



Developing inorganic coatings with nano-TiO₂ for heritage concrete and assessing their self-cleaning performance by a new laboratory test

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ARTICLE INFO

Keywords:

Marble
Cement mortar
Capillary absorption
TEOS
Hydroxyapatite
Artificial soiling
Artificial rain
Application procedure
Photocatalytic TiO₂

ABSTRACT

Heritage concrete and cement mortars urgently need preventive treatments which slow down their deterioration, allow to avoid extensive demolition and reconstruction, and preserve the aesthetic significance of texturized surfaces. In this paper new inorganic treatments were developed, which combine the self-cleaning behaviour of nano-TiO₂ and the beneficial effect of inorganic consolidants. In a preliminary phase, two consolidants were investigated for the incorporation of titania nanoparticles, namely diammonium phosphate and ethyl silicate (TEOS), and the latter one was selected as the most promising one. In the second phase, combined treatments with TEOS and titania nanoparticles were developed and applied by different techniques to cement mortars manufactured to mimic historic substrates, providing a novel and valuable solution for heritage concrete protection that is unprecedented in the literature. Besides evaluating the photoactivity of the treatments in terms of methylene blue discolouration, a novel test was developed in this study to assess in a more realistic way the actual ability of the treatments to boost the removal of soiling by rain. The combination of TEOS and nano-TiO₂ into a single treatment has the potential to slow down carbonation and chloride diffusion, to help the removal of soiling and to provide the substrates with antimicrobial activity, hence it can be considered highly innovative. The results also showed that more realistic laboratory assessment procedures are necessary to predict the actual effectiveness of the treatments when applied to real substrates and exposed to real outdoor conditions. The novel test proposed and applied in this study may serve as a basis for the development of a new procedure of assessment of self-cleaning ability.

1. Introduction

Cement-based mortars and concrete have been playing a very important and distinctive role in modern architecture, often having a strong cultural significance [1–3]. Thanks to their moldable nature, these materials can be given a variety of appearances determined by different shapes, textures and colours as desired by the architect or artist [1]. For this reason, they widely spread since the second half of the Nineteenth century, for structural functions and expressive and decorative purposes. These materials include decorative cements, texturized concrete, artificial stones, and stone-imitating renders, which diffused in Art Nouveau, Art Deco, Rationalism, Brutalism and in many movements of contemporary architecture [4]. The fact that modern and contemporary buildings constructed with these materials may belong to our cultural heritage and deserve conservation just like ancient ones is more and more frequently recognized. In fact, several XX century concrete buildings were included in the UNESCO World Heritage list, such as the

Unity Temple Frank by Lloyd Wright, the Centennial Hall Max Berg and the Architectural Work of Le Corbusier.

Cement-based materials, which usually incorporate steel reinforcements, are affected by several deterioration processes [5], related to natural carbonation process, exposure to polluted and/or marine environment, and climate changes. In particular, they are affected by:

- corrosion of steel reinforcement due to carbonation and/or chloride diffusion [6]
- soiling, i.e., deposition of airborne particles over the surfaces leading to their blackening. Particulate matter owing to motor vehicles and home heating is still one of the major air quality problems in many European cities, although air pollution has been significantly reduced in recent decades [7]. Soiling is particularly severe when the surface is characterized by some texture or roughness [8], as in many cement-based materials.

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<https://doi.org/10.1016/j.conbuildmat.2024.138282>

Received 18 June 2024; Received in revised form 17 August 2024; Accepted 8 September 2024

Available online 11 September 2024

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- biofilm growth [9,10], possibly accelerated by the presence of soiling.

These problems cannot be solved using the same techniques used for ordinary concrete's repair [11], which involve extensive demolition and reconstruction of the original materials, because they would cause a loss of significant materials, fighting the principles of heritage conservation [12]. XX century architectural heritage requires innovative conservation solutions [13], which not necessary overlap those already well-established for ancient building materials [14]. In fact, no well-developed, universally implemented conservation methodologies are available for the investigation, repair or long-term maintenance of concrete [15], and the studies about this topic are necessary and quickly increasing [16]. As a promising approach, it was highlighted that preventive treatments that can arrest or slow deterioration may minimize or delay more invasive repair [11] should be pursued.

Preventive surface treatments can be used first to fight carbonation and chloride diffusion in historic reinforced concrete. Organic treatments are the most used ones, as they provide good protective effect, but they also exhibit a limited service-life and some tendency to crack and detach [17,18]. Inorganic surface treatments are silicates (mainly sodium silicate, i.e., the so called "waterglass"), which exhibit better durability performance, but are less deeply investigated [17]. The standard EN 1504-2:2004 [19] groups surface treatments into three classes according to their function rather than composition: hydrophobic impregnation, impregnation, and coatings. All of them may exhibit some drawbacks. Hydrophobic impregnation, consisting in the application of water-repellents like those used for ancient buildings, exhibit a short-term effectiveness due to polymers' ageing [20–22]. On the other hand, impregnation and coatings form totally (or almost totally) impermeable layers, which may cause compatibility issues when applied to porous substrates, which is frequently the case of historic concrete, leading to cracks and detachment [23]. Cementitious coatings are also available, consisting in cement-based mortars manufactured with a huge number of polymers, and exhibiting a certain water vapor diffusivity and a higher resistance to cracking [23], but they can be hardly applied over texturized and aesthetic surfaces without losing their significance. Some studies suggested that ethyl silicate (tetraethyl orthosilicate, TEOS), used long since for the consolidation of stone, can be a valid alternative to current surface treatments for reinforced concrete structures [24]. In fact, the silica gel produced by its hardening is durable and exhibits some pozzolanic behaviour [25], thus providing excellent adhesion and compatibility (limited porosity reduction and colour alteration), and an effective protection in terms of chloride, carbonation and abrasion resistances also in comparison to sodium silicate and nanosilica [26]. Afterwards, other studies investigated the use of TEOS for surface treatment of concrete [27,28]. It was shown that ethyl silicate alone or in conjunction with nanolime improves mechanical strength and water repellence while conserving the original colour and gloss [29]. In another cases, TEOS together with other two normally used silica-based agents (Na_2SiO_3 and silane) [30] and modified TEOS [31] were successfully used for surface treatment of concrete.

Preventive surface treatments can be used also to fight the deposition of soiling and the growth of biofilm, by exploiting the self-cleaning ability of photocatalytic nano- TiO_2 in the anatase form. However, the studies mainly focus on their application to historic materials, such as stone, and in some cases lime-based mortars [32], following two main approaches:

- the dispersion of titania nanoparticles in organic water repellents [33]
- the direct spray application of aqueous dispersions of nanoparticles to the surface [34].

The main drawback of the first approach is that titania catalyses the degradation of the organic polymer matrix [35], while the main

drawback of the second approach is the easy leaching of TiO_2 nanoparticles, if not effectively attached to the surface, by rain [35,36]. To improve the adhesion of TiO_2 nanoparticles to the surface and avoid the use of polymers, the combination of TiO_2 with hydroxyapatite [37], the dispersion of titania inside a silica matrix [38,39], or the use of a silicatic coupling agent [40] were recently proposed.

However, there are still no studies, to the authors' best knowledge, on titania-based surface treatments for heritage concrete. Conversely, there is a broad literature on the incorporation of nano-titania in cement-based materials for depolluting, antimicrobial and self-cleaning purposes [41–44]. The self-cleaning ability of cementitious composites with nano- TiO_2 is the sum of two phenomena taking place under UV radiation:

- the superhydrophilicity of the surface which allows, when in contact with water, the formation of a continuous thin film between the substrate and the dust, which more effectively washes away the particles deposited on the surface [45]
- the catalysed oxidation reactions occurring in the organic molecules, which are destroyed and transformed into easily washed compounds [46]. This also limits biological growth on concrete surface, e.g., owing to algae [45], providing it with antimicrobial activity [47].

In this paper, new inorganic coatings were developed based on the incorporation of photocatalytic nano- TiO_2 into inorganic matrices, by different methods. The idea is to combine the benefits of inorganic treatments with the self-cleaning ability of nano- TiO_2 , for the employment in the preventive conservation of heritage concrete surfaces, a task which has no precedents in the literature, to the authors' best knowledge. The inorganic matrix is also expected to guarantee the adhesion of titania nanoparticles to the substrates and to prevent their removal by rain.

The experimental program was developed in consequential steps. First the photocatalytic activity of two different kinds of TiO_2 nanoparticles alone was assessed. Then, they were combined, by different methods, with two matrices, i.e. TEOS and hydroxyapatite. These treatments were applied by different procedures to marble and cement mortar and their effectiveness was investigated, also after exposure to artificial rain. Given its better performance on cement mortar, TEOS was selected as a matrix for development of the treatments, which were applied over cement mortar substrates in a further step. The self-cleaning effectiveness of the treatments was investigated by the methylene blue discoloration test and by a new purposely designed experimental procedure developed by the authors and aimed at assessing the ability of the surface to help the removal of soiling by rain.

The proposed treatments are expected:

- to combine the beneficial effects of TEOS (consolidation of the surface layer and protection from carbonation and chloride ingress) and the self-cleaning ability of titania
- to ensure that TiO_2 nanoparticles remain effectively and durably anchored to the substrate.

2. Materials and methods

2.1. Materials

Two different substrates were used in the tests, namely cement mortar and Carrara marble. Although cement mortar is the final target for the application of the developed treatments, marble was used as well in the first screening tests, for the following purposes:

- to assess the photoactivity of the nanoparticles alone. Marble is a simple and very suitable substrate for this assessment, because it is characterized by a basically uniform mineralogical composition (CaCO_3), an even surface and a basically zero porosity

- to evaluate the most promising treatments for further testing. In fact, marble was widely investigated in previous literature studies on self-cleaning treatments, hence it was considered a good substrate for comparison's sake.

After selecting the most promising treatments, these were applied to cement mortars only, evaluating their performance.

The cement mortar (**CEM**) was prepared in a Hobart mixer according to the manufacturing procedure in EN 196–1, by mixing 450 g of Portland cement (CEM II/A-LL 32.5 R), 1350 g of standard quartz sand EN 196–1 and 270 g of tap water. The relatively high water to cement ratio (0.6) and the low strength cement were selected to mimic early cement-based mixes used at the beginning of XX century. Prisms of size $40 \times 40 \times 160 \text{ mm}^3$ were prepared and cured at relative humidity $> 95 \%$ for 28 days, according to EN 194–1, then slices of mortar having size $40 \times 40 \times 5 \text{ mm}^3$ were cut by sawing from the prisms and further cured for at least 3 months in the same conditions. This procedure allowed to obtain samples having a smooth surface (for comparison with marble) and fully carbonated as historic substrates. The carbonation was confirmed before further tests through the thymolphthalein method. The final properties of the mortar used, averaged on three samples, are: bulk density $2.02 \pm 0.02 \text{ kg/l}$, water absorption at 24 hours $9.40 \pm 0.16 \text{ wt}\%$, open porosity $19.03 \pm 0.42 \%$.

The Carrara marble (**MAR**) used was quarried in the Apuan Alps in Italy and supplied by Imbellone Michelangelo s.a.s., Bologna, Italy. This stone is mainly composed of calcite (98 %), with small traces of dolomite. Samples having size $50 \times 50 \times 5 \text{ mm}^3$ were cut by sawing from a single marble slab having thickness 5 cm, to avoid any problem related to stone variability. In the light of the types of characterization tests used in this study, the slight difference in the size of mortar and marble samples (having however the same thickness) was not considered prejudicial for the results.

All the mortar and marble samples were dried in a ventilated oven at 40°C before any treatment. The properties of marble, averaged on three samples, are: bulk density $2.75 \pm 0.06 \text{ kg/l}$, water absorption at 24 hours $0.16 \pm 0.02 \text{ wt}\%$, open porosity $0.45 \pm 0.02 \%$.

Two materials were used to prepare the self-cleaning treatments:

- a commercial TiO_2 fine-particulate (Aeroxide TiO_2 P 25, Evonik), labelled as **TP**. It is composed of crystalline titania predominantly in the anatase form and exhibits high purity ($>99.50 \%$) and high specific surface area ($35\text{--}65 \text{ m}^2/\text{g}$, by BET)
- a nano- TiO_2 suspension (AT20 SG01, Colorobbia Consulting srl), containing 3 wt% of N-doped TiO_2 nanoparticle suspended in ethanol labelled as **T-SUSP**.

Two inorganic matrices were used for the treatments' development.

The first was ethyl silicate (Estell 1000, CTS, Italy), composed of tetraethylorthosilicate, **TEOS** (40 % monomers, 35 % dimers/trimers, also containing 1 % dibutyltin dilaurate as catalyst), in 25 wt% white spirit. TEOS is among the most widely used consolidants for stone, its consolidating action being due to hydrolysis and condensation reactions that lead to the formation of silica gel inside the pores of the treated material. These reactions produce a high consolidating efficacy especially in materials containing some silica [48]. The main advantages of TEOS consolidant are:

- its compatibility with historic inorganic substrates,
- the formation of volatile by-products during its hardening reactions,
- the absence of significant pore-clogging effect and limited permeability alteration [49].

The good consolidating and protecting performance of TEOS in cement-based substrates was also demonstrated [24,26], owing to the pozzolanic reaction between silica gel and portlandite contained in hardened cement [25], hence a combined treatment TEOS- TiO_2 could

provide substantial benefits not only in terms of self-cleaning behaviour but also in terms of increased resistance to carbonation and chloride diffusion.

The second matrix used was hydroxyapatite (**HAP**). HAP was proposed some years ago as a protecting and consolidating material for marble and limestone [50], and recently experienced a quick diffusion for a variety of materials [51] including mortars [52], due to its compatibility, effectiveness and durability [51,53,54]. The treatment is based on the in-situ formation of HAP and other calcium phosphate (CaP) phases in the substrate, by the application of an aqueous solution of diammonium hydrogen phosphate (DAP), whose PO_4^{3-} ions react with the Ca^{2+} ions coming from millimolar dissolution of the substrate and/or externally supplied, forming CaP phases [51]. In this research, based on previous studies [52], a DAP solution composed of 1 M DAP, 1 mM CaCl_2 and 10 vol% ethanol in deionized water was used. The presence of calcium ions from CaCl_2 and ethanol is expected to contribute to the densification of the CaP phases formed.

2.2. Screening tests

2.2.1. Assessment of titania's effectiveness

Tests were carried out on marble and mortar substrates to assess the effectiveness of the two types of nano- TiO_2 , also in relation to the application method. In this case, no matrix was employed.

Two types of nano- TiO_2 suspensions were used:

- **T-SUSP**, described in Section 2.1
- **TP-SUSP**, prepared by adding 3 wt% of TP powder to a solution of water:isopropanol 4:1 by mass, stirring the dispersion for 5 minutes and then sonicating it for 15 minutes to avoid particles' aggregation.
- The following treatments were applied to MAR and CEM samples:
 - **T-SUSP-BRU**: the suspension T-SUSP was applied by brushing for three subsequent times (the brush was immersed 3 times in the suspension)
 - **T-SUSP-IMM**: the suspension T-SUSP was applied by immersion for three subsequent times (the face of the sample to be treated was immersed in the suspension 3 times for 5 seconds each)
 - **TP-SUSP-BRU**: the suspension TP-SUSP was applied by brushing for three subsequent times (the brush was immersed 3 times in the suspension).

Both the suspensions were kept under stirring during the application on the samples.

The mass of the samples was measured before and immediately after the treatments, i.e., in wet conditions. Then, the samples were let dry at laboratory conditions for 1 week. One sample of each material was treated for each kind of substrate and treatment.

The fact that the concentration of nanoparticles in the treatments was kept constant and the use of thorough, realistic and repeatable application procedures in this study were considered fundamental to obtain reliable and repeatable results also for further studies. However, it is noteworthy that historic substrates exhibit variable (and often significant) porosity, hence they may absorb the treatments by capillarity at different rates and retain different amounts of products. Here, the control of the amount of products absorbed was carried out by measuring the mass of the samples before and after the treatments' application.

The water capillary absorption rate of the untreated (**UT**) and treated samples was measured according to EN 15801 [55], although the size of the samples was different for that indicated in the standard. After drying, the same samples used for the water capillary absorption test were subjected to the methylene blue discoloration test [56]. Two spots of about 0.10 ml each of methylene blue solution (concentration 50 mg/l) were released over the surface and let dry in the dark for 24 hours. Then, the samples were placed in a custom-designed box equipped with UV-A lamps (wavelength range: 315–400 nm, radiation power: 1.5 W;

distance sample-lamp: 30 cm), for prefixed time intervals. The discoloration at different time interval was visually assessed.

2.2.2. Evaluation and selection of the matrices

Two different matrices were tested for nano-titania embedding, namely TEOS and HAP. Both kinds of substrates MAR and CEM were used.

The following treatments were prepared and applied:

- Treatment **TEOS-TP**, where TP powder was simply added to the commercial TEOS, in a concentration of 3 wt% (5 mins stirring, then 10 mins of sonication). The application of this treatment to the samples was carried out by immersion (samples were immersed 2 times for 5 seconds each), keeping the suspension slightly stirred
- Treatment **HAP-TP**, where TP powder was simply added to the DAP solution described above, in a 3 wt% concentration (5 mins stirring, then 10 mins of sonication). The application of this treatment was carried out by immersion (samples were immersed 2 times for 5 seconds each), keeping the suspension slightly stirred. To promote the formation of HAP, the treated surfaces were wrapped for 24 hours with a plastic film not to avoid the evaporation of liquid phases, then they were unwrapped and gently rinsed with deionized water
- Treatment **TEOS-T-SUSP**, where TEOS was applied to the samples by immersion (2 times for 5 seconds each) and then the suspension was applied by poulticing. The poulticing was carried out by applying a 5 mm-thick poultice constituted of cellulose pulp and titania dispersion (mass ratio 1:4) over the samples after the TEOS drying and wrapping the samples in plastic film for 24 hours. Then, the film and the poultice were removed, the samples' surface was gently rinsed with deionized water and the samples were left in laboratory conditions for 2 months for curing. This procedure of application was selected after some preliminary tests, aimed at finding out the best method
- Treatment **HAP-T-SUSP**, where the DAP solution previously described was applied by immersion (as above) and then the T-SUSP was applied by poulticing (as above). The same application procedure used for TEOS was adopted, for comparison's sake.

After the treatments' application, the samples were let dry and cure at room conditions for 2 months. 2 samples were treated for each kind of substrate and treatment.

The selected TiO_2 concentration in the treatments (3 wt%) was kept quite high compared to other literature studies, because the focus of this study was the assessment of the self-cleaning ability.

The untreated (UT) and treated samples were then subjected to the capillary absorption test and then to the methylene blue discoloration test, as described above. The methylene blue discoloration at each time interval was assessed by spectrophotometry with a 3NH Lab Colorimeter series NH310, on each stain. The measurement positions on samples were marked by drawing circles having the same diameter as the colorimeter spot, to ensure the measurement of discoloration always in the same positions and obtain consistent results.

2.3. Combined TEOS- TiO_2 treatments for cement-based mortars

Given the results obtained in the screening tests (see Section 3.1.2 of Results and discussion), TEOS was selected as the most promising matrix for embedding nano-titania in the treatment of cement-based substrates. Both types of nano- TiO_2 , alone and in combination with TEOS, were applied to cement mortar samples CEM. For each type of nanoparticles, the application procedure was kept the same when they were applied alone and with the matrix, to evaluate whether the matrix inhibits titania's effectiveness. The treatments in Table 1 were applied to the cement-based mortar slabs (8 slabs for each condition).

The poulticing was carried out as described above. All the samples

Table 1

Treatments applied to cement mortar samples.

| Treatment | Application procedure |
|-------------|---|
| TP-SUSP | Immersion (two times for 5 seconds each) |
| TEOS-TP | Immersion (two times for 5 seconds each) |
| T-SUSP | Poulticing |
| TEOS-T-SUSP | Immersion in TEOS (two times for 5 seconds each) followed by poulticing of T-SUSP |

were left in laboratory conditions for 2 months for curing. Two untreated (UT) CEM samples were used as reference.

After curing, 2 samples for each condition were subjected to an artificial rain exposure in laboratory, according to the experimental fixture developed in [44], to evaluate the permanence of the treatments after rain washout. In brief, the mortar slabs were put with a slope of 45° under an artificial rain system, which provides a constant dripping of deionized water (pH 5.9) at a rate of 1800 ml/h on each sample. The test was run for a time corresponding to the total rainfall of about 11 years in Bologna, Italy, where the annual average rainfall is 80 cm [57]. The samples were let dry at laboratory conditions before any further test.

The samples subjected and not subjected to the artificial rain were tested by the methylene blue discoloration test described above (2+2 samples per condition). Furthermore, 3 sample per condition were tested by a purposely designed experimental procedure aimed at assessing the ability of the treatment to favour the soiling removal by rain.

This latter test was developed to mimic what is expected to happen in real surfaces treated with self-cleaning coatings, and consists of different phases (Fig. 1). After colour measurement by spectrophotometer, the samples were exposed to artificial soiling deposition. The artificial soiling composition was adapted from ASTM standard D7897 – 18 “Standard practice for laboratory soiling and weathering of roofing materials to simulate effects of natural exposure on solar reflectance and thermal emittance”, even if the purpose of the test in the standard is different from that pursued in the present study. In order to perform the artificial soiling test, the soiling mixture simulating moderate summer and cold winter climates was chosen from those presented in the aforementioned standard. This mixture was selected because it closely resembled the climate conditions observed in Bologna. The solution was prepared by combining three soiling agents: a dust water suspension, salt, and soot. The composition of the soiling mixture and of the soiling agents are as follows:

- 61 wt% of dust water suspension (Fe_2O_3 3 g/L; montmorillonite 20 g/L - the latter substituting bentonite suggested in the standard - added to 1 L of distilled water)
- 31 wt% aqueous salt solution (NaCl 3 g/L; NaNO_3 3 g/L; $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ 4 g/L dissolved in 1 L of distilled water)
- 8 wt% soot water solution (commercial carbon black, Aqua-Black 001, Tokai Carbon Co. Ltd, 13.7 g/L diluted in 1 L of distilled water).

The concentration of chemical species composing the soiling agent and the deposition weight of the soiling mixture were conveniently adjusted to mimic 100 years of soiling.

Samples were placed on a horizontal plane, and the soiling mixture was applied perpendicularly over their surfaces using an airbrush (pressure 1.4 atm, distance between the airbrush nozzle and sample surface 27 cm), ensuring uniform deposition of the soiling mixture on the surface of the treated samples.

An amount of soiling much higher than that indicated in the standard was deposited over the samples, i.e. the deposited wet mass was 27 mg/cm², aiming at producing a visible soiling accumulation similar to those observed in real buildings. Then, the samples were kept for 10 minutes under an infrared lamp at temperature 70°C for drying. Once dried out, the samples' colour was measured through the colorimeter described

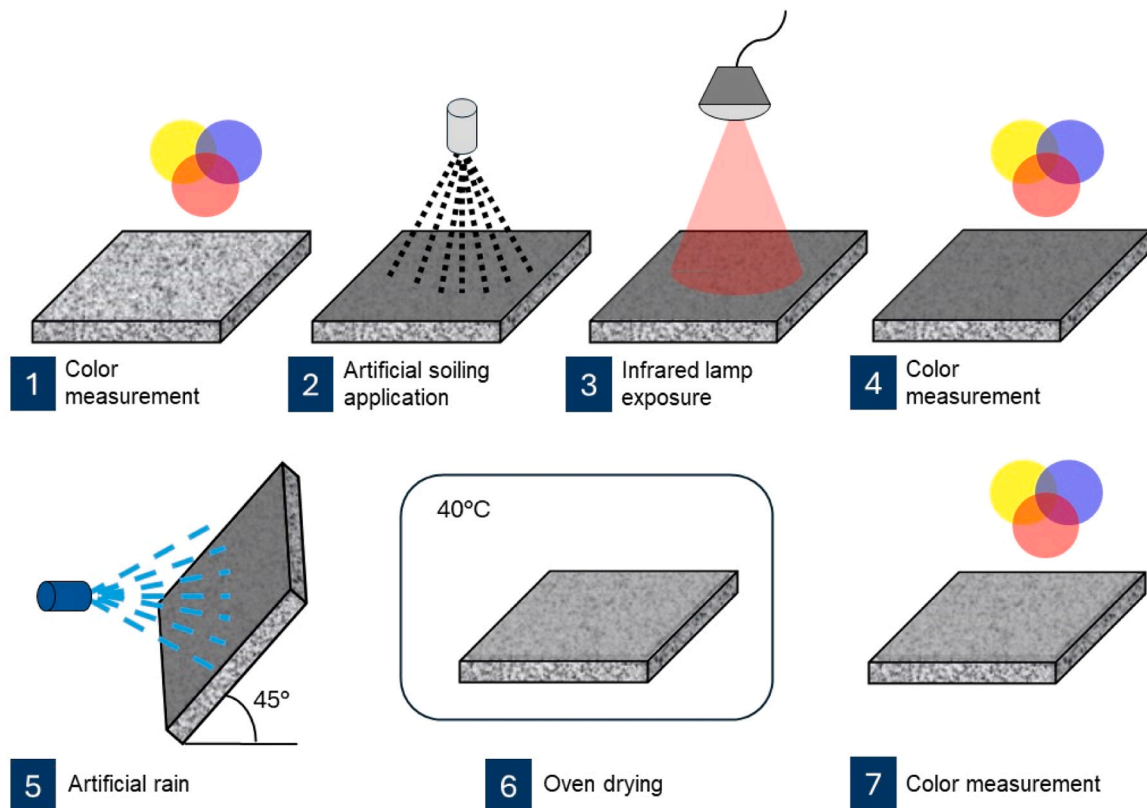


Fig. 1. Phases of the laboratory procedure to assess the ability of the treatments to help the removal of soiling by rain.

above. Afterwards, the samples were exposed to UV radiation for 1 hour, in the same apparatus used for the previous tests, for photoactivation and then they were immediately subjected to artificial rain. In particular, the samples were put 45° tilted and an amount of water equal to 1-month average precipitation in Bologna (50 mm) was sprayed onto them by a spray bottle. Finally, the samples were dried in oven at 40°C up to constant mass and their colour measurement was repeated.

3. Results and discussion

3.1. Screening tests

3.1.1. Assessment of titania's effectiveness

The mass increase of the samples due to the different treatments is reported in Table 2. Due to its porosity, the mortar obviously absorbed more than marble. The application by immersion caused an increase in the absorption of T-SUSP with respect to brushing, especially in marble, which is barely porous. Conversely, the major absorption due to immersion is more limited in cement mortar, as it exhibits a high absorption also in brushing application.

The results of the methylene blue discoloration test (Fig. 2) show that all the treatments exhibited a marked photocatalytic activity, while the UT samples were unaffected by the exposure to UV. Moreover, the

Table 2

Mass increase of the MAR and CEM samples due to the treatments immediately after their application, i.e., in wet conditions.

| Treatment | Mass increase due to the treatment, in wet conditions (mg/cm ²) | |
|-------------|---|------|
| | MAR | CEM |
| TP-SUSP-BRU | 7.7 | 33.1 |
| T-SUSP-BRU | 6.8 | 33.0 |
| T-SUSP-IMM | 27.3 | 37.8 |

methylene blue drops showed a bigger spreading on the treated samples than on the untreated ones, suggesting a hydrophilicity increase due to the treatments, as expected. The discoloration effectiveness is higher in MAR than in CEM, despite the higher absorption of the latter one (Table 2). This is ascribed, on the one hand, to the fact that all the TiO₂ nanoparticles are retained on the surface in the case of marble and, on the other hand, to the fact that a fraction of the methylene blue drop is absorbed by the mortar and hence cannot be deteriorated by the UV light exposure. Comparing the two suspensions, both applied by brushing, it can be seen that the methylene blue drops spread more and were more discoloured in substrates treated with TP-SUSP than in those treated with T-SUSP, suggesting a higher effectiveness for the first one, notwithstanding the identical percentage of titania contained in both suspensions. The application of T-SUSP by immersion gave a higher effectiveness with respect to brushing (especially on MAR), and in fact a higher amount of titania was found on the surface in the first case (Table 2), indicating that the application method plays a key role in the treatments' outcome.

The rate of water capillary absorption of the samples is reported in Table 3. It is very important to evaluate how this parameter changes for the treatments applied to historic building materials, because a strong decrease in the speed of water absorption might suggest incompatibility issues due to pore clogging effect, but also a strong increase might cause detrimental effects, such as a higher exposure to frost damage. In the case of marble, a certain increase in the water capillary absorption rate can be observed for the treatments that also caused the strongest methylene blue discoloration (TP-SUSP-BRU and T-SUSP-IMM). However, the porosity of marble is so low and the amount of water absorbed in the samples so small that the determination of the slope of the first linear part of the absorption curves is quite challenging and the values in Table 3 should be considered as affected by some degree of uncertainty. In the case of CEM mortar:

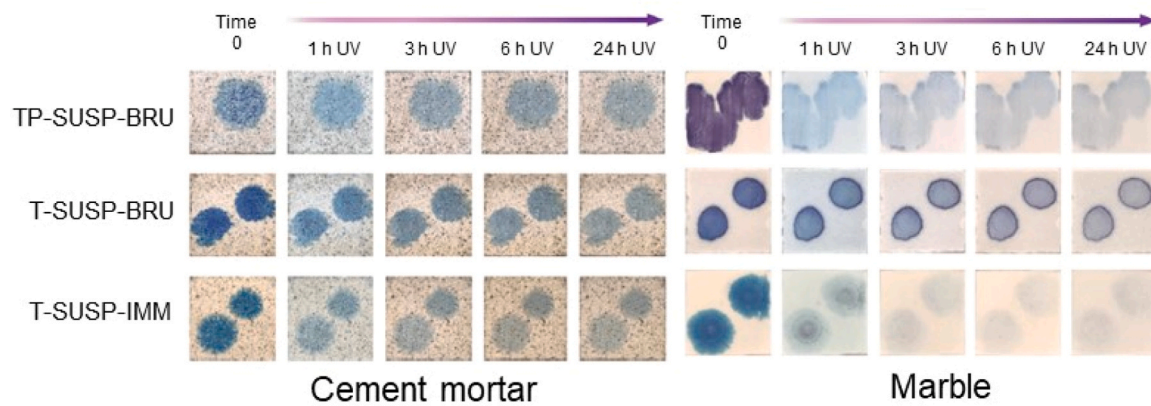


Fig. 2. Methylene blue discoloration test for the CEM and MAR samples treated with the TiO_2 without any matrix.

Table 3

Water capillary absorption rate of the untreated and untreated samples.

| Treatment | Capillary absorption rate ($\text{mg}/\text{cm}^2\text{s}^{1/2}$) | |
|-------------|---|------|
| | MAR | CEM |
| UT | 0.10 | 2.80 |
| TP-SUSP-BRU | 0.19 | 3.37 |
| T-SUSP-BRU | 0.09 | 3.17 |
| T-SUSP-IMM | 0.27 | 2.34 |

- the treatments applied by brushing caused a slight increase in the capillary absorption rate with respect to the untreated samples
- the treatment applied by immersion, which was the one giving the highest retention of TiO_2 nanoparticles in the samples (mass increase in Table 2), slightly decreased the capillary absorption rate.

However, considering the natural variability between mortar samples, these modifications can be considered not so significant, hence no substantial pore clogging effect or increase in the speed of absorption of rain can be expected for these coatings.

Given the good performance of both types of nano- TiO_2 , they were used also for the following step of selection of the matrix.

3.1.2. Selection of the matrices

In terms of capillary water absorption rate (Table 4), none of the treatments caused significant changes with respect to UT samples, hence all of them can be considered compatible with the substrates from this point of view.

The discoloration of the methylene blue stain at increasing time of UV exposure is reported in Fig. 3 for all the samples, allowing the following observations.

- All the treatments caused an increase in the discoloration with respect to UT samples, however to a different extent depending on the treatments, substrates and time of exposure to UV.

Table 4

Water capillary absorption rate for untreated and treated marble and cement mortar samples.

| Treatment | Capillary absorption rate ($\text{mg}/\text{cm}^2\text{s}^{1/2}$) | |
|-------------|---|------|
| | MAR | CEM |
| UT | 0.10 | 2.80 |
| TEOS-TP | 0.12 | 2.07 |
| TEOS-T-SUSP | 0.07 | 1.84 |
| HAP-TP | 0.04 | 3.46 |
| HAP-T-SUSP | 0.05 | 2.47 |

- The treatments with TEOS seem more effective on cement mortar than on marble, while the treatments with HAP seem more effective on marble than on cement mortar. This is particularly evident in the first hour of exposure to UV, when the discoloration of methylene blue on both marble treated with TEOS-titania and mortar treated with HAP-titania is barely detectable at sight (the threshold of visibility in the colour change is generally considered $\Delta E=2-3$). After 24 hours of exposure to UV, the discoloration increased to different extents in the different substrates, however the treatments with TEOS confirm their superior performance in cement-based mortar and the best treatment is the one with TP nanoparticles dispersed in TEOS before application (TEOS-TP).

The good performance of the treatments combining HAP and TEOS on marble can be explained by observing the microstructures formed over marble surface in the case of HAP-TP (Figs. 4–5).

The application of DAP over marble produced different kinds of CaP phases having acicular and flower-like microstructures (Fig. 4: A and B-1, and Fig. 5: A-1), as already observed in previous studies (e.g., [58]). The coverage of the surface with these phases is wide, although not complete. In the EDS maps of Fig. 4 (B-1/3) and 5, it can be observed that the presence of Ti is mostly in correspondence of the phases containing P, owing to the fact that the rough phosphatic phases promote the adhesion of nanoparticles, as pointed out in [45]. Conversely, Fig. 6 shows the surface of MAR sample treated with TEOS-TP. Here it can be observed that the TEOS treatment does not give any film forming effect, confirming that it does not significantly alter the stone permeability. However, titania nanoparticles tend to agglomerate into limited spots on the surface.

Fig. 7 shows the aspect of CEM samples in the untreated condition (A) and when treated with HAP-TP (B-1). Also in this case, no film forming effect was observed, but the CaP phases distributed non-homogeneously on the surface. In particular, Fig. 7 (B-1/2) shows that some zones rich in Si (likely aggregates) did not show any coating, while others clearly exhibit a phosphatic coating that also contains Ti. This confirms that CaP phases successfully retain nano- TiO_2 , but in the case of CEM substrates the distribution of these phases is inhomogeneous and particularly deficient over the quartzitic aggregates. Such uneven distribution of P and consequently also of Ti is confirmed by Fig. 8: Ti is coupled with P in zone 11, while the quartz aggregate in zone 12 is basically not covered by any coating. The limited presence of CaP phases over silica compared to calcite was expected, considering that the DAP-based treatment was first proposed for the consolidation of carbonate stones in cultural heritage conservation, postulating the possibility of an epitaxial growth of HAP crystals over calcite ones. Even if such epitaxial growth was not observed in past studies, a better growth of CaP phases over MAR sample, containing plain calcite crystals surface, with respect to CEM samples was clearly observed. Moreover, almost no acicular or

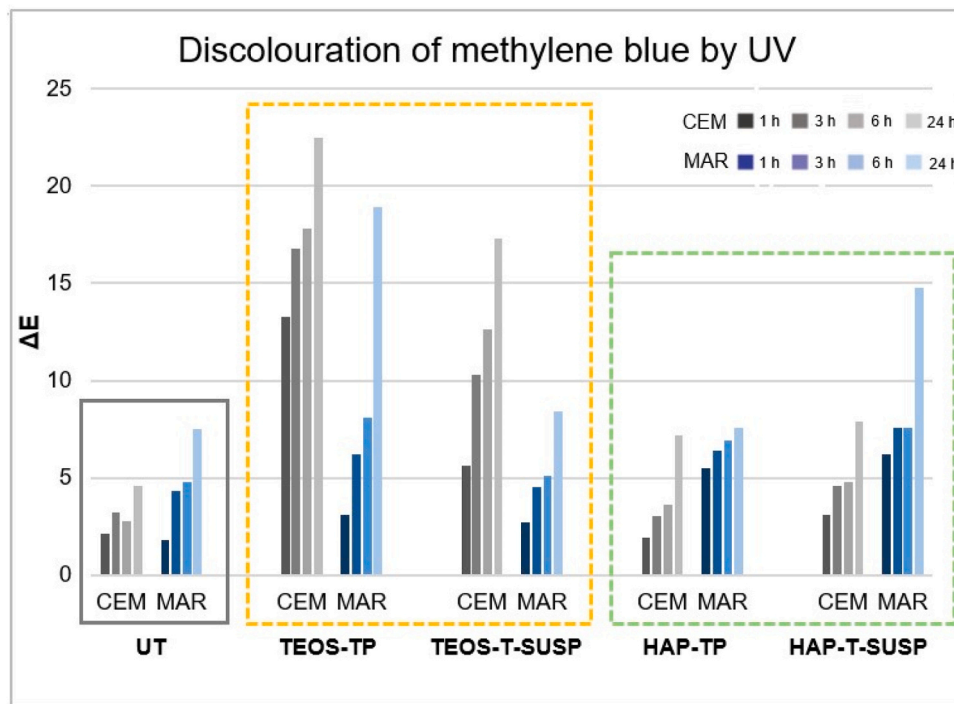


Fig. 3. Discolouration of the methylene blue stain on the untreated and treated marble and cement mortar samples, when exposed to UV light for increasing times.

flower-like phases were found over CEM samples treated with HAP-TP, suggesting that also in correspondence of the cement paste (which is rough and heterogeneous) the formation of CaP phases' crystals is harder. In the case of TEOS-TP treatment applied to CEM samples, Fig. 9 confirms the absence of film-forming effect already observed and suggests that Si and Ti are distributed rather uniformly over the substrate. This should not surprise, considering that ethyl silicate is very prone to binding silicatic substrates.

These results suggest that the matrix used for the treatments not only helps the bonding of the TiO₂ nanoparticles to the substrates, but also plays a pivotal role in the distribution of such nanoparticles. In fact, HAP treatment spreads and grows more effectively over marble than over cement mortars, also driving a better distribution of TiO₂ on marble. Conversely, TEOS binds more effectively and evenly over cement mortar, driving a better distribution of TiO₂ on such substrate.

Based on the results of these tests, TEOS was selected as a matrix for the development of combined treatments with TiO₂ on cement mortar.

3.2. Combined TEOS-TiO₂ treatments on cement-based mortars

The mass increase of the samples after the treatments is reported in Table 5. The amounts of nanoparticles deposited on the samples are comparable for the two suspensions and extremely limited, as expected. The mass increases due to the two combined treatments were comparable and of course higher than the previous ones, due to the presence of TEOS.

The results of the methylene blue discoloration test are reported in Fig. 10 for all the samples. The untreated samples exhibited an almost negligible photodegradation activity, as expected. Before the artificial rain, all the treated samples experienced a marked discoloration. The effectiveness of the nanoparticles alone (T-SUSP and TP-SUSP) is barely dependent on the time of UV exposure, because the discoloration observed after 1 hour increases only slightly after 24 hours, and it seems better for TP-SUSP. On the contrary, the discoloration caused by the combined treatments (TEOS-T-SUSP and TEOS-TP) strongly increases passing from 1 hour to 24 hours of UV exposure, suggesting that the presence of the silica matrix slows down the photocatalytic effect.

However, even if a certain slowing of the photocatalytic effect was observed, the final performance of the combined treatments with TEOS was better than the performance of nano-TiO₂ alone. Moreover, when combined with TEOS, the two kinds of nanoparticles exhibited similar performances. After artificial rain, the nanoparticles of the treatment TP-SUSP suffered a certain removal and in fact a lower discoloration was registered in the test, while T-SUSP was almost unaffected by rain. Interestingly, the combined treatments were not so affected by artificial rain, especially TEOS-TP, which even slightly improved.

Concerning the removal of artificial soiling, the results are shown in Fig. 11 in terms of colour change. The values "after artificial soiling" indicate the darkening of the surface, hence the "residual soiling after simulated rain" should indicate the self-cleaning ability of the treatments, i.e., should be zero in case of complete soiling removal. Some interesting observations can be derived from the data:

- In the untreated samples (UT), only a very limited amount of soiling was removed by artificial rain.
- The effectiveness of the treatments with the nanoparticles alone (T-SUSP and TP-SUSP) in promoting the soiling removal is very different from what could be expected based on the results of the methylene blue discoloration test. In fact, TP-SUSP was almost ineffective (same cleaning of the untreated samples), while T-SUSP removed approximately 24 % of the initial darkening. These data seem to indicate that the photodegradation ability of nano-TiO₂ and its self-cleaning potential are distinct and should be separately investigated.
- The combined treatments exhibit a better self-cleaning ability than the nanoparticles alone and also in this case T-SUSP seems more effective. This is a very encouraging result because it indicates that the combination of nano-TiO₂ with the silica matrix does not hinder the nanoparticles' photocatalytic behaviour. However, in no case was the removal of artificial soiling complete, and the best performance obtained was an approximate halving of the darkening (for TEOS-T-SUSP treatment) for an amount of water equivalent to 1 month of precipitation in Bologna.

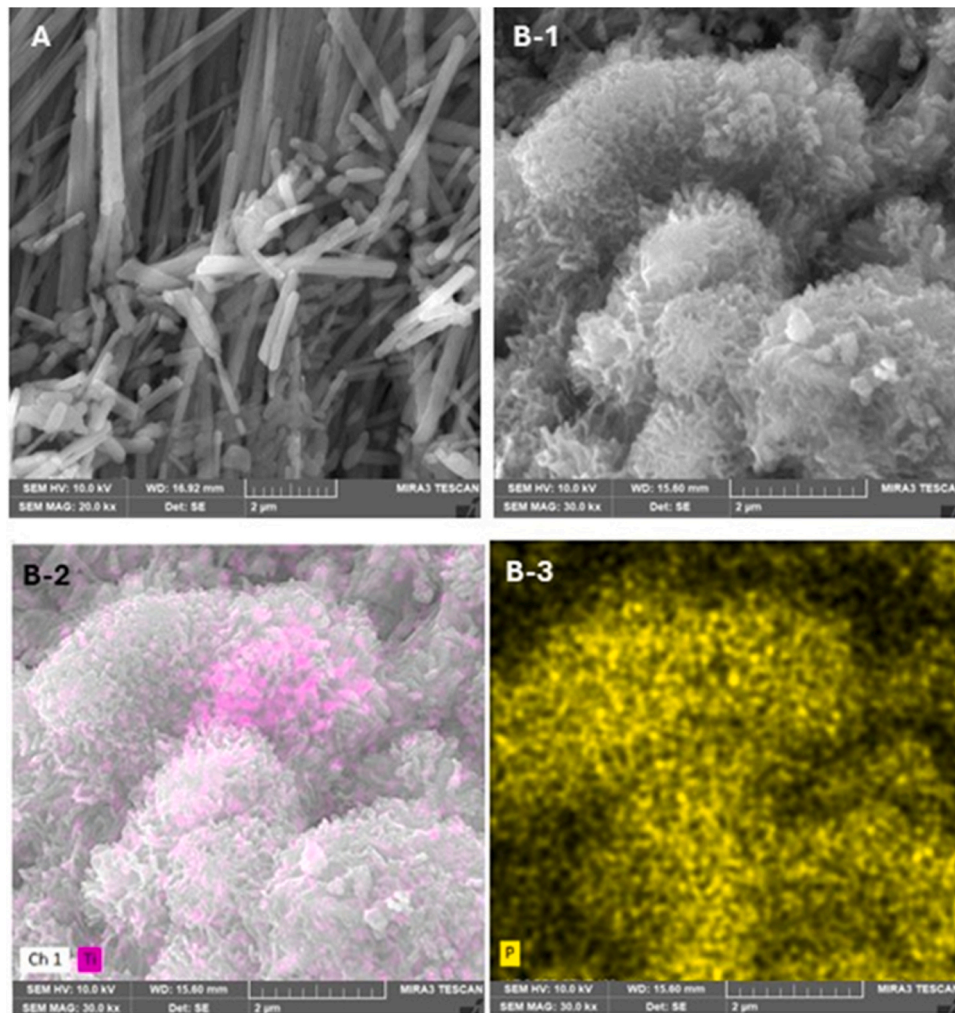


Fig. 4. SEM images and EDS mapping of marble samples treated with HAP-TP. Different shapes of the CaP phases formed by the treatment (A and B-1); distribution of titanium (B-2) and phosphorus (B-3) in the area shown in B-1. Marker 2 μm .

4. Conclusions

In this paper, after some preliminary assessment and screening tests, two different combined inorganic treatments were developed, exploiting ethyl silicate as a matrix and titania nanoparticles as photoactive components, and they were applied to cement mortar samples. In the first treatment, TEOS was first applied by immersion and then a commercial dispersion of nano-TiO₂ was applied by poultice. In the second treatment, TEOS was directly mixed with a second type of titania nanoparticles and applied by immersion to the samples. The concentration of nano-TiO₂ was kept constant and equal to 3 wt%. The performance of these two treatments was evaluated compared to the two nano-TiO₂ applied alone and to the untreated samples.

The following conclusions can be drawn.

- The incorporation of TiO₂ nanoparticles into the silica matrix formed by TEOS' curing does not significantly reduce their photocatalytic activity, although a longer time of exposure to UV seems necessary to achieve a strong photodegradation of methylene blue.
- The effectiveness of the combined TEOS-TiO₂ treatments seems unaffected by an amount of artificial rain equivalent to 11 years of precipitation in Bologna, while one of the treatments with nanoparticles alone (TP-SUSP) was likely affected by water washout.
- The purposely developed test for the self-cleaning ability toward artificial soiling gave quite different results compared to the ordinary

methylene blue discoloration test, suggesting that such ability should be specifically investigated and not given for granted based on tests on photodegradation. In fact, the performance of the two nano-TiO₂ alone was reversed in the methylene blue discoloration test (TP-SUSP better than T-SUSP) and in the soiling removal test (T-SUSP better than TP-SUSP).

- The performance of the combined TEOS-TiO₂ treatments in the soiling removal test was better than the nanoparticles alone, and this is very encouraging in the development of these treatments, which may overcome the limitations of current self-cleaning treatments.
- However, none of the treatments allowed the complete removal of artificial soiling by simulated rain and the best result obtained was a reduction of the darkening slightly lower than 50%. This could be partly ascribed to the short duration and the “delicacy” of simulated rain, but in any case, the results suggest that the actual self-cleaning ability of TiO₂-based treatments deserves further investigation.
- The procedure developed to test the self-cleaning ability through artificial soiling and simulated rain might constitute an interesting basis for the future development of a standard testing procedure.

The present paper focused on evaluating the self-cleaning performance of the developed treatments, but further advantages can be expected by using TEOS for protection, as highlighted in the Introduction. The ability of the treatments to prevent the growth of biofilm over concrete surface is currently under evaluation.

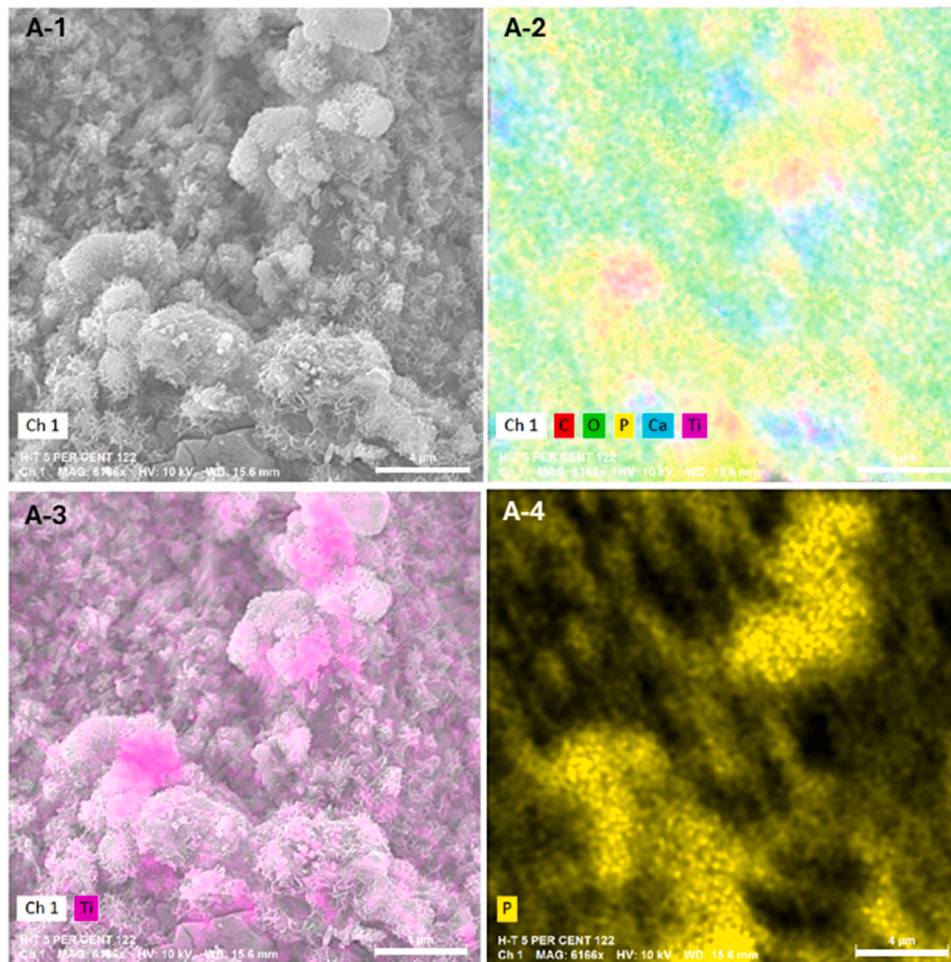


Fig. 5. SEM images and EDS mapping of marble samples treated with HAP-TP. In the observed area (A-1), titanium is concentrated in the zones where phosphorus is more abundant (A-2), as confirmed also by the comparison of the titanium (A-3) and phosphorus (A-4) maps. Marker 4 µm.

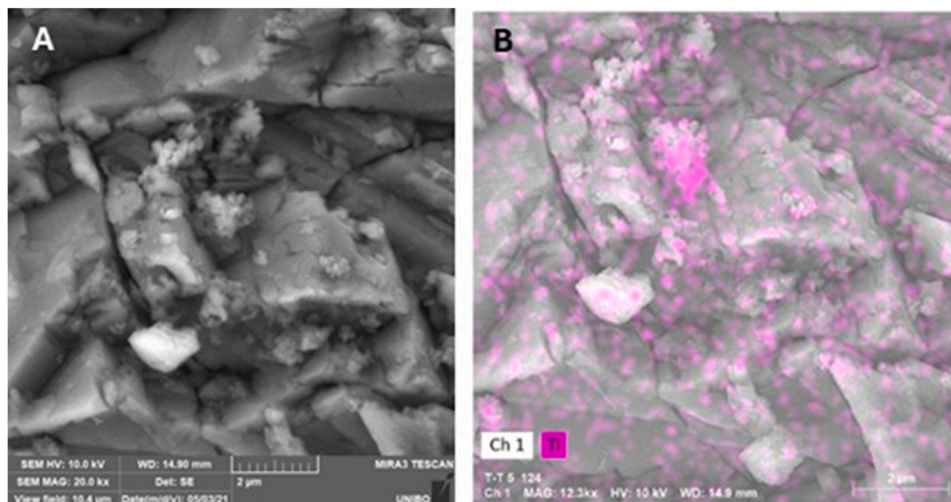


Fig. 6. SEM images and EDS mapping of marble samples treated with TEOS-TP. In the observed area titania nanoparticles agglomerates can be seen (A), as confirmed by the EDS mapping of titanium (B). Marker 2 µm.

The novel treatments developed in this study showed the potential of being an innovative and valuable solution for heritage concrete protection, combining the benefits of inorganic protection with those of anti-soiling action, in a durable way. Concerning the novel test

developed and used in this study, this allows a more effective and realistic assessment of the self-cleaning ability of the surfaces compared to the methylene blue discolouration test. This test could be the basis for the development of a new procedure of assessment of self-cleaning

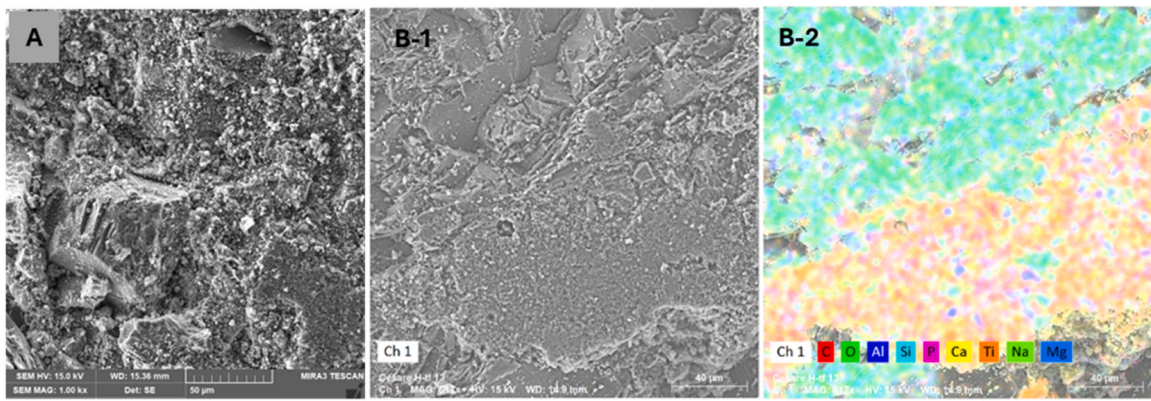


Fig. 7. SEM images of CEM samples: untreated (A) and treated with HAP-TP (B-1). B-2: EDS mapping of the area in B-1. Marker: 50 μm (A) and 40 μm (B1 and B-2).

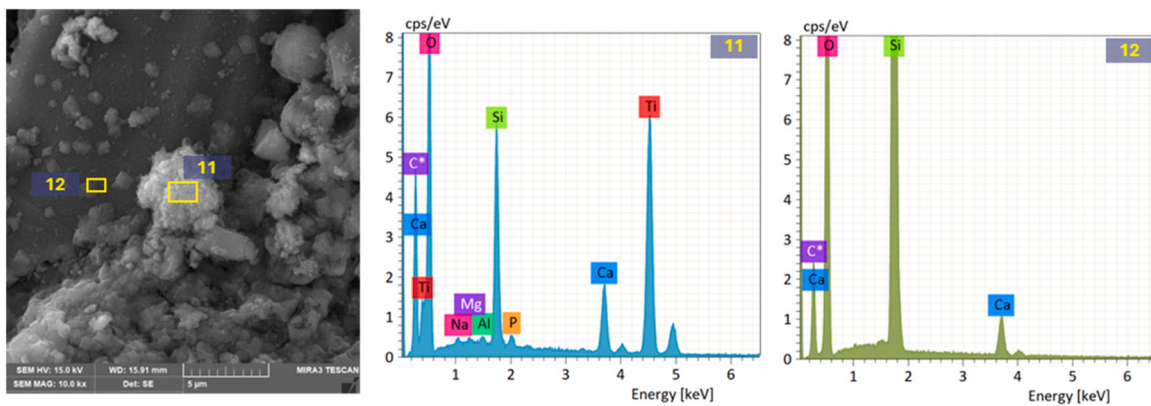


Fig. 8. SEM image of CEM sample treated with HAP-TP, and EDS analysis of the two areas indicated by rectangles in the image (11 and 12).

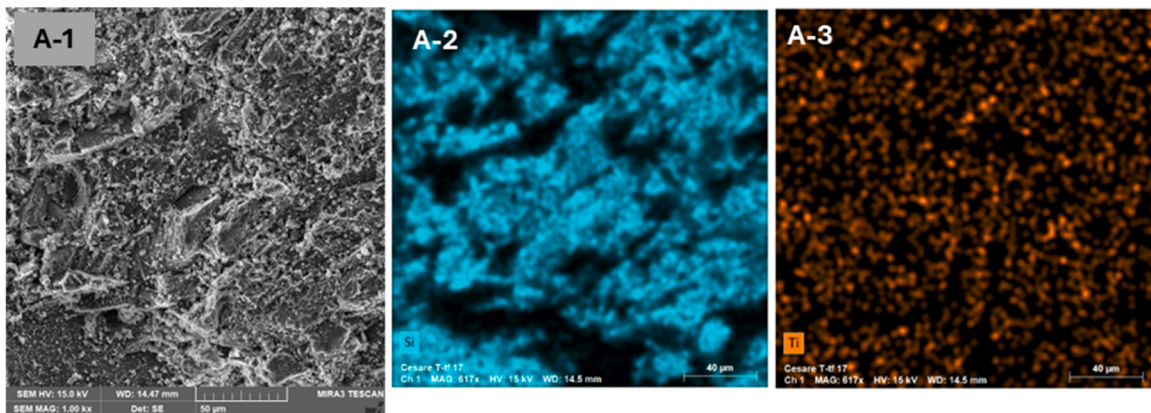


Fig. 9. SEM image of CEM sample treated with TEOS-TP (A-1) and EDS mapping of Si (A-2) and Ti (A-3) in the same area. Marker 50 μm.

Table 5

Mass increase of the samples due to the different treatments. The mass was measured after curing at laboratory conditions.

| Treatment | Mass increase due to the treatment, after curing (mg/cm ²) |
|-------------|--|
| T-SUSP | 4.38 ± 1.95 |
| TP-SUSP | 3.13 ± 2.29 |
| TEOS-T-SUSP | 11.02 ± 3.57 |
| TEOS-TP | 10.23 ± 1.10 |

performance in laboratory.

CRediT authorship contribution statement

Riccardo Fabris: Writing – review & editing, Methodology, Investigation. **Elisa Franzoni:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Cesare Pizzigatti:** Writing – review & editing, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

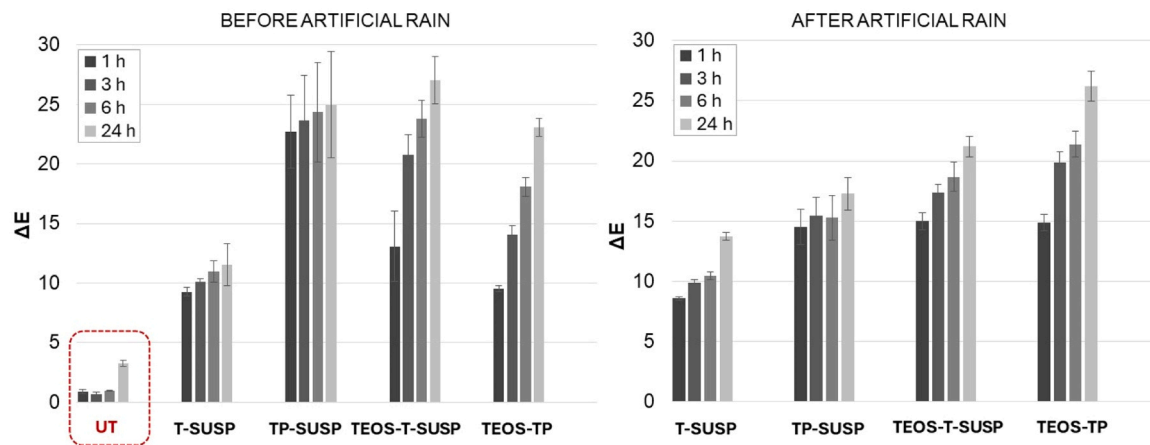


Fig. 10. Discolouration of the methylene blue stain on the cement mortar samples, both untreated and treated with the combined TEOS-TiO₂ treatments, when exposed to UV light for increasing times.

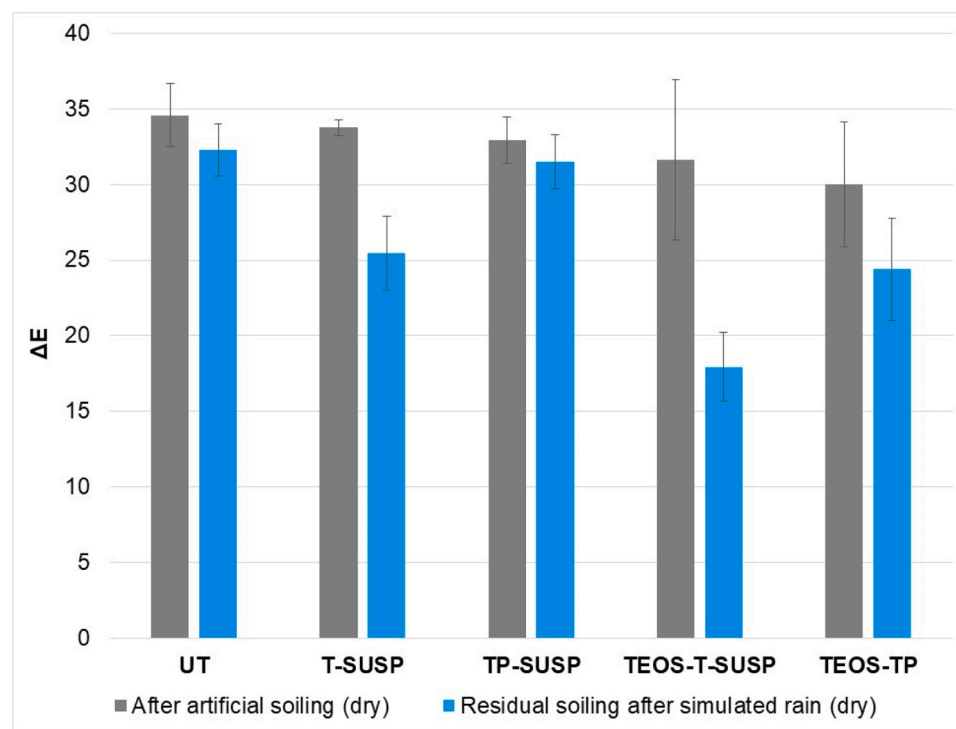


Fig. 11. Colour change of the cement mortar samples, both untreated and treated with the combined TEOS-TiO₂ treatments, after the deposition of artificial soiling and after the subsequent artificial rain, both related to the initial condition (i.e., before the application of the soiling).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors are unable or have chosen not to specify which data has been used.

Acknowledgements

Luca Scordamaglia is gratefully acknowledged for his help in the experimental testing. We would like to thank Prof. Noni Maravelaki for

the fruitful discussion that we had over last years on nano-TiO₂.

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