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Copper(I)oxide microparticles – Synthesis and antimicrobial finishing of textiles

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Copper containing particles are of high interest to provide antibacterial activity to textiles for medical products, hygiene application or where odor formation as result of bacterial activity has to be controlled. Cu(I)oxide microparticles with a rather uniform diameter between 1.5 and 2 µm can be prepared by controlled reduction of alkaline Cu(II)-tartaric acid complexes. Such particles can be bound to textile surfaces by means of a pigment binder system used in pigment dyeing. By a simple pad-dry process textile fabrics with a Cu-content of 250 – 270 mg Cu / kg fabric could be prepared. The samples (fabrics) exhibited a reduction in viability of 100 % for *Staphylococcus aureus* and 84 % for *Klebsiella pneumonia* as estimated by the ASTM E2149 antimicrobial test. Simulated wash procedures led to a reduction in Cu-content to 60 – 50 % of the initial value. Reduction in viability remained at 99 % for *Staphylococcus aureus* and 78 % for *Klebsiella pneumoniae*. The new process is of high value to impart antimicrobial properties to textile products because an antimicrobial product with good wash permanence can be delivered using rather simple processing and ordinary chemicals.

1. Introduction

Copper based antimicrobials have been studied extensively for applications in medical products, the coating of surfaces and in textiles as well as technical products.[1-3] The antimicrobial properties of copper alloy surfaces makes them the preferential material for touch surfaces e.g. door knobs in hospitals, when compared to stainless steel parts.[4] Doping of paints with copper particles of different sizes demonstrated the highest antifouling potential when nano-particles were used, e.g. compared to micro-particles.[5]

Copper doped $CaSiO_3$ coatings have been investigated to provide antimicrobial properties to titanium surfaces of metallic implants.[6] Formation of TiO_2 as surface layer and incorporation of copper as antimicrobial agent has been proposed to introduce antimicrobial surface properties on Ti-implants.[7]

Besides chemical deposition from solution, alternative processes which can build up an active copper layer are CVD, magnetron sputtering or the use of nano-carriers for controlled copper release.[8-10] By gel spinning fibrous structures of $CuFe_2O_4$ could be prepared and subsequently loaded with Ag-nanoparticles to obtain high antibacterial magnetic fibres. The $CuFe_2O_4$ fibres did not show antibacterial properties. This demonstrates that release of Cu-ions into the surrounding medium is required to achieve antimicrobial efficiency.[11]

For insertion/deposition of copper into textile fibres and fabrics different techniques can be applied. A general concept is to impregnate the material with Cu(II) salt, followed by reduction to Cu(I) or Cu.[12,13] Secondly Cu containing particulate material is prepared in a first step e.g. as colloidal solution or nanoparticles and then deposited on the fibrous textile structure.[14,15] Other concepts utilise the complex formation of Cu(II)-ions with selected polymers to bind Cu(II)-ions in stable complexes.[16,17]

Controlled deposition of Cu(I)-oxide from alkaline solutions of Cu(II)-D-gluconate complexes has been reported to introduce antimicrobial properties in cellulose fibres. The nano-scaled particles however exhibited limited stability against washing procedures. Approximately 70 – 80 % of the initially present copper content was removed during 5 gentle washes.[18] The remaining amount of copper was still sufficient to provide antimicrobial properties.

In this study the preparation of an antimicrobial fabric from PES-microfiber fabric with use of Cu(I)-microparticles was investigated. The Cu(I)-microparticles were obtained by reduction from alkaline Cu(II)-tartaric complexes. As these particles did not exhibit affinity to the polyester fibres a polymer binder system for pigment dyeing was utilised to fix the particles on the fibre surface. The technical concept is not dependent on a certain fibre property, thus can be applied for most textile fibres used at present. The treated fabrics were characterised by microscopy, FTIR spectroscopy, determination of mechanical properties, Cu-content and antimicrobial properties against *Staphylococcus aureus* and *Klebsiella pneumoniae*, including also an investigation of the wash permanence Cu-content and antimicrobial effects. The transfer to existing textile processing machinery will be possible without significant changes, which will permit straightforward implementation in textile production.

2. Experimental

Material and Chemicals

Two different polyester based knitted fabrics were used for the experiments as provided by the manufacturer (REZI , Lustenau, Austria). Material A has been produced by splitting of bi-component fibres into micro-fibres thus the knitted texture of the fabric is covered by a dense layer of microfibers present in material A and additionally by a polyurethane coating in Material B. Details are given in Table 1.

Table 1 Details of materials used

Sample	Composition % w/w	Mass per area g/m²
A	90 polyester 10 polyamide	325
B	90 polyester 10 polyamide polyurethane coated	336

$CuSO_4.5H_2O$ (Fluka, Buchs, Switzerland), potassium-sodium tartrate tetrahydrate $KNaC_4H_4O_6{\cdot}4H_2O$ (Zeller, Dornbirn, Austria), NaOH, HNO_3 and glucose monohydrate (Merck, Darmstadt, Germany) were analytical grade chemicals. Elastomer binder Tubifast BN35 (acrylonitrile-butadiene-styrene copolymer, CHT Austria R. Beitlich, Meiningen, Austria) and dispersing agent Setamol WS (Lignosulfonate, BASF, Ludwigshafen, Germany) were technical grade products.

Preparation of Cu_2O microparticles

For the preparation of the Cu_2O microparticles 5 ml solution of glucose monohydrate (10 g/l, 0.050 M) was added to a mixture of 100 ml solution containing $CuSO_4.5H_2O$ (3 g/l, 0.012 M), and 100 ml potassium sodium tartrate tetrahydrate (20 g/l, 0.071 M) and NaOH (5 g/l, 0.125 M). The mixture was kept in a water bath at 80 °C for 1h to perform the reduction reaction. The microparticles settled to the ground and the colourless supernatant was decanted off. The particles were rinsed three times with distilled water.

Impregnation of textile fabric

The microparticles were used for the impregnation of the textile fabric without intermediate drying by adding to 200 ml of an aqueous solution of the elastomer based binder (Tubifast BN35, 50 g/L) and a dispersing agent to support dispersion in the solution (Setamol WS, 5 g/l). The impregnation solution must be agitated continuously to avoid settling of the particles and to achieve homogenous addition.

Impregnation of samples (31 x 20.5 cm) was performed on a laboratory padding unit (RT, speed 0.5 m/min, nip pressure 2 bar). The samples then were treated with hot air at 150 °C for 5 min to fix the Cu_2O particles with the binder system on the fabric. Two samples of each fabric quality were prepared.

For the simulated washing, impregnated samples of approx. 6 x 12 cm were placed in 250 ml bottles and 250 ml of a detergent solution (1 g/l tap water; Claro, Claro Products, Mondsee, Austria) was added. The samples then were treated in a water bath for 30 min at 60 °C. The procedure was repeated 5 times or 10 times. The samples were dried at ambient conditions for 24 h.

Analytical procedures

Microphotographs of Cu_2O particles were taken with a light microscope attached with a digital camera (CX41 RF, Olympus, Tokyo, Japan). Scanning electron micrographs and energy-dispersive X-ray (EDX) analysis were recorded with a JEOL JSM-7100F (JEOL Munich, Germany) without coating on the specimens.

The X-ray powder diffraction patterns (XRPD) were obtained with a X'Pert PRO diffractometer (PANalytical, Almelo, The Netherlands) equipped with a theta/theta coupled goniometer in transmission geometry, Cu-Kα1,2 radiation source (wavelength 0.15419 nm) with a focussing mirror, a 0.5° divergence slit, a 0.02° soller slit collimator and a 0.5° anti-scattering slit on the incident beam side, a 2 mm anti-scattering slit, a 0.02° soller slit collimator, a Ni-filter and a 1d-PIXcel solid state line detector (255 channels) on the diffracted beam side. The patterns were recorded at a tube voltage of 40 kV, tube current of 40 mA, applying a stepsize of 0.013° 2θ with an exposure time of 79s per step in the angular range of 2° to 70° 2θ.

The simulated patterns for Cu_2O and CuO were calculated from the single crystal structure data (ICSD collection codes 31057 and 31059 respectively[19]) using Mercury CSD 3.5.1 software (wavelength: Cu-Kα1,2 - 1.54056/1.54439 Å, ratio 1:0.5; step size: 0.02° 2θ).

ATR-FTIR spectra were recorded in the wavenumber range of 400 – 4000 cm^{-1} using a Vector 22 FTIR spectrophotometer (Bruker, Germany) equipped with a diamond ATR stage (32 scans, resolution 4 cm^{-1}).

Atom absorption spectroscopy (AAS) was used to determine the copper content of the samples before and after the washing tests. Samples were weighed and placed in 100 ml bottles. After adding 10 ml concentrated HNO_3 (ρ=1.4 g/cm^3) the samples were shaken for 2 h at RT. The extract was transferred into a 100 ml volumetric flask. The residual material in the bottles was shaken with 10 ml deionised water for 10 min at RT twice and the extracts were added to the nitric acid extract in the volumetric flask. The volumetric flasks were filled up to 100 ml and the extract then was filtered to remove any solids (filter paper, MN 615 - ∅ 110 mm, Machery and Nagel) before AAS was performed. The AAS analysis was performed at wavelength of 324.8 nm (AAS spectrophotometer contrAA 300 HR-CS analytic jena, Jena Germany). Three replicates were made.

Physical testing

The air permeability test was performed on a test area of 20 cm² using a Textest instrument FX3030 (TEXTEST, Austria), according to DIN 53887:1977. Results are given in litres/m² min at a pressure difference of 200 Pa. Mean value and standard deviation of three repetitions were calculated.

The sample flexural rigidity was characterised through determination of the bending length of sample strips of 2.5 cm width according to DIN 53362:1970. The material was tested in one direction and with bending on the same side. Mean value and standard deviation of six repetitions were calculated.

Antibacterial activity

The antibacterial activity tests for copper treated fabrics were performed using the standard test method for the determination of the antimicrobial activity of immobilized antimicrobial agents under dynamic contact conditions ASTM E2149-01.[20] Briefly, a specimen is measured by weight and 2 g were placed in 250 ml wide-necked, screw-capped Erlenmeyer flasks containing 50 ml of a suspension of *Staphylococcus aureus* ATCC 6538 or *Klebsiella pneumoniae* ATCC 4352 (approx. 3.0 x 10^5 cells per ml) in 0.3 mM KH_2PO_4 buffer solution (pH 7.2). Flasks were vigorously shaken for intervals of 0 min, 1h, 3h, 6h and 24h at 25°C. At the end of each time interval 1 ml of

bacterial suspension was removed, serial diluted and plated on nutrient agar. The bacteria were incubated at 37°C for 24 h and the number of viable cells (CFU) was determined. The antibacterial activity was evaluated by calculating the reduction of bacteria according to Eq. (1).

$$R\% = \frac{(A-B)}{A} * 100 \qquad (1)$$

where R% is the percentage of reduction bacteria viability. For calculation of the control fabrics (untreated samples), A is the number of viable bacteria (CFU/ml) at contact time = 0 and B is the number of viable bacteria (CFU/ml) after contact time = x h. For calculation of the treated samples (CFU/ml), A is the number of viable bacteria (CFU/ml) of the untreated fabrics at contact time = x h, and B is the number of viable bacteria (CFU/ml) after contact time = x h with copper coated fabrics. According to the ASTME2149-01 method two replicates were made.

3. Results and discussion

Cu_2O microparticles

The preparation of the Cu_2O microparticles followed an adapted reaction scheme of Fehling's test for aldehydes. Glucose was used as a reducing aldehyde and an alkaline solution of Cu(II)-tataric acid complex was added as a source of Cu(II)-ions. The rate of reduction can be controlled by adjusting the concentration of NaOH in the assay and by temperature.
Smaller particles are generated when rapid formation of Cu_2O is initiated by higher concentrations of NaOH and temperatures near to the boil.[21] By reducing the NaOH concentration we could achieve slow controlled growth of microparticles to reach an average diameter of approximately 1.5 - 2µm (Figure 1).

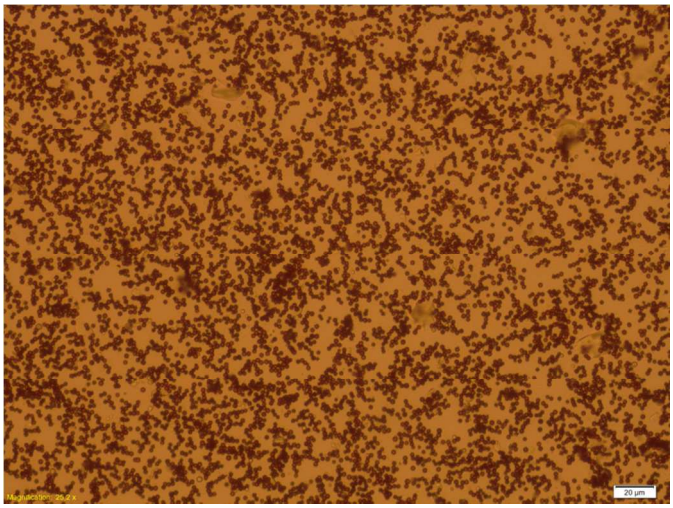

Fig. 1 Light microscope images of Cu_2O microparticles

The Cu_2O microparticles were allowed to settle down and rinsed with water to remove chemicals from the reduction step. The particles were then directly used to prepare the aqueous dispersion for impregnation. An X-ray powder diffraction pattern of the solid red precipitate is shown in Figure 2. The analysis proves that the red microparticles consist of Cu_2O.

Preparation of textiles

The textile fabrics were impregnated with the dispersion of Cu_2O particles by means of a laboratory padder. Due to their size the Cu_2O particles did not exhibit strong binding forces to the fibre surface, thus a commercial binder system for pigment dyeing was used to fix the micro-particles at the fibre surface.
The uptake of impregnation liquid was determined with 110 % w/w for sample A and with 64 % w/w for sample B, which can be explained with the more closed structure of the elastomer coated sample B.

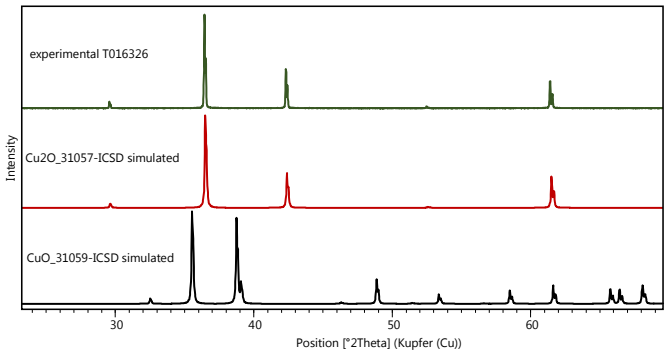

Fig. 2 Comparison of the experimental PXRD pattern of Cu_2O particles (TO16326) with the simulated pattern of Cu2O and CuO

Changes in the mechanical properties and permeability of the treated samples were monitored by analysis of air permeability and flexural rigidity, characterised by the bending length required to achieve a 41.5° bending of a 2.5 cm wide stripe under its own weight.

Table 2 Air permeability and flexural rigidity (bending length) of untreated and Cu2O/binder treated samples (mean ± standard deviation)

Sample	Air permeability l/m² min	Bending length mm
Sample A		
Untreated	198 ± 14	24 ± 4
Cu_2O binder	322 ± 24	52 ± 1
Sample A		
Untreated	243 ± 14	33 ± 4
Cu_2O binder	267 ± 38	61 ± 2

Material A consists of micro-fibres which were formed through splitting after knitting the fabric, thus resulting in a very bulky fibrous surface. Through the padding and drying processes the voluminous structure is slightly compressed and fibres are partly bonded together by the binder. Thus more and larger voids between the fibres are formed and the already high air permeability increases further. Material B already had been coated with polyurethane before the Cu_2O/binder treatment thus the influence of the binder addition on air permeability is within the statistical error of the measurements. The binder treatment reduces mobility of individual fibres in the textile structure thus the stiffness of the samples increases. For treated samples the length required to bend a stripe under its own weight to an angle of 41.5° almost doubles. In the flexural rigidity test the applied forces for bending are rather low, thus the indicated change in stiffness is significant but handle of the material still is perceived soft and flexible.
The thickness of the binder layer can be estimated from the liquid uptake, the concentration of binder used and the solids content of the binder. When a binder system with 50 % solids is

used with a concentration of 50 g/l and a liquid uptake of 100 %, then a total amount of 25 g binder is deposited on 1000 g fabric. On a fibre with a diameter of 10 µm the layer thickness then can be calculated with 60 – 70 nm.
An electron micrograph and an EDX analysis of the deposited particles on a single fibre of sample material A is shown in Figure 3. As expected from the estimates the thickness of the binder film too low to be visible (additional micrographs are shown in the supplementary material Figs. S1 – S4).

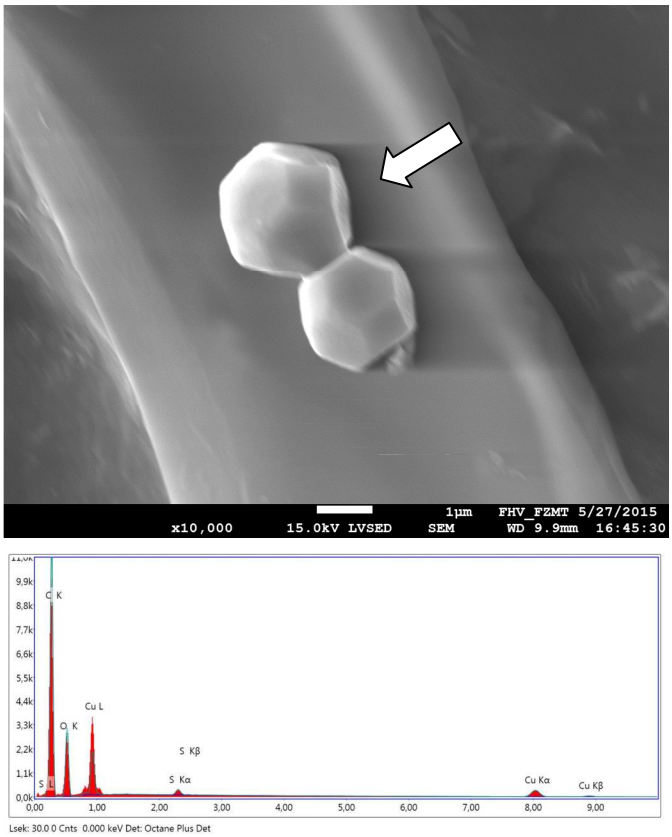

Fig.3 Electron micrographs of Cu_2O/binder treated sample A and EDX analysis (arrow indicates Cu_2O particle)

The Cu-content of the samples and references was analysed by AAS after nitric acid extraction of the Cu and appropriate dilution (Table 3). The uniformity of impregnation on macroscopic scale of 1 cm² can be assessed form the standard deviation of the Cu-analysis, which is in the dimension of ± 10 %. For comparison the Cu-content of samples with pigment binder alone were analysed and a Cu-content of approximately 10 mg Cu per kg of fabric was found.
To study the durability of the deposited Cu_2O the decrease of the Cu-content as a function of 5x and 10x of repetitive simulated washing was studied. The results shown in Table 3 indicate a substantial decrease in Cu-content from the initial 248 mg/kg (sample A) and 272 mg/kg (sample B) with and increased number of washes. More than 50 % of the Cu-content initially bound on the treated samples was determined after 10 washes, with 139 mg/kg for sample A and 170 mg/kg for sample B. This is a substantially lower decrease in Cu-content compared to results reported in a related study, where 80 % of the Cu was removed during 5 repetitive washes.[18] In the study presented in reference 18 the Cu_2O particles were formed on cellulose fibres by an in-situ reduction without use of any polymer binder. Thus particle release and dissolution of Cu-ions occurs more rapid, which results in high antimicrobial activity. High reduction in viability of *Staphylococcus aureus* already was observed within 3 hours, as a result of the more rapid release of Cu-ions into the bacterial suspension.

Table 3 Cu-content of fabric samples (std.dev. = standard deviation)

	Cu-content mg/kg	(std.dev.) mg/kg	Cu-content mmol/kg
Sample A			
Binder alone	7.6	±4.4	0.12
Binder alone, 5X washed	7.7	±5.7	0.12
Cu_2O binder	248.1	±26.7	3.90
Cu_2O binder 5X washed	166.3	±63.6	2.62
Cu_2O binder 10X washed	139.7	±30.7	2.20
Sample B			
Binder alone	13.2	±3.8	0.21
Binder alone, 5X washed	12.2	±3.6	0.19
Cu_2O binder	272.3	±30.2	4.29
Cu_2O binder 5X washed	192.8	±30.7	3.03
Cu_2O binder 10X washed	170.1	±23.9	2.68

An electron micrograph and EDX analysis of a particle on the Cu_2O/binder treated sample A after 10 x washing are shown in Figure 4. The shape of the particles seems almost unchanged, which supports the assumption that a major loss of Cu-content during washing may be due removal of particles through frictional and shear forces.

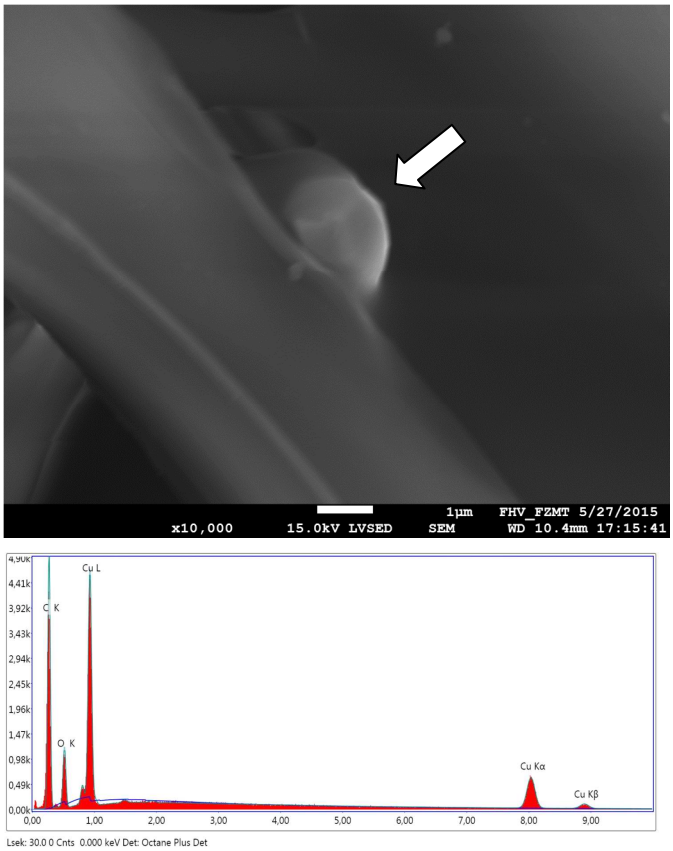

Fig.4 Electron micrographs of 10 x washed Cu_2O/binder treated sample A and EDX analysis (arrow indicates Cu_2O particle)

The modification of the fabric surface also was investigated by FTIR-ATR spectroscopy. As a representative example the FTIR

spectra of untreated sample A and samples treated with binder and Cu_2O microparticles are shown in Figure 5.
While all three infrared spectra show the characteristic vibrations for polyester (e.g. ν(C=O) at 1720 cm^{-1}, ν(C-H) at 2920 cm^{-1} and 2880 cm^{-1}, ν(C-O) at 1250 cm^{-1},) and a minor amount of polyamide (e.g. ν(N-H) at 3300 cm^{-1}) there are no significant differences between the three spectra to indicate the presence of a binder system. This can be explained with the amount of binder present on the fabric, which can be estimated to be lower than 1 % w/w and thus is expected to range below the detection limit of the method.

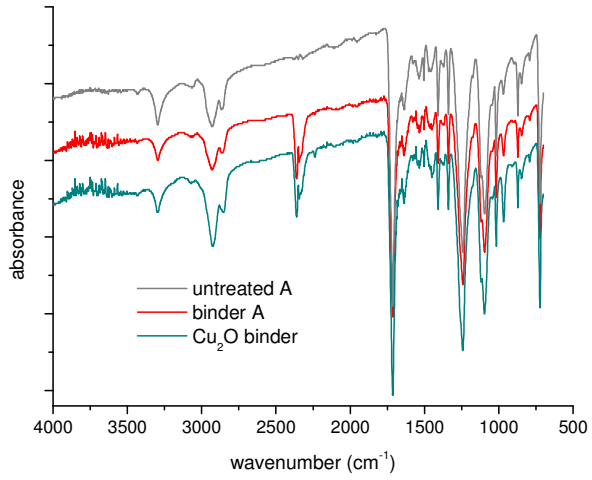

Fig. 5 FTIR-ATR spectra of untreated sample A, sample with binder alone and Cu_2O and binder treated sample

Antimicrobial properties

To determine the antibacterial activity of the Cu_2O microparticles containing samples the fabrics and relevant reference samples without Cu_2O particles were tested against the Gram-positive *Staphylococcus aureus* (ATCC 6538) and the Gram-negative *Klebsiella pneumoniae* (ATCC 4352). ASTM E2149-01 was chosen as standard method for determination of the antimicrobial activity of immobilized antimicrobial agents (Tables 4 and 5).

Table 4 Reduction in bacterial viability of *Staphylococcus aureus* as a function of time (blank = untreated fabric)

	Time 1h	3h	6h	24h
Sample A				
Blank	0	0	0	0
Ref. Binder	0	4	5	0
Cu_2O	16.2	41.5	45.7	100
Cu_2O (5x wash)	9.1	35.4	48.2	100
Cu_2O (10x wash)	8.2	27.1	44.6	99.6
Sample B				
Blank	0	0	0	0
Ref. Binder	0	4.3	5.1	0
Cu_2O binder	10.3	21.2	35.4	84.2
Cu_2O (5x wash)	0	30.1	45.3	97.1
Cu_2O (10x wash)	0	4.7	35.5	82.1

As references both untreated fabric and fabric treated with the pigment binder system alone were included to identify possible antimicrobial properties of other components present in the material or binder chemicals.
As can be seen in Tables 4 and 5 under the test conditions both the fabric material itself and the pigment binder chemicals did not cause a significant reduction in bacterial viability.
All Cu_2O containing samples exhibited antimicrobial activity. Washing procedures caused a reduction in the antimicrobial activity, as expected from the Cu-analysis in the fabric.
As expected for an immobilised antibacterial agent reduction in bacterial viability in the chosen test protocol depends on the experimental time scale. A 84 - 100 % reduction in viability was observed for *Staphylococcus aureus* after 24 h and 85.3 - 92.8 % reduction was observed in the same time for *Klebsiella pneumoniae*. Washing processes in general decrease the Cu-content and in parallel a lower reduction of bacterial viability is observed. Remarkably a higher reduction in bacterial viability was observed after 5 washings. Most probably the thin binder film on Cu_2O particles partly was removed through the action of the detergent thus besides Cu_2O losses also the surface activity of the remaining particles was increased. After 10 washes, dependent on material and test culture reduction in bacterial viability still reached 78 – 99.6 %, indicating that the amount of Cu present in the fabric is sufficient enough to exhibit antimicrobial properties.

Table 5 Reduction in bacterial viability of *Klebsiella pneumoniae* as a function of time (blank = untreated fabric)

	Time 1h	6h	24h
Sample A			
Blank	0	0	0
Ref. Binder	0	0	0
Cu_2O binder	28.2	83.1	92.8
Cu_2O binder (10x wash)	0	58.6	78.1
Sample B			
Blank	0	0	0
Ref. Binder	0	0	0
Cu_2O binder	27.4	58.1	85.3
Cu_2O binder (10x wash)	0	45.4	80.5

In an extensive study of the minimal inhibitory concentration (MIC) of various antimicrobials a MIC of 2 mM (127 mg/l) for copper sulphate was reported for 22 isolates of *S. aureus*, while the majority of *E. coli* isolates was able to tolerate much higher Cu concentrations resulting in a MIC of 20 mM (1270 mg/l).[22]
For Cu-nanoparticles a minimum inhibitory concentration for *S. aureus* has been reported in literature with 2.2 mM.[23]
Under the test conditions applied in this work 2 g of the test specimen was agitated in 50 ml of culture medium, thus the maximum concentration of Cu theoretically possible in a solution would be around 0.16 - 0.17 mM for the unwashed samples and 0.09 – 0.11 mM for the 10x washed samples. These values are substantially below the MIC for Cu in solution and indicate that the antimicrobial effect is not based primarily on a rapid release of Cu-ions into the culture medium. According to literature, leaching of Cu-ions and formation of Cu-peptides complexes in the near environment of the particles leads to oxidative stress and cytotoxicity.[24] This explains the time dependent antimicrobial effects observed in this study, as the cytotoxic effects of the Cu-microparticles mainly will be localised close to the immediate fabric surface.

4. Conclusions

The formation of Cu_2O microparticles from the alkaline Cu(II)-tartaric acid complex can be steered in such manner, that

microparticles with almost uniform size distribution around 1.5 – 2 µm can be prepared. These particles can be fixed on textile fabric made from synthetic fibres by use of a commercial pigment binder system applying a pad-dry process.
The prepared samples showed a Cu-content of 250 – 300 mg Cu / kg fibres. A distinct reduction in bacterial viability for both tested cultures *Staphylococcus aureus* and *Klebsiella pneumoniae* was observed. The bound Cu_2O particles behave as an immobilised antimicrobial agent thus time dependent reduction in bacterial viability was observed.
After 10 repetitive washes a significant reduction in Cu-content to 60 – 50 % of the initial value was observed. Despite the lowered Cu-content of 140 – 170 mg Cu / kg of fibre substantial reduction in bacterial viability of 78 – 99 % was observed, this indicates that the remaining Cu is still sufficient to maintain antimicrobial properties.
The application of Cu_2O microparticles on textile fabric by use of a commercial pigment binder system is of high value for future technical applications because

- the technique permits direct transfer into production scale
- the process is independent of the type of textile fibre as the binder system can be applied on all major types of fibres
- high reduction in viability can be achieved at low Cu-content.

Further studies to investigate the effect of particle size and preparation conditions in more detail would be of interest to elucidate the principles behind the reported findings further.

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Copper(I)oxide microparticles were be bound to textile surfaces by means of a pigment binder system to provide antibacterial activity with good wash permanence, using rather simple processing and ordinary chemicals.