XII CONVEGNO INTERNAZIONALE

Diagnosis for the Conservation and Valorization of Cultural Heritage

Napoli, 9 - 10 dicembre 2021

ATTI DEL CONVEGNO

a cura di

Luigi Campanella, Ciro Piccioli, Anna Rendina, Valeria Romanelli

A.I.E.S. BENICULTURALI
Associazione Italiana Esperti Scientifici

POLO museale SAPIENZA

CERVINO EDIZIONI

Atti del XII Convegno Internazionale
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Progetto e realizzazione grafica: *Maria Fece*
Thanks to Nick Ritz from Pixabay

Stampa: Press Up

ISBN 978 88 95609 61 4

CERVINO EDIZIONI
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Con il patrocinio di

Evento realizzato con la collaborazione di

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> Summary / Sommario

Ciò che chiamiamo realtà
deriva dalla nostra partecipazione attiva
alla sua costruzione.

Ilya Prigogine

Prefazione

Il XII convegno AIES giunge, nuovamente in presenza, in un tempo profondamente segnato dalla pandemia da Covid-19 e da tutto quello che da essa è scaturito. La profonda crisi generata dal virus non è stata solo sanitaria ma ha colpito vari settori della nostra esistenza.

Ci ha colpiti nella nostra fragile umanità, costringendoci a ripensare i tempi, a scandirli in una maniera nuova e condividerli più di quanto fossimo abituati a fare.
Ci ha colpiti nel delicato processo di formazione scolastica dei nostri giovani; ne sono testimoni i giovani ricercatori le cui tesi - di laurea magistrale e di dottorato - sono state ammesse agli atti.

Ci ha colpiti nell'economia, costringendoci spesso a rivedere interi processi di marketing e a guardare alle tecnologie informatiche con più fiducia e maggiore interesse. Anche in questi atti ce n'è testimonianza.

La pandemia ha anche colpito particolarmente il settore dei beni culturali e della cultura in generale che, solo da poco, grazie alle nuove normative di accesso e fruizione, riesce a ripartire. Questo ci rende doppiamente felici di essere nuovamente al MANN, testimoni che la vita nei luoghi della cultura è finalmente ripresa.

La ripartenza del convegno AIES si presenta ricca di lavori: abbiamo ricevuto infatti un numero molto consistente di contributi di altissimo valore scientifico e di variegata natura che ci permetteranno di esplorare lo stato dell'arte da diversi punti di vista. Accanto a temi classici e cari ad AIES come diagnosi e conservazione, verrà affrontato il tema delle nuove tecnologie a supporto del complesso lavoro di valorizzazione ma anche studi di natura sociologica e culturale, come quello sui fattori che spingono le persone a donare per progetti culturali.

Un ulteriore aspetto di novità che merita una particolare attenzione è rappresentato dalla presenza fra i lavori di contributi dedicati alla *Chimica Green* applicata ai beni culturali. .La chimica europea deve affidarsi alla green chemistry per competere con successo nel mercato.internazionale con la concorrenza dell'estremo e del medio oriente favorita da bassi costi di manodopera e di infrastrutture. La green chemistry ha trovato applicazioni di successo nell'alimentare, nell'energetico, nel farmaceutico, non ancora nel campo dei beni culturali che pure per un Paese come il nostro e per l'Europa in generale rappresenta un' eccellenza. Siamo felici che il nostro Convegno possa rappresentare una tappa di avvicinamento in questa direzione.

La scienza riflette il tempo. Questo tempo in cui si avverte la necessità di ritornare ad una spensierata socialità, lascia il segno anche negli articoli che leggerete. Non è un caso che quest'anno, in allegato agli atti, verranno distribuite le "Linee-guida per la promozione e lo sviluppo della raccolta fondi ad uso delle comunità attive per la gestione e valorizzazione dei beni comuni e per le loro reti", un piccolo libretto di indicazioni sul fundraising per i beni comuni che parte dall'esperienza dei beni comuni napoletani che coincidono con beni culturali di pregio.

Dietro a questo convegno c'è un lavoro che parte da lontano e che scandisce un tempo lungo 12 mesi. Parafrasando Cesare Brandi nella sua descrizione della struttura ritmica del tempo dell'opera d'arte, si può ritrovare la struttura ritmica persino nel convegno AIES:

- la durata: che non è di due giorni a dicembre ma che ci vede tutti impegnati per tutto l'anno: a ricercare, a studiare, a sperimentare, a connettere tutto ciò
- l'intervallo: o gli intervalli che sono le scadenze imposte nella call; le dead line sono indispensabili per la buona riuscita del convegno
- l'attimo: il momento in cui ci ritroviamo di nuovo insieme, a Napoli, per parlare di scienza, di cultura, di nuove sinergie, di futuri progetti
-

Tutto questo non sarebbe possibile senza lo straordinario supporto del Comitato Scientifico che, con molta cura e dedizione, valida tutti i lavori che ci vengono sottoposti e stimola, di anno in anno, la crescita del convegno sottoponendo nuovi temi e nuove strade da percorrere per arricchire sempre di più questo momento di incontro.

Senza la coniugazione di tutti questi lassi di tempo non esisterebbe il convegno AIES che, di anno in anno, cresce e si fortifica grazie a due punti cardine: il coordinamento delle attività ed il conforto della tecnologia.

Infine, non saremmo mai capaci di guardare abbastanza lontano senza il connubio tra lungimiranza ed esperienza che sono alla base della storia di AIES e la caratterizzano, rendendola un'esperienza sempre nuova e multidisciplinare.

Questa particolare edizione del convegno ci spinge ad una riflessione profonda sul Tempo, una variabile familiare ma forse poco approfondita della nostra vita, ed è per questo che in apertura degli atti vogliamo proporre una considerazione sul rapporto tra la valorizzazione ed il tempo.

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Ciro Piccioli
Anna Rendina
Valeria Romanelli

> Diagnosis
> Conservation
> Valorization
> Micro and nanostructured
materials for innovative conservation
> Emerging digital technologies
for Cultural Heritage
> Best Thesis Award 2021

> Diagnosi
> Conservazione
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> Materiali micro e nano strutturati
per approcci conservativi innovativi
> Tecnologie digitali emergenti
per i Beni Culturali
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Culture Economy: innovative strategies to sustainable restoration of artistic heritage.
Part I - Development of natural gels for cleaning the stone materials of cultural heritage from iron stains and biodeteriogenic microorganisms

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Key words >
calcareous stone, cleaning procedure, iron stain, enzymatic surfactant, metal chelator, biodeterioration, alginate-biocide hydrogel.

Abstract > A wide spread of multidisciplinary results was obtained for the Smart Cities and Communities and Social Innovation project supported by MIUR and entitled "Product and process innovation for the maintenance, conservation and sustainable restoration of cultural heritage". The project basically suggested the opportunity to avoid emergency closures of sites of high historical, architectural and cultural value, to proceed with planned interventions that regularly guarantee the well-being of the site and its conservation. A new organization of the protection, conservation and maintenance system was thus proposed (Part I and Part II). The choice of the test materials was suggested by their widespread use in the monumental heritage of Southern Italy and in particular in 'The Sassi and the Park of the Rupestrian Churches of Matera – UNESCO World Heritage Site" which was the site where part of the lab activity was transferred "in situ". In particular, the reported activity in Part I was aimed at ensuring a sustainable restoration based on safe cleaning methods on calcareous stones, able to reduce professional diseases and environmental pollution. Trying to replace traditional products with new derivatives, some natural products, as enzymatic surfactants or natural metal chelators, for iron stains and new biocompatible systems, i.e. oxidative alginate-biocide hydrogels, against biodeteriogenic attacks are proposed.

Introduction
A recent statistic revealed that our country, the richest in UNESCO World Heritage Sites, is also among those whose return in terms of points of GDP remains below the European average, despite the efforts of the competent Ministry. The United Kingdom,

for example, with a number of UNESCO sites equal to half of ours, has an economic return almost double, with a yield therefore 4 times higher. The reasons for this situation are political, but perhaps more of an organizational and technical nature.
Any intervention on the built heritage requires a multidisciplinary approach able to primarily describe the cultural value of the architectural asset and its state of conservation. Every cognitive aspect, from the reconstruction of historical events to the formal relief of the building, from the characterization of the construction typology to specialist diagnostic investigations, contributes equally to the overall view as a single piece of a complex mosaic.
The acquisition of the most complete knowledge possible of the state of conservation of the property is essential both to guarantee the effectiveness of the interventions and to act in a preventive perspective through the scheduled maintenance of the architectural heritage. The Smart Cities and Communities and Social Innovation project entitled "Product and process innovation for the maintenance, conservation and sustainable restoration of cultural heritage" has to be seen.
A new organization of the protection, conservation and maintenance system was thus proposed, together with the application of innovative methods and processes and natural products safer for the environment and for the operators themselves. As regards the first point, the project basically suggests the opportunity to avoid emergency closures of sites of high historical, architectural and cultural value, to proceed with planned interventions that regularly guarantee the well-being of the site and its conservation.
Innovative products and process with low environmental impact were experimented on stone materials (Part I), trying to replace traditional products, for the various phases of the restoration starting from cleaning from enzymatic surfactants to natural metal chelators, from new consolidants generation to new procedures for applying antimicrobials. These innovations can give restoration interventions greater stability and durability.
With particular attention to calcareous stones and their sulfation with the formation of black crusts, an optimization algorithm of the scheduled maintenance issues was implemented (Part II).
In detail, Part I concerns:

1. Use of natural products to clean iron stains in stone materials.
    a. Specific chelating agents suitable to be dispersed in a natural gel consisting of polyvinyl alcohol (PVA) and sodium alginate as an optimal supporter, showing for iron (III) a high selectivity with respect to the calcium ions of the constituent carbonate material. The gelled chelating agents that gave the best results on marble specimens appositely stained were Deferiprone, a tridentate chelate widely studied and used in the treatment of iron overload [1] and Glutathione, a tripeptide formed by three amino acids, cysteine glutamic acid and glycine, which has both chelating and oxidizing properties [2].
    b. Two natural proteins, Lactotransferrin (Ltf) and Ovotransferrin (Ovt), identified for their high affinity "in vivo" for iron (III), and tested for the removal of iron-based stains on marble surfaces, after extraction from their natural matrices. The protein extracts were then immobilized using a common cellulose pulp and compared in details as reported in reference [3] and references therein cited.
2. The development of new biocompatible systems, i.e. oxidative alginate-biocide hydrogels, for cleaning limestone subject to biodeteriogenic attack, both from phototrophic organisms (cyanobacteria, microalgae, mosses, lichens, plants), and from he-

terotrophic ones (bacteria and fungi). The research focused on the development and application of a non-toxic, biocompatible and biodegradable polysaccharide hydrogel, in which the biocide can be incorporated in order to remove the biocontaminants from the stone material [4-5].

3. "In situ" application and monitoring of this hydrogel-biocide and protective and/or consolidant products developed by Icap-Leather Chem SpA [6] within the rock churches of San Pietro Barisano and Madonna dei Derelitti in Matera.

Materials and Methods

Materials and cleaning products for iron stains

Deferiprone and Glutathione, active in vivo at neutral pH as chelating agents for ferric ions, were dissolved at a concentration of 0.2% in a gel consisting of PVA and sodium alginate, which allowed the iron stains on marble surfaces to be treated within a time of 24 hours, with both chelating agents, although they have different chelation mechanisms [1,2]. Their efficacy for the removal of iron stains, when dispersed in this natural gel, was compared by repeated laboratory test using Travertine and Carrara marble specimens that were appositely stained [7,8] by oxidizing iron bars on their surface, through monthly exposure in the external environment. Attention was paid to the gel constituents, in order the final product to be effective, easy-to-apply, and not prone to produce alterations and or residues on the treated artefacts. The structural formula of both Glutathione ($C_{10}H_{17}N_3O_6S$) and Deferiprone ($C_7H_9NO_2$) provided by Aldrich in form of standard powders, was also verified by XPS analysis.

Artificial bio-degradation of Lecce stone

The Lecce stone samples were soaked in a glass chamber, containing backwater added with fertilizers, and exposed to the sunlight to favor the growth of microorganisms, which was evaluated every week until the desired degree of contamination was reached; the specimen was then extracted, dried and subjected to analysis.

Hydrogel-biocide system

We prepared alginate hydrogels, an unbranched binary copolymer composed of monomer units of β-D-mannuronate and α-L-guluronate ionically crosslinked by Ca^{2+}.

Thanks to the encapsulation in the hydrogel matrix, the amount of the biocide can be significantly reduced compared to its application in solution, as the gel allows a much longer contact time of the biocide on the material [4]. In addition, the viscosity of the different formulations can be modified through the use of variable quantities of gelling agent, which allows their application on the support by brush or spatula; in both cases, the hydrogels adhere perfectly to the surfaces, even if vertical. Finally, their removal can be easily done with water, with tweezers or using a cotton gauze.

For our purpose, hypochlorite ion (ClO^-), titanium dioxide (TiO_2) and sodium dichloroisocyanurate (NaDCC) were selected among the usually used biocide agents [5,9].

Monumental Heritages for "in situ" bio-cleaning: rupestrian churches of San Pietro Barisano and Madonna dei Derelitti in Matera

In the church of San Pietro Barisano some small areas were identified in the central and right naves, which differed both in construction material and in the degree of biocontamination. In particular, two little stone reliefs were selected on the balustrade that separates the central nave from the right one, a small hypogeal area located on the right nave of the church (ossuary) and a brick present on one of the columns of the central nave.

The second "in situ" activity was performed inside the small rupestrian church called

Madonna dei Derelitti, located on the side of the Gravina opposite the one on which the Sassi districts stand. Already in this first phase of "in situ" experimentation, some problems were highlighted with respect to the tests carried out in the laboratory, since rupestrian environment was characterized by high relative humidity e poor ventilation. Stone surfaces were wet, with a moisture content greater than 90%; this meant that, after 24 hours, the hydrogel was not perfectly dry and cannot be removed from the treated areas. Since the treated areas were not very extensive, the hydrogel was dried using a thermo-convector but, in view of an application on larger areas, the use of ventilators, convectors or infrared lamps is advisable.

Photos and Colorimetry

To assess the degree of biodegradation of stone materials and the effectiveness of hydrogel treatments to refresh the original chromaticity, photo images and colorimetric measurements were performed. Digital photos were taken with Canon EOS 1300D. Color parameters measurements were acquired on three different points of the surfaces, before and after treatment, using a MINOLTA CM-508d spectrophotometer (Minolta, Osaka, Japan), equipped with D65 illuminator in SCE mode with a 10° standard observer. The color difference, with respect to a properly selected reference surface, was determined according to $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$.

Digital microscopy and image processing

The color variation was measured with a portable digital microscope, Dino-Lite AM4815ZT, and the micro-photos acquired before and after the treatment were processed with the software for image analysis "Image J" (https://imagej.nih.gov/ij/index.html). Using the RGB (Red/Green/Blue) profiler plug-in for the color processing, it was possible to obtain histograms of the average RGB values of the individual pixels, useful for evaluating chromatic variations relating to the removal of iron oxides.

X-ray Photoelectron Spectroscopy (XPS) - XPS spectra were acquired with a SPECS Phoibos 100- MCD5 spectrometer operating at 10 kV and 10 mA, in medium area (Ø=2 mm) mode, using achromatic MgKα (1253.6 eV) and AlKα(1486.6 eV) radiations. The pressure in the analysis chamber was always better than 10-9 mbar during acquisition. Wide spectra were collected in FAT (Fixed Analyzer Transmission) or FRR (Fixed Retarding Ratio) modes with a constant pass energy of 20 eV and channel widths of 1.0 eV. Detailed spectra were all acquired in FAT mode with a constant pass energy of 9 eV and channel widths of 0.1 eV and were curve-fitted using a well-established program, Googly [10,11]. Peak areas and positions (binding energies, BE) as derived by curve-fitting were, respectively, normalized using proper sensitivity factors and referenced to C1s aliphatic carbon, as an internal standard, set at 285.0 eV [12]. XPS analysis was performed on marble specimens properly treated and sized. In alternative, by gently scraping their surface, following the current sampling normative. The powder collected from the marked zones were firstly homogenized in an agate mortar and then pressed on to a double-sided copper tape, properly fixed on a steel sample holder, to be safely introduced in the analysis chamber. The energy scale reported on figures is not corrected for surface charging but the peak assignments (reported on XPS table) and peak labels in graphics are referred to the analysis of standard compounds, to NIST XPS online database (https://srdata.nist.gov/xps/default.aspx) and literature data.

1H-NMR Relaxometry

The portable NMR apparatus is the mq-ProFiler (Bruker Biospin, Italy). Since the proton NMR signal in the sample is proportional to the total amount of water confined in the pore space, analysis of the proton relaxation signal can be used to evaluate the porosity of the material when fully saturated with water. It is also possible to obtain information about the dimensions of the pores and pore-size distribution through the distributions of relaxation times of the transverse (T2) components of the nuclear magnetization. Moreover, ^{1}H NMR measurements carried out during capillary water absorption up to saturation, allow to assess the effects of treatments in terms of hydration kinetics and moisture content variations with respect to a reference untreated sample. The capillary water absorption was performed according to UNI 10859.

Results and Discussion

Use of natural products to clean iron stains in stone materials

Figure 1 shows the cleaning procedure adopted on Carrara marbles (100x100x20 mm) properly sized for XPS analysis and the chromatic variations following just one treatment with Glutathione (A) and Deferiprone (B).

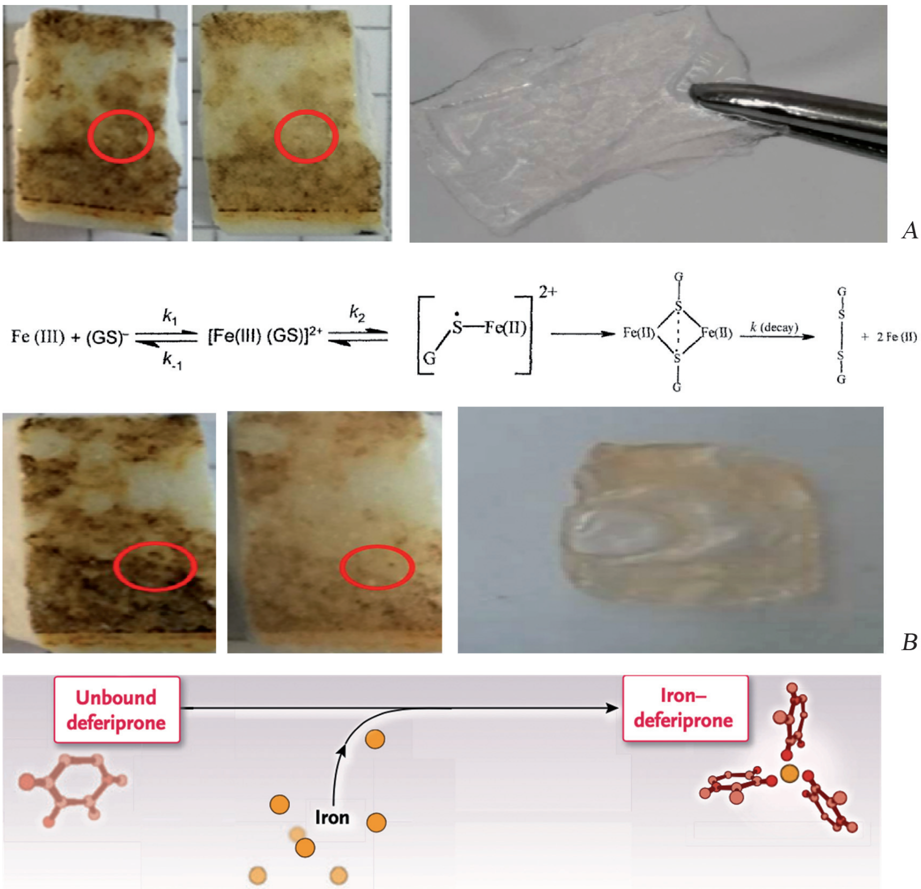

Figure 1. Rusted marble specimens before (left) and after (right) treatment with gelled Glutathione (A) and Deferiprone (B). The gel- containing chelants was spread on marble surface and removed after the established contact time. After treatments, it shows different coloration depending on the chelation mechanism: red for the complex Deferiprone-Fe(III) in the ratio 3:1 [from Reference 1] and light grey for the Glutathione complex following the redox mechanism reported on the above scheme [from Reference2].

A number of rust marble specimens were analyzed, pre- and post- treatments with both the gelled chelants, by digital processing equipment for the color comparison and by XPS over the sampled medium areas (red circles in Fig. 1) for the variation of their surface composition. Some examples of the Fe/Ca ratio particularly indicative of the cleaning efficacy are shown below in the Table for Travertine and Carrara marbles, pre- and post- treated with both chelants.

Stained Travertine marbles	**Fe/Ca**		Stained Carrara marbles	**Fe/ Ca**
Pre- and post- treated with Glutathione	.39→.13		Pre- and post- treated with Glutathione	.05→.02
Pre- and post- treated with Deferiprone	.34→.10		Pre- and post- treated with Deferiprone	.09→.05

The XPS data exemplify the correlation of the obtained results with the different marbles porosities, the entity and extension in depth of the produced iron patches and their association with environmental contaminants of different origin, as well as with the gel thickness, time of contact and evaporation control of the water solvent therein contained [7]. It could be foreseen, for both chelating agents, a second treatment and an optimization of the contact time, in order to proceed in depth with the cleanliness of the specimen, depending on the initial staining conditions.
The use of Ltf and Ovt, two proteins of the transferrin's family extracted by milk and egg matrices was also proposed by the Rome research unity as an alternative method. The extraction and cleaning procedures are fully illustrated in Reference 3, in this case, the two extracted proteins are immobilized into a common cellulose pulp being not suitable, Ltf particularly, to be gelled as the Glutathione and Deferiprone chelants. The applications reported in Reference 3, show their best use on larger marbles resembling artifacts of a certain surface extension and delicacy, of the type visible in detail in Fig. 2. In such a case, XPS analysis was performed on powders collected by gently scraping the surfaces of the pre- and post- treated areas. Like the two chelants, the two proteins (Ltf and Ovt) supported in the cellulose pulp have proved highly selective in solubili-

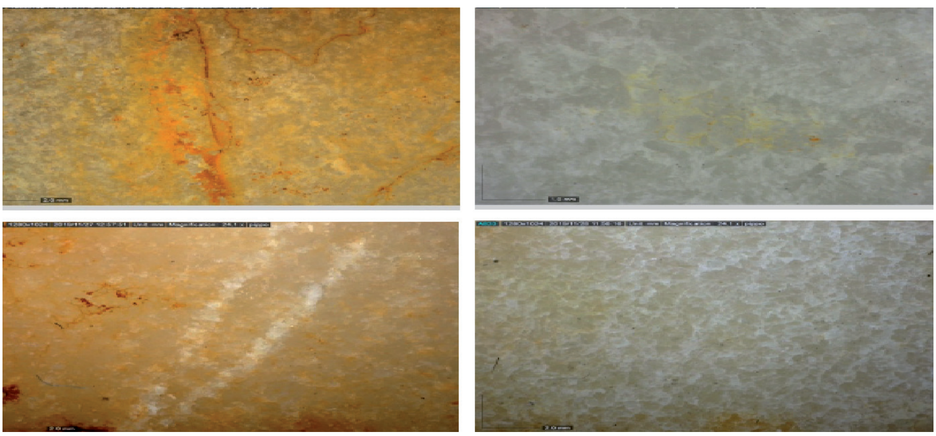

Figure 2. Stained Carrara marble surfaces, before (left) and after (right) cleaning with Lactotransferrin, Ltf, (upper photographs) and with Ovotransferrin, Ovt, (lower photographs).

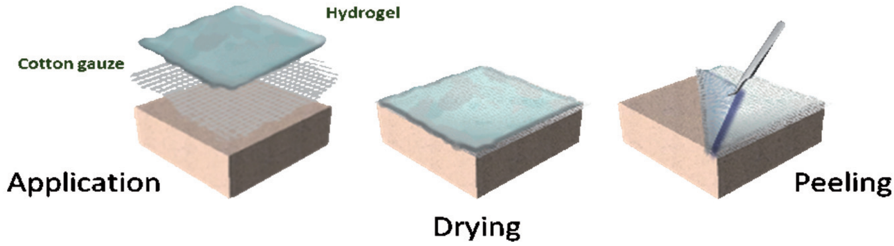

Figure 3. Representation of the phases of application, drying and removal of the hydrogel supported on cotton gauze.

zing the rusty patches without affecting the CaCO3 substrate. The XPS analyses show a percentage increase in carbonaceous components on the treated surfaces probably due to extraction residues that may possibly mask traces of iron not yet removed. However, a subsequent application with the cellulose pulp has proven the possibility of removing further residues left on surfaces and softened by the first application, thus improving the cleaning effectiveness and maintaining the safety of the intervention.

The results so far obtained with both methods indicate how the surface patina induced by iron corrosion contributes to the surface alteration of stone artefacts. In fact, the presence and the growth of iron oxides on carbonate stones is associated also to absorption of other components, organic and inorganic, all contributing to the weathering process

The laboratory results are very promising and are fully considered to suggest new actions for the restoration of cultural heritages and to evaluate the performance of the tested products in the real location of Smart Cities sites. In this perspective, the alternative methods and different supports will be chosen in dependence of the specific cases. The choice should also consider the working situation; for example, vertical surfaces will require supporting materials with a low tendency to slide, while surfaces located in a humid environment the control of potential biological attacks and so on. The reduction of occupational diseases and pollution will be extremely advantageous considering the greater extension of the indoor/outdoor surfaces to be treated.

Preparation of polysaccharide hydrogels added with oxidizing biocides, for the removal of biological contaminants from Lecce stone

Preliminary studies were carried out to optimize the composition of the hydrogel in terms of concentration of alginate and Ca2+ ions, to modulate its mechanical properties, and of the biocide to modulate its bioactive properties. To evaluate the efficiency of the treatment, standardized Lecce stone specimens were chosen and the following analyses were carried out, both before and after the cleaning procedure: stereoscopic microscopy, to assess the degree of biological colonization; colorimetry, in order to establish that the treatment does not alter the original color of the object; unilateral NMR relaxometry, to evaluate the hydration behavior of the porous stone materials.

The first tests for the removal of biological contaminants were carried out using hypochlorite ion as biocide in two different percentages by weight (0.8 and 2%), to be selected according to the degree of contamination [4]. The hydrogel was applied to the surface of the stone sample (Fig. 3), with the aid of a cotton gauze to facilitate the subsequent removal of the dry gel. A few minutes after its application, the contaminants lost part of their initial color; once dry condition was reached, the gauze was removed, leaving the treated surface totally cleaned.

Microscopic analyzes, colorimetry and surface porosity measurements showed that the treatment completely removed the biological contamination without altering either the original color of the stone or the capillary properties of the clean stones. The only drawback to note in these hydrogel-biocide systems are their low stability in terms of loss of biocidal activity and gel consistency, effects probably due to the oxidizing action of hypochlorite on the polysaccharide matrix.

For this reason, hypochlorite was replaced with sodium dichloroisocyanurate (NaDCC), which slowly releases hypochlorous acid. Here too, numerous preliminary tests were carried out to identify the most effective formulations [5].

After the treatment with the optimized hydrogel, the images taken with the stereomicroscope and the colorimetric analyzes showed both the total removal of contaminants from the stone samples and the restoration of the initial color of the same. The surface porosity measurements highlighted a slowdown at the beginning of the kinetic of water absorption, probably due to the partial occlusion of the surface pores that, however, not affect the chromaticity of the stone surface.

Hydrogels added with NaDCC not only was effective in removing contaminants but resulted much more stable than those added with hypochlorite and, if stored at 4 °C, showed good antimicrobial activity even after a week of their preparation.

"In situ" application of biocompatible hydrogels containing biocides and coatings developed by Icap-Leather Chem SpA, inside the rupestrian churches of San Pietro Barisano and Madonna dei Derelitti in Matera

"In situ" activity was carried out in Matera inside the rupestrian churches of San Pietro Barisano (September 2018) and of Madonna dei Derelitti (October 2019).

Two hydrogels were used, containing the hypochlorite ion in two different percentages by weight (0.4 and 1%), chosen based on the degree of contamination. The hydrogels were applied to the selected areas and some of the results obtained are here reported (Fig. 4).As can be seen, the biocidal activity of the hydrogel was practically unchanged compared to the tests performed in the laboratory, apart from the brick, in which even after several treatments with the hydrogel, the removal of contaminants was never complete. It is therefore evident that the type of stone surface to be treated is also crucial for an effective removal of contaminants. Probably the different porosity of the support, as well

Figure 4. San Pietro Barisano Church (Matera) - a little stone statue (on the right), on the balustrade that separates the central nave from the right one and a brick (on the left) on one of the columns of the central nave: images regarding the "in situ" cleaning procedure with hydrogel containing hypochlorite ions. For both items, before and after treatment images are shown.

Before treatment *After treatment*

Figure 5. Madonna dei Derelitti Church (Matera): an area of the “in situ” cleaning activity with hydrogel containing NaDCC and consolidating treatment with Polyrest P2, one of the new coating products developed by Icap-Leather Chem SpA. Images before and after interventions.

as any whitewashing interventions, which incorporate the contaminants in a carbonate matrix, contributed to their partial removal. The second “in situ” activity was performed inside the small rupestrian church called Madonna dei Derelitti, located on the side of the Gravina opposite the one on which the Sassi districts stand. To evaluate the effects of the treatment with both the biocidal hydrogel and the protective-consolidant products developed by Icap-Leather Chem SpA (Polyrest AC012 and Polyrest P2), photographic documentation, X-ray photoelectron spectroscopy (XPS), colorimetric tests and “peeling tests” were performed. Different areas of intervention were identified according to the type of biodeterioration. For the cleaning treatment, the hydrogel added with NaDCC was used [5]. As previously reported, the gel was applied using a cotton gauze as a support to facilitate its removal once dried. To speed up the drying phase, infrared lamps and ventilators were used. In almost all the selected areas, the gel was particularly effective after just one application, as evidenced by the following images (Fig. 5).
The sampling for XPS analysis of the stones under study was performed by gently scraping their surface before and after the cleaning treatment. The main signals of the detected elements were labeled and were the same in both wide spectra (data not shown). The curve fitting results of all the detailed spectra are summarized on the pie graphs reported in Fig. 6 (Upper graphs). An increase in intensity of silicium, accompanied by a decrease in sulfur and organic carbon after the treatment is immediately evident at first glance.
The changes in intensity and/or spectral shape can be highlighted and evaluated by the analysis of the detailed regions acquired at higher resolution in energy. The curve fitting result is reported for the C1s regions (Fig 6 Lower graphs), the most susceptible to variation of the peak components, after treatments. The figures clearly show the inversion of relative intensities of the carbonate and C-C components, after treatment.
Altogether the comparison of pre-and post-treated spectra shows the abatement of carbon and sulfur- containing contaminants, after treatment, accompanied by the surface discoloration as evidenced by the photo of the treated portion in Fig. 5. The efficacy of the adopted biocide is extremely satisfactory because the removal of the overlapping layers brings to light the prominent calcareous structure together with siliceous components, typical of ‘calcarenite’ stones, as it can be observed by the pie charts comparison. This may mean that the underlying structure does not show serious damage and that the biocidal action is effective over the surface contaminating layers. The colorimetric parameters clearly showed that the differences in brightness and color variation after the

treatment were similar to those of the reference, which, also in this case, were very variable due to the alternation of living rock and lime due to processes of whitewashing.
Previously, for what concerns the evaluation of protective and/or consolidant products [6], three types of calcarenite were selected with lab experiments. Three calcareous stones, Lecce, Matera and Montescaglioso, and eight products were chosen: three largely used commercial products (Acrylic 33, Tegovakon V100 and Paraloid B72) and five experimental nanolatexes from Icap-Leather Chem SpA (Polyrest P1, Polyrest P2, Polyrest AC012, Polyrest AC013, Consolidante 1). The concentrations were chosen in order to obtain the same dry residue for all products and the treatment involved only one of the two sides of the specimens. The application of the products was carried out by brush, until saturation (wet surface for one minute), twice a day every 4 h through 3 days. The protective efficacy of non-commercially available nanopolymers was investigated in comparison with coatings employed in the conservation field, using non-destructive and non-invasive analytical techniques. 1H NMR measurements carried out during capillary water absorption up to saturation, allowed to assess the effects of treatments in terms of hydration kinetics and moisture content variations. Gravimetric data supported the analyses for the three different limestones: Lecce, Montescaglioso, and Matera. Besides pointing out the different pore structures of reference stone systems, NMR results permitted to establish which products could meet the optimum requirements for the lithotypes under consideration. Among the coatings developed by Icap Leather Chem, the

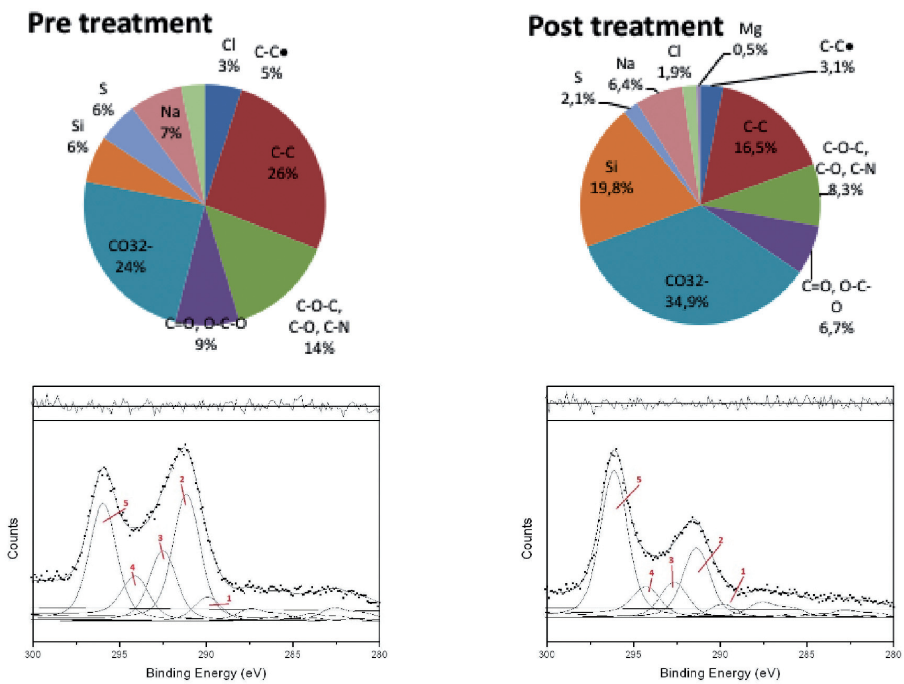

Figure 6. Upper: Percentage composition derived by curve-fitting results of pre- and post- treatment spectra. Lower: curve fitting comparison of detailed C1s regions of pre- (on the left) and post- (on the right) spectra. The assignments were based on the reference peak #2 (Internal Standard C-C) set at 285.0 eV. Peak #1 refers to the lower band energy zone of C-C with carbide, graphite and polycyclic contributions. Peak #3 refers to COC and CN, peak #4 to C=O, OCO and peak #5 to CO_3^{2-}.

most effective ones are AC012 and P1, which, by slowing down hydration kinetics, reconcile protective terms with interactions between stone materials and the environment. Colorimetric data revealed negligible variations for nanopolymer products, contrary to the high darkening and yellowing observed on samples after treatment with some other commercial products. The chromatic effects of the treatment in terms of total color variation were more pronounced in Montescaglioso than in the other lithotypes. Anyway, the treatments with Polyrest P1, Polyrest P2, and Polyrest AC012 on Montescaglioso stones were not particularly critical from a chromatic point of view, since the respective color differences resulted lower than the threshold value.
Finally, after the cleaning treatment, on some church areas, the two Icap-Leather Chem SpA products, Polyrest AC012 and Polyrest P2, were applied.
The peeling tests showed that both products significantly reduced (about 90%) the chalking of the stone.

Conclusions

The studied cases here presented are representative of the wider research actions performed to meet the directives of the project Smart Cities, with specific reference to the stone materials constituent of Matera sites.
The project is aimed at gaining an accurate knowledge of the process of degradation of cultural heritages made of stone materials, caused by atmospheric agents and abiotic biotic agents with deteriogenic capacity [13-14], and ensuring a sustainable restoration based on safe cleaning methods able to reduce professional diseases and environmental pollution. The salient points of Part I show the importance of multi-technical and multidisciplinary approaches for the diagnostic phase and of the combined cleaning actions through the use of natural supports, mostly in gelled forms. The gelled solutions are an interesting alternative to traditional solvents, less selective and more aggressive, and greatly improve and enhance the application possibilities. The advantages related to the use of supporting agents, summarized, are many: they allow the use of biocides, reducing the toxicological risk, to limit the penetration of solvents, slow down their evaporation and therefore lower the level of toxicity, and also allow to proceed in a stratigraphic manner in the cleaning operation. In fact, compared to the traditional cleaning with organic solvents in free form, the supporting agents allow a greater selectivity towards the substances to be removed, since the same intervention can be carried out with solvents with a lower polarity and therefore more selective. Starting from the postulate that every work of art is an unrepeatable unicum, the most delicate restoration operation, namely cleaning, cannot be separated from the preliminary analysis of the executive technique and the state of conservation; it will thus be possible to choose the most suitable support for the specific case.

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Finito di stampare
nel mese di novembre 2021
ISBN 978 88 95609 61 4
CERVINO EDIZIONI