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Antimicrobial Fabrics Impregnated with Ag Particles Included in Silica Matrices

Katerine Igal and Patricia Vázquez

Abstract

A hospital that has a high incidence of acquired infections during the stay of patients in it is not considered efficient, since as Florence Nightingale, an English lady who died in 1910 and founder of the modern school of nursing, said: “the first thing that doesn’t a hospital must do is get sick.” Filamentous fungi, given their ability to grow on various substrates, are considered within the most damaging organisms. Among the fungi that are generally found in environments inhabited by humans in urban areas, we can mention *Alternaria*, *Aspergillus*, and *Cladosporium*, among others. With the incorporation of biocides into textiles, different methodologies are being studied depending on the stage they are performed; if it is at the finishing of the fabric, among the most used methods is the pad-dry-cure. The objective of this work was to synthesize modified silica by including Ag and C, where the latter is extracted from disused batteries and then added as antimicrobial additives to obtain antimicrobial fabrics.

Keywords: silica, silver, carbon, antimicrobial additives, antimicrobial fabrics

1. Introduction

The concern of human beings related to health care has always existed, and the increase in diseases caused by the enormous population density has forced us to look for effective technological solutions. Materials such as textiles, used for fabric production, can be easily colonized by a high amount of microorganism or can even be deteriorated by them. The microbial colonization on fabrics generates esthetic problems and can also lead to the degradation of the material, leaving it in disuse. Fungi are heterotrophic organisms that commonly colonize organic surfaces, such as coatings used in construction materials, paints, or fabrics, and due to the substrate type, they can be metabolized by them. This not only generates problems into the domestic environment, where many objects are built by organic substrates, but also the fungal growth can affect the human health by the production of allergens, irritants and mycotoxins. Therefore, antimicrobial additives need to be not only effective in fungal growth control but also safe and environmentally friendly chemical substances in their preparation.

In the last decades, different impregnation methods in fabrics [1, 2] and a wide variety of antimicrobial additives such as silver, quaternary ammonium salts [3], polyhexamethylene biguanide [4], triclosan [5], and chitosan [6], N-halamine

compounds [7], and peroxy acids [8] have been studied. For example, an ecological and viable method has been used to re-coat cotton fabrics with silver nanoparticles [9, 10]. In studies conducted by Mahltig et al. [11], the sol-gel method was used to coat textiles with inorganic SiO₂ by the construction of layers containing Ag nanoparticles. The formation of these particles was investigated according to the curing treatment variables performed after the coating. Inorganic coatings containing Ag inhibited the growth of *Aspergillus niger* fungal strain and *Bacillus subtilis* and *Pseudomonas putida* bacteria [12].

Tomšič et al. [13] studied dry curing and the method was thoroughly compared. The antimicrobial solution was prepared from different concentrations of dispersed commercial silver chloride, with a reactive organic-inorganic binder (RB) using cotton fabrics. Washing cycles were carried out and then antifungal (against *Aspergillus niger* and *Chaetomium globosum*) and antibacterial assays (*Escherichia coli*) were evaluated, being more effective the exhaustive method, and also better results were obtained against bacteria compared with fungi. The results were different according to the Ag concentrations and the method of application in the cotton fabrics.

In other work [14], Ag nanoparticles have been used within polystyrene-block-polyacrylic acid copolymer (PS-b-PAA) micelle nuclei, synthesized by the free-radical polymerization method, in different relations. It has been determined that the impregnation method into the fabric is by an esterification reaction between PAA and the hydroxyl groups on the surface of the fabric. Another method studied is the use of new nanostructures and techniques that allow the production of nanoparticles for its application, in various sectors, in order to improve processes and increase productivity. For example, electrospinning method [15] is simple, inexpensive, and used in a wide variety of materials, making it one of the most used. The structures obtained have unique characteristics, such as large contact area and high porosity. Due to these properties, nanofibers are of great interest to be applied in different areas, such as biomedical, textile, and food, obtaining beneficial results.

Textiles and clothing are in daily contact with microorganisms of the environment and the human skin. In general, fabrics can be an excellent substrate for microbial growth, because they have an organic composition that provides an adequate base for human sweat and biofilm fixing. The human skin contains a complex mixture of microorganisms; even a “clean” skin has a typical population of between 100 and 1000 microorganism/cm². At these levels, they do not represent a health problem or bad smell. On the contrary, its presence and a balanced population are essential for human health [16]. But when the optimal growth conditions are provided, microorganisms are multiplied rapidly and can produce problems such as the generation of odors, loss of performance, discoloration of fabrics, and possibly infection. In the most extreme case, microorganisms can produce serious problems, such as rotting of the fabric, stains, unpleasant odors and health problems ranging from simple discomfort to physical irritation, allergic sensitization, toxic responses, infections, and diseases. Many of the characteristic malodors associated with the human body are due to the presence of large populations of microorganisms. Therefore, control of the undesirable effects of microbes on textiles is becoming an important issue in the textile industry. Currently, there is much interest in hygienic fabrics that offer an advantage compared with cleaning and odor prevention as a result of their antimicrobial properties or reduced bacterial growth.

The advantage of using an oxide matrix associated with an antimicrobial agent resides in its protective function that lead to a longer useful life of the material obtained maintaining its bioactivity over time, and the sol-gel method is an appropriated way to obtain this immobilization [17–19].

The aim of the present work was to obtain silica-based solids whose active phase is formed by C, from the recycling of disused batteries, and Ag particles.

In relation to the used carbon, the idea of recycling the metals that make up the batteries is to look at the exhausted batteries as a resource and not as a waste, since they contain valuable metals in high concentrations that, if the batteries are thrown in the trash, contaminate soil and water; on the other hand, if they are seen as raw material for the recovery of metals, they become an important resource since minerals are reused that are otherwise extracted from the mines with the consequent environmental impact that this activity entails.

To obtain recycled Zn, different elements are obtained, including coal, which is obtained by means of a biohydrometallurgical process for the treatment and recovery of metals from spent batteries. Biohydrometallurgy is a branch of metallurgy that uses biooxidation and/or bioleaching processes, referred to by a general term: biomining [20–24]. Biohydrometallurgy is the application of microbiological processes for the recovery of metals, mainly used by the mining industry. The acid bioleaching of unsaturated minerals uses the acidic reducing medium biogenerated by microorganisms for the solubilization of metals.

The materials synthesized were characterized by potentiometric titration, textural properties, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Subsequently, the synthesized solids were used as antimicrobial additives in fabrics, using the pad-dry-cure method. *Aspergillus* sp., *Chaetomium globosum*, and *Cladosporium* sp. fungi were selected to evaluate the antifungal activity from biodeteriorated fabrics [25]. These fungi were selected for their ability to grow on indoor surfaces and to be negative to human health to produce a variety of different compounds including mycotoxins [26–28]. The agar diffusion method was used to evaluate the antibacterial activity of impregnated fabrics (*E. coli* and *S. aureus*).

This work is focused on the preparation of new materials that can provide solutions to the technological and environmental challenges in different areas.

2. Materials and methods

2.1 Synthesis of the additives

The solids were synthesized by the sol-gel method, under N₂ atmosphere in order to reach an inert condition. Tetraethyl orthosilicate (TEOS) (Aldrich, 98%) was used as the precursor for silica solids, absolute ethanol (EtOH, Baker 99.9%) and distilled water as solvents, and ammonium hydroxide as catalyst (basic hydrolysis). The precursor/catalyst/EtOH/H₂O molar ratios were 1:1:5:4, respectively, in all the synthesis. Besides, different amounts of carbon, recycled from zinc-carbon batteries, were added into the reaction mixture.

Zinc-carbon batteries contain a cathode, which is a mixture of manganese oxide and conductive carbon, usually in the form of black [29] coal, and the anode, composed of a high-purity zinc alloy, is also the container that encloses battery active materials. The recycled carbon was milled with a ball mill, then sieved with a mesh of 200, and, finally, added to the synthesis. The obtained mixture was stirred for 2 h and dried at room temperature for 1 week. The nomenclature of samples are as follows: SB (without C), SB1 (0.1 C p/p), SB2 (1 C p/p), and SB3 (10 C p/p), respectively. Subsequently, two samples were selected: sample SB (without C), which was modified including during the synthesis process 4% w/w of silver nitrate (Aldrich, 99.9%), was called SB_{Ag}, and the sample SB3 (10% w/w C) which was treated in the same way including Ag and was called SB3_{Ag}.

2.2 Characterization of the additives

The acidic properties of the solids were evaluated by potentiometric titration with *n*-butylamine, in a Metrohm 794 Basic Titrino titrator (Switzerland) with a double-junction electrode. First, 0.025 g of sample was suspended in 45 mL of acetonitrile and stirred for 540 s, and second, 0.025 mL/min of an *n*-butylamine solution in acetonitrile (0.025 N) was added, while stirring constantly. The textural properties of the additives, such as the specific surface area (S_{BET}), the pore volume, and pore size, were determined by adsorption/desorption in Micromeritics Accusorb 2100 equipment (USA), using N_2 as absorbable gas at 77 K. Before the measurement, each sample was degassed at 100°C for 12 h and under 30 mmHg. The X-ray diffraction (XRD) diagrams were obtained in Philips (Holland) PW-1390 (channel control) and PW-1394 (motor control) equipment coupled to a scanning graphical recorder, using $\text{Cu K}\alpha$ ($\alpha = 1.5417 \text{ \AA}$) radiation, Ni filter, 20 mA and 40 kV in the voltage source, a 5–60 2θ scanning angle range, a scanning rate of 2°/min, and 2000 counts/s for the amplitude of the vertical scale. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained using Bruker Vertex 70 equipment (Germany) and pellets of the sample in KBr (Aldrich, 99 wt% FT-IR purity), measured in a range between 400 and 4000 cm^{-1} at room temperature. Two hundred scans were collected at a resolution of 4 cm^{-1} and averaged. Scanning electron microscopy (SEM) was used to obtain different micrographs of the additives, in Philips 505 equipment (Holland), using a voltage of 15 kV. Samples were supported on graphite and metallized with a sputtered gold film. The micrographs were obtained with an ADDAI acquisition device (Soft Imaging System). Transmission electron microscopy (TEM) was performed with a JEOL microscope (100 CX) (Japan), with an accelerating voltage of 100 kV. Samples were prepared by their suspension in ethanol and placing an aliquot over carbon-coated copper grids, allowing the samples to dry in a desiccator for 30 min at room temperature. X-ray mapping was acquired by using a Talos F200X HR-TEM microscope operating at 200 kV equipped with a SuperX EDS spectrometer (composed of 4 EDS SDD detectors).

2.3 Assessment of the antifungal activity of the additives

Aspergillus sp., *Chaetomium globosum*, and *Cladosporium* sp. fungi were selected to evaluate the antifungal activity of the solids, based on their cellulolytic ability in agar plate assays. *Aspergillus* sp. and *Cladosporium* sp. were previously isolated from bio-deteriorated fabrics by conventional microbiological techniques, whereas *C. globosum* was selected from the CIDEPINT culture collection [30]. From subcultures growing in Petri dishes, inoculums of cited fungi were obtained using a solution of 0.85% p/v NaCl and 0.005% p/v Tween 20, being the concentration of the suspension adjusted to 106 spores/mL employing a Neubauer chamber. The composition of the culture medium used was 1.5 g agar (Parafarm), 1 g dextrose (Anedra, analytical reagent), 0.5 g proteose peptone (OXOID), 0.1 g KH_2PO_4 (Anedra, analytical reagent), 0.05 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Anedra, analytical reagent), and distilled water (Laboratory). Two different silver concentrations were selected to carry out the agar plate assays, 60 and 120 ppm. The Petri dishes were inoculated in the center with 20 mL of spore suspension of each fungus per triplicate and incubated at 28°C for 10 days. With the obtained results, the inhibition percentage (I%) was calculated according to Eq. [31]: $\text{inhibition \%} = [(C - E)/C] \times 100$, where C and E correspond to the average diameter of each fungus in the control plate and on the plate with the tested solids, respectively. Three measurements of the fungal growth diameter were made in each plate, and the standard deviation was determined.

3. Results and conclusions of additives

Figure 1 shows the synthesized samples of silica with different concentrations of carbon whose images were obtained digitally. If we look at **Figure 1**, the SB sample is the one obtained with ammonium hydroxide and is taken as a control sample (it does not contain carbon), while the other images provide a light gray to dark gray coloration for higher carbon contents. For the three cases presented, the granulometry is similar when they are already dry, it is not significant compared to the SB, and only the S3B has larger granules.

The determination of the structure of the synthesized silicas was carried out by XRD. Thus the amorphous character of the synthesized materials that have only wide peaks in the 15–30° 2 θ interval was confirmed and the band located around 23° 2 θ was observed, which is the typical structure of this type of silica. The acid properties of the silicas measured through the potentiometric titration with *n*-butylamine were studied, which allows the evaluation of the number of acid sites and their acid strength. To interpret the results obtained, it is known that the initial electrode potential (E_i) indicates the maximum acid strength of the surface sites and the values (meq/g solid) where the plateau is reached indicate the total number of acidic sites [32]. The acid strength of surface sites can be classified according to the following ranges: very strong sites $E_i > 100$ mV; strong sites $0 < E_i < 100$ mV; weak sites $-100 < E_i < 0$ mV, and very weak sites $E_i < -100$ mV, respectively [30]. It is important to clarify that this technique only indicates the trend of mass acidity of the synthesized samples. Bulk carbon has an E_i value of 37.1 mV, while silica without carbon has an E_i of 157.9 mV. It is interesting to note that the potentiometric curves have a similar shape to each other, with continuous and relatively rapid decrease in potential, which would indicate that their acidic sites are very few, regardless of the change in the amount of carbon they contain, this could be that compounds that impurity carbon tend to be basic in nature. In any case, the potentiometric curves have a strong parallel with the behavior of pure silica and not of bulk carbon.

The FT-IR spectrum of the SB silica shows characteristic bands at 3748 and 3473 cm^{-1} assigned to the interactions between the hydroxyl groups on the silica surface and the water presented in the surrounding atmosphere. These bands can be related to the presence of isolated groups (Si–OH) and OH stretch bands, caused by hydrogen-bound water molecules (HOH..H) and surface silanol groups, hydrogen-bound to water molecular (SiO–H...H₂O). The other characteristic bands that confirm the hydrophilic character of the silica are located at 968 and 1883 cm^{-1} and are directly related to the Si–O interaction of the silanol groups. At 1640 cm^{-1} , an intense band associated with the adsorption of water on the surface of the sample is also observed due to its hydrophilic nature. Bands in the range 1200–1000 cm^{-1} and 800 cm^{-1} were also detected. These interactions can be related to antisymmetric and

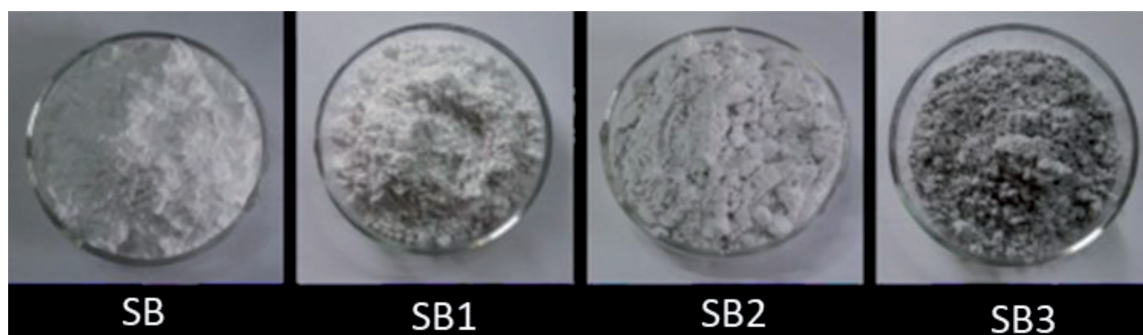


Figure 1.
Digital images of silicas.

symmetric vibration between Si–O–Si with a minimum of 1076 cm^{-1} and 801 cm^{-1} , respectively. The vibration mode that appears at 1231 cm^{-1} can be assigned to the symmetric deformation of C–H in CH_2 groups, corresponding to the residual non-hydrolyzed alkoxy groups ($-\text{OC}_2\text{H}_5$) in the silica xerogel. The characteristic interaction band was observed at 1381 cm^{-1} , which may be related to the C–H interaction of the ethyl radicals on the silica surface. These radicals can be formed as a product of condensation reactions between $\text{Si}(\text{OH})_4$ and $\text{Si}(\text{OC}_2\text{H}_5)_4$. Carbon-containing samples show similarity to pure silica [33].

The immobilization of antimicrobial agents within multiple materials obtained by sol-gel has recently been investigated. For example, Copello et al. [34] studied the incorporation of dodecyl-di (aminoethyl) glycine in a matrix of SiO_2 -xerogel for use as an antimicrobial in glasses, and Marini et al. [35] incorporated quaternary ammonium salts in an organic and inorganic hybrid coating for plastics. This methodology offers the possibility of obtaining materials of different porosity, as well as allowing the introduction of metals and other molecules through a simple impregnation, dissolution, or suspension of the metal precursors in the gel [36, 37]. In particular, several investigations are found in the literature on the use of immobilized Ag in materials obtained by sol-gel [38, 39]. Generally, materials impregnated with Ag consist of Ag ions integrated in inert ceramic, zeolite, or vitreous matrices. The sol-gel method became an effective procedure for linking organic and inorganic molecules in the same matrix and offers a unique opportunity to incorporate metal components into an organically modified inorganic matrix. The methods are entrapment, electrostatic interaction, adsorption, and covalent bonding.

The samples with Ag included are SBAG, without C, and 4% Ag that possess an Ei of 113.5 mV and S3BAG, with 10% C, and 4% Ag that showed an Ei of 67.7 mV. This could be due to the electrons of the ammonium groups that would be induced to OH more acids and may result in a redox reaction of Ag^{1+} to Ag^0 . The potentiometric curves of SBAG and S3BAG are similar to the previous samples without Ag. The area under the curves is more open, indicating a greater amount of acid sites. The adsorption/desorption isotherms of N_2 corresponding to samples obtained using ammonium hydroxide as a catalyst could be included in Langmuir type II, characteristics of low porous solids, with meso- and macroporosity. Point B is where the coverage of the monolayer is complete and multilayer adsorption is about to begin. This kind of isotherm is a characteristic of nonporous solids or macroporous adsorbents. For the SBAG and S3BAG samples, the isotherms are similar which would indicate that the dopants (Ag and C) do not influence the basic hydrolysis that prevails in the synthesis of these samples. Regarding the FT-IR spectra, the samples show a shift, with respect to the SBAG. The bands are at 1182, 1094, 860, 674, and 464 cm^{-1} , but they are not substantial so that it can induce the variation of links in the siliceous network.

In the case of using ammonium hydroxide, in SEM (**Figure 2**), it can be seen that the particles of laminar morphology of the silica with acid hydrolysis become rounded. This generates a sharp decrease in the specific area and is independent of the dopants included, both in the SBAG and in the S3BAG, respectively.

It should not be forgotten when discussing this point that the sol is defined as a stable suspension of colloidal solid particles in a liquid [40]. For the existence of the sun, the colloidal particles that form it, denser than the surrounding liquid, must be small enough not to precipitate, being suspended by the repulsion of weak forces, such as those of van der Waals, or by surface charges that keep them in suspension. To meet these requirements, the particles must have sizes between 1 and 100 nm, which corresponds to the existence of 103–109 atoms per particle [41]. In the case of TEM (**Figure 3**), the rounded forms of silica and the superficial presence of Ag particles in both samples can be distinguished.

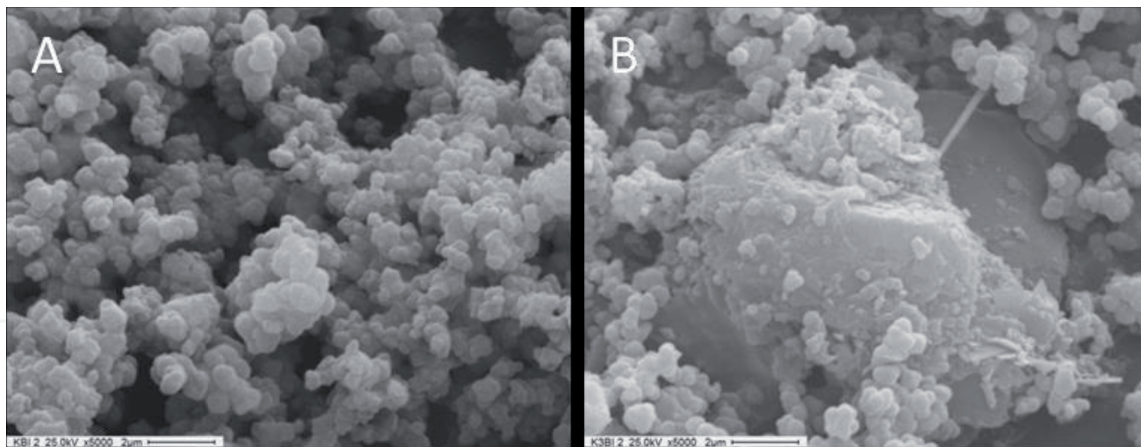


Figure 2.
SEM micrographics of samples: (A) SBAg and (B) S₃Ag (5000×).

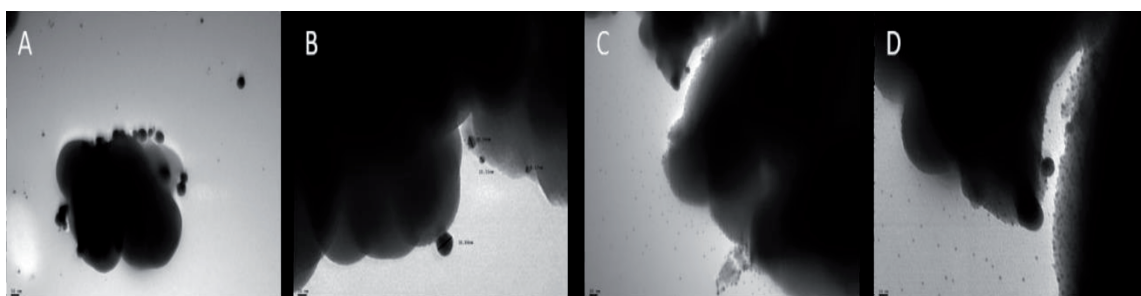


Figure 3.
TEM micrographics of samples: (A) SBAg (100,000×), (B) SBAg (270,000×), (C) S₃Ag (100,000×), and (D) S₃Ag (270,000×).

Babapour et al. [42] studied the inclusion of silver in a siliceous matrix through the sol-gel method and analyzed the materials by X-ray photoelectronic spectroscopy, to elucidate the chemical state of the silver nanoparticles on the surface. They observed that at 100°C, the silver particles have a high tendency to accumulate on the surface, but, at higher temperatures, they diffuse from the surface to the matrix. Also, they found that in dry samples (in air at 100°C) more than 90% of the concentration of Ag on the surface is in the Ag⁰ (metallic) state. However, after treating the materials thermally at 200°C, the silver particles oxidize, presenting an increase in the surface concentration of Ag⁺ and Ag²⁺, which continues to grow up to 400°C, the results being independent of the concentration of silver in the siliceous matrix.

4. Antimicrobial fabrics

4.1 Insulation of fungi from biodeteriorated fabrics

To obtain the biodeteriorated fabric, source of the strains used in this work, samples of 100% cotton (plain weave fabric), 5 cm × 5 cm in size, previously moistened with distilled water, were exposed to accelerate the process of biodeterioration. They remained for 30 days in an indoor environment, under conditions of high relative humidity. It should be noted that this type of fabric is used in the hospital field as stretchers and oxygen tube covers, sheets, both (shirt and pants), etc. At the end of the exposure time of the samples, they were superficially decontaminated to orient the isolation to the fungal species that were growing in the fabric. According to the observations made, the isolates that presented the highest cellulolytic activity (halo ≥ 0.4 cm) were found to be used as bioindicators: *Aspergillus*

and *Cladosporium*, respectively. On the other hand, a strain of *Chaetomium globosum* (KU936228) was also selected as a bioindicator considering that it is widely known for its cellulolytic activity (**Figure 4**).

4.2 Fabric preparation: pad-dry-cure method

Pad-dry-cure or exhaust-dry-cure is a finishing process applied to textiles to impart different finish treatments, such as waterproofing, softening, antibacterial or anti-odor finishes. The textile is passed through a water-based solution bath containing the Ag-silica additives; in this case, this method [13, 43] consisted in the inclusion of cotton fabric (4 cm × 4 cm), and the total immersion was carried out at 20°C for 10 min. Then, it was dried at 40°C for 2 h and, finally, cured for 1 h at 140°C. These impregnated fabrics were exposed against the *Chaetomium globosum* and *Aspergillus* sp. strains, to measure their antifungal activity.

4.2.1 Wash cycles

To evaluate the durability of the adhesion of the additives to the tissue, durability tests were performed against washing. Each sample was subjected to 1, 5, and 20 wash cycles of 15 min each. Each cycle consisted of placing the impregnated fabrics in a 400-ml beaker in contact with a solution of sodium lauryl sulfate 2 g/l for 15 min. Then, the fabrics were rinsed, removed with tweezers, and placed in another beaker with distilled water; this procedure was performed twice, and, finally, each cloth was rinsed again with a water slug dragging all traces of soap (**Figure 5**). The new nomenclature [44] is SBAg (KBI) and S3BAg (K3BI).

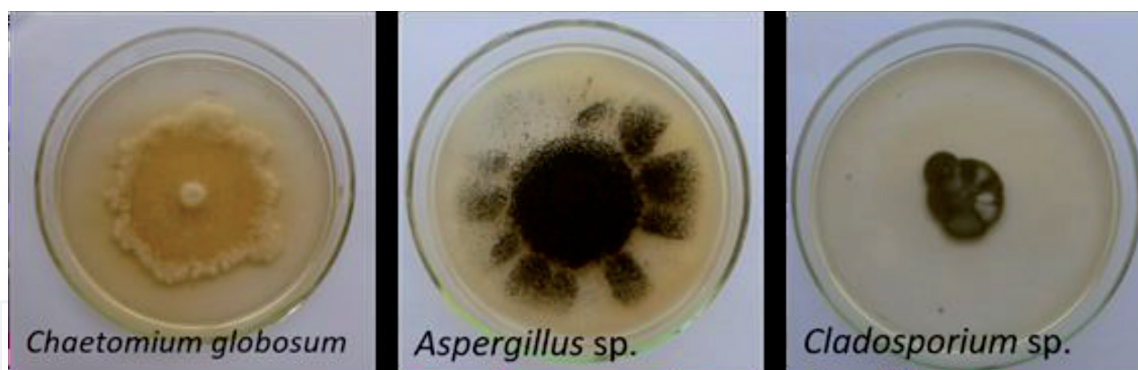


Figure 4.
Photographs of the strains used as bioindicators.



Figure 5.
Photographs of the fabric with KBI after a first wash cycle (left), 5 wash cycles (center), and 20 wash cycles (right).

The nomenclature is changed in this section that is subsequent to all changes suffered by the selected fabric. This makes the identification of pure silica-based additives based on those incorporated into the fabric simpler as explained previously.

4.3 Evaluation of the antifungal activity of fabrics

The antifungal activity of the fabrics treated with the modified silicas was estimated with the bioindicators: *Aspergillus* sp. and *C. globosum* (KU936228) according to the standard modified method DIN 53931390. The culture medium used consists of 1 g of KH_2PO_4 , 1 g of KNO_3 , 0.5 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.5 g of KCl, 0.2 g of glucose, 0.2 g of sucrose, and 15 g of agar per 1 l of distilled H_2O . It is a less nutritious culture medium, allowing more delicate colony growth and an easier evaluation of the antifungal activity of the fabric. About 100 μl of the spore suspension (inoculum) previously obtained was inoculated, spread with the Drigalski spatula to obtain a homogeneous lawn of the strain, and incubated in an oven at 28°C for 24 h. Subsequently, the impregnated fabrics (4 cm \times 4 cm) were sterilized by UV radiation and placed in the center of the previously grown plate working in the laminar flow.

Then, they were incubated in an oven 28°C for 14 days. After that time, the antifungal activity was determined in terms of mycelial growth on the surface of the cotton fibers and the intensity of the sporulation. To ensure statistical validity, the test was performed in triplicate.

4.3.1 Results

Analyzing the data after 20 wash cycles, some of the antifungal activities is lost. Both SBAg and S3BAg samples have no noticeable differences in growth inhibition, achieving only a dispersed growth of between 5 and 10% (eye

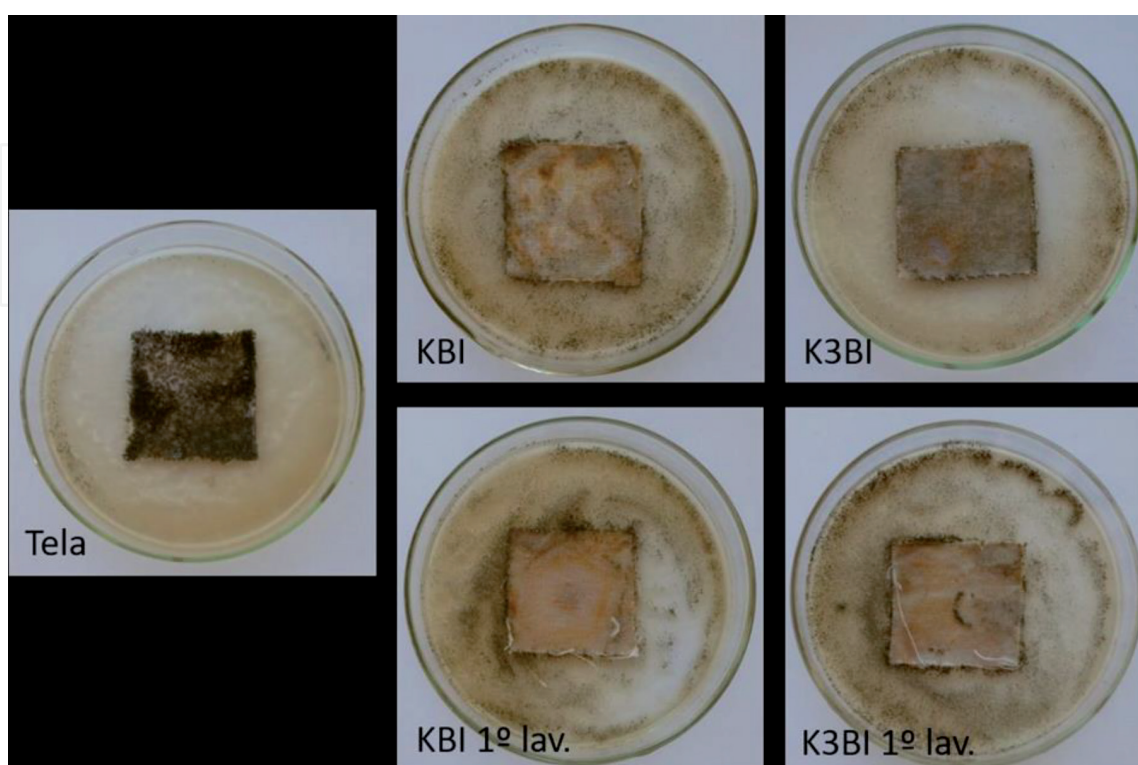


Figure 6.
Antifungal test of the fabrics impregnated with the pad-dry-cure method against *C. globosum*.

observation). As can be seen in **Figure 6**, which shows the photographs of the test against *Chaetomium globosum*, there is a greater sporulation concentrated in the control fabric, while in the other fabrics containing Ag there is only to a lesser extent on the edges of the fabric. The nomenclature is as follows [44]: control (Tela), SBAg 1 wash cycle (KBI 1 lav.), and S3BAg 1 wash cycle (K3BI 1 lav.).

Figure 7 shows SEM micrographs of the fabrics tested. Here the difference in growth in the control fabric with respect to the fabrics with KBI and K3BI versus *C. globosum* is noticeable, although the KBI gives less growth than the fabric containing K3BI. It can be seen that KBI has lower growth than K3BI, which has poor and scattered growth. The micrographs, which are shown by way of example, can be seen

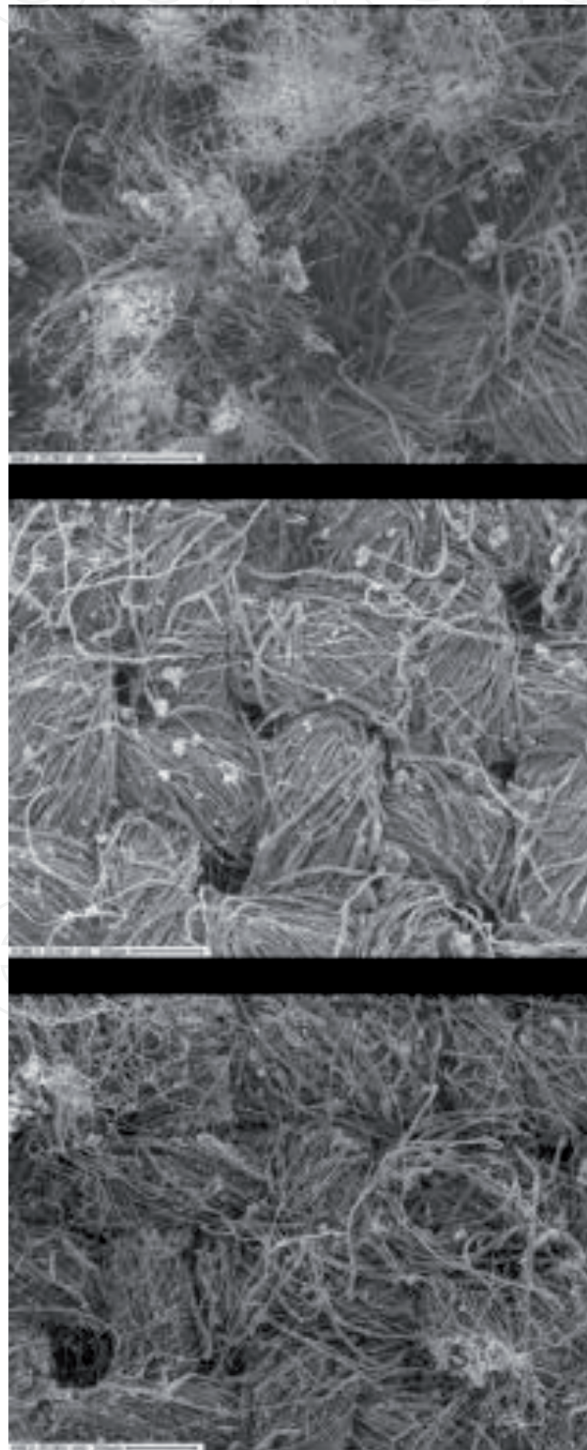


Figure 7. SEM micrographs of the control fabric (above) and the fabrics impregnated with the pad-dry-cure method KBI and K3BI (medium and down), tested against *C. globosum*.

again that *Aspergillus* sp. (**Figures 8 and 9**) has scattered and weakened specialized hyphae (conidiophores), in fabrics containing KBI and K3BI, with respect to the control fabric where they are more abundant and with normal characteristics.

As a conclusion of this section regarding the additives impregnated with the fabrics, these samples were synthesized with basic hydrolysis, the KBI does not contain carbon, and there is only impregnation of Ag in the sample of the previous stage. For the K3BI, there is presence of C together with Ag. If the activity is compared, these samples gave good results. Regarding the washing cycles, there is no difference between the samples for the fungi tested, there may be loss of the additive with the number of washes, but there is no variation between 1 cycle and 20 cycles, which leads to good adhesion of the additives to the fabric, that is, the method tested has a good rating to continue using it.

4.4 Evaluation of the antibacterial activity of fabrics

For the test of antimicrobial activity, a first general classification of the method to be used is carried out depending on the type of evaluation of the population of microorganisms. Reduction in intimate contact with an agar culture medium inoculated with the test bacteria (DIN EN ISO 20645-2001, AATCC 147). If diffuse or leaching antibacterial activity is present, it will be possible to observe a clear area around the treated sample compared to the surrounding bacterial growth zone and the untreated control sample after the same contact time. However, this method cannot be applied to nondiffusible or fixed antimicrobial substances [45].

4.4.1 Agar diffusion method (SN 195920-1992)

To study the antibacterial efficacy of the impregnated fabrics, the agar-based diffusion method was performed (SN 195920-1992). Bacterial strains for test in *E. coli* and *S. aureus* (**Figure 10**) were selected to be abundant in the

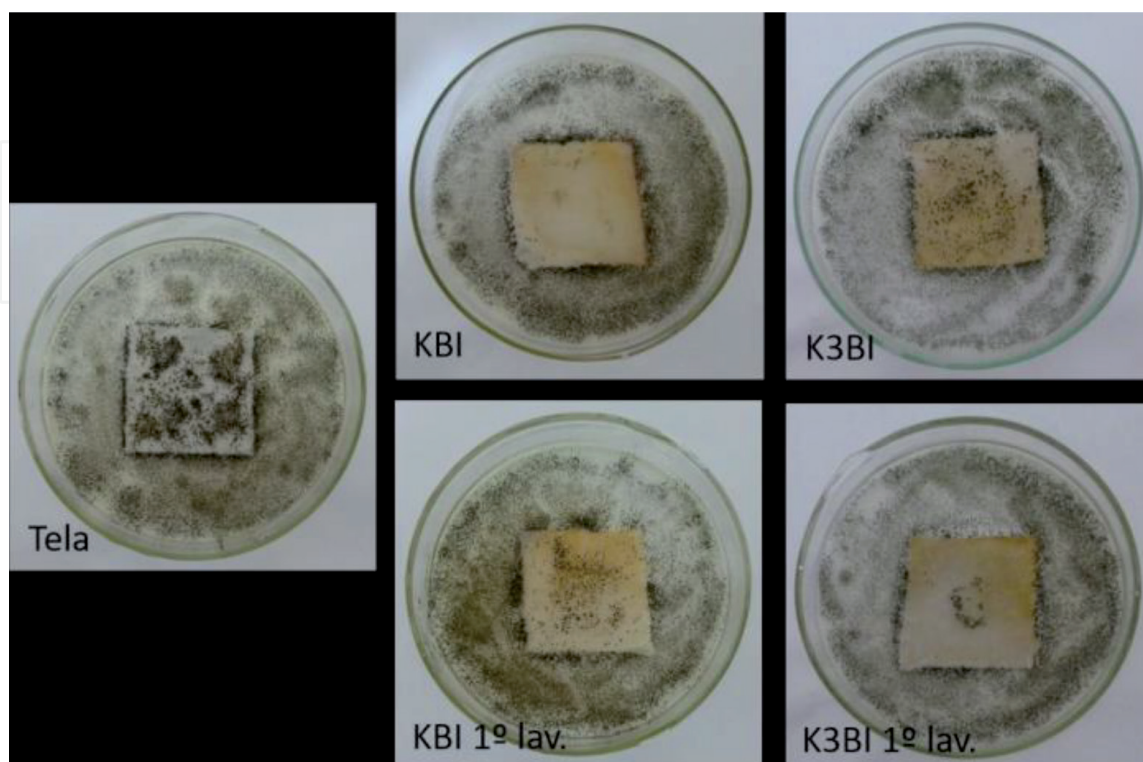


Figure 8.
Antifungal test of fabrics impregnated with the pad-dry-cure method against Aspergillus sp.

environment and be related to pathologies affecting human health. The culture medium used is BVAC: 5 g NaCl, 5 g yeast extract, 10 g casein peptone, and 15 g of bacteriological agar 1 l of distilled water. Then, plates were prepared with 15 ml of the culture medium BVAC and inoculated with the inoculum previously prepared, which spread throughout the plate with sterile swabs. Finally, the fabrics were added treated and untreated. The plates were incubated for 24 h at 37°C [14, 46].

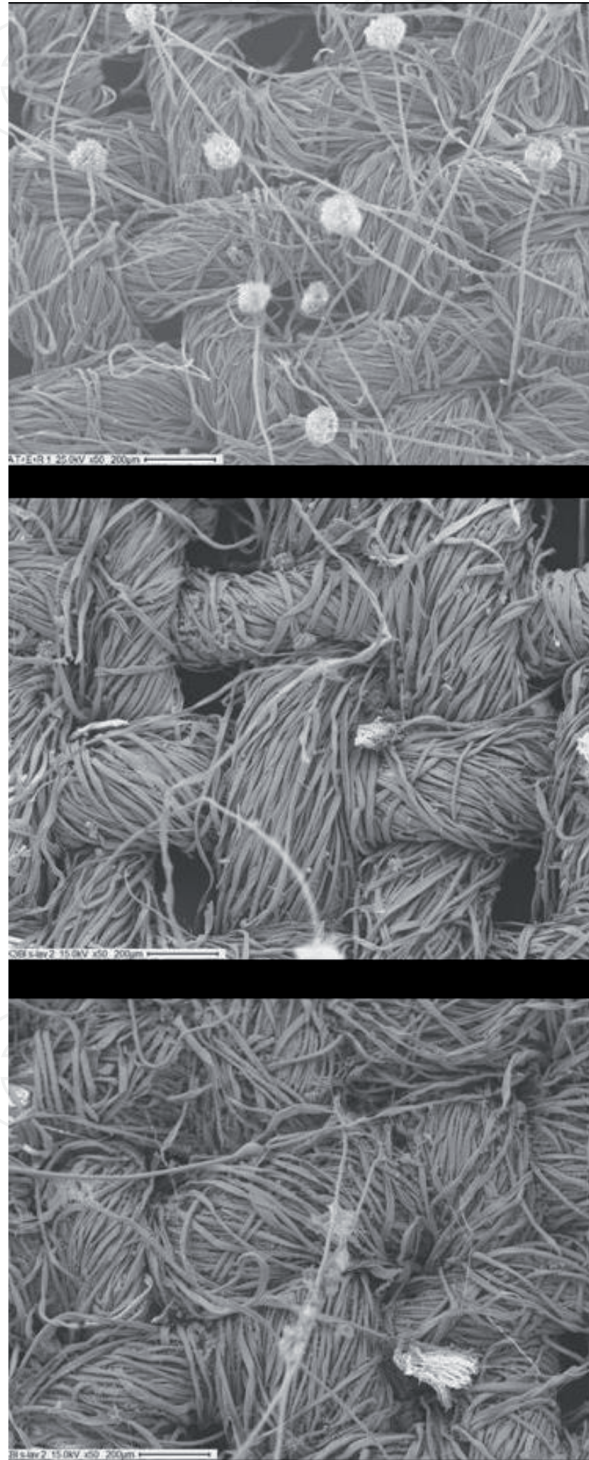


Figure 9. SEM micrographs of the control fabric (above) and the fabrics impregnated with the pad-dry-cure method KBI and K3BI (medium and down) and the fabrics impregnated with the pad-dry-cure method, tested against *Aspergillus sp.*

The inoculum was made from 24-h cultures that were in an oven at 37°C. Suspensions with physiological solution were obtained by adjusting the turbidity to 0.5 of the McFarland scale (1.5×10^8 Ufc/ml). A dilution was then made to obtain a bacterial suspension of 1.5×10^6 . After the incubation period of the plates inoculated with the selected strains, the zone of inhibition (ZOI) was recorded. The results were obtained from the average of four measurements taken for each triplicate. In addition, the standard deviation between measurements was determined. **Figures 11** and **12** show the photographic records of the trial and those observed through the magnifying glass of the fabrics against *E. coli*. It can be seen that there is an inhibition halo that is identified as a space adjacent to the fabric (transparent culture medium). There are no noticeable differences in the measures of the ZOI of the fabrics that contained the additives in spite of the washing cycles; therefore it can be concluded that the impregnation method has high durability against washing. Taking into account the values of ZOI, 0.6 ± 0.2 for KBI and 0.7 ± 0.2 for K3BI, it can be said that only at 20 wash cycles there is a decrease in the antibacterial effect.

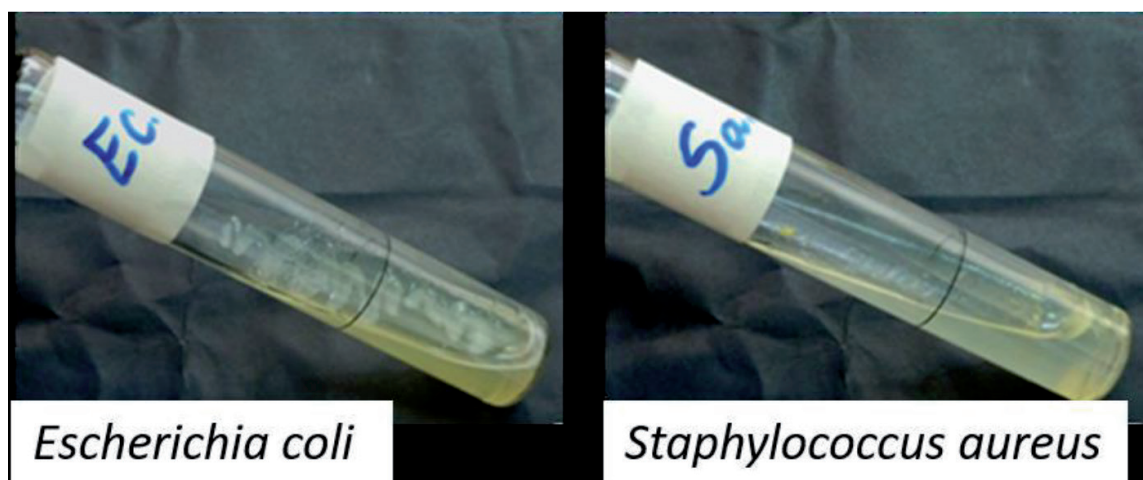


Figure 10.
Photographs of bacterial strains used in the assay.

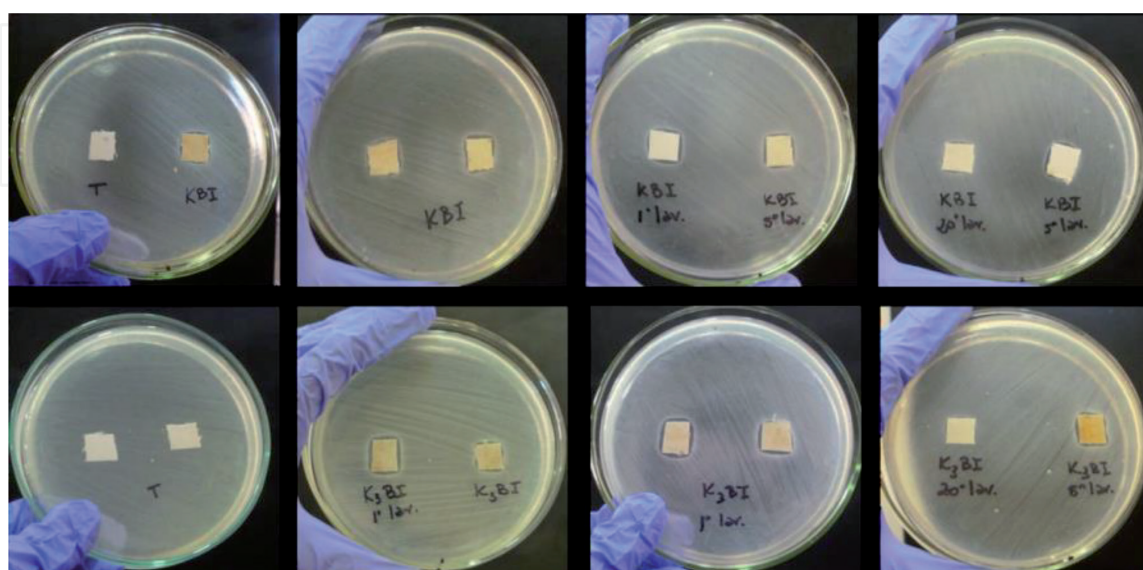


Figure 11.
Antibacterial test of fabrics impregnated with the pad-dry-cure method against *Escherichia coli*.

The photographs of the agar diffusion test against *S. aureus* are shown in **Figures 13** and **14**, in which a halo of inhibition is observed for the fabrics impregnated with the biocide while in the control fabric there is growth throughout the plate.

The photographs obtained through the magnifying glass clearly show the interface of fabric-culture medium-bacterial growth for fabrics with biocide, thus affirming their inhibitory effect. With respect to the washing cycles, they have the same tendency as described for *E. coli*, producing a slight decrease in activity only in the washing cycle number 20.

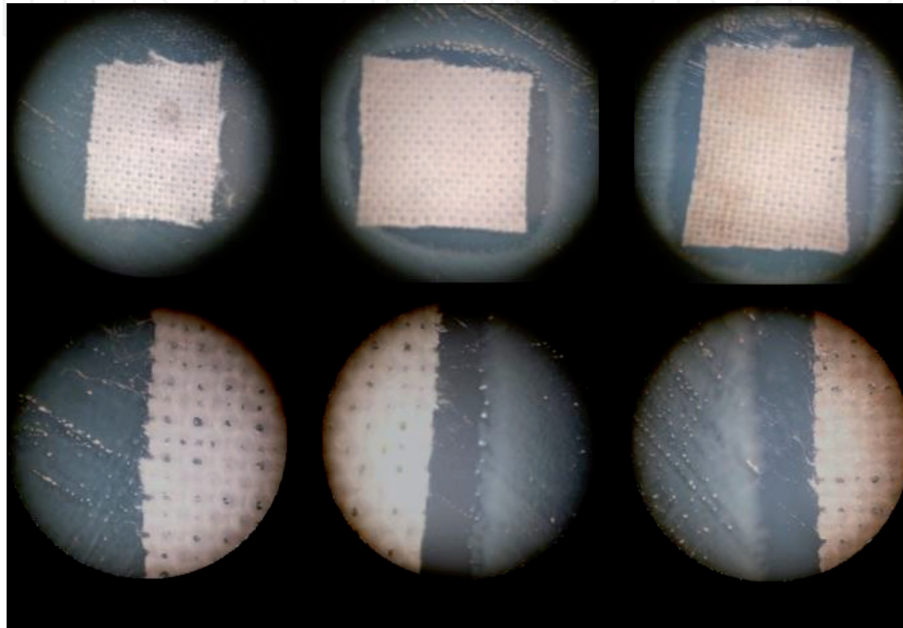


Figure 12. Images observed with magnifying glass of the control fabric and the fabrics impregnated with the pad-dry-cure method, tested against *Escherichia coli*.

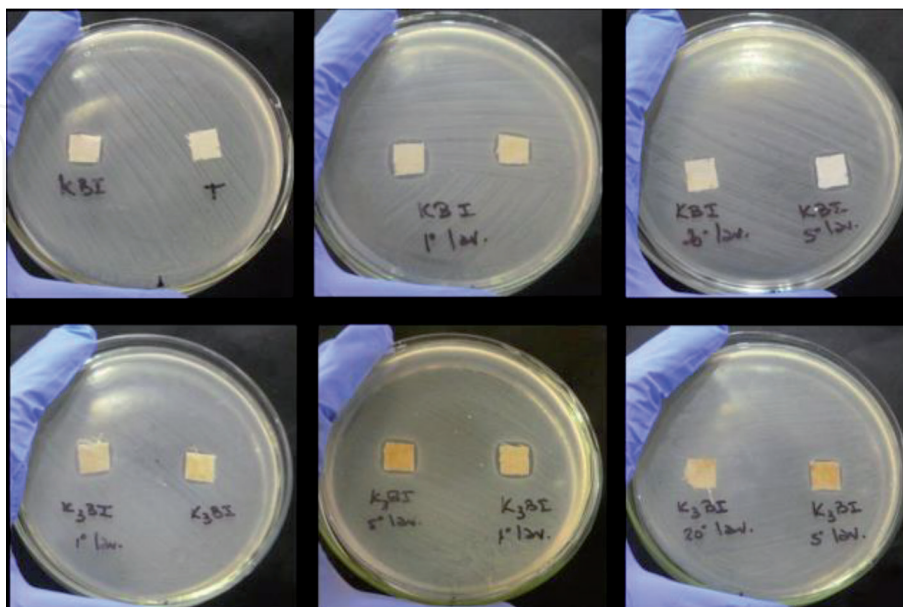


Figure 13. Antibacterial assay of fabrics impregnated with the pad-dry-cure method against *Staphylococcus aureus*.

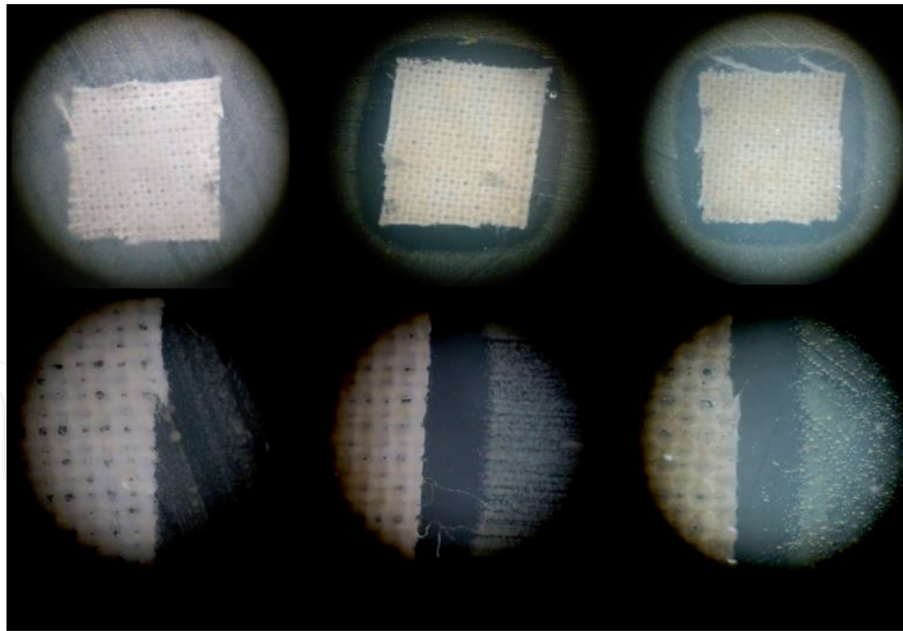


Figure 14. Images observed with magnifying glass of the control fabric and the fabrics impregnated with the pad-dry-cure method, tested against *Staphylococcus aureus*.

5. Conclusions

As a closing of this chapter, it can be concluded that antimicrobial fabrics were obtained from the pad-dry-cure method, using the samples synthesized on silica base with C and Ag. The cotton cloth used was evaluated in antifungal tests with strains *C. globosum* and *Aspergillus* sp., according to the modified standard method DIN 5393, and by antibacterial assays through the agar-based diffusion method (SN 195920-1992), against *E. coli* and *S. aureus*.

On the other hand, the results were good for both the inhibition of fungal and bacterial strains. In addition, there was a high degree of persistence of the additives after the wash cycles before antimicrobial tests, with inhibition being recorded up to 20 cycles.

Since most of the work focuses on the inhibitory effect of Ag against bacteria, the mechanisms of inhibition or lethality of surfaces with antifungal compounds are poorly understood. In recent years there has been an effort to increase research on antimicrobial fabrics, but the vast majority of these publications focus on bacterial research and only some conduct resistance tests against fungi. If the number of investigations in general is reviewed, a marked increase is observed in the last 5 years. However, the number of investigations on antibacterial fabrics is higher than the number of investigations on antifungal fabrics. However, taking into account the importance of fungal infections in human health, considering that the incidence of fungal infections is increasing and the associated health costs are high, studies should also focus on this field and interest on antifungal fabrics should be growing.

The antimicrobial properties of silver have been known for many years, but recently it has begun to understand the mechanisms by which silver inhibits the growth of microorganisms, although much remains to be investigated. There are several investigations about the biocidal effect and mode of action of silver ions against bacteria, especially against *E. coli*; however, the antifungal effects and the mode of action of nano-Ag against fungi have not yet been studied in depth, and it remains unknown.

Some investigations assume that Ag atoms bind to thiol groups (–SH) in enzymes and subsequently cause them to be deactivated by denaturation. Stable S–Ag bonds would be generated with compounds that contain thiol in the cell membrane and that would be involved in the generation of transmembrane energy and in the transport of ions [43]. The result would be a loss of fluids and electrolytes from microorganisms, which are dried and shrink. In literature it was shown that the cells suffered great damage when contacted with Ag, a treatment that finally destroyed the cell wall and the cell membrane. Damage to the cell membrane could lead to cell cytoplasm filtration, which would result in dehydrated and shrunken cells [43].

The method to obtain the carbon used in these samples comes from a process that can be applied to the treatment of residues with high metal contents, which resemble a non-sulfide mineral, for example, batteries, computer waste, slags from the metallurgical industry, etc. The acid medium can be generated in situ in biopiles directly on the mineral or residue, or produced in bioreactors where the microorganisms are grown, and then put in contact with the mineral or residue; the latter is the case studied in this work. In recent years, scientific papers have been reported on this process applied to the recovery of metals from different wastes, among others, batteries and batteries, bibliographic references previously placed, although no existing commercial facilities have been reported to date [47, 48].

It can be concluded, in general terms, that the proposed objectives have been achieved, since antimicrobial additives were synthesized through a simple and rapid method of obtaining, such as the sol-gel method, which allowed the inclusion of the biocide, Ag, in oxidic matrices. They could be incorporated effectively in the preparation of antimicrobial fabrics.

Acknowledgements

This work was supported by the National Scientific and Technical Research Council (CONICET) and the National University of La Plata (UNLP).

Conflict of interest

The authors declare no conflict of interest.

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