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# Antiviral leather: A functional coating based on SiO<sub>2</sub>-AgNPs to eliminate pathogens

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## ABSTRACT

A bovine leather material functionalized with SiO<sub>2</sub>-Ag nanoparticles (NPs) composite, which possesses highly efficient antimicrobial activity against the SARS-CoV-2 virus and *Staphylococcus aureus* (*S. aureus*) bacteria, has been developed. The characterization of this material was conducted using scanning and transmission electron microscopy (SEM and TEM), energy dispersive X-ray spectrometry (EDS), atomic force microscopy (AFM), Fourier-transform infrared spectroscopy (FTIR), and x-ray photoelectron spectroscopy (XPS). The immobilization of SiO<sub>2</sub>-AgNPs within the collagen fibers of the leather resulted in surface modification, leading to an increase in material roughness (from 8.93 nm  $\pm$  1.55–12.36 nm  $\pm$  1.76 nm) and the contact angle (from 76° to 81°) of the SiO<sub>2</sub>-AgNPs coated leather. This functionalized leather exhibited an impressive efficacy of 99.93% against SARS-CoV-2% and 99.99% against *S. aureus*, attributed to the oxidizing properties of the Ag NPs and the enhanced production of reactive oxygen species (ROS). These results highlight that the immobilization of SiO<sub>2</sub>-AgNPs on the surface of bovine leather is an simple, effective and low-cost strategy for obtaining new surfaces with high antimicrobial activity.

## 1. Introduction

With the aggravation of environmental pollution and the global epidemic of infectious diseases, there is an increased demand for antimicrobial surfaces that can safely and efficiently eliminate microorganisms.[1,2] Transmission occurs through direct or indirect contact, either through microorganism-laden airborne droplets or contaminated surfaces of objects. Direct infections are challenging to control as they depend on anthropological factors Indirect contaminations, particularly through fomites, contribute significantly to infections and can also exacerbate surface biofouling, facilitating cross-species transmission and rapid propagation of contaminations, especially in emerging diseases.[3,4] At the early stage of the global emergency of the COVID-19 pandemic, some studies have concluded that microorganisms, such as SARS-CoV-2, can survive on several different types of surfaces for several days after being expelled by human fluids, and their viability is influenced by the nature of the surface and its maintenance [5–7].

In this scenario, different approaches for controlling

microorganisms, including SARS-CoV-2, have been developed based on the use of bioactive organic molecules and various types of materials. [8–10] Specifically, natural biopolymers like cellulose, starch, chitosan, pectin, leather, etc., have been gaining prominence for their use as antimicrobial agents. [11–13] Their antimicrobial property is intrinsic to the polymer or can be achieved through chemical and physical modifications. Recently, Yan et al. developed new polymeric materials based on hyperbranched dialdehyde carboxymethyl cellulose (HPD) with significant performance in eliminating Staphylococcus aureus (S. aureus) and Escherichia coli (E. coli).[14] Dang et al. obtained an antibacterial and biocompatible polymer through oxidized starch by grafting indoleacetic acid monomers onto the oxidized starch.[15] In another study, Baysal et al. obtained biodegradable composite films based on corn starch, wheat gluten, and silver nanoparticles (AgNPs) with high antimicrobial activity.[16] Wu et al. produced size-tunable AgNPs for their application in cotton fabrics. [17] These works are clear examples of the synthesis and development of biopolymers with enhanced antimicrobial properties.

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Among natural polymers, leather has significant importance in the industry, especially in the clothing sector, due to its versatility, durability, and ease of production. Therefore, the development of leatherbased materials with antimicrobial properties provides an effective solution for producing clothing and other everyday items that can inhibit the growth of microorganisms.[18-20] However, due to the composition of animal skins, which contain high concentrations of lipids, carbohydrates, and proteins, leather is susceptible to microbial proliferation. To address this issue, organic and inorganic materials have been used to confer antimicrobial activity to leather through surface treatments.[21-26] AgNPs have received extensive attention both in fundamental research and technological fields due to their unique antimicrobial activity. Liu et al. conducted a study where they used a spray tanning method to functionalize animal leather samples with gallic acid-modified AgNPs. [27] Elsayed et al. functionalized the surface of bovine leather through the in-situ deposition of AgNPs using trisodium citrate.[28] In another work, Nguyen et al. were able to immobilize biosynthesized AgNPs from leaf extracts on pig leather, resulting in highly antibacterial and antifungal functionalized leather. [29] One of the challenges of using AgNPs is their stabilization on the leather surface, as it can lead to the loss of antimicrobial activity over time. The use of amorphous silica (SiO<sub>2</sub>) to stabilize Ag nanoparticles (AgNPs) is an intriguing strategy. This approach allows for the convenient attachment of the particles to the leather material, providing enhanced stability and mitigating the risk of AgNPs leaching [30].

Our research group has conducted several studies on the antimicrobial properties of a variety of materials, aiming to mitigate the spread of infections caused by resistant microorganisms, with a special focus on those caused by the SARS-CoV-2 virus. [29–33] More specifically, we synthesized SiO<sub>2</sub>-AgNPs with a highly antiviral response against SARS-CoV-2, with efficacy exceeding 99% after just 15 min of contact. [34]. The inactivation mechanism is driven by the generation of reactive oxygen species (ROS), including hydroxyl (•OH) and hydroperoxyl (•OOH) radicals. As a result, this composite material exhibited a highly effective antiviral response against SARS-CoV-2, with efficacy exceeding 99% after just 15 min of contact. [34] Recently, by combining experimental data with first-principles calculations, we gain deep insight into the intricate connection between the structure, properties, and antimicrobial activity of SiO<sub>2</sub>-AgNPs composites [35].

In this study, we synthesized SiO<sub>2</sub>-AgNPs composite to be applied as coatings on bovine leather. The coating was applied to the leather by spray, using an aqueous solution of SiO<sub>2</sub>-AgNPs and polyethylene glycol. The resulting materials were subjected to characterization using scanning and transmission electron microscopy (SEM and TEM), energy dispersive X-ray spectrometry (EDS), atomic force microscopy (AFM), Fourier-transform infrared spectroscopy (FTIR), and x-ray photoelectron spectroscopy (XPS). We evaluated the antimicrobial activity of the SiO<sub>2</sub>-AgNPs functionalized leather against the gram-positive bacterium S. aureus and the SARS-CoV-2 virus. The maintenance of antimicrobial activity was also evaluated by analyzing the activity of the functionalized leather after successive washings. Additionally, we conducted an analysis of ROS production from SiO<sub>2</sub>-AgNPs to establish a correlation with the antimicrobial activity, thus serving as a proof of concept. The article is structured into three additional sections. Section 2 focuses on the synthesis and experimental techniques employed. The subsequent section presents and discusses the obtained results. Finally, the concluding section summarizes the findings of this study, highlighting the potential application of this simple SiO<sub>2</sub>-AgNPs functionalized leather as an antimicrobial material.

### 2. Materials and methods

### 2.1. Synthesis SiO<sub>2</sub>-Ag NPs

The SiO<sub>2</sub>-AgNPs were synthesized following a previously established method within our research group.[34] In summary, 0.850 g of AgNO<sub>3</sub>

(Cennabras, 99.8%) was dissolved in 100.0 mL of distilled water at 90 °C. Then, 1.0 mL of a 1% wt/wt aqueous solution of dehydrated sodium citrate (Sigma-Aldrich, >99%) was added to the solution, resulting in a yellowish solution. After allowing the solution to age for 5 min, 11 g of SiO<sub>2</sub> (Sigma-Aldrich, 99.8%) was added, and the system was stirred for 10 min. The solvent was subsequently evaporated at 90 °C, and the resulting powder was dried in a conventional oven at 125 °C for 12 h.

## 2.2. Leather coating

The white bovine leather samples utilized in this study were generously provided by JBS S.A. (São Paulo, Brazil). The leather was initially tanned with 6% chromium (III) solutions and re-tanned with 4% chromium (III) solutions. After this process, they were deacidified to pH 5.5 using sodium bicarbonate and naturally dried. The leather surface was functionalized by applying a spray of the previously prepared composite material. To achieve optimal conditions, the parameters of spray flow, concentration, and conveyor speed were optimized as described below. A solution was prepared by adding 0.100 g of SiO<sub>2</sub>-AgNPs and 0.200 g of polyethylene glycol (PEG 6000, Sigma-Aldrich, 99.8%) to 100.0 mL of water. This proportion was used as it demonstrated the best adhesion of SiO<sub>2</sub>-AgNPs to the leather. This solution was stirred continuously at room temperature for 12 h. Subsequently, the solution was sprayed onto the leather surface at a constant flow rate of 3.0 mL/min using an automatic conveyor belt set at a speed of 1 m/min. After the application, the samples were washed with distilled water to simulate the conditions encountered during leather manufacturing and then air-dried at room temperature.

#### 2.3. Characterizations

The chemical composition of the leather samples, both with and without functionalization, was analyzed using FTIR. Measurements were performed at room temperature using a Bruker Vertex 70 spectrophotometer, equipped with an attenuated total reflectance (ATR) system, with a spectral range of 400–4500  $\text{cm}^{-1}$ , resolution of 4  $\text{cm}^{-1}$ , and 32 scans. The oxidation states of the elements present on the sample surfaces were investigated through XPS. A Scientia Omicron ESCA+ spectrophotometer equipped with an Al-Ka monochromatic X-ray source (1486.7 eV) was used for the analysis. The incident power was set at 280 W, and a constant power mode of 50 eV was employed. Surface analysis was performed using a Zeiss SEM model Supra 35 VP. TEM images were obtained using an FEI TECNAI F20 microscope operating at 200 kV. AFM images were acquired using a Nano Observer ATM microscope from CSInstruments, France. The cantilever size and parameters used for imaging were provided. Contact angle analyses were conducted using the sessile drop method in static mode on a Ramé -hart goniometer model 260-F4. A 5-µL drop of distilled water was deposited on the surface of each sample, and the contact angle formed between the drop and the leather or leather-SiO2-Ag surfaces was measured using DROPimage Advanced software. The analyses were performed in triplicate, and the data were treated using harmonic media. Statistical analysis was carried out using a two-way ANOVA with GraphPad Prism 5.00 software (p < 0.05) for the contact angle analyses, and multiple comparisons were determined using the Newman-Keuls tests.

## 2.4. Antiviral activity

The antiviral activity of the leather samples was evaluated using a modified version of ISO 21702, which is a standard method for measuring the antiviral activity on non-porous surfaces.[33,34] The leather samples measuring  $2 \times 2$  cm were placed individually in Petri dishes and exposed to the viral solution, ensuring that the entire surface of the leather came into contact with the virus. Subsequently, the samples were incubated at 37 °C for 15 and 30 min. After the incubation

period, a dilution process was carried out as described in the previous section. The viral titer was determined using the 50% Tissue Culture Infectious Dose ( $TCID_{50}$ ) method. The results were expressed relative to the viral particles of the SARS-CoV-2 (Omicron) stock solution on both the non-virucidal control leather and the treated leather samples. Each test was conducted with five repetitions and repeated on three separate occasions to ensure reliability and reproducibility of the results.

#### 2.5. Antibacterial activity

The bactericidal activity of the leather samples against S. aureus (ATCC 6538 P) was evaluated according to ISO 22194, which is a standard method for measuring antibacterial activity on non-porous surfaces. The test microorganism was prepared by culturing the bacteria on Mueller-Hinton agar plates for two days. The bacteria were then suspended in test tubes containing the same medium, and the inoculum was standardized by adjusting the turbidity to a value of 0.5 on the McFarland turbidity scale. The turbidity was measured at a wavelength of 620 nm using a JASCO spectrophotometer. The standardized bacterial solution, representing approximately  $1.5 \times 10^8$  CFU (colony-forming unit), was diluted 1:10 in saline (0.9%) to obtain an initial concentration of  $2.2 \times 10^6$  CFU/mL. To inoculate the leather samples, 100 µL of this bacterial solution was spread on the surface of each  $2 \times 2$  cm sample and covered with sterile plastic film to ensure even distribution. The samples were then incubated at 37 °C for 24 h. After the incubation period, the inoculum was recovered by adding 10 mL of soya casein digest lecithin polysorbate (SCDLP) broth to each sample. Serial dilutions of the recovered inoculum were made in phosphate-buffered saline (PBS) solution, and each dilution was plated on Mueller-Hinton agar. The agar plates were then incubated at 37 °C for 24 h, and the number of CFU was determined. All tests were conducted with five repetitions and repeated on three separate occasions to ensure reliability and reproducibility of the results. To assess the maintenance of antibacterial activity after repeated washing, the samples were washed and centrifuged ten times before performing the antibacterial tests again.

## 3. Results and discussion

#### 3.1. TEM, SEM, AFM and EDS

The SEM and TEM images shown in Fig. 1(a-b) reveal that the SiO<sub>2</sub>-AgNPs composite exhibits significant agglomeration, with the Ag-NPs dispersed within the  $SiO_2$  matrix. The EDS image in Fig. 1(c) confirms the presence of small amounts of AgNPs in the composite. XPS analysis (Fig. S1) further confirms the presence of Ag in the composite, with binding energies of 368.01 eV and 374 eV for Ag 3d<sub>3/2</sub> and Ag 3d<sub>5/2</sub>, respectively. The deconvolution of the peaks indicates the presence of Ag in other chemical states, suggesting interaction with SiO<sub>2</sub>.[36] The SEM images in Fig. 1(d-e) show that the surface of the sample without the composite exhibits decreased uniformity, while the functionalized leather surface with SiO<sub>2</sub>-AgNPs deposition appears rougher. This change in surface morphology indicates the adhesion of the composite to the leather sample. The adhesion can be attributed to interactions between the hydroxyl groups in PEG and the amine, carboxyl, and amide groups present in the collagen fibers of leather. According to Xiao et al., these interactions can involve hydrogen bonds, van der Waals forces, and electrostatic interactions, contributing to the adhesion process [37].

The AFM images presented in Fig. 1(f-g) confirm the topographical differences on the surface of the samples, consistent with the SEM observations. The deposition of SiO<sub>2</sub>-AgNPs on the leather surface led to an increase in surface roughness, as evidenced by the measurements of 8.93 nm  $\pm$  1.55 nm for the untreated sample and 12.36 nm  $\pm$  1.76 nm for the functionalized sample. Colorimetric analysis using parameters of the CIELab system showed that the incorporation of SiO<sub>2</sub>-AgNPs did not



Fig. 1. (a) SEM, (b) TEM, and (c) EDS images of SiO<sub>2</sub>-AgNPs. SEM and AFM images of the composite (d-f) and (e-g) functionalized leather. (h) Contact angle of the leather samples.

significantly affect the color of the leather, which remained white. This is evident from the close proximity of the coordinates a\* and b\* values measured at different points on the sample (Fig. S2a). The parameter of luminosity (L) determined by CIELab also indicated that the functionalization of the material did not cause a significant change in this aspect (Fig. S2b). All measured points fell within the same region, indicating that the visual appearance of the leather was preserved.

The introduction of SiO<sub>2</sub>-AgNPs onto the leather surface resulted in notable changes in the surface properties, as demonstrated by the SEM and AFM images. These changes also had an impact on the wettability of the functionalized leather, which was investigated through water contact angle measurements.[38] The contact angle measurement results (Fig. 1h) showed that the leather modified with SiO<sub>2</sub>-AgNPs exhibited a contact angle of 81°, whereas the pure leather had a contact angle of 76°. This increase in contact angle indicates that the functionalized leather surface became more hydrophobic. The improved water repellency of the sample is an important characteristic for leather and its products. According to Foksowicz-Flaczyk et al., [39] the addition of metallic NPs with antimicrobial properties anchored in silica compounds can enhance the hydrophobicity of different material surfaces. This enhancement in hydrophobicity contributes to improved resistance to moisture and temperature changes, inhibiting the conditions favorable for the growth of microorganisms. As a result, the functionalized leather may exhibit increased durability, resistance to dirt, and self-cleaning properties. [39] The enhanced hydrophobicity achieved by functionalizing the leather with SiO2-AgNPs has several advantages and potential applications, as it can prolong the lifespan of the material and contribute to its antimicrobial properties.

## 3.2. FT-IR and XPS

Fig. 2a shows the FT-IR spectra of the leather samples. As can be seen, in the region between 3190 and 3490 cm<sup>-1</sup> there are bands corresponding to the vibrations of the N-H stretching of amide groups. [40] The three absorbance peaks recorded at 2965, 2936 and 2853 cm<sup>-1</sup> are very similar to those reported by Hedberg et al., who attributed them to

the stretching of the C-H bond easily found in fatty acids that make up animal tissue fat.[41] The bands located at 1886, 1544, and 1096 cm<sup>-1</sup> are associated with stretching vibrations of the C=O bond, bending vibrations of the N-H bond coupled with the C-N bond of the amide band I and II,[42] and C-O stretch, respectively.[43] The amide III band is shown around 1241 cm<sup>-1</sup>.[40].

The chemical composition of the leather samples was analyzed by XPS to confirm the presence of the SiO<sub>2</sub>-AgNPs composite on the surface of the sample and determine the oxidation states of the elements. The XPS survey spectra shown in Fig. 2b exhibit clear signals of the elements O, C, and Si. Fig. 2c displays the deconvoluted C 1 s peak of the nonfunctionalized leather sample, revealing the presence of two peaks at binding energies of 286.40 eV and 289.12 eV, corresponding to the C-H and  $\pi$ - $\pi$  bonds, respectively.[44,45] In contrast, the C 1 s spectrum of the leather sample containing SiO<sub>2</sub>-AgNPs shows a downward shift of both peaks to lower energies (282.66 eV and 283.95 eV, respectively) (Fig. 2d), indicating the presence of C-Si bonds, as reported by Meskinis et al.[42] Regarding the high-resolution O 1 s spectra of the samples, Fig. 2e shows three peaks for the non-functionalized sample in the region of 532.03 eV, 530.46 eV, and 527.85 eV, corresponding to C-O, C=O, and  $O^{2-}$  bonds, respectively. [46,47] In contrast, the two peaks observed in the sample containing SiO<sub>2</sub>-AgNPs (Fig. 2f) exhibit a shift towards higher energy values (530.87 and 530.16 eV) compared to the deconvoluted peak of the non-functionalized sample. This shift can be attributed to the presence of the C=O bond observed in the triple helix conformation of collagen, which is composed of amino acids and serves as the primary component of leather.[48] Lastly, the presence of Si in the sample modified with SiO<sub>2</sub>-AgNPs can be better observed through the deconvolution of the spectrum illustrated in Fig. 2g, which corresponds to Si 2p3/2 (99.96 and 100.78 eV). These values are consistent with the reported energies for the Si-O bond, confirming the presence of the heterostructure on the surface of the functionalized leather and supporting the surface changes observed in the previous techniques.[42] It is not possible to observe the presence of Ag in the leather functionalized with SiO<sub>2</sub>-AgNPs, as the concentration of Ag is extremely low. The presence of Ag can only be detected in the analysis of SiO2-AgNPs, as



Fig. 2. (a) FTIR and (b) full-range XPS spectra of the pure and functionalized leather, and deconvoluted XPS (c-d) C 1 s, (e-f) O 1 s and (g) Si 2p peaks of pure leather and the functionalized leather, respectively.

demonstrated previously by TEM and EDS (Fig. 1), and later confirmed by XPS (Fig. S1).

XPS is indeed an excellent technique for surface characterization, but it is known to be a point analysis technique. In order to analyze the presence of Ag, XPS analyses were conducted on pure SiO<sub>2</sub>-AgNPs samples. Fig. S1 presents the survey spectrum and the high-resolution spectrum of Ag 3d. Fig. S1-b displays the experimental and deconvoluted core level spectra of the Ag 3d peaks. The two-component peaks at 374 and 368 eV can be attributed to the Ag  $3d_{3/2}$  and Ag  $3d_{5/2}$  peaks, respectively.[49,50] The species identified in the Ag  $3d_{3/2}$  and  $3d_{5/2}$ peaks can be qualitatively determined through deconvolution of each peak. In the SiO<sub>2</sub>-AgNPs sample, both Ag<sup>0</sup> and Ag<sup>+</sup> species are observed in both Ag  $3d_{3/2}$  and  $3d_{5/2}$  peaks. The results indicate that the enhancement of Ag<sup>0</sup> and Ag<sup>+</sup> in the sample can be determined by the ratio of the most intense Ag  $3d_{5/2}$  peak at 374 eV. The obtained percentages for Ag<sup>+</sup> and Ag<sup>0</sup> are 30.57% and 20.38%, respectively. These results confirm the presence of Ag in the SiO<sub>2</sub>-AgNPs sample [36].

## 3.3. Antimicrobial activity and proposed mechanism

The effectiveness of the material in eliminating infectious pathogens was investigated. This preliminary analysis aimed to demonstrate the potential use of this material in coatings for various sectors of the leather industry. The composition of the material creates favorable conditions for bacterial growth, including appropriate humidity and temperature, which can lead to unpleasant odors and decreased resistance.[50] The antimicrobial activity of the functionalized leather against gram-positive S. aureus bacteria was assessed by comparing the growth percentage with control samples of microorganisms incubated in the culture medium. The data in Table 1 demonstrate the remarkable effectiveness of the leather containing SiO<sub>2</sub>-AgNPs, exhibiting a 99.99% reduction in S. aureus CFU after 24 h. Furthermore, even after 10 wash cycles, the material exhibited a 99.99% reduction in S. aureus CFUs after 24 h, whereas the pure leather showed no reduction. This result indicates the sustained antibacterial activity of the functionalized material and supports the earlier findings regarding the interaction between leather collagen fibers and SiO<sub>2</sub>-AgNPs deposited through spraying.

The ability of the samples to inactivate the SARS-CoV-2 virus was evaluated at contact intervals of 15 and 30 min. As depicted in Fig. 3a, a 56.38% reduction in virus copies was observed after 15 min of contact. Increasing the analysis time to 30 min resulted in an impressive antiviral activity of 99.93% against SARS-CoV-2. In contrast, no reduction in virus copies was observed in the pure leather samples. These findings confirm that the functionalization with SiO<sub>2</sub>-AgNPs enhances the antimicrobial activity of the leather. This finding is consistent with previous studies that have reported the synergistic effect of SiO<sub>2</sub>-AgNPs in creating materials with high efficacy in eliminating various pathogens. [33,51] Given the limited research on the antiviral properties of leather-based materials, this study represents a significant advancement for the leather industry and related sectors, particularly in the context of

#### Table 1

Quantitative antibacterial re	ults according to ISO 22194.
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S. aureus (ATCC 6538)				
	Zero-time bacteria count	Bacteria counter after 24 h (CFU/ mL)*	Reduction in relation to control	
			Logarithmic reduction	Percentage reduction
Leather	$2.2  imes 10^6$	$9.0 imes10^6$	-	-
Leather – SiO <sub>2</sub> -Ag	$2.2\times10^{6}$	$1.0  imes 10^1$	5.95	99.99%
Leather – SiO <sub>2</sub> -Ag (after 10 washes)	$2.2  imes 10^6$	$1.1  imes 10^1$	5.90	99.99%

CFU/mL - colony forming units per milliliter.



**Fig. 3.** (a) Antiviral results of copies per mL of SARS-CoV-2 at different times and percentages of inhibition and (b) proposed mechanisms for the interaction between functionalized leather collagen protein and  $SiO_2$ -Ag-NPs and the inactivation of bacteria and viruses.

the COVID-19 pandemic.

Previous studies have explored the use of functionalized leathers as microbial coating strategies. Ngwabebhoh et al. investigated purple goatskin leather with the addition of polyaniline to combat S. aureus and K. pneumoniae bacteria, leveraging its photocatalytic activity.[52] However, the antibacterial activity of the material was moderate, with bacterial growth percentages close to 25%. Elsayed et al. applied AgNPs-functionalized crust bovine leather to treat bacteria such as B. subtilis and S. aureus, achieving 99.99% inhibition efficiency.[28] However, a concentration of 1000 AgNPs was added to the leather in situ to achieve this result. Alexe et al. described sheepskin leather treated with different mixtures and TiO<sub>2</sub>, including TiO<sub>2</sub>-SiO<sub>2</sub>-Ag-PDPA. [53] The conventionally treated leather exhibited 99.80% and 99.86% antibacterial activity against E. coli and S. aureus, respectively. Similarly, Liu et al. investigated the addition of chitosan-PEGylated AgNPs as an antibacterial coating for ovine leather through immersion, resulting in a 99% inhibition of E. coli and S. aureus, respectively.[54] It is worth noting that there are currently no reports of functionalized leather applied to virucidal tests with SARS-CoV-2. In Table S1, the antimicrobial results obtained in this study are compared with those reported in the literature for different types of leather functionalized with antimicrobial activity.

Compounds that contain AgNPs are recognized for their efficient antimicrobial properties. This attribute can be attributed to various factors, including the localized surface plasmon resonance (SPR) behavior exhibited by AgNPs. [61] AgNPs have the ability to eliminate bacteria and viruses by disrupting the bacterial cell wall upon contact with immobilized nanoparticles in the coating. Additionally, they can induce the migration of silver ions (Ag<sup>+</sup>) and the generation of reactive oxygen species (ROS), which can trigger cell apoptosis.[55,56] The confirmation of this mechanism as a potential means of microorganism inactivation was achieved by investigating the generation of ROS using appropriate scavengers, as presented in the supplementary material (Fig. S3). In photocatalysis tests using RhB dye, it was observed that the SiO<sub>2</sub>-AgNPs nanocomposite exhibited a maximum photo discoloration capacity of 53.78% within 1 h under ultraviolet (UV) irradiation (Fig. S3a). Furthermore, when inhibitory agents such as ascorbic acid (AA), AgNO<sub>3</sub>, p-benzoquinone (p-bq), ammonium oxalate (AO), and tert-butyl alcohol (TBA) were used to suppress the  $\bullet$ OOH, e<sup>-</sup>,  $\bullet$ O<sub>2</sub>, h<sup>+</sup>, and •OH species, respectively, a reduction in photocatalytic activity was observed. The degradation of RhB without scavengers was decreased by 66.96%, 6.81%, 94.72%, 79.16%, and 82.62% with the addition of AA, AgNO<sub>3</sub>, p-bq, AO, and TBA, respectively. This behavior suggests the efficient formation of electron/hole pairs (e<sup>-</sup>/h<sup>+</sup>) resulting from the photoexcitation of the catalyst by incident light radiation (Fig. S3b). Subsequently, the  $e^{-}/h^{+}$  pairs interact with water (H<sub>2</sub>O) and molecular oxygen (O<sub>2</sub>), leading to the generation of highly reactive radicals, including •OH, •O<sup>2</sup><sub>2</sub>, and •OOH. These radicals can then interact with the genetic material of viruses and bacteria, initiating irreversible damage processes.[33].

The combination of the oxidizing power of AgNPs and the enhanced production of ROS such as  $\bullet$ OH,  $\bullet$ O<sub>2</sub>, and  $\bullet$ OOH in the amorphous SiO<sub>2</sub> semiconductor leads to irreversible damage to bacteria and viruses.[33, 34,53,57] Gaidau et al. demonstrated that the antimicrobial activity of leather can be enhanced by spraying TiO<sub>2</sub>-AgNPs onto its surface, resulting in active self-cleaning properties.[58] Based on these findings, we propose the biocidal mechanisms of action of the functionalized leather (Fig. 3b).

## 4. Conclusions

In this study, we evaluated the antimicrobial activity of leather functionalized with a SiO<sub>2</sub>-AgNPs composite against the SARS-CoV-2 virus and S. aureus bacteria. Through TEM, EDS, and XPS techniques, we determined the composition of the leather and confirmed the presence of the SiO<sub>2</sub>-AgNPs composite. The results obtained from FTIR, SEM, XPS, AFM, and contact angle measurements demonstrated effective adhesion of SiO<sub>2</sub>-AgNPs to the leather surface, resulting in increased roughness and hydrophobicity. The functionalized leather exhibited remarkable antimicrobial activity, with 99.93% inactivation of the SARS-CoV-2 virus after 30 min and 99.99% reduction of S. aureus bacteria after 24 h. These findings suggest the involvement of the oxidizing power of AgNPs and the enhanced production of ROS (•OH and •OOH) by the SiO<sub>2</sub>-AgNPs composite in causing irreversible damage to viruses and bacteria. The application of SiO2-AgNPs functionalized leather holds great promise as an effective and feasible antimicrobial strategy for the leather industry and related sectors.

## CRediT authorship contribution statement

G.N.M, R.Y.N.R and L.K.R.: Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing, Visualization. L.G.P.S. and D.T.M: Data curation, Formal analysis, Investigation, Methodology, Funding acquisition, Resources. J. A., M.A., L.H.M. and E.L.: Funding acquisition, Resources, Supervision, Writing - original draft, Writing - review & editing, Visualization.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data Availability

Data will be made available on request.

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### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2023.110919.

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