

Antimicrobial effect of coated leather based on silver@silica nanocomposites

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Abstract

Nowadays, the antimicrobial properties of different materials are a significant feature for a wide range of products, not only in the healthcare sector, but also in sports, housekeeping, etc. In the case of footwear, microorganisms, such as bacteria, fungi and viruses, are likely to proliferate in the shoe environment under appropriate temperature and humidity conditions. Their multiplication is the cause for the development of odour in areas that are worn close to the skin and also for the development of infections in the case of pathogen organisms. Consequently, the demand for new and different coatings for footwear materials that enable good antibacterial protection has increased.

Currently, existing biocides include some antimicrobial agents, most of them being organic compounds, that are extremely irritant, harmful and toxic for the environment and human health. Therefore there is a growing interest in finding ways to formulate new types of safe and ecological materials.

Such problems and needs have currently led to resurgence in the use of silver-based (Ag) antiseptics which have been used for centuries as antimicrobial agents for the treatment of burns, water treatment processes and wound disinfection¹. Today, these properties have been enhanced through nanotechnology, which has allowed the size of metal nanoparticles to be modularly and accurately reproduced. Previous studies revealed high antimicrobial activity of silver nanoparticles (AgNPs) against a broad spectrum of microorganisms. The advantage of the antimicrobial mechanism of silver is the ability to produce an antibacterial effect at very low concentrations (oligodynamic effect).

Therefore, this work is aimed to develop coated leathers with enhanced antimicrobial properties, thus providing a solution to avoid the problems mentioned above. To achieve this objective, nanosilver colloidal solutions were synthesised using different reductors such as borohidru², gelatine/glucose³ and an aloe vera phenolic extract⁴ (Figure 1). The first one is a control of the others, which were considered as green methods because they do not require the use of organic solvents. In all cases, the formation of Ag-NPs was further determined by using UV-visible spectroscopy (Figure 2) as a function of time. Furthermore, in order to improve nanoparticle stability and avoid their aggregation, silver-silica nanocomposites were synthesised by a modified Stöber method⁵.

In this study, we evaluated the properties of a novel silver-silica nanocomposite used as an antimicrobial additive for leather and compared its efficacy to that of AgNPs. A representative transmission electron micrograph of AgNPs and silver-silica nanoparticles is shown in Figure 3A and 3B. The nanocomposite consists of aggregate silica matrix particles where silver metal particles are located within the matrix and are also embedded within the matrix.

The silver nanoparticle morphology and dispersability were evidenced by transmission electron microscopy (TEM) measurement. AgNPs embedded within the silica matrix were also evaluated by TEM and EDX analysis. In addition, scanning electron microscopy (SEM) was performed on the AgNPs-silica nanospheres, allowing also the size of the nanospheres to be determined.

Synthesised AgNPs and Ag-silica nanoparticles were applied to different leathers to obtain antimicrobial coatings. The treated leathers studied include metal-tanned leather (chrome, titanium, aluminium) and oxazolidine-tanned leather. For this purpose, leather samples were treated with the corresponding silver solutions by applying 50 µL of the solution on the grain side, and 50 µL on the flesh side, allowing them to dry for at least 24h at room temperature. In order to verify the presence of AgNPs and AgNPs-silica nanocomposites on the leather matrix, SEM analysis was performed on both the grain and flesh sides and also, with the leather matrix, on the side of criofractured leather samples to test nanoparticles and nanospheres penetration (Figure 3C).

Finally, the antimicrobial activity of the treated leathers was tested by means of liquid and solid (agar diffusion) antibacterial tests against both gram positive (*Staphylococcus aureus* and *Bacillus subtilis*) and gram negative bacteria (*Escherichia coli* and *Klebsiella pneumoniae*). All the different treated leather samples showed a strong antibacterial activity in liquid medium (Figure 4A). In agar diffusion test, titanium- and aluminium-tanned leathers showed also a synergistic effect along with silver on *B. subtilis* survival (Figure 4B).

The results show that the functionalisation of leather with AgNPs, and especially with AgNPs-silica nanocomposites represents a promising alternative to create leather with enhanced antifungal and antimicrobial properties. Some advantages of the silver-silica nanocomposites are the dispersion of the discrete silver particles throughout the silica (which prevents agglomeration of the silver particles), the small diameter of the silver particles (which results in a large surface area and release of a large amount of Ag^+ , which results in high antimicrobial efficiency), and the small size of the silver-silica nanocomposite (which allows the material to be uniformly dispersed and readily incorporated into leathers but also into a variety of substrates, including synthetic fibres, coatings, plastics, etc.). A further advantage is that the immobilization of silver nanoparticles within the silica structure limits the potential for release and disposal of the nanoparticles themselves. This property may be highly desirable because of the possible abilities of nanoparticles to go through biological membranes and other barriers.

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References

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Figures

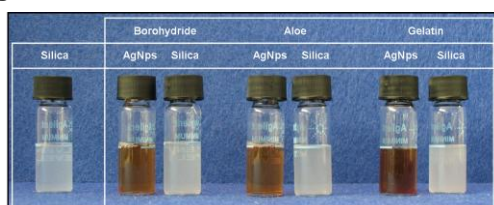


Fig. 1. Nanosilver and silica nanocapsules obtained with the different synthesis methods.

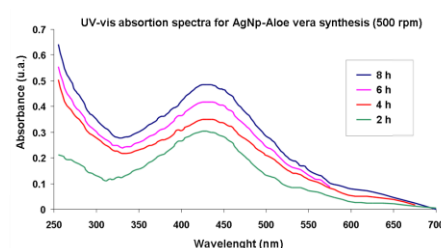


Fig. 2. Uv-vis characterisation of the AgNPs solutions synthesised with Aloe vera extract, at different periods of the synthesis process.

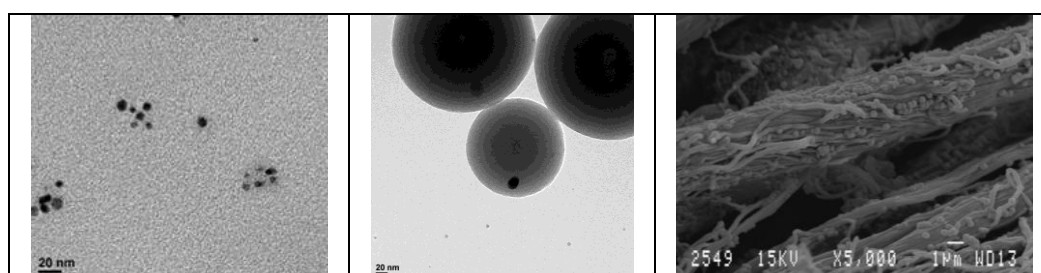


Fig. 3. TEM micrographs corresponding to: A) AgNPs colloidal solution; B) Ag-silica nanocomposites; C) SEM micrograph corresponding to leather fibres treated with Ag-silica nanocomposites.

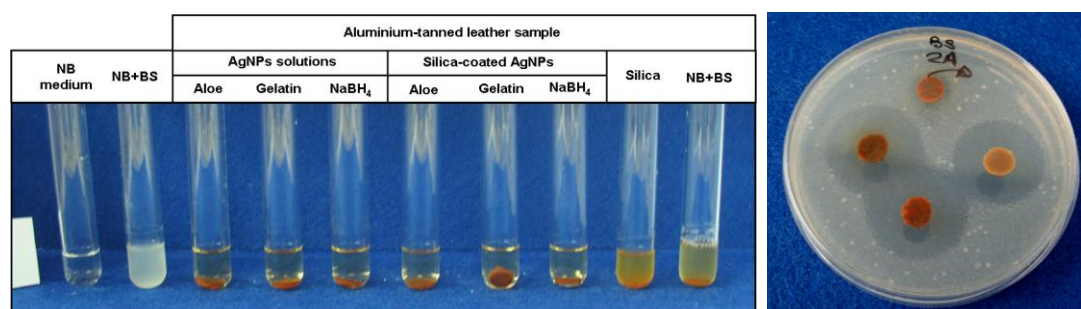


Fig. 4. Liquid NB medium assay showing the antibacterial effect of aluminium-tanned leather with all the 6 AgNPs containing solutions against *Bacillus subtilis* (BS) (left). Petri dish showing the antimicrobial effect of titanium-tanned leather treated with silica-coated AgNps against BS (right).