ANALYSIS REGARDING THE INCREASE IN THE RESISTANCE OF CEMENTITIOUS SELF-HEALING COMPOSITES TO THE ACTION OF MICROORGANISMS BY INDUCED PHOTOACTIVATION CAPACITY

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Abstract

The development of biofilms of micro-organisms on the surface of buildings, in addition to the negative impact and risk to the health of the population, leads to their degradation and the need for continuous sanitation operations. Inducing superhydrophilicity and self-cleaning performance of cement surfaces by adding TiO_2 nanoparticles to the composite matrix, as a result of photoactivation reactio. This method, can become an effective for the production of new materials in order to increase the durability of buildings and to increase the degree of hygiene, due to the ability of these new materials to inhibit the growth of microorganisms. Experimental results have shown that in case of contamination with two types of moulds (Aspergillus niger, Penicillium notatum) and four types of bacteria (Escherichia Coli, Pseudomonas Aeruginosa, Staphylococus Aureus, Streptococus Pyogenes) respectively, the development of harmful biofilm is inhibited. This performance was monitored using the dimensional development of the specific inhibition halo as a quantifiable indicator. It can be said that it is influenced by the type of contaminant and the nanoparticle content of the cementitious composite matrix, but is manifested in all cementitious composites containing TiO_2 nanoparticles photoactivated under laboratory conditions.

***Key words**: biocidal effect, photocatalysis, self-cleaning cementitious composites, TiO_2 nanoparticles.*

INTRODUCTION

Today, worldwide, especially in developed countries, but not exclusively, there is a change in people's lifestyles, with more and more activities taking place inside buildings. Microorganisms such as moulds, bacteria, viruses, algae, lichens or mites, have a negative impact on building surfaces. This is known to have negative effects on the health of the population if the growth occurs on the surfaces of indoor living spaces. Also, the growth of microorganism films on the built surface has a negative effect on the durability and operational safety of buildings, accelerating their degradation and contributing on the degree of environmental pollution. Each tonne of manufactured cement (the main raw material used in the construction industry) is responsible for the release of 0.8-1.1 tons of CO_2 into the atmosphere because of fuel combustion and limestone calcination (International Energy Agency, 2009). "Sick building syndrome (SBS)" (Farrag et al., 2021; Gawande et al., 2020; Sarkhosh et al., 2021; Wang et al., 2022; Gao et al., 2021; Huo et al., 2020) is known as having negative impact on the health of users and is recognized worldwide as, manifesting itself in people who work, partially or totally, inside buildings. They can be affected by deposits of microorganisms, as a result of the degradation of indoor air quality through contamination with spores and toxins emanating (Andersen et al., 2011; Baxter et al., 2005; Żukiewicz-Sobczak et al., 2013; Haverinen-Shaughnessy, 2012; Giannantonio et al., 2009; Sökmen et al., 2001; Sökmen et al., 2008). These mould spores, toxins emanating in the normal life cycle of micro-organisms, or even the micro-organisms themselves, reach the human body both through the air breathed in and through direct contact with contaminated surfaces.

Cheap and handy antibacterial methods can become a very important method for the development of simple, new types of materials. This issue is actual and very important because, in recent years, damage caused by harmful microorganisms has become a serious social problem (Yandav et al., 2016; Wang et al., 2017). Exterior surfaces act as reservoirs for the development of microorganisms that could, in turn, lead to the spread of infections or become the main cause of various health conditions (Kühn et al., 2003). The conceptually, simple and promising technology, in which applications of the photocatalytic process of TiO_2 nanoparticles (NT), generate an inhibition in the growth of some microorganisms, moulds or bacteria, becomes an alternative to the use of chemical disinfectants (Drugă et al., 2018; Machida et al., 2005; Watts et al., 1995; Jakubickova et al., 2020; Khannyra et al., 2022; Wang et al., 2022). In general, NT is found as a mixture of rutile and anatase (both being crystallographic forms of TiO_2). There is also the situation where the crystallographic form anatase is predominant (over 90%), and, according to the literature, TiO_2 nanoparticles could be added dry, by direct mixing with cement powder, followed by the addition of hydration water. Water does not chemically react with any crystallographic form of titanium dioxide, nor does a chemical reaction occur between the photosensitive nanoparticles. The hydration-hydrolysis phases of the cement and the hydration-hydrolysis reactions are not chemically influenced by the chemical reaction (Quagliarini et al., 2012). The major influence of these nanoparticles on the performance of cementitious composites is to induce a superhydrophilicity of the surface, with a sustained self-cleaning capacity and also increased resistance to the action of microorganisms The developed materials could also present an imparting a biocidal effect.

Under the action of UV rays, as a semiconductor with a band gap of about 3.0 eV and by absorbing energy, titanium dioxide generates electrons (e^-) and holes (h^+). Ti (IV) cation to the Ti (III) ion is reduced by the above mentioned and holes oxidize O_2^- anions. This process will release oxygen, creating vacancies on the surface of the titanium dioxide. This vacancies will allow the water molecules to bind with the release of hydroxyl groups (OH^-). Literature indicates that, in the case of TiO_2-containing cementitious composite surfaces (Jakubickova et al., 2020; Khannyra et al., 2022; Wang et al., 2022; Matsunaga et al., 1988; Drugă et al., 2018) that photogenerated (h+) voids (holes) cause the bond length within the TiO_2 structure to increase bringing the surface into a metastable state. Simultaneously with the formation of new hydroxyl groups and the release of a proton, this allows the adsorption of molecular water (Figure 1) (Zhang et al., 2010; Matsunaga et al., 1988).

Using the energy provided by UV radiation, simultaneously with the development of superhydrophilicity, which is greater than the valence band gap of TiO_2, electron pairs (e^-) and holes (h^+) are generated. Those react with O_2 and H_2O forming anionic radicals (O_2^-) and (OH). These oxidative species $(h^+, \cdot O_2^-)$ and (OH) are all highly reactive and participate to the destruction of microorganism cells (Haleem Khan & Mohan Karuppayil, 2012). Research to date has led to a number of hypotheses regarding the biocidal effect indicating that the cell membrane is photocatalytically destroyed (Sunada et al., 2003). This is also supported by reports by Oguma et al. (Oguma et al., 2002) who propose a destruction mechanism explained by both cell wall destruction and induction of disruption at the cellular level following contact of the microorganism with TiO_2, while Saito et al. (Saito et al., 1992) propose the hypothesis of a destruction mechanism explained by the inhibition of the bacterial cell's respiratory function once in contact with TiO_2.

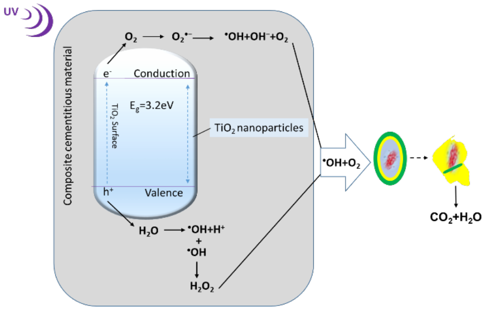

Figure 1. Sequential representation of the biocidal mechanism

The aim of this paper is to analyse the biocidal capacity of cementitious composites containing with TiO_2 nanoparticles (NT).

MATERIALS AND METHODS

The samples were produced using NT-added cement paste, with AEROXIDE® TiO_2 P25. The TiO_2 nanoparticles were characterized by an average particle size of 21 nm, a specific surface of 35-65 m^2/g and 99.5% purity, containing more than 70% anatase, were prepared for the experimental tests. The composite cementitious paste was prepared and conditioned as shown in Figure 2, with mixture P1 as a control sample (0% NT).

According to literature references (Hope, 2013; Rosen & Heseltine, 2009; Fisk et al., 2007; Mudarri & Fisk, 2007; Jaakkola et al., 2005) and based on preliminary research, since NT has a low density and a necessity for water, it was not possible to maintain a constant amount of preparation water without affecting the consistency and workability of the fresh material. In order to determine the standard consistency of the paste, the Tetmayer probe was chosen as a constant parameter and the mixing water was determined for each individual cement/TiO_2 nanoparticles ratio. The mix design ratio is presented in Figure 2, with a water/cement ratio ranging of 0.45-0.5.

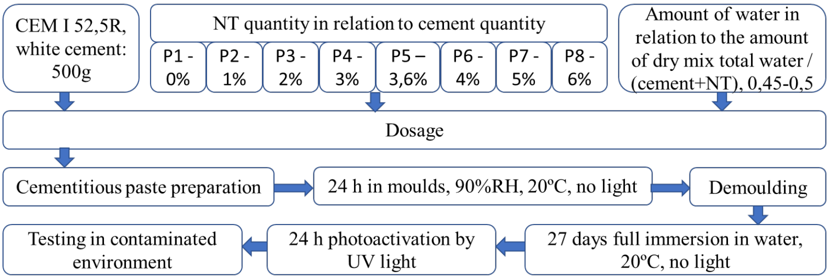

Figure 2. Methodology for the production of the test specimens

Cementitious composite specimens, made in the form of 17.4 mm diameter discs and 24 mm x 30 mm plates respectively, were photoactivated by holding them for 24 hours under UV light using a light source within the range of 400-315 nm UVA band. The lights were displaced at a distance of 10 cm above the specimen surface, resulting in a light flux intensity of 860 lux.

For each contaminating microorganism (mould/bacteria) an experimental stand was constructed to eliminate the risk of cross-contamination. For each case, the repeatability of the results was demonstrated by repeating the tests for at least 3 similar specimens.

The final result is expressed as the average of the individual results. The contamination material used consisted of pure cultures of *Penicillium notatum* (Fag19002) and *Aspergillus niger* (FAg18003), obtained from USAMV Cluj-Napoca, respectively, *Streptococcus pyogenes* (ATCC 19615), *Pseudomonas aeruginosa* (ATCC 27853), *Escherichia coli* (ATCC 25922) and *Staphylococcus aureus* (ATCC 25923) commonly used in laboratory medicine practice. Exposure to contaminants was affected by applying solutions prepared from mold/bacterial reference cultures and introducing 2 colonies (2 loops of 1μl) biological material into 1 ml saline.

Since there is no generally accepted standard of analysis for evaluating the behaviour of cementitious composites in the presence of mould/bacteria, the antibiogram method was taken as the starting point for testing. This method is a common method, mainly used in medicine. Consequently, the test specimens were made, taking as indicative sizes the samples used in laboratory medical practice (Hernandez-Carnerero et al., 2021).

Petri dishes, φ 90 mm, were prepared for each case analysed, in which nutrient substrate was placed to grow bacterial cultures (agar for *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococus aureus*, respectively blood agar for *Streptococcus pyogenes*), or mould cultures (Potato Dextrose Agar - PDA, 39 g/l) which were also sterilised under UV light. In each Petri dish the nutrient substrate was contaminated uniformly over the entire surface with 1 ml of the solution prepared as described above. Then, the light-activated cementitious composite specimen was placed centrally and 0.5 ml of biological material - mould/bacteria suspension - was applied directly to the surface of the specimen, after which the whole system was closed and isolated. For each type of mould or bacteria used samples were produced and, subsequently, control samples (P0). The control sample was considered as the sample for demonstrating the viability of the mould/bacteria spores in the suspensions used, following the development of the culture, which was also confirmed by rapid and intense growth.

The growth systems prepared for testing were placed under laboratory conditions at (30±2)°C, constant temperature and (55±2)% relative humidity. The systems were examined visually and microscopically, at regular intervals, for signs of growth/development of biological material (colonies) and the existence/development of the inhibition halo was observed. Quantification of the resistance of cementitious composites to the action of microorganisms was achieved by identifying the existence and measuring the inhibition halo in the case of specimens exposed to a mould-contaminated environment, and by assessing the microbiological load of the system, respectively, according to STAS 12718/1989 in the case of specimens exposed to the action of bacteria. The degree of development of bacterial material in the system was recorded in agreement with STAS 12718/1989 where the following classes are specified: Class 0(-) indicating no growth (sterile); Class 1(+) indicating 1-10 colonies of microorganisms; Class 2(++) indicating over 10 colonies of micro-organisms; Class 3(+++) indicating areas with confluent colonies and Class 4(++++) indicating growth over the entire area.

The entire experimental testing process, i.e. preparation of the cementitious composite with/without the addition of NT, production of test specimens (casting in moulds, demoulding after 24 h, storage for 27 days in water for maturation), 24 h UV photoactivation, creation of a contaminated environment system in Petri dishes (creation of specific substrate for mould or bacteria growth, soaking with solution containing contaminating microorganism, placing photoactivated cementitious composite test tube, applying solution containing contaminating microorganism on the surface of the test tube, closing and sealing the system), were carried out once for each test tube in the test batch. As specified, for each cementitious composite and for each type of microorganism (2 types of mould and 4 types of bacteria) three test specimens were made. Therefore, the test batch was composed of: 8 types of cementitious composite x 6 types of contaminant medium x 3 test specimens for each situation, i.e. 144 test specimens, each of them contained in an individual, closed, sealed test system (Petri dish). After sealing the individual test system, no additional photoactivation of the specimens in the cementitious composite was performed and the contaminant medium was not altered by enrichment with additional volumes of solution containing mould spores or bacteria. For the identification and measurement of the inhibition halo and for taking the example photographs, the individual, closed, sealed system was not opened, as these operations may have been performed through the transparency of the Petri dish lid. This mode of operation allowed the same specimen to be followed over time, in the same contaminant environment, without inducing possible elements of additional variation. Also, the monitoring of the size of the halo of indifference was carried out each time by the same operator, with the same calibrated measuring instrument. Therefore, it can be appreciated that the uncertainty of measurement remained constant throughout the experimental test, for all the cases analysed.

The durability of the biocidal effect was examined by analysing the maintenance of the inhibition halo for 7 days under constant temperature and humidity conditions and natural lighting (natural day-night cycles), without intervening with a new dose of UV radiation.

Additionally, in order to compare the production cost of the cementitious composites with NT with that of the control cement composite, based on the raw material mixture, the cost/m^3 was calculated. Based on this cost price, it was assumed that panels, with dimensions 50 cm x 50 cm x 2 cm, are made of concrete with NT content, class C20/25. These panels will be used for wall cladding of a building. In this hypothesis, it was calculated how much the cost of making the coating would increases for the use of cementitious composite with the addition of NT, compared to the situation of using a classic concrete. For testing to demonstrate the biocidal effect of NT under laboratory conditions, a UV photoactivation plant was used. Given the intended use of these materials, i.e. outside buildings, this photoactivation will take place naturally, either from sunlight. If these materials will be used inside buildings, literature (Khannyra et al., 2022; Machida et al., 2005; Kühn et al., 2003; Matsunaga et al., 1988) indicates that indoor light sources such as neon bulbs, for example, or natural lunation incident on the cement surface during the period of ventilation of spaces by opening windows, provide sufficient light radiation to achieve this photoactivation process. Therefore, the cost of electricity used by the photoactivation system in the laboratory was not included in the calculated cost. Furthermore, the literature (Khannyra et al., 2022; Machida et al., 2005; Kühn et al., 2003; Matsunaga et al., 1988) indicates that, in cementitious composites, so, in the present SiO_2, NT photoactivation, once performed under UV, is kept active for several days without the need for a new UV dose.

RESULTS AND DISCUSSIONS

The results of the experimental investigations, as shown in Figure 3 to Figure 8, showed a number of aspects proving the biocidal ability of NT-containing cementitious composites.

In the case of exposure of the cementitious composite in an environment contaminated with *Penicillium notatum*, Figure 3a). the existence of the inhibition halo is observed in all specimens of cementitious composite material, including the control sample (P1-0% NT). However, with regard to the test system carried out with the control sample, a reduced size of the inhibition halo is identified and, after 3 days of exposure, its disappearance.

Regarding the behaviour of the photoactivated NT-containing cementitious composite material (P2-P8) in *Penicillium notatum*-contaminated environment, the appearance and maintenance of the inhibition halo throughout the test is identified, even if, over time, this inhibition halo undergoes reductions in diameter, which means a reduction in the inhibition power of the biological film development. After 4 days of testing, it can be said that there is a tendency for the phenomenon to stabilise, from a kinetic point of view (Figure 3a), since the decrease in the diameter of the inhibition halo is much smaller between two consecutive days (measurements), compared to the situation during the first 3 days of testing.

In the case of exposure of the cementitious composite in an environment contaminated with *Aspergillus niger*, Figure 3b) the existence of the inhibition halo is observed in all specimens of cementitious composite material, including the control sample (P1-0% NT).

The maintenance of the inhibition halo, in the case of this mould species, occurs during the first 4 days of testing in all specimens, including the control specimen, after which its disappearance is observed both for the control and for the cement composite specimens prepared with the addition of 1% NT and 2% NT. Even in the case of the 3% NT cement composite, the mould film develops on the nutrient substrate, covering it completely after the 5th day of testing, but without any signs of mould growth on the surface of the cement specimen. Also, similarly to the behaviour of specimens exposed to *Penicillium notatum* contaminated medium, a tendency of stabilization of the inhibition halo diameter is observed in the last 3 days of testing, which would suggest a stabilization of the phenomenon from a kinetic point of view.

At the same time, by comparing the results presented in Figure 3a) and 3b), it can be said that *Aspergillus niger* species shows a higher aggressiveness than *Penicillium notatum* species. Both were based on the inhibition diameters values and as a result of the ability of this species to grow even when there are composites with 1%, 2% and even 3% NT in the system.

It is therefore considered that, in the case of these mould species, frequently encountered in everyday life, good protection could be obtained by using quantities of at least 3% NT as an addition to the cementitious composite, in relation to the quantity of cement, provided, of course, that a good cost/benefit ratio is maintained. Based on the calculation made by the simplified methodology, presented above, under the current price conditions, it can be said that the costs of cladding with concrete panels increase by 6-20 euro/m^2 for the use of a quantity of 1-3% NT in the cementitious composite, respectively by over 25 euro/m^2 if the amount of NT used is at least 4% (relative to the quantity of cement). The frequency and complexity of decontamination, washing, maintenance, etc. of surfaces will of course vary from case to case, depending on the characteristics of the construction, location, intended use, etc. However, it is considered that reducing the frequency with which these maintenance operations are required will result in a cost/benefit balance in favour of the use of cementitious composites with added NT. Despite this increase in the cost of the initial investment, in the case of using NT-enhanced material, as a result of biocidal capacity, the costs of washing, sanitizing and surface maintenance will decrease. Moreover, it is appreciated that thus, indirectly, the impact on the health of the population will improve, so that possible treatment costs in the medical system will be reduced. No signs of mould growth were observed on the surface of the composite specimens for any of the species used as biological aggressors (*Penicillium notatum*/*Aspergillus niger*).

Significant examples in terms of inhibition halo evidence are shown in Figure 9a) and 9b) for for cases of exposure to mold, respectively, Figure 9c) for the case of exposure to the *Escherichia coli* bacteria.

Microscopic analysis revealed, for all test systems in which the specimen was made of cementitious composite with NT, 3 circular areas of contamination and growth of biological material (Figure 10 and Figure 11). In the immediate vicinity of the specimen, the inhibition halo is formed, with variable diameter (D) depending on the amount of NT in the composite and the type of contaminant (mould/bacteria).

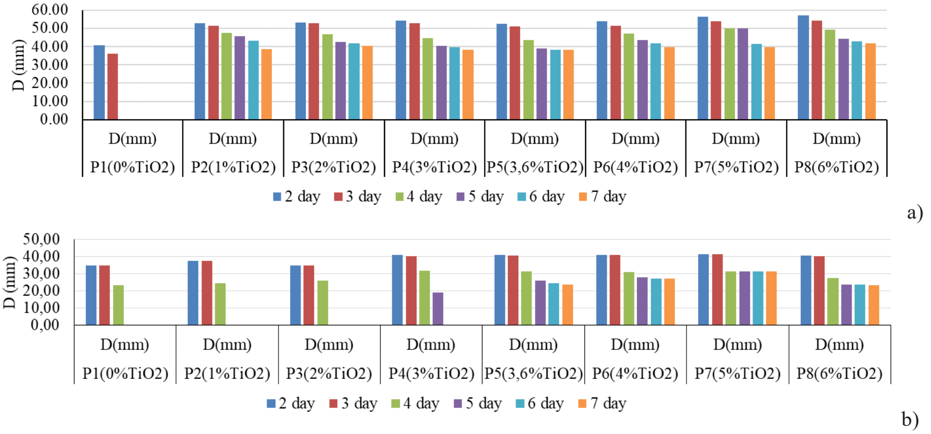

Figure 3. Variation of inhibition halo diameter during 7 days of testing for specimens exposed to *Penicillium notatum* (a) and *Aspergillus niger* (b) contaminated medium

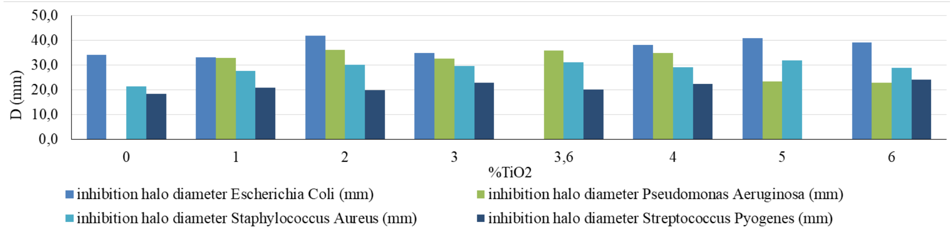

Figure 4. Inhibition halo diameter for specimens exposed 2 days in medium contaminated with *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*

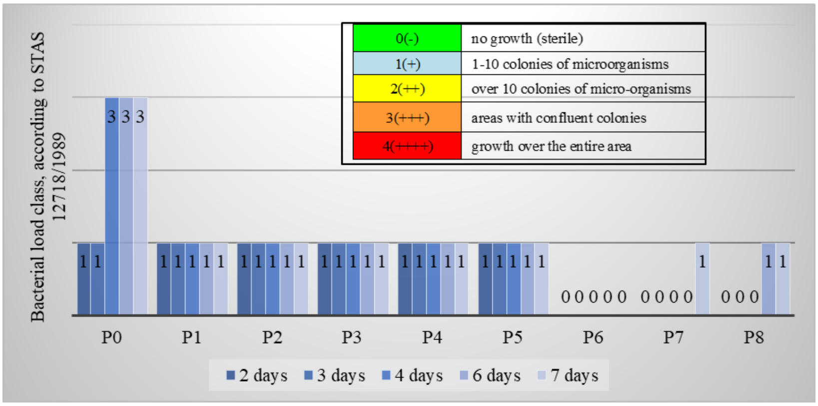

Figure 5. The degree of development of bacterial material (Class acording to STAS 12718/1989) in case of environment contaminated with *Escherichia coli*

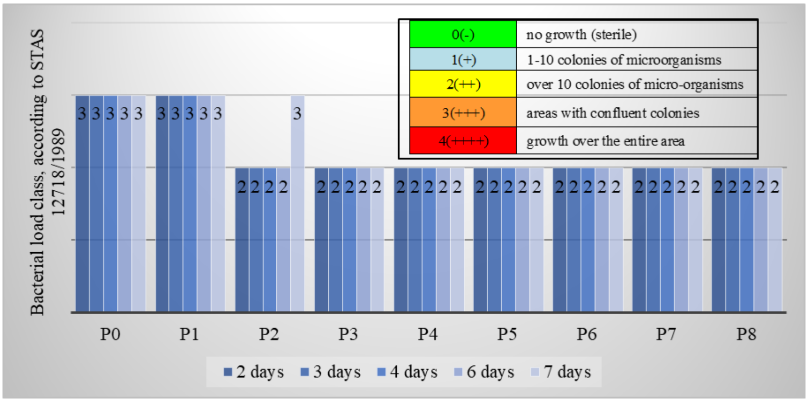

Figure 6. The degree of development of bacterial material (Class acording to STAS 12718/1989) in case of environment contaminated with *Pseudomonas aeruginosa*

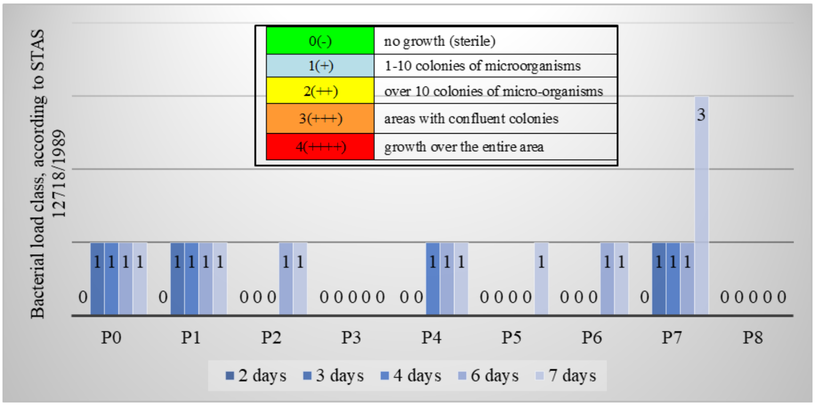

Figure 7. The degree of development of bacterial material (Class acording to STAS 12718/1989) in case of environment contaminated with *Staphylococus aureus*

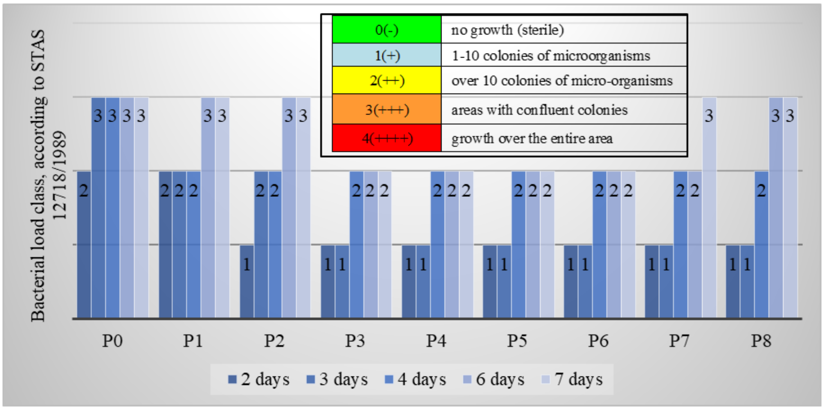

Figure 8. The degree of development of bacterial material (Class acording to STAS 12718/1989) in case of environment contaminated with *Streptococus pyogenes*

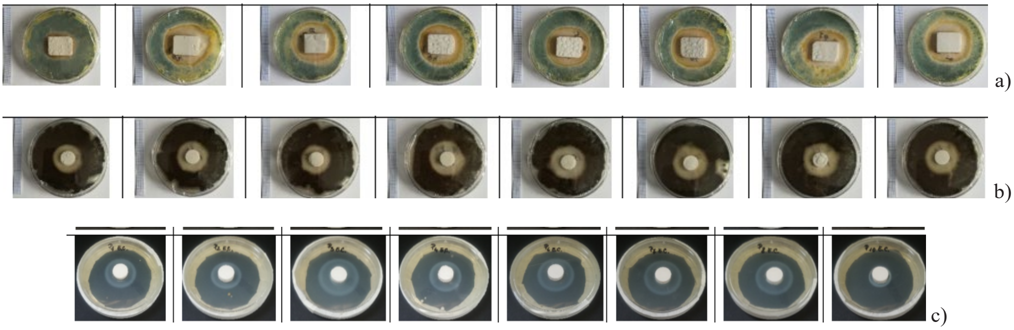

Figure 9. Evidence of inhibition halo - example for sample exposed 3 days in medium contaminated with *Penicillium notatum* (a), *Aspergillus niger* (b) *Escherichia Coli* (c) (P1 - P8, from left to right)

The inhibition halo is characterized, according to STAS 12718/1989, corresponding to a growth of maximum 1-10 colonies, or "sterile". Subsequently, a transition zone is identified in which biological growth begins to intensify, reaching a maximum of intense growth, in which independent units of biological material can no longer be identified and reach confluence.

As regards the behaviour of the photoactivated NT-containing cementitious composite material (P2-P8) in a bacterially contaminated environment, some similarities and some differences can be observed compared to the behaviour in the presence of moulds. Thus, the appearance of inhibition halos is identified (Figure 4), which are much smaller in diameter than in the cases of the two mould species, but remain constant throughout the test.

Microscopic analysis shows the appearance of bacterial colonies on the surface of the nutrient substrate, but not on the surface of the cementitious specimen. As shown in Figures 5-8, the biological load was quantified for each test system (Petri dish with nutrient substrate, with cementitious composite specimen and with biological contaminant material) separately. Each type of bacteria has a different degree of aggressiveness and a different strength of resistance and growth in the presence of the control or NT-enriched cementitious composite. Thus, a graded classification of bacterial aggressiveness can be appreciated, with the most aggressive behaviour exhibited by *Pseudomonas aeruginosa* bacteria and the least aggressive by *Staphylococus aureus* and *Escherichia coli.*

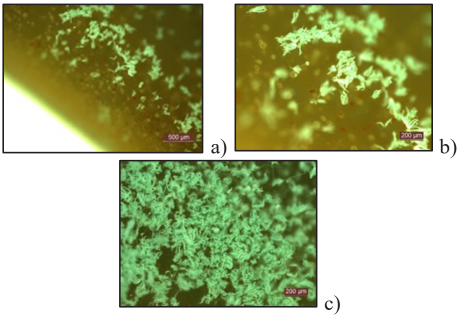

Figure 10. Sample captures for microscopic analysis in which the following can be identified: a). inhibition halo; b). transition zone; c). zone of intense growth - sample exposed 7 days in *Penicillium notatum* contaminated medium

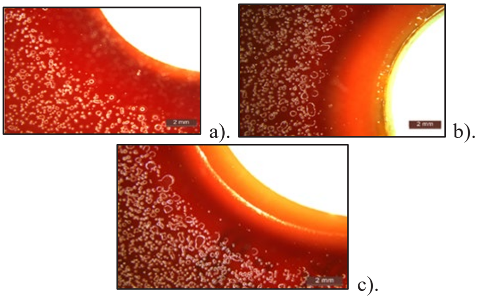

Figure 11. Sample captures for microscopic analysis in which the following can be identified a) inhibition halo; b) transition zone; c) zone of vigorous growth - sample exposed 7 days in *Streptococcus pyogenes* contaminated medium

Analysing the evolution of the biological load in the system during the 7 days of analysis, Figures 5-8, together with the fact that the inhibition halo, although small, is also maintained throughout the evaluation period, it can be appreciated that the biocidal effect is maintained over time and that an amount of min. 1% NT, in relation to the amount of cement, as an addition to the cementitious mixtures, is sufficient. However, if this range of concentration of photoreactive material (NT) were to be analysed in conjunction with the behaviour against mould aggressiveness, it is estimated that the minimum NT required would be 3%, relative to the amount of cement.

CONCLUSIONS

The aim of the work was to investigate the ability of TiO_2 nanoparticle-enriched photoactivated UV-enriched cementitious composites to reduce the risk of mould and bacteria growth on building surfaces. Thus, eight cementitious mixtures were designed, based on white cement, to which TiO_2 nanoparticles were added in an amount of 0-6% of the cement. For each of these situations, test specimens were made and, after UV photoactivation, exposed to media contaminated with *Aspergillus niger*, *Penicillium notatum*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* or *Streptococcus pyogenes* for a period of 7 days.

Based on the above, it can be considered that the biocidal effect induced by the addition of nanoparticles in the composite cement matrix under UV photoactivation is manifested for all cases analysed. However, the effectiveness of this effect is influenced by the type of contaminant and the species to which it belongs. Also, this effect of increasing the resistance of cementitious composite materials to the action of microorganisms is influenced by the amount of nanoparticles used as additive. Although in the case of bacteria an addition of 1% NT would be sufficient, as the inhibition haloes would be maintained throughout the evaluation, in the case of mould species, a minimum of 3% NT would be required, relative to the amount of cement.

Among the bacteria used as contaminants, *Pseudomonas aeruginosa* was found to be more resistant and aggressive, *Staphylococcus aureus* and *Escherichia coli* were found to be less resistant in the presence of NT-added cementitious composites, and *Aspergillus niger* was found to be more aggressive than *Penicillium notatum*.

In terms of the durability of this effect over time, it was found that, in the absence of other influencing factors, under constant temperature conditions and under daylight exposure conditions corresponding to day-night cycles, the growth of microorganism films is inhibited without the need for additional surface photoactivation over and above the initial one.

The experimental results obtained are encouraging arguments for further research in this area. At this stage of the research, the number of experimentally obtained data is insufficient to start a statistical analysis, which is one of the directions for further research.

Also, the encouraging experimental results lead to a new research direction, namely a cost/benefit analysis applied to the concrete case of an existing building for which it is proposed to finish the exterior with cladding panels based on cementitious composite with added NT, under specific climatic and environmental contaminant exposure conditions.

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