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Bio-Protected Flax Nanocomposites as Basis for Manufacturing of High-Tech Eco-Products

V. N. Galashina, P. A. Moryganov, and N. S. Dymnikova

Krestov Institute of Solution Chemistry, Russian Academy of Sciences, ul. Akademicheskaya 1, Ivanovo, 153045 Russia
e-mail: vng@isc-ras.ru, poul.m@mail.ru, nsd@isc-ras.ru

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Abstract—Data on biodegradation of flax fibers of different chemical composition, structure of cellulose, and included natural impurities (pectic compounds, lignin, and hemicelluloses) are presented. The influence of silver nanoparticles immobilized in the fiber on biodegradation of the objects under study is evaluated. It is demonstrated that this effect depends on the concentration and size of nanoparticles in the polymer matrix.

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INTRODUCTION

Materials for industrial use based on flax fibers are characterized by high performance and consumer properties and an ability to provide the consumer with a high level of comfort. However, these materials have low biological stability and are liable to degradation during operation under conditions favorable for the development of microbial cultures (high humidity and temperature, contact with soil microflora etc.). Therefore, it is an extremely important and challenging problem to ensure bio-protection of cellulose-containing textile materials.

At present the most acceptable methods of protection in terms of practical implementation are techniques based on introduction of biocide agents into textile materials. Mechanisms of their influence on microbial cultures are different including inhibition of energy metabolism processes, functioning of membranes, synthesis of proteins, nucleic acids metabolism, synthesis of peptide-glucans of the cell wall of microorganisms etc. Factors overcoming resistance of microbial cultures to the effect of biocides include intensification of the biocide agent transportation into the cell by increasing permeability of the cell membranes and inhibition of the bacterial enzymes-inactivators of antimicrobial reagents [1].

Only few biocide agents out of a great number of well-known biocides are widely-applied in practice. The reason for that is their noncompliance with the applicability criterion of three E: Efficiency, Environmental friendliness, and Economic feasibility. As a rule, high efficiency of biocides in relation to microbial cultures is also the reason for low eco-friendliness. Therefore, continuously increasing requirements to environmental safety of biocide agents and rapid adaptation of microbial cultures to unfavorable factors dictate the necessity to improve their compositions and application technologies.

One of the promising brand-new ways for solution of these problems is immobilization or generation of ultrafine metal particles in flax fibers. According to a number of researchers, such particles can possess an abnormally high biological activity. A possibility to ensure bio-protection of cellulosic materials applying minimal amounts of metal nanoparticles is of great scientific and practical interest.

Flax Fiber Degradation under Influence of Microbial Cultures

Low biological stability of plant cellulose fibers is related to the fact that cellulose and its companions are feed and energy sources for many microorganisms, the influence of which leads to changes in the composition and structure of the fibers, to deterioration and sometimes loss of their aesthetic, functional, and performance properties. The most widespread cases of microbiological damage of cellulosic materials are caused by fungi, bacteria, and actinomycetes [2].

The biodegrading effect of fungi is defined by their morphological, physiological, and genetic characteristics, ensuring their high reproduction rate and high level of contact with the polymer. Their rapid growth and the formation of air and/or substrate mycelium with the development of hyphae (filaments 2–3 μm thick) on the surface or penetrating into the internal layers of the fibers, as well as the ability of fungi to form toxic products increase their competitiveness with regard to utilization of the material. Apart from that, fungi are biochemically active organisms, playing an environment-forming role in microbiocenoses, forming an environment saturated with products of their metabolism around them, which promotes the development of bacteria and other microbial cultures [3].

A characteristic feature of all biodegraders is their existence in the form of populations. Apart from such natural sources of biodegraders as air, water, and soil, plant cellulose fibers are a kind of ecological niche for microbiocenoses of epiphytic microflora, inhabiting the surface of stems and feeding on the secretions of plants. There are more than 40 species of different microbial cultures living on flax stems, including microscopic fungi, aerobic and anaerobic bacteria, and actinomycetes [4].

Bio-stability of cellulosic materials varies; it depends on the content of cellulose companions in the fiber and their accessibility for microbial cultures. For example, increased microbiological stability of flax fibers is explained by the presence of lignin, waxy substances, and a significant number of microelements, including heavy and rare-earth metals (Cu, Zn, Mn, Pb etc.) [5, 6]. On the contrary, pectic substances, hemicelluloses, and certain agents applied on fibrous materials in the treatment process (for example, starch) are a growing medium for microbial cultures. It is found [7–9] that biodegradation of cotton and flax fibers starts from utilization of easily hydrolysable polysaccharides; therefore, a high content of the polysaccharides in native fibers is responsible for a higher degree of biodegradation of products made from coarse fibers as compared to fibers purified from foreign and natural impurities.

One of the important reasons of cellulosic materials bio-vulnerability is their high sorption capacity. On the one hand, the presence of the system of pores and capillaries, available internal volume and highly-developed surface of the polymer, on the other hand, the ability of biological objects to change upon contact with the substrate, adapting to it, predetermine efficient progress of sorption processes [10]. An increase in the number of defective areas resulting from mechanical treatment of fibers and appearance of a great number of interfiber spaces in the process of formation of the textile materials structure contributes to their vulnerability to microorganisms. On the contrary, application of reagents and finishing agents, shielding the surface of the materials, improves their bio-stability.

As observations show, under conditions favorable for the development of microorganisms it is possible to observe changes happening to fibers, including appearance of clusters of colored spores, mycelium, stains, and odor, as well as damage, or even degradation of the fibers structure. The color of stains located along the fibers in the form of irregular sections can vary significantly. It is determined by the color of the pigment produced by microbial cultures or emerges as a result of the reactions of microbial waste products with coloring agents [11]. Pigmentation is mostly related to the development of fungi, especially mold fungi, and only rarely stains in damaged fiber areas are caused by bacteria, for example, thermophilic anaerobes (light yellow areas). Stains emerging on the fibrous material in the process of microbial cultures life activities are hard to remove and they do not disappear after washing or application of chemical reagents. Defects of textile materials caused by fungi are usually characterized by a strong musty odor or a more unpleasant putrid smell in case of bacterial cultures.

However, visual assessment does not give an adequate picture of the degrading effect of microbial cultures; it can only testify to their adaptability to existence on the substrate. According to the theory of biological degradation of textile materials developed by Professor I.A. Ermilova [12], deep biodegradation of fibers is considered as a process of appearance and development of defects of their structure, affecting the molecular and supramolecular levels of the cellulose structure, micro- and macrostructure of fibers (elementary and industrial), and the structure of textiles materials (yarn and fabric). Development of the defects from macro- to micro-objects is determined by the fact that the structure of coarser formations (industrial fibers and roving) is characterized by significant interspaces or incompactness of packing, i.e. a higher sorption capacity; apart from that, such formations contain easily hydrolysable cellulose companions. In turn, biodegradation of the main building component, cellulose, is accompanied by changes in its supramolecular structure, which is reliably controlled by the X-ray diffraction method.

In this case degradation is a consequence of mechanical damage of the substrate inflicted directly by microbial cultures, for example, growing mycelium of the fungi, penetrating into the pores and cracks of the material, or destruction of the fiber shell, formation of hollows in the fiber walls under the influence of bacterial cultures etc. [13, 14]. However, the main negative factor in biodegradation of materials is the chemical effect of microbial waste products, including enzymes and organic acids (oxalic, fumaric, succinic, malonic, malic, gluconic, tartaric, citric, and lactic acids), on polymers. According to the modern scientific ideas, the general mechanism of all biochemical reactions catalyzed by enzymes involves the formation of an active enzyme-substrate complex with the manifestation of complementarity between the active site of the enzyme and the area of the substrate macromolecular chain [15]. As microbial waste products are not limited to enzymes but include acids as well, biodegradation can affect hardly accessible crystallite zones of cellulose [16].

Bio-protected flax nanocomposites should provide materials, manufactured on their basis, with resistance to various types of microflora. Earlier we performed a number of research works demonstrating limited possibilities of individual microbes, separated from the surface of bio-damaged flax fiber (*Penicillum sp*., strains 105 and 96; *Bacillus sp*., strain 25), and their artificially created associations to cause flax degradation [17]. It was found that active degradation took place upon contact with soil microflora or under the influence of the natural complex of microflora, i.e. microbiocenosis developed on flax plants in the process of their growth and sorbed on flax fibers in the course of their processing and storage.

Experimental Assessment of Bio-Protection of Flax Nanocomposites Containing Silver

As specified above, one of the ways to ensure flax fibers bio-protection is to immobilize metal nanoparticles contained in them, in particular, nanoparticles of silver. Theoretical statements regarding the factors defining biological activity of nanoparticles have not been developed yet; therefore, the efficiency of their impact on microorganisms is determined empirically.

Among modern methods for synthesis of nanoparticles the most cost-effective way is based on dispergation of metals in solutions in the presence of stabilizing agents. Application of polymers as stabilizers ensuring aggregative stability of ultrafine particles significantly extends the range of variation of the synthesized materials properties, as in this case synergism of properties both of the central core materials and the stabilizing component can manifest itself [19]. It is considered that application of natural polymer compounds in the formation of nanoparticles is an affordable and efficient method for obtainment of environmentally sound composites with a complex of controlled properties, including high biological activity. However, the list of such natural polymers is not long and includes exotic high-molecular compounds, the extraction of which from plant raw materials is a complicated and expensive process. As for flax fibers, due to their morphological characteristics and varied component composition they are also capable of ensuring aggregative stability of nano-objects. Moreover, high-molecular compounds, accompanying flax cellulose, can reduce toxicity of the applied metals and increase environmental safety of the obtained products.

Development of nanocomposites with immobilized silver particles raises special interest, as they possess significant advantages over a great number of other antimicrobial agents. Silver compounds, possessing antimicrobial and antifungal effects, are in many respects devoid of drawbacks related to the problem of resistance of pathogenic microorganisms to them; at the same time, they differ from other metals by low toxicity to humans [20]. It is known that bacteria resistant to penicillin and biomycin are susceptible to the destructive effect of silver and silver-containing agents. It should be noted that certain experiments demonstrated a higher stability of gram-negative bacterial cultures to mercury compounds than to silver compounds [21]. It should be emphasized that it is the ability of microbial cultures to adapt to unfavorable factors which raises concerns of medical specialists and microbiologists in connection with the increasing global scale of application of products with bio-effects.

Results of the influence of metal nanoparticles on microbiological objects depend on their concentration and size, the state of metal (ionic, zero-valent), the nature of the stabilizing agent, the stability of nanoparticles, and the presence of resistant microbial cultures. Therefore, materials with immobilized nanoparticles can exhibit bactericidal (fatal for microbes) or bacteriostatic (inhibition of microbial growth) properties, as well as they can make no noticeable impact

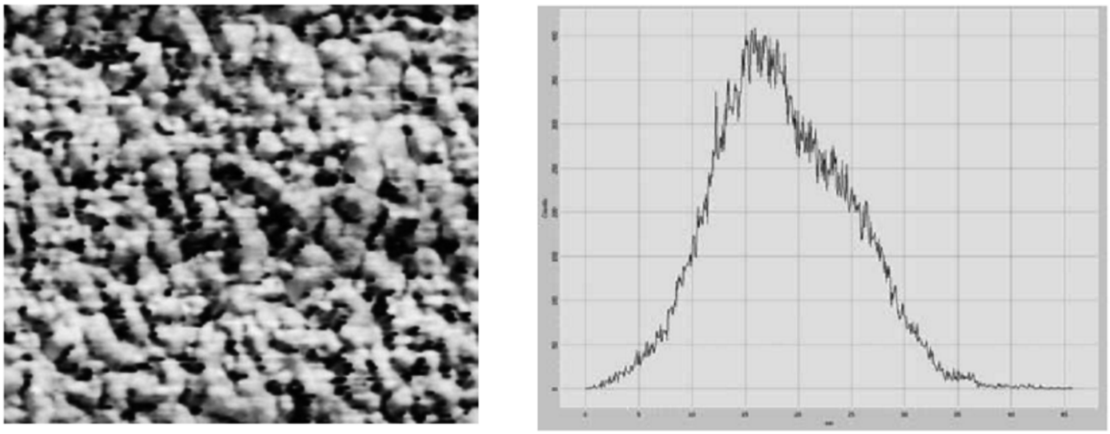

Fig. 1. Picture of silver-containing flax composite sample (left) and diagram of silver nanoparticles distribution in polymer cellulose Matrix according to particle size (right).

on biological objects. For example, there are data [22] saying that in case of changes in silver content of nanocomposites, stabilized with polyvinyl pyrrolidone, the level of antimicrobial activity varies nonlinearly and nanocomposites with a high silver content (20–70%) and a low silver content (0.8–4%) display much less activity in relation to microbial cultures as compared to the agent containing 8% of silver. The high biological activity of the latter is associated with a significant number of silver nanoparticles with a radius of ~2 nm contained in its composition.

This agent represented by high-dispersion silver, stabilized with polyvinyl pyrrolidone, was used in our studies of the process of biodegradation of flax fibers with different chemical composition, cellulose structure, and the content of associated natural compounds (pectic substances, lignin, and hemicelluloses). Subjects of the research included samples of native flax fiber, structurally and chemically modified fibers, and bio-protected flax nanocomposites, which were obtained through immobilization of silver nanoparticles in native flax fibers and flax fibers preliminarily treated under conditions ensuring complete conversion of cellulose crystalline regions into C II modification, an increase in the content of its carboxyl groups by an order of magnitude, and partial extraction of natural compounds associated with cellulose [16].

The X-ray diffraction analysis of the agent and the produced flax nanocomposite of silver showed independence of the dimensions of silver particles immobilized in the fiber from their concentration and invariability of the particle size during conversion from the agent to the flax material. This fact makes it possible to conclude on the stability of silver nanoparticles and their even distribution in the flax fiber matrix. The dimensions of silver nanoparticles in the agent and the flax fiber determined on the basis of the X-ray diffraction method amounted to 15 nm.

Figure 1 shows a picture of the sample of flax nanocomposite with immobilized silver nanoparticles made with the use of the scanning probe microscope Solver47-PRO and a diagram of metal particles distribution in accordance with their dimensions constructed on the basis of the experimental data. The presented results testify to the predominant content of silver nanoparticles of 15–19 nm in the fiber, which confirms the stability of silver nanoparticles in the cellulose matrix.

The samples under investigation were subjected to the effect of microbial cultures. Initiation of biodegradation of flax fibers and flax nanocomposites with a natural complex of microflora was ensured by holding the test samples in a thermostat at 29±0.2°C and humidity of 98–100% for 14 days. Under humid conditions there is an activation of both vital processes of microorganisms and diffusion processes in cellulosic materials. With an increase in the flax fiber moisture content from 10 to 50% bacterization of the fiber rises more than 6000-fold – from 1.4 mln to 9000 mln cells/g of fiber [18].

The depth of destructive transformations of the materials was evaluated visually, based on the changes in their appearance, and quantitatively, based on the changes in the content of cellulose companions, loss of weight, and decreased strength indicators. The factor of resistance to microbiological degradation (Π), characterizing the ratio of the breaking strength of the material after its contact with soil microflora (P_t) to the initial value (P_0), was calculated according to the following formula:

$$\Pi\ (\%) = P_t \times 100/P_0.$$

According to the State Standard GOST 9.060 the material is considered resistant to microbiological degradation if the resistance coefficient $\Pi \geq 80\pm5\%$.

As demonstrated by the experimental data, the result of the impact made by microbial cultures and their metabolites on the flax fibers under investigation is the degradation of natural substances, i.e. cellulose companions, contained in the fiber. After cultivation of microflora the content of pectic substances in native fibers is reduced by 60%, of hemicelluloses – by 40%, and of lignin – by 22%. With a decrease in the initial content of cellulose companions there is a certain reduction (1.5–9-fold) in the level of their destructive transformations under the influence of microorganisms. Thus, microbial cultures cause less degradation of pectins and hemicelluloses (only 11.5–30%) in the material with structurally modified cellulose, as alkaline solutions affect the chemical composition of the fiber: easily hydrolysable part is removed and the remaining high-molecular part is more resistant to microbes. A significant increase in preservation of natural compounds under conditions of cultivation of microbial cultures is ensured in flax nanocomposites containing silver, which is evidenced by a higher content of pectic substances, hemicelluloses, and lignin in them. Moreover, the degree of degradation of polysaccharides in flax nanocomposites based on native fibers reach 34 and 19%, while this value for composites based on structurally modified cellulose amounts to 15 and 11%.

An objective evidence of biodegradation of fibrous materials is their loss of weight. The loss of weight of native flax fibers as a result of biodegradation reaches 26.5% with degradation of the controlled substances accounting for only 6.5% of them. This fact indicates that flax cellulose is significantly degraded during the considered period of exposure to the natural complex of microflora. There is a significant increase in the cellulose susceptibility to biodegradation related to the growth in the amount of amorphous zones after the structural modification of cellulose, i.e. after an increase in accessibility of its internal structure for penetration of microbes and their metabolic products. The total weight loss increases to 32%, while a loss related to the removal of pectic substances, hemicelluloses, and lignin accounts for only 1.9%. At the same time, fibers containing chemically modified cellulose and, consequently, characterized by high accessibility for microbial cultures, but containing more carboxyl groups lose only 10% of their weight. Apparently, the reason for high bio-stability is the absence of complementarity between pyranose units of cellulose, containing carboxyl groups, and cellulase enzymes, produced by microbes. This fact points at the efficiency of passive protection of cellulose from enzymes, which is traditionally performed through introduction of substituents into its anhydroglucose units.

In case of flax fibers with native and structurally modified cellulose biodegradation affects ordered crystallite regions, which is evidenced by a reduction in their weight content. In these circumstances the initially (prior to biodegradation) higher content of amorphous zones in the second sample (with structurally modified cellulose) is the reason for crystallite regions of modified cellulose to experience degradation to a lesser extent (only 109 mg/g of fiber) as compared to crystallite regions of unmodified cellulose (118 mg/g of fiber). The permanence of the crystalline particles weight in fibers with chemically modified cellulose indicates that in case of partial replacement of hydroxyl groups in pyranose cycles of flax cellulose with carboxyl groups biodegradation of flax fibers is limited to amorphous zones.

Introduction of only 0.3 wt % of silver nanoparticles into the structure of native and modified flax fibers significantly increases preservation of cellulose and its natural companions. The loss of weight of flax bio-composites under conditions of cultivation of microbial cultures amounts to 4.0–6.1% with a lower degree of reduction (35 mg/g of fiber) or even permanence of the crystallite content.

At present there is active development of methods for synthesis of agents containing silver nanoparticles for manufacturing of bio-protected materials. However, application of many of those methods is limited due to low concentrations of nanoparticles, their insufficiently high efficiency, or high costs. Therefore, a search for cost-effective methods to form silver nanoparticles with high biological activity is still relevant.

We performed comparative evaluation of antimicrobial activity of silver agents in relation to gram-positive (Staphylococcus) and gram-negative

(*Escherichia coli*) microflora at microbial load of not less than 10^6 cell/ml (see the table). The agents are synthesized using different methods and characterized by different nanoparticle size and state of metal (ionic, electroneutral). Agents no. 5 and no. 6 are synthesized using cost-effective methods involving application of available and relatively cheap precursors. For the formation of agent no. 6 compounds with biocidal properties were used.

In order to control the size of metal nanoparticles in solutions the spectrophotometric method is mostly used [23]. According to the published data, the more small particles there are, the more prominent is the absorption maximum in the region of metal nanoparticles and the more it is shifted into the short-wave region.

The optical absorption spectra of high-dispersion solutions with silver nanoparticles were registered within a range of 300–600 nm using the spectrophotometer Specord M-400 and a quartz cell with the optical length of 1 cm. It was possible to judge on the concentration and size of nanoparticles in the solutions based on the position and intensity of bands in the absorption spectra [24].

Figure 2 shows the optical absorption spectra of the solutions containing high-dispersion silver particles formed in the presence of polyvinyl pyrrolidone and reducing agents of different nature. The obtained spectra are typical for aqueous solutions of high-dispersion silver. The maxima of nanoparticles absorption bands are located within a range of 400–420 nm, which is in compliance with the available published data regarding the position of the extremum for silver nanoparticles. They point at the dependence of the number and size of the forming silver nanoparticles from the nature of the reducing agent. Thus, if glucose is used as a reducer, the maximum optical density value is registered at 410 nm; if another reducing agent, conditionally labeled as R, is applied,

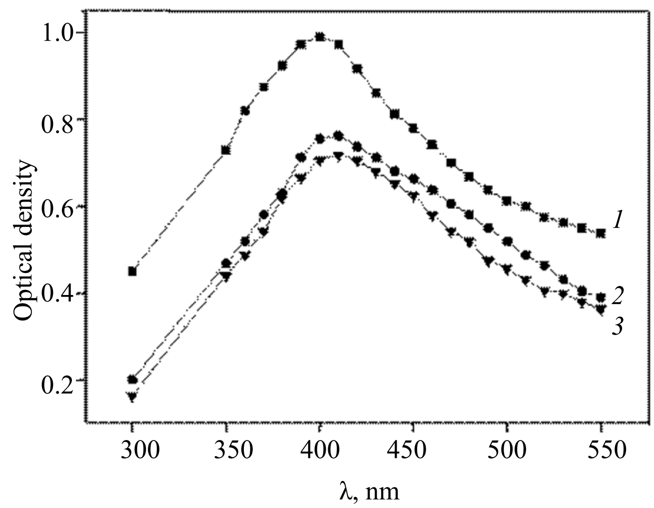

Fig. 2. UV absorption spectra of solutions with silver nanoparticles synthesized using $AgNO_3$ (0.01 M) in the presence of polyvinyl pyrrolidone and reducing agents (0.01 M): (*1*) sodium borohydride; (*2*) R-reducing agent; and (*3*) glucose .

Indicators of biological activity of flax nanocomposites containing silver

Agent, concentration of silver nanoparticles in solution, (dimensions of nanoparticles)	Diameter of test culture growth inhibition zone, mm		Content of nanoparticles in flax fibers, %	Coefficient of flax fiber resistance to microbiological degradation, %
	Escherichia coli	*Staphylococcus*		
1. Ag^+, salt solution, 27.0×10^{-3} M	1.8	4.2	0.3	77
2. Ag^+_{nano}, aqueous-organic solution, 2.65×10^{-3} M (7–11 nm)	2.1	4.5	0.03	72
3. Ag^+_{nano}, aqueous solution, 2.65×10^{-3} M (7–11 nm)	0	3.9	0.03	70
4. Ag^0_{nano}, water-soluble substance, 27.0×10^{-3} M (15—19 nm)	1.9	4.6	0.3	93
5.Ag^0_{nano}, aqueous solution, 23.2×10^{-3} M (40–45 nm)			0.25	92
6. Ag^0_{nano}, aqueous solution, 6.5×10^{-3}, M (40–60 nm)			0.07	89
7. Antiseptic agents	2.0–3.1	4.2–4.9	>1	95
8. Absence of agents			–	3–5

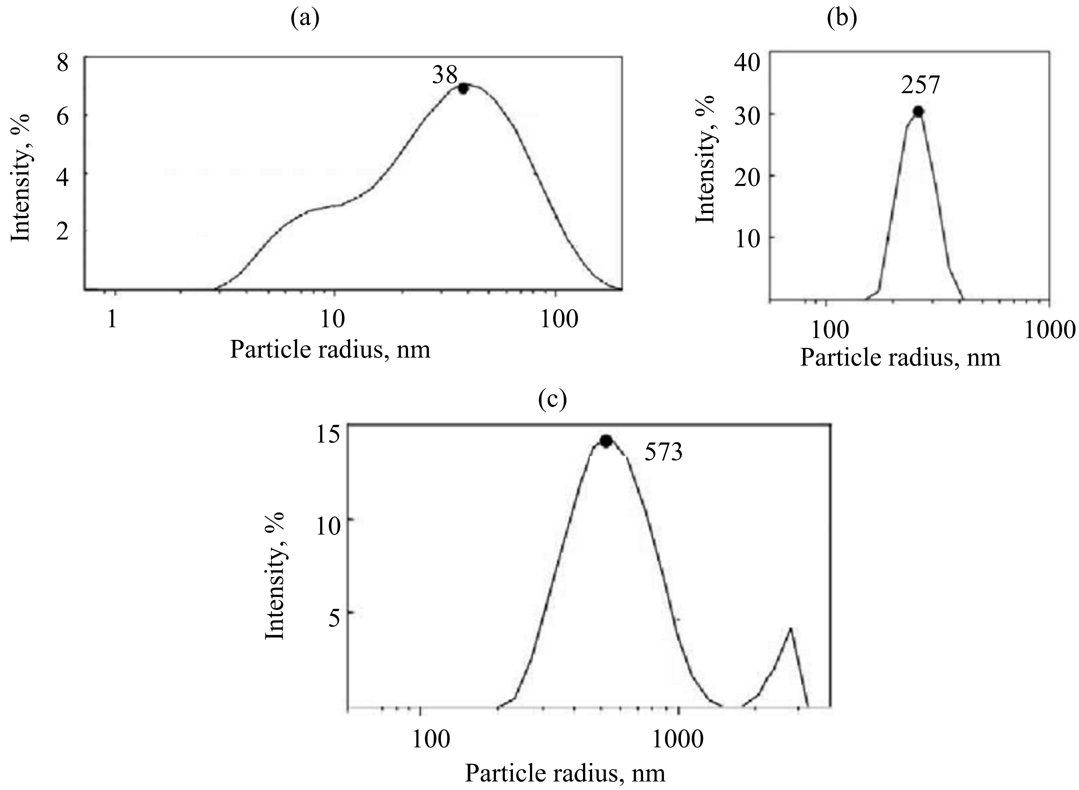

Fig. 3. Curves of distribution of silver nanoparticles, obtained using (a) sodium borohydride, (b) R-reducer, and (c) glucose as reducing agents, in solution according to nanoparticle size. Registration method is photon correlation spectroscopy.

the maximum value corresponds to 407 nm, while in case of sodium borohydride it is registered at 400 nm. The displacement of the extremum point into the short-wave region is associated with the decrease in the size of nanoparticles, while the growth in the absorption intensity is connected to the increase in the number of obtained particles. Therefore, application of sodium borohydride as a reducing agent makes it possible to synthesize a greater number of silver nanoparticles of smaller size. The obtained data are confirmed by the spectra registered on the basis of the photon correlation spectroscopy method using Zetasizer Nano ZS (Fig. 3). The spectral curves indicate that the dimensions of silver nanoparticles (including the shell of the stabilizing agent) are much smaller in case a strong reducing agent, i.e. sodium borohydride, is applied.

Another evidence of the provided data is the color of the obtained solutions: yellow if glucose is applied as a reducing agent, light brown in case of R-reducer, and dark brown when sodium borohydride is used.

Antiseptic agents display a selective effect in relation to the specified types of microflora (see the table). In case of Staphylococcus the inhibition zone diameter around biologically active flax materials reaches 4.2–4.9 mm, while for *Escherichia coli* this value is only 2.0–3.1 mm. Similarly, silver-containing flax fibers exhibit a much lower activity with regard to the coliform bacterium *Escherichia coli*. For objects obtained through distribution of 0.03–0.3 wt % of silver in the form of nanoparticles in the volume of the fibrous matrix the diameter of the *Staphylococcus* growth inhibition zone is 3–4 mm. The fact that in case the metal concentration is reduced by an order of magnitude, the microflora growth inhibition zone changes so negligibly testifies to the dependence of antimicrobial activity from the properties of the applied agents, and, consequently, from the conditions of the formation and stabilization of metal particles. It is indicative that the silver nanocomposites under development can be obtained at a low concentration of nanoparticles in the cellulose matrix, which makes it possible to increase toxicological safety of the materials and enjoy economic benefits of the manufactured products.

The greatest contrasts between untreated flax fibers and flax nanocomposites are observed after their contact with soil microflora. The native flax fiber is almost completely degraded and its breaking strength is reduced by more than 95%, which corresponds to an extremely low coefficient of resistance to biodegradation equal to 5%. Under similar conditions flax nanocomposites display high resistance to biodegradation and their coefficients (89–93%) are significantly higher than the standard value specified in the State Standard GOST 9.060 (not less than 80%).

The efficiency of agent no. 6 should be particularly noted, as application of this agent ensures high stability of nanocomposites at minimal content of silver nanoparticles in the fibers equal to 0.07%. It is unquestionable that application of composites based on agents containing silver nanoparticles increases the economic effectiveness and environmental safety both of the technologies and the end products. Apart from that, a decrease in concentrations of silver nanoparticles, giving color to materials under treatment, makes it possible to reduce the influence of the background in the process of subsequent dyeing of the products manufactured from these materials.

CONCLUSIONS

Application of bio-protected flax nanocomposites containing silver and other metals should lead to the creation of a wide range of high-quality eco-products based on non-woven materials of the original structure. In particular, it will be possible to produce environmentally sound fabric-like non-woven cellulose materials, heat- and sound-insulation products, and easily recyclable sorbents, as well as to ensure import substitution of analogous products (hypoallergenic insulation boards, eco-insulation materials etc.) manufactured on the basis of wood and cotton cellulose. It should be taken into account that it is the combination of unique natural and synthetic fibers which makes it possible to create non-woven materials able to compete with products manufactured by the best world producers.

Development of this area of activity can also solve an extremely important national objective ensuring the demand for products based on currently inefficiently used short flax fiber and flax production waste, which account for 70–75% of the total volume of flax raw materials. Such approach will make it possible to break the tendency to reduce Russian flax production, to increase cost-effectiveness of flax processing, and to contribute to an increase in the development of flax cultivation and, eventually, to the development of the raw material base for manufacturing of high-quality products, including strategically important articles.

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