Cellulose (2022) 29:287–302
https://doi.org/10.1007/s10570-021-04296-6

ORIGINAL RESEARCH

Biodegradation of cellulose fibers functionalized with CuO/Cu_2O nanoparticles in combination with polycarboxylic acids

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Received: 4 August 2021 / Accepted: 27 October 2021 / Published online: 12 November 2021

Abstract Sustainable biodegradation of cellulose fibers is critical for composting after the end of a product's life. In this study, we aimed at investigating the effect of in situ synthesized CuO/Cu_2O nanoparticles (NPs) with biocidal concentration on the biodegradation behavior of cotton fibers pretreated with 1,2,3,4-butanetetracarboxylic acid (BTCA) and succinic acid (SUC). Biodegradation of the fibers was evaluated by soil burial tests in garden soil and in model compost after different soil burial times. The results showed that the application of BTCA, SUC, and CuO/Cu_2O NPs did not affect the hydrophilicity of the samples and allowed a smooth biodegradation process. The morphological and chemical changes during biodegradation, evaluated by FESEM and FTIR analyses, showed that the presence of CuO/Cu_2O NPs slightly hindered biodegradation of the fibers after 18 days in soil. However, biodegradation was much faster in the model compost, where all samples, regardless of their chemical modification, almost completely degraded after only 11 days. Intense microbial growth on the surface of all samples after nine days of burial in garden soil and model compost was confirmed by the presence of proteins produced by the microorganisms. The total number of microorganisms in the garden soil remained almost unchanged and increased in the model compost after the burial test. The only exception was the sample with the highest concentration of CuO/Cu_2O NPs, which caused a reduction in microbial growth but not complete growth inhibition. These results clearly showed that during material degradation, the cellulosic material supporting microbial growth prevailed over the suppression of microbial growth by CuO/Cu_2O NPs.

Keywords Biodegradation · CuO/Cu_2O nanoparticles · Cotton · BTCA · Succinic acid · Model compost

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Introduction

The biodegradation behavior of cellulose fibers classifies them as an eco-friendly textile material, which greatly facilitates their handling and treatment after entering the waste stream. Since soil microorganisms readily degrade cellulose macromolecules, on the one hand, cellulose-based materials can be advantageously

composted after the end of the products' life. This is very important to the environment as more than 60% of post-consumer textile waste continues to be disposed of in landfills or illegal dumps (US EPA 2021).

On the other hand, biodegradability of cellulose fibers is not always a desirable property in textile products. In fact, biodegradability can lead to esthetic changes and reduce the value of products due to mold and decay of the fibers when exposed to appropriate conditions. In addition, biodegradability is usually incompatible with antimicrobial activity, which is a desired property of cellulose fibers that are used for medical and health purposes. In these cases, the application of antimicrobial agents is essential to protect the user from pathogenic microorganisms. However, usually, these antimicrobial agents are also destructive to microorganisms which are the main actors in the biodegradation process of the fibers. Therefore, the development of cellulose textile material with simultaneously effective antimicrobial activity during use and preserved biodegradability of fibers at the products' end of life continues to be one of the greatest challenges in the field of chemical finishing of textiles.

In order to achieve specific antimicrobial properties, there are various approaches for applying finishing agents with different chemical structures, particle sizes, and efficacy to textile fibers. In particular, nanofinishing of textiles with metal and metal oxide nanoparticles (NPs) as an alternative to conventional antimicrobial finishing has received considerable attention, mainly because small amounts of highly reactive nanosized particles can provide exceptional antimicrobial activity against a wide range of microorganisms, including drug-resistant bacteria (Verbič et al. 2019; Rezaie et al. 2018; Radetić and Marković 2019; Saleem and Zaidi 2020; Rashid et al. 2020; Montes-Hernandez et al. 2021). Metal and metal oxide NPs such as Ag, Cu, CuO, Cu_2O, TiO_2 and ZnO and their combinations have already been established as excellent antimicrobial agents for textiles (Sedighi et al. 2014; Errokh et al. 2016; Montazer et al. 2015; Sedighi and Montazer 2016; Gorjanc and Šala 2016; Zarbaf et al. 2017; Kanade and Patel 2017; Zahid et al. 2018; Marković et al. 2018a, b, 2020a; Marković et al. 2018a, 2020a; Ibrahim et al. 2019; Aalipourmohammadi et al. 2019; Jatoi et al. 2019; Zhang et al. 2019; Marković et al. 2019a, b, c; Karagoz et al. 2020; Čuk et al. 2021). The antimicrobial activity of metal and metal oxide NPs is very complex and is attributed to the release of metal cations and NPs from the textile surface, as well as to the generation of the reactive oxygen species (ROS) in the photocatalytic reaction under UV radiation. The antimicrobial efficacy is influenced by several important factors, including the chemical and morphological properties of the NPs, their concentration, the photocatalytic efficiency to produce ROS, and the environmental conditions.

In addition to development of the manufacturing processes of textile fibers functionalized with metal and metal oxide NPs, many studies, including that of our research team, have been devoted to investigating the influence of metal and metal oxide NPs on the biodegradability of chemically modified textile materials at the end of product life (Klemenčič et al. 2010; Tomšič et al. 2011, 2017; Lazić et al. 2015; Milošević et al. 2017; Bras et al. 2017; Marković et al. 2019a; Saleem and Zaidi 2020). Previous studies have shown that the excellent antimicrobial activity of Ag NPs significantly inhibited the biodegradation of cotton and cotton/polyester fabric in soil (Klemenčič et al. 2010; Tomšič et al. 2011; Lazić et al. 2015; Ibrahim and Hassan 2016). In addition to outdoor temperature, soil composition, and moisture, the concentration of charged Ag NPs has been shown to play an important role in suppressing the cotton biodegradation process (Lazić et al. 2015; Milošević et al. 2017). A similar effect in relation to biodegradation of cotton and cotton/polyester fabrics loaded with Ag/TiO_2 NPs has been found (Milošević et al. 2017). In contrast to Ag NPs, there was no significant difference in biodegradation behavior between control cotton fabric and cotton fabric impregnated with commercial TiO_2 NPs Degussa P25 (Marković et al. 2019b). Similar biodegradation behavior has also been observed in untreated cotton fabric and fabric pretreated with corona discharge and subsequently dip-coated into colloidal TiO_2 NPs synthesized by acid hydrolysis of $TiCl_4$ (Tomšič et al. 2017). It has also been observed that plasma pretreatment of cotton fibers promoted biodegradation in soil, despite inhibition by coated ZnO NPs (Primc et al. 2016). Another study also found that incorporation of ZnO into fiber blends of viscose, flax, and lyocell did not stop fiber biodegradation or significantly affect soil contamination (Malis et al. 2019). These results confirm that the antimicrobial activity of TiO_2 and ZnO, which is mainly driven by

the generation of ROS under UV radiation, decreased significantly when the samples were buried in the dark. At the same time, it is also known that the antimicrobial activity of TiO_2 and ZnO against fungi, which constitute many soil microorganisms, is not as effective as compared with bacteria (Blake et al. 1999; Gao et al. 2019).

To the best of our knowledge, the effect of Cu-based NPs on the biodegradation of textile materials in terrestrial environments has not yet been reported. On the other hand, extensive studies have been conducted on the toxic effects of different forms of copper on soil and plants (Keller et al. 2017; Rajput et al. 2018, 2019; Peng et al. 2020; Samarajeewa et al. 2021). In these studies, CuO NPs have been considered to be highly toxic to the microbiota and plants, as they cause biological toxicity through the release of Cu cations and the formation of ROS. However, no definitive or generalized conclusions can be drawn about the harmful effects of NPs on the microbial community, as this phenomenon is directly influenced by the type and concentration of NPs as well as soil properties (Jośko et al. 2019). Accordingly, many questions remain unexplored in this area, and studies on biodegradability of cellulose fibers functionalized with Cu-based NPs would be extremely valuable to provide additional information on the possibility of composting these textile materials after they enter the waste stream.

Therefore, in this study, we aimed at elucidating the influence of CuO/Cu_2O NPs on the biodegradation behavior of cotton fabric while determining their potentially deleterious effect on the microbial community in garden soil and model compost. To this end, cotton samples previously modified with 1,2,3,4-butanetetracarboxylic acid (BTCA) and succinic acid (SUC) and subsequently functionalized with CuO/Cu_2O NPs were selected for study. Subsequently, we reported that pretreatment of cotton fiber surface with polycarboxylic acids provides sufficient carboxyl groups necessary for complexation of Cu^{2+} ions, which were further reduced, leading to the formation of CuO/Cu_2O NPs with strong antimicrobial activity (Marković et al. 2018a, 2019a; Marković et al. 2019a, b, c). The biodegradation process in garden soil and model compost was assessed by a standard soil burial test. Morphological and chemical changes in cotton fibers were evaluated by SEM and FTIR analyses, respectively. A standard microbial counting method was used to determine the total number of microorganisms in the garden soil and model compost after the cotton samples had completed the biodegradation process.

Experimental

Materials

The desized and bleached cotton (CO) woven fabric (117.5 g/m^2, 52 picks/cm, 27 ends/cm, thickness of 0.26 mm) was kindly supplied by the Slovenian textile company Tekstina d.d. Ajdovščina (Ajdovščina, Slovenia). Nonionic washing agent Felosan RG-N was provided by CHT Switzerland AG (Montlingen, Switzerland). All other reagents of p.a. grade were applied in the experiments without any further purification. 1,2,3,4-butanetetracarboxylic acid (BTCA) and succinic acid (SUC), the catalyst sodium hypophosphite (SHP) and sodium borohydride were purchased from ACROS Organics (Carlsbad, USA). Copper(II)sulphate pentahydrate was supplied by Centrohem, (Stara Pazova, Serbia). Luria–Bertani agar (LA, Oxoid, UK) for heterotrophic bacteria, mannitol soy flower agar (MSF) for spore-forming bacteria and Sabouraud dextrose agar (SAB, Difco, UK) were used.

Preparation of fabric

In order to eliminate impurities in the CO fabric, it was washed in a bath containing 0.1% Felosan RG-N (liquor-to-fabric ratio of 50:1) at 50 °C for 15 min. After rinsing with warm water (50 °C) and subsequent thorough rinsing with cold water, the fabrics were dried at room temperature. Cleaned, untreated fabric as a control sample was labeled as CO_UN.

Impregnation of fabrics with succinic and BTCA acids

Our previous research indicated that CO fabric impregnated with 10 w/v% BTCA and Cu-based NPs contained almost twice the Cu content as the sample impregnated with 6 w/v% BTCA (Marković et al. 2018a, 2019a). However, they exhibited equivalent antibacterial activity. A further decrease in BTCA concentration to 4 w/v% led to a significant

drop in Cu content, and consequently, to unsatisfactory antibacterial activity (Marković et al. 2019a). Therefore, the CO fabric samples, in the current study, were impregnated with 6 w/v% SUC and BTCA by dipping 0.50 g of the fabric and adding 1.24 g of the catalyst SHP into 20 mL of the acid solution. After one hour, the fabric samples were dried at 80 °C for 3 min and cured at 170 °C for 3 min. The fabrics were subsequently rinsed with distilled water and dried at room temperature. The CO fabrics impregnated with 6 w/v% BTCA and SUC were labeled as CO_BTCA and CO_SUC, respectively.

In situ synthesis of CuO/Cu_2O nanoparticles

First, 0.50 g CO_BTCA and CO_SUC fabric samples were immersed into 25 mL of 10 mM solution of $CuSO_4$ for 2 h. In order to remove the excessive Cu^{2+}-ions, the samples were rinsed three times with deionized water. Then, 0.050 g of sodium borohydride was dissolved in 25 mL of 0.1 mM NaOH solution, and the samples were immediately soaked in the prepared solution, followed by the reduction process for 30 min at room temperature. After a thorough rinsing with distilled water, the fabric samples were left to dry at room temperature. These samples were labeled as CO_BTCA + Cu and CO_SUC + Cu. Our previous studies provided detailed information about the chemical and morphological properties of the fabricated samples (Marković et al. 2018a, 2019a). In these studies, the XRD and XPS analyses revealed that the mixture consisting of CuO/Cu_2O NPs was in situ synthesized on the CO_BTCA + Cu and CO_SUC + Cu samples. Regardless of the type of polycarboxylic acid, the XRD revealed the presence of the monoclinic crystal phase of CuO and the crystal plane of cubic Cu_2O on the surface of the cotton samples.

Biodegradation testing of fabrics in soil and model compost

Biodegradation of the CO_UN, CO_BTCA, CO_SUC, CO_BTCA + Cu, and CO_SUC + Cu fabric samples was evaluated by a soil burial test according to ISO 11721-1:2001 and ISO 11721:2003 standards. According to standard procedure, a container was filled with the model compost-containing garden soil. A constant soil water content of 60 ± 5% of its maximum moisture retention capacity was maintained during the test by spraying with water. The pH of the soil ranged between 4.0 and 7.5. The samples were buried in the soil for 3, 9, and 18 days. After certain incubation times, the samples were removed from the soil, rinsed with running tap water, soaked in 70% ethanol for 30 min, and dried at room temperature.

The soil burial test in model compost was accomplished by placing 5 samples (3 × 10 cm) into containers (volume of 2 L, 26 × 17 × 17 cm) filled with 600 g of model compost soil. (Šašek et al. 2006; Ponjavic et al. 2017). The samples were buried approximately at half the depth of the container (2 cm under the top and 2 cm above the bottom). Initially, 200 mL of tap water was added to the model compost and the moisture was maintained by the addition of 20 mL of tap water dropwise on top of the model compost every 4 days. Containers were kept at 30 °C for 3, 6, 9, and 11 days. The samples were cleaned with water, soaked in 70% ethanol for 30 min, and dried at room temperature.

Characterization of samples before and after biodegradation testing

The existence of CuO/Cu_2O NPs on the surface of the CO_SUC + BTCA and CO_SUC + Cu fibers was detected by field emission scanning electron microscopy (FESEM, Tescan Mira3 FEG). The samples were coated with a thin layer of Au prior to analysis. The obtained FESEM images were used to determine of the size and size distribution of the synthesized NPs using the freely available imaging software tool "ImageJ". Energy-dispersive X-ray spectroscopy (EDS) of these fibers was conducted using a JEOL JSM 5800 SEM with a SiLi X-Ray detector (Oxford Link Isis series 300, UK).

The total Cu content in CO_BTCA + Cu and CO_SUC + Cu fabric samples was determined by inductively coupled plasma-mass spectroscopy (ICP-MS) using a PerkinElmer SCIED Elan DRC spectrophotometer. A sample of 0.5 g was prepared in a Milestone microwave system by acid decomposition with 65% HNO_3 and 30% H_2O_2. Copper concentrations values are given as the mean of two measurements made for each sample.

The fiber morphology of the CO_UN, CO_BTCA, CO_BTCA + Cu, CO_SUC, and CO_SUC + Cu samples before and after specified times of exposure

to garden soil and model compost microflora was analyzed by a JEOL JSM 5610 and 6060 LV scanning electron microscope. The samples were coated with carbon and Au/Pd (90%/10%) alloy before SEM analysis.

Fourier-transform infrared (FT-IR) spectra were collected over the range of 4000–600 cm^{-1} using 32 scans at a resolution of 4 cm^{-1} by a Spectrum ™ 3 spectrophotometer (Perkin Elmer, Great Britain) equipped with an attenuated total reflection (ATR) cell and a diamond crystal (n = 2.0).

The wickability of untreated and functionalized samples was explored using a thin-layer wicking (TLW) test of wettability, which was performed in the horizontal direction in accordance with Chibowski and Gonzales-Caballero (1993) method. The samples were cut into strips (1 cm × 10 cm) and dried for 30 min at a temperature of 100 °C. Each dry sample was inserted between two glass plates with a ruler and put into deionized water in a Petri dish. Starting from the moment when the water started to penetrate into the sample, the time at which the water penetrated a certain distance in the sample was measured. At least 10 measurements were made for each sample and the average value was presented as a result.

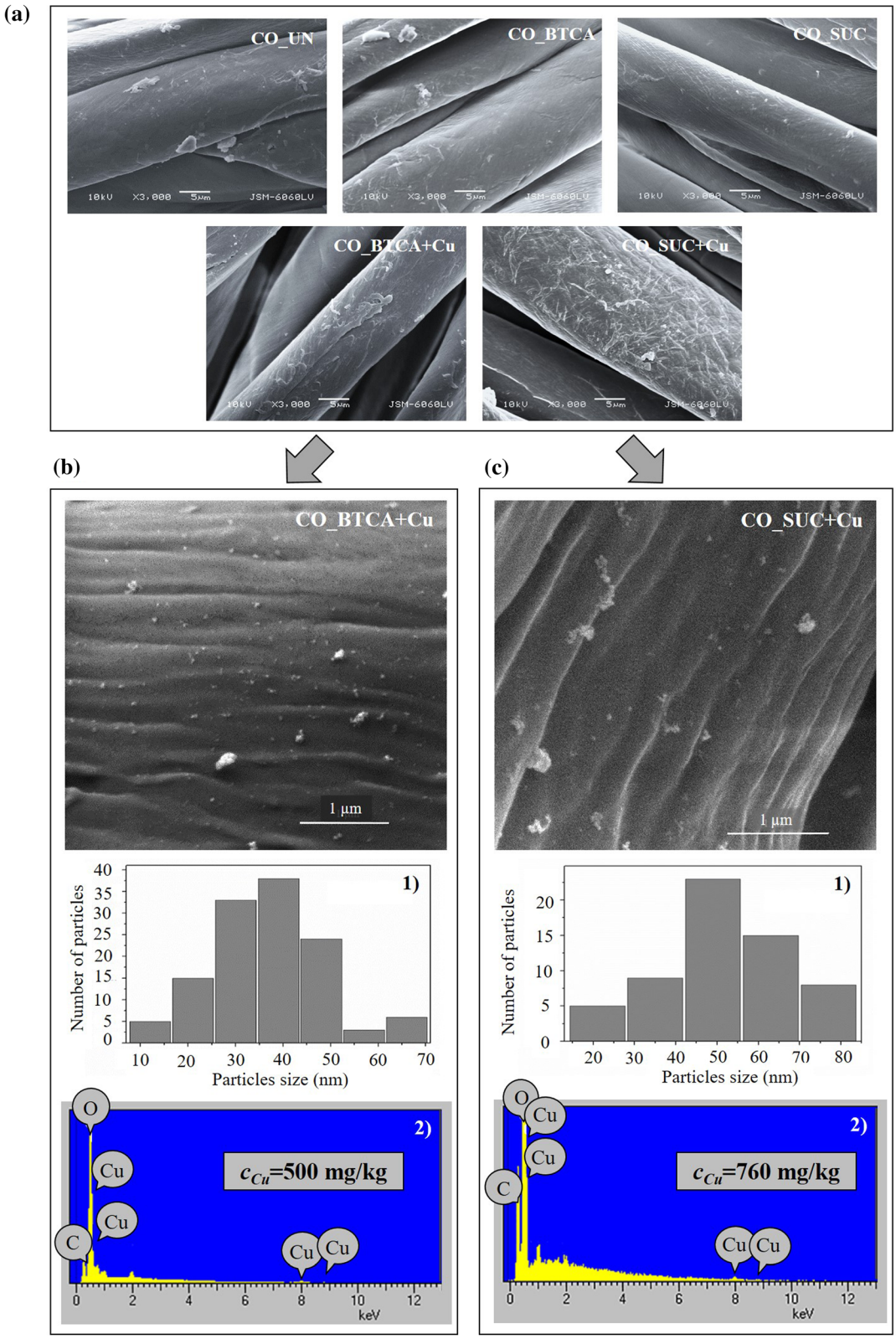
Microbial cell counts

To determine the number of microbial cells per gram of garden soil and model compost, aliquots (1 g) before and after the soil burial of textile samples were taken and the standard culture-dependent enumeration procedure was applied (Lawlor et al. 2000; Lee et al. 2021). Soil micro-organisms were also cultured at 30 °C on three types of agar media: Luria–Bertani agar (LA, Oxoid, UK) for heterotrophic bacteria; mannitol soy flower agar (MSF) (Hobbs et al. 1989) for spore-forming bacteria; and Sabouraud dextrose agar (SAB, Difco, UK) for fungi. Bacterial counts were made 48 h after plating, fungal counts after 5 days and expressed as colony forming units per gram of soil (CFU/g).

Results and discussion

The morphological and chemical changes of the untreated and modified cotton samples after functionalization were studied by SEM and EDS analyses (Fig. 1). No obvious morphological changes were visible on the SEM images, indicating a thin layer of both crosslinkers BTCA and SUC, while the CuO/Cu_2O NPs were too small to be detected by SEM (Fig. 1a). FESEM and EDS analysis confirmed the successful in situ synthesis of CuO/Cu_2O NPs on the fiber surfaces of the CO_BTCA and CO_SUC samples (Fig. 1b, c). The FESEM images of the CO_BTCA + Cu and CO_SUC + Cu samples showed non-uniform deposition of single and agglomerated CuO/Cu_2O NPs on the surface of the fibers. The average sizes of the NPs synthesized on CO_BTCA and CO_SUC fibers were 41 ± 12 nm and 54 ± 16 nm, respectively. The size distribution of the synthesized NPs on the surface of both samples is shown in Fig. 1b, c. The presence of Cu-based NPs on the fibers was also confirmed by the EDS analysis as peaks corresponding to Cu appeared in the EDS spectra of both samples. However, this technique could not provide quantitative data on the amount of deposited copper in the samples. This was further verified by ICP-MS analysis, which revealed that the CO_BTCA + Cu and CO_SUC + Cu samples contained 500 and 760 mg/kg of copper, respectively. This indicated that at the same concentration of Cu precursor in the solution, the amount of total copper content was about 1.5 times higher in the CO_SUC + Cu sample than that in the CO_BTCA + Cu sample.

During the biodegradation process, moisture content has a significant influence on the degree of growth and multiplication of microorganisms. This is especially true for fungi, as it has been found that fungi grow readily on cellulosic fibers at 80% relative humidity, while their growth is reduced or even stopped at 50% relative humidity (Montegut et al. 1991). Accordingly, the hydrophilicity of fibers, which is a prerequisite for their good water wettability, is crucial for maintaining conditions for the biodegradation process (Yaacob et al. 2016; Sülar and Devrim 2019), as it promotes the interactions between microorganism cells and the fiber surface in the adhesion process. Since the wettability of textile fibers is directly related to their wicking property (Sun and Stylios 2004), the effect of impregnating cotton fabric with BTCA or SUC followed by immobilization of CuO/Cu_2O NPs on the wicking properties was investigated by TLW measurements, and the results are shown in Fig. 2. The results showed that the impregnation with SUC had no effect on the wicking effect on


(a)
CO_UN
CO_BTCA
CO_SUC
CO_BTCA+Cu
CO_SUC+Cu
(b)
CO_BTCA+Cu
1 µm
Number of particles
Particles size (nm)
1)
2)
O
Cu
Cu
C
Cu
Cu
c_{Cu}=500 mg/kg
keV
(c)
CO_SUC+Cu
1 µm
Number of particles
Particles size (nm)
1)
2)
O
Cu
Cu
C
Cu
Cu
c_{Cu}=760 mg/kg
keV

◀**Fig. 1** (**a**) SEM images of untreated and modified cotton samples; FESEM images of the (**b**) CO_BTCA + Cu and (**c**) CO_SUC + Cu samples with corresponding particle size distribution (1) and EDS spectra (2)

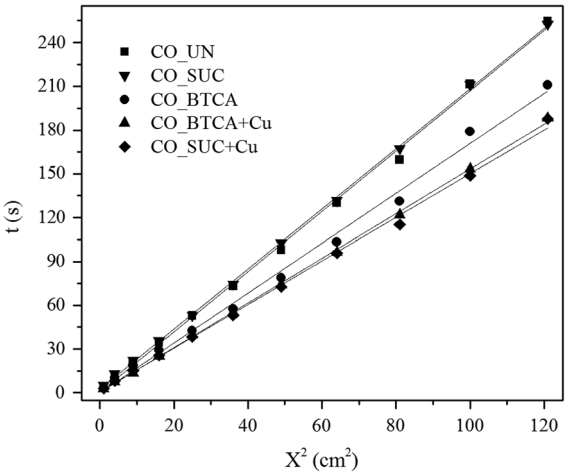


Fig. 2 Rate (x^2/t) of thin-layer wicking of water into control and modified samples

the cotton fabric, it remained the same as the untreated CO_UN sample. The application of BTCA increased the wicking of the CO_BTCA sample as compared with the CO_UN sample, and this phenomenon was even more pronounced when CuO/Cu_2O NPs were present. Interestingly, the TLW rate of water was the same in the CO_BTCA + Cu and CO_SUC + Cu samples, which clearly showed that the application of both carboxylic acids and CuO/Cu_2O NPs did not hinder the hydrophilic properties of the CO fabric and allowed a fluent water uptake of the samples. This maintains good contact between microorganisms in the medium (water, soil, or model compost) and the fiber surface, allowing the microorganisms to adhere and penetrate the amorphous regions of the fibers during the biodegradation process.

The influence of BTCA, SUC, and CuO/Cu_2O NPs on the biodegradation behavior of functionalized cotton samples was investigated by soil burial tests in garden soil and model compost. Initially, the aim was to compare the biodegradation behavior of the samples in garden soil and model compost within the same time frame, i.e., 3, 9, and 18 days. However, this was not possible, as the first experiment showed much faster degradation in the model compost than in garden soil and this indicated that the planned duration of 18 days was too long for assessing the biodegradation process for this medium. Therefore, to gain better insight into the rate of biodegradation in the model compost, the experiments were limited to 11 days and the samples were taken from the model compost after 3, 6, 9, and 11 days. Photographs of the tested samples after a certain period of burial in the garden soil and model compost are shown in Fig. 3. The greater the color change of the samples, the more intense their decomposition (Klemenčič et al. 2010). The comparison of untreated and functionalized samples showed that within 3 days after burial in garden soil, no significant color change occurred in all samples (Fig. 3a, b). However, significant decomposition, and hence color change, in the sample CO_UN was seen after 9 days of burial in garden soil. During the same period, the color of the CO_SUC and CO_SUC + Cu samples also changed to brownish tones. In contrast, the CO_BTCA and CO_BTCA + Cu samples remained almost unaffected, with only a few barely visible pale brown spots appearing. While this phenomenon was observed in both CO_BTCA and CO_BTCA + Cu samples, the reason for the lower cotton biodegradation could be due to BTCA and not copper. Indeed, BTCA with four carboxyl groups in its structure is a known crosslinking agent that cross-links cellulose macromolecules in the amorphous region via covalent bonds formed with hydroxyl groups of cellulose (Schindler and Hauser 2004). This could have an important effect on the rate of cotton fiber biodegradation, and was not observed in the case of SUC with two carboxyl groups, which cross-linked the cellulose macromolecules via much weaker noncovalent interactions, including ionic and intermolecular hydrogen bonds (Mitra et al. 2013).

Significant decomposition of the CO_UN sample due to biodegradation became evident after 18 days of burial in the garden soil, which is consistent with our previous results (Marković et al. 2019a). Over the 18-day period, biodegradation of all functionalized samples continued, confirming that the presence of BTCA and CuO/Cu_2O NPs did not completely stop the progress of biodegradation, but only slowed it down. These results are in accordance with the literature, where inhibition of the action of microorganisms in soil was previously achieved when Ag NPs were immobilized on CO fibers (Klemenčič et al. 2010; Lazić et al. 2015).

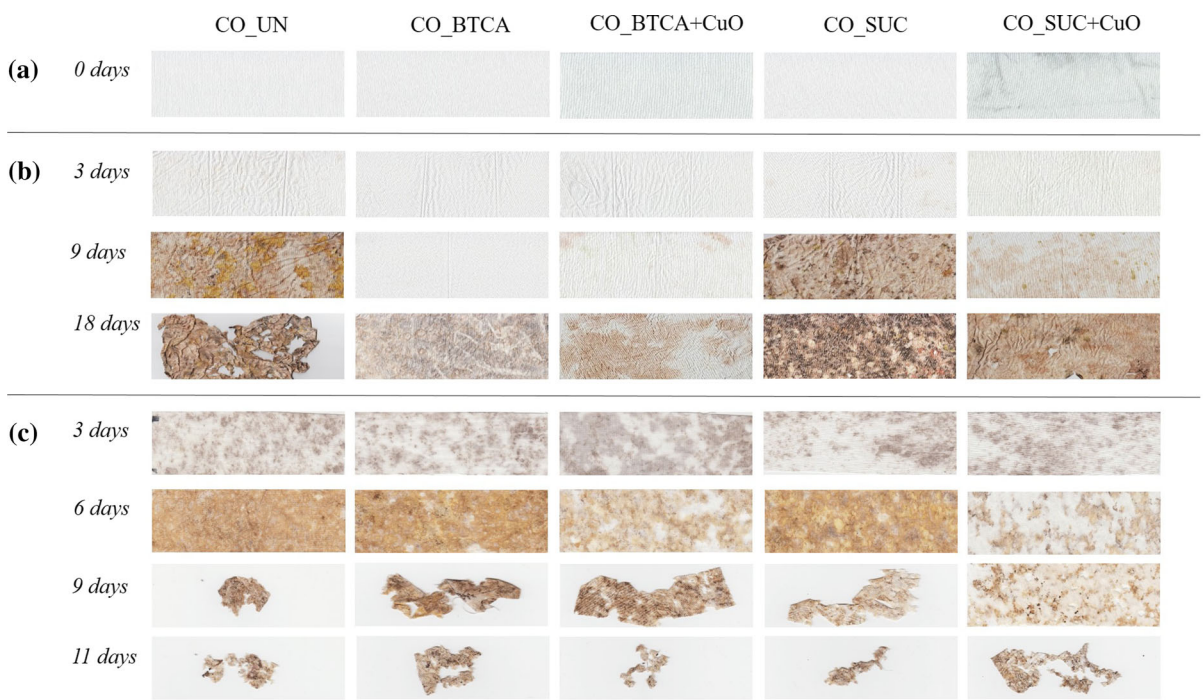


Fig. 3 Photographs of control and impregnated fabrics: **a** before, **b** after certain periods of burial in garden soil, **c** in model compost

In contrast to the garden soil, much faster biodegradation of the investigated samples took place in the model compost (Fig. 3c). Obviously, the decomposition of all studied samples, regardless of their functionalization, was detectable already after 3 days of incubation, which radically progressed in the case of samples CO_UN, CO_BTCA, and CO_SUC during the following 3 days. The decomposition of the CO_SUC + Cu and CO_BTCA + Cu samples was less pronounced, suggesting that the presence of CuO/Cu_2O NPs slows down the cellulose biodegradation. However, the difference in biodegradation rates among the samples disappeared after 11 days, when all samples severely biodegraded and only decomposed sample pieces remained, regardless of the presence of CuO/Cu_2O NPs.

Significantly faster biodegradation of the studied samples in the model compost as compared with those in the garden soil confirms the fact that the time for complete degradation of cotton materials is influenced by temperature, moisture content, and textile composition (Park et al. 2004; Lazić et al. 2015), as well as strongly depends on the nature of the soil, especially the composition of the microbial community in the soil and its ability to degrade cellulose. These phenomena could also explain the different rates of cotton biodegradation, as recent studies have reported that cotton knitted fabrics buried in soil took 4–5 months to fully decompose (Sülar and Devrim 2019; Smith et al. 2021).

Without doubt, it can be concluded that the antimicrobial activity of CuO/Cu_2O NPs inhibited cellulose decomposition during the initial period of burial in garden soil, which accelerated with increasing burial duration. The reason for this is the gradual but persistent leaching of the CuO/Cu_2O NPs from the CO_BTCA + Cu and CO_SUC + Cu samples during burial. For the sample CO_BTCA + Cu, the Cu concentration determined by ICP-MS analysis decreased from an initial 500 mg/kg to 130 and 63 mg/kg after 3 and 18 days of burial in the soil garden, respectively, while for the sample CO_SUC + Cu, the Cu concentration decreased from 760 mg/kg to 260 and 78 mg/kg, respectively. The much faster biodegradation process of the studied functionalized samples in the model compost as compared with the garden soil may be attributed to the enriched microbial community in the model compost. In this case, the content of CuO/Cu_2O NPs on the samples was too small to hinder the biodegradation of cotton, as the

CO_BTCA + Cu and CO_SUC + Cu samples disintegrated into pieces after only 11 days of burial. Their biodegradation rate was comparable to that of the CO_UN sample.

Morphological changes induced by the biodegradation process were assessed by SEM analysis. SEM images of untreated and functionalized samples before and after 3 and 9 days of burial in garden soil and model compost are shown in Fig. 4. While no significant morphological changes appeared on the untreated and functionalized cellulose fibers after 3 days of burial in garden soil, fine cracks were visible on the fiber surface after 3 days of incubation in the model compost for all the samples studied, confirming partial decomposition of the fibers. Wide and deep cracks appeared on the CO_UN fibers after 9 days of burial in garden soil, indicating decomposition of fibers by biodegradation, and the observed morphological changes were very similar to those reported in the literature (Arshad et al. 2014). The microcracks formed facilitated the colonization of microorganisms, and thus accelerated the biodegradation process (Yaacob et al. 2016; Sülar and Devrim 2019; Smith et al. 2021). Similar cracks were observed in the CO_SUC and CO_SUC + Cu samples. In the case of the CO_BTCA + Cu sample, most of the fibers were not obviously decomposed after 9 days of burial in the garden soil, but some of them were severely damaged and the onset of their defibration was evident. In contrast, the same incubation time of the studied samples in the model compost resulted in much more disintegration of the fibers. It is obvious that the CO_UN fibers have completely disintegrated. The CO_BTCA sample exhibit severe fiber disintegration and the CO_SUC sample exhibits even fiber opening. It appears that the samples with immobilized CuO/Cu_2O NPs were more resistant, regardless of the presence of BTCA or SUC, which is consistent with the photos in Fig. 3.

However, a closer look at the SEM images of the CO_BTCA and CO_SUC samples after 9 days of soil burial revealed important differences between the two crosslinkers. While hardly any defibration is seen in the CO_BTCA sample, this phenomenon is clearly visible in the CO_SUC sample. Considering that fungi play the main role in the biodegradation process of cellulose fibers by penetrating the amorphous region of the fibers via superficial cracks and degrading the

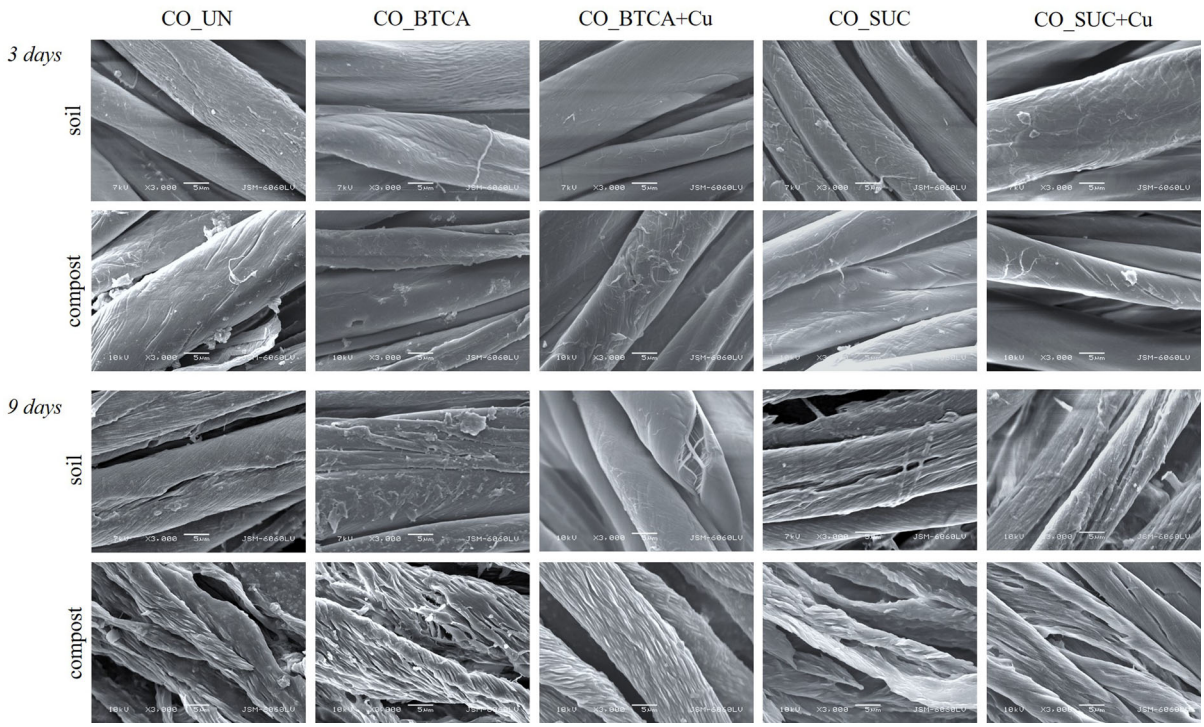


Fig. 4 SEM images of untreated and functionalized cotton samples after 3 and 9 days of burial in soil and model compost

fibers from within (Montegut et al. 1991), the lack of defibration in the CO_BTCA sample suggests that BTCA strengthened the amorphous regions of the cotton fibers much more during the crosslinking reaction as compared with SUC, which hinders the penetration of fungi into the amorphous regions. This indicates that in addition to the presence of CuO/Cu_2O NPs, the crosslinker also has some influence on the biodegradability of the functionalized cotton samples.

The chemical changes resulting from the biodegradation process were analyzed by FTIR spectroscopy. The FTIR spectra of the control samples (dashed black line) and the samples buried in garden soil (green line) and model compost (blue line) after 9 days of burial are shown in Fig. 5. The characteristic fingerprint of cellulose in the range 1400–890 cm^{-1} is clearly visible in all spectra and was analyzed in detail in our previous report (Tomšič et al. 2017). The appearance of intense absorption bands at 1640 and 1540 cm^{-1} in the excavated samples after 9 days of burial is assigned to amide I and amide II of secondary polyamides. They originate from the proteins produced during the growth of microorganisms and remain permanently bound to the fibers (Klemenčič et al. 2010; Tomšič et al. 2011). It is also evident that the intensities of the bands were more pronounced in the samples buried in model compost than in garden soil, indicating greater microbial growth. These results obviously confirmed the growth of microorganisms on the surface of all samples, which was not stopped due to the presence of copper. Furthermore, the band at 1730 cm^{-1} appeared in the spectra of the CO_UN sample after 9 days of burial with higher intensity when buried in model compost than in garden soil. This band is attributed to the C=O vibrations of the aldehyde and carboxyl groups generated during the hydrolysis and strong oxidative degradation of cellulose during the biodegradation process (Bras et al. 2017).

The total number of cultivable microorganisms was counted for biodegradation in both experimental setups (Fig. 6). The comparison of the graphs in Fig. 6a, b confirms that the model compost is about 100 times richer than the garden soil in all three groups of microorganisms studied, i.e., heterotrophic bacteria, sporulating bacteria, and fungi. During the biodegradation of the samples in the soil, the total numbers of microorganisms remained almost unchanged, suggesting a harmless effect of the samples on microbial growth. The only exception was the CO_SUC + Cu sample, which caused a visible reduction in sporulating bacteria (Fig. 6a). However, at the same time, this sample did not hinder the growth of heterotrophic bacteria and fungi, as the number of the latter even increased tenfold as compared with the garden soil before the burial experiment.

In the model compost system, a general increase in total microbial counts was observed after the burial experiment, with heterotrophic bacteria and fungi

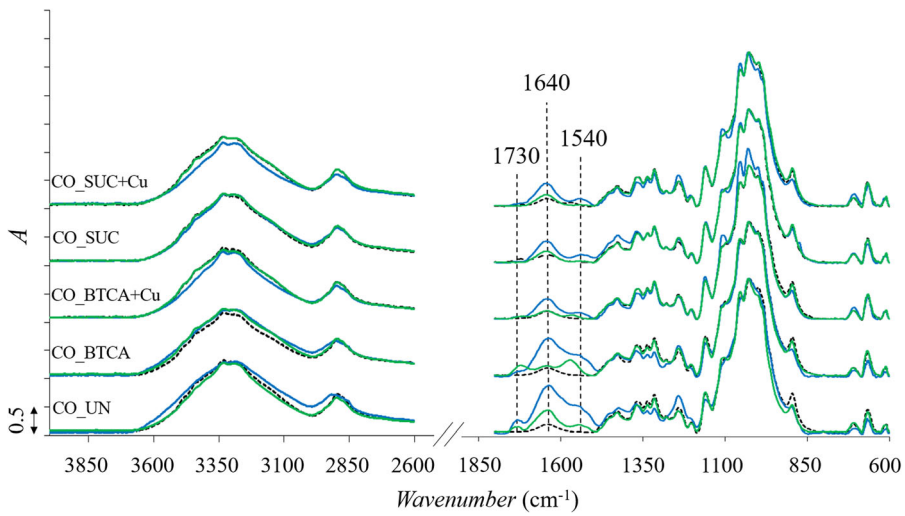


Fig. 5 FTIR spectra of control and impregnated fabrics before (dashed black) and after 9 days of burial in soil (green) and model compost (blue)

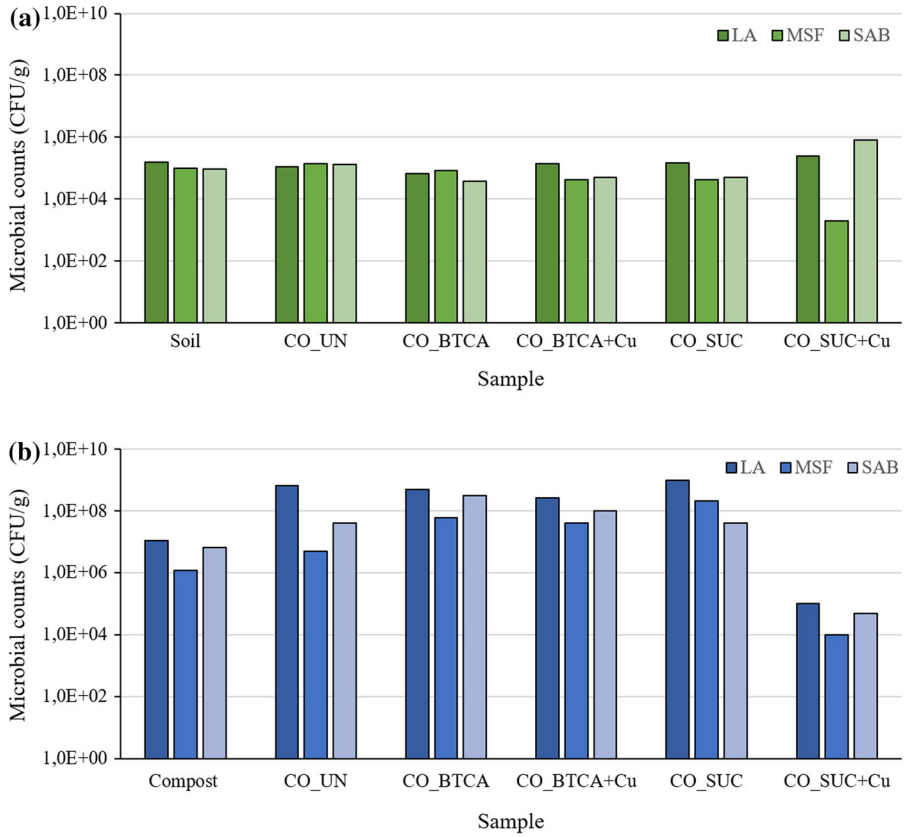


Fig. 6 Microbial growth in garden soil (**a**) and model compost (**b**) before (samples marked as Soil and Compost) and after biodegradation experiments of studied cotton samples. LA, heterotrophic bacteria; MSF, sporulating bacteria (such as *Bacillus* spp.and *Streptomyces* spp.); SAB, fungi

increasing the most (Fig. 6b). It appears that the cellulose samples and the decomposition products stimulated active bacterial and fungal growth and proliferation. The only exception was the CO_SUC + Cu sample, which caused the reduction of all types of studied microorganisms with the highest 1000-fold reduction in sporulating bacteria (Fig. 6b). These results show that the sporulating bacteria are the most sensitive to copper present in the CO_SUC + Cu sample. The same results were obtained in the case of the microorganisms in the garden soil. The reduction of microbial growth in the presence of CO_SUC + Cu was attributed to the copper content in this sample, which was 1.5 times higher than that in the CO_BTCA + Cu sample. This finding confirms the fact that the growth of microorganisms in soils. However, the representative images of the agar plates of the studied culture media after the end of the CO_SUC + Cu sample burial clearly show that the growth of microorganisms was not completely inhibited by this sample (Fig. 7), even though almost 90% of the CuO/Cu_2O NPs from the CO_SUC + Cu sample were leached in the garden soil (i.e. from the initial 760 mg/kg to the 78 mg/kg at the end of burial). Since bacteria and fungi are abundant and active in soils, rapid turnover times have been estimated (Rousk and Bååth 2011), which means that despite the observed reduced growth, this was not significant enough to endanger the microbial community either in the garden soil or in the compost. It can be concluded that that cellulosic material in both of the CO_BTCA + Cu and CO_SUC + Cu samples supported the growth of microorganisms in garden soil and model compost to a much greater extent than it was suppressed by CuO/Cu_2O NPs.

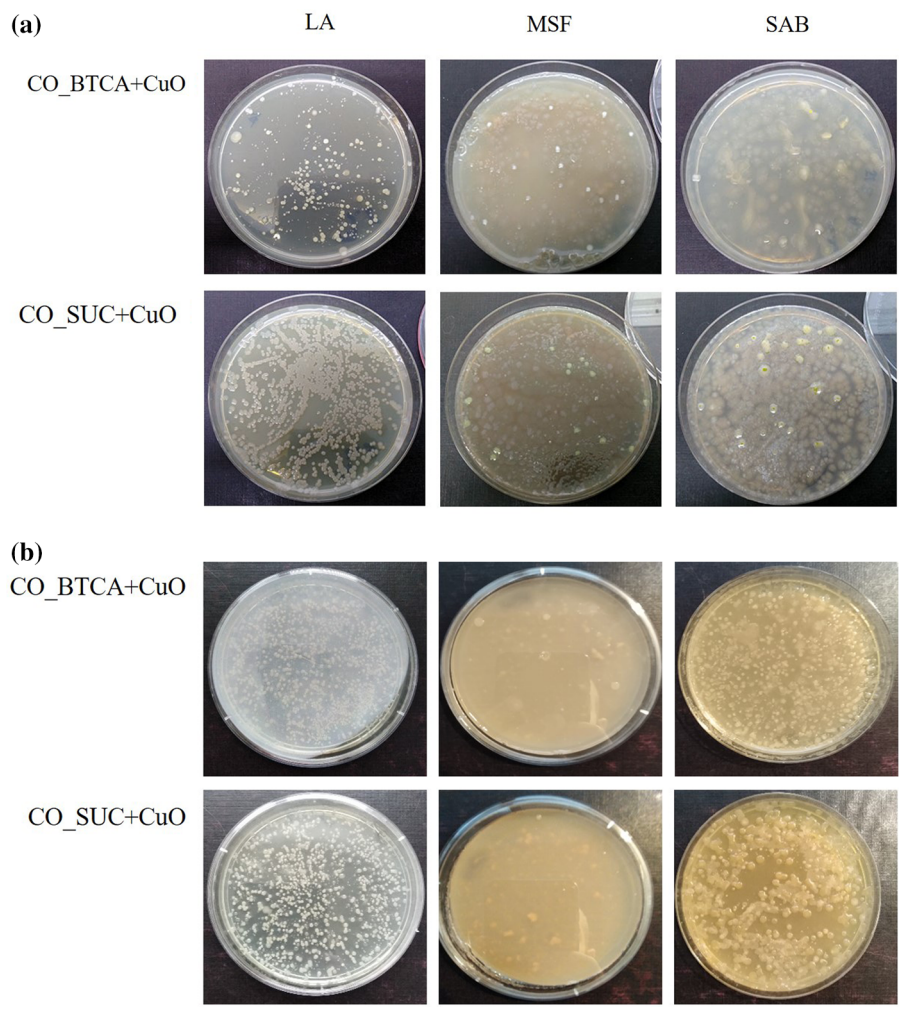


Fig. 7 Photographs of CFU overgrown on different culture media at the end of burial of the CO_BTCA + Cu and CO_SUC + Cu samples in garden soil (**a**) and model compost (**b**). LA, heterotrophic bacteria; MSF, sporulating bacteria (such as *Bacillus* spp. and S*treptomyces* spp.); SAB, fungi

Conclusions

This study provides valuable results regarding the biodegradation process of functionalized cotton fibers pretreated with BTCA or SUC and finished with the biocidal concentration of CuO/Cu_2O NPs. The results showed that the biodegradability of the fibers was affected by both their chemical modification and the test soil, using compost-containing garden soil and model compost enriched with microorganisms.

Pretreatment of the cotton sample with SUC resulted in a 1.5-fold higher concentration of adsorbed CuO/Cu_2O NPs as compared with the sample pretreated with BTCA, leading to an inhibition of microorganism growth in the garden soil and the model compost with the highest reduction in sporulating bacteria, which was reflected in the slowdown of the biodegradation process of the sample. However, in the case of compost burial, this phenomenon was observed only in the first burial periods and the sample disintegrated into pieces after 11 days of burial, very similar to the untreated and the other functionalized cotton samples. This suggests that the concentration of CuO/Cu_2O NPs on the sample was too low to hinder the biodegradation of cellulose in the presence of a rich microbial community, where the influence of CuO/Cu_2O NPs was less pronounced. Since the biodegradation of all samples was significantly faster in the model compost than in the garden soil, these results clearly indicate that the biodegradation rate is strongly influenced by the soil type.

In addition to the CuO/Cu_2O NPs, the biodegradation process of cotton fibers in soils during the initial period of burial was also affected by pretreatment with

BTCA, which, unlike SUC, cross-linked the cellulose macromolecules via covalent bonds, thus reinforcing the amorphous regions of the fibers. This made it more difficult for the fungi to penetrate the interior of the fibers and degrade them from the inside. The crosslinking effect became negligible after a longer incubation period in the soils.

The maintenance and even growth of all three studied groups of microorganisms in the garden soil and model compost after the burial experiment clearly confirmed that the fiber degradation products and the leaching of copper from the samples during burial did not significantly affect active bacterial and fungal growth and propagation, which is crucial for composting products after their end of life.

Acknowledgments The financial support for this study was provided by the Slovenian Research Agency (Programme P2-0213 Textiles and Ecology) and the Ministry of Education, Science and Technological Development of Republic of Serbia (451-03-9/2021-14/200135 and 451-03-68/2021-14/200287). This research has been done under the umbrella of the bilateral cooperation between Republic of Slovenia and Republic of Serbia (337-00-21/2020-09/43).

Author contributions Investigation, writing, review BT, methodology, validation, writing DM, investigation VJ, conceptualization, supervision, writing, review BS, investigation, writing, review JRN, investigation TIT, conceptualization, supervision, writing, review MR.

Funding This work was financially supported by the Slovenian Research Agency (Programme P2-0213 Textiles and Ecology) and the Ministry of Education, Science and Technological Development of Republic of Serbia (451-03-9/2021-14/200135 and 451-03-68/2021-14/200287).

Declarations

Conflict of interest The authors have no conflicts of interest to declare that are relevant to the content of this article.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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