

Antibacterial Activity of Textiles Functionalized with SilverSil

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Natural (cotton) and synthetic (polyester) fabrics functionalized with the SilverSil xerogel powder dispersed in water-repellent, eco-friendly commercial textile finishings, acquire substantial antibacterial activity against both Gram-positive and Gram-negative bacteria. Here demonstrated against *Staphylococcus aureus* and *Escherichia coli*, said activity is due to the Ag nanoparticles sol-gel entrapped within the organically modified silica

matrix. Cotton fabrics treated with SilverSil using the rod-coating method show a reduction in bacterial growth of 90.1% for *S. aureus* and 99.0% for *E. coli*. Ease of deposition using the rod-coating method, low application rate, and enhanced physical and chemical stability of the ORMOSIL-entrapped Ag nanoparticles are promising toward the production of durable antimicrobial fabrics and garments, minimizing antimicrobial resistance.

1. Introduction

The development of antimicrobial garments is an important health and safety objective of contemporary applied research.^[1] Particularly relevant is the development of antimicrobial textiles capable of not driving antimicrobial resistance (AMR), a process in which microorganisms evade the effects of multiple drug classes through mechanisms such as drug target modification, enzymatic degradation or inactivation, reduced membrane permeability, and increased efflux from the bacterial cell. This is particularly important in hospital settings, where it helps reduce the microbial load on healthcare workers' clothing to levels low enough to lower the rate of hospital-acquired infections (HAIs), infections acquired during hospitalization.^[2] Nearly 8% of hospitalized patients develop HAI, 20% of which could be caused by a multidrug-resistant organism (bacteria or fungi). Methicillin-resistant

Staphylococcus aureus (MRSA) and *Escherichia coli* ESBL (extended-spectrum β -lactamase producing) were amid the four multidrug-resistant bacteria identified in a clinical study carried out in Spain between 2011 and 2014. The study found that hospital infections caused by multidrug-resistant organisms increase mortality, readmissions, and visits to the emergency department compared with those produced by conventional bacterial strains.^[3]

Unlike conventional antimicrobials, nanoparticulate silver has recently been rediscovered due to broad-spectrum antimicrobial activity, targeting a wide range of pathogens, including fungi, and its multiple mechanisms of action, such as disrupting bacterial cell membranes, generating reactive oxygen species, and interfering with DNA replication, making it harder for microorganisms to develop resistance, thereby minimizing AMR.^[4] Thanks to the joint activity of Ag^+ ions, Ag atomic clusters, and nanoparticles (NPs), a synergistic antimicrobial mechanism is established. In this process, dead bacteria may act as reservoirs for active silver species, which can be subsequently released and transferred to other bacteria, thereby propagating the bactericidal effect and contributing to the minimization of AMR.^[5] The synergistic antimicrobial mechanism of nanoparticulate silver, furthermore, minimizes AMR.^[6]

Smaller Ag NPs exhibit a higher surface area-to-volume ratio, enhancing their contact with bacterial membranes and their ability to penetrate the bacterial cell wall. Surface charge influences electrostatic interactions with the negatively charged bacterial surface, while the oxidation state governs the continuous release of Ag^+ ions, which are primarily responsible for the antimicrobial activity.^[6]

A review published in early 2013 found that triclosan, silane quaternary ammonium compounds, zinc pyrithione, and silver-based compounds were the main species used to functionalize antimicrobial textiles.^[7] Synthetic organic compounds were found to dominate the market, but nanoscale silver and silver salts offering "clear potential benefits for textile use"^[6] due to very low application rates.

However, conventional silver-based antimicrobials, such as those incorporating silver nitrate or silver sulfadiazine (SDD),

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often suffer from poor durability and bioactivity loss due to faster silver loss. For example, in clinical applications of silver nitrate and SSD in wound dressings, ionic silver is quickly inactivated by proteins and chloride present in wound exudates, necessitating frequent reapplication (up to 12 times daily in some cases) to maintain antimicrobial efficacy.^[8] In contrast, nanocrystalline silver provides an initial large release of silver followed by a slow and sustained release due to lower reactivity with negatively charged biological components.

In their 2020 publication, Albo, Pagliaro, and Ciriminna suggested that antimicrobial formulations based on microencapsulated Ag NPs will be amid next-generation antimicrobials.^[4] Without microencapsulation, silver deposited on textiles readily leached into the water, and bioactivity was lost. For example, researchers in Germany evaluated the durability of 11 silver-containing antimicrobial textile products and found that all of them lost their antimicrobial activity rapidly after laundering.^[9] In the same year, Albo's team in Israel, along with Pagliaro's team in Italy, reported promising *in vitro* antimicrobial activity of the sol–gel organically modified silica (ORMOSIL) xerogel coatings.^[10]

The material, referred to as “SilverSil,” immersed in water, showed nearly leach-proof nature, releasing only 3.46 ppm of silver after seven washing cycles.^[10] Despite this low release, both the rinsing water and the residual xerogel retained significant antibacterial efficacy. The pronounced activity of the washing solutions was attributed to the potent effect of silver ions present in extremely low concentrations. A similar outcome was observed in previous studies, where even trace amounts (e.g., 2 ppb) of silver remaining on fabrics after extended washing cycles were sufficient to suppress over 99.9% of *E. coli* proliferation.^[11]

This makes nanocrystalline silver, and by extension, silver-based nanomaterials embedded in stable matrices like ORMOSIL, a promising alternative for longer-lasting antimicrobial functionality. Nontoxic silica-based waterborne nanosols used to produce thin and durable ORMOSIL coatings share uniquely excellent health and safety profile.^[12] Besides low production costs resulting from the current low market price of Si alkoxides, the key advantage provided by the sol–gel encapsulation of Ag nanoparticles in the ORMOSIL organoceramic matrix lies in the high chemical and physical stability imparted by the sol–gel matrix to the encapsulated Ag NPs. Alongside providing stability toward leaching, the sol–gel encapsulation of the Ag NPs enhances the nanoparticle stability toward oxidation, agglomeration, and thermal degradation.^[13]

Recently, a new alcohol-free synthesis protocol for SilverSil, specifically designed to enable scalable and practical applications on textile materials, has been optimized.^[14] This advancement is particularly relevant since conventional sol–gel formulations based on alkoxysilanes generally contain flammable alcohols, which help control gelation kinetics and stability. However, their presence can hinder scalability. Alcohol-free formulations are therefore essential for promoting the industrial implementation of sol–gel coatings, especially for safety reasons in textile manufacturing.^[15] Furthermore, this new formulation offers both uniform and high encapsulation efficiency of Ag NPs, effectively minimizing metal nanoparticle aggregation. The uniform dispersion of small Ag nanoparticles within the silica matrix enhances antimicrobial activity and minimizes cytotoxicity.^[16]

In this study, the antimicrobial activity of both natural (cotton) and synthetic (polyester) fabrics functionalized with SilverSil using different methods is reported, demonstrating effectiveness against both Gram-positive and Gram-negative bacteria, specifically *S. aureus* and *E. coli*. A readily scalable and convenient functionalization method based on rod-coating for cotton textiles was optimized with the aim of enabling the first practical applications of the versatile SilverSil sol–gel coating to produce long-lasting antimicrobial fabrics.

2. Materials and Methods

2.1. Materials

Tetraethylorthosilicate (TEOS, purity >99%), methyltriethoxysilane (MTES, purity >99%), 3-(aminopropyl)trimethoxysilane (APTMS, purity >99%), AgNO₃ (purity >99.999%), and NaBH₄ powder (purity >98%) were purchased from Sigma Aldrich. HNO₃ (65%) was purchased from Merk Millipore. Absolute ethanol and aqueous ammonia (≈25% in water) were purchased from Fluka Chemical.

Cotton ISO 105-F02 (hereafter, CO) and Polyester ISO 105-F04 (hereafter, PE) textile garments were kindly provided by Testfabrics Inc. (West Pittston, PA, USA). Pluvion Dry 2030 BS and Vision Sugar 4.0 commercial resins, Catalizzatore is Green used as the crosslinking agent, and Gel Ftr Liq. used as an acrylic-based thickener, were kindly provided by F.T.R. Srl (Albano Sant'Alessandro, Italy). Naigard BB-WR, Naigard BB-AC, and Katalin S/CL NEW (crosslinking agent) were kindly provided by Nearchimica Srl (Legnano (MI), Italy). The antibacterial tests were conducted on *S. aureus* ATCC 6538 and *E. coli* ATCC 11229 bacteria obtained from the American Type Culture Collection (ATCC) supplied by Biogenetics Diagnostics (Ponte San Nicolò (PD), Italy). The medium used in the ASTM E 2149–13 standard method was Yeast Extract Agar supplied by Merck Life Science (Milano, Italy).

2.2. ORMOSIL Preparation

Blank and doped SilverSil ORMOSILs containing different amounts of silver nanoparticles (Table 1) were prepared following the optimized sol–gel route recently reported.^[14] A mixture of tetraethylorthosilicate (TEOS, 3.94 mL, 17.8 mmol) and methyltriethoxysilane (MTES, 7.85 mL, 39.4 mmol) in 13.3 mL of ultrapure

Table 1. Blank and doped ORMOSILs, theoretical Ag NPs%, and bacteria reduction %.

ORMOSIL	Ag [wt%]	Bacterial reduction [%]	
		<i>S. aureus</i>	<i>E. coli</i>
BlankC	0.0	30.7 ± 7.5	41.6 ± 15.5
SilverSilC1	0.01	67.4 ± 5.1****	91.0 ± 3.1****
SilverSilC2	0.05	74.7 ± 2.1****	95.1 ± 0.6****
SilverSilC3	0.1	97.6 ± 0.4****	99.6 ± 0.5****
SilverSilC4	1	99.5 ± 0.0****	100.0 ± 0.0****

water was slowly added with 6 mL 0.2 M HNO₃ under stirring at room temperature. After 10 min, a 0.125 mL aliquot of 3-(aminopropyl)trimethoxysilane (APTMS, 0.716 mmol) was added, and the mixture was further stirred for 1 h. Ethanol generated during the hydrolysis of the Si alkoxides was removed under reduced pressure and replaced with the same volume (11 mL) of ultrapure water.

For SilverSilC1, C2, and C3, different aliquots of a 6.36 mM AgNO₃ solution were added dropwise: 0.5 mL for SilverSilC1, 2.5 mL for SilverSilC2, and 5 mL for SilverSilC3. The volume was then adjusted with ultrapure water to obtain a 0.024 Si alkoxide/water molar ratio. In the case of SilverSilC4, a 7.95 mL aliquot of 40 mM AgNO₃ solution and 2.05 mL of ultrapure water were used to achieve the same ratio. For the blank sample, the amount of AgNO₃ solution was replaced with ultrapure water. Gelation was initiated by the slow addition of 3 mL of 0.2 M aqueous ammonia solution. The resulting wet hydrogel was aged for 48 h at room temperature and subsequently dried in an oven at 70 °C for 3 days.

A 1 g portion of each doped xerogel precursor was suspended in 10 mL of ultrapure water (20 mL in the case of SilverSilC4) and added under stirring with a 0.03 M NaBH₄ solution in 1:100 molar ratio with respect to AgNO₃. After 1 h stirring, the resulting reduced xerogel suspension was filtered and washed thoroughly with 500 mL of ultrapure water, followed by 200 mL of EtOH:H₂O (1:1 volume ratio) solution. Each washed xerogel was dried in an oven at 40 °C for 5 h.

2.3. Coating Deposition Procedures

The preparation of coated textiles was carried out via dip-pad-dry-cure and the rod-coating method.

The coating formulation was prepared by adding powdered ORMOSIL samples (BlankC or doped SilverSil powders: SilverSilC1, C2, C3, or C4), at a concentration of 7.5 wt%, to partly biobased textile finishings used to provide hydrophobicity (Pluvion Dry 2030 BS, Naigard BB-WR, Naigard BB-AC, or Vision Sugar 4.0). Alternatively, a concentration of 3.5 wt% ORMOSIL was added to the aforementioned resins diluted with ultrapure water (10% w/v). An exception was made for Naigard BB-WR, which was diluted in acidic water (pH 5.5). A homogeneous dispersion was obtained by vigorous stirring at room temperature for 5 min, followed by

sonication in a bath for additional 5 min. Subsequently, cotton or polyester fabrics (10 × 10 cm square samples) were immersed in the coating dispersion for 5 min to ensure the formation of a uniform coating. The wet fabrics were then squeezed using a glass lab roller to achieve ≈100% wet pick-up, calculated according to Equation (1).

$$\text{Wet pick-up (\%)} = \frac{m_1 - m_0}{m_0} \times 100 \quad (1)$$

where m_1 and m_0 are the weights of wet and untreated fabrics, respectively.

Finally, the fabrics were dried in an oven at 100 °C for 5 min, followed by thermal treatment at 170 °C for 2 min (Table 2).

The formulations used for applications by the rod-coating method were prepared by mixing a diluted aqueous solution of each resin (acidic aqueous solution in the case of Naigard BB-WR), along with its crosslinking agent, and with a proper amount of BlankC and doped SilverSilC4 added separately under vigorous stirring. Subsequently, a defined amount of acrylic-based thickener was added to each mixture, resulting in four viscous pastes doped with ORMOSIL xerogels. Control samples without the presence of xerogel powders were also prepared.

Scoured cotton fabrics were coated with these formulations using a rod-coating method with a laboratory-scale K101 control coater (URAI, Assago, Italy). This coater featured a spreadable surface of 170 × 250 mm and an adjustable speed range of 30–250 mm s^{−1}. To apply the coating, the cotton fabric was first securely fixed on the coater's table. The ORMOSIL-based formulations were then deposited on the fabric substrate, using a Mayer bar to evenly distribute the dispersion by forming a uniform coating. The coating process was carried out at a rate of 55 mm s^{−1}. A video of the deposition process can be viewed online at the URL: <https://t.ly/7DXtv>.

Finally, all coated samples were dried at 100 °C for 5 min and polymerized at 170 °C for 2 min, thus obtaining the cotton-treated textiles listed in Table 2.

In the case of dip-pad-dry-cure, or a single layer deposition in the case of the rod-coating method, a single impregnation step was conducted to achieve the dry add-on % value calculated according to Equation (2).

$$\text{Add-on (\%)} = \frac{W_1 - W_0}{W_0} \times 100 \quad (2)$$

Table 2. Wet pick-up, add-on, and bacterial reduction values for cotton (CO) and polyester (PE) fabrics treated with 3.5 wt% of BlankC or SilverSilC4 (1% Ag NPs) dispersed in different resins.

ORMOSIL	Textile	Resin	Weight pick-up [%]	Add-on [%]	Bacterial reduction [%] <i>S. aureus</i>
BlankC	PE	Naigard BB-WR	106	9.7	0.0 ± 0.0
SilverSilC4	PE	Naigard BB-WR	103	8.9	33.6 ± 4.0****
BlankC	PE	Pluvion Dry 2030 BS	102	3.7	61.8 ± 2.5
SilverSilC4	PE	Pluvion Dry 2030 BS	104	9.2	91.1 ± 1.2****
BlankC	CO	Naigard BB-WR	103	6.1	89.9 ± 2.0
SilverSilC4	CO	Naigard BB-WR	97	5.8	99.5 ± 0.0***
BlankC	CO	Pluvion Dry 2030 BS	100	6.1	86.0 ± 2.1
SilverSilC4	CO	Pluvion Dry 2030 BS	98	5.7	89.9 ± 3.7

where W_1 and W_0 are the dry weights of treated and untreated fabrics, respectively, after thermal treatment.

2.4. Antibacterial Tests

The antibacterial activity of SilverSil and blank ORMOSILs against *S. aureus* ATCC 6538 (Gram-positive) and *E. coli* ATCC 11229 (Gram-negative) bacterial strains was assessed both before and after application on finished textiles. The antibacterial activity was evaluated according to ASTM E 2149-2013a "Standard test method for determining the antimicrobial activity of antimicrobial agents under dynamic contact conditions." The bacteria strains were obtained from the ATCC: Gram-positive *Staphylococcus aureus* ATCC 6538 and Gram-negative *Escherichia coli* ATCC 11229. The primary cultures were prepared using lyophilized bacteria kits supplied by KwikStik; the suspensions were put into a Petri dish containing 20 mL of yeast extract agar for microbiology (Sigma-Aldrich 01497-500 g, suitable for *E. coli* and *S. aureus*) for 24 h at 37 °C. The test cultures were created by suspending the bacteria in a nutrient broth (Buffered Peptone Water for microbiology, VWR Prolabo Chemicals) for 24 h at 37 °C. The bacteria concentration was measured with a spectrophotometer (following the absorbance at 475 nm) and diluted in a pH 7.2 $\pm$ 0.1 buffer solution (Honeywell FlukaTM, 0.25 M KH_2PO_4 , with fungicide) to yield a concentration of $1.5\text{--}3.0 \times 10^5$ CFU (colony-forming unit) mL^{-1} (working dilution). The bacterial inoculum was put in contact with the antibacterial materials (materials/inoculum ratio 1:50 w/v) under shaking at 190 rpm at room temperature for 1 h. After this time, a 1 mL aliquot of said inoculum was first diluted 1000 times with buffer solution at pH 7.2 until reaching a concentration of $1.5\text{--}3.0 \times 10^2$ CFU mL^{-1} and then plated in Petri dishes in 15 mL of Yeast Extract Agar (Sigma-Aldrich).

Inoculated plates were incubated at 37 °C for 24 h, and surviving bacteria colonies were counted using the plate count method. The antibacterial activity was expressed as a percentage reduction in microorganism colonies after contact with the test specimen compared to the number of bacterial colonies in the control plate, according to Equation (3).

$$\% \text{ bacterial reduction (CFU mL}^{-1}\text{)} = \frac{B - A}{B} \times 100 \quad (3)$$

where A is the bacterial concentration in CFU mL^{-1} after contact with the specimen under testing and B at contact time $t = 0$ (inoculum control).

All tests were conducted in triplicate.

2.5. FTIR Analysis

Fourier transform infrared (FTIR) analysis was performed using the attenuated total reflection (ATR) sampling technique with a Bruker (Billerica, MA, USA) spectrophotometer equipped with a transit platinum ATR probe and a diamond crystal apparatus. Measurements were carried out in the $4000\text{--}600$ cm^{-1} range, with a lateral resolution of 4 cm^{-1} and 128 scans for each sample. Spectra were recorded using OPUS 7.0 software and normalized to the band at 1313 cm^{-1} for cotton and 1337 cm^{-1} for polyester

fabrics, as these peaks fall in a region where siloxane absorptions are absent.

2.6. TEM Analysis

The scanning transmission electron microscopy (STEM) images of blank ORMOSIL (BlankC) and SilverSil xerogels were obtained using a Tescan MAGNA (Tescan, Brno, Czechia) ultra-high-resolution field emission scanning electron microscope equipped with a STEM detector. Samples were prepared by suspending a small amount of xerogel powder in distilled water, followed by sonication in an ultrasonic bath and drop casting on a carbon film supported 200 mesh copper grid. All samples were dried at room temperature before analysis. The STEM analysis was performed in bright and dark fields at an accelerating voltage of 30 keV.

2.7. Data Processing

Experimental data were processed using the version 2024 of the Origin(Pro) software (OriginLab, Northampton, MA, USA).

The antibacterial tests were performed in triplicate, with independent microbial cultures for antimicrobial assays. The results obtained were analyzed using "GraphPad Prism 8.0" software, validating the statistical significance by the one-way analysis of variance (ANOVA) test, with Bonferroni and Dunnett corrections. In all cases, p -values < 0.05 were considered statistically significant.

3. Results and Discussion

The STEM images in Figure 1 show that all ORMOSILs are comprised of aggregated submicron organosilica particles exhibiting a good dispersibility of the Ag NPs within the inner mesoporosity of the organosilica matrices, particularly evident in SilverSilC4 (Figure 1C). Homogeneously distributed within the mesoporous organosilica matrix, the Ag NPs appear as black spots in bright-field images or bright spots in dark-field images. In contrast, Ag NPs are not detectable in SilverSilC3 (Figure 1b) due to their lower concentration and high dispersibility.

The Ag NPs entrapped in SilverSilC3 and SilverSilC4 are quasi-spherical with a uniform size distribution around 20–25 nm in diameter. Formation of larger clusters (100 nm) in SilverSilC4 was likely due to the higher concentration of Ag^+ undergoing aggregation during the reduction process with NaBH_4 .

The size and shape of Ag NPs are two critical factors influencing the release of Ag^+ ions from Ag NPs. Nanoparticles with a small size and a spherical or quasispherical shape are more prone to release Ag^+ ions due to their lower thermodynamic stability.^[17] Furthermore, Ag NPs with a size of 10–20 nm exhibit enhanced activity due to internalization and interaction with intracellular components (while larger (>20 nm) NPs chiefly act through the release of Ag^+ ions).^[18]

Entries in Table 1 show the bacterial reduction percentage of SilverSil powders after 1 h inoculation of *S. aureus* and *E. coli* bacterial strains in the presence of BlankC and SilverSil ORMOSILs.

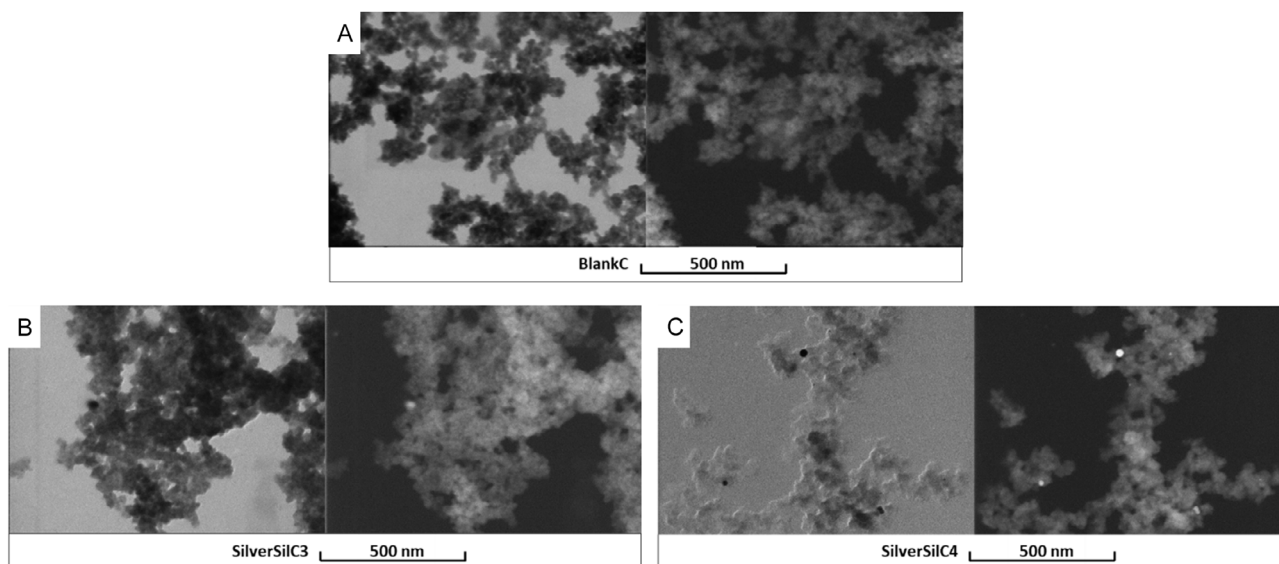


Figure 1. STEM images (left, bright field; right, dark field) of: A) BlankC (non-doped), B) SilverSilC3 (doped with 0.1% Ag NPs), C) SilverSilC4 (doped with 1% Ag NPs).

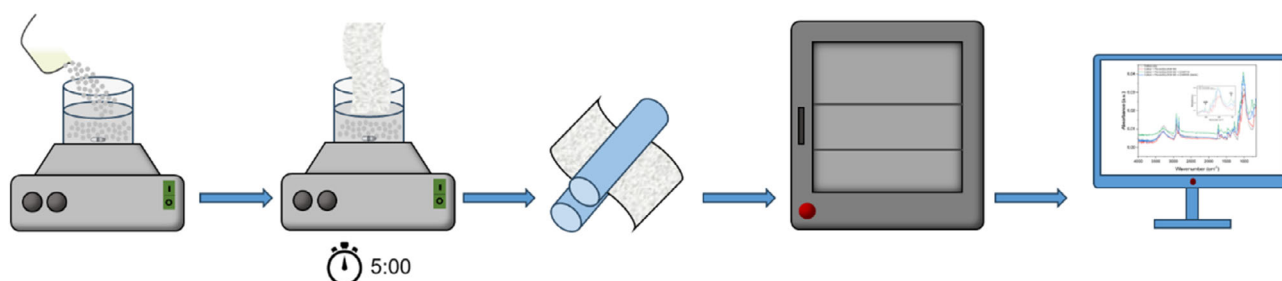
Bacterial reduction (%) was reported as the mean of values obtained from assays in triplicate $\pm$ standard deviation. Statistical significance was examined by the one-way ANOVA test, with Dunnett's correction ($p < 0.05$). Asterisks indicate the statistical significance respect to the control (BlankC) (**** $p < 0.0001$; *** $p < 0.001$; ** $p < 0.01$; and * $p < 0.05$); the absence of asterisks indicates absence of significance. The antibacterial activity of the blank material (a bacterial reduction of 30.7 and 41.6% against *S. aureus* and *E. coli*, respectively) can be ascribed to the presence of the primary amine group of aminopropylsilane at the outer surface of the xerogel. Aminoalkyl moieties, indeed, exert antibacterial activity.^[19]

Further inspection of Table 1 outcomes shows that the ability of the doped SilverSil to reduce bacterial growth is significantly greater than that of the blank sample and clearly dependent on the concentration of Ag NPs. Notably, all SilverSil powders showed higher activity against *E. coli* (more than 90% bacterial reduction with a 0.01% theoretical load of Ag NPs). This enhanced activity is likely due to structural differences between bacterial cell walls. While Gram-positive bacteria possess a thick, peptidoglycan-rich wall, Gram-negative bacteria feature a thinner wall with a negatively charged outer membrane. The negative charge promotes the attraction of positively charged Ag^+ ions, released by Ag NPs in

aqueous media, thereby facilitating their penetration into the cytoplasm. Combined with silver in nanoparticulate form, this interaction results in synergistic cell disruption.^[17]

Based on the results of the antibacterial tests with powdered samples, a first set of coated cotton and polyester fabrics was prepared via the dip-pad-dry-cure method (**Scheme 1**), by dispersing BlankC and SilverSilC4 ORMOSILs at a concentration of 7.5% into four as-received biobased resins.

These finishes were selected to align with the growing demand for sustainable, nontoxic, and environmentally safe textile treatments. Indeed, for the textile treatments under investigation, resins with a biobased content of around 50% were selected, as Pluvion Dry 2030 BS and Naigard BB-WR. As additional compliance with the abovementioned sustainability requirements, several chemical products involved in the formulations are currently included in the approved chemical substances list of ecological labels such as "Global Organic Textile Standard (GOTS) version 7.0:2023" (Catalizzatore is green, Gel Ftr Liq. and Katalin S/CL NEW), "Zero Discharge of Hazardous Chemicals (ZDHC)" - level 3 (Catalizzatore is green, Gel Ftr Liq., Pluvion Dry 2030 BS, Katalin S/CL NEW), and "bluesign" (Catalizzatore is green, Pluvion Dry 2030 BS and Katalin S/CL new).^[20] Preliminary investigation (data not shown) showed



Scheme 1. Dip-pad-dry-cure process for textile functionalization.

nearly 100% bacterial reduction against both bacterial strains using both BlankC or SilverSilC4 dispersed in Pluvion Dry 2030 BS or Naigard BB-WR. In contrast, when the same amount of blank and SilverSil samples was dispersed in Vision Sugar 4.0 and Naigard BB-AC, the bacterial reduction against both *S. aureus* and *E. coli* was lower than 20%.

These differences in antibacterial activity may originate from the varying composition of the biobased resins and their specific interactions with the ORMOSIL particles. For example, as reported in the literature, the application of silica NPs to polyester fabrics using a water-based polyurethane dispersion (PUD) as a binder through the impregnation method may result in non-uniform NPs distribution due to agglomeration issues within the polymer matrix.^[21]

Said effect in the case of SilverSil (or blank) ORMOSIL xerogel microparticles might hinder the uniform distribution of the materials on the textile surface. Moreover, silica nanoparticle concentrations $\geq 6\%$ promote aggregation on fiber surfaces, leading to uneven coatings that may negatively impact the functional performance of the treated fabrics.^[22]

Initial screening allowed adjustment of the formulation by lowering the amount of SilverSil (or blank) dispersed in Pluvion Dry 2030 BS or Naigard BB-WR materials to 3.5 wt% after diluting the resins in water at 10 w/v concentration. This minimizes any potential interference of the resin with powder distribution and consequently with the biological activity. Cotton (Figure 2) and polyester (Figure 3) fabrics, after heat treatment with the blank and doped ORMOSILs dispersed in diluted resins, show a uniform aspect. The wet pick-up% and add-on% values for each treatment displayed in (Table 2 and S1, Supporting Information), show evidence of good antibacterial activity of the coated fabrics against *S. aureus* in the case of polyester fabrics coated with SilverSilC4 dispersing in the Pluvion Dry 2030 BS resin, as well as of cotton fabrics coated with SilverSilC4 dispersed in the Naigard BB-WR resin.

In Table 2, the bacterial reduction (%) was reported as the mean of values obtained from assays in triplicate $\pm$ standard deviation. Statistical significance was examined by the one-way ANOVA test, with Bonferroni's correction ($p < 0.05$). Asterisks indicate the

statistical significance respect to each respective control (BlankC) (**** $p < 0.0001$; *** $p < 0.001$; ** $p < 0.01$; and * $p < 0.05$); the absence of asterisks indicates absence of significance.

The FTIR spectra of untreated cotton (Figure 4) and polyester (Figure 5) fabrics (see also Figure S2 and S3, Supporting Information) were compared with those treated with resin alone (Pluvion Dry 2030 BS or Naigard BB-WR) or with resins embedding dispersed SilverSil and blank ORMOSIL xerogel powders. All spectra were recorded after thermal treatment of the fabrics.

In agreement with previous findings concerning sol-gel functionalization of cotton fibers (silanol groups at the surface of ORMOSIL particles condense with the hydroxyl groups of the cellulose forming strong covalent bonds),^[23] the spectra of Pluvion Dry 2030 BS and Naigard BB-WR, respectively, show evidence of silanization of the cotton fibers (Figure 4A,B).

The peak at 770 cm^{-1} characteristic of symmetric $\nu_s\text{Si-O-Si}$ vibration mode is present in spectra of cotton fabrics treated with blank and doped SilverSil dispersed in Pluvion Dry 2030 BS (Figure 4A) and Naigard BB-WR (Figure 4B), while the peak at around 1270 cm^{-1} is due to the stretching vibration mode of Si-CH_3 groups.^[24]

The broad band centered at 3270 cm^{-1} , characteristics of the O-H stretching region of cellulose in cotton fibers, overlaps with the N-H stretching vibration of the NH_2 functional group of APTMS, and residual silanol groups (Si-OH) located at the surface of the organosilica particles. Signals in the range $2980\text{--}2800$ and $1433\text{--}1428\text{ cm}^{-1}$, assigned to C-H frequency stretching and C-H in-plane bending frequency of cellulose,^[25] respectively, are masked by the stretching vibrations of C-H bonds of aliphatic -CH_2 groups in the resins.

The same trend was observed in polyester fabrics (Figure 5A,B and S2, Supporting Information). Here, however, the absence of peaks between 3200 and 3400 cm^{-1} is likely due to condensation reaction of oxygen-containing functional groups (i.e., OH or COOH) of the polyester fabrics during the heat treatment.

As mentioned above, the results of antibacterial screening against *S. aureus* of this set of fabrics showed high bacterial reduction (equal or higher than 86%) for both BlankC and



Figure 2. Cotton fabrics after coating with 3.5% of BlankC and SilverSil xerogels (doped with different amounts of Ag NPs) dispersed in A) Naigard BB-WR and B) Pluvion Dry 2030 BS.



Figure 3. Polyester fabrics after coating with 3.5% of BlankC and SilverSil xerogels (doped with different amounts of Ag NPs) dispersed in A) Naigard BB-WR and B) Pluvion Dry 2030 BS.

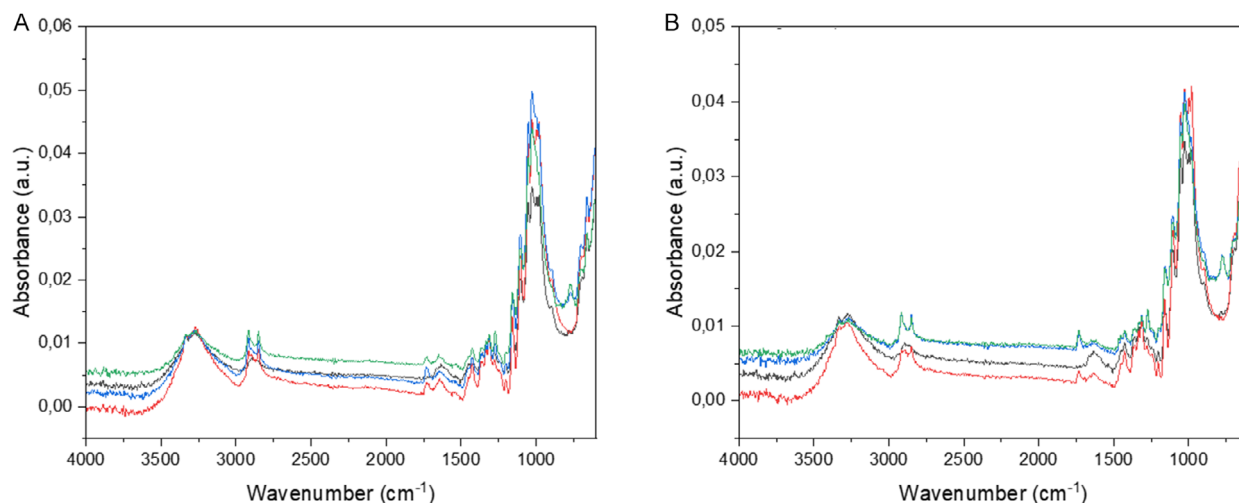


Figure 4. FTIR spectra of cotton fabric treated with BlankC and SilverSilC4 (1% Ag NPs) dispersed in A) Pluvion Dry 2030 BS and B) Naigard BB-WR. Black line: untreated cotton. Red line: cotton with resin only. Blue line: cotton with resin and BlankC. Green line: cotton with resin and SilverSilC4. Normalization at 1313 cm^{-1} of cotton.

SilverSilC4 dispersed in cotton (Table 2). Coated polyester fabrics, on the other hand, showed inconsistent results likely due to the nonhomogeneous distribution of the ORMOSIL submicron microparticles in the fabrics during the impregnation and curing steps. The uniform distribution of silica nanoparticles to polyester fabrics, indeed, is influenced by the drying temperature during the coating process.^[26]

To validate the result found by testing the coated cotton fabrics, the deposition of BlankC or SilverSilC4 at 3.5 wt% load in diluted Pluvion Dry 2030 BS was performed by impregnation (viz., using a foulard, in which the textile to be treated is impregnated using a finishing bath) using two different methodologies. In Meth1, the suspensions were prepared using powders BlankC and SilverSilC4 at a concentration of 3.5 wt%, stirred, and immediately used for fabric impregnation. The fabrics were dried in an oven at 100°C for 5 min, polymerized at 170°C for 2 min, and conditioned at room temperature for 24 h.

Employing Meth2 the fabric was functionalized using a suspension layering technique in three steps. For the first layer, a suspension with BlankC at a concentration of 3.5 wt% was prepared using water, resin, crosslinking agent, and surfactant, left to settle for a few minutes. Only the liquid part was used for application. The residue was then used to prepare a second suspension, using the same amount of water, resin, and crosslinking agent, left to settle for a few min, using only the liquid part for application. The same procedure was used to prepare the third layer. Between each layer, the fabric was dried in an oven at 100°C for 5 min. After drying the third layer, the sample was cured at 170°C for 2 min and conditioned at room temperature for 24 h.

Results of the antibacterial tests performed using different portions of finished cotton textile obtained by foulard impregnation were poor (Table 3). The bacterial reduction (%) was reported as the mean of values obtained from assays in triplicate $\pm$ standard deviation. Statistical significance was examined by the

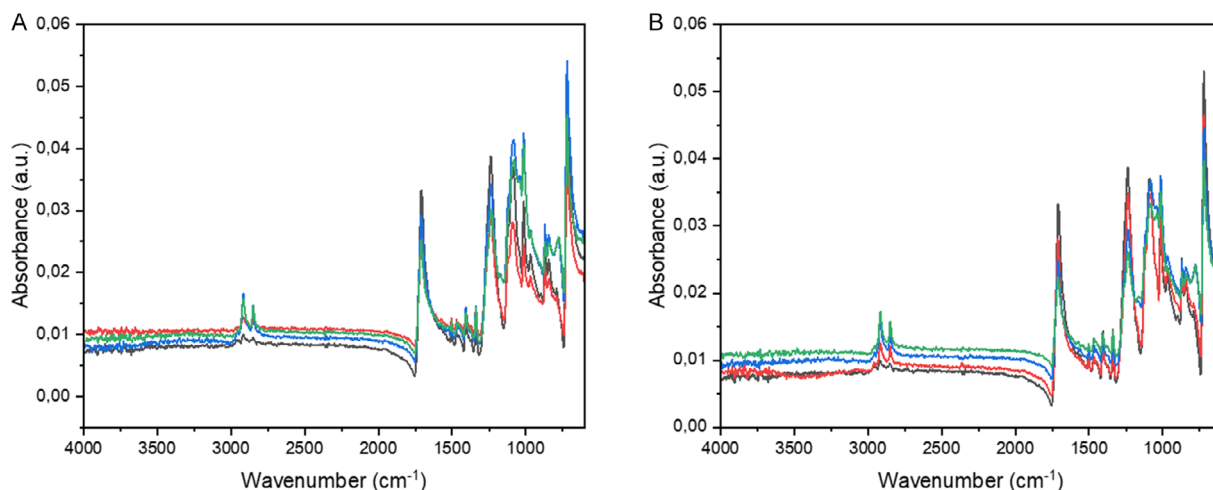


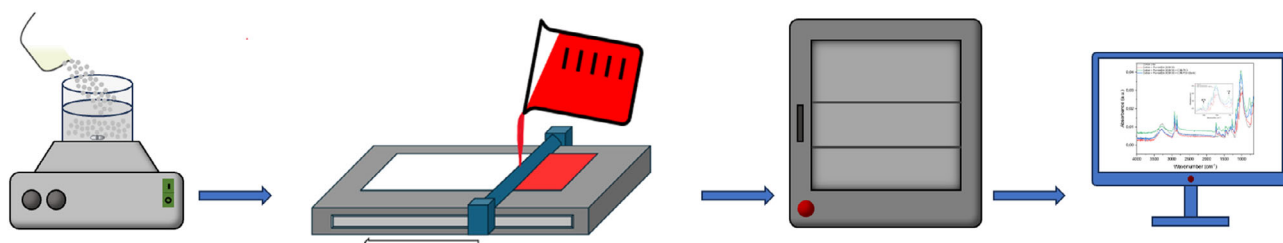
Figure 5. FTIR spectra of polyester fabric treated with BlankC and SilverSilC4 (1% Ag NPs) dispersed in: A) Pluvion Dry 2030 BS and B) Naigard BB-WR. Black line: untreated polyester. Red line: polyester with resin only. Blue line: polyester with resin and BlankC. Green line: polyester with resin and SilverSilC4. Normalization at 1337 cm^{-1} of polyester.

Table 3. Composition and antibacterial results of finished cotton by foulard impregnation. ^{a)}			
ORMOSIL	Surfactant [wt%]	Bacterial reduction [%]	
		<i>S. aureus</i>	<i>E. coli</i>
BlankC Meth1	–	8.2 ± 6.8	0.0 ± 0.0
SilverSilC4 Meth1	–	$45.5 \pm 3.4^{****}$	$94.0 \pm 0.6^{****}$
BlankC Meth2	0.35	$22.5 \pm 7.9^*$	0.0 ± 0.0

^{a)}Resin is Pluvion Dry 2030 BS; textile is cotton (CO); crosslinking agent: catalizzatore is green.

one-way ANOVA test, with Dunnett's correction ($p < 0.05$). Asterisks indicate the statistical significance respect to the control (BlankC Meth1) ($****p < 0.0001$; $***p < 0.001$; $**p < 0.01$; and $*p < 0.05$); the absence of asterisks indicates absence of significance.

This shows evidence that fabric impregnation by foulard affords a non-homogeneous coating in both cases. To overcome the limitations of the foulard impregnation in applying SilverSil materials, we switched to the rod-coating method, which is a far better approach for achieving a more uniform distribution of functional coatings on fabric.^[27] Hence, a film was coated on cotton fibers of $\approx 40\text{ }\mu\text{m}$ thickness, made of BlankC and SilverSilC4 mixed with diluted Naigard BB-WR and Pluvion Dry 2030 BS resins, along with their respective crosslinking agent and acrylic-based thickener (Scheme 2).



Scheme 2. Rod-coating process for textile functionalization.

The rod-coating method was introduced and tested for fabricating uniform, thin films on treated textile samples to ensure good dispersion of the particles in the deposited paste and promote controlled and scalable deposition.^[28] This approach enables the production of thin films with tunable thicknesses, improving the adhesion between the film and the treated fabrics, which is ultimately realized by the subsequent drying process. The continuity and precision of this technique make industrial scalability possible, overcoming the limitations of the abovementioned impregnation method.

Results in Table 4 show evidence that now excellent antibacterial activity of the coated cotton fabrics was obtained when dispersing the SilverSil xerogel (but not the blank ORMOSIL). Again, nearly bactericidal action was observed against *E. coli* strains, whereas 90% bacterial reduction was observed against *S. aureus*.

The bacterial reduction (%) was reported as the mean of values obtained from assays in triplicate $\pm$ standard deviation. Statistical significance was examined by the one-way ANOVA test, with Dunnett's correction ($p < 0.05$). Asterisks indicate the statistical significance respect to the control (BlankC), for each resin ($****p < 0.0001$; $***p < 0.001$; $**p < 0.01$; and $*p < 0.05$); the absence of asterisks indicates absence of significance.

A proposed mechanism of action of SilverSil is illustrated in Figure 6.

In the said mechanism, Ag NPs and Ag^+ ions interact with bacteria leading to membrane disruption, penetration into the

Table 4. Composition and antibacterial results of coated cotton obtained by rod-coating method (concentrations are reported in brackets).^{a)}

ORMOSIL [wt%]	Resin [g/L]	Crosslinking agent [wt% resin]	Add-on ^{b)} [%]	Bacterial reduction [%]	
				<i>S. aureus</i>	<i>E. coli</i>
–	Pluvion Dry 2030 BS (100)	Catalizzatore is green (7.0)	9.6	0.0 ± 0.0	0.0 ± 0.0
BlankC (3.5)	Pluvion Dry 2030 BS (100)	Catalizzatore is green (7.0)	18.2	0.0 ± 0.0	1.9 ± 0.2
SilverSilC4 (3.6)	Pluvion Dry 2030 BS (100)	Catalizzatore is green (7.0)	19.3	90.9 ± 2.3****	96.2 ± 1.4****
–	Naigard BB-WR (100)	Katalin S/CL NEW (10.0)	9.6	0.0 ± 0.0	0.0 ± 0.0
BlankC (3.4)	Naigard BB-WR (100)	Katalin S/CL NEW (10.0)	18.0	0.0 ± 0.0	0.0 ± 0.0
SilverSilC4 (3.4)	Naigard BB-WR (100)	Katalin S/CL NEW (10.0)	19.4	90.1 ± 1.4****	99.0 ± 1.2****

^{a)}Thickener was GEL FTR LIQ. (≈1.0 wt%). ^{b)}Standard deviation <2%.

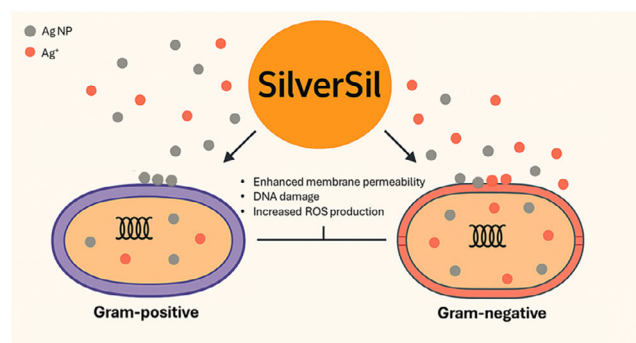


Figure 6. Proposed mechanism of action of SilverSil against bacterial cells.

cytoplasm, and subsequent intracellular damage. The SilverSil submicron organosilica particles physically and chemically stabilize the sol–gel entrapped Ag NPs. Slow and modest leaching of silver in water upon prolonged contact with aqueous solution, releasing only 3.46 ppm of silver after seven washing cycles,^[10] is promising toward development of a silver-based antimicrobial textile coating showing long-term stability upon washing.

4. Conclusions

In summary, functionalization of both natural (cotton) and synthetic (polyester) fabrics with the SilverSil sol–gel coating using different methods imparts antimicrobial activity to the functionalized fabrics against both Gram-positive and Gram-negative bacteria, here demonstrated against *S. aureus* and *E. coli* bacteria. On cotton fabrics treated via the rod-coating method with SilverSilC4 dispersed in Pluvion Dry 2030 BS, bacterial growth inhibition reached 90.9% against *S. aureus* and 96.2% against *E. coli*. Similarly, cotton fabrics functionalized using Naigard BB-WR showed 90.1 and 99.0% inhibition against *S. aureus* and *E. coli*, respectively.

The simple and readily scalable rod-coating method adapted to functionalize cotton textiles involves the dispersion of the SilverSil xerogel powder in eco-friendly commercial textile finishings, along with their respective crosslinking agents and an acrylic-based thickener. The eco-friendly resins used are durable water-repellent finishing for textiles, partly sourced from

biological resources, both free of fluorinated compounds and formaldehyde.

First optimized in view of practical applications of the SilverSil versatile sol–gel coating to produce long-lasting antimicrobial cotton fabrics, the rod-coating method may be further refined using different fabrics to ensure uniform coating penetration throughout the fabric structure, ensuring long-term durability and consistent antimicrobial performance, particularly under repeated washing conditions.^[27] This is of fundamental practical relevance because most silver-containing antimicrobial textile products rapidly lose their antimicrobial activity after laundering,^[7] with silk and cotton products functionalized with Ag-based antimicrobial products showing “no deliverable antimicrobial effect even in their original state.”^[9]

In conclusion, this work introduces an innovative strategy that combines the outcomes of sol–gel material chemistry optimization research^[14] with sustainable textile finishing in a scalable process. The dual advantage of antimicrobial efficacy and environmental safety represents a breakthrough in the field of functional textiles, moving beyond conventional silver-based approaches that often rely on toxic and flammable solvents or unsustainable materials, addressing the limitations of traditional silver-based antimicrobial coatings.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: antimicrobial textile · coating · silver · SilverSil · sol–gel

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