# EVALUATION OF $TIO_2$ BASED TREATMENTS ON STONE SURFACES EXPOSED TO A POLLUTED URBAN ENVIRONMENT

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## Abstract

Over the last few years, titanium dioxide based products have been used in the field of construction materials as self-cleaning, non-polluting and antibacterial functions. These products are currently applied to construction material for external use and interior furnishing material such as cement mortars, exterior tiles, paving blocks, glass and PVC fabrics. These products have also been proposed in the field of Cultural Heritage but up to now their experimental use has been quite limited. For this reason, a systematic research was carried out on some $TiO_2$ based products applied to various types of natural stones exposed in a urban polluted environment. The treatment was evaluated in terms of its efficiency, durability and harmfulness to the treated stones. Three types of natural stones (white marble, travertine and limestone) were treated and exposed for eight months in a polluted environment in the centre of Rome. Three $TiO_2$ based products, in form of nanoparticles or mixed with hydrophobic polymers, were used for the experiment. Each stone was investigated before and after the application of the products and after natural ageing, by means of colorimetric measurements, surface observations by SEM, contact angle measurements, Rodamina test, ion chromatography measurements, elemental analysis by EDS and XRF. The results showed that the photocatalytic products have a mild self-cleaning effect related to the porosity of the stone. Moreover, the products tend to be washed away from the stone surface by the rain.

**Keywords:** photocatalytic product, self-cleaning effect, stone treatment, maintenance



## 1. Introduction

In the framework of the activities related to the preventive conservation and maintenance of Cultural Heritage, the application of titanium dioxide ($TiO_2$ in the allotropic form of anatase) based treatments on stone surfaces could greatly contribute in limiting cleaning interventions. Nowadays several $TiO_2$ based products, such as mineral and organic coatings, are available for use in new building (European project PICADA; Italcementi company: http:/ www.italcementigroup.com). Because of its photo-catalytic properties, $TiO_2$ is able to induce the photo-decomposition of inorganic (e.g. $NO_x$) and organic pollutants (e.g. benzene and other aromatic compounds) adsorbed on its surface and has been proven to be very active in bacterial destruction (Fujishima et alia 2008). For this reason the $TiO_2$ photo-catalysis produces non-polluting, self-cleaning and antibacterial effects (Heller, 1995; Fujishima, 1999; Fujishima et alia 2000). $TiO_2$ based products have been scarcely tested on stone surfaces of artistic and historical interest (Luvidi et alia 2010). The aim of this paper is to test these innovative products for use in the field of conservation of Cultural Heritage. In particular, the present work was carried out to verify the effectiveness of these products and the absence of damage on stone surfaces. It should be noted that $TiO_2$, in the photocatalytic form of anatase, induces a superhydrophilicity of the surface when exposed to UV light. On the other hand the treated surfaces are more exposed to the degradation agents such as acidic/alkaline rain water. This is, of course, a negative aspect in the case of materials of interest in the field of Cultural Heritage. Concerning the possible side effects of the photo-catalytic reactions, particular attention should be focused on investigating the degradation mechanism of $NO_x$ (Toma et alia 2004; Devahasdin et alia 2003). This molecule, in fact, under the catalytic action of $TiO_2$ can lead to the formation of calcium nitrate. Therefore, the soluble salt content of treated specimens is an indicator of the potential damage that can be caused by the photocatalytic activity of the $TiO_2$.

In the present paper, the investigated $TiO_2$ based products include a water solution of titanium dioxide in the form of nanoparticles and two different products where $TiO_2$ is mixed with organic material. In the latter products the combination with a water repellent is useful because it limits water penetration. Rhodorsil H 224 was taken into account as a reference water repellent material. For an effective use of these photocatalytic products, on surfaces of historical buildings and monuments, these innovative materials have to undergo various tests. In particular, colorimetric tests were carried out to evaluate any possible colour changes and soiling of the surface, while the adhesion of the treatment and its durability were studied by SEM, before and after ageing. The surface concentration of titanium, measured by EDS and XRF, was related to the photocatalytic efficiency obtained by monitoring the discolouration of rhodamine B, an organic dye, applied to the stone surface (Ruot et alia 2009). Contact angle measurement was carried out to evaluate the hydrophilicity introduced by $TiO_2$ based products and the durability of treatment after outdoor exposure on the stones. The analysis of the soluble salts present in the samples treated with $TiO_2$ based products was important to find evidence of possible degradation factors.



## 2. Experimental procedure

### 2.1 Stone materials and products

The three investigated stones were white marble (calcite based stone), with a total open porosity equal to 0.95%; travertine from Tivoli (mostly calcite) with a pore size ranging from 1.6 to 9% and Lecce stone with a porosity of around 35% and prevalent composition of calcite (88 ÷ 97%). Samples measuring 5x10x2 cm were taken of these stone types and treated with the following products containing $TiO_2$ and/or some hydrophobic material: - Bioxy air (CIR Ltd.), micro-dispersion of silanes mixed with photocatalytic $TiO_2$; - Nama07 (Colorobbia Italy SpA), nanoparticles of titanium dioxide in aqueous solution (pH 5.61); - an experimental treatment supplied by the Acep Ltd., which consists of two products to be applied in sequence: a primer, composed of fluorinated acrylic polymer and a product based on alkyl silanes and photocatalytic $TiO_2$ in aqueous dispersion; - Rhodorsil H 224 (RH 224), alkyl polysiloxane polymer in aliphatic hydrocarbons, diluted 1:10. Each treatment was applied to the specimens on a single face (5x10cm). The amount of product applied was determined by taking into account the porosity of the three lithotypes and the degree of absorption of the products. On marble we used: 1 ml (0,5+0,5 ml) of Acep, 0,7 ml of Bioxy, Nama and RH 224.

On travertine we used: 2 ml (1+1 ml) of Acep, 1 ml of Bioxy, Nama and RH 224. On Lecce stone we used: 10 ml (5+5 ml) of Acep, 5 ml of Bioxy, Nama and RH 224. The treatment on the Lecce stone was applied on partially wet samples (10 ml of water) to avoid that the product containing $TiO_2$ penetrated too deep. The untreated and treated samples were exposed to a high level of traffic pollution for eight months.

### 2.2 Characterization procedures

**Colorimetric measurements -** Colorimetric analyses were carried out according to the EN standard 15886: 2010 by Spectrophotometer Konica Minolta CM 2600d in total reflectance (measurement area 800 MAV). The colour changes ($\Delta E$) were evaluated by the *L*a*b**system (CIE 1976). Thirty measurements were carried out on each stone sample before and after the $TiO_2$ based treatment.

**SEM-EDS analysis –** A morphological analysis and elemental distribution of the products on the stone surface was carried out by a SEM-EDS analysis using a EVO 60 Zeiss scanning electron microscopy, equipped with a Lanthanum Hexaboride filament cathode. The investigation was conducted at a variable pressure of 100Pa without any pre-treatment of the samples, and the images were obtained by backscattered electrons.

**XRF analysis -** A portable spectrometer developed ad hoc for application in the case Cultural Heritage at CNR-ITABC was used for the measurements 9 Ferretti et alia 2007). The system combines an X-ray tube working at 60kV, 1.5mA and a 30mm$^2$ Si-drift detector. In such conditions and with a measuring time of 120s, detection limits range from a few tens to a few hundreds of mg/kg, depending on the element and the matrix; the analysed spot being about 6mm in diameter.

**Static contact angle measurements -** The static contact angle of treated and untreated stone specimens was determined, according to the EN standard 15802: 2009, by using a Lorenz&Wettre instrument. For each sample, the contact angle, expressed in degrees, was obtained by the average of thirty measurements. The measurements were performed only on marble and Lecce stone because in the case of travertine the measurements are strongly influenced by the heterogeneity of surfaces and therefore are insignificant.

**Soluble salt analysis -** Ion chromatography technique was used to monitor the presence of soluble salts due to the photocatalytic activity of the $TiO_2$. Stone specimens (5x3x2 cm) were immersed in 30 ml of deionized water in closed plastic containers under stirring for 48 h. After extraction of the soluble ions in water and consequent filtering, dissolved cations and anions were determined using a Dionex DX-100 ion chromatograph with a 25 μl sample loop. For each sample at least three analyses were performed.

**Photocatalytic activity assessment -** Photo-catalytic activity evaluation of $TiO_2$ based products by colourimetric test was carried out on both untreated and treated samples stained with rhodamine B (0.05% in ethanol) and exposed to xenon light using a Suntest CPS+ apparatus (Heraeus, Germany) irradiated with 30kJ/m2 per min. The discoloration of the rhodamine B was measured after 0.5, 2, 5 and 8 h by Spectrophotometer Konica Minolta CM 2600d.

## 3. Results and discussion

### 3.1 Colorimetric measurements

Colorimetric measurements were performed on all the different stone samples before and after treatment and then exposed in a polluted urban environment. Colorimetric changes (ΔE) of the treated samples were calculated with respect to the values of the colorimetric coordinates of the respective untreated stones and before ageing. The results are reported in Table 1. Before being exposed outdoor, treatment with Bioxy and RH 224 produce very slight colour changes within ΔE = 3, on the specimens of marble. In the case of Nama there is a stronger change of colour as shown by the yellow and dark colour of the samples. The dark colour effect of Acep is less than that of Nama. After outdoor exposure, the untreated marble samples show scarcely visible variations of colour while the samples with Acep become lighter moving closer to the values of the untreated. The samples with Bioxy remain unchanged after exposure. The Nama treatment that shown a strong dark effect moves closer to the colour of untreated, losing even the yellow effect. RH 224 when exposed to rain becomes noticeably darker and yellow in colour.

**Table 1.** Colour variation (ΔE) of stone samples untreated (NT) and treated with different products before and after outdoor exposure.

| Treatment | MARBLE | | LECCE STONE | | TRAVERTINE | |
|---|---|---|---|---|---|---|
| | BEFORE EXPOSURE | AFTER EXPOSURE | BEFORE EXPOSURE | AFTER EXPOSURE | BEFORE EXPOSURE | AFTER EXPOSURE |
| **NT** | | 1,7±1,4 | | 16,2±1,8 | | 4,0±1,7 |
| **Acep** | 4,7±0,5 | 2,8±1,3 | 2,9±1,4 | 15,2±2,3 | 6,1±0,8 | 3,5±0,7 |
| **Bioxy** | 2,7±0,5 | 3,4±1,1 | 1,1±0,6 | 7,7±1,5 | 1,9±0,6 | 4,3±1,2 |
| **Nama** | 9,2±1,6 | 3,1±1,2 | 3,9±0,8 | 13,0±3,2 | 7,5±1,7 | 2,6±1,1 |
| **RH 224** | 0,8±0,5 | 7,1±1,3 | 1,7±1,0 | 11,5±3,0 | 7,4±0,9 | 10,3±1,7 |



Before outdoor exposure, colour changes produced by treatment on the stone of Lecce prior to exposure are insignificant except in the case of Nama (ΔE = 3.9) where there is a slight difference. After outdoor exposure, untreated and treated Lecce samples show a marked darkening effect, and strong yellow patches appear on the samples treated with Nama. Only in the case of Bioxy aged samples is shown a self-cleaning effect, in the other cases this effect is very mild. Before outdoor exposure, on travertine every kind of treatment produces a dark and yellow colour effect on the samples, apart from Bioxy that does not produce any noticeable effects. After outdoor exposure, the untreated samples show slight variations in colour. The treatments in all cases do not appear to have a self-cleaning effect, and in addition the treatment with RH 224 leads to a marked increase of colour variations (ΔE = 10).

### 3.2 SEM-EDS analysis

The morphologies of the various $TiO_2$ based products applied to the lithotype surfaces, were studied by SEM observations of the samples of marble, travertine and Lecce stone (figs. 1 and 2). The elemental microanalysis EDS (table 2) made it possible to estimate, although semi-quantitative because of the reduced area of analysis, the characteristic elements (titanium and silicon) of the products present on the treated surface. The behaviour of the different products applied to low porosity compact stone, such as marble and travertine, is similar. Bioxy and Nama (fig. 1 left and fig. 2 left) create a layer of a glassy appearance, with the presence of micro-cracks due to micro-shrinkage and detachment of the layer from the surface, while on the specimens treated with Acep (fig. 2 right) these morphologies are not evident.

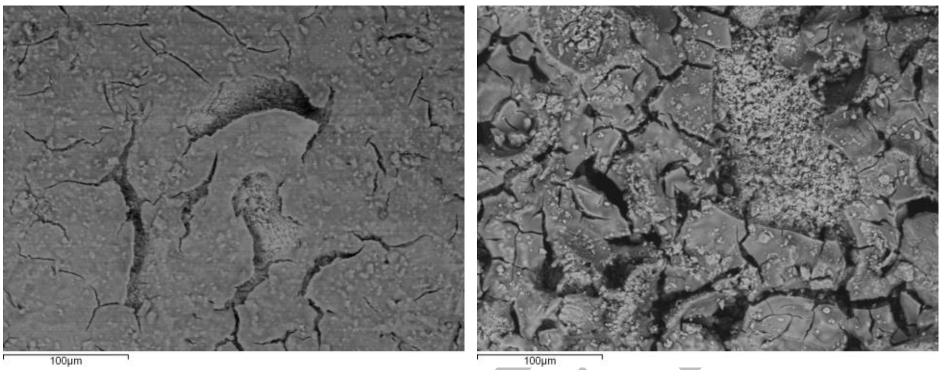


**Figure 1.** SEM-BSE images of marble (left) and Lecce stone (right) before exposure; both samples are treated with Bioxy

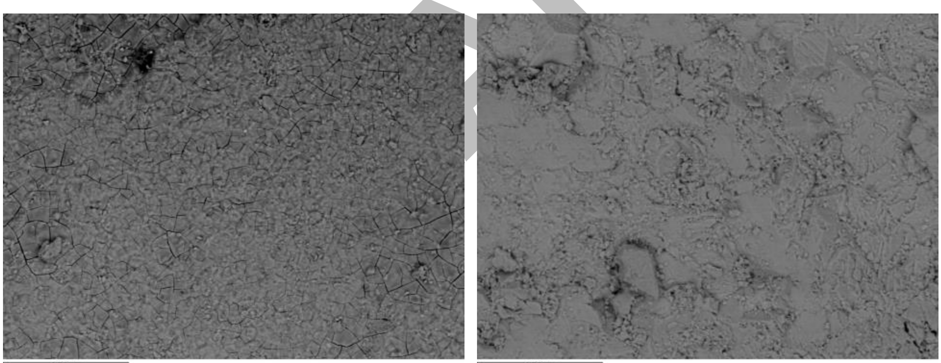


**Figure 2.** SEM-BSE images of travertine treated with Nama (left) and marble treated with Acep (right) before exposure

This behaviour can also be explained also by the results of a microanalysis (table 2) which shows a much higher percentage of titanium in the Nama and Bioxy treatments than in the Acep treatment. Regarding the Lecce stone, these phenomena are less visible as a greater quantity of the different products is absorbed due to the higher porosity of this lithotype; only in the case of treatment with the Bioxy (fig. 1 right) is it possible to notice the formation of micro-cracks caused by shrinkage. An analysis of the SEM images and the corresponding microanalysis show that the cracking and detachment of these layer makes it easier for them to be carried away by atmospheric elements during outdoor exposure. As far as the results of the microanalysis on marble before ageing is concerned, Bioxy treatment presents a slightly higher amount of titanium with respect to the Nama treatment and a much higher amount than in the case of Acep. Among the various kinds of treatment that present hydrophobic properties the Bioxy has also the largest amount of silicon. After outdoor exposure the samples treated with Acep maintain the low initial values of Ti and Si, while in the case of treatment with Nama the titanium is reduced by about 1/3 but nonetheless maintains high values. Treatment with Bioxy seems to disappear after exposure. In the case of travertine, EDS analysis data show that, before exposure, the Nama treatment presents a higher amount of titanium with respect to Bioxy and in both cases lead to larger quantity of Ti with respect to Acep.

After outdoor exposure the samples treated with Nama maintain the initial content of titanium while the Bioxy and Acep treatment lose part of the initial Ti. In the case of the Lecce stone, the microanalysis shows that before of outdoor exposure, the Bioxy treatment present the highest content of titanium. It is likely that the nanoparticles of titanium dioxide (Nama) are more easily absorbed by the porous structure of the Lecce stone with respect to the $TiO_2$ bound to the polymer of the Bioxy and Acep. In both the cases of Acep and Nama samples exposed outdoor, maintain about half of their original values of titanium while in the Bioxy treatment it decreases considerably. Also in all cases of specimens treated with Nama was detected the presence of chlorides and sodium ions on the surface; these elements after outdoor exposure are no present probably due they are washed away from the surface by the rain.

As regard these results it should be taken into account that the areas to be analyzed were chosen by us and not at random as was the case with the XRF analysis.



**Table 2.** EDS analysis of stone surfaces before and after outdoor exposure; the content of Ti and Si, with respect to the total of the elements, is reported in percentage by weight as minimum and maximum value

| | **Marble** | | | | **Lecce stone** | | | | **Travertine** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **NOT AGED** | | **AGED** | | **NOT AGED** | | **AGED** | | **NOT AGED** | | **AGED** | |
| | Ti | Si | Ti | Si | Ti | Si | Ti | Si | Ti | Si | Ti | Si |
| **NT** | - | - | - | - | - | 2÷3 | | 4÷5 | - | - | - | 2 |
| **Acep** | 3÷4 | 2÷3 | 6÷3 | 2÷3 | 3÷5 | 2÷3 | 2÷5 | 7÷13 | 15÷16 | 9÷10 | 6 | 3 |
| **Bioxy** | 30÷40 | 15÷22 | 1÷3 | 1÷4 | 38÷56 | 16÷27 | 4÷6 | 3÷5 | 26÷28 | 16÷17 | 6 | 3 |
| **Nama** | 31÷35 | - | 10÷11 | 1 | 5÷10 | 1÷2 | 10÷15 | 3÷4 | 34÷49 | 1 | 21÷46 | 1÷3 |

## 3.3 XRF analysis

The suitability of X-ray fluorescence (XRF) to monitor the Ti surface content of the samples was tested through preliminary measurements. This technique boasts several advantageous features, such as rapidity (the measuring time is about 120s) and non-destructiveness (Ferretti 2000), which means that the same samples can be analysed as many times as necessary during ageing. Moreover, if the XRF spectrometer is equipped with a scanning system, it can provide significant data regarding the whole sample surface. Table 3 reports the Ti content on the sample surface before and after exposure for each type of stone and each product. Given the inhomogeneous depth distribution of $TiO_2$, it makes no sense speaking of concentration, as it cannot be referred to an identified analytical volume. The figures are therefore given as Ti K-lines intensity (counts/s) (Solé et alia 2007), which, however, do not preclude comparisons. Low porosity stones, such as marble and travertine, show similar behaviour. In particular, the Ti K-lines intensity of the Nama treatment is very high before outdoor exposure and is reduced after exposure, nonetheless always maintaining the highest values of all the other kinds of treatment. In the case of the Acep treatment, although the initial amount of titanium is lower than in the Nama treatment, after exposure this treatment loses less Ti. In the case of the Bioxy treatment a very low amount of Ti remains on the surface after exposure. In the case of each treatment on the Lecce stone, the high porosity of the samples leads to very different results. Before exposure, as far as the titanium content is concerned it is reasonable to assume that Acep and Nama are easily absorbed by the Lecce stone

**Table 3.** Ti K-lines intensities for each type of stone and each product before and after outdoor exposure

| | **$TiO_2$-based product** | **Ti before exposure [counts/s]** | **Ti after exposure [counts/s]** |
|---|---|---|---|
| **Marble** | Acep | 175 | 37 |
| | Bioxy | 418 | 5 |
| | Nama | 1057 | 82 |
| **Travertine** | Acep | 159 | 67 |
| | Bioxy | 450 | 9 |
| | Nama | 1089 | 216 |
| **Lecce stone** | Acep | 71 | 33 |
| | Bioxy | 1099 | 55 |
| | Nama | 108 | 81 |

whereas in the case of Bioxy it remains on the surface due to its hydrophobic behaviour. After ageing, the amount of Ti is similar in all case of treatment, with the exception of Bioxy where there is a great decrease in the percentage of Ti counts/s.

### 3.4 Static contact angle measurements

In Table 4 are reported the static contact angle measurements of marble and Lecce stone treated respect to the untreated samples.

**Table 4.** Contact angle measurements of stone samples untreated (NT) and treated before and after outdoor exposure

| | **Treatment** | **Not aged** | **Outdoor exposure** |
|---|---|---|---|
| **Marble** | **NT** | **85±4** | **119±4** |
| | **Acep** | **79±15** | **118±5** |
| | **Bioxy** | **125 ±4** | **93±12** |
| | **Nama** | **Absorbed** | **108±5** |
| | **RH 224** | **132±8** | **129±6** |
| **Lecce stone** | **NT** | **Absorbed** | **Absorbed** |
| | **Acep** | **137±5** | **125±3** |
| | **Bioxy** | **> 140** | **111±14** |
| | **Nama** | **Absorbed** | **Absorbed** |
| | **RH 224** | **> 140** | **> 140** |

Before ageing, the marble samples show that hydrorepellency is high in the case of treatment with Bioxy and RH and weak in the case of Acep and NT, in the case of Nama there is hydrophilicity. The low value of the contact angle of Acep is probably due both to the hydrophilic effect of the $TiO_2$ and the poor presence of a water repellent component (as evident from SEM-EDX analysis). After ageing, the RH 224 treatment on the marble maintains the same degree of water repellency while the contact angle of Acep is similar to the values of NT because of the decrease of $TiO_2$ on the surface.

The Bioxy treatment reduces its hydrophobic properties showing a loss of hydrorepellent material which is also confirmed by the SEM-EDX/XRF analyses. The Nama samples show a degree of hydrorepellency similar to that of NT as a result of the loss of titanium dioxide that was initially present. The increase in hydrophobicity of the untreated marble is probably due to the deposit on the surface of slightly polar organic compounds from the environment. The surface of the Lecce stone samples treated with products containing water-repellent component (Bioxy and RH 224) maintain the hydrorepellency even after exposure to rain, with just a slight decrease in the case of Bioxy. The Nama treatment, due to the presence of the $TiO_2$ nanoparticles, induces an increase of hydrophilicity compared to untreated samples: the water drops deposited on Nama for the measurement are absorbed more quickly than on the untreated surface. A particular behaviuor, on the Lecce stone, is shown by the Acep treatment. In this case probably the $TiO_2$ is adsorbed while the hydrophobic component remains on the surface.



### 3.5 Soluble salts analysis

The analysis of the soluble salts in the aged stone samples shows insignificant variations in the ion content of the untreated samples (NT) with respect to the samples treated with the different $TiO_2$ based products. Therefore, after eight months of outdoor exposure, the potential damage due to the photocatalytic activity of the $TiO_2$ is not evident. Here is reported just an example of the analysis results expressed in milliequivalent of anion or cation per gram (meq/g) of dry mass of the sample for the marble (Table 5).

**Table 5.** Concentration of anions and cations in the supernatant liquid of the mixtures: stone/water

| **Marble** | **$Cl^-$ x$10^{-5}$ (meq/g)** | **$NO_3^-$ x$10^{-5}$ (meq/g)** | **$SO_4^{2-}$ x$10^{-5}$ (meq/g)** | **$K^+$ x$10^{-5}$ (meq/g)** | **$Na^+$ x$10^{-5}$ (meq/g)** | **$Ca^{2+}$ x$10^{-5}$ (meq/g)** |
|---|---|---|---|---|---|---|
| NT not aged | **2,1** | **1,0** | **4,4** | **0,8** | **6,0** | **39,6** |
| NT | **6,5** | **1,6** | **4,8** | **0,8** | **7,8** | **33,7** |
| ACEP | **3,5** | **1,2** | **6,3** | **0,7** | **5,1** | **47,2** |
| BIOXY | **4,5** | **1,6** | **4,2** | **0,6** | **4,6** | **71,7** |
| NAMA | **4,1** | **2,0** | **6,0** | **1,2** | **4,2** | **111,0** |

### 3.6 Photocatalytic activity assessment

Rhodamine B discoloration tests highlight the different photoefficiency of the $TiO_2$ based treatment also with respect to the exposed samples in a polluted environment. Results are shown as colour changes ($\Delta E$) of samples stained with rhodamine B monitored after 30 min, 2, 5 and 8 h of irradiation.

In fig. 3 is reported the different behaviour of the marble samples before and after ageing.

Nama treatment gives a discoloration more efficient than the other forms of treatment (fig. 3 left), the results indicate that photocatalysis is most effective within the first 30 min of irradiation, otherwise all treatments give ΔE values higher with respect to the NT samples. After ageing (fig. 3 right), the ΔE values of Acep, Bioxy and Nama are shown to decrease with respect to the not aged values due to the lower content of $TiO_2$ remaining on the surface. However, Nama remains the most effective treatment for marble. Regarding exposed Lecce stone and Travertine samples stained with rhodamina (fig. 4), Bioxy and Nama in the case of the former lithotype while Acep and Nama in the latter case exhibit a higher discoloration than in the untreated stone.

These results show that the photocatalytic efficiency of the $TiO_2$ based treatment is mainly influenced by the type of photocatalytic product and then by the porosity of the stone material. Photocatalysis is much more efficient in the case of the Nama treatment where $TiO_2$ is present in finely divided particles and highly dispersed because it offers the greatest surface exposure to the surrounding environment.

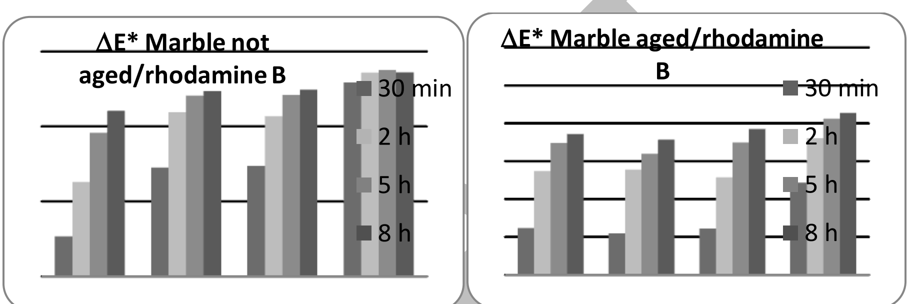


**Figure 3.** Colour difference (ΔE) with time of irradiation (30 min, 2, 5 and 8 h) of rhodamine B applied on marble samples before (left) and after (right) ageing in a polluted environment.

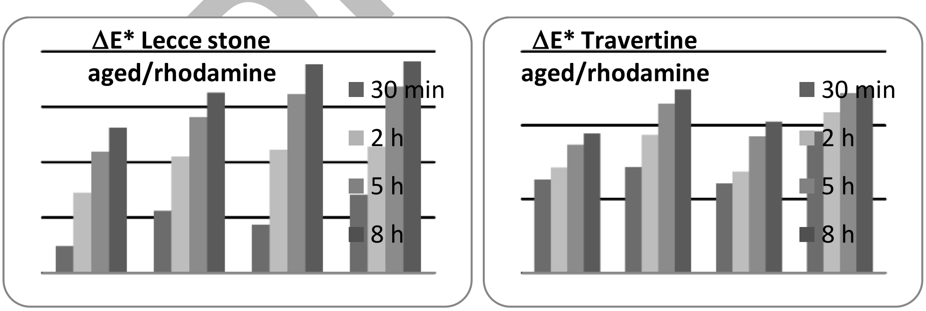


**Figure 4.** Colour difference (ΔE) with time of irradiation (30 min, 2, 5 and 8 h) of rhodamine B applied on Lecce stone samples (left) and Travertine (right) after ageing in a polluted environment.

## 4. Conclusions

Photocatalytic products tested in this research have shown a different behaviour also with respect to the three stones. After a natural ageing in a polluted urban area they show only mild self-cleaning effects but no harmful effect, due to the increased of soluble salts on the stones, is detected. The Nama product containing only nanoparticles of $TiO_2$ presents the most efficiency photocatalytic activity due to the greatest surface exposure to the surrounding environment. However, this product is not sufficient attached to the substrate and consequently after exposure only a  a little amount remains on the surface. Nama also makes the stone surface more hydrophilic. Both Bioxy and Acep, present a lower photocatalytic activity, however Bioxy is much more effective on the surface of  porous Lecce stone than Nama which is easily adsorbed. Acep and Bioxy contain both a hydrorepellent component useful to counteract the superhydrophilicity introduced by $TiO_2$. However, after ageing all forms of treatment disappear from the surface, in particular in the case of Bioxy and Nama and as result the self-cleaning effect is limited.

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