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Yunusov K.E., Sarymsakov A.A., Mirxolisov M.M.
Institute of Polymer Chemistry and Physics, Uzbekistan Academy of Sciences
Rogachev A.A., Agabekov V. E., Ihnatovich Zh.V.
Institute of Chemistry of New Materials of the NAS of the Republic of Belarus

PHYSICOCHEMICAL CHARACTERISTICS OF BIOMATERIALS BASED ON CELLULOSE FIBRES COATING SODIUM-CARBOXYMETHYLCELLULOSE CONTAINING NANOPARTICLES OF SILVER

Presently, there is a great practical interest in the elaboration of cellulose fibers and textile biomaterials and products on their bases possessing a high bactericidal activity against pathogenic fungus and bacteria [1]. Bactericidal and bacteriostatic activity in the bases of cellulosic biomaterials and their products may take place by incorporating silver ions in their structure and following their reduction into nanoparticles, their interaction with the polymer matrix is carried out through the formation of coordinational bonds [2]. Silver (Ag) and Ag-based compounds have become the most widely represented and studied inorganic antimicrobial agents for use in textiles [3].

The aim of this investigation is to prepare and physicochemically characterize textile biomaterials obtained from cotton fiber containing silver nanoparticles (AgNPs) stabilized with sodium-carboxymethylcellulose (Na-CMC).

In the first stage of the investigation, the formation of AgNPs in 0.2-0.4 wt.% solutions of Na-CMC with degree of substitutions (DSs) - 0.85 and degree of polymerization (DP) - 400 were carried out by photochemical reduction of Ag^+. It has been established that adding Ag^+ to a Na-CMC solution increases the viscosity of the solution owing to the decreased solubility of Ag^+CMC^- complexes generated due to the formation of coordination bonds between the carboxylate groups ($-COO^-$) of Na-CMC macromolecules and Ag^+.

For the photochemical generation of AgNPs in the Na-CMC solution, one can suppose that the negative charges of the carboxymethyl groups ($-COO^-$) "trap" Ag^+ ions. Then, the reaction sequence according to the Mott-Gurney mechanism is represented as follows:

$$R\text{-}COO^- + (Ag^+)_n \xrightarrow{h\nu} R\text{-}COO^{\bullet} : Ag^0, \quad (1)$$

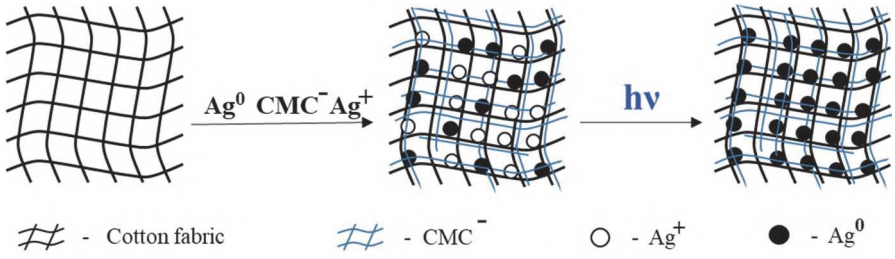
$$R\text{-}COO^{\bullet} : Ag^0 + e^- \longrightarrow R\text{-}COO^- : Ag^0, \quad (2)$$

$$R\text{-}COO^- : Ag^+ + Ag^0 \xrightarrow{h\nu} R\text{-}COO^{\bullet} : Ag^0{}_2. \quad (3)$$

$$R\text{-}COO^- : Ag^0{}_2 \xrightarrow{h\nu} R\text{-}COO^- : (Ag^0)_n. \quad (n)$$

Based on the results, the following conditions were determined for the formation of homogeneous, spherical, and stable AgNPs with sizes of 5-35 nm: UV-irradiation for 30 minutes and solution concentrations of 0.2 wt.% Na-CMC and 0.0086 wt.% $AgNO_3$.

To obtain bactericidal c/f, they were treated with Ag^0CMC solutions. At this low concentration of Na-CMC solution, the sizes of the AgNP and ions enabled their penetration between fibers and within the intermolecular free spaces of cellulose materials. The obtained wet cellulose materials were subjected to additional UV-irradiation, where the reduction of unreacted Ag^+ within the Na-CMC matrix was carried out (Figure 1).



Cotton fabric — Ag^0 CMC^-Ag^+-loaded cotton fabric — The cotton fabric contained Ag^0 CMC

a. Cotton fibres

a. Fibre bundles

b. Individual cellulose fibres

Figure 1 – Supposed scheme of the formation and fixation of AgNPs in the structure of cotton fibres (a), fibre bundles (b), and individual cellulose fibres (c).

Bactericidal activity of the obtained samples of cotton fabrics grafted with the solution of Na-CMC, containing AgNPs in test cultures of *Staphylococcus epidermidis* and *Candida albicans*, was studied in the laboratory of the Institute of Microbiology, Academy of Sciences, Republic of Uzbekistan.

It was established that the replaced Ag^+ in Na-CMC macromolecules is mainly subject to restoration and plays the role of "nanoreactors" in which the carboxylic groups of a negative ion, according to the theory of Mott-Gurney, are the "trap" for positively charged ions of silver and promote the photostimulated formation of AgNPs.

Investigations showed that spherical AgNPs with sizes of 5-35 nm were present in Na-CMC, whereas 0.0086 wt.% AgNPs sized 2-30 nm formed in cotton fabric, exhibiting high bactericidal activity.

It was established that depending on the concentration of polymeric substrate, silver ions and UV irradiation, spherical and rod-like stabilized AgNPs of different sizes form in the structure of Na-CMC. The conditions of the formation of AgNPs with different shapes and sizes in dependence on components interaction reaction parameters and photochemical restoration were revealed.

Correlation dependence between the size and shape of AgNPs in Na-CMC structure and their biological activity was established. It was shown that the size of the AgNPs decreasing promotes the increase of their antimicrobial activity at the same concentrations in a polymeric matrix.

It was found that the grafted cotton fibre within cotton fabric stabilized by AgNPs possessed high bactericidal and bacteriostatic properties. Stabilization of AgNPs within the structure of the c/f helped preserve their bactericidal and bacteriostatic activity even after five washes.

The obtained bactericidal biomaterials, based on the cellulose-containing stabilized AgNPs, possessed the antifungal effect, prevented offensive odor, decreased the level of pathogenic germs, and preserved the fungal disease. Cellulose-contained biomaterials could be used as face masks for air filtration.

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