Textile artefacts conservation using nanomaterials – Review

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ABSTRACT – REZUMAT

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Continuous research is necessary for the field of cultural heritage conservation to maintain up-to-date knowledge regarding new treatments and methods for preserving artefacts. Cultural heritage conservation is not only necessary for preserving the memory of our predecessors but is also meaningful for future generations. History museums around the world contain impressive collections of heritage textiles in various stages of degradation. The main method of preservation is maintaining the objects a microclimate to limit degradation by adjusting the temperature, humidity, and brightness of the rooms in which they are exposed or stored. Biodegradation is influenced by the presence of microorganisms, the availability of oxygen, temperature, humidity, light, and chemical factors (pH, electrolytes, etc.). This paper aims to provide scientific information on how heritage textiles have been studied and characterized, as well as the methods of preservation reported in the literature. Particular attention is being paid to nanomaterials, as they have been intensively studied for various applications and demonstrated to exhibit antimicrobial effects, which can be utilized to treat heritage objects and slow down degradation processes.

Keywords: *historical textiles, conservation, nanomaterials, microbial degradation, characterization*

Conservarea artefactelor textile folosind nanomateriale – studiu de literatură

Cercetarea continuă este necesară pentru ca domeniul conservării patrimoniului cultural să mențină cunoștințele la zi, cu privire la noile tratamente și metode de conservare a artefactelor. Conservarea patrimoniului cultural nu este necesară doar pentru păstrarea memoriei predecesorilor noștri, ci este și semnificativă pentru generațiile viitoare. Muzeele de istorie din întreaga lume conțin colecții impresionante de textile de patrimoniu aflate în diferite stadii de degradare. Principala metodă de conservare este menținerea obiectelor într-un microclimat pentru a limita degradarea prin reglarea temperaturii, umidității și luminozității încăperilor în care sunt expuse sau depozitate. Biodegradarea este influențată de prezența microorganismelor, disponibilitatea oxigenului, temperatură, umiditate, lumină și factori chimici (pH, electroliți etc.). Această lucrare își propune să ofere informații științifice despre modul în care au fost studiate și caracterizate textilele de patrimoniu, precum și despre metodele de conservare raportate în literatura de specialitate. Se acordă o atenție deosebită nanomaterialelor, deoarece acestea au fost studiate intens pentru diverse aplicații și s-a demonstrat că prezintă efecte antimicrobiene, care pot fi utilizate pentru a trata obiectele de patrimoniu și pentru a încetini procesele de degradare.

Cuvinte-cheie: *textile istorice, conservare, nanomateriale, degradare microbiană, caracterizare*

INTRODUCTION

Since the advent of the first civilizations, textiles have been indispensable objects for mankind. Textiles have a long history and reflect the different levels of social and cultural development and the evolution of technology and materials used by different civilizations [1]. The term "textiles" comes from the Latin language (texere) and means "to weave". Textile materials are obtained from textile fibres that are transformed into yarns, which are then subjected to various operations, such as weaving, knitting, crocheting, knotting, etc. Finally, textiles are subjected to finishing processes (e.g., dyeing) [2]. The final products represent an interconnection of the resources, technology, and lifestyle of society during the time at which the textiles were manufactured. Hence, the interest of the archaeology research community in conserving textile artefacts originates from the importance of textiles as a relevant index of exchange economics and available technology, in addition to their aesthetics and traditions in civilization as clothing [3, 4]. Textile artefacts are sensitive and susceptible to degradation *via* depolymerization, leading to fading and low resistance to tears [5]. The biodegradation of textile objects depends on their composition.

Compared to synthetic fibres, natural fibres are much more susceptible to degradation [6]. Additionally, natural fibres degrade at a different rate depending on their nature. The main component of vegetable fibre is cellulose. In addition, fibres contain lignin and other organic, noncellulose components. The susceptibility of textiles to degradation is strongly influenced by the presence of these components, as well as their nature. The presence of noncellulose components, such as lignin and wax, increases the resistance to degradation. On the other hand, pentosans and pectins present in the composition of plant fibres decrease the resistance to degradation [7]. In animal fibres, the main component is proteinaceous and includes keratin (wool), fibroin and sericin (silk) [8].

Recent progress in nanoscience has paved the way for a wide range of possibilities due to the broad spectrum of applicability of new nanomaterials [9]. Many studies have demonstrated that certain nanoparticles (NPs) exhibit deacidification, UV-blocking and antimicrobial properties, which make them attractive candidates for conservation treatments [10–12]. Studies have also examined the use of metals, metal oxides, and metal composites for textile finishing due to the antimicrobial properties of these materials [13].

This paper aims to provide scientific documentation on how textile cultural heritage has been studied and characterized, as well as describe the methods of preservation reported in the literature. Particular attention is being focused on the nanomaterials used, especially silver NPs (AgNPs), as they exhibit a well-known antibacterial effect, which can be exploited in treating heritage objects to slow down the degradation processes.

TEXTILES BIODEGRADATION

The biodegradation of textile objects is a slow process that depends on the composition of the objects and occurs in the following stages: biodeterioration, biofragmentation and assimilation. The biodegradation of textiles is the result of several combined degrading factors, such as mechanical degradation, thermal degradation and degradation due to the presence of moisture, oxygen, ultraviolet light and environmental pollutants [14]. Due to these factors, a large number of microorganisms adhere to the surface of textiles. Biofragmentation is the process by which the population of microorganisms grows and secretes enzymes and free radicals, reducing the degree of polymerization. As a result, the macromolecules break down into oligomers, dimers, and monomers. Assimilation involves metabolic products being released from microorganisms and the adhesion of these products to the surface of textiles [15].

CHARACTERIZATION OF TEXTILE ARTEFACTS

The analysis of heritage objects must be performed, as much as possible, by nondestructive or microdestructive techniques that do not affect the integrity of the artefacts. The main characterization techniques used in the field are presented below.

Textural analysis of textile artefacts

The techniques used to perform textural analysis are based on microscopy. The textural analysis provides information on the type of fibre, its diameter, and the degradation state of the objects [16]. Scanning electron microscopy (SEM) is among the common microscopy techniques used to evaluate fibre morphology and assess the possible deposits formed during the degradation processes [17].

Structural analysis of textile fibres

The main techniques used for the structural analysis of materials are X-ray diffraction (XRD), thermogravimetry (TGA), differential scanning calorimetry (DSC), gel permeation chromatography (GPC), viscometry and others. XRD is a non-destructive technique and can be used to evaluate the crystallinity of textiles, while TGA and DSC are microdestructive techniques used to observe the thermal stability and phase transition of samples [18, 19]. GPC, also known as size-exclusion chromatography (SEC), is a microdestructive technique for determining the molar mass distribution (Mw) of polymers [20]. Furthermore, the textile's average degree of polymerization can be calculated by performing viscometry measurements. Thus, it is possible to assess the changes in textile fibres [21].

Chemical composition and metal assessment

Fourier transform infrared spectroscopy (FTIR) is a technique that is commonly used to determine the functional groups present in the chemical composition of samples. By coupling an attenuated total reflection (ATR) module to this technique, the analysis can be performed directly on the samples and no additional sample preparation is necessary, unlike the traditional technique [22, 23]. Therefore, nondestructive analysis of the chemical composition can be conducted. Moreover, the information can be completed by performing Raman spectroscopy, a complementary technique that can provide information regarding the dyes used on textile fabrics [24].

For assessing metals, X-ray fluorescence spectroscopy (XRF) or energy-dispersive X-ray spectroscopy (EDX) are the most appropriate techniques for textile artefacts, as they are nondestructive or microdestructive (for EDX) and previous sample preparation is not necessary. Moreover, these techniques can also provide information regarding nonmetallic elements [25]. However, these techniques can provide only semiquantitative information and are unable to detect metal traces. For quantitative analysis, atomic absorption spectroscopy (AAS) or inductively coupled plasma (ICP) might be performed. Nevertheless, the main disadvantage of these techniques is related to the expense of the instruments and resources, as well as the necessary sample preparation [26, 27].

Chromatic analysis

In the field of conservation-restoration of heritage objects it is important that the treatment does not change the colour of the artefacts or, in the case of restoration, slightly intensifies the colour tones, for objects that have faded over time [26]. The most common method to evaluate chromatic changes involves recording the visible spectrum of a sample, using a special spectrophotometer, which reports the data as in the CIE L*a*b* system of colours [29].

Microbiological analysis

Microbial contamination of textile artefacts can be achieved by fingerprinting or clone library construction methods. The first step is to perform cell lysis, followed by isolation, fragmentation, and amplification of DNA residues, by polymerase chain reaction (PCR) [30]. Next, the clone library construction method involves inserting DNA fragments into vectors, which are implanted into host cells. Afterwards, functional screening and/or sequencing-based screening is performed [31]. The fingerprinting method involves analysing PCR products by electrophoresis [32].

CONSERVATION OF TEXTILE ARTEFACTS

The main method of preservation is to maintain a suitable microclimate, in which the relative humidity is 65% and the temperature does not exceed 22°C [33]. In addition to maintaining the microclimate, the literature describes several physical and chemical methods for disinfecting heritage objects with the aim of preventing biodegradation [34]. The physical methods described in the literature are inducing dehydration to inhibit the growth of microorganisms, exposing the artefacts to gamma rays using cobalt 60 isotopes and exchanging the oxygen in the atmosphere with inert gases, such as argon or carbon dioxide [35, 36]. Chemical methods involve the use of biocidal substances that belong to different classes of compounds, such as alcohols (e.g., ethanol), alkylating agents (e.g., ethylene oxide and formaldehyde), azole compounds (e.g., imidazole, triazole, thiabendazole), quaternary ammonium salts (e.g., dimethyl-lauryl-benzyl ammonium bromide and lauryl-dimethyl-carboethoxy-methyl ammonium bromide), and, more recently, essential oils [37–39].

NANOMATERIALS IN ARTEFACTS CONSERVATION

The nanostructures studied for their potential application in cultural heritage conservation are metal (e.g., AgNPs), metal-oxide (e.g., TiO_2, MgO, ZnO) and hydroxide NPs (e.g., $Ca(OH)_2$ or $Ba(OH)_2$) and modified nanoclays (e.g. Montmorillonite hybrids), due to their antimicrobial and deacidification properties [40–44].

Nanomaterials in stone and cellulose-based artefact conservation

Another mechanism to prevent the degradation of cultural heritage objects involves deacidification. Hydroxide NPs, such as calcium, magnesium, and barium hydroxide NPs, have been applied on limestone, paper, wood, and canvas artefacts through brushing or spraying during restoration and conservation processes. Due to their alkaline character, these hydroxide NPs proved to be efficient for deacidifying artefacts and hence decelerating the degradation process [45–47]. Moreover, in addition to their deacidification efficiency, $Ca(OH)_2$ NPs also exhibited antifungal properties, which can be enhanced by mixing with TiO_2 and/or ZnO NPs. Such antifungal coatings have been used to protect limestone monuments against deterioration [48].

The antimicrobial properties of certain oxide NPs, such as MgO, ZnO, and TiO_2, are strongly related to their photocatalytic mechanism. These NPs have been intensively studied in the process of conserving and restoring calcareous stone, paper, and wood heritage [11, 49, 50].

Water repellence is another mechanism that leads to microorganism growth inhibition. SiO_2, Al_2O_3, and SnO_2 NPs have been used for wood and stone artefacts and even stone building conservation due to their water-repellent properties [51].

The use of AgNPs has also been intensively studied for applications in cultural heritage conservation. AgNPs and AgNP-based nanocomposites are well-known antimicrobial agents due to Ag cytotoxicity [52]. AgNPs are a promising conservation treatment due to their antimicrobial effectiveness and because they can be easily and greenly synthesized from various plant extracts [11, 40]. AgNPs and AgNP-based nanocomposites have been used as conservation treatments for stone [53], paper [11, 54], and even parchment artefacts [55].

Another category of nanomaterials studied for cultural heritage conservation are nanoclays. Halloiste, sepiolite, montmorillonite, and laponite have been applied for wood, paper, and stone deacidification, cleaning, and surface protection [44].

Nanomaterials in textile conservation

NPs have been employed in finishing textiles to manufacture functional textile fabrics, such as antimicrobial textiles, UV-absorbers, water-repellents, and dirt repellents [56, 57]. Inspired by the studies conducted on paper deacidification, the use of alkaline nanomaterials, such as calcium or magnesium hydroxide, has been proposed to protect the canvas from acidic degradation [58]. The most intensely studied nanomaterial for textile artefact conservation is AgNPs due to their remarkable antimicrobial properties. The literature describes several methods for AgNP deposition, such as solution immersion, layer-by-layer deposition, and sonochemical methods (figure 1) [59].

The Beata Gutarowska research group conducted a study that assessed microorganism contamination in several museums and archives. In the Central Museum of Textiles in Lodz, an average number of 2.5×10^2 microbes was found in the air, consisting of 15.44% fungi and 84.56% bacteria. Additionally, the average number of microbes on the surfaces was 1.5×10^2, consisting of 30.73% fungi and 69.27% bacteria. The identified microbes are listed in table 1 [60]. Gutarowska proposed a disinfection method using a misting chamber in which silver colloid was injected with heated and humidified air and sprayed from four sides (Patent no. P-399 507) [61].

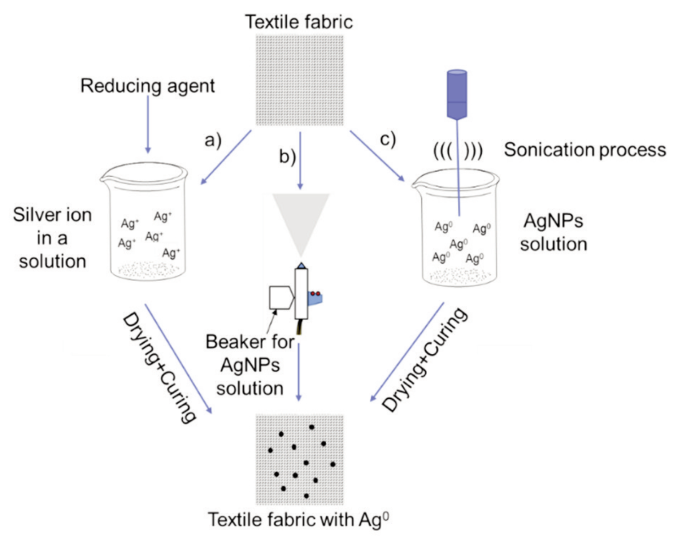

Fig. 1. Methods for AgNP deposition: *a* – solution immersion; *b* – layer-by-layer deposition; *c* – sonochemical deposition [59]

Table 1

MICROORGANISMS IDENTIFIED IN THE CENTRAL MUSEUM OF TEXTILES IN LODZ [60]	
Type of microorganism	**Microorganism species**
Gram-negative rods	-
Gram-positive cocci	*Micrococcus sp., Kocuria varians/rosea, Staphylococcus xylosus*
Gram-positive endospore-forming rods	*Bacillus sp., Bacillus firmus, Bacillus pumilus, Bacillus subtilis, Brevibacillus laterosporus, Lactobacillus delbrueckii*
Mesophilic actinomycetes	-
Moulds	*Alternaria alternata, Alternaria consortiale, Aspergillus niger, Aspergillus versicolor, Botrytis sp., Cladosporium sp., Cladosporium cladosporoides, Mucor hiemalis, Mucor racemosus, Penicillium carneum, Penicillium polonicum, Penicillium radicola, Rhizopus nigricans*
Yeast-like fungi	*Candida sphaerica, Rhodotorula mucilaginosa*

Based on these data, Katarzyna Pietrzak described in a later publication that the AgNPs misting was effective in disinfecting cotton fabrics, demonstrating a high efficiency in reducing bacterial development on cotton fabrics (from 87% to 99%) [62].

The researchers also studied the antimicrobial properties of AgNPs against biofilm formation by *Pseudomonas sp.* on pre- and post-Columbian archaeological textiles and suggested that AgNP treatments can be very promising in the antimicrobial protection of archaeological textiles [63]. The percentages of microbe reductions are shown in table 2.

Table 2

THE REDUCTION IN MICROORGANISM NUMBERS (R) AFTER TREATING THE COTTON FABRIC WITH AgNPs [62, 63]	
Microorganism	**R (%)**
Bacillus subtilis I	87.39
Escherichia coli	99.95
Staphylococcus aureus	99.65
Pseudomonas aeruginosa	97.10
Aspergillus niger	31.57
Penicillium chrysogenum	53.54

Given the abundance of publications that document the remarkable antimicrobial properties of AgNPs and the applicability of AgNPs for disinfecting textiles, AgNPs constitute a promising treatment with a wide range of possible variates in the field of artefacts conservation [64–66]. The new challenges consist of finding optimal synthesis pathways to fulfil both the efficiency and environmental friendliness, as well as the cost-effectiveness criteria [64, 66, 67]. Therefore, green alternatives constitute an attractive solution that involves the use of enzymes, microorganisms, oligosaccharides, polysaccharides, DNA, bacteria, yeast, fungi, plant extracts, and sometimes intact plants for AgNP synthesis [68].

Other nanomaterials, such as TiO_2 and ZnO, can be exploited for this purpose, as they also demonstrate antibacterial activity [69–71].

CONCLUSIONS

It is impossible to prevent the degradation of heritage objects. Degradation can occur slowly or quickly, depending on the nature of the object and the storage conditions. The analysis of degradation processes that impact textile fabrics can be performed using a variety of techniques. Several preservation methods have been reported in the literature, including the following: physical methods (dehydration, exposure to gamma radiation, change of atmosphere, etc.) and chemical methods (alcohols, phenols, alkylating agents, azoles, quaternary ammonium compounds, essential oils, etc.). Recently, special attention has been given to nanomaterials, such as alkali NPs ($Ca(OH)_2$ or $Ba(OH)_2$) due to their deacidification properties; silica NPs (SiO_2) due to their hydrophobic character, which provide water-repellent properties; etal oxide NPs (TiO_2 and ZnO NPs), due to their UV-blocking and antimicrobial properties; and AgNPs due to their antimicrobial properties and versatility.

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