A review in using agar gels for cleaning art surfaces

A REVIEW IN USING AGAR GELS FOR CLEANING ART SURFACES

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Keywords: cleaning, agar gel, chemical composition, water state, chelating properties

Abstract

Cleaning an artwork is an extremely delicate and irreversible procedure in a conservation work. Art conservators constantly work to identify an appropriate and correct cleaning method according to the requirements of different substrates and in order to solve different removal problems. In recent years, gels positively responded to the conservation requests becoming a valid help and, in some cases, the best alternative compared to traditional cleaning methods. This paper proposes a summary of the most recent results regarding agar gels and their applications for cleaning art surfaces; moreover, the application of agar gels specifically formulated to address different conservation problems is also discussed.

Introduction

Cleaning is often a challenge when conservators are called to work on a delicate art surface. In the so-called “chemical cleaning”, several different systems can be chosen depending on the desired results to be obtained: pure solvents, solvent mixtures and solutions. The addition of surfactants or chelating agents or other chemicals also contributes to the required conservation achievements. The obtained fluid could be used by swab, brush or by gel pad directly on the art surface. As an alternative, the fluid system can be supported by an inert material, such as cellulose microfibers, clay or micronized silica, preparing a paste which can be applied to the area of interest [1-5]. In doing this, the operator improves the fine control of the cleaning procedure.

It is worth noting that many scientific publications [6-28] and conferences [29] have focused on this specific topic. Since the 1990s, when thickeners based on cellulose ethers and solvent gels were introduced, the development of these types of cleaning systems and the study of their effectiveness

have been gradual and have pointed to different conservative problems (e.g. residues on the treated surface) [6-8].

Recently, gelling agents able to control the fluid release to the substrate avoiding evident residues have raised the interest of the conservation community. In fact, in recent decades, many efforts have been made to prepare new gelling systems capable of retaining liquid compounds and being easily removable. Responsive gels were considered the new frontier of thickeners because of their promising properties [11,12]. Unfortunately, the specialized literature shows that peelable gels have had the greatest success so far in the conservation practice [16,17, 29]. Agar gel and gellan gum can be included in this category even if they are natural gelling systems [9,10,13-15,22]. Both gels are usually applied in the cleaning of artworks thanks to their great effectiveness and ease of application on a huge variety of substrates, from the firmest, like stone surfaces or plaster with consistent soiling [20, 23, 27], to the most fragile, like paper [18,21,30].

In general, gels can be considered as soft materials consisting of interconnected long polymer chains dispersed into a fluid (water and/or organic solvent), forming a three-dimensional network [31]. They allow to use less solvent than in “free solvent” cleaning, thus improving the sustainability of the treatment [32,33]. Moreover, reproducible cleaning processes can be easily and effectively obtained by controlling the contact time of gels with the surface underneath. However, the risk of leaving organic residues on the treated surfaces must be taken into account for these systems, because of the difficulty of completely removing the gel residues from the substrates. Such a risk can be prevented with several washings by swabs soaked in suitable solvents, or it can be avoided by using semi-rigid gels [17] and, in particular, agar gels [10, 34].

Agar is a natural polysaccharide extracted from several orders of red seaweeds (Gelidiales and Gracilariales), able to form semi-rigid, thermo-reversible and hydrophilic gels by simply dispersing the agar raw powder in water, subsequent heating and final cooling. During the last step, agar chains arrange into an ordered structure, where aggregates of co-axial helices form the junctions of the three-dimensional gel network [9,35]. This peculiar supramolecular structure provides interesting properties for its application as salt bridge in electrochemistry, gelatine substitute in the food industry, growth media for microbiological cultures, and many others [36]. Hence, agar gels allow the confined release of the solvent at the interface between gel and substrate, and display other interesting features for the conservation field: high effectiveness and versatility in removing different types of soiling from different substrates, low impact on the artwork, low cost, “green” approach and applicability in different forms and environmental conditions [10]. These properties are particularly useful when water sensitive substrates are involved. In fact, water is one of the most important solvents used in cleaning painting materials, murals, metals and stones. Despite its fundamental role in cleaning processes, several materials (such as gypsum, stuccoworks, etc.) cannot tolerate water effects (e.g. solvent action and decrease of the substrate mechanical features). Thus, especially in

these situations, the use of agar gel widens the potential of water cleaning by controlling the contact time and, consequently, the release of water.

The conservation of sensitive substrates, i.e. plaster and gypsum works, introduces some issues, which steered conservators toward the use of agar gels already during the first decade of the new century. These substrates exhibit specific physical, mechanical and chemical properties which demand care procedures: light colour, porosity and consequent water absorption, weak mechanical resistance, especially when the materials are wet, just to name a few. Moreover, the artworks, especially gypsum works, quite often display a composite structure, with insertion of materials as iron bars, wood elements or vegetable fibres; in those cases, cleaning problems, such as the application of a liquid phase and its confinement, can dramatically increase.

The practical effects provided by the use of agar gels in the cleaning of artworks have been studied for more than a decade. Best practices suggest preparing agar gels by dissolving raw powders in water in the range 0.5-5% w/v [10,37]. Moreover, new application methods were developed drawing inspiration by the polysaccharide characteristics, and new trends of use were opened in different types of conservation interventions [37, 38]. In particular, for the removal of metal stains from building materials, an improvement in agar gel performances was obtained by adding functional chemicals, such as ethylenediaminetetraacetic acid (EDTA), triammonium citrate (TAC) or specific amino acids [23,39,40].

However, the effectiveness of gel cleaning is strictly related to the soiling removal mechanism, which is not known in detail yet [23]. On the other hand, it is known that the environmental conditions of growth of red seaweed affect the chemical composition of the raw material, thus influencing the gel structure and its cleaning performances [24,41,42].

Given these premises, this review provides an overview of recent works published on agar gels as cleaning materials, focusing especially on the following aspects:

1. summarize the chemical differences among the raw materials currently present on the market, in order to understand how the supplier influences the final cleaning performances;
2. elucidate the water bonds in the agar network (in the following refereed as water state), that could be linked to the “release issue”;
3. highlight the chelating action of agar gels towards metals;
4. exemplify the practical versatility of agar gels in several conservation cases

The applied multi-analytical approach

Compositional, structural and functional features of different agar raw materials and gels have been elucidated by a multi-analytical approach [24, 26]. Each analytical technique provided specific information, and, in several cases, one technique completed the information recorded by the others. In the attempt to identify and clarify all the factors that might influence the effectiveness of agar gels in cleaning procedures, different formulations of agar gels were used, both pristine and added with

disodium EDTA and triammonium citrate [23,24,26]. Four raw materials used in several application fields were compared and studied. Table 1 reports the name and the supplier of the selected raw materials. AgarArt and Agar Purissimo are the most used material by conservators in Italy, whereas the other materials are usually applied in biological cultures and in the food industry (in the following named Agar Food). In particular, agar purchased by Sigma Aldrich was used as a reference. Agar solutions of 1, 3 and 5 % w/v were chosen since they are the most used concentrations applied by conservators. For gel preparation, agar powder was dissolved in the proper amount of Milli-Q water, then the solution was heated for 2 min in a microwave oven at 700W and then it was cooled in the air. In the case of EDTA and TAC-added gels, the proper amount of additives was introduced in the solution just before cooling.

The general compositional screening and the chemical characterization of the different agar formulations were performed by infrared spectroscopy (FTIR), Fourier Transform Raman Spectroscopy (FT-Raman) and pyrolysis - gas chromatography/mass spectrometry (Py-GC/MS). In particular, FT-Raman analyses were carried out to avoid the fluorescence effects observed in conventional Raman spectroscopy. For Py-GC/MS analyses, the thermally assisted hydrolysis and methylation method (THM) [43-45] was applied to obtain detailed information on the monosaccharides present in agarose and agaropectin chains and on the way the monosaccharide units are linked to each other.

The characterization of the agar gel structure was focussed on the evaluation of several issues, such as the water state and its release, investigating the chelating properties and performances as well [23, 26]. Different stone substrates were used for different purposes: Noto calcarenite for the determination of water absorption and veined Carrara marble for the reproduction of the copper green stains observed on real cases. Water release was determined by capillarity test according to Italian Standard UNI 10859 [46] substituting the multifilter paper with agar gels at different concentrations. ^{1}H NMR analyses were also performed to evaluate the water state in the gel and in a highly porous (36.2%) stone [47].

Copper stains were reproduced on specimens according to the recipe suggested by Bakhtiani et al. [48], synthesizing brochantite [$Cu_4(SO_4)(OH)_6$] directly on the marble surface. Before staining (at time t_0), laboratory marble surfaces display at the optical microscope a compact surface without morphological flaws (Figure 1a), whereas after staining copper compounds do not remain as external formations, but penetrate into subsurface regions (Figure 1b), probably in correspondence with more porous areas (at time t_1). After application of the agar gel (Figure 1c) on the stained specimens for the required time (t_2, 30 and 60 min), the microscope images allowed to verify that in general copper compounds were removed from the intergranular spaces, leaving them brighter in colour [23].

Moreover, thermal analyses, such as thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC), were fundamental to give an insight into the water state in agar gel at different concentrations [26].

The agar gel chelating properties and its performances for metal stain removal were investigated by electron paramagnetic resonance (EPR) and induced coupled plasma optical emission spectrometry (ICP-OES) [23]. In particular, EPR spectroscopy characterized Cu(II) centres symmetry in gels, highlighting that also agar gels have the intrinsic capacity to coordinate metals. Furthermore, ICP-OES spectroscopy allowed to quantify the total copper amount extracted by agar gels from substrates, suggesting the best formulation applicable to a specific conservative problem.

The chemical differences among raw materials

As already reported in the introduction, literature strongly correlates the specificity of the raw materials to their properties and performances. In particular, the environmental conditions of algae growth can affect agar gel properties in terms of chemical composition, gel strength and, as a consequence, in cleaning performances. The research published by the authors demonstrates the compositional differences among the four different commercial raw materials reported in Table 1 [24]. Table 2 lists the assignments of all specific FTIR absorption and FT-Raman scattering bands for agar samples. In general, the FTIR patterns of different raw agar powders are too similar to discriminate differences in composition [24, 49-53]**.** On the other hand, spectral subtraction of FT-Raman spectra was found to be a valuable tool to highlight the presence of specific spectral pattern, e.g. in Agar Purissimo and in Agar Food, which can be well correlated to the presence of crystalline glucose [54].

These data were confirmed also by Py-GC/MS analyses, which show the presence of galactose linked on position C3, both in agarose and agaropectine, as well as glucose signals, thus supporting the spectroscopic results. Moreover, three additional peaks of 4-O-substituted glucose, typical compounds of cellulose, were detected in AgarArt and Agar Purissimo, pointing to a different purification level of the seaweed from which the samples were extracted (Table 3).

Importantly, Py-GC/MS analyses carried out without derivatization allowed to perform a semi-quantitative evaluation of the anhydrous fraction responsible of the gel strength [55]. The analyses demonstrate a variable content of anhydrous and non-anhydrous units. In particular, under pyrolysis Agar Sigma, which is the purest raw agar, produced comparable amounts of galactopyranose and anhydro-galactopyranose, whereas Agar Purissimo recorded the lowest content of the anhydrous compound. This compositional information was in good agreement with rheological measurements. In fact, Agar Food gels contains the highest percentage of anhydrous units and the greatest viscoelastic moduli has been detected [55].

Finally, thermogravimetric analyses also showed slight differences in the weight loss profiles of different types of agar. AgarArt and Agar Sigma were found to be more thermally stable than Agar Purissimo and Agar Food. The first two samples exhibited a fast and steep weight loss at around 200 °C, which was shifted at approximately 140 °C in the other two agar gels. This difference was possibly correlated to the free glucose volatilization.

The water state and its release

The cleaning selectivity of agar gel is strongly correlated to several specific properties of gels, such as the spontaneous release of the liquid phase (syneresis), its diffusion capacity into porous substrates thanks to an ion concentration gradient, and finally osmosis phenomena [56]. The main advantages in using gel cleaning systems, compared to the traditional cleaning methods (free solvent, mechanical methods or their combination), are the fine control of the liquid release into the substrate and the reduced evaporation of solvents, thus limiting the aggressiveness of the cleaning process.

Water in gels is commonly classified into three main types: non-freezable bound water with strong water-polymer connection, freezable bound water with weak water-polymer connection and free (freezable) water without water-polymer connection [57,58]. The quantification of the different types of water allows to understand at what extent the agar structure and composition influence the transport phenomena.

Starting from the evaluation of the water release, modified capillary test were performed on Noto calcarenite, substituting the multilayer filter paper pad with AgarArt gel at increasing concentrations [23]. The amount of water (Qi) absorbed by capillarity into substrates was studied by capillarity absorption measurements on five Noto calcarenite specimens kept in contact with agar gel. Absorption capillary coefficients (CA), proportional to the absorption rate, were calculated as suggested in UNI 10859 [46] and are reported in Table 4. Results show that both the amount of water absorbed by capillarity and the water absorption rate decrease when the agar gel concentration increases. In particular, the asymptotic value of the gel 1 % curve is very similar to the one obtained for a multilayer filter paper pad [59], used as reference. Thus, agar gel 1% almost performs as a “free” water reservoir.

Unilateral ^{1}H-NMR analyses were also carried out to support the water transport capillarity results with further information on mobility of the various water components as a function of gel concentration. The longitudinal and transverse magnification decays of the different types of water exhibit a multi-exponential trend, different from the mono-exponential decay trend of bulk water [26]. In fact, agar samples display a mono-exponential trend in longitudinal relaxation time (T_1), whereas a bi-exponential trend is recorded in transverse relaxation time (T_2). Longitudinal relaxation time exhibits a linear correlation with agar concentration, indicating that water mobility decreases with the density of the polymeric network. For what concern the “bound” and “free” water, transverse relaxation time can be described by two proton species characterized by a short (T_{2A}) and long (T_{2B}) transverse relaxation time, respectively. Both relaxation times decrease when the agar concentration increases, which affects more the mobility of free water than bound water, further confirming that water mobility is strongly hampered by the polymer network and its inner interconnections.

The amount of bound water is very low, around 4-7% of the total water, while the free water content is in the range of 93-96% in all samples. Moreover, the self-diffusion coefficient of water molecules was investigated by diffusion ^{1}H NMR measurements on Noto calcarenite mock-ups with agar gels at different concentration. In all commercial agar gels, also the diffusion decays exhibit a linear correlation with agar concentration: the self-diffusion coefficients of water in agar gels were slower than those observed for bulk water ($2.5*10-9$ m^2/s at 25 °C) and decreased with increasing agar concentration. At higher concentrations of agar, water mobility is hindered both by interactions with the agar hydroxyls and by the greater density of the polysaccharide matrix [26]. AgarArt exhibits a slower translational motion of water molecules and therefore more water release if compared to Agar Sigma, in which a tendency to collapse has been observed after a certain release of water (between 60 and 240 min).

The amount of freezable bound water and freezable free water in different agar gels was also estimated by thermal analyses [26]. In general, freezable bound water melts at lower temperature than free water. By monitoring the gel drying by DSC, the melting signal of bound water increased at the expense of the free water melting signal. Moreover, the heat of melting of freezable free water is always lower than in bulk water, confirming the different behaviour of water in bulk or in a network. Concerning the correlation between the different types of water and agar concentration, DSC analyses highlighted that freezable water is not affected by agar concentration, but the amount of bound water changes reaching approximately 20 wt% of the total water content. This is probably correlated to the gel microstructure: the smaller is the porosity, the greater the interfacial area and the greater the number of bound water sites. This happens until a concentration limit, in this case 5% w/v, beyond which the binding sites for water become less accessible.

The correlation of the water release with the gel microstructure is a difficult task because porosity and especially the pore connectivity are difficult to observe on hydrogels, even with an Environmental SEM (E-SEM) equipment. For such an investigation, hydrogels can be lyophilised (i.e. freeze-dried) immediately after contact with stained specimens, in order to obtain a polymeric network without the liquid phase, called xerogels [60]. In fact, ad hoc prepared xerogels may be considered representative of the morphology of the related hydrogels, since fast freezing in liquid nitrogen leads to the formation of amorphous ice, which does not expand the hydrogel network structure unlike ice crystals. The authors' research is moving exactly in this direction, trying to correlate water release and cleaning effectiveness with the gel microstructure.

Chelating properties of agar gels

In order to better understand the chemical mechanisms involved and to evaluate the cleaning effectiveness, the removal of artificial copper stains from marble specimens was investigated by ICP-OES and the chelating properties of agar gels were investigated by EPR spectroscopy [23].

As prepared agar gels contain negligible amounts of copper. After 1 h contact with artificially stained marble specimens, ICP-OES data showed that the amount of copper detected in pristine gels (1, 3, 5 % w/v) was rather small, below 15 μg/cm^2 (Figure 2a, b, c). By using agar gel 3 % containing additives (EDTA and TAC), the removal of copper was about twice more effective, with no significant differences among the used additives (Figure 2d, e). The higher effectiveness displayed by agar gels containing additives with respect to pristine gels is in agreement with the results obtained in other researches about copper ion removal from wastewaters [61].

For what concerns the study of copper coordination, all pristine agar gels displayed weak axial EPR signals (Figure 3a), having values of g and A tensor components (Table 5) consistent with those of Cu (II) centers in a tetragonal symmetry field of oxygen atoms [62,63]. Thus, these signals were attributed to Cu (II) centres coordinated by agar gels, from now on termed as Cu-agar.

For gel 3 % w/v added with TAC (Fig. 3b), resonances attributable to Cu-agar species were observed. In addition, an isotropic intense broad band was observed (g ~2), attributable to interacting Cu (II) centres in frozen water solution [63,64].

Gel 3 % added with EDTA showed two different axial signals, attributable to two different Cu (II) centres in a tetragonal symmetry field of oxygen atoms (Figure 3c). The weaker one has the same EPR parameters as those observed for pristine agar gels (Cu-agar), while the other signal has higher intensity and tensor components ($g_{||}$ = 2.07 $g^{\perp}$ = 2.29 $A_{||}$ = 149 G), which can be attributed to Cu (II) centres coordinated by the additive, from now on termed Cu-EDTA.

Thus, EPR spectra showed that in all the studied samples copper centres are coordinated both by agar gels and by additives, when present. Moreover, in 3% w/v gels added with TAC some copper dispersed in water was also found. Thus, all agar gels with chelators were found to be equally effective in removing copper stains, even if they host metals in different ways [23].

Understanding some agar features through the practical experience of conservators

Usually conservators identify the proper cleaning procedure with agar gels taking into consideration the soiling, the substrate characteristics and the following variables:

- specific type of raw material
- agar concentration
- gel thickness
- application mode
- contact time

Some of the above parameters have been already discussed. As for thickness, it usually ranges in the millimetre scale, depending on the application mode and substrate morphology. Rigid gels are usually the thickest, reaching 1 cm. Considering the empirical experiences collected so far, the thickness of the gel significantly influences the cleaning effectiveness, and consequently, the release of liquid phase. Although this issue is not scientifically confirmed by a systematic study aimed at

clarifying the correlation between thickness and a quantitative value of the released liquid, if one wants to apply gels for a prolonged contact time, their thickness must be carefully controlled to prevent the gel from drying out on the artwork surface. Moreover, it is worth noting that several practical experiences of conservation interventions suggest the combined action of mechanical and chemical processes to remove particles detached form the surface of artworks, especially when the gel is used in the viscous sol form, without compromise the integrity of the treated surfaces [18, 20, 23, 65].

Aqueous solutions of agar show a sol–gel transition temperature in the range from 32°C to 47°C [66]. Hence, the use of agar gel at room temperature allows its application in the rigid form, cutting it in pads of the desired shape to be placed on flat surfaces. Otherwise, warm agar solutions can be applied as viscous fluids, with viscosity depending on the temperature of the solution and on the agar concentration.

Agar gels, both in the rigid and fluid form, have successfully cleaned large three-dimensional figures as well as detailed decorative architectural surfaces. Gullotta reported one of the first researches where empirical observations have been completed and interpreted through scientific laboratory studies [20].

So far a lot of experience in the use of agar gels on several different materials such as marble (both conserved in indoor environment or exposed to outdoor conditions), wall paintings, panel or canvas paintings or wooden sculptures, has been collected [8-10, 18, 20, 22, 27- 29, 32, 37-40, 66-71]. Such a variety of case studies led to addressing a wide range of different cleaning problems, related to both the substrate features (morphology, dimensions, hydrophilicity, absorption features, etc.), and the soiling nature (chemical composition, thickness, adhesiveness, cohesion). The versatility of agar gels makes the conservation procedure flexible, according to operational needs. This happens because agar ensures a good control of water release and limited colour changes in the substrates. A sequence of repeated applications allows a satisfactory selectivity, even when the desired result does not entail the total removal of soiling. This is possible because rigid agar gels can be easily removed by a simple peeling, avoiding more aggressive mechanical actions and limiting subsequent rinsing.

A double process of heating/cooling is recommended as standardized procedure for the preparation of rigid agar gels in order to obtain a transparent gel with a better consistency, which leads to an improved cleaning effectiveness.

Rigid gels prepared at increasing concentrations exhibit different final mechanical properties [55]. Moreover, the increase in concentration implies a decrease in water release. These empirical features were confirmed by Bertasa et al. [26], who found a linear dependence of the polysaccharide concentration versus the total amount of *free* water in the gel. F*ree* water is considered to be the main responsible of soiling extraction.

It is also possible to use agar gels in a paste form, purchasable on the market under the registered

trademark name of Nevek®; the product is ready-to use and sold in the form of small rigid particles stabilized by ethanol and a very low amount of isopropanol (~ 0.1 %). Nevek® can be added to apolar solvents such as ligroin, thus increasing the variety of possible removable soiling. In general, the possibility of adding different chemicals, such as organic solvents (both polar and apolar), chelating agents or surfactants, enormously widens the potential of agar gels as cleaning materials. Finally, it is worth mentioning a recent study in which good results for sensitive materials were obtained combining the cleaning with agar gels with Nd:YAG laser sources [67] and paving the way for new strategies of intervention. The combined cleaning of laser-agar demonstrated an interesting sensitivity in removing different kind of soiling: colorimetric measurements recorded minimal chromatic variation under the threshold (ΔE ~ 3) of eye sensibility. Moreover, optical microscope observations showed no changes in the morphology and integrity of the treated surfaces.

In Table 6, the possible application modes are summarized, each one with related benefits and drawbacks.

When the gel is prepared with a standard procedure its pH is close to neutrality (in the range 6.5/7.5 pH units); as mentioned above, several additives and solvents can be added to the gel modifying its chemical and physical properties, including pH. It is worth noting that the gelling properties are strongly dependent on pH values, hence it is possible that moving from neutrality, the gel does not form correctly.

The gel cleaning potential changes by working on a specific pH: for instance, agar gels can work on hydrophobic surfaces by adding a surfactant, or as an alternative, they can be used to extract insoluble salts by adding chelating agents. More specifically, above pH 8 insoluble calcium salts (sulphate, carbonates and oxalate) can be extracted by gels added with EDTA and citrate [72]: EDTA has a higher capacity of chelating Ca^{2+} compared to citrate.

According to the practical experience, the cleaning action of the system gel-chelating agent is improved at minor chelator concentration (lower than 1%) [40]. As already mentioned, Nevek® achieved good results when added with solvents (both polar and apolar), up to about 40% of the weight, depending on the solvent. As a matter of fact, on the same artwork cleaning methods can be varied depending on the specific state of conservation and decay phenomena. In the following, some examples of conservative work with agar gel are reported, showing the wide range of potential that it can offer.

Stoldo Lorenzi was an Italian mannerist sculptor active both in Tuscany and in Milan: the “Adamo” marble figure, sculpted in 1575 and currently in the Milan Museum of Ancient Art collection (Sforza Castle), exhibited an extremely critical conservation state. Fluid agar gel at 3% w/v was used in several repeated applications, focusing on the removal of thick and adherent surface deposits, patination and retouching, while the stains on the back side of the sculpture were treated by Nevek ® *ready-to-use*, with the addition of acetone (Figure 4a). Moreover, fluid agar gel added with TAC at 0.2%, was applied on specific zones, characterized by an intense coloration due to decay, with

different contact time, until a complete drying of the gel itself. In particular, the halo of the stain was progressively contained by applying the agar gel at slightly greater size than the stain itself, increasing the chelating agent concentration or prolonging the contact time [68].

A combination of gel and laser cleaning were used on two extremely delicate areas: i) at the head of the sculpture (Figure 4b), characterized by very weak conditions, since even a minimal mechanical treatment could have created a weakening of the surface material, and ii) on the black areas of the lower part of the sculpture as well, in order to reduce the coloured retouching still present on the sculpture. After the laser ablation and several applications of fluid agar, a veil of yellowish deposits remained on the head surface, thus matching the correct chromatic tone, which is suggested by the museum curators and the supervisors of the Italian Ministry of Cultural Heritage [40,67,68].

Agar gel in different application modes was used with good results also on the XIV century mural painting in San Miguel Chapel (Pedralbes Monastery, Barcelona) [71]. The variety of the observed painting techniques was respected by intervening with a targeted and diversified way according to the conservation state of the painting and the chemical composition of pigments and binders. In this case, agar in three different application forms, such as rigid, fluid form and Nevek© with and without additives, was tested in order to evaluate the best formulation in accordance to the specific conservative problem (Figure 5a). All formulations were adapted to obtain different removal levels of vegetal glue (probably gum arabic). After evaluating advantages and drawbacks (see Table n. 6), Nevek® agar was applied both pristine and with chelating agents, such as triammonium citrate with tetraethylammonium and trisodic EDTA. Chelating agents were used in the concentration range of 0.3 -1% w/v, with different contact times (from 15 min to 4 hour) continuously controlling pH level (safety range according to the different painting layer: 6.53 for oil paint and 7.25 for fresco). Furthermore, two levels of Japanese paper were applied on the surface to precisely control the cleaning level and detect the eventual paint detachment [71].

An extremely innovative application of the agar gel system, not yet published, undoubtedly regards the wax sculpture “Portinaia” by Medardo Rosso, part of a private collection. The alkyd paint on the wax sculpture was removed after a softening step obtained by a layer of Nevek® directly applied on the surfaces. Nevek® agar gel has been also used to remove adherent deposits on the surface of another wax sculpture entitled “Ecce Puer” by the same author: in this particular case, Nevek® was applied on Japanese tissue in order to protect the rippled and uneven surface (Figure 5b).

Summary and open questions

The research reviewed in this article has the ambition to provide a deep and innovative insight into agar gel properties and cleaning mechanisms. Several issues were investigated with a multi-analytical approach in order to characterize compositional, structural and functional features which affect agar-based cleaning methods. Agar raw materials purchased by different supplier are characterized by intrinsic chemical differences depending on the application field and the different

purification level. Such a result was neither confirmed nor denied by the companies which sell the product.

The evaluation of water release and state in different gels shows significant differences in the overall content of water according to the polymer concentration. The research underlined that agar at 1% w/v performs as a free water source. This result suggests the application of a more concentrated gels in order to better control the water release at the surface, as confirmed by ^{1}H-NMR analyses. In fact, water mobility is strongly hindered by the polymer network due to the increase of double helices population and their interconnection. These data are in agreement with thermal analyses, which detected a lower amount of freezable water compared to bulk water in the different gels, suggesting that water in gels is in a more dispersed state than bulk water.

Copper centres can be coordinated both by agar gels and by additives (when present). All copper centres are coordinated in gels added with EDTA, while they are also dispersed in water within gels added with TAC. Thus, all agar gels with additives are equally effective for copper stain removal, even if they host copper in different ways. This suggests that the cleaning of stains on stones starts with the diffusion of water at the gel-stone interface, but copper coordination, both by agar sites and additives, is the driving force.

The conservators' experience highlights the extreme versatility of the agar gel that can be applied on different types of material and according to the conservation needs.

Overall, agar gel has renewed the concept of the conservation intervention, starting from the sustainability of the material and the versatility of the application mode, to the possibility of solving open conservative problems. The presence of gel residues on the surface of the treated artworks or, in a pessimistic view, inside the artwork has not yet been thoroughly investigated, although a few works have been reported in the literature [10, 18, 65, 73].

In a sense agar gel is comparable to other gelling agents, but it becomes superior in the ability to adapt to different situations, with the possibility to tailor its physical and chemical properties.

Acknowledge

The authors would like to thank the authors *C. Riedo, T. Poli, O. Chiantore, V. Di Tullio, D. Capitani, N. Proietti, A. Botteon, L.Brambilla, M. Lazzari, A. Dodero, S. Vicini, M. Castellano, M. Alloisio* for the collaboration during the research.

Compagnia di San Paolo and University of Torino are gratefully acknowledged for funding Project Torino_call2014_L2_181 through "Bando per il finanziamento di progetti di ricerca di Ateneo – anno 2014" (Project title: Polymer gels for cultural heritage).

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Tables

Table 1 - Agar raw materials

Agar name	**Purchased by**
AgarArt	*CTS*, Italy
Agar Purissimo	*Bresciani*, Italy
Agar Sigma	*Sigma Aldrich* (A7002_CAS:9002-18-0)
Agar Food	UK supplier

Table 2 - Assignments of specific absorption and scattering bands of agar samples

Wavenumber (cm^{-1})	Assignment		Intensity		References
			FT-Raman	IR	
3400-3300	ν O–H		w	m	[24]
2900-2800	ν C–H	R_3-CH; R-CH_2	vs	vs	[24]
1470-1460	δ_s CH_2		m-s	m-s	[24]
1430-1200	δ O–H		m-w	w	[24]
1390-1370	ν_{as} S=O		m	vs-s	[53], [24]
1200-1188	ν_a S=O		vs-s	vs-s	[49], [50], [51], [52], [53], [24]
1150-1075	$\nu_{out\text{-}of\text{-}phase}$ C–C–O	Secondary alcohols	m-s	s	[52], [24]
1070	$\nu_{out\text{-}of\text{-}phase}$ C–C–O	3,6-anhydrogalactose	s	s	[50], [24]
1075-1000	$\nu_{out\text{-}of\text{-}phase}$ C–C–O	Primary alcohols	m-s	s	[51], [53], [24]

930	ν C–O	3,6-anhydrogalactose	vw	w	[49], [51], [52], [53], [24]
900-800	$\nu_{\text{in-phase}}$ C–C–O	Primary /secondary alcohols	vs-m	m	[50], [51], [52], [53], [24]
867	C–O–SO_3	On C6 of galactose	vw	vw	[50], [51], [24]
845	C–O–SO_3	On C4 of galactose	m	-	[49], [50], [52], [24]
815–820	C–O–SO_3	On C6 of galactose	sh	-	[49], [50], [52], [24]
770-740	Skeletal vibr	Galactose ring	vw-m	m-s	[51], [53], [24]
500-400	δ C–C–O	Primary /secondary alcohols	-	m-w	[24]

Table 3 - Characteristic pyrolysis products of agar samples derivatized with TMAH (table modified from Bertasa M. et al., 2017)

Assignment	Tentative sugar assignments	m/z	MM*
2-hydroxypropanoic acid, methyl ester	-	45	104
Methoxyacetic acid, methyl ester	-	45	104
2-methoxypropionic acid, methyl ester	-	59	118
Unknown (m/z 144, 131, 113, 99, 71)	-	71	-
1,2,4-trimethoxybenzene	-	168	168
tri-O-methyl-3-deoxy-2-methoxymethyl-d-erythro-pentonic acid, methyl ester	GLU 4-O substituted	173	236
tri-O-methyl-3-deoxy-2-methoxymethyl-d-threo-pentonic acid, methyl ester	GLU 4-O substituted	173	236
tri-O-methyl-3-deoxy-d-arabino-hexonic acid, methyl ester	GLU	129	206
tetra-O-methyl-3-deoxy-d-arabino-hexonic acid, methyl ester	GLU	129	220

tri-O-methyl-3-deoxy-d-xylo-hexonic acid, methyl ester	GAL	129	236
tetra-O-methyl-3-deoxy-2-methoxymethyl-d-erythro/threo-pentonic acid, methyl ester	GLU 4-O substituted	129	264
tetra-O-methyl-3-deoxy-d-xylo-hexonic acid, methyl ester	GAL	129	250
tri-O-methyl-3-deoxy-d-ribo-hexonic acid, methyl ester	GLU	129	206
tetra-O-methyl-3-deoxy-d-ribo-hexonic acid, methyl ester	GLU	129	220
tri-O-methyl-3-deoxy-d-lyxo-hexonic acid, methyl ester	GAL	129	236
tetra-O-methyl-3-deoxy-d-lyxo-hexonic acid, methyl ester	GAL	129	250

* MM = Molecular Mass

Table 4 - Adsorption capillarity coefficients (CA) on Noto calcarenite in contact with AgarArt gel at different concentration.

Gels	CA ($mg/cm^2\ s^{-1/2}$)
UNI 10859	11.3 ± 0.9
AgarArt 1%	6.1 ± 0.9
AgarArt 3%	0.6 ± 0.2
AgarArt 5%	0.13 ± 0.01

Table 5 - Parameters of EPR signals observed on agar gels after 1 h contact with laboratory-stained specimens.

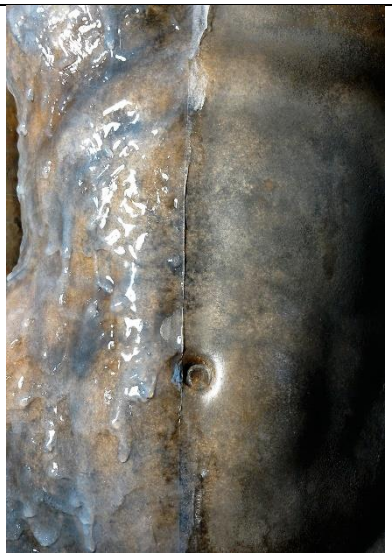
Sample		g// ± 0.01	A// ± 5 G	g⊥ ± 0.01	Attribution
AgarArt 1 %	Pristine	2.39	135	2.08	Cu-agar
AgarArt 3 %	Pristine	~ 2.4	″	″	Cu-agar
	with TAC	2.39	“	“	Cu-agar
		~ 2.1	n.d.	“	Interacting Cu(II) centres
	with EDTA	2.39	135	“	Cu-agar
		2.29	149	2.07″	Cu-EDTA (predominant)
AgarArt 5 %	Pristine	“	135	″	Cu-agar

n.d. = not detected

682

683 **Table 6** - Agar gel properties according to the application methods

684 *[Images - courtesy of M. Anzani]*

Rigid agar gel		· Minimal adhesion · Limited water release · Moderate and controllable removal of the soiling · Substrate should present perfect planarity · The gel can be cut and shaped, according to the substrate surface, desired regular thickness and the gel concentration · Good transparency · Possibility to be simply peeled off
Fluid agar gel		· Very good adhesion · Light increase in water release · Irregularity in thickness · Combination of chemical and mechanical cleaning · Good Transparency · Possibility to be simply peeled off

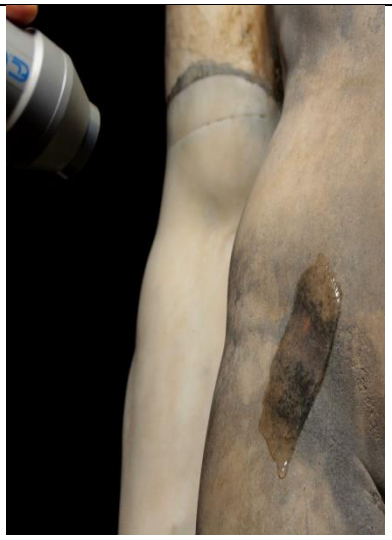
Nevek ®	. 	· Adhesion minimised · Slight increase in water release · Moderate soling removal · Limited transparency · Easy removal · Possibility to add apolar solvents
Foam agar gel	. 	· Very good adhesion · Minimal water release · Moderate soiling removal · Higher effectiveness increasing the volume due to the increase of specific surface · No transparency · Easy removal
Agar gel in combination with laser methodology	. 	· Preliminary step in cleaning · Wetting agent on the surface during the laser irradiation · Control of the thermic peak and limitation of the mechanical stress · No fall down mechanisms and fixing of soiling · Limitation of colour variations

Figure Captions

Figure 1 - Optical microscope images of Carrara marble laboratory specimens before (a), after the staining process (b) and after cleaning for 30 and 60 min with AgarArt 3% w/v added with EDTA 1% w/v (c) (scale bar 1 cm).

Figure 2 - Copper content per agar surface area after 1 h cleaning of laboratory specimens with agar gels: 1% (a), 3% (b), 5 % (c), 3% + TAC (d), 3% + EDTA (e).

Figure 3 - EPR spectra of agar gels after 1 h cleaning of laboratory specimens with agar gels: 5 % (a), 3% +TAC (b), 3% + EDTA (c).

Figure 4 - The peelable agar gel with yellowish deposit (a); thinning of the veil of yellowish deposits by laser ablation (b). *[Images - courtesy of M. Anzani]*

Figure 5 - Application of Nevek ® formulation and Japanese paper on XII century mural painting (a) and on Medardo Rosso sculture (b). *[Images - courtesy of M. Anzani]*

Figure 1

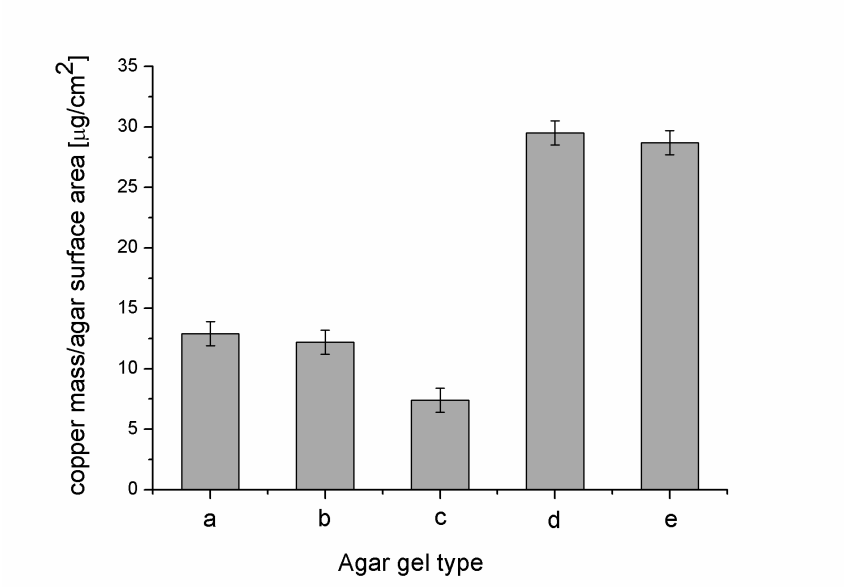


Figure 2

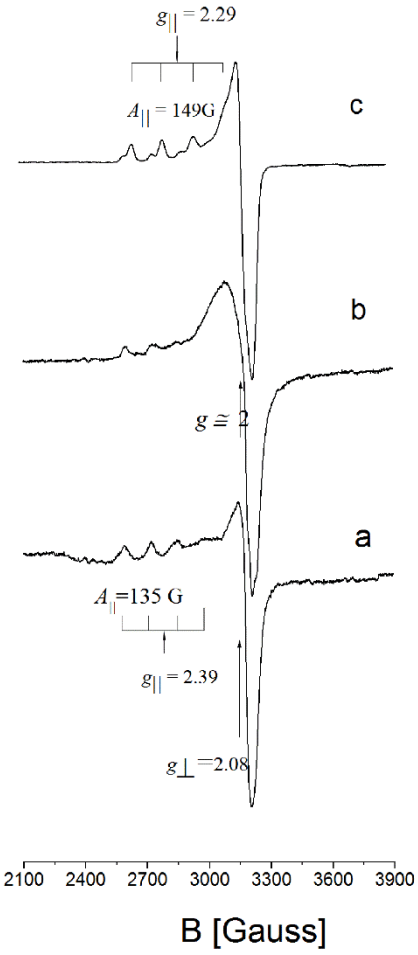


Figure 3

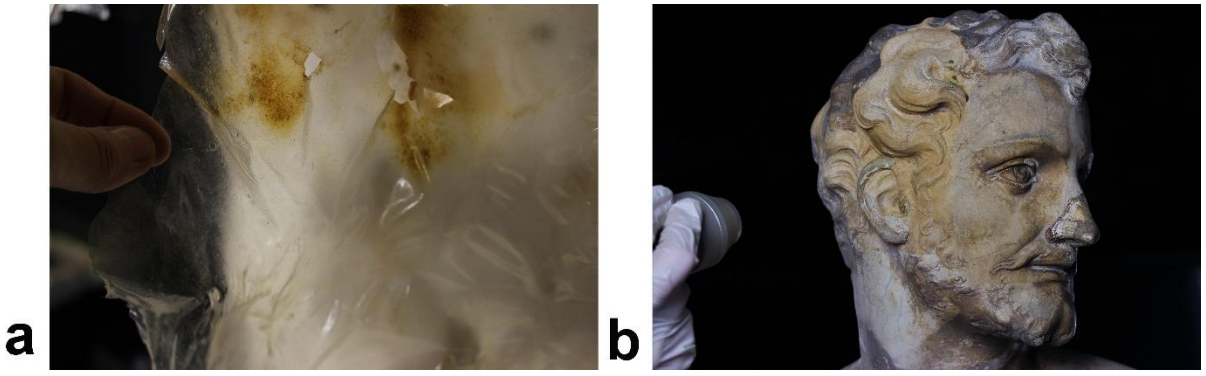


Figure 4

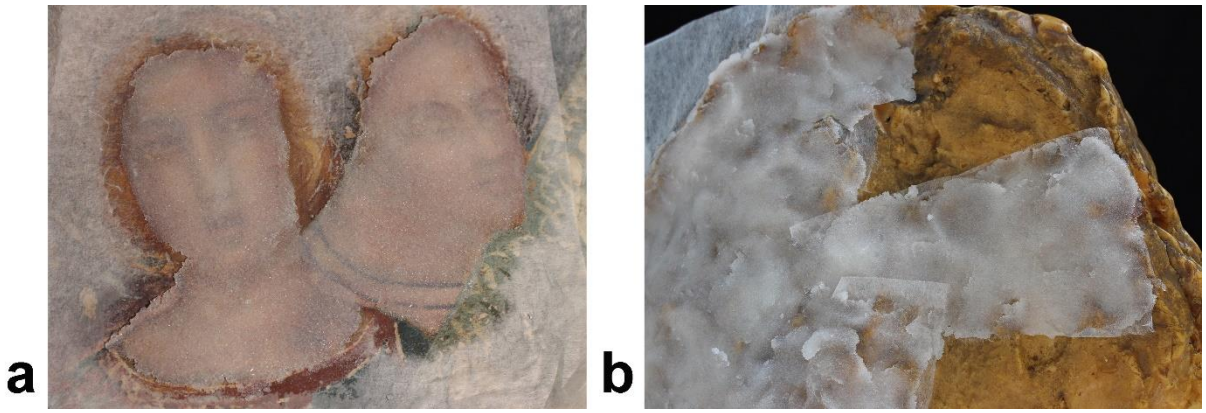


Figure 5