TEKSTİL VE KONFEKSİYON

VOL: 31, NO. 1

DOI:10.32710/tekstilvekonfeksiyon.724693

Antibacterial and Washing Resistance Improvement of Cotton Fabric Using Some Metal Oxides

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ABSTRACT

Cu_2O, CuO, ZnO-microparticles with different size and morphology directly influences their antimicrobial potential. In this study, the possible improvement of the antibacterial and washing resistance up to 20 washing cycles performance of 100% cotton fabrics were investigated. At high temperatures, carboxylic acids form ester-type crosslinking with cellulose molecules and provide antibacterial activity. For this purpose, carboxylic acids such as BTCA and CA were used in this study.The purpose of this research was to evaluate 1,2,3,4-butantetracarboxylic acid (BTCA) and citric acid monohydrate (CA) as an crosslinking agent for washing resistance of 100% cotton textile substrates against, Staphylococcus aureus (ATCC 43300), Bacillus subtilis (NRRL NRS-744), Escherichia coli (ATCC 35218) and Klebsiella pneumoniae (ATCC 70063). Cupper oxide and zinc oxide were assimilated in the coating bath for the antibacterial property. BTCA concentration in the solutions influenced the antibacterial and washing properties of the cotton fabrics. The Fourier Transform Infra-Red -Attenuated Total Reflection (FTIR-ATR) spectra showed a new summit that confirmed the ester linkage formation and crosslinking reaction for application.

ARTICLE HISTORY
Received: 21.04.2020
Accepted: 28.01.2021

KEYWORDS

Antibacterial, cotton fabric, copper oxide, zinc oxide, washing resistance.

1. INTRODUCTION

Novel materials, including textiles for specific applications have to satisfy consumers' growing demands. Due to various applications, clothing and also economic aspects, it is necessary for a material to perform several functions. Intensive development of nanotechnology in the area of micro- and nano-structure generation offers the possibility of creating novel textile materials with protective properties for human beings and for their natural environment.

Nanoparticles (NPs) of some metal-oxides such as copper(I)oxide (Cu_2O) and zinc (ZnO) belong to a group of compounds with antibacterial properties.

The usage of nanoparticles, as new agents for inhibition of microbial growth, has developed due to the development of antibiotic resistance [1-3].The particle with 1-100 nm size that behaves as a whole unit with respect to transport and properties is called nanoparticle [4-6]. These particles which have much higher surface area than conventional materials are currently considered as antimicrobial agents[1]. Among these nano-materials, nano-metals, such as copper and zinc oxide have been used more because of their less toxicity [7-8]. The copper and zinc oxide micro and NPs were studied in most related research, exhibiting antibacterial effect at low concentrations.

Ionic nanoparticulate metal oxides are among the potentially interesting antimicrobial agents because of their extremely high surface areas and special crystalline structures with high number of edges and corners and other reactive sites [9]. Copper oxide nanoparticle (CuO NP) is the simplest member of the Cu compounds that reveal a range of potential physical properties and is much cheaper than silver oxide. It can be mixed easily with polymers to provide composites with unique physio-chemical

To cite this article: Koruyucu A, Erdal B, Kurç MA, Gülen D. 2021. Antibacterial and Washing Resistance Improvement of Cotton Fabric Using Some Metal Oxides, *Tekstil ve Konfeksiyon*, 31(1), 19-26.

properties. Also, these CuONPs have high surface areas and special crystalline structures to give antimicrobial activity that is application dose dependent [10].

Metal ions, e.g. silver (Ag) [11], zinc (Zn) [12] and copper (Cu) [13-14] exhibit strong antibacterial activity. For a long time, the antimicrobial properties of Ag have been known, which are very useful both in the textile industry and in medicine [1-6,15]. In recent years many examples of antibacterial activity of Zinc oxide(ZnO)[8-10,16-18]. Titanium oxide(TiO_2)and other metal oxides have been described in literature [18-23]. It was demonstrated that the highest activity against bacteria was exhibited by Ag nanoparticles (NPs) with dimensions of 1-10 nm [24] and also by TiO_2 NPs with dimensions of below 20 nm [25].

Copper oxide also has good antibacterial, antiviral and antifungal properties [26-31]. Although small concentrations of CuO are sufficient, quite often, higher doses are used to inhibit the growth of certain microorganisms and achieve bactericidal activity[32]. Permanent biocidal properties of textiles containing 3-10% of CuO were described. In recent years, new antibacterial materials based on CuONPs have been developed[14, 33-35].

As potential novel antibacterial agents, metal oxide nanoparticles like CuO and ZnO are being thoroughly investigated. Their relatively low toxicity against human cells [36], low cost[37], size-dependent effective inhibition against a wide range of bacteria, ability to prevent biofilm formation [38] and even eliminate spores[39] make them suitable for application as anti-bacterial agents in the fabric [38], skincare products[40], biomedical[41] and food-additive industries[42] .

CuO and ZnO, being constituted by essential elements, are more biocompatible than other metal oxides and their toxicity is lower than, for example, silver- or nickel-based NPs[43-46].

Since nanoparticular passes from cell to cell by passing the semi-permeability control mechanism of the cells, their us for health is unfavorable. For this reason, micro copper (I), copper(II) and zinc oxide particles were used in this study.

Cu_2O was used in this research because of its better antibacterial properties [47]. Therefore, in our study basis and below 5 μm particles copper (I) oxide, below 10 μm particles copper(II)oxide and below 5 μm particles zinc oxide were used for antibacterial activity and antibacterial effect was assesment after repeated washings (1-3-5-7-10-13-15-17-20).

The BTCA (1,2,3,4-butantetracarboxylic acid) and CA (citric acid) were used as crosslinking agents to hold CuO, Cu_2O and ZnO particles on cotton fabric to obtain antimicrobial properties with high washing resistance.

Since it is important to maintain the antibacterial activity of fabrics in conditions of use, the antibacterial activity of unwashed fabrics was also compared with washed fabrics.

2. MATERIAL AND METHOD

2.1 Material

100 % cotton fabric was used for this study which was selected due to its wide usage in surgical textile protective clothing. The substrates were characterised with respect to their weight and thickness, the data of which is shown in Table 1.

The cotton fabric had a twill weave, with a weight of 336,79 g/m^2,and a thickness of 0,4545 mm.

Metal oxides

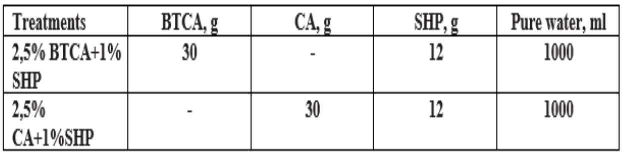
Basis and below 5 μm copper(I)oxide particles, below 10μm copper(II)oxide particles and below 5 μm zinc oxide particles (Sigma Aldrich) pattern were used as supplied.

Cross-linkings

At high temperatures, carboxylic acids form ester-type crosslinking with cellulose molecules and provide antibacterial activity. For this purpose, BTCA and CA were used in this study. Since these two carboxylic acids make effective cross-linking in the combined use of phosphorus-containing acids with inorganic salts, sodiumhypophosphite was added as a catalyst in pre-treatment bath.

BTCA was obtained in powder form from Fluka and CA was obtained from Sigma-Aldrich. The both chemicals were used as supplied. The composition of pre-treatment baths including BTCA and SHP, and CA and SHP were presented in Table 1. Cupper oxide and zinc oxide were assimilated in the coating bath for the antibacterial property. Coating bath formulation containing 90% of the arcylate binder is given in the Table 2.

Table 1. Composition of pre-treatment baths [49]



Treatments	BTCA, g	CA, g	SHP, g	Pure water, ml
2,5% BTCA+1% SHP	30	-	12	1000
2,5% CA+1%SHP	-	30	12	1000

Table 2. Coating bath formulation containing 90% of the arcylate binder [49]

Polyacrylate binder 1	45%
Polyarcylate binder 2	45%
BTCA/CA	5%
Cu_2O, CuO and ZnO	1%
Emulsified, dispersing material	3%
Thickener	1%
Coating thickness	0,1mm
Drying	100^0 C/ 2 min
Curing	150^0 C/ 2 min

2.2 Determination of antibacterial effects of treated fabrics

In this study as gram-positive bacteria (*Staphylococcus aureus* (ATCC 43300) and *Bacillus subtilis* (NRRL NRS-

744)) and as gram-negative bacteria (*Esherichia coli* (ATCC 35218) and *Klebsiella pneumoniae* (ATCC 70063)) were used. The culture medium Nutrient Agar (NA) used for the cultivation of the bacterial strains deployed in this work, were prepared according to the instructions of the manufacturer.

Antibacterial activity of cotton fabrics were tested against bacterial strains before washing and after 20 wash cycles according to the JIS L 1902-Halo Method (2008) protocol. The culture medium Nutrient Broth (NB) and Nutrient Agar (NA) were used for the cultivation of the bacterial strains. Culture media were dissolved directly after being weighed in deionized distilled water, and then sterilized by autoclaving for 15 min at 121 ºC [48].

The protocol from JIS L 1902–Halo Method was performed as follows: The bacteria was incubated for 24 h at 37°C in nutrient broth (NB). Then, 1.0±0.1 ml from the inoculum with 1×10^7 CFU/ml was added to 15 ml of NA warmed at 45-46°C. After agar solidification, the cotton fabrics (size 25 x 25 mm) were placed on the agar surface and incubated at a temperature of 37°C for 24 hours. Then, the diameter of the fabrics were measured by measuring the diameter around the fabric (inhibition zone diameter)[48].

2.3 Metal oxide applications

Cotton fabric were double padded in the dispersion of micro copper(I)oxide (Cu_2O), cupper(II)oxide (CuO) and zinc oxide (ZnO) particles (with concentration of $1g/dm^3$) in the nano-styrene acrylate copolymer binders finishing bath using a laboratory padding and 0,1 mm coating thickness. Then the cotton samples were dried at 100 ^{0}C for 2 min and cured at 150°C for 2 min [49].

2.4 Measurements

Infrared spectra of the samples were recorded in reflection mode using a Fourier-Transform Perkin Elmer 2000 FT-IR spectrometer. An attenuated total unit was fitted with a 45^0 entrance angle. Thirty scans were taken for each sample.
A field emission scanning electron microscope was used to observe the samples spattered with a 82.9 µm thick layer.

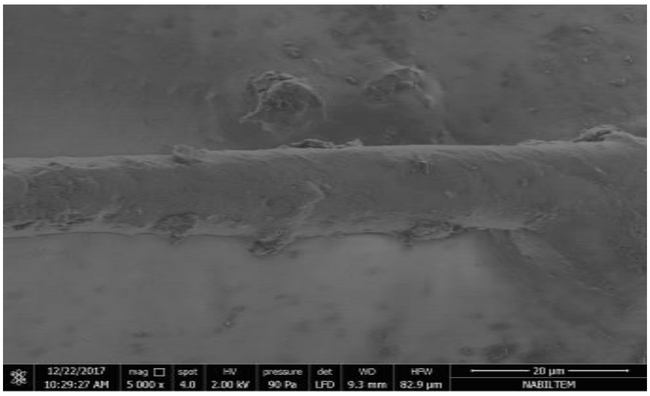
3. RESULTS AND DISCUSSION

3.1. Morphology of treated cotton fabric samples through SEM

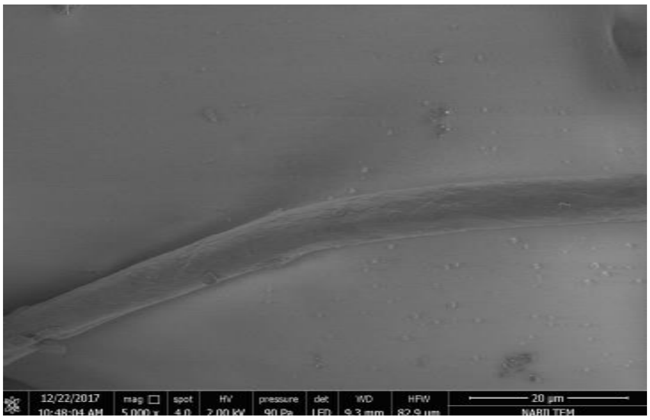
The distribution of basis and micro copper (I) oxide particles on the structure of the fabric after nano-styrene acrylate copolymer coatings were investigated by SEM analysis [49].

All samples were washed in distilled water to remove soluble and superficially attached reagents. The images showed an obvious change in the surface morphology of the treated samples with respect to the untreated cotton fabric.
The untreated cotton fabric as observed by SEM showed typical longitudinal fibrils on the surface [49].

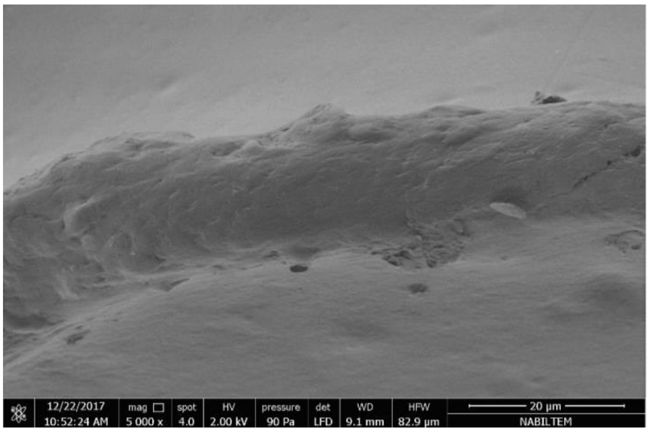
The SEM images of the uncoated and basis and micro-copper oxide applied fabrics particles were given in Figure 1. When SEM images were considered, the presence of basis and micro particles on fabric structure was clearly observed. It could be seen from the SEM images that micro-sized copper oxide particles penetrated to the fiber surface and showed a homogenous distribution. It was observed that hard and soft acrylic binders used in the coating application were polymerized and they were hold on the surface [49].



A:Cu(I)O<5µm [49]



B: Cu(II)O<10µm [49]



C:ZnO<5µm [49]

Figure 1. Cotton fiber surfaces before and after antibacterial coating processes (A: Cu(I)O< 5µm, B: Cu(II)O<10 µm, C: ZnO <5µm [49]

3.2 FTIR spectra after applications

The FTIR spectra of pretreated and then antibacterial coated cotton fabric samples were shown in Figures 2, 3, 4, 5 and 6.

Figure 2 showed the FTIR spectra of cotton fabric pretreated BTCA and SHP and then treatment with arylic coating polycarboxylic acids, the bands OH and CH (2900 and 2161 cm $^{-1}$), OH and CH bending (1646,1428 and 1315 cm $^{-1}$) CC and CO tensile (1160,1108 and 1030 cm $^{-1}$) bands were obtained dense band at 1646 cm $^{-1}$ is the C=0 stresses from the hydrogen bonded carboxylic acid and the change in the transmittance band at 1646 cm $^{-1}$ is due to the deformation vibration of the hydroxyl groups.

The two bands in 1315 and 1030 cm $^{-1}$ are due to the deformation of the hydrogen-linked carboxylic acid in the plane sequence and the C-O strain[47]. As a result, the change in the bands 3000-2800 cm $^{-1}$ and 1200-800 cm $^{-1}$ indicated that the number of OH groups increased after the procedure.

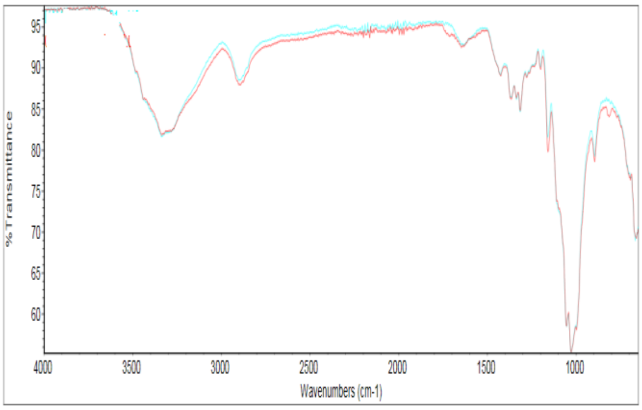


Figure 2. FTIR-ATR spectra of cotton fabric treated with Cu(I)O basis antibacterial particle and arylic coating antibacterial after application of BTCA[49]

Figure 3 showed the FTIR spectra of cotton fabric pretreated CA and SHP and then treatment with arylic coating polycarboxylic acids with Cu(I)O basis antibacterial particle. The bands formed after the process showed similarity with Figure 2. The change in the bands 3000-2800 cm $^{-1}$ indicated that the number of OH groups increased after the CA polycarboxylic acid. In summary, the change in the FTIR-ATR spectrum of cotton fabric treated with CA followed by Cu (I) O basis antibacterial particle via acrylic coating appears to be greater than the one treated with BTCA.

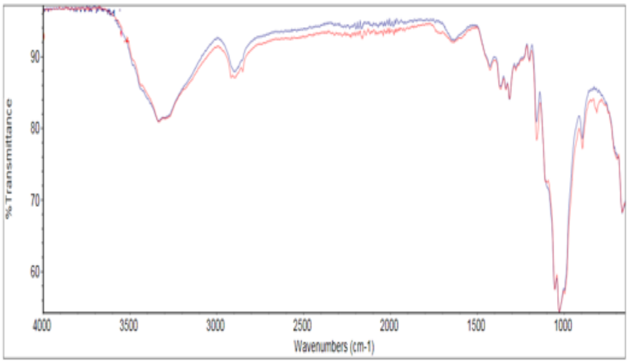


Figure 3. FTIR-ATR spectra of cotton fabric treated with Cu(I)O basis antibacterial particle via acrylic coating after application of citric acid monohydrate [49]

Figure 4 showed the FTIR spectra of cotton fabric pretreated BTCA and SHP and treatment with arylic coating polycarboxylic acids with Cu(I)O< 5 μm antibacterial particle.

The spectra obtained from pretreated and then antibacterial coated cotton fabric samples are very similar, but the spectra for BTCA and SHP pre-treated cotton showed some difference in the peaks of two strong bands at 2161cm $^{-1}$, 1730cm $^{-1}$ and 1570 cm $^{-1}$ which are due to the ester and carboxylate carbonyls, respectively[50-52].

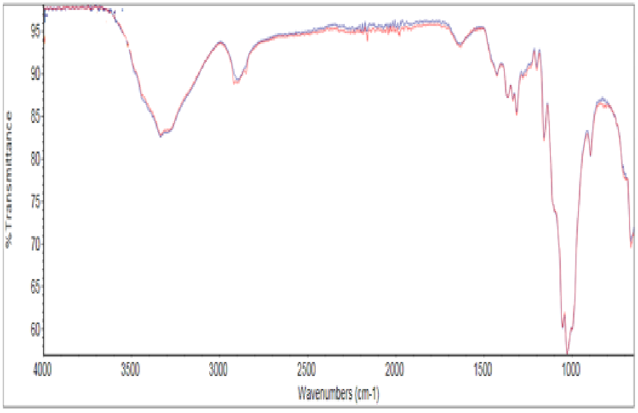


Figure 4. FTIR-ATR spectra of cotton fabric treated with Cu (I) O <5 μm antibacterial after application of BTCA[49]

Figure 5 showed FTIR-ATR spectra of cotton fabric pretreated with citric acid monohydrate and then treated arylic coating polycarboxylic acids with Cu (I)O< 5 μm antibacterial particle. The bands formed after the process were similar to the ones presented in Figure 4.The two bands in 1315 and 1030 cm $^{-1}$ were due to the OH deformation and C-O stretching of the hydrogen bonded carboxylic acid outside the plane. O-H bands at 1645 cm $^{-1}$ were completely closed.

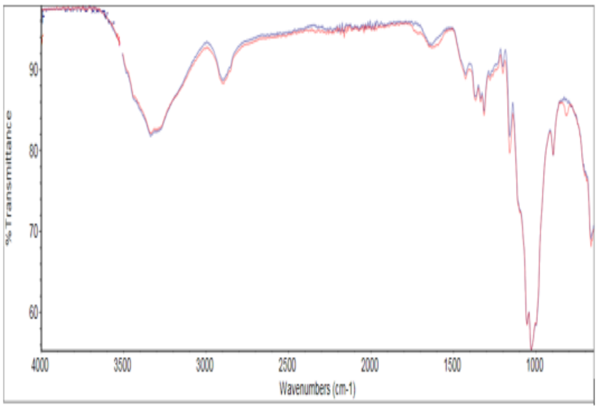


Figure 5. FTIR-ATR spectra of cotton fabric treated with Cu(I)O<5 μm antibacterial particle via acrylic coating after the application of citric acid monohydrate[49]

Figure 6 showed FTIR-ATR spectra of cotton fabric treated with citric acid monohydrate and then treated with ZnO<5μm antibacterial particle via acrylic coating. As a result, the change in the bands of 3000-2800 cm $^{-1}$ and 1200-800 cm $^{-1}$ indicated that the number of OH groups increased after the procedure. The change in the band of 2161 cm $^{-1}$

and 1646 cm $^{-1}$ showed that the citric acid monohydrate, which is a polycarboxylic acid, was bound to free hydroxyl groups of cotton.

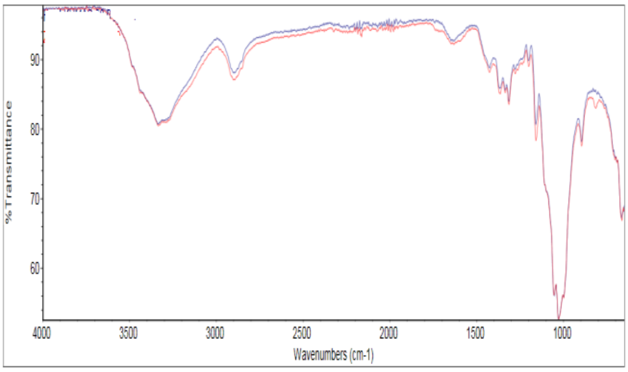


Figure 6. FTIR-ATR spectra of cotton fabric treated with ZnO<5μm antibacterial particle via acrylic coating after the application of citric acid monohydrate [49]

3.3 Comparision of antibacterial effects of treated fabrics according to wash cycles

To evaluate the antimicrobial efficiency according to protocol of the treated fabrics JIS L 1902-Halo Method (2008), the inhibition zones of the attempted fabrics formed on selected microorganisms were assessed.

In order to determine the resistance of the antibacterial treatments to washing the fabric samples were washed with twenty times. However, after the seventeenth wash no zone formation was observed. The treated fabrics were laundered in an Atlas Launder-Ometer according to AATCC Test Method 61, Test 1A. The test is intended to simulate five home launderings. The antibacterial efficiency of the laundered fabrics were evaluated again after the wash tests. Results of these experiments are presented in Tables 2,3, 4,5.

Table 2. Inhibition zones of treated fabrics after wash cycles against S. aureus (ATCC 43300)[49]

Fabric no	Inhibition zone (mm)									
	-	1st	3rd	5th	7th	10th	13th	15th	17th	20th
Cu(I)O<5μm +BCA	32	31	27	27	27	27	27	26	26	0
Cu(I)O<5μm +CA	27	26	0	0	0	0	0	0	0	0
Cu(I)O basis+CA	33	32	30	30	0	0	0	0	0	0
Cu(I)O basis+BTCA	30	29	26	0	0	0	0	0	0	0
Cu(II)O<10μm +BTCA	32	0	0	0	0	0	0	0	0	0
Cu(II)O<10μm +CA	29	0	0	0	0	0	0	0	0	0
ZnO<5 μm+ BTCA	27	27	0	0	0	0	0	0	0	0
Zno<5μm+ CA	32	32	27	0	0	0	0	0	0	0

The antimicrobial efficiency of the unwashed fabrics; ZnO+CA treated fabric had showed the best antibacterial activity for *B. subtilis* (37 mm) and Cu(I)O<5μm+BTCA treated fabric had good effect against *E. coli* (36 mm) (Table 2) (Figure 7,8,9,10).

Table 3. Inhibition zones of treated fabrics after wash cycles against B. subtilis (NRRL NRS-744)[49]

Fabric no	Inhibition zone (mm)									
	-	1st	3rd	5th	7th	10th	13th	15th	17th	20th
Cu(I)O<5μm +BCA	35	32	30	29	26	26	26	0	0	0
Cu(I)O<5μm +CA	26	26	26	26	0	0	0	0	0	0
Cu(I)O basis+CA	36	30	28	28	28	28	0	0	0	0
Cu(I)O basis+BTCA	29	28	26	26	0	0	0	0	0	0
Cu(II)O<10μm +BTCA	33	30	0	0	0	0	0	0	0	0
Cu(II)O<10μm +CA	33	0	0	0	0	0	0	0	0	0
ZnO<5 μm+ BTCA	27	27	27	27	0	0	0	0	0	0
Zno<5μm+ CA	37	34	26	26	0	0	0	0	0	0

Table 4. Inhibition zones of treated fabrics after wash cycles against E. coli (ATCC 35218)[49]

Fabric no	Inhibition zone (mm)									
	-	1st	3rd	5th	7th	10th	13th	15th	17th	20th
Cu(I)O<5μm +BCA	36	31	31	31	28	0	0	0	0	0
Cu(I)O<5μm +CA	27	27	0	0	0	0	0	0	0	0
Cu(I)O basis+CA	33	30	28	27	0	0	0	0	0	0
Cu(I)O basis+BTCA	30	29	0	0	0	0	0	0	0	0
Cu(II)O<10μm +BTCA	0	0	0	0	0	0	0	0	0	0
Cu(II)O<10μm +CA	29	0	0	0	0	0	0	0	0	0
ZnO<5 μm+ BTCA	28	0	0	0	0	0	0	0	0	0
Zno<5μm+ CA	31	29	0	0	0	0	0	0	0	0

Table 5. Inhibition zones of treated fabrics after wash cycles against K. pneumoniae (ATCC 70063)[49]

Fabric no	Inhibition zone (mm)									
	-	1st	3rd	5th	7th	10th	13th	15th	17th	20th
Cu(I)O<5μm +BCA	32	31	31	27	0	0	0	0	0	0
Cu(I)O<5μm +CA	31	27	26	26	0	0	0	0	0	0
Cu(I)O basis+CA	32	30	26	26	0	0	0	0	0	0
Cu(I)O basis+BTCA	0	0	0	0	0	0	0	0	0	0
Cu(II)O<10μm +BTCA	0	0	0	0	0	0	0	0	0	0
Cu(II)O<10μm +CA	28	0	0	0	0	0	0	0	0	0
ZnO<5 μm+ BTCA	0	0	0	0	0	0	0	0	0	0
Zno<5μm+ CA	32	31	30	0	0	0	0	0	0	0

1 g. Cu (I) O basis + BTCA as well as 1g. ZnO + BTCA were the largest samples in the area of the fabric samples containing acrylic coating. As it could be seen from Table 4, 5 inhibition zones were not detected on the Cu(I)O basis+BTCA, Cu(II)O<10μm+BTCA and ZnO+ BTCA againts *E. coli* or *K. pneumoniae.*

Antibacterial activity of washed treated fabrics against Gram positive bacteria (*S. aureus* and *B. subtilis*) and was greater than that against Gram negative bacteria (*E. coli* and *K. pneumoniae*). Samples with the highest inhibition zone against bacteria were 30g/L BTCA, 12 g /L sodium hypophosphite pretreatment applied by Cu(I)O<5μm+ BTCA. When the washing stability of these different bacteria was compared, it was determined that Cu(I)O<5μm+BTCA had good antibacterial effects even after 17 washes against *S. aureus* and 13 washes against *B. subtilis* and 7 washes against *E. coli*. But after 20 washes, it did not show antibacterial effect for *S.aureus* (Table 2). Likewise, Cu(I)O basis+CA had good antibacterial effects even after 10 washes against *B. subtilis* (Figure 11,12,13).

Some treated fabrics had lost antimicrobial activity in their first washings. Especially, Cu(II)O<10μm+CA fabric did not show antimicrobial effect after the first wash against all microorganism. Likewise, with washing of Cu(II)O<50nm+ CA and Cu(II)O<10μm+BTCA fabrics, *no inhibition zone was observed against* S. aureus *and in* ZnO+ BTCA fabric against *E.coli.*

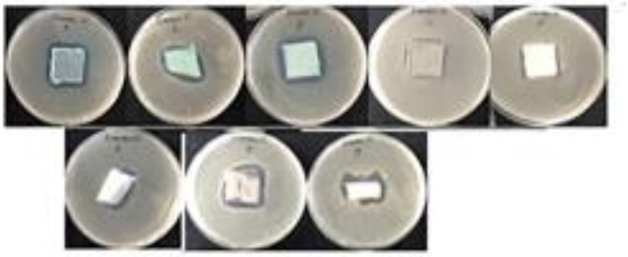


Figure 7. Inhibition zones of treated fabrics before washing against S. aureus (1:Cu(I)O<5μm+BTCA, 2:Cu(I)O basis+BTCA, 3:Cu(I)O basis+CA, 4:Cu(II)O<10μm+ CA, 5:ZnO<5μm+BTCA, 6:Cu(I)O<5μm+CA, 7:Cu(II) O<10μm+BTCA, 8:ZnO<5μm+CA)[49]

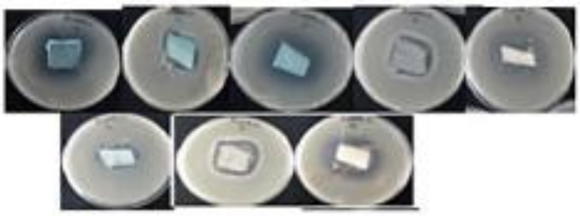


Figure 8. Inhibition zones of treated fabrics before washing against B. subtilis (1:Cu(I)O<5μm+BTCA, 2:Cu(I)O basis+BTCA, 3:Cu(I)O basis+CA, 4:Cu(II)O<10μm+ CA, 5:ZnO<5μm+BTCA,6:Cu(I)O<5μm+CA, 7:Cu(II) O<10μm+BTCA, 8:ZnO<5μm+CA)[49]

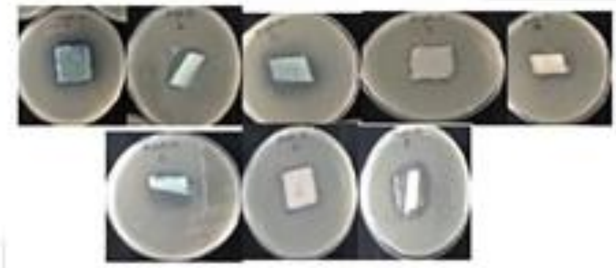


Figure 9. Inhibition zones of treated fabrics before washing against E. coli (1:Cu(I)O<5μm+BTCA, 2:Cu(I)O basis+BTCA, 3:Cu(I)O basis+CA, 4:Cu(II)O<10μm+ CA, 5:ZnO<5μm+ BTCA, 6:Cu(I)O<5μm+CA7: Cu(II)O<10μm+BTCA, 8:ZnO<5μm+CA)[49]

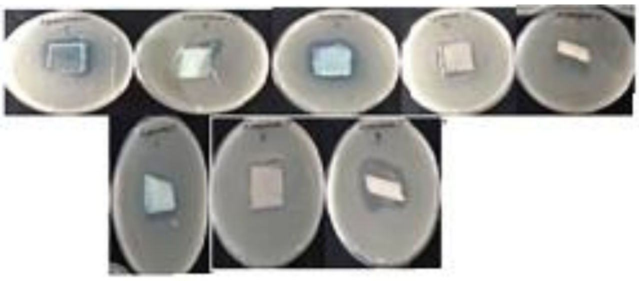


Figure 10. Inhibition zones of treated fabrics before washing against K. pneumonia (1:Cu(I)O<5μm+BTCA, 2:Cu(I)O basis+BTCA, 3:Cu(I)O basis+CA, 4:Cu(II) O<10μm+CA, 5:ZnO<5μm+ BTCA, 6:Cu(I)O<5μm+ CA, 7:Cu(II)O<10μm+BTCA, 9:ZnO<5μm+CA)[49]

Figure 11. Inhibition zones of Cu(I)O<5μm+BTCA fabrics after 1,5,10,15,17 wash cycles against S. Aureus[49]

Figure 12. Inhibition zones of Cu(I)O<5μm+BTCA fabrics after 1,5,10,15,13 wash cycles against B. Subtilis[49]

Figure 13. Inhibition zones of Cu(I)O basis+CA fabrics after 1,5,10 wash cycles against B. Subtilis[49]

4. CONCLUSIONS

The results of the usage of some metal oxides on the antibacterial and washing resistance properties of cotton fabrics were investigated. The relationship between the structural and morphological properties of CuO, Cu2O and ZnO-coated fabrics was presented. The uniform coating of the cotton fabrics with CuO, Cu2O and ZnO microparticles were confirmed by FTIR and SEM. The inhibition zones of treated fabrics after multiple wash cycles were studied. The antibacterial activities of the optimized sample were tested using some species of gram-positive and gram-negative bacteria.

Experimental results showed that the most inhibited species were B.subtilis and S.aureus. It is well known that microparticles of some metal-oxides such as copper (Cu2O) and zinc (ZnO) belong to a group of compounds with antibacterial properties. In this research, the samples with the highest inhibition zone were observed with 30g/L BTCA and 12 g/L sodium hypophosphite pretreatment which were applied by Cu(I)O<5μm+BTCA nano-styrene arcylate copolymer coating treated fabric. When the stability and antibacterial efficiency of this treated fabric on different bacteria against washing were compared, it was determined that Cu(I)O<5μm+BTCA had good antibacterial resistance even after 17 washes against S. aureus, after 13 washes against B. subtilis and after 7 washes against E. coli.

Acknowledgements

This work was supported by the Namık Kemal University Scientific Research Projects Commission (NKUBAP. 06.GA.16.064)

Declaration

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article. The author(s) also declared that this article is original, was prepared in accordance with international publication and research ethics, and ethical commitee permission or any special permission is not required.

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