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Antifouling coatings for underwater archaeological stone materials

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A B S T R A C T

This research is part of the Italian national project entitled COMAS (Planned COnservation, "in situ", of underwater archaeological artefacts), concerning the degradation phenomena occurring during the permanence of archaeological items in underwater environment and their conservation in situ by means of new methodological approaches. One of the activities within the project was devoted to the formulation and testing of products for the conservation of stone materials against biofouling, which is the most aggressive degrading agent in underwater environment.

This research has been focused on the application of metal oxide nanoparticles on stone surfaces. They have been dispersed in siloxane wax in order to bond the nanoparticles to the stone, and to make it possible to apply the mixture directly underwater.

Several formulations have been prepared, applied on marble specimens, and tested in laboratory to check the hydrophobicity and the colorimetric variation induced by the products. Moreover, treated specimens have been hold in underwater environment for two years, to study the bio-colonization on treated surfaces. The underwater archaeological park of Baia (Naples, Italy) in the area of the *Villa con ingresso a protiro*, has been chosen for the in situ tests. Transmitted light optical microscopy and scanning electron microscopy (SEM) coupled with microanalysis (EDS) were used to study the biological colonization and the interactions with treated and untreated stone specimens, observed in different exposure periods. Results showed a significant slowdown of the biological colonization on treated surfaces.

1. Introduction

In recent decades, interest in studying degradation phenomena occurring on archaeological site located in underwater environment considerably increased. Different researches are focused both on the degradation phenomena on the stone materials located in underwater environment [31,7,19,21,22] and on innovative approaches for their protection.

As well known, one of the most damage of submerged archaeological artefacts is due to biological colonization (bio-fouling) which develops differently according to a variety of environmental conditions along with the textural and structural features of the materials [8,21,28,31].

The most recent guidelines of scientific and international cultural heritage protection organisms agree in willing the promotion, protection and in situ preservation of underwater archaeological and historical Heritage (UNESCO Convention on the Protection of the Underwater Cultural Heritage, 2 November 2001).

The present research, which is a part of the COMAS project (Planned COnservation, "in situ", of underwater archaeological artefacts, national project PON01_02140) was focused on the testing of new protective products for preventing the biological growth directly in situ, by using materials with antifouling property and an acceptable environmental impacts [6].

Science applied to conservation of Cultural Heritage has an increasing interest toward nanotechnology [3]. In particular, photo-catalytic materials have a great potential due to their antimicrobial and photocatalytic features [2,10,12,13,33]. ZnO and TiO_2 are photocatalytic materials, characterized by high chemical stability, non-toxicity, high photo-reactivity, broad-spectrum activation, antibiosis and cheapness; they have been used as biocide against various microorganisms: bacteria, fungi and viruses [11,14,25,26,38,32]. The activity of photocatalytics can be enhanced by adding small amounts of metals in the materials [39,40], [9,12,13], [15,20,24]. In particular the Ag doping can also cause the denaturation of proteins present in bacterial cell walls and slow down bacterial growth [25], leading to a synergic effect.

For this reason, we focused our attention on nano-powdered TiO_2, ZnO and Ag, which have been selected, and then, an experimental procedure has been carried out, aimed to making

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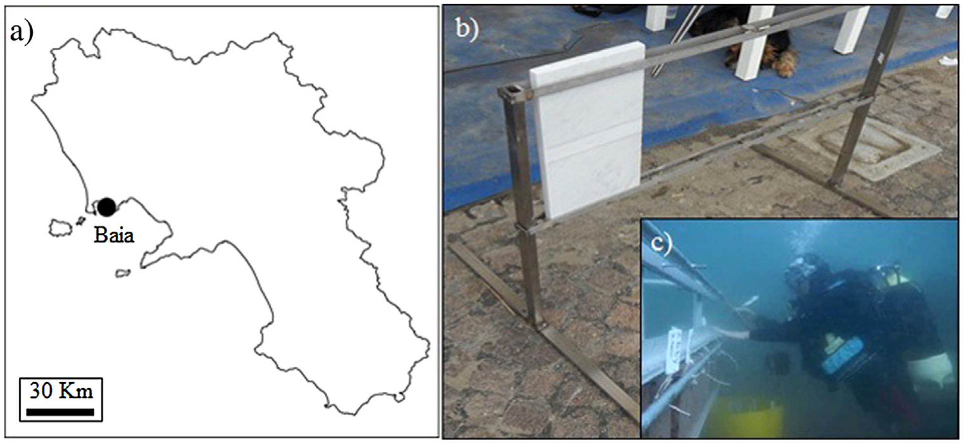

Fig. 1. a) Location of Baia in the Campanian region, Italy; b) Portion of the sample holder and c) positioning of marble specimens in underwater environment.

Table 1
Summary of the formulated mixtures.

Formulation ID	Nanoparticles		
	TiO_2 (% wt)	Ag (% wt)	ZnO (% wt)
U	Untreated		
B	Treated with only the binder		
TL	0.1	–	–
TH	1	–	–
TAL	0.1	0.001	–
TAH	1	0.01	–
ZL	–	–	0.1
ZH	–	–	1
ZAL	–	0.001	0.1
ZAH	–	0.01	1

antifouling products suitable for the protection of stone materials in underwater environment [34]. The nanomaterials were dispersed in siloxane wax in different compound, and tested on marble specimens in different amounts.

Wax has been selected as binding material due to the possibility to apply the product directly in underwater environment, by rubbing the product on the stone surface. The choice of marble was linked both to their presence in the underwater archaeological sites [29,30], and for the strong biological degradation phenomena occurring on its submerged surface [21]. The application of the products was carried out in laboratory on specimens, and then contact angle and colorimetric measurements have been carried out. Another set of specimens have been treated, anchored on a sample holder and immersed in the underwater archaeological park of Baia (Naples, Italy) in the area of the *Villa con ingresso a protiro*, at a depth of about 5 m. Procedures for monitoring degradation forms were carried out in 4 stages in order to identify and quantify the biodeterioration on the treated and untreated stone surfaces at different stages of immersion.

2. Materials and methods

Nanoparticles of TiO_2, ZnO and Ag (Sigma Aldrich, USA) (particles mean diameter 100 nm) were dispersed in different amounts in a binder made of melted (T–60 °C) siloxane wax (Wacker W23, Wacker AG, Germany) (Table 1). These amounts have been chosen according to the results reported in literature on similar formulations [18,23,34] in terms of efficacy and colorimetric variation due especially to silver. Dispersions have been left overnight at room temperature to cool and solidify. A first analytical step has been carried out in laboratory. The formulations have been applied on stone specimens (5 × 5 × 2 cm) immersed in water, by rubbing the solid wax on the stone surface directly into the water; the average amount of applied product was about 25 g/m^2. Treated surfaces have been analysed by means of the following techniques:

i Colorimetric tests carried out using a CM-2600d Konica Minolta spectrophotometer, to assess chromatic variations. Chromatic values are expressed in the CIE L*a*b* space, where L* is the lightness/darkness coordinate, a* the red/green coordinate (+a* indicating red and −a* green) and b* the yellow/blue coordinate (+b* indicating yellow and −b* blue). This analysis was aimed to assess the colour variation induced by the treatment.
ii Contact angle measurements carried out in order to determine the wettability of the treated surface, this parameter could influence the adhesion on the microorganisms in the submerged environment. In all the experiments, the first step of the measurement consisted in the placement of a water drop of defined volume (10μl) on the solid sample surface. Drop shape was recorded with a camera and automatically evaluated in terms of contact angle, which represents the angle between the substrate surface and the tangent from the edge to the contour of the drop.

All formulations (Table 1) were also applied on larger marble specimens (36 × 46 × 2 cm). Each treatment has been applied on three specimens. These specimens have not been subjected to laboratory assessment. They were anchored to several sample holders (Fig. 1b–c) and immersed in the archaeological area of Baia at a depth of about 5 metres (Fig. 1). All samples were exposed vertically in order to avoid the accumulation of sediments, which could affect significantly the colonization of the surfaces. All samples were placed simultaneously, and at time intervals, some specimens were recovered and subjected to investigations. In all steps of the submerged experimentation, untreated samples (U) were used to make a comparison with treated samples. Moreover, samples treated with only the binder (B) has been exposed in order to assess the effect of the bare binding agent on the biofouling formation. Procedures for monitoring the efficacy of treatments were carried out in four stages (4, 12, 20 and 24 months) (Fig. 2), in order to identify the biodegradation products and to assess changes occurring in samples during the period of permanence in seawater.

In order to examine the efficacy of the treatments and possible degradation products microscopic investigations were carried out, as follows:

i Stereomicroscope observations of the samples by using a EMZ-5D, MEIJI EM in order to preliminarily identify the biological communities in relation to the total surface of the fragments and