

Preparation of photochemical coatings of metal films (copper, silver and gold) on dielectric surfaces and studying their antimicrobial properties.

by

P.A.Abdurazova^a, U.B.Nazarbek^a, A.A.Bolysbek^a, N.K.Sarypbekova^a, G.S. Kenzhibayeva^a, G.A.Kambarova^a, M.S.Sataev^a, Sh.T.Koshkarbaeva^a, A.B.Tleuova^a, S. Perni^b, P. Prokopovich^{b,c*}.

^a South Kazakhstan State University, Shymkent, Kazakhstan

^b School of Pharmacy and Pharmaceutical Science, Cardiff University, Cardiff, UK

^c School of Engineering, Cardiff University, Cardiff, UK

* *Corresponding author:*

Dr. Polina Prokopovich e-mail: prokopovichp@cardiff.ac.uk

School of Pharmacy and Pharmaceutical Sciences

Cardiff University

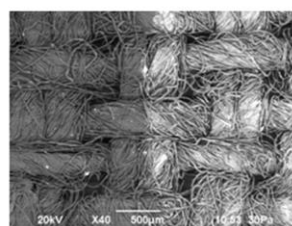
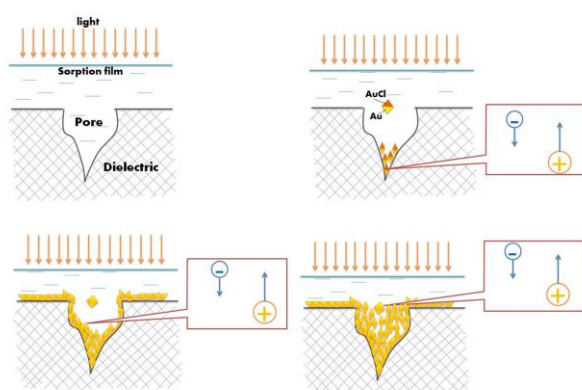
Redwood Building, King Edward VII Avenue

Cardiff, CF10 3NB, UK

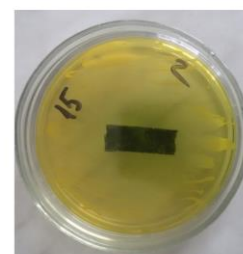
Tel: +44 (0)29 208 75820

Fax: +44 (0)29 208 74149

Graphical abstract



Irradiated screened



Highlights:

- a new photochemical technique to prepare antimicrobial metal films on the textiles materials is developed.
- gold, copper, silver and its combination coatings are obtained on fabrics.
- antimicrobial activity of these coatings depends on type, combination, concentration and ratios of metals formed.
- obtained coatings are resistant to washing and creasing of the fabrics.

Abstract

The metals of the copper subgroup (copper, silver, gold) are known for its antibacterial properties for a long time. For example, among the antimicrobial properties of copper, it should be noted its ability effectively inactivate MRSA and influenza a virus including subtype H1N1, called "swine flu". In this study we developed a number of methods of gold, copper and silver and its mixture coatings of dielectric materials and applied these coatings on textile fabrics. Subsequent antimicrobial testing of coated fabrics were conducted using two bacteria *E. coli* and *S. aureus*. Obtained coatings were subjected to numerous washing and creasing to prove its resistance.

Keywords: copper; silver; gold; metal coatings; antimicrobial surfaces.

1. Introduction.

The metals of the copper subgroup (copper, silver, gold) are known for its antibacterial properties for a long time. Although the antimicrobial action of copper is 4-5 times weaker than that of silver, taken together, these metals greatly enhance the properties of each other [1].

Among the antimicrobial properties of copper, it should be noted its ability effectively inactivate MRSA [2] and influenza a virus including subtype H1N1, called "swine flu" [3,4]. The antimicrobial ability of copper was confirmed by the fact that the US Agency for environmental protection (US EPA) formally granted to copper and several copper alloys status of substances with antibacterial surface properties [4].

Among the copper subgroup silver possesses the highest antimicrobial properties. Spectrum of silver antibacterial action extends to 650 types of bacteria, whereas the antibacterial spectrum of any antibiotic only to 5-10 types of bacteria [5,6]. Currently silver and its formulations are widely used as antimicrobials for different textile materials for household and medical purposes [7-11]. These fabrics can be used for the manufacture of medical devices, various types of military uniforms, sports wear, lingerie, holsters for weapons, protecting them from various kinds of microorganisms [12,13].

The bactericidal activity of gold is 2-3 times lower than silver, however, the best bactericidal effect is achieved using the bimetallic composition of Ag/Au = 5, where a small addition of gold enhances the silver activity [14]. For example, the combination of gold and silver nanoparticles can significantly extend the silver antimicrobial action which is used in the manufacture of antimicrobial clothing [15].

Various coating methods were developed for deposition of antimicrobial metals of copper subgroup on dielectric materials such as vacuum metallization [16-19], vapor deposition or laser sputtering [20-23], chemical deposition [23-28]. There are advantages and disadvantages for each method, for example, for chemical deposition sometimes toxic reducing agents are employed [29-35]. Also a photochemical preparation of copper, silver and gold containing nanoparticles on polymer microspheres became popular [36-38]. It was noted that the surface of the microspheres

of polymers, acting as sorption centres of metal nanoparticles provide the possibility of obtaining the latter in the form of stable dispersions. The disadvantage of this method is that the photochemical reaction with the formation of metals occurs only on a certain structure of the dielectric materials which significantly narrows the scope of the method.

In this study we developed a number of methods of gold, copper and silver and its mixture coatings of dielectric materials and applied these coatings on textile fabrics. Subsequent antimicrobial testing of coated fabrics were conducted using two bacteria *E. coli* and *S. aureus*.

2. **Materials and Methods.**

Chemical reactions:

The basis of the proposed method is a photochemical method of gold and copper recovery by light rays action. Let's consider the mechanism of this method on the example of gold.

The photochemical reaction occurs in the sorption layer of a gold chloride solution on the surface of the dielectric material. In this system, one possible reaction is the formation of monovalent gold ions.



This reaction is thermodynamically possible, since the standard potentials of the reaction are:



and:



Under normal conditions, the direction of reaction (1) is strongly shifted to the left, so the allocation of a significant amount AuCl and the formation of oxygen and HCl (H⁺) are not observed. The drying of the sorption layer increases AuCl₃ concentration, which increases the oxidizing capability of trivalent gold. In addition, the contact of the sorption layer with the solid-phase surface, which represents the centers of crystallization, facilitates the appearance of AuCl solid-phase layer. This enhances the possibility of reaction with the formation of low-soluble monovalent gold.

The monovalent gold chloride possesses semiconductor properties and, therefore, under the light a photochemical reaction occurs.



The occurrence of this photochemical reaction shifts the equilibrium of reaction 1 to the right, and the overall reaction in this case would be:



Oxidation capacity of copper chloride is lower than that of gold chloride, therefore, the reaction (1) in the case of copper is impossible.

Cotton fabrics at 97-98% composed of cellulose is very sensitive to oxidants due to the presence of alcohol and hydroxyl groups. As a result of these groups oxidation the formation of new carbonyl and carboxyl functional groups occurs. Oxidation starts from the surface of the fabric and then gradually progresses into the fabric, whereby first the amorphous parts get oxidized, and then the crystalline areas oxidised [39].

Consequently, the formation of chloride of monovalent copper can be explained by the reaction:



where R is the elementary unit of cellulose.

It is obvious that for gold chloride both reaction (6) and reaction (1) can take place.

Film preparation:

Laboratory studies were performed on a gauze fabric (SKU AA010278) widely used for medical purposes. For preparation of gold or copper films tissue samples were immersed in a solution of gold (III) chloride or in a solution of copper (II) chloride respectively for 1-3 minutes.

Due to the poor water solubility of silver chlorides, to obtain in one step a homogeneous sorption layer containing silver is impossible. Therefore, to obtain silver films initially a copper film was formed and treated in a solution of silver nitrate by completely replacing copper to silver.

For this the sample was put for 5-6 hours in a solution containing 1-2 g/l of silver nitrate (AgNO_3) and 0.5 g/l of nitric acid (HNO_3) [25]. The process of formation of silver was provided by the reaction:



For the copper-silver film preparation re-photochemical method was re-applied to achieve the required amount of copper. Similarly, preparation of gold-silver-copper films were carried by applying gold-copper on priority deposited silver films. Concentration of each metal was 30 g/l. For preparation of two or three metal containing coating solutions were equal concentration giving a total of 30 g/l metal concentration in the coating.

In some experiments, a part of the tissue surface was screened by a polymeric washer to distinguish the boundary between the irradiated and not irradiated parts of the sample. Then the sample was exposed to General Electric 28 W Biax 2D compact fluorescent lamp at 20 °C until completely dried. After that, the washer was removed and the sample was thoroughly rinsed with distilled water.

Film characterisation:

The thickness of the coating was determined by the method described in [40]. The structure and composition of the films deposited on textile materials were studied using scanning electron microscope ISM-6490-LV.

Antimicrobial testing:

The antibacterial properties of metal coated fabrics were studied against two bacteria, *E. coli* ATCC 25922 and *S. aureus* ATCC 25923, according to ISO20743-2012 and 019/2011 standards. Prior antimicrobial testing all tissue samples were subjected to 10-fold washing in washing powder (SMS) of 2 g/l solutions at 50 degrees with constant mixing following by water rinsing (3-5 L during 10 minutes). Fabrics were placed in nutrient medium Endo (differential-diagnostic nutrient medium designed for the isolation of enterobacteria) and in medium ZHSA (yolk -salt agar medium for isolation of staphylococci, contains up to 10 percent of sodium chloride, which inhibits

most bacteria contained in the material) respectively. Then samples were incubated at room temperature for three days. Preliminary experiments showed that no changes occurred after longer exposure to bacteria.

3. Results and Discussions.

Various steps of film preparation are shown in Fig. 1. Untreated fabric (Fig. 1a) is presented against a fabric treated with gold (II) chloride (Fig. 1b), a fabric after irradiation (Fig. 1c), a fabric treated using the polymeric washer as a screening tool to distinguish between irradiated and not irradiated parts of the sample (Fig. 1d), a gold coated fabric after washing (Fig. 1e) and a fabric with hidden parts after washer removal and rinsing (Fig. 1f).

The course of photochemical reactions was confirmed by the study of the composition of the films formed on the tissue when irradiated. Figure 2 shows an electronic image of the border between the illuminated and shielded polymeric washer areas.

Elemental analyses of individual sites (Table 1), indicates which sites were illuminated by the photos and produced elemental gold, shielded sections of the chloride of gold remains unchanged. The presence of small amounts of gold on shielded areas is associated with the existence of some sections in the tissue structure that are able to restore chemically to the metal. In general, the amount of gold chloride (99%) remains unchanged and is removed after washing.

The thickness of the gold and copper films produced depends on several factors: the intensity of the light rays, the structure of the tissues, the concentration of metal ions, the degree of recovery, temperature of drying, the presence of impurities. It is very difficult to account for these factors. But the main factor will be the concentration of metal ions. The dependence of this factor are given in Table 2.

The study of the structure of films consisting of metals of the copper subgroup found that in all cases they are formed in the form of spherical particles average diameter ranges from several to several hundred nanometers (Fig. 3).

Studies of tissue samples on the counter numerous washings (10-15 times) and mechanical actions (50-70 times) showed that the composition of the film remains practically unchanged. This allows us to suggest the following scheme of formation of the film (Fig.4).

This suggests that the formation of primary crystals of monovalent chlorides begins in the depths of the pores, as the topography of these areas is energetically more favorable for the formation of new crystalline phase. The penetration of the light photons on the surface of these crystals leads to the occurrence of photochemical reactions (4) with the formation of metal atoms. Moreover, this process will begin with a border of crystals monovalent chlorides, which have large distortion of the crystal lattice. This scheme of the original metal pore filling can be a possible explanation of the film stability obtained by the photochemical method to washing and sinanian.

By using solutions with different concentrations of copper and gold to create a sorption layer it is possible to obtain films containing these elements in the desired quantities and proportions.

It was shown experimentally that the ratio of copper and gold in the solutions used to obtain the sorption layer on the tissue is same with the ratio of these elements in the film resulting from photochemical reactions (Table 3).

If one considers that copper can easily be replaced by silver, the photochemical method allows obtaining films of almost any desired composition of these elements. The compositions of the films of the elements of the subgroup of copper obtained from dilute and concentrated solutions are shown in Figures 5 and 6 and Tables 4 and 5.

Antimicrobial tests were performed determining the zone of inhibition created by the prepared coating for *E. coli* ATCC 25922 and *S. aureus* ATCC 25923 (Table 6); an example of the resulting bacterial plates is presented in Figure 7. For both organisms rested, bacteria growth was not prevented by samples without film; on the other hand, on coated samples, bacteria did not grow in an area close to the fabric (zone of inhibition).. In general, on the basis of data given in Table 6 bactericidal activity of the studied films decreases in the following order: silver, copper+silver,

copper+silver+gold, copper+gold, gold+silver, copper, gold. Moreover, *E. coli* exhibited smaller zone of inhibition than *S. aureus* for all samples.

The zone of inhibition is caused by the release of antimicrobial compounds from the sample and because of the localised origin of this agent, the concentration decreases from the surface of the sample towards the plate edges. Each microorganism can grow when the concentration of a potential antimicrobial agent is below a certain value (Minimal Inhibitory Concentration - MIC) thus bacterial growth can be observed far from the sample edge, on the contrary if the antimicrobial concentration close to sample is above the MIC, no growth is noticeable and a zone of inhibition is defined. The higher the sensitivity of a microorganism to the antimicrobial agent the bigger the zone of inhibition.

If the specific antibacterial properties of subgroup metals of copper are taken into account, bactericidal properties of metallic films can be linked to their ability to ionize in a given environment. So if you compare the standard potentials of ionization of these elements, for gold, this value is +1,68 V for the formation of monovalent ions and 1.42 V for the formation of trivalent ions; while for silver the value is + 0.8 V and for copper and 0.52 V. for the formation of monovalent ions and +0.34 V for divalent ions.

This implies that ionization of gold in this environment is minimal hence bacteria were capable of growing close to the samples. On the contrary, the ionization of copper occurs to a greater extent and the resulting compounds of copper are diffusing into the test environment, thus resulting in greater inhibition zones. Also a positive role of a higher concentration of copper compounds (for comparison with gold) contributes to this effect. In favor of this assumption is the evidence of the appearance of dark halo around the samples coated with films containing copper (4,6,7,8 positions in the Table 6). This halo is caused by compounds of copper, usually with dark color.

Antimicrobial properties of silver and copper are relatively well reported and similarly gold is known not to prevent bacterial growth [41]-[45]; in this context the results presented here are consistent with these works. Antimicrobial activity of deposited metals is not usually explained in

terms of reduction potential as we did here and such providing an additional perspective in the antimicrobial activity of materials coated with metals.

Bactericidal properties of other metals such as nickels, zinc, aluminium, are less effective and shown for specific microorganisms only. Besides, film coating using these metals are complex and expensive technologically.

4. Conclusions

In this study we reported a preparation of metal films (copper, gold and silver and its combinations at various ratios) on fabric surfaces using a relatively simple photochemical method. Combining various metals in the coating, allowed to extend the range of their antibacterial properties and replaced expensive gold and silver to copper which is cheaper. Considering that the metal films also formed in the grooves and pores of the fabric, these coated textiles can withstand repeated washing and creasing of the fabric. This makes this technology is promising for obtaining antimicrobial medical devices and antimicrobial clothing.

5. References

- [1] <http://www.allbest.ru/...http://www.inauka.ru/...le83902.html>
- [2] <http://www.epa.gov/pesticides/factsheets/copper-alloy-products.htm>
- [3] <http://www.coppertube.ru-wieland.ru/h1n1.html>
- [4] Copper Facts. EPA 738-F-06-014. United States Environmental Protection Agency 2008; 1-5.
- [5] A.B. Lansdown. Silver. 1. Its antibacterial properties and mechanism of action. *J Wound Care* 2002;11:125–130.
- [6] S. Thomas, P. McCubbin. A comparison of the antimicrobial effects of four silver-containing dressings on three organisms. *J Wound Care* 2003;12:101–107.
- [7] R.O. Darouiche. Anti-infective efficacy of silver-coated medical prostheses. *Clin Infect Dis* 1999;29:1371–1377.
- [8] F. Furno, K.S. Morley, B.Wong, B.L. Sharp, P.L. Arnold, S.M. Howdle, R. Bayston, P.D. Brown, P.D. Winship, H.J. Reid. Silver nanoparticles and polymeric medical devices: a new approach to prevention of infection? *J Antimicrob Chemother* 2004;54:1019–1024.
- [9] J. Heggors, R.E. Goodheart, J. Washington, L. McCoy, E. Carino, T. Dang, P. Edgar, C. Maness and D. Chinkes. Therapeutic efficacy of three silver dressings in an infected animal model. *J Burn Care Rehabil* 2005;26:53–56.
- [10] I.P. Margaret, S.L. Lui, V. K. M. Poon, I. Lung, A. Burd. Antimicrobial activities of silver dressings: an in vitro comparison. *Journal of medical microbiology* 2006;55:59-63.
- [11] N.N. Shkil, N.A. Shkil, V.A. Burmistrov, M.Y. Sokolov. Antimicrobial properties, pharmotoxicological characteristics and therapeutic effectiveness preparation argovit in gastroenteritis diseases of calves. *KubGAU Scientific journal* 2011; №68(04), <http://ej.kubagro.ru/2011/04/pdf/46.pdf>.
- [12] A.B.G. Lansdown. *Silver in Healthcare: Its Antimicrobial Efficacy and Safety in Use*. Royal Society of Chemistry 2010; p. 159.
- [13] S. Duquesne. *Multifunctional barriers for flexible structure: textile, leather, and paper*. Springer-Verlag Berlin Heidelberg 2007; p.26.

- [14] E.A. Konovalova. Preparation, crystallo stability, adsorptive and antimicrobial properties of silver, gold and silver-gold nanoparticles in zoles and on substrates. PhD. Moscow.
- [15] <http://www.goldbulletin.org>.
- [16] M. Hoking, V. Vasatasri, P. Sidki. Metal and ceramic coating: preparation, properties and application. Mir 2000: p. 518.
- [17] A.I. Kashirin, O.F. Klyuyev, T.V. Buzdygar, A.V. Shkodkin. Particle sedimentation formation by kinetic energy application. Patent R.F. IZ № 2257423 published on 27.07.2005. Patent R.F. IZ № 2257423 published on 27.07.2005.
- [18] O.F. Klyuev, A.I. Kashirin, T.V. Buzgygar, A.V. Shkodin. Technology of repair, recovery, hardening and renewal of cars, mechanisms, equipments and metal containing constructions. Conference Proceedings. 4th Russian Practical Conference. Sankt-Petersburg, 16-18 April of 2002; pp.136-140.
- [19] Yu Xingwen, C. Chunan, Ya. Zhiming, Z. Derui, Y. Zhongda. Study of double layer rare earth metal conversion coating on aluminum alloy LY12. Corrosion Science 2001;43:1283-1294.
- [20] A.A. Bessonov, N.B. Morozova, N.V. Gelfond, P.P. Semyannikov, S.V. Trubin, Yu.V. Shevtsov, Yu.V. Shubin, L.K. Igumenov. Dimethyl-gold(DI) Carboxylates as New Precursors for Gold CVD. Surf. Coat. Tech. 2007; 201: 9099-9103.
- [21] A.S. Kuch'yanov, A.I. Plehanov, I.K. Igumenov, B.M. Kuchumov, P.G. Parhomenko, S.V. Trubin. Sedimentation method of gold nanoparticles on silica microspheres based on thermo-decomposition of light gold compounds. Patent R.F. № 2489230 MIIK: B22F9/12. Published on 10.08.2013.
- [22] A.J. Tujeushev, V.N. Lisizin, U.J. Tuleaujev, V.N. Volodin, S.N. Kim. Preparation method of precious metal and its alloys coatings. Patent № 2214476 MIIK: C23C14/16. Published on 20.10.2003.
- [23] A. Hadji Begli, C. Baatz, N. Decker, W. Prusse, K.-D. Forlop. Gold catalyst on the substrate. Patent RF. №2378048, B01J 23/52, published in 2010.
- [24] S. T. Koshkarbaeva, S.Z. Nauryzova, M.S. Sataev and A.B. Tleuova. Low-temperature Gas-phase Metallization of Dielectrics. Oriental journal of chemistry 2012; 28(3):1281-1283.
- [25] M.S. Sataev, S.T. Koshkarbaeva, A.B. Tleuova, S. Perni, S.B. Aidarova, P. Prokopovich. Novel process for coating textile materials with silver to prepare antimicrobial fabrics. *Colloids and Surfaces A: Physicochemical and Engineering* 2014; 442: 146–151.
- [26] M.S. Satayev, Sh.T. Koshkarbayeva, A.B. Tasboltaeva. Metallization of the products of textile production. *Izvestiya Vysshikh Uchebnykh Zavedenii, Seriya Tekhnologiya Tekstil'noi Promyshlennosti*, 2013; 348 (6):102-104
- [27] M.S. Sataev, S.T. Koshkarbaeva, S. Perni, S.Z. Nauryzova, P. Prokopovich. A galvanic-chemical method for preparing diamond containing coatings. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2014; 480: 384-389.
- [28] M.S. Satayev, S.T. Koshkarbayeva, A.S. Tukibayeva, E.Z. Tuleshova. Decorative Coatings of Crystallite Type on Metallic and Non-metallic Surfaces. *Asian Journal of Chemistry* 2013; 25 (18), 10329.
- [29] S. Q. Jiang, E. Newton, C. W. M. Yuen, C. W. Kan. Chemical silver plating and its application to textile fabric design. *Journal of Applied polymer science*. 2005; 96 (3): 919–926.
- [30] S. Q. Jiang E. Newton C. W. M. Yuen C. W. Kan. Chemical Silver Plating on Cotton and Polyester Fabrics and its Application on Fabric Design. *Textile Research Journal*. 2006; 76(1):57-65.
- [31] M. Kato, Yu. Okinaka. Some recent developments in non-cyanide gold plating for electronics applications. *Gold Bulletin*.2004; 37(1): 37–44.
- [32] H. Jiandong, L. Wei, Ch. Jian, Zh. Xiaohui, Zh. Xiangyang. Novel plating solution for electroless deposition of gold film onto glass surface. *Surface and Coatings Technology*. 2008; 202 (13): 2922–2926.
- [33] Ch.-Y. Lee, T.-H. Huang. Electroless gold plating method for forming inductor structures. Patent. US 6030877 A. 2000.

- [34] IPC-4552. Specification for Electroless Nickel / Immersion Gold (ENIG) Plating for Printed Circuit Boards. 2002. pp.1-25.
- [35] T.N. Vorob;eva, T.N. Vrublebskya, A.V. Vengura. Solutions for non electrolysis sedimentation of gold films on nickel surfaces. Patent. BUN№10283, MIIK C23C18/31, published on 2008.02.18.
- [36] E.I. Isaeva, O.B. Svistunova, V.V. Gorbunova, T.B. Boizova. Photochemical synthesis of gold nanoparticles in elastomeric polybutylene latex films. *Journal of General Chemistry*. 2007; 77(12): 1968-1971.
- [37] E.I. Isaeva, T.B. Boizova, V.V. Gorbunova. Photochemical synthesis of gold nanoparticles in latex. *Journal of Applied Chemistry*. 2006; 79(4):683-685.
- [38] E. Sacher, J.J. Pireax, S.P. Kowalczyk. *Metallization of Polymer*. Washington D.C.:ACS, Symp.Ser. 1990; 440(1): 282-288.
- [39] V.I. Azarov. *Chemistry of woods and synthetic polymers*. 1999; p. 629.
- [40] P.A. Abdurazova, M.S. Satayev, Sh.T. Koshkarbayeva, Y.B. Raiymbekov, U.B. Nazarbek. Method for determining the thickness of metal coating deposited on the surface of dielectric material. *Bulletin of the Karaganda university* 2017; 85(1): 1-27.
- [41] G. Tommasi, S. Perni, P. Prokopovich. An Injectable Hydrogel as Bone Graft Material with added Antimicrobial Properties. *Tissue Eng. A* 2016;22(11-12):862-872.
- [42] S. Perni, V. Hakala, P. Prokopovich. Biogenic Synthesis of Silver Nanoparticles Capped with L-cysteine. *Coll. Surfaces A* 2014;460:219-224.
- [43] M.S. Sataev, S.T. Koshkarbaeva, A.B. Tleuova, S. Perni, S.B. Aidarova, P. Prokopovich. Novel Process for Coating Textile Materials with Silver to Prepare Antimicrobial Fabrics. *Coll. Surfaces A* 2014;442:146-151.
- [44] Shankar S, Rhim JW. Facile approach for large-scale production of metal and metal oxide nanoparticles and preparation of antibacterial cotton pads. *Carbohydr Polym*. 2017;163:137-145.
- [45] Mishra SK, Mary DS, Kannan S. Copper Incorporated Microporous Chitosan-Polyethylene Glycol Hydrogels Loaded With Naproxen for Effective Drug Release and Anti-Infection Wound Dressing. *Int J Biol Macromol* 2016;95:928-937.

Tables

Table 1. Elemental analysis of screened and irradiated parts of fabric.

| Element | Content of screened part, % (weight) | Content of irradiated part, % (weight) |
|---------|--------------------------------------|--|
| C | 49.29 | 45.88 |
| O | 48.95 | 44.73 |
| Si | 0.84 | 0.95 |
| Cl | 0.09 | 0.04 |
| Ca | 0.19 | 0.09 |
| Au | 0.64 | 7.87 |

Table 2. Influence of gold and copper chloride concentration on metal film thickness obtained using photochemical method.

| № | Coated metal salt solution concentration, g/l | Gold film thickness, um | Copper film thickness, um |
|---|---|-------------------------|---------------------------|
| 1 | 1 | 0.009-0.01 | 0.012-0.016 |
| 2 | 10 | 0.12-0.15 | 0.2-0.27 |
| 3 | 100 | 1.3-1.5 | 3.2-3.7 |
| 4 | 300 | - | 4-5 |

Table 3. Copper and gold ratios in the initial salt solutions used for the sorption layers and in final photochemical films obtained.

| № | Initial solutions used for sorption layers | | | Photochemical films | |
|---|--|------------------------------|--------------|--------------------------|--------------|
| | Salt concentration, g/l | Elemental concentration, g/l | Ratio Cu/ Au | Elemental composition, % | Ratio Cu/ Au |
| 1 | Cu Cl ₂ -150 AuCl ₃ -20 | Cu -70.5 Au- 13 | 5.4 | Cu -47.45 Au- 8 | 5.9 |
| 2 | Cu Cl ₂ -120 AuCl ₃ -20 | Cu -56.4 Au- 13 | 4.3 | Cu -39 Au- 9.35 | 4.17 |
| 3 | Cu Cl ₂ -150 AuCl ₃ -20 | Cu -2.35 Au- 0.65 | 3.6 | Cu -1.08 Au- 0.34 | 3.17 |

Table 4. Elemental analysis of films obtained from diluted solutions (CuCl₂-4 g/l, AuCl₃-2 g/l with additional treatment with 100 ml of 30 mg/l AgNO₃ solution).

| Element | Content, %(weight) |
|---------|---------------------|
| C | 47.88 |
| O | 41.95 |
| Si | 0.84 |
| Cl | 0.09 |
| Ca | 0.18 |
| Cu | 0.52 |
| Ag | 1.90 |
| Au | 0.64 |

Table 5. Elemental analysis of films obtained from concentrated solutions (CuCl_2 -120 g/l, AuCl_3 -20 g/l with additional treatment with 100 ml of 1 g/l AgNO_3 solution).

| Element | Content, %(weight) |
|---------|---------------------|
| C | 6.60 |
| O | 8.45 |
| Cl | 0.06 |
| Ca | 0.64 |
| Cu | 31.12 |
| Ag | 45.07 |
| Au | 8.06 |

Table 6. Antimicrobial properties of obtained films as dimension of zone of inhibition.

| | Film composition | Bacteria | |
|---|---------------------|----------------|------------------|
| | | <i>E. coli</i> | <i>S. aureus</i> |
| 1 | Control sample | 0 | 0 |
| 2 | Gold | 14±1 mm | 18±1 mm |
| 3 | Silver | 20±2 mm | 24±1 mm |
| 4 | Copper | 16±1 mm | 19±2 mm |
| 5 | Gold- silver | 17±1 mm | 20±1 mm |
| 6 | Silver-copper | 19±2 mm | 22±2 mm |
| 7 | Gold-copper | 18±1 mm | 20±1 mm |
| 8 | Gold- silver-copper | 19±2 mm | 21±2 mm |

Figure captions

Figure 1. *Images of fabric samples at various stages of gold coating photochemical process.*

a-untreated fabric; b-fabric after coating with gold chloride; c- fabric after irradiation; d-fabric with the polymer screening washer; e-fabric with gold coating after rinsing; f-screened by washer fabric parts after washer removal and rinsing.

Figure 2. *SEM image of borders between irradiated (b) and screened (a) by a polymeric washer fabric parts.*

Figure 3. *Structure of copper subgroup metal films obtained by a photochemical method.*

Figure 4. *Stages of copper (I) and gold (I) chloride crystals formation and growth in the process of sorption layer preparation in fabric pores.*

1-initial stage; 2-formation of initial chloride crystals; 3- pore closure as a result of photochemical reaction (4); 4- closure of other fabric parts as a result of photochemical reaction.

Figure 5. *SEM image of a film obtained from the diluted solution.*

Figure 6. *SEM image of a film obtained from the concentrated solution.*

Figure 7. *Example of the influence of film compositions on antimicrobial properties against S. aureus.*

1 – control sample (fabric without a film); 2 – gold coating; 3 – silver coating; 4 – copper coating; 5 – gold+silver coating; 6 – copper+silver coating; 7 – copper+gold coating; 8 - copper+silver+gold coating.

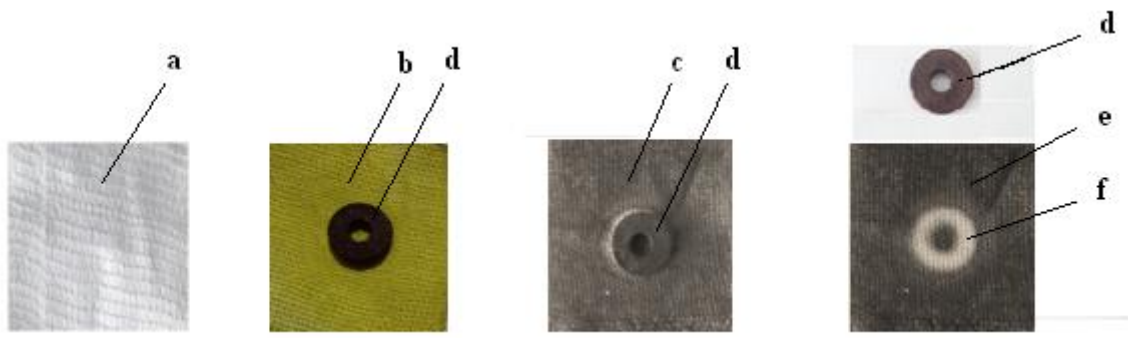
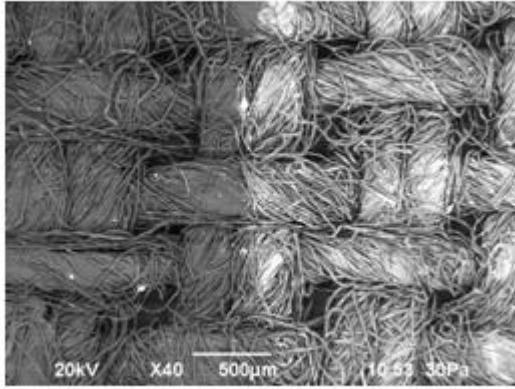


Figure 1.



a

b

Figure 2

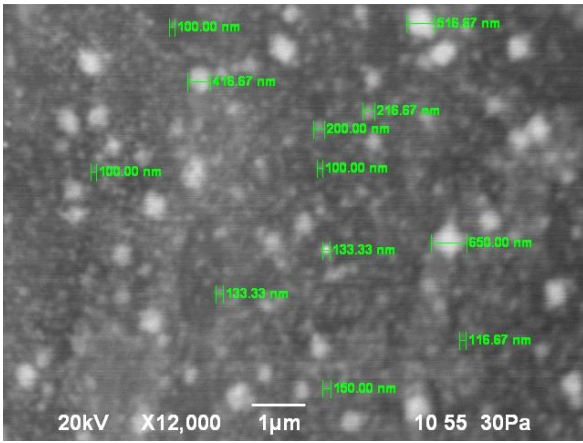


Figure 3

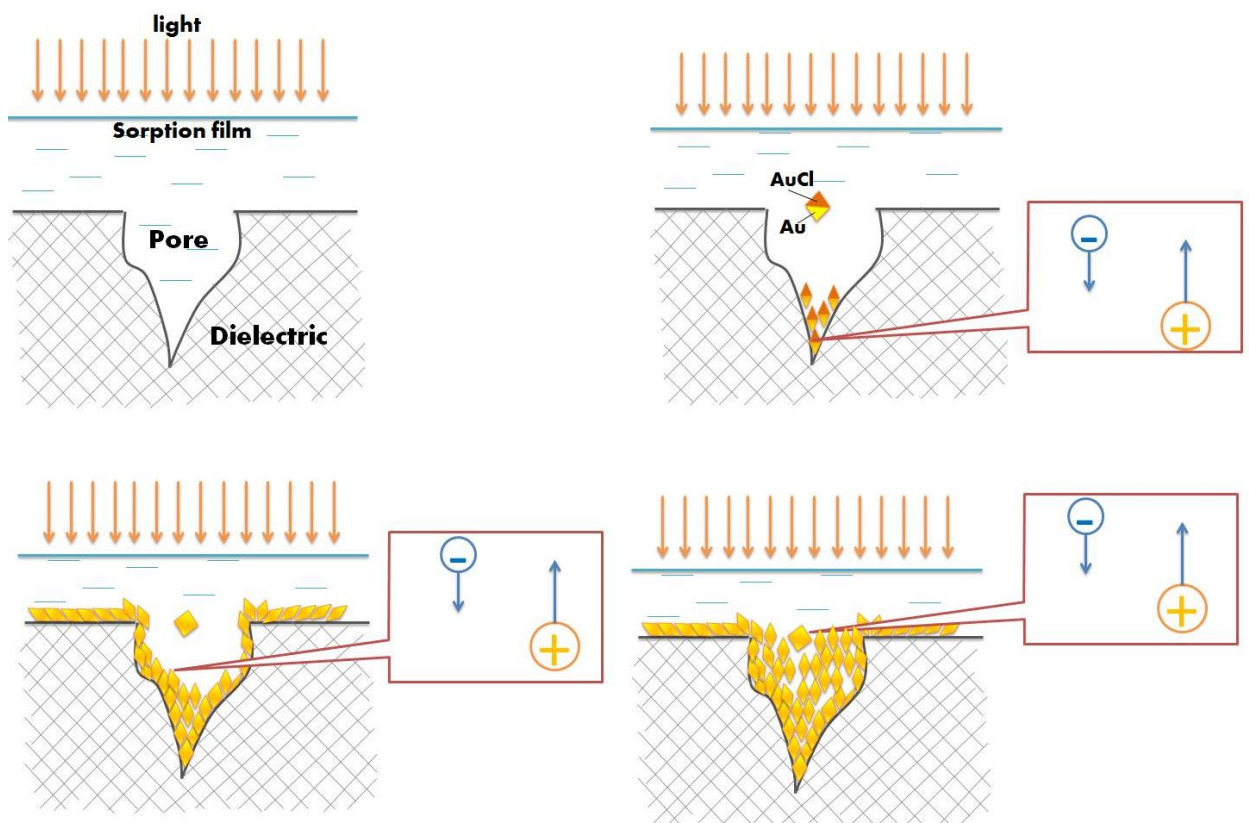


Figure 4

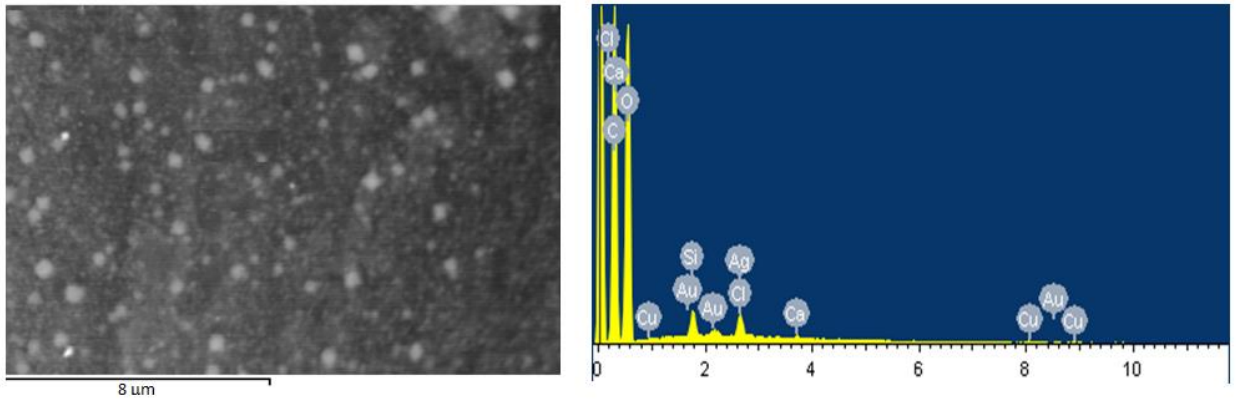


Figure 5

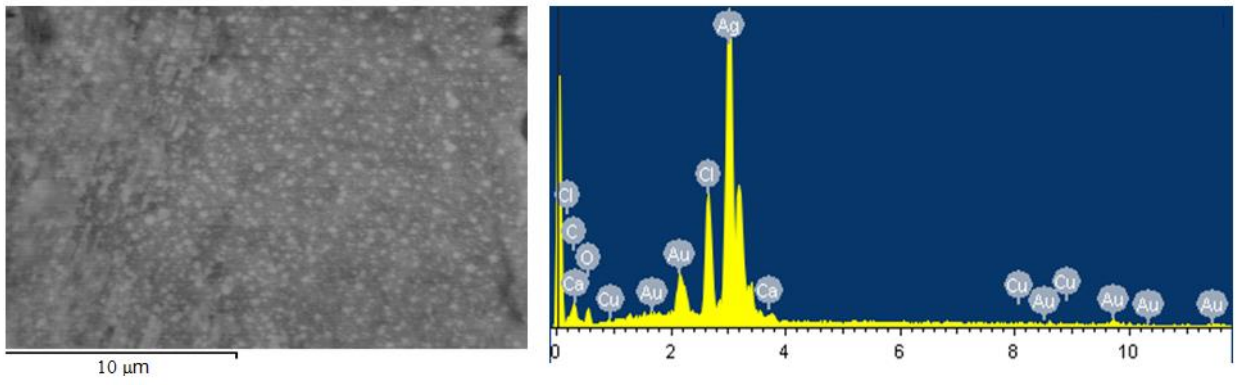


Figure 6

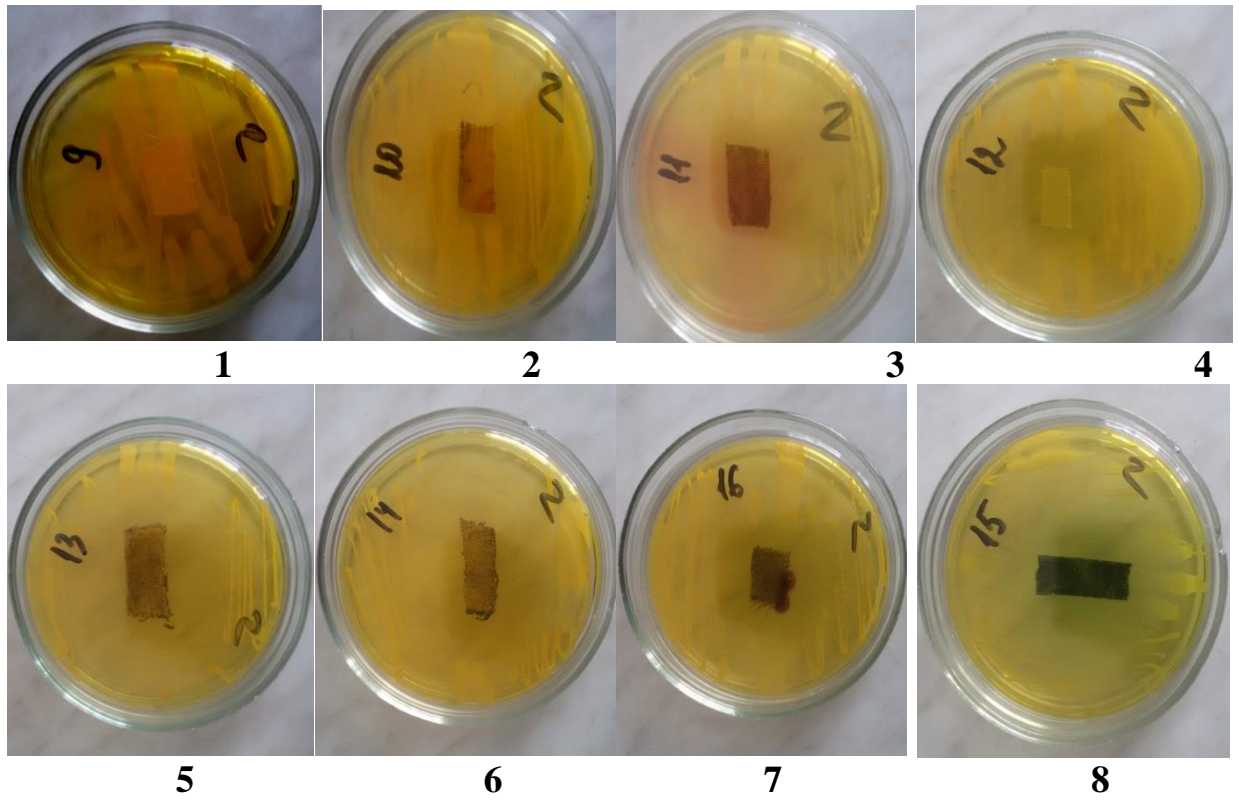


Figure 7