DEVELOPMENT OF CERAMIC TILES WITH VIRUCIDAL PROPERTIES

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1. INTRODUCTION

Up until now, the development of biocidal ceramic tiles has mainly focused on obtaining surfaces with bactericidal properties. However, the recent health crisis caused by the worldwide spread of the SARS-CoV-2 virus has led to an increase in demand for products capable of creating safe environments and providing protection against such viral pathogens [1][2].

Bacteria are prokaryotic micro-organisms of just a few micrometres in size, whereas viruses are sub-microscopic infectious agents that are not considered living organisms and only replicate within living cells. The different infection and proliferation mechanisms of the two types of pathogens means that any action directed at creating antimicrobial surfaces has to be specific for each type of micro-organism [1][3].

The VIRUCER project aims to develop ceramic surfaces with virucidal activity by first studying different virucidal agents such as copper, silver and titanium dioxide. In addition, traditional and digital application methods have been assessed. This paper specifically explains the development of titanium dioxide (TiO_2) with photocatalytic effect in a traditional application.

TiO_2 has been identified as a potent virucidal alternative to chemical disinfectants, thanks to its broad-spectrum biocidal activity, its long-lasting effect, and its high efficacy in small doses [4]. The biocidal activity of TiO_2 is based on a photocatalytic effect that is activated when it receives ultraviolet (UV) radiation, which generates species with a high oxidising capacity. The generated oxidising species exert a toxic effect on microorganisms in contact with the surface of the photocatalyst, inactivating them and thus preventing their proliferation [5][6]. The sunlight spectrum contains a small amount of ultraviolet light, comprising approximately 5% of the radiation received during the day. However, that is enough to activate a photocatalytic effect, so that in tiles installed outdoors on roofs or façades, the photocatalytic reactions take place at a suitable rate. In the case of tiles fitted indoors, given the low intensity of available UV radiation, the photocatalyst needs to be modified by doping it with other elements to obtain a material that is sufficiently active in the lighting conditions present in indoor spaces [7].

Two of the main characteristics that optimise the photocatalytic property of TiO_2 are the anatase crystalline phase content and particle size in the nanometric range. This is why a nanostructured coating of TiO_2 is generally used when applied on surfaces with that purpose in mind. In the case of ceramic tiles, as their manufacture involves heat treatment at more than 1000°C, developing permanent biocidal properties calls for a study of the most suitable method of incorporating TiO_2 onto the surface in order to obtain a sufficiently active and durable product validated by the relevant regulations [8][9].

Our research has investigated the development of virucidal ceramic tiles through the application of an active TiO_2 coating in indoor environments. For that purpose, two coating systems have been studied, which allow the nanoparticles of the photocatalyst to be anchored to the ceramic surface by using a low-temperature heat treatment in one case, and by drying in the other.

2. EXPERIMENTAL

In this study, ceramic tiles have been developed with virucidal capabilities based on a photocatalytic effect. To do so, a suspension of nitrogen-doped TiO_2 (TiO_2-N) nanoparticles that is active in visible light was used [10]. The surfaces were prepared by applying the photocatalytic suspension to an industrially fired ceramic tile intended for use as a wall cladding. To this end, the method for anchoring the nanoparticles to the most suitable surface was studied using an aqueous suspension of a fusible glass and a suspension based on SiO_2 nanoparticles as the intermediate layer.

First, the anchoring of TiO_2 nanoparticles to the ceramic surface was investigated, using an aqueous suspension of a fusible glass. For that purpose, the glass suspension was applied by means of an automatic adjustable speed applicator with a layer thickness of 30 μm on fired ceramic pieces, and the TiO_2-N suspension was then sprayed at a laydown of 60 g/m^2.

The coated pieces were heat treated in an electric kiln at four maximum temperatures of 500, 550, 600 and 650ºC (TV-500, TV-550, TV-600 and TV-650). The photocatalytic properties of the pieces obtained were evaluated by monitoring the variation in concentration of a 5ppm aqueous solution of Rhodamine B (RB) when exposed to UV radiation in contact with the surface of the coated tiles. The RB solution was exposed to radiation in an insolation chamber with a lamp emitting UV radiation at a UVA radiation intensity of 10 W/m^2. The absorbance required to obtain concentration of the RB solutions was determined using a visible spectrophotometer. The influence of photolysis on the decrease in concentration of the compound was determined by testing the uncoated specimen (TR) and a soda-lime glass in parallel to the coated tiles.

Secondly, development of the virucidal surfaces was studied using an aqueous suspension based on SiO_2 nanoparticles (primer) as an intermediate layer. To obtain the surfaces, the SiO_2 primer (6 g/m^2) and the photocatalytic TiO_2-N suspension (60 g/m^2) were sprayed successively on the ceramic piece. The coated surface was dried at a temperature of 50ºC. The functional properties on the resulting surface (TS1) were evaluated by determining its photocatalytic activity with RB following the method indicated above. In addition, the microstructure of the coating was analysed using microscopy techniques. For that purpose, a fresh fracture specimen of the coated tiles was taken, observed, photographed and analysed in cross-section with a field emission scanning electron microscope (SEM) fitted with an energy dispersive X-ray microanalysis (EDX) system.

Finally, surface virucidal capability was determined in accordance with ISO 18061:2014, which describes the test method for construction products with photocatalytic materials incorporated into the mass of the material or with photocatalytic coatings applied onto the surface [11]. The method described in the standard validated the surface's virucidal activity by quantifying the reduction in bacteriophage Qbeta infectivity after exposure to UV light. The UV radiation intensity used in the tests was only 0.25 mW/cm^2, which is equivalent to natural light exposure in an indoor space behind a window. The bacteriophage Qbeta is a type of virus that exclusively infects bacteria, not animals or humans, and its behaviour serves as a model simulant of Influenza viruses. In this test, 6 replicates of the sample with the photocatalytic material were inoculated with a bacteriophage Qbeta suspension of known titre and exposed to UV radiation for a period of 8 hours. The titre of the bacteriophage on the pieces was determined by counting plaque-forming units (PFUs). For this purpose, the bacteriophage was recovered by washing the pieces and the resulting wash solutions were mixed with suspensions of *Escherichia coli*, a bacterium sensitive to bacteriophage Q-beta. Mixtures of the test solutions and the recipient bacteria were seeded on agar plates and incubated to obtain plaque-forming unit counts. The bacteriophage titre (PFU) obtained from the pieces irradiated with photocatalytic antiviral material was compared with that obtained from the uncoated tiles used as control, and with that of the treated and untreated samples with photocatalytic material kept in the dark for the same period of time, and the photocatalytic antiviral activity with UV irradiation was calculated.

The results of the test are expressed as viral lethality, which represents in percentage terms the inactivation of microorganisms attributable only to the photocatalytic effect of the sample, eliminating both the reduction that occurs in the control tile with no photocatalyst exposed to radiation and that which occurs when the photocatalytic sample remains in the dark.

The influence of the applied amount of TiO_2-N on surface activity was studied in order to determine optimal conditions of use. To this end, pieces were coated with the same SiO_2 suspension laydown but with the TiO_2-N suspension laydown reduced to 30 g/m^2. The resulting pieces (TS2) were characterised by determining their photocatalytic properties and their virucidal activity using the methods described above.

Finally, a wear test was carried out to evaluate the durability of the surfaces developed under indoor conditions. For this purpose, the SiO_2 suspension and the TiO_2-N coating were applied to the tiles with laydowns of 6 and 40 g/m^2, respectively. The wear test was carried out using the accelerated wear method proposed by C.J. Strautins [12] to assess changes in flooring slip resistance. This method is based on the Gardco washability and wear testing device used in the paint industry, where a horizontally moving linear slider drags an abrasive element over the floor surface, alternating the direction of travel. Given the deformability of the abrasive pad, this method generates surface abrasion and constitutes an alternative way of simulating actual wear [13]. Considering that the intended use of the surfaces developed in this project is for wall tiles, the tests were conducted by subjecting the surface to 100 cycles of slider displacement using water and a cloth as abrasive element.

3. RESULTS AND DISCUSSION

3.1. DEVELOPMENT OF SURFACES WITH FUSIBLE GLASS

The ceramic surfaces with the TiO_2-N coating using glass as anchoring layer were prepared according to the method described in Section 2, which produced test specimens fired at 500, 550, 600 and 650ºC. After firing, it was observed that in samples TV-500 and TV-550, sintering of the glass had not taken place and, as a result, the surface had a powdery appearance and the coating peeled off easily.

The surfaces on which the coating had been successfully anchored (TV-600 and TV-650) were characterised to determine their photocatalytic activity and confirm the functionality provided by the coating and the effect of thermal treatment on it. Test specimen photocatalytic activity was assessed by monitoring the degradation of an aqueous solution of RB in contact with the surface when exposed to UV radiation. Figure 1a shows the variation of RB concentration versus time of exposure to radiation for the TV-600 and TV-650 pieces, and for both an uncoated piece (TR) and the glass used as a blank. The curves obtained indicate a decrease in RB concentration with exposure time in all samples, although it was lower in the glass and TR piece, where it is exclusively due to photolysis of the colourant, than in the coated pieces.

The greater RB degradation obtained in the coated tiles indicates their photocatalytic activity; the sample fired at 650ºC (TV-650) was less effective, possibly due to the fact that at that temperature, part of the TiO_2 was transformed from anatase into rutile (from 600ºC onwards).

In the case of the blank (TR) and the glass, the variation of concentration with time fits a zero-order kinetics with an equation of the type shown below, where k is the reaction rate constant.

$$C = C_0 - k \cdot t (1) \qquad (1)$$

The fit of the experimental data to the above equation provides a rate constant of photolytic degradation of the RB (produced by the radiation itself) (Table 1).

Sample	C_0 (ppm)	k .10^2 (ppm/h)	r^2
TR	4.6	69.7	0.979
Glass	4.6	70.0	0.991

Table 1. *Fit parameters obtained to the zero-order kinetic equation for the RB solution of the uncoated specimen (TR) and of the glass specimen.*

The photocatalytic degradation of RB follows an equation that corresponds to a pseudo-first order kinetics [14].

$$-\frac{dC}{dt} = k' \cdot C \xrightarrow{\text{integrating}} ln\left(\frac{C_0}{C}\right) = k' \cdot t \qquad (2)$$

Plotting the data corresponding to $\ln(C_0/C)$ versus time produces a straight line (Figure 1b), the slope of which is the rate constant k' or photocatalytic activity constant. By way of comparison and merely as a reference with respect to the coated pieces, the line obtained from the concentration values of the TR and glass samples is also included in the graph. Table 2 shows the photocatalytic activity constants calculated by fitting the data to the kinetic equation. The values obtained confirm the higher activity of the TV-600 piece and the decline in photocatalytic efficiency with increasing firing temperature in the TV-650 piece.

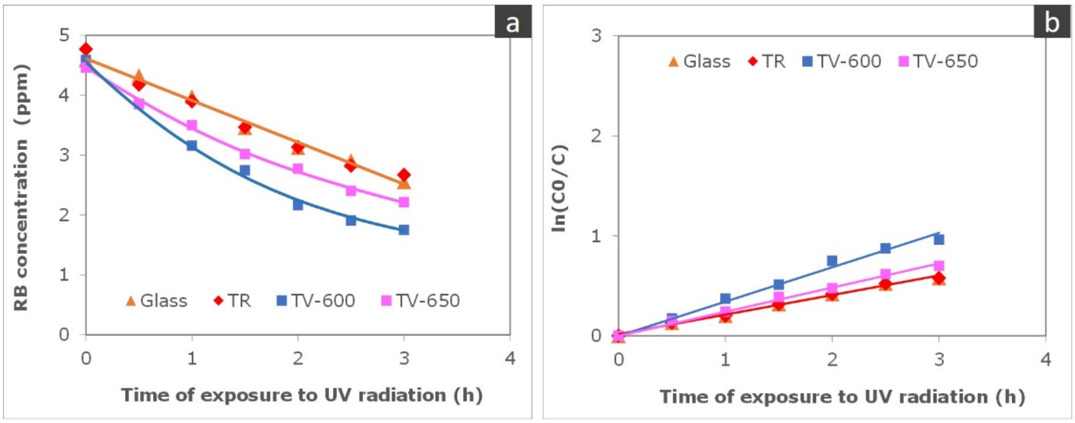

Figure 1 a) *Variation of RB concentration, b) Variation of ln (C_0/C) with time of exposure to UV radiation obtained for the TV-600, TV-650, TR pieces and the glass.*

Sample	k' 10^2 (h^{-1})	r^2
TV-600	34	0.996
TV-650	24	0.998

Table 2. *Photocatalytic activity constant and linear regression coefficients of the kinetic fit obtained for the TV-600 and TV-650 pieces.*

The results show that, with the tested suspension of fusible glass, the optimum temperature for obtaining the new double-layer coating is 600ºC. At lower temperatures the intermediate coating does not form a vitreous coat and does not anchor the nanoparticles, while at higher temperatures, a reduction in photocatalytic efficiency occurs, possibly as a result of the transformation of TiO_2 from anatase into rutile [9][15].

3.2. DEVELOPMENT OF SURFACES WITH AN INTERMEDIATE SIO_2 COATING

In order to avoid the temperature of the thermal after-treatment affecting photocatalytic efficiency, development of the surfaces using an aqueous suspension based on SiO_2 nanoparticles was studied, which, once the coating has been applied and dried, allows sufficient adhesion of the TiO_2-N nanoparticles to be achieved without any need for additional thermal treatment.

The piece was coated following the method detailed in Section 2, depositing a 60 g/m^2 laydown of the photocatalytic suspension on the previously applied intermediate coating, yielding the workpiece referenced TS1.

The photocatalytic activity of the TS1 piece was evaluated using the RB degradation method indicated above. Figure 2a shows the decrease in RB concentration seen in the solution in contact with the TS1 piece compared with that of the uncoated specimen (TR) and that of the glass used as blank. The significant degradation of the colourant obtained for the TS1 sample compared with that of the glass and that of the TR tile evidences the photocatalytic activity of the developed surface.

The $\ln(C_0/C)$ data for the TS1 piece have been plotted in Figure 2b. The fit of the experimental data to the kinetic equation (2) yielded the surface photocatalytic activity constant, resulting in a value of 0.75 h^{-1} (Table 3). This constant is clearly higher than the 0.34 h^{-1} obtained for the TV-600 sample (Table 2) prepared with the same TiO_2-N laydown, which shows how the heat treatment influences the photocatalytic efficiency of the developed surface.

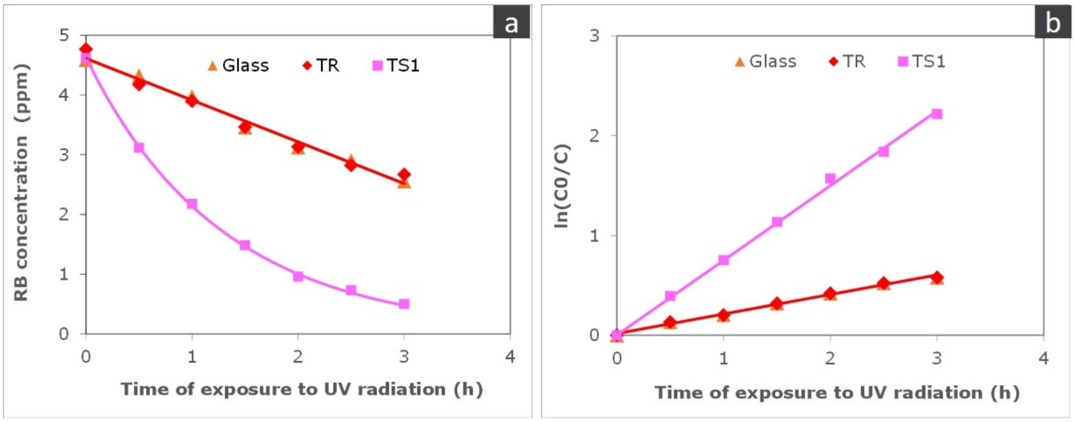

Figure 2. a) *Variation of RB concentration, (b) Variation of ln (C_0/C) with time of exposure to UV for the TS1 and TR pieces and the glass.*

Sample	k' 10^2 (h^{-1})	r^2
TS1	75	0.999

Table 3. *Photocatalytic activity constant and linear regression coefficients of the kinetic fit obtained for piece TS1.*

In order to characterise the microstructure of the experimental coating, cross-sectional scanning electron microscopy (SEM) analysis of the piece was carried out. The following figure shows the micrographs obtained at different magnification levels and the two layers that make up the coating applied to the surface of the fired piece. EDX analysis of the layers, marked as zones 1 and 2 in Figure 3b, detected a higher amount of SiO_2 in the bottom layer (Figure 3c) and of TiO_2 in the top layer Figure 3d). The different thickness of the layers is logical given that the TiO_2-N suspension laydown (60 g/m^2) is 10 times higher than that of the SiO_2 (6 g/m^2).

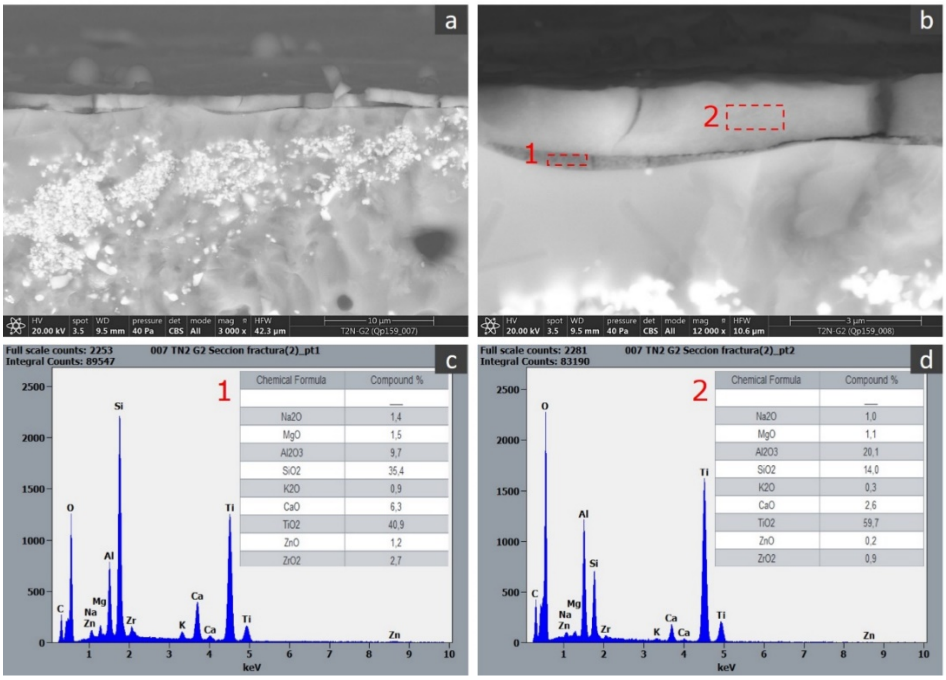

Figure 3. *SEM micrograph of the TS1 sample cross-section at different magnifications (a and b). EDX analysis (% by weight) of the highlighted particles and area (c and d).*

Validation of virucidal activity was performed in accordance with the methodology described in the ISO 18061:2014 standard, which gives a specific test method for photocatalytic surfaces in construction products such as ceramic tiles. The results obtained showed the virucidal activity of the TS1 surface with a viral lethality of 97% of the inoculated viruses. This parameter represents the inactivation of microorganisms attributable only to the photocatalytic effect of the sample and eliminates the reduction achieved both in the uncoated piece (TR) exposed to radiation and when the piece remains in the dark. At this point, it should be noted that the test standard used does not set a viral lethality value at which a surface can be considered virucidal, but rather states that the higher the parameter is, the greater the surface's activity.

STUDY OF THE INFLUENCE OF THE APPLIED TiO_2-N LAYDOWN

In order to test the influence of the applied TiO_2-N coating on the activity of the resulting surfaces, pieces were prepared in accordance with the method described above, reducing photocatalytic suspension laydown by half (30 g/m^2). The functional properties of the resulting piece (TS2) were characterised by determining its photocatalytic and virucidal activity.

Figure 4a shows the curves representing RB degradation versus length of UV radiation exposure time for the TS2 piece, as well as for the uncoated piece (TR) and the glass used as a blank.

The greater decrease in RB concentration in the solution in contact with the TS2 piece reveals the photocatalytic activity of the surface. The fit of the experimental data to the kinetic equation plotted in Figure 4b returned a photocatalytic activity constant for the coating (Table 4) of 0.48 h^{-1}. When the activity of TS2 is compared with that of TS1 and TV-600 (0.75 and 0.34 h^{-1}), it can be seen that the reduced applied TiO_2-N laydown produces lower effectiveness of the surface, although it still displays greater photocatalytic activity than that obtained with the TV-600 prepared with a higher photocatalyst laydown.

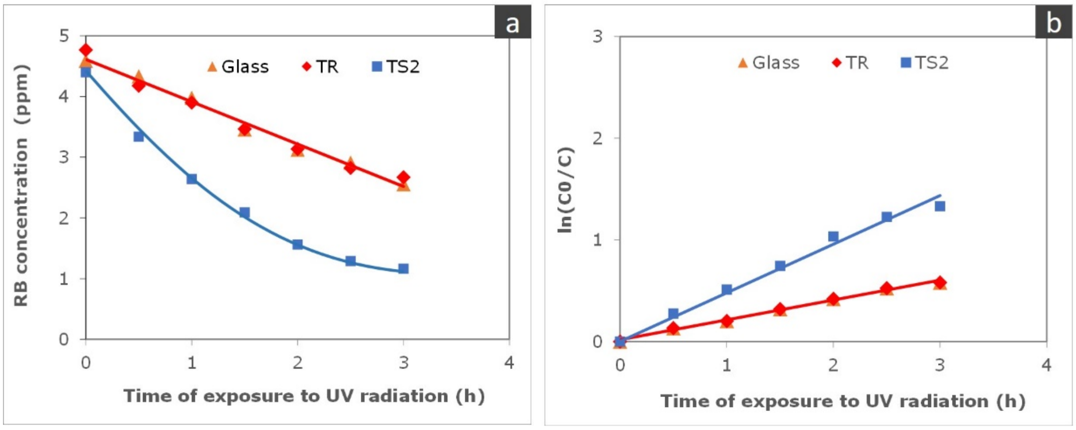

Figure 4. a) *Variation of RB concentration, (b) Variation of ln (C_0/C) with time of exposure to UV radiation for the TS2 and TR pieces and the glass.*

Sample	k' 10^2 (h^{-1})	r^2
TS2	48	0.996

Table 4. *Photocatalytic activity constant and linear regression coefficients of the kinetic fit obtained for the TS2 piece.*

The virucidal activity of workpiece TS2 was determined in accordance with ISO standard 18061:2014, resulting in a viral lethality of 93%. The significant inactivation of the viruses inoculated on the surface shows that, as already observed in the photocatalytic activity test, despite reducing photocatalyst laydown by 50%, the surface continues to display high virucidal capacity.

STUDY OF COATING DURABILITY

Coating durability was studied by simulating wear on the surface under indoor usage conditions with a cloth and water as explained in Section 2. For that purpose, the surfaces were prepared by spraying the TiO_2-N suspension with a laydown of 40 g/m^2 onto the previously applied intermediate SiO_2 coating.

The photocatalytic properties of surface TS3 were evaluated to determine the coating's durability. Figure 5 shows RB degradation with UV exposure time for the piece with the coating before (TS3) and after (TS3 wear) the wear test, compared with that of the TR piece and the glass. The abrasive effect produced on the coating manifests itself in the form of lower RB degradation and a decrease in the photocatalytic activity constant of the piece after wear (Table 5). However, it should be noted that, although a decrease in efficiency is seen, the surface is still active, as shown by the greater RB degradation generated compared with that of the uncoated piece.

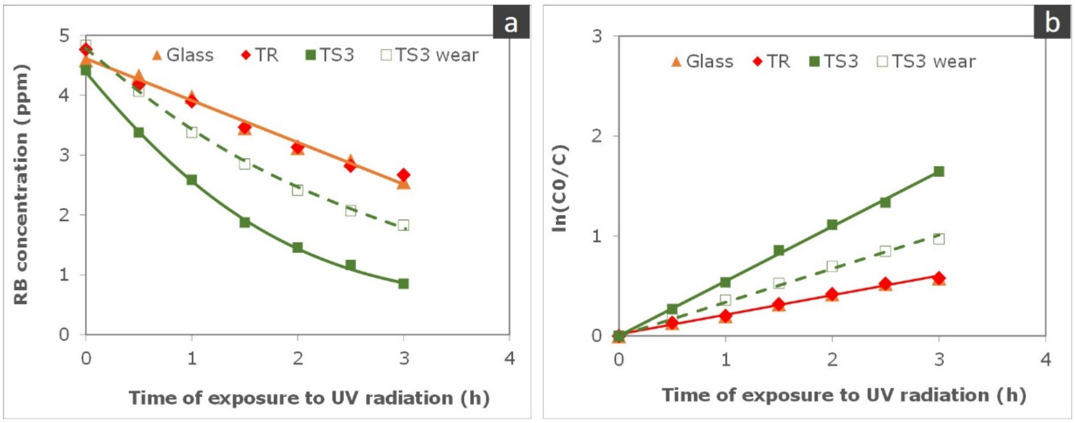

Figure 5. a) *b) Variation of RB concentration, b) Variation of ln (C_0/C) with time of exposure to UV radiation for piece TS3 before and after the wear test, piece TR and the glass.*

Sample	k' 10^2 (h^{-1})	r^2
TS3	55	0.999
TS3 wear	34	0.999

Table 5. *Photocatalytic activity constant and linear regression coefficients of the kinetic fit obtained for piece TS3 before and after the wear test.*

In order to measure the effect of coating wear on the surface's biocidal properties, the virucidal activity of the TS3 surface was determined after subjecting it to the wear test, obtaining a viral lethality percentage of 98% of the inoculated viruses. Therefore, as already observed in the characterisation with the organic colourant, the surface continues to be active even after being subjected to wear by the test method used.

4. CONCLUSIONS

Photocatalytic virucidal ceramic surfaces were developed by applying TiO_2-N coatings to fired wall tiles. The following conclusions can be drawn from the study:

- The application of a fusible glass as an intermediate coating between the ceramic surface and the TiO_2-N coating was studied. With the tested suspension of fusible glass, the optimum temperature to produce the experimental double-layer coating is 600ºC. At lower temperatures, the intermediate coating does not anchor the nanoparticles, while at higher temperatures, there is a marked reduction in photocatalytic efficiency, possibly due to the transformation of TiO_2 from anatase into rutile.
- A second coating system was investigated using a suspension based on SiO_2 nanoparticles which, after the coating is applied and dried, enables the TiO_2-N nanoparticles to adhere sufficiently well without further heat treatment. The surfaces obtained with this system exhibit photocatalytic activity with UV radiation. Microbiological characterisation of the surface under radiation conditions in an indoor environment confirmed its virucidal properties, resulting in 97% viral lethality of inoculated viruses, tested in accordance with the ISO 18061:2014 standard with bacteriophage Q-beta (Influenza surrogate virus).
- A 50% reduction in TiO_2-N laydown on pieces prepared with the intermediate SiO_2 coating reduces viral lethality to 93% but the surface still exhibits high virucidal activity.
- The durability of the surface developed with TiO_2-N and the intermediate SiO_2 coating was studied by performing a test that simulates wear under indoor conditions. Characterisation of the surface after wear resulted in a viral lethality of 98%, confirming its continued virucidal activity.
- The surfaces obtained on the basis of the SiO_2-TiO_2-N system do not require heat treatment to anchor the nanoparticles and are suitable for use in wall claddings in both indoor and outdoor environments.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

[1] J. Rangineni. Post-pandemic emphasis on hygiene–Ceramic tile and test methods. In: Qualicer 2022: XVII World Congress on Ceramic Tile Quality. Castellón: Cámara Oficial de Comercio, Industria y Navegación.

[2] M. Mili, M., V. Hada, T. Mallick, A. Singhwane, A. Tilwari, S. Hashmi, A. Srivastava, S. Sagiri, S. Verma. Advances in Nanoarchitectonics of Antimicrobial Tiles and a Quest for Anti-SARS-CoV-2 Tiles. Journal of Inorganic and Organometallic Polymers and Materials, 32, 3355–3367, 2022.

[3] V. Rodríguez-Gonzalez, S. Obregon, O.A. Patrón-Soberano, C. Terashima, A. Fujishima. An approach to the photocatalytic mechanism in the TiO_2-nanomaterials microorganism interface for the control of infectious processes. Applied Catalysis B: Environmental 270, 2020, 118853.

[4] S. Talebian, G. Wallace, A. Schroeder, F. Stellacci, J. Condeet. Nanotechnology-based disinfectants and sensors for SARS-CoV-2. Nature Nanotechnology 15, (2020) 618-621.

[5] G.L. Guerrini. Photocatalysis and virus. From theory to applications. Journal of Photocatalysis 2, 2021, 25-34.

[6] H.M. Coleman, C.P. Marquis, J.A. Scott, S.S. Chin, R. Amal, Bactericidal effects of titanium dioxide-based photocatalysts, Chem. Eng. J. 113 (2005) 55–63.

[7] R. Fagan, D.E. McCormack, D.D. Dionysiou, S.C. Pillai. A review of solar and visible light active TiO_2 photocatalysis for treating bacteria, cyanotoxins and contaminants of emerging concern. Materials Science in Semiconductor Processing, 42, 2–14, 2016.

[8] J.J. Reinosa, E. Enríquez, V. Fuertes, S. Liu, J. Menéndez, J.F. Fernández. The challenge of antimicrobial glazed ceramic surfaces. Ceramics International, 48, 7393-7404, 2022.

[9] V. La Torre, E. Rambaldi, G. Masi, S. Nici, D. Ghezzi, M. Cappelletti, M.C. Bignozzi, Validation of antibacterial systems for sustainable ceramic tiles. Coatings, 11, 1409, 2021.

[10] COLOROBBIA CONSULTING S.R.L. Nitrogen-doped TiO_2 nanoparticles and the use thereof in photocatalysis. WO2019211787 (A1). 2019-11-07.

[11] ISO 18061:2014. Fine ceramics (advanced ceramics, advanced technical ceramics)— Determination of antiviral activity of semiconducting photocatalytic materials — test method using bacteriophage Q-beta.

[12] C.J. Strautins, Sustainable slip resistance: An opportunity for innovation. In QUALICER 2008: X World Congress on Ceramic Tile, Castellon, Spain.

[13] G. Silva, A. Muñoz, A. Beltrán, R. Domínguez, A.M. López, M. Bañuls. Estudio comparativo de métodos para simular el desgaste en condiciones reales de uso. In Qualicer 2020: XVI World Congress on Ceramic Tile Quality. Castellón: Cámara Oficial de Comercio, Industria y Navegación.

[14] A.R. De Araujo Scharnberg, A.C.D. Loreto, T.B. Wermuth, A.K. Alves, S. Arcaro, P.A.M.D. Santos, A.D.A.L. Rodriguez, Porous ceramic supported TiO_2 nanoparticles: Enhanced photocatalytic activity for Rhodamine B degradation. Boletín de la Sociedad Española de Cerámica y Vidrio, 59, 230–238, 2020.

[15] T. Da Silva Dassoler, E. de Sousa Cordeiro, D. Hotza, A. De Noni Junior. Photocatalytic activity of ceramic tiles coated with titania supported on kaolinite. Open Ceramics, 13, 100331, 2023.