Chapter

Silver Nanoparticles in the Cultural Heritage Conservation

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Abstract

Our cultural heritage is our invaluable social and environmental resource and concern. Moreover, it is a key global economic driver. However, they are subjected to deterioration process and aging. Particularly, microorganisms are nowadays considered harmful agents of biodeterioration of artistic materials due to the fact that their interactions with the material cause not only an esthetical damage due to their visible growth on the surface, but they may affect the interested materials in different ways and at different degrees via mechanical and biochemical processes leading to the formation of pitting, scaling and, in the worst scenario, to the loss of material by its detachment. To protect our shared tangible cultural heritage from biodeterioration and preserve it for future generations, several methods have been developed. Notably, using nanomaterials, with antimicrobial features, has been considered an interesting and economical method to preserve valuable heritage materials. In this chapter, we will present an overview of the decay mechanisms that participate in the deterioration of tangible artworks, in particular microorganisms' colonization. Next, current works that have been developed to use silver nanoparticles to protect heritage items from microbial colonization and prevent their deterioration have been detailed.

Keywords: silver, nanoparticles, microorganisms' colonization, stone biodeterioration, conservation, heritage materials

1. Introduction

Cultural heritage consists of tangible or intangible assets that history has left for a country and its future generations [1]. Heritage refers to the cultural legacies that we inherit from the past, maintain in the present, and pass on to succeeding generations. Moreover, investments in cultural heritage are frequently considered as having positive effects on a local economy, including increased employment and revenue as well as cultural consumption. However, famous works of art and historical artifacts have been marred. The alteration of cultural assets is the consequence of the continuous cycle of disintegration, by losing cohesion or strength, and reconstruction. Generally, in a natural condition, matter undergoes processes of alteration, degradation, or decomposition, which means that original chemical, physical, and optical characteristics are lost [2].

Among the decay mechanisms, the most known are as follows: (i) Physical or mechanical processes: where the behavior of the material is modified without altering the chemical composition of the material due to the contribution of several mechanical forces such as traction and compression. (ii) Chemical processes: where the matter is transformed due to a chemical reaction. (iii) Biological processes: where living organisms, such as microorganisms, insects, plants, rodents, and others, can chemically attack the material [1]. For that reason, the preservation of monuments becomes an obligation. Several products and methodologies have been studied and developed for the preservation of monuments from decay [3].

Traditionally, solvents (both aromatic and non-aromatic), chelating agents in addition to other cleaning products (including strong and mild acids and bases), have been widely used in the restoration field and are applied on different materials such as stones, paintings, and wall paintings [4]. However, the irreversibility of this technique and the risk of altering the artwork as well as the toxicity of certain products make this method not suitable for application on historic buildings [4]. Biocleaning has been suggested and studied as an alternative to the traditional cleaning techniques [5]. This method is based on using microorganisms for the treatment of deteriorated historical materials by removing undesired sulfates, nitrates, and organic matter [6]. Despite the efficiency of this method under laboratory conditions, the need of a specified condition to ensure the viability of these microorganisms makes its practical application very difficult and subject to further study [4]. The laser has been considered a friendly technique for cleaning heritage structures as well as for the environment. Its ability to alter and affect the artifacts' surface on a variety of materials, such as wood [7], paper [8], stone [9], easel paintings [10], and wall paintings [11] makes this technique attract high attention. Nevertheless, the high cost of this method is still the barrier to its widespread use.

Several products have been also developed and used as protective and consolidation agents with the aim to preserve the historic buildings from decay such as polymers [12, 13], biopolymers [14], gels [15], microemulsions [16], and ionic liquids [17]. However, the application of the abovementioned products requires caution owing to the toxicological risks to the artwork and the operator in addition to the high cost of maintenance. More recently, nanomaterials have been proposed as an alternative method in the maintenance of the historical artifacts, particularly in the consolidation and protection treatments of damaged art materials [18]. Unlike conventional materials such as polymers that are frequently used in conservation, engineered nanomaterials do not modify the original physical and chemical properties of artifacts as well as have a low environmental impact [19].

When the dimensions of particles decrease to be about 1–100 nanometers, the properties of materials change considerably from those at larger scales. In this sense, nanomaterials have larger surface areas compared with similar masses of larger-scale materials, which enhance their chemical reactivity [18]. Moreover, due to the particle size, these nanomaterials can deeply penetrate into the damaged stone materials.

The application of Nanoscience in the field of artifacts as a preservative agent reverts to the end of the 1980s through the restoration of the wall paintings (i.e., Renaissance paintings) in the "*Brancacci Chapel*" in Florence, Italy [20]. After that, different kinds of inorganic nanomaterials have been used as consolidant products [21] such as calcium hydroxide ($Ca(OH)_2$) nanoparticles, which have been applied on rocks (limestones and dolostones) and mortars [22–24]. In addition, consolidant products based on $Mg(OH)_2$ nanoparticles have been used for the conservation of cultural heritage [25] and paper-based cultural archives [26]. Barium hydroxide

($Ba(OH)_2$) has been extensively used as a consolidant product for carbonate stones for decades [27, 28]. Strontium hydroxide ($Sr(OH)_2$) nanoparticles obtained by bottom–up approach and their use as a consolidant product and also as a desulfating agent for stone, mortars, and wall paintings were proposed [22, 29]. More recently, studies concerning the behavior of commercial water-based silica dispersions, with different particles size (from 9 to 55 nm), as consolidant products on heritage materials have been performed on limestone (Lecce stone) [30]. Silicon-based hybrid polymer nanocomposites have also taken an interest in the domain of preservation of historical materials. Alkoxysilane-based formulations, notably, tetraethoxysilane (TEOS) and methyltrimethoxysilane (MTMOS), have been the most broadly used stone consolidants principally due to their ability to penetrate easily inside the porous matrix [18]. Another approach has been developed in order to reduce the cracking of the consolidant products through the addition of different metal colloidal oxide particles to the TEOS-based polymeric resins [31]. Recently, Verganelaki et al. proposed a novel crack-free calcium oxalate-silica nanocomposite for protecting historic building materials [32]. During the last years, the use of polymeric materials with hydrophobic properties has been broadly studied. The incorporation of inorganic oxide nanoparticles, such as aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), and tin dioxide (SnO_2), has been performed as a method to improve the hydrophobic character of synthetic polymers such as silicone or hybrid siloxanes polymers, which leads to super-hydrophobic coatings with higher water-repellent capacity. Recently, the area of interest dealing with the treatment of monument materials for their preservation from microorganisms' colonization and pollution is shifting into the application of nanotechnology with self-cleaning properties [18]. Heterogeneous photocatalysis using semiconductors such as TiO_2 and ZnO has been considered an interesting method, used extensively to preserve heritage materials [33–39]. The particular activity of these oxides, based on the generation of reactive oxygen species (ROS) when they are exposed to UV light, makes them very attractive compounds [40].

Recently, nanoparticles of different elements (e.g., Ag, Ti, Cd, Fe, Pd, Zn, Pt, and Co) have been investigated due to their interesting attributes. Indeed, the low cost, nontoxicity, chemical stability, biological inertness, suitability toward visible or near-UV light, sustained photoactivity, high conversion efficiency as well as higher quantum yield [41]. In fact, these nanoparticles could react with an extensive range of substrates and have high adaptability to several environments and good absorption in the domain of the solar spectrum [41]. In addition, treatments by using the abovementioned nanoparticles can provide water-repellent features and inhibit the damage generation performed by water [42]. In particular, Ag NPs display good antimicrobial properties in comparison to other metals, which makes them widely used for several applications, in particular, conservation of heritage materials from biodeterioration [43]. To our knowledge, this is the first report on the application of silver nanoparticles in cultural heritage conservation.

Several variables need to be taken into account in order to have an adequate protective coating by selecting materials and procedures to be used. The intrinsic properties of historic material, the environmental factors, the compatibility between tested products and affected heritage materials, the durability of applied products, the biological colonization, in addition to the application method, are significant factors that have to be taken into consideration [22]. However, it is essential to identify firstly the main factors considered as threats to heritage materials, in order to delay the deterioration processes [1] as much as possible.

2. Decay mechanisms of cultural heritage materials

Historic materials are subject to several decay phenomena. The main deteriorating factors will be explicated in the following sections.

2.1 Water

Many processes that can alter historical materials are often driven by water. In fact, water is one of the most significant abiotic factors of deterioration of porous stones, which are more susceptible to water. Highly porous materials with average porosity values between 30 and 40% and above have been widely used over the world as historic building materials [33]. When water penetrates the pores through capillary force, water performs its deteriorating effect via both chemical and physical phenomena such as dissolution of carbonate component of the stone, freezing/thawing cycles, salt crystallization, and deposition [44, 45]. Such processes can affect the physical as well as mechanical properties of stone in addition to inducing some changes in its structure such as modification of porosity and pore structure, loss of stone cohesion, and development of cracks [46]. The need of the surface protection, especially against water penetration, is mandatory to conserve historical artifacts.

Dissolution is usually caused by water that frequently contains acid due to dissolved carbon dioxide. It is able to dissolve minerals from a rock body, leaving cavities in the rock. These cavities may generate cave features [47].

The freezing-thawing cycles of the water inside the stone pores result in the development of internal stresses, which can lead to cracking and progressive desegregation of material [46]. Particularly, this phenomenon is widely observed in cold regions exposed to excessive freezing and thawing during the year. Tensions that frequently increase and decrease due to the formation of successive layers of ice result in the fracture of the material [46]. The formation of ice in the pores creates a crystallization pressure, that is, a pressure caused by the crystallization of ice against the pores in walls of the material. This phenomenon can affect even stone with very fine pores, (diameter smaller than 0.1 μm). Water freezes at temperatures considerably under 0°C; the freezing of water causes internal stresses that are the direct cause of the damage. The pressure rises as the temperature decreases [48].

2.2 Salt crystallization

Salt crystallization affects heritage materials constructed from rocks. Indeed, plenty of architectural heritage materials around the world are constructed principally of carbonate rocks. However, historical monuments are frequently affected by several degradation and alteration processes typically due to salt crystallization [49]. Such phenomenon is considered as one of the most powerful weathering factors in the case of porous materials, particularly limestone rocks. This problem affects monuments and historical buildings around the world, from the cooler and wetter conditions found in the United Kingdom to hyper-arid desert environments and Mediterranean climates. Macroscopically, such a type of deterioration process produces enormously aggressive damages such as loss of material, erosion, flaking, exfoliation, and occasionally, even the complete disaggregation of the material [44]. Once a salt-rich solution enters into the pore structure of stone material, in favorable supersaturating and thermodynamic conditions, the salt crystallization occurs. Besides, nucleation and growth of salt crystals inside the pore spaces can promote alteration and degradation of the stone [50]. Many factors would affect the damage of the material such as the supersaturation of the salt, the shape of crystals, the pore size, and the repulsion force between the salt and the walls of the pores [51]. Porosity represents a critical parameter in the process of salt crystallization since it regulates the fluid mobility inside the material. Salt crystals exert pressure on the capillary wall, namely the linear pressure, which is proportional to crystal size and salt concentration and inversely proportional to the radius of the pore.

2.3 Microorganisms' colonization

Physical and chemical processes were commonly assumed to be the principal factors in the degradation of materials. However, since 1967 and in later decades, dogma has changed, and today, it is believed that one of the main causes of deterioration of archaeological stone materials is the microbial action, leading to biodeterioration [1]. Biodeterioration can be defined as "any undesirable change in a material brought about by the vital activities of organisms." The biodeterioration of cultural heritage can also be defined as "the physical or chemical damage caused by microorganisms on objects, monuments, or buildings that belong to the cultural heritage" [1]. The main microorganisms that play a role in biodeterioration are both autotrophic and heterotrophic bacteria, fungi, cyanobacteria, algae, and lichens [1]. Microbial populations present in a stone foundation are generally the result of successive colonization of different microorganisms over many years [52].

Many types of research on the biological deterioration of stone monuments have been performed, and results showed that bacteria, algae, fungi, and lichens are the microorganisms mainly responsible for artifacts biodegradation [53]. Whereas, mosses have received relatively less attention because their impact has been considered mainly esthetic [53]. In fact, bacteria were isolated from many archaeological statues (e.g., in the Museum in Zagreb, Croatia [54]), deteriorated marble (e.g., Moscow Kremlin masonry [55]), from wall paintings [56] and found in caves and catacombs [57]. Fungi were also isolated frequently from historic limestone buildings and antique marble from different sites in many countries such as Germany, Portugal, Italy, Russia, Namibia, and Spain. On the other hand, it was stated that cyanobacteria and chlorophyta (green algae) are considered the pioneering inhabitants in the colonization of stone works of art [58].

Microorganisms damage stone in different ways, including discoloration, water retention, material breakage, growth stimulation of heterotrophic organisms, disintegration of the material, degradation (corrosion), formation of patinas, and alkaline dissolution. On the other hand, many antique and precious historical items are suffering from serious microbial invasions that cause in some cases the closure of archeological sites, as in the case of the caves of Lascaux in France [59].

Biofilms, which are made by a complex microbial organization mainly containing bacteria and fungi, contribute also to degrade historical statues. All they need are surface, moisture, nutrients, and microorganisms. The role of biofilms in the biodeterioration of cultural heritage materials has been reported for several decades and is related to: (a) accumulation of water that enters the matrix causing swelling and amplified conductivity; (b) alterations in pH values and ionic concentrations; (c) releasing enzymes that lead to embrittlement and loss of mechanical stability and others [1, 60].

There is a general agreement that microbial activity contributes to altering and deteriorating historical relics. The question now is why and how microorganisms are able to degrade the works of art. Some artifacts such as parchment, wood, leather, or textiles are made with organic materials, which microbes like to feast on. It used to be common for artists to use egg tempera, pigments mixed with egg yolks as a binding agent, which has left their paintings more susceptible to infestation. Fungi are among the most active microorganisms in these processes where they can use organic support as nutrients. Moreover, in the case of inorganic supports, several metabolites that are excreted may react with the support in different ways [53]. In the case of stone materials, their mineralogical nature, surface features, and environmental conditions play a role in the colonization by microorganisms [1]. Due to their heterotrophic nature, fungi promote biological deterioration by synthesizing certain compounds, such as inorganic and organic acids, which allow them to utilize the contents of the inorganic supports [53]. On the other hand, inorganic materials have been also considered as good substrates for a high number of different microorganisms. It was reported that most kinds of microorganisms are able to attack and degrade marble materials [53]. It is now generally agreed that fungi and bacteria not only cause serious aesthetical problems but also reside and penetrate inside the materials, resulting in a material loss due to acid corrosion, enzymatic degradation, and mechanical attack [61]. Acidic compounds can also corrode metals. Algae and cyanobacteria, as an example, are able to adapt to different light qualities [61] and environments (humid, semiarid, and arid) [62] and to be developed on stone in archaeological hypogea (e.g., an underground chamber). Such an environment is characterized by low light intensities (i.e., crypts, caves, and catacombs). Cyanobacteria cause esthetic damage to marble surfaces; their endolithic mode of life contributes to the collapse of rock crystalline structures [62].

2.4 Climatic conditions

The climatic conditions play an important role in deterioration mechanisms. Particularly, the architectural structures and historical monuments, which are exposed outdoors, are susceptible to several climatic conditions such as the wind that wears the rock eroding it, the solar radiation causing discoloration, the rain, the humidity, and the snow that induce physical and chemical wear [1]. These factors affect significantly the stability of stone matrix by inducing chemical corrosion through hydration and oxidation reactions, the dissolution of carbonates as well as solubilization of some mineral components.

On the other hand, the climate has an effect on microbial colonization species. In moderate or humid climates, the fungal communities on the rock are predominant. Whereas in arid and semiarid environments, such as those found in the Mediterranean area, the climatic conditions are overly extreme, consequently the communities shift toward the so-called black yeasts and microcolonial fungi [61]. Moreover, the role of bacteria in the weathering of rock depends mostly on the environmental conditions: while bacteria might evolve in humid environments and form biofilms inside the porous space of building stone, in arid and semiarid environments, their occurrence might be limited [61].

Climate change is another potential risk since it increases the anticipated degradation rates and/or participates to the occurrence of new decay phenomena [63]. In fact, climatic changes are able to aggravate the chemical, physical, and biological processes producing deterioration by influencing the composition and/or structure of the affected heritage materials [64]. Climate change could also affect the intensity as well as the frequency of dangerous events such as floods, landslides, and droughts with unavoidable extensive impacts, also on the cultural heritage materials. The United Nations Educational, Scientific and Cultural Organization (UNESCO) has considered that changes in the temperature, wind intensity, precipitation, desertification, atmospheric moisture in addition to the interaction between air pollution and climatic changes have been identified as threats to cultural heritage [65].

There are synergisms that take place between different parameters, leading to direct and indirect, immediate, and long-term impacts on a widespread variety of objects, buildings, materials, and sites. Changes in the conservation conditions because of climate-related degradation processes are inevitable phenomena for immovable and movable cultural heritage materials [63].

3. Silver nanoparticles

Due to their distinctive physical and chemical features, silver nanoparticles (Ag NPs) have been extensively used in a several domains, including medicine, health care, food, and others [66]. The exceptional features of silver NPs are the main factor for the extensive range of their application in several fields. **Figure 1** illustrates the main application fields of Ag NPs.

In general, Ag NPs with size lower than 100 nm contain around 20–15,000 silver atoms and have exceptional chemical, physical, and biological features compared with their bulk materials. The optical, catalytic, and thermal characteristics of Ag NPs are intensely affected by their size and shape. In particular, Ag NPs are characterized by the localized surface plasmon resonance (LSPR), which has attracted considerable attention over the past few years in the photocatalytic field. Thanks to their broad-spectrum antimicrobial capacity, Ag NPs have also become the highest used sterilizing nanomaterials. It is well known that silver compounds are highly effective to kill microorganisms such as bacteria in addition to certain fungi and viruses. The use of silver as a biocide in the form of nanoparticles has grown significantly due to the higher fraction of surface atoms of silver nanoparticles, which leads to a better antimicrobial activity compared with bulk silver metal. Numerous studies have been reported in order to clarify the inhibitory effect of silver nanoparticles on bacteria. Reports declared that the electrostatic attraction between negatively charged

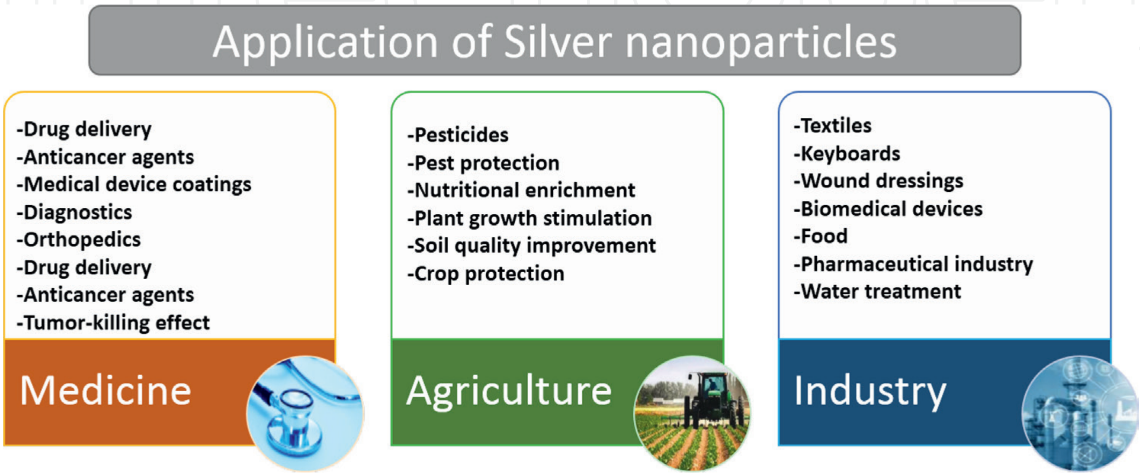

Figure 1.
Silver nanoparticles' application in different domains [66–68].

bacterial cells and the positively charged nanoparticles plays a key role in the activity of nanoparticles as bactericidal materials. Nevertheless, Sondi and Salopek-Sondi synthesized negatively charged silver NPs [69]; and results revealed that they show excellent antibacterial activity against *E. coli*. Authors suggested that the negative surface charge of nanoparticles interacts with the building elements of the bacterial membrane, provoking structural changes in addition to degradation and, lastly, cell death. EDS analysis proved the existence of the elementary silver in the membranes of treated bacteria; such observation confirmed the incorporation of silver NPs into the membrane structure. Yamanaka et al. [70] proposed that the inhibitory activity of silver on the microorganisms growth could be due to the toxic effect on the DNA replication causing the inactivation of vital cellular proteins. Another suggestion reported by Choi and Hu [71], based on the fact that the cell death can be attributed to the formation of free radicals, particularly, reactive oxygen species (ROS) from the surface of Ag. The generation of free radicals can attack membrane lipids and lead to a collapse of membrane function. It has also been stated that Ag ions can bind with the sulfhydryl groups of the proteins disturbing the membrane function that bound enzymes of the respiratory chain [72]. Although the biocidal effect of nanosized silver particles against bacteria was widely studied, the mechanism of the growth-inhibitory effects of Ag nanoparticles on microorganisms is still not fully understood. The different hypotheses concerning the antibacterial effect of silver nanoparticles are described in detail in the literature [73].

4. Application of silver nanoparticles for the preservation of heritages materials

Heritage buildings are subject to different decay phenomena. In particular, microorganisms' colonization affects them in different ways and at different degrees starting from esthetical problems and formation of patinas, often causing total breakage and loss of the materials. Archival documents and library collections such as paper, parchment, textile, glue, leather, and photographs are of high cultural importance. However, microorganisms could easily attack them, particularly in high humidity conditions. Therefore, protecting heritage materials has become a necessity. Applying silver NPs has been suggested as a promising and effective method. In this context, several groups have worked on exploiting silver nanoparticles to protect heritage items from microbial colonization and prevent their deterioration.

Gutarowska et al. are among the first groups who worked on applying silver nanoparticles to museum collections and archives, which are contaminated by microorganisms [74]. The authors worked precisely on analyzing the sensitivity of microorganisms to Ag NPs in six different museums and archives in Poland. Results showed that microorganisms can be effectively removed from the surface of artifacts at a concentration of 90 parts per million (ppm). While a concentration of only 45 ppm was able to remove 94% of all tested microorganisms with the exception of *Staphylococcus xylosus* and *Bacillus subtilis* that showed higher resistance. The study revealed that silver NPs could be considered a promising disinfectant for the surfaces of historical materials and archival documents. The Lodz team developed also a novel procedure for disinfecting cultural artifacts by nebulizing Ag NPs from a dispersion over the paper, textiles, or canvas [75]. These researchers discovered that the degree of relative humidity affected the misting disinfection procedure, as moisture facilitates the entry of NPs into microbial walls. Furthermore, they found that vegetative cells (mycelium and bacteria) are more susceptible to Ag NPs antimicrobial activity than fungal or bacterial spores. Next, F. Bellissima et al. have synthesized silver nanoparticles according to a seed-based procedure in order to preserve Serena stone (SS, 5–10% open porosity) from biodeterioration [76]. The ability of Ag NPs to hinder bacterial colonization was investigated through the inactivation of *Bacillus subtilis*. Aiming to chemically graft silver NPs to SS surface, tetraethylorthosilicate (TEOS) was used as a grafting agent, and dimethylamine was used as a catalyst to promote the condensation of a silane precursor on NPs surface. Antimicrobial activity on stones was evaluated through "spot on spot" method. Results showed that applied nano-coatings did not induce significant color changes on the stone surface after treatment ($\Delta E < 2$) and provided good antibacterial activity with a reduction in cell viability between 50 and 80%, with the most efficient nanoparticles concentration equal to 6.7 $\mu g/cm^2$. A.M.M. Essa and M.K. Khallaf have studied the efficiency of Ag NPs suspensions as an antimicrobial agent to preserve Edfu (Sandstone) and the tomb of Teti's son Teti-ankh-km at Sakkara (Limestone) [77]. Both archaeological buildings are localized in Egypt. Silver NPs were elaborated biologically through volatile metabolites formed during the aerobic growth of *N. halobius* and then mixed with acrylic polymers (Primal AC33 polymer) and silicon as a consolidation polymer at a concentration of 40 mg/ml. Small Ag particles with diameters of 10–20 nm were obtained as displayed by scanning electron microscopy analysis. The antimicrobial properties of prepared NPs were studied against *Streptomyces parvulus* as Gram-positive bacterial strain and *Aspergillus niger* as a fungal strain. Findings showed high antibacterial performance of the applied nano-coatings against *S. parvulus*. The treated sandstone samples showed a significant decrease in the percentage of bacterial cell recovery (98.4% and 97.2%) by using functionalized silicon polymer and acrylic polymer, respectively. Moreover, treated limestone specimens exhibited a clear reduction in the percentage of *S. parvulus* cell recovery that achieved 97.1% and 98.6% with the impregnated acrylic polymer and the functionalized silicon polymer, respectively. On the other hand, a significant inhibition growth of *A. niger* on both the surfaces of the sandstone and limestone samples coated by silver NPs and silicon or acrylic polymers occurred compared with untreated stones on which a prominent growth of *A. niger* was observed. MacMullen et al. have investigated that the efficiency of silver NPs (<100 nm) enhanced aqueous silane/siloxane emulsions performance to protect and improve the facade interface of historical buildings [78]. Different emulsions were prepared and applied on mortar samples. Results showed that all treated samples exhibited water-repellent character with water contact angles higher than 100°; however, treatment induced a color modification higher than that which is considered tolerable for application on cultural heritage with $\Delta E > 5$. Authors declared also that adequate concentrations (<0.5% wt) were needed to reach considerably beneficial enhancements. Capillary absorption analysis showed that water absorption was considerably reduced in the case of treated mortars compared with the untreated ones, despite that negligible difference was observed when Ag NPs were incorporated. Therefore, the authors considered that silver treatments are not suitable for marine or flood applications where there is prolonged water exposure. Next, R. Carrillo-González et al. have prepared silver NPs through a green process using leaf aqueous extracts of *T. stans* and *F. vulgare* [79]. The inhibitory growth of biosynthesized NPs at different doses was tested against microorganisms, which are isolated from biofilms developed on the surfaces of three kinds of stony historic monument walls located in the pre-Hispanic city, Teotihuacan (Mexico). *In vitro* biocontrol of isolated microorganisms revealed that Ag NPs prepared from *F. vulgare* were more efficient to inhibit microbial growth than those prepared from *T. stans*. Results also showed that bacterial strains were less sensitive to silver NPs than fungal strains and that sensitivity is principally related to the microbial strain and the plant extract utilized to elaborate silver NPs. Therefore, the authors considered that using Ag NPs as a corrective or preventive treatment to reduce microbial colonization from historical walls was effective. K. Pietrzak et al. [80] have investigated the efficiency of Ag NPs misting as a decontamination process compared with the effect of two other disinfection procedures such as thyme essential oil microatmosphere (TEO) and low-temperature plasma (LTP), to inhibit microbial growth from two archival books through culture-dependent method and RNA analysis. In this study, two books with observable signs of biodegradation obtained from Jozef Pilsudski Regional and Municipal Public Library in Lodz (Poland) and National Archive in Prague (Czech Republic) were used. in the study. Results revealed that Ag NPs misting process was more efficient for bacterial inhibition (R = 60–100%), while the two other methods showed less effectiveness with LTP (R = 25–100%) and TEO (R = 12–100%). Furthermore, it was stated that all tested methods showed less efficiency against fungi (R = 0–99.8%). Another study performed by K. Pietrzak et al. [81] to explore Ag NPs misting method in order to disinfect historical textile materials, precisely, five pre-Columbian fibers (1250–1450 A.D., Argentina). Microscopic analyses indicated that tested items were fabricated from sisal, cotton, and wool, and they were contaminated by dust and mineral impurities. The reduction in microbial population ranged from 30.8 to 99.9%, depending on the variety of microbial colonization and its concentration. In fact, the sensitivity of microorganisms toward silver NPs was fluctuated in most resistant endospore-forming bacteria *Bacillus*, while *Oceanobacillus*, *Paracoccus, Kocuria*, and molds *Penicillium*, *Cladosporium* were more easily inhibited. Interestingly, it was found that Ag NPs misting process does not harmfully affect the pH and the chemistry of textiles. The same group worked on evaluating the anti-biofilm capabilities of Ag NPs to protect textiles from *Pseudomonas sp* [82]. In the study, textile materials were collected during excavations in Santa Rosa de Tastil, Puna Argentina (1967–1969). Microscopic observations revealed that the bacterial strain including *Pseudomonas aeruginosa* and *Clostridium sp.* was presented on examined archaeological textile items through lipolytic and proteolytic activities. Results demonstrated that using Ag NPs with particles size ranged from 10 to 80 nm and a concentration of 90 ppm was effective to protect archaeological textiles against *P. aeruginosa* growing by 63%–97%. Authors stated that the inhibition ability of NPs was influenced by the kind of strain and the exposition time. Aerial algae are a central biological factor contributing to the degradation of building materials as well as facades. In this regard, P. Nowicka-Krawczyk et al. have examined the effect of silver NPs on *Apatococcus lobatus* as an algal model due to its frequent presence in aerial biofilms formed on historical building facades [83]. Authors stated that changes in the chloroplasts structure and the photosynthetic activity of the tested cells have been observed through confocal laser microscopy and digital image analysis due to exposition to Ag NPs. The rate of growth inhibition was estimated through a biomass test, and results showed that the average biomass of control samples was 3.7 mg/l chl *a*. While after exposition to Ag NPs, the biomass was decreased by 26% for 8 ppm, 56% for 15 ppm, 65% and 68% for 20 and 107 ppm, respectively. Authors recommended that Ag NPs could be employed as a biocide against aerial algal coatings, with caution in terms of nanoparticle concentration. More recently, Z. Li et al. [84] have developed a colorimetric sensor array (CSA) by using printed inks of 10 nm Ag NPs with different capping agents as an alternative process to passive sampling indicators, which were traditionally used by conservators. CSAs have been used as "optoelectronic nose" to detect and identify individual compounds and highly similar complex mixtures such as oxidants, acids, and aldehydes from ppm to tens of ppb levels. In fact, for artifacts, the levels of pollutant exposure are generally recommended at a few ppb or even sub-ppb concentrations. Authors found that the developed CAS was ultrasensitive and able to identify quantitatively 11 common contaminants related to the preservation of cultural heritage items and museums. Thanks to changes in localized surface plasmon resonance of metallic NPs, in particular silver, due to sintering of solid-state NPs, alterations in color during exposure to pollutants can be observed.

Nanocomposite coatings have been suggested as heterojunction systems to enhance the light absorption of semiconductors such as (TiO_2 and ZnO) and separate the charge carrier by localizing photogenerated holes and electrons to different regions in the system. In this regard, Ag NPs have been suggested to be coupled with semiconductors to develop several biocidal coatings with other interesting features to be applied to heritage building materials in order to conserve them. In this context, M. Aflori et al. [85] have compared the antibacterial/antifungal efficacy of silsesquioxane-based hybrid nanocomposites with methacrylate units containing only Ag NPs to its counterpart containing Ag/TiO_2 NPs as protective coatings for heritage stone surfaces. The antibacterial and antifungal efficiency of the prepared nanocomposites was evaluated through the inactivation of *Escherichia coli* (*E. coli*) and *Candida albicans* (*C. albicans*), respectively. Findings revealed that the coatings composed of Ag/TiO_2 NPs showed higher activity against *E. coli* and *C. albicans* than the coatings composed of only Ag NPs. Pinho et al. prepared hydrophobic and self-cleaning Ag-TiO2-SiO2 coatings for outdoor applications [86]. Findings revealed that prepared nanocomposites efficiently inhibit the penetration of water into the pores of the tested stones based on the total water uptake values, which were close to zero for all treated samples, and remarkably attained lower values compared with untreated ones. Such results prove the water-repellent feature of the developed coating since water causes many decay mechanisms to porous materials. Indeed, when water penetrates the pores by capillary force, it performs its deteriorating effect through salt crystallization; chemical dissolution of the carbonate component of the stone, and freezing/thawing cycles. On the other hand, incorporation of high amounts of Ag (5% w/w) leads to an undesired color alteration on studied stones and would prevent the sol–gel transition of the nanocomposite coatings (10% w/w). In fact, one of the conditions to accept the application of such treatment, according to Normal 20/85 [87], is that a protective product should not cause a visible alteration and must be stable over time. Moreover, authors found that the incorporation of silver into TiO_2-SiO_2 network notably improves the photodegradation activity of the coating containing 1% (w/v) TiO_2 thanks to the enhanced absorption under visible light and larger surface area of the photocatalyst. L. Graziani et al. [88] have compared the efficiency of Ag NPs incorporated in TiO_2 sol nanocoatings for the preservation of brick-based heritage materials compared with their Cu-TiO_2 counterpart. The concentration of Ag or Cu nanoparticles was set at 1% (molar weight/TiO_2 weight), and the total color variation at that concentration was higher than the value accepted for treatments on historical buildings, which is fixed to 5. The self-cleaning test showed that untreated samples achieved an efficacy of around 9%, while specimens treated with Cu/or Ag-TiO_2 were about 46 and 33%, respectively. Interestingly, Ag-TiO_2 nanocomposite showed a higher ability to hinder algal growth than Cu-TiO_2 treatment, which revealed the efficiency of Ag NPs as a biocide agent. J. Becerra et al. [89] investigated

Nanomaterials	Particles size	Substrate	Obtained results	References
SiO_2/Ag NPs	5–15 nm	Buildings Materials stone	Biocidal efficiency up to > 90%. Hierarchical roughness attributed to creation of Ag/SiO_2 NPs clusters. Improved contact with the cell walls. Easy removal of the dead cells. Good durability of the treatment.	[90]
Ag NPs	10 nm	Paper: Ancient manuscripts and books.	Suitable sensors for the detection, identification, and quantification of pollutants to the preservation of cultural heritage objects.	[84]
Ag-TiO_2NPs	11.8 ± 3.6 nm	Fossiliferous limestone	Treatment with self- cleaning activity. Ag NPs prevent the growth of *E. coli* and *S. cerevisiae* in the dark. Ameliorated inhibition growth of the coatings applied on the stone up to a 20% (*S. cerevisiae*) and 70% (*E. coli*).	[93]
PMAA@Ag NPs	200 nm	Paper, wood, or stone	PMAA@Ag nanostructures revealed an efficient fungicidal activity against *Aspergillus niger*. Nanomaterials can be used on cultural heritage materials for preventive conservation	[94]
Ag/N-SiO_2NPs	50–100 nm	Cement mortars	Efficient anti-fouling surface treatments. Multifunctional superhydrophobic/biocide treatment was obtained.	[91]
Ag NPs	7.2 nm ± 1.8 nm	Paper	A total removal of dirt from the paper samples, Softening of the dirt from the canvas, without affecting the integrity or leaving residues of the treated art works.	[95]

Table 1.
Application of silver nanomaterials for the treatment of historical artifacts (references are presented in a chronological order).

the suitability and the efficacy of nanocomposite treatments based on TiO_2 and/or Ag NPs to inhibit the biodegradation of limestone heritage materials. Findings revealed that Ag and TiO_2 nanocomposites when stabilized by citrate reach a good biocide effect by inducing a substantial reduction of the biopatina growth: and retaining the color modifications at an acceptable level. Next, R. Zarzuela et al. [90] have developed multifunctional treatment by incorporating Ag NPs grafted to functionalized silicon dioxide NPs in an organically modified silica matrix (Ag/N-SiO_2). This treatment was applied to different kinds of stone specimens that are frequently used to construct heritage building by spray method in order to enhance the mechanical resistance of the stone-based monuments, improve water permeability, and produce biocidal surfaces. Authors stated that thanks to coupling Ag NPs with SiO_2, the biocidal efficiency reached 90% values, since Ag NPs raise the stability of the treatment and improve the contact with the cell walls. Furthermore, the synergistic effect facilitates the removal of dead cells, ameliorating treatment durability. The same Ag/N-SiO_2 nanocomposite was used in another study performed by M. Domínguez et al. [91] as an anti-fouling agent. Authors studied the impact of surface features such as roughness/texture, surface free energy, and charge of the surface on the biocidal efficiency of NPs and the interaction with the cell walls. Authors stated that the functionalization of SiO_2 NPs with the positively charged –NHx groups considerably improved their interaction capability with the negatively charged cell walls through the electrostatic forces. For that reason, this interaction between biocide agent and *Phormidium sp*. was the lowest due to the presence of a positively charged mucopolysaccharide sheath cell wall. R. Zarzuela et al. [92] have elaborated Ag/modified-TiO_2 nanoparticles (Ag /N-TiO_2) for numerous applications (environmental, self-cleaning, antifouling, etc.). The biocidal efficiencies of Ag/TiO_2 nano-powders were evaluated through mixed cultures composed of three biofilm-forming phototrophic microorganisms isolated from building façades. Whereas, the photocatalytic activity of the obtained nanocomposite was assessed through the degradation of methylene blue dye under solar spectrum lamp. Results showed that the incorporation of Ag NPs into TiO_2 surface noticeably ameliorates the absorption of the semiconductor under the visible spectrum thanks to the surface plasmon resonance band provided by silver ions and, consequently, improved photodegradation capacity of TiO_2 NPs. Moreover, findings showed that Ag/TiO_2 was able to hinder microalgae growth under visible irradiation, whereas pure TiO_2 NPs were ineffective. The prepared functionalized nanocomposites were then used as protective treatment for porous ceramic materials. Nanocoatings exhibited superhydrophobic performance, high capacity to degrade pollutants, and good biocidal properties on surface stones [93]. **Table 1** summarizes the main application of Ag NPs as preventive and consolidant treatments in the recent years (2019–2022).

5. Drawbacks, challenges, and perspectives

Silver nanoparticles become more broadly used in the field of protection of cultural heritage materials. However, the transport of NPs in different environments is still not clearly understood. In general, nanoparticles have the potential to leach into the environment and cause ecotoxicity in soil, water, and related biota [96]. The major form of the toxic action and toxic effects are usually related to the dissolution of the metal into metal ions, and then it is introduced into the environment. Zhang et al. [97] pointed out the necessity of investigating NPs' toxicity in natural waterways. To clearly understand the toxicity of nanoparticles in natural water, authors studied the harmfulness of Ag NPs toward unicellular green alga "*Chlorella pyrenoidosa*" in four freshwater bodies. Findings revealed that water chemistry had a deep impact on dissolution, aggregation, and algal toxicity of nanoparticles. Authors stated that the ecotoxicity of silver NPs was generally attributed to the release of the harmful ions. Indeed, the dissolved Ag^+ might be principally responsible for the toxicity of Ag NPs. On the other hand, Franco-Castillo [98] stated that Ag NPs are regularly cytotoxic and consequently have an impact on the health, the safety, and environmental implications for restorers-conservators, curators, and general public.

The potential of using engineered nanoparticles for the preservation of heritage structures has been developed for the restoration of deteriorated materials, production of self-cleaning surfaces or developing surfaces as a biocide to minimize biodeterioration. However, several studies need ideally to be carried out *in situ*, or in the real environment, such as outdoors, in archives, where the anthropogenic circumstances could be investigated appropriately. The period of the research projects, the time required for the implementation of medium-to-long-term *in situ* investigation by collaborative programs including research centers, museums, and professionals in conservation and restoration, needs to be taken into account [98]. Studies should not be limited only to the efficiency of antimicrobial treatment but also to the entire procedure involving the design, application, investigation of the progressive evolution of the treatment, detachment, leaching, or ions release. Moreover, a protocol concerning the removal or clearance of treatment needs to be taken into consideration, in accordance with conservation rules. Several works have been performed to conserve heritage materials through the application of Ag NPs, these NPs are still far away from being routine treatments. There exists limited understanding concerning the impact of engineered nanoparticles on the environment after being released from the treated surfaces. Nevertheless, it is important to control their impact on the different nearby non-target organisms and ecological processes [99].

6. Conclusion

Tackling the deterioration of cultural heritage needs a global effort. Material scientists are asked to elaborate novel nanomaterials and develop new methods for the conservation of heritage artwork. In this study, we have particularly focused on the different works that have been developed to use Ag NPs to preserve heritage materials from deterioration. In this chapter, the different degradation mechanisms of cultural heritage materials have been presented in detail. An overview about different nanomaterials used as protective and consolidation agents with the aim to preserve the historic buildings from deterioration has been provided. Next, the different works that have been performed to exploit silver nanoparticles used alone or coupled with semiconductors for cultural heritage conservation have been described. Studies showed that silver NPs revealed high capability to protect heritage materials from biodeterioration. The main risks of using silver NPs for conservation purpose in addition to the different challenges to make Ag NPs widely used in this field have also been discussed. More importantly, the effect of NPs after their application on heritage materials surfaces needs extensive studies, to be assured about them being harmless to the environment and human beings.

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References

[1] Rivera LEC, Ramos AP, Sánchez JIC, Serrano MED. Origin and control strategies of biofilms in the cultural heritage. In: Kırmusaoğlu S, editor. Antimicrobials, Antibiotic Resistance, Antibiofilm Strategies and Activity Methods. London, UK, Rijeka: IntechOpen; 2018

[2] De Leo F, Marchetta A, Capillo G, Germanà A, Primerano P, Schiavo SL, et al. Surface active ionic liquids based coatings as subaerial anti-biofilms for stone built cultural heritage. Coatings. 2021;**11**:26. DOI: 10.3390/coatings11010026

[3] Chobba MB, Weththimuni ML, Messaoud M, Bouaziz J, Licchelli M. Enhanced Gd doped TiO_2 NPs-PDMS nanocomposites as protective coatings for bio-calcarenite stone: Preliminarily analysis. In: Walha L, Jarraya A, Djemal F, Chouchane M, Aifaoui N, Chaari F, Abdennadher M, Benamara A, Haddar M, editors. Design and Modeling of Mechanical Systems - V. Cham: Springer International Publishing; 2023. pp. 885-893. DOI: 10.1007/978-3-031-14615-2_99

[4] Balliana E, Ricci G, Pesce C, Zendri E. Assessing the value of green conservation forcultural heritage: Positive and critical aspects ofalready available methodologies. International Journal of Conservation Science. 2015;**7**:185-202

[5] Sanmartín P, Cappitelli F, Mitchell R. Current methods of graffiti removal: A review. Construction and Building Materials. 2014;**71**:363-374

[6] Alfano G, Lustrato G, Belli C, Zanardini E, Cappitelli F, Mello E, et al. The bioremoval of nitrate and sulfate alterations on artistic stonework: The case-study of Matera Cathedral after six years from the treatment. International Biodeterioration and Biodegradation. 2011;**65**:1004-1011

[7] Tang QH, Zhou D, Wang YL, Liu GF. Laser cleaning of sulfide scale on compressor impeller blade. Applied Surface Science. 2015;**355**:334-340. DOI: 10.1016/j.apsusc.2015.07.128

[8] Kolar J, Strlič M, Müller-Hess D, Gruber A, Troschke K, Pentzien S, et al. Laser cleaning of paper using Nd:YAG laser running at 532 nm. Journal of Cultural Heritage. 2003;**4**:185-187. DOI: 10.1016/S1296-2074(02)01196-2

[9] Sabatini G, Giamello M, Pini R, Siano S, Salimbeni R. Laser cleaning methodologies for stone façades and monuments: Laboratory analyses on lithotypes of Siena architecture. Journal of Cultural Heritage. 2000;**1**:S9-S19. DOI: 10.1016/S1296-2074(00)00144-8

[10] Staicu A, Apostol I, Pascu A, Urzica I, Pascu ML, Damian V. Minimal invasive control of paintings cleaning by LIBS. Optics and Laser Technology. 2016;**77**:187-192. DOI: 10.1016/j.optlastec.2015.09.010

[11] Gaetani C, Santamaria U. The laser cleaning of wall paintings. Journal of Cultural Heritage. 2000;**1**:S199-S207. DOI: 10.1016/S1296-2074(00)00137-0

[12] Licchelli M, Malagodi M, Weththimuni ML, Zanchi C. Water-repellent properties of fluoroelastomers on a very porous stone: Effect of the application procedure. Progress in Organic Coating. 2013;**76**:495-503. DOI: 10.1016/j.porgcoat.2012.11.005

[13] Weththimuni M, Crivelli F, Galimberti C, Malagodi M, Licchelli M.

Evaluation of commercial consolidating agents on very porous biocalcarenite. International Journal of Conservation Science. 2020;**11**:251-260

[14] Ocak Y, Sofuoglu A, Tihminlioglu F, Böke H. Protection of marble surfaces by using biodegradable polymers as coating agent. Progress in Organic Coating. 2009;**66**:213-220. DOI: 10.1016/j.porgcoat.2009.07.007

[15] Domingues JAL, Bonelli N, Giorgi R, Fratini E, Gorel F, Baglioni P. Innovative hydrogels based on semi-interpenetrating p(HEMA)/PVP networks for the cleaning of water-sensitive cultural heritage artifacts. Langmuir. 2013;**29**:2746-2755. DOI: 10.1021/la3048664

[16] Baglioni P, Giorgi R, Dei L. Soft condensed matter for the conservation of cultural heritage. Comptes Rendus Chimie. 2009;**12**:61-69. DOI: 10.1016/j.crci.2008.05.017

[17] Greer AJ, Jacquemin J, Hardacre C. Industrial Applications of Ionic Liquids. Molecules. 2020;**25**:5207. DOI: 10.3390/molecules25215207

[18] Sierra-Fernandez A, Gomez-Villalba L, Rabanal M, Fort R. New nanomaterials for applications in conservation and restoration of stony materials: A review. Materiales de Construcción. 2017;**67**:107. DOI: 10.3989/mc.2017.07616

[19] Baglioni P, Carretti E, Chelazzi D. Nanomaterials in art conservation. Nature Nanotechnology. 2015;**10**:287-290. DOI: 10.1038/nnano.2015.38

[20] Baglioni P, Berti D, Bonini M, Carretti E, Dei L, Fratini E, et al. Micelle, microemulsions, and gels for the conservation of cultural heritage. Advances in Colloid and Interface Science. 2014;**205**:361-371. DOI: 10.1016/j.cis.2013.09.008

[21] Ion R-M, Doncea S-M, Caruțiu DȚ. Nanotechnologies in cultural heritage - Materials and instruments for diagnosis and treatment. In: Kyzas GZ, Mitropoulos AC, editors. Novel Nanomaterials. London, UK, Rijeka: IntechOpen; 2017. DOI: 10.5772/intechopen.71950

[22] Licchelli M, Malagodi M, Weththimuni M, Zanchi C. Nanoparticles for conservation of bio-calcarenite stone. Applied Physics A. 2014;**114**:673-683. DOI: 10.1007/s00339-013-7973-z

[23] Poggi G, Toccafondi N, Melita LN, Knowles JC, Bozec L, Giorgi R, et al. Calcium hydroxide nanoparticles for the conservation of cultural heritage: New formulations for the deacidification of cellulose-based artifacts. Applied Physics A. 2014;**114**:685-693. DOI: 10.1007/s00339-013-8172-7

[24] López-Arce P, Gómez-Villalba LS, Martínez-Ramírez S, de Buergo MÁ, Fort R. Influence of relative humidity on the carbonation of calcium hydroxide nanoparticles and the formation of calcium carbonate polymorphs. Powder Technology. 2011;**205**:263-269. DOI: 10.1016/j.powtec.2010.09.026

[25] Baglioni P, Giorgi R. Soft and hard nanomaterials for restoration and conservation of cultural heritage. Soft Matter. 2006;**2**:293-303. DOI: 10.1039/B516442G

[26] Saoud K, Saeed S, Soubaih R, Samara A, Ibala I, Ladki D, et al. Application of $Mg(OH)_2$ nanosheets for conservation and restoration of precious documents and cultural archives. Bioresources. 2018;**13**:3259-3274. DOI: 10.15376/biores.13.2.3259.3274

[27] Karatasios I, Kilikoglou V, Colston B, Theoulakis P, Watt D. Setting process of lime-based conservation mortars with barium hydroxide. Cement and Concrete Research. 2007;**37**:886-893. DOI: 10.1016/j.cemconres.2007.03.007

[28] Rodrigues JD, Pinto APF. Laboratory and onsite study of barium hydroxide as a consolidant for high porosity limestones. Journal of Cultural Heritage. 2016;**19**:467-476. DOI: 10.1016/j.culher.2015.10.002

[29] Ciliberto E, Condorelli GG, La Delfa S, Viscuso E. Nanoparticles of Sr(OH)2: Synthesis in homogeneous phase at low temperature and application for cultural heritage artefacts. Applied Physics A. 2008;**92**:137-141. DOI: 10.1007/s00339-008-4464-8

[30] Aggarwal P, Singh RP, Aggarwal Y. Use of nano-silica in cement based materials—A review. Cogent Engineering. 2015;**2**:1078018 https://doi.org/10.1080/23311916.2015.1078018

[31] Miliani C, Velo-Simpson ML, Scherer GW. Particle-modified consolidants: A study on the effect of particles on sol–gel properties and consolidation effectiveness. Journal of Cultural Heritage. 2007;**8**:1-6. DOI: 10.1016/j.culher.2006.10.002

[32] Verganelaki A, Kilikoglou V, Karatasios I, Maravelaki-Kalaitzaki P. A biomimetic approach to strengthen and protect construction materials with a novel calcium-oxalate–silica nanocomposite. Construction and Building Materials. 2014;**62**:8-17. DOI: 10.1016/j.conbuildmat.2014.01.079

[33] Chobba MB, Weththimuni ML, Messaoud M, Urzi C, Bouaziz J, Leo FD, et al. Ag-TiO2/PDMS nanocomposite protective coatings: Synthesis, characterization, and use as a self-cleaning and antimicrobial agent. Progress in Organic Coating. 2021;**158**:106342. DOI: 10.1016/j.porgcoat.2021.106342

[34] Chobba MB, Weththimuni ML, Messaoud M, Sacchi D, Bouaziz J, De Leo F, et al. Multifunctional and durable coatings for stone protection based on Gd-doped nanocomposites. Sustainability. 2021;**13**:11033. DOI: 10.3390/su131911033

[35] Weththimuni M, Ben Chobba M, Tredici I, Licchelli M. ZrO2-doped ZnO-PDMS nanocomposites as protective coatings for the stone materials. ACTA IMEKO. 2022;**11**:5. DOI: 10.21014/acta_imeko.v11i1.1078

[36] Weththimuni ML, Chobba MB, Sacchi D, Messaoud M, Licchelli M. Durable polymer coatings: A comparative study of PDMS-based nanocomposites as protective coatings for stone materials. Chemistry. 2022;**4**:60-76. DOI: 10.3390/chemistry4010006

[37] Cinteză LO, Tănase MA. Multifunctional ZnO nanoparticle: Based coatings for cultural heritage preventive conservation. In: Ares AE, editor. Thin Films. London, UK, Rijeka: IntechOpen; 2020. DOI: 10.5772/intechopen.94070

[38] Luna M, Gatica JM, Vidal H, Mosquera MJ. Use of Au/N-TiO2/SiO2 photocatalysts in building materials with NO depolluting activity. Journal of Cleaner Production. 2020;**243**:118633. DOI: 10.1016/j.jclepro.2019.118633

[39] Kapridaki C, Xynidis N, Vazgiouraki E, Kallithrakas-Kontos N, Maravelaki-Kalaitzaki P. Characterization of photoactive Fe-TiO_2 lime coatings for building protection: The role of iron content. Materials. 2019;**12**:1847. DOI: 10.3390/ma12111847

[40] Ben Chobba M, Messaoud M, Bouaziz J, De Leo F, Urzì C. The effect of heat treatment on photocatalytic performance and antibacterial activity of TiO_2 nanoparticles prepared by sol-gel method. In: Chaari F, Barkallah M, Bouguecha A, Zouari B, Khabou MT, Kchaou M, Haddar M, editors. Advances in Materials, Mechanics and Manufacturing. Cham: Springer International Publishing; 2020. pp. 71-79. DOI: 10.1007/978-3-030-24247-3_9

[41] Aziz AA, Cheng CK, Ibrahim S, Matheswaran M, Saravanan P. Visible light improved, photocatalytic activity of magnetically separable titania nanocomposite. Chemical Engineering Journal. 2012;**183**:349-356. DOI: 10.1016/j.cej.2012.01.006

[42] Colangiuli D, Calia A, Bianco N. Novel multifunctional coatings with photocatalytic and hydrophobic properties for the preservation of the stone building heritage. Construction and Building Materials. 2015;**93**:189-196. DOI: 10.1016/j.conbuildmat.2015.05.100

[43] Ben Chobba M, Weththimuni ML, Messaoud M, Bouaziz J, Salhi R, De Leo F, et al. Silver-doped TiO_2-PDMS nanocomposite as a possible coating for the preservation of serena stone: Searching for optimal application conditions. Heritage. 2022;**5**:3411-3426. DOI: 10.3390/heritage5040175

[44] La Russa MF, Ruffolo SA, Belfiore CM, Aloise P, Randazzo L, Rovella N, et al. Study of the effects of salt crystallization on degradation of limestone rocks. Periodico Di Mineralogia. 2013;**82**:113-127. DOI: 10.2451/2013PM0007

[45] Ricca M, Le Pera E, Licchelli M, Macchia A, Malagodi M, Randazzo L, et al. The CRATI Project: New Insights on the Consolidation of Salt Weathered Stone and the Case Study of San Domenico Church in Cosenza (South Calabria, Italy). Coatings. 2019;**9**:330. DOI: 10.3390/coatings9050330

[46] Martins L, Vasconcelos G, Lourenco P, Palha C. Influence of the freeze-thaw cycles on the physical and mechanical properties of granites. Journal of Materials in Civil Engineering. 2015;**28**:04015201. DOI: 10.1061/(ASCE)MT.1943-5533.0001488

[47] Abd El-Aal A. Climate change and its impact on monumental and historical buildings towards conservation and documentation Ammon temple, Siwa Oasis, Egypt. Journal of Earth Science & Climatic Change. 2016;**7**. DOI: 10.4172/2157-7617.1000339

[48] Stryszewska T, Kańka S. Forms of damage of bricks subjected to cyclic freezing and thawing in actual conditions. Materials. 2019;**12**:1165. DOI: 10.3390/ma12071165

[49] Belfiore CM, La Russa MF, Pezzino A, Campani E, Casoli A. The Baroque monuments of Modica (Eastern Sicily): Assessment of causes of chromatic alteration of stone building materials. Applied Physics A. 2010;**100**:835-844. DOI: 10.1007/s00339-010-5659-3

[50] Weththimuni ML, Licchelli M, Malagodi M, Rovella N, Russa ML. Consolidation of bio-calcarenite stone by treatment based on diammonium hydrogenphosphate and calcium hydroxide nanoparticles. Measurement. 2018;**127**:396-405. DOI: 10.1016/j.measurement.2018.06.007

[51] Scherer GW. Stress from crystallization of salt. Cement and Concrete Research. 2004;**34**:1613-1624. DOI: 10.1016/j.cemconres.2003.12.034

[52] De Leo F, Marchetta A, Urzì C. Black fungi on stone-built heritage: Current knowledge and future outlook. Applied Sciences. 2022;**12**:3969. DOI: 10.3390/app12083969

[53] Abdelhafez AAM, El-Wekeel FM, Ramadan EM, Abed-Allah AA. Microbial deterioration of archaeological marble: Identification and treatment. Annals of Agricultural Science. 2012;**57**:137-144. DOI: 10.1016/j.aoas.2012.08.007

[54] Čavka M, Glasnović A, Janković I, Sikanjic P, Perić B, Brkljacic B, et al. Microbiological analysis of a Mummy from the archeological Museum in Zagreb. Collegium Antropologicum. 2010;**34**:803-805

[55] Doronina N, Li T, Ivanova E, Trotsenko I. Methylophaga murata sp. nov.: A Haloalkaliphilic aerobic methylotroph from deteriorating marble. Mikrobiologiia. 2005;**74**:511-519

[56] Pangallo D, Kraková L, Chovanová K, Šimonovičová A, De Leo F, Urzì C. Analysis and comparison of the microflora isolated from fresco surface and from surrounding air environment through molecular and biodegradative assays. World Journal of Microbiology and Biotechnology. 2012;**28**:2015-2027. DOI: 10.1007/s11274-012-1004-7

[57] De Leo F, Iero A, Zammit G, Urzì C. Chemoorganotrophic bacteria isolated from biodeteriorated surfaces in cave and catacombs. International Journal of Speleology. 2012;**41**:1-12. DOI: 10.5038/1827-806X.41.2.1

[58] Macedo M, Miller A, Dionísio A, Saiz-Jimenez C. Biodiversity of cyanobacteria and green algae on monuments in the Mediterranean Basin: An overview. Microbiology (Reading, England). 2009;**155**:3476-3490

[59] Bastian F, Alabouvette C. Lights and shadows on the conservation of a rock art cave: The case of Lascaux Cave. International Journal of Speleology. 2009;**38**

[60] Milanesi C, Baldi F, Borin S, Vignani R, Ciampolini F, Faleri C, et al. Biodeterioration of a fresco by biofilm forming bacteria. International Biodeterioration and Biodegradation. 2006;**57**:168-173. DOI: 10.1016/j.ibiod.2006.02.005

[61] Sterflinger K, Piñar G. Microbial deterioration of cultural heritage and works of art — tilting at windmills? Applied Microbiology and Biotechnology. 2013;**97**:9637-9646. DOI: 10.1007/s00253-013-5283-1

[62] Lamprinou V, Mammali M, Katsifas EA, Pantazidou AI, Karagouni AD. Phenotypic and molecular biological characterization of cyanobacteria from marble surfaces of treated and untreated sites of propylaea (Acropolis, Athens). Geomicrobiology Journal. 2013;**30**:371-378. DOI: 10.1080/01490451.2012.690021

[63] Bertolin C. Preservation of cultural heritage and resources threatened by climate change. Geosciences. 2019;**9**:250. DOI: 10.3390/geosciences9060250

[64] Sesana E, Gagnon A, Ciantelli C, Cassar J, Hughes J. Climate change impacts on cultural heritage: A literature review. WIREs Climate Change. 2021;**12**. DOI: 10.1002/wcc.710

[65] UNESCO World Heritage Centre. Climate Change and World Heritage. Report on Predicting and Managing the Impacts of Climate Change on World Heritage and Strategy to Assist States Parties to Implement Appropriate Management Responses. Paris, France: UNESCO; 2007

[66] Zhang X-F, Liu Z-G, Shen W, Gurunathan S. Silver nanoparticles: Synthesis, characterization, properties, applications, and therapeutic approaches. International Journal of Molecular Sciences. 2016;**17**:1534. DOI: 10.3390/ijms17091534

[67] Kale SK, Parishwad GV, Patil AS. Emerging agriculture applications of silver nanoparticles. ES Food & Agroforestry. 2021;**3**:17-22

[68] Jaskulski D, Jaskulska I, Majewska J, Radziemska M, Bilgin A, Brtnicky M. Silver nanoparticles (AgNPs) in urea solution in laboratory tests and field experiments with crops and vegetables. Materials. 2022;**15**:870. DOI: 10.3390/ma15030870

[69] Sondi I, Salopek-Sondi B. Silver nanoparticles as antimicrobial agent: A case study on E. coli as a model for Gram-negative bacteria. Journal of Colloid and Interface Science. 2004;**275**:177-182. DOI: 10.1016/j.jcis.2004.02.012

[70] Yamanaka M, Hara K, Kudo J. Bactericidal actions of a silver ion solution on *Escherichia coli*, studied by energy-filtering transmission electron microscopy and proteomic analysis. Applied and Environmental Microbiology. 2005;**71**:7589-7593. DOI: 10.1128/AEM.71.11.7589-7593.2005

[71] Choi O, Hu Z. Size dependent and reactive oxygen species related nanosilver toxicity to nitrifying bacteria. Environmental Science & Technology. 2008;**42**:4583-4588. DOI: 10.1021/es703238h

[72] Rai M, Yadav A, Gade A. Silver nanoparticles as a new generation of antimicrobials. Biotechnology Advances. 2009;**27**:76-83. DOI: 10.1016/j.biotechadv.2008.09.002

[73] Bruna T, Maldonado-Bravo F, Jara P, Caro N. Silver nanoparticles and their antibacterial applications. International Journal of Molecular Sciences. 2021;**22**:7202. DOI 10.3390/ijms22137202

[74] Gutarowska B, Skora J, Zduniak K, Rembisz D. Analysis of the sensitivity of microorganisms contaminating museums and archives to silver nanoparticles. International Biodeterioration and Biodegradation. 2012;**68**:7-17. DOI: 10.1016/j.ibiod.2011.12.002

[75] Gutarowska B, Rembisz D, Zduniak K, Skóra J, Szynkowska M, Gliścińska E, et al. Optimization and application of the misting method with silver nanoparticles for disinfection of the historical objects. International Biodeterioration and Biodegradation. 2012;**75**:167-175. DOI: 10.1016/j.ibiod.2012.10.002

[76] Bellissima F, Bonini M, Giorgi R, Baglioni P, Barresi G, Mastromei G, et al. Antibacterial activity of silver nanoparticles grafted on stone surface. Environmental Science and Pollution Research. 2014;**21**:13278-13286. DOI: 10.1007/s11356-013-2215-7

[77] Essa AMM, Khallaf MK. Biological nanosilver particles for the protection of archaeological stones against microbial colonization. International Biodeterioration and Biodegradation. 2014;**94**:31-37. DOI: 10.1016/j.ibiod.2014.06.015

[78] MacMullen J, Zhang Z, Dhakal HN, Radulovic J, Karabela A, Tozzi G, et al. Silver nanoparticulate enhanced aqueous silane/siloxane exterior facade emulsions and their efficacy against algae and cyanobacteria biofouling. International Biodeterioration and Biodegradation. 2014;**93**:54-62. DOI: 10.1016/j.ibiod.2014.05.009

[79] Carrillo-González R, Martínez-Gómez MA. Inhibition of microorganisms involved in deterioration of an archaeological site by silver nanoparticles produced by a green synthesis method. Science of The Total Environment. 2016;**565**:872-881

[80] Pietrzak K, Otlewska A, Danielewicz D, Dybka K, Pangallo D, Kraková L, et al. Disinfection of archival documents using thyme essential oil, silver nanoparticles misting and low temperature plasma. Journal of Cultural Heritage. 2017;**24**:69-77. DOI: 10.1016/j.culher.2016.10.011

[81] Pietrzak K, Puchalski M, Otlewska A, Wrzosek H, Guiamet P, Piotrowska M, et al. Microbial diversity of pre-Columbian archaeological textiles and the effect of silver nanoparticles misting disinfection. Journal of Cultural Heritage. 2017;**23**:138-147. DOI: 10.1016/j.culher.2016.07.007

[82] Pietrzak K, Otlewska A, Puchalski M, Gutarowska B, Patricia G. Antimicrobial properties of silver nanoparticles against biofilm formation by Pseudomonas aeruginosa on archaeological textiles. Applied Environmental Biotechnology. 2016;**1**:1. DOI: 10.18063/AEB.2016.02.001

[83] Nowicka-Krawczyk P, Zelazna-Wieczorek J, Koźlecki T. Silver nanoparticles as a control agent against facades coated by aerial algae—A model study of Apatococcus lobatus (green algae). PLoS One. 2017;**12**:e0183276. DOI: 10.1371/journal.pone.0183276

[84] Li Z, Wang Z, Khan J, LaGasse MK, Suslick KS. Ultrasensitive monitoring of museum airborne pollutants using a silver nanoparticle sensor array. ACS Sensors. 2020;**5**:2783-2791. DOI: 10.1021/acssensors.0c00583

[85] Aflori M, Simionescu B, Bordianu I-E, Sacarescu L, Varganici C-D, Doroftei F, et al. Silsesquioxane-based hybrid nanocomposites with methacrylate units containing titania and/or silver nanoparticles as antibacterial/antifungal coatings for monumental stones. Materials Science and Engineering B. 2013;**178**:1339-1346. DOI: 10.1016/j.mseb.2013.04.004

[86] Pinho L, Rojas M, Mosquera MJ. Ag–SiO_2–TiO_2 nanocomposite coatings with enhanced photoactivity for self-cleaning application on building materials. Applied Catalysis B: Environmental. 2015;**178**:144-154. DOI: 10.1016/j.apcatb.2014.10.002

[87] NORMAL 20/85. Interventi conservativi: progettazione esecuzione e valutazione preventiva, Milan, Italy. 1996

[88] Graziani L, Quagliarini E, D’Orazio M. The role of roughness and porosity on the self-cleaning and anti-biofouling efficiency of TiO2-Cu and TiO2-Ag nanocoatings applied on fired bricks. Construction and Building Materials. 2016;**129**:116-124. DOI: 10.1016/j.conbuildmat.2016.10.111

[89] Becerra J, Zaderenko AP, Sayagués MJ, Ortiz R, Ortiz P. Synergy achieved in silver-TiO2 nanocomposites for the inhibition of biofouling on limestone. Building and Environment. 2018;**141**:80-90. DOI: 10.1016/j.buildenv.2018.05.020

[90] Zarzuela R, Carbú M, Gil MLA, Cantoral J, Mosquera M. Ormosils loaded with SiO_2NPs functionalized with Ag as multifunctional superhydrophobic/biocidal/consolidant treatments for buildings conservation. Nanotechnology. 2019;**30**:345701. DOI: 10.1088/1361-6528/ab1ff0

[91] Domínguez M, Zarzuela R, Moreno-Garrido I, Carbú M,

Cantoral JM, Mosquera MJ, et al. Antifouling nano-Ag/SiO2 ormosil treatments for building materials: The role of cell-surface interactions on toxicity and bioreceptivity. Progress in Organic Coating. 2021;**153**:106120. DOI: 10.1016/j.porgcoat.2020.106120

[92] Zarzuela R, Moreno-Garrido I, Gil MLA, Mosquera MJ. Effects of surface functionalization with alkylalkoxysilanes on the structure, visible light photoactivity and biocidal performance of Ag-TiO2 nanoparticles. Powder Technology. 2021;**383**:381-395. DOI: 10.1016/j.powtec.2021.01.050

[93] Zarzuela R, Carbú M, Gil A, Cantoral J, Mosquera MJ. Incorporation of functionalized Ag-TiO2NPs to ormosil-based coatings as multifunctional biocide, superhydrophobic and photocatalytic surface treatments for porous ceramic materials. Surfaces and Interfaces. 2021;**25**:101257. DOI: 10.1016/j.surfin.2021.101257

[94] Kainourgios P, Tziveleka L-A, Kartsonakis IA, Ioannou E, Roussis V, Charitidis CA. Silver nanoparticles grown on cross-linked poly (methacrylic acid) microspheres: Synthesis, characterization, and antifungal activity evaluation. Chemosensors. 2021;**9**:152. DOI: 10.3390/chemosensors9070152

[95] Oliveira MJA, Otubo L, Pires A, Brambilla RF, Carvalho AC, Santos PS, et al. Silver nanoparticles-based hydrogels synthetized by ionizing radiation for cleaning of tangible cultural heritage surfaces. Radiation Physics and Chemistry. 2022;**199**:110345. DOI: 10.1016/j.radphyschem.2022.110345

[96] Reyes-Estebanez M, Morales O, Chan M, Granados-Echegoyen C, Camacho-Chab J, Pereañez Sacarias J, et al. Antimicrobial engineered nanoparticles in the built cultural heritage context and their ecotoxicological impact on animals and plants: A brief review. Heritage Science. 2018;**6**

[97] Zhang L, Li J, Yang K, Liu J, Lin D. Physicochemical transformation and algal toxicity of engineered nanoparticles in surface water samples. Environmental Pollution. 2016;**211**:132-140. DOI: 10.1016/j.envpol.2015.12.041

[98] Franco-Castillo I, Hierro L, de la Fuente JM, Seral-Ascaso A, Mitchell SG. Perspectives for antimicrobial nanomaterials in cultural heritage conservation. Chem. 2021;**7**:629-669. DOI: 10.1016/j.chempr.2021.01.006

[99] de Gannes V, Hickey, WJ. Genetic Adaptations of Bacteria for Metabolism of Polycyclic Aromatic Hydrocarbons. In: Cravo-Laureau C, Cagnon C, Lauga B, Duran R, editors. Microbial Ecotoxicology. Cham: Springer; 2017. pp 133-164. DOI: 10.1007/978-3-319-61795-4_7