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Original article

Is nano-TiO_2 alone an effective strategy for the maintenance of stones in Cultural Heritage?

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ABSTRACT

TiO_2-based nanocoatings have been becoming more and more widespread during last years in Cultural Heritage: they seem to be able to keep stone surfaces self-cleaned and to prevent the formation of biofouling. However, the efficiency of these coatings is strongly dependent on the substrate (i.e.: porosity and roughness) and on the amount of TiO_2. Thus, this study experimentally investigates on the self-cleaning and anti-biofouling efficiency of a nano-TiO_2 dispersion (without any organic or inorganic additive) applied on six different types of natural stones (three limestones, two sandstones and one tuff) usually used in Cultural Heritage, where high porosity and roughness can be found and the TiO_2 amount cannot be increased in order to avoid any chromatic variation of the substrate. Water was used as solvent so as to reduce the risk of exposition of hazardous materials and to eliminate any chemical action on stones. The self-cleaning power of the coating was evaluated by measuring its ability at discolouring organic dye Methylene Blue, while its anti-biofouling efficiency was assessed by an accelerated growth test under controlled climatic conditions of two algal microorganisms, namely *Chlorella mirabilis* and *Chroococcidiopsis fissurarum*. Results show that, even if the photocatalytic and biocide power of nano-TiO_2 itself is well known in literature, its application for the maintenance of stones in Cultural Heritage does not seem to be an effective strategy, especially when stones are highly porous and rough. Roughness and porosity of stones, in fact, can limit the efficiency of TiO_2, which is thus not able to powerfully keep the stone substrate cleaned or slow down algal proliferation.

1. Research aim

Innovative conservation treatments of building materials used in Cultural Heritage based on TiO_2-nanocoatings have been becoming more and more widespread during last years: they seem to be able to keep the various substrates self-cleaned and to prevent the formation of biofouling, as some previous studies of the same research group have underlined. However, some recent researches have pointed out that the efficiency of these coatings is strongly dependent on the substrate itself (i.e.: porosity and roughness) and on the amount of TiO_2. Thus, this study experimentally investigates on the self-cleaning and anti-biofouling efficiency of only nano-TiO_2 (without any organic or inorganic additive) applied on natural stones used in Cultural Heritage where high porosity and roughness can be found and it is not often possible to increase the TiO_2 amount in order to avoid a chromatic variation of the substrate. Besides, water was used as solvent so as to reduce the risk of exposition of hazardous materials and to eliminate the chemical action on stones.

2. Introduction

The use of natural stones in Cultural Heritage is widespread all over the world from ancient times. Main stones used for masonries, finishes and decorations were sandstone, limestone and tuff. Local availability, esthetical reasons and their resistance to weather encouraged their use outdoor. However, after many years of exposition, soiling (especially in urban areas) inevitably occurs. This can compromise their aesthetic aspect, as well as their integrity. Besides, bio-degradation, related to the adhesion of

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microorganisms like algae, may also occur by inducing the formation of a patina that alters their original aspect, and by promoting the damage of the stone surface in critical cases [1–4].

An innovative and very promising strategy to prevent building materials used in Cultural Heritage from polluting and biofouling seems to be the use of TiO_2 nanocoatings [5–8], because of their ability to photo-decompose pollutants under UV irradiation, their durability and affordable costs [9–15].

TiO_2-based nanocoatings were applied on many stone materials such as marbles, travertine, dolostones and limestone, and a review can be found in literature [16]. Some first results seemed to encourage their use especially as an efficient method to prevent aesthetic problems caused by the adhesion of organic and inorganic substances that produce discolouration, chromatic variations and black crusts, as some previous studies of the same authors of this paper have underlined [12,16–19].

At the same time, the efficiency of these coatings to limit biofouling such as algal proliferation on stones is currently under investigation, and they seem to be successful only in case of ideal conditions of the substrate [20–22].

However, recent studies, some of them from the same authors of this paper on other building materials, have pointed out that intrinsic characteristics of the substrate such as porosity and roughness could play a key role [20,23–27]. High values of these parameters could nullify (or limit considerably) the beneficial effects of TiO_2, both in case of self-cleaning and anti-biofouling [20,22], whereas the efficiency of these coatings is also strongly dependent on the amount of TiO_2.

In the field of Cultural Heritage, with a predominant presence of high porous and rough stone materials, the limited effects of TiO_2, caused by the morphology of the substrate, could be thus a real problem. Besides, in this field, low amounts of TiO_2 have to be used for having compatible chromatic variations.

In this way, in this paper, an only-based nano-TiO_2 coating (without any organic or inorganic additive) was applied on typical stones used in Cultural Heritage, such as limestone, sandstone and tuff. A preliminary study was conducted to understand its photocatalytic and self-cleaning power, and then an accelerated growth test was carried out to study algal biofouling on treated and untreated specimens. This could help to evaluate the real opportunity to use TiO_2 in Cultural Heritage for self-cleaning and biofouling prevention, taking into account the compatibility with the substrate, and preserving the original aspect of stones. Besides, since many chemicals such as solvent, raw materials, reagents, and template materials, have been used in order to produce nanomaterials, and the concept of green chemistry was recently introduced to chemical science and industry to reduce or eliminate the generation of undesirable products and to decrease the use of hazardous materials in chemical processes [28], in this study water was used as green solvent.

3. Material and methods

3.1. Tested stones and characterization

Three types of limestone, two types of sandstone and one tuff were tested. These types of stones were selected because they are building materials usually used in Cultural Heritage. For each type of stone, six prismatic ($80 \times 80 \times 30$ mm^3) specimens were prepared. Fig. 1 presents a classification of the tested specimens with their original visual aspect.

Preliminary tests were conducted to characterize the selected stones in terms of porosity, roughness and colour. Porosity was analyzed by a mercury intrusion porosimeter (Micromeritics, Autopore III) following ASTM D4404-10 standard procedure [29].

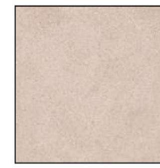
Sample ID	Description – Site	Visual aspect
CRC	Limestone – Caccamo lake	
CRF	Limestone – Furlo gorge	
CBC	Limestone – Cingoli	
ARC	Sandstone – Camerino	
ART	Sandstone – Tennacola torrent	
T	Tuff – Lazio region	

Fig. 1. Tested specimens in the biofouling-accelerated test. Each group includes six specimens.

Total porosity (p), and average pore diameter (d) were assessed. The surface roughness was measured by using a Diavite DH-5 rugosimeter on a base length of 1.25 cm with a cut- off length of 1.25 mm. Eight measurements, with different orientations, were considered to calculate the average surface roughness (Ra) and the geometric average height of roughness irregularities (Rq), according to UNI EN ISO 4287:2009 [30].

The colour of the original stones was measured by a portable spectrophotometer (Konica Minolta CM2600D) using a 3 mm aperture, a daylight illuminant (D65), and 10° observer angle, as recommended in UNI EN 15886:2010 [31]. Nine measurements were repeated for each specimen, obtaining 54 data for each type of stone, and then all the data were averaged to obtain the original aspect of each stone. Results were expressed in CIELab colour space.

$$\Delta E = \sqrt{\left(L^* - L_0^*\right)^2 + \left(a^* - a_0^*\right)^2 + \left(b^* - b_0^*\right)^2}$$

Colour measurements were repeated on treated specimens in order to detect any chromatic variation due to the application of the TiO_2 nanocoating. The colour difference (ΔE) between the original

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