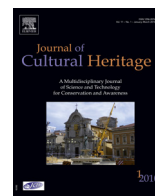




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Short note

Diethyl oxalate as a new potential conservation product for decayed carbonatic substrates



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ARTICLE INFO

Article history:

Received 11 April 2013

Accepted 8 August 2013

Available online 23 September 2013

Keywords:

Diethyl oxalate

Consolidant product

Calcium oxalate

Caoxite

Raman Spectroscopy

ABSTRACT

This note shows the first results of a study concerning the development of a new method for the consolidation of decayed carbonatic matrices. On the basis of the results achieved with ammonium oxalate, the authors tested a different mechanism to crystallize calcium oxalate phases in calcium carbonate substrate using diethyl oxalate solution. Raman spectroscopy provided a significant analytical support on the study of diethyl oxalate hydrolysis allowing to monitor the reaction and to suppose the occurrence of a reaction intermediate. The investigation of the newly-formed calcium oxalate phases after the reaction of diethyl oxalate with calcite powder allowed to verify the reactivity of the proposed solution and to highlight the crystallization of caoxite, an uncommon calcium oxalate phase.

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1. Introduction

During the last decades, different kinds of organic and inorganic products have been proposed for the conservation of the monument surfaces [1] to increase the cohesion and water-repellence of the material. Several studies [2,3] highlighted the importance to investigate the reactions occurring below the surface of a treated stone or plaster; the penetration depth, the distribution of the applied product and the chemistry that may develop are the crucial factors for the evaluation of the efficacy of a treatment. Recently, Raman spectroscopy has been proposed to investigate the inner portion of plasters treated with ammonium oxalate $(\text{NH}_4)_2\text{C}_2\text{O}_4$ [3,4], a product increasingly and widely used for some years to protect carbonatic surfaces; ammonium oxalate reacts with the carbonatic matrix inducing the transformation of calcium carbonate to calcium oxalate, a substance characterized by a very low solubility in water and generally also in strong acids, thus providing better resistance to decay phenomena [5]. Micro-Raman mapping revealed that the penetration depth achieved by ammonium oxalate in plaster specimens is very low, at most approximately 700 μm [4]. The ionic interaction between the salt and the carbonatic matrix could hinder the penetration of the oxalate ions into the inner portion of the substrate [6], therefore the consolidant action of this treatment is limited only to the first few hundred microns.

This finding brought the authors to test a new mechanism of calcium oxalate crystallization into the carbonatic substrates using diethyl oxalate $(\text{C}_2\text{H}_5)_2\text{C}_2\text{O}_4$. In neutral conditions the hydrolysis mechanism of this molecule should avoid the ionic interaction during its penetration. Therefore as in the case of other organic compounds [6] diethyl oxalate should achieve a better penetration depth compared with that of ammonium oxalate. The consolidation action of diethyl oxalate should have a high chemical affinity with the substrate because, as ammonium oxalate, calcium carbonate changes into calcium oxalate. In this report preliminary findings obtained with Raman spectroscopy are shown; in particular the kinetics and the mechanism of the hydrolysis of diethyl oxalate have been monitored as well as the interaction between a diethyl oxalate aqueous solution and calcite crystals has been reported and discussed.

2. Experimental

2.1. Raman spectroscopy

Raman experiments were carried out with a Bruker Senterra dispersive μ -Raman spectrometer equipped with 400 and 1200 grooves/mm gratings and coupled to an Olympus BX51 microscope with 20 \times , 50 \times and 100 \times objectives in light and dark field. Exciting line used is 532 nm (50 mW), with a Peltier cooled CCD detector (1024 \times 256 pixels).

Measurements have been carried out in a liquid contained in a quartz cuvette using 20 \times objective, in the 100–3600 cm^{-1} range,

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3–5 cm^{-1} of spectral resolution, exposure time 40s, 3 accumulations and a maximum of 50 mW laser power at the sample.

2.2. Analytical procedure

The hydrolysis reaction of diethyl oxalate has been monitored analysing a solution of diethyl oxalate (Sigma Aldrich, purity $\geq 99\%$) 3% v/v in water. Raman spectra have been acquired every 6 hours for 7 days.

As a further step, the reaction between diethyl oxalate and a marble powder has been studied in order to check the newly crystalline phases formed. Therefore, a stoichiometric amount of marble powder has been added to a solution of diethyl oxalate (3% v/v in water). Raman spectra have been acquired after 7 days on the dried reacted powders.

3. Results and discussion

Raman spectra of the reference compounds are reported in Fig. 1. In the CH stretching region diethyl oxalate shows two lines at 2905 and 2976 cm^{-1} for CH_3 and at 2878 and 2944 cm^{-1} for CH_2 ; the line at 1761 cm^{-1} is assigned to the stretching vibration of $\text{C}=\text{O}$, the line at 1455 cm^{-1} to the bending of CH_2 and 1399 cm^{-1} to the umbrella motion of the methyl group; the stretching vibration of $\text{C}-\text{C}$ gives rise to two lines at 1025 and 1098 cm^{-1} , while 873 cm^{-1} is assigned to the stretching of CCO ; however, a clear distinction between the skeletal modes is qualitative since it is known that strong intramolecular coupling takes place in this frequency range. Finally, in the low-wave number region the deformation vibrations of COO is observed at 383 and 322 cm^{-1} probably coupled with lattice modes. Raman spectra acquired during 7 days allowed to observe the decrease of diethyl oxalate and the increase of ethanol (Figs. 2–3). No lines ascribed to oxalic acid have been observed. The disappearing of diethyl oxalate can be inferred observing the line at 1761 cm^{-1} (Fig. 2), absent in the Raman spectrum of ethanol, the shift of one of the two lines of $\nu\text{C}-\text{C}$ from 1025 cm^{-1} to 1052 cm^{-1} and the shift of the line of νCCO from 873 cm^{-1} to 883 cm^{-1} (Fig. 3). After 3 days no lines of diethyl oxalate can be observed; the conductometric measures acquired on the diethyl oxalate solution with the same time as those of Raman allowed determining that after 3 days 84% of diethyl oxalate has hydrolyzed. As it can be seen in Fig. 3, a slow decrease and disappearance of a line at 853 cm^{-1} is observed; this line can be reasonable ascribed to the decreasing fraction of monoethyl oxalic acid (Fig. 1–b). The analysis with

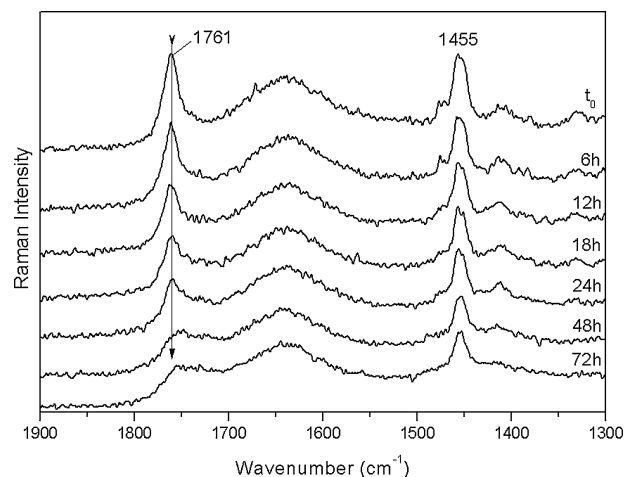


Fig. 2. Time decreasing in the 1300–1900 cm^{-1} range of diethyl oxalate monitored by Raman in an aqueous solution.

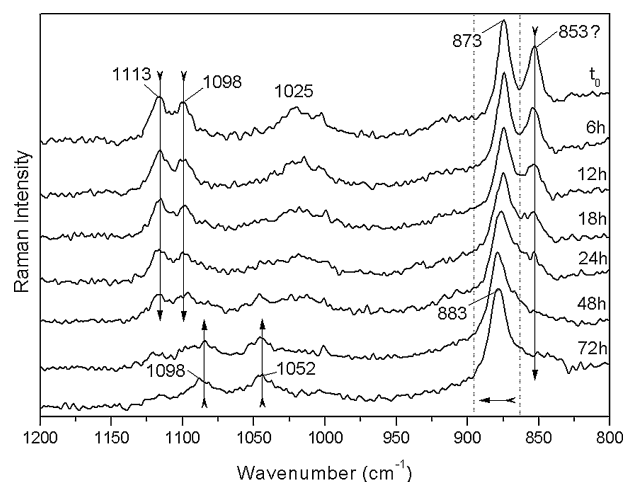


Fig. 3. Time decreasing in the 800–1200 cm^{-1} range of diethyl oxalate and increasing of ethanol monitored by Raman in an aqueous solution.

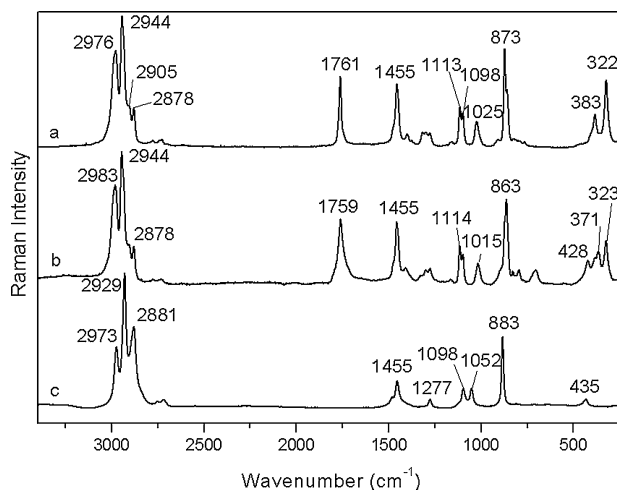


Fig. 1. Raman spectra of pure diethyl oxalate (a), monoethyl oxalate (b) and ethanol (c).

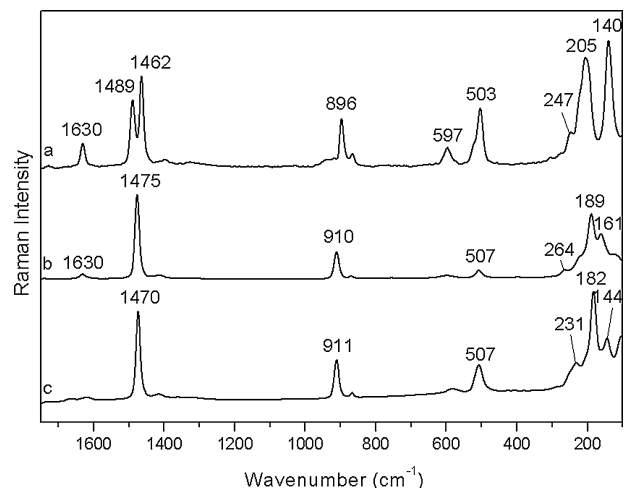


Fig. 4. Raman spectra of whewellite (a) and weddellite (b). The third spectrum (c) is ascribed to coxite.

micro-Raman of the products of the reaction between diethyl oxalate and marble powder shows the predominant presence of calcite. Therefore, the calcite did not completely react. With respect to calcium oxalates whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), weddellite ($\text{CaC}_2\text{O}_4 \cdot (2+x)\text{H}_2\text{O}$) and caoxite ($\text{CaC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$) have been detected. Whewellite and weddellite are the most common forms of calcium oxalates, while caoxite is rarely observed in nature and it has never been detected as a reaction product of ammonium oxalate treatment [3,4]. To the best of our knowledge no Raman spectra of caoxite were published so far. Raman spectrum shown in Fig. 4 has been ascribed to caoxite after the X-Ray diffraction analysis that revealed the characteristic pattern of this mineral. A sharp line at 1470 cm^{-1} can be obviously ascribed to the stretching vibrations of the O–C–O group of caoxite; in fact whewellite and weddellite show two lines at 1460 and 1475 cm^{-1} , respectively.

4. Conclusions

Raman spectroscopy turns out to be an effective tool to monitor the compounds involved in the hydrolysis of diethyl oxalate. The conductometric data support that Raman is able to monitor the hydrolysis up to the almost complete consumption of the reagent. The presence of a reaction intermediate has been inferred. Further knowledge is necessary to assess the hydrolysis mechanism of the diethyl oxalate; this may support the existence of a reaction intermediate, as for instance the monoethyl oxalic acid, which may

play a relevant role when it reacts with the carbonatic substrate. The slow rate of the hydrolysis reaction could favour the crystallization of calcium oxalates inside the material at higher depths compared to those achieved with ammonium oxalate. The analyses of the reaction products formed after the reaction between diethyl oxalate and calcite revealed the unexpected occurrence of caoxite, in addition to whewellite and weddellite. The mineralogical fraction of the material has received a sound support from XRD experiments. A new optical evidence of caoxite is given by its Raman spectrum.

References

- [1] V. Horie, *Materials for conservation*, Elsevier Butterworth-Heinemann, Burlington, MA, 2005.
- [2] F. Casadio, L. Toniolo, Polymer treatments for stone conservation: methods for evaluating penetration depth, *J. Am. Inst. Conserv.* 43 (2004) 3–21.
- [3] C. Conti, C. Colombo, M. Matteini, M. Realini, G. Zerbi, Micro-Raman mapping on polished cross sections: a tool to define the penetration depth of conservation treatment on cultural heritage, *J. Raman Spectrosc.* 41 (2010) 1254–1260.
- [4] C. Conti, C. Colombo, D. Dellasega, M. Matteini, M. Realini, G. Zerbi, Ammonium oxalate treatment: evaluation by μ -Raman mapping of the penetration depth in different plasters, *J. Cult. Her.* 12 (2011) 372–379.
- [5] B. Doherty, M. Pamplona, R. Selvaggi, C. Miliani, M. Matteini, A. Sgamellotti, B. Brunetti, Efficiency and resistance of the artificial oxalate protection treatment on marble against chemical weathering, *Appl. Surf. Sci.* 253 (2007) 4477–4484.
- [6] A.P. Ferreira Pinto, J. Delgado Rodrigues, Stone consolidation: the role of treatment procedures, *J. Cult. Her.* 9 (2008) 38–53.