Antifungal characteristics of warp-knitted cotton fabrics treated with various metal complexes

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ABSTRACT – REZUMAT

Antifungal characteristics of warp-knitted cotton fabrics treated with various metal complexes

This study investigates the antifungal properties of warp-knitted cotton fabrics treated with metal-based compounds containing sodium tetrahydroxocuprate (Cu), silver diamine (Ag), and sodium zincate (Zn), synthesised via novel, efficient methods designed to reduce processing complexity and cost. Treatments were applied at concentrations of 0.5% and 1%, and antifungal efficacy was assessed against Candida albicans over 28 days. Surface morphology and chemical composition analyses were conducted using scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and Fourier-transform infrared spectroscopy (FTIR). Results revealed uniform particle distribution on fabric surfaces. It was found that Cu-based particles tended to accumulate more densely and demonstrated stronger adhesion on the yarn surfaces. In contrast, in comparison, this effect became gradually weaker in the samples containing Ag and Zn particles. Antifungal testing demonstrated that Cu-treated fabrics exhibited the highest reduction in fungal load, achieving a 4 log_{10} (10,000-fold) decrease at 1% concentration by day 7, with sustained activity through day 28. Ag treatments resulted in up to a 3.04 log_{10} reduction, while Zn treatments showed reductions up to 3.22 log_{10} at 1%. The 1% metal complex concentration consistently outperformed 0.5% across all metals. Findings highlight Cu compounds as particularly effective for healthcare textiles due to rapid and robust antifungal activity, whereas Ag and Zn compounds offer stable, long-term protection.

Keywords: *antifungal textiles, metal-based coatings, chemical synthesis, warp-knitted cotton fabric, Candida albicans*

Caracteristicile antifungice ale tricoturilor din urzeală din bumbac tratate cu diferiți complecși metalici

Acest studiu investighează proprietățile antifungice ale tricoturilor din urzeală din bumbac tratate cu compuși pe bază de metal care conțin tetrahidroxocuprat de sodiu (Cu), diamină de argint (Ag) și zincat de sodiu (Zn) sintetizați prin metode noi și eficiente, concepute pentru a reduce complexitatea și costul procesării. Tratamentele au fost aplicate la concentrații de 0,5% și 1%, iar eficacitatea antifungică a fost evaluată împotriva Candida albicans timp de 28 de zile. Morfologia suprafeței și analizele compoziției chimice au fost efectuate folosind microscopia electronică de baleiaj (SEM), spectroscopia cu dispersie de energie (EDS) și spectroscopia în infraroșu cu transformată Fourier (FTIR). Rezultatele au evidențiat o distribuție uniformă a particulelor pe suprafețele tricoturilor. S-a descoperit că particulele pe bază de Cu au avut tendința de a se acumula mai dens și au demonstrat o aderență mai puternică pe suprafața firului, în timp ce, în comparație, acest efect a devenit treptat mai slab în probele care conțin particule de Ag și Zn. Testele antifungice au demonstrat că tricoturile tratate cu Cu au prezentat cea mai mare reducere a încărcăturii fungice, obținând o scădere de 4 log_{10} (10.000 de ori) la concentrația de 1% până în ziua 7, cu activitate susținută până în ziua 28. Tratamentele cu Ag au dus la o reducere de până la 3,04 log_{10}, în timp ce tratamentele cu Zn au prezentat reduceri de până la 3,22 log_{10} la 1%. Concentrația de 1% a complexului metalic a depășit în mod constant concentrația de 0,5% pentru toate metalele. Rezultatele evidențiază compușii de Cu ca fiind deosebit de eficienți pentru textilele utilizate în domeniul medical datorită activității antifungice rapide și robuste, în timp ce compușii Ag și Zn oferă o protecție stabilă, pe termen lung.

Cuvinte-cheie*: textile antifungice, acoperiri pe bază de metal, sinteză chimică, tricoturi din urzeală din bumbac, Candida albicans*

INTRODUCTION

Cotton represents a significant share of natural textile resources and is extensively utilised in modern society. It is valued for its softness, comfort, hydrophilic property, biocompatibility, and demanded mechanical strength. However, its high moisture retention, natural characteristics, and porous structure render it more vulnerable to microbial growth [1, 2]. Thus, antimicrobial treatment of cotton fabrics is an essential process to enhance their resistance against microbial growth, thereby improving hygiene, durability, and wearer comfort [3]. Metal-based bactericidals and therapeutic agents are commonly used for the antimicrobial treatment of textiles through coating [4, 5], sol-gel coating [6], electroless-plating [7], microencapsulation [8], padding-drying-curing [9], exhausting [10], plasma treatment [11], spraying [12, 13], electrospraying [14], photodeposition [15], and atomic

layer deposition [16], etc. Extensive research is still being conducted to improve the antimicrobial properties of cotton textiles through alternative treatment techniques, as well as the various synthesising methods of metal complexes.

Silver (Ag) has been widely utilised for its antimicrobial properties, particularly in the treatment of cotton fabrics to provide antifungal protection through disrupting microbial cell membranes and inhibiting enzymatic activity [17–19]. Studies have shown that Ag-treated cotton exhibits strong antifungal efficacy against common textile-deteriorating fungi such as *Aspergillus niger* and *Candida albicans*, making it an ideal choice for medical textiles, sportswear, and other functional fabrics [20–22]. However, factors such as particle size, concentration, and binding methods significantly influence the long-term effectiveness of Ag coating [23]. Numerous laborious and complicated studies have been conducted on the synthesis of Ag-containing chemical compounds for their application in the production of antifungal cotton fabrics. Arenas-Chávez et al. investigated the antifungal properties of a nanocomposite based on Ag nanoparticles and carboxymethyl chitosan against *Candida albicans* using various qualitative and quantitative methods. Results demonstrated that the functionalized cotton fabric exhibited strong antifungal effects, suggesting its potential use in hospital garments to reduce nosocomial infections [24]. Hedayati et. al. synthesised silver nanoparticles (AgNPs) on a β-CD/ ketoconazole composite and applied it to cotton fabric using a cross-linking agent. The findings indicated that AgNPs on the composite increased antifungal properties, enhanced washing durability, and potential suitability for medical applications, wound dressings, and sportswear for sensitive skin [25]. For maintaining long-lasting hygiene in textiles and reducing the limitations of traditional antimicrobial treatments, reliable alternative research is still needed in terms of silver ion-based antifungal applications.

Copper has gained significant attention for its antimicrobial properties, particularly in the antifungal treatment of cotton fabrics [26]. Copper ions (Cu^{2+}) exhibit strong biocidal activity by disrupting fungal cell membranes, generating reactive oxygen species, and interfering with essential enzymatic functions [27]. Compared to silver, copper offers a more cost-effective alternative while still ensuring high antimicrobial performance [28]. Recent studies revealed that various innovative methods have been recorded in the literature. Nosheen et al. designed a pilot-scale setup incorporating a jigger dyeing machine, a high-pressure hydraulic roll-press (padder), and a stenter machine to expose the cotton fabric to the electroless deposition in a $CuSO_4$-based bath with controlled pH. Treated samples exhibited 91% (1.87 log10) reduction in the fungal spores of *Aspergillus niger* [29]. Swierczynska and Kudzin reported an alternative antimicrobial cotton material by utilising chemical deposition of copper sulfide. The process consisted of two phases, which included the chelation of copper sulfate onto the cellulose chains, and second, the precipitation of copper as copper sulfide. Antifungal effectiveness was evaluated against *Chaetomium globosum* and *Aspergillus niger*, and the results presented that clear inhibition zones with sizes of 1 to 2 mm were detected, without any evident growth of micro-organisms [30]. To establish more efficient hygiene management, researchers continue to overexert about developing new, durable, non-toxic, and biodegradable compounds regarding the adoption of copper-based antifungal treatments of textiles.

Zinc (Zn) has been widely explored for its antimicrobial properties, particularly in the antifungal treatment of cotton fabrics. Zn-based complexes are commonly used due to their broad-spectrum antimicrobial activity, biocompatibility, thermal conductivity, low production cost, and UV-protective properties [2, 31]. Lately, investigations indicated that Zn-based agents at the same dose had both bactericidal influence on micro-organisms and non-toxic effects on human cells [32]. Latest studies have been published in the literature regarding a novel approach to the treatment of antifungal textiles with Zn compounds. Roy et. al. synthesised Zinc Oxide nanoparticles (ZnO NPs) and applied them onto cotton fabrics by using the dip coating technique through different mole (M) concentrations. Disk diffusion test method revealed that 2M ZnO-coated cotton fabric has shown the highest zone of inhibition (14 mm) against *Aspergillus niger*. Researchers have also indicated that as the size of nanoparticles increases, their adhesion to cotton fabric decreases, making them more easily removed during washing. In contrast, smaller nanoparticles exhibit stronger adhesion and greater penetration into the fabric. However, at specific molar concentrations, nano-sized particles were prone to agglomeration, which might impact their effectiveness [33, 34]. Kudzin et. al. coated cotton fabric with Zn by utilising a DC magnetron sputtering system. The antifungal activity of the coated samples was evaluated against *Aspergillus niger* and *Chaetomium globosum* fungal mould species. Findings presented apparent zones of fungal growth inhibition around the coated samples in Petri dishes [35]. Since Zn-based metals exhibit less soluble characteristics [35, 36], exploring new Zn-based compounds is strongly encouraged to develop more effective antifungal treatments for textile materials.

This study aims to yield various facile and viable metal-based compounds incorporating Cu, Ag and Zn through alternative and novel synthesis methods by eliminating long processing time, complex and expensive equipment, and multiple steps for deposition. The other objective of the current research is to evaluate the antifungal efficacy of the warp-knitted cotton fabrics treated with varying concentrations of the synthesised metal-based compounds.

EXPERIMENTAL

Materials and methods

Materials

During the experiments, 100% cotton bandages were produced in the FITTEX (model 080S) warp knitting machine with a gauge of 14 needles per inch. The properties of the open-end cotton yarn used during production and the warp knitted cotton fabric manufactured are presented in table 1 and table 2, respectively.

Table 1

PROPERTIES OF THE PRODUCED WARP KNITTED COTTON FABRIC	
Related properties	**Values**
Yarn count	Ne 29.5
Linear density of the yarn (tex)	20
Fabric weight (g/m^2)	54.2
Tensile strength (N)	42
Elongation (%)	11.4
Length of produced knitted bandage (m)	5
Width of produced knitted bandage (cm)	14
Humidity ratio (%)	6
Air permeability (1 atm) (dm^3/m^2*sec)	1420

Table 2

CHARACTERISTICS OF 100% CARDED COTTON OPEN-END YARN	
Related properties	**Average value**
Linear density of yarn (tex)	20.1
Coefficient of variation in linear density (%)	1.6
Breaking load (cN)	281.2
Coefficient of variation for breaking load (%)	9.8
Specific breaking load (cN/tex)	13.9
Elongation (%)	3.93
Breakage at 1000 cycles/hour	54

Chemical compounds used for the synthesis of antifungal agents

Analytical grade silver nitrate ($AgNO_3$), copper sulfate ($CuSO_4$ $5H_2O$), and zinc acetate ($Zn(O_2CCH_3)_2$ in pure form used in this research were purchased from Ural Bor (Uralsk, Russia). Ascorbic Acid ($C_6H_8O_6$) was supplied by Luwei Pharmaceutical Group (China). Analytical grade aqueous ammonia (NH_4OH) was ordered from JSC Kupavnareaktiv (Russia).

Experimental processes

Experimental research was carried out in the M. Auezov Engineering Testing Laboratory (Kazakhstan) and an accredited training and testing laboratory in Tashkent (Uzbekistan).

Before carrying out the experimental work, 14x14 cm warp knitted cotton fabrics were boiled at 100 ºC for 30 minutes with the addition of 3% NaOH. Then, the samples were washed with distilled water for neutralisation. Then, they were dried in a drying cabinet (SNOL 75/350, Russia) at 95–100ºC for 30 minutes. Finally, the samples were kept in a desiccator at a constant standard humidity of 8%.

Deposition of copper particles

Initially, copper sulfate solutions with varying concentrations of 0.5% and 1% were prepared. 14×14 cm knitted fabrics were placed in separate beakers. Then, 100 ml of copper sulfate solutions of various concentrations were poured into each beaker. Approximately 40% sodium hydroxide (NaOH) solution was added to each solution to completely dissolve the copper hydroxide ($Cu(OH)_2$), which was formed in the initial stage. As a result of the chemical interaction, a complex molecule of sodium tetrahydroxocuprate (II) $Na_2[Cu(OH)_4]$ is generated, which served as an intermediary (precursor) compound in the process (Chemical reactions a and b). To ensure complete impregnation of the samples with copper ions, the knitted fabrics were kept in the solution for 10 min.

a) Formation of copper hydroxide: Adding a NaOH solution to a $CuSO_4$ solution results in the precipitation of $Cu(OH)_2$.

$$CuSO_4 + 2NaOH \rightarrow Cu(OH)_2\downarrow + Na_2SO_4$$

b) Dissolving copper hydroxide in an excess amount of sodium hydroxide: With further addition of NaOH, copper hydroxide dissolves and a complex compound, sodium tetrahydroxocuprate (II), is formed.

$$Cu(OH)_2 + 2NaOH \rightarrow Na_2[Cu(OH)_4]$$

The samples were then squeezed from the surplus precursor solution and placed in another solution containing 4 g/l ascorbic acid, which is stirred for 10–15 seconds before being rinsed with distilled water to eliminate any excess reducing agent. After that, samples were dried in a drying cabinet (SNOL 75/350, Russia) at 95–100ºC for 30 minutes, before being transferred to a desiccator to maintain a constant normalised humidity of 8%.

Deposition of silver particles

At the outset, varying concentrations (0,5% and 1%) of silver nitrate ($AgNO_3$) solutions were obtained. Knitted bandages measuring 14×14 cm were placed in different beakers. Following that, 100 ml of ($AgNO_3$) solutions of varying concentrations were added to each beaker. During the process, silver chloride (AgCl) was formed and precipitated. In order to completely dissolve the AgCl and make its distribution in the solution homogeneous, 1–2 ml of 25% ammonia solution ($NH_3 \cdot H_2O$) was added to the mixture (Chemical reactions c and d). The samples were left in the solution for 10 minutes to ensure that the silver ions were completely absorbed into the fabric and impregnated equally throughout the material.

c) Formation of silver chloride precipitate: If chloride ions are present in the silver nitrate solution (as a contaminant), a silver chloride (AgCl) precipitate may occur.

$$AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$$

d) Dissolving silver chloride in ammonia: Once 25% ammonia is added, the silver chloride precipitate dissolves, yielding a complex silver diamine compound.

$$AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]^{++}Cl^-$$

Afterwards, the samples were squeezed out of the excess precursor solution and immersed in a 4 g/l ascorbic acid solution for 10–15 seconds. Following that, they were washed with distilled water to remove any remaining reducing agent. Ultimately, specimens were dried in the drying cabinet (SNOL 75/350, Russia) at 100 ºC until they had completely dried, before being transferred to a desiccator to maintain a constant normalised humidity of 8%.

Deposition of zinc particles

At this stage, zinc acetate ($Zn(CH_3COO)_2$) solutions were prepared at concentrations of 0,5% and 1%. Knitted fabric samples of 14×14 cm were placed separately in each of five beakers. Then, 100 ml of ($Zn(CH_3COO)_2$) solution was added to each beaker. NaOH solution was added to the mixture until the zinc hydroxide $Zn(OH)_2$, which was formed in the first step, was completely dissolved, which led to the formation of sodium zincate, an intermediate compound (precursor) (Chemical reactions e and f). The samples were left in the solution for 20 minutes to ensure that the chemical agent was completely absorbed by the fabric.

e) Formation of zinc hydroxide: When NaOH is introduced to the zinc acetate solution, zinc hydroxide is formed.

$$Zn(CH_3COO)_2 + 2NaOH \rightarrow Zn(OH)_2 + 2CH_3COONa$$

f) Dissolution of zinc hydroxide to generate sodium zincate: By continuing to add NaOH to the mixture, zinc hydroxide dissolves to form sodium zincate:

$$Zn(OH)_2 + 2NaOH \rightarrow Na_2[Zn(OH)_4]$$

Next, the fabrics were soaked in a 4 g/l ascorbic acid solution for 15–20 seconds. They were subsequently washed with distilled water to get rid of any residual reducing agent. Finally, they were put in a drying cabinet (SNOL 75/350, Russia) at 80 ºC until totally dried, before being transferred to a desiccator to maintain a constant normalised humidity of 8%.

SEM and EDS analyses of the samples

The surface morphology and elemental composition of sputter-coated (80/20%; gold/palladium) untreated and treated warp-knit cotton fabrics were analysed using scanning electron microscopy (SEM; Jeol JSM 5910LV), at an accelerating voltage of 20 kV, coupled with energy-dispersive spectroscopy (EDS; Oxford Instruments Inca X-Sight 7274).

FTIR analyses of the samples

FTIR analysis was performed using a Shimadzu IRPrestige-21 spectrometer equipped with a Pike Total Internal Reflection (TIR) accessory (USA). The measurements were taken at a resolution of 2 cm^{-1} with 50 scans over a wavenumber range of 500 to 4000 cm^{-1}. The data were analysed using IRSolution software version 1.6.

Antifungal test procedure

Chemicals for microbiological testing

Phosphate Buffered Saline (PBS, pH 7.2): Prepared by dissolving 8.0 g NaCl, 0.2 g KCl, 1.44 g Na_2HPO_4 and 0.24 g KH_2PO_4 in 1 L of distilled water. After adjusting the pH to 7.2, it was sterilised by autoclaving at 121 ºC for 15 minutes.

PBS containing 0.2% Tween 80: 0.2% (v/v) Tween 80 was added to the prepared PBS, then filter sterilisation (0.22 µm) was applied and made ready for use.

Sabouraud Dextrose Agar (SDA): Commercial powder form was prepared according to the manufacturer's instructions (65 g/L), dissolved by boiling and sterilised at 121 ºC for 15 minutes. After cooling, it was poured into Petri dishes in a sterile environment and used.

Antifungal test procedure

Candida albicans (ATCC 10231) strain was used as a test organism to evaluate the antifungal activity of textile samples. Warp-knitted cotton fabrics were cut into 1×1 cm squares and sterilised under UV light. Fungal suspension containing approximately 10^6 CFU/mL was prepared using phosphate-buffered saline (PBS) at pH 7.2. The suitability of the suspension was confirmed by inoculating with serial dilutions at 1:10 and 1:100 on Sabouraud Dextrose Agar (SDA) by the spread plate method and colony formation in the range of 30–300 CFU. The antifungal activity test protocol was based on modifications of the JIS L 1902:2002 and ISO 20743:2013 standards for antimicrobial testing of textiles [37].

Each procedure was carried out with four parallel samples. Accordingly, sixteen samples from each fabric type were placed in sterile Petri dishes. 0.1 mL of previously verified fungal suspension was applied to each piece of fabric by taking it with a pipette. This application was recorded as T_0 (start). Petri dishes were kept partially closed at 22±3 ºC and 50±5% relative humidity for 4 hours in order to ensure the interaction of fungal cells with the fabric. After this period, the dishes were kept at 30°C in dark conditions for incubation.

Incubation periods were determined as 7, 14, 21 and 28 days. At each time point, the fabric pieces were taken into separate sterile tubes and 5 mL of sterile PBS (containing 0.2% Tween80) was added and vortexed for 30 seconds, thus ensuring complete separation of fungal cells from the fabric. Serial dilutions were prepared from the obtained suspensions at 1:10 and 1:100 ratios; 0.1 mL of each dilution was taken and plated on the SDA surface using the spread plate method. The plates were incubated at 30 ºC for 48 hours; then the colonies formed were counted manually. The countable colony range was accepted as 30–300 CFU.

RESULTS AND DISCUSSION

SEM Analysis

Figures 1–4 present the SEM images and EDS spectra of untreated and treated warp-knitted cotton fabrics. The SEM micrograph of the untreated fabric (figure 1, *a*) revealed a smooth fibre surface, with no detectable chemical particles. Furthermore, EDS analysis of the untreated cotton fabric (figure 1, *b*) identified carbon (C) and oxygen (O) as the primary elemental constituents. The weight, atomic, and theoretical percentages of these elements aligned with the expected composition of cellulose-based materials under standard conditions [38].

In contrast, SEM analysis of the treated samples demonstrated a uniform distribution of chemical particles across the fibre surface, with no evidence of particle agglomeration. It was observed that fibre deposition of chemical particles was lower at 0.5% concentration (figure 2, *a*, figure 3, *a* and figure 4, *a*) and higher at 1% concentration (figure 2, *b*, figure 3, *b* and figure 4, *b*). Furthermore, it was observed that copper-based particles were more densely distributed and exhibited stronger adhesion on the yarn surfaces, whereas this effect diminished progressively in the silver- and zinc-based samples. Additionally, EDS elemental analysis of the treated samples confirmed that the weight and atomic ratios were in agreement with the theoretical values.

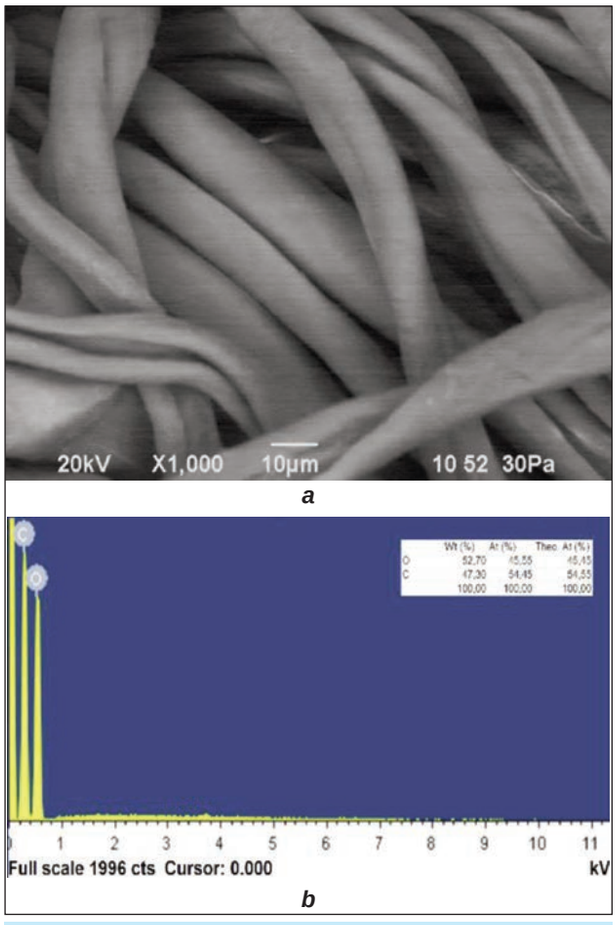


Fig. 1. SEM and EDS micrographs of untreated cotton fabric: *a* – SEM; *b* – EDS

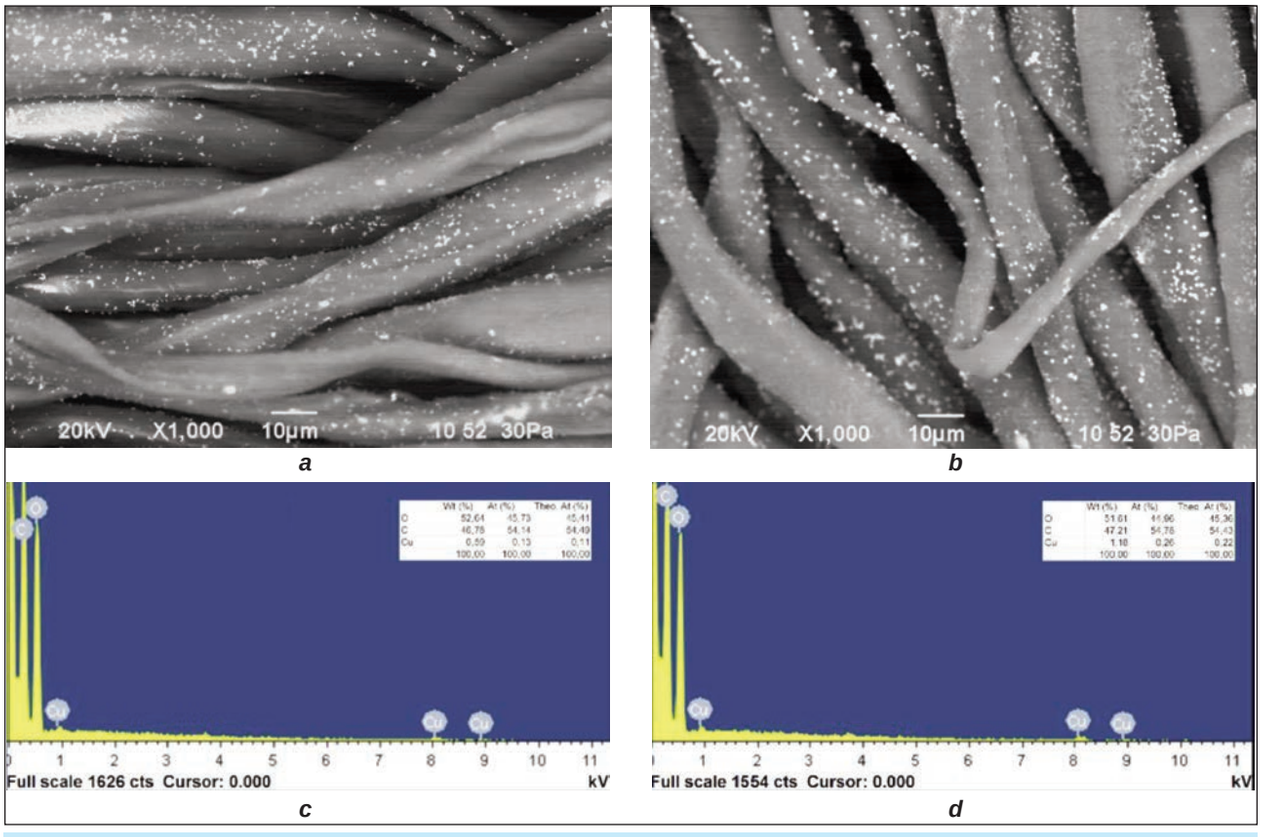


Fig. 2. SEM and EDS micrographs of Cu treated cotton fabric: *a* – SEM pictures of Cu-0.5%; *b* – SEM pictures of Cu-1%; *c* – EDS spectra of Cu-0.5%; *d* – EDS spectra of Cu-1%

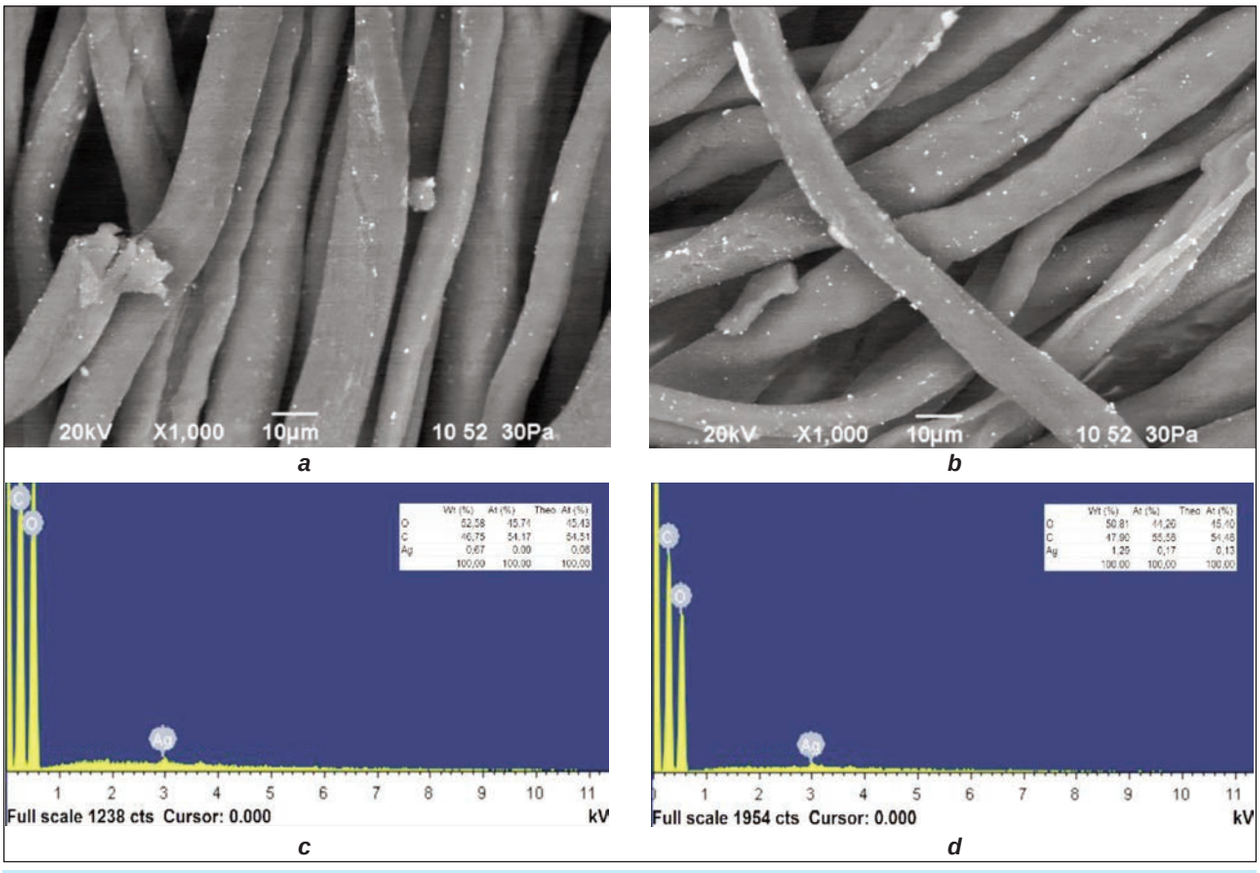


Fig. 3. SEM and EDS micrographs of Ag-treated cotton fabric: *a* – SEM pictures of Ag-0.5%; *b* – SEM pictures of Ag-1%; *c* – EDS spectra of Ag-0.5%; *d* – EDS spectra of Ag-1%

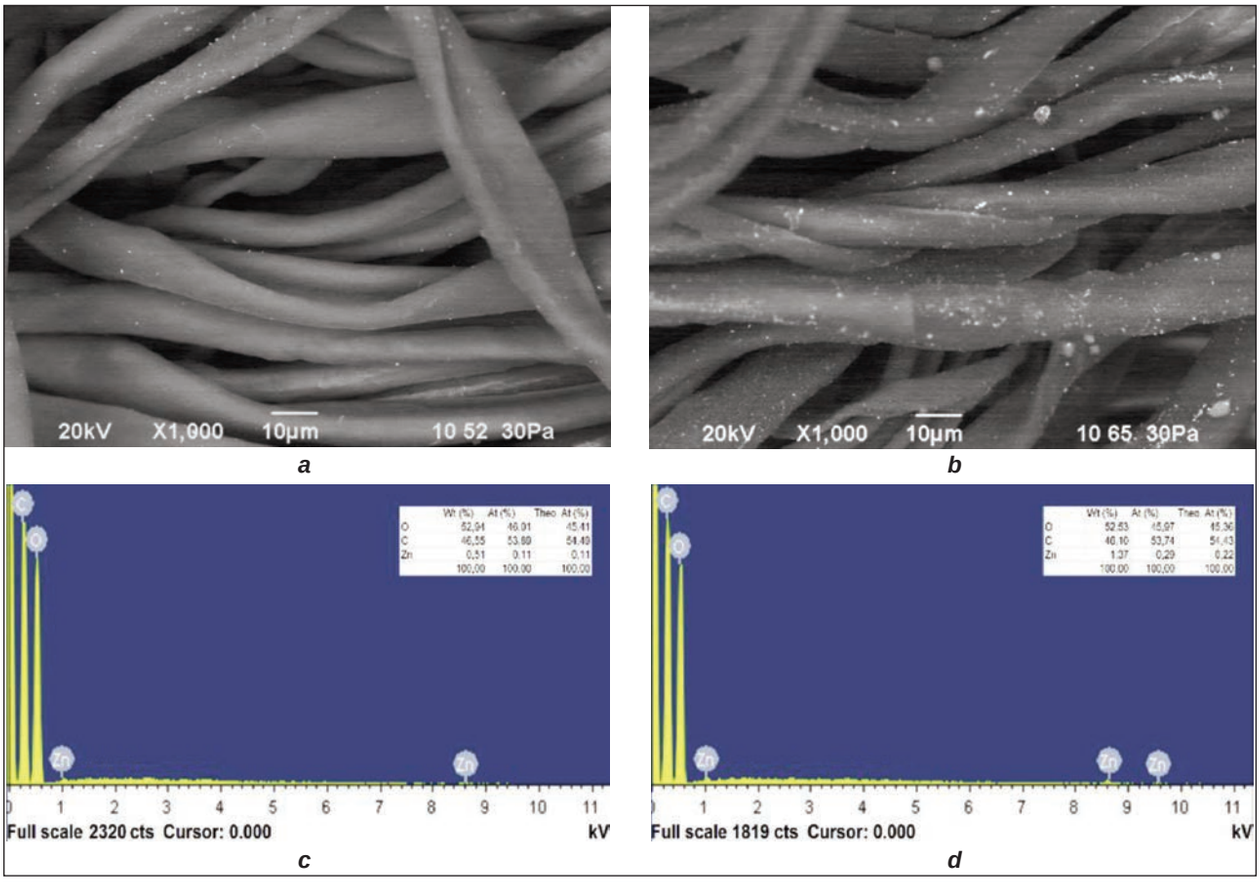


Fig. 4. SEM and EDS micrographs of Zn-treated cotton fabric: *a* – SEM pictures of Zn-0.5%; *b* – SEM pictures of Zn-1%; *c* – EDS spectra of Zn-0.5%; *d* – EDS spectra of Zn-1%

FTIR analysis

FTIR analysis of cotton fabric treated with sodium tetrahydroxocuprate (II)

FTIR spectrum of untreated and sodium tetrahydroxocuprate (II) (Cu) treated cotton fabric samples is depicted in figure 5. The peak observed at 3300 cm^{-1} corresponds to O–H stretching and appears as a broad band due to hydrogen bonding between the -OH groups. This frequency range also encompasses both intermolecular and intramolecular hydrogen bond vibrations in cellulose. A broad peak observed between 3000–2800 cm^{-1} is attributed to C–H stretching, a characteristic feature of all hydrocarbons [39–41]. The peak at 1428 cm^{-1} is associated with CH_2 scissoring, which shifts to 1420 cm^{-1} for the Cu-1% sample, accompanied by a decrease in intensity [42]. The peak at 1161 cm^{-1} is related to the anti-symmetric C(1)–O–C(4) bridge stretching mode, which slightly shifts to 1156 cm^{-1} for the Cu-0,5% and Cu-1% samples, respectively [43, 44]. The peak at 1105 cm^{-1} represents the asymmetric ring stretching mode and disappears in the treated cotton samples [45]. The peak at 1050 cm^{-1} is assigned to C–O stretching, with a notable reduction in intensity for the treated cotton fabrics [46]. The peak at 897 cm^{-1} is linked to the β-linkage of cellulose that can determine the degree of crystallinity [42, 47, 48]. The peak at 1024 cm^{-1}, associated with the C–O bond [49], shifts to 1020 cm^{-1} for the treated samples. Additionally, the peak at 665 cm^{-1}, attributed to -OH out-of-plane bending of cellulose, shows a significant decrease in intensity for the treated samples [42]. It is also observed that the peaks in the fingerprint region (550–600 cm^{-1}) for untreated and Cu-0,5% samples nearly vanish in the Cu-1% sample.

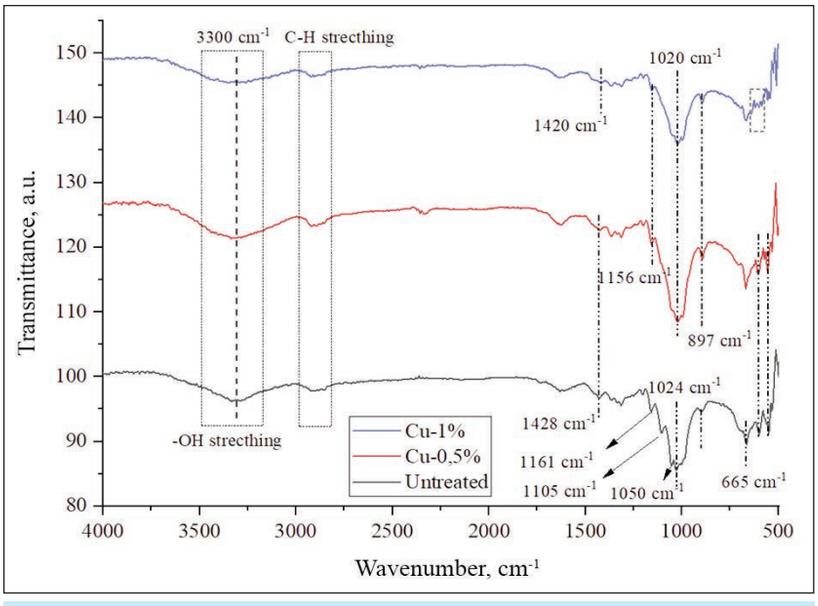


Fig. 5. FTIR spectra of untreated and Cu treated cotton fabrics

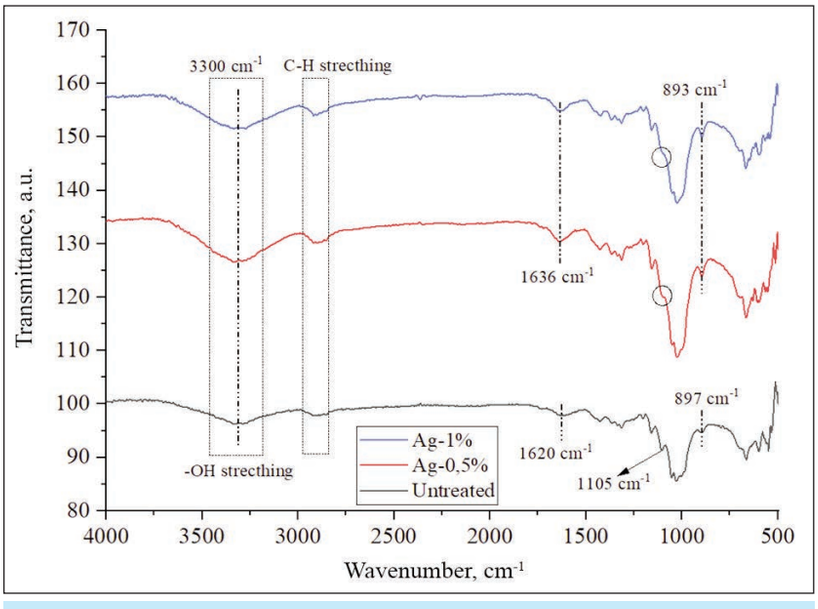


Fig. 6. FTIR spectra of untreated and Ag-treated cotton fabrics

FTIR analysis of cotton fabric treated with diamine silver compound

Figure 6 presents the FTIR spectra of untreated and treated cotton fabrics impregnated with diamine silver compound (Ag). In general, the untreated cotton sample displays characteristic peaks corresponding to cotton cellulose. However, for the treated samples, some of these peaks exhibit shifts, and their intensities have been modified. The broad peak observed at 1620 cm^{-1}, which is typically associated with the bending vibration of OH groups [50], shifts to 1636 cm^{-1} for Ag-0.5% and Ag-1% samples. Additionally, the peak at 1105 cm^{-1}, corresponding to the C-O-C glycosidic ether bond, almost completely disappears in the treated samples [51]. Another prominent peak, characteristic of cotton cellulose at 897 cm^{-1}, shifts to 893 cm^{-1} in the treated fabrics. These changes in peak positions and intensities suggest potential molecular interactions between the cellulose and the diamine silver compound.

FTIR analysis of cotton fabric treated with sodium zincate

Figure 7 illustrates the FTIR spectra of untreated and treated cotton fibres coated with sodium zincate (Zn). Overall, the untreated cotton sample exhibits distinct peaks associated with cotton cellulose; however, for the treated samples, some of these peaks undergo shifts, and their intensities are

altered. The broad peak at 1620 cm^{-1}, typically attributed to the bending vibration of OH groups [50], shifts to 1644 cm^{-1} for the Zn-0.5% sample and completely disappears for the Zn-1% sample. The peak at 1428 cm^{-1}, corresponding to CH_2 scissoring [45], is absent in the treated samples. Additionally, the peak at 1050 cm^{-1}, assigned to C–O stretching, shows a noticeable reduction in intensity for the treated cotton fibres [46]. These observed changes in peak positions and intensities suggest the occurrence of molecular interactions between the cellulose and the sodium zincate.

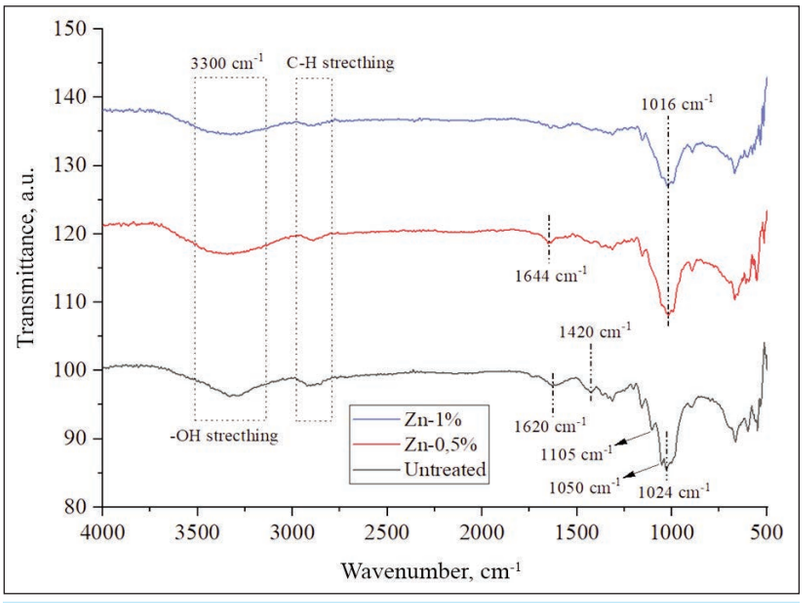


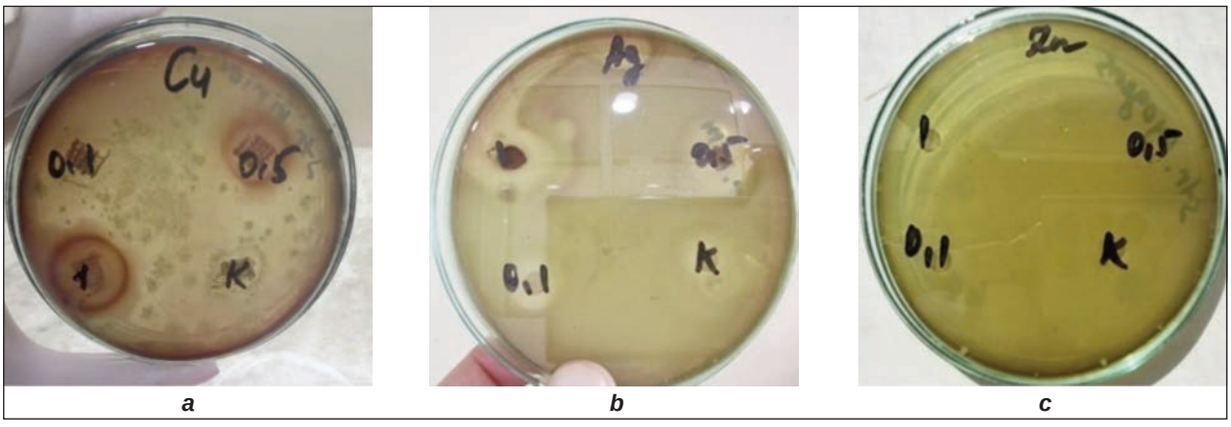
Fig. 7. FTIR spectra of untreated and Zn-treated cotton fabrics

Antifungal activity of the treated samples

The antifungal efficacy of Cu-, Ag-, and Zn-based compounds, applied at varying concentrations, was assessed based on their impact on *Candida albicans* over incubation periods of 7, 14, 21, and 28 days (the initial stage of the loaded petri dishes has been presented in figure 8). All tests were initiated with a fungal load of 10^6 CFU, and reductions in viable fungal cells were quantified as $\log_{10}$ values. The residual CFU counts were presented on a logarithmic scale. The corresponding quantitative results are summarised in table 3. Based on these findings, the temporal variation in antifungal activity at concentrations of 0.5% and 1% for each metal compound is graphically illustrated in figures 9 and 10, respectively.

The highest antifungal effect was observed in samples containing Cu. At the end of the 7th day, the fungal load decreased to the level of 10^2 with a decrease of 4 $\log_{10}$ (10,000-fold decrease) for Cu-1% sample as well as 3.74 $\log_{10}$ for Cu-0,5%. Although this effect partially decreased over time, the fabrics treated with Cu maintained their strong antifungal properties even on the 28th day. This is consistent with previous reports by Nosheen et al. [52], who demonstrated significant antifungal activity in copper-treated fabrics using electrolytic deposition techniques. The antifungal effect, which persisted over four weeks, may be due to disruption of the fungal cell membrane, the formation of reactive oxygen species (ROS), and the mechanism of enzymatic systems, as reported by Swierczynska and Kudzin [53]. These versatile mechanisms of action enable copper ions (Cu^{2+}) to act rapidly and extensively on fungal cells, making copper one of the most promising antifungal agents for long-term hygienic applications [54–56].

In Ag-treated samples, a maximum reduction of 3.04 $\log_{10}$ was achieved on day 7 (approximately 1000-fold) for Ag-1% sample as well as 3 $\log_{10}$ for Ag-0,5%. This is consistent with previous studies by Arenas-Chávez et al. [57], which highlighted the inhibitory potential of Ag-based nanocomposites against *Candida albicans*. The level of antifungal effect was largely maintained over time, with only a small decrease observed. The stability of the antifungal effect of silver over 28 days confirms the findings of Hedayati et al. [58], who emphasised the sustained release of Ag



a *b* *c*

Fig. 8. Initial stage of the antifungal tests of metal coated warp knitted cotton samples: *a* – Petri dish including Cu coated samples; *b* – Petri dish having Ag-treated samples; *c* – Petri dish with Zn-coated samples

Table 3

ANTIFUNGAL TEST RESULTS OF THE TREATED SAMPLES				
Microorganism/day	**Cu-1%**		**Cu-0.5%**	
	Final CFU*	**Logarithmic decrease**	**Final CFU***	**Logarithmic decrease**
Candida albicans 7th day	0	log 4	18	log 3.74
Candida albicans 14th day	21	log 3.67	62	log 3.20
Candida albicans 21st day	41	log 3.42	73	log 3.12
Candida albicans 28th day	59	log 3.23	81	log 3.07
Microorganism/day	**Ag-1%**		**Ag-0.5%**	
	Final CFU*	**Logarithmic decrease**	**Final CFU***	**Logarithmic decrease**
Candida albicans 7th day	90	log 3.04	101	log 3
Candida albicans 14th day	94	log 3.02	117	log 2.93
Candida albicans 21st day	96	log 3.01	135	log 2.86
Candida albicans 28th day	97	log 3.01	151	log 2.82
Microorganism/day	**Zn-1%**		**Zn-0.5%**	
	Final CFU*	**Logarithmic decrease**	**Final CFU***	**Logarithmic decrease**
Candida albicans 7th day	60	log 3.22	145	log 2.83
Candida albicans 14th day	71	log 3.14	172	log 2.76
Candida albicans 21st day	76	log 3.12	178	log 2.74
Candida albicans 28th day	79	log 3.1	183	log 2.73

Note: *Following the antifungal assessment of the metal-coated samples, a residual microbial load of 10^6 colony-forming units (CFU) was detected in the culture medium.

and its surface interaction with microbial membranes. Although silver is generally known for its strong antimicrobial effect, in this study, its effect on *Candida albicans* was slightly weaker than Cu. This may be due to the lower ion exchange rate of Ag in the fabric matrix or the intrinsic resistance of *Candida albicans* to silver; this was also noted by Nasrollahi et al. [37]. Furthermore, factors such as particle size and coating homogeneity may have influenced the effectiveness of Ag, as previously shown in studies by Perelshtein et al. [59] and Gutarowska & Michalski [60].

Antifungal activity in textile samples treated with zinc ions was shown to be between 3.22 $\log_{10}$ for Zn-1% sample as well as 2.83 $\log_{10}$ for Zn-0,5% on the 7th day, supporting previous studies by Roy et al. [61] and Kudzin et al. [62] demonstrating that ZnO nanoparticles are effective antifungal agents when dispersed homogeneously. Although Zn ions are less soluble than Cu and Ag ions [62, 63], their interaction with microbial enzymes and membrane destabilisation mechanisms remains important [64]. The lower but stable antifungal performance observed here is consistent with the findings of Emam and Abdelhameed [65], who highlighted the photostability of Zn-based coatings on cotton surfaces. Furthermore, the relatively lower toxicity of zinc compared to copper

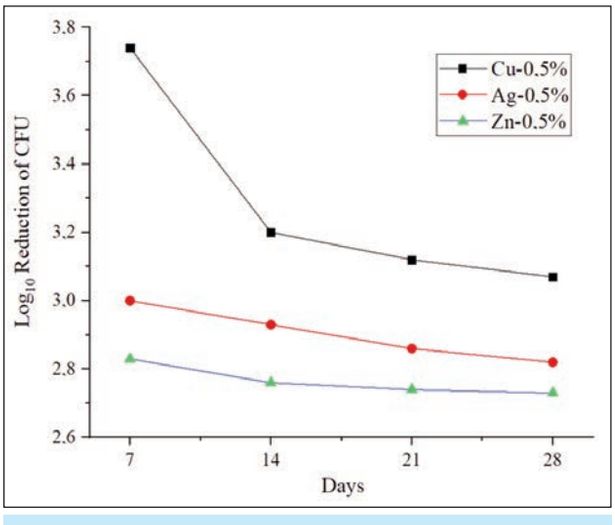


Fig. 9. Antifungal activity of 0,5% metal treated samples over 28 days

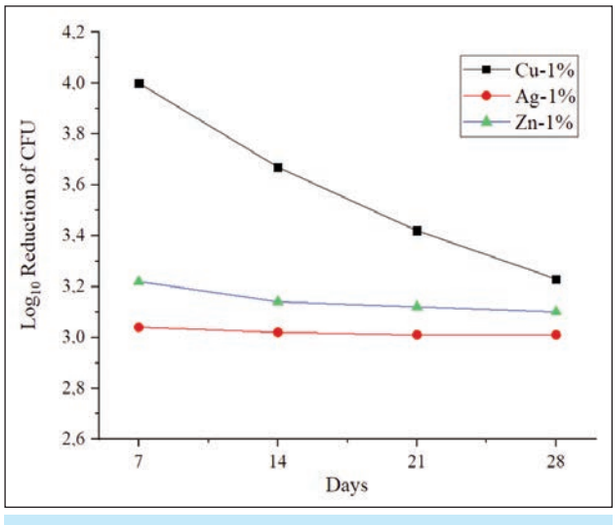


Fig. 10. Antifungal activity of 1% metal treated samples over 28 days

makes it a suitable candidate for applications where prolonged skin contact is expected.

The comparative analysis demonstrates that textiles treated with a 1% concentration of metal complexes exhibited superior antifungal efficacy compared to those treated with a 0.5% concentration. It has also been observed that Cu based compound is particularly suitable for antifungal needs in healthcare or high-risk health environments. Ag and Zn-based compounds, although less effective, are thought to provide more stable and predictable long-term protection in applications where gradual ion release is critical [57, 64, 66]. The cost-effectiveness of Cu [56], combined with the biocompatibility of Zn and the broad-spectrum activity of Ag [67, 68], suggests that the appropriate metal selection should be tailored to the intended textile application.

CONCLUSION

This study demonstrated effective synthesis and application of copper, silver, and zinc metal complexes onto warp-knitted cotton fabrics, verified by SEM, EDS, and FTIR analyses, which confirmed uniform particle distribution and molecular interactions with cellulose. Antifungal testing against *Candida albicans* revealed that copper-treated fabrics at 1% concentration achieved the highest antifungal activity, reducing fungal load by 4.00 $\log_{10}$ (from 10^6 to 10^2 CFU) within 7 days and maintaining significant efficacy through 28 days. Copper at 0.5% concentration also showed strong activity with a 3.74 $\log_{10}$ reduction at day 7. Silver treatments at 1% and 0.5% concentrations yielded reductions of 3.04 and 3.00 $\log_{10}$, respectively, on day 7, maintaining stable antifungal performance over 28 days. Zinc-treated fabrics at 1% and 0.5% concentrations showed reductions of 3.22 and 2.83 $\log_{10}$ at day 7, with consistent but lower activity compared to copper and silver. Across all metals, 1% concentration treatments outperformed 0.5%, confirming the positive impact of higher metal loading on antifungal efficacy. The rapid and sustained reduction in fungal viability highlights copper's superior biocidal action, making it optimal for healthcare and high-risk applications. Silver and zinc offer reliable and biocompatible alternatives suited for applications requiring prolonged antimicrobial effects. These quantitative results provide a basis for selecting appropriate metal-based antifungal treatments tailored to specific textile applications, balancing efficacy, durability, cost, and safety.

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