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1 **The role of roughness and porosity on the self-cleaning and anti-biofouling efficiency of**  
2 **TiO<sub>2</sub>-Cu and TiO<sub>2</sub>-Ag nanocoatings applied on fired bricks.**

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4

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8 **Keywords:** Porosity, Roughness, fired brick biodeterioration, Titania, Ag and Cu, nano-Coatings

9

10

11 **Abstract**

12 From the advent of nanotechnologies in building constructions, many materials were functionalized to create  
13 composite material with new properties.

14 Titania (TiO<sub>2</sub>) is actually the most promising nanotechnology to create composite materials with self-  
15 cleaning and anti-microbial properties. TiO<sub>2</sub> was able to limit algae adhesion and their growth, even if, in  
16 case of high porous and rough substrata, their inhibitory effect seems to be limited. This way, in this study,  
17 silver and copper nano-particulate enhanced an aqueous nano-titania solution were applied on brick  
18 specimens and their inhibitory effects were tested during accelerated laboratory tests.

19 Extent of biofouling on specimens' surface was assessed by measuring the aesthetical alteration and  
20 correlations between algal growth and key parameters of substrata were discussed.

21 Results confirm the key role of porosity and roughness on the biofouling process on untreated specimens,  
22 and their effect on the photocatalytic power of the tested nano-coatings toward algal adhesion.

23 Results from this study were compared with previous findings in the literature on the same types of  
24 specimens only treated with the same aqueous nano-titania solution. No significant improvements were  
25 detected by the addition of metal nanoparticles.

26 Experimental curves were overlapped to analytical model calculated by Avrami's law, and its validity was  
27 confirmed where latency time could be observed. Whereas no latency time was detected, that is a very fast  
28 adhesion of algal cells occurred, the experimental curves were modelled by using a four parametric logistic  
29 model that was able to describe numerically the biofouling process.

30

## 31    **1. Introduction**

32    The use of nanotechnologies in building construction was rapidly developed from its discovery [1], bringing  
33    to a new generation of functionalized building materials able to respond to new needs from the market.  
34    In the fields of restoration of ancient buildings, and maintenance of new constructions, the use of titanium  
35    dioxide (TiO<sub>2</sub>) finds large applications in components for self-cleaning and air pollution reduction [2–9].  
36    An emerging application of this nanotechnology is the prevention of biodeterioration caused by  
37    microorganisms able to adhere on building's components where ideal conditions of light, temperature and  
38    moisture is present whereas this last one is a needful factor [10]. Green algae and cyanobacteria can be  
39    considered the most abundant colonisers of building façades, and microorganisms can produce aesthetical  
40    alterations like stains or colour variations depending on species.  
41    The formation of biofilm helps to establish other vegetative species like lichens or bryophytes that increase  
42    water retention by substrata. Under these conditions, hydrodynamic of porous media changes [11],  
43    degradation mechanisms accelerate [12–14], and energy efficiency of the building could be reduced.  
44    The use of nano-coatings is currently the new trend in biofouling prevention and many research papers can  
45    be found in the literature [15–31].  
46    Recently, their application was studied for anti-biofouling scope on natural materials like stone [32–34], and  
47    man-made materials like brick [18,26,27,35], concrete [23,24,36] and mortar [17,25,28].  
48    Literature shows anti-biofouling efficiency of nano-particles is strictly related to intrinsic characteristics of  
49    substrata, mainly porosity and roughness [10,35,37–41]. The influence of these parameters on inhibitory  
50    efficiency of TiO<sub>2</sub> was previously studied also on clay brick [26] and TiO<sub>2</sub> was unable to stop algal growth  
51    when it was applied on high porous material with rough surface, like clay brick applied in Cultural Heritage.  
52    In these conditions, porosity helps retention of water and nutrient for algal growth, while roughness favours  
53    the adhesion of algal cells to substrata and the inhibitory effect of TiO<sub>2</sub> is limited [26].  
54    Some studies investigate the possibility of enhancing the photocatalytic power of TiO<sub>2</sub> by the addition of  
55    other metal nanoparticles, meanly silver (Ag) [42–44], and copper (Cu) [45].  
56    A TiO<sub>2</sub>-Ag solution was deposited on titania surface to test sanitation of *Escherichia coli*, and results show  
57    antibacterial properties also under visible light [42]. A sol–gel TiO<sub>2</sub>-based coating with bioactive silver has  
58    been proposed as a promising strategy for controlling in vitro biofilm formation of *Escherichia coli* and

59 *Staphylococcus epidermidis* [43]. Results of this study showed that AgCl–TiO<sub>2</sub> nano-composite coated  
60 surfaces inhibited the development of biofilm over a period of 10 days in accelerated conditions.  
61 These two studies were carried out on neutral substrata, and it is not possible to find the effect of substrata  
62 (i.e. building materials) on the biocide power of nano-coating.  
63 Silver nano-particulate enhanced aqueous silane/siloxane emulsion was applied on mortar surface, and a  
64 significant reduction of biofouling surface coverage and its intensity were observed [44]. The author  
65 provides also information about silver concentration, indeed a concentration above 0.5% (wt) could cause  
66 aesthetical alteration, and water contact angle improvement was negligible against increased material cost  
67 [44]. Thus, a synergism between antimicrobial properties and photo-disinfection properties of TiO<sub>2</sub> was  
68 observed in the literature.  
69 In this study, two nanostructured solutions of TiO<sub>2</sub>-Ag and TiO<sub>2</sub>-Cu were respectively applied on two  
70 different clay brick substrata to investigate their inhibitory efficiency toward algae and cyanobacteria.

71

## 72 **2. Material and methods**

### 73 *2.1. Material preparation and characterization*

74 In order to consider the effect of substrata, two types of specimens were prepared with different total  
75 porosity and roughness.

76 High porous specimens (group A) were moulded in rectangular moulders and left at ambient conditions until  
77 the dry weight was reached. Specimens were then removed from the moulds and fired at about 700°C. This  
78 production method was used because it replicates traditional clay brick production methods used in Cultural  
79 Heritage.

80 Low porous specimens (group N) were produced by modern technique. After mixing, they were extruded  
81 and then fired at about 1200°C. This production process is currently used to produce fired clay elements for  
82 application in building façades and ventilated building façades.

83 Eighteen specimens were prepared for each group with final dimensions equal to 80x80x30 mm<sup>3</sup>.

84 Surface roughness parameters were evaluated according to European standards [46,47] by using a Diavite  
85 DH-5 portable rugosimeter. Arithmetic average (*Ra*), maximum profile peak height (*Rz*) and maximum  
86 height of the profile (*Rmax*) were calculated according to UNI EN ISO 4287:2009 [47]. Each parameter was



obtained by ten measurements on a track of 15mm with a cut-off length of 0.8mm. The first and last values were excluded to limit measurement's noise. Thus, the active track of measurement was equal to 13.4mm. Porous structure (total porosity and porous distribution) were measured onto five N and five A additional samples by a mercury intrusion porosimeter (Micromeritics Autopore III) following the ASTM D4404–10 standard [48].

## 2.2. Nano-coating application

Two types of aqueous TiO<sub>2</sub>-based solutions were studied in this paper. The first TiO<sub>2</sub> solution was doped with silver nanoparticles, while the other one was doped with copper nanoparticles. TiO<sub>2</sub>-Ag nano-powders were composed by TiO<sub>2</sub> and a concentration of silver and copper nanoparticles equal to 1% (molar weight/TiO<sub>2</sub> weight). Concentration of TiO<sub>2</sub>-Cu solution was equal to 1% (weight/TiO<sub>2</sub> weight). Final concentration of aqueous solutions was equal to 1% (weight/volume of water). Thus, 100ml of solution contains 1g of TiO<sub>2</sub> and 0.02g of Ag and 0.01g of Cu, respectively.

These concentrations were chosen to avoid browning of nano-film during UV irradiation, as demonstrated by preliminary tests (not reported in this paper). This phenomenon was also previously shown in the literature with a concentration of Ag equal to 1.48mol% to titania [42].

Both aqueous solutions were manually applied on the specimens' surface by spray coating. An air spray gun with a nozzle of 0.8 mm diameter was connected to an air compressor at a pressure of 7 bar and was used to spray the solutions from a distance of 250 mm. Specimens were then dried at 60°C for 1 h to accelerate the drying process.

For each group (A and N), three specimens were treated with TiO<sub>2</sub>-Ag (AAg and NAg) and TiO<sub>2</sub>-Cu (ACu and NCu) respectively, whereas three specimens remained untreated (ANt and NNt) to be used as references. Colour measurements were made in accordance to UNI-EN 15886 [49] with a portable spectrophotometer (Konica Minolta CM 2600d).

Colour variation between original specimens and treated ones was calculated following equation 1:

$$\Delta E = \sqrt{(L_0^* - L^*)^2 + (a_0^* - a^*)^2 + (b_0^* - b^*)^2} \quad 1)$$

113 where  $L^*_0$ ,  $a^*_0$  and  $b^*_0$ , and  $L^*$ ,  $a^*$  and  $b^*$  are colour coordinates of original specimens and treated ones  
114 respectively.

115

### 116 2.3. Photocatalytic efficiency of nano-coatings

117 Self-cleaning ability of TiO<sub>2</sub> nano-coating was evaluated by considering the degradation of organic dye  
118 (Methylene Blue – MB) following the same methods proposed in the literature [50].

119 Briefly, 0.5ml of MB aqueous solution (MB content: 100 µmol/L) was deposited on an area of 2200 mm<sup>2</sup> on  
120 the surface of brick specimens (80x80x30 mm<sup>3</sup>) by using a syringe, while one specimen for each type  
121 remained untreated, and it was considered as control.

122 UV irradiation was provided by an 8W Blacklight Blue neon (working at 365nm) at a distance of about 15  
123 cm from the specimens' surface. In this way, UV irradiance value was equal to about 10 W/m<sup>2</sup>.

124 Colour values were detected before UV irradiation and after 1, 2, 4 and 26 hours as specified by standard  
125 [51]. The discoloration efficiency ( $R_E$ ) was measured during time by equation 2, and it was expressed as  
126 percentage.

$$R_E (\%) = \frac{|\Delta E_t^* - \Delta E_0^*|}{\Delta E_0^*} \times 100 \quad 2)$$

127

128  $\Delta E_t^*$  in equation 2 is the average colour variation between the measured colour after 1, 2, 4 and 26 hours and  
129 the original surface colour before MB application, and  $\Delta E_0^*$  is the average colour variation between the  
130 measured colour after MB application and the original surface colour.

131

### 132 2.4. Accelerated growth test and biofouling evaluation

133 Biofouling process was simulated into 100x40x53 cm<sup>3</sup> glass chamber whose architecture has been previously  
134 described [26,27,35]. Scheme of apparatus is illustrated in Fig. 1.

135 Broth culture was composed by *Chlorella cf. mirabilis* and *Chroococcidiopsis fissurarum*. The initial  
136 concentration of composed microbial suspension was about 4mg of algal cells in one litre.

137 Temperature and relative humidity (RH) inside the glass chamber were recorded every 5 min over the entire  
138 period of accelerated test by using a remote data logger (Lascar Electronics model EL-USB-2). Plot in Fig. 2  
139 shows climatic conditions inside the chamber near the specimens' position.

140 In order to furnish necessary light for photosynthesis of algal cells, two neon lamps with a light temperature  
141 of 5000 K were inserted in the chamber, while UV radiation for TiO<sub>2</sub> activation was provided by one  
142 Blacklight Blue neon at a distance of about 150mm from the specimens' surface. In this way, nanocoating  
143 was irradiated with an average UV intensity of 8 W/m<sup>2</sup>. The day/night period was equal to 14/10 hours  
144 respectively.

145 Above the samples, a 10 mm diameter PVC rail containing three 2 mm holes for each specimen, was  
146 attached to the rack. The distance from the rails to the sample surface was approximately 30 mm and  
147 designed to allow water to fall approximately 10 mm from the top of the sample.

148 The chamber contained one 500 L/h water pumps attached to both rails using T-connectors. The run/off  
149 cycle of water was 15 min for a duration of 6 h (3 h run and 3 h off).

150 Biofilm causes stain on the substratum both by the presence of extracellular polysaccharides (EPS) on the  
151 surface of biofilm [52], and by the presence of organic colored pigments like chlorophyll a and b  
152 (responsible of green colour) or carotenoids (responsible of orange colour).

153 For this reason, the colour of each specimens was also measured during the accelerated growth test following  
154 the same procedure described in section 2.2.

155 In order to collect data about the extension of algal fouling, the surface of each specimen was periodically  
156 (weekly) digitized by an office scanner. The adopted resolution was 600dpi because it was able to show the  
157 comparison of algal spot (equal to one pixel) with a side of about 40µm. Obtained images were filtered and  
158 binarized to isolate pixels occupied by algae, then colonized area was counted by ImageJ software, and  
159 percentage of coverage was calculated from the total area of each specimen equal to 80x80 mm<sup>2</sup>.

## 160 2.5. Numerical modelling of biofouling

161 In this paper, experimental results were overlapped to analytical curves calculated by the Avrami's law (3)  
162 that shown to be adequate in the literature [53,54], especially in case of biofouling process with sigmoidal  
163 trend.

$$X(t) = 1 - e^{-K(t-t_1)^n} \quad 3)$$

164 where  $t_1$  is the latency time (corresponding to the comparison of the first algal spot),  $K$  is a constant of the  
165 material, and  $n$  is the Avrami's exponent calculated as indicated in equation 4.

$$n = q + 3 \quad 4)$$

166 The  $q$  parameter was derived from general equation of the growth that was linear in time, thus  $q$  can be  
167 assumed equal to one and  $n=4$  consequently.

168 The  $K$  parameter includes other parameters dependent on the material properties, and it can be calculated  
169 from equation 5.

$$K = A k_g k_c^2 \quad 5)$$

170 where  $k_g$  is the rate of the nucleation of new particles,  $k_c$  is the specific growth rate constant, and  $A$  is a  
171 constant calculated by equation 6.

$$A = \frac{2}{(q+1)(q+2)(q+3)} \quad 6)$$

172 In case of specimens covered by algae partially (covered area < 100%), equation 7 was used instead of  
173 equation 3 as previously proposed in the literature [54].

$$X(t) = (1 - e^{-K(t-t_1)^n}) \times S_{\max} \quad 7)$$

174

### 175 **3. Results and discussion**

#### 176 *3.1. Properties of substrata*

177 Table 1 shows results about porosity and roughness of tested specimens. The differences between the two  
178 different substrata are evident. Specimens of group A were characterized by a total porosity of about 37%,  
179 twice than total porosity of specimens of group N. Moreover, average pore diameter of A specimens was  
180 about 0.4μm, while porosity of group N was composed by average pore diameter of about 0.1μm. Thus,  
181 specimens of group A had high porosity composed by low pores with large diameter, while group N was  
182 characterized by many pores with small diameter. This finding was confirmed by values of total pore area,  
183 indeed total pore area of group A was about three times of group N.

184 This last result was important because total pore area controls movements of water at the interface between  
185 material and microorganisms as previously demonstrated [26,35].  
186 Manufacturing methods also influenced morphology of the surface, particularly the roughness. The average  
187 roughness of A specimens was about three times  $R_a$  of group N, while other roughness's parameters ( $R_z$  and  
188  $R_{max}$ ) were about twice in case of A specimens if compared with specimens of group N (Table 1).

189

### 190 3.2. Colour variation after treatment

191 The application of the coatings caused colour variations as indicated in Table 2.  $TiO_2$ -Ag sol caused a  
192 difference in lightness in both A and N specimens; in case of A specimens,  $\Delta L^*$  was twice than N specimens.  
193 The same trend was notable in case of specimens treated with  $TiO_2$ -Cu solution. By looking at  $a^*$  and  $b^*$   
194 coordinates, a higher variation of colour coordinates was visible in N specimens.  
195 Thus, after coating applications, clay bricks showed whitening (higher  $L^*$ ), and they become less red and  
196 more yellow (lower  $a^*$  and  $b^*$ ). Total colour variation ( $\Delta E$ ) was about the same in all specimens.  $\Delta E$  was  
197 greater than the just noticeable difference (JND) by naked eye fixed to 2.3 [55], and it was also a bit greater  
198 than the value accepted for preservative treatments of historical building surfaces fixed to 5 [56].  
199 Colour variation of specimens' surfaces was about the same observed on specimens treated with only  $TiO_2$   
200 solution [50], as expected.

201

202

### 203 3.3. Self-cleaning ability of nano-coatings

204 Fig. 3 shows the self-cleaning efficiency  $R_E$  of tested specimens. Group A shows no efficiency of  
205 nanocoatings, indeed AAg and ACu have the same trend of untreated ANt specimens. At the end of the test  
206 the curves can be considered overlapped. Conversely, N specimens show a different trend. In this last case  
207 untreated specimens reached an efficiency of about 9%, while  $R_E$  of NAg was about 33% and it reached  
208 about 46% in case of NCu specimens. Thus,  $TiO_2$ -based solutions shown a noticeable (three time higher)  
209 self-cleaning ability in case of low porous specimens. Inefficiency of treatments in case of A specimens can

210 be ascribable to high porosity and roughness of substrata of course [10,35,37–40]. Secondly, it can be  
211 associated to micro-cracks on the surface of treatment that limits the photocatalytic efficiency of nano-  
212 coating [50].

213

214

215

### 3.4. Biofouling evaluation and discussion

By considering the colour variation, no significant difference exists between untreated A specimens and treated ones (Fig. 4 a). In case of low porous specimens N (Fig. 4 b),  $\Delta E$  of untreated specimens was about twice than  $\Delta E$  of treated ones at the end of the accelerated test.

No significant differences were notable between specimens treated with  $\text{TiO}_2\text{-Ag}$  sol and  $\text{TiO}_2\text{-Cu}$  sol in both A and N specimens. Anyhow,  $\text{TiO}_2\text{-Ag}$  specimens showed minor colour variation than  $\text{TiO}_2\text{-Cu}$  specimens. Colour change was related to phototropic activity of algal biofilm, and it was capable to detect the presence of algal cells, but it was not adequate to describe the extension of algal adhered to substrate. Thus, this technique was coupled to digital image analysis to measure the percentage of algal coverage as described in section 2.4 (Fig. 5).

Fig. 5 shows algal coverage during time of the accelerated growth test.

Investigating the anti-biofouling effect of nano-coatings, it is possible to conclude that  $\text{TiO}_2\text{-Ag}$  was able to inhibit algal growth better than  $\text{TiO}_2\text{-Cu}$  treatment, especially in case of A specimens

Algal coverage of  $\text{TiO}_2\text{-Ag}$  specimens was always lower than  $\text{TiO}_2\text{-Cu}$  specimens, in both A and N specimens (Fig. 5).

The effect of the coatings was better visible in case of N specimens, indeed the maximum coverage of treated samples was about 8%, while untreated samples reached about 22% (about three times higher).

A decrease of algal coverage was visible in Fig. 5 b after ten weeks on both control specimens and treated ones. The decrease was also visible on A specimens (Fig. 5 a) after eight weeks. These decreases were ascribable to natural dispersal phase of biofilm that enables biofilm to spread and colonize new surfaces.

This phase starts after biofilm growth and maturation, when fluid is able to employ adequate forces (in relation to biofilm's thickness) [57]. Since biofouling process on A specimens was faster than on N specimens, the detachment phase occurred two weeks before.

These findings are in line with results from self-cleaning test (Section 3.3), indeed the higher is  $R_E$ , the higher is the ability to stop algal growth on specimens and vice versa.

By comparing the results from this study with previous finding on the same specimens only treated with  $\text{TiO}_2$  sol [26], it is possible to highlight the effect of Ag and Cu addition.

High porous specimens with rough surface treated with  $\text{TiO}_2$  sol reached  $95.45 \pm 1.36\%$  of algal coverage [26], while  $\text{TiO}_2\text{-Ag}$  and  $\text{TiO}_2\text{-Cu}$  reached  $94.88 \pm 3.24\%$  and  $96.43 \pm 0.95\%$  respectively. Thus, no significant differences were notable comparing the results, and the addition of Ag and Cu to  $\text{TiO}_2$  sol (in the percentage used in this study, that is, so as to not altering the aesthetic appearance too much) does not produce the expected increment of biocide power.

Low porous specimens with less rough surface were covered by  $3.64 \pm 0.50\%$  if treated by only  $\text{TiO}_2$ , while they reached  $6.66 \pm 1.50\%$  with  $\text{TiO}_2\text{-Ag}$ , and  $8.24 \pm 2.74\%$  with  $\text{TiO}_2\text{-Cu}$ .

In this last case, it seems that Cu and Ag promote algal growth on specimens' surface, but this phenomenon could be caused by other factors (morphology of nano-coating, nano-particles deposition, etc...), and further investigations are required before giving a conclusion.

Results from this study are in contrast with other finding in the literature [42–44], underling how the efficiency of any coating cannot be assessed without testing them directly on each substratum they could be applied. In fact, the previous contrast is mainly ascribable to different substrata (in vitro assay [42,43], and mortar samples [44]) that play a key role in the biocide activity of titania [26].

The effects of intrinsic characteristics of substrata (porosity and roughness) is visible at a glance in Fig. 5. The A specimens (with higher porosity and roughness) reached total coverage around at the fifth week of test (Fig. 5 a), while N specimens (with low porosity and roughness) reached maximum 20% of algal coverage at around the tenth week (Fig. 5 b). This phenomenon was foreseeable, indeed the influence of porosity and roughness on clay brick was previously studied in the literature [26,35].

Porosity and roughness play a synergetic effect: the first contributes to retain water and nutrient into the substrata, while the second offers asperities required for adhesion of algal cells,

Not only trend of algal coverage was confirmed, but also values of maximum algal extension was substantially the same of previous researches [26].

266

### 267 3.5. Modelling of biofouling process

268 Fig. 6 shows the analytical curve, obtained by the Avrami's law, overlapped to experimental data. In case of  
269 N specimens, the Avrami's law was used to modelize the biofouling process, and it was adequate to describe  
270 the biofouling processes.



271 In case of specimens of group A, Avrami's law was very aloof from the experimental data. This result is  
 272 explicable by observing the shape of the biofouling process. In fact, no latency time was observed during the  
 273 experimental phase. The high porosity and roughness of the specimens caused a very fast adhesion of algal  
 274 cells, and biofouling process started immediately.

275 The existence of a latency time ( $t_1$  exponent in equation 3), an exponential growth, and a stationary phase are  
 276 at the basis for the application of the Avrami's law, and they were not observed on specimens of group A  
 277 (Fig. 6 b).

278 Then, a different approach was followed and a four parametric logistic model (4PL) was used to describe  
 279 numerically the biofouling of group A (equation 8).

$$y = A + \frac{B - A}{1 + \left(\frac{C}{x}\right)^D} \quad 8)$$

280 In the 4PL model,  $A$  is the minimum  $y$ ,  $B$  is the top of the plateau of the curve (highest  $y$ ),  $C$  represents the  $x$   
 281 at the inflection point of the S-shaped curve, and  $D$  is the slope factor. Under these hypotheses,  $A$  was fixed  
 282 to zero,  $B$  was the maximum value of algal coverage varying from sample to sample, and  $C$  was equal to  
 283 seven (days) because the curve changed its curvature after the first week due to the very fast biofouling  
 284 growth (Fig. 5 a). The slope factor  $D$  was calculated by minimizing the standard deviation between  
 285 experimental and analytical curves. Results obtained by this operation are reported in Fig. 7.

286 The parameters obtained by the two models were resumed in Table 3 and Table 4.

287 In case of Table 3, the most indicative parameter to describe the biofouling process is  $K_c$  that represents the  
 288 speed of the growth of algal spot. NNt shows higher  $K_c$  (both experimental and calculated) than NAg and  
 289 NCu specimens. This means that nano-coating influenced the biofouling process, and slowed down its  
 290 expansion. In this way, biofouling on NAg and NCu specimens was less extended than biofouling on NNt  
 291 specimens (see Fig. 5 b and Fig. 6 a). In addition, Table 3 allows to compare the results of this research with  
 292 results of a previous research with only  $TiO_2$  treatment on the same type of specimens [54], and it permits to  
 293 extend the range of Avrami's parameter in case of clay brick specimens.

294 Table 4 shows no significant difference between untreated samples and treated ones, indeed values indicate  
 295 the same trend. A little difference is visible in case of slope of the curves ( $D$ ). In this case, AAg and ACu

show smaller D than ANt specimens. This means that the biofouling process was lightly slowed down by the treatment, but the nanocoating was not able to stop the growth of algal cells that cover the specimens' surfaces almost completely.

299

#### 300 **4. Conclusions**

301 Previous researches on innovative treatments for biofouling prevention on brick substrata by the use of TiO<sub>2</sub>  
302 nanocoatings have shown how these are able to limit algae adhesion and their growth, even if, in case of high  
303 porous and rough substrata, their inhibitory effect seems to be limited. This way, this paper investigates on  
304 how the addition of Ag and Cu could fill in this gap.

305 Two types of brick were tested in order to simulate both ancient and contemporary brick façades.

306 Accelerated algal growth test was then carried out to study the effect of the addition of these nano-metals to  
307 TiO<sub>2</sub> sol. Test was conducted in the same way of previous researches, and specimens with the same  
308 characteristics were tested.

309 This study confirms the key role of porosity and roughness on the biofouling process, and on the biocide  
310 effect of the tested nano-coatings. Besides, it underlines how the efficiency of any coating cannot be assessed  
311 without testing them directly on each substratum they could be applied.

312 Anyway, the addition of silver and copper nano-particles to TiO<sub>2</sub> sol does not produce the expected effect on  
313 like-ancient brick surface, while a certain decrement of algal adhesion was observed in modern brick  
314 substrata. On the contrary, the results encourage the application of TiO<sub>2</sub> based nano-coatings for the  
315 production of new composite material and components to prevent algal adhesion on modern building façades  
316 and reduce the maintenance costs consequently.

317 Finally, in this paper, the validity of Avrami's law was confirmed to be adequate to predict the biofouling  
318 processes that were described by a sigmoidal curve composed by an initial latency time, an exponential  
319 growth, and a stagnation phase. In cases in which these three phases are not present, the hypotheses at the  
320 base of Avrami's law are not no longer valid, and four parametric logistic model was proposed to modelize  
321 the biofouling process. Analytical models (both Avrami's model and 4PL model) confirmed findings from  
322 experimental data, and they could have the potentiality to predict biofouling process of algae on brick  
323 specimens.

324 Further researches are currently under way to optimize the photocatalytic power of nano-coatings toward  
325 biofilm formation.

326

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479

480

481 **Figure captions**

- 482 **Fig. 1** Side view, and front view of test apparatus.  
483 **Fig. 2** Climatic conditions in the glass chamber (two days are represented).  
484 **Fig. 3** Results of self-cleaning test. Efficiency  $R_E$  was reported for specimens of group A a) and group N b).  
485 **Fig. 4** Total color variation at the end of water run-off test on A specimens (a), and N specimens (b).  
486 **Fig. 5** Percentages of area covered by the biofilm during the water run-off test on A specimens (a), and N specimens (b). Bars  
487 represent standard error.  
488 **Fig. 6** Overlapping of analytical curve, obtained with Avrami's law, to experimental data. Overlapping in group A b) is clearly  
489 inappropriate.  
490 **Fig. 7** Overlapping of 4PL logistic model to experimental data of group A.  
491

492 **Table captions**

- 493 **Table 1** Intrinsic characteristics of tested clay brick specimens (mean value  $\pm$  standard deviation). Each sample is representative of  
494 three specimens.  
495 **Table 2** Average color variation after coating application expressed as CIELab color coordinates and total color differences ( $\Delta E$ ).  
496 **Table 3** Calculated parameters of N group (Avrami model)  
497 **Table 4** Calculated parameters of A group (4PL model)  
498

**Table 1** Intrinsic characteristics of tested clay brick specimens (mean value  $\pm$  standard deviation). Each sample is representative of three specimens.

Sample	Treatment	Total porosity (%)	Ra ( $\mu\text{m}$ )	Rz ( $\mu\text{m}$ )	Rmax ( $\mu\text{m}$ )
ANt	Untreated				
AAg	TiO <sub>2</sub> - Ag	36.65 $\pm$ 0.65	8.90 $\pm$ 0.90	57.00 $\pm$ 8.00	68.00 $\pm$ 14.00
ACu	TiO <sub>2</sub> - Cu				
NNt	Untreated				
NAg	TiO <sub>2</sub> - Ag	19.13 $\pm$ 1.66	2.80 $\pm$ 0.50	27.00 $\pm$ 4.00	39.00 $\pm$ 6.00
NCu	TiO <sub>2</sub> - Cu				



**Table 2** Average color variation after coating application expressed as CIELab color coordinates and total color differences ( $\Delta E$ ).

Sample	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$	$\Delta E$
ANt	---	---	---	---
AAg	6.22	-1.51	-2.05	6.73
ACu	6.36	-1.74	-2.71	7.13
NNt	---	---	---	---
NAg	3.13	-3.52	-6.88	8.34
NCu	2.23	-2.98	-6.21	7.24

Table 3 Calculated parameters of N group (Avrami model)						
Sample	$t_1$ (day)	$k_g$ ( $\times 10^{-10}$ ) (Spot/ $\mu\text{m}^2$ day <sup>2</sup> )	$k_c$ ( <i>exp</i> ) ( $\mu\text{m}/\text{day}$ )	$K$ ( $\times 10^{-6}$ ) (Spot/day <sup>4</sup> )	R (%)	$k_c$ ( <i>calc</i> ) ( $\mu\text{m}/\text{day}$ )
NNt	21	568.52	45.91	0.23	26.28	23.11
NAg	28	1512.4	27.74	1.41	27.21	10.80
NCu	35	904.65	32.66	0.86	16.66	13.19

Table 4 Calculated parameters of A group (4PL model)					
Sample	$t_1$ (day)	$A$ (%)	$B$ (%)	$C$ (days)	$D$
ANt	0	0	89.21	7	2.02
AAg	0	0	90.41	7	1.49
ACu	0	0	94.91	7	1.59

Figure 1  
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