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ASSESSING THE VALUE OF GREEN CONSERVATION FOR CULTURAL HERITAGE: POSITIVE AND CRITICAL ASPECTS OF ALREADY AVAILABLE METHODOLOGIES

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Abstract

In recent years, the use and the necessity of green materials and methodologies have been promoted in the field of cultural heritage, aiming to a low impact on the operator health and the environment. For a long time, in restoration and conservation science, the main goal was searching for the most compatible solutions with the materials of the artefacts not thinking sometimes about the possible issues for the operator and/or for the environment. Recently, thanks also to an increasing attention to a respectful consumption of environmental resources and waste management, new scientific methodologies have been proposed for more sustainable and green interventions, promoting furthermore the concept of preventive conservation. The aim of this work is to present an overview about some of the most interesting technologies and methodologies already available as alternative to traditional and more invasive/dangerous restoration treatments towards artefact, operators and environment. In particular, the methods described in this paper have been critically analysed focusing on which might be the positive and negative points considering the convenience of use by the restorers and the reasons why these methods are still not well known and diffused.

Keywords: *Eco-compatibility; Cultural heritage; Risk-assessment; Human health.*

Introduction

Conservation and restoration of cultural heritage is a challenging field, often difficult to approach due to many peculiarities and necessities. Despite the increase of research being developed concerning cultural heritage, most of the available and commonly used products and methodologies have been borrowed from other fields and are often adapted considering specific and crucial requirements of preservation, such as effectiveness, compatibility, etc.

Unfortunately, main efforts are focused on "the health" of the artefacts and scarce attention is given to other aspects, such as the toxicological risks, the restorers themselves, the environment and waste disposal. Only in the last few years there has been an increasing demand for the substitution of commonly used, out-of-date and high-risk products (e.g. white spirit, xylene, etc. [1]), with safer alternative compounds and protocols, thanks to national legislations and international regulations. Nowadays, it is essential to meet the demands of the cultural heritage field with ecological, economic and social aspects.

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"Quale sostenibilità per il restauro?", "Restauro sostenibile 2.0" and "Green Conservation of Cultural Heritage" [2, 3] are examples of conferences, where the necessity of green and sustainable alternatives for the cultural heritage field has been highlighted and discussed. Up until now, few universities and research centres have focused their efforts on developing new green methodologies for the restoration field, thanks to specific research projects [4, 5].

One of the main problems concerns the accessibility of new products to restorers, in line with newly proposed green solutions and methodologies. Moreover, the use of green and sustainable solutions, though potentially effective, needs specialised professional and specific testing before they can be used safely within the cultural heritage field.

Another crucial aspect that impedes the use of innovative products and methodologies, is the off-target dissemination of information; the results of these studies are often published in specific journals that are not always aimed at restorers (i.e. Journal of colloid and interface, Microchemical Journal, Analytica Chimica Acta, Polymer Degradation and Stability).

In order to promote a green approach to the conservation of cultural heritage, we believe that attention should be given not only to the products used, but in particular to all the phases that characterise a restoration project. Aspects such as waste disposal, the Life Cycle Assessment (LCA) of the products, impact of the intervention on society and the economy, etc. should also be considered for a complete, holistic "green restoration". In this sense, a close collaboration between operators, companies, and researchers is fundamental for proposing up-to-date solutions and to promote economic investments for the research on cultural heritage.

The aim of this paper is to briefly present, evaluate and critically analyse some of the available green and sustainable products and methodologies for cleaning, consolidation and protection operations within cultural heritage application. Additionally, environmental and operational risk-assessment, compatibility with artworks and commercial availability will all be further presented and discussed.

Cleaning

Cleaning is commonly considered the most critical and time-expensive operation in a restoration project, mainly due to its irreversibility, the difficulty in defining the cleaning level and the possibility of damaging the artwork [6].

Traditionally, solvents, both aromatic and non-aromatic, and other cleaning products (i.e. chelating agents, mild and strong acids and bases) are largely used within the conservation field and are applied on several different materials such as paintings, stones, wall-paintings, etc. Despite their toxicity, due to their efficiency and fast-action, these products are still preferred by restorers as they are often less expensive and better established [7, 8]. For instance, common commercial products based on N-methylpirrolidone, dichloromethane, phenolic solvents or chlorinate, are still used nowadays to remove graffiti from historic walls, despite being banned or their use restricted by REACH regulation [9].

Recently, alternative products and methodologies have been developed and proposed to avoid and limit the use of toxic solvents, in particular for the removal of old and degraded polymeric treatments. Some examples and applications of microemulsion, biocleaning, ionic liquids, laser cleaning and gels are reported below as the most promising green and sustainable cleaning methods.

Microemulsions

Microemulsions have been applied as cleaning agents mainly on wall-paintings [10-12] and stones [13], thanks to their controllability and transparency. Microemulsions can be considered green as they require a small amount of solvent, thus reducing their toxicity and environmental impact.

A microemulsion composed of dimethyldodecane-1-amine oxide (DDAO) and diethyl carbonate (DC) dispersed in water, is given by Baglioni et al. [14] for the removal of deteriorated polymers on wall-paintings. The DDAO is a surfactant characterized by good biodegradability and eco-compatibility, suitable for application in cultural heritage conservation. Laboratory testing and in situ application of the DDAO-DC system demonstrates its efficiency in removing the aged polymeric layer of nitrocellulose, acrylic polymers and soluble salts. Take for example the tests performed on the wall-paintings of the Mayan archaeological site in Tulum, Mexico, [14] where the altered coatings were removed with no mechanical actions respecting the fragile structure of the artwork. Furthermore, the microemulsion system is poorly absorbed on the substrate leaving no residues after cleaning treatment, is easy to use and not affected by the possible presence of divalent metal ions, often existent on wall-paintings. The main drawback of DDAO-DC formulations, as of other microemulsions, [15] is the fact that they are not yet commercially available for the restoration field as ready-to-use solutions. Moreover, a diffused and common application of these new products is limited because a vast majority of research and results are published only in specific journals that may not reach restorers.

Biocleaning

Biocleaning is a biological and sustainable alternative to traditional chemical and mechanical cleaning of artworks. Despite the fact that microorganisms are commonly associated with negative effects on the durability of cultural heritage materials, it has been proved that selected microorganisms can be used as cleaning agents on mural paintings, stone surfaces, paintings, paper [16, 17]. Recently, the use of microorganisms for cleaning purposes has been successfully tested on undesirable substances, often present on artwork's surfaces, such as soluble salts (nitrates, sulphates), natural and artificial polymers and coatings, graffiti, etc. [18-24].

An example of biocleaning application on cultural heritage is given by Gioventù et al. [25], where the bacteria *Desulfovibrio vulgaris* is applied as a cleaning agent to remove black crust from marble surfaces. The cleaning test, performed on a sample of Carrara marble from a balcony of the Florence Cathedral, demonstrates its high efficiency in comparison to traditional methods, allowing a more homogeneous, gradual and controllable action, whilst avoiding the risk of damaging the original substrate. The great versatility of biocleaning is further clarified in the case presented by Mazzoni et al. [20] for the removal of deposits composed of inorganic compounds and a protein layer at the loggia of Casina Farnese in Rome. Three strains of bacteria, applied with laponite compress, were selected in order to solubilise phosphates (*Pseudomonas koreensis*), sulphates and carbonates (*Cellulosmicrobium cellulans*) and proteins (*Stenotrophomonas maltophilia*). Bacteria and laponite contributed synergistically to the removal of the patinas: the former solubilising the material through metabolic activities; the latter humidifying and softening the layers of material to be removed. A complete, gradual and non-invasive removal of the undesired layers was obtained with high selectivity, sustainability and the safety of the operators and environment.

In terms of operating costs, an analysis made by Lustrato et al. [26] underlined the fact that there is no economic advantage of using traditional chemical methods. Moreover, chemical methods can only be used when the layer to remove is thick, otherwise there is the risk of damaging the original substrate. On the contrary, biocleaning is able to act in advance and in a preventive way, due to its high-level controllability.

In prospect of implementing a marketable and routine application of biological restoration, the main difficulties to overcome are: how to keep the microorganisms alive as they need specific growing conditions; the need of specialized personnel and the realization of a ready-to-use kit for restorers.

Ionic liquids

In recent years, ionic liquids (ILs) have attracted significant interest and have been used for many applications in different field such as electrochemistry, solvent and metals extraction, etc. [27-32]. ILs are liquids composed solely of cations and anions. The great interest in ILs is mainly due to their promising and unique characteristics, such as extremely low-vapour pressure, non-flammability, good thermal stability, etc [27]. By changing the combination of cations and anions, properties like viscosity, acidity/basicity and melting temperature can be tuned in order to meet specific demands. This makes ionic liquids attractive as valuable substitutes for dangerous cleaning methods in the conservation of artworks.

The primary applications of ILs, as a green alternative in the field of cultural heritage, are assessed by Pacheco et al. [32] and by Hrdlickova Kuckova et al. [33]. Throughout the studies, a range of different pure and ionic liquids were tested for the removal of common natural and artificial resins on easel paintings. Pacheco et al. use ILs for the removal of Dammar as natural resin, poly(vinyl acetate) and cyclohexanone as synthetic resins. Twelve available ILs are selected according to their commercial availability, polarity and miscibility with solvents of low toxicity (e.g. ethanol), etc. Analysis shows that after the application of ILs, the surface morphology is similar to the original unvarnished one, proving the effectiveness of the operation. Nevertheless, in most cases, the presence of ionic liquid residue has been observed. Hrdlickova Kuckova tests the use of two different, commercially available ILs, in combination with an acidic enzyme (pepsine) and an alkaline enzyme (form *Aspergillum soiae*) for the removal of proteinaceous materials from painted surfaces. The enzymes are selected according to their stability and optimal performance in the different pH range. The different combination of ILs and enzymes gives good results in terms of selectivity, cleaning action and compatibility. In particular, above all the tested mixtures, the formulations based on IL 1-butyl-3-methylimidazolium fluoride-boron trifluoride ([bmim][BF4]) give the best results in removing the natural aged varnishes. The effectiveness of [bmim][BF4] is significant because this ionic liquid is the most commonly used in green chemistry and its properties have been studied in detail [27, 34-37].

The advantages of using ionic liquids are related to their versatility and selectivity. When comparing to traditional solvents, the main drawback concerns cost, as ILs have only become commercially available recently [27]. Furthermore, in terms of compatibility, the residues of ionic liquids do not leave the surface easily, due to their low vapour pressure, and therefore could interact with the substrate or promote degradation processes. Thirdly, ionic liquids have only ever been tested on laboratory specimens, whilst it is fundamental to test them on real artworks, where the nature of the deposit to be removed could be unknown or highly altered. Ionic liquids are promising, however still far from being widely used for restoration purposes. Further studies regarding solubility parameters, kinetics of degradation and compatibility with traditional art materials are therefore necessary.

Laser

Laser has been used as a selective and environmentally friendly technique for cleaning, due to its ability to neither alter or effect the artefact’s surface on a variety of materials, such as wood [38], metal [39], paper [40], stone [41], easel paintings [42] and wall paintings [43]. Further details about laser systems and parameters used within the restoration field are reported within literature [44-46].

The first applications of laser techniques for cleaning purposes, dates back to the late 60s and 70s where ink imprints were removed from paper [47], followed shortly by the intervention on the marble sculptures of Santa Caterina Church and Palazzo Ducale in Venice [48, 49]. From then on, owing to technological advances, further applications and thus a more extensive use of laser as a cleaning technique has been made within the field of cultural heritage. Nowadays, laser cleaning is considered to be a well-established and sustainable cleaning technique as it involves material selectivity and precision, preservation of the underlying substrate, self-controlled action, immediate feedback, does not involve mechanical contact or abrasion of the substrate, etc. [50, 51]. Furthermore, laser cleaning has been combined with other laser techniques, such as Laser Induced Breakdown Spectroscopy (LIBS), to spectroscopically characterise the material surface before, during and after the ablation, in order to improve and have better control over the cleaning process [52].

Laser cleaning can be considered a common alternative to traditional organic solvents for the removal of graffiti from historical buildings [8, 53-55]. For example, Ortiz et al. [56] compares laser techniques to pressurized water and chemical methods, for the removal of different types of spray and markers from a dolomitic white marble. Test results show that the chemical methods and the laser ablation always yield similar cleaning effects. However, the laser seems to be more compatible with the materials and does not cause penetration of the dissolved paints. The authors, however, underline the main drawbacks of the laser techniques due to its long application period and economical costs. The high costs make this technique, in many cases, unaffordable for large and routine applications, though its effectiveness and low environmental impact are evident.

Gels

The use of gel, as a supporting material or effective cleaning product, is quite common and widespread in cultural heritage applications. The higher viscosity of gel allows a gradual release of solvents, reducing their solubilising action, a reduction of the solvent's evaporation and consequently a limitation in the penetration of solvents within the original substrate [57]. The low evaporation rate of the compounds is also a drawback, as it is responsible for the so-called "residue question" thoroughly discussed by Stulik et al. [58]. Typical gels used in cultural heritage are both natural compounds, like cellulose ether derivatives, and synthetic products, like the so-called "Wolbers' solvent gels" [57, 59] or polyacrylic acid. Adjacent to these well know gels, new natural polymeric compounds, such as Gellan and Agar, are also commonly used, in particular for water-sensitive surfaces [59-61].

As a consequence, many studies have been carried out with the aim of selecting gelled systems which are not only able to retain a liquid phase and guarantee an effective cleaning action, but also can ensure an easy and complete removal after its use [62-65]. For example, Carretti et al. [62] exploits the properties of isothermally (at room temperature) rheoreversible organogels, that can easily be removed by converting them to a low-viscosity fluid *in situ*. The conversion happens as the gelator, usually a polyamine, reacts with CO_2 yielding a high-viscous compound. The CO_2 converts the amino groups in ionic couples made of ammonium (cation) and carbamate (anion). These attractive interactions make the compound highly viscous. To re-convert the gel in solution, a small amount of a weak acid is applied and the carbamate groups are converted into ammonium. In this way, the interactions between ionic couples become repulsive and the gel becomes liquid again. The tested gel is based on an ammonium/carbamate gelator of polyethyleneimine (PEI) loaded with low toxic solvents, such as alcohols and 1-methyl-2-pyrrolidone (MP), plus acetic acid for its complete removal. The system is used for the removal of aged natural varnish (Dammar) from a 18th century gilded frame and a 15th century wood panel, and for the removal of aged acrylic resin from the *a secco* wall paintings by Vecchietta in the Old Sacristy of Santa Maria della Scala, Siena, Italy. Analytical data show that the system is effective in all cases and no signs of gel residue are detected on the surface of the artworks. More tests are however necessary in order to assess whether the $PEICO_2$ polymer diffuses into the painted layers after mild acidification. Following the cleaning effect, the second most positive aspect is that this particular system can easily be prepared by restorers from commercially available and inexpensive components.

An interesting work is that of Bonini et al. [63], on the use of a magnetically responsive nanosystem as a cleaning method. The nanomagnetic sponge is obtained by cross-linking magnetic nanoparticles through a polymer network, based on polyethylene glycol (PEG) and acrylamide. This obtained nanomagnetic sponge is later loaded with a microemulsion, made up of a mixture of nitrodiluents and p-xylene as the oil phase, and applied on a marble surface sample, covered with an 8-year-old layer of Paraloid B72. Complete removal of the resin is obtained and no residue of the sponge is present on the surface after application. After cleaning, the nanomagnetic gel can be dried and reused, reducing the waste of materials and of toxic residues. It is worth noting is that the evaporation of the volatile organic solvents (p-xylene and nitrodiluent) in the microemulsion is much slower than expected for a pure solvent, due to the confinement effect played by the gel structure. Thus exposure to toxic vapours and VOCs emissions is drastically reduced. However, whilst the removal of the gel is simple, many difficulties can be encountered by restorers during the cleaning process because of the colour of the sponge that is, in fact, totally black and does not allow constant control of the cleaning action.

Carretti et al. [64] propose a poly(vinyl alcohol)-borate (PVA-borate) hydrogel system loaded with 1-propanol/hydrogels for the solubilisation of oxidized varnishes, used in past conservation treatments, on the oil-based-painted surface of the wood panel “Santo Stefano” painted by Ludovico Cardi, called il Cigoli. The peculiar elastic properties of PVA-borate 1-propanol/hydrogel allow the gel to be safely and easily peeled from the surface, in contrast to other gels commonly used in art conservation (i.e. poly(acrylic acid) or carboxymethylcellulose). In addition to 1-propanol, PVA-borate matrix can be loaded with other solvents such as cyclohexanone, 1-pentanol and 1-butanol, which all have low-toxicity. The varnish was effectively removed from the wooden panel with repeated treatments and with the aid of slight mechanical action. The cleaning action was still gradual, controllable and selective, demonstrating that the use of peelable gel could be a viable method for the removal of unwanted layers from a delicate surface, with low impact on the restorer’s health.

Domingues et al. [65] also develops a high biocompatible hydrogel system to accomplish rising demands for materials with a low environmental impact from their production process to their disposal. The system is based on the biocompatible polymers poly(2-hydroxyethyl methacrylate), or p(HEMA), and poly(vinyl pyrrolidone) (PVP). These polymers, widely used in pharmaceutical, cosmetic and food industries [66-68], give to the hydrogel system mechanical features and hydrophilicity, respectively. A test to assess the effectiveness of the hydrogel is carried out on a water-sensitive surface (i.e. cotton canvas covered with a layer made of $CaCO_3$ and animal glue, painted with *tempera magra* technique) soiled with an artificial hydrophilic grime mixture. The results show a gradual, selective and controllable action of the hydrogel system mainly dependant on the gel application time.

Analyses show that no residues of hydrogel are present on the canvas after treatment, resolving the well-known problem of possible swelling or residue [58]. The gel is able to well retain micellar systems and microemulsions, it allows to replace organic solvents, and it can be effectively used to remove also lipophilic layers, particularly from water-sensitive materials such as watercolour paintings. Other specific features of the hydrogel can be adjusted during synthesis by varying its component ratios (water, PVP, HEMA, etc.) so that its mechanical behaviour and affinity to water can be modified as required. Moreover, the hydrogel is transparent allowing easy manipulation; it exhibits good adhesion, higher softness and higher water retention capability than ordinary chemical gels; and the application procedure does not require any mechanical action.

Development and improvement of gels for cultural heritage seems to be a promising research field and nowadays many research teams are carrying forward the pending issues of compatibility, selectivity, retention, etc. [69, 70]. Despite the recognized positive aspects and results, the use of gels is not yet widespread between restorers due to technical difficulties in the preparation process. Few types of gels are commercially available but their costs are high and are predominantly unaffordable for extensive use.

Consolidation

Consolidation represents a very difficult and delicate operation in the conservation and restoration field, as it might cause undesirable effects, such as yellowing, formation of aggressive substances, heterogeneous distribution into the support [71-73]

Most of the synthetic products (as acrylic and vinyl polymers, silicon based, etc.) have a high environmental impact and their application requires the use of volatile organic solvents, such as white spirit or methyl ethyl ketone, which can be recognized as potentially carcinogenic [9]. An improvement in terms of toxicity and solubility is achieved with the implementation of synthetic polymers as water emulsion or in solvents of reduced risk (i.e. acetone, ethanol, etc.) [74-76]. The water-organic system overcomes some drawbacks of the traditional organic polymers, but issues related to their stability over time and sensitivity to humidity are still pending [77, 78]

In the work of Sassoni et.al. [79], the use of phosphate-based consolidant (forming hydroxihapatite, HAP) is proposed as an alternative to traditional ethyl silicate based products (ES) for the intervention on weathered limestones. The authors investigated the products in terms of effectiveness (i.e. ability to improve chemical-mechanical properties, penetration depth, resistance to abrasion, etc.) and compatibility (i.e. compatibility with substrate, colour change, pore size distribution, etc.). Based on the obtained results, the two products give similar results, but the HAP is able to overcome the limitations of ES in terms of prolonged curing time and temporary hydrophobicity. In comparison with commercially available consolidants, HAP treatment is highly innovative and appealing for several reasons: the product is applied as aqueous solution, free from any organic solvent thus completely green; the viscosity is similar to water and contains no particles avoiding limitations in penetration rate and effectiveness also of nanolimes products [80].

Following the discussion of green products and methodologies, a separate discussion has to be made regarding nanotechnologies and bioconsolidation, that up until now may well represent the most sustainable and eco-compatible methodologies for consolidation treatments in cultural heritage.

Nanotechnologies

From the 1959, when nanotechnologies were firstly introduced by Richard P. Feynman [81], the applications and developments of nanotechnologies have widely expanded and reached multidisciplinary fields (i. e. medicine, biology, industry, etc.) with significant economic and industrial implications. Owing to the increasing use of nanotechnologies, in 2008 the European Commission adopted the ‘‘Code of Conduct for responsible research in the field of nanotechnology,’’ which aims at promoting a sustainable and responsible research approach. Nanotechnology is still, in fact, an emerging research field, that has many open questions regarding the real benefits and possible risk for human health and the environment in the long term. [69, 82-85],

The application of nanotechnologies has seen a rapid and consistent development, in particular in the field of construction and cultural heritage, giving a significant innovation to traditional methodologies and products [86, 87].

The use of nanoparticles in cultural heritage has provided promising research and there are already many specific research projects and applications for different materials, such as paper [88], canvas [89], stone [90], wall paintings [80], wood [91], etc. Nanoparticles have been used in different conservation operations [69, 87];

Given all the different applications in cultural heritage, the use of nanoconsolidants, for many researchers, may represent one of most promising and innovative methodologies in terms of sustainability and eco-compatibility for restorers and the environment. The peculiar properties of nanomaterials are in fact crucial in all the cases where the size of the materials needs to be controlled to achieve the best results, as in the case of consolidation and protection.

Nanotechnologies offer the possibility to improve traditional inorganic consolidant products (based on calcium, magnesium and barium hydroxide) and propose innovative methods, such as colloidal dispersions with silica and titania nanoparticles [92, 93].

The publication of Chelazzi et al. [80] gives an interesting and in-deep overview over the last 15 years of the use of hydroxide nanoparticles for the consolidation of porous carbonate materials (i.e. wall paintings, stones, plasters). In this particular paper review, Chelazzi considers the synthesis and preparation of colloidal systems suitable for cultural heritage application, such as physico-chemical compatibility, efficiency, etc. Inorganic nanoproducts are commonly used as water or alcohol dispersed solutions, thus resulting in being green for operators and the environment. As pointed out by the authors, the collaboration between scientists and conservators is crucial for proposing state-of-the-art solutions capable of providing reliable and easy-to-use methodologies for the conservation and preservation of artworks [80].

Next to hydroxide nanoconsolidants, the work of De Rosario et al. [94] represents the first example of the use of a new green surfactant-synthesised nano-alkosylane as *in situ* consolidant for granite.

The authors test the nanomaterial UCA-2o, a sol consists of Dynasilan 40 and n-octylamine surfactant, against the two traditional consolidants: Paraloid B-82, an acrylic resin based on methyl-methacrylate prepared in an ethanol water solution, and Estel 1000, an ethyl silicate dispersed in White Spirit D40. The products are first tested on specimens in the laboratory, in order to evaluate their effectiveness and were then applied on the granitic Romanesque Church of Santa María del Campo (A Coruña, Spain). The UCA-2o, as traditional alkosylane products, is able to polymerize *in situ* inside the pore structure with a good penetration efficiency, thanks to its reduced viscosity. An important point to consider in term of sustainability and eco-compatibility are that the process is extremely simple and the consolidant can be prepared directly *in situ* in common outdoor conditions and no volatile compounds (VOCs) are added to the sol. Moreover, the UCA-2o is available on the market at a low cost under the corresponding exploiting patent [95].

Despite its commercial availability, nanoconsolidants (CaLoSil, the first commercially available stone consolidant, Nanorestore, Nano-Estel, Ludox, etc.) are still rarely used by restorers and are uncommon for stone materials due to their high costs. However, they are used for the consolidation of pictorial surfaces (i.e. mural paint) due to reduced penetration [80, 96].

Despite the increasing interest and research into nanoconsolidants, seldom are the *in situ* applications on a large scale and there are still open questions regarding their physico-chemical stability, compatibility with human health and the environments and their Life Cycle Assessment (LCA) [97].

Bioconsolidation

Bioconsolidation is a new methodology based on selected microorganisms that are able to settle on stone materials and produce inorganic compounds with binding properties [98, 99]. Bioconsolidation does not require the use of organic solvents overcoming compatibility issues, reducing toxicity and environmental impact [20, 100, 101].

An example of bioconsolidation of carbonatic materials is given by Rodriguez-Navarro et al. [100] that exploits the carbonatogenic ability of the bacterium *Myxococcus xanthus* for the consolidation of porous limestone specimens. The bacterium strain is inoculated in the stone by immersion of the specimens in the liquid culture media. The new precipitated biocrystals, calcite and vaterite (a $CaCO_3$ polymorph), cement the limestone grains without filling the pores and allowing vapour permeability. The effectiveness of the treatment is demonstrated, but the penetration depth of the bioconsolidant is limited only to 1 mm and the experiment is carried out only in laboratory conditions.

In order to promote a more sustainable application and to avoid possible fauna contamination, Jimenez-Lopez et al. [102] experiment with the possibility of activating the biomineralization by the inhabiting microorganisms colonizing the stone material [103]. The authors compared this new approach with the Rodriguez-Navarro's method which uses *M. xanthus* bacterium. The results of the experiment show that the autochthonous microbial community promotes a more intense but slower $CaCO_3$ precipitation than *M. xanthus*. The studies by Rodriguez-Navarro et al. and Jimenez-Lopez et al. prove the possibility, at least in laboratory conditions, to use selected microorganism for consolidation of porous carbonatic materials, but there are only few examples of *in situ* applications [104]. The bioconsolidation methodology may be considered completely harmless towards workers and the environment. In terms of environmental compatibility, the use of inhabiting microorganisms may be preferred over any new bacteria introduced within the original surface.

On the other hand, bioconsolidation presents some drawbacks: risks posed by aesthetic and structural changes [101]; physico-chemical stability and efficiency over time with the original substrate; compatibility with previous operations, as the use of chemicals during cleaning could inhibit the growth of precipitating microorganisms [105]. Moreover, the selected bacteria strains should not produce endospores, preventing the possibility of incurring an uncontrolled and undesired proliferation [100]. This technology is still in its infancy and it is not yet available for routine application as the methodologies require specialised operators and strict bacterium growing condition.

Protection

Most of the well-known synthetic protectives are often applied by means of volatile organic solvents, such as toluene, white spirit and chloroform [71] with evident risk for restorers and the environment. In order to reduce toxicity, several studies have been carried out which were aimed at testing acrylic aqueous dispersions as protective agents [106-108]. Advantages of water disperse products include non-toxicity and non-flammability, aspects which are particularly important when the surface in question is extended and therefore high volumes of solvents are required.

Recently, innovative methodologies for the protection of outdoor-exposed cultural heritage assets have focused on the possible application of biopolymers and of coatings doped with nanometric TiO_2 [109-112].

Biopolymers

The use of biopolymers in the conservation of cultural heritage may well present advantages in terms of eco-compatibility, reversibility and biodegradability.

The work of Ocak et al. [109] tests the efficiency of four different biopolymers - Chitosan, Zein, polyhydroxybutyrate (PHB), high and low molecular weight poly-L-lactide (HMWPLA and LMWPLA) - as protective coatings for marble surfaces subject to sulphation processes [113]. The biopolymers have been applied to the marble and diluted in different solvents: ethanol for Zein, acetic acid/water for Chitosan and chloroform for PHB and PLA. The collected data shows that Chitosan and Zein are highly hygroscopic, therefore not suitable as protective agents at all. PHB and PLA demonstrate beneficial properties, such as water repellency and permeability of water vapour. In particular, regarding sulphation process, HMWPLA ensured best SO_2 barrier of the all tested biopolymers, but its high brittleness may prevent its use for cultural heritage application.

Another study by Ocak et al. [110] proposes the use of a PLA matrix filled with nanometric montmorillonitic clay. Results show that the bio-nano composite coating is effective and has good protective properties, although vapour permeability is worsened because nanometric particles typically occlude pores [114-116]. As regards safety issues, it is proven that biopolymers have a drastically lower environmental impact and toxicity than oil derivatives [117]. Nevertheless, during application, some of these biopolymers, such as PLA, need to be dissolved in chloroform, which is toxic and a recognised environmental pollutant [118, 119].

Nonetheless, solutions in chloroform may well be preferable as traditional methods see the use of more toxic and carcinogenic products, as demonstrated in Giuntoli's case study [111] that concerns outdoor bronze monuments. Protection interventions on bronze are normally carried out through the extended use of a solution of toluene, acrylic resin and benzotriazole (BTA) [120]. BTA is harmful for the environment and carcinogenic to humans [121, 122] but remains one of the most effective products for metal protection. In the case study, a copolymer made of PLA and BTA (PLLA-BT_5) is tested as a protective agent on bronze specimens. The PLLA-BT_5 copolymer is highly stable with no significant optical changes, and its toxicity is drastically reduced as BTA is chemically bond to PLA polymeric chains.

Biopolymers and in particular PLA based products are a potentially viable alternative to synthetic polymers as their production is sustainable and green, but additional studies are required for substituting the toxicity solvents. These products are not yet widespread due to their production costs, which are still unaffordable and prevent biopolymers from being properly known and tested for cultural heritage application; and compatibility problems, such as brittleness, low-heat distortion temperature, reduced hydrophobicity, etc. [110] that limit their use as protective coatings.

TiO_2 nanoparticles

Nowadays, great interest is given to the possibility of adding nanoparticles of titanium dioxide (TiO_2) to traditional products, mainly as self-cleaning and microbial photo catalytic coatings for civil and historical applications [5, 93, 123-132].

The research by Franzoni et al. [112] is only one of the recent studies that focuses on the use of aqueous dispersion of nano-TiO_2, as self-cleaning and anti-microbial, on plaster specimens from the Ex-Albergo del Corso in Bologna. The product proves to be effective for both aims, but demonstrates evident wettability. In fact, the treated surfaces show drastic reduction of contact angle and water absorption time, as TiO_2 makes the surface super-hydrophilic [133], something that is not acceptable for products advertised as protective. The authors selected brushing application in order to reduce risk of inhalation, as the side effects of TiO_2 nanoparticles are not yet well known. This induced super-hydrophilicity can be attenuated by using nano-TiO_2 in emulsions with acrylic and polyurethane polymers [123, 124].

However, this property is still in question as, according to a study by Quagliarini et al. [127], it allows water to make a homogeneous film that flows on the surface, without being consistently absorbed within the porous substrate. The green aspects of TiO_2 application relate to its versatility and green production [131]; the possibility to use TiO_2 in aqueous dispersion, avoiding traditional toxic solvents; its eco-compatibility and low-level impact on chemical compositions of materials. Important issues are still pending regarding the effectiveness and long-term stability of the titanium coatings *in situ*, as most of the application studies and characterization tests have been carried out in laboratory conditions. As for other innovative materials, such as nanolimes, the impact of nano-TiO_2 on human health and the environment is still a matter of debate, due to the lack of sufficient data and thorough investigation [134].

Conclusions

Owing to an increased general awareness of product toxicology and the introduction of new legislations and regulations on chemical production, use and treatment, only in the last few years has there been an increasing demand for alternatives to traditional products and methodologies that are evidently dangerous. Alternative green products and methodologies are already available for the interventions on cultural heritage, however rarely reach restorers in due course as they are often published in certain journals that do not target the restorer specifically (i.e. Journal and Colloid and Interfaces, Microchemical Journal, Analytica Chimica Acta etc.). In worse cases, some products do not even reach the production step, as they are not economically or industrially competitive. Furthermore, many of the available green alternatives are still difficult to find on the market and their use and preparation requires specialized professionals and specific evaluation protocols. Even so, some of these products still require further testing regarding their effectiveness, alongside risk assessments for both human health and the environment.

Parallel to the development of green solutions, it is now mandatory to inform and to educate restorers on their use, preparation, etc. In this sense a close collaboration between operators, companies, and researchers is therefore fundamental.

It is now essential to meet the demands of the cultural heritage field ecologically, economically and socially with aims of a completely green approach for conservation. When planning a restoration or conservation intervention, besides the safety of the artefacts, the main goal should be to consider all the phases that characterise a restoration project. The focus should be on a completely green and holistic direction, fulfilling social, cultural, economical and environmental needs.

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