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USE OF NANOMATERIALS FOR THE PROTECTION OF HISTORIC STONE ARCHITECTURE: LABORATORY METHODS FOR THE EVALUATION AND INVESTIGATION OF PHOTOCATALYTIC ACTIVITY

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KEYWORDS
Nano-TiO₂, Nanocomposites, Stone Protection, Photocatalysis, Self-Cleaning

ABSTRACT
The use of nanomaterials in the conservation of natural and artificial stone materials has been an active research topic over the last fifteen years, showing a potential for tackling different aspects of conservation, from consolidation of de-cohesinates substrates to hydrophobation and protection against chemical and biological decay agents.

Currently, the NanoCathedral H2020 project is aimed at developing a systematic approach to the use of TiO₂-based nanomaterials for stone protection, by evaluating the performance of an array of innovative products for the treatment of a set of lithotypes posing different challenges in terms of conservation.

The products set up in the frame of the NanoCathedral project are nanocomposites relying on the combination of different TiO₂ nanoparticles with a variety of silane/siloxane matrixes. As such, they are expected to provide the treated stone with self-cleaning photocatalytic behaviour and water-repellent properties.

As it is well known, no standard protocol exists to-date for the evaluation of photocatalytic activity on stone substrates. The existing methods, i.e. the organic colourant discoloration and the NOx degradation tests, suffer from a number of drawbacks, that include issues of reproducibility in the case of the organic colourant discoloration test, and high operational costs, in the case of the NOx degradation test.

The aim of this paper is compare the two methods by considering their similarities/differences in terms of response. To this purpose, we discuss the photocatalytic performance of two nanocomposites on three different lithotypes. Then, an attempt is made to correlate the experimental values of photocatalytic activity with the properties of the selected lithotypes and their interaction with the considered nanomaterials.

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INTRODUCTION

Stone materials in outdoor architecture are naturally subjected to a host of decay phenomena, among which those related to the penetration of water are particularly relevant. Furthermore, in a polluted environment, as the one offered by most present-day urban areas, natural agents of decay combine with anthropogenic ones, not only represented by carbo-naceous particulate matter but also by inorganic gaseous pollutants like sulphur dioxide and nitric oxides, thus making up a synergistic action [1-2].

Strategies for stone protection have become increasingly concerned with tackling these different sources of decay through a multi-functional approach: reducing water penetration on one side and the soiling and corrosion from air-borne pollutants on the other.

Over the last 25 years, photocatalysis has been regarded as a very powerful tool by environmental science, thanks to its potentialities in the fast oxidative degradation of organic pollutants [3]. Photoactive nanomaterials, especially TiO$_2$ nanoparticles, have also been applied in the manufacturing of building materials, such as cement [4]; more recently, their use in the field of natural stone protection has met encouraging results, also thanks to the good aesthetic compatibility of these products with stone substrates [5]. An improvement in some of the properties of these materials has been achieved through the development of nanocomposites, i.e. nanostructured materials relying on the combination of two or more components, in this case TiO$_2$ or ZnO nanoparticles and a polymer matrix of silanic or acrylic nature [6-7]. These composite materials show better adhesion to the stone substrates with respect to nanoparticle dispersions and display hydrophobic features combined with a self-cleaning photocatalytic action.

For the characterization of photoactive materials, it is of great importance to have a reliable method for the measurement of photocatalytic activity. As far as stone protection is concerned, such measurements are currently performed through the organic colourant discoloration [8-13] and the NO$_x$ degradation tests [8, 11-12, 14-16]. The latter monitors the degradation of nitric oxide (NO) through the intermediate nitrogen dioxide (NO$_2$) onwards to nitrate ion (NO$_3^-$) as a result of UV irradiation. Similarly, the discoloration test involves depositing a given amount of colourant solution, generally Rhodamine B or Meth-ylene blue, on a treated stone specimen and visually monitoring its degradation at various time intervals while irradiating the specimen by means of a UV/Vis light source. Colourimetric measurements are usually employed for the monitoring.

However, there are a number of drawbacks to these tests. Firstly, the reliability of the measurements can be an issue when dealing with substrates with high surface roughness like natural stone materials, since results strongly depend on the amount of treatment on the surface and its coverage. Then, as far as the NO$_x$ degradation test is concerned, the high cost of the required apparatus sets a limit to the applicability of the test. Finally, regarding the discoloration test, it is difficult to achieve a homogeneous deposition of a water-based colourant solution on a surface with hydrophobic features.

A more detailed knowledge of the factors underlying the measurement of photocatalytic activity, both in terms of substrate variability and test procedure, may thus help to understand the inherent limits of the tests, clarify the differences between them and also contribute to a correct interpretation of results.

In this work, we try to account for these factors by considering three lithotypes of different porosity (open porosity) and two different nanocomposites that are presently under study in the framework of the Nano-Cathedral project (European Project H2020 G.A. n.646178).

We start by discussing the results of the NO$_x$ degradation test in the light of available information on lithotype porosity and of data on the amount of absorbed treatment (§ 3.1).
Then, concerning the organic colourant discoloration test, an adjusted test procedure is adopted with the aim of reducing the variability from the deposition of colourant solution (§ 2.5 and § 3.2). The results are finally discussed and compared with those of the NO₅ degradation test (§ 3.2).

MATERIALS AND METHODS

2.1. Products

The two nanocomposites, hereafter referred to as TSA and TSW, consist of TiO₂ nanoparticles embedded in alkyl alkoxysilane matrices, hence they are expected to display water-repellent as well as photocatalytic properties.

2.2. Lithotypes

The stone specimens (2.5x2.5x2 and 5x5x1 cm³ blocks) belong to three different lithotypes: Baleb gem limestone, Apuan marble and Obernkirchen sandstone. Baleb gem limestone is a stone from the Ghent region (Belgium), quite compact in texture despite featuring many millimetre-sized cavities. Its open porosity amounts to 8±1 %vol [17] and on a mineralogical level it is composed of siliceous clastic arenite (40.1% quartz and 4.9% feldspars) with sparitic cementation (53.1% calcite). Apuan marble (from Carrara region, Italy) is almost purely made up of calcite (99.6%) and its open porosity is very low, around 0.2 %vol [18]. Obernkirchen sandstone is a fine-grained and porous stone (16-21 %vol, [19]) coming from lower Saxony (Germany), and its composition includes quartz (89.6%) and subordinately kaolinite (7.7%).

2.3. Treatments

Before undergoing any treatment, the specimens were gently polished with abrasive paper (P180 carborundum paper), kept in deionized water for an hour in order to remove soluble salts, dried in oven for 24 hours at 50°C and finally stored in a silica gel desiccator at 55% RH. The nanocomposites were applied by capillary absorption according to EN16581:2014 for 6 hours. In order to determine the amount of dry matter absorbed, all specimens were weighed before the treatment and then after solvent evaporation until constant weight was achieved (a minimum of 48 hours). Four 5x5x1 cm³ specimens per each lithotype and treatment were prepared for the NO₅ degradation test. In addition, four specimens treated with Silres BS290 (Wacker) were chosen as blank for each lithotype. Three 2.5x2.5x2 cm³ specimens (named A, B and C) per each lithotype and treatment were prepared for the organic colourant discoloration test. For each lithotype three untreated specimens were also chosen as reference. The values of dry matter absorbed per unit area are reported in Table 1. For 5x5x1 cm³ specimens, only average values calculated from four specimens per lithotype and treatment are reported (named D).

<table>
<thead>
<tr>
<th>specimen</th>
<th>BALEGEM</th>
<th>APUAN MARBLE</th>
<th>OBERNKIRCHEN</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TSW</td>
<td>TSA</td>
<td>TSW</td>
</tr>
<tr>
<td>A</td>
<td>0.0044</td>
<td>0.0133</td>
<td>0.0002</td>
</tr>
<tr>
<td>B</td>
<td>0.0039</td>
<td>0.0056</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>C</td>
<td>0.0075</td>
<td>0.0058</td>
<td>0.0001</td>
</tr>
<tr>
<td>D</td>
<td>0.005</td>
<td>0.007</td>
<td>0.001</td>
</tr>
</tbody>
</table>

Table 1: values of dry matter per unit area (g/cm²) absorbed by the specimens treated with TSW and TSA.

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2.4. NOx degradation test

The degradation of nitrogen oxides NOx (NOx = NO + NO2) was monitored for 100 minutes in a photoreactor (Colorobbia Consulting S.r.l.) equipped with an Ultraviolet Osram lamp (50 W/m² irradiance) and a chemiluminescence-based detection system. The analysis was conducted by mixing dry air, moist air and NO in such proportions as to obtain a 500±50 ppbv NO concentration and an atmosphere having 41±1 % RH at the temperature of 25±2 °C. Six samplings were performed every 20 minutes during the test, each with a duration of 5 minutes. The values (%) of NOx degradation for TSW and TSA at 0, 40 and 100 minutes were calculated through the formula

$$\frac{C_0 (NO_x) - C_t (NO_x)}{C_0 (NO_x)} \times 100$$

where $C_0 (NO_x)$ [= C0 (NO)] is the initial NOx concentration and $C_t (NO_x)$ [= C_t (NO)+Ct (NO2)] is the NOx concentration at time t.

2.5. Organic colourant discolouration test

Before starting the test 10 colour measurements were performed on each specimen through a Konica Minolta CM-600D Vis reflectance spectrophotometer. Then, a 0.05 g/L Rhodamine B solution was prepared by mixing ethanol and water in 7:3 ratio. The addition of ethanol helped to achieve a homogeneous deposition of the colourant. This choice was made after checking by a preliminary test that no significant difference in the value of photocatalytic activity arises from the presence of ethanol with respect to a purely water-based solution. 500 μL of colourant were deposited on each specimen by using a pipette. Then, the specimens were allowed to dry at room temperature for 72 hours, while being kept away from light sources. Finally, they were irradiated for 150 minutes in a solar box (Suntest XLS®, URAI S.p.A.) equipped with a Xenon arc lamp (cut-off filter for λ<295 nm, 765 W/m² irradiance). The temperature on the surface of the specimens was kept at 65±2 °C throughout the irradiation. Colour measurements (10 measurements per specimen) were performed at 0, 30, 90 and 150 minutes during the test in order to monitor colour change. For the assessment of photocatalytic activity the $a^*$ value from each measurement was considered, which represents the red colour component in the CIE Lab colour space. The extent of discolouration (D*) was then evaluated according to the formula

$$D^* (%) = \frac{a^*(t) - a^*(0)}{a^*(ns) - a^*(0)} \times 100$$

where $a^*(t)$ and $a^*(0)$ stand for the $a^*$ value at time t and 0, respectively, while $a^*(ns)$ refers to the specimen before the deposition of the Rhodamine solution. In order to take into account the contribution of photolytic and thermal degradation of Rhodamine as distinct from the photocatalytic process itself, D* values for treated specimens (D*$_{tr}$) at 150 minutes were divided by the corresponding values of untreated lithotypes (D*$_{ns}$) and will be reported as parameter for the evaluation of photocatalytic activity.

Three repetitions of the test were performed on different specimens (A, B and C). In each test, the standard deviation of $a^*$ values ($σ a^*$) of each specimen (resulting from 10 measurements) at the beginning of the test was considered as an indication of the inherent variability of specimen surfaces.

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RESULTS AND DISCUSSION

3.1. NOx degradation test

In Figure 1 the variation of NO, NO2 and NOx (=NO+NO2) concentrations for TSW, TSA and Silres BS290 during the degradation test is shown. The values (%) of NOx degradation for TSW and TSA at 0, 40 and 100 minutes are reported in Table 2.

![Graphs showing concentration changes over time for NO, NO2, and NOx](image)

Figure 1: time variation of NO, NO2 and NOx concentrations for TSW (--), TSA (---) and Silres BS290 (----) during the degradation test on Balegem stone (▲), Apuan marble (●) and Obernkirchen stone (■).

<table>
<thead>
<tr>
<th>time (min)</th>
<th>BALEGEM TSW</th>
<th>BALEGEM TSA</th>
<th>APUAN MARBLE TSW</th>
<th>APUAN MARBLE TSA</th>
<th>OBERNKIRCHEN TSW</th>
<th>OBERNKIRCHEN TSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td>35</td>
<td>38</td>
<td>3</td>
<td>20</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>100</td>
<td>60</td>
<td>49</td>
<td>8</td>
<td>32</td>
<td>52</td>
<td>32</td>
</tr>
</tbody>
</table>

Table 2: values (%) of NOx degradation at 0, 40 and 100 minutes for TSW and TSA.

These results indicate that the two nanocomposite products are both photoactive, but display rather different behaviours. From the graphs (Figure 1), it is clear that:

1. the kinetics of TSA in the first reaction step, i.e. NO degradation, is much faster than in the second NO2 degradation step. This leads to a rapid increase in NO2 concentration and negatively affects the overall photocatalytic performance, which is evaluated from
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the total, cumulative NOx degradation;

2. in spite of a lower rate of NO degradation, TSW exhibits comparable rates in the first and second steps, so that only a minor NO2 increase results and overall a better photocatalytic performance is observed.

Moreover, from an inspection of Table 2, it is clear that a difference between lithotypes also exists:

1. both products yield the best performance on Balegem stone and show less brilliant but still consistent behaviour on Obernkirchen stone;

2. the results from Apuan marble look puzzling: unlike the case of Balegem and Obernkirchen stones, TSW shows almost no activity, whereas the performance of TSA is comparable to that measured on the other two lithotypes;

3. the values of dry matter absorbed by the specimens (see specimens D in Table 1) show that, as compared to TSW, TSA is absorbed to a greater extent. This behaviour is more pronounced on Obernkirchen stone and Apuan marble, while in the case of Balegem stone the two products behave more similarly.

3.2. Organic colourant discolouration test

In Table 3 are reported the D* / D* values at 150 minutes obtained from the three tests A, B and C and in Table 4 the resulting average values.

<table>
<thead>
<tr>
<th></th>
<th>BALEGEM</th>
<th></th>
<th>APUAN MARBLE</th>
<th></th>
<th>OBERNKIRCHEN</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TSW</td>
<td>TSA</td>
<td>TSW</td>
<td>TSA</td>
<td>TSW</td>
<td>TSA</td>
</tr>
<tr>
<td>Test A</td>
<td>D* / D* 150 min</td>
<td>1.0</td>
<td>1.2</td>
<td>1.6</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>σ a*(ns)</td>
<td>0.4</td>
<td>0.2</td>
<td>0.04</td>
<td>0.06</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>σ a*(0)</td>
<td>0.7</td>
<td>2</td>
<td>7</td>
<td>5</td>
<td>0.4</td>
</tr>
<tr>
<td>Test B</td>
<td>D* / D* 150 min</td>
<td>1.5</td>
<td>1.4</td>
<td>1.1</td>
<td>0.9</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>σ a*(ns)</td>
<td>0.78</td>
<td>0.94</td>
<td>0.09</td>
<td>0.03</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>σ a*(0)</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>Test C</td>
<td>D* / D* 150 min</td>
<td>1.2</td>
<td>1.4</td>
<td>1.2</td>
<td>0.8</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>σ a*(ns)</td>
<td>0.2</td>
<td>0.3</td>
<td>0.04</td>
<td>0.04</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>σ a*(0)</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 3: D* / D* values at 150 minutes in the tests A, B and C, standard deviations of a* values (σ a*) from 10 colour measurements (before Rhodamine deposition and at time 0).

<table>
<thead>
<tr>
<th></th>
<th>BALEGEM</th>
<th></th>
<th>APUAN MARBLE</th>
<th></th>
<th>OBERNKIRCHEN</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TSW</td>
<td>TSA</td>
<td>TSW</td>
<td>TSA</td>
<td>TSW</td>
<td>TSA</td>
</tr>
<tr>
<td>μ</td>
<td>1.2</td>
<td>1.3</td>
<td>1.3</td>
<td>1.0</td>
<td>1.3</td>
<td>0.89</td>
</tr>
<tr>
<td>σ</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.01</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>17</td>
<td>8</td>
<td>15</td>
<td>20</td>
<td>23</td>
<td>1</td>
</tr>
<tr>
<td>av. dry matter (g/cm²)</td>
<td>0.005</td>
<td>0.008</td>
<td>0.0002</td>
<td>0.0005</td>
<td>0.007</td>
<td>0.016</td>
</tr>
<tr>
<td>σ (g/cm²)</td>
<td>0.002</td>
<td>0.004</td>
<td>0.0001</td>
<td>0.0002</td>
<td>0.001</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Table 4: average D* / D* values at 150 minutes (μ) from tests A, B and C, with standard deviation (σ) and relative standard deviation (RSD), and average dry matter per unit area absorbed by the specimens (A, B, C), with standard deviation σ (see Table 1 for values of dry matter absorbed by each specimen).
The results shown in Tables 3-4 indicate that:

1. the average value of photocatalytic activity, represented by $D^*/D^*_{at}$ values in Table 4, does not vary much from one lithotype to the other, with two notable exceptions. These are represented by TSA on Apuan marble and especially Obernkirchen stone, for which significantly lower $D^*/D^*_{at}$ values are observed;

2. among the two products, TSW shows an overall better photocatalytic performance, with similar average results on all lithotypes. TSA displays a more variable performance, ranging from results on Balegem stone comparable with those of TSA to negative performances on Apuan marble and Obernkirchen stone (Table 4);

3. the measurement of photocatalytic activity is affected by a marked variability between different specimens of each single lithotype, as indicated by high RSD values (Table 4);

4. considerable variability also exists in the amounts of dry matter absorbed by the specimens of each single lithotype (Table 1);

5. a direct correlation between these amounts and the photocatalytic activity of the corresponding specimens cannot be observed. Although it is evident that increasingly porous lithotypes (for data on lithotype porosity, see Materials and methods § 2.2) absorb greater amounts of product (Obernkirchen stone → Balegem stone → Apuan marble) and that TSA is absorbed in much greater amount than TSW by all lithotypes, it turns out that the amount of absorbed dry matter does not correlate with the value of $D^*/D^*_{at}$;

6. as far as the test procedure is concerned, it can be noticed (Table 3) that the standard deviations of $a^*$ values at the beginning of the test $\sigma a^*(0)$ on Balegem and Obernkirchen stones are comparatively low, indicating that no serious issue of homogeneity in the deposition of Rhodamine solution occurs. In Apuan marble a certain inhomogeneity appears to be there, particularly in specimens treated with TSW, but this could be due to the fact that, on a compact surface as that of Apuan marble, TSW tends to accumulate in some areas of the surface, giving rise to an inhomogeneous distribution of the treatment and, consequently, of the colourant solution.

From the above said (in particular, from points 3, 4 and 6), it appears that the variability observed for each lithotype in the results of the organic colourant discoloration test is primarily a result of the inherent substrate variability rather than a limit of the test itself.

In this regard, a comparison between the results of the organic colourant discoloration and the NO$_x$ degradation tests may suggest the following considerations:

1. for Balegem and Obernkirchen stones the two datasets are mutually consistent (see Table 2 and Tables 3-4): indeed, considering the two products as an ensemble, we may say that in both tests the best performance overall is achieved on Balegem stone (1.2 and 1.3, 60% and 49% for TSW and TSA, respectively). Then, the results of TSW on Obernkirchen stone in both tests are comparable with those on Balegem stone (1.3 and 1.2 vs. 52% and 60%), and the results of TSA are likewise consistent (0.89 and 1.3 vs. 32% and 49%);

2. on Apuan marble, the results from the two tests are in good agreement in the case of TSA, but totally divergent as regards the performance of TSW, for a good photocatalytic activity observed in the discoloration test corresponds to almost no activity in the NO$_x$ degradation test. We have not yet come up with a thorough explanation of this phenomenon, but some observations can be made. Firstly, Apuan marble is a low porosity (0.2 %vol.) and low roughness stone and we know that the coverage and protection of such materials is much more critical than the protection of medium and high porosity substrates, because treatments find particularly difficult to penetrate and settle inside the
material. Among the two products we are dealing with, TSW shows in all cases a lower tendency to penetrate as compared to TSA. Furthermore, optical microscope observations on specimen surfaces clarified that in the case of marble TSW is not homogenously distributed on the surface and it forms aggregates, whose specific surface area is likely very low. We then know that heterogeneous catalytic processes, as is the case of NO₂ degradation, occur through a preliminary adsorption step that is all the more efficient if the catalyst displays a high specific surface area, so that a greater number of reactant molecules are able to interact with it. If this is not the case, the adsorption step proceeds at lower rate and the overall reaction rate is accordingly reduced [8]. These qualitative observations only take a pace towards explaining the difference observed between the two tests, but a dedicated investigation would be needed in order to clarify the matter.

It may therefore be concluded that the two tests seem to provide substantially comparable results on Blegem and Oberndorf stones, most probably related to the high and medium porosities of these lithotypes, whereas the conflicting results observed on Apuan marble require a further investigation.

CONCLUSIONS

In this work, we compared two laboratory methods for the evaluation of photocatalytic activity, the NO₂ degradation and the organic colourant discoulouration tests, by considering three different lithotypes and two different nanocomposites.

The results of the two tests were discussed and their similarities/differences were highlighted. A good correlation was found between the tests on medium and high porosity substrates, so that we might say that the information provided by them appears to be equivalent. On the other hand, on a low porosity stone like Apuan marble the tests provide conflicting results, so that a complete evaluation of photocatalytic activity requires to perform both tests.

Concerning the discoulouration test, we considered a multiplicity of factors that may have an effect on the photocatalytic activity and its variability. In particular, the test procedure itself, the influence of the different stone materials and of the different nanocomposites were taken into account. It emerged that the observed variability is primarily related to the intrinsic variability of stone substrates rather than the test procedure itself. Furthermore, an obvious correlation between stone porosity, the amount of dry matter absorbed and the photocatalytic activity could not be found, suggesting that the properties of stone specimens, in particular their pore-size distribution, the properties of nanocomposites, particularly the size of their components and the solvent, and their distribution on the stone surface should be considered.

The evaluation of the interaction between nanocomposites and lithotypes is under study and we are obtaining promising results from an innovative surface characterization technique based on streaming current measurements.

ACKNOWLEDGMENTS

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REFERENCES


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