

# An innovative and sustainable approach to Graffiti removal from Istrian stone through the silica sol-gel chemistry

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## Abstract

A sustainable methodology to synthesise and screen new libraries of low-environmental impact products, suitable for removing graffiti and murals from historic building, masonries and stone artworks has been developed. This approach provided a novel series of two-component systems by combining silica sol-gel chemistry and dimethyl carbonate. The solid matrixes were hybrid silica gels synthesised in basic conditions by using ethylene and propylene glycols as organic co-solvents. Dimethyl carbonate (DMC) was the green organic solvent to load into the gel. The efficiency of three new systems in adsorbing/trapping commercial red aerosol spray paint was investigated through an *ad hoc test tube* extraction evaluation and on mock stained samples of Istrian stones. Data provided by NMR spectroscopy and FT-IR spectroscopy led to the identification of a promising cleaning agent, paving the way to its full characterisation and features improvement.

## Keywords

Graffiti removal agents, conservation and restoration of Cultural Heritage, green methodology, Istrian stone, organic carbonates, silica gels.

## 1. Introduction

In the last decades, Conservation Science has not been exempted from the worldwide urge to embrace a sustainable and bio-compatible chemistry. As a consequence, restorers and art conservators have been forced to review some of their working practices, in order to avoid or limit the use of those chemicals, once commonly employed, but now classified as hazardous material to the environment and human health (e.g. chlorine-based organic solvents and salts) by international and European regulations.

In this scenario, the development of efficient and cost-effective *ad hoc* procedures to protect and restore stone artworks and masonries belonging to the Cultural Heritage often clashes with the restrictions imposed, especially in the field of graffiti removal [1,2]. In fact, graffiti – in the negative exception – represent an act of vandalism and thus a borderline case in a conservation plan, inasmuch they cannot be foreseen and controlled [3]. Different techniques and methods have been reported either as protection of stone material such as coating agents [4,5] or to extract synthetic polymer colours from stone material such as the use of chemicals, blasting [6], laser [7,8], application of organic gels, [9] microbial degradation [10,11]. However, up to date no low cost and low impact strategy has been yet conceived, which acts efficiently against graffiti, without altering the treated material.

Herein we propose a novel approach for cleaning graffiti based on the use of two components system: a silicate-based polymer as a matrix and dimethylcarbonate (DMC) as the organic solvent. Our investigation was focused on the efficiency of silica gel/DMC system as cleaning agent for spray painted Istrian stone samples. Istrian stone or Orsera stone is considered the local stone of Venice and its Lagoon UNESCO site as it has been widely employed in the last 700 hundred years for the realization of sculptures, architectural and structural elements and historical buildings façade such as those of Palazzo Ducale and Ponte di Rialto. This limestone's low water absorption, porosity (0.5 – 0.6%) and high compactness (apparent density 2.67 – 2.69)

rendered it an ideal barrier against the rising damp. This phenomenon affects all the Venice area and may cause serious damages to masonries and stone works – up to 3.5 m above the sea level – if it is not properly hindered [12,13].

Therefore, Istrian stone have been deemed as a model substrate to evaluate novel silica gel/DMC systems as graffiti removal agents and to develop a practical methodology for cleaning historical (and non-historical) buildings marred by paints.

Silicon-based materials are well known coating [14,15] and consolidating (e.g. ethyl silicate) [16,17] agents commonly used both to protect and restore stone artifacts. Among these materials, silica gels represent versatile supports that can be rather easily synthesised and functionalised via sol-gel chemistry in mild reaction conditions. Numerous procedures to produce silica gels in neutral, basic and acidic catalysis and in aqueous and non-aqueous conditions have been reported in the literature [18-20].

DMC is a green solvent belonging to the family of dialkyl carbonates (DACs) come to the fore as valid and sustainable alternative to chlorine chemicals both as reagents and solvents [21-22]. Besides, DMC – as well as few other DACs such as diethylcarbonate (DEC), ethylenecarbonate (EC) and propylenecarbonate (PC) –, is already present in low amount as co-solvent into formulates and microemulsions employed to remove a variety of resins, i.e. waxes, glues, varnishes, etc., from artworks [23,24]. By including DMC into a silica gel, we aim to obtain an absorbent product, which combines the features of a safe organic volatile solvent (DMC b.p. is 90 °C) with those of an adsorbing inorganic support.

The main operational goals meant to be achieved by using these new inorganic/hybrid gels are:

- a facile application of the gel over the painted area affecting the stone material;
- an easy removal of the dried gel from the stone material without altering it;
- the development of a general operational approach, which limits the exposure of operators and environment to chemicals.

## 2. Materials and Methods

### 2.1 Gels production

Four hybrid-silica gels **G1-G4** were synthesised by mixing tetramethyl orthosilicate (TMOS) or tetraethyl orthosilicate (TEOS) (1.00 eq) with ethylene glycol or propylene glycol (12.00 eq) followed by the addition of a 0.30 M NH<sub>3</sub> aqueous solution (0.08 eq) under stirring. The gelation time depended on the orthosilicate, the diol, as well as the reaction conditions (Table 1). Once the gelation point was reached, each gel was left aging for 72 h and then either loaded with DMC to give a *wet* gel or dried to give a powder gel.

*Wet* gels (**G1a-G4a**; Table 1) were achieved by placing aged gels in flasks filled with DMC and crushing them into small particles. DMC was renewed twice a day for 4 days, to ensure removal of diols and alcohol generated during the gel formation.

**Table 1.** Reaction conditions to obtain Silica gels.

entry <sup>a</sup>	Alkyl silicate	Reaction mixture	Gelation conditions <sup>b</sup>	Gel aspect
<b>G1</b>	TMOS (1.00 eq)	EG (12.00 eq) + 0.30 M NH <sub>3</sub> aq. sol. (0.08 eq)	stirring for 1 h at 20 °C	<b>G1a</b> : faint white gelatin-like gel <b>G1b</b> : pale yellow powder
<b>G2</b>	TEOS (1.00 eq)	EG (12.00 eq) + 0.30 M NH <sub>3</sub> aq. sol. (0.08 eq)	stirring for 84 h at 20 °C	<b>G2a</b> : faint white gelatin-like gel <b>G2b</b> : yellow powder
<b>G3</b>	TMOS (1.00 eq)	PG (11.00 eq) + 0.30 M NH <sub>3</sub> aq. sol. (0.08 eq)	stirring for 1 h at 20 °C	<b>G3a</b> : clear gelatin-like gel <b>G3b</b> : pale yellow powder
<b>G4<sup>c</sup></b>	TEOS (1.00 eq)	PG (11.00 eq) + 0.30 M NH <sub>3</sub> aq. sol. (0.08 eq)	Stirring for 14 d at 80 °C	<b>G4a</b> : Partial gelation

<sup>a</sup> **G1a-G3a** wet gels and **G1b-G3b** dried gels. <sup>b</sup> After a 72 h aging: **G1a-G3a** obtained by washing out diols and alcohol and loading with DMC; **G1b-G3b** obtained by solvents elimination through a drying process; <sup>c</sup> **G4a** gave partial gelation, thus it was not further investigated.

The general procedure to obtain a dried gel (**G1b-G3b**; Table 1) as a powder consisted in treating the aged gel with H<sub>2</sub>O (3 times), in order to wash out the residual diol and the alcohol generated during the gel formation. Then the so-called *hydrogel* was washed with toluene, dried under vacuum and kept for 1 week at 120 °C in an open flask, prior to crushing it finely in a mortar.

## 2.2 Silica gels for extraction of a synthetic polymer colour in DMC

Gels (**G1-G3**) efficiency in trapping colour polymers was firstly investigated by comparison with those of silica gel for chromatography (**SGC**; 60A Carlo Erba) and micronized silica gel (**MSG**; Aerosil 200®), commonly used as thickening agent by restorers. Commercially available red aerosol paint (Rubin Red, Enamel Acrylic Spray, Arexons) was sprayed over a glass plate, let dried and then scraped off to obtain a red powder. For each gel, 5.00 mg of polymer colour powder was placed in a Pyrex test tube, suspended in DMC (1.00 mL) prior to adding a powder gel (0.25 g) or a wet gel (1.25 g of the mixture of Si gel/DMC corresponding to 0.17-0.21 g of dried gel) and further diluting the mixture with DMC (up to 4.00 ml in total). Then the test tube was vigorously shaken and the mixture was left 1 h to equilibrate. The supernatant was then decanted, the residual gel washed with DMC (2 x 2.00 mL) and the collected liquid fractions were concentrated under vacuum to give a yellow oil residue analysed by FT-IR and NMR spectroscopy. The gels were dried under vacuum and analysed via FT-IR spectroscopy by mixing samples with KBr. Each experiment was repeated at least three times

## 2.3 Silica-gel/DMC systems application on mock samples of stained Istrian stone

Istrian stone samples with dimensions 10 cm x 10 cm x 2 cm were stained using commercially available red aerosol spray paint, (Rubin Red, Enamel Acrylic Spray, Arexons). The latter was sprayed over stone samples from a distance of 20 cm and with an angle of approximatively 45°. Two layers of paint were applied over specimens that were stored in laboratory at 20 °C for one week prior to being used.

**G1a-G3a** systems and **MSG/DMC** – slurry – were applied over stained samples by using a spatula and covering a surface of 10-20 cm<sup>2</sup>. Each stone was then protected with a PVC film to further limit the solvent evaporation. Experiments were performed leaving the silica-gel/DMC systems acting for 10, 30, 60, 120 min or 1 day. Stones were then uncovered, and gels were let dried on open air for 60 min and then removed by a soft brush. Eventually treated areas were gently washed with water to remove silica gel particles residual. Silica gels collected at end of the tests were further dried under vacuum and analysed via FT-IR spectroscopy by mixing samples with KBr. Each experiment was repeated at least three times.

# 3. Result and Discussion

The general reaction mechanism leading to sol-gels involves the hydrolysis in basic or acidic conditions of at least one alkoxy group of a tetraalkyl orthosilicate molecule, followed by the condensation through siloxane bonds formation and so forth until the – so called – gelation point (Scheme 1) [18]. Under basic catalysis, the hydrolysis steps of silicates have been reported to get progressively faster than condensations steps. As a result, a colloidal gel may be generated from small branched oligomers or small polymers crosslinked with each other (Scheme 1A). On the other hand, under acidic catalysis the rate of hydrolysis steps is progressively slower than that of condensation steps, which preferentially involve terminal silanol groups. Therefore, the gel may grow as chain like structures (Scheme 1B).

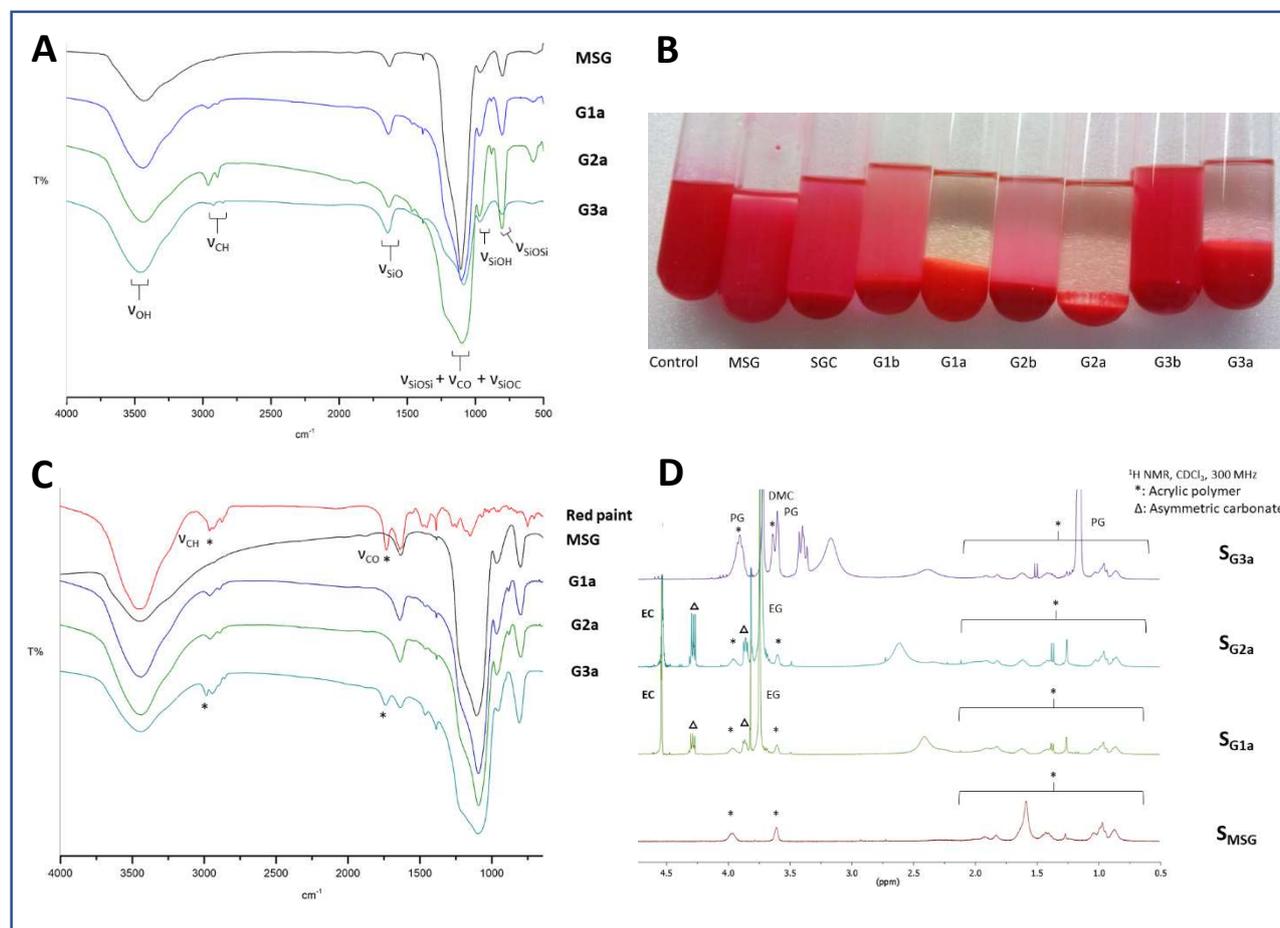
In this paper we report the synthesis of hybrid silica gels (**G1-G3**; Table 1) by using TMOS and TEOS as silicate precursors and EG and PG as organic solvents instead of alcohols (Scheme 1C). As described by Ștefănescu *et al.* [25,26], EG and PG can react with a tetraalkyl silicate through the formation of a covalent bond Si-O, and thus be directly involved in the gel formation, acting as a spacer between two silicon atoms. TEOS is often



bonded. On the other hand, FT-IR spectrum of dried **G3a** shows a broader band of OH stretching, suggesting the formation of a less branched gel with a lower degree of propylene glycol inclusion in the structure [25,26].

### 3.1 Evaluation of Silica gels extraction efficiency in DMC

Silica gels **G1-G3** were then tested for extraction of a commercially available red aerosol paint by using DMC as solvent; each experiment was carried out in a test tube (see section 2.2 for details). After 1 h equilibration, solely the experiments conducted with **G1a-G3a** and **MSG** exhibited a clear separation between gel and liquid phase; the former phase showed an intense red colour and the latter a pale-yellow colour (Figure 1B). Instead, **G1b** and **G2b** needed 7 h to extract the red pigment from DMC completely, whereas in the case of the tests with chromatographic silica gel (**SGC**) and **G3b** pigment adsorption resulted incomplete. Moreover, gels **G1a** and **G3a** appeared swelled in comparison to **G2a**. The swelling may be ascribable to the different gel structures, strictly related to the degree of hydrolysis and condensation of their silicate precursors TMOS (**G1a** and **G3a**) and TEOS (**G2a**).



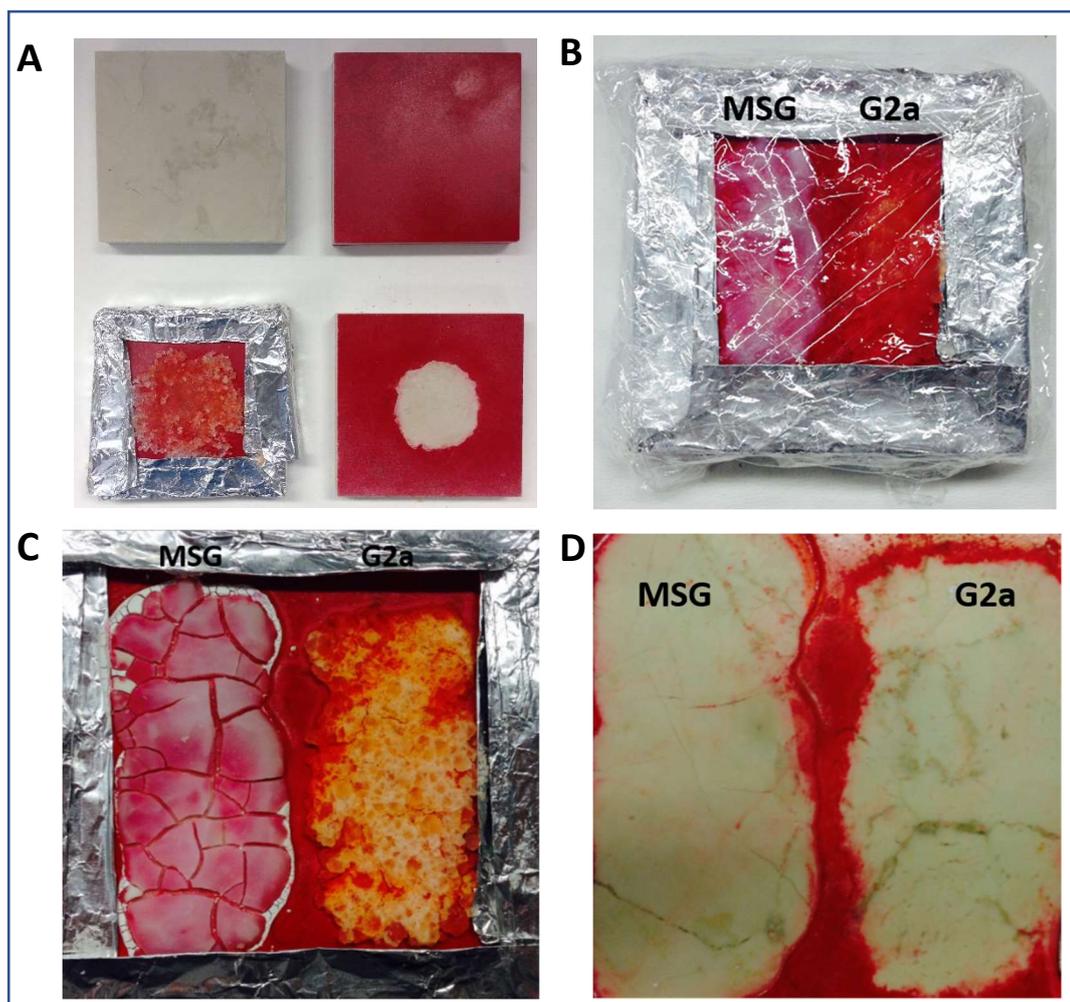
**Figure 1.** Silica gels extraction in DMC. **(A)** FT-IR analysis of G1a-G3a and MSG dried gels. **(B)** Test Tube analysis with red paint. **(C)** FT-IR analysis of **G1a-G3a** and **MSG** dried gels after the Test Tube analysis. **(D)** <sup>1</sup>H NMR analysis S<sub>G1a</sub>-S<sub>G3a</sub> and S<sub>MSG</sub> of concentrated supernatant liquid phases of the Test Tube analysis. (\*) = acrylic polymer; (Δ) = asymmetric carbonate.

**G1a-G3a** and **MSG** were thus the most efficient gel of this series in trapping the red pigment from the paint dissolved in DMC. Once the supernatant liquid phases were decanted, the gels were washed with DMC (no loss of colour was detected) and dried under vacuum. FT-IR analyses of these reddish powder were compared with that of dried red paint (**RP**) mixed with KBr (Figure 1C). Dried post pigment extraction samples of **G1a**, **G2a** and **MSG** exhibited no clear band ascribable to the red paint. Instead dried **G3a** spectra showed two

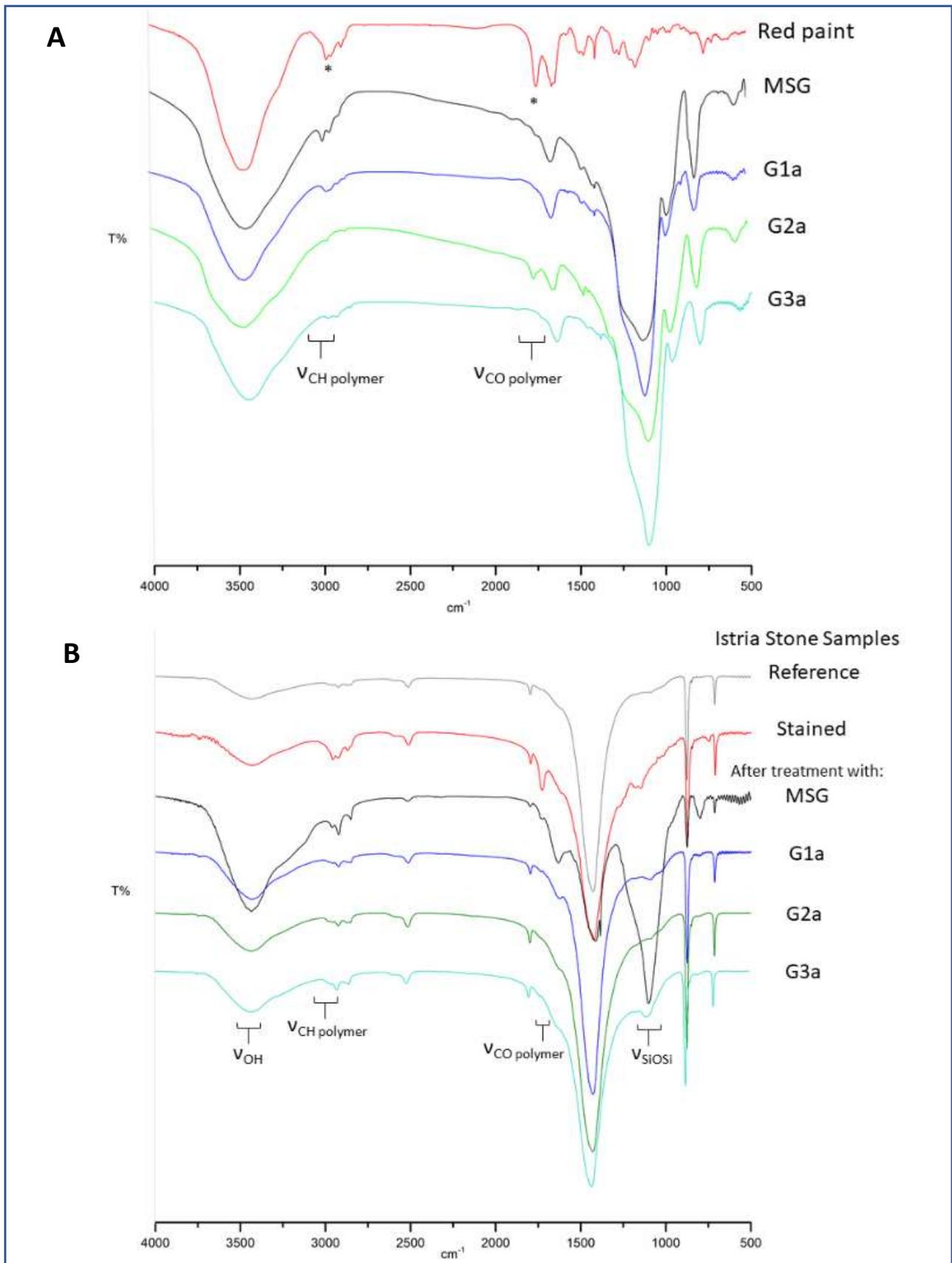
bands characteristics of acrylic polymers, i.e. **RP**, one at around  $2950\text{ cm}^{-1}$  relative to a C-H stretching and the other one around  $1730\text{ cm}^{-1}$ , relative to a C=O stretching. Their corresponding clear liquid phases, namely **S<sub>G1a</sub>-S<sub>G3a</sub>** and **S<sub>MSG</sub>**, were concentrated under vacuum to afford residues analysed by NMR spectroscopy (Figure 1D).  $^1\text{H}$  NMR spectra of each solution highlighted the extraction of acrylic polymer contained into the paint spray by DMC. A low amount of residual glycol was detected in each **S<sub>G1a</sub>-S<sub>G3a</sub>**. Signals corresponding to ethylene carbonate and an asymmetric organic carbonate were presents in **S<sub>G1a</sub>-S<sub>G2a</sub>** spectra. These organic carbonates were produced during DMC loading step by reaction of DMC and EG in basic conditions and they may act as co-solvents in the gel/DMC systems increasing their efficiency. Besides, the amount of polymer dissolved in **S<sub>G3a</sub>** appeared less than that dissolved in the other gels confirming the incomplete polymer extraction from the red paint by DMC.

### 3.2 Evaluation of Silica gel/DMC systems extraction efficiency over stained Istrian stone

Istrian stone samples were stained using commercially available red aerosol spray paint. The most efficient gels identified in the previous study, i.e., **G1a-G3a**, and **SGC/DMC** system were then applied over stained surface according to the procedure described in section 2.3. The efficiency of **G1a-G3a** and **MSG/DMC** systems in extracting and trapping red paint from Istrian stone mock samples was evaluated considering different time of applications of the gel systems, i.e., 10, 30, 60, 120 min and 1 day. Typically, the experiments were completed within 2 hours and their visual evaluation showed that the absorption involved solely the surface of gels directly in contact with the stone surface.



**Figure 2.** Silica gels/DMC systems application on red stained Istrian stone samples. **(A)** Istrian stone samples pre-, intra- and post-treatment; **(B-D)** Comparison between **MSG/DMC** and **G2a**.



**Figure 3.** Preliminary evaluation of Silica gels/DMC systems efficiency on red stained Istrian stone samples. **(A)** FT-IR analysis of dried **G1a-G3a** and **MSG** sample removed after 2 h from red stained Istrian stones. **(B)** FT-IR analysis of red stained Istrian stones samples pre- and post- treatment with **G1a-G3a** and **MSG/DMC** systems.

**G2a** and **MSG/DMC** systems provided comparable overall results over the treated stone surface. However, after gels removal the area treated with **MSG/DMC** system presented an accumulation of red paint along the border of the untreated area. On the contrary **G2a** provided smooth edges all around treated surface. This implies that **MSG** retained DMC less than **G2** and thus the **MSG/DMC** system action is not completely circumscribed under the covered stained surface (Figure 2A).

Moreover, the removal of dried **G2a** by a soft brush showed a homogeneously cleaned surface even over areas containing stylolites and sedimentary joints, which are common elements of Istrian stone texture [25,26] with higher porosity and permeability.

After treatment with **MSG/DMC** system, these elements showed a reddish discontinuous colour, most likely, ascribable to the presence of particles of **MSG** with low average size ( $\leq 3 \mu\text{m}$ ). Although these particles effectively adsorbed the red paint, more vigorous brushings were needed to remove them from highly porous stone areas. **G1a** and **G3a** partially removed red paints from stone surface. A second application of both was needed to obtain an extraction comparable to those achieved by means of **G2a** and **MSG/DMC** systems.

FT-IR analysis of dried gels samples, after application over stained Istrian stone, confirmed that **G2a** and **MSG** better extracted and trapped the acrylic polymer than **G1a** and **G3a** (Figure 3A). **MSG** spectrum showed a characteristic C-H stretching band of the acrylic polymer, which instead appeared rather covered from O-H stretching band in the dried **G2a** spectrum. However, this latter exhibited a clear C-O stretching band of the acrylic polymer, not easily identifiable in the **MSG** analysis.

FT-IR analysis of red stained Istrian stone samples of pre- and post- treatment with gel systems highlighted that **G1a** and **G3a** cleaning action was incomplete, inasmuch recognisable stretching band of acrylic polymer were detected on stone samples (Figure 3B). Moreover, the spectra of stone samples treated with **G3a** and **MSG/DMC** systems showed a band at  $1100 \text{ cm}^{-1}$  ascribable to the asymmetric stretching of Si-O-Si bond and thus confirming the presence of silica particles over the stone surface after the gel removal procedure. No bands ascribable to acrylic polymer and silica gel were identified in the dried **G2a** spectrum.

## Conclusions

In this communication the synthesis and preliminary evaluation of a novel class of silica gel/DMC graffiti removal systems have been described. Three Si gel/DMC systems were achieved through an opportunely modified and optimised sol-gel like methodology and their potency to adsorb paint (synthetic polymer colour) were tested. This investigation involved firstly an easy to set up and cost-effective comparative extraction of a paint dissolved in DMC using new wet gels **G1a-G3a**, their powder version **G1b-G3b**, a micronized silica gel and a silica gel for chromatography. Data collected by  $^1\text{H}$  NMR and FT-IR analyses allowed to identify silica wet **G1a-G3a** and **MSG/DMC** systems as lead systems of this studies. Then their efficiency as cleaning agents was assessed on Istrian stone stained samples. **G2a** provided promising results in extracting aerosol spray paint from the treated stone material. As a consequence, it has been deemed as the best candidate to focus on, in order to achieve further improvements and performed a complete product and product-treated surface interaction characterisation.

Eventually, the reported approach allows to easily develop and screen a variety of libraries of silica gels/DACs by using different synthetic procedures, introducing functionalities onto silica matrix and by adding different organic carbonates or using them in mixture with other solvents [27,28] which can:

- dissolve dye, polymer and additives of the aerosol paint and trap them into the gel through the drying, without damaging the surface of the stone material;
- decrease the rate of the solvent evaporation, which in turn may prolong the solvation action and limits the operator exposition;
- be obtained via a convenient, environmental friendly and scalable production.
- be easily storable.

The investigation of gels features, a deep study of their interactions with stone surface and spray paints were considered beyond the aim of this Communication. They will be addressed along with gels efficiency evaluations on different substrates (e.g. paint and tapestry) [29,30] in a future ongoing work.

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