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Improving the Washing Resistance of Antibacterial Fabrics with Different Crosslinkers

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ABSTRACT

The durability and effectiveness of antibacterial agents are a major factors for consumer use. In this study, copper(I)oxide and copper(II)oxide<5µm particles were used as antibacterial agents. These particles were applied to cotton fabrics with five different structures of polycarboxylic acid crosslinkers such as CA, DL-malic, fumaric, itaconic, BTCA and also ethylmetacrylate via knife-over coating method and antibacterial properties were imparted. The aim is to impart permanent antibacterial properties to cotton fabric by using copper(I)oxide and copper(II)oxide<5µm particles with six different structures of cross-linkers and to compare the aid of cross-linkers in terms of the particles antibacterial properties. The best result for gram-negative bacteria *Klebsiella pneumonia* (ATCC 70063) was obtained by using copper(I)oxide<5µm particles with CA crosslinker treated cotton fabric samples at inhibition zone of 31.53 mm as well as for gram-positive bacteria *Staphylococcus aureus* (ATCC 43300) the best result was obtained by using copper(I)oxide<5µm particles with CA crosslinker on treated cotton fabric samples at inhibition zone of 31.02 mm even after 20 repeated washing cycles.

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KEYWORDS

Antibacterial property, copper oxide microparticles, cotton, inhibition zone diameter, repeated washings

1. INTRODUCTION

Coating has been used to give functional properties to fabrics (1). The main advantages of the coating process are less water and chemical consumption as well as savings in energy costs (2). Inorganic antibacterial substances have potential applications in sectors such as food, packaging, cosmetics, pharmaceuticals, textiles and healthcare.

Copper(I) and copper (II)oxide particles were used on textile materials for imparting antibacterial property. Copper oxide nanoparticles have high surface area, low toxicity and antimicrobial properties. Additionally, these nanoparticles have antibacterial activity against both gram-positive and gram-negative bacteria via reactive oxygen species (ROS) formation (3). Copper (II)oxide and copper(I)oxide particles have been used as antibacterials because they are cheap and easier to mix with polymers. Besides copper ions indicated antimicrobial activity against microorganisms, such as *Staphylococcus aureus* (*S.aureus)* and *Escherichia coli* (*E.coli)* (4-6).

In the literature, recent advancements could be summarized as follows:

Metal-based NPs were adsorbed to the bacterial surface by Sanchez-Lopez et al. (7) because they were positively charged through electrostatic interaction. Copper micro- and NPs have similar effects on the cell membrane. Adsorption of copper ions into bacterial cells occurred because of the antibacterial mechanism. Additionally, concentration-dependent antibacterial activity was obtained by Raffi et al. (8). The bacterial effect of copper NPs on gram-positive bacteria was obtained to be better than gram-negative bacteria by Tiwari et al. (9) and Ahamed et al.(10) evaluated the lowest inhibition zone diameter of CuONPs against *Klebsiella pneumonia (K. pneumonia)* bacteria.

Din & Rehan (11) obtained the copper oxides by using inert atmosphere and coatings in the synthesis of copper particles. Due to the strong affinity of Cu to amines and carboxy groups in bacteria, Cu NPs were used by Ekthammathat et al. (12) as an effective antibacterial.

Copper ions bound to the bacterial cell surface have shown good bactericidal properties. Copper ions released from nanoparticles caused adhesion and bioactivity through electrostatic forces. Ohsumi et al. (13) and Dan et al.(14) investigated the effective surface area of copper

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nanoparticles in binding to bacteria. In addition, Dehabadi et al. (15) analyzed the samples composed of Cu, finding that the best bacterial killing ability due to the release of Cu ions.

The antibacterial properties of CuO NPs depend on the size and shape of the nanoparticles. Additionally, the antibacterial activity mechanism of CuO NPs was determined in three steps. First, the release of copper ions, second, direct contact of CuO NPs with bacteria and third, the production of reactive oxygen species was achieved by Mu et al.(16) and Roman et al.(17). As a result, it was determined that a textile material containing CuO has antiviral properties.

Ruparelia et al.(18) and Li et al.(19) evaluated the antibacterial properties of silver and copper by the disc diffusion test method. CuO NPs were more effective against *Bacillus subtilis* (*B.subtilis)* bacteria than silver particles due to the affinity of *B.subtilis* to amines and carboxyl groups. Additionally, the antibacterial properties of ROS (Reactive Oxygen Species) and $Cu(OH)_2$ was discussed by Li et al.(19). They claimed that the use of Ag and Cu as active antibacterial materials.

Copper-containing particles provided antibacterial activity. The antibacterial properties of micro/nano copper particles were evaluated by Chalayon & Tangwongsan (20) against *Escherichia coli* (*E.coli)*, *Salmonella, Staphylococcus aureus (S.aureus)* and *Staphylococcus epidermidis (S.epidermidis)* bacteria. They discovered that the copper ions must be oxidized to be released. Behzadinasab et al.(21) investigated the dissolved copper and copper(I)oxide had a strong effect in killing bacteria. For antimicrobial coatings, diffusion of Cu^+ ions must be allowed. Cu^+ ions transported through the coating and reach bacteria. Additionally, Turalija et al. (22) investigated the copper(I)oxide microparticles that were attached to the medicinal products via a pigment binder. Using very simple processes and ordinary chemicals, finding that an antibacterial product was obtained resistant to washing.

The antibacterial performance of 100% cotton fabrics was evaluated by Koruyucu et al. (23) after 20 repeated washings. 1,2,3,4-butanetetracarboxylic acid (BTCA) and citric acid (CA) were used as crosslinkers for the washing resistance of 100% coated cotton fabrics against *Staphylococcus aureus (S.aureus*) (ATCC 43300), *Bacillus subtilis* (*B.subtilis)*(NRRL NRS), *Escherichia coli* (*E.coli)* (ATCC 35218) and *Klebsiella pneumonia (K.pneumoniae)* (ATCC 70063) bacteria. The stability of coated fabric samples against repeated washings and their antibacterial activity on different bacteria were tested. Copper (I)oxide<5µm+BTCA showed good antibacterial activity against *S.aureus* even after 17 washing cycles, against *B.subtilis* after 13 washing cycles, and against *E.coli* even after 7 washing cycles.

The inhibition zone of modified wool and cotton knitted fabrics against *Staphylococcus aureus (S.aureus)* and *E.coli* bacteria was evaluated by Ivanauskas et al.(24) before and after the treatment. Consequently, it was determined that the modified wool fabric had the best antibacterial property against *S.aureus* bacteria. The maximum inhibition zone was obtained as 19.3 mm for *S.aureus* and 18.3 mm for *E.coli*.

The commercial (ZnPT) zinc pyrithone organometallic compound was used to obtain antimicrobial textile material by Ugras S & Sarı U (25). After the application process, it was determined that the textile samples containing 70% cotton and 30% polyester gained good antimicrobial property and formed an inhibition zone diameter larger than 30 mm around the textile materials up to 10 repeated washing cycles.

The aim of this study was to evaluate the inhibition zone diameters of acrylic coated nurses' gowns after repeated washings to assess antibacterial activity. According to, the binding mechanism of the polymer with fabric, antibacterial copper oxide particles and different structures of polycarboxylic acid cross-linkers were found to be effective in obtaining good antibacterial activity. The antibacterial activities of coated cotton fabrics were evaluated against two standard bacterial isolates, methicillin-resistant *Staphylococcus aureus (S.aureus)* (MRSA) and *Klebsiella pneumonia (K.pneumoniae)*. MRSA was preferred due to bacterium frequently observed in hospital infections. The type of fabric used in nurses' gowns was of great importance in terms of the comfort and durability. These types of fabrics are breathable and offer comfort even for long-term use. In addition, having anti-bacterial and easy to clean properties are of great importance in terms of hygiene. Nurses' gowns are produced from 100% cotton fabric because of their significant mechanical performance and flexible structure. Cotton has been used as the most popular fibre for the production of nurses' gowns in medical textiles and provides comfort throughout the working period. The features of 100% cotton fabrics include non-allergenic, high strength, ease of use.

In the literature, studies generally focused on the bacterial effect of copper NPs on gram-positive bacteria was to be better than gram-negative bacteria, the strong affinity of Cu to amines and carboxy groups in bacteria and the surface area of copper nanoparticles was effective in binding to bacteria with fabrics in effective antibacterial coating performance.

2. MATERIAL AND METHOD

2.1. Application onto fabrics

The 100% cotton fabric had a twill weave, with a weight of 330 g/m^2, and a thickness of 0,4545 mm. Copper(I)oxide and copper(II)oxide<5µm particles were used for antibacterial activity. At high temperatures, carboxylic acids formed ester-type cross-linking with cellulose molecules and provided antibacterial activity. For this purpose, crosslinkers such as BTCA (1,2,3,4-butantetracarboxylic acid), CA (citric acid), DL-malic acid, itaconic acid and fumaric acid were used. And also, ethylmetacrylate crosslinker was used. Coating

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bath formulation containing 90% of the arcylate binder was given in the Table 1. All the chemicals were used analytical purity.

Table 1. Coating bath formulation

Polyacrylate soft binder	45%
Polyarcylate hard binder	45%
Crosslinking	5%
Cu_2O, CuO	0.5%
Emulsified, dispersing material	3.5%
Thickener	1%
Coating thickness	0.2 mm
Drying	120 ˚C/ 5 min
Curing	150 ˚C/ 1 min

Cotton fabric were coated with the copper(I)oxide (Cu_2O), copper (II)oxide (CuO)<5µm particles in the acrylate copolymer binders using a laboratory knife-over coating method and 0.2 mm coating thickness. All the coated cotton fabric samples were dried at 120 ˚C for 5 minutes and cured at 150 ˚C for 1 minute. The hard and soft acrylic binders used in the coating application were polymerized and they were hold on the surface. Cellulose molecules formed ester bonds with the carboxyl groups in polycarboxylic acid crosslinkers (26-28). Copper(I)O<5µm and copper(II) O<5µm particles were fabricated on cationic woven cotton fabrics by knife-over coating method. For cationic surface charge, cotton fabrics pretreated with 2.5% CA+ 1% SHP by padding method. When phosphorus was present in the structure of CA, sodium hypophosphite was used as a catalyst to achieve effective crosslinking with inorganic salts.

2.2. Characterization

In order to determine the presence of copper(I)O<5µm film on the surface of cotton fabrics, FT-IR and SEM analyzes were performed. The chemical structure of samples was obtained with FE-SEM microscope in ranging from 4000 cm^{-1} to 500 cm^{-1}.

2.3. Determination of antibacterial activity of coated fabrics

In this study, the antibacterial properties of copper oxide coated fabrics were evaluated using a gram-positive bacteria *S.aureus* (ATCC 43300) and as gram-negative bacteria *K.pneumoniae* (ATCC 70063).

Antibacterial resistance of cotton fabrics were tested according to the JIS L 1902-Halo test method (2008) before washing and after repeated washings (1-3-5-7-10-13-15-17-20) (29). A mixture of nutrient broth and nutrient agar was dissolved in deionized distilled water, and then sterilized by autoclaving for 15 min at 121℃. Then, 2.0±0.1 ml from the inoculum with 1×10^7 CFU/ml was added to 30 ml of NA warmed at 45-46℃. After agar solidification, the cotton fabrics (size 20x20 mm) were placed on the agar surface and incubated at 37 ˚C for 24 hours. Uncoated fabric samples were used as negative controls in each experiment. After incubation, the inhibition zone diameter was measured. All antibacterial assays were performed in triplicate, and results are expressed as mean ± standard deviation (SD). All the table in this study were analyzed by Excel Windows Microsoft 365 and GraphPad Prism 8.0.

2.4. Determination of repeated washing of coated fabrics

Repeated washings of coated fabrics were tested using ECE phosphate detergent in 150 ml liquor volume at 40℃ 30 minutes according to ISO 105 C06-A1S test method. All coated cotton fabrics exhibited excellent antibacterial activity against *S.aureus* and *K.pneumoniae* bacteria. Gram-positive bacteria, such as *S.aureus* (methicillin-resistant *S.aureus*) have been observed more frequently, particularly in immunocompromised patients, burns, organ transplant recipients and as causative agents of hospital-acquired infections (30). Similarly, gram-negative bacteria such as *K.pneumoniae* was also important pathogen causing hospital-acquired infections. One study examined the contamination rates of gowns and gloves of healthcare workers caring for patients with carbapenemase producing *K.pneumoniae* and non-carbapenemase producing *K.pneumoniae*. Contamination rates with *K.pneumoniae* species were found to be similar to contamination rates with methicillin-resistant *S.aureus* and vancomycin-resistant enterococci. The results showed that 31 of 220 (14%) healthcare worker-patient interactions resulted in contamination of gloves and gowns (31). Consequently, their ability to survive on surfaces for long periods of time makes these bacteria a suitable model for evaluating the antimicrobial properties of textile products (32). Copper (I)oxide<5µm and copper(II)oxide<5µm particles were used for antibacterial activity. Antibacterial effect was assesment after repeated washings (1-3-5-7-10-13-15-17-20).

3. RESULTS AND DISCUSSION

3.1. Binding mechanism of cellulose to carboxylic acids

The hydroxyl groups in cotton had an anionic charge. The aqueous environment caused to bond with oppositely charged molecules. Polycarboxylic acids linked to the cellulose molecule through ester group (33). The binding mechanism of cellulose to polycarboxylic acids was shown in Figure 1.

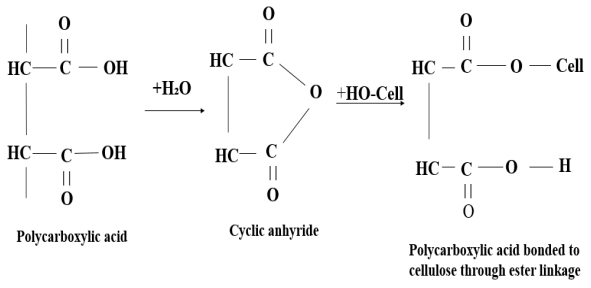


Figure 1. The binding mechanism of cellulose to polycarboxylic acids (34)

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In the coating process, firstly, cyclic anhydride was obtained with -OH groups and the hydroxyl group in cellulose was attached to the polycarboxylic acid with the ester group (35-36).

The linking of DL-malic acid (DL-MLA), citric acid (CA), 1,2,3,4-butanetetracarboxylic acid (BTCA), fumaric acid and itaconic acid (IA) to the fabric surface was shown in Figure 2.

3.2. Surface Morphology of the Coated Cotton Fabrics

Figure 3 and Figure 3a displayed the the uncoated and copper(II)oxide applied fabrics particles. FE-SEM analysis was performed for the coating of polycarboxylic acid on the cotton fabric surface. SEM images of untreated and polycarboxylic acid+ SHP treated cotton fabrics are shown in Figure 3 and Figure 3a. When SEM images were considered, the presence of copper(I)O<5µm and copper(II)O<5µm particles on fabric structure was clearly observed. As a result, the micro-sized copper oxide particles penetrated to the fiber surface and homogeneously distributed on the surface of cotton fabric and this was due to the good adhesion between copper oxide particles and hydroxyl(-OH) group in the structure of cotton. Another result is that the copper oxide microparticles are hydrogen bonded to the hydroxyl groups of the cotton.

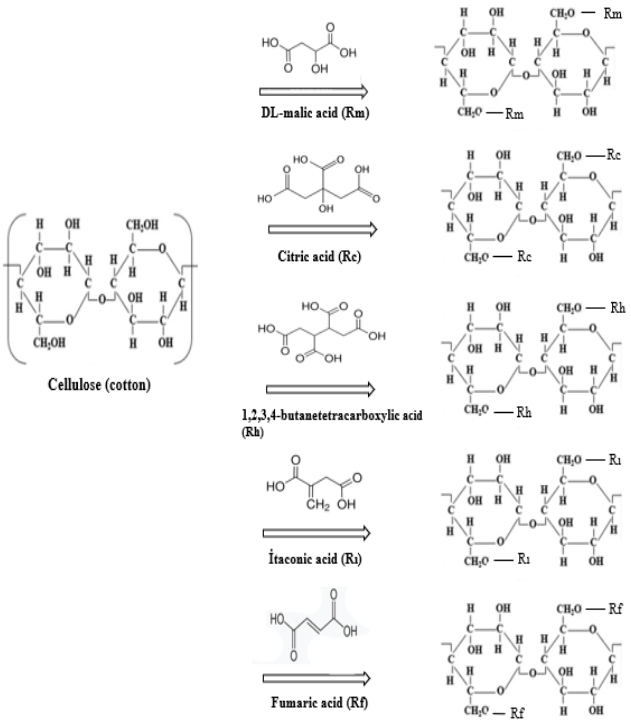


Figure 2. Linking of cellulose to carboxylic acids (35)

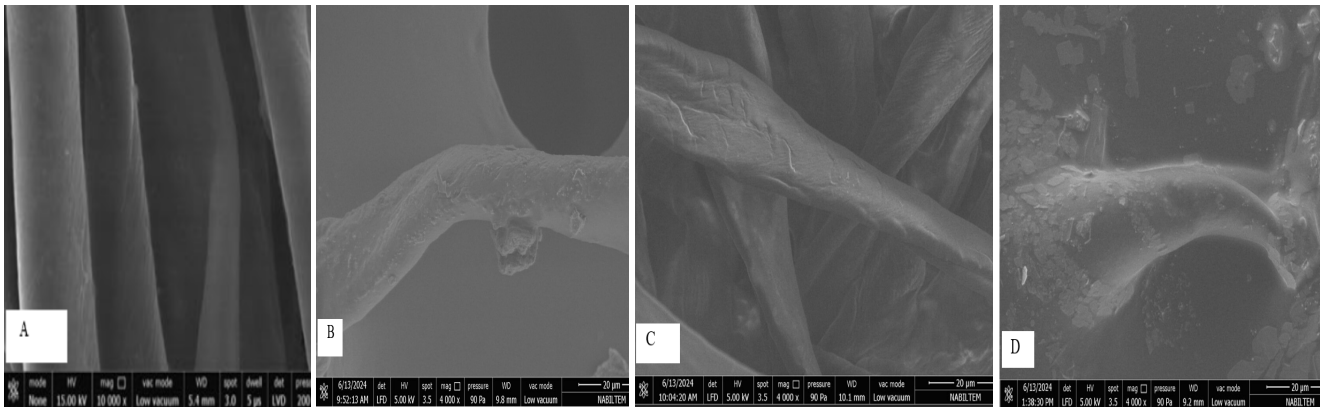


Figure 3. SEM images of cotton fabric before and after antibacterial coating processes (A: untreated cotton fabric, B: BTCA with Cu(II)O<5µm coated cotton fabric, C: CA crosslinker with Cu(II)O<5µm coated cotton fabric, D: DL-malic acid with Cu(II)O<5µm coated cotton fabric)

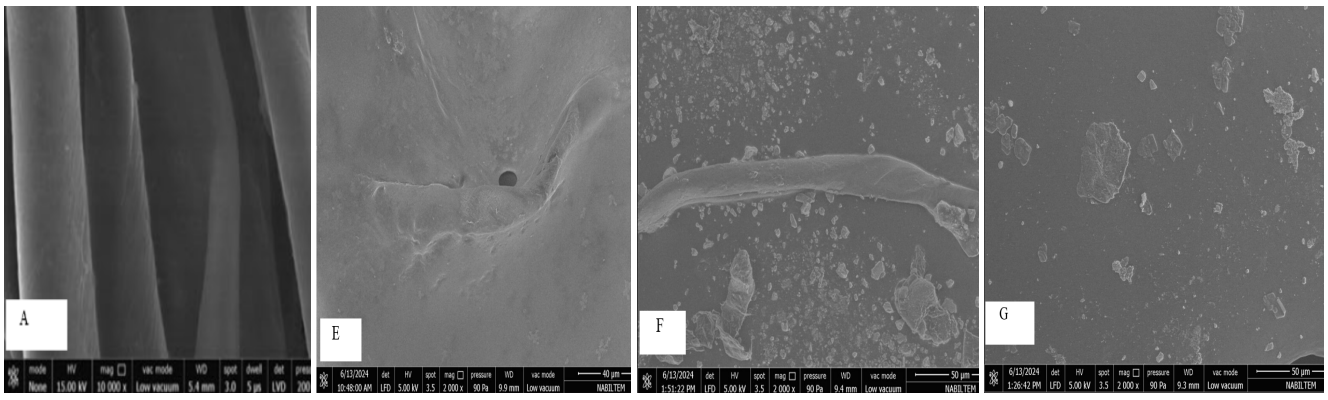


Figure 3a. SEM images of cotton fabric before and after antibacterial coating processes (A: untreated cotton fabric, E: itaconic acid with Cu(II)O<5µm coated cotton fabric, F: Fumaric acid with Cu(II)O<5µm coated cotton fabric, G: Ethylmetacrylate with Cu(II)O<5µm coated cotton fabric)

Figure 4 and Figure 4a showed the uncoated and copper(I) oxide particles applied to cotton fabrics.

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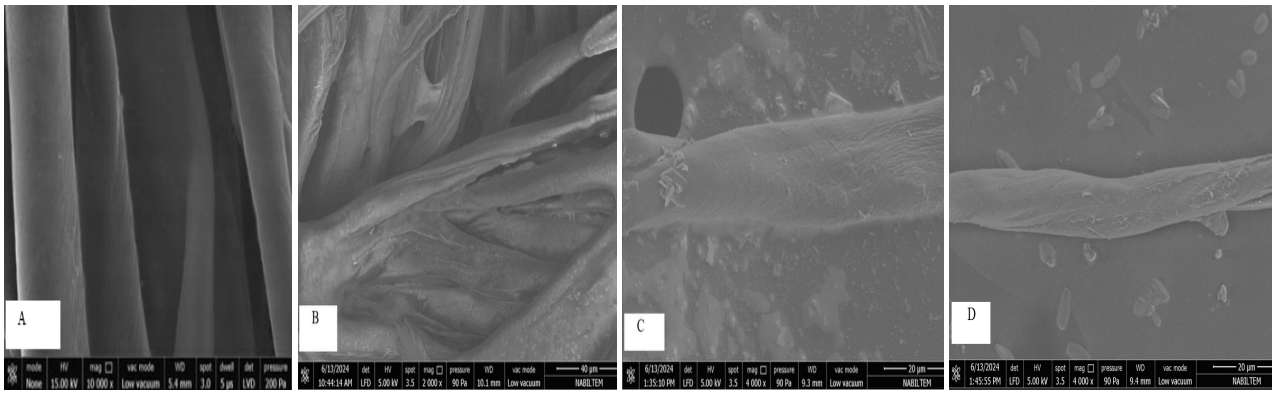


Figure 4. SEM images of cotton fabric before and after antibacterial coating processes (A: untreated cotton fabric, B: BTCA with Cu(I)O<5µm coated cotton fabric, C: CA with Cu(I)O<5µm coated cotton fabric, D: DL-malic acid with Cu(I)O<5µm coated cotton fabric)

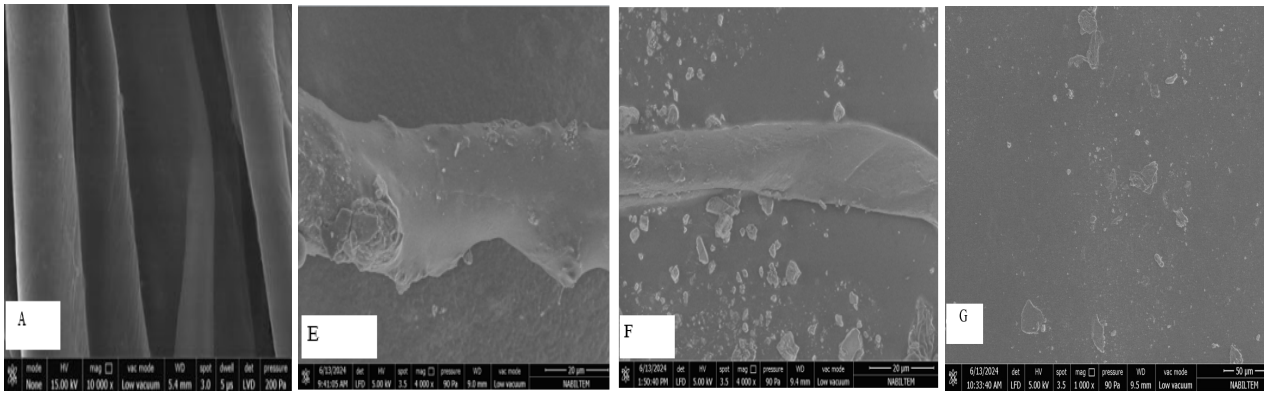


Figure 4a. SEM images of cotton fabric before and after antibacterial coating processes (A: untreated cotton fabric, E: itaconic acid with Cu(I)O<5µm coated cotton fabric, F: Fumaric acid with Cu(I)O<5µm coated cotton fabric, G: Ethylmetacrylate with Cu(I)O<5µm coated cotton fabric)

3.3. FTIR spectra after applications

Figure 5, 5a, 6 and 6a illustrated the FTIR spectrum of pretreated and then antibacterial coated cotton fabric samples.

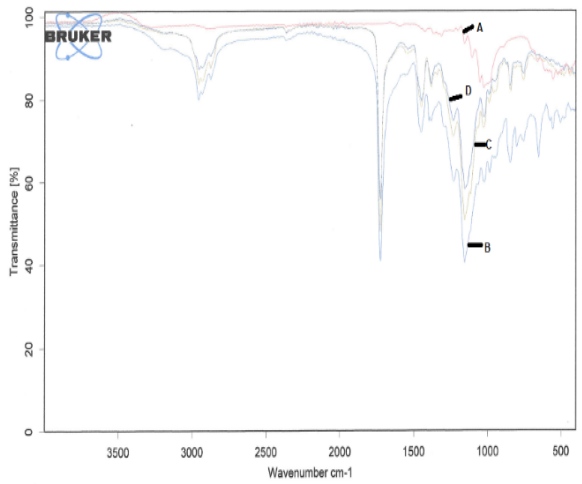


Figure 5. FTIR spectrum of cotton fabric treated with Cu (II)O<5µm with (A: uncoated cotton fabric, B: BTCA crosslinker, C: Ethylmetacrylate crosslinker, D: Itaconic crosslinker)

FTIR spectrum band of cotton fabric treated with copper(II)O<5µm in the range of 500 to 4000 cm^{-1} are seen in Figure 5 and Figure 5a. FTIR spectra of cotton fabric pretreated with CA and SHP followed by arylic coating polycarboxylic acids, OH and CH bands (2900 and 2161 cm^{-1}), OH and CH bending (1646,1428, 1315 cm^{-1}) with CC and CO. The bands located at 1646 cm^{-1} and 1263 cm^{-1} are due to the C=O and C–O stretching vibrations from the carboxylic groups, accordingly.

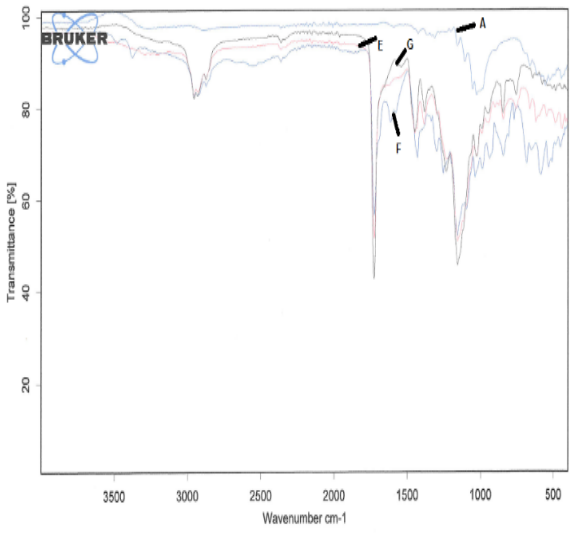


Figure 5a. FTIR spectrum of cotton fabric treated with Cu (II)O<5µm with (A: uncoated cotton fabric, E: CA crosslinker, F: DL-malic crosslinker, G: Fumaric crosslinker)

The ester bond formed a strong band at 1723.3 cm^{-1}, which is the stretching vibration peak of the carbonyl. Also a peak

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at 2926 cm^{-1} indicated that H-OH bond between the cellulose and carboxylic acid crosslinkers. Further, a peak at 1020 cm^{-1} indicated that (C=0) carbonyl group. The band at 2876 cm^{-1} represented the stretching vibration of (C–H) present in cellulose. The band at 1736 cm^{-1} indicated that ester and aldehyde groups (>C=O) were shown in BTCA, CA, DL-malic and itaconic acid with copper(II)O<5µm. The band at 1611.2 cm^{-1} corresponded to the aromatic bonding of the alkene group (C=C). The change in the 3000-2800 cm^{-1} and 1200-800 cm^{-1} bands showed that the number of OH groups increased.

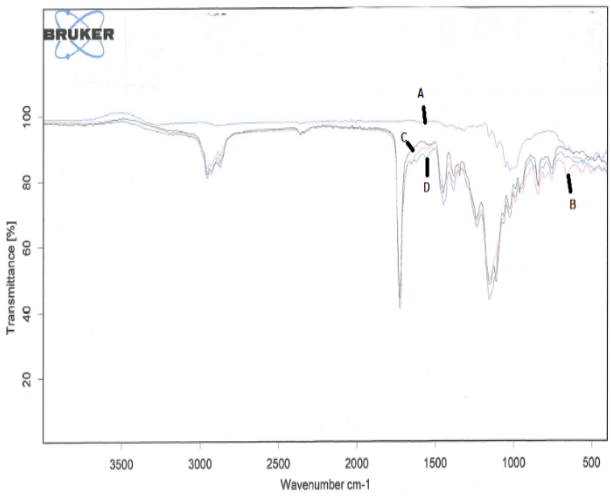


Figure 6. FTIR spectrum of cotton fabric treated with Cu (I)O<5µm with (A: uncoated cotton fabric, B: BTCA crosslinker, C: Ethylmetacrylate crosslinker, D: Itaconic crosslinker)

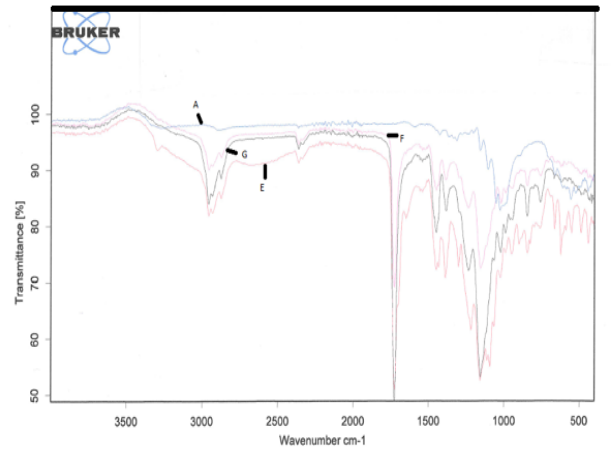


Figure 6a. FTIR spectrum of cotton fabric treated with Cu (I)O<5µm with (A: uncoated cotton fabric, E: CA crosslinker, F: DL-malic crosslinker, G: Fumaric acid crosslinker

The FTIR spectrum band of cotton fabric treated with copper(I)O<5µm particles in the range of 500 to 4000 cm^{-1} are presented in Figure 6 and Figure 6a. The broad band at 3360 cm^{-1} designated the OH functional groups found in cellulose. The ester carbonyl band at 1722 cm^{-1} (>C=0<) and the anhydride carbonyl band at 1778 cm^{-1} were obtained. The carbon-carbon double bond (>C=C<) was obtained at 1648 cm^{-1}. The strong absorption band at 1030 cm^{-1} indicated in cellulose (C-C, C-O and C-O-C vibrations) functional groups.

3.4. Comparison of antibacterial effects of treated fabrics after repeated washing cycles

To evaluate the antibacterial efficiency according to the treated fabrics JIS L 1902-Halo Method (2008), the inhibition zones of the coated fabrics were assessed [29]. The antibacterial efficiency of the coated fabrics were evaluated after repeated washing tests. The antibacterial effectiveness results are given in Tables 2, 3, 4, 5.

The antibacterial activity of copper(I)O<5µm film coated cotton fabrics after repeated washing processes against *K.pneumoniae* bacteria was seen in Figure 7 and Table 2. It was formed as a zone inhibition as a result of repeated washing process with antibacterial effect on copper(I) O<5µm coated fabric samples.

Antibacterial effect was formed as inhibition zones on the fabric coated with copper(I)O|<5µm film after 9 repeated washings with 1,2,3,4-butanetetracarboxylic acid crosslinker. After co-coating with BTCA crosslinker, an inhibition zone diameter of (33.27 mm) against *K.pneumoniae* bacteria was obtained after 5 washes, (33.17 mm) after 10 repeated washes, and (33.04 mm) after 15 and 20 repeated washes.

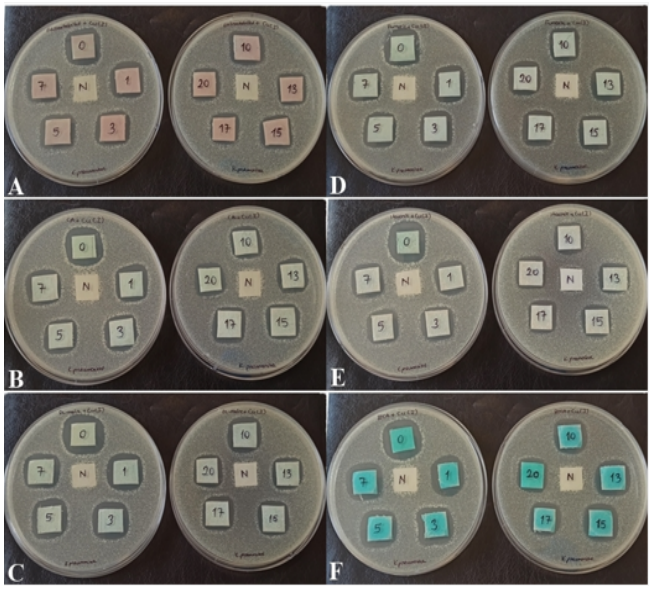


Figure 7. Inhibition zones of coated/uncoated Cu(I)O<5µm fabrics after repeated washings against *K.pneumoniae* (A: Ethylmetacrylate, B: CA, C: DL-Malic, D: Fumaric, E: Itaconic, F: BTCA)

As a result, the antibacterial effectiveness of fabric samples coated with copper(I)O<5µm particles after twenty repeated washings against *K.pneumoniae* bacteria, an 8.32% decrease in the inhibition zone of the fabric samples coated with 1,2,3,4-butanetetracarboxylic crosslinker and a zone diameter of (33.04 mm) were obtained (Figure 7f).

Besides, 12.73 % reduction in the inhibition zone of fabric samples coated with copper(I)O<5µm particles with citric acid cross-linker and 16.07 % reduction in the antibacterial zone diameter with itaconic acid crosslinker were achieved. In order to determine the presence of copper(I)O<5µm film on the surface of cotton fabrics, FT-IR and SEM analyzes were performed.

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Table 2. Inhibition zones of coated/uncoated Cu(I)O<5µm fabrics after wash cycles against *K.pneumoniae*

Fabric No		Ethylmethacrylate	CA	DL-malic	Fumaric	Itaconic	BTCA
Inhibition Zones After Washing (Mean± **SD.mm)	*N	***ND	***ND	***ND	***ND	***ND	***ND
	0	35.03±0.50	36.13±0.76	40.04±0.96	39.03±1.00	36.02±0.98	36.04±1.02
	1	33.36±0.58	36.10±1.00	35.24±0.50	30.57±0.49	35.58±0.69	35.27±0.58
	3	32.23±0.35	36.03±0.70	35.08±0.62	30.40±0.43	35.32±0.60	35.11±0.29
	5	32.13±0.19	34.70±0.93	35.04±1.06	30.33±0.45	35.32±0.39	33.27±0.58
	7	32.09±0.08	34.50±0.53	35.02±0.12	30.23±0.54	35.25±0.52	33.24±0.52
	10	30.46±0.77	33.53±0.46	35.01±0.11	30.17±0.43	35.02±0.12	33.17±0.23
	13	30.39±0.66	33.50±0.53	32.02±0.89	30.17±0.43	32.25±1.05	33.11±0.30
	15	30.36±0.31	33.00±0.85	31.21±0.35	30.14±0.20	30.52±0.50	33.04±0.88
	17	30.29±0.39	32.53±0.80	31.04±0.06	30.07±0.08	30.35±0.56	33.04±0.04
	20	29.46±0.61	31.53±0.80	30.54±0.51	30.03±0.03	30.23±0.23	33.04±0.04

*N: Uncoated fabric, **SD: Standard deviation, ***ND: None diameter
(***ND: None diameter: It means that no antibacterial activity effect observed at the uncoated Cu(I)O<5µm fabrics)

After 20 repeated washing cycles, the fabric samples coated with copper(I)O<5µm+ BTCA showed an antibacterial zone diameter of 33.04 mm against *K.pneumoniae* bacteria (Figure 7f), whereas after the same particle was coated with the same crosslinker, a zone diameter of 32.02 mm was obtained against *S.aureus* bacteria (Figure 8f). Antibacterial activity of washed treated fabrics against gram negative bacteria (*K.pneumoniae*) was greater than that against gram positive bacteria (*S.aureus*). Good antibacterial effects were determined with coated copper(I)O<5µm after 20 repeated washing cycles against *K.pneumoniae* and *S.aureus* (Tables 2 and 3).

The coated cotton fabrics after repeated washing processes against *S.aureus* bacteria was seen in Figure 8 and Table 3.

Antibacterial effect against *S.aureus* bacteria was obtained with BTCA crosslinker, an inhibition zone diameter of (33.41 mm) after 5 washings, an inhibition zone diameter of (32.21 mm) after 10 repeated washings, (32.15 mm) after 15 repeated washings and (32.02 mm) after 20 repeated washings (Figure 8f). As seen in Table 3, the minimum antibacterial zone diameter (30.03 mm) was obtained Cu(I)O<5µm particles with ethylmethacrylate crosslinker after 20 repeated washings against *S.aureus* bacteria.

In addition, after 20 repeated washings of fabric samples coated with copper(I)oxide<5µm particles and BTCA crosslinker, 15.83 % decrease in the inhibition zone diameter and 21.04 % decrease in the antibacterial zone diameter with ethylmethacrylate crosslinker were obtained against *S.aureus* bacteria. In order to determine the presence of copper(I)oxide<5µm film on the surface of cotton fabrics, FTIR and SEM analyzes were performed.

The antibacterial activity of copper(II)O<5µm film coated cotton fabrics after repeated washing processes against *K.pneumoniae* bacteria was shown in Figure 9 and Table 4. After 20 repeated washings of fabric samples coated with Cu(II)O<5µm particles, 13.46 % reduction in inhibition zone diameter was achieved with CA crosslinker. With CA crosslinker, antibacterial zone diameter of (37.01 mm) and (33.06 mm) after 5 washings, (32.29 mm) after 10 washings, (32.09 mm) zone diameter after 15 washings and (32.03 mm) antibacterial zone diameter after 20 repeated washings were obtained against *K.pneumoniae* bacteria (Figure 9b). There are three carboxyl groups in the structure of the CA crosslinker. It formed two ester bonds with the coated fabric samples.

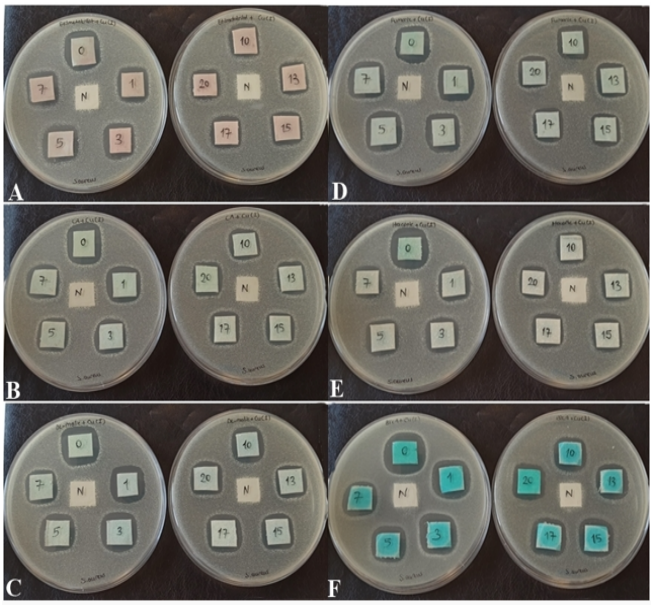


Figure 8. Inhibition zones of coated/uncoated Cu(I)O<5µm fabrics after repeated washings against *S.aureus* (A: Ethylmetacrylate, B: CA, C: DL-Malic, D: Fumaric, E: Itaconic, F: BTCA)

In order to determine the presence of copper(II)O<5µm film on the surface of cotton fabrics, FTIR and SEM analyzes were performed.

The antibacterial efficiency of the washed fabrics after twenty repeated washing cycles, copper(II)O<5µm+CA treated fabric showed the best antibacterial activity for *K.pneumoniae* (32.03 mm) and the same particle coated with the same crosslinker treated fabric showed the best antibacterial for *S.aureus* (31.02 mm) (Figure 9b, Figure 10b). Antibacterial activity of washed treated fabrics against gram negative (*K.pneumoniae*) was greater than that against gram positive bacteria (*S.aureus*). Good antibacterial effects determined with coated copper(II)O<5µm after 20 repeated

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washing cycles against *K.pneumoniae* and *S.aureus* bacteria (Table 4 and Table 5).

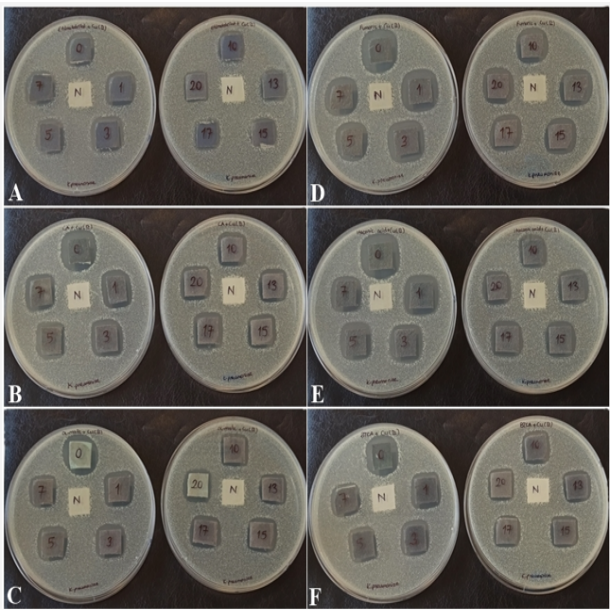


Figure 9. Inhibition zones of coated/uncoated Cu(II)O<5µm fabrics after repeated washings against *K.pneumoniae* (A: Ethylmetacrylate, B: CA, C: DL-Malic, D: Fumaric, E: Itaconic, F: BTCA)

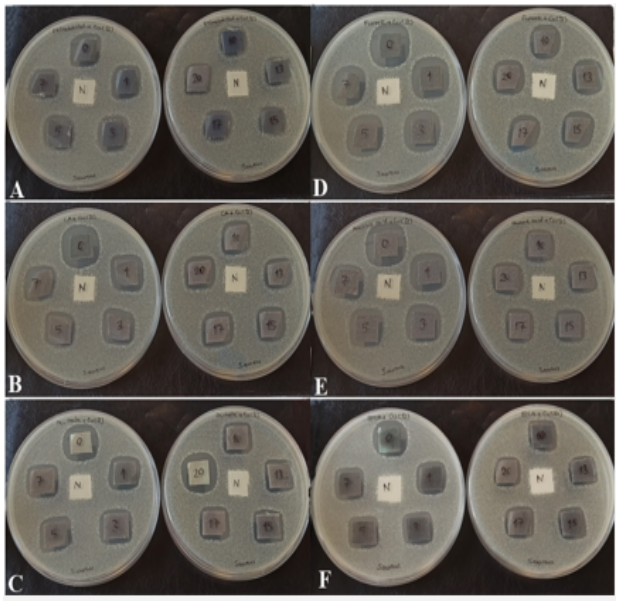


Figure 10. Inhibition zones of coated/uncoated Cu(II)O<5µm fabrics after repeated washings against *S.aureus* (A: Ethylmetacrylate, B: CA, C: DL-Malic, D: Fumaric, E: Itaconic, F: BTCA)

Table 3. Inhibition zones of coated/uncoated Cu(I)O<5µm fabrics after wash cycles against *S.aureus*

Fabric No		Ethylmethacrylateate	CA	DL-malic	Fumaric	Itaconic	BTCA
Inhibition Zones After Washing (Mean±**SD.mm)	*N	***ND	***ND	***ND	***ND	***ND	***ND
	0	38.03±0.50	37.02±0.03	40.10±1.00	35.67±0.53	40.03±1.00	38.04±0.06
	1	35.36±0.60	35.02±0.96	38.13±0.28	35.37±0.61	35.27±0.78	35.11±0.37
	3	32.16±0.18	34.42±0.53	37.03±0.70	35.17±0.23	33.33±1.38	35.01±0.11
	5	32.09±0.23	34.32±0.51	32.40±0.38	35.14±0.35	32.23±0.54	33.41±0.87
	7	32.09±0.14	33.32±0.39	32.37±0.38	35.04±0.38	32.17±0.43	32.42±0.96
	10	32.09±0.12	33.25±0.22	32.17±0.25	34.24±0.52	32.10±0.31	32.21±0.35
	13	31.06±0.08	31.25±1.05	32.00±0.05	33.01±0.83	32.07±0.26	32.21±0.35
	15	30.23±0.29	31.23±0.23	30.67±1.03	30.37±0.61	30.17±0.25	32.15±0.60
	17	30.13±0.12	31.18±0.32	30.53±0.80	30.17±0.23	30.13±0.19	32.04±0.06
	20	30.03±0.11	31.02±0.03	30.20±0.87	30.04±0.04	30.10±0.13	32.02±0.12

*N: Uncoated fabric**,** **SD: Standard deviation, ***ND: None diameter

((***ND: None diameter: It means that no antibacterial activity effect observed at the uncoated Cu(I)O<5µm fabrics)

Tablo 4. Inhibition zones of coated/uncoated Cu(II)O<5µm fabrics after wash cycles against *K.pneumoniae*

Fabric No		Ethylmethacrylate	CA	DL-malic	Fumaric	Itaconic	BTCA
İnhibition Zones After Washing (Mean±**SD.mm)	*N	***ND	***ND	***ND	***ND	***ND	***ND
	0	33.43±0.55	37.01±0.09	35.10±0.09	38.14±0.16	43.13±0.37	35.10±0.09
	1	33.39±0.43	35.20±0.40	34.50±0.53	35.24±0.32	40.17±0.43	34.50±0.53
	3	33.19±0.69	35.03±0.03	32.57±0.70	31.58±0.50	35.33±0.45	32.57±0.70
	5	31.45±0.66	33.06±0.74	31.50±0.53	31.38±0.64	35.27±0.98	31.50±0.53
	7	30.49±0.64	33.03±0.09	31.20±1.23	30.42±0.38	32.03±0.10	31.20±1.23
	10	28.38±0.38	32.29±1.31	30.53±0.58	30.38±0.64	31.23±0.54	30.53±0.58
	13	28.25±1.05	32.13±0.36	30.50±0.53	30.38±0.64	31.23±0.54	30.50±0.53
	15	25.57±0.63	32.09±0.40	30.43±0.43	30.35±0.49	31.07±0.08	30.43±0.43
	17	25.52±0.50	32.07±0.14	30.40±0.38	30.35±0.49	30.50±0.91	30.40±0.38
	20	25.30±0.48	32.03±0.50	30.32±0.39	29.20±1.32	30.10±0.14	30.32±0.39

*N: Uncoated fabric, **SD: Standard deviation,***ND: None diameter

(***ND: None diameter: It means that no antibacterial activity effect observed at the uncoated Cu(II)O<5µm fabrics)

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Table 5. Inhibition zones of coated/uncoated Cu(II)O<5µm fabrics after wash cycles against *S.aureus*

Fabric No		Ethylmethacrylate	CA	DL-malic	Fumaric	Itaconic	BTCA
İnhibition Zones After Washing (Mean± **SD.mm)	*N N	***ND	***ND	***ND	***ND	***ND	***ND
	0	38.03±0.50	37.02±0.03	40.10±1.00	35.67±0.53	40.03±1.00	38.04±0.06
	1	35.36±0.60	35.02±0.96	38.13±0.20	35.37±0.61	35.27±0.78	35.11±0.37
	3	32.16±0.18	34.42±0.53	37.03±0.70	35.17±0.23	33.33±1.38	35.01±0.11
	5	32.09±0.23	34.32±0.51	32.40±0.38	35.14±0.35	32.23±0.54	33.41±0.87
	7	32.09±0.14	33.32±0.39	32.37±0.38	35.04±0.38	32.17±0.43	32.42±0.96
	10	32.09±0.12	33.25±0.22	32.17±0.25	34.24±0.52	32.10±0.31	32.21±0.35
	13	31.06±0.08	31.25±1.05	32.00±0.05	33.01±0.83	32.07±0.26	32.21±0.35
	15	30.23±0.29	31.23±0.23	30.67±1.03	30.37±0.61	30.17±0.25	32.15±0.60
	17	30.13±0.12	31.18±0.32	30.53±0.80	30.17±0.23	30.13±0.19	32.04±0.06
	20	30.03±0.11	31.02±0.03	30.20±0.87	30.04±0.04	30.10±0.13	30.20±0.12

*N: Uncoated fabric, **SD: Standard deviation, ***ND: None diameter

(***ND: None diameter: It means that no antibacterial activity effect observed at the uncoated Cu(II)O<5µm fabrics)

The antibacterial activity of copper(II)O<5µm film coated cotton fabrics after repeated washing processes against *S.aureus* bacteria was shown in Figure 10 and Table 5. Fabric samples coated with Cu(II)O<5µm particle and CA cross-linker showed the best antibacterial activity against *S.aureus* bacteria at (31.02 mm) (Figure 10b). In this study, copper(II)oxide demonstrated significant reduction in antibacterial zone diameter with itaconic acid crosslinker after 20 repeated washings against *K.pneumoniae* and *S.aureus* bacterias (Table 4 and Table 5).

Fabric samples coated with Cu(II)O<5µm particles with CA cross-linker had an antibacterial zone diameter of (34.32 mm) against *S.aureus* bacteria after 5 washings, a zone diameter of (33.25 mm) after 10 washings, a zone diameter of (31.23 mm) after 15 washings and an inhibition zone diameter of (31.02 mm) after 20 washings. After 20 repeated washings of fabric samples coated with Cu(II)O<5µm particles with CA cross-linker against *S.aureus* bacteria, 16.21 % reduction in inhibition zone diameter was achieved. The maximum antibacterial zone diameter was achieved with CA cross-linker.

In order to determine the presence of copper(II)O<5µm film on the surface of cotton fabrics, FT-IR and SEM analyzes were performed.

In the coating of textile surfaces with polymers, the fabric surface must be homogeneously coated to obtain good antibacterial property [37].

In this study, the antibacterial activity rate of fabrics coated with CuO microparticles after washing was obtained to be slightly lower than without washing. It was related to the decrease in the amount of CuO (copper(II) oxide) and Cu_2O (copper(I) oxide) on the fabric surface and was due to the dissolution of Cu^{+} and Cu^{+2} ions in the washing solution. This finding was similar to the result of another study [38]. Thus, repeated washings did not significantly affect the antibacterial behavior of fabrics functionalized with CuO NPs [38]. And also, this situation explained by the binding of antibacterial inorganic metal oxides and carboxylic acid crosslinkers to the textile fabric samples with binders [39].

4. CONCLUSIONS

In this study, copper(I)oxide<5µm and copper(II) oxide <5µm particles, five different structures of polycarboxylic acid and ethylmethacrylate crosslinkers were used for the antibacterial and washing resistance properties of cotton fabrics. Microparticles rather than nanoparticles were used to avoid possible health issues with nanoparticles. After repeated washings, the antibacterial properties of cotton fabric samples coated with copper(II)oxide and copper(I) oxide<5µm particles were compared. The main results are summarized as follows:

The structural and morphological properties of copper(I) oxide <5µm and copper(II)oxide<5µm coated fabrics were presented. The homogen coating of the cotton fabrics with copper(II)oxide <5µm and copper(I)oxide<5µm were observed by FT-IR and SEM.

As seen in FT-IR results, the ester carbonyl bond, ester and aldehyde groups were illustrated at 1722 cm^{-1} peak and at 1736 cm^{-1} peak in cotton fabrics coated with copper(I) oxide<5µm and copper(II)oxide<5µm, respectively. Also good antibacterial zone diameter was obtained after 20 repeated washing cycles.

This study demonstrated that the coated cotton fabrics showed antibacterial efficiency against *S.aureus* and *K.pneumoniae* bacteria even after 20 repeated washings. When assessed for antibacterial activity by disc diffusion test method, the copper(I)oxide<5µm particles and BTCA crosslinker treated fabric samples showed a maximum inhibitory effect against *K.pneumoniae* with inhibition zone of 33.04 mm followed by *S.aureus* with inhibition zone of 32.02 mm and are shown in the Figure 7f and Figure 8f, respectively. Due to BTCA crosslinker was an expensive product, CA (citric acid) crosslinker was used to obtain antibacterial properties.

After 20 repeated washings of cotton fabric samples coated with copper(I)oxide<5µm particles with CA cross-linker, an antibacterial zone diameter (31.02 mm) was obtained against *S.aureus* bacteria. In addition, after 20 repeated washings of fabric samples coated with copper(I)oxide

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<5µm particle and CA crosslinker, 16.21 % decrease in inhibition zone diameter and 24.80 % decrease in inhibition zone diameter with itaconic acid (IA) crosslinker were obtained.

The maximum antibacterial zone diameter was obtained copper(II)oxide<5µm particle with CA cross-linker after 20 repeated washings against *K.pneumoniae* bacteria. At the same time, after 20 repeated washings of fabric samples coated with copper(II)oxide<5µm particles and CA cross-linker, 13.46 % decrease in the inhibition zone diameter was obtained, and 30.21 % decrease in the inhibition zone diameter of the same particle with itaconic acid crosslinker was obtained. With CA crosslinker, antibacterial zone diameter (33.06 mm) after 5 washings, (32.29 mm) after 10 washings, (32.09 mm) zone diameter after 15 washings and (32.03 mm) antibacterial zone diameter after 20 repeated washings were obtained against *K.pneumoniae* bacteria (Figure 9b). Fabrics without any treatment had negative percent reduction test values because the final cell count was much higher than before. Initial cell count as it was not bactericidal. The results were found to be zero. CA crosslinker formed two ester bonds with the coated cotton fabric due to the three carboxyl groups in the structure of this crosslinker.

In this study, high zone diameter was obtained in fabric samples pretreated with 30g/L CA and 12g/L sodium hypophosphite and then coated with copper(I)oxide<5µm and copper(II)oxide<5µm particles with CA crosslinker. The results showed that the crosslinker structure affected the zone diameter after repeated washing cycles. Different structures of crosslinkers used in coating process provided good antibacterial activity to the washing cycles. The main antibacterial effect was due to drying of the bacteria onto the copper(I)oxide and copper(II)oxide particles and the presence of dissolved Cu^{+} and Cu^{+2} ions. The efficiency was tested against *S.aureus* and *K.pneumoniae* bacteria. As a result of this study, it was determined that antibacterial textile was most effective against *K.pneumoniae* bacteria.

Cotton fabric samples coated with copper(I)oxide<5µm particle and CA crosslinker showed high antibacterial activity after repeated washing cycles.

Application of cationization and the binding of copper(I)oxide<5µm and copper(II)oxide<5µm particles with crosslinkers to the 100 % cotton fabric samples with binders increased the antibacterial activity.

As a conclusion, the structure of crosslinkers and the polycarboxylic acid crosslinkers bonded to cellulose via ester linkage have positive effect on improving the washing resistance of coated antibacterial fabric samples.

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Declaration

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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