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The role of roughness and porosity on the self-cleaning and anti-biofouling efficiency of TiO₂-Cu and TiO₂-Ag nanocoatings applied on fired bricks.

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- 8 Keywords: Porosity, Roughness, fired brick biodeterioration, Titania, Ag and Cu, nano-Coatings
- 9
- 10

11 Abstract

From the advent of nanotechnologies in building constructions, many materials were functionalized to createcomposite material with new properties.

- 14 Titania (TiO_2) is actually the most promising nanotechnology to create composite materials with self-15 cleaning and anti-microbial properties. TiO₂ was able to limit algae adhesion and their growth, even if, in
- 15 cleaning and anti-interobian properties. 110_2 was able to finite argae addesion and their growth, even it, in 16 case of high porous and rough substrata, their inhibitory effect seems to be limited. This way, in this study,
- silver and copper nano-particulate enhanced an aqueous nano-titania solution were applied on brickspecimens and their inhibitory effects were tested during accelerated laboratory tests.
- Extent of biofouling on specimens' surface was assessed by measuring the aesthetical alteration andcorrelations between algal growth and key parameters of substrata were discussed.
- Results confirm the key role of porosity and roughness on the biofouling process on untreated specimens,
 and their effect on the photocatalytic power of the tested nano-coatings toward algal adhesion.
- Results from this study were compared with previous findings in the literature on the same types of specimens only treated with the same aqueous nano-titania solution. No significant improvements were 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
- adhesion of algal cells occurred, the experimental curves were modelled by using a four parametric logisticmodel 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 (TiO₂) 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 facades, 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], degradation mechanisms accelerate [12–14], and energy efficiency of the building could be reduced. 43 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 substrata, mainly porosity and roughness [10,35,37–41]. The influence of these parameters on inhibitory 49 50 efficiency of TiO_2 was previously studied also on clay brick [26] and TiO_2 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 the adhesion of algal cells to substrata and the inhibitory effect of TiO_2 is limited [26]. 53 Some studies investigate the possibility of enhancing the photocatalytic power of TiO₂ by the addition of 54 55 other metal nanoparticles, meanly silver (Ag) [42–44], and copper (Cu) [45]. 56 A TiO₂-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_2 -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 ₂ 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 ₂ was
68	observed in the literature.
69	In this study, two nanostructured solutions of TiO ₂ -Ag and TiO ₂ -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
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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].

92

93

2.2. Nano-coating application

Two types of aqueous TiO_2 -based solutions were studied in this paper. The first TiO_2 solution was doped

95 with silver nanoparticles, while the other one was doped with copper nanoparticles. TiO_2 -Ag nano-powders

96 were composed by TiO_2 and a concentration of silver and copper nanoparticles equal to 1% (molar

97 weight/TiO₂ weight). Concentration of TiO₂-Cu solution was equal to 1% (weight/TiO₂ weight). Final

98 concentration of aqueous solutions was equal to 1% (weight/volume of water). Thus, 100ml of solution

99 contains 1g of TiO_2 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 thedrying process.

107 For each group (A and N), three specimens were treated with TiO₂-Ag (AAg and NAg) and TiO₂-Cu (ACu

and NCu) respectively, whereas three specimens remained untreated (ANt and NNt) to be used as references.

109 Colour measurements were made in accordance to UNI-EN 15886 [49] with a portable spectrophotometer

110 (Konica Minolta CM 2600d).

112

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

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

where L*₀, a*₀ and b*₀, and L*, a* and b* are colour coordinates of original specimens and treated ones
respectively.

115

116 *2.3. Photocatalytic efficiency of nano-coatings*

117 Self-cleaning ability of TiO₂ nano-coating was evaluated by considering the degradation of organic dye

118 (Methylene Blue – MB) following the same methods proposed in the literature [50].

Briefly, 0.5ml of MB aqueous solution (MB content: 100 µmol/L) was deposited on an area of 2200 mm² on

- 120 the surface of brick specimens (80x80x30 mm³) 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^2 .

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.

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

127

128 ΔE_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 ΔE_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*

Biofouling process was simulated into 100x40x53 cm³ glass chamber whose architecture has been previously
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.

Temperature and relative humidity (RH) inside the glass chamber were recorded every 5 min over the entire
period of accelerated test by using a remote data logger (Lascar Electronics model EL-USB-2). Plot in Fig. 2
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_2 activation was provided by one

142 Blacklight Blue neon at a distance of about 150mm from the specimens' surface. In this way, nanocoating

was irradiated with an average UV intensity of 8 W/m^2 . The day/night period was equal to 14/10 hours

144 respectively.

Above the samples, a 10 mm diameter PVC rail containing three 2 mm holes for each specimen, was

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

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).

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

In order to collect data about the extension of algal fouling, the surface of each specimen was periodically (weekly) digitized by an office scanner. The adopted resolution was 600dpi because it was able to show the comparison of algal spot (equal to one pixel) with a side of about 40µm. Obtained images were filtered and

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 $80 \times 80 \text{ mm}^2$.

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)

that shown to be adequate in the literature [53,54], especially in case of biofouling process with sigmoidal

trend.

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

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

$$n = q + 3 \tag{4}$$

The q parameter was derived from general equation of the growth that was linear in time, thus q can be 166

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.

$$K = A k_{g} k_{c}^{2}$$
⁵

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

$$A = \frac{2}{(q+1)(q+2)(q+3)}$$
(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].

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

174

175 3. Results and discussion

3.1. Properties of substrata 176

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 about 0.4µm, while porosity of group N was composed by average pore diameter of about 0.1µm. Thus, 180 181 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.

This last result was important because total pore area controls movements of water at the interface betweenmaterial 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 Ra of group N, while other roughness's parameters (Rz and

188 *Rmax*) 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

difference in lightness in both A and N specimens; in case of A specimens, ΔL^* 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 (ΔE) was about the same in all specimens. ΔE was

197 greater than the just noticeable difference (JND) by naked eye fixed to 2.3 [55], and it was also a bit greater

than the value accepted for preservative treatments of historical building surfaces fixed to 5 [56].

Colour variation of specimens' surfaces was about the same observed on specimens treated with only TiO₂
solution [50], as expected.

201

202

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

Fig. 3 shows the self-cleaning efficiency R_E of tested specimens. Group A shows no efficiency of
nanocoatings, indeed AAg and ACu have the same trend of untreated ANt specimens. At the end of the test
the curves can be considered overlapped. Conversely, N specimens show a different trend. In this last case
untreated specimens reached an efficiency of about 9%, while R_E of NAg was about 33% and it reached
about 46% in case of NCu specimens. Thus, TiO₂-based solutions shown a noticeable (three time higher)
self-cleaning ability in case of low porous specimens. Inefficiency of treatments in case of A specimens can

- be ascribable to high porosity and roughness of substrata of course [10,35,37–40]. Secondly, it can be
- associated to micro-cracks on the surface of treatment that limits the photocatalytic efficiency of nano-coating [50].
- 213
- 214
- 215

216 *3.4. Biofouling evaluation and discussion*

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

220 No significant differences were notable between specimens treated with TiO₂-Ag sol and TiO₂-Cu sol in both

A and N specimens. Anyhow, TiO_2 -Ag specimens showed minor colour variation than TiO_2 -Cu specimens.

222 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.

227 Investigating the anti-biofouling effect of nano-coatings, it is possible to conclude that TiO₂-Ag was able to

228 inhibit algal growth better than TiO_2 -Cu treatment, especially in case of A specimens

229 Algal coverage of TiO₂-Ag specimens was always lower than TiO₂-Cu specimens, in both A and N

specimens (Fig. 5).

231 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.

236 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.

239 These findings are in line with results from self-cleaning test (Section 3.3), indeed the higher is R_E , the

240 higher is the ability to stop algal growth on specimens and vice versa.

241 By comparing the results from this study with previous finding on the same specimens only treated with

TiO₂ sol [26], it is possible to highlight the effect of Ag and Cu addition.

- High porous specimens with rough surface treated with TiO_2 sol reached 95.45±1.36% of algal coverage
- [26], while TiO₂-Ag and TiO₂-Cu reached 94.88 \pm 3.24% and 96.43 \pm 0.95% respectively. Thus, no significant
- 245 differences were notable comparing the results, and the addition of Ag and Cu to TiO₂ sol (in the percentage
- used in this study, that is, so as to not altering the aesthetic appearance too much) does not produce the
- 247 expected increment of biocide power.
- Low porous specimens with less rough surface were covered by $3.64\pm0.50\%$ if treated by only TiO₂, while
- they reached $6.66\pm1.50\%$ with TiO₂-Ag, and $8.24\pm2.74\%$ with TiO₂-Cu.
- 250 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.
- 253 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
- 256 mortar samples [44]) that play a key role in the biocide activity of titania [26].
- 257 The effects of intrinsic characteristics of substrata (porosity and roughness) is visible at a glance in Fig. 5.
- 258 The A specimens (with higher porosity and roughness) reached total coverage around at the fifth week of test
- 259 (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].
- 262 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,
- 264 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*

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

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

$$y = A + \frac{B - A}{1 + \left(\frac{C}{x}\right)^D}$$
(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. The parameters obtained by the two models were resumed in Table 3 and Table 4. 286

In case of Table 3, the most indicative parameter to describe the biofouling process is K_c that represents the 287 speed of the growth of algal spot. NNt shows higher K_c (both experimental and calculated) than NAg and 288 NCu specimens. This means that nano-coating influenced the biofouling process, and slowed down its 289 expansion. In this way, biofouling on NAg and NCu specimens was less extended than biofouling on NNt 290 specimens (see Fig. 5 b and Fig. 6 a). In addition, Table 3 allows to compare the results of this research with 291 292 results of a previous research with only TiO_2 treatment on the same type of specimens [54], and it permits to extend the range of Avrami's parameter in case of clay brick specimens. 293 294

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 thetreatment, 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_2 302 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

 TiO_2 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

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.

Anyway, the addition of silver and copper nano-particles to TiO_2 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

substrata. On the contrary, the results encourage the application of TiO_2 based nano-coatings for the

315 production of new composite material and components to prevent algal adhesion on modern building façades

and reduce the maintenance costs consequently.

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

growth, and a stagnation phase. In cases in which these three phases are not present, the hypotheses at the

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).
- Fig. 5 Percentages of area covered by the biofilm during the water run-off test on A specimens (a), and N specimens (b). Bars
 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

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

498

Sample	Treatment	Total porosity (%)	Ra (µm)	Rz (µm)	Rmax (µm)
ANt	Untreated				
AAg	T_iO_2 - Ag	36.65 ± 0.65	8.90 ± 0.90	57.00 ± 8.00	68.00 ± 14.00
ACu	T_iO_2 - Cu				
NNt	Untreated				
NAg	$T_iO_2 - Ag$	19.13 ± 1.66	2.80 ± 0.50	27.00 ± 4.00	39.00 ± 6.00
NCu	T_iO_2-Cu				

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

Sample	ΔL^*	Δa^*	∆b*	ΔΕ
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 2 Average color variation after coating application expressed as CIELab color coordinates and total color differences (ΔE).

Table 3Click here to download Table: Table 3.docx

Sample	t ₁ (day)	k_g (x 10 ⁻¹⁰) (Spot/µm ² day ²)	k _c (exp) (μm/day)	<i>K</i> (x 10 ⁻⁶) (Spot/day ⁴)	R (%)	<i>k_c (calc)</i> (μm/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 3 Calculated parameters of N group (Avrami model)

Table 4Click here to download Table: Table 4.docx

Sample	t_1 (day)	A (%)	В (%)	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

 Table 4 Calculated parameters of A group (4PL model)









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