Old maps and the effectiveness of chitosan as antimicrobial agent

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ABSTRACT – REZUMAT

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In the case of tangible cultural heritage items made of natural fibres, biodegradation due to microorganisms can lead over time to undesirable deterioration, including physical, mechanical and chemical damage as well as aesthetic alteration of materials. In this study, the antifungal activity tests were performed on 3 old maps (on silk, on canvas and on paper) using the AATCC 30-2004 test method. Map samples were immersed in a chitosan solution (10 g/l) and evaluated using Scanning Electron Microscopy (SEM) with a Field Emission Scanning Electron Microscope (ULTRA 55, ZEISS). The process showed that, due to its antimicrobial effect, chitosan treatment is effective for removing external agents and microorganisms present on fibre surfaces. The technique is simple, efficient and the results indicated that chitosan can be transformed into a very good and cheap antimicrobial solution for the conservation and preservation of heritage objects.

Keywords: *old maps, natural fibres, fungi, impurities, chitosan, antimicrobial*

Hărțile vechi și eficiența chitosanului ca agent antimicrobian

În cazul bunurilor materiale din patrimoniul cultural realizate din fibre naturale, biodegradarea datorată microorganismelor poate duce în timp la o deteriorare nedorită, inclusiv degradarea fizică, mecanică și chimică, precum și la afectarea proprietăților estetice ale materialelor. În acest studiu, teste privind activitatea antifungică au fost efectuate pe 3 hărți vechi (pe mătase, pânză și hârtie) folosind metoda de testare AATCC 30-2004. Mostrele de hartă au fost scufundate într-o soluție de chitosan (10 g/l) și evaluate utilizând microscopia electronică cu scanare (SEM). S-a folosit un microscop electronic cu scanare cu emisie de câmp (ULTRA 55, ZEISS). Procesul a arătat că, datorită efectului său antimicrobian, tratamentul cu chitosan este eficient pentru îndepărtarea agenților externi și a microorganismelor prezente pe suprafețele fibrelor. Tehnica este simplă, eficientă și poate fi transformată într-o soluție antimicrobiană foarte utilă și ieftină, care poate fi folosită pentru conservarea și prezervarea obiectelor de patrimoniu.

Cuvinte cheie: *hărți vechi, fibre naturale, fungi, impurități, chitosan, antimicrobian*

INTRODUCTION

People are becoming increasingly aware of the importance of the human values that form the common heritage that must be passed on to future generations and at the same time, it must be protected. It is our duty to transmit these values as we have found them and to contribute to their preservation, protection and promotion, they remain living testimonies of the old tradition [1–4]. The role of cultural heritage in defining the national identity is unquestionable [5, 6], each community identifies itself through the cultural inheritance received and transmitted from generation to generation [7–9].

In 1962, UNESCO considered it necessary to protect both natural and man-made environments that are of cultural interest. This approach to defining cultural heritage can also be seen in "The Architectural Heritage Charter in Amsterdam" (1975). All these normative definitions can be found in detail in the Granada Convention for the Protection of European Architectural Heritage (1985). Beginning with the mid-1970s, international documents were drawn up that tried to define the general criteria for the purpose of being reunited in a code all the documents – the tangible and intangible achievements of the human activities that become valuable – must be protected. The tangible component of the cultural heritage includes works of art, manuscripts, photographs, maps and various documents, but also buildings, locations, paintings, sculptures, etc.

In this were analysed three aged heritage maps from different archives, made of natural fibres, that are highly susceptible to biodegradation due to microorganisms, impurities etc.:

- an old map of Switzerland, on a sheet of paper glued to the canvas, dating from 1866;
- the old map of Crișana, on paper, dating from 1919;
- the double silk map or escape map dates from 1953; this type of map was first made during World War II, being used by the British and US military to escape behind enemy lines.

The tangible cultural heritage items are very sensitive, especially when made of natural fibres; they are very susceptible to biodegradation due to microorganisms, dust etc. Classical methods [10–13] for species identification given in this study offer an accurate image of the fungal biodeterioration process on heritage textiles samples which were analysed. Antifungal activity tests on map materials were determined by AATCC Test Method 30-2004.

Some studies analysed the mechanism, innovation and safety of chitosan on textiles and antibacterial proprieties; biocompatibility, biodegradability and bioactivity of chitosan and its importance for humans [14–27]. In Romania, it was also investigated the use of chitosan in the surface modification of textile fabric and its antimicrobial effects. We can mention in this sense the papers of: Enescu [28], Buşilă et al. [29], Bou-Belda et al. [30] and Indrie et al. [31] etc.

Application of chitosan solutions on natural fibres [32–37] has given very good results in removing the impurities so that it can be a very good and cheap antimicrobial solution [38–40].

ANTIFUNGAL ACTIVITY AND ASSESSMENT ON MAP MATERIALS

Material & method

The antifungal activity tests were performed on old maps samples using the AATCC 30-2004 test method [41] in the laboratories of Ege University, Dokuz Eylül University, Turkey, University of Oradea, Romania, Trakia University, Faculty of Technics and Technologies, Bulgaria.

The aim of this test method was to determine the susceptibility of textile materials to mildew and rot and to evaluate the efficacy of fungicides on textile materials. *Aspergillus niger* ATCC 6275 was grown on the Czapek Dox Agar at 28°C for approximately 10 days to produce abundant growth spore formation. The spores were collected by appropriate methods [42–47] and the prepared spore suspension was used as the inoculum.

- the double silk map or escape map dates from 1953; this type of map was made during World War II, being used by the British and US military to escape behind enemy lines;
- the old map of Crișana (Romania), on paper, dating from 1919;
- an old map of Switzerland, on a sheet of paper glued to the canvas, dating from 1866.

Test specimens: sample A – Map on silk, B – Map on paper support, from 1919; C – Map on paper, book from 1866; discs were cut, 1.5±0.1 cm diameter. The discs were pre-wet without rubbing or squeezing in water containing 0.05% of a nonionic wetting agent (Triton X-100) and placed on the Agar surface. 0.1 ml of the inoculum was distributed evenly over each sample disc by means of a sterile pipette. Duplicated test materials were incubated for 10 days at 28°C.

Application of chitosan for treatment of the aged maps

Chitosan Medium Molecular Weight was purchased from Sigma Aldrich, for the treatment of the samples (figure 1), at the Textile and Paper Department, Universitat Politècnica de València, Spain; acetic acid was supplied by Panreac. The concentration prepared for chitosan was 10 g/l. It was added 5 ml/l of Acetic acid, because of the chitosan solubility in water at acid pH. The resulted solution was magnetically stirred (24 hours).

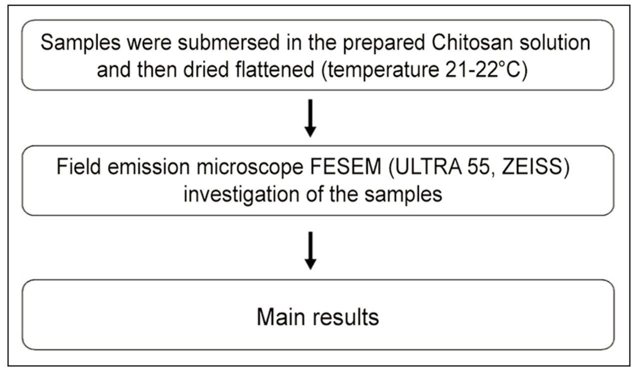

Fig. 1. Method of investigation of old maps samples treatment with chitosan

Samples were submersed in a chitosan solution (10 g/l) and passed through two squeezing rolls. Afterwards, samples were flattened dried at room temperature (21–22 °C) for 24 hours.

The observation of the samples was carried out by means of Scanning Electron Microscopy (SEM) with a Field Emission Scanning Electron Microscope (ULTRA 55, ZEISS). Every treated map was placed on a flat surface. To increase the conductivity of the materials, each sample was covered with a very thin gold layer [15]. The samples were analysed with the appropriate magnification and with an acceleration voltage of 1 KV.

RESULTS & DISCUSSION

At the end of the incubation period, the percentage of the surface area of the discs covered with the growth of *Aspergillus niger* was observed macroscopically and microscopically. Antifungal activity tests result of map materials were given in figure 2.

The main purposes of this test method [48–53] are to determine the susceptibility of materials to mildew and rot and to evaluate the efficacy of fungicides on textile materials. Mildew resistance in textile material is defined as resistance to the development of unsightly fungal growths and accompanying unpleasant, musty odours on textile materials exposed to conditions favouring such growths while rot resistance in textile material, resistance to deterioration of a textile material as a result of fungal growth in or on it [41].

According to the macroscopic observations (figure 2), the contact zones were seen for all specimens, clearly. These results show that all map materials have rot resistance, but not mildew resistance.

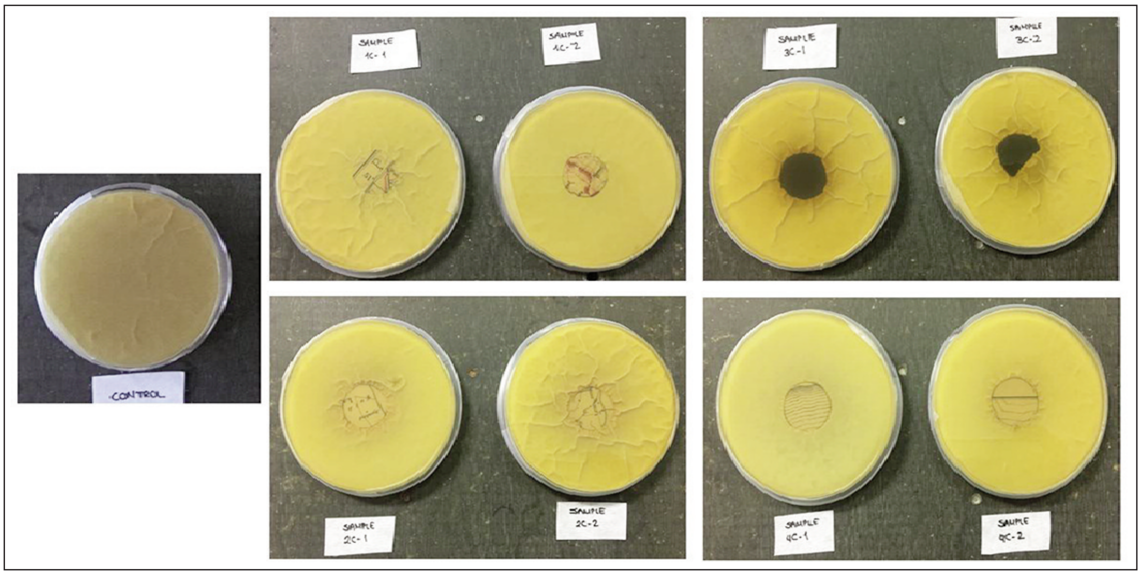

Fig. 2. AATCC Test Method 30 results of all specimens

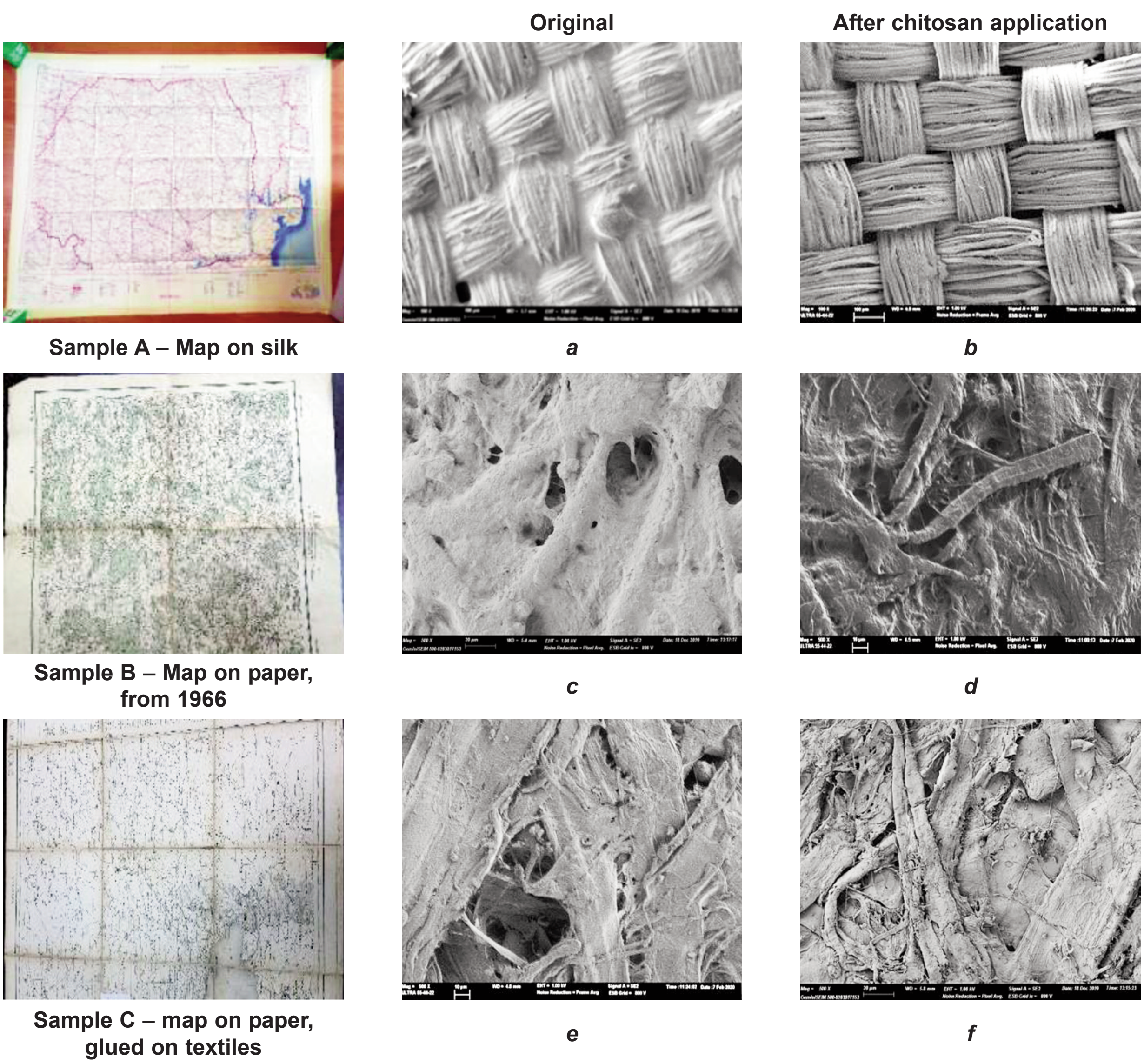

Fig. 3. SEM images reflecting the effect of chitosan treatment on the samples of aged maps: *a* – SEM image of the fibres from sample A at 100 × magnification; *b* – SEM image of the fibres from sample A at 100 × magnification; *c* – SEM image of the fibres from sample B, at 500 × magnification; *d* – SEM image of the fibres from sample B, at 500 × magnification; *e* – SEM image of the fibres from sample C, at 500 × magnification; *f* – SEM image of the fibres form sample C, at 500 x magnification

Results-application of chitosan on the samples

The effect of chitosan treatment on the samples of aged maps can be observed in figure 3, which shows SEM images at different magnifications. Sample A shows some kind of fine coating which disappears when treated with chitosan, despite some little particles that can still be appreciated on the surface. Sample B shows a surface partially coated and some fibres morphology can be sensed below the coating. Once the sample has been treated, some differences can be appreciated. The coating still remains although it seems to be in the deepest fibres, and not on the ones placed on the upper part. It seems that the most superficial ones have lost the superficial coating. Something similar also occurs in the case of sample C. Once the chitosan treatment is applied, fibres seem to have lost the superficial coating from the original samples. When the chitosan treatment is applied, it can be clearly observed that the small particles have disappeared. Antifungal activity tests and new results on map materials were done and they did not reveal microorganisms after applying chitosan to the test samples.

CONCLUSIONS

The procedure described in this study is simple and it does not need high technological resources. Once the product is solved, a chitosan solution can be applied to it. The treatment is easy to apply and capable to remove part of the odd substance on the samples, reducing the potential damage which can be conferred to the sample. According to observations, the results highlight that all the samples have rot resistance but not mildew resistance. Chitosan treatment shows good compatibility, biodegradability, and environment friendly and it has revealed adequate efficiency in removing the odd agent on the fibre surfaces. It can also have a long-term future antibacterial effect. The findings of the study suggest a potential application of chitosan on textiles, such as those analysed: silk, paper, textile support of the aged maps, to provide the optimal physical and antimicrobial properties.

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