

Research Article

The Antibacterial and Antifungal Textile Properties Functionalized by Bimetallic Nanoparticles of Ag/Cu with Different Structures

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We reported a preparation and characterization of five kinds of impregnation solutions, containing Ag/Cu in the form of bimetallic nanoparticles (alloy and core-shell) as well as ionic species. The cotton-polyester textiles were successfully impregnated during the washing and ironing process by as-prepared solutions to have antibacterial and antifungal properties against to *Escherichia coli*, *Staphylococcus aureus*, and *Candida albicans*. Moreover, we have reported the effect of type of the fabric used and number of washing/impregnation cycles (in a laboratory scale) on the bactericidal and fungicidal activity of obtained textiles. The results indicated that all tested samples after 5, 10, 15, and 20 washing/impregnated cycles exhibited an antimicrobial activity. The antifungal tests showed that only textile impregnated with solutions containing $\text{Ag}^+/\text{Cu}^{2+}$ and Ag NPs/ Cu^{2+} exhibited a strong inhibition of fungi growth of the after 5 (99.99%) and 15 (100%) washing/impregnation cycles, respectively.

1. Introduction

Textiles are excellent substrates for a bacterial growth and microbial proliferation under appropriate moisture, nutrients, and temperature conditions. In the hospital environment, polluted textiles can be an important source of bacteria, viruses, and fungi that may primarily contaminate the patients and clinician personnel. Additionally, the contamination of textiles in the clinical settings may contribute to the dispersal of pathogens to the air, which then fall down and infect the immediate and nonimmediate environment. Thus, transfer of microorganisms from the contaminated surface to the susceptible patients is one of the most common reasons of nosocomial infections (hospital-acquired infections) [1]. The most common pathogen microorganisms responsible for nosocomial infections include *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Legionella*, and *Mycobacterium tuberculosis* [2–6].

On the other hand, cotton, wool, and synthetic textiles containing metal nanoparticles, such as silver [7–9] or copper [10–12], in order to impart antimicrobial properties are used as commercial biomedical products. The nanoparticles, even in very small amounts, can provide the final product with bacteriostatic properties due to the fact that nanoscaled materials have a high ratio of a surface area to volume [13]. Silver in its metallic state is inert but it reacts with the moisture and gets to ionize. The ionized silver is highly reactive, as it binds to tissue proteins and brings structural changes in the bacterial cell wall and nuclear membrane leading to cell distortion and death. Silver nanoparticles also bind to bacterial DNA and RNA by denaturing and inhibiting bacterial replication [14, 15]. On the other hand, copper nanoparticles, such as Cu and CuO, exhibit a high antimicrobial activity against wide spectrum of microorganisms, including fungi and Gram-positive and Gram-negative bacteria [16]. According to the literature,

the mechanism of antibacterial activity of copper NPs is generally based on metallic ions [17–20].

It was found that the antimicrobial properties of silver and copper nanoparticles are dependent on the size and shape of particles, which resulted from the preparation route [21, 22]. Generally, monodisperse nanoparticles composed of silver and copper could be obtained by chemical reduction [23–29], electrochemical [30–35], photochemical [36–41], and sonochemical methods [42–45] as well as using pulsed laser deposition [46–51]. Among all these methods, chemical reduction in aqueous solution is still one of the most commonly used methods due to (i) low cost of raw materials and equipment, (ii) low process temperature, (iii) simplicity, (iv) tight control of size, shape, and structure of NPs, and (v) possibility of deposition of nanoparticles on different substrates to create new features (such as antimicrobial properties). Cabal et al. [52] obtained silver NPs immobilized on kaolin crystal using thermal and chemical reduction. They found that silver NPs revealed a high antimicrobial activity against *Escherichia coli JM 110* and *Micrococcus luteus* bacteria. Suárez et al. [53] synthesized diatom containing metallic silver NPs by chemical reduction method. The diatom-silver nanocomposite has proved to be a selective green inorganic biocide which reduces the starting concentrations of *Escherichia coli* and *Micrococcus luteus*. Diatom-nAg can be considered as a selective inorganic biocide particularly suitable for the food and pharmacological sectors.

The antimicrobial and antifungal properties of textiles modified with monometallic nanoparticles such as copper [10, 54–58] and silver [7, 8, 54] are well established. However, only limited data on the possible antimicrobial and antifungal activity of textiles modified by combination of silver and copper in the form of bimetallic nanoparticles as well as ionic species are available [59]. Moreover, although the preparation methods of bimetallic nanoparticles of Ag/Cu are well-described in the literature [60–65], then the antimicrobial properties of those particles were mentioned in only a few papers [66–68]. Additionally, one of the scientific challenges is how to produce antimicrobial textiles in easy and cheap way to apply them in facilities with a high risk of infection by pathogens (mainly hospitals facilities).

In view of this, we recently obtained and characterized a series of colloidal solutions to impregnate fabrics that will exhibit antibacterial and antifungal properties [69]. In this work we show the application of selected five types of impregnation solutions, containing Ag/Cu in the form of bimetallic nanoparticles (alloy and core-shell) as well as ionic species, for textiles impregnation. For the first time, the composition of Ag/Cu-based solutions in relation to their antibacterial and antifungal properties as well as their ability to functionalize the surface of textile during washing and ironing process has been investigated [70]. Antibacterial and antifungal activity was tested against *Escherichia coli*, *Staphylococcus aureus*, and *Candida albicans*, respectively. The effect of impregnation solution composition ($\text{Ag/Cu}_{(\text{alloy})}$, $\text{Ag}_{\text{core}}\text{Cu}_{\text{shell}}$, Cu^0/Ag^+ , $\text{Ag}^0/\text{Cu}^{2+}$, and $\text{Ag}^+/\text{Cu}^{2+}$) and the type of textile on the antimicrobial features of the impregnated textile were systematically investigated. The functionalized textiles, showing

antibacterial and antifungal properties, could be used for production of bed linen and work wear used in medical facilities, nursing homes, and hotels.

2. Materials and Method

2.1. Materials and Instruments. Copper acetate received from Avantor Performance Materials Poland S.A. was used as the precursor for the preparation of samples. Silver citrate was prepared according to the procedure given in Supplementary materials (see Supplementary Material available online at <http://dx.doi.org/10.1155/2016/6056980>). Reagents needed to synthesize silver citrate such as sodium citrate (III) and silver carbonate were provided by Sigma-Aldrich and citric acid, sodium hydroxide, and acetic acid were received from Avantor Performance Materials Poland S.A. Sodium borohydride 99% was provided by Aldrich and used as the reducing agent. Polyvinylpyrrolidone (PVP) was received from Sigma-Aldrich and was used as the stabilizers. Isopropanol and distilled water were used as the reaction media. All the chemicals were used without the further purification.

The textiles used in the tests were commercially available: Malwa 150-Optical White, barrier textile ESD 150-gray (Producer: ANDROPOL S.A., Poland).

Prewash has been carried out with used Turbo Break (Detergent 1), (NaOH 25–30%), Silex Emulsion (Detergent 2) (fatty alcohol ethoxylates 10–20%, NaOH 10–20%); main wash has been made with used Turbo Break (Detergent 1), Silex Emulsion (Detergent 2), and Ozonit Performance (Detergent 3) (acetic acid 25–30%, hydrogen peroxide 10–20%, peracetic acid 10–20%) and rinsed with used Finale Liquid (Detergent 4) (formic acid 10–90%). Detergents used in washing cycles came from the Ecolab Sp. Z o.o. company (Poland).

The diffuse reflectance UV-Vis absorption spectra of the samples were obtained using a spectrophotometer UV-Vis Thermo model: Nicolet Evolution 220. TEM analysis was performed on the FEI Tecnai F20 X-Twin microscope with the spectrometer EDX (r-TEM SUTW, EDAX). The samples were observed under bright-field (BF STEM) and SE mode (detection of secondary electrons, information about the morphology of the surface). Samples were suspended in ethanol (99.8%) and were put into an ultrasonic bath (Inter-Sonic IS-1K) for 5 seconds. Then, the drop (4 μL) was collected and placed on a copper mesh coated with a carbon layer with holes (Plano, type Lacey Cu 400 mesh). The solvent was evaporated at room temperature. The morphology of the textiles was investigated with scanning electron microscope (SEM) using LEO Electron Microscopy Ltd., model 1430 VP (2001) equipped with X-ray spectrometer, Quantax 200 detector XFlash 4010 production of Bruker AXS, Germany (2008), and tungsten cathode, accelerating voltage from 200 V to 30 kV. The textile size samples of 1.3 \times 1.3 cm were blowing with inert gas in order to remove surface contamination. Then the sample was attached to the microscope stage with double sided discs of coal. The carbon contained in the discs creates a conductive layer providing discharge static electricity of the samples.



TABLE 1: Properties of textiles used for impregnation.

Textiles label	Fabric type	Color	Composition		Specific surface area (g/m ²)	Fiber diameter (μm)	Number of filaments per 1 dm
			Polyester (%)	Cotton (%)			
Malwa 150-Optical White	Usual	White	50	50	150	~7.5	296 ± 6
Barrier textile ESD 150-gray	Barrier	Grey	44	54.6	125	~13	320 ± 6

2.2. *Preparation of Solutions for Textile Impregnation.* To obtain bimetallic nanoparticles, 50 ppm of silver citrate and 50 ppm of copper acetate as a metal precursors, water-isopropanol solution with volume ratio 3 : 1 as a solvent, and PVP (tenfold excess relative to the precursor) as a stabilizer and NaBH₄ (twofold excess relative to the precursor) as a reducing agent were used. Depending on the route of synthesis, various types of bimetallic nanoparticles have been achieved. In order to obtain Ag/Cu alloy single-step reduction and to obtain the core-shell nanoparticles a double-step reduction has been used. Ionic solutions (Ag⁺, Cu²⁺) have also been received without reduction.

2.3. *Antibacterial and Antifungal Activity Measurements.* The JIS L 1902:2002 absorption method is designed to quantitatively test the ability of textiles that have been treated with this antibacterial agent to prevent a bacterial growth and to kill bacteria, for over an 18-hour period of contact. This method is based on the quantitative determination of the potential effect and activity of functionalized samples, by the direct contact with a suspension of bacterial cells. For each prepared strain of $1.0 \pm 0.3 \times 10^5$ cells/mL inoculum using nutrient broth was diluted with water of 1 : 20 (v : v). Samples of fabrics controlled and treated with antimicrobial substances 15 × 15 mm have been sterilized UV and next placed in sterile tubes and inoculated with an inoculum volume of 0.2 mL. The samples were incubated for 18 h at 37°C (bacteria) and 30°C (fungi). For each strain used for the control samples after 0 time as well as control and test samples after 18 h of incubation cultures were performed to determine the number of microorganisms: to each tube containing the fabric sample 2 mL of sterile saline containing 0.2% Tween 80 was added. The contents thoroughly were mixed on the vorteks and have done serial dilutions in sterile saline. From the mixture baseline and serial dilution 1 mL was taken. Next, the seeds were performed on blood agar nutrient by flood method. After 48 h of incubation at 37°C (bacteria) and 30°C (fungi) the cells have been counted. In order to carry out the judgment of test effectiveness, the growth value was calculated according to the following equation:

$$F = Mb - Ma. \quad (1)$$

When the growth value is more than 1.5, the test is judged to be effective, and when the growth value is 1.5 or less, the test is judged to be ineffective. When the test is in effective, a retest is necessary. When the quantitative test has been

effective, the bacteriostatic activity value should be calculated in accordance with the equation

$$S = Mb - Mc \quad (2)$$

and the bactericidal activity according to

$$L = Ma - Mc, \quad (3)$$

where F is the growth value and S and L are the bacteriostatic and bactericidal activity values, respectively. Ma is the average of common logarithm of the number of living bacteria on the test pieces immediately after inoculation of inoculum on standard cloth. Mb is the average of common logarithm of the number of living bacteria on the test pieces after 18 h incubation. Mc is the average of common logarithm of the number of living bacteria on the test pieces after 18 h incubation on antibacterial treated sample. Traditionally, bacteriostatic means prevention of multiplication of bacteria without destroying them, whereas the bactericidal effect implies forthright killing of the organisms [71].

2.4. *Washing and Impregnation Procedures.* The washing cycle in the laboratory scale reflected the cycle conditions in the technological scale. The tests were carried out on textiles with 10 × 10 cm size. The properties of fabrics used for impregnation with Ag/Cu particles are shown in Table 1. The washing cycle consisted of three stages: prewash at the temperature of 38°C via 5 min, main wash at 60°C via 5 min, and rinse at 45°C via 5 min manually in the separate flasks. The amount of water used and the type of detergent determined in accordance with the guidelines of the company EKO-STYL Rental Sp. Z o.o Sp.k [70]. Each stage of washing was carried out using the ultrasounds (washing simulation). Then the fabric was impregnated with previously prepared solutions containing Ag/Cu nanoparticles. It was the postgrafting method. The samples were treated with hot air and next pressed at 200°C for about 1 min to fix the particles with the binder system on the fabric. The process of washing and impregnation route is shown in Figure 1S (supporting materials). The procedure was repeated 5 times or 20 times depending on the textiles antimicrobial activity. A yellow tint appears because of the oxidation of part of silver and copper to the oxides Ag₂O and CuO.

3. Results and Discussion

3.1. *Characterization of Impregnation Solutions.* Preparation conditions, particle size, and color of the impregnation solutions selected for the antibacterial and antifungal tests have



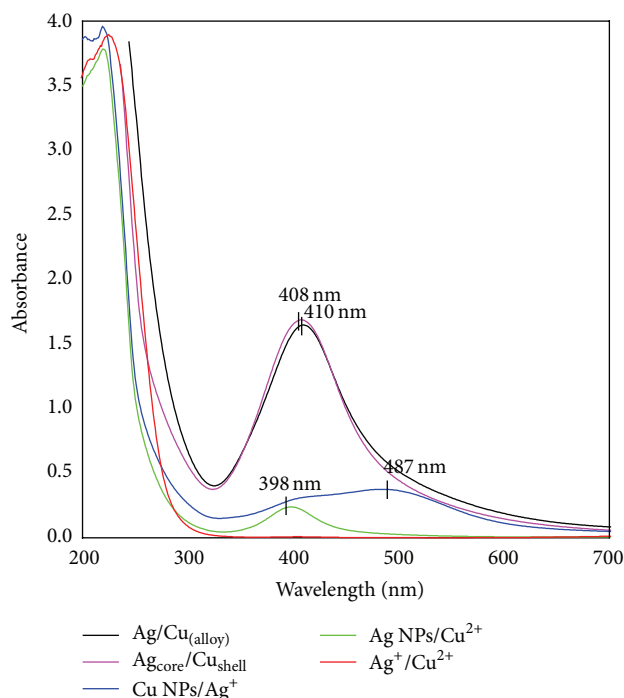


FIGURE 1: UV-Vis spectra of obtained impregnation solution.

been shown in Table 2. Different combinations of silver and copper species suspended or diluted in the aqueous solution have been used, such as alloy Au/Cu nanoparticles, core-shell Au/Cu nanoparticles, $\text{Ag}^0/\text{Cu}^{2+}$, Cu^0/Ag^+ , and $\text{Ag}^+/\text{Cu}^{2+}$ mixtures. It was found that the color of solutions containing Au and Cu nanoparticles and/or ions have changed from light yellow to dark brown depending on the composition (see details in Table 2).

Figure 1 shows the UV-Vis spectra of the obtained nanoparticles in aqueous solution. The spherical Ag and Cu NPs exhibit single plasmonic band, whereas the anisotropic NPs show two or more bands because of quadrupole and multipole plasmon excitations [72]. The bimetallic particles have a strong localized surface plasmon resonance peak at 408 nm and 410 nm for the $\text{Ag}_{\text{core}}/\text{Cu}_{\text{shell}}$ and $\text{Ag}/\text{Cu}_{\text{(alloy)}}$, respectively. Single fine band represents the formation of spherical nanoparticles. Taner et al. [66] suggest that displacement of LSPR to 420 nm could be attributed to the formation of alloy structure of Ag/Cu NPs. In the case of core-shell structure of the Ag/Cu nanoparticles the position of the absorption spectra depends on the thickness of the copper shell [73]. The UV-Vis spectra also confirm the presence of combination of NPs (Ag or Cu) with ions (Ag^+ or Cu^{2+}). The Ag NPs/ Cu^{2+} sample exhibited absorption bands at 398 nm and 230 nm, confirming the presence of silver particles and copper ions, respectively. On the other hand, the Cu NPs/ Ag^+ sample revealed absorption band at 484 nm, which could be ascribed to the presence of copper nanoparticles. The most intensive absorption band (ca. 230 nm) was observed for ionic Ag. It is evident that for samples containing only ions of silver and copper it was observed peak at about 235 nm.

The morphology of the structure creation of Ag/Cu NPs was studied using Cs-corrected STEM (High Angle Annular Dark Field, HAADF) with EDXS mapping. Therefore, it is possible to get images in a high resolution with z-contrast based on the elastic scattering of the primary beam with the sample. Figure 2 shows the morphology of Ag/Cu bimetallic nanoparticles obtained by chemical reduction method with corresponding particle size distribution. The average Ag/Cu size ($d_{\text{Ag/Cu}}$) was calculated from the statistical average size of 100 Ag/Cu NPs. Results reveal nanoparticles ranging from 1 to 90 nm. However it is needed to be highlighted that particles with diameter >50 nm result from the agglomeration of smaller particles. The sample $\text{Ag}/\text{Cu}_{\text{(alloy)}}$ is formed mainly by particles with sizes ranging from 1 to 30 nm, with the higher contribution of the 1–15 nm nanoparticles (Figure 2(a)). However, the $\text{Ag}_{\text{core}}/\text{Cu}_{\text{shell}}$ sample formed mainly particles with diameter 1–40 nm (90%), Figure 2(b).

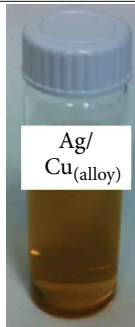

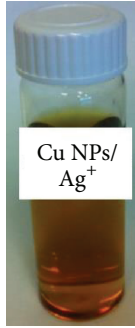
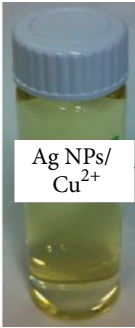
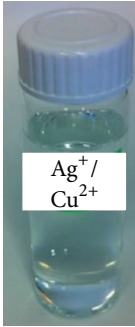
In order to investigate the properties of the individual nanoparticles, we chose one particle from each sample. Figures 3(a)-3(b) show the alloy Ag/Cu spherical nanoparticle with diameter ~ 20 nm. The uniform distribution of silver (navy blue region) and copper (bright blue region) within one particle is observed which corresponds to the alloy structure of obtained NPs. Moreover, the EDXS mapping confirmed that Ag and Cu signal occurred in the same area as shown in Figure 2(b). It was observed that metals were well mixed in its composition.

The morphology of Ag/Cu nanoparticle obtained by two-step reduction is shown in Figures 4(a)-4(b). The observed bimetallic particle had spherical shape with diameter ~ 18 nm. EDXS analysis revealed that silver content is higher than a copper content in the BNPs core, while the shell of BNPs region is richer in copper. The structure of bimetallic nanoparticles is dependent on (1) relative strengths of homo- and heteronuclear bonds, (2) surface energies of bulk metals, and (3) standard reduction potential of both metals [74]. Based on the experimental studies the silver has the lowest surface energy (1.25 J/m^2) compared to copper (1.79 J/m^2) [75]. The metal with lower surface energy has the susceptibility to segregate on the surface of other metals [76]; thus it could be expected that silver tends to segregate in the surface layer of Cu NPs. On the other hand, the reduction of silver ($E_o = 0.79 \text{ V}$) and copper ($E_o = 0.521 \text{ V}$) potential was not significantly different. The abundant literature shows that a large difference in the reduction potential usually results in a core-shell structure and a small difference in reduction potential usually leads to an alloy structure [77]. Generally, according to the theoretical and experimental studies, Ag-Cu composition tends to form core-shell structure. However, based on the TEM analysis, it could be stated that as-prepared bimetallic nanoparticles obtained by the one-step and two-step reduction revealed alloys and core-shell structures, respectively.

4. Characterization of Impregnated Textiles

4.1. The Effect of Washing Cycles on the Antibacterial and Antifungal Properties of the Textiles. Table 3 shows details about the type of used microorganisms, the impregnation solutions

TABLE 2: Preparation route and characteristics of bimetallic colloids.

Sample label	Preparation route	Particle size (nm)	Structures of metal	Image of impregnation solution
Ag/Cu _(alloy)	Ag ₃ C ₆ H ₅ O ₇ , C ₄ H ₆ O ₄ Cu as a precursors, single step reduction with NaBH ₄ , and stabilizer PVP	~20 nm	Alloy	
Ag _{core} /Cu _{shell}	Ag ₃ C ₆ H ₅ O ₇ , C ₄ H ₆ O ₄ Cu as a precursors, double step reduction with NaBH ₄ , and stabilizer PVP	~18 nm	Core/shell	
Cu NPs/Ag ⁺	First solution: Ag ₃ C ₆ H ₅ O ₇ ; second solution: C ₄ H ₆ O ₄ Cu as a precursor, single step reduction with NaBH ₄ , stabilizer PVP; mixing of previously prepared solutions (1 and 2) in volume ratio 1 : 1	NPs Cu ~30 nm	NPs/ions	
Ag NPs/Cu ²⁺	First solution: C ₄ H ₆ O ₄ Cu; second solution: Ag ₃ C ₆ H ₅ O ₇ as a precursor, single step reduction with NaBH ₄ , stabilizer PVP; mixing of previously prepared solutions (1 and 2) in volume ratio 1 : 1	NPs Ag ~18 nm	NPs/ions	
Ag ⁺ /Cu ²⁺	Ag ₃ C ₆ H ₅ O ₇ , C ₄ H ₆ O ₄ Cu as a precursors in the H ₂ O solution	—	Ions/ions	



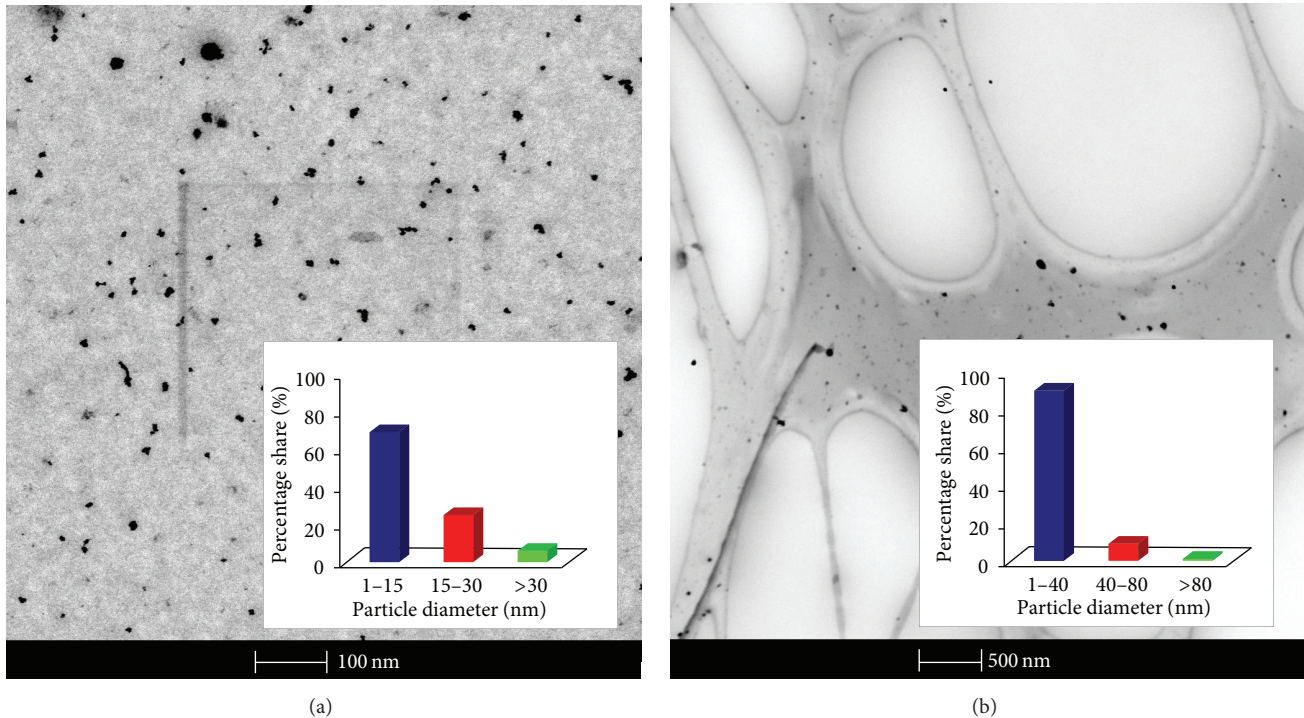


FIGURE 2: TEM images and particle size distribution of (a) $\text{Ag}/\text{Cu}_{(\text{alloy})}$ and (b) $\text{Ag}_{\text{core}}/\text{Cu}_{\text{shell}}$ nanoparticles.

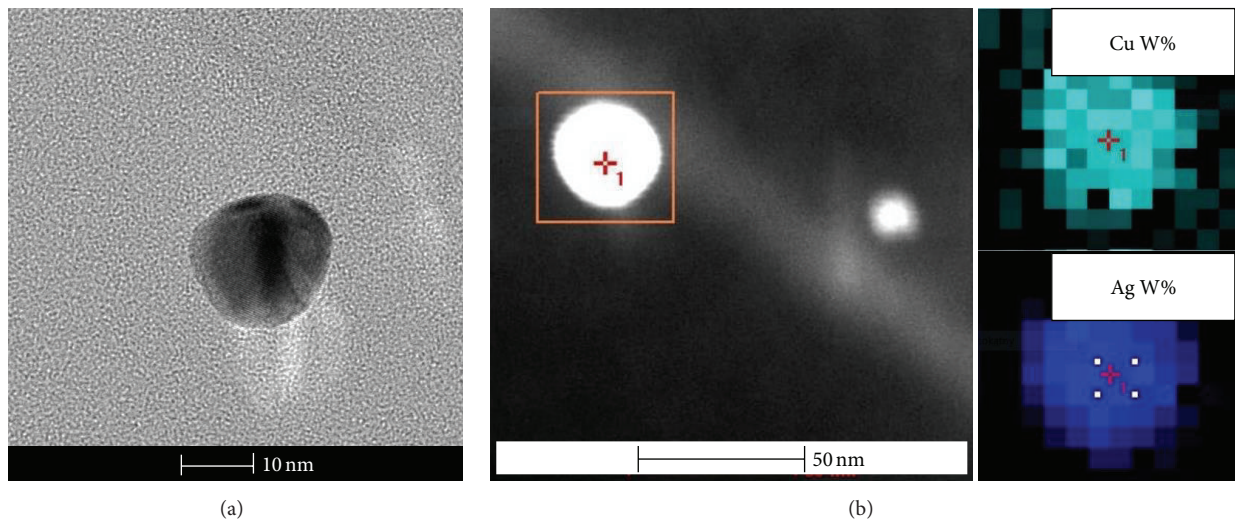


FIGURE 3: TEM images of obtained bimetallic $\text{Ag}/\text{Cu}_{(\text{alloy})}$ nanoparticles, (a) SE mode, and (b) point chemical analysis EDX.

and the concentration of the inoculum. Experimental trials were made on the textile Malwa 150-Optical White with different types of impregnation solutions with Ag/Cu metals used. The materials details are used as shown in Table 3. Textile samples were tested after 5, 10, 15, and 20 cycles of the washing and impregnation process.

It was observed that all tested samples in the next washing/impregnated exhibited an antimicrobial activity.

In all cases the percentage of reduction in cell growth relative to the control samples was 100%, which suggests

the strong bactericidal and bacteriostatic properties. The antifungal tests showed that only textile impregnated with solutions made of $\text{Ag}^+/\text{Cu}^{2+}$ and Ag NPs/ Cu^{2+} exhibited a strong inhibition of fungi growth after 5 (99.99%) and 15 (100%) washing/impregnation cycles, respectively. For the other solutions, fungal growth was observed even after 20 washing/impregnation cycles. The inhibition of growth for *Candida albicans*, in relation to the reference sample, equaled 4.89%, 20.3%, and 27.23% for textile impregnated with solutions composed of Cu NPs/ Ag^+ , $\text{Ag}/\text{Cu}_{(\text{alloy})}$, and

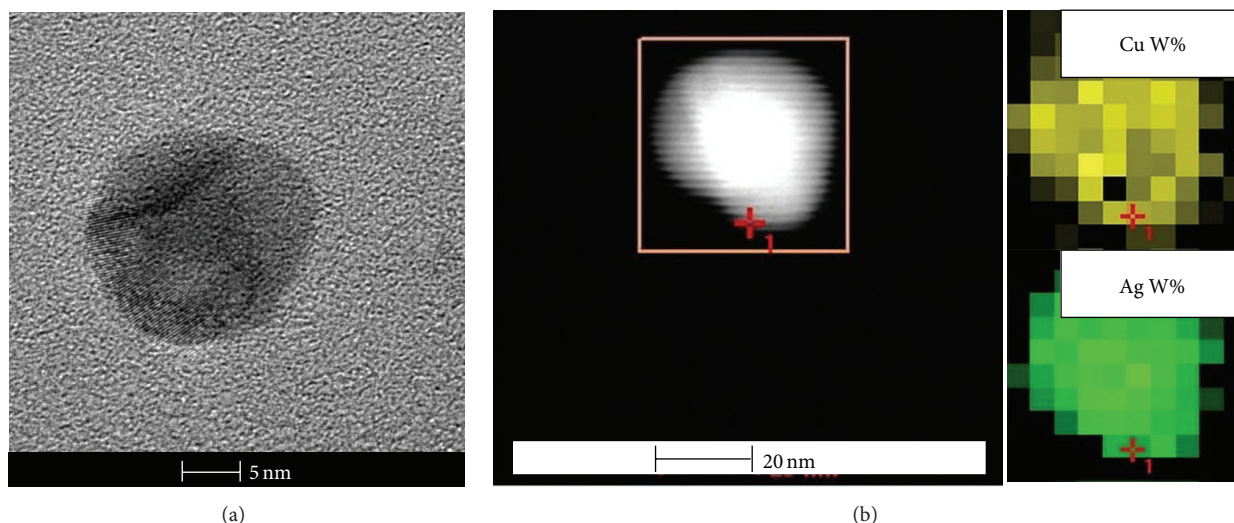


FIGURE 4: TEM images of obtained bimetallic $\text{Ag}_{\text{core}}/\text{Cu}_{\text{shell}}$ nanoparticles, (a) SE mode, and (b) point chemical analysis EDX.

$\text{Ag}_{\text{core}}/\text{Cu}_{\text{shell}}$, respectively. The strongest bactericidal and fungicidal features of the textile sample impregnated with $\text{Ag}^+/\text{Cu}^{2+}$ ions could be attributed to the existence of silver and copper in the form of (i) Ag^+ and Cu^{2+} ions; (ii) nanoparticles Ag/Cu ; and (iii) metal oxides (Ag_2O , CuO), formed *in situ* during the washing and ironing process due to the chemical reaction between Ag^+ and Cu^{2+} ions with washing chemicals and under high temperature (38, 60, 45, and 200°C for washing, rinsing, and ironing, resp.). The coexistence of silver and copper in the three forms (Ag^+ , Ag^0 , and Ag_2O and Cu^{2+} , Cu^0 , and CuO) could enhance microbial activity of impregnated textiles. Morones et al. [78] observed that silver nanoparticles adhere to the surface of the cell membrane of bacteria and drastically disturb its proper function. They stated that Ag NPs are able to penetrate inside the bacteria and cause further damage by possibly interacting with sulfur- and phosphorus-containing compounds such as DNA. Ag^+ ions also cause cell replication damage by binding with bacterial DNA [79]. Copper metal ions also play an important role in the mechanism of action, suppressing cell growth by inhibiting activity of DNA gyrase, an essential bacterial enzyme that maintains superhelical twists in DNA [80]. Summarizing of the mechanisms for their bactericidal effects, the silver or copper ions released by the nanoparticles may attach to the negatively charged bacterial cell wall and rupture it, thereby leading to protein denaturation and cell death [68]. In this way Ag and Cu NPs can be widely used in antimicrobial coatings in medical instrument. Turalija et al. [81] stated that textiles containing Cu_2O exhibited the antimicrobial activity. The washing processes caused decreases in the Cu content in textiles but it still retains the antimicrobial properties. Matyjas-Zgondek et al. [13] investigated the antibacterial efficiency of silver-finished textiles using *Escherichia coli* and *Bacillus subtilis*. The authors conclude that the obtained results proved the good and long-lasting bacteriostatic efficiency of silver nanoparticles applied during the finishing of cotton.

According to the literature, the bimetallic nanoparticles of Ag/Cu exhibited enhanced antimicrobial activity compared to pure elements and were associated with the synergetic effect of two metals [67, 68, 82]. High antimicrobial and antimycotic properties of tissues impregnated with the low concentrations of Ag and Ag/Cu nanoparticles (in the range 0.06–0.25 wt% for Ag and 0.015–0.13 wt% for Ag/Cu) were confirmed in the experiments with a wide range of bacteria and fungi: *Escherichia coli*, *Enterobacter aerogenes*, *Proteus mirabilis*, *Klebsiella pneumoniae*, *Candida albicans* yeasts, and micromycetes. Textile materials with Ag NPs demonstrated a high antibacterial activity, while fabrics doped with bimetallic Ag/Cu had pronounced antimycotic properties. Bactericidal and antifungal properties of the obtained materials did not change after washing and ironing pressing at 200–220°C [59]. Geranio et al. [83] revealed that Ag in the particulate fraction >450 nm is probably the predominant form of Ag released into the washing liquor. On the one hand the release of Ag from the textiles depends on the form and the amount of Ag in the textiles but also on the medium that is used for washing. Additionally, the detergents contain bleaching agent that rapidly oxidizes nano-Ag and results in a fast release of dissolved Ag^+ [9]. However, the NPs-suspension showed that the presence of different surfactants at concentrations relevant to washing has only a small influence on the oxidative dissolution of $\text{Ag}(0)$ [83].

Figure 5 shows an example of the plates with fungi *Candida albicans* corresponding to the solution obtained after washing inoculum from the control and test samples: textile impregnated with the solutions Ag NPs/ Cu^{2+} after 20 washing cycle and Cu NPs/ Ag^+ after 10 washing cycles. It is clearly visible inhibition of fungal growth on the plate with textile impregnated with Ag NPs/ Cu^{2+} (99.99% reduction in cell growth) as opposed to Cu NPs/ Ag^+ (0% reduction in cell growth).

TABLE 3: The effect of washing cycles on the microbial activity of textile Malwa 150-Optical White. The static activity was determined in accordance with the following equation: $S = Mb - Mc$ (see details in Section 2). The lethal activity was determined in accordance with the following equation: $L = Ma - Mc$ (see details in Section 2).

Bacterial strain	<i>Candida albicans</i> ATCC 10231		<i>Escherichia coli</i> ATCC 8739		<i>Staphylococcus aureus</i> ATCC 6538	
Inoculum (cell/mL)	$0.9 \pm 0.3 \times 10^5$		$1.5 \pm 0.2 \times 10^5$		$1.3 \pm 0.2 \times 10^5$	
Value of growth (F)	1.54		1.54		1.50	
Type of solution	Ag/Cu _(alloy)					
Number of washing cycles	(S)/(L)*	R**	(S)/(L)	R	(S)/(L)	R
5	-0.11/-1.64	0%	Absence***	100%	Absence	100%
10	-0.02/-1.56	0%	Absence	100%	Absence	100%
15	-0.12/-1.66	0%	Absence	100%	Absence	100%
20	0.10/-1.44	20.3%	Absence	100%	Absence	100%
Type of solution	Ag _{core} /Cu _{shell}					
Number of washing cycles	(S)/(L)	R	(S)/(L)	R	(S)/(L)	R
5	0.12/-1.41	25%	Absence	100%	Absence	100%
10	-0.04/-1.58	0%	Absence	100%	Absence	100%
15	-0.02/1.56	0%	Absence	100%	Absence	100%
20	0.14/-1.40	27.23%	Absence	100%	Absence	100%
Type of solution	Ag NPs/Cu ²⁺					
Washing cycle	(S)/(L)	R	(S)/(L)	R	(S)/(L)	R
5	-0.04/-1.58	0%	Absence	100%	Absence	100%
10	0.07/-1.46	15.59%	Absence	100%	Absence	100%
15	4.57/2.96	100%	Absence	100%	Absence	100%
20	4.09/2.49	99.99%	Absence	100%	Absence	100%
Type of solution	Cu NPs/Ag ⁺					
Washing cycle	(S)/(L)	R	(S)/(L)	R	(S)/(L)	R
5	-0.06/-1.66	0%	Absence	100%	Absence	100%
10	-0.15/-1.75	0%	Absence	100%	Absence	100%
15	-0.05/-1.66	0%	Absence	100%	Absence	100%
20	0.02/-1.58	4.89%	Absence	100%	Absence	100%
Type of solution	Ag ⁺ /Cu ²⁺					
Number of washing cycles	(S)/(L)	R	(S)/(L)	R	(S)/(L)	R
5	4.02/2.48	99.99%	Absence	100%	Absence	100%

*The activity of static (S)/lethal (L). **The % reduction in cell growth relative to the control samples.

***Absence means the complete elimination of microorganisms. The sample is active microbiologically.

4.2. *The Effect of the Type of Textiles on the Antibacterial and Antifungal Properties.* To investigate the effect of the textiles type the two commercially available textiles were used: usual fabric textile Malwa 150-Optical White and barrier textile ESD 150-gray. Barrier textiles are used in hospitals, pharmaceutical industry and electronics due to their impermeability for pollution particles $<0.5 \mu\text{m}$ or a human sweat. Solution composed of $\text{Ag}^+/\text{Cu}^{2+}$ ($C = 50 \text{ ppm}$ for each metals) was applied as an impregnation factor due to its strongest bactericidal and fungicidal properties. Based on the experimental results (shown in Table 4) both textiles exhibited the strong antibacterial and antifungal properties. Therefore, it could be concluded that the antibacterial and antifungal properties of fabrics do not depend on the type of fabric but only on the solution used for the impregnation.

Takai et al. [84] demonstrated that there are differences in antibacterial properties among commercially available antimicrobial-finished textile products containing Ag. Additionally, the antibacterial properties of these textiles in the clinical setting may be of limited value. Therefore it seems to be appropriate to apply the special barrier materials. Lorenz et al. [9] reported the antibacterial activity depends on the textiles kinds, fiber compositions, and forms of silver. They stated that textiles modified with silver nanoparticles exhibited a very high antimicrobial activity and clearly outperformed all the other textiles. Many forms of silver can be applied to textiles, but not all of them show the antibacterial activity, which in fact is related to the respective release rates of Ag^+ . This is especially apparent for the textile with the silver wire, which had no antimicrobial activity, although its

TABLE 4: The effect of the type of textiles on the antibacterial and antifungal properties with use solution of $\text{Ag}^+/\text{Cu}^{2+}$. The static activity was determined in accordance with the following equation: $S = Mb - Mc$ (see details in Section 2). The lethal activity was determined in accordance with the following equation: $L = Ma - Mc$ (see details in Section 2).

Bacterial strain	<i>Candida albicans</i>		<i>Escherichia coli</i>		<i>Staphylococcus aureus</i>	
	ATCC 10231		ATCC 8739		ATCC 6538	
Inoculum (cell/mL)	$1.1 \pm 0.2 \times 10^5$		$0.9 \pm 0.2 \times 10^5$		$1.2 \pm 0.2 \times 10^5$	
Value of growth (F)	1.53		1.51		1.56	
Type of textiles	Malwa 150-Optical White					
Washing cycle	(S)/(L)*	R^{**}	(S)/(L)	R	(S)/(L)	R
5	4,02/2,48	99.99%	Absence***	100%	Absence	100%
Type of textiles	Barrier textile ESD 150-gray					
Washing cycle	(S)/(L)	R	(S)/(L)	R	(S)/(L)	R
5	Absence	100%	Absence	100%	Absence	100%

*The activity of static (S)/lethal (L). **The % reduction in cell growth relative to the control samples.

*** Absence means the complete elimination of microorganisms. The sample is active microbiologically.

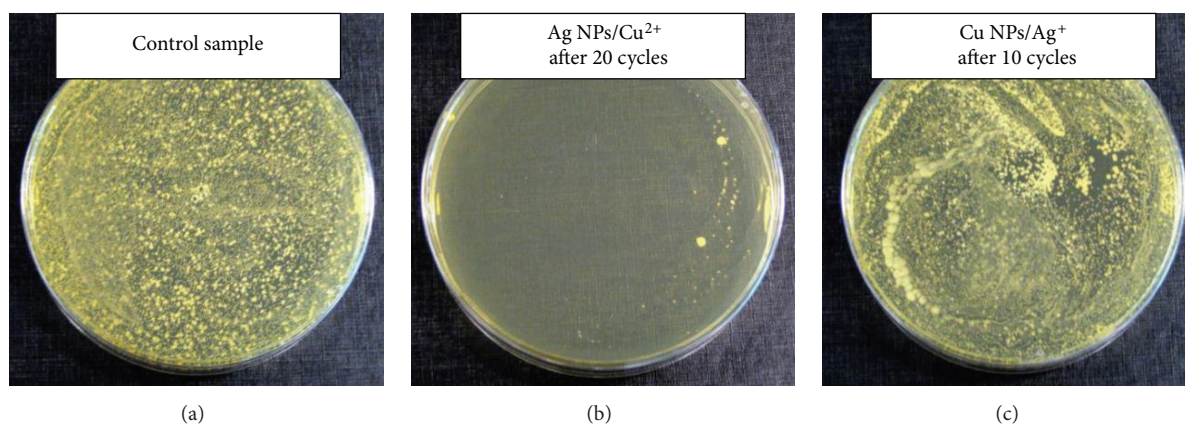


FIGURE 5: Examples of the plates corresponding to the solution obtained after washing inoculum from the control and test samples, *Candida albicans*.

Ag content was much higher than other two nanotextiles. Presumably, the silver ion releasing surface was too small to attain potent concentrations, indicating again much better functionality of “nano” based silver-formulations [9, 85].

In summary, in our investigation the strongest bactericidal and fungicidal properties were observed for the textile sample impregnated with $\text{Ag}^+/\text{Cu}^{2+}$. It could be caused by an existence of silver and copper as ions, nanoparticles, and oxides. Textiles modified by $\text{Ag}^+/\text{Cu}^{2+}$ exhibited definitely higher bactericidal and fungicidal properties. The effect of ions on bacteria can be observed by the structural and morphological changes. When the ions penetrate inside the bacterial cell the DNA molecule turns into condensed form and loses its replication ability leading to cell death [14, 86].

4.3. SEM/EDX Analysis of Impregnated Textiles. The scanning electron microscopy images of the barrier textile ESD 150-gray impregnated with the solution containing $\text{Ag}^+/\text{Cu}^{2+}$ ($C = 50$ ppm) are presented in three different approximations in Figures 6(a)–6(c). It was observed that Ag/Cu were formed

dominantly and uniformly distributed on textile surface (Figures 6(b)–6(c)). The average size of fiber was about $9 \mu\text{m}$.

This textile sample was selected because it exhibits a very high level of the bactericidal activity. The textile sample, after impregnation with ionic solution was pressed at 200°C . The high temperature resulted in thermal reduction of Ag^+ and Cu^{2+} ions whereby nanoparticles of Ag/Cu were formed *in situ* on the textile surface. Moreover, cotton fibers consist of more than 99% of cellulose containing oligosaccharides, which can be used as a reducing agent. Aldehyde functional groups from oligosaccharides can favor the process of silver and copper ion reduction [59]. It was observed that nanoparticles diameters were in the range of 100–200 nm (Figure 6(c)).

From the EDX analysis (Figure 7) which was used to determine the elemental composition, it can be observed a uniform dispersion of Ag and Cu nanoparticles at the surface of textile. The EDX analysis showed that the main components of the surface layer are carbon and oxygen. A high content of C and O is derived from cellulose. Based on the SEM analysis it has been shown that on the surface of

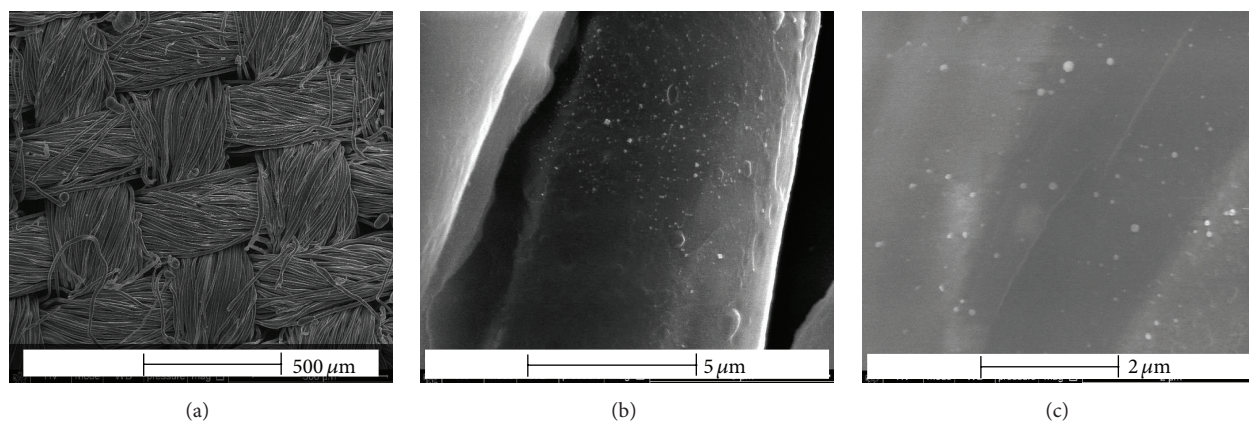


FIGURE 6: SEM images of barrier textile impregnated with solution of $\text{Ag}^+/\text{Cu}^{2+}$, (a) piece of textile, (b) one fiber, and (c) single nanoparticles on the fiber.

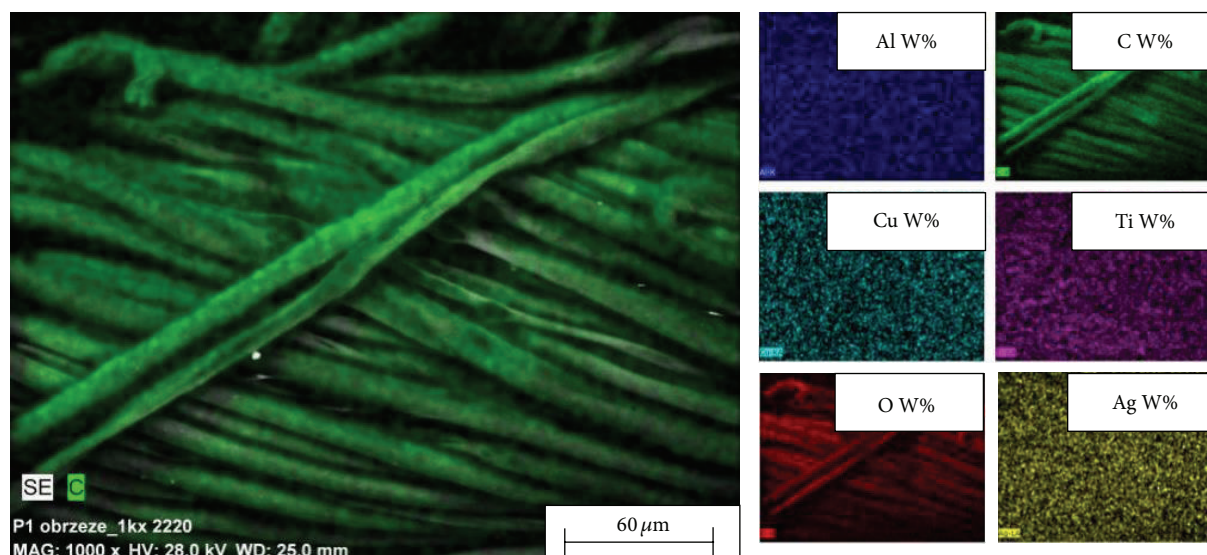


FIGURE 7: SEM and EDX analysis for the barrier textiles impregnated with solution of $\text{Ag}^+/\text{Cu}^{2+}$.

barrier textile are not only ions Ag^+ and Cu^+ but also Au/Cu nanoparticles were formed *in situ* method. Additionally, the textile was uniformly coated with the solution according to the SEM analysis.

5. Conclusions

In this work we show the application of selected five types of impregnation solutions, containing Ag/Cu in the form of bimetallic nanoparticles (alloy and core-shell) as well as ionic species, for textiles impregnation. A very strong antibacterial activity and the persistent antibacterial ability against *Escherichia coli* and *Staphylococcus aureus* were observed for all tested samples after 5, 10, 15, and 20 next washing/impregnation cycles. The percentage of dead cells already reached 100% on *Escherichia coli* and *Staphylococcus*

aureus after 18-h incubation. The antifungal tests showed that only the textile sample impregnated with solutions containing $\text{Ag}^+/\text{Cu}^{2+}$ and Ag NPs/ Cu^{2+} exhibited a strong inhibition of the *Candida albicans* growth after 5 (99.99%) and 15 (100%) washing/impregnation cycles, respectively. Moreover, based on the obtained results it could be stated that the antibacterial and antifungal properties of fabrics do not depend on the type of fabric but mainly on the composition and dose of the solution used for the impregnation. The functionalized textiles that exhibit antibacterial and antifungal properties could be used for production of bed linen and work wear used in medical facilities, nursing homes, and hotels.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

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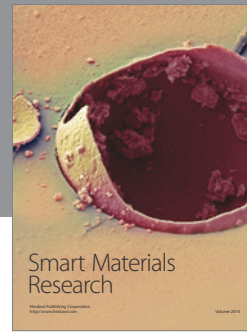
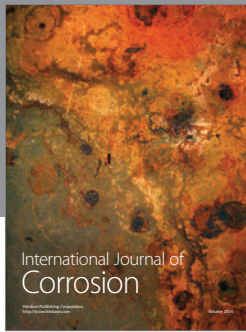


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