materials with the receipt of a socially useful product for medicine, hygiene, and sports is promising.

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