Available green conservation methodologies for the cleaning of cultural heritage: an overview

Marta Gueidão[1]; Eduarda Vieira[1]; Rui Bordalo[1]; Patrícia Moreira[1,2]

[1] Universidade Católica Portuguesa (UCP)-Centro Regional do Porto, Escola das Artes, Centro de Investigação em Ciência e Tecnologia das Artes (CITAR), Portugal

[2] Universidade Católica Portuguesa, Centro de Biotecnologia e Química Fina (CBQF), Portugal

Abstract

The introduction of new guidelines and regulations on chemical production, use, treatment or disposal demanded the development of greener alternatives to conventional products and methodologies. This review briefly presents some of the most promising innovative systems applied in the cleaning of cultural heritage – lasers, green solvents, microemulsions or micellar solutions, bacterial cells or enzymes, ionic liquids and gels. Their advantages and drawbacks are discussed, along with further improvements.

Keywords

Sustainability, Safety, Compatibility, Human health, Ecological.

Introduction

Owing to the growing awareness about climate change and the depletion of natural resources, multiple industries were forced to adopt more sustainable production processes and rethink strategies and products (Lancaster, 2002; Karagölge & Gür, 2016). Aiming at environmental sustainability and safer health conditions for operators, they have implemented measures to mitigate energy consumption, better resource use, reduce waste production and extend materials' usable life, among others (De Silva & Henderson, 2011). In the last few decades, concern about the impact that environmental issues may have on the conservation of cultural heritage has been raised by different entities involved in its preservation (Colette, 2007). Research studies predict that climate change will result in irreversible damage and ultimately in the loss of «material heritage and the intangible dimensions with which it is interwoven» (Hall et al., 2015, p.10) due to the development of more destructive forms of bio-deterioration, climate changes (pollution, atmospheric moisture, temperature, pH, wind), desertification and sea-level rise (Colette, 2007; Hall et al., 2015). Accordingly, conservators have become more conscious about the effect that their short-term actions (treatments and products used) may have in accentuating future heritage deterioration (De Silva & Henderson, 2011; Hall et al., 2015). Moreover, concern has been raised about the need to increase the resistance of cultural assets through ecofriendly solutions with higher durability (De Silva & Henderson, 2011; Balliana et al., 2016; Wolbers, 2017a).

Influenced by the principles that regulate green chemistry (Anastas & Warner, 1998; International Union of Pure and Applied Chemistry, 2016 and Wolbers, 2017a), the field of cultural heritage conservation has been improving its practices towards greener solutions based on environmentally sustainable and safer procedures/materials (P. Baglioni, Chelazzi & Giorgi, 2015; Balliana et al., 2016; Wolbers, 2017a). Research groups and a few universities or organizations have been promoting the development of strategies centered on biotechnology or nanotechnology, that reduce the volume of reagents and waste, while simultaneously increasing their compatibility with historic materials and efficiency in cleaning, consolidating or protecting. Thus, toxic solvents are being replaced wherever possible by products and protocols less harmful to the conservator or the environment and less invasive to cultural heritage objects. Preference is also given to the use of multi-functional reagents and materials, as these allow "doing more with less" and reduce, in the long-term, the amount and diversity of chemical interactions between heritage substrates and conservation materials (Wolbers, 2017a).

In Portugal, these innovative approaches are frequently promoted and updated through seminars and workshops (Universidade Católica Portuguesa, 2016, 2018a, 2018b, 2019a), oral presentations in conferences such as the II Colloquium Investigations in Heritage Conservation held in Faculdade de Belas-Artes da Universidade de Lisboa (Pérez Bento et al., 2020), the 3rd International Conference - Green Conservation of Cultural Heritage (UCP, 2019b) and the Symposium - Conservation of Cultural Heritage and Sustainability: challenges and experiences (Faculdade de Ciências e Tecnologia-Universidade Nova de Lisboa, 2019), or through publications of R&D projects such as BIO4MURAL (UCP, 2018c), PlasCO2 and CleanART (FCT-UNL, 2021).

This review summarizes some of the research and critical analyses done on the most promising available alternatives to conventional methodologies applied in heritage cleaning, given that it is «commonly considered the most critical» operation in a conservation project (Balliana et al., 2016, p.186). Undesired materials or layers vary greatly in composition (from soil to natural or synthetic coatings) (P. Baglioni, Chelazzi & Giorgi, 2015; Palla & Barresi, 2017). Therefore, the removal of these compounds, often deposited over textured, sensitive and highly deteriorated surfaces, can be extremely time-consuming and demanding. Besides being irreversible, cleaning is the operation most associated with the risk of deterioration (Carretti et al., 2005; P. Baglioni et al., 2014; Palla & Barresi, 2017; Bonelli et al., 2019). The cleaning action of the products used must be restricted and cause no physical or chemical alteration that might induce further deterioration. Thus, knowledge about the cultural asset itself (history, composition and technique) and the different alternatives available is crucial to select a compatible cleaning system.

In this context, the separate or synergic use of green approaches – i.e. environmentally sustainable and/or safer alternatives to both operator and historic materials – based on the use of lasers, green solvents, microemulsions or micellar solutions, bacterial cells or enzymes, ionic liquids and gels, constitute promising alternatives to the excessive use of organic solvents and toxic cleaning products. The properties, action mechanisms and advantages of each method are discussed along with disadvantages and further improvements, and then summarized in Table 1.

Laser

Laser systems are an alternative well-established method in cultural heritage preservation, which has been used for cleaning purposes and improved for decades (Siano, 2008; Doehne & Price, 2010; Balliana et al., 2016). It permits a less invasive removal of oxidized and polymerized coatings, encrustations, pollutants or overpaints without the use of solvents or harmful products and without any mechanical or chemical contact with historic materials (Fotakis et al., 2007). The different types of commercially available lasers allow conservators to select the most adequate for any specific conservation work. Hence, they achieve a controlled and selective cleaning of a wide range of materials (e.g.: stone, wood, metal, paper or canvas) without interfering with the surface or underlying substrate (Rodríguez-Navarro et al., 2003; Siano, 2008; Siano et al., 2012; Lahoz et al., 2013).

In contrast to traditional methods, laser cleaning is an effective, precise and versatile technique, suitable for the treatment of sensitive surfaces (noncontact system). Through its combination with Laser-Induced Breakdown Spectroscopy (LIBS) or other analytical techniques, its effectiveness can be monitored in real time, to better control its cleaning action and to prevent any further deterioration (Rodríguez-Navarro et al., 2003; Fotakis et al., 2007; Siano et al., 2012).

Though being a greener and non-invasive alternative, laser cleaning is still considered not easily available and therefore inadequate for routine application in cultural heritage conservation (Lahoz et al., 2013; Balliana et al., 2016). It is a more expensive method that requires preliminary study and extensive knowledge about the interaction between the laser and the materials to select the appropriate laser parameters (Fotakis et al., 2007; Siano et al., 2012). Its misuse can induce further deterioration (e.g.: chromatic alterations) and cause irreversible short- or long-term effects (Fotakis et al., 2007; Doehne & Price, 2010).

Green Solvents

Owing to the hazard posed by the use of mostly harmful solvents and in compliance with one of the principles of green chemistry – the «use of harmless or non-toxic reagents» (Wolbers, 2017a, p.5) –, green solvents have been implemented and promoted in conservation as an alternative cleaning approach (Volpi, 2017; Gonçalves, 2018; Macchia et al., 2019; Ricci et al., 2020).

Different organizations have made available guides classifying solvents according to their impact on environment, health and safety (EHS), their life cycle assessment (LCA) and inherent energy costs of manufacture, application and reuse or disposal (Alfonsi et al., 2008, F.P. Byrne et al., 2016 and Gonçalves, 2018). However, these various guides differ in compounds' classification due to the influence of the companies' individual preferences, differences in the numerical calculation of the gradings and the diversity of type and number of parameters considered. The collaborative project CHEM21, developed jointly by entities that have written some of the previously mentioned selection guides, highlights this lack of consensus (F.P. Byrne et al., 2016; Gonçalves, 2018).

In most guides, a limited number of classes of organic solvents (only alcohols and esters) are placed as green solvents, along with water (Alfonsi et al., 2008; F.P. Byrne et al., 2016; Gonçalves, 2018). Solvents of biological origin (produced with biomass) are also mentioned as substitutes for different protic solvents, esters, ketones and ethers (F.P. Byrne et al., 2016). However, none meet all the requirements of a "completely green" solvent (F.P. Byrne et al., 2016; Häckl & Kunz, 2018). Most of the alternatives for non-recommended solvents only address one of their negative properties (e.g.: they have lower toxicity, but the energy consumption of their production equals that of the non-green solvent) (Gonçalves, 2018). For instance, water generally gets the higher rating in solvent classification and, in conservation, the use of aqueous methods instead of organic solvents is one of the mostly used safe and "environmentally friendly" approach. Nevertheless, its complete sustainability can be called into question if its high energy cost is taken into greater consideration (F.P. Byrne et al., 2016; American Institute for Conservation, 2018). For example, the production process of distilled water is extremely time-consuming, requires high amounts of energy to produce small quantities and it represents about 95% waste of the initial quantity (AIC, 2018). Although, in some cases, distilled water can be substituted by deionized or tap water, resorting to aqueous systems still can't be considered completely sustainable due to water scarcity.

Increasing the sustainability of a conservation treatment or minimizing toxicity without simultaneously compromising effectiveness is often one of the most challenging aspects in the development of greener products and processes. To select the most appropriate solvent it is crucial to consider the properties of the surface in treatment and the layers to be removed (Gonçalves, 2018). Some alternative substances and solvents, although greener, do not apply to the intended use, so a critical analysis of the substitute products determined by the available guides is advised. To assist in solvent selection for heritage conservation purposes, different databases were developed: for example, the Solvent Solver® program, by the US National Archives and Register Administration (NARA, 2016; AIC, 2018); the TriSolv® program, by Istituto Centrale per il Restauro (ICR, 2020); and the Modular Cleaning Program®, by the Getty Conservation Institute in collaboration with California State University, Winterthur/University of Delaware Art Conservation Program and Winterthur Museum Conservation Division (Conservation OnLine, 2009; Stavroudis & Doherty, 2013). They help the conservator to tailor solvent mixtures, solvent gels or aqueous systems, adjust them to the same dissolving power as a more harmful product and be more compatible with each case study (CoOL, 2009; Stavroudis & Doherty, 2013; NARA, 2016; AIC, 2018; ICR, 2020).

Nonetheless, this sustainable approach by itself does not solve one of the main drawbacks of the use of organic solvents in cultural heritage conservation – the invasiveness of free-fluid solvents, their impregnation and retention in the substrate. It needs to be combined with systems structured by a 3D matrix capable of sustaining a liquid phase and releasing it gradually (e.g.: gel).

Microemulsions and micellar solutions

Nanostructured fluids (microemulsions and micellar solutions) are considered one of most valuable innovative strategies for cultural heritage conservation (P. Baglioni, Chelazzi & Giorgi, 2015). Microemulsions and micellar solutions are both liquid dispersions stabilized by aggregates of the surfactant's amphiphilic molecules that form above the critical micelle concentration. However, microemulsions are constituted by a dispersed phase that is insoluble in the continuous phase (solvent) (Carretti et al., 2005). Microemulsions are greener and more efficient systems formed by a high percentage of water (75-99%) and a reduced organic content (>0.5%-15% including both solvents and surfactants). They combine the detergency properties of surfactants with the solvation action of organic solvents, requiring smaller amounts of solvents in their formulation. Hence, the toxicity and environmental impact of the cleaning treatment is reduced without compromising its action (Carretti et al., 2005; P. Baglioni, Chelazzi & Giorgi, 2015; P. Baglioni et al., 2014, 2019).

These thermodynamically stable systems ensure selective cleaning of mainly wall paintings and stone surfaces through the formation of a hydrophobic barrier that prevents impregnation and retention of the solvent and limits its action to the surface (Balliana et al., 2016; P. Baglioni & Giorgi, 2006). Their optical transparency acts as an additional aid in managing its cleaning action (Carretti et al., 2005). The chemical and physical properties of these solutions based on amphipathic molecules allow the removal of synthetic materials used in previous conservation treatments, that were otherwise unremovable (Giorgi et al., 2010; P. Baglioni et al., 2013, 2014; M. Baglioni et al., 2015; P. Baglioni, Chelazzi & Giorgi, 2015). They optimize cleaning solution-undesired material interaction, increasing swelling/solubilization rate and therefore facilitating removal. Once detached, the undesired hydrophobic material is surrounded by a hydrophilic phase that prevents redeposition. Thus, research groups have assessed their application on water-sensitive substrates (e.g.: canvas, paper, wood) and found that loading them into hydrogels can enhance their performance (Gorel, 2010), allowing the controlled release of the liquid phase and cleaning agents (P. Baglioni, Chelazzi & Giorgi, 2015).

The main drawbacks of micelle-based systems are the lack of commercially available formulations and the dissemination of most of the research via journals outside the conservation field (Balliana et al., 2016).

Biocleaning

Another sustainable cleaning solution consists in biologically based systems that resort to the action of microorganisms and enzymes (Silva, 2017). Most of the enzymes selected are hydrolases, which can break down polymer structures (e.g.: proteinaceous materials, starch paste, adhesives, acrylic coatings or drying oils). Commercial hydrolases such as proteases, amylases, lipases and esterases (isolated from animal, vegetal and microbial sources) are pointed out as safer alternatives to conventional acid- and alkaline-based cleaning treatments (Palla & Barresi, 2017).

Biocleaning systems require a careful selection of the appropriate bioagent(s) in order to ensure a good performance in the removal of undesired substances (e.g.: soluble salts, organic matter, natural and artificial polymers, or graffiti) and avoid promoting further deterioration (Fernandes, 2006; Bosch-Roig et al., 2014; Balliana et al., 2016). Thus, microorganisms' selection must take into consideration a previous chemical and physical characterization of the decay and give preference to non-pathogenic, environmentally-friendly strains (ideally non-spore forming to simplify elimination after treatment) (Palla & Barresi, 2017).

Bioagents' cleaning action can be optimized by loading them into a delivery system that provides the right environmental conditions and nutrients, controls their interaction with the surface (minimizing invasiveness) and facilitates formulation, application and removal (Palla & Barresi, 2017; Silva, 2017). Enzymes or bacterial cells can be combined with ionic liquids (Kuckova et al., 2014) and poultices or gels (Bosch-Roig et al., 2014; Balliana et al., 2016 and Bosch-Roig et al., 2017) to enhance their effectiveness, selectivity and compatibility (Fernandes, 2006; Cremonesi, 2015; Palla & Barresi, 2017). Bacteria's metabolism is then able to easily dissolute the undesired materials with the complementary action of the gelled systems (humidification and mollifying of layers) (Balliana et al., 2016). Their delivery in cotton wool or Japanese paper has also been mentioned by Palla & Barresi (2017).

Biocleaning is classified has a highly versatile strategy with low impact on cultural assets, the operator and the environment, that allows a more homogeneous, gradual and controllable action. Several research groups consider it a viable remediation treatment for historical architectural monuments, mural paintings, stone surfaces and sculptures, paper and paintings (Bosch-Roig et al., 2014; Palla & Barresi, 2017; Silva, 2017). Nonetheless, unlike other alternative approaches, biocleaning systems are not commercially available in a large scale as a ready-to-use formulation (Balliana et al., 2016) and are still at an early stage of application in case studies (Bosch-Roig et al., 2017). Bosch-Roig et al. also refer application problems, such as the incorrect adherence of some delivery systems to irregular surfaces and «the need to maintain optimal temperature and relative humidity for bacteria to metabolize [which] reduces the number of works that can withstand such stress» (Bosch-Roig et al., 2017, p.119).

Ionic Liquids

Ionic liquids (ILs) have been recently introduced as a greener and safer approach to the preservation of cultural heritage (Kozigóg & Wysocka-Robak, 2017). They are formed exclusively by cations and anions, are recyclable, thermally and chemically stable and non-inflammable, have generally higher viscosity (lower penetration rate) than conventional solvents and the capacity to dissolve (in)organic or polymeric materials (Chowdhury et al., 2007; Poole, 2004; Kozigóg & Wysocka-Robak, 2017; Lo Schiavo et al., 2020). Alterations in the combination of its components allow the adjustment of viscosity, pH and melting point according to surface and substrate's properties (Balliana et al., 2016; Lo Schiavo et al., 2020).

Research studies have mentioned ILs' ability to remove calcium crusts from stained glass or synthetic and natural varnishes (Lo Schiavo et al., 2020). Some have also assessed the efficiency of commercially available ILs, alone (Pacheco et al., 2013) and in combination with enzymatic solutions (Kuckova et al., 2014), for the removal of natural or artificial resins and proteinaceous materials from polychrome surfaces. Lo Schiavo et al. characterize ILs as solutions with «good antifouling activity on different stone substrates» and refer to them as possible contributions «to the production of new formulations of antifouling and antimicrobial surface coatings, developed as gel materials and other forms» (Lo Schiavo et al., 2020, p.13). ILs' variety of combinations and capacity to inhibit microbial activity and buffer pH have also placed them as potential deacidification, disinfection (biocolonization) and disinfestation (insects and rodents) methods for paper heritage preservation (Kozigóg & Wysocka-Robak, 2017; Dimitrić et al., 2019). Schmitz et al. mention that «the persistence of growth-free halos around IL inoculation sites throughout the observation period of four weeks indicated long-term stability and inertness of the tested ILs towards fungal decay or abiotic factors» (Schmitz et al., 2019, p.9), referring to ILs as possible solutions for long-term biocolonization inhibition in archived documents.

This alternative approach has showed good results in terms of versatility, compatibility, selectivity and cleaning action. Nonetheless, concerns were risen regarding its cost and the detection of residues attributed to its extremely low vapor pressure and consequent difficult removal, which can promote or induce deterioration (Balliana et al., 2016). Further research is needed regarding its application in case studies with different substrates, its biodegradability and compatibility with traditional materials, solubility parameters and kinetics of deterioration (Balliana et al., 2016; Lo Schiavo et al., 2020).

Gels

Gels are used not only as delivery systems for many of the cleaning solutions listed above but also as sustainable cleaning methods (Gulotta et al., 2014; Carretti & Dei, 2006; P. Baglioni et al., 2009; Carretti et al., 2009; M. Baglioni et al., 2012; Kavda et al., 2017; Chelazzi et al., 2018; Al-Emam et al., 2019). A gel is defined, according to IUPAC, as a «non-fluid *colloidal network* or *polymer network* that is expanded throughout its whole volume by a fluid» (Jones, 2007, p.1806); i.e. it is formed by the transition from liquid to a disordered solid (Dudukovic, 2015; Volpi, 2017), through the formation of a 3D matrix of polymeric chains – that are crosslinked (covalent polymer network) or "physically *aggregated"* «by hydrogen bonds, crystallization, helix formation, complexation, etc.» (Jones, 2007, p.1806) – dispersed in a continuous phase (Bertasa et al., 2017).

Gels stand out for their capacity to «retain large amounts of liquid» (P. Baglioni et al., 2019, p.183) in a matrix that releases them gradually and incorporate «different liquid media like organic solvents, micellar solutions, o/w microemulsions, or aqueous solutions containing enzymes or chelates» (P. Baglioni et al., 2014, p.365). Therefore, they are considered one of the most efficient materials in the controlled and non-invasive cleaning of cultural heritage (P. Baglioni et al., 2014; P. Baglioni, Chelazzi & Giorgi, 2015; Bonelli et al., 2019). Despite being a promising greener methodology, the cost of some gelator components hinders its extensive use and further studies need to be carried out to improve their compatibility, selectivity and retentiveness. (Balliana et al., 2016).

The need for versatile cleaning methods highlighted by the generally complex chemical nature of the materials to be removed is matched by the wide variety of gel formulations. Researchers have established different classes and types of gelled systems according to their chemical and physical properties and the advances in the field (P. Baglioni, Chelazzi & Giorgi, 2015; Volpi, 2017; Vázquez Pérez, 2018; Bonelli et al., 2019). P. Baglioni et al. (2014, 2019) divide them into traditional thickeners and physical gels, introduced by Wolbers in the 1990s (Carretti et al., 2008), and innovative nanostructured gels or gel-like systems (responsive gels and peelable systems).

Traditional thickeners and gels

Soft solvent gels were one of the first high-viscosity cleaning methods used in cultural heritage conservation and, therefore, are classified as traditional thickeners and physical gels. They combine or intensify the action of miscible solvents and are generally formed by natural (cellulose-derived ethers) or synthetic (polyacrylic acid, PAA) water-soluble polymers/macromolecules (P. Baglioni et al., 2014), that act as thickeners and viscosity modifiers reducing the fluidity of a solvent and/or solution and decreasing the diffusion rate (A. Byrne, 1991; Volpi, 2017). Cellulose-derived ethers (methyl, hydroxypropyl, methylhydroxypropyl cellulose) are miscible and soluble in water or polar organic solvents, forming a poultice widely applied in conservation due to their low cost and practical formulation (Volpi, 2017). In turn, PAA-based cleaning systems are activated by adding a weak basic non-ionic surfactant that causes a neutralization reaction and enhances their thickening properties through the formation of a salt (P. Baglioni et al., 2014; Volpi, 2017).

Soft gels have a greater tendency to leave solid residues (mainly gelling polymer) after removal due to the weaker bonds established between polymer chains (Carretti et al., 2008). The required additional rising solutions and/or mechanical action have showed to produce alterations similar to those observed in non-confined solvent applications (P. Baglioni et al., 2019). Since the complete removal of some residues «is not achieved even using rising solvents and mechanical action» (Bonelli et al., 2019, p.340), gelled systems formed by these thickeners or viscosity modifiers should be avoided in textured or irregular surfaces (P. Baglioni et al., 2014; Bonelli et al., 2019).

Other traditionally applied physical gels are based on biodegradable natural polysaccharides (e.g.: gellan gum and agar) that aim at minimizing the impact of water application on highly sensitive and porous substrates (P. Baglioni et al, 2014; Volk & Van den Berg, 2014; Royo Fraguas et al., 2015; Cremonesi & Casoli, 2017; Maranesi, 2017; Puoti et al., 2017; Kanth et al., 2018). These semi-rigid, hydrophilic gels are structured in a 3D mesh of double-helices, interlinked via secondary interactions, such as hydrogen bonds or Van der Waals forces (P. Baglioni et al., 2014, 2019; Bertasa et al., 2017; Wolbers, 2017b).

The resulting cleaning system is an extremely useful and versatile tool widely applied in conservation due to its thermoreversible 3D network junction points – i.e. its non-covalent interactions can be broken or re-established by heating or cooling, returning to a fluid solution or re-hardening (Armisén & Galatas, 2009; Zucca et al., 2016; Wolbers, 2017b). Thus, it can be applied directly onto the surface in rigid or viscous form and easily removed in solid state at room temperature. This guarantees full coverage of textured surfaces and minimizes the risk of deterioration with subsequent chemical or mechanical action (P. Baglioni et al., 2019; Bertasa et al., 2017). The efficiency and invasiveness of its cleaning action varies according to the concentration of the gelator (Tortajada Hernando & Blanco Domínguez, 2013) and the addition of reagents – solvents, enzymatic solutions, non-ionic surfactants or weak chelating agents can be loaded into the hydrogel without compromising its retentiveness (Gorel, 2010; Scott, 2012; Cremonesi, 2015, 2016). However, incorrect manipulation can lead to various forms of deterioration. Its light extraction power may cause the migration of components from different layers or the substrate and its use at an excessively high temperature may create surface staining or cause the decomposition of agar solutions («resulting in a net lower gel strength after temperature decrease and gel formation», Wolbers, 2017b, p.381). The presence of solid residues after removal (due to its application with reduced thickness) may also induce biological colonization (Tortajada Hernando, 2011; Tortajada Hernando & Blanco Domínguez, 2013; Wolbers, 2017b).

Innovative gels and gel-like systems

Owing to the disadvantages of traditional gels, scientific research focused on the formulation of alternative gelled systems. P. Baglioni et al. (2014) subdivide innovative nanostructured gels or gel-like systems into responsive gels and peelable systems, both having chemical and physical properties that allow the minimization or complete elimination of analytically detectable residues.

Responsive gels' chemical structure allows a «rapid, complete and non-invasive removal via a response to "chemical" or to "physical" stimuli» (P. Baglioni et al., 2014, p.366). They include rheoreversible gels based on polyamines and nanomagnetic sponges with a polyacrylamide network.

Polyallylamine or polyethyleneimine solutions are easily transformed into gels upon reacting with CO_2 and forming a 3D polymeric structure (Carretti et al., 2003, 2004, 2008; Suzuki & Hanabusa, 2010; P. Baglioni et al., 2014, 2019). These gels can in turn be completely removed with cotton swabs, after adding a few drops of a weak acid solution (mineral or organic), and converting them into a liquid (Carretti et al., 2010; P. Baglioni et al., 2019). Although this rheoreversible system can be highly effective, it is still scarcely applied and in need of further improvements: its intrinsic thixotropy hampers its correct handling and control (P. Baglioni et al., 2014) and its removal method restricts its use to less porous artefacts.

Nanomagnetic sponges are «obtained by functionalizing an acrylamide-based polymer network with ferrite nanoparticles» (P. Baglioni et al., 2019, p.187). This enhances the hydrogel elasticity and makes it responsive to magnetic fields, enabling its complete removal by simply lifting it with a permanent magnet (P. Baglioni et al., 2014). Hence, they are a safe cleaning approach with a non-invasive removal method that can be applied onto surfaces with high sensitivity to mechanical stress (Carretti et al., 2010; P. Baglioni et al., 2019). The micrometric porosity of these gel-nanoparticle systems allows the controlled release of cleaning agents such as aqueous solutions, micellar systems or o/w microemulsions (Carretti et al., 2010).

Another innovative cleaning system based on poly(methyl methacrylate) (PMMA) organogels has been studied in order to assess its potential in cultural heritage conservation. MMA form a «solid system, non-crystalline, thermoreversible (thermoplastic) and viscoelastic» gel (Pianorsi, 2017, p.100) with a wide range of pure organic solvents (Suzuki & Hanabusa, 2010). Its properties can be tuned by adjusting «the amount of cross-linker and the monomer-solvent phase ratio during the synthesis of the gel» (Pianorsi, 2017, p.78; P. Baglioni et al., 2019). Since organogels are «chemical networks where the confined liquid phase is composed of organic solvents» (P. Baglioni et al., 2015, p.858) and «the loaded solvents have lower polarity that those typically confined in hydrogels» (P. Baglioni et al., 2019, p.190), they represent a versatile cleaning method capable of swelling and dissolving a large variety of materials (e.g.: adhesives, wax, natural and synthetic coatings) from canvas paintings and paper artifacts (P. Baglioni et al., 2015, 2019; Pianorsi, 2017; Pianorsi et al., 2017). PMMA organogels can be applied directly onto the surfaces and easily removed with light mechanical action using cotton swabs (leaving no detectable residues). Their optical transparency aids in the control of its cleaning action during application (P. Baglioni et al., 2015; Pianorsi, 2017).

According to P. Baglioni et al., peelable systems are formulations with «high intrinsic elasticity» (P. Baglioni et al., 2014, p.366) that enables their easy removal from sensitive surfaces residue-free through a peeling action (Carretti et al., 2010). They include highly viscous polymeric dispersions (HVPDs) based on polyvinyl alcohol (PVA) and semi-interpenetrated polymer networks (semi-IPNs) based on polyvinylpyrrolidone (PVP) and polyhydroxyethyl methacrylate (pHEMA) (P. Baglioni et al., 2014, 2019; Bonelli et al., 2019).

The most commonly used HVPD results from a condensation reaction between PVA's hydroxyl groups and borax (Natali et al., 2011; Riedo et al., 2015; Riedo et al., 2017). Its efficiency and invasiveness are regulated by the concentration of both components, pH and temperature, degree of PVA hydrolysis, and «the composition of the continuous embedded aqueous phase» (P. Baglioni et al., 2014, p.369; Baglioni et al., 2019; Angelova et al., 2017; Fialová & Kotlík, 2017; Varadinova-Papadaki, 2017). Significantly high quantities of organic solvents can be added to alter its viscoelastic properties without compromising thermodynamic stability (P. Baglioni et al., 2014). PVA/borax HVPD's transparency and its simply adjustable mechanical and viscoelastic properties grant more control and selectivity to its cleaning action.

Bonelli et al. (2019) assessed another cleaning system formed by adding PVP (highly hydrophilic) to PVA-based hydrogels, influencing their hydrophilicity, porosity and rheological behavior. PVA/PVP formulations show high mechanical resistance and the ability to completely remove soil from textured polychrome layers due to an enhanced adhesion to irregular surfaces.

As a (semi-IPN)-based cleaning approach P. Baglioni et al. (2014, 2019) refer to a biphasic chemical hydrogel system formed by PVP and pHEMA, that combines polymeric substances with different polarity, the hydrophilicity of one component and the mechanical strength of the other. The retentiveness, porosity, viscoelastic behavior and hydrophilicity of this semi-IPN can be tailored to the substrate or surface in treatment by altering its formulation (P. Baglioni et al. 2014, p.369; Giorgi et al., 2013). Several organic solvents with different solubility parameters and aqueous cleaning agents (e.g.: enzyme or micellar solutions and o/w microemulsions) can also be added to promote the removal of different materials (soil, varnish, adhesives, other aged conservation materials) in water-sensitive artifacts (Domingues et al., 2013a, 2013b, 2014; P. Baglioni et al., 2014; Sun et al., 2015; Eriksson et al., 2017). Semi-IPN have a higher peelability, optical transparency and water-retention than traditional rigid gels (Domingues et al., 2013b; P. Baglioni et al., 2014, 2019).

Green Cleaning Methodologies	
Laser	**Advantages** Less invasive No use of solvents No mechanical or chemical contact with artefacts Different types are commercially available Suitable to clean wide range of materials No alteration to the surface or underlying substrate Controlled and selective cleaning action Can be monitored in real time **Disadvantages** Expensive method Requires preliminary study and extensive knowledge on the technique
Green Solvents	**Advantages** Reduced impact on EHS LCA taken into account Programs to assist in solvent selection and mixture are available **Disadvantages** Disparity in classification Limited number of solvents considered green Some alternatives do not apply to intended use Free-fluid solvents invasiveness Possible impregnation and retention in substrate Need to be combined with other systems
Microemulsions and micellar solutions	**Advantages** Require smaller amounts of solvents Reduced impact on EHS Thermodynamically stable throughout wide range of environments Prevent impregnation and retention of solvents Optical transparency Can be loaded into hydrogels Increased swelling/solubilization rate Prevent redeposition of undesired materials **Disadvantages** Lack of commercially available formulations Off-target dissemination of research

Green Cleaning Methodologies	
Biocleaning	**Advantages** Safer than conventional acids and alkaline-based cleaning treatments Can be loaded into delivery system (facilitate formulation, application and removal; optimize cleaning action; and control interactions with surface) Possible synergistic cleaning action with delivery system Highly versatile, effective and selective strategy Low impact in heritage artifacts More homogeneous, gradual and controllable cleaning action **Disadvantages** Require careful selection of appropriate bioagents Not commercially available in a large scale Still in preliminary stages of application to case studies Application problems (adherence to overly textured surfaces) Need to maintain optimal hygrothermal conditions for bioagents to remain viable
Ionic Liquids	**Advantages** Can be used as delivery system or as cleaning method alone Recyclable Thermally and chemically stable Formed exclusively by cations and anions Non-inflammable Lower penetration rate (high viscosity) Adjustable mechanical and chemical properties Antimicrobial activity pH buffer capacity Long-term stability and inertness Commercially available formulations Versatile, compatible and selective **Disadvantages** High cost Detection of residues Difficulty in removal (can promote or induce deterioration) processes Need of more research regarding application in different substrates

Green Cleaning Methodologies	
Gels	**Advantages** Can be used as delivery system or as cleaning method alone Can be loaded with different classes of liquid media Capable to retain large amounts of fluid Ability to retain liquid in matrix and release it gradually Decreased diffusion rate Reduced impact of water on highly sensitive and porous substrates Efficient, controlled and non-invasive cleaning action Versatile cleaning system (wide variety of gelled systems) Tunable chemical and mechanical properties Advances in research to overcome traditional thickeners and physical gels' disadvantages (facilitate removal and enhance compatibility) Innovative gels or gel-like systems can be removed residue-free and with no impact on surfaces Optical transparency of some systems allows better control of cleaning action **Disadvantages** Need to improve compatibility with some materials, selectivity and retentiveness High cost of some gelator components Problems with complete removal (traditional thickeners and physical gels) Problems with complete adherence to irregular surfaces (traditional thickeners and physical gels) Some innovative gels or gel-like systems are still scarcely applied and need further improvements

Table 1 – Comparison of green conservation methodologies for cultural heritage cleaning.

Conclusion

Over the last few decades, several scientific studies have been carried out to develop innovative cleaning methodologies or greener suitable materials that provide greater safety for the conservator, the environment and the cultural heritage artefacts (summary in Table 1). These alternative systems aim at the decrease of diffusion and retention rates, the reduction of reagent volume, the optimization of cleaning action and the increase of operational time. They have proven to be more efficient, controllable and compatible than conventional methodologies based on organic solvents or harmful products and can be tailored to meet specific demands (Wolbers, 2017a).

Though potentially more effective and non-invasive, most sustainable cleaning solutions require specialized professionals and significant knowledge about the technique in order to be formulated and used safely in cultural heritage conservation (Balliana et al., 2016). Thus, parallel to the development and the improvement of greener treatments, it is crucial to invest in dissemination and training for conservators on their preparation and application methods, through the collaboration between operators, companies, and researchers.

The frequent off-target dissemination of information and the reduced amount of commercially available alternatives also hinder their widespread use (Balliana et al., 2016). Many of these innovative methodologies are not easily accessible, not marketed in ready-to-use formulations or do not even reach the production phase (they are deemed economically or industrially nonviable). Further investigation needs to be carried out to improve technical difficulties in preparation, optimize and simplify formulation and make them practical and easy to use.

References

Al-Emam, E., Motawea, A.G., Janssens, K., & Caen J. (2019). Evaluation of polyvinyl alcohol-borax/agarose (PVA-B/AG) blend hydrogels for removal of deteriorated consolidants from ancient Egyptian wall paintings. *Heritage Science, 7(22)*, 1-18. https://doi.org/10.1186/s40494-019-0264-z

Alfonsi, K., Colberg, J., Dunn, P.J., Fevig, T., Jennings, S., Johnson, T.A., Kleine, H.P., Knight, C., Nagy, M.A., Perry, D.A., & Stefaniak, M. (2008). Green chemistry tools to influence a medical chemistry and research chemistry-based organisation. The Royal Society of Chemistry. *Green Chemistry, 10(1)*, 31-36. https://doi.org/10.1039/b711717e

American Institute for Conservation (2018). Sustainability and Chemicals.https://www.conservation-wiki.com/wiki/Sustainability_and_Chemicals

Anastas, P.T., & Warner, J.C. (1998). *Green Chemistry: Theory and Practice.* Oxford University Press.

Angelova, L.V., Berrie B.H., & Weiss, R.G. (2017). Poly(vinyl alcohol)-borax 'gels': a flexible cleaning option. In Angelova, L.V., Ormsby, B., Townsend, J.H., & Wolbers, R. *Gels in the Conservation of Art* (pp.231-236). Archetype Publications.

Armisén, R., & Galatas, F. (2009). Agar. In Phillips, G.O., & Williams, P.A.(Ed.) Handbook of hydrocolloids (2nd ed.) (pp.82-107). Woodhead Publishing Limited.

Baglioni, M., Benavides, Y.J., Desprat-Drapela, A., & Giorgi, R. (2015). Amphiphile-based nanofluids for the removal of styrene/acrylate coatings: Cleaning of stucco decoration in the Uaxactun archeological site (Guatemala). *Journal of Cultural Heritage, 16(6)*, 862-868.https://doi.org/10.1016/j.culher.2015.03.008

Baglioni, M., Giorgi, R., Berti, D., & Baglioni, P. (2012). Smart cleaning of cultural heritage: a new challenge for soft nanoscience. *Nanoscale, 4(1)*, 42-53. https://doi.org/10.1039/C1NR10911A

Baglioni, P., Baglioni, M., Bonelli, N., Chelazzi, D., & Giorgi, R. (2019). Smart Soft Nanomaterials for Cleaning. In Lazzara, G., & Fakhrullin, R. (Eds.). *Nanotechnologies and Nanomaterials for Diagnostic, Conservation, and Restoration of Cultural Heritage*. Advanced Nanomaterials Series (pp.171-204). Elsevier. https://doi.org/10.1016/B978-0-12-813910-3.00009-4

Baglioni, P., Berti, D., Bonini, M., Carretti, E., Dei, L., Fratini, E., & Giorgi, R. (2014). Micelle, microemulsions, and gels for the conservation of cultural heritage. *Advances in Colloid and Interface Science, 205*, 361-371.https://doi.org/10.1016/j.cis.2013.09.008

Baglioni, P., Bonelli, N., Chelazzi, D., Chevalier, A., Dei, L., Domingues, J., Fratini, E., Giorgi, R., & Martin, M. (2015). Organogel formulations for the cleaning of easel paintings. *Applied Physics A, 121*, 857-868.https://doi.org/10.1007/s00339-015-9364-0

Baglioni, P., Chelazzi, D., & Giorgi, R. (2015). *Nanotechnologies in the Conservation of Cultural Heritage: A compendium of materials and techniques*. Springer. https://doi.org/10.1007/978-94-017-9303-2

Baglioni, P., Chelazzi, D., Giorgi, R., & Poggi, G. (2013). Colloid and Materials Science for the Conservation of Cultural Heritage: Cleaning, Consolidation, and Deacidification. *Langmuir, 29(17)*, 5110-5122.https://doi.org/10.1021/la304456n

Baglioni, P., Dei, L., Carretti, E., & Giorgi, R. (2009). Gels for the Conservation of Cultural Heritage. *Langmuir, 25(15)*, 8373-8374.https://doi.org/10.1021/la900961k

Baglioni, P., & Giorgi, R. (2006). Soft and hard nanomaterials for restorations and conservation of cultural heritage. *Soft Matter, 2(4)*, 293-303.https://doi.org/10.1039/B516442G

Balliana, E., Ricci, G., Pesce, C., & Zendri, E. (2016). Assessing the value of green conservation for cultural heritage: positive and critical aspects of already available methodologies. *International Journal of Conservation Science, 7(1)*, 185-202.http://hdl.handle.net/10278/3672441

Bertasa, M., Chiantore, O., Poli, T., Riedo, C., di Tullio, V., Canevali, C., Sansonetti, A., & Scalarone, D. (2017). A study of commercial agar gels as cleaning materials. In Angelova, L.V., Ormsby, B., Townsend, J.H., & Wolbers, R. *Gels in the Conservation of Art* (pp.11-18). Archetype Publications.

Bonelli, N., Poggi, G., Chelazzi, D., Giorgi, R., & Baglioni, P. (2019). Poly(vinyl alcohol)/poly(vinyl pyrrolidone) hydrogels for the cleaning of art. *Journal of Colloid and Interface Science, 536*, 339-348.https://doi.org/10.1016/j.jcis.2018.10.025

Bosch-Roig, P., Lustrato, G., Zanardini, E., & Ranalli, G. (2014). Biocleaning of Cultural Heritage stone surfaces and frescoes: which delivery system can be the most appropriate?. *Annals of Microbiology, 65(3)*, 1227-1241.https://doi.org/10.1007/s13213-014-0938-4

Bosch-Roig, P., Regidor Ros, J.L., Soriano Sancho, M.P., Montes Estellés, R., & Roig Picazo, P. (2017). Biocleaning of wall paintings on uneven surfaces with warm agar gels. In Angelova, L.V., Ormsby, B., Townsend, J.H., & Wolbers, R. *Gels in the Conservation of Art* (pp.119-221). Archetype Publications.

Byrne, A. (1991). Wolbers cleaning methods: introduction. *AICCM Bulletin, 17(3-4)*, 3-11. https://doi.org/10.1179/bac.1991.17.3-4.001

Byrne, F.P., Jin, S., Paggiola, G., Petchey, T.H.M., Clark, J.H., Farmer, T.J., Hunt, A.J., McElroy, C.R., & Sherwood, J. (2016). Tools and Techniques for solvent selection: green solvent selection guides. *Sustainable Chemical Processes, 4(7)*, 1-24. https://doi.org/10.1186/s40508-016-0051-z

Carretti, E., Bonini, M., Dei, L., Berrie, B.H., Angelova, L.V., Baglioni, P., & Weiss, R.G. (2010). New Frontiers in Materials Science for Art Conservation: Responsive Gels and Beyond. *Accounts of Chemical Research, 43(6)*, 751-760.https://doi.org/10.1021/ar900282h

Carretti, E., & Dei, L. (2006). Gels as cleaning agents in cultural heritage conservation. In Weiss, R.G., & Terech, P. (Eds.) *Molecular Gels* (pp.929-938). https://doi.org/10.1007/1-4020-3689-2_28

Carretti, E., Dei, L., Baglioni, P., & Weiss, R.G. (2003). Synthesis and Characterization of Gels from Polyallylamine and Carbon Dioxide as Gellant. *Journal of the American Chemical Society, 125(17),* 5121-5129.https://doi.org/10.1021/ja034399d

Carretti, E., Dei, L., Macherelli, A., & Wiess, R.G. (2004). Rheoreversible Polymeric Organogels: The Art of Science for Art Conservation. *Langmuir, 20*, 8414-8418.https://doi.org/10.1021/la0495175

Carretti, E., Dei, L., Weiss, R.G., Baglioni, P. (2008). A new class of gels for the conservation of painted surfaces. *Journal of Cultural Heritage, 9(4)*, 386-393.https://doi.org/10.1016/j.culher.2007.10.009

Carretti, E., Grassi, S., Cossalter, M., Natali, I., Caminati, G., Weiss, R.G., Baglioni, P., & Dei, L. (2009). Poly(vinyl alcohol)-Borate Hydro/Cosolvent Gels: Viscoelastic Properties, Solubilizing Power, and Application to Art Conservation. *Langmuir, 25(15)*, 8656-8662.https://doi.org/10.1021/la804306w

Carretti, E., Salvadori, B., Baglioni, P., & Dei, L. (2005). Microemulsions and Micellar Solutions for Cleaning Wall Paintings Surfaces. *Studies in Conservation, 50(2)*, 128-136.https://doi.org/10.1179/sic.2005.50.2.128

Chelazzi, D., Fratini, E., Giorgi, R., Mastrangelo, R., Rossi, M., & Baglioni, P. (2018). Gels for the Cleaning of Works of Art. In Horkay, F., Douglas, J.F., & Del Gado, E. (Eds.) *Gels and Other Soft Amorphous Solids.* ACS Symposium Series, vol.1296 (pp.291-314). http://dx.doi.org/10.1021/bk-2018-1296.ch015

Chowdhury, S.A., Mohan, R.S., & Scott, J.L. (2007). Reactivity of ionic liquids. *Tetrahedron, 63(11)*, 2363-2389.https://doi.org/10.1016/j.tet.2006.11.001

Colette, A. (Ed.) (2007). *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*. World Heritage reports 22. UNESCO World Heritage Centre.

Conservation OnLine (2009). The Modular Cleaning Program. https://cool.culturalheritage.org/byauth/stavroudis/mcp/

Cremonesi, P. (2015). Rigid Gels and Enzyme Cleaning. *Smithsonian contributions to museum conservation, 3*, 179-183.

Cremonesi, P. (2016). Surface cleaning? Yes, freshly grated Agar gel, please. *Studies in Conservation, 61(6)*, 362-367.https://doi.org/10.1179/2047058415Y.0000000026

Cremonesi, P., & Casoli, A. (2017). Thermo-reversible rigid agar hydrogels: their properties and action in cleaning. In Angelova, L.V., Ormsby, B., Townsend, J.H., & Wolbers, R. *Gels in the Conservation of Art* (pp.19-28). Archetype Publications.

De Silva, M., & Henderson, J. (2011). Sustainability in conservation practice. *Journal of the Institute of Conservation, 34(1)*, pp.5-15. https://doi.org/10.1080/19455224.2011.566013

Dimitrić, N., Spremo, N., Vraneš, M., Belić, S., Karaman, M., Kovačević, S., Karadžić, M., Podunavac-Kuzmanović, S., Korolija-Crkvenjakov, D., & Gadžurić, S. (2019). New protic ionic liquids for fungi and bacteria removal from paper heritage artefacts. *Royal Society of Chemistry Advances, 9(31)*, 17905-17912.https://doi.org/10.1039/C9RA03067K

Doehne, E., & Price, C. (2010). *Stone Conservation: An Overview of Current Research* (2^{nd} Ed.). Research in Conservation Series. The Getty Conservation Institute.

Domingues, J., Bonelli, N., Giorgi, R., & Baglioni, P. (2014). Chemical semi-IPN hydrogels for the removal of adhesives from canvas paintings. *Applied Physics A, 114(3)*, 705-710. https://doi.org/10.1007/s00339-013-8150-0

Domingues, J., Bonelli, N., Giorgi, R., Fratini, E., & Baglioni, P. (2013a). Innovative method for the cleaning of water-sensitive artifacts: synthesis and application of highly retentive chemical hydrogels. *International Journal of Conservation Science, 4*, 715-722.

Domingues, J., Bonelli, N., Giorgi, R., Fratini, E., Gorel, F., & Baglioni, P. (2013b). Innovative Hydrogels Based on Semi-Interpenetrating p(HEMA)/PVP Networks for the Cleaning of Water-Sensitive Cultural Heritage Artifacts. *Langmuir, 29(8)*, 2746-2755. https://doi.org/10.1021/la3048664

Dudukovic, N.A. (2015). The principles of molecular gel formation. [Doctoral dissertation, Graduate College, University of Illinois at Urbana-Champaign]. http://hdl.handle.net/2142/88186

Eriksson, H., Wedberg, I., Nessow, J., & Bronmark-Thorlund, M. (2017). The use of Nanorestore gels in the conservation of lime-based wall paintings. In Angelova, L.V., Ormsby, B., Townsend, J.H., & Wolbers, R. *Gels in the Conservation of Art* (pp.270-273). Archetype Publications.

Faculdade de Ciências e Tecnologia-Universidade NOVA de Lisboa (2019). Symposium: "Conservation of Cultural Heritage and Sustainability: challenges and experiences". October 14, 2019. Benfica Museum Auditorium Cosme Damião, Lisbon, Portugal.https://www.fct.unl.pt/en/sustainability-at-fct-nova/event/2020/10/symposium-conservation-cultural-heritage-and-sustainability-challenges-and-experienc

Faculdade de Ciências e Tecnologia-Universidade NOVA de Lisboa (2021). Investigação em Conservação e Restauro-Projectos.https://www.dcr.fct.unl.pt/investigacao/projectos.

Fernandes, P. (2006). Applied microbiology and biotechnology in the conservation of stone cultural heritage materials. *Applied Microbiology and Biotechnology, 73(2)*, 291-296.https://doi.org/10.1007/s00253-006-0599-8

Fialová, A., & Kotlík, P. (2017). Poly(vinyl alcohol)-borate gels as carriers of microemulsions. In Angelova, L.V., Ormsby, B., Townsend, J.H., & Wolbers, R. *Gels in the Conservation of Art* (pp.277-279). Archetype Publications.

Fotakis, C., Anglos, D., Zafiropulos, V., Georgiou, S., & Tornari, V. (2007). *Lasers in the preservation of cultural heritage: Principles and Applications.* Series in Optics and Optoelectronics. Taylor & Francis Group. https://doi.org/10.1201/9780367800857

Giorgi, R., Baglioni, M., Berti, D., & Baglioni, P. (2010). New Methodologies for the Conservation of Cultural Heritage: Micellar Solutions, Microemulsions, and Hydroxide Nanoparticles. *Accounts of chemical research, 43(6)*, 695-704.https://doi.org/10.1021/ar900193h

Giorgi, R., Domingues, J.A.L., Bonelli, N., & Baglioni, P. (2013). Semi-interpenetrating p(HEMA)/PVP hydrogels for the cleaning of water-sensitive painted artifacts: Assessment on release and retention properties. In Rogerio-Candelera, M.A., Lazzari, M., & Cano, E. (Eds.) *Science and Technology for the Conservation of Cultural Heritage* (pp.291-294). Taylor & Francis Group. https://doi.org/10.1201/b15577

Gonçalves, B. (2018). An Introduction to Less Toxic Approaches for the Cleaning of Paintings: The Particular Case of Acrylics [Master's thesis, ENSAV La Cambre].

Gorel, F. (2010). Assessment of agar gel loaded with micro-emulsion for the cleaning of porous surfaces. *Conservation, exposition, Restorauration d'Objects d'Art*, 1-9. https://doi.org/10.4000/ceroart.1827

Gulotta, D., Saviello, D., Gherardi, F., Toniolo, L., Anzani, M., Rabbolini, A., & Goidanich, S. (2014). Setup of a sustainable indoor cleaning methodology for the sculpted stone surfaces of the Duomo of Milan. *Heritage Science, 2(6)*, 1-13. https://doi.org/10.1186/2050-7445-2-6

Häckl, K., & Kunz, W. (2018). Some aspects of green solvents. *Comptes Rendus Chimie, 21(6)*, 572-580.https://doi.org/10.1016/j.crci.2018.03.010

Hall, C.M., Baird, T., James, M., & Ram, Y. (2015). Climate change and cultural heritage: conservation and heritage tourism in the Anthropocene. *Journal of Heritage Tourism*, 1-15. https://doi.org/10.1080/1743873X.2015.1082573

International Union of Pure and Applied Chemistry (2016). Green chemistry and sustainable development. https://iupac.org/greeniupac2016/

Istituto Centrale per il Restauro (2020). Interactive triangle of solvents and solubility. http://www.icr.beniculturali.it/pagina.cfm?umn=297&uid=505&usz=1

Jones, R.G. (2007). Definitions of terms relating to the structure and processing of sols, gels. Networks, and inorganic-organic hybrid materials. *Pure Applied Chemistry, 79(10)*, 1801-1829. https://doi.org/10.1351/pac200779101801

Kanth, A.; Singh, M., & Pandey, S.C. (2018). Optimizing the rigidity of gellan and agar gels for cleaning sensitive acrylic emulsion painted surfaces. *International Journal of Conservation Science, 9(3)*, 451-462.

Karagölge, Z., & Gür, B. (2016). Sustainable Chemistry: Green Chemistry. *Journal of the Institute of Science and Technology, 6(2)*, 89-96. https://doi.org/10.21597/jist.2016218851

Kavda, S., Dhopatkar, N., Angelova, L.V., Richardson, E., Golfomitsou, S., & Dhinojwala, A. (2017). Surface behaviour of PMMA: Is gel cleaning the way to go?. *Studies in Conservation, 61(2)*, 287-299. https://doi.org/10.1080/00393630.2016.1200858

Kozigóg, A., & Wysocka-Robak, A. (2017). Application of Ionic Liquids in Paper Properties and Preservation. In Handy, S. (Ed.). *Progress and Developments in Ionic Liquids* (pp.51-72). IntechOpen. https://doi.org/10.5772/65860

Kuckova, S.H., Krizkova, M.C., Pereira, C.L.C., Hynek, R., Lavrova, O., Busani, T., Branco, L.C., & Sandu, I.C.A. (2014). Assessment of Green Cleaning Effectiveness on Polychrome Surfaces by MALDI-TOF Mass Spectrometry and Microscopic Imaging. *Microscopy Research and Technique, 77(8)*, 574-585.https://doi.org/10.1002/jemt.22376

Lahoz, R., Angurel, L.A., Brauch, U., Estepa, L.C., & de la Fuente Leis, G.F. (2013). Laser Applications in the Preservation of Cultural Heritage: An Overview of Fundamentals and Applications of Lasers in the Preservation of Cultural Heritage. In Varella, E.A.(Ed.). *Conservation Science for the Cultural Heritage: Applications of Instrumental* Analysis (pp.294-332). Springer. https://doi.org/10.1007/978-3-642-30985-4

Lancaster, M. (2002). *Green Chemistry: An Introductory Text*. The Royal Society of Chemistry.

Lo Schiavo, S., De Leo, F., & Urzì, C. (2020). Present and Future Perspectives for Biocides and Antifouling Products for Stone-Built Cultural Heritage: Ionic Liquids as a Challenging Alternative. *Applied Sciences, 10(18)*, 1-17. https://doi.org/10.3390/app10186568

Macchia A., Rivaroli L., & Gianfreda B. (2019). The GREEN RESCUE: a 'green' experimentation to clean old varnishes on oil paintings. *Natural Product Research*, 1-11. https://doi.org/10.1080/14786419.2019.1675061

Maranesi, G. (2017). Using rigid gellan gel for the stratigraphic cleaning of a canvas painting. In Angelova, L.V., Ormsby, B., Townsend, J.H., & Wolbers, R. *Gels in the Conservation of Art* (pp.129-131). Archetype Publications.

Natali, I., Carretti, E., Angelova, L., Baglioni, P., Weiss, R.G., & Dei, L. (2011). Structural and Mechanical Properties of "Peelable" Organoaqueous Dispersions with Partially Hydrolyzed Poly(vinyl acetate)-Borate Networks: Applications to Cleaning Painted Surfaces. *Langmuir, 27(21)*, 13226-13235.https://doi.org/10.1021/la2015786

National Archives and Records Administration (2016). Preservation-Solvent Solver. https://www.archives.gov/preservation/solvent-solver

Pacheco, M.F., Pereira, A.I., Branco, L.C., & Parola, A.J. (2013). Varnish removal from paintings using ionic liquids. *Journal of Materials Chemistry A, 1(24)*, 7016-7018.https://doi.org/10.1039/C3TA10679A

Palla, F., & Barresi, G. (Eds.) (2017). *Biotechnology and Conservation of Cultural Heritage*. Springer. https://doi.org/10.1007/978-3-319-46168-7

Pérez Bento, P., Regidor Ros, J.L., & Roig Picazo, P. (2020). Emulsion system without surfactant as an alternative to the use of solvent gel. *ARP-Conservar Património, 34*, pp.101-108.https://doi.org/10.14568/cp2018051

Pianorsi, M.D. (2017). Synthesis and application of novel materials for cleaning and protection of historical documents. [Doctoral dissertation, Università Degli Studi Firenze]. http://hdl.handle.net/2158/1079131

Pianorsi, M.D., Raudino, M., Bonelli, N., Chelazzi, D., Giorgi, R., Fratini, E., & Baglioni, P. (2017). Organogels for the cleaning of artifacts. *Pure and Applied Chemistry, 89(1)*, 3-17. https://doi.org/10.1515/pac-2016-0908

Poole, C.F. (2004). Chromatographic and spectroscopic methods for the determination of solvent properties of room temperature ionic liquids. *Journal of Chromatography A, 1037(1-2)*, 49-82. https://doi.org/10.1016/j.chroma.2003.10.127

Puoti, F., Jervis, A.V., Ciabattoni, R., Cossa, E., Di Giovanni, A., Giuliani, M.R., Guida, G., & Ioele, M. (2017). Evaluation of leather cleaning with a rigid hydrogel of gellan gum on two composite Amharic shields from the Museo Nazionale Preistorico Etnografico 'Luigi Pigorini', Rome. In Angelova, L.V., Ormsby, B., Townsend, J.H., & Wolbers, R. *Gels in the Conservation of Art* (pp.82-86). Archetype Publications.

Ricci, C., Gambino, F., Nervo, M., Piccirillo, A, Scarcella, A., Zenucchini, F., Pozo-Antonio, J.S. (2020). Developing New Cleaning Strategies of Cultural Heritage Stones: Are Synergistic Combinations of a Low-Toxic Solvent Ternary Mixtures Followed by Laser the Solution?. *Coating, 10(466)*, 1-22. https://doi.org/10.3390/coatings10050466

Riedo, C., Caldera, F., Poli, T., & Chiantore, O. (2015). Poly(vinylalcohol)-borate hydrogels with improved features for the cleaning of cultural heritage surfaces. *Heritage Science, 3(23)*, 1-11. https://doi.org/10.1186/s40494-015-0053-2

Riedo, C., Rollo, G., Scalarone, D., & Chiantore, O. (2017). Improved PVA gels for the cleaning of paint surfaces. In Angelova, L.V., Ormsby, B., Townsend, J.H., & Wolbers, R. *Gels in the Conservation of Art* (pp.283-286). Archetype Publications.

Rodríguez-Navarro, C., Elert, K., Sebastian, E., Esbert, R.M., Grossi, C.M., Rojo, A., Alonso, F.J., Montoto, M., & Ordaz, J. (2003). Laser cleaning of stone materials: an overview of current research. *Studies in Conservation, 48(1)*, 65-82. https://doi.org/10.1179/sic.2003.48.Supplement-1.65

Royo Fraguas, C., Morales Almonacid, M., Espinosa Ipinza, F., Chiostergi Picchio, S. (2015). Resultados exploratórios de la aplicación de geles de agar-agar para la limpieza de superfícies de yeso: una propuesta metodológica. Selección CNCR. *Conserva, 20*, 141-148.

Schmitz, K., Wagner, S., Reppke, M., Maier, C.L., Windeisen-Holzhauser, E., Benz, J.P. (2019). Preserving cultural heritage: Analyzing the antifungal potential of ionic liquids tested in paper restoration. *PLoS ONE, 14(9)*, 1-12. https://doi.org/10.1371/journal.pone.0219650

Scott, C.L. (2012). The use of agar as a solvent gel in objects conservation. *AIC Objects Specialty Group Postprints, 19*, 71-83.

Siano, S. (2008). Principles of Laser Cleaning in Conservation. In Schreiner, M, Strlič, M., & Salimbeni, R. (Eds.) *Handbook on the Use of Lasers in Conservation and Conservation Science*, COST G7 (pp.2-20).

Siano, S., Agresti, J., Cacciari, I., Ciofini, D., Mascalchi, M., Osticioli, I., & Mencaglia, A.A. (2012). Laser cleaning in conservation of stone, metal, and painted artifacts: state of the art and new insights on the use of the Nd:YAG lasers. *Applied Physiscs A: Materials Science & Processing, 106*, 419-446.https://doi.org/10.1007/s00339-011-6690-8

Silva, M. (2017). Novel Biocides for Cultural Heritage [Doctoral dissertation, Institute for Advanced Studies and Research, University of Évora]. http://hdl.handle.net/10174/21001

Stavroudis, C., & Doherty, T. (2013). The Modular Cleaning Program in Practice: Application to Acrylic Paintings. *Smithsonian Contributions to Museum Conservation, 3*, 139-145.

Sun, M., Zou, J., Zhang, H., & Zhang, B. (2015). Measurement of reversible rate of conservation materials based on gel cleaning approach. *Journal of Cultural Heritage, 16(5)*, 719-727.https://doi.org/10.1016/j.culher.2014.11.006

Suzuki, M., & Hanabusa, K. (2010). Polymer organogelators that make supramolecular organogels through physical cross-linking and self-assembly. *Chemical Society Reviews, 19(2)*, 455-463.https://doi.org/10.1039/B910604A

Tortajada Hernando, S., & Blanco Domínguez, M.M. (2013). Cleaning plaster surfaces with agaragar gels: evalution of the technique. *Ge-conservación, 4*, 111-126.https://doi.org/10.37558/gec.v4i0.153

Tortajada Hernando, S. (2011). El gel de agar como método de limpieza para escultura. *Pátina, 16*, 290-292.

Universidade Católica Portuguesa (2016). Workshop de Limpeza superficial e remoção de substâncias filmogénias em arte antiga e contemporânea. https://citar.artes.porto.ucp.pt/pt/central-eventos/workshop-limpeza-superficial-e-remocao-substancias-filmogenias-arte-antiga-e.

Universidade Católica Portuguesa (2018a). Workshop de Soluções aquosas e solventes para tratamento de obras de arte em papel. https://www.porto.ucp.pt/pt/central-eventos/workshop-solucoes-aquosas-e-solventes-para-tratamento-obras-arte-papel

Universidade Católica Portuguesa (2018b). Workshop de Soluções aquosas e solventes para tratamento de obras de arte em papel: aplicação a documentos, arte antiga e contemporânea. https://www.porto.ucp.pt/pt/central-oferta-formativa/2019-solucoes-aquosas-e-solventes-para-tratamento-obras-arte-papel?

Universidade Católica Portuguesa (2018c). R&D BIO4MURAL innovative biotechnology solutions for black stains removal and preventive conservation of historical and culturally important mural paintings. https://citar.artes.porto.ucp.pt/en/node/18085

Universidade Católica Portuguesa (2019a). Seminar in Green Conservation of Cultural Heritage. https://artes.porto.ucp.pt/pt/central-oferta-formativa/2019-green-conservation-cultural-heritage?

Universidade Católica Portuguesa (2019b). 3rd International Conference-Green Conservation of Cultural Heritage. https://artes.porto.ucp.pt/en/greenconservation2019?

Varadinova-Papadaki, S. (2017). Gels for removing varnish and surface stains from Bulgarian icons. In Angelova, L.V., Ormsby, B., Townsend, J.H., & Wolbers, R. *Gels in the Conservation of Art* (pp.292-293). Archetype Publications.

Vázquez Pérez, S. (2018). Revisión de sistemas de limpieza y consolidación de superfícies pictóricas modernas sensibles al agua y/o a los dissolventes orgânicos polares [Bachelor's degree, Faculty of Fine Arts, University of Seville].

Volk, A., & van den Berg, K.J. (2014). Agar-A New Tool for the Surface Cleaning of Water Sensitive Oil Paint?. *Issues in Contemporary Oil Paint*, 389-406.https://doi.org/10.1007/978-3-319-10100-2_26

Volpi, F. (2017). Green strategies for the cleaning of works of art. Setting up of an analytical protocol for the evaluation of cleaning [Doctoral dissertation, University of Bologna]. https://doi.org/10.6092/unibo/amsdottorato/8050

Wolbers, R. (2017a) Gels, green chemistry, gurus and guides. In Angelova, L.V., Ormsby, B., Townsend, J.H., & Wolbers, R. *Gels in the Conservation of Art* (pp.3-8). Archetype Publications.

Wolbers, R. (2017b) Terminology and properties of selected gels. In Angelova, L.V., Ormsby, B., Townsend, J.H., & Wolbers, R. *Gels in the Conservation of Art* (pp.381-394). Archetype Publications.

Zucca, P., Fernandez-Lafuente, R., & Sanjust, E. (2016). Agarose and Its Derivatives as Supports for Enzyme Immobilization. *Molecules, 21(11)*, 1-25. https://doi.org/10.3390/molecules21111577

Authors' *Curriculum Vitae*

Marta Gueidão graduated in Art Conservation and Restoration from UCP (2018). She is currently completing a MA in Conservation and Restoration of Cultural Heritage from UCP, specializing in green conservation methodologies for the cleaning and preservation of plaster- and cement mortar-based sculptures.

Contact: marta.costa792@gmail.com

Eduarda Vieira holds a PhD in Conservation and Restoration of Historical and Artistic Heritage by the UPV (Spain). She is currently an Assistant Professor at the School of Arts of UCP (Porto) and a permanent researcher at CITAR, a research unit of which she has been director since July 2019. She is the principal investigator of the GEO-SR Reference nº 031304 project and an associate researcher for the BIONANOSCULP and BIO4MURAL projects. She operates in the areas of Humanities-Arts, with an emphasis on Conservation and Restoration of Cultural Heritage, Sustainable Conservation (risk mitigation and heritage resilience).

Contact: evieira@porto.ucp.pt

Rui Bordalo is graduated in Art Conservation (2003). He holds a PhD in the area of Heritage Sciences by the Courtauld Institute of Art (2011), specialized in the analytical characterization of artistic materials. At present, he is an integrated member of CITAR where he is developing research within the GEO-SR project.

Contact: rbordalo@porto.ucp.pt

Patrícia Moreira holds a PhD in Biotechnology with specialization in Biochemical Engineering by the UCP. She is an Assistant Professor at the School of Arts of UCP (Porto). She is an integrated member of CITAR, coordinates the CITAR's Focus Area of Study and Conservation of Cultural Heritage and is a collaborator of CBQF. Her main research area is innovation in Biotechnology and Nanotechnology for Cultural Heritage with emphasis on biodeterioration, sustainability, circular economy and green conservation. She co-represents the Green Conservation movement in Portugal and at the moment coordinates the BIONANOSCULP PTDC/EPH-PAT/6281/2014 and BIO4MURAL PTDC/HAR-ARQ/29157/2017 projects.

Contact: prmoreira@porto.ucp.pt

Article received on 02/02/2021 and accepted on 21/06/2021