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Original article

Synergistic effect of the consolidant and the photocatalytic coating on antifungal activity of porous mineral substrates

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ABSTRACT

The goal of the paper is the investigation of synergistic action of newly developed consolidants and LDH_TiO_2 photocatalytic suspension on the characteristics (antifungal efficiency and surface properties) of the selected mineral substrates: brick and render. There were two different application protocols employed: protocol (1) the fresh photocatalytic suspension was applied on already consolidated substrates aged for 1, 2, 4 and 7 months, and protocol (2) only once on all specimens aged 1 month after the consolidant application. This study provides an insight into the synergistic effect of the applied materials on the antifungal activity, hydrophilicity and performances of the substrates' surface during UV irradiation. The decrease of OH^- ions on the surface, revealed from the photocatalytic suspension, showed a positive effect on the surface stability and antifungal properties of the mineral surface. Based on the obtained results, the most suitable protocol for the application of the photocatalytic suspension on the already consolidated and aged porous substrates has been adopted.

1. Introduction

Porous mineral building materials are susceptible to degradation processes when affected by water and/or environmental pollution. Pollution is usually deposited on the surface of the materials and it penetrates further into their bulk. Degradation processes alter the material structure, which leads to its limited service life and changes of its aesthetic appearance. In addition to chemical and physical degradation processes, the presence of water in the porous structure of building materials presents a suitable environment for the development of microorganisms on the surface and their progressing into the bulk [1]. Degradation phenomena are more prominent in the field of cultural heritage where historic materials are exposed to environmental conditions for a long period. Among many factors, atmospheric pollution represents the most important one. This is followed by the creation of surface contamination (formation of patina, development of different microorganisms and lichens, and more complex organisms, e.g. moss) [2].

In order to preserve the historic building materials from further degradation caused by the presence of microorganisms, special materials have been employed for both surface and bulk protection. The use of TiO_2 photocatalytic suspensions for surface protection of building materials is a prospective research area and many papers have been devoted to their development [3,4]. These materials possess self-cleaning properties, which include photocatalytic activity (promote decomposition of various organic and inorganic pollutants) and photo-induced surface hydrophilicity activated by UV–vis light irradiation, which makes them suitable for the protection of surfaces [5]. The TiO_2 suspensions have been extensively tested and they can be safely used in many different areas such as the protection of cultural heritage, surface sterilization, medicine, microbiology [6–10]. The antibacterial, antifungal and antiviral nature of TiO_2 photocatalytic suspensions has also been confirmed [11,12]. Although the antimicrobial properties of TiO_2 photocatalytic suspensions have been established, it is difficult to compare the results of various authors. This is due to different experimental procedures, which are the consequence of the absence of a universal standard testing method with good practical settings [13].

The primary aim of bulk restoration of historic materials is the improvement of mechanical properties and the reduction of further deterioration using various consolidants. The most significant properties of the consolidants regularly stressed in literature are the consolidating value, depth of penetration, effect on appearance, compatibility with the substrate, durability of treatment, effect on

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Table 1
Testing systems with protective materials.

Protected mineral substrate	Porous mineral substrate	Protective material
HB_CS	Brick	Consolidant (CF4)
HB_CS_PF	Brick	Consolidant (CF4) + photocatalytic coating (PF)
HR_CL	Render	Consolidant (CFW)
HR_CL_PF	Render	Consolidant (CFW) + photocatalytic coating (PF)

CF4: silicate ester; CFW: soluble calcium compound.

liquid water and vapour permeability, health and safety issues, while the antimicrobial testing of the consolidants are not common [14,15].

Regardless of the preservation type (bulk or surface), it is important to balance the characteristics of protective materials and the overall properties of the coated substrates. It has been shown that effectiveness of the photocatalytic coatings strongly depends on the substrate morphology and textural characteristics [16]. Furthermore, during the study of self-cleaning properties of photocatalytic suspensions, Hashimoto et al. have introduced the concept of metastable state of the surface structure of TiO_2 [17]. They suggested that the appearance of the metastable state could be the result of the increase of the number of hydroxyl groups on the TiO_2 surface. This concept emphasizes the significance of understanding the mutual effect of the substrate and protective material properties, as well as of environmental conditions on the characteristics of the coated substrate.

2. Research aims

This study provides an insight into the synergistic effect of the consolidant and the photocatalytic suspension on the values of antifungal activity of the surface of mineral substrates (bricks and renders with similar characteristics to historic materials found at the Bač Fortress, Serbia). It also gives information about the performance, chemical characteristics and hydrophilicity of the consolidated samples of brick and render, before and after the application of the photocatalytic suspension, during the experimental period of seven months. Thus, determination of an efficient application protocol of the photocatalytic suspension onto the consolidated porous substrates was the main objective of this paper.

3. Materials and methods

Four groups of testing systems (Table 1) were set up in order to examine the surface properties and antifungal activity of the porous mineral substrates (brick and render) after the application of the consolidants and the photocatalytic suspension. The TiO_2 photocatalytic suspension (PF) based on layered double hydroxides (LDH) was applied onto the already consolidated surface with the consolidant formulation:

- based on soluble calcium compound (CFW);
- based on silicate ester (CF4).

The two consolidants and the photocatalytic material represent the outputs of the HEROMAT project (ENV-NMP.2011.3.2.1-1 NMP) [18].

3.1. Consolidants

The consolidant CF4 was applied onto the brick surface. It was prepared by mixing 50 wt.% ethyl polysilicate (WACKER TES 40 WN, Wacker Silicones), 20 wt.% 1,3-dioxolane (DOX, 99%, Sigma Aldrich), 5 wt.% diethylethanolamine (DEEA, 99.5% Sigma Aldrich) and 25 wt.% of the mixture of C11–C13 alkanes (paraffin, Samson Kamnik, CAS: 64742-48-9). The preparation of the consolidant CF4 was described in detail elsewhere [19].

Render samples were consolidated by the CFW, already described in detail elsewhere [19,20]. CFW is a water solution of calcium acetoacetate $Ca(OAcAc)_2$. Additionally, 0.05 wt. % of a catalyst, ethylenediamine (Acros Chemicals), was added into the consolidant before the application.

Density at 20 °C conducted according to SIST ISO 758:1995 of the consolidant formulations CF4 and CFW was 0.91 and 1.02 g/mL, respectively.

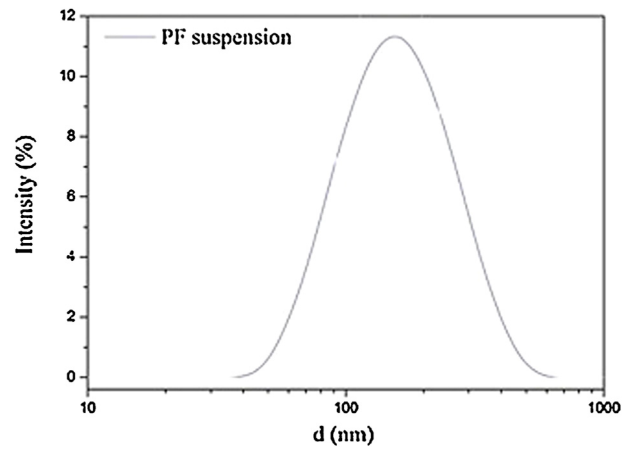

Fig. 1. Particle size distribution (PSD).

3.2. Photocatalytic suspension

Modified low super saturation co-precipitation method was performed in order to obtain a newly synthesized nanomaterial based on LDH (e.g. anionic clays) and photocatalytic active TiO_2 particles [18]. The Zn and Al salts were continually added (4 mL min^{-1}) together with 10 wt.% TiO_2 suspensions (VP Disp.W 2730 X Evonik). The alkali solution [mixture of $NH_4(CO_3)_2$ and NaOH] was used in order to maintain a constant pH value (pH = 8–9) during the synthesis process. The newly synthesized nanocomposite was further stabilized by a dilution procedure adding an appropriate polyelectrolyte stabilizer [18].

The results of the particle size distribution (PSD) measurements of the photocatalytic suspension showed that the synthesized suspension possesses had a monomodal profile, with an average diameter of the particles around 289 nm (Fig. 1). Based on the rheology assessment, it was concluded that the obtained suspension is a Newtonian liquid with a viscosity value of 10^{-3} Pas, which is close to the properties of demineralised water. Mineralogical analysis of this suspension revealed the presence of sharp XRD peaks (Fig. 2) suggesting a well-defined crystal LDH structure [21].

Technical characteristics of the photocatalytic suspension, with a presumed consumption per m^2 of a mineral substrate, are presented in Table 2. Based on these characteristics, the developed suspension can be underlined as an environmentally friendly material, close to the water properties.

3.3. Mineral substrates – preparation

Two types of substrates were used during the investigation: handmade brick samples (HB), air-dried for two weeks and fired in a laboratory kiln at 980 °C; handmade render samples (HR), prepared by hot lime mix method (lime putty, micronized dolomitic quicklime, sand and water with mass ratio 1.85:0.08:3.5:0.2,