Chapter

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 SiO_2 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/cm^2. 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 N_2 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/H_2O 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 SBAg, and the sample SB3 (10% w/w C) which was treated in the same way including Ag and was called SB3Ag.

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 Cu Kα (α = 1.5417 Å) 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 ADDAII 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 biodeteriorated 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 $MgSO_4.7H_2O$ (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]: 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° 2θ interval was confirmed and the band located around 23° 2θ 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 (Ei) 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 Ei > 100 mV; strong sites 0 < Ei <100 mV; weak sites −100 < Ei <0 mV, and very weak sites Ei < −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 Ei value of 37.1 mV, while silica without carbon has an Ei 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 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....H_2O). 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

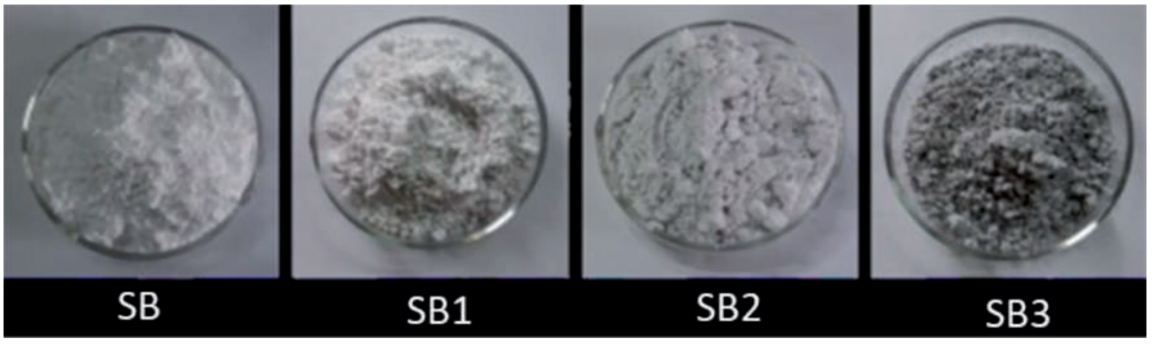

Figure 1.
Digital images of silicas.

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 (–OC_2H_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 $Si(OH)_4$ and $Si(OC_2H_5)_4$. 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.

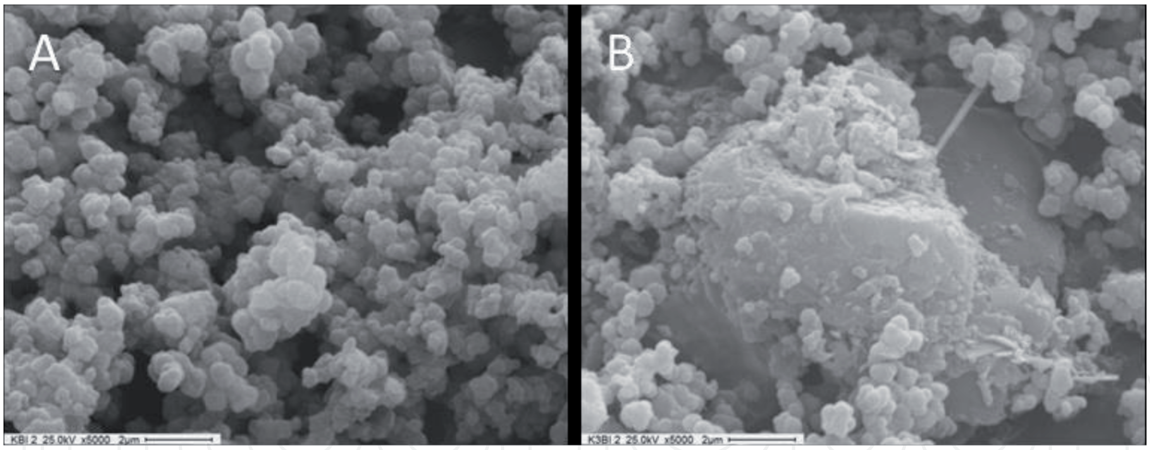

Figure 2.
SEM micrographics of samples: (A) SBAg and (B) S3Ag (5000×).

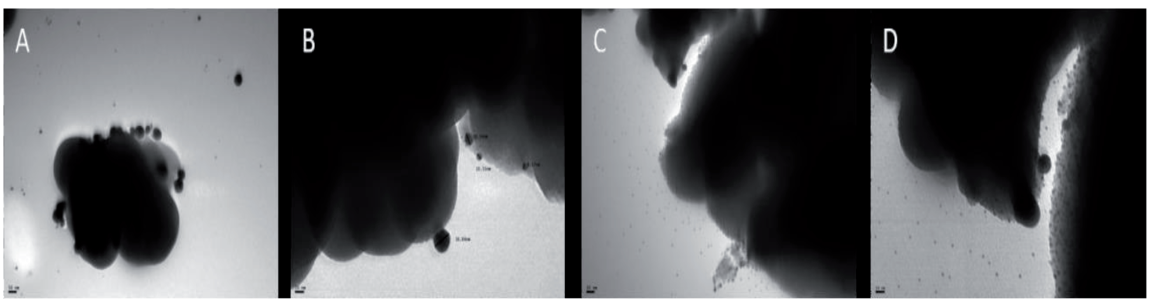

Figure 3.
TEM micrographics of samples: (A) SBAg (100,000×), (B) SBAg (270,000×), (C) S3Ag (100,000×), and (D) S3Ag (270,000×).

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 Ag^0 (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 Ag^{2+}, 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 surficially 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-cry 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).

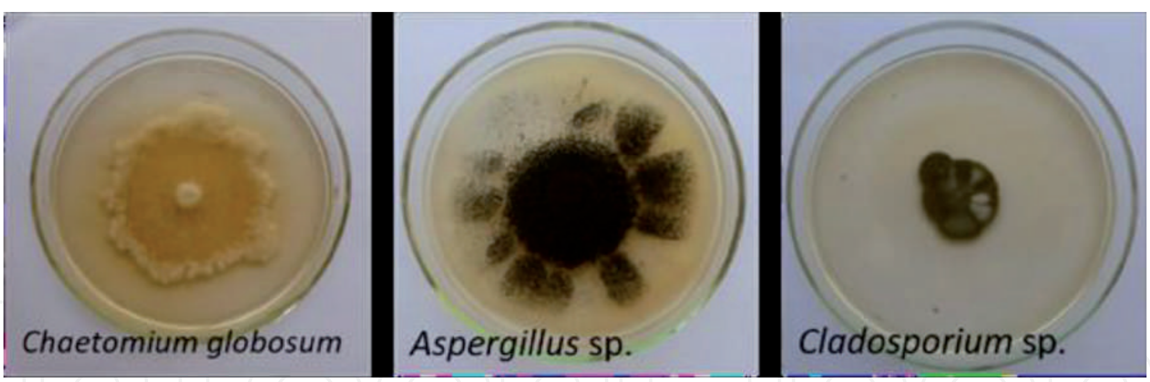

Figure 4.
Photographs of the strains used as bioindicators.

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 $MgSO_4.7H_2O$, 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 × 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

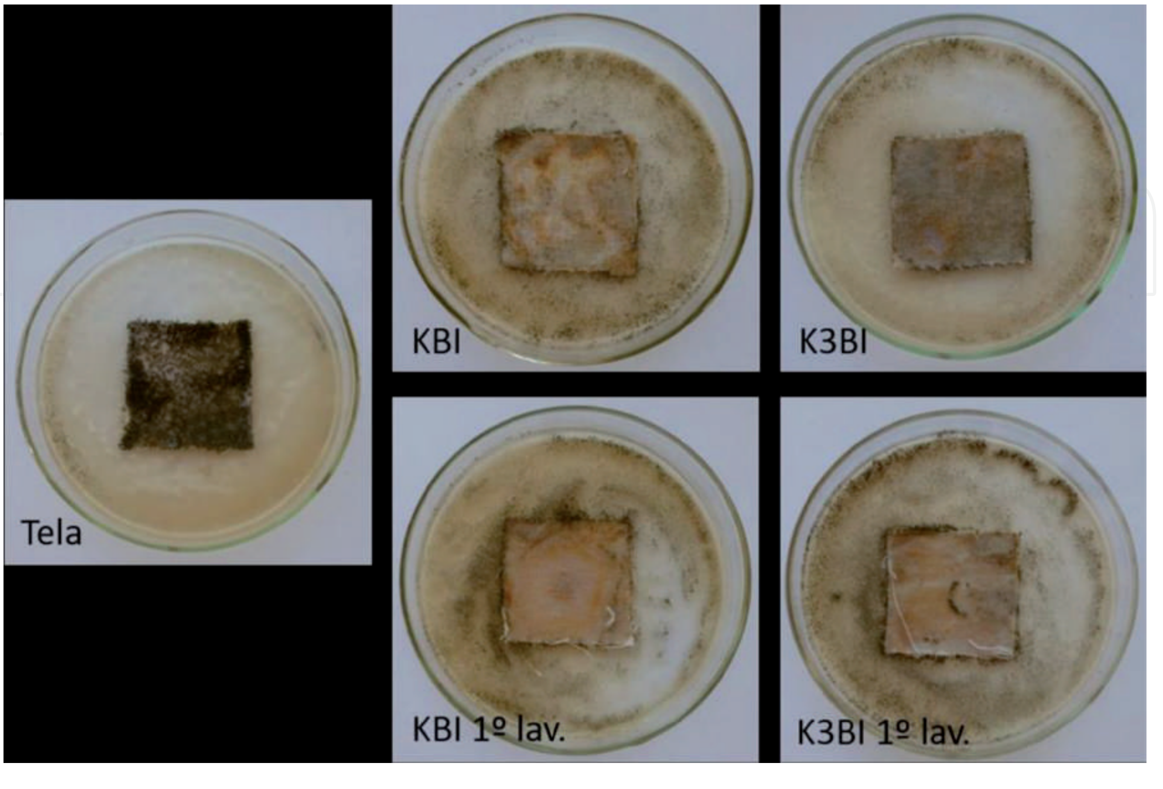

Figure 6.
Antifungal test of the fabrics impregnated with the pad-dry-cure method against C. globosum.

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

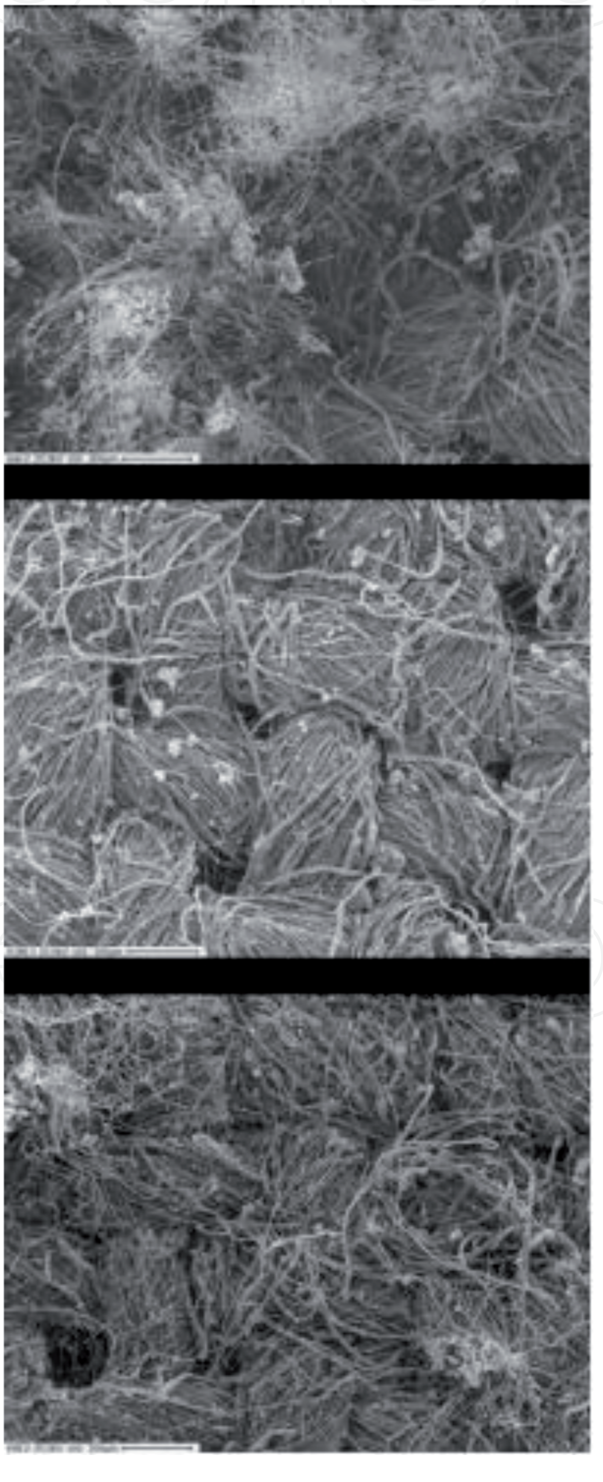

Figure 7.
SEM micrographs of the control fabric (above) and the fabrics impregnated with the pad-dry-cure method KBI and K3BI (medium and down), tested against C. globosum.

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

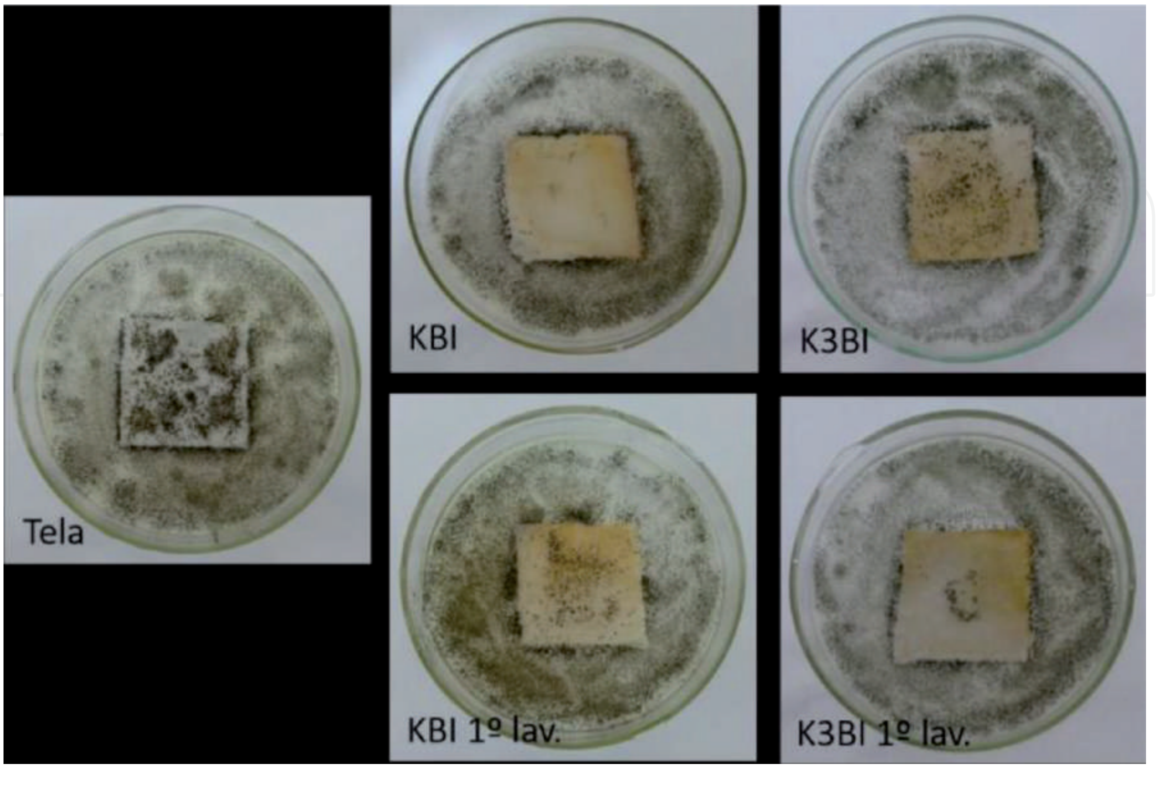

Figure 8.
Antifungal test of fabrics impregnated with the pad-dry-cure method against Aspergillus *sp.*

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].

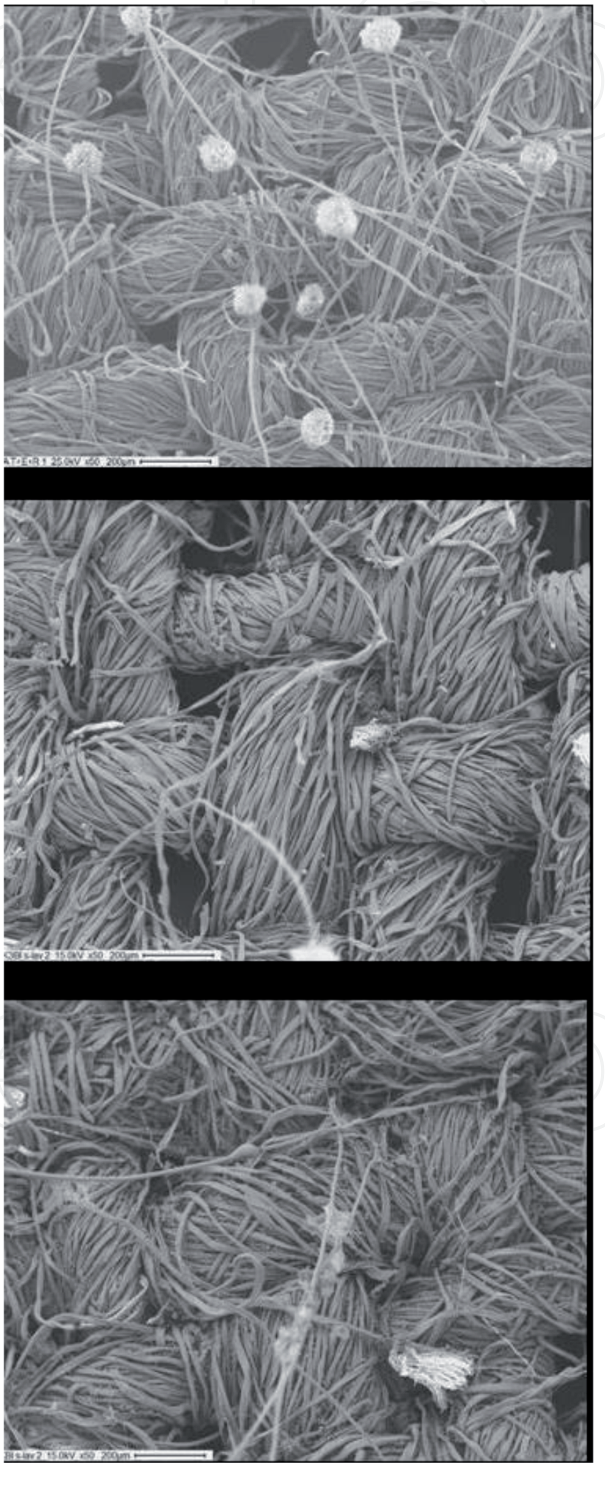

Figure 9.
SEM micrographs of the control fabric (above) and the fabrics impregnated with the pad-dry-cure method KBI and K3BI (medium and down) and the fabrics impregnated with the pad-dry-cure method, tested against Aspergillus *sp.*

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 (1.5×108 Ufc/ml). A dilution was then made to obtain a bacterial suspension of 1.5×106. 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.

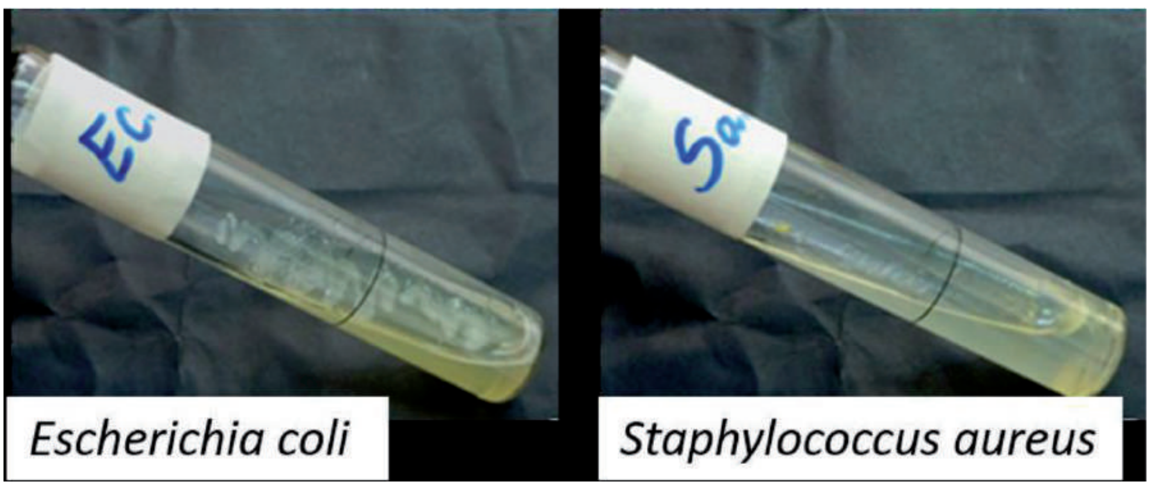

Figure 10.
Photographs of bacterial strains used in the assay.

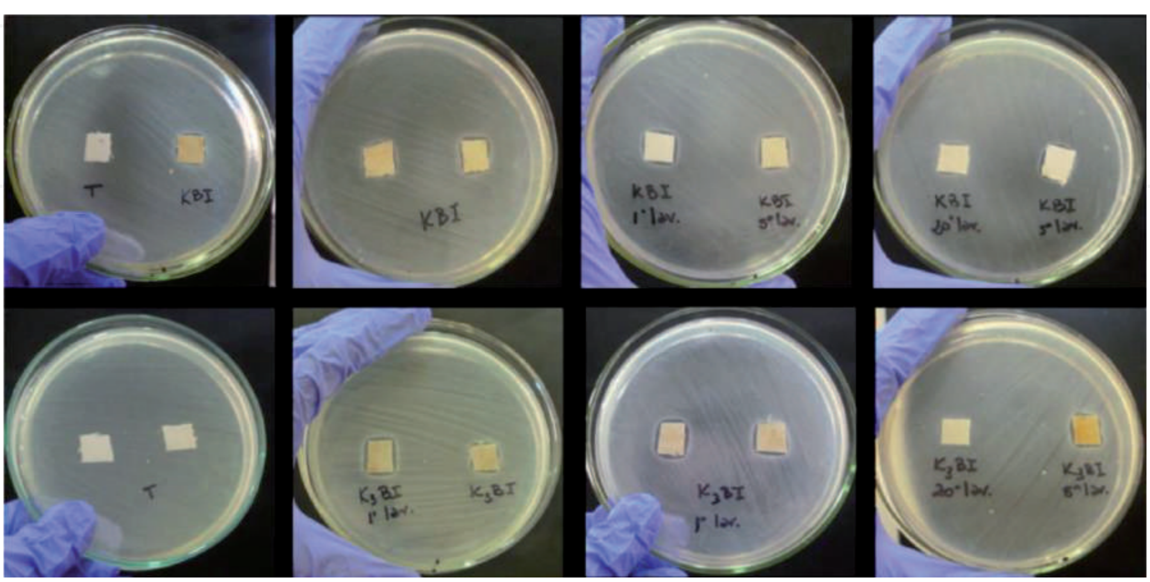

Figure 11.
Antibacterial test of fabrics impregnated with the pad-dry-cure method against Escherichia coli.

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.

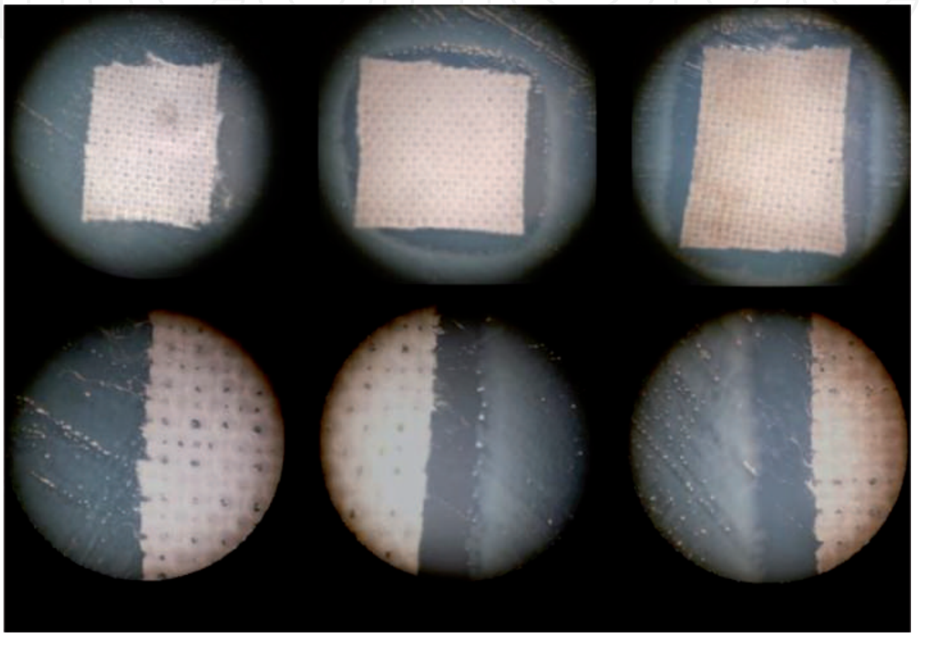

Figure 12.
Images observed with magnifying glass of the control fabric and the fabrics impregnated with the pad-dry-cure method, tested against Escherichia coli.

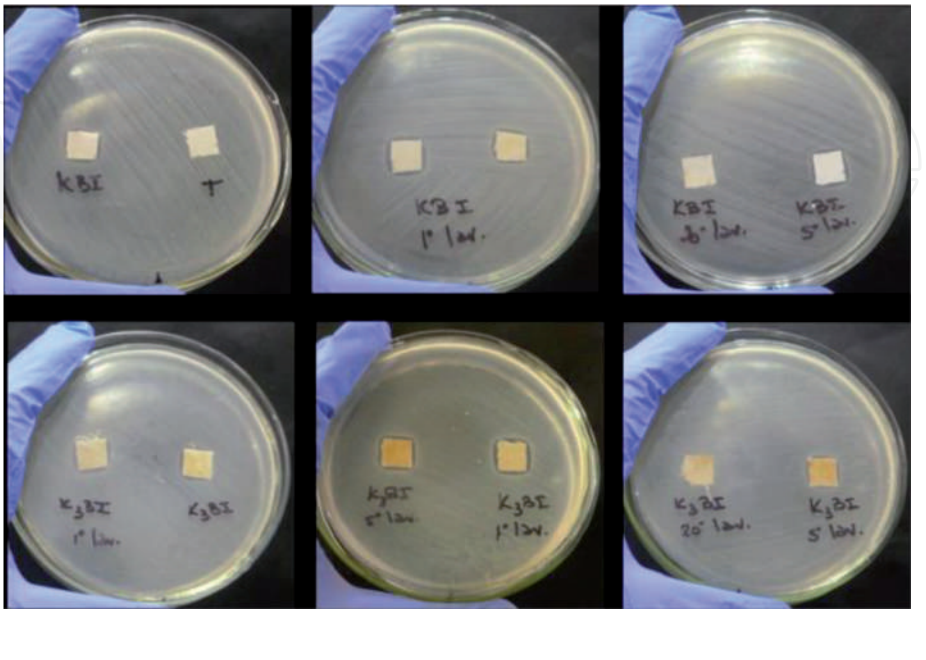

Figure 13.
Antibacterial assay of fabrics impregnated with the pad-dry-cure method against Staphylococcus aureus.

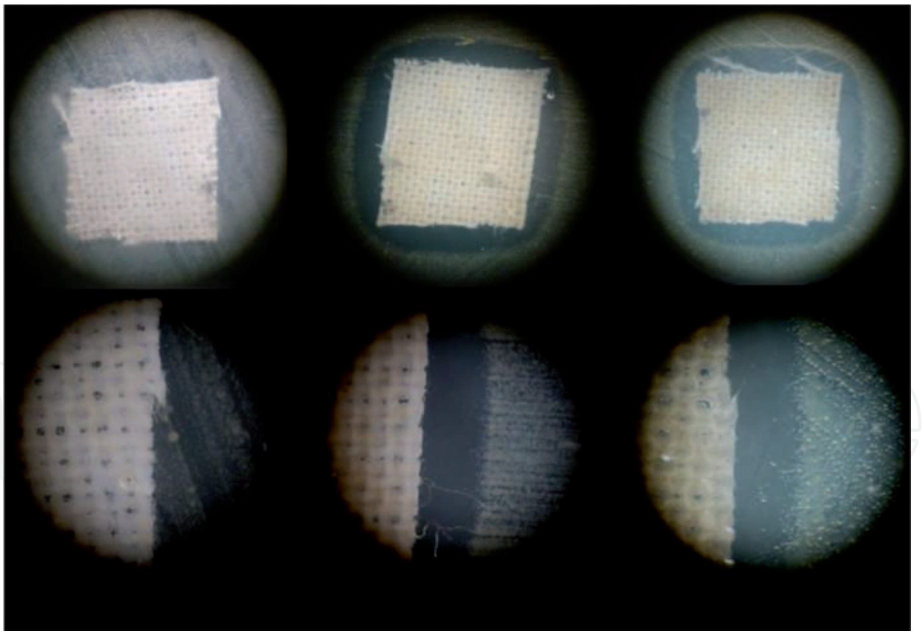

Figure 14.
Images observed with magnifying glass of the control fabric and the fabrics impregnated with the pad-dry-cure method, tested against Staphylococcus aureus*.*

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

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Conflict of interest

The authors declare no conflict of interest.

Author details

Katerine Igal and Patricia Vázquez*
Center for Research and Development in Applied Sciences (CINDECA), National Scientific and Technical Research Council (CONICET), La Plata University, La Plata, Argentina

*Address all correspondence to: vazquez@quimica.unlp.edu.ar

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Chapter

The Waste Problem of Antimicrobial Finishing

Candan Akca

Abstract

Growing awareness of health and hygiene has increased the demand for bioactive or antimicrobial textiles. As a result the global market of antimicrobial textile products has been growing day by day. Antimicrobial finishing protects the wearer from microorganisms for aesthetic, hygiene, or medical reasons and protects the textile from biodeterioration caused by mold, mildew, and fungi. Antimicrobial textile products have crucial functions such as ensuring hygienic conditions and preventing spread of diseases especially crowded places like hospitals, baby nurseries, and barracks. However the antimicrobial agents used in antimicrobial finishing have adverse effects (toxic, allergic, and carcinogenic) on wearer and all the living organisms during the antimicrobial textile product's production and serving life. The effects of finish content released in waste water bath and the release of finish content to surrounding skin of user and its contact/inhalation/consumption by other living species require studies. The contamination substances in the sludge may be consumed by the cultivated plants, eventually becoming component in feed and food. Contamination is also possible in water and soil organisms. The chapter is about the waste problem of the antimicrobial finishing (especially metal-based antimicrobial finishing and triclosan-based antimicrobial finishing).

Keywords: antimicrobial finishing, heavy metal, silver, triclosan, waste, environment, pollution, toxicology

1. Introduction

The foundations of the textile industry were laid in Britain; spinning and weaving technologies developed here. However, in the aftermath of this development, in the nineteenth century, textile production shifted to Europe and North America following pace with the industrial modernization in these regions. In the preceding years, almost all countries have realized industrialization and development processes via the textile industry. Countries undergoing the development process continue to produce more traditional textile products, whereas countries that have already completed their development processes and have achieved an advanced level of technology continue to produce high-tech technical textiles [1].

While the textile industry was initially in a traditional position that met basic requirements, such as yarn and fabric production, clothing, and home textiles, the development of technology over time and the increase in human needs have resulted in the industry being much more technological and functional today as a result of diversification [1].

Looking at the global textile market volume in 2015 and beyond, it is observed that it reached $667.5 billion in 2015. Europe accounted for 54.6% of this volume and the Asia-Pacific region 20.6%. When the 2018 data is examined, the global textile market volume is estimated to be $858 billion, up to 5% from 2019, and estimated to reach $1.207 billion by 2025 [1, 2]. It is also estimated that interest in high-tech textile products will continue to increase in the coming years and that the market in this field will continue to grow in Europe (especially Germany, France, and Italy) [2].

In recent years, consumers' desire to feel comfort, be hygienic, feel good and control odor, and be protected from microorganisms has led to the rapid growth of the market of antimicrobial textiles [1, 3, 4]. The current uses of antimicrobial textiles range from outdoor applications such as tents, tarpaulins, awnings, blinds, parasols, sails, and waterproof clothing to indoor applications such as shower curtains and mattress ticking. They are also used in some consumer textiles such as sportswear, T-shirts, and socks and also in medical purpose such as masks, surgical clothing, wound dresses, and bandages [5]. Global antimicrobial textile market volume in 2019 reached $9468 million. And it is estimated to reach $12,313 million in 2024 [6]. According to the 2015 data, the market volume of global finishing chemicals is 1.14 million tons, and there is an increase of 6.1% each year by 2025. A significant portion of this amount consists of antimicrobial finishing agents [7]. The volume of the global wet wipe and wet napkin market is thought to have the potential to increase by $5.75 billion between 2020 and 2024 [8]. And by 2016, the volume of diapers will be $46.50 billion and is estimated to reach $67.46 billion by the end of 2022 [9].

By 2025, the world's population is estimated to be 8.2 billion. Growing world populations, rising living standards, and fast fashion trends are causing the global textile industry to grow day-by-day. This also means large amounts of raw materials and resource usage, ultimately producing pollution and a high rate of waste [1, 10].

In this section, the issue of antimicrobial textile production (especially metal-based antimicrobial textile production, triclosan-based antimicrobial textile production) and subsequent product life spans are investigated.

2. Textile and waste

The word waste is defined as things that people do not need and want to get rid of. Waste according to their physical form can be classified as solid, liquid, and gas. It is also possible to classify waste according to its original uses (packaging waste, textile waste, etc.), according to its materials (glass, metal, fiber, etc.), according to its physical characteristics (recyclable, composite, fuel, fertilization, etc.), according to its origin (domestic, commercial, industrial, agricultural, etc.), and according to its safety level (dangerous or hazardous) [9]. Household waste and commercial waste are classified together as solid municipal wastes. Excessive and unnecessary consumption in all areas of daily life increases the burden of a clogged-up world [10].

European Union member states have targeted a 50% reduction of municipal waste by 2020 through reuse and recycling [10].

In the textile industry, during the production of textile products, high amounts of solid, liquid, and gas in the form of wastes are produced as well as during the lifetime of textile products by the consumer and after the end of its lifespan [1, 10, 11].

Aged textile processes, which include pre-finishing, dyeing, printing, and finishing processes, usually consist of chemical applications, fixation, washing, and drying steps. In particular dyeing and finishing processes are processes where the highest amount of water is used [1, 11]. In textile production, a very large amount of water, chemicals, dyeing, and auxiliary chemicals are used. Therefore, textile wastewater is contaminated with these substances, has alkaline at high concentrations, is sharply scented, has the need for high biological oxygen (BOD) and for chemical oxygen (COD), and contains highly dissolved solids if it is not properly removed, which can cause environmental complications [1, 11].

Textile products other than disposable products are repeatedly exposed to washing, drying, ironing, and dry cleaning during their lifetime [12]. Wastewater contaminated with detergent, stain remover, and softener in washing baths are toxic to marine creatures [13]. With each washing, the active finishing chemicals applied on the textile product also leave the textile surface and pass on to the washing water subsequently increasing the waste load. Active finishing chemicals can leave the textile surface not only with bathing but also when faced with bodily fluids during use. This condition can cause itching, skin sensitivity, and allergies in people with sensitive skin [14].

The average life expectancy of textile products is 2 years, and then they continue to be waste loads by being stored in landfills. The amount of textile waste that has completed its life span is 10.5 million tons per year in the United States, 350,000 tons in the UK, and 287,000 tons in Turkey [10]. In particular, some studies and trends have been initiated to evaluate textile products that have completed their life spans in the United States and Europe. These studies can be summarized as recycling, reuse, energy production, second-hand clothing trends, vintage clothing trends, and slow fashion trends [10, 15]. According to 2009 data, only 15% of the textile products that have completed their life in the United States are utilized through recycling or donation, and the remaining 85% are left to solid waste landfills. However, it is thought that it is possible to utilize up to 95% with successful waste management [10].

The textile industry also produces waste in gas form, causing air pollution. Especially in spinning and weaving processes, a large amount of dust and sublimates are emitted into the operating environment. This condition can cause respiratory diseases and chronic lung diseases in workers [10].

From an environmental point of view of the textile industry, energy consumption, gas emissions, solid waste, and odor problems are also important issues, but the main problem is the chemical waste load produced in large quantities of wastewater and the chemicals in the wastewater [10].

2.1 Toxic or hazardous waste in the textile industry

Toxic or hazardous waste is waste that is dangerous for the environment and human health or has the potential to create harmful effects. Toxic and hazardous waste can occur in the form of solid, liquid, gas, and sludge as a result of various industrial production activities [16].

There are many toxic and dangerous chemicals in textile wastewater caused by different production processes [10]. Some of these are as follows [10]:

- Chlorinated solvents: chlorinated solvents are used in many processes such as bleaching, scouring, and dyeing in the textile industry. They are known to have allergic, carcinogenic, and toxic properties for human and environmental health.

- Hydrocarbon solvents-aliphatic hydrocarbons: hydrocarbons of organically structured compounds consisting of aliphatic compounds and carbon and hydrogen elements are aliphatic. They can be straight-chained, branched, or ringed and are divided into two: saturated and unsaturated. They are flammable and have sultry properties. They are known to cause nervous system diseases and cancer.

- Hydrocarbon solvents-aromatic hydrocarbons: it is very difficult to purify textile wastewater from aromatic hydrocarbons. Aromatic hydrocarbons are not easily dissolved in water. Most aromatic hydrocarbons stick to solid particles, settling in lake and riverbeds and blending into groundwater. These compounds are known to cause cancer in the long term.

- Oxygenated solvents (alcohols/glycollics/ethers/esters/ketones/aldehydes): oxygenated solvents are solvents with a high solvent feature containing an oxygen molecule. These solvents (methanol, ethanol, propane, ethylene glycol, etc.) are widely used in textile processes. They are harmful to both human health and all flora and fauna. Exposure to high amounts of these compounds can lead to sudden deaths. Prolonged exposure can cause blindness, irregular heartbeat, and damage to the kidney and lungs. Some of these compounds are in the carcinogenic category for humans. Glycol ethers can cause developmental impairment in the fetus and infertility in men. Regular exposure to these solvents can cause memory and hearing loss, depression, headache, coordination disorders, and skin disorders. Exposure to the vapors of these solvents can cause ailments such as asthma or shortness of breath.

- Grease and oil contaminated waste: grease can be animal-based, oil-based, and synthetic-based. Wastewater contaminated with grease is toxic to marine life in the long run.

- Used oils: some of the oils used in textile processes are carcinogenic to human health if they are in physical contact with humans or digested.

- Dye materials and pigments containing harmful substances: the presence of dye substances and treatment of textile wastewater are serious problems because most dye materials are stable and are not easy to parse with traditional treatment methods. The chemical structures and contents of the dyes have an effect on toxicity sites:

- Organohalogens: pigments can contain fluorocarbon, chlorocarbon, bromocarbon, or iodo-carbon bond and contains toxic elements such as lead, cadmium, mercury, valve, chromium, cobalt, nickel, arsenic, etymon, and selenium and are toxic and dangerous.

- Organic compounds (such as benzyte, methane, paraffin) are made up of carbon and hydrogen elements; they are found in coal, crude oil, natural gas, and vegetables. Hydrocarbons, pesticides, dyes, and plastics are the cornerstone of numerous product groups.

3. Textile antimicrobial treatments

Antimicrobial finishing applied to textile material should be effective against microorganisms as well as meet a number of requirements including the fact that antimicrobial finishing is suitable for the textile process; is resistant to washing, dry cleaning, and hot press; and is not harmful to the environment [17].

Different antimicrobial methods of finishing may be preferred depending on the genus, structure, surface characteristics, and usage area of textile material. Antimicrobial finishing can be carried out during the phase of finishing procedures, as well as the application of antimicrobial agents into the polymeric matrix during the production phase of synthetic fiber. The activity against microorganisms occurs through contact and/or diffusion. There are no antimicrobial agent disperses in activity through contact and show impact on the microorganism at the time of contact. In the event of diffusion, the antimicrobial agent reaches the outer environment away from the fiber surface, or polymer matrix, and shows activity on the microorganism [17–21].

A living germ, bacteria, or fungal has a cell wall of polysaccharides on the outermost surfaces. This structure ensures their integrity and protects them against the external environment. There is a semipermeable cell membrane on the cell wall. The cell wall and membrane stores, protects, and performs the cell's vital organelles, enzymes, genetic information, and transport. The type of activity of the antimicrobial agent against the microorganism is the main factor in its classification. If the antimicrobial agent only prevents the growth of the microorganism, it is called a biostatic effect; if it kills microorganisms, it is called biocidal effect [22–24].

Antimicrobial finishing processes have three different mechanisms [25]:

3.1 Controlled release

Most antimicrobial substances operate with a controlled oscillation mechanism. In this mechanism, the antimicrobial substance, which has already been applied to the textile material, is released at a certain speed in a controlled manner during use. This type of antimicrobial substance, which is removed when the textile material is washed, is very effective against microbes on or around the fiber surface. However, since it is constantly released during use, the amount of the textile material is gradually depleted at the end of the antimicrobial substance, and therefore the exhaustion process is depleted. On the other hand, the environmentally released antimicrobial substances are toxic to beneficial microorganisms and other creatures [24–26].

In recent years, studies have increased the use of silica carriers such as zeolite and microencapsulation technology for controlled oscillation in order to increase the strength of antimicrobial process or effect and cause less damage to the environment [25–27].

3.2 The regeneration principle

The renewal model was formulated by Gagliardi in 1962. This model, described in Gagliardi's article, is based on the application of a chemical finishing process product to fabrics that produce active germ killer (antiseptic) substances that are constantly renewed by adding bleaching substances during washing or exposure to ultraviolet light. This regeneration occurs when the covalent bonds in the chemically modified fiber are severed as a result of washing or photochemical effects, so that the model has an unlimited antimicrobial repository [27]. Although the regeneration technique has not yet been implemented, the microencapsulation technique is close to performing the function of this model. However, although the surface is suitable for a long period of time, microencapsulated antimicrobial substance storage is not unlimited [25, 27, 28].

3.3 Blocking or the blocking effect

The blocking or blocking mechanism for the protection of fabrics from microorganisms can be divided into two: (a) inert (ineffective) physical obstacle layers or coatings that are simply resistant to the passage of microorganisms into fabric or (b) layers or coatings with direct surface contact effect against microbial proliferation [27].

Fire, water, weather, and mildew resistant (FWWMR) end process is an example of obstacle coating. In this process, fabrics are coated with a mixture of organic and anorganic compounds containing fungicide. The blocking or blocking mechanism has been used to protect fabrics from mold yeast and decaying fungi with resin applications or chemical modification of cellulose with cyanoetylation or acetylation. When the finishing process containing flame-retardent agents and resins forms of finishing agent with covalent bonds, they are the most effective products against mold [27].

The product of the only antibacterial finishing process based directly on the concept of surface contact attachment obstruction is an organosilicon polymer containing hanging quaternary ammonium groups that form a biobarrier in the fabric [27].

Most of the antimicrobial agents used to manufacture commercial textiles have biocidal effects, but they show activity on microorganism in different ways [17]:

- They damage or inhibit the synthesis of the cell wall, which is critical for life and survival.
- They damage intracellular and non-cell matter transport by inhibiting cell membrane function.
- They cause the death of the microorganism by inhibiting the synthesis of the proteins that make up the building rocks of the cell and enzymes.
- By inhibiting nucleic acid (DNA and RNA) synthesis, they prevent the survival and proliferation of the cell.
- By inhibiting metabolic processes, they cause the death of the microorganism.

4. Antibacterial agents used in the textile industry

The most common antimicrobial substances used to give textile materials antimicrobial properties are quaternary ammonium compounds (QAC), polyhexamethylene biguanide (PHMB), chitosan, regenerated N-halamine compounds, peroxy acids, metal/metal salts, and triclosan. In addition, there are antimicrobial-enabled paints (e.g., metallic paints) that allow simultaneous dyeing and antimicrobial finishing processes [25]. The chapter is about metal-based antimicrobial finishing and triclosan-based antimicrobial finishing.

4.1 Metal-based antimicrobial finishing

Many heavy metals are toxic to microorganisms, both freely and in compounds, even at very low concentrations. Other heavy metals such as copper, zinc, and cobalt are also used in the production of antimicrobial textiles, but the most preferred are silver and silver compounds for this purpose [17, 29, 30]. In recent years, the nano-forms of metal and metal compounds have attracted attention as new generation biocides [30]. According to 2018 data, the most commonly used antimicrobial substances in the production of antimicrobial medical textiles are metal/metal salts (39.6%) [31]. The most commonly used metallic salts are silver, copper, zinc, and cobalt [31–33]. The global nano-silver market volume is estimated to exceed $3.3 billion in 2024 [34].

Metal and metal compounds cause oxidative stress in the microorganism, causing damage to microorganism lipid, protein, and DNA, resulting death [30]. The mechanism of action of the nano-forms of metal/metal compounds is similar. Silica such as zeolite, polymer matrixes, and various cross linking agents are used to stabilize nanoparticles in the structure, to provide controlled oscillation, and to ensure washing durability [30].

In synthetic fibers, metal and metal compounds can be added to the environment before fiber extraction or in the polymer stage before electrospinning and nano-fiber production. During its lifetime, metal ions are released causing biocidal effects in the presence of moisture. The amount of metal ion released varies depending on the chemical structure of the fiber, its surface feature, and the amount of metal/metal salt on the fiber [29].

The application of metals to natural fibers can only be done during the finishing process. Various strategies have been developed to improve binding and durability. Cotton was pre-treated with succinct acid anhydrites. Succinic acid anhydride acts as a ligand (atom, molecule, or ion attached to the central atom) for metal ions and provides very effective antibacterial activity by increasing the retention of metal salts (Ag^+ and Cu^{2+}) on the surface. In protein fibers (e.g., wool), aspartyl and glutamyl residues are thought to be binding groups for free carboxyl groups, most likely metal ions. Binding capacity can be further increased with EDTA with the ability to skip the tannin acid or metal ions that increase the serious restrictions due to technical and environmental problems; therefore, it is not accepted in commercial production [29].

4.1.1 Silver-based antimicrobial finishing

Silver has been used in many areas for centuries as a broad-spectrum antimicrobial substance with antibacterial, antifungal, and antiviral properties. Metallic silver, silver nitrate, and silver sulfadiazine forms have been used for many years to treat burns, wounds, and numerous bacterial infections [35]. Most metal ions are also known to have antimicrobial properties, but silver is best effective against bacteria, viruses, and other eukaryotic microorganisms [35]. Silver has very important advantages as an antibacterial substance. These benefits include the fact that silver is a very broad-spectrum antibiotic and has almost no bacterial resistance to silver, and there is no toxicity in low concentrations [35–37].

It is known that the use of silver in the treatment of burns and chronic ulcers in water disinfection dates back to the 1000 BC. In the literature, it is mentioned that silver was used as an eye drop in the 1800s, and then its used was reduced with the presence of penicillin, but 0.5% silver nitrate solution in the 1960s was widely used in burn treatment. In these years, silver's effectiveness against bacteria such as *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *Escherichia coli* has been proven. In 1968, silver sulfadiazine cream was obtained by combining silver nitrate with sulfonamide. This cream has been widely used in the treatment of burns due to its effectiveness against many microorganisms. The literature states that silver sulfadiazine is active against bacteria such as *E. coli*, *S. aureus*, *Klossiella* sp., and *Pseudomonas* sp. and also has antifungal and antiviral activities [35]. 1% silver nitrate solution is still used as eye antiseptic for various purposes in newborn babies [38]. Today, wound dresses containing different amounts of silver against antibiotic-resistant bacteria are used [35].

Concentrations greater than 0.5% are not generally preferred in silver solutions used for medical purposes. In these concentrations, silver allergy is not reported.

However, when using wound dress containing a high amount of silver ion in large wounds, a disease called argyrism can be found in the form of bluish and brown lesions in the skin and mucous membrane. This disease causes the removal of silver ions from the open wound for a long time [35, 39].

Metallic silver is actually inert, but when it comes into contact with the skin, the moisture and fluid of the wound on the skin make it ionized. Iodine silver is highly reactive. It connects to tissue proteins, causing structural changes in the bacterial cell wall and then the nuclear membrane, causing the death of the microorganism [35].

4.1.2 Mechanism and toxicity of silver

The mechanism of killing microorganisms by silver is still not very clear. The mechanism was attempted to be clearer by examining morphological and structural changes caused by metallic silver, silver ions, and silver nanoparticles in the bacterial cell. In light of the studies, it is known that silver is connected to the bacterial cell wall and cell membrane, interacting with thiol groups to inhibit respiratory enzymes, thus leading to the death of the microorganism [35, 36].

Liau and his colleagues studied the effect of silver ions on amino acids containing thiol (–SH) groups in 1997 [40].

A 2000 study by Feng and colleagues examined the morphological changes that silver ions have on gram-positive *S. aureus* and gram-negative *E. coli* bacteria. AgNO3 was used as an ion source in the study. Gram-positive *S. aureus* has been shown to be able to better resist silver ions due to its thick cell wall, which is typical of positive bacteria. Again, the study reported that DNA, which can only be copied while free, has become a more intense form within the cell, which shows that DNA has lost its ability to copy itself [41].

In his 2005 study, Holt and colleagues reported that the increase in the amount of potassium in the environment was detoxicated by the toxicity of silver against microorganisms [42].

Li and colleagues studied the antibacterial effect mechanism of silver nanoparticles on *E. coli* in a 2010 study. In this study, silver nanoparticles first disrupted the structure of the cell membrane and entered the cell and then inhibited the respiratory enzymes by relocating the hydrogen atoms (–S–Ag–) in the cysteine thiol (–SH) groups. The development and proliferation of bacteria stop if cell member permeability and respiratory of cell deteriorate [43].

Many studies are being conducted on the antimicrobial mechanism of nano-silver particles, but there is not enough work on toxicity. A limited number of studies conducted in in vitro conditions show that nano-silver particles are much more toxic than conventional silver and other heavy metals [35, 44]. Shapes, particle sizes, crystalline, surface properties, ambient humidity, ambient pH, cations in the environment, and their concentrations are among the particles that affect the toxicity of silver nanoparticles [45]. In vitro studies reveal that nano-silver particles cause damage to the brain, liver, and reproductive cells in mammals. In 1999, the FDA warned that the use of colloidal silver solutions containing micro- or nanoparticles could lead to neurological problems, headaches, skin irritation, weakness, stomach ailments, and kidney ailments. It is also reported that silver nanoparticles will affect rivers, lakes, and all living things that make up the ecosystem by blending into the food chain by mixing into the water. Washing machines produced in recent years, using nano-silver technology, are also objectionable in this context. In order to further clarify this issue, a large number of independent animal and clinical trials that are not supported by producers must be performed [35, 43, 46].

4.1.3 Silver contaminated waste and silver accumulation

Silver and its different forms are wide spectrum antibiotics. They have low risk of bacterial resistance, and their low concentrations are not toxic, and they have ease of application and low cost. Because of these advantages, silver and other forms of it are widely used in most areas and surfaces, which are being antimicrobial desired. It is also widely used in the production of antimicrobial textiles in different forms of Ag and silver (colloidal silver, silver salts, and elemental silver in powder form) [35–37].

Ag particles are applied to the textile surface using binder or cross-binding substances; it is possible to increase washing resistance. However, as a result of washing both during antimicrobial textile production and throughout its life cycle, most of the Ag particles on the textile surface mix into rivers, lakes, and groundwater along with wastewater, causing the accumulation of silver in the ecosystem. Disposable hygiene products are a similar situation [36]. Most antimicrobial textile products are released into washing water for 50% of the amount of silver at the end of three washings. And the textile products release 10–98% content of the silver into washing water at the end of 10 washings [47]. According to a study, up to 75% of silver may be released from textiles impregnated with Ag NPs in one washing cycle [48]. It is clear that silver accumulated in the ecosystem, water or soil, will have a toxic effect on all living organisms and reach the food chain [14, 35].

According to a study conducted in 64 countries on the release of silver from different products into nature, the United States is the country that releases the most silver into the environment, globally. The Asian continent is the continent which has the most silver emissions directly into the aquatic environment and land [49]. According to a report, 68% of the global silver consumption is used for water treatment and 32% for other uses. And 3.4–40 metric tons of silver are used in textiles per year [5]. In the United States, 29% of the silver used in different industries is released into the aquatic environment, and 69% are known to be dumped in solid waste storage [50]. In recent years nano-silver consumption in textiles like other industries has been increasing rapidly also [51]. The regions where antimicrobial medical textiles containing metallic salts such as copper, zinc, cobalt, mainly silver most used are North America (39% of market volume), Europe (23% of market volume), the Asia Pacific regions (30% of market volume) and the rest of the world (7% of the market volume) respectively [31, 48]. The highest use rate belongs to North America because hospital infection and cardiovascular disease rates are high in this region [31].

4.2 Triclosan-based antimicrobial finishing

Triclosan has been widely used in commercial products for many years as an antimicrobial substance used in soaps, deodorants, cosmetics, cleaning lotions, plastics, toothpastes, and antibacterial textiles [52–56]. The European Union's consumption of triclosan in 2006 is reported to be approximately 450 tons. It is reported that 85% of this is used in personal care products, 5% in textile products, and 10% in plastics and products that come into contact with food [54, 57]. Triclosan is also frequently used in the textile industry. Triclosan is used to prevent the formation of bad odor in wool; to prevent the reproduction of bacteria and fungi in synthetic, mixtures, and non-woven textile materials; and to keep mites away from textile materials [57].

75–210 metric tons of triclosan are used in textiles per year globally [5]. According to a 2009 report by the Australian government, between 2001 and 2005, the amount of triclosan contained in textile products exported to Australia varied between 1 and 20%. The report stated that between 2001 and 2005, textile products containing approximately 1 ton of triclosan were used. In the same report, it is stated that triclosan in used in Australia in wool bed-duvet production, upholstery fabrics, towels, woolly textile products, preparatory fabric production, marine and sports clothes, socks, underwear, shoe linings, zippers, gloves, surgical masks, non-woven products, sleeping bags, and insulation textiles [57]. Triclosan can be added to the textile materials during the fiber production stage and can be applied as a finishing process or transferred in the form of coating [57].

4.2.1 Mechanism and toxicity of triclosan

Triclosan is known to have bacteriologic effects on gram-positive and gram-negative bacteria, as well as antifungal and antiviral properties [53, 56]. Triclosan inhibits lipid synthesis by blocking enoyl-acyl reductase (ENR) of the microorganism. Thus, it prevents the development of the microorganism and its proliferation of division [53].

In 1986 in accordance with the European Union Cosmetics Directive, triclosan has been confirmed that it can be used in materials in contact with foods of up to 0.3% concentration as protective material, 5 mg/kg textile materials (especially in sportswear), and 0.3% concentration of plastic (plastic packaging, brushes) materials [54]. The Japanese government has stated that in cosmetics, the maximum amount of triclosan that can be used is 0.1%. In oral care in Canada, the amount of triclosan allowed in their products is 0.03%, and in cosmetic products it is 0.3%. According to a 2009 report by the Australian government, with regard to triclosan, eyes, respiratory system, and skin have been described as being irritating and toxic to inhalation [57].

Studies on the effects of triclosan on human health are usually carried out with mice, rabbits, dogs, and monkeys [53, 54]. Triclosan is taken into the body through the skin, nose, and mouth during contact with products containing triclosan. In addition, triclosan has contaminated the sea, lake, and groundwater and has reached the food chain, especially from foods such as seafood; triclosan enters the human body [53]. A study of 36 breastfeeding mothers who stated that they used personal care products containing triclosan as a result of a series of studies in America found triclosan in the mothers' milks [53]. Studies have shown that triclosan affects androgens in the male body and estrogen in the female body. Triclosan was found to affect the transport between the fetus and the placenta in the bodies of pregnant sheep, which has been reported that this can cause abnormal development. It has also been reported that triclosan can trigger breast cancers, especially in females. A number of studies on rabbits have been reported to reduce the sperm count in male rabbits and cause tissue destruction in reproductive organs, disrupting masculinity hormones [53].

The thyroid is known to have vital effects on development and metabolism. The thyroid hormone is a highly effective hormone in the development of fetuses and young children. Studies have shown that triclosan lowers thyroid hormone levels in rabbits and changes metamorphosis time in frogs [53, 58].

4.2.2 Triclosan contaminated waste and triclosan accumulation

Water supplies all over the world have been contaminated with triclosan due to wide commercial use in commercial products. In a 1999–2000 study conducted in the United States, samples from different water sources were examined in terms of 95 different chemicals, and as a result, one of the chemicals with the highest concentration was triclosan. Again, the researchers found a very high amount of triclosan in the bodies of marine creatures in particular. The Environmental Protection Agency reported that some of the triclosan in the environment was disrupted by the effect of ultraviolet rays and turned into toxic dioxins. It is reported that the access of dioxins to the food chain will have bad consequences [52]. Because the demolition products of triclosan are also toxic [59]. Again, the formation of cancer is associated with triclosan exposure [59]. According to a study, antimicrobial textile products containing triclosan are sold in 64–84% of the triclosan wash water at the end of 10 washings [57].

5. Bioactive plant-based environment-friendly antimicrobial finishing

Bio-functionalization of textiles with natural bioactive agents with antimicrobial properties is becoming increasingly important because they are not toxic, skin, and environment-friendly. These antimicrobial compounds extracted from most plants are phenols, polyphenols (simple phenols, phenolic acids, quinines, flavonoids, tannin, coumarin, etc.), terpenoids, essential oils, alcoholicoids, lectins polypeptides, and polyacethylenes. Most of these substances obtained from plants are colorful and are natural antimicrobial dyes and pigments used for the dyeing of both natural and synthetic fibers [30, 60–65]. Eco-friendly pigments can be obtained with fermentation of bacteria and fungi [30, 66, 67]. Different methods are mentioned in the literature to increase washing habits of bioactive vegetable-based antimicrobial compounds uncinated on textile fiber: resin application with cross-binding agent, glyoxal, and glycol [30, 68]; sol-gel matrix of liquid bioactive compounds, such as essential oils [30, 69]; and application with microcaps or with the pad-dry-cure method [30, 70–72].

Hydrogen peroxide is a natural antimicrobial produced against invasive bacteria in human cells. It is also found in honey as a preservative. Antimicrobial activity of hydrogen peroxide against bacteria, mold, fungi, algae, and viruses is known. The finishing processes and substances with hydrogen peroxide have become popular and commercialized in recent years [14].

It is thought that the importance of antimicrobial-effective herbal (such as vegetable wastes etc.) and animal-derived natural materials will increase for reducing the waste load (production, during its lifetime, and at the end of its lifespan) and engaging in more environment-friendly manufacturing [14].

6. Conclusion

In today's world, the role of the textile industry is very important. While the textile industry initially met traditional human needs such as dressing with yarn and fabric production and home textiles, today due to rising living standards, textiles have become much more technological and functional with diversified human requirements. It is also an important industry sector for both countries in the growth and development process (rather than traditional textile production) and countries that have completed their development (rather than high technological textile production). However, despite all these advantages, the textile industry causes a large amount of waste and environmental pollution.

At different stages of textile production, numerous chemicals and auxiliary substances are used, many of which are toxic and harmful to the environment and human beings. As a result of these production stages, a large amount of solid, liquid, gas, and sludge form waste is exposed and causes pollution. Noise pollution is also another negative result of the textile industry. Textile finishing operations are the processes where high amounts of water are used, so high amounts of wastewater (with high chemical load) occur. Therefore, the biggest problem of the textile industry is this wastewater burden. According to some studies, 20% of all fresh water pollution is made by textile treatment and dyeing [73]. Textile wastewater needs to be properly purified to reduce environmental damage. In this context, the selection of chemicals and dyes with less environmental damage or environment-friendly finishing operations is also important in this context.

Any textile product has been subjected to washing, dry cleaning, and ironing many times during its service life. With each wash, the active chemical finishing agent in its structure is mixed into washing water, which then threatens the entire ecosystem by mixing into the sea, lakes, and underground waters, and is consequently used by water and soil plants contaminated with antimicrobial lice chemicals to be included in the food chain. Again, the seas and rivers contaminated with antimicrobial substances threaten water creatures and the human health as a result of consuming these creatures.

Studies on antimicrobial textiles have focused mainly on the synthesis of antimicrobial matter and its performance against microorganisms and washing durability. However, the effects of waste/wastewater content on the user's skin and health and all other creatures through contact/respiratory/consumption are needed to be further studies during the production of antimicrobial textiles, during and at the end of its lifecycle [74]. Antimicrobial agents derived from natural sources are safe for human and the environment, but the spectrum of activity and efficiency is not as good as the synthetic ones. To achieve this, more research work is needed in the field. Hence, natural antimicrobial agents derived from plant sources would be of prime importance in the future [75]. It is so urgent to protect and conserve the natural ecosystem of the earth, thereby restoring the global sustainability.

Author details

Candan Akca
Candan Akca Textile Technology Department, Salihli Vocational School, Manisa Celal Bayar University, Manisa, Turkey

*Address all correspondence to: candanakca@yahoo.com; candan.can@cbu.edu.tr

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Chapter

Textile Wastes: Status and Perspectives

Burçin Ütebay, Pinar Çelik and Ahmet Çay

Abstract

The world population has grown tremendously in the past few decades, and the same period also witnessed improvements in living standards in general. These two developments have augmented the consumption of textiles, which in turn increased textile production. Global production of all apparel and textile fibers amounted to more than 110 million tons annually, leading to the generation of high amount of textile wastes. In order to ensure sustainability and reduce environmental impacts in the textile and apparel sector, utilizing a circular economy model is of utmost importance. Recycling of textile waste is a requirement for the implementation of a circular model. This study presents a general evaluation of management of textile wastes, in terms of ensuring sustainability and minimizing environmental impacts.

Keywords: textile wastes, sustainability, waste management, recycling, circular economy

1. Introduction

Textile is an ancient industry that goes back to the beginning of the history of humanity, and its products range from products of daily usage to technical ones. All kinds of garments obtained by processing knitted, woven and nonwoven fabrics are categorized as the apparel sector. Actually, textile production is one of the main industries that affect global environmental pollution, as both the production and the processing of the necessary raw materials are contributing factors to pollution. Another important aspect of the problem is the waste that results from both production and consumption of the textile goods. Though technically all waste in the textile and garment sector can be recycled, unfortunately, only a small amount is recycled. As long as the linear system currently utilized in the production goes on, it seems that we will not be able to use the resources efficiently and reduce the environmental pollution.

Given that the current global trends persist, by 2050, the textile sector is expected to represent a quarter of the world carbon budget—26%, to be precise. The figures are colossal: If the current trends do not shift, the textile and apparel sector's nonrenewable raw material usage will reach 300 million tons and the amount of microplastic released to the oceans will reach 22 million by 2050 [1].

One key concept to analyze and understand the situation is the linear economy. As the dominant model of production at least since the Industrial Revolution, linear economy basically works as "subtract the raw material from the source, convert it into a product, sell the product to the consumer, which eventually gets disposed of by the consumer after usage." Under this model, products discarded by the consumer become waste and are generally disposed of ending up in landfills or by incineration [2].

The basis of the linear economy approach is the consumption of the raw material required for production. It seems that the limited resources available to us in the world will not provide the conditions for the current dominant economic model to go on as today. The actual perception of raw materials is not sustainable. Moreover, linear economy-oriented production and business models become a burden for the environment—the environmental aspect, the damages they cause and the waste that results from them are generally not considered.

An alternative to this traditional production model is what is called a "circular economy": "A circular economy is based on the principles of designing out waste and pollution, keeping products and materials in use, and regenerating natural systems" [3].

In contrast to the negative aspects of the linear economic approach, the circular economy is seen as a sustainable development model for the future and increasingly stands out as an approach that is becoming widespread in the world. The circular economy is a systems model in which every part of a product is considered as a valuable resource that should be handled with care and resources are circulated again and again through closed loops.

The basis of the circular economy model is to expand the life-span of a product via repair, reuse, remanufacturing and recycling, so that resources are used more efficiently and the need for new products and virgin raw material is reduced or ideally eliminated [2].

In order to ensure sustainability and reduce environmental impacts in the textile and apparel sector, utilizing a circular economy model is of utmost importance. Recycling of textile waste is a requirement for the implementation of a circular model. This study presents a general evaluation of recycling of textile wastes, in terms of ensuring sustainability and minimizing environmental impacts.

2. Fashion and sustainability

Decisions of consumption have obtained a significant role in today's world—the choice of what you eat, where you go, what you wear and so on has become decisive factors of showing who you are and what you want to be, of displaying one's social identity. When one talks about consumer behavior in the textile sector, fashion is the key concept. Fashion presents the markers for social differentiation, mobility and identity, and allows a person to present one's identity—moreover, this dynamism and speed of fashion allow people to change their conceived identity [4–6].

Certain historical, social and cultural changes can be said to have shaped contemporary fashion. The first big leap was the Industrial Revolution—the possibility of producing *en masse* made it possible for the consumers to pick their desired products from a much wider range at lower prices, which, in turn, meant that a wider portion of the society could afford to have the pleasure of purchasing the desired products. In other words, "...fashion, which had been the epitome of luxury, was democratized and consumption behavior began to change" [7]. Industrialization also triggered changes in the economic structures: Autarky lost ground and urbanization has become a widespread phenomenon. The fact that an increasing number of people started to move into cities enhanced the commercial activities. Starting with the 1900s, new types of trade companies and retail shops emerged in the cities. Consumption, which was mainly a subject of certain periodical trade events, has become a fundamental part of the daily routine of the people. The new shops enabled people to buy clothes any given day. This new dynamism of fashion provided retailers and marketers with new commercial opportunities, as "being fashionable" became an important aspect of consumer behavior [7, 8].

Although the modern concept of "consumer culture" goes as far back as three centuries, the last few decades have witnessed unprecedented growth of purchasing and disposal of textile goods. The emergence of fashion as a defining force in consumer behavior resulted in overconsumption. The logic of fashion constantly pushes forward the need for change, which results in generating more and more requests to supply newer, fresher and more contemporary goods [9, 10]. Until the 1990s, the general tendency of fashion retailers was to release two main collections—spring/summer and autumn/winter—each year; however, during the 1990s, drastic changes occurred: The so-called era of "super cheap and super fast" arrived [11]. The increasing ability to outsource production to low-cost regions of a globalized world and thus to produce much cheaper clothes, combined with the inherent dynamism of fashion, paved the way for the emergence of what we nowadays conceive as the "modern fashion business" [12].

This fundamental role of dynamism inevitably positioned time as a crucial factor for the competitiveness of fashion companies. Consumers are conditioned to expect newness; thus, brand new products need to arrive at the stores with short time intervals constantly. This objective is accompanied by limited ranges and rapid stock turnaround for the companies [13].

The dominance of fast fashion and just-in-time production in the textile industry has led to more frequent seasons and minicollections in-between seasons, which has led to the arrival of new cheap items to the stores every week, even, in some cases, every day. It is a chain reaction: increase in the creation of new fashion trends, desires to experience the new spurring out of control, consumers buying more and more, and eventually overconsumption. This new concept of seasonal new collection brings about more incentives of buying for the consumer and, thus, increases the rate of textile consumption. However, the fashion industry not only has an impact on people but also has a big impact on the environment [10, 14].

The concerns about the environment are rapidly growing in today's world and are shared by the fashion firms and the consumers. Textile production is an important source of human-made adverse impact on the environment, as the sector uses huge amounts of water, pesticides and chemicals. Attempts to establish guidelines for sustainability in the production phase, such as ISO 14000, are a reflection of this fact, and this aspect is quite relevant for fashion firms. On the other hand, the consumers are getting more and more conscious about the social and environmental problems, which have a direct effect on the consumption choices of the consumers, as in eco-fashion consumption [15–17].

Even though this burning issue is gaining more importance in all sectors, it can be said that textile lags behind other sectors, for example the industrial design, in terms of research and development about modes of production that would be more efficient for the conservation of the environment or ways to get the consumers more engaged in topics of sustainability. The industry needs more innovation in the aspects of design, manufacture, consumption and business within a sustainable framework [18, 19].

Sustainability is indeed a burning issue, and the following data demonstrate how important it is for the world to achieve greater success in the textile sector. Textile production, a sector that goes back to ancient times and has always maintained its pivotal role in human life, still has a paramount place in industry if one takes a look at the global output and employment numbers [20]. According to the Zion Market Research's report, the textile market was approximately valued at USD 858 billion in 2018 globally and is estimated to generate around USD 1207 billion by the year 2025, at a CAGR of around 5% between 2019 and 2025 [21]. The global garment and textile industries employ 60 million to 75 million people worldwide [22]. The total volume of the production of the sector around the world is expected to exceed 99 million tons annually. These numbers are evidence to the importance of the applications of the industry for environment [23].

Clothing is an essential human need, and the textile and clothing industry delivers goods to satisfy this basic necessity. But this vital sector presents serious social and ecological problems in many instances of the supply chain—from fiber production, spinning, fabric production, dyeing and finishing, to clothing production [24, 25]. However, the increasing price pressure over fashion companies in the last decades does not help the companies in developing more sustainable production models. The price pressure has led many textile companies to outsource their production, which caused the bulk of the European and US clothing production shift to developing economies in Asia. The part of the value creation chain that remains in the Western countries is mostly limited to value-added services such as design and overall brand management. This production shift, with the relocation of a big part of the value chain in lower labor cost countries, presents a new challenge for sustainability, as the surveillance and control over labor and ecological practices in the production sites of the supply chain have become much more complicated [25, 26].

Sustainability, a word more frequently used every day nowadays, may sound very familiar, but it is difficult to define, understand and adopt in industrial practices. An apt definition for the term sustainable development, coined by Brundtland (formerly the World Commission on Environment and Development), is as follows: "The development that meets the needs of the present without compromising the ability of future generations to meet their own needs" [27]. Below is a list of the main obstacles for an environmentally sustainable textile and apparel sector:

2.1 Consumption of water

Studies show that, in terms of consumption and pollution of clean water, textile and related industries are only surpassed by agriculture [28]. The sheer amount of water used during textile production, especially wet processing, tells a lot: to process a kilogram of fabric, 80 to 150 liters of water is used, along with other chemicals [29]. About 4% of global freshwater withdrawal, which corresponds to 93 billion cubic meters of water, is utilized annually by the textile sector, if cotton farming is included. Clothing is responsible for more than 60% of this amount [1].

2.2 Global warming

The average temperature on Earth is constantly increasing, but especially since the Industrial Revolution, the rate at which the average temperature on Earth has been rising is too rapid—the phenomenon known as global warming. Various estimates put the rise at 0.6–0.8°C, which corresponds to a rise 10 times faster than the calculated normal. This man-made global warming is due to the amount of greenhouse gases released, such as carbon dioxide and chlorofluorocarbon, of the use of fossil fuels as well as of other developments [30].

Textile and apparel production has a major role in this global phenomenon. In 2015, greenhouse gas (GHG) emissions from textile production were responsible for 1.2 billion tons of CO_2 equivalent of greenhouse gas (GHG). This figure exceeds the emissions that result from all international flights and maritime shipping combined—two fundamental means of transportation [1]. Transferring final products produced in developing countries to the shops in the developed ones necessitates long-distance maritime transportation, which further increases the total consumption of nonrenewable fuel [31].

Given that the actual trends of the sector do not alter, by 2050, 26% of the carbon budget and 300 million tons of crude oil will be consumed by the textile industry—a significant change compared with 2% and 98 million tons, respectively, in 2015 [1].

The textile industry utilizes much energy with little efficiency. The chemical processing leg of the production mostly utilizes thermal energy to heat water and dry fabrics, while spinning and weaving legs of the production mostly utilize electrical power [32, 33]. The consumption of electricity to produce 60 billion kilograms of fabrics worldwide per year is calculated to be nearly 1 trillion kilowatt hours [30].

Textile manufacture is also a source of NOx and SOx emissions, solvent release during drying of coatings or cleaning operations and volatile organic compounds (VOCs) [31].

2.3 Environmental pollution

About a quarter of chemicals produced globally are used in the textile industry [34]. Numerous chemicals are used for textile production, mainly in the wet processing. Of these nearly 2000 different chemicals, many have adverse impacts on health. Some chemicals evaporate, while others are dissolved in treatment water—which ultimately goes back to the environment—and some chemicals remain in the product [31]. Cotton clothing, which, after all, is regarded as particularly natural and healthy, calls for cotton farming, which currently needs 0.2 million tons of pesticides and 8 million tons of fertilizer globally. Although cotton cultivation accounts for only 2.5% of worldwide agricultural land, it is responsible for 16% of global pesticide utilization. Furthermore, the physical health of cotton farmers gets negatively affected from the chemicals used for cultivating cotton, and cases of acute poisoning from pesticides among cotton farmers are commonplace. About 4% of all nitrogen and phosphorus fertilizers used around the world go to cotton production, and these chemicals are a main source of clean water pollution. If merged into the rivers, these chemicals can lead to algal blooms, which starve the river of oxygen. Producing cellulose-based fibers also necessitates large amounts of chemicals and some of the chemicals used are sources of concern. However, the agricultural part of textile production is not solely responsible for the chemical use of the industry. Producing the fibers requires using chemicals too, for example for dyes or finishing treatments. This part of the production is estimated to use approximately 43 million tons of chemicals globally [1].

The microplastics contaminating the oceans are attracting more and more attention from concerned scientists, even though we still do not fully understand its long-term impacts. Microfibers discharged from textiles during washing processes add to the increasing plastic pollution in the oceans [1]. George Leonard, Chief Scientist for The Ocean Conservancy, estimates that the amount of microfibers on seafloor could have reached to the sheer figure of 1.4 million trillion [35].

The waste generated by producing and consuming textiles is another major concern. Textile consumption around the world is calculated to be over 100 million tons [23]. However, the rate of recycling is rather low: Barely 13% of the total material input is in some way recycled after usage. Of this recycled 13%, a minuscule part is used to produce new clothing—less than 1%. The rest is recycled into other, lower-value items such as insulation material, wiping cloths or mattress stuffing [1].

Additionally, odor problems and noise pollution are also negative effects of the textile industry on the environment. Odor pollution is an indicator of environmental change that affects health and human well-being. Odor impacts people by strong, unpleasant or offensive smells that can interfere with one's enjoyment of life especially if they are frequent and/or persistent [36]. When it comes to noise pollution, there are different processes in the textile chain that can produce noise level above 90 dB(A), the allowed limit, and can cause problems especially for the workers. The dry processes produce more noise than the wet processes, due to the fast-moving parts in the processing machines, which is another danger for the workers along with the hearing problems [37].

3. General outlook of the current situation of the textile fibers

The world population has grown tremendously in the past few decades, and the same period also witnessed improvements in living standards in general. These two developments have augmented the consumption of textiles, which in turn increased textile production [38]. The effect of the rising living standards can be seen in the fact that the worldwide consumption of textiles is growing faster than the world population. The demand is expected to grow from around 30 million tons in 1980 to more than 130 million tons in 2025. The figure translates into a growth of over 400%—or an average annual growth rate of 4.3%. In the same period, the world population has been growing by only 1.7% [39].

Global production of all apparel and textile fibers amounted to 110 million tons in 2018, according to the Discover Natural Fibers Initiative (DNFI). This number points to an increase of 4 million tons compared with the previous year and of 35 million tons compared with a decade ago. Natural fibers represent 29%—a 12% decrease since 2008. In 2018, cotton represented 81% of natural fiber production by weight, which overshadows the share of jute, coir and wool, which account for 7%, 3% and 3%, respectively. Cellulosic fiber production represented 6%, synthetic filament 45% and synthetic staple 20% of the total production in 2018. Polyester is the leading synthetic fiber, which represents almost 90% of world filament production and 70% of world synthetic staple production. The rest of the synthetic fibers are mostly composed of nylon, acrylic and polypropylene. However, the figures do not translate into a plunge in the production of natural fibers. The share of natural fibers in total fiber production has decreased in the last decade because the production of polyester has increased exponentially. Synthetic filament production, which is mainly used for the production of fast-fashion apparel, has risen from 26 million tons to 50 million in a decade after 2008, almost doubling in size. During the same period, synthetic staple production increased from 15 million tons to 22 million. Natural fiber production also increased from 2008 to 2018, but the rate was nowhere close to the others: from 31 million tons to 32 million [40].

The global market is prevailed by two types of fibers: polyester, a synthetic fiber, and cotton, a natural fiber. The trend mentioned in the previous paragraph is clearly reflected when the figures for these two fibers are examined. The demand for polyester has doubled—a significant rise that resulted in the fact that polyester has succeeded cotton, the most widely used fiber until the 2000s. Polyester fiber production is estimated to increase to be 3 times more than cotton production in order to meet the still-growing demand, while the production of cotton fibers remained stable. Increasing the production of cotton depends on the land and water resources, which are limited, and the fact that the opportunities to increase yields of cotton cultivation are narrow does not help either. These constraints on cotton production are very significant to understand the growth of the synthetic fiber market [39].

Still, it is important to point out that, despite the growth of synthetic fiber production, cotton, a product with very good fiber characteristics, remains to be considered as the most popular fiber. It is not expected that cotton would largely be replaced or eliminated in the short or medium term from the textile production. Thus, sustainability strategies for cotton will persist to be paramount for the conservation of the environment [25, 41].

Synthetic polymers are mainly produced from petroleum—a nonrenewable resource. But this is not limited to synthetic fibers: Renewable natural polymers such as cotton also depend on nonrenewable resources, because their production needs energy and chemicals that are actually produced from nonrenewable resources. The petroleum reserve of the world might last for several more centuries if the current consumption rates continue, but it does not change the fact that petroleum—like many other natural resources—cannot be replaced in practical terms [42]. Therefore, deciding if natural fibers or manufactured fibers are more eco-friendly is impossible. The production of all types of fibers comes with its own challenges. Some fibers need a lot of water, while others demand lots of energy to produce. The synthetic fibers are not fully biodegradable like the natural and cellulosic fibers, which broadens the waste aspect of the problem. Synthetic fibers are generally petroleum by-products, which makes them nonrenewable materials; however, this gives them the advantage to get conveniently recycled into a good-quality material like polyester—a contrast with cotton, which generally gets down-cycled. But recently, the market has also started to receive recycled, high-quality cotton [19, 20].

Made-By, a nonprofit organization, carried out a study called "The Environmental Benchmark for Fibres." The study focuses on the prevalent fibers in the clothing industry and compares the environmental impact of the production of these materials. The production of the fibers is analyzed from the raw material up until the preparation of the fiber to be spun, thus excluding the later stages, such as spinning itself, fabric manufacturing, dyeing and finishing, garment making, transportation of the product and consumption. The study lists 28 fibers from Class A to Class E (Class A being the most benign) not regarding their quality, durability or performance, but their direct effects on the environment: greenhouse gas emissions, human toxicity, eco-toxicity, energy input, water input and land use [43].

The results demonstrate that all mechanically recycled fibers and organic fibers score "positively," while both natural and synthetic fibers obtained by conventional production methods are far behind in sustainability ranking. Class A materials include mechanically recycled nylon, mechanically recycled polyester, organic flax (linen), organic hemp, recycled cotton and recycled wool, while Class E materials include bamboo viscose, conventional cotton, cuprammonium rayon, generic viscose, rayon, spandex (elastane), virgin nylon and wool [43].

To protect not just human life on Earth, but Earth itself, we have to use the natural resources adequately. The rates at which natural resources are generated and consumed have to be appropriate for the sustainability of the planet. The 2011 annual report of the United Nations Environment Programme (UNEP) predicts the rate of consumption to triple the current rate by the year 2050 [44]. One alternative way to approach the solution of this problem is gradually replacing the traditional linear economy model—which relies on extraction/cultivation of raw materials, use of the product and disposal of the waste in landfills—with the circular material flow—which focuses on reusing and recycling.

4. Textile wastes and recycling

Consumption of textile products has two main aspects that trigger environmental change: the pollution and waste brought about, and the natural resources expended. Pollution is generated not only during the production phase but also during the consumption of the products. The Earth has a natural system that can naturalize pollutants and stabilize a natural equilibrium to a certain extent, but the rate and degree of the release of man-made pollutants into nature challenge this natural equilibrium of the planet [45, 46].

The second factor is the depletion of limited natural resources of the planet through the consumption of goods. Conventional modes of production and consumption dictate utilizing both renewable and nonrenewable resources. Manufacturing processes required during production need natural resources such as fossil fuels (coal, oil and natural gas) to generate energy and raw materials for the actual products (as in the example of plastic, which generally is produced from petrochemicals). Furthermore, in most cases, more natural resources are used up to consume the products themselves. Unfortunately, the utilization of both nonrenewable and renewable resources has a major impact on both localized and global environmental change. As a result of the depletion of resources and generation of pollution, both producing and consuming goods by humans are important sources of environmental change [45, 46].

A significant amount of research has been conducted and published on the environmental impacts of the production and consumption of textiles. The research has helped to inform policy-makers and the public on reducing toxicity of chemicals in production stages, creating industry standards for production and promoting more sustainable ways of cleaning textiles. However, sustainability of the disposal of textiles was not paid much attention until recently.

Textile production is a burden for the environment. Textiles cost significant amounts of natural resources, and the use of toxic chemicals and generation of large quantities of carbon dioxide further augment the problem. However, despite this huge cost, millions of tons of textile products are disposed of every year. In Europe and America, 10 million tons of disposed textile products are predicted to be disposed of, while the estimation for China is double this amount. This textile waste pollutes our environment and clogs landfills around the world on top of all the natural resources used for their production.

Western lifestyle, with its dependence on the culture of consumption, amplifies landfill waste. Not only is the consumption at a high level, but also products are generally overpackaged in the West, which translates into more waste—and to the consumption of natural resources required for packaging. Landfill capacity is not growing at the pace of the increase of the generation of waste, which inevitably means that the cost of waste disposal rises further. This is a major concern for businesses as they need to reduce the overhead costs [38].

The disposal of textile wastes is crucial for the textile industry globally. Tons of textile products get discarded by the consumers and end up in landfills all over the world. Estimates suggest that a vast majority, as high as 95 percent, of the discarded product could in fact be used again—re-worn, reused or recycled, depending on their condition. Indeed, the conditions are pushing the trend, because, as natural resources are limited and cost of waste disposal is increasing, more waste is getting recycled or reused [47].

Textile wastes account for almost 5% of all landfill spaces, according to the US Environmental Protection Agency (USEPA); however, the recycled postconsumer textile wastes are barely 15% annually, and thus, a huge 85% of the waste ends up in landfills. Certain organizations, including the Council for Textile Recycling (CTR), are endeavoring to raise consciousness about keeping the postconsumer textile wastes out of the solid waste streams, with the aim of reaching the level of zero textile waste going to landfills by 2037 [44].

Textile waste is produced through a number of streams including the fiber, textile and clothing manufacturing industry, consumers and the commercial and service industries. CTR categorizes textile recycling material as pre- or postconsumer waste [48, 51].

Preconsumer textile waste, according to CTR, is the waste generated during production—by processing fibers, and the production of finished yarns and textiles, technical textiles, nonwoven, garments and footwear, including offcuts, selvages, shearings, rejected materials and/or B-grade garments. Preconsumer textile waste is usually what is considered as "clean waste." Preconsumer textile wastes are produced by the original manufacturers and never make it to consumers [44, 48].

Postconsumer textile waste refers to textile products that the consumer disposes for any reason—they might be run-down or not liked by the consumer anymore. Generally, postconsumer textile wastes tend to be of good quality, which can be recovered or reused as second-hand clothing, and are generally sold to poorer regions of the world. Even the textile products that will most likely not be used by the consumers can potentially be shredded into fiber to be reused for manufacturing [48].

The fast fashion era has skyrocketed the rate at which textile products are discarded, as "going-out-of-fashion" has become one of the main reasons for "not liking the product anymore." The implementation of a convenient recycling regime can turn these wastes into raw materials to be used in producing future, value-added products. This is the current aim for the ongoing development of textile waste management systems, which seek to produce value-added products through recycling [44]. Textile waste treatment strategies include reducing, reusing and recycling, as shown in **Figure 1**. The first and most preferred approach, reducing, is aimed at, if possible, avoiding any waste entirely. The second approach, reusing, aims literally for the item to be reused by a consumer after it has been discarded by another. The third and last approach is recycling: the materials of discarded items are transformed into new products [49]. Wastes can be recycled to products for the same purpose with their first use, or they can be upcycled or downcycled. In upcycling, wastes are converted into high-value products with different purposes than the original use, while in downcycling, valuable products are converted into lower-value materials [50].

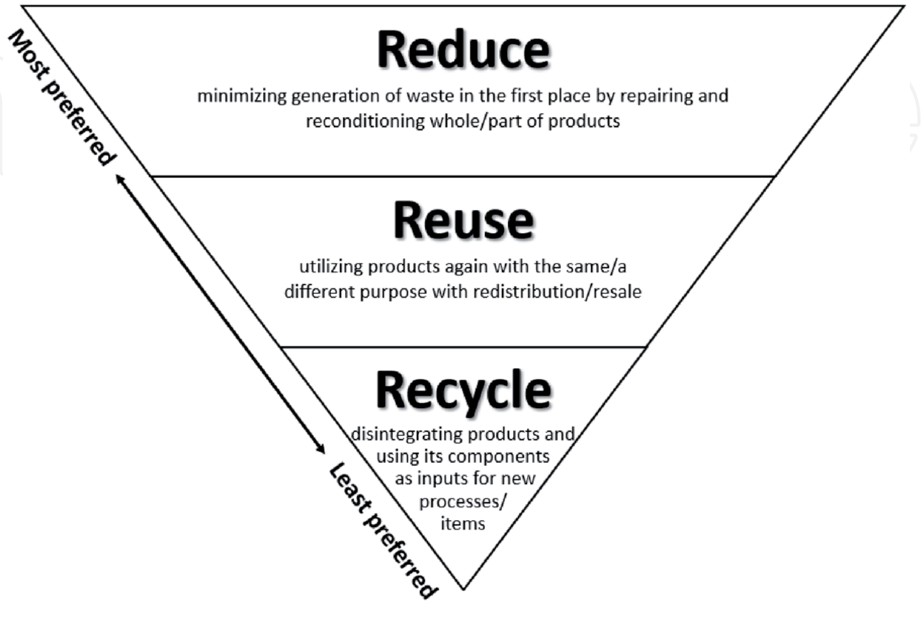

Figure 1.
Textile waste treatment strategies 3R concept.

Sustainability aspires to derive maximum benefit from products by extending their life. Studies conducted by economists and environmentalists on technical and economic requirements for sustainability reveal that it is imperative to reduce waste generation and increase recycling. Below are a few reasons why recycling is important [51, 52]:

- Economical reasons: recycling programs cost less than waste disposal programs. The high water, energy and manufacturing consumption makes it much cheaper to recycle than to produce some new textile products. Recycling can be made financially rewarding, as people can receive money for turning in certain recyclable products.

- Social reasons: recycling creates jobs. Recycling centers create four jobs for every one job in the waste disposal industry. The method can also create opportunities for small businesses.

- Environmental reasons: recycling conserves natural resources such as water, oil and natural gas; saves energy as it requires less energy compared with manufacturing brand new products; produces less greenhouse gases; and prevents the destruction of natural habitats.

Recycling and recovery of textile products are not as common as the material groups such as glass, metal, plastic and paper and product groups such as electronic, packaging and automotive. Recycling activities related to the textile sector are mainly focused on the treatment of chemical wastes and polluted water—problems that arise during production processes. The number of scientific or practical studies on the recycling of solid wastes is extremely limited [53].

Even though the textile and apparel sector is one of the most intense consumption sectors, implementation of recycling throughout the sector is not satisfying. However, parallel to the increasing global awareness of environmental problems, the awareness of consumers about sustainability has also started to increase. Consumers are now demanding recycled textile products and manufacturers are seeking ways to meet this demand [53, 54].

The waste generated by the textile sector contributes to land, water and air pollution. Decomposing textiles generate greenhouse gases and thus air pollution. The vast amount of chemicals used for producing textile goods unavoidably pollutes the rivers. And discarded textile products fill up landfills, which are already scarce. All these wastes are resources that could have been used to create value-added products. Not only this potential is lost, but also more raw materials are required to be used, which in turn results in more energy to be consumed [55].

Wasted materials can be recovered through reusing a product as is and converting the waste into a product. A material should get to be reused as much as possible and the consumer finally decides to discard it, and then recycling would be a good alternative to reduce the carbon footprint [56].

Recycling technologies tend to be divided into primary, secondary, tertiary and quaternary approaches, and all these four methods are applicable to recycle fibers. Primary approaches refer to the process of recycling a material to what it was originally. Secondary recycling means melt processing a plastic product into a lower-quality but nevertheless a new one. Tertiary recycling refers to processes that convert the plastic wastes into basic chemicals or fuel, such as pyrolysis and hydrolysis. Quaternary recycling involves burning the fibrous solid waste and converting it into a source of energy exploiting the heat generated through burning [38, 57].

Obviously, the most fruitful method of recycling is the primary approach. This approach, also called closed-loop recycling, is only applicable to man-made fibers such as PET or PA. This primary approach includes collecting textile waste discarded by the user and using this in new clothing as material for the production of yarn. The most common method of recycling actually is what is called open-loop recycling. In this method, the output material does not have a high-enough level of quality to produce new clothes; thus, it gets downgraded. The study on cotton fibers by Ütebay et al. demonstrates the deterioration in fiber quality. Downgraded material can be used as mattress upholstery or isolation material in cars. Through open-loop recycling, some value is recuperated from the textile waste, which would otherwise have been incinerated. However, this does not help to reduce the necessity of raw materials to produce clothing. Therefore, closed-loop recycling remains to be an attractive alternative. A closed-loop supply chain provides the advantage to recover more value from used products [56, 58, 59].

The most recycled textile waste is thermoplastic polymer-based fibers because they are easy to process and can be given different forms and shapes afterwards. Nevertheless, natural fibers such as cotton, wool and silk are also finding their ways into the recycling stream through downcycling or upcycling [44].

Recycling of textiles today is not a wide industry. The number of companies that offer services of recycling of textile fibers is limited because it is economically not beneficial and technologically not advanced. The lack of technological innovation and the continuing supply of cheap fabrics into the markets hinder the motivation for research, development and application of recycling techniques; however, it does not totally block the development of new technologies for recycling textile waste. Soon, certain obstacles will need to be faced and resolved to further increase textile waste recycling [10, 60].

In terms of technology, the fundamental question is the fiber composition of textile materials. The current garments in today's markets vary more in terms of design and fiber content than in the past. The other compounded factors are issues/difficulties in separating the blended components, efficiency of separation, quality of separated material and hence the recycled material's quality and so on. As recycled fibers and fabrics still provide a low level of quality, virgin natural and synthetic fibers remain to be popular options [10, 38, 56].

There are some recycling technologies available on the market today. Others are on the way, albeit few. Other changes need to accompany these research and trial endeavors—in terms of economy, processing costs should be reduced; in terms of policy, relevant standards should be implemented; and in terms of governance, textile waste should be recollected much more efficiently. Apart from increasing the efficiency of recycling methods and processes, the market for recycled products should grow. In short, recycling needs more encouragement, wherever it is economically and technically feasible [47].

There are important benefits of recycling textiles, both environmental and economical. It reduces the need for landfill space, consumption of already scarce virgin resources, pollution as well as water and energy consumption and the demand for dyes and fixing agents [61]. However, even though recycling offers ways to reduce environmental negative impacts, it is not exempt from certain problems. Wang [38] lists the following as challenges:

- The mechanical, chemical or biological processes to recycle waste still require a certain amount of energy.
- The recycling processes continue to require new raw material input.
- The recycling processes still generate emissions into air, water and land.

Evidently, recycling is not always the preferred approach, when not only the environmental context but also the competitiveness of the final product in the market is taken into account. The existing recycling technologies need to get better, cleaner, more energy efficient and less costly [38].

Textile recycling, a key concept for sustainability, currently faces hurdles related to cost, time and technology. But as sustainability becomes more and more important, more initiatives are getting incentivized and sponsored by both manufacturers and other organizations in the textile sector to help advance the results of textile recycling. This tendency can be seen through the fact that certain textile recycling companies have shown promising growth. Different strategies and policies were coined in different regions to promote an efficient way of recycling for conserving the environment more and increasing the economic efficiency [38].

Many voluntary and nonprofit organizations run campaigns to conserve natural resources by creating awareness of both downcycling and upcycling recycling

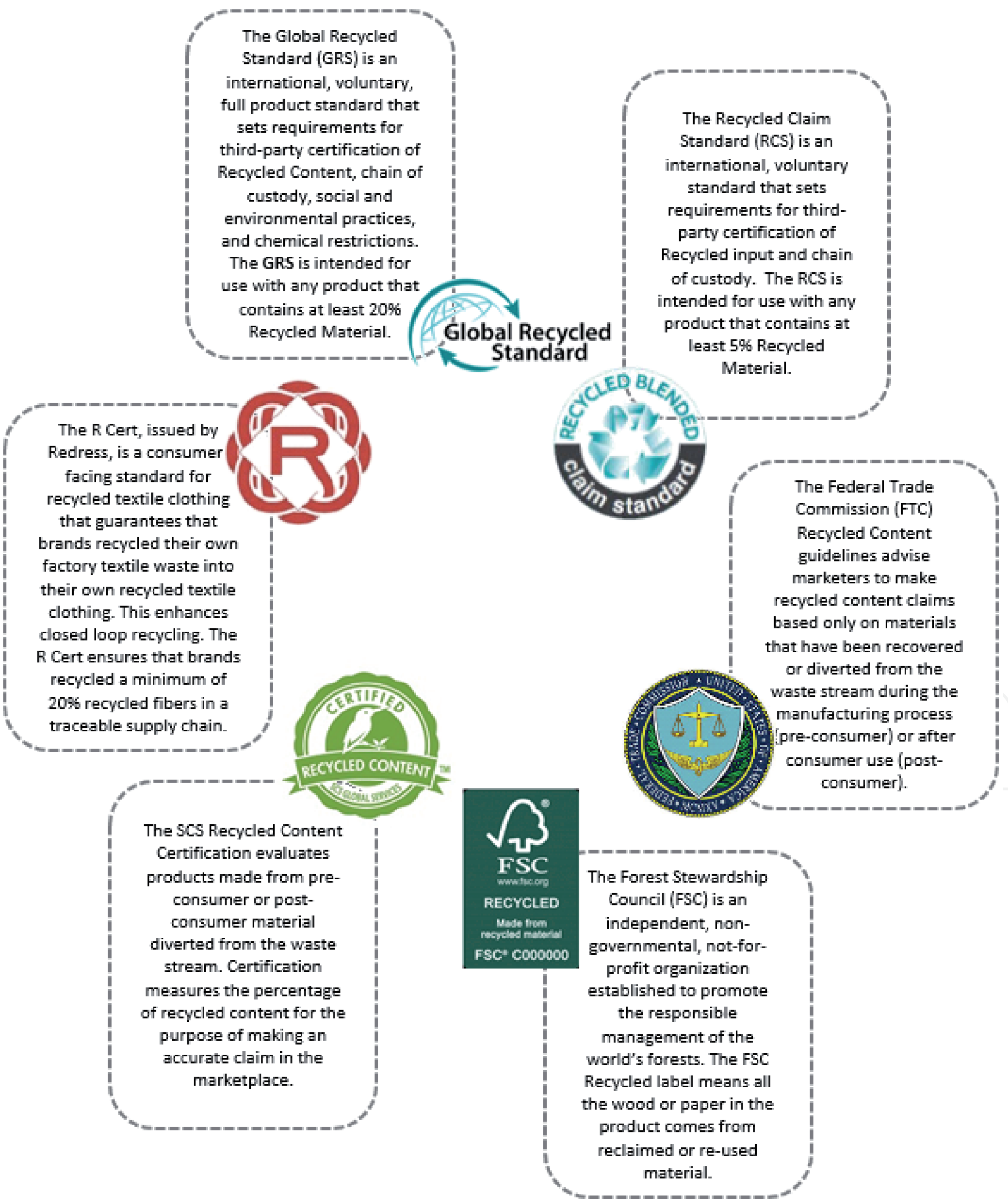

Figure 2.
Labels for recycled products.

concepts. The campaigns aim to convince the consumers that using recycled products is an esteemed way of adding value to oneself, the product and the world.

Examples of commercially available labels for recycled products are given in **Figure 2** [62–68]. All these initiatives are expected to promote environmentally appropriate, socially beneficial and economically viable management systems [44].

In addition to these certifications, some standards such as Social Responsibility Standard (ISO 26000), Environmental Management System (ISO 14001), Occupational Health and Safety Management System (ISO 45001) and Energy Management System (ISO 50001) also support sustainability and social responsibility practices and contribute to their dissemination [69–72].

An unsustainable consumption of textile goods ensures the deterioration of the environmental degradation. To achieve environmental integrity and sustainability, incentivizing the textile companies to produce more environment-friendly products is not enough—the behavior of consumers also needs to change, creating more awareness toward the conservation of the environment [45]. In this context, Connolly and Prothero [73] write: "Rather than focus on the issue of whether green consumption can work as a strategy, we should perhaps try to gain a greater understanding of the process that has led people to believe that they, as individuals, can help solve global environmental problems."

5. Conclusion

The fibers obtained by recycling are generally evaluated in the production of lower-value products (downcycling) compared to the original product. However, nowadays, recycling fibers have started to increase their evaluation in high value-added products (downcycling). On the other hand, the perspective that focuses only on the cost aspect of the production of recycled garments is not correct. Considering water consumption as well as pesticides and artificial fertilizers used, the textile industry is known to be one of the most polluting and waste-generating sectors. From this point of view, recycling of textiles and garments is of great importance in terms of reducing the use of natural resources (e.g., water used to grow seeds or oil used in the production of synthetic fibers) and CO_2 emissions. Recycling will also save energy and chemicals to produce new textiles, as well as prevent pollution from the production process. In this context, it is important for the future of our world to review all production and consumption processes and supply chains in the focus of circular economy and sustainability. Therefore, the recycling of textile industry waste is very important.

The future of textile recycling mostly depends on its implementation in the industry and gaining more experience and grounds for more innovative methods. Clothing retailers are key actors on this front, as they are uniquely positioned to be able to influence and improve consumers' approach in favor of sustainability. Not only do clothing retailers have the potential to influence consumer decisions, but also they are in a position to alter consumption patterns. People can learn the importance of recycling as well as reuse and resales by the help of companies, and this is not limited to developing countries. Through such actions, consumer awareness about sustainable consumption would increase, leading to less environmental damage in the future.

Author details

Burçin Ütebay[1*], Pinar Çelik[2] and Ahmet Çay[2]

1 Üniteks R&D Center, İzmir, Turkey

2 Faculty of Engineering, Department of Textile Engineering, Ege University, İzmir, Turkey

*Address all correspondence to: burcin@uniteks.com.tr

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