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1 Photocatalytic degradation of dyes in water with micro-sized TiO₂ as
2 powder or coated on porcelain gres tiles
3

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13
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26 ABSTRACT

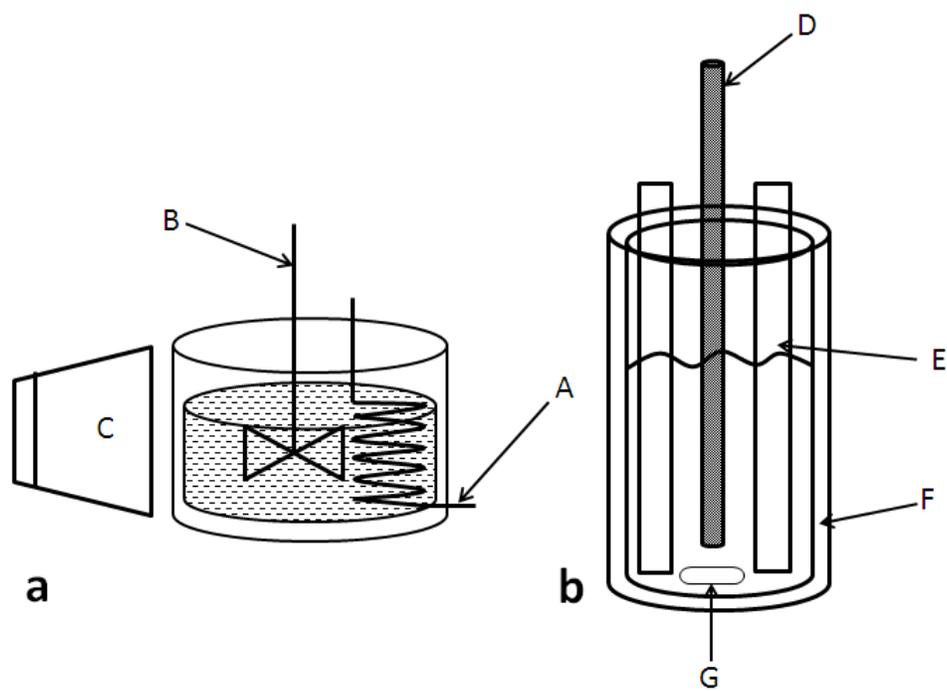
27 Some particular drawbacks due to the industrial use of nano-sized TiO_2 (safety, recovery) in
28 photocatalytic processes for water remediation can be avoided choosing micro-sized TiO_2 . Tests
29 on both micro-sized TiO_2 powder and industrially prepared photocatalytic tiles, having the
30 surface of porcelain gres tiles hot-coated with the same photocatalyst, were performed. Good
31 photocatalytic performance in the degradation of three organic dyes (Rhodamine B, Crystal
32 Violet and Methylene Blue) in water phase were achieved. Photocatalytic tiles can really
33 represent a good alternative to TiO_2 suspensions and pave the way for the fully industrial use of
34 photocatalysis in environmental remediation.

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37

38 TOC



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Polluted water



Clear water

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42

43 1. INTRODUCTION

44 Titanium dioxide (TiO_2) is worldwide considered as one of the best semiconductor to be used as
45 photocatalyst for pollutants degradation. Exposition under UV light promotes redox reactions
46 and charges separation that lead to oxidative processes as reported by Razavi et al.[1]. TiO_2 is
47 often used in powdery form as nano-sized particles with high surface area, so as to enhance its
48 photoactivity. Most of the literature reports consequently the use of nanometric TiO_2 materials
49 for many purposes, from disinfection [2] and air purification [3] to decomposition of organic
50 matter [4] or heavy loads metals in waste waters [5]. However, some recent papers have
51 underlined the possible side-effects on human health due to both use and exposure to
52 nanoparticles [6,7], as the ultra-small particles can penetrate inside human body from skin and
53 nose especially when they are used in products like paints or simply cold-coated on materials
54 surfaces for air purification and a loss of photoactive powder cannot be neglected.

55 Problems can be observed in liquid phase as well, where nano-sized powder can affect the
56 catalyst recovering at the end of the reaction, hindering an industrial use of TiO_2 nanopowders,
57 due to the extreme difficulty in the final filtering necessary to separate photocatalytic powder and
58 the cleaned solution, as reported by Schulze et al.[8].

59 On this basis, a great attention is focused on the potential of TiO_2 micro-sized powders to be
60 used as photocatalyst for the degradation of organic contaminants. Recent results for both NO_x
61 and VOC degradation in gas phase seem to be very promising [9] but no data are available for
62 the degradation of pollutants in liquid phase yet.

63 Main target of the present work is to investigate the performance of a commercial micro-sized
64 TiO_2 (1077 by Kronos) used as photocatalyst in the degradation of three different dyes
65 (Rhodamine B, Crystal Violet and Methylene Blue) in water. Micro-sized sample was used as

66 received, so to compare the obtained results with the classical nano-sized commercial P25 by
67 Evonik, always used as photocatalyst reference material.
68 Previously Marcos et al. [10] reported the deposition of TiO₂ layers on common ceramic glazed
69 tiles using the screen-printing process, which is a low cost and common technique used for
70 decoration in the ceramic industry. Labrincha et al. [11] deposited several commercial titania
71 powders by jet spray on ceramic tiles, then fired to stabilize the layers. In both cases a good
72 activity of nano-sized TiO₂ photocatalytic layers on ceramic tiles was demonstrated in the
73 degradation of Orange II dye. In the present case, micro-sized 1077 was industrially hot-coated
74 at the surface of a porcelain gres tile (Orosei ActiveTM). Tests using photoactive tiles were
75 carried out to verify the efficacy of the coated catalyst to degrade dyes in water media to obtain a
76 stable and very easy way to separate the solution at the end of the reaction from the photoactive
77 catalyst.

78

79 2. EXPERIMENTAL

80 2.1 Materials and Characterization

81 TiO₂ 1077 by Kronos was chosen as micro-sized photocatalyst, commercially classified as
82 pigment. Characterization of this sample was previously carried out and elsewhere reported [12].
83 However, principal features (crystallographic phase and crystallites size by XRD, specific
84 surface area (S.S.A.) by BET, and OH/O_{TOT} by XPS measurements) are summarized in Tab. 1.
85 1077 is also used in commercially available photoactive porcelain gres tiles (named Orosei
86 ActiveTM). TiO₂ was mixed industrially with a silica-based compound, sprayed on the tiles
87 surface, fired in industrial kiln a 680°C and cleaned with a rotating wire brush to remove the
88 TiO₂ weakly stuck at the tile surface, as already reported [13].

89 Rhodamine B (RhB, dye content ~95%, $C_{25}N_3H_{30}Cl$, PM 409 g/mol), Methylene Blue (MB, dye
90 content $\geq 97\%$, $C_{28}H_{31}ClN_2O_3$, PM 479 g/mol) and Crystal Violet (CV, dye content $\geq 90\%$,
91 $C_{28}H_{31}ClN_2O_3$, PM 479 g/mol) were used as organic pollutant. Each dye (Sigma Aldrich) was
92 used without further purification.

93

94 **Table 1** Physico-chemical features of either 1077 and P25 powders.

95

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97

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100

Sample	crystallographic phase	S.S.A. ($m^2 g^{-1}$)	crystallite size (nm) (XRD)	OH/O _{TOT} (XPS)
P25	75/25 anatase/rutile	50	26	0.14
1077	anatase	12	110	0.32

101

102 Two different dye concentrations were used in the present paper: 1×10^{-4} M and 1×10^{-5} M,
103 depending on the reaction set-up. The most concentrated solution was used to verify the
104 efficiency in the photodegradation of organic molecules in water of powdered micro-sized TiO_2
105 as stressing conditions. These results were compared to the results already obtained by P25 by
106 several authors in the past [14,15] and reconfirmed in this text. The less concentrated solution,
107 higher than the one reported by Marcos et al. [10], were used to test the performance of Orosei
108 ActiveTM tiles.

109 The solutions were prepared by dissolving the dye in distilled water and without any pH
110 adjustment, but leaving them at their spontaneous values.

111 1077 powder has been characterized by HR-TEM (Jeol JEM 3010 instrument, equipped with

112 LaB₆ filament and operating at 300 kV). HR-SEM-EDX analysis were performed on as received

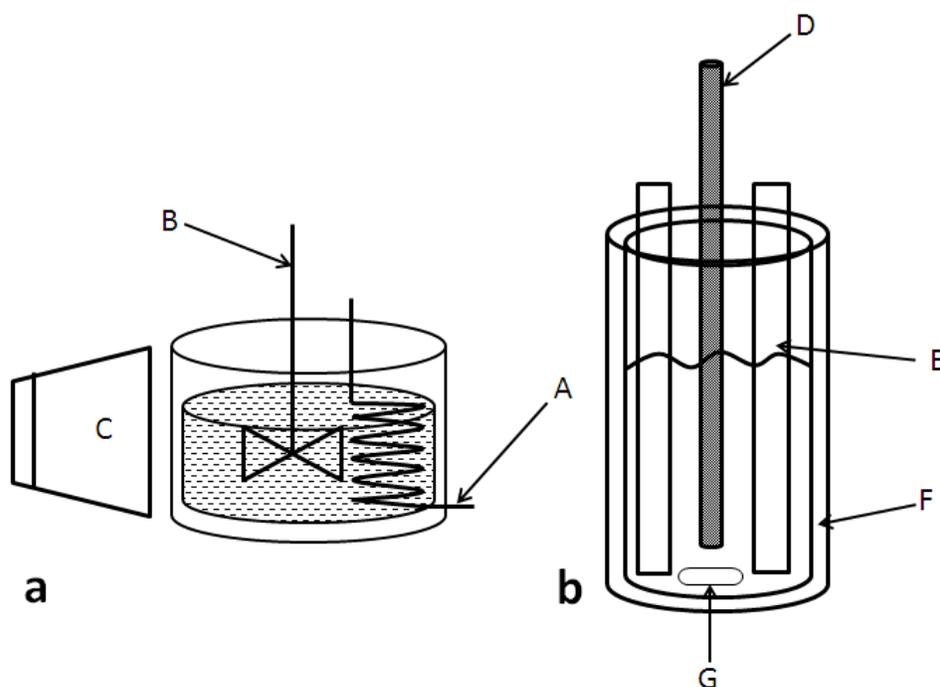
113 Orosei Active™ tiles (Field Emission Gun Electron Scanning Microscopy LEO 1525,
114 metallization with Cr. Elemental composition was determined using Bruker Quantax EDS.).

115

116 2.2 Photocatalytic test using powdered nano and micro-TiO₂ catalysts

117 Dyes degradation in water media was performed in a slurry reactor (Fig. 1a) of 0,5 L volume
118 [16]. Irradiation was allowed by the use of an external UV lamp (500W, Jelosil®, HG500, halide
119 lamp), emitting in the range 315-400 nm and with a emitting power evaluated in the middle of
120 the reactor by a radiometer instrument (Delta OHM, model HD2102.2) of 75 W/m². The reactor
121 was equipped by an internal refrigerating serpentine system.

122



123

124 **Figure 1 - a:** Continuous stirred slurry reactor. A: refrigerating serpentine system; B: Stirrer; C:
125 UV lamp. **b:** Cylindrical batch reactor used for photocatalytic experiments. D: UV lamp; E:
126 Orosei Active® tiles; F: Cooling jacket; G: Magnetic stirrer.

127 Dye adsorption tests have been carried out in the dark using a catalyst amount of 1 g/L at four
128 different dyes solution (concentration ranged between 10^{-6} - 10^{-4} M) for six hours.
129 Photolysis tests have been performed for six hours; the same for photocatalysis performed using
130 fresh 0,1 g/L TiO_2 in powder form. Dyes degradation was checked every 60 min. Analytic
131 determination of the dyes concentrations in water solution was performed by a UV-vis
132 spectrophotometer analyzer (T60 UV-vis PG LTD instruments), using water as the reference.
133 Pure CV has an absorbance maximum at 590 nm, RhB at 555 nm and MB at around 670 nm.

134

135 **2.3 Photocatalytic test using photoactive TiO_2 tiles**

136 A cylindrical batch reactor of 1 L volume was used for dye degradation tests in presence of ten
137 photoactive tiles (0.03 m^2 total surface photoactive area) immersed into the liquid solution, as
138 schematically shown in Fig.1b. Refrigeration was allowed by a cooling jacket. Two different
139 lamps directly immersed into the dye solution were used with this setup: a typical germicidal 9
140 W UV-C lamp (Philips TUV BL-S, model AEPL-7913 mercury vapor low pressure), with a UV-
141 A illuminance at the tiles surface of 1 W/m^2 and a 125 W UV-A lamp (Jelosil, mercury vapor
142 low pressure), with an illuminance of 65 W/m^2 .

143 The same batch of Orosei ActiveTM tiles was used for all the tests reported in the present paper;
144 after each test the tiles were simply washed using deionized water and acetone and then left in
145 deionized water all night long.

146 Adsorption tests were carried out by dipping the tiles into the dyes solutions in dark conditions
147 for six hours. To avoid any alteration of both irradiating conditions and fluid dynamic of the
148 system, photolysis was performed with the tiles still inside the reactor but with the active faces
149 turned towards the dark side of the reactor, thus preventing the photoactivation of the TiO_2

150 catalyst. During photocatalytic tests the TiO₂ active faces of the tiles were turned towards the UV
151 light.

152 The same dyes solution described in the 2.1 section were used in the present setup at a
153 concentration of 1×10^{-5} M. Kinetics were monitored by UV-vis spectrophotometric analysis as
154 described in 2.2

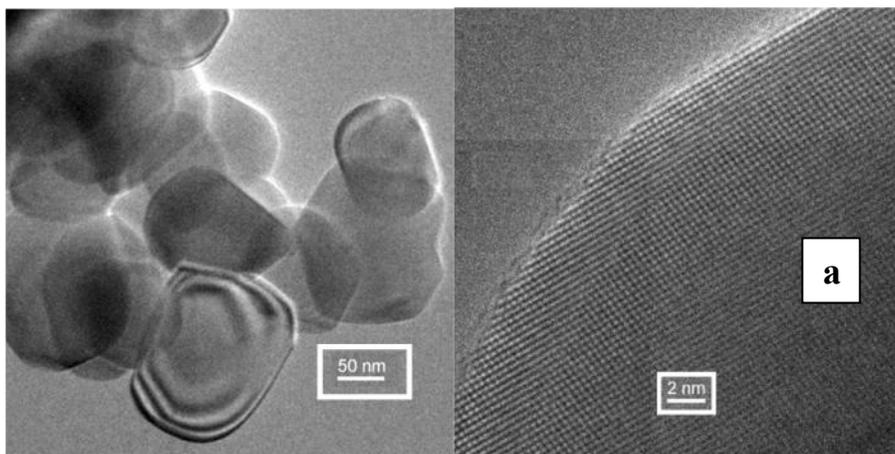
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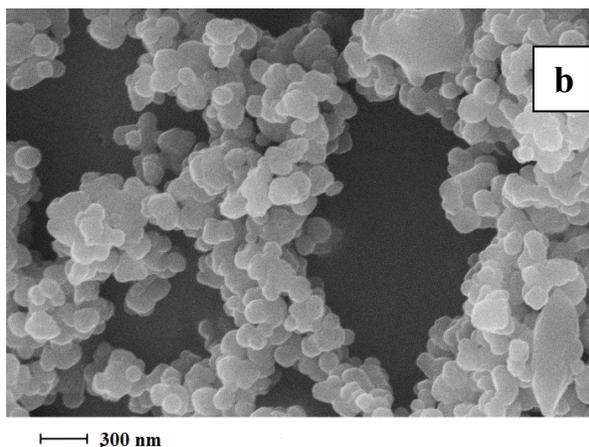
157 RESULTS AND DISCUSSION

158 **3.1 Powders and tiles characterization**

159 Conventional and HR-TEM investigations indicate that (almost) no ultrafine crystallites are
160 evident for the plain 1077 powder (see Figure 2a, left-hand section): in particular, all particles
161 exhibit well-ordered crystallographic terminations (see Figure 2a, right-hand section), all
162 belonging to the anatase phase (mostly to the (101) family of planes), as also reported in [12],
163 referring to XRD analysis performed on the same sample. HR-SEM images of Orosei[®] tiles
164 show a homogeneous distribution of TiO₂ crystallites in the micro-sized range without ultrafine
165 particles [13].



166



167

168 **Figure 2.** 2a: TEM images of pure 1077 in powder form. 2b: HR-SEM images of Orosei
169 Active™ tiles refer to 100.00K X.

170

171 A further magnification (Fig.2b) reveals the particles dimension that ranges between 100 and 125
172 nm as already obtained by XRD (Tab.1). By EDX analysis it was possible to determine the
173 quantity of TiO₂ coated on the tiles surface as 1.1 g/m². Related to the ten tiles used in our tests

174 with the total photoactive surface of 0.03 m^2 , a quantity of 0.033 g/L of TiO_2 was estimated to
175 work during the photocatalysis tests.

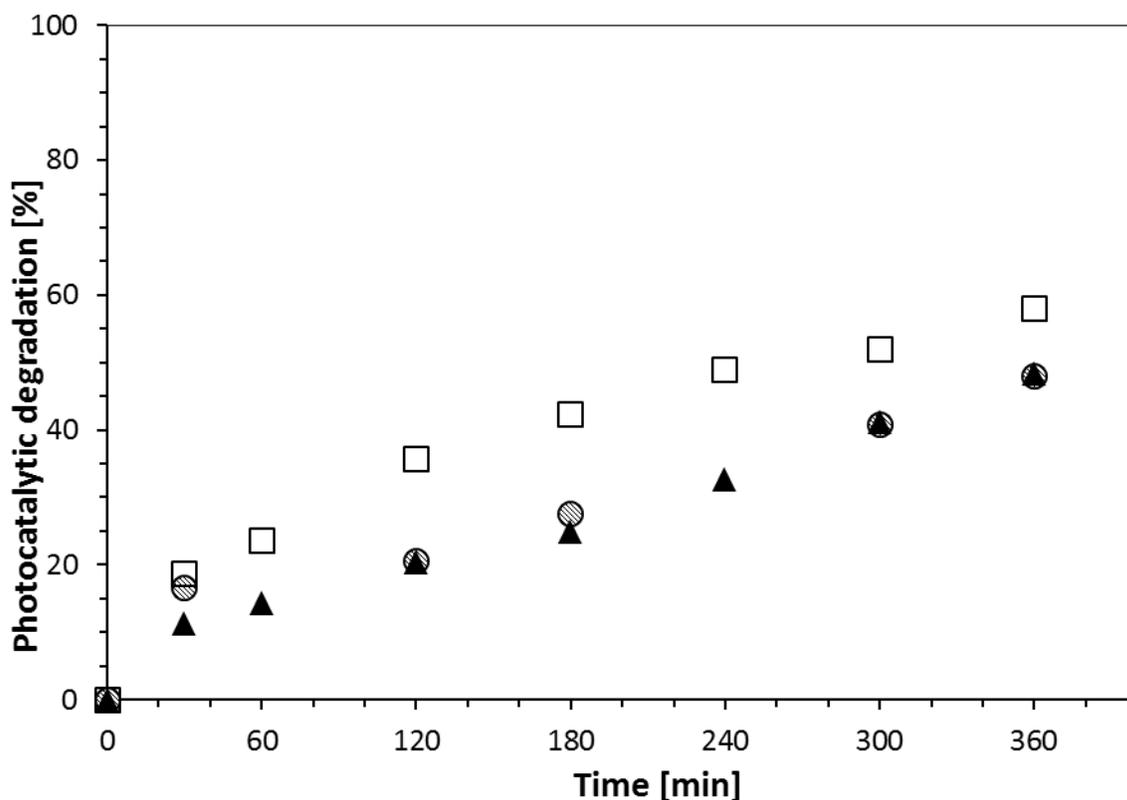
176

177 **3.2 Photocatalytic degradation of dyes in presence of TiO_2 powders**

178 Experimental dark tests have shown a very low adsorption of all the dyes on both P25 and 1077
179 catalyst at the spontaneous pH we have in our working conditions. Notwithstanding P25 has
180 specific surface area double than 1077 ($25 \text{ m}^2/\text{g}$ and $12 \text{ m}^2/\text{g}$, respectively) photolysis of CV and
181 MB are almost negligible for both the catalysts (6% for both dyes for P25, 9% and 4% for CV
182 and MB, respectively, for 1077). 12% of dye degradation for simple photolysis (10% for P25)
183 was achieved for RhB.

184 The dye molecules here considered are all cationic organic-based ones with a several benzene
185 rings and high molecular weight, being thus quite complex systems to be degraded.

186 Photocatalytic tests show good results in dyes abatement. Nano-sized powder shows the best
187 results for all the considered dyes achieving the complete decolorizing of the water solution in 6
188 hours in the case of CV (Fig.5SI), but also micro-sized sample are able to degrade the pollutants
189 with a good efficiency (ranging from 48 to 58% depending on the dye in six hours) (Fig.3).



190
 191 **Figure 3.** Photocatalysis of dyes performed with powdered micro-TiO₂ catalyst (1077):
 192 □ Crystal Violet; ▲ Methylene Blue; ● Rhodamine B.

193
 194 A study on the reaction rate has been done by elaborating the kinetic constants for both 1077 and
 195 P25 samples. Photocatalysis generally follows a Langmuir-Hinshelwood mechanism [17]:

$$197 \quad r = k\theta = \frac{kKC}{1 + KC} \quad (1)$$

198
 199 where r is the reaction rate for the oxidation of the reactant, k is the true kinetic constant,
 200 including the mass of catalyst and the flux of efficient photons, θ is the coverage fraction of the
 201 material, C is the dye concentration in solution and K is the adsorption equilibrium constant.

202 Eq. 1 can be approximated to a pseudo-first order kinetic with respect to the negligible
203 adsorption of the dyes by the micrometer catalyst used:

204 the classical equation can be approximated to a pseudo-first order kinetic with respect to the
205 negligible adsorption of the dyes by the micrometer catalyst used:

206

$$207 \quad r = -\frac{dC}{dt} = k_{app} C \quad (2)$$

208

209 where k_{app} is the apparent first order rate constant and t is the time. The integral form in function
210 of time of the Eq. 1 can be withdrawn and the slope of the straight line interpolated represents
211 the k_{app} . The rate constants were consequently calculated for both samples and for all the tested
212 dyes and are all in the 10^{-3} magnitude order. (data in Tab. 2). It is worth noting that both nano-
213 and micro-powders exhibit k values in the same order of magnitude, most likely because the
214 photocatalytic process follows a similar pathway despite the dimensions of the TiO_2 powder.

215

216 **Table 2** Rate constant calculated for both 1077 and P25 samples.

217

Sample	RhB rate constant $*10^{-3} (\text{min}^{-1})$	MB constant rate $*10^{-3} (\text{min}^{-1})$	CV constant rate $*10^{-3} (\text{min}^{-1})$
1077	1.78	1.78	2.64
P25	5.0	5.1	8.2

222

223

224 The possibility to recover the powdered catalyst was checked by simply filtering the final
225 degraded solution in a standard Büchner funnel equipped with a filter paper or directly
226 centrifuging it in a laboratory scale equipment working at 10000 rpm.

227 For 1077 sample the simple centrifugation was sufficient to recover all the used photocatalyst.
228 The powder was washed several times in deionized water and reused in the same dye
229 degradation test (CV discoloration) with no loss of photoactivity. On the other hand, no recovery
230 of P25 was possible neither filtering or centrifuging the solution. The nano-powder passed
231 completely through the filter paper and it was not separated by the solution by centrifugation
232 remaining very well-dispersed in water.

233 The lower efficiency of 1077 micro-sized TiO_2 in the degradation of dyes in water than nano-
234 sized photocatalyst is fully rewarded by the facility to recover the photoactive powder from the
235 solution at the end of the purification reaction and reuse it eventually after a simple washing in
236 water.

237

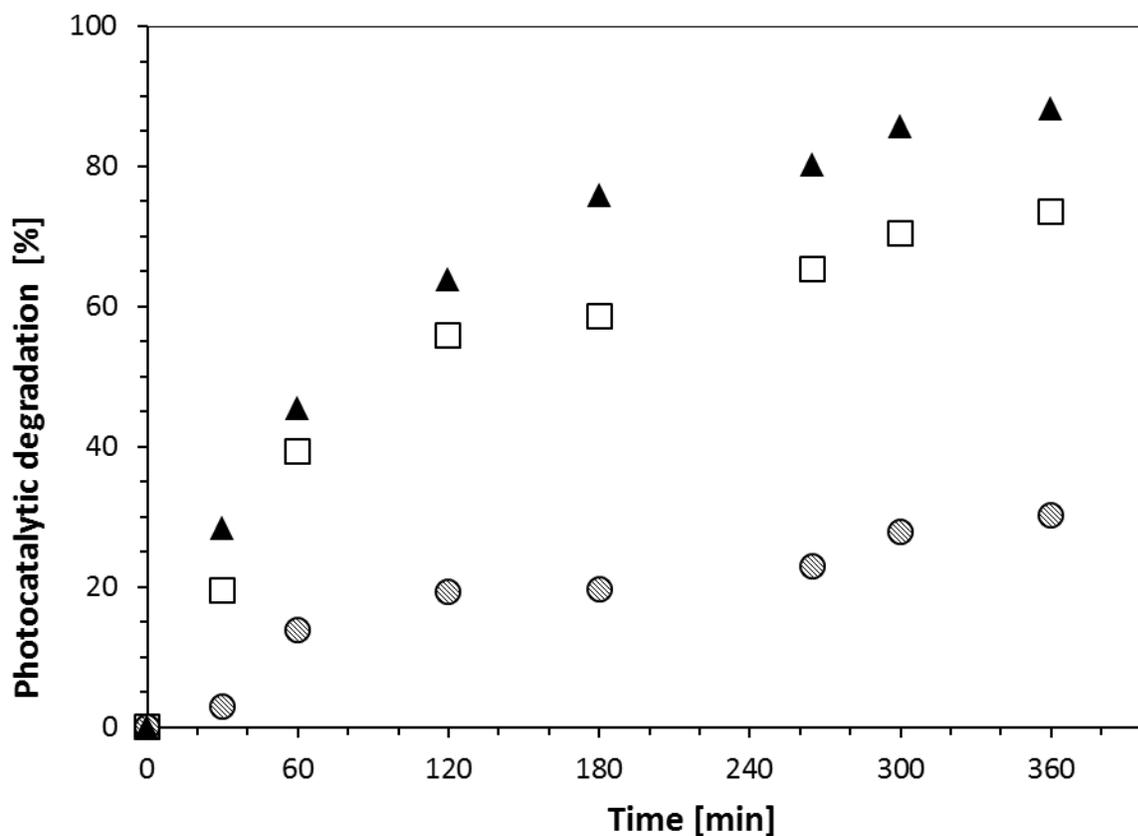
238 **3.3 Photocatalytic degradation of dyes in presence of TiO_2 activated tiles**

239 According to the previous results obtained by the use of micro-sized TiO_2 catalyst, the activity of
240 1077 industrially hot-coated onto porcelain tiles was evaluated in another experimental setup
241 verifying the material efficiency with two different UV lamps immersed inside the dyes solution.
242 Control experiments of photolysis and adsorption of dyes on the tiles were carried out. Dark tests
243 shown a 25% adsorption of CV and MB, while RhB adsorption is on the contrary almost
244 negligible. However, dyes were exclusively fixed in the backside and lateral sides of the ceramic
245 pieces, i.e. in the surfaces uncovered by the photocatalytic layer.

246 Direct photolysis highlights different results depending on the used lamp: a percentage
247 degradation of 64% for CV, 70% for MB and 14% for RhB was achieved for 9W immersion
248 lamp, a very high result in comparison to the photolysis tests reported in section 2.2. However in
249 this case this was a germicidal lamp and therefore an emission in the UV-C region is present and
250 is probably enhancing the photolysis process.

251 Lower results were obtained using the 125W UV-A immersion lamp. The absence of UV-C
252 allows to have dyes degradation due to pure photolysis within 30% for CV and MB, 10% for
253 RhB (we have not to forget that tiles are already immersed not to alter the reactor flow dynamic
254 and therefore adsorption process is still present).

255 Results obtained by photocatalytic tests, carried out by using the coated micro-TiO₂ catalyst onto
256 the tiles surface are showed in Fig. 4 for 9W lamp.



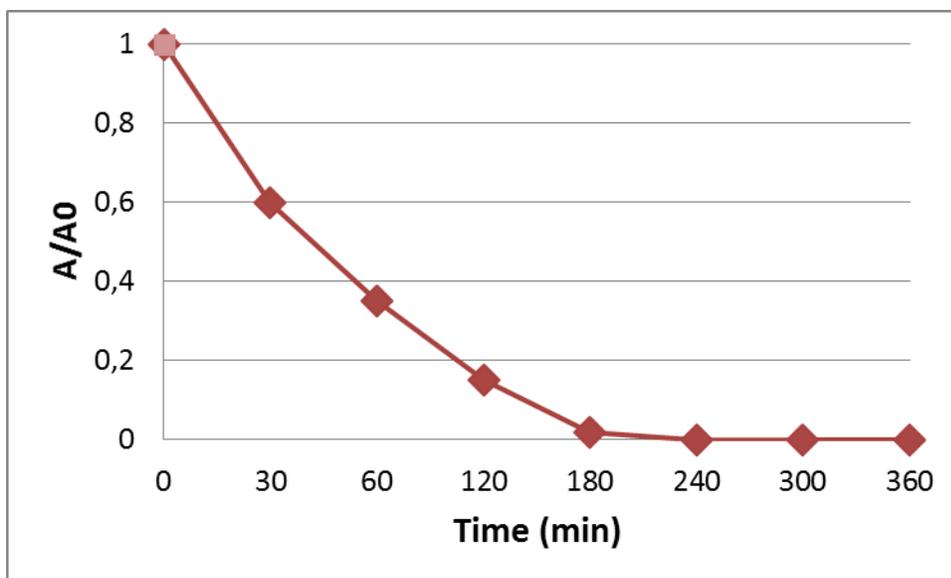
257
 258 **Figure 4.** Photocatalysis with Orosei™ Active tiles and UV-light irradiation (9W immersion UV
 259 lamp); □ Crystal Violet; ▲ Methylene Blue; ● Rhodamine B.

260
 261 Degradation of dyes is improved by the use of the photoactive tiles; in fact after a six hours
 262 reaction, the percentage degradation value obtained is 78% for CV, 88% for MB, and the 30%
 263 for RhB, revealing an increase of about 15% of degradation on all dyes in comparison to the
 264 simply photolysis tests.

265 Tests with the 125W UV-A lamp lead to the complete degradation of CV (Fig. 5) and MB in less
 266 than three hours and the disappearance of 71% RhB in 6 h.

267

268



269

270 Figure 5 Attenuation of the 590 nm absorbance peak of CV by Orosei™ Active tiles and UV-
 271 light irradiation (125W immersion UV-A lamp)

272

273

274 4. CONCLUSIONS

275 Main target of the present work was thus to verify the possibility to use micro-sized TiO₂,
 276 instead of the classical nanopowders, in the degradation of organic molecules in water phase.

277 The obtained results have to be considered with great importance as using micro-sized TiO₂ the
 278 health risks related to nano-sized particles can be avoided; moreover such a micro-sized powder
 279 can be easily filtered and recovered, in order to be immediately reused for further
 280 photodegradation reactions, opening the way of a fully industrial use of photocatalysis in
 281 environmental remediation.

282 A further improvement can be achieved coating micro-TiO₂ on porcelain tiles surfaces. The
 283 photocatalytic materials described here can be reused, just after mere rinsing of the tiles in
 284 distilled water, and without affecting the photocatalytic activity. In fact all the tests performed in

285 the present work were done using the same batch of ten samples obtained from industrially
286 prepared tiles (Orosei ActiveTM), and no loss in their photoactivity was monitored.
287 This indicates that the TiO₂ deposited layers are not deactivated during the reaction either by loss
288 or poisoning of the catalyst, and can be reutilized in subsequent runs.
289 These new industrial ceramic materials are surely an interesting alternative to TiO₂ suspensions,
290 for example in photocatalytic applications avoiding the removal of the particles at the end of the
291 process.

292

293 **Acknowledgement**

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295 measurement performed on the tiles.

296

297

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