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# Antibacterial and Antimycotic Activity of Cotton Fabrics, Impregnated with Silver and Binary Silver/Copper Nanoparticles

A. M. Eremenko<sup>1\*</sup>, I. S. Petrik<sup>1</sup>, N. P. Smirnova<sup>1</sup>, A. V. Rudenko<sup>2</sup> and Y. S. Marikvas<sup>2</sup>

## Abstract

Effective method of obtaining of the bactericidal bandage materials by impregnation of cotton fabric by aqueous solutions of silver and copper salts followed by a certain regime of heat treatment is developed. The study of obtained materials by methods of optical spectroscopy, electron microscopy, and X-ray phase analysis showed the formation of crystalline silver nanoparticles (NPs) and bimetallic Ag/Cu composites with the corresponding surface plasmon resonance (SPR) bands in the absorption spectra. High antimicrobial and antimycotic properties of tissues with low concentrations of Ag and Ag/Cu nanoparticles (Ag/Cu NPs) (in the range 0.06–0.25 weight percent (wt%) for Ag and 0.015–0.13 wt% for Ag/Cu) is confirmed in experiments with a wide range of multidrug-resistant bacteria and fungi: *Escherichia coli*, *Enterobacter aerogenes*, *Proteus mirabilis*, *Klebsiella pneumoniae*, *Candida albicans* yeasts, and micromycetes. Textile materials with Ag NPs demonstrate high antibacterial activity, while fabrics doped with bimetallic composite Ag/Cu have pronounced antimycotic properties. Bactericidal and antifungal properties of the obtained materials do not change after a washing. Production of such materials is extremely fast, convenient, and cost-effective.

**Keywords:** Bactericide cotton fabrics, Silver, Silver/copper nanoparticles, Antibacterial and antimycotic activity

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## Background

Silver and copper in the nanosize state are known for the antibacterial properties in relation to the wide spectrum of pathogenic and opportunistic bacteria. Last year in connection with development of steady strains of bacteria, their resistance to the antibiotics and bactericidal preparations is growing. Efficiency of silver as an antibacterial agent is known during centuries, and with the appearance of silver nanoparticles (Ag NPs), their use in different biomedical devices is growing sharply. Ag NPs in the colloid state have a large area of surface that results in the continuous release of Ag ions from the surface of Ag NPs and as a consequence to prolonged bactericidal effect. A few of reviews are devoted to the study of synthesis and antibacterial properties of silver NPs [1–3].

The mechanisms of silver NPs' effect on a bacterial cell are discussed in the literature as the following: anchoring to the cell wall, accumulation of NPs, destruction of cell membrane by free radicals, interaction of silver with respiratory enzymes, release of reactive (singlet) oxygen, destruction of cell, and interaction with sulfur and phosphorus atoms of DNA [4]. A bactericidal action depends on the method of NP synthesis, their size and form, and also from the nature of stabilizer that protects NPs against oxidization and aggregation. In the case of NPs' deposition on an inorganic or organic carrier, as a silica, polymer, colloid, or textile, the surface and chemical nature of carrier directly influence the release of active atoms and/or ions of metals and kinetics of their bactericidal action as well as the tendency to aggregate. Ag NPs are the original deposited form of silver ions, constantly generating and eliminating from the NP surface in the process of binding to biological substrates. Thus, locally (near the surface of the particles), generating high ion concentrations, is harmful to germs.

\* Correspondence: annaerem@ukr.net

<sup>1</sup>Chuiiko Institute of Surface Chemistry of National Academy of Science of Ukraine, 17 General Naumov str., Kyiv 03164, Ukraine

Full list of author information is available at the end of the article

58 Herewith, the size of viruses is comparable with the sizes  
59 of cluster and colloid particles of silver. Ionizing potential  
60 of Ag NPs with the sizes of 1–2 nm is lower on 1.5 eV as  
61 compared to that of bulk silver, i.e., from the developed sur-  
62 face of NPs, the ions of silver are considerably generated  
63 easier. It provides more soft, prolonged action of prepara-  
64 tions of cluster and colloid silver [5]. Unique properties  
65 have also copper nanoparticles (Cu NPs), which are less  
66 toxic, than ions of copper, and initial substances for a Cu  
67 NPs production is on a few orders cheaper than those that  
68 are used for the synthesis of Ag NPs. The free  $\text{Cu}^{2+}$  ions in  
69 high concentration can generate toxic effects, in particular  
70 due to the creation of reactive singlet oxygen, destroying  
71 amino acids and DNA [6]. Antibacterial activity of NPs is  
72 varied depending on the taxonomical location of microor-  
73 ganisms. For example, it was shown that Cu NPs have  
74 higher affinity to the amines and carboxyl groups on the  
75 surface of *Bacillus subtilis* than Ag NPs and therefore  
76 higher antibacterial activity [7]. The efficiency of Cu NPs  
77 synthesized in a chitosan [8] in relation to a *Collibacillus*  
78 is comparable with that of AgNPs. Cu NPs are easily  
79 oxidizable in air; at the same time, copper oxide demon-  
80 strates high enough bactericidal action [9–11]. In [12], the  
81 evolution of surface plasmon resonance (SPR) spectrum  
82 of Cu NPs in time is shown because of the formation of  
83 oxide layer and the decrease of the diameter of NPs' core;  
84 herewith, the bactericidal action of the material remains  
85 high. Author [13] showed that the initial stage of damage  
86 of bacteria by different NPs (Ag, Hg, Cu) consists in the  
87 inhibition of cellular energy and structural changes of cel-  
88 lular surface. In [14], increased (as compared to their con-  
89 stituents) bactericidal ability of bimetallic nanoparticles  
90 (BMNP) Ag/Cu obtained by the method of chemical re-  
91 duction in solution in the presence of stabilizers was  
92 shown; however, their stability was very low due to the  
93 separation into mono Ag and Cu particles and their ox-  
94 idization. As stabilizers of NPs, surfactants, polymers, and  
95 amino acids are usually used. The last years a biogenic or  
96 "green" synthesis of metal NPs is popular with the use of  
97 bacteria, mushrooms, water plants, and plants. The advan-  
98 tage of biogenic methods is that NPs are reduced from  
99 ions and stabilized by the biomolecules produced by mi-  
100 croorganisms that can be familiar to the human organism  
101 [15, 16]. In [17], to obtain Ag and Cu NPs, and also car-  
102 bides and oxides of metals in air and in the atmosphere of  
103 nitrogen at temperatures from 160 to 600 °C, the suspen-  
104 sions of crystalline cellulose as a reducing agent has been  
105 used; a method is attributed also to the green synthesis.  
106 Previously, we reported photochemical and chemical syn-  
107 theses of nanosized silver, gold, copper, and BMNP Ag/Au  
108 and Ag/Cu in the colloid state and on the surface of silica,  
109 saving high bactericidal activity during a few months [18].  
110 BMNP Ag/Au possesses the expressed antitumoral action  
111 [19]. In accordance with XPS data [20], Ag/Cu nanoalloy

in ultrathin polyelectrolyte films possesses high bactericidal 112  
activity. However, there is no doubt that antimicrobial 113  
drugs based on nanosized silver and copper have an irritat- 114  
ing and toxic effect on the body. It can be assumed that the 115  
toxicity of NPs within the fabric is much less compared to 116  
that of other carriers due to the strong binding to the tissue 117  
structure, while maintaining availability for microorgan- 118  
isms. Thus, economically beneficial route to the creation of 119  
safe and effective biocidal materials with a simple method 120  
of preparation and storing a long time of application is an 121  
urgent task. This direction is of great scientific and applied 122  
interest. The very perspective is the introduction of NPs in 123  
woven fabrics for clinical application. Impregnation of Ag 124  
NPs in wool [21], cotton, covered by a hydrophobic poly- 125  
mer (norgine, rubbery anionic polysaccharide from red 126  
water plants) [22], viscose, nylon, and polyamide [23] have 127  
been presented. The impregnation of silver NPs in wool, 128  
polymeric, and cotton fabrics by the methods of plasma or 129  
thermal sputtering, electrochemical way [24, 25], laser abla- 130  
tion, and flaming synthesis [26–29] are presented. Ag NPs 131  
connect with the surface of the fabric in the form of crystal- 132  
lites and inhibit the expansion of polyresistant bacteria. The 133  
depth of penetration of NPs in a cotton is approximately 134  
30 Å [30]. The thermal way of synthesis of Ag/Cu BMNP is 135  
comfortable from the point of view of lowering their melt- 136  
ing temperatures; the alloy of Ag/Cu is formed without big 137  
energy expenses. Ag enhances oxidizing activity of copper, 138  
and BMNP Ag/Cu have higher surface reactivity as compar- 139  
ed to their constituents [31]. In this work, the original 140  
method of impregnation of silver and bimetallic Ag/Cu 141  
NPs in bandaging cotton fabrics by their saturation with 142  
water solutions of silver and copper salts without applica- 143  
tion of chemical-reducing agents, at certain mode of heat 144  
treatment, not requiring substantial power inputs and 145  
special equipment is proposed. 146

## 147 Methods

We use  $\text{AgNO}_3$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  from Aldrich. Gauze 148  
and madapollam fabrics were used as cotton samples. 149  
The surface of gauze is  $36 \text{ g/m}^2$  and that of madapollam 150  
is  $94 \text{ g/m}^2$ . 151

## 152 Production of Bactericidal Tissues Containing Ag NPs

Cotton textile was immersed in the water solutions of 153  
 $\text{AgNO}_3$  ( $1 \cdot 10^{-4} \div 1 \cdot 10^{-1}$  molar (M)) for 15 min then 154  
squeezed thoroughly and then evenly ironed at 200– 155  
220 °C by means of metallic press during  $5 \div 10$  min. 156  
Fabric is dyed in yellow or yellow-brownish color de- 157  
pending on the amount of silver on the unit of the fab- 158  
ric surface. A brownish tint appears because of the 159  
oxidization of part of silver to the oxide  $\text{Ag}_2\text{O}$ . The 160  
concentration of silver on fabrics calculated from the ad- 161  
sorption isotherms of  $\text{AgNO}_3$  is 0.06–0.25 wt%. (60–250 162  
percent per million (ppm)) 163

**Table 1** The results of action of fabrics impregnated with different concentrations of Ag NPs on bacteria, fungi of the genus *Candida* and mikromycetes

Test-culture		E.coli	K. pneumoniae	E. aerogenes	P. vulgaris	P. aeruginosa	S. aureus	E. faecalis	C. albicans	C. non-albicans	Rhodotorula glut.	Rhodotorula spp.	A.niger	A.flavus	Penicillium spp.	Alternaria alternata
t1.3	nano-particles in colloid	Ag/glycerin	+	+	+	+	+	0	0	+	n/s	n/s	n/s	n/s	n/s	n/s
t1.4		Ag/SDS/PVP	+	+	+	+	+	0	+	+	n/s	n/s	n/s	n/s	n/s	n/s
t1.5		Ag	0	0	0	0	0	0	0	0	n/s	+	+	+	+	+
t1.6	non-particles on SiO <sub>2</sub> powder	Ag	0	0	0	0	0	0	0	0	n/s	+	+	+	+	+
t1.7			0	0	0	n/s	0	n/s	+	+	+	+	+	n/s	+	+
t1.8	nonoparticles on the cotton fabrics	Ag/ Cu (10 <sup>-3</sup> )	0	0	0	n/s	0	n/s	+	+	+	+	+	n/s	+	+
t1.9		gause	0	n/s	0	n/s	0	n/s	+	+	n/s	n/s	n/s	n/s	n/s	n/s
t1.10		Ag/Cu (1·10 <sup>-3</sup> )	0	0	0	n/s	0	0	+	+	+	n/s	+	n/s	+	+
t1.11		Ag/Cu (1·10 <sup>-1</sup> )	0	0	0	n/s	0	0/+	+	+	+	n/s	+	n/s	+	+
t1.12		Ag (1·10 <sup>-3</sup> )	+	+	0	+	+	0	+	+	n/s	+	+	0/+	+	+
t1.13		Ag (1·10 <sup>-2</sup> )	0	0	0	0	0	0	0	0	n/s	+	+	0/+	+	+
t1.14		Ag (1·10 <sup>-1</sup> )	0	0	0	0	0	0	0	0	n/s	+	+	0/+	+	+
t1.15		Ag (1·10 <sup>-3</sup> )	0	+	+	+	+	+	+	+	n/s	n/s	n/s	0/+	n/s	n/s
t1.16		Ag (1·10 <sup>-2</sup> )	0	0	0	0	0	0	0	0	n/s	+	+	0/+	+	+
t1.17		Ag (1·10 <sup>-1</sup> )	0	0	0	0	0	0	0	0	n/s	n/s	+	0/+	+	+
t1.18	ions on the cotton fabrics	Ag+/Cu <sup>2+</sup> (1·10 <sup>-3</sup> )	+	+	+	n/s	+	+	n/s	+	n/s	n/s	n/s	n/s	n/s	n/s
t1.19			+	+	+	n/s	+	+	n/s	+	n/s	n/s	n/s	n/s	n/s	n/s
t1.20		Ag+/Cu <sup>2+</sup> (1·10 <sup>-2</sup> )	+	+	+	n/s	+	+	n/s	+	n/s	n/s	n/s	n/s	n/s	n/s
t1.21			+	+	+	n/s	+	+	n/s	+	n/s	n/s	n/s	n/s	n/s	n/s
t1.22		Ag+/Cu <sup>2+</sup> (1·10 <sup>-1</sup> )	+	+	+	n/s	+	+	+	+	+	n/s	+	n/s	+	+
t1.23			+	+	+	n/s	+	+	+	+	+	n/s	+	n/s	+	+
t1.24		Cu <sup>2+</sup> (1·10 <sup>-3</sup> )	+	+	+	n/s	+	+	n/s	+	n/s	n/s	+	n/s	n/s	n/s
t1.25		Cu <sup>2+</sup> (1·10 <sup>-2</sup> )	+	0	0	n/s	+	0	n/s	+	n/s	n/s	+	n/s	n/s	n/s
t1.26		Cu <sup>2+</sup> (1·10 <sup>-1</sup> )	0	+	0	n/s	0	0	+	+	+	n/s	+	n/s	+	+
t1.27		Ag+(1·10 <sup>-3</sup> )	0	+	0	n/s	+	+	n/s	+	n/s	n/s	n/s	n/s	n/s	n/s
t1.28		Ag+(1·10 <sup>-2</sup> )	0	0	0	n/s	0	0	n/s	+	n/s	n/s	n/s	n/s	n/s	n/s
t1.29		Ag+(1·10 <sup>-1</sup> )	0	0	0	n/s	0	0	+	+	+	n/s	+	n/s	+	+

t1.30 0 - no growth of test cultures under samples

t1.31 + - Is the growth of test cultures

t1.32 n/s - studies have not been conducted

### 164 Production of Tissues Containing Copper

165 Cotton textile was saturated with water solutions of  
 166  $\text{CuSO}_4$  then squeezed thoroughly and evenly ironed at  
 167 200–220 °C by means of metallic press during 5 +  
 168 10 min. Fabric acquires a greenish-brownish color de-  
 169 pending on the amount of copper on the unit of the  
 170 fabric surface. It should be noted that all samples of  
 171 fabrics containing copper did not show the expressed  
 172 bactericidal activity.

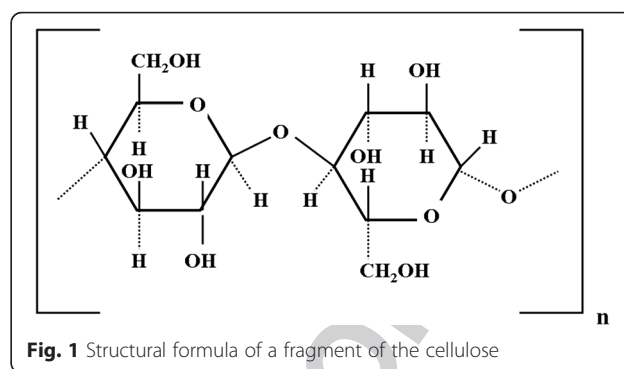
### 173 Production of Bactericidal Tissues Containing BMNP

#### 174 Ag/Cu

175 Natural fabrics like gauze or madapolam were impreg-  
 176 nated with mixture of water solutions  $\text{AgNO}_3$  and  
 177  $\text{CuSO}_4$  with ratio Ag:Cu = 1:1 within the fabric, then  
 178 squeezed thoroughly and evenly ironed at 200–220 °C  
 179 during 5–10 min. In fabrics with BMNP, ratio of Ag:Cu is  
 180 equal within 0.015–0.13 wt% (15–70 ppm) depending on  
 181 the concentration of initial impregnating solutions. These  
 182 amounts were determined on the correlation of area  
 183 under maximum absorption spectrum by Gaussian expan-  
 184 sion. A calibration was performed as dependence of corre-  
 185 sponding area and intensity of SPR spectrum on silver  
 186 amount calculated from an adsorption isotherm. Fabric is  
 187 dyed in a red-brownish color; the tint of that depends on  
 188 the amount of the appearance of the metal on the unit of  
 189 textile surface. Red-brownish tint appears because of the  
 190 formation of protoxide and oxide of copper. The produc-  
 191 tion of bactericidal fabrics by the ironed wet materials  
 192 with the metal ions at a temperature near 200–220 °C  
 193 does not require the use of chemical reductant and pro-  
 194 longed warming up; the surface of press is not painted  
 195 and not corroded, allowing to save time and facilities at  
 196 the production of material.

197 The results of action of fabrics impregnated with dif-  
 198 ferent concentrations of Ag NPs and Ag/Cu BMNP on  
 199 bacteria, fungi of the genus *Candida*, and micromycetes  
 200 are shown. We indicated the concentrations of initial  
 201 salt solutions used for the impregnation of fabrics before  
 202 their thermal treatment near each sample. Since the  
 203 preparation conditions of the tissues, namely, the con-  
 204 centration of the salt solutions and the time of impreg-  
 205 nation and drying of tissues were similar for all samples.

TI 206 Table 1 shows the concentration of the impregnation so-  
 207 lutions near the symbol of each sample that will facilitate  
 208 the reproduction of the results. Usually, a piece of cotton  
 209 (10 g) was immersed in a 100 ml of solution of a certain  
 210 concentration of silver, copper, or Ag/Cu salts for  
 211 30 min. Amounts of adsorbed salts were determined  
 212 spectrophotometrically. Amounts of appearing Ag and  
 213 BMNP Ag/Cu were determined on calibration bands of  
 214 diffusion reflectance spectra (DRS) of dry fabrics after  
 215 the ironing procedure.



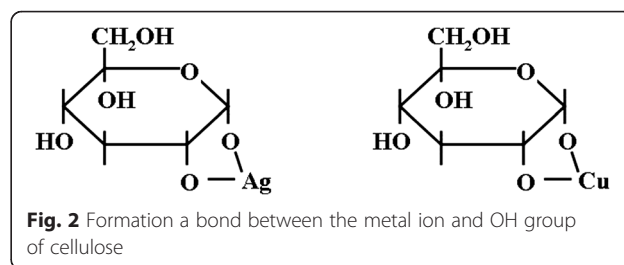
f1.1

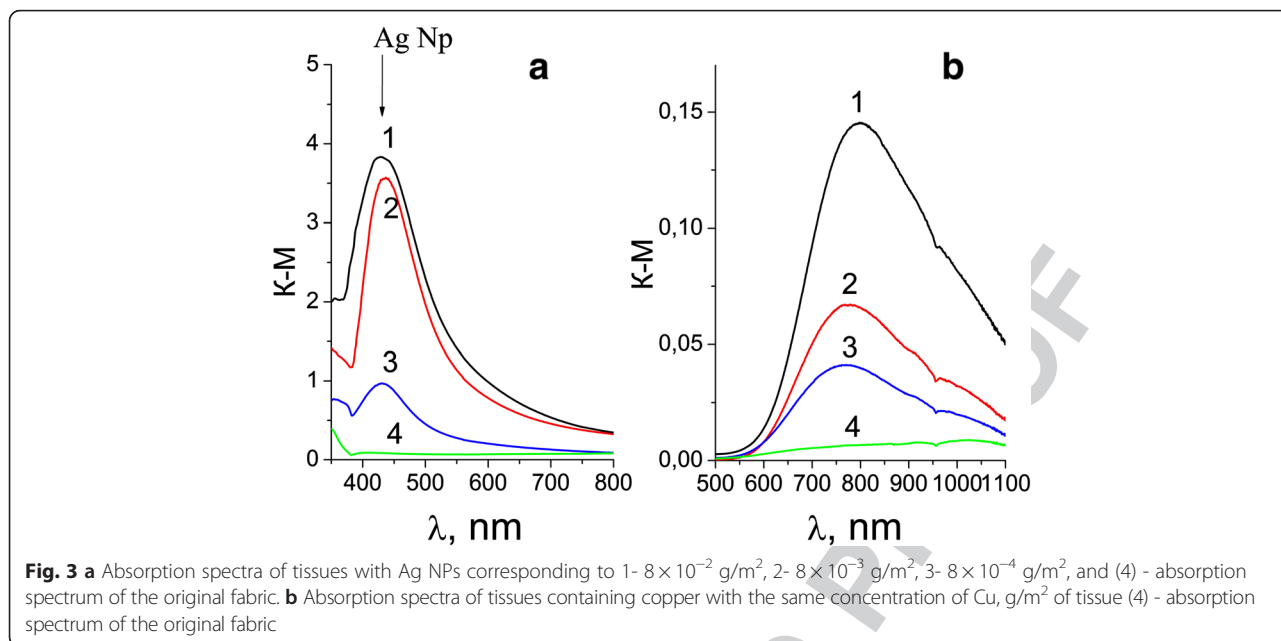
The DRS of the fabrics with NPs were registered by  
 means of spectrophotometer PerkinElmer Lambda Bio  
 UV-vis with the integrating sphere of Labsphere RSA-PR-  
 20 in the range of waves 200–1000 nm. XRD analysis was  
 performed by means of diffractometer DRON-407 with a  
 nickel filter in the radiation of  $\text{CuK}\alpha$  ( $\lambda = 0.15418$  nm) in  
 the reflected bunch and registration geometry for Bregg-  
 Brentano ( $2\theta = 10^\circ\text{--}60^\circ$ ).

To determine the effect of fabric materials impregnated  
 with different concentrations of Ag and Ag/Cu nanoparti-  
 cles on bacteria and micromycetes, we used a classic mi-  
 crobiological method. Petri dishes were filled with the  
 respective test culture agar for bacteria and Sabouraud for  
 fungi. Then, cotton fabrics were cut into equal-sized round  
 pieces 10 mm × 10 mm, and the test cultures of bacteria  
 ( $10^6$  CFU), yeasts of the genus *Candida* ( $10^5$  CFU), and the  
 mold-forming fungi, micromycetes ( $10^5$  CFU) were placed  
 on the cooled agar and carefully triturated with a spatula  
 Drygalski on the surface of the agar. After drying up of  
 inoculation, the tissue of investigated samples were applied  
 onto the agar surface (1 cm × 1 cm) and Petri dishes were  
 cultured in the conditions of thermostat: for bacteria at  
 37 °C for 24 h, for fungi of the genus *Candida* at 36 °C  
 for 48 h, and for micromycetes at 28 °C for 3–5 days.  
 The results of the action of fabrics impregnated with Ag  
 NPs and Ag/Cu composites and the comparison of silver  
 ions on the test cultures are presented in Table 1.

### Results and Discussion

The mechanism of reduction of metal ions to the NPs  
 on the surface of the cotton by gentle heat treatment

f2.1  
f2.2

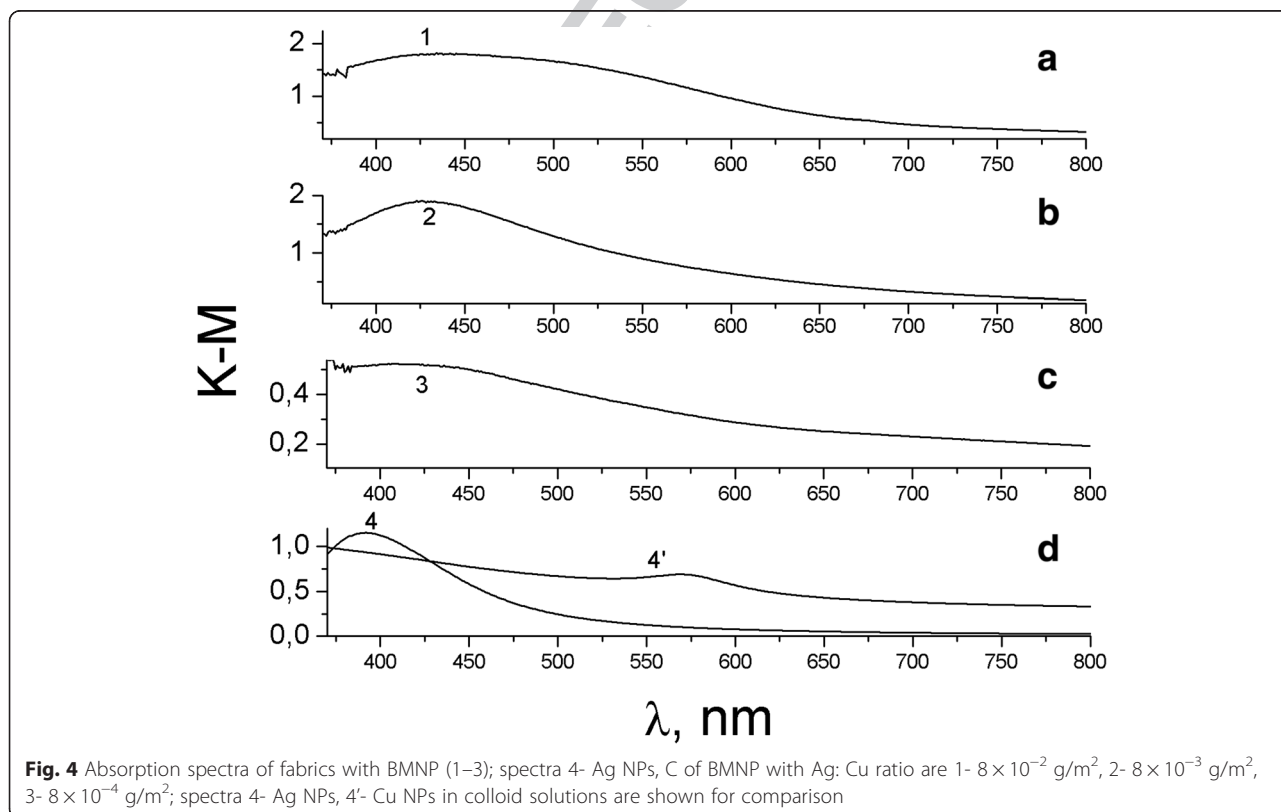


f3.1  
f3.2  
f3.3

246 and their stability in relation to leaching of the metal  
247 particles or ions upon contact with water and biological  
248 fluids is not entirely clear. It is known that cotton is  
249 99.6 % cellulose, and the rest is ash-like substance.  
250 Cellulose is a long chain polymer molecule consisting of  
251 repeating glucosidic residues, 300–10,000 glucose

residues, without side loops. Cellulose contains reducing  
oligosaccharides. Their aldehyde function presumably  
can promote the process of silver and copper ion reduction  
(probably analogous to the reaction of “silver mirror”).  
Figure 1 shows a fragment of the polymeric chain of cellulose.

252  
253  
254  
255  
256 **F1**  
257



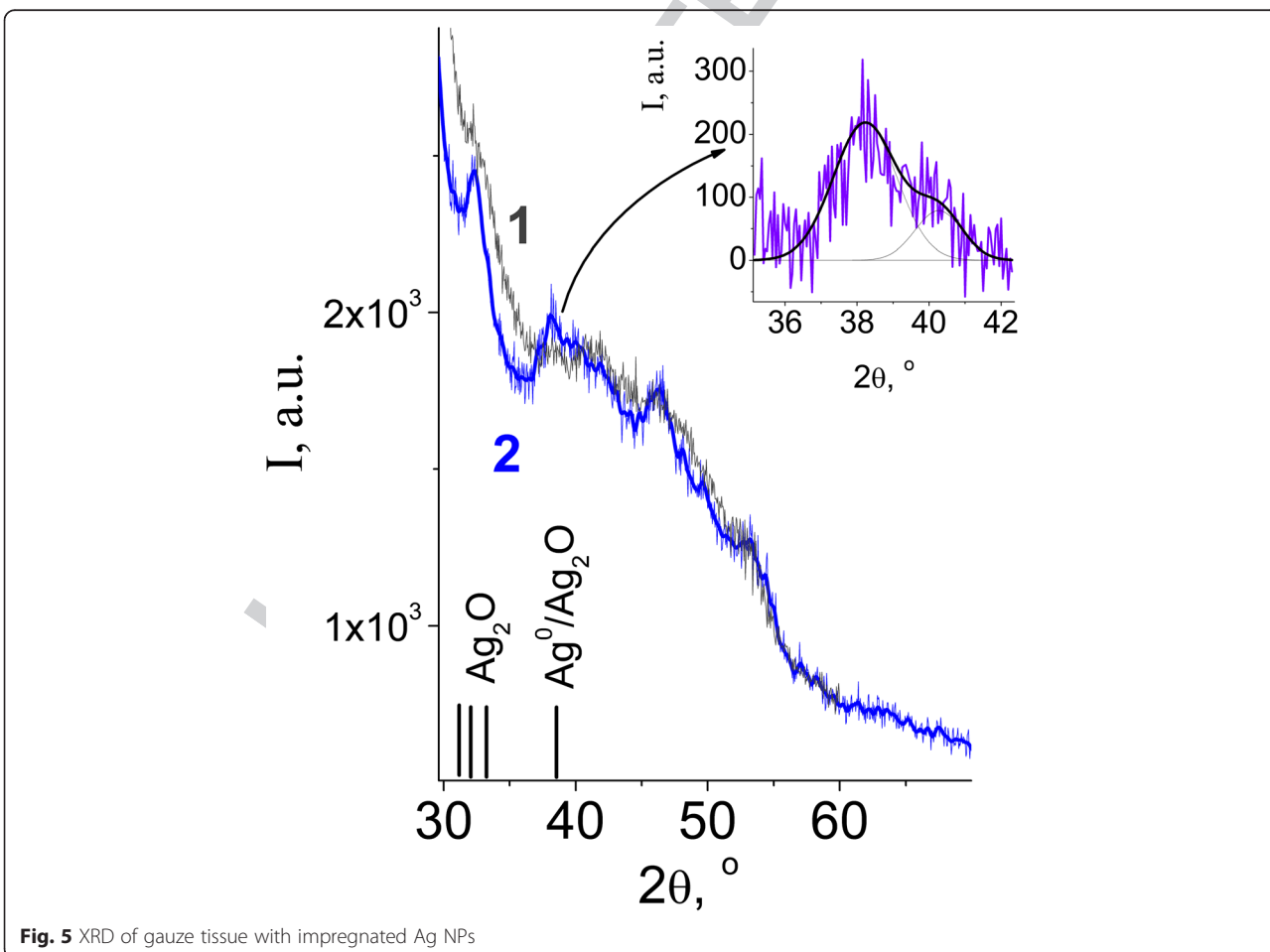
f4.1  
f4.2

258 We can assume also the concentration of metal ions  
 259 around OH<sup>-</sup> groups and the bond formation between  
 F2 260 the metal cations and hydroxyls of cellulose (Fig. 2). The  
 261 water molecules are included in the coordination sphere  
 262 of metal ions, simultaneously forming a hydrogen bond  
 263 with OH<sup>-</sup> groups of cellulose. The Ag<sup>+</sup> ions have a rela-  
 264 tively high reduction potential and are reduced to Ag  
 265 atoms at low temperature (160–200 °C in air). The re-  
 266 duction of copper ions requires a higher temperature;  
 267 however, when impregnated in the cotton, there is a  
 268 danger of destruction of tissue due to carbonization  
 269 process. Therefore, the ironing of tissues soaked in a salt  
 270 solution was carried out in all cases at temperatures of  
 271 200 to 220 °C. The OH<sup>-</sup> groups of cellulose are oxidized  
 272 to carboxyl groups. The fabric retains its structure; here-  
 273 with according to FTIR [17], stretching band at 1720 cm<sup>-1</sup>  
 274 <sup>-1</sup> decreases due to the interaction between carboxyl  
 275 groups and metal ions.

F3 276 Figure 3 shows the electronic absorption spectra of  
 277 cotton samples with different numbers of silver and  
 278 copper particles after ironing, recalculated according  
 279 to the equation of Kubelka-Munch. The presence of  
 280 absorption band with a maximum at 430–440 nm

(SPR) in Fig. 3a is indicative of the formation of silver  
 281 NP<sub>s</sub> in the structure of cotton. 282

On the contrary, the wide absorption band in Fig. 3b  
 283 does not correspond to the SPR spectrum of Cu NPs 284  
 (max of SPR spectrum of Cu NPs is 565 nm) and rather 285  
 belongs to the copper oxides on the fabric. The 286  
 color of tissues changes from yellow to yellow- 287  
 brownish for Ag and from greenish-brownish to 288  
 brown for Cu depending on the metal amount. We 289  
 assume that the impregnation of tissue with both silver 290  
 and copper salts and subsequent heat treatment 291  
 results in the reduction of the ions Ag<sup>+</sup> and Cu<sup>2+</sup> to 292  
 nanoparticles of silver, yellow-brownish oxide Ag<sub>2</sub>O 293  
 and a red-brown protoxide Cu<sub>2</sub>O. Metal particles re- 294  
 main in the structural micropores and on the surface 295  
 of the fabric in the form of NPs or small aggregates. 296  
 Formation of bimetallic particles Ag/Cu is compli- 297  
 cated because of substantial distinction of oxidizing 298  
 potentials—0.337 V for copper and 0.799 V for silver. 299  
 Therefore, to control the process of simultaneous re- 300  
 duction of ions is difficult. In the absorption spectra 301  
 of fabrics with BMNP on Fig. 4, a wide band with 302  
 max near 750 nm is more typical for aggregates of 303



f5.1 **Fig. 5** XRD of gauze tissue with impregnated Ag NPs

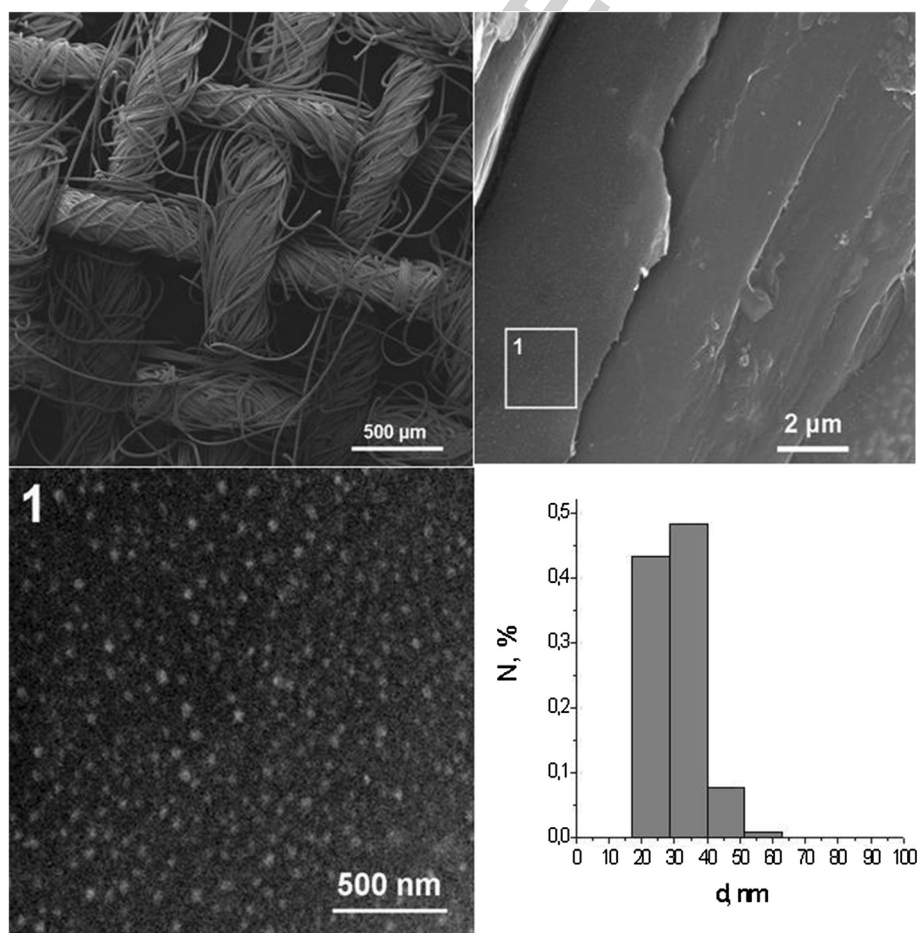
304 Ag NPs. It is possible to suppose that in a bimetallic  
 305 composites at heat treatment, Ag NPs precipitate on  
 306 the copper oxide particles as a shell. As a whole, it is  
 307 possible to suppose that under the impregnation and  
 308 heat treatment of cotton with salts of metals, a basis  
 309 of cotton, a cellulose, is simultaneously the reductant  
 310 of ions and stabilizer of appearing NPs. This question  
 311 needs further investigation.

312 In [19], the spectrum of Ag/Cu BMNP in a thin  
 313 film of polyelectrolyte is attributed by the authors to  
 314 the alloy also only slightly differs in the position of  
 315 SPR of Ag NPs, though one would expect a much  
 316 larger wavelength shift in the case of formation of the  
 317 alloy. According to [19], in Ag/Cu alloy, silver and  
 318 copper are close to each other in electrical contact  
 319 and have a disordered random distribution of Ag and  
 320 Cu atoms inside an enclosed structure and therefore  
 321 do not possess crystallinity.

F5 322 Figure 5 shows the diffraction pattern of the tissue  
 323 sample with silver NPs. Peak at  $2\theta = 32^\circ$  is character-  
 324 istic of silver oxide  $\text{Ag}_2\text{O}$  and shows that the Ag NPs

325 on the surface of the fabric are located in the shell of  
 326 the silver oxide and a broad low-intensity band in the  
 327 region of  $2\theta = 38^\circ$  can be attributed to  $\text{Ag}^0$ . Electron  
 328 microscopic image of the BMNPs-impregnated gauze  
 329 F6  
 330 at different magnifications is shown in Fig. 6 (the  
 331 scale bar is  $500\ \mu\text{m}$  on the left above,  $2\ \mu\text{m}$  on the  
 332 right above, and  $500\ \text{nm}$  on the left down), as well as  
 333 the size distribution of BMNP on the surface of the  
 334 fabric. Ag/Cu NPs can be seen as white spherical  
 335 spots which are uniformly disposed on the whole  
 336 gauze surface. Average size of NPs is approximately  
 337  $20\text{--}30\ \text{nm}$ . Agglomeration of silver nanoparticles into  
 338 larger clusters was also observed. The results showed  
 339 that silver particles are sufficiently bound to the cot-  
 340 ton fabric, which can retain good bacteriostatic prop-  
 341 erties even after washing.

341 Bactericide action of Ag NPs and BMNP are shown  
 342 in Table 1. The samples of Ag-modified gauze and  
 343 madapollam samples effectively kill the harmful bac-  
 344 teria and fungi. In the last two columns of Table 1,  
 345 the results of bactericide activity of Ag NPs on the



f6.1 **Fig. 6** Electron microscopic image of the sample with BMNPs on gauze

346 dispersive silica surface as well as of aqueous solution  
 347 of colloidal silver obtained by us early are shown for  
 348 comparison. Apparently, the activity of the obtained  
 349 fabrics is comparable with such for Ag NPs in a col-  
 350 loid and on the developed surface of dispersive silica.  
 351 Thus, advantages of fabrics are the substitution of  
 352 noble metal silver on copper, simplicity of their pro-  
 353 duction and storage, stability after washing, and main-  
 354 tenance of bactericidal action for a long time.

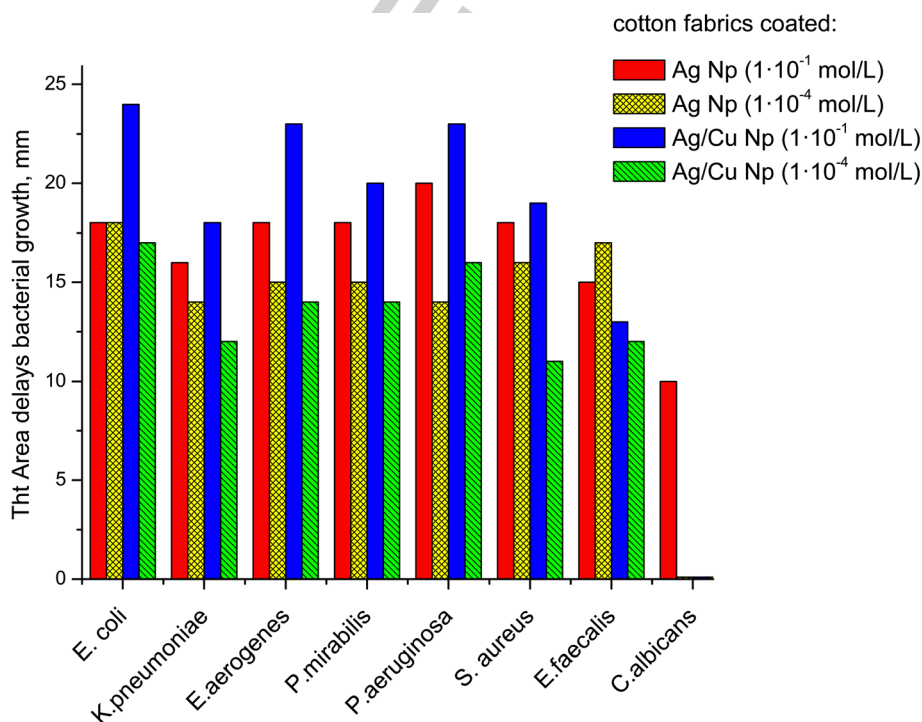
355 The results of determining the effect of tissue samples  
 356 with nanoparticles of silver and copper in clinical iso-  
 357 lates of bacteria, fungi of the genus *Candida*, and micro-  
 F7 358 mycetes are shown in the diagram (Fig. 7).

359 Ratio Ag:Cu in BMNPs in gauzes is 1:1 (blue), with  
 360 the content of metal  $1.3 \cdot 10^{-5}$ : $1.3 \cdot 10^{-1}$  g/m<sup>2</sup>. Tissues  
 361 with a corresponding number of binary Ag/Cu have  
 362 pronounced bactericidal activity. As can be seen from  
 363 the above data, the fabrics impregnated with BMNPs  
 364 are the most effective in relation to most of the in-  
 365 vestigated test cultures. The maximal area of growth  
 366 inhibition around the tissue for all studied bacteria,  
 367 fungi, and micromycetes are detected for bimetallic  
 368 composites. Cu ions and particles in the fabric do not  
 369 found expressed antibacterial action. Kinetics of  
 370 leaching of NPs with water from tissue samples were  
 371 studied for 24 h. Metal ions were not detected in the  
 372 solution, indicating the strong fixation of the particles

on the fabric. Bactericidal activity is maintained for  
 more than 6 months. 373 374

### Conclusions 375

Highly efficient bactericidal and antimycotic materials  
 based on cotton fabrics contain nanoscale particles of  
 silver and bimetallic Ag/Cu composition in an amount  
 of 0.015–0.13 wt% obtained by impregnating a fabric  
 with water solutions of corresponding metal salts followed  
 by even ironing at 200 °C. The samples were characterized  
 by optical spectroscopy, X-ray diffraction and electron mi-  
 croscopy and contain crystalline NPs of silver compounds  
 with relevant SPR bands in the absorption spectra and bi-  
 metallic Ag/Cu composition—presumably the nanoparti-  
 cles of copper oxide coated with silver NPs. High  
 antimicrobial properties of tissues with Ag NPs and Ag/  
 Cu composites are confirmed in experiments with a wide  
 range of multidrug-resistant bacteria *Escherichia coli*, *En-*  
*terobacter aerogenes*, *Proteus mirabilis*, *K. pneumoniae*,  
*Candida albicans* yeasts, and micromycetes, and activity  
 remains high throughout 6 months. Presumably under the  
 impregnation of cotton with salts of metals and ironing at  
 200 °C, a basis of cotton, a cellulose, is simultaneously the  
 reductant of ions and stabilizer of appearing NPs. Antibac-  
 terial fabrics do not reduce their activity after washing. A  
 method developed for such material is extremely fast,  
 cost-effective, and convenient. 391 392 393 394 395 396 397 398



f7.1  
 f7.2

**Fig. 7** The effect of tissue samples with nanoparticles of silver and copper in clinical isolates of bacteria, fungi of the genus *Candida*, and micromycetes



399 **Abbreviations**

400 A300: fumed silica; BMNP: bimetallic nanoparticles; M: molar;  
401 NPs: nanoparticles; wt%: weight percent.

402 **Competing Interests**

403 The authors declare that they have no competing interests.

404 **Authors' Contributions**

405 AE carried out the study and drafted the manuscript. IP was involved in the  
406 synthesis of the nanocomposites and the spectrophotometrical investigations.  
407 AR and JM carried out the investigation biocidal and antimycotic activity of  
408 samples. AR and IP helped to draft the manuscript. AE and AR participated in  
409 the design and coordination of the study. All authors read and approved the  
410 final manuscript.

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413 on A300 powder and in colloid.

414 **Author details**

415 <sup>1</sup>Chuiko Institute of Surface Chemistry of National Academy of Science of  
416 Ukraine, 17 General Naumov str., Kyiv 03164, Ukraine. <sup>2</sup>Institute of Urology of  
417 Academy of Medical Science of Ukraine, Yu Kotsyubynskogo, 9-A, Kyiv 04053,  
418 Ukraine.

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