INFLUENCE OF 1,2,3,4-BUTANETETRACARBOXYLIC ACID CONCENTRATION ON *IN SITU* SYNTHESIS OF CuO/Cu_2O NANOPARTICLES ON COTTON AND VISCOSE RAYON FABRICS

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This study discusses the possibility of *in situ* synthesis of Cu-based nanoparticles (NPs) on cotton and viscose rayon fabrics previously modified with 1,2,3,4-butanetetracarboxylic acid (BTCA) of different concentrations, with the aim to obtain antibacterial protection. The changes in the chemical structure of the fibers caused by the modification with BTCA were assessed by FTIR spectroscopy. The higher the concentration of the applied BTCA, the larger the amounts of free carboxyl groups in both fabrics. AAS analysis showed that the samples modified with higher concentration of BTCA provided larger Cu^{2+}-ions uptake and consequently, higher content of Cu after Cu^{2+}-ions reduction. The presence of Cu-based NPs on the fabrics was confirmed by FESEM and EDS analyses. XRD analysis revealed that NPs appeared as a mixture of CuO and Cu_2O. Synthesized NPs imparted excellent antibacterial activity to both fabrics against *E. coli* and *S. aureus*, including methicillin-resistant *S. aureus*.

Keywords: cotton, viscose, Cu-based nanoparticles, BTCA, antimicrobial activity, controlled release

INTRODUCTION

The development of new antimicrobial textile materials, particularly for medical use, has been gaining significant scientific attention and industrial acceptance for a long time. Among various antimicrobial agents, such as metal salts, quaternary ammonium compounds, polyhexamethylene biguanides, triclosan, N-halamine, N-containing reagents with polycarboxylic acids and peroxyacid, metal (Au, Ag, Cu) and metal oxide (TiO_2, ZnO, CuO, Cu_2O) nanoparticles (NPs) have been proven to be efficient in imparting antimicrobial properties to textile materials.[1-7] Ag NPs are widely exploited as an efficient antimicrobial agent against various microorganisms.[3,8-10] However, Ag NPs demonstrated shortcomings mainly reflected in the possibility to develop argyria (blue-grey coloration of the skin) after prolonged therapy and the appearance of Ag-resistant bacteria.[11]

Lately, the impregnation of textiles with NPs based on Cu and/or its oxides has come into the focus of many research groups due to their excellent antimicrobial activity against numerous bacteria and relative inexpensive precursors, compared to those applied in the synthesis of Ag NPs.[12-24] Cu-based NPs could be incorporated into textile materials by *ex situ* and *in situ* methods.[19] *Ex situ* or indirect methods include the preparation of Cu-based NPs dispersions and loading textile substrates with NPs.[20,25,26] However, the dominant methods for the fabrication of textile nanocomposites with Cu-based NPs are *in situ* syntheses, with lower consumption of chemicals and better fastness properties, compared to *ex situ* methods.[19] This

approach relies on the adsorption of Cu^{2+}-ions on textile substrates and their *in situ* reduction with appropriate reducing agents, such as sodium borohydride, hydrazine, hydroxyl amine, glucose, ascorbic acid, *etc*.[15-17,27] Recently, da Costa *et al*. performed *in situ* reduction of Cu^{2+}-ions on cotton fabric using an ascrorbic acid or hydroxylamine as reducing agent, along with polyvinylpyrrolidone or lactose as protective agent when Cu_2O NPs have been formed.[28] In order to enhance the Cu^{2+}-ion uptake and hence, the final content of Cu-based NPs, carboxyl groups are often applied to textiles with cellulosic fibers by coating with an adequate polymer or by chemical modification.[13,17,21,22] Errokh *et al*. applied TEMPO-mediated oxidation of cotton fabric for the formation of carboxylate groups, necessary for binding of Cu^{2+}-ions, which were further reduced in an alkaline solution of hydrazine and hydroxylamine.[17] Yang *et al*. proposed a different approach, relying on the synthesis of Cu/CuO NPs on cotton fibers previously modified with dopamine, which comprises amino groups.[29]

Recently, we have successfully fabricated antibacterial cotton fabric modified with various polycarboxylic acids (succinic, cytric, and 1,2,3,4-butanetetracarboxylic) and Cu_2O/CuO NPs, which could be utilized for wound dressings.[22] The modification of cotton fabrics with polycarboxylic acids induced an improved uptake of Cu^{2+}-ions and consequently, the generation of larger amounts of NPs on the fiber surface and better antibacterial performance.[22] Taking into account that cotton fabric modified with 1,2,3,4-butanetetracarboxylic acid (BTCA) ensured higher content of NPs, compared to other investigated acids, the intention of the present work was to broaden the research and to explore the influence of initial BTCA concentration on the fabrication of Cu-based NPs on cotton and viscose rayon fabrics, which can be considered as the most exploited wound dressing materials. Viscose fiber is the most important substitute for cotton due to its excellent hygroscopicity, wettability, sorption capacity, breathability *etc*.[30] The antibacterial activity of fabricated textile nanocomposites was tested against *E. coli*, *S. aureus* and methicillin-resistant *S. aureus* as one of the most common antibiotic-resistant pathogens that cause nosocomial and community infections. Antifungal activity was tested against yeast *C. albicans*. The release of Cu^{2+}-ions in physiological saline solution was also explored since the controlled release is one of the major precautions for efficient wound dressing material.

EXPERIMENTAL

Preparation of the fabrics

Desized and bleached cotton (CO) woven fabric (117.5 g/m^2, 52 picks/cm, 27 ends/cm, thickness of 0.26 mm) and viscose rayon (CV) fabric (107.8 g/m^2, 44 picks/cm, 34 ends/cm, thickness of 0.27 mm) were used as substrates. The fabrics were cleaned in a bath containing 0.05% nonionic washing agent Felosan RG-N (Bezema) at a liquor-to-fabric ratio of 50:1. Washing of both fabrics was performed at 50 ^oC for 15 min. Afterwards, the fabrics were rinsed first with warm water (50 ^oC) and then thoroughly with cold water. They were left to dry at room temperature.

Modification of the fabrics with BTCA

The modification of CO and CV fabrics with BTCA was carried out by immersion of 0.50 g of the samples in 20 mL of 4 w/v% and 6 w/v% BTCA aqueous solutions in the presence of 0.8 g and 1.24 g of the catalyst sodium hypophosphite (SHP), respectively. After one hour, the samples were dried at 80 ^oC for 3 min and cured at 170 ^oC for 3 min. The samples were then rinsed in distilled water and dried at room temperature. CO and CV fabrics modified with 4 w/v% and 6 w/v% BTCA are marked as CO+BTCA4, CO+BTCA6, CV+BTCA4 and CV+BTCA6, respectively.

In situ synthesis of Cu-based NPs

0.50 g of the sample (CO+BTCA4, CO+BTCA6, CV+BTCA4 and CV+BTCA6) was soaked in 25 mL of 10 mM solution of $CuSO_4$ for 2 h. In order to eliminate the excessive Cu^{2+}-ions, the samples were rinsed three times (1 min) with distilled water. 0.050 g of the sodium borohydride ($NaBH_4$) was dissolved in 25 mL of 0.1 mM NaOH solution and the samples were immediately dipped into the solution at room temperature. After 30 min of the reduction, the samples were thoroughly rinsed with deionized water and left to dry at room temperature. These samples are labeled as CO+BTCA4+Cu, CO+BTCA6+Cu, CV+BTCA4+Cu and CV+BTCA6+Cu.

Characterization

Determination of carboxyl groups content in CO and CV fabrics modified with BTCA

Determination of carboxyl groups content in CO+BTCA4, CO+BTCA6, CV+BTCA4 and CV+BTCA6 fabrics was based on the calcium acetate method described by Kumar and Yang[31] and modified by Praskalo *et al*.[32] 0.50 g of the sample was treated with 0.01 M HCl for 1 h, followed by washing with distilled water. In the next step, the samples were soaked into 30 mL of 0.25 M calcium acetate and 50 mL of distilled water. After 2 h of reaction with continuous shaking, 30 mL aliquots were titrated with

0.01 M NaOH using phenolphthalein as an indicator. The carboxyl group content (mmol/g) was calculated in accordance with:

$$\text{COOH} = \frac{\frac{80}{30}\cdot 0.01M\cdot V(NaOH)}{m\cdot\left(1-\frac{w}{100}\right)} \quad (1)$$

where 0.01 M is the concentration of NaOH, V(NaOH) is the volume (mL) of NaOH solution used for titration, m is the weight of treated fabrics (g) and w is the moisture content (%).

FTIR analysis

Fourier transform infrared (FTIR) spectra of the control fabrics, the fabrics modified with BTCA and the fabrics modified with BTCA after 30 min long immersion in the 0.1 M NaOH solution were recorded in the ATR mode, using a Nicolet 6700 FTIR Spectrometer (Thermo Scientific) at 2 cm^{-1} resolution, in the wavenumber range from 500 to 4000 cm^{-1}.

FESEM and EDS analyses

The morphology of the control fibers and the fibers impregnated with Cu-based NPs was analyzed by field emission scanning electron microscopy (FESEM, Tescan Mira3 TC). The samples were coated with a thin layer of Au prior to analysis. Energy-dispersive X-ray spectroscopy (EDS) of the fibers impregnated with Cu-based NPs was performed using a JEOL JSM 5800 SEM with a SiLi X-ray detector (Oxford Link Isis series 300, UK).

XRD analysis

The XRD powder patterns were acquired using a Philips PW 1050 powder diffractometer with Ni-filtered Cu-K_λ radiation (λ = 1.5418 Å). The diffraction intensity was measured by the scanning technique (a step size of 0.05° and a counting time of 50 s per step).

AAS analysis

The amounts of adsorbed Cu^{2+}-ions on CO+BTCA4, CO+BTCA6, CV+BTCA4 and CV+BTCA6 fabrics from $CuSO_4$ solution were calculated on the basis of the concentration of residual Cu^{2+}-ions in the solution, which was measured using a Spectra AA 55 B (Varian) atomic absorption spectrometer (AAS). The Cu^{2+}-ions uptake (q) was calculated according to:

$$q = \frac{(C_{Cu0} - C_{Cu})\cdot V}{m} \quad (2)$$

where C_{Cu0} is the initial concentration of Cu^{2+}-ions in the solution (mol/L), C_{Cu} is the concentration of Cu^{2+}-ions in the solution after 2 h long adsorption (mol/L), V is the volume of the $CuSO_4$ solution (L) and m is the weight of CO and CV fabrics (g).

The total Cu content in CO and CV fabrics after the reduction process was also determined by AAS. These fabrics were immersed into a 1:1 HNO_3 solution for 24 h.

Antimicrobial test

The antimicrobial activity of the fabrics was tested against *E. coli* ATCC 25922, *S. aureus* ATCC 25923, methicillin-resistant *S. aureus* (MRSA) ATCC 43300 and yeast *C. albicans* ATCC 24433, using a standard method for determining the antimicrobial activity of immobilized antimicrobial agents under dynamic contact conditions ASTM E 2149-01 (2001). The inocula were prepared by growing the microorganism in 3 mL of tryptic soy broth (Bacto™, Becton, Dickinson and Company, USA) at 37 °C. Erlenmeyer flasks containing 50 mL of sterile physiological saline solution (pH 7.2) were inoculated with 0.5 mL of microbial inocula (exponential stage of growth). Per one gram of the control CO and CV fabrics, and CO and CV fabrics loaded with Cu-based NPs (previously treated with UV light for 30 min and cut into small pieces) were shaken in flasks for 2 hours. 1 mL aliquots from the flask were diluted with physiological saline solution and placed onto a tryptic soy agar (Difco™, Becton, Dickinson and Company, USA). After 24 h of incubation at 37 °C, the zero time and two hour counts of viable bacteria/yeast were made. Time zero counts (initial number of bacteria/yeast colonies) were made by removing 1 mL aliquots from the inocula, which were diluted with physiological saline solution and placed onto a tryptic soy agar.

Cu^{2+}-ions release study was performed by immersing 0.25 g of fabricated nanocomposites into 25 mL of physiological saline solution (9 g/L NaCl) at 37 ºC under static conditions. The concentration of released Cu^{2+}-ions was measured after 1, 3, 6 and 24 hours by AAS. All the experiments were done in triplicate.

RESULTS AND DISCUSSION

Chemical and morphological characterisation of nanocomposite material

Chemical changes induced by the modification of CO and CV fabrics with BTCA were assessed by FTIR spectroscopy. Figure 1a shows the FTIR spectra of CO, CO+BTCA6 and CO+BTCA6 immersed into NaOH solution (CO+BTCA6+NaOH). The FTIR spectra of CV, CV+BTCA6 and CV+BTCA6 immersed into NaOH solution (CV+BTCA6+NaOH) are presented in Figure 1b. The bands characteristic of cellulose are clearly seen in all the spectra. The appearance of the band with a peak centered at 1720 cm^{-1} in the spectra of CO+BTCA6 and CV+BTCA6 fabrics indicates the formation of ester bonds between the hydroxyl groups of cellulose and the carboxyl groups of BTCA.[33] The immersion of the CO+BTCA6 and CV+BTCA6 samples into 0.1 M NaOH solution resulted in the formation of a new band centered at 1565 cm^{-1}.[34]

This band is assigned to the carboxylate groups, which were formed due to the deprotonation of free carboxyl groups. The existence of both bands at 1720 cm^{-1} and 1565 cm^{-1} in these spectra proved that BTCA was bound to cellulose by ester bonds, but a certain number of carboxyl groups of the BTCA remained free. The possible mechanism of esterification of cellulose fibers with BTCA is illustrated in Figure 2.[35-37] It was suggested that the esterification of cellulose fibers with BTCA involves the formation of cyclic anhydrides in the first step, which subsequently react with the hydroxyl groups of cellulose fibers establishing the ester.[35-37]

The total amount of free carboxyl groups in CO+BTCA4, CO+BTCA6, CV+BTCA4 and CV+BTCA6 samples was determined titrimetically. The results presented in Table 1 indicate that the number of free carboxyl groups on the CO and the CV fabrics depends on the concentration of applied BTCA solution. The higher the BTCA concentration, the larger the content of free carboxyl groups in the samples. Obviously, the influence of BTCA concentration was more pronounced in the case of CO samples. Our previous report showed that the free carboxyl groups content in the CO fabric cross-linked with 10 w/v% solution of BTCA under the same experimental conditions was by 30% and 82% higher compared to CO+BTCA6 and CO+BTCA4 samples, respectively.[22]

A larger number of free carboxyl groups as potential sites for binding of Cu^{2+}-ions provided better uptake of Cu^{2+}-ions from $CuSO_4$ aqueous solution and, eventually, larger amounts of copper after the reduction process in alkaline solution of $NaBH_4$ (Table 1). The Cu content in the CO+BTCA6+Cu and CV+BTCA6+Cu samples increased by 75% and 45%, compared to the CO+BTCA4+Cu and CV+BTCA4+Cu samples, respectively. The results shown in Table 1 are in line with recent reports.[21,22,38] It is evident that the total Cu content in the impregnated CO and CV fabrics is almost equal for the same concentrations of applied BTCA. The total Cu content found in the CO+BTCA6+Cu sample (5.65 mg/g) is equivalent to the Cu content in the CO sample modified with chloroacetic acid prior to the fabrication of Cu NPs in a similar manner (5.70 mg/g).[13]

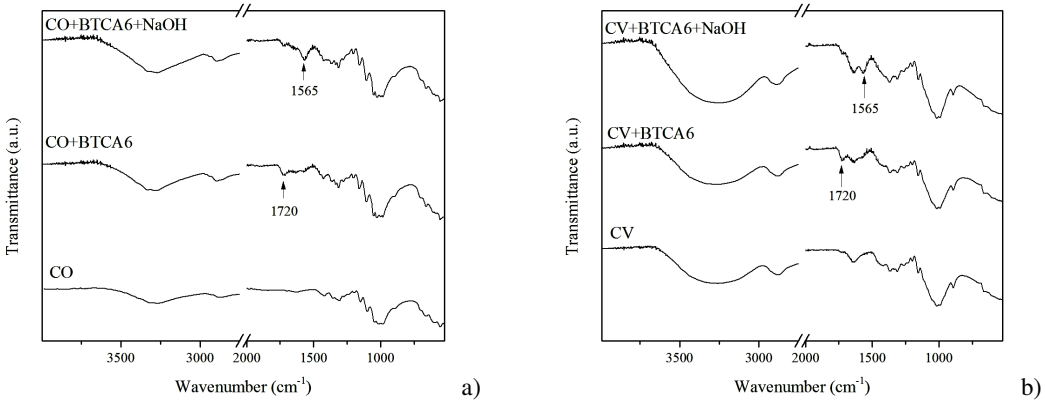


Figure 1: FTIR spectra of (a) control CO sample, CO+BTCA6+Cu sample and Co+BTCA6+Cu sample immersed into 0.1 N NaOH solution; and (b) control CV sample, CV+BTCA6+Cu sample and CV+BTCA6+Cu sample immersed into 0.1 N NaOH solution

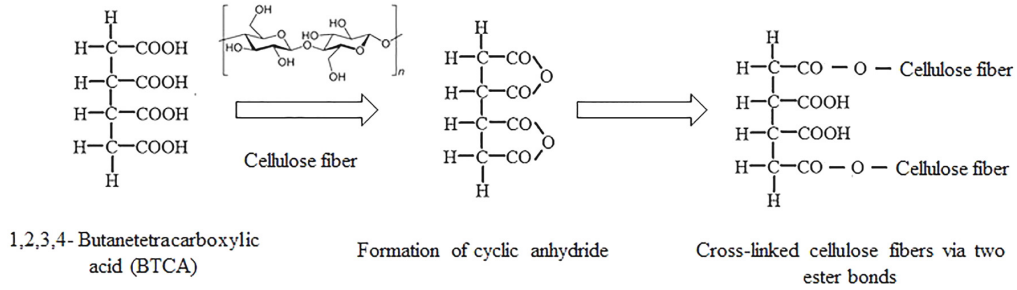


Figure 2: The schematic illustration of esterification of cellulose fibers with BTCA

Table 1
Free carboxyl group content, Cu^{2+}-ion uptake and total content of Cu after Cu^{2+}-ion reduction in CO and CV fabrics modified with BTCA

Sample	Carboxyl group content (μmol/g)	Cu^{2+}-ion uptake (μmol/g)	Total content of Cu after reduction (μmol/g)
CO+BTCA4	453±21	56±6.4	51±1.4
CO+BTCA6	635±54	101±6.1	89±3.4
CV+BTCA4	519±13	62±5.1	58±4.1
CV+BTCA6	580±61	85±6.7	84±5.5

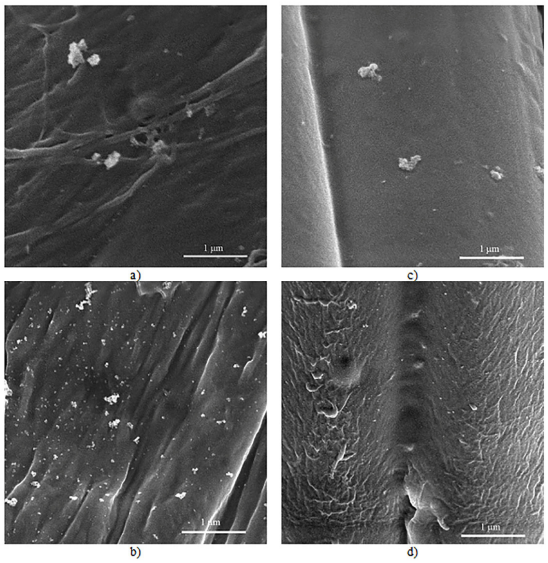


Figure 3: FESEM images of (a) CO+BTCA4+Cu, (b) CO+BTCA6+Cu, (c) CV+BTCA4+Cu and (d) CV+BTCA6+Cu fibers

Recently, Emam *et al.*[19] synthesized Cu_2O micro-needles on CV fabric by two step synthesis: alkalization and sorption of Cu^{2+}-ions. In comparison with these results, our synthesis route provided higher Cu content on the CV fabric for the same concentration of precursor salt.

The surface morphology of CO and CV fibers after *in situ* synthesis of Cu-based NPs was assessed by SEM analysis (Fig. 3). Figure 3 reveals uneven distribution of synthesized NPs across the surface of all modified samples. The presence of agglomerated NPs is clearly visible on all the samples. As expected, larger amounts of NPs were present on the surface of the samples that were cross-linked with BTCA solutions of higher concentration (Fig. 3b and 3d). The SEM images are in good correlation with the results summarized in Table 1. The presence of Cu on the surface of CO and CV fibers modified with BTCA and Cu based NPs is confirmed by EDS analysis. The peaks corresponding to Cu are clearly visible in all EDS spectra (Fig. 4).

Each synthesis step induced a visible color change of the samples. The adsorption of Cu^{2+}-ions resulted in a color change of the samples from white to blue. Afterwards, the reduction step altered the color of the samples to dark brown/black. The color obtained after reduction with sodium borohydride was attributed to the formation of metallic Cu.[13] The samples gradually became green during the drying process in the air. The observed color transformation is in agreement with literature data.[13,21,22] The color yield of the samples depends on the concentration of BTCA, *i.e.* the amounts of synthesized Cu-based NPs. In other words, the larger the amounts of fabricated Cu-based NPs, the greener the samples. The instability of metallic copper based nanostructures synthesized with sodium borohydride as a reducing agent is reflected in rapid oxidation when exposed to air.[39] It could be avoided by drying/storing the samples in inert atmosphere[27] or by protection with capping agents, which form compact monolayers on the NPs surface.[40]

XRD analysis was employed to determine the composition of NPs on the surface of CO and CV fabrics. The XRD patterns of the CO, CO+BTCA6+Cu, CV and CV+BTCA6+Cu fabrics are shown in Figure 5. The shoulders (marked with rectangles) at 2θ~35.5° and 38.7° in the diffractograms of both composites indicated the formation of the (-111) and (111) crystal planes of base centered monoclinic crystal phase of CuO (ICDD 01-089-5899). A broad peak (shoulder) at 2θ~29.5° and the low intensity peak at 2θ~37.2° are assigned to the shifted peak characteristic for the (110) and (111) crystal plane of cubic Cu_2O (ICDD 01-077-0199), respectively.

The XRD patterns clearly implied that NPs are present on the CO and CV fiber surface as a mixture consisting of CuO and Cu_2O crystalline structures. It is interesting to note that the NPs synthesized on the TEMPO modified CO fabric in the same manner contained the mixture of metallic Cu and Cu_2O.[18]

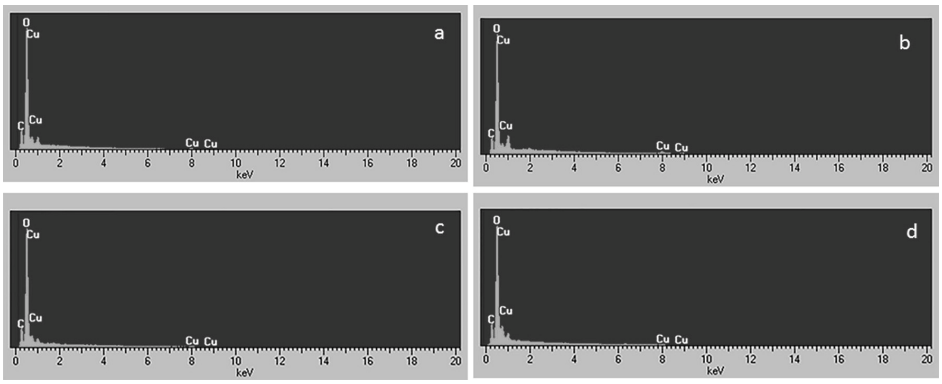


Figure 4: EDS spectra of (a) CO+BTCA4+Cu, (b) CO+BTCA6+Cu, (c) CV+BTCA4+Cu and (d) CV+BTCA6+Cu fibers

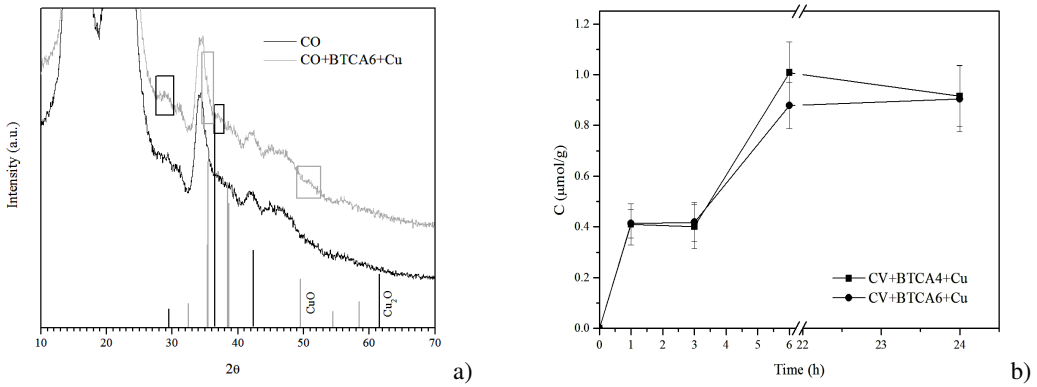


Figure 5: XRD patterns of (a) Co and Co+BTCA6+Cu and (b) CV and CV+BTCA6+Cu samples

Antimicrobial activity of nanocomposite material

The antimicrobial activity tests were carried out on the CO and CV fabrics modified with BTCA and fabrics additionally impregnated with CuO/Cu_2O NPs. The CO and CV fabrics modified with BTCA did not show any antimicrobial activity. The results given in Table 2 demonstrate that all the samples modified with CuO/Cu_2O NPs ensured maximum reduction of the number of the tested bacteria. Apparently, there is no significant difference in antimicrobial activity between impregnated CO and CV fabrics. It should be stressed that these nanocomposites exhibited very strong antibacterial activity even against MRSA, which is more problematic for treatment than antibiotic-susceptible pathogens. In hospitalized and immuno-compromised patients, bacterial infections, especially infections caused by antibiotic-resistant bacteria, are one of the leading causes of morbidity and mortality. Furthermore,

the treatment of bacterial infections could be complicated due to the formation of biofilms, agglomerates of bacterial colonies that adhere to a surface, and resist traditional means of killing by avoiding contact with antibiotics.[41] Therefore, alternative solutions are required. The obtained results open new avenues for further research as small amounts of CuO/Cu_2O NPs on CO or CV fabrics offer intrinsic bactericidal activity against the investigated antibiotic-resistant bacteria.

However, the synthesized samples did not provide antifungal activity against the tested yeast. Obviously, the Cu content in all the samples was not sufficient for achieving the desired antifungal protection. Based on the results presented in Tables 1 and 2, it can be suggested that approximately 50 µmol of Cu per gram of CO or CV fabric was sufficient for the desired level of antibacterial protection, even against MRSA. On the other hand, for imparting antifungal protection to these fabrics, more than 90 µmol/g of Cu is required. The obtained results are comparable with the literature data. Emam *et al*.[27] showed that Cu_2O-containing lyocell fibers with Cu content of 17.61 µmol/g provided 99.8% reduction of *S. aureus*. Later, Emam *et al*. reported that viscose fibers modified with Cu_2O micro-needles did not reach maximum antibacterial (*E coli* 48% and *S. aureus* 56%) and antifungal (*C. albicans* 38% and *A. niger* 36%) reduction, even with Cu content of 68 µmol/g.[16]

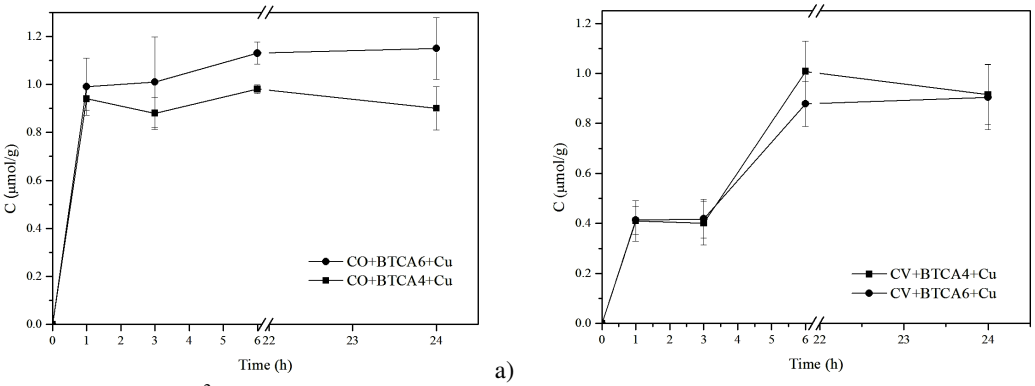
The general mechanism of antimicrobial activity of copper and copper oxide NPs has not been completely understood yet. Several hypotheses can be found in the literature.[13] Some studies propose the same mechanism of antimicrobial action as the one assumed for Ag NPs.[42] Silver or copper ions released from NPs react with negatively charged bacterial cell wall, leading to protein denaturation and cell death.[42] It is difficult to distinguish microbial activity between the NPs and the ions released from the NPs.[42] Another approach assumes that Cu^{2+}-ions released from NPs may attack the DNA molecules and destroy the helical structure by reacting with nucleic acid.[42] It is also reported that characteristic organism-metal particle surface interactions may cause the contact killing, which further leads to bacterial cell death.[43,44] Hong *et al*. suggested that Cu induced peroxidation of unsaturated fatty acid of cytoplasmic membrane results in membrane depolarization, inhibition of respiration and finally cell death.[44] On the contrary, Ballo *et al*.[45] implied that oxidative damage of the cytoplasmic membrane did not have a primary role in metal contact killing.

Release study

Keeping in mind that the fabricated nanocomposites would be potentially applied as wound dressing materials, it was necessary to investigate the release of Cu^{2+}-ions. The cumulative release of Cu^{2+}-ions in the physiological saline solution is presented in Figure 6. Figure 6a reveals that the release of Cu^{2+}-ions was the fastest during the first hour in the case of both CO+BTCA4+Cu and CO+BTCA6+Cu samples. Subsequently, the release of Cu^{2+}-ions slowed down. Similar release profiles for TEMPO oxidized CO fabric impregnated with Cu/Cu_2O NPs and CO fabric modified with succinic acid and CuO/Cu_2O NPs were reported.[18,19] The CV+BTCA4+Cu and CV+BTCA6+Cu samples exhibited considerably different release profiles (Fig. 6b). Similar amounts of Cu^{2+}-ions leached out from CV+BTCA4+Cu and CV+BTCA6+Cu within the whole investigated period. Approximately 98% of Cu remained on the CO and CV fabric after 24 h of release, indicating that stabile nanocomposites have been fabricated.

Table 2
Antimicrobial activity of CO and CV fabrics impregnated with CuO/Cu_2O NPs

Sample	*E. coli*	*S. aureus*	*S. aureus* (MRSA)	*C. albicans*
	Number of microbial colonies (CFU)			
Inoculum	4.0×10^5	1.1×10^5	$3.1\ 10^8$	3.0×10^5
Control CO	1.5×10^5	6.6×10^4	$2.07\ 10^5$	1.1×10^5
CO+BTCA4+Cu	65	730	30	1.5×10^5
CO+BTCA6+Cu	<10	<10	20	9.1×10^4
Inoculum	$4.4\ 10^5$	$7.0\ 10^4$	$3.1\ 10^7$	3.0×10^5
Control CV	4.3×10^5	6.8×10^4	$1.51\ 10^5$	1.5×10^5
CV+BTCA4+Cu	<10	<10	<10	6.7×10^4
CV+BTCA6+Cu	<10	<10	<10	5.2×10^4



a) b)

Figure 6: Cu^{2+}-ion release from CO and CV fabrics impregnated with CuO/Cu_2O NPs into physiological saline solution

Taking into account that leaching of metal ions from fibrous nanocomposites is difficult to control and, in most cases, it leads to an overloading of the release medium, fabricating stabile fibrous nanocomposites with immobilized CuO/Cu_2O NPs was desirable.[10] It should be emphasized that all the fabricated nanocomposites ensured controlled release of Cu^{2+}-ions within a short time interval (less than 24 h), which is sufficient for providing the antibacterial activity necessary for preventing infections, even against MRSA strains.

CONCLUSION

Cross-linking of cotton and viscose rayon fabrics with BTCA imparted the free carboxyl groups necessary for an uptake of Cu^{2+}-ions. The application of higher concentration BTCA solutions brought about a larger uptake of Cu^{2+}-ions and the fabrication of larger amounts of nanoparticles on both samples. The total content of Cu in both fabrics was similar after reduction. FESEM analysis proved that larger amounts of nanoparticles have been synthetized on the surface of cotton and viscose fiber modified with the BTCA solution of higher concentration. The XRD measurement of impregnated CO and CV fabrics revealed that the formed nanoparticles are present on the fibers as a mixture of CuO and Cu_2O. The amounts of Cu-based nanoparticles on all the studied cotton and viscose fabrics was sufficient for obtaining 99.9% reduction of *E. coli*, *S. aureus* and methicillin-resistant *S. aureus*. In spite of their excellent antibacterial activity, the synthesized nanocomposites did not provide any antifungal activity against *C. albicans*. All the tested fabrics ensured controlled release of Cu^{2+}-ions in the physiological saline solution, which is required for wound dressings.

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REFERENCES

[1] Y. Gao and R. Cranston, *Text. Res. J.*, **78**, 60 (2008), https://doi.org/10.1177/0040517507082332
[2] B. Simončič and B. Tomšič, *Text. Res. J.*, **80**, 1721 (2010), https://doi.org/10.1177%2F0040517510363193
[3] M. Radetić, *J. Mater. Sci.*, **48**, 95 (2013), https://doi.org/10.1007/s10853-012-6677-7
[4] C. Yang, G. L. Liang, K. M. Xu, P. Gao and B. Xu, *J. Mater. Sci.*, **44**, 1894 (2009), https://doi.org/10.1007/s10853-009-3247-8
[5] O. Demiryurek and T. Tulunay, *Cellulose Chem. Technol.*, **53**, 163 (2019), http://www.cellulosechemtechnol.ro/pdf/CCT1-2(2019)/p.163-173.pdf
[6] J. Y. Min and H. M. Choi, *Cellulose Chem. Technol.*, **52**, 891 (2018), http://www.cellulosechemtechnol.ro/pdf/CCT9-10(2018)/p.891-901.pdf
[7] M. M. Ibrahim, A. Mezni, H. S. El-Sheshtawy, A. A. Abu Zaid, M. Alsawat *et al.*, *Appl. Surf. Sci.*, **479**, 953 (2019), https://doi.org/10.1016/j.apsusc.2019.02.169
[8] V. V. Shinde, P. R. Jadhav, J. H. Kim and P. S. Patil, *J. Mater. Sci.*, **48**, 8393 (2013), https://doi.org/10.1007/s10853-013-7651-8
[9] I. Vukoje, V. Lazić, V. Vodnik, M. Mitrić, B. Jokić *et al.*, *J. Mater. Sci.*, **49**, 4453 (2014), https://doi.org/10.1007/s10853-014-8142-2

[10] H. J. Lee, S. Y. Yeo and S. H. Jeong, *J. Mater. Sci.*, **38**, 2199 (2003), https://doi.org/10.1023/A:1023736416361
[11] S. Hamdan, I. Pastar, S. Drakulich, E. Dikici, M. Tomic-Canic *et al.*, *ACS Central Sci.*, **3**, 163 (2017), https://doi.org/10.1021/acscentsci.6b00371
[12] H. Palza, S. Gutierrez, K. Delgado, O. Salazar, V. Fuenzalida *et al.*, *Macromol. Rapid. Comm.*, **31**, 563 (2010), https://doi:10.1002/marc.200900791
[13] N. C. Cady, J. L. Behnke and A. D. Strickland, *Adv. Funct. Mater.*, **21**, 2506 (2011), https://doi.org/10.1002/adfm.201100123
[14] Z. K. Nia, M. Montazer and M. Latifi, *Colloid. Surface. A*, **439**, 167 (2013), http://dx.doi.org/10.1016%2Fj.colsurfa.2013.03.003
[15] A. Sedighi, M. Montazer and S. Nasrin, *Carbohyd. Polym.*, **110**, 489 (2014), https://doi.org/10.1016/j.carbpol.2014.04.030
[16] M. Montazer, M. Dastjerdi, M. Azdaloo and M. M. Rad, *Cellulose*, **22**, 4049 (2015), https://doi.org/10.1007/s10570-015-0764-2
[17] A. Errokh, A. M. Ferraria, D. S. Conceição, L. F. Vieira Ferreira, A. M. Botelho de Rego *et al.*, *Carbohyd. Polym.*, **141**, 229 (2016), http://dx.doi.org/10.1016/j.carbpol.2016.01.019
[18] N. R. Dhineshbabu and V. Rajendran, *IET Nanobiotechnol.*, **10**, 13 (2016), https://doi.org/10.1049/iet-nbt.2014.0073
[19] H. E. Emam, H. B. Ahmed and T. Bechtold, *Carbohyd. Polym.*, **165**, 255 (2017), https://doi.org/10.1016/j.carbpol.2017.02.044
[20] P. Kanade and B. Patel, *Fashion and Textiles*, **4**, 10 (2017), https://doi.org/10.1186/s40691-017-0094-0
[21] D. Marković, M. Korica, M. Kostić, Ž. Radovanović, Z. Šaponjić *et al.*, *Cellulose*, **25**, 829 (2018), https://doi.org/10.1007/s10570-017-1566-5
[22] D. Marković, C. Deeks, T. Nunney, Ž. Radovanović, M. Radoičić *et al.*, *Carbohyd. Polym.*, **200**, 173 (2018), https://doi.org/10.1016/j.carbpol.2018.08.001
[23] H. N. Rubin, B. H. Neufeld and M. M. Reynolds, *ACS Appl. Mater. Interfaces*, **10**, 15189 (2018), https://doi:10.1021/acsami.7b19455
[24] R. J. B. Pinto, M. C. Neves, C. P. Neto and T. Trindade, *Eur. J. Inorg. Chem.*, **2012**, 5043 (2012), https://doi.org/10.1002/ejic.201200605
[25] I. Perelstein, Y. Ruderman, N. Perkas, J. Beddow, G. Singh *et al.*, *Cellulose*, **20**, 1215 (2013), https://doi.org/10.1007/s10570-013-9929-z
[26] S. Anita, T. Ramachandran, R. Rajendran, C. V. Koushik and M. Mahalakshmi, *Text. Res. J.*, **8**, 1081 (2011), https://doi.org/10.1177/0040517510397577
[27] H. E. Emam, A. P. Manian, B. Široká, H. Duelli, P. Merschak *et al.*, *Surf. Coat. Tech.*, **254**, 344 (2014), http://dx.doi.org/10.1016/j.surfcoat.2014.06.036
[28] W. V. da Costa, B. da Silva Pereira, M. Camotti Montanha, E. Kimura, A. A. Winkler Hechenleitner *et al.*, *Mater. Chem. Phys.*, **201**, 339 (2017), https://doi.org/10.1016/j.matchemphys.2017.08.046
[29] J. Yang, H. Xu, L. Zhang, Y. Zhong, X. Sui *et al.*, *Surf. Coat. Tech.*, **309**, 149 (2017), https://doi.org/10.1016/j.surfcoat.2016.11.058
[30] Z. Peršin, U. Maver, T. Pivec, T. Maver, A. Vesel *et al.*, *Carbohyd. Polym.*, **100**, 55 (2014), https://doi.org/10.1016/j.carbpol.2013.03.082
[31] V. Kumar and T. Yang, *Carbohyd. Polym.*, **48**, 403 (2002), https://doi.org/10.1016/S0144-8617(01)00290-9
[32] J. Praskalo, M. Kostić, A. Potthast, G. Popov, B. Pejić *et al.*, *Carbohyd. Polym.*, **77**, 791 (2009), https://doi.org/10.1016/j.carbpol.2009.02.028
[33] O. Šauperl, K. Stana-Kleinschek and V. Ribitsch, *Text. Res. J.*, **79**, 780 (2009), https://doi.org/10.1177/0040517508096222
[34] H. Awada, D. Montplaisir and C. Daneault, *Ind. Eng. Chem. Res.*, **53**, 4312 (2014), https://doi.org/10.1021/ie500101n
[35] T. Harifi and M. Montazer, *Carbohyd. Polym.*, **88**, 1125 (2012), https://doi.org/10.1016/j.carbpol.2012.02.017
[36] O. Šauperl and K. Stana-Kleinschek, *Text. Res. J.*, **80**, 383 (2010), https://doi.org/10.1177/0040517509343818
[37] S. A. Aksoy and E. Genç, *Cellulose Chem. Technol.*, **49**, 405 (2015), http://www.cellulosechemtechnol.ro/pdf/CCT5-6(2015)/p.405-413.pdf
[38] P. Liu, K. Oksman and A. P. Mathew, *J. Colloid. Interf. Sci.*, **464**, 175 (2016), https://doi.org/10.1016/j.jcis.2015.11.033
[39] B. Jia, Y. Mei, L. Cheng, J. Zhou and L. Zhang, *ACS Appl. Mater. Interfaces*, **4**, 2897 (2012), https://doi.org/10.1021/am3007609
[40] P. Kaninen, C. Johans, J. Merta and K. Kontturi, *J. Colloid. Interf. Sci.*, **318**, 88 (2008), https://doi.org/10.1016/j.jcis.2007.09.069
[41] H. A. Hemeg, *Int. J. Nanomed.*, **12**, 8211 (2017), https://doi.org/10.2147/IJN.S132163
[42] J. P. Ruparelia, A. K. Chatterjee, S. P. Duttagupta and S. Mukherji, *Acta Biomater.*, **4**, 707 (2008), https://doi:10.1016/j.actbio.2007.11.006
[43] H. Pang, F. Gaob and Q. Lu, *Chem. Commun.*, **45**, 1076 (2009), https://doi.org/10.1039/b816670f
[44] R. Hong, T. Y. Kang, C. A. Michels and N. Gaduraa, *Appl. Environ. Microb.*, **78**, 1776 (2012), http://doi:10.1128/AEM.07068-11
[45] M. K. S. Ballo, S. Rtmi, J. Kiwi, C. Pulgarin and J. M. Entenza, *J. Photch. Photobio. B*, **174**, 229 (2017), https://doi.org/10.1016/j.jphotobiol.2017.07.030