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1 **Solar photocatalysis of TiO₂ supported natural palygorskite nanofibers elaborated by a**
2 **one_pot mechanochemical route**

3

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23 **Abstract:**

24 This study reports the successful synthesis of supported TiO₂_Palygorskite nanocomposites by
25 a one-pot dry mechanochemical route. Indeed, the elaboration procedure involved an in-situ
26 reaction between accessories carbonates present in raw fibrous palygorskite clay and titanyl
27 sulfate (TiOSO₄) precursor under variable grinding conditions, essentially ball/solid matter
28 mass ratio and rotation velocity. This yielded after air annealing at 600°C for 1 h to the
29 immobilization of anatase TiO₂ nanoparticles (≈ 8 nm of average size) as evidenced by XRD
30 and TEM analyses. Once the conditions of elaboration were optimised, the photocatalytic
31 properties were evaluated under 3 conditions: artificial UV radiation, artificial solar radiation
32 (UV+visible range) and under dynamic solar illumination taking into account the
33 discontinuities of the solar resource. The results allowed the estimation and comparison of the
34 catalyst's capabilities and showed its ability to work under natural irradiation. The so developed
35 supported photocatalysts TiO₂/Palygorskite exhibited a good activity towards the removal of
36 Orange G (OG) dye from aqueous media under artificial UV and natural solar radiations.

37

38 **Keywords:** TiO₂, palygorskite, mechanochemical synthesis, nanocomposite, solar
39 photocatalysis, wastewater treatment.

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46 **1. Introduction**

47 Heterogeneous photocatalytic oxidation recently has emerged as an efficient alternative process
48 for wastewater treatment [1–6]. The principle of this technique relies on the creation of reactive
49 species as holes (h^+) and hydroxyl radicals (OH^\bullet) upon irradiating a semiconductor oxide with
50 an energy source ($h\nu$) higher than its energy band gap [1,6]. In optimized processes, the highly
51 oxidizing species so generated are able to induce complete mineralization of organic pollutants
52 into CO_2 and H_2O [1]. TiO_2 anatase is the most active semiconductor oxide in photocatalysis
53 and is besides widely used owing to its numerous advantages, for instance, non-harmfulness,
54 low cost, and chemical inertness [1]. Several wet methods, including sol-gel [7–9], flame
55 aerosol [10], solvothermal [11] were reported for the synthesis of TiO_2 powder. Interestingly,
56 a dry method based on grinding powders of carbonate compound, namely Na_2CO_3 and a Ti
57 molecular precursor such as titanium sulfide (TiS_2) [12,13] and titanyl sulfate ($(TiOSO_4 \cdot 2H_2O)$
58 [14–16] was also reported to synthesize pure TiO_2 powder. However, the direct use of TiO_2 in
59 the form of nano-powder (*e.g.*, commercial Degussa P25 powder [10]) raises several problems
60 such as agglomeration of the nanoparticles during the process, which reduces photocatalytic
61 efficiency [17]. Additionally, recovering of micron sized aggregated particles from water
62 decontaminated by TiO_2 slurry needs to implement costly microfiltration processes [2,6,17,18].
63 To overcome these drawbacks, researches focused on improving photocatalytic processes by
64 the development of TiO_2 supported photocatalysts, in particular starting with natural highly
65 dispersed materials as support.

66 The solar resource is a sustainable energy by definition and available for many applications.
67 For photo-oxidation applications, capacities are limited because most catalysts are only
68 sensitive to ultra violet (UV) radiation in the spectrum. This represents only 5% of the solar
69 radiation, resulting in limited performance for solar installations. A second characteristic of the
70 solar resource is its intermittent nature, which is due to the daily (day/night) and seasonal cycle,

71 but also to meteorological effects such as the passage of clouds or heavy cloud cover. Thus, to
72 meet these constraints, the catalysts developed must have photocatalytic properties that allow
73 the use of the solar resource and manage the fluctuations linked to this resource. This implies
74 catalysts with both photo-excitation characteristics to produce radicals and sorption
75 characteristics to store the molecules during low sunlight phases.

76 Among the support materials envisaged, clay minerals are considered promising owing to their
77 interesting inherent multi-functional properties such as their adsorption capacity, high surface
78 area, multiscale porosity, and ability to be grafted by chemical compounds [18–25]. In this
79 respect, some authors more recently reported CeO₂_WO₃_Palygorskite/TiO₂ catalysts
80 elaborated by impregnation method [26] and TiO₂ supported on three natural clays with
81 different morphologies carried out by sol-gel route [27]. In the same way, we reported some
82 years ago the immobilization of TiO₂ anatase nanoparticles (NPs) with an average size of 10
83 nm onto particles surfaces of beidellite [28] and nanofibers surfaces of palygorskite [29] via a
84 colloidal sol-gel route. Beidellite and palygorskite were both natural clay minerals sampled in
85 Morocco from Agadir basin and Marrakech High Atlas regions, respectively. They were
86 purified, characterized, and specifically functionalized to be used as catalytic supports in the
87 wet synthesis methods employed [30,31]. Photocatalytic tests performed in presence of these
88 TiO₂ supported clay nanocomposites towards the degradation of Orange G dye (OG) were
89 promising in that they interestingly exhibited a photoactivity normalized to the TiO₂ amount
90 higher than that of pure TiO₂ micropowder commercially available as Degussa P25.

91 Nevertheless, the synthesis of these supported photocatalysts is generally achieved via colloidal
92 [21,29] or solvothermal [32] or pillaring [20] wet routes, which on one hand required previous
93 purifying and/or homoionisation with Na⁺ ions of clay minerals. On the other hand, these
94 elaboration methods involved several steps so that they are laborious, time and solvents
95 consuming and yielding to small laboratory amounts. Thereby, they have a low capacity to be

96 transferred to industrial scale. Thus, there is a need to find out alternative synthesis method to
97 overcome these wet routes issues.

98 The aim of this work is to show the potential of these materials for a solar photo-oxidation
99 application. It is divided into three parts. The first part aims at elaborating TiO₂ supported
100 palygorskite by a free-solvent one-pot mechanochemical method starting from powders of raw
101 palygorskite (Pal) clay and titanyl sulfate (TiOSO₄·2H₂O) precursor. This dry synthesis route
102 was smartly based on *in-situ* reaction between carbonates accessorially available in raw clay and
103 a Ti molecular precursor to immobilize resulting TiO₂ particles on the surface of palygorskite
104 fibers or in the vicinity of their surface in the tangle of fibers. Synthesis conditions were
105 optimized by studying the influence of the composition ratio palygorskite clay / TiOSO₄·2H₂O
106 and grinding velocity. The second step is to select the optimal conditions for the development
107 of a material in order to control the photocatalytic properties. The so elaborated TiO₂-Pal
108 nanocomposites were afterwards characterized at a multi-scale level using *in situ* X-ray
109 diffraction (XRD (X'pert powders Philips diffractometer)), Scanning Electron Microscopy
110 (SEM (SEM-FEG, Hitachi S-4500)) and Transmission Electron Microscopy (TEM (JEOL JEM
111 2010)). The originality lies in a global approach starting from the elaboration of the catalysts,
112 their optimization to test their photocatalytic potential. The aim being to evaluate the photo-
113 oxidation capacities under solar conditions, our step-by-step approach involves three stages.
114 Measurements are carried out under controlled irradiation conditions, both in terms of spectral
115 distribution and flux density (artificial UV and solar irradiation) with the aim of modelling the
116 photo-oxidative capacities of the catalysts. Finally, the photo-oxidation capacities are measured
117 and modelled under natural irradiation, taking into account the characteristics of solar radiation:
118 spectral distribution and flux density discontinuities. Thus, photo-activities were evaluated
119 towards the removal from aqueous medium of Orange dye (OG) considered as a model pollutant

120 under UV radiations and solar light by using indoor lab-scale reactors equipped with an artificial
121 solar light and a larger outdoor pilot irradiated by natural solar light.

122 **2. Experimental details**

123 **2.1- Materials and synthesis**

124 Natural raw clay, involved herein, was sampled from Marrakesh – High Atlas region. Detailed
125 characterizations performed by Rhouta *et al.* [30] on this clay revealed that it is made up of fine
126 clay fraction ($< 2 \mu\text{m}$) ($> 65\%$) along with accessory minerals, namely quartz ($< 5\%$) and
127 carbonates ($\approx 30 \text{ wt}\%$) in the forms of calcite ($\text{Mg}_{0.03}\text{Ca}_{0.97}\text{CO}_3$) and ankerite
128 ($\text{Ca}_{1.01}\text{Mg}_{0.45}\text{Fe}_{0.54}(\text{CO}_3)_2$). The extracted fine fraction ($< 2 \mu\text{m}$) was found to be exclusively
129 composed of fibrous clay minerals, namely palygorskite ($\approx 95\%$) exhibiting predominant
130 dioctahedral character and deficiency into zeolitic water along with sepiolite ($\approx 5\%$). The
131 composition of this palygorskite was found on the basis of 26 oxygens to be
132 $(\text{Si}_{7.97}\text{Al}_{0.03})(\text{Mg}_{2.17}\text{Al}_{1.46}\text{Fe}_{0.40}\text{Ti}_{0.05})(\text{Ca}_{0.03}\text{Na}_{0.07}\text{K}_{0.03})\text{O}_{20.18}(\text{OH})_{1.94}(\text{H}_2\text{O})_{3.88}, 2.43 \text{ H}_2\text{O}$. Its
133 Cation Exchange Capacity (CEC), Brunauer-Emmet-Teller method (BET) specific surface area
134 and total porous volume were assessed to be $21.2 \text{ meq.}100 \text{ g}^{-1}$, $116 \text{ m}^2.\text{g}^{-1}$ and $0.458 \text{ cm}^3.\text{g}^{-1}$
135 respectively.

136 The Ti precursor considered herein is the titanyl sulfate ($\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$) purchased from Aldrich
137 and used without further treatment.

138 In contrast to our previous works [24-27, 30] in which the synthesis of clay minerals supported
139 photocatalysts implied several laborious and time-consuming steps including purifying,
140 homoionisation and fine fraction recovering before its functionalization, the elaboration herein
141 was accomplished according to a one-pot route starting directly from raw clay. Indeed, given
142 amounts of raw palygorskite clay and $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$ powders were introduced in an alumina
143 jar of planetary ball mill PM100 from Retsch for being grinded using six alumina balls of 20
144 mm in diameter. The synthesis of TiO_2 supported on palygorskite fibers was achieved by *in-*

145 *situ* reacting carbonates accessorially present (≈ 30 wt%) in raw clay with $\text{TiOSO}_4 \cdot 2\text{H}_2\text{O}$
146 precursor according to different conditions. Indeed, the amount of each reactant was chosen in
147 such a way to have a total mass of reactants of 50 g per run by considering two raw clay /
148 TiOSO_4 mass ratios of 0.6/1 and 3.3 /1, which corresponded to mixtures in which both
149 compounds were in stoichiometric or in excess proportions, respectively. The grinding was
150 performed at a rate of 500 rpm for different times (10, 15, 20 and 30 min). As-grinded samples
151 were thereafter air annealed for 1 h at different temperatures (400, 500, 600 and 700°C).
152 Samples were designated Pal_ $\text{TiO}_2(x)$ _G_y_T_z by referring to the composite nature of the sample
153 (Pal_ TiO_2), the reactant mass ratio ($x = \text{TiO}_2/\text{Pal}$), the grinding time (G_y) and the post-heat-
154 treatment temperature (T_z). The obtained powdered materials were finally stored for further
155 uses.

156

157 **2.2- Characterizations**

158 The structural changes of TiO_2 upon heating of as-grinded samples were analyzed *in*
159 *situ* versus the temperature by XRD over the two-theta range 2_60 deg using a Bruker D8
160 Advance diffractometer equipped with a Vantec Super Speed detector and an Mid- Infrared
161 (MIR) radiation heating chamber (Bragg-Brentano configuration; Ni filtered Cu K_α radiation).
162 The diffractograms were recorded every 50°C from the room temperature to 950°C. An
163 isotherm was maintained at each level for 40 min to record the pattern then the temperature was
164 increased using a ramp of 1 deg.s⁻¹ up to the next level. Also XRD at room temperature was
165 recorded on TiO_2 _Pal samples prior to air annealing at different temperatures in the same
166 angular range using a Seifert XRD 3000TT diffractometer equipped with a graphite
167 monochromator (Bragg-Brentano configuration; Cu K_α radiation).

168 The microstructure, morphology and uniformity of the samples were analyzed at
169 different steps of the synthesis by a Scanning Electron Microscope (SEM; Leo-435VP)

170 equipped with an Oxford energy dispersive spectrometer (EDS, (EDS, KEVEX Si(Li) assisted
171 software Brüker)). Also, a JEOL JEM 2010 TEM equipped with a Tracor EDS analyzer was
172 used for characterizing clay particles and performing local elemental composition.

173

174 **2.3- Photocatalytic activity**

175 The photocatalytic activity of different samples was evaluated using three kinds of set-
176 ups: a laboratory-scale set-up, an indoor solar simulator and an outdoor solar pilot.

177 As far as the first set-up is concerned, the degradation reaction was performed in a batch quartz
178 reactor ($40 \times 20 \times 36 \text{ mm}^3$) placed in a thermostated chamber (25°C) under the UV light of a
179 lamp (HPLN Philips 125 W) emitting at 365 nm. The reactor was irradiated with a photon flux
180 of about $100 \text{ mW}\cdot\text{cm}^{-2}$ by adjusting the distance to the lamp so that it simulates the UV intensity
181 of solar spectrum on the earth [33]. This lamp was chosen because the OG absorption is
182 negligible at this wavelength and, as a result, the direct photolysis of the solution (*i.e.* without
183 photocatalyst) was found negligible for more than 24 h. The photoactivity of different samples
184 was assessed at pH around 6 by measuring the decomposition rate of OG in aqueous solutions
185 containing the supported photocatalyst according to a procedure previously reported [34] and
186 adapted to the dispersion of supported powder photocatalysts in previous papers [28,35]. The
187 photocatalyst powder of TiO_2 _Pal nanocomposites was added to 25 cm^3 of OG solution (10^{-5}
188 M) in an amount equal to $0.8 \text{ g}\cdot\text{dm}^{-3}$. This catalyst mass was found as optimum to avoid excess
189 of catalyst and to ensure an efficient absorption of photons [36]. The dispersion was agitated
190 with an inert Teflon magnetic stirrer. To determine the dye concentration, aliquots were taken
191 from the mixture at regular time intervals and centrifuged at 12500 rpm for 5 min. The OG
192 concentration in the supernatant was determined by measuring the absorbance at 480 nm using
193 a UV-VIS-NIR spectrophotometer (Perking Elmer lambda 19).

194 Sunlight is particularly weak in the UV spectral region and, in addition, it changes along the
195 day due to day-night and seasonal cycles [37,38]. Thus, prior optical and kinetic studies have
196 to be performed to determine on one hand optimal catalyst mass allowing the maximum (\approx
197 90%) of the absorption of photons (considered as reactant) and, on the other hand, kinetic
198 constants to achieve process efficiency in an outdoor solar pilot [37,39]. Therefore, optical
199 properties of photocatalysts suspensions differing in mass concentrations were studied by an
200 optical experimental setup described in details elsewhere [37,39]. Practically, the light supplied
201 by a source simulating solar radiation (maximum intensity equal to $1000 \text{ W}\cdot\text{m}^{-2}$ in the full
202 spectral range, *i.e.* $50 \text{ W}_{\text{uv}}\cdot\text{m}^{-2}$ in the UV range) came across a Polymethyl methacrylate
203 (PMMA treated to be UVA transparent, Sunactive® GS2458) cell 2 cm thick (*i.e.* optical
204 length) containing under stirring the TiO_2 _Pal dispersions whose concentrations ranged from
205 0.1 to $4 \text{ g}\cdot\text{L}^{-1}$. This cell was placed at the inlet of an integrating sphere. The direct radiation as
206 well as scattered radiation transmitted hence collected from the integration sphere were directed
207 via an optical fiber towards a spectrophotometer permitting the detection of wavelengths
208 ranging from 250 to 1100 nm (ultraviolet, visible and near-infrared). The transmission of light
209 was hence assessed versus catalyst powder concentration to determine the mass concentration
210 at which the 90% absorbency was reached. Afterwards, kinetic study of OG dye degradation
211 was carried out versus mass concentration of catalysts powders dispersion by using an indoor
212 solar simulator set-up. For a given mass concentration the catalyst dispersion was kept under
213 stirring in a 150 mL quartz bucket (suspension height of 5 cm), then it was irradiated by sunlight
214 simulator ($1000 \text{ W}\cdot\text{m}^{-2}$) under constant photons flow. At different time intervals, aliquots were
215 picked up from media, centrifuged and resulting supernatants analyzed by spectrophotometry
216 to determine the dye concentration according to the way described above.

217 Afterwards, the efficiency of TiO_2 _Pal catalysts towards the photodegradation under sunlight
218 of OG dye was tested by using an outdoor solar pilot described in details by Janin *et al.*, [40]

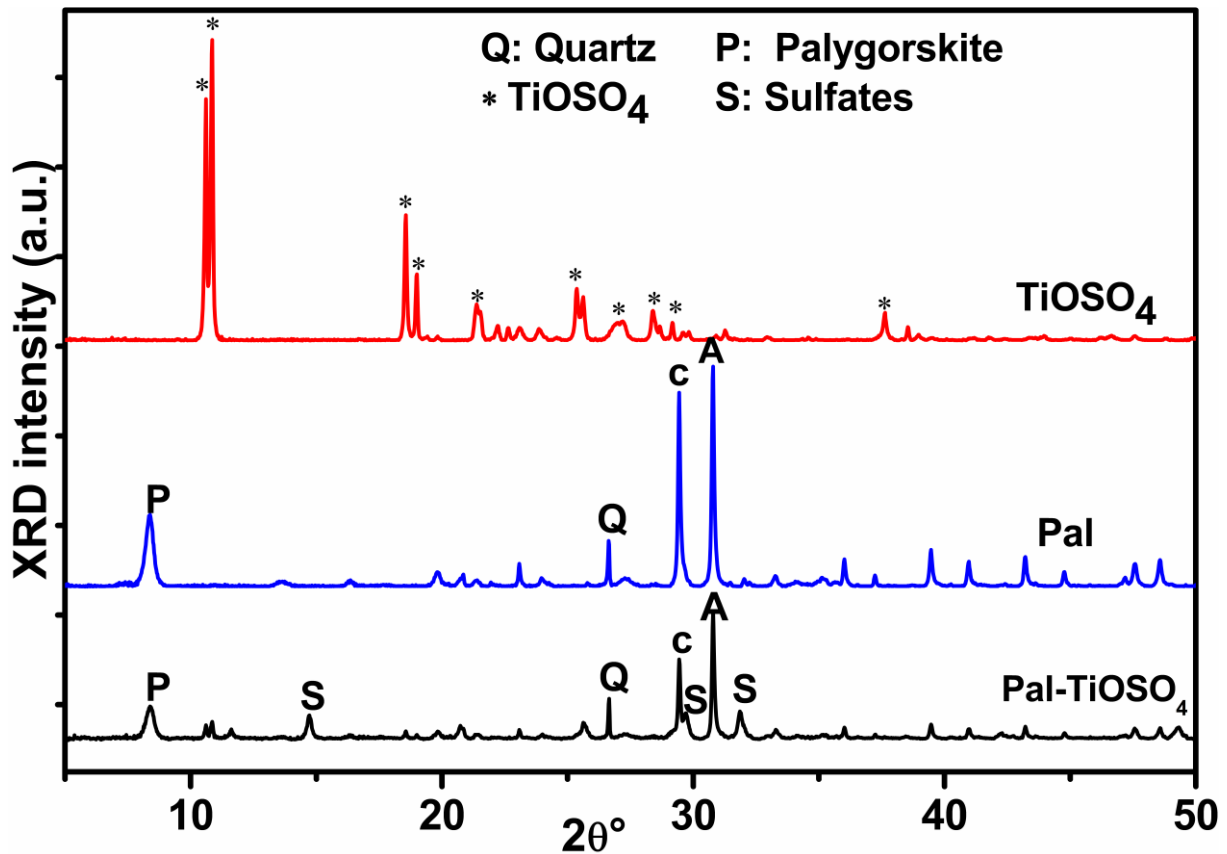
219 (picture given in the supplementary [figure 1S](#)). Briefly, a mass concentration of TiO₂_Pal that
220 permitting 90% of photons absorption was dispersed under stirring in an OG dye solution and
221 stored in a stainless steel tank (with a maximum volume of 50 L). Then 6 L of effluent were fed
222 into a flat solar panel (30 × 100 × 2 cm³) from the bottom to the top via a liquid pump and
223 recirculated into the tank. This panel was covered with a special PMMA plate to prevent
224 evaporation of compounds and to ensure watertight. This flat reactor was oriented southwards
225 and inclined at an angle around 42° in order to maximize the average solar irradiation
226 throughout the year. This was controlled by two equipments: a pyranometer whose wavelength
227 domain varies between 380 to 2800 nm and an UV radiometer (UVA-Sensor CT-UVA 3)
228 measuring the corresponding spectrum in the range of 310 – 400 nm;

229

230 **3. Results and discussion**

231 **3.1- Structural characterizations**

232 Figure 1 shows an overview of the room temperature XRD diagrams of the two starting
233 materials after a grinding for 30 min at 500 rpm: titanyl oxysulfate precursor (TiOSO₄) and
234 palygorskite-rich raw clay (Pal). Also, the XRD diagrams of a mixture of TiOSO₄ and Pal clay
235 in a mass ratio of 0.6/1 after grinding for 30 min at 500 rpm is reported (Pal_TiOSO₄).



236

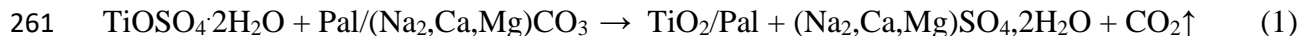
237 Fig.1: Room temperature XRD patterns of TiOSO₄, raw clay (Pal) and Pal_TiOSO₄ mixture in
238 mass ratio of 0.6/1 after grinding of each of these samples at 500 rpm for 30 minutes.

239

240 The diffractogram pertaining to the milled titanium precursor revealed only the reflections at
241 the 2θ angular positions of 10.67° (8.35 Å), 10.95° (8.20 Å), 18.61° (4.79 Å), 19.07° (4.69 Å),
242 21.43° (4.16 Å), 25.44° (3.50 Å), 25.70° (3.47 Å), 28.47° (3.13 Å), 29.25° (3.05 Å), 37.70 (2.38
243 Å), 38.61 (2.33 Å) corresponding to the compound TiOSO₄ (ICDD file N°14-503) without
244 evidence for the formation of any other crystalline phase, especially TiO₂. In the same sense,
245 the XRD pattern of the grinded Pal raw clay showed several reflections corresponding to the
246 fibrous mineral, *i.e.* palygorskite, at the angular positions described by Rhouta *et al.*, [30]. The
247 characteristic basal reflection is at $2\theta \approx 8.38^\circ$ (10.56 Å) in addition to the peaks ascribed to the
248 accessory minerals, namely the carbonates in the form of calcite (C) Mg_{0.03}Ca_{0.97}CO₃ (ICDD

249 file: 01-089-1304) and ankerite (A) $\text{Ca}_{1.01}\text{Mg}_{0.45}\text{Fe}_{0.54}(\text{CO}_3)_2$ (ICDD: 01-084-20 2066) as well
250 as quartz (Q) (ICDD file: 03-065-0466) whose strongest reflections were observed at 29.46°
251 (3.03 \AA), 30.82° (2.90 \AA) and 26.64° (3.34 \AA), respectively.

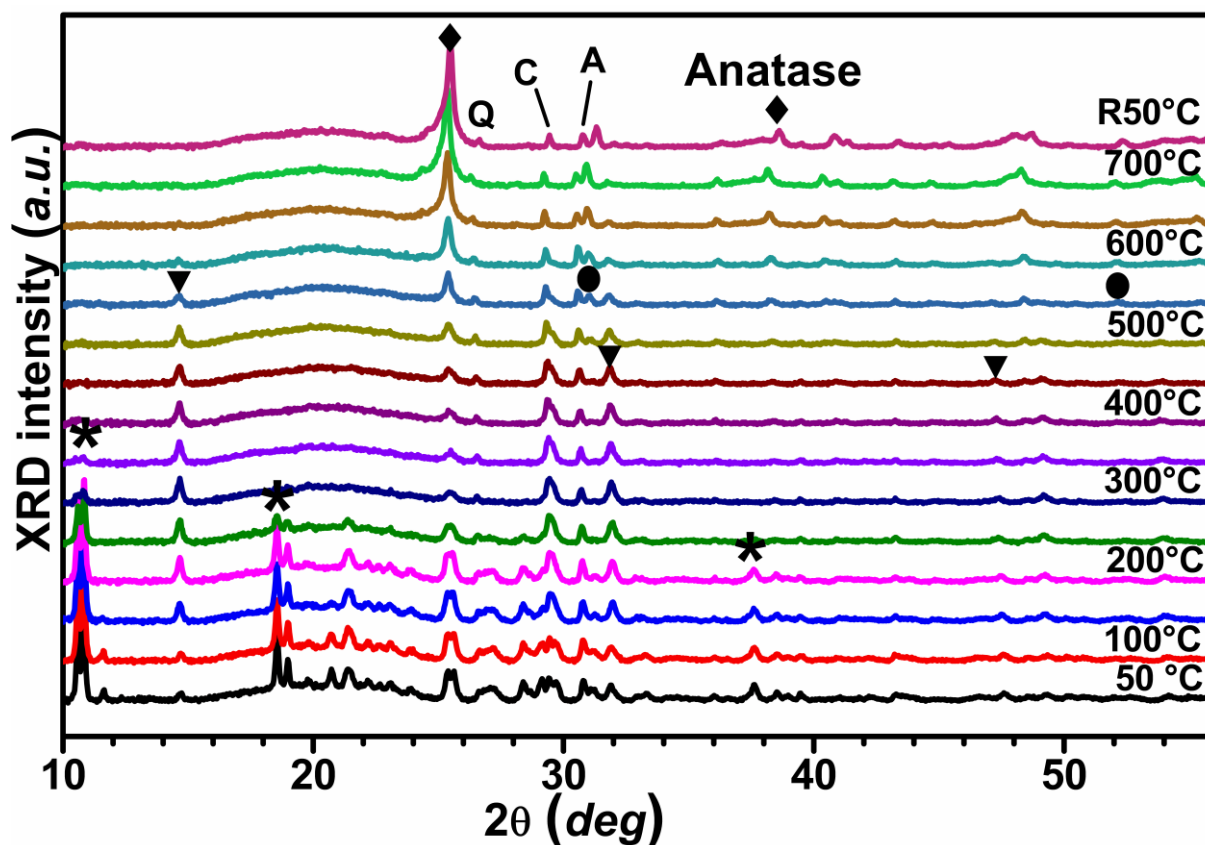
252 This result showed that both the palygorskite and the accessory phases, constituting the raw Pal
253 clay, were apparently not affected by the grinding operation in the mechanosynthesis jar since
254 their crystallographic structure remained stable. On the other hand, these grinding conditions
255 of the Pal_TiOSO₄ mixture caused a drastic decrease in the XRD intensities of TiOSO₄
256 reflexions at the point to disappear, as well as those of the carbonates (calcite and ankerite),
257 while preserving the clay structure confirmed by the persistence of the corresponding peaks.
258 The disappearance of TiOSO₄ reflexions can be due to its amorphisation but the major event
259 during grinding is the trigger of reaction (1), according to which TiOSO₄ reacts with the
260 carbonates present among the accessory minerals in the raw clay Pal:



262
263 The occurrence of this reaction was further confirmed by the production of the hydrated sulfate
264 compound $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ evidenced by the presence in the composite sample Pal_TiOSO₄ of
265 the characteristic peaks noted S on the diffractogram (Fig. 1) at angular positions 2θ of 14.71°
266 (6.00 nm), 29.71° (3.00 nm) and 31.86° (2.80 nm) in agreement with the ICDD file 01-081-
267 1848. The near-consumption of the TiOSO₄ precursor revealed by XRD may be due to the fact
268 that the low value of the mass ratio TiOSO₄:clay (0.6:1) would be the driving force of reaction
269 (1).

270 Furthermore, the reaction (1) also showed that titanium dioxide has to be formed but no
271 diffraction peaks of this oxide was observed in Figure 1 suggesting that the as-prepared TiO₂
272 phase must be amorphous after the mechanosynthesis step (TiOSO₄:clay = 0.6:1; 500 rpm; 30

273 min). Subsequently, a mixture of TiOSO_4 and Pal raw clay with the mass ratio 3.3/1, *i.e.* with
 274 Ti precursor in excess was grinded for 30 min at 500 rpm. Then, XRD patterns of this composite
 275 sample were recorded *in-situ* in air as a function of the temperature (Figure 2).



276
 277 Fig. 2: X-ray diffractograms recorded *in-situ* in air as a function of the sample temperature of a
 278 $\text{TiOSO}_4/\text{Pal}$ (3.3/1) mixture after mechanosynthesis (Step 1). These diagrams were recorded
 279 every 50°C; they represented the effect of calcination as 2nd step of the synthesis process. They
 280 showed the main compounds that disappeared were TiOSO_4 (★), calcite (C), ankerite (A), while
 281 the compounds that formed were $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ (▼), CaSO_4 (●), TiO_2 anatase (◆), and the most
 282 thermally stable accessory compounds like quartz (Q).

283
 284 For as-milled sample, the diagram recorded at 50°C revealed that, as mentioned above,
 285 amorphous TiO_2 and the hydrated CaSO_4 product were formed during the grinding stage as a

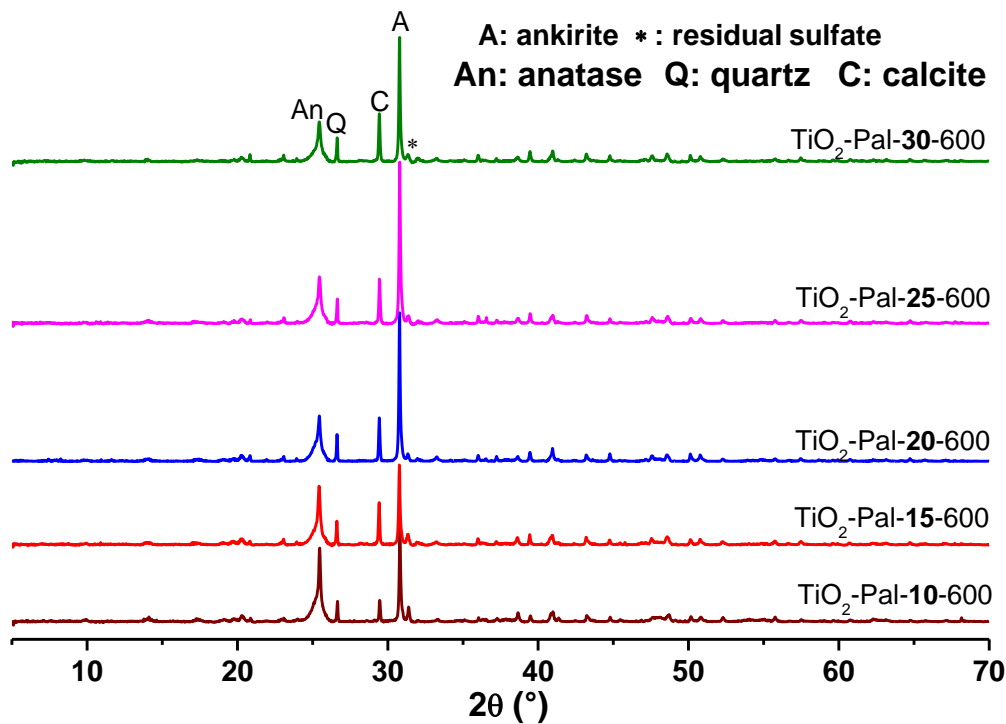
286 result of the above reaction (1). In this respect, a significant proportion of the carbonates were
287 consumed by the reaction with TiOSO_4 (that was in excess) has shown by the decrease of their
288 XRD intensity. This was further supported by a huge decrease in carbonate content determined
289 by coulometric analysis. Indeed, the carbonate content has been reduced approximately by a
290 factor of 2, from 28 ± 2 wt % in the raw clay Pal to $13 \pm 2\%$ wt % in the grinded TiOSO_4 / Pal
291 (3.3/1) mixture.

292 By increasing the temperature, it can be seen that the crystallization of anatase TiO_2 started
293 from 450°C as shown by the emergence of the corresponding peaks at angular positions 2θ of
294 about 25.44° (3.51 \AA) and 38.53° (2.33 \AA) (ICDD Data Sheet 01-021-1272). As the temperature
295 increased further, the anatase peaks became more intense and well resolved, indicating the
296 improvement of its crystallization. The anatase peaks remained observable up to 700°C , without
297 the appearance of any XRD peaks of the less photoactive rutile variety. This strongly denoted
298 the remarkable stability of the anatase formed under the conditions of this study. Palygorskite
299 peaks were observable up to 400°C , beyond which their intensities severely reduced. This can
300 be ascribed to the occurrence of structural collapse of the clay mineral. However, this can be
301 also due to an absorption filter induced by the conformal coverage of anatase particles on
302 palygorskite fibers as suggested by Rhouta *et al.*, [28] and Bouna *et al.*, [29] and confirmed by
303 the TEM analyses shown in the next section.

304 In order to examine the effect of grinding time on the reactivity of TiOSO_4 with the carbonates
305 present in the Pal raw clay, a mixture of the two compounds in a ratio of 0.6 / 1 was ground at
306 500 rpm for 10, 15, 20, 25 and 30 min and then air annealed at 600°C for 1 h. The
307 superimposition of the corresponding XRD diagrams (Fig. 3) clearly showed the formation of
308 anatase TiO_2 for all the samples investigated regardless grinding time. Nevertheless, the anatase
309 crystallinity appeared to improve with the grinding time as evidenced by the gradual narrowing
310 of its characteristic peak at about 2θ around 25° . In this respect, by referring to quartz, which is

311 an insensible and stable accessory mineral under the applied grinding conditions, the increase
312 of the intensity ratio of the main anatase/quartz peaks is noteworthy. This probably reflected an
313 increase in the amount of anatase phase formed with the increase of grinding time.

314



315

316 Fig. 3: Stacking of XRD patterns of TiO₂_Pal photocatalysts prepared by grinding TiOSO₄ and
317 Pal raw clay in a mass ratio of 0.6/1 during 10, 15, 20, 25 and 30 min at 500 rpm.

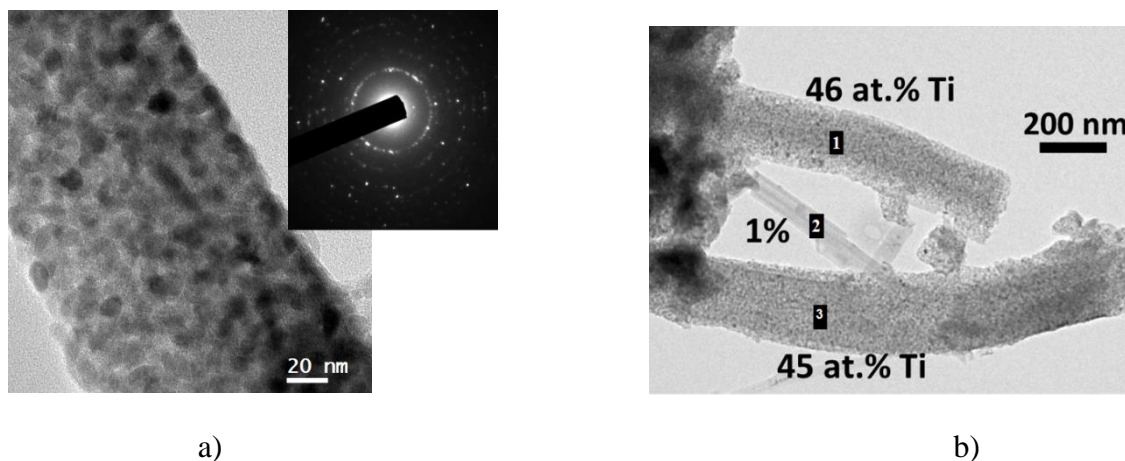
318

319 3.2- Microstructural characterizations

320 XRD results were further supported by TEM characterizations. Indeed, depending on the
321 grinding conditions, TEM analysis after the first step showed palygorskite fibers of 30-70 nm
322 in diameter and 650 nm in length mixed with TiOSO₄ platelets of 400-600 nm with an average
323 thickness of 3-5 μm. At this stage, no evidence for crystallized anatase nanoparticles (NPs) was
324 found confirming this oxide phase was amorphous. After annealing at 600°C in air for 1 h, TEM
325 revealed that palygorskite fibers were entirely wrapped with homogeneous monodisperse and

326 spherical TiO₂ anatase NPs 10-15 nm in diameter (Fig. 4a). Only a few palygorskite fibers were
327 not covered as revealed by EDS analysis. For most of them, a granular and conformal TiO₂
328 coverage formed a uniform cladding (Fig. 4b).

329



330

331

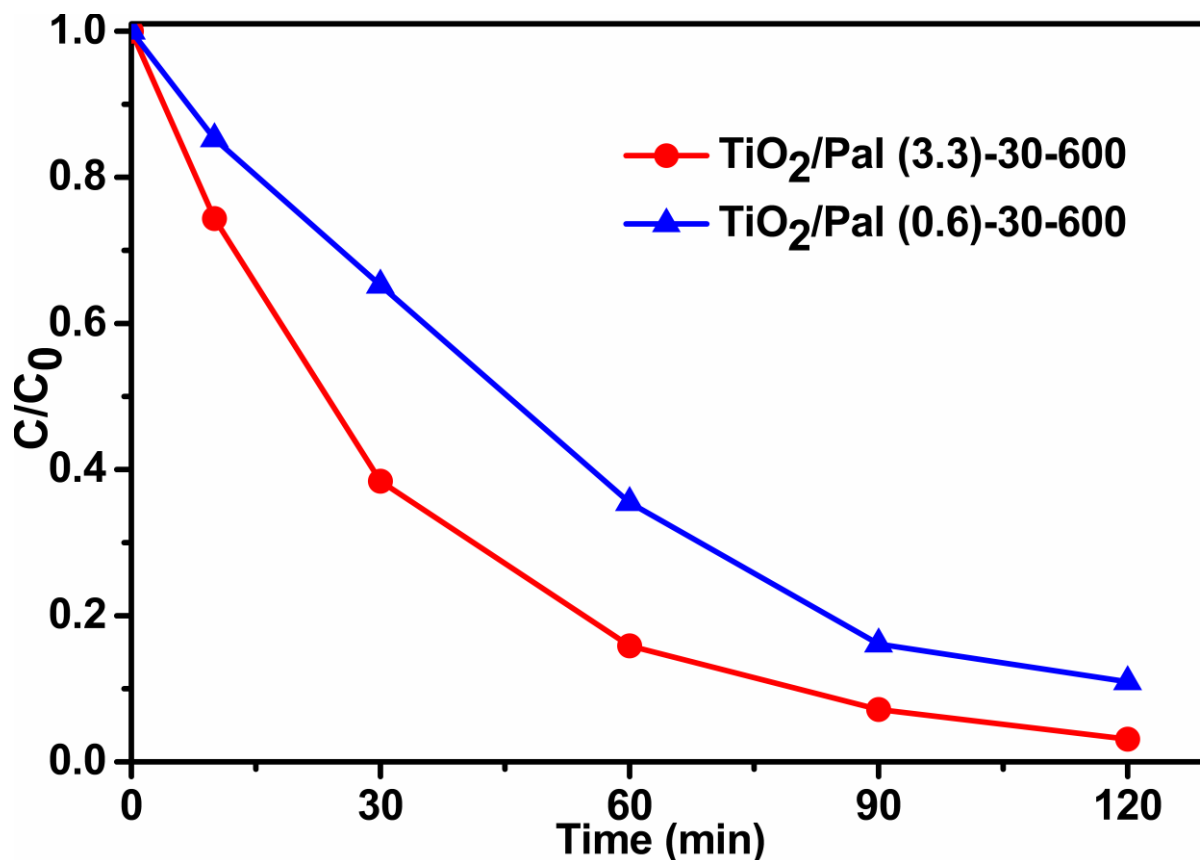
332 Fig. 4: TEM micrographs and corresponding electron diffraction pattern indexed as TiO₂
333 anatase (a) and EDS local analysis showing uncoated (point 2) and uniformly coated point 1
334 and 3) palygorskite fibers (b).

335

336 3.3- Photocatalytic properties under UV light

337 The photocatalytic activity of different TiO₂-Pal composite samples elaborated by
338 mechanosynthesis was tested towards the degradation under UV light of OG dye by using the
339 laboratory set-up described in the experimental section (2.3). The results in Figure 5 showed
340 that photocatalytic efficiency significantly increased with the amount of TiOSO₄ used in
341 photocatalyst synthesis and thus the amount of TiO₂ present in TiO₂-Pal nanocomposite. This
342 was evidenced by on one hand the strong decrease of OG concentration for instance in the first
343 10 min, revealing a high initial degradation rate of the pollutant around $2.6 \times 10^{-2} \text{ s}^{-1}$ for TiO₂/Pal
344 mass ratio of 3.3/1 with respect to that determined for the mass ratio of 0.6/1 ($\approx 1.5 \times 10^{-2} \text{ s}^{-1}$).
345 On the other hand, the almost total elimination of the OG dye from the solution was achieved
346 within about 2 h when using TiO₂/Pal mass ratio of 3.3/1 whilst almost 10% of the dye remained

347 after the same time of UV irradiation in presence of TiO₂/Pal mass ratio of 0.6/1 (but a plateau
348 has not yet been reached).

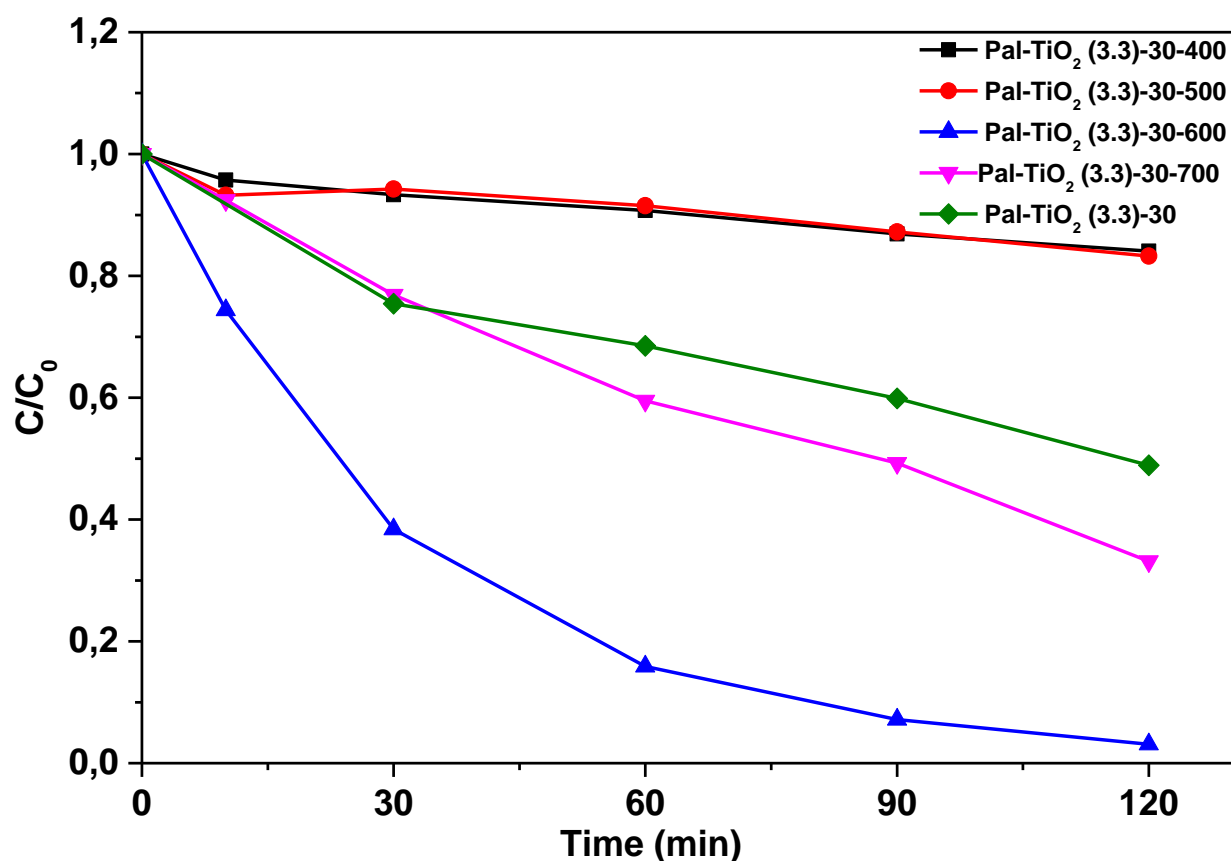


349
350 Fig. 5: Change in the concentration of OG (where C₀ and C denote the concentrations of OG at
351 the initial time t = 0, and after an elapsed time t of the photocatalytic reaction) vs. UV irradiation
352 time of the samples, differing in TiOSO₄/ Pal mass ratio (0.6/1 and 3.3/1), grinded during 30
353 min at 500 rpm and afterwards air annealed at 600°C for 1 h.

354
355 The influence of annealing temperature on the photocatalytic activity towards the removal of
356 OG dye of TiO₂_Pal was afterwards studied on the most active one corresponding to TiO₂/Pal
357 mass ratio = 3.3/1. Figure 6 interestingly showed that the unheated as-milled Pal_TiOSO₄
358 mixture (sample Pal_TiO₂_(3.3)_30) already exhibited photoactivity under UV irradiation.
359 Indeed, 50% of the initial quantity of OG decreased after 2 hours of irradiation. This is due to
360 the formation of photoactive TiO₂ resulting, as beforehand mentioned, from the heterogeneous

361 solid-state reaction between TiOSO_4 and the carbonate phases (calcite + ankerite) present as
362 accessory minerals in the Pal raw clay (reaction 1). Although the TiO_2 formed in as-grinded
363 material was amorphous, as ascertained above by XRD, this is not exceptional since it was
364 already shown that amorphous TiO_2 can be active in photocatalysis under UV irradiation [41].
365 Indeed, from a general point of view, even if amorphous semiconductors have less efficient
366 electronic properties than their crystallized counterparts, they nevertheless find specific
367 applications as in photovoltaic.

368



369

370 Fig. 6: Change in the concentration of OG vs. UV irradiation time of TiO_2 _Pal elaborated by
371 mechano-synthesis (TiOSO_4 /Pal mass ratio = 3.3/1, grinding at 500 rpm for 30 min) and air
372 annealing at 400, 500, 600 and 700°C.

373

374 Samples annealed at 400 and 500°C showed quite similar photo-degradation curves of the OG
375 and paradoxically showed a lower photoactivity compared to as-grinded sample, allowing the
376 removal of only 15% after 2 hours of illumination. This annealing temperature range is
377 therefore insufficient to ensure a good crystallization of TiO₂ in the form of anatase but, on the
378 other hand, it seems to be sufficient for inducing a detrimental diffusion of species that trap
379 excitons (Pal clay cations for example), thus affecting the photocatalytic efficiency of the
380 composite. Calcination at 600°C promoted the most efficient active palygorskite-supported
381 TiO₂ photocatalyst since it allowed almost complete degradation of the OG after 2 hours of UV
382 irradiation. This improvement was attributed to the good crystallinity of TiO₂ anatase upon the
383 sample calcination at 600°C as confirmed above by XRD. On the other hand, when the sample
384 was annealed at 700°C, photocatalytic activity again decreased. This reduction in photocatalytic
385 activity may be due to the growth of TiO₂ particles beyond the optimal nanocrystalline size,
386 which promotes the recombination of charge carriers. Also, a partial phase transformation of
387 the more active anatase TiO₂ phase into the less photoactive rutile variety as reported by Bouna
388 *et al.*, [29] and Rhouta *et al.*, [28] is not excluded although none of the corresponding peaks
389 have yet been detected at 700°C, the presence of other crystalline phases can hide them.

390

391 **3.4- Photocatalytic properties under sunlight**

392 Owing to its high photoactivity under UV evidenced above by the tests on the laboratory set-
393 up, the TiO₂_Pal nanocomposite with mass ratio TiO₂/Pal of 3.3/1 was thereafter retained for
394 performing the study of photocatalytic activity under sunlight towards the removal of OG dye.

395

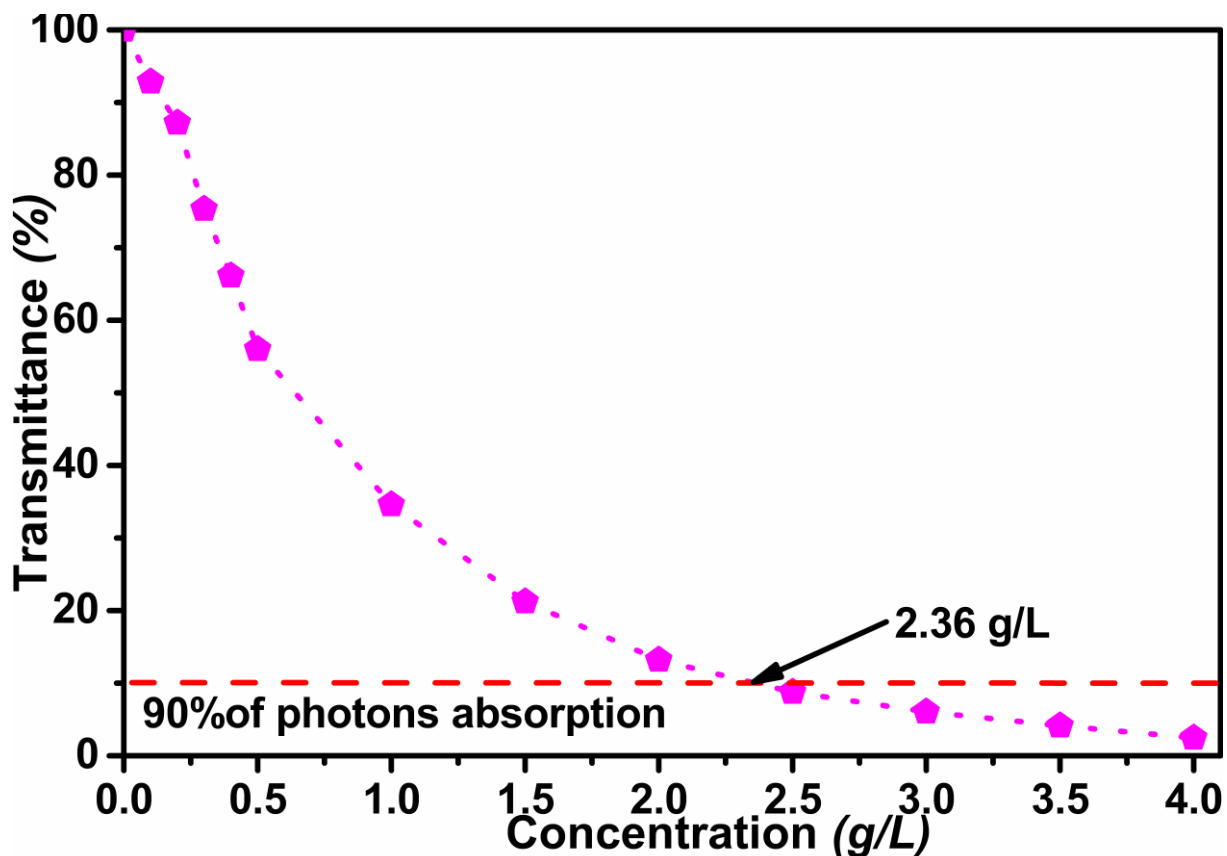
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398

399 **3.4.1- Activity under constant solar irradiation – indoor experiments**

400 For studying optical properties of TiO₂-Pal, the change in transmittance (%), defined as the
401 ratio of transmitted (I_t) to incident (I_i) intensities, was followed versus catalyst slurry mass
402 concentration. Figure 7 showed that the necessary amount for the absorption of 90% of incident



403
404 Fig. 7: Variation of transmittance in the spectral range 250 -1100 nm (artificial solar light
405 1000 W.m⁻²) as a function of the catalyst dispersion concentration in an aqueous suspension.

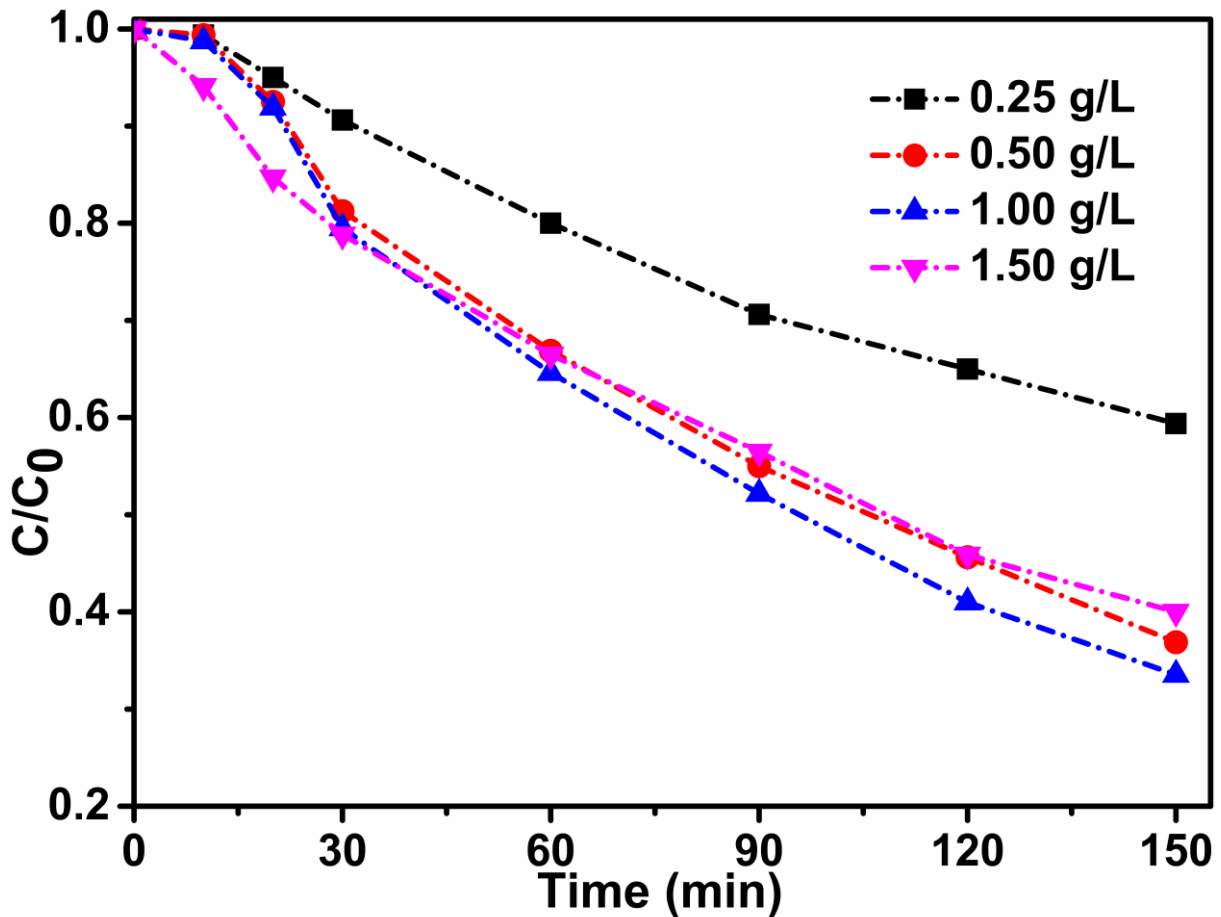
406
407 light simulating sunlight (1000 W/m²) for a catalyst dispersion thickness of 2 cm (C_{2cm}) was
408 around 2.36 g/L, *i.e.* 1.34 g/L of TiO₂ taking into account its proportion of 57 wt% assessed by
409 Individual Counting by single Particle (ICP) in the nanocomposite. Photocatalytic tests in batch
410 mode using the indoor solar simulator described in the experimental section were performed by
411 varying the amount of TiO₂_Pal dispersed in OG solution of 5 cm of thickness around the
412 optimum amount (C_{5cm} = 2/5×C_{2cm} ≈ 0.95 g/L) allowing maximum absorption.

413

414 Figure 8 showed that very low amount of TiO₂_Pal, *e.g.* 0.25 g/L, exhibited a relatively low
415 photocatalytic activity leading to the removal of about only 40% of OG after 150 min of
416 irradiation with an initial photo-degradation rate of about $5 \times 10^{-3} \text{ s}^{-1}$. Nevertheless, by increasing
417 the TiO₂_Pal mass concentration beyond 0.5 g/L up to 1.5 g/L, a better efficiency occurs and a
418 quite similar photocatalytic behavior of the photocatalyst towards OG elimination was
419 observed. Indeed, the OG photodegradation considerably increased as evidenced on one hand,
420 by the strong decrease of OG concentration for instance in the first 20 min, revealing a high
421 initial degradation rate ($\approx 7 \times 10^{-3} \text{ s}^{-1}$) of the pollutant and, on the other hand, by the elimination
422 of almost 60% of OG dye from the solution within the same time of irradiation. These results
423 showed that around the optimal mass concentration of TiO₂_Pal ($\approx 0.95 \text{ g/L}$) beforehand
424 determined by optical measurements, the catalyst exhibited maximal photoactivity for dye
425 removal due to highest light absorption. Thus, an increase in the mass concentration of the
426 photocatalysts beyond its optimal mass concentration is unnecessary since the maximum
427 absorption of incident light has already been reached. This is in agreement with Plantard *et al.*,
428 [42] who reported that for a given pollutant and a fixed initial concentration, the degradation
429 kinetic constants obtained for the same photocatalyst depended solely on the quantity of
430 photons absorbed. As a result, degradation by photocatalysis is function to the concentration of
431 the catalyst in suspension, up to a threshold value at which all the incident radiation is almost
432 absorbed.

433

434



435

436 Fig. 8: Variation of the relative OG concentration versus time (where C_0 and C denote the OG
 437 concentrations at the initial time $t = 0$, and after an elapsed time t) in the 1000 W.m^{-2} solar
 438 simulator recorded for different mass concentrations of the $\text{TiO}_2\text{-Pal}$ composite photocatalyst.

439

440

441 Besides photocatalyst mass concentration in the aqueous suspension, photons fluxes also
 442 constituted a crucial parameter influencing heterogeneous photocatalysis process especially
 443 under solar light characterized by the variation of irradiation intensity. Figure 9, representing
 444 OG proportion change versus solar irradiation time at different photons fluxes in presence of
 445 0.94 g/L of $\text{TiO}_2\text{-Pal}$ revealed that in general, and as expected, an increase of the radiation
 446 intensity led to an increase of the OG pollutant degradation. This is the result of the increase of
 447 quantity of photons absorbed. It is obviously well known that this is only the UV part of the

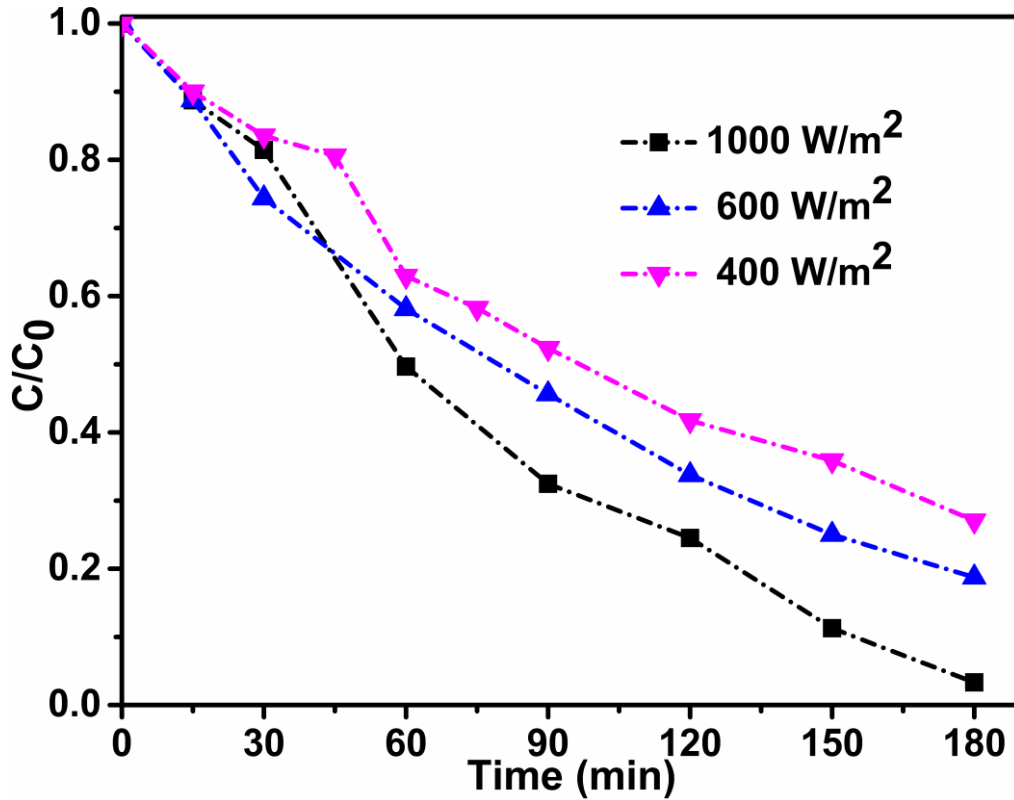
448 solar spectrum that is effective for photocatalytic treatment with TiO₂ as active component.
449 With the solar simulator UV intensity is directly proportional to the total intensity delivered by
450 the lamp. It is almost the case for solar natural irradiation (even if the UV percentage is
451 influenced by the weather conditions). So, we made the choice to keep the total radiation
452 intensity received as the reference. It is the energy flux received by the surface of a reactor
453 working in outdoor conditions.

454
455 For being transposed to solar photocatalysis treatment, OG photodegradation kinetic should be
456 modulated taking into account the irradiation intensity key parameter. In photodegradation of a
457 target molecule (OG herein) using a slurry catalyst (TiO₂_Pal), rates can be approached by the
458 modified Langmuir-Hinshelwood (L-H) relationship (1) [43]:

459

$$460 \quad \frac{dC}{dt} = k(I) \frac{C}{1+\beta.C} = -\left(\alpha \cdot \frac{S}{V_T} \cdot I\right) \frac{C}{1+\beta.C} \quad (1)$$

461 With $k(I)$ the apparent kinetic constant (s^{-1}) function of the intensity, C the OG concentration
462 ($g.L^{-1}$), β ($L.g^{-1}$) a constant determined by comparison between calculated and experimental
463 data. In the simplest case, $k(I)$ is directly proportional to the intensity I received by unit volume
464 of solution (V_T in L) with an irradiated surface S (m^2). α ($J.L^{-1}$) is the second unknown
465 parameter. If necessary, a dependence of k according to a law in power of the irradiation can
466 be introduced to account of additional limiting phenomena such as the charge recombination.



467

468 Fig. 9: Variation of the OG proportion versus time (s) upon irradiation simulating sunlight at
 469 400, 600 and 1000 W.m⁻² in presence of TiO₂_Pal (0.94 g/L) composite photocatalyst.

470

471

472 For a constant irradiation intensity, the integration of equation (1) leads to the expression (2):

$$473 \quad f\left(\frac{C}{C_0}, \beta\right) = \ln\left(\frac{C}{C_0}\right) + \beta \cdot C_0 \cdot \left(\frac{C}{C_0} - 1\right) = -k(I) \cdot t \quad (2)$$

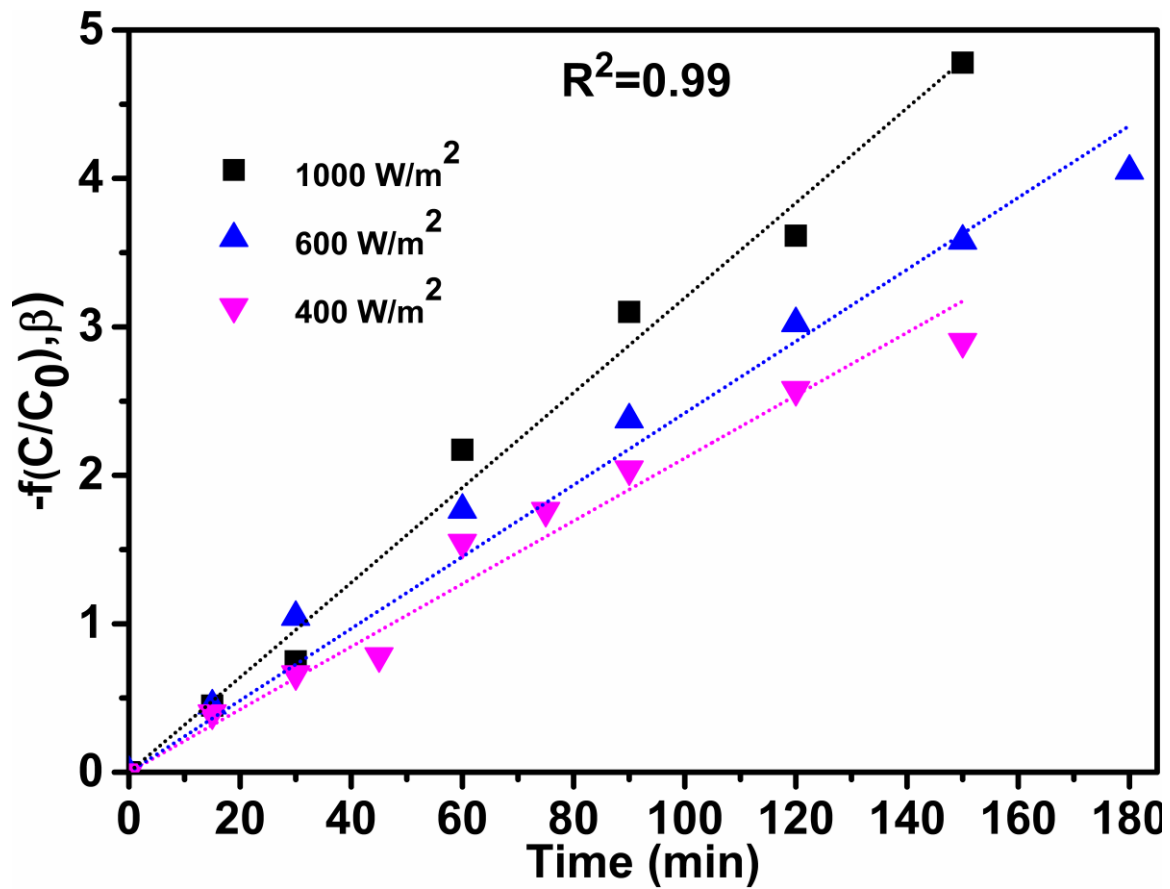
474 To be valuable, the value of β has to be constant whatever is the irradiation. It is determined
 475 simply by considering the left part of equation 2 depends linearly on time. Figure 10 depicted
 476 experimental profiles of the logarithmic adimensional concentration C/C_0 as a function of the
 477 time with a value of $\beta = 0.65 \text{ L.g}^{-1}$. It showed linear dependence with a satisfactory agreement.

478 This ascertained pseudo first-order kinetics whose the slope k depends on the intensity of the
 479 irradiation according to the relationship (3).

$$480 \quad k(I) = \frac{S}{V_T} \cdot \alpha \cdot I \quad (3)$$

481

482

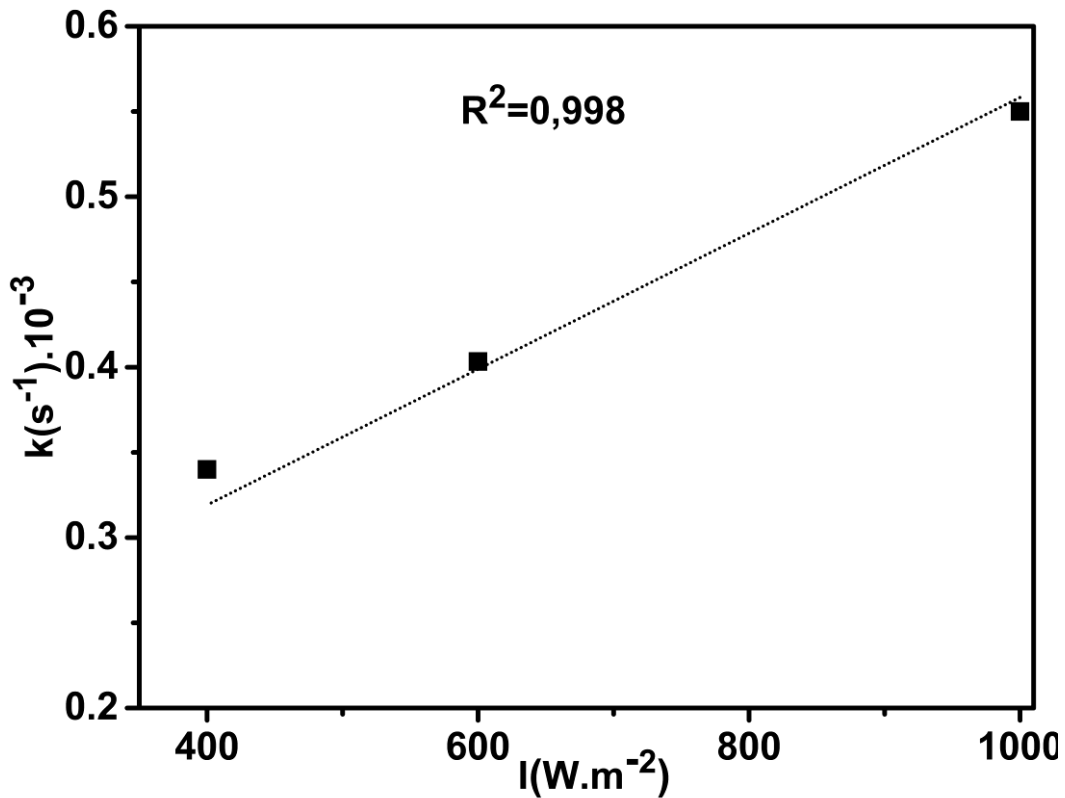


483

484 Fig.10: Linear variation of $\ln(C/C_0)$ of OG versus time (s) for different irradiation intensities
485 simulating sunlight in the presence of 0.94 g/L of $\text{TiO}_2\text{-Pal}$ catalyst for $\beta = 0.65 \text{ L.g}^{-1}$
486 confirming a pseudo first order kinetics. Continuous colored lines represent the best agreement
487 between the experimental data and a linear regression for each level of irradiation.

488

489 Likewise, the variation of the apparent kinetic constant k versus irradiation intensity (I) (Fig.
490 11) showed a linear trend supported by a reasonable degree of accuracy of about 0.99. Hence,
491 the value of the kinetic constant (α), deduced from the slope, can be assessed to be around 1.5
492 L/kJ.



493

494 Fig. 11: Linear variation of the kinetic constant k of OG photodegradation versus the
 495 irradiation intensity I simulating sunlight onto TiO_2 _Pal photocatalyst slurry. The continuous
 496 gray line simulates the data according to equation (3).

497

498 By introducing the values of α and β in the expression (2), the C/C_0 plots versus time show a
 499 very good fitting between the experimental and simulated data for all irradiation flux densities,
 500 as expected from the good agreement already reported in Figures 10 and 11. This result
 501 validates the proposed kinetic model described by equation (2).

502

503 3.4.2- Activity under natural discontinuous irradiation - outdoor solar pilot

504 The photocatalytic tests for the removal of OG dye from aqueous solution were carried out in
 505 presence of TiO_2 _Pal slurry by using an outdoor solar pilot and according to conditions
 506 described in the experimental section (2.3). Nonetheless, owing to the variation of solar

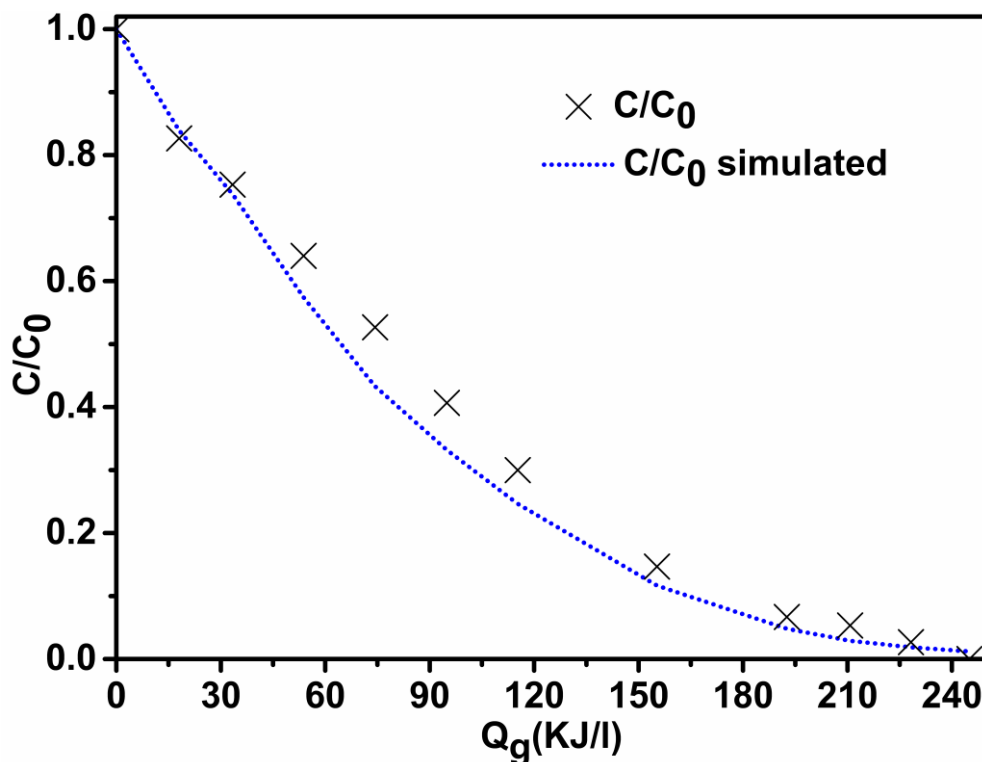
507 irradiation along a day, the change of OG dye during these tests should be versus the cumulative
 508 energy Q_g ($J.L^{-1}$) received by the reactor given by the relationship (4) [44]:

$$509 \quad Q_g = \frac{S}{V_T} \cdot \int_0^{t_i} I(t) dt \quad (4)$$

510 with t_i (s) the time at which an aliquot was taken for being centrifuged and analyzed by the
 511 spectrophotometer and $I(t)$ the solar irradiation intensity measured over time using the sensors
 512 mounted on the pilot as described in the experimental section.

513

514 Figure 12 shows, like data obtained with the indoor solar simulator in "batch" mode, a decrease
 515 in OG dye proportion upon solar irradiation, which thus confirms the photoactivity of TiO_2_Pal
 516 under solar light. In this respect, 50% of the OG dye was removed with a cumulated energy of
 517 74.2 kJ/L whilst the total removal of the dye required a cumulated energy of 250 kJ/L.



518

519 Fig. 12: Change of the experimental relative concentration of the OG (×) and simulated data
 520 (dotted curve) versus the total cumulated energy obtained for TiO_2_Pal composite
 521 photocatalyst.

522

523 Besides, by introducing the numerical values of α (1.5 L/kJ) and β (0.65 L.g⁻¹) beforehand
524 determined in the relationship (5) derived from the above one (2) after substituting I(t) by Q_g(t),
525 a good agreement between simulated and experimental data was observed with a good degree
526 of accuracy.

$$527 \quad \frac{c(t)}{c_0} = e^{-[(\alpha \frac{S}{V_T} Q_g(t)) + (\beta c_0 (\frac{c}{c_0} - 1))]} \quad (5)$$

528 This confirmed the validation of the kinetic model proposed and ascertained that the OG
529 photodegradation in presence of TiO₂_Pal slurry was of first order with a kinetic constant of
530 **1.5 L/kJ** and did not involve adsorption phenomenon.

531

532 **4. Conclusion**

533 TiO₂ photocatalyst supported onto natural palygorskite clay mineral fibers (TiO₂_Pal) was
534 successfully elaborated by a one-pot dry mechanical method. This elaboration process is very
535 interesting because it directly uses palygorskite clay without the multiple purification steps that
536 wet processes frequently required. Furthermore, it is solvent free, eco-friendly and based on
537 smart *in situ* solid-state reaction between carbonates accessory minerals contained in the raw
538 clay and a cheap molecular Ti precursor. As a result, it can be easily scaled up to an
539 economically viable large-scale production.

540 Structural analysis and microstructural characterization using XRD and TEM respectively
541 showed that TiO₂_Pal, revealed homogeneous monodisperse TiO₂ NPs in the form of anatase
542 wrapping palygorskite fibers. This sample was shown to be the most photoactive under UV
543 irradiation towards the removal of OG dye from aqueous solution upon the use of a laboratory
544 set-up. Then photocatalytic tests carried out by an indoor solar simulator set-up on OG dye
545 solution containing an optimal mass concentration of TiO₂_Pal nanocomposite was found to

546 assure the maximum of the elimination of OG. In this respect, a good agreement was
547 demonstrated between experimental and simulated data using a pseudo first order kinetic model
548 for the dye photodegradation. The same photocatalytic behavior was also obtained with an
549 outdoor solar pilot confirming the photoactivity of these supported TiO₂_Pal photocatalysts
550 under sunlight.

551

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569 **References**

- 570 [1] P.K.J. Robertson, Semiconductor photocatalysis: an environmentally acceptable
571 alternative production technique and effluent treatment process, *J. Clean. Prod.* 4 (1996)
572 203–212. doi:10.1016/S0959-6526(96)00044-3.
- 573 [2] J. Herrmann, Heterogeneous photocatalysis: fundamentals and applications to the
574 removal of various types of aqueous pollutants, *Catal. Today.* 53 (1999) 115–129.
575 doi:10.1016/S0920-5861(99)00107-8.
- 576 [3] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, 1 (2000) 1–21.
577 doi:10.1016/S1389-5567(00)00002-2.
- 578 [4] A. Fujishima, X. Zhang, Titanium dioxide photocatalysis: present situation and future
579 approaches, *Comptes Rendus Chim.* 9 (2006) 750–760. doi:10.1016/j.crci.2005.02.055.
- 580 [5] Y. Paz, Preferential photodegradation - why and how?, *Comptes Rendus Chim.* 9
581 (2006) 774–787. doi:10.1016/j.crci.2005.03.032.
- 582 [6] O. Carp, Photoinduced reactivity of titanium dioxide, *Prog. Solid State Chem.* 32
583 (2004) 33–177. doi:10.1016/j.progsolidstchem.2004.08.001.
- 584 [7] R. Ghosh Chaudhuri, S. Paria, Visible light induced photocatalytic activity of sulfur
585 doped hollow TiO₂ nanoparticles, synthesized via a novel route, *Dalt. Trans.* 43 (2014)
586 5526–5534. doi:10.1039/c3dt53311e.
- 587 [8] M.A. Alvarez Lemus, H. Monroy, T. López, E.N. De la Cruz Hernández, R. López-
588 González, Effect of surface modification on the bioactivity of sol–gel TiO₂-based
589 nanomaterials, *J. Chem. Technol. Biotechnol.* 91 (2016) 2148–2155.
590 doi:10.1002/jctb.4915.
- 591 [9] C.B.D. Marien, C. Marchal, A. Koch, D. Robert, P. Drogui, Sol-gel synthesis of TiO₂
592 nanoparticles: effect of Pluronic P123 on particle's morphology and photocatalytic
593 degradation of paraquat, *Environ. Sci. Pollut. Res.* 24 (2017) 12582–12588.

- 594 doi:10.1007/s11356-016-7681-2.
- 595 [10] A. Moiseev, M. Krichevskaya, F. Qi, A.P. Weber, J. Deubener, Analysis of
596 photocatalytic performance of nanostructured pyrogenic titanium dioxide powders in
597 view of their polydispersity and phase transition: Critical anatase particle size as a
598 factor for suppression of charge recombination, *Chem. Eng. J.* 228 (2013) 614–621.
599 doi:10.1016/j.cej.2013.05.038.
- 600 [11] A.H. Mamaghani, F. Haghghat, C.S. Lee, Hydrothermal/solvothermal synthesis and
601 treatment of TiO₂ for photocatalytic degradation of air pollutants: Preparation,
602 characterization, properties, and performance, *Chemosphere.* 219 (2019) 804–825.
603 doi:10.1016/j.chemosphere.2018.12.029.
- 604 [12] T. Umebayashi, T. Yamaki, H. Itoh, K. Asai, Band gap narrowing of titanium dioxide
605 by sulfur doping, *Appl. Phys. Lett.* 81 (2002) 454. doi:10.1063/1.1493647.
- 606 [13] T. Umebayashi, T. Yamaki, S. Yamamoto, A. Miyashita, S. Tanaka, T. Sumita, K.
607 Asai, Sulfur-doping of rutile-titanium dioxide by ion implantation: Photocurrent
608 spectroscopy and first-principles band calculation studies, *J. Appl. Phys.* 93 (2003)
609 5156–5160. doi:10.1063/1.1565693.
- 610 [14] P. Billik, G. Plesch, V. Brezová, L. L’Kuchta, M. Valko, M. Mazúr, Anatase TiO₂
611 nanocrystals prepared by mechanochemical synthesis and their photochemical activity
612 studied by EPR spectroscopy, *J. Phys. Chem. Solids.* 68 (2007) 1112–1116.
613 doi:10.1016/j.jpcs.2007.02.010.
- 614 [15] P. Billik, G. Plesch, Mechanochemical synthesis of anatase and rutile nanopowders
615 from TiOSO₄, *Mater. Lett.* 61 (2007) 1183–1186. doi:10.1016/j.matlet.2006.06.080.
- 616 [16] M. Čaplovičová, P. Billik, Ľ. Čaplovič, V. Brezová, T. Turáni, G. Plesch, P. Fejdi, On
617 the true morphology of highly photoactive anatase TiO₂ nanocrystals, *Appl. Catal. B*
618 *Environ.* 117–118 (2012) 224–235. doi:10.1016/j.apcatb.2012.01.010.

- 619 [17] M. Houari, M. Saidi, D. Tabet, P. Pichat, H. Khalaf, The Removal of 4-chlorophenol
620 and Dichloroacetic Acid in Water Using Ti-, Zr- and Ti/Zr-Pillared Bentonites as
621 Photocatalyst, *Am. J. Appl. Sci.* 2 (2005) 1136–1140.
622 doi:10.3844/ajassp.2005.1136.1140.
- 623 [18] J. Liu, M. Dong, S. Zuo, Y. Yu, Solvothermal preparation of TiO₂/montmorillonite and
624 photocatalytic activity, *Appl. Clay Sci.* 43 (2009) 156–159.
625 doi:10.1016/j.clay.2008.07.016.
- 626 [19] M. Nieto-Suárez, G. Palmisano, M.L. Ferrer, M.C. Gutiérrez, S. Yurdakal, V.
627 Augugliaro, M. Pagliaro, F. del Monte, Self-assembled titania–silica–sepiolite based
628 nanocomposites for water decontamination, *J. Mater. Chem.* 19 (2009) 2070.
629 doi:10.1039/b813864h.
- 630 [20] T. An, J. Chen, G. Li, X. Ding, G. Sheng, J. Fu, B. Mai, K.E. O’Shea, Characterization
631 and the photocatalytic activity of TiO₂ immobilized hydrophobic montmorillonite
632 photocatalysts, *Catal. Today.* 139 (2008) 69–76. doi:10.1016/j.cattod.2008.08.024.
- 633 [21] P. Aranda, R. Kun, M.A. Martín-Luengo, S. Letaïef, I. Dékány, E. Ruiz-Hitzky,
634 Titania–Sepiolite Nanocomposites Prepared by a Surfactant Templating Colloidal
635 Route, *Chem. Mater.* 20 (2008) 84–91. doi:10.1021/cm702251f.
- 636 [22] B. Rhouta, H. Kaddami, J. Elbarqy, M. Amjoud, L. Daoudi, F. Maury, F. Senocq, A.
637 Maazouz, J.-F. Gerard, Elucidating the crystal-chemistry of Jbel Rhassoul stevensite
638 (Morocco) by advanced analytical techniques, *Clay Miner.* 43 (2008) 393–403.
639 doi:10.1180/claymin.2008.043.3.05.
- 640 [23] L. Bouna, B. Rhouta, M. Amjoud, A. Jada, F. Maury, L. Daoudi, F. Senocq,
641 Correlation between eletrokinetic mobility and ionic dyes adsorption of Moroccan
642 stevensite, *Appl. Clay Sci.* 48 (2010) 527–530. doi:10.1016/j.clay.2010.02.004.
- 643 [24] O. Lakbita, B. Rhouta, F. Maury, F. Senocq, M. Amjoud, A. Jada, L. Daoudi, ,

- 644 Supported Photocatalyst Based on CuO – TiO₂/Palygorskite Nanocomposite Material
645 for Wastewater Treatment, *J. Colloid Sci. Biotechnol.* 5 (2016) 1–7.
646 doi:10.1166/jcsb.2016.1150.
- 647 [25] O. Lakbita, B. Rhouta, F. Maury, F. Senocq, M. Amjoud, L. Daoudi, On the key role of
648 the surface of palygorskite nanofibers in the stabilization of hexagonal metastable β -
649 Ag₂CO₃ phase in palygorskite-based nanocomposites, *Appl. Clay Sci.* 172 (2019).
650 doi:10.1016/j.clay.2019.02.023.
- 651 [26] W. Xie, G. Zhang, B. Mu, Z. Tanga, J. Zhang, The promoting effect of palygorskite on
652 CeO₂-WO₃-TiO₂ catalyst for the selective catalytic reduction of NO_x with NH₃, *Appl.*
653 *Clay Sci.* 192 (2020) 1–10. doi:10.1016/j.clay.2020.105641.
- 654 [27] A. Wu, D. Wang, C. Wei, X. Zhang, Z. Liu, P. Feng, X. Ou, Y. Qiang, H. Garcia, J.
655 Niu, A comparative photocatalytic study of TiO₂ loaded on three natural clays with
656 different morphologies, *Appl. Clay Sci.* 183 (2019) 1–12.
657 doi:10.1016/j.clay.2019.105352.
- 658 [28] B. Rhouta, L. Bouna, F. Maury, F. Senocq, M.C. Lafont, A. Jada, M. Amjoud, L.
659 Daoudi, Surfactant-modifications of Na⁺-beidellite for the preparation of TiO₂-Bd
660 supported photocatalysts: II-Physico-chemical characterization and photocatalytic
661 properties, *Appl. Clay Sci.* 115 (2015) 266–274. doi:10.1016/j.clay.2015.04.025.
- 662 [29] L. Bouna, B. Rhouta, M. Amjoud, F. Maury, M.-C. Lafont, a. Jada, F. Senocq, L.
663 Daoudi, Synthesis, characterization and photocatalytic activity of TiO₂ supported
664 natural palygorskite microfibers, *Appl. Clay Sci.* 52 (2011) 301–311.
665 doi:10.1016/j.clay.2011.03.009.
- 666 [30] B. Rhouta, E. Zatile, L. Bouna, O. Lakbita, F. Maury, L. Daoudi, M.C. Lafont, M.
667 Amjoud, F. Senocq, A. Jada, A. Aït Aghzzaf, Comprehensive physicochemical study
668 of dioctahedral palygorskite-rich clay from Marrakech High Atlas (Morocco), *Phys.*

- 669 Chem. Miner. 40 (2013) 411–424. doi:10.1007/s00269-013-0579-3.
- 670 [31] L. Bouna, B. Rhouta, L. Daoudi, F. Maury, M. Amjoud, F. Senocq, M.C. Lafont, a.
671 Jada, a. A. Aghzzaf, Mineralogical and Physico-Chemical Characterizations of
672 Ferruginous Beidellite-Rich Clay from Agadir Basin (Morocco), Clays Clay Miner. 60
673 (2012) 278–290. doi:10.1346/CCMN.2012.0600305.
- 674 [32] L. Bouna, B. Rhouta, F. Maury, A. Jada, F. Senocq, M.-C. Lafont, Photocatalytic
675 activity of TiO₂/stevensite nanocomposites for the removal of Orange G from aqueous
676 solutions, Clay Miner. 49 (2014) 417–428. doi:10.1180/claymin.2014.049.3.05.
- 677 [33] K. Hofstadler, R. Bauer, S. Novalic, G. Heisler, New Reactor Design for Photocatalytic
678 Wastewater Treatment with TiO₂ Immobilized on Fused-Silica Glass Fibers:
679 Photomineralization of 4-Chlorophenol, Environ. Sci. Technol. 28 (1994) 670–674.
680 doi:10.1021/es00053a021.
- 681 [34] C. Sarantopoulos, E. Puzenat, C. Guillard, J.-M. Herrmann, A.N. Gleizes, F. Maury,
682 Microfibrous TiO₂ supported photocatalysts prepared by metal-organic chemical vapor
683 infiltration for indoor air and waste water purification, Appl. Catal. B Environ. 91
684 (2009) 225–233. doi:10.1016/j.apcatb.2009.05.029.
- 685 [35] O. Lakbita, B. Rhouta, F. Maury, F. Senocq, M. Amjoud, L. Daoudi, Influence of the
686 crystal structure of Ag₂CO₃ on the photocatalytic activity under visible light of
687 Ag₂CO₃-Palygorskite nanocomposite material, Appl. Surf. Sci. 464 (2019) 205–211.
688 doi:10.1016/j.apsusc.2018.09.053.
- 689 [36] L. Bouna, B. Rhouta, F. Maury, Physicochemical Study of Photocatalytic Activity of
690 TiO₂ Supported Palygorskite Clay Mineral, 2013 (2013) 2–7.
691 doi.org/10.1155/2013/815473
- 692 [37] F. Correia, V. Goetz, G. Plantard, D. Sacco, A model for solar photocatalytic
693 mineralization, J. Sol. Energy Eng. Trans. ASME. 133 (2011) 2–6.

- 694 doi:10.1115/1.4004242.
- 695 [38] G. Plantard, T. Janin, V. Goetz, S. Brosillon, Solar photocatalysis treatment of
696 phytosanitary refuses: Efficiency of industrial photocatalysts, *Appl. Catal. B Environ.*
697 115–116 (2012) 38–44. doi:10.1016/j.apcatb.2011.11.034.
- 698 [39] G. Plantard, V. Goetz, Correlations between optical, specific surface and photocatalytic
699 properties of media integrated in a photo-reactor, *Chem. Eng. J.* 252 (2014) 194–201.
700 doi:10.1016/j.cej.2014.04.055.
- 701 [40] T. Janin, V. Goetz, S. Brosillon, G. Plantard, Solar photocatalytic mineralization of 2,4-
702 dichlorophenol and mixtures of pesticides: Kinetic model of mineralization, *Sol.*
703 *Energy.* 87 (2013) 127–135. doi:10.1016/j.solener.2012.10.017.
- 704 [41] Z.-G. Sun, X.-S. Li, X. Zhu, X.-Q. Deng, D.-L. Chang, A.-M. Zhu, Facile and Fast
705 Deposition of Amorphous TiO₂ Film under Atmospheric Pressure and at Room
706 Temperature, and its High Photocatalytic Activity under UV-C Light, *Chem. Vap.*
707 *Depos.* 20 (2014) 8–13. doi:10.1002/cvde.201307088.
- 708 [42] G. Plantard, V. Goetz, D. Sacco, TiO₂-coated foams as a medium for solar catalysis,
709 *Mater. Res. Bull.* 46 (2011) 231–234. doi:10.1016/j.materresbull.2010.11.011.
- 710 [43] J.M. Herrmann, Photocatalysis fundamentals revisited to avoid several misconceptions,
711 *Appl. Catal. B Environ.* 99 (2010) 461–468. doi:10.1016/j.apcatb.2010.05.012.
- 712 [44] S. Malato, J. Blanco, A. Vidal, C. Richter, Photocatalysis with solar energy at a pilot-
713 plant scale: An overview, *Appl. Catal. B Environ.* 37 (2002) 1–15. doi:10.1016/S0926-
714 3373(01)00315-0.
- 715 [45] P. Aranda, R. Kun, M.A. Martín-Luengo, S. Letaïef, I. Dékány, E. Ruiz-Hitzky,
716 Titania–Sepiolite Nanocomposites Prepared by a Surfactant Templating Colloidal
717 Route, *Chem. Mater.* 20 (2008) 84–91. doi:10.1021/cm702251f.
- 718 [46] B. Rhouta, L. Bouna, F. Maury, F. Senocq, M.C. Lafont, A. Jada, M. Amjoud, L.

719 Daoudi, Surfactant-modifications of Na⁺-beidellite for the preparation of TiO₂-Bd
720 supported photocatalysts: II—Physico-chemical characterization and photocatalytic
721 properties, Appl. Clay Sci. 115 (2015) 266–274.
722 doi:<http://dx.doi.org/10.1016/j.clay.2015.04.025>.
723