Gas phase oxidation of *n*-decane and PCE by photocatalysis using an annular photoreactor packed with a monolithic catalytic bed coated with P25 and PC500

Ricardo A.R. Monteiro¹, Sandra M. Miranda¹, Caio Rodrigues-Silva¹, Adrián M.T. Silva^{2,*}, Rui A.R. Boaventura¹, Vítor J.P. Vilar^{1,*}

¹**LSRE - Laboratory of Separation and Reaction Engineering**

²**LCM - Laboratory of Catalysis and Materials**

Associate Laboratory LSRE/LCM

Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

* Authors to whom correspondence should be addressed:

Tel. +351 918257824; Fax: +351 225081674; E-mail addresses: adrian@fe.up.pt (Adrián M.T. Silva); vilar@fe.up.pt (Vítor J.P. Vilar).

25 **Abstract**

26 Perchloroethylene (PCE) and *n*-decane are persistently present in the indoor air of
27 several industrial/corporate facilities and households. The present paper reports studies
28 on the photocatalytic oxidation (PCO) of *n*-decane and PCE using an annular
29 photoreactor packed with a cellulose acetate monolithic structure coated with two
30 commercially available TiO₂, namely PC500 and P25, irradiated by simulated solar
31 light. The influence of the type of photocatalytic film employed, feed flow rate,
32 pollutant concentration, relative humidity, presence or absence of gas-phase molecular
33 oxygen and incident irradiance, on the pollutants photocatalytic conversion was
34 assessed. PC500 film showed higher conversion of both pollutants in comparison with
35 P25 despite the lower mass of catalyst used for film coating. Photocatalytic conversions
36 close to 100 % were obtained for *n*-decane and PCE ($C_{\text{dec, feed}} = 71$ ppm and
37 $C_{\text{PCE, feed}} = 1095$ ppm, respectively) operating at $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$ ($\tau = 88$ s),
38 $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ and $RH = 20$ %. The mineralization of PCE showed no differences
39 regarding the photocatalytic films employed, however, PC500 film enabled the
40 complete mineralization of *n*-decane (100 % out of 100 % of converted *n*-decane) while
41 over P25 film only 69 % out of 86 % of converted *n*-decane was mineralized
42 ($C_{\text{dec, feed}} = 71$ ppm and $C_{\text{PCE, feed}} = 1095$ ppm, respectively) in the following conditions:
43 $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$ ($\tau = 88$ s), $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ and $RH = 40$ %). In addition,
44 competitive adsorption between the pollutants and water molecules on the TiO₂ film
45 surface was observed above 20 % of RH . Results obtained at low RH suggest that
46 chlorine radicals chain propagation reactions may be included in the PCO mechanism of
47 PCE. Finally, the absence of oxygen drastically impairs the photoreaction.

48 **Keywords:** Solar photocatalysis; air decontamination; *n*-decane; perchloroethylene;
49 TiO₂ PC500 and P25.

50 **1. Introduction**

51 VOCs represent a very active group of air pollutants discharged into the
52 atmosphere by household and industrial activities, such as fuel combustion, residential
53 cleaning agents, among several others. For example, Teixeira *et al.* [1] reported a large
54 concentration of VOCs (including PCE and *n*-decane) in the indoor air of different
55 stages of a wastewater treatment plant (WWTP), mainly associated with the aeration
56 and mechanical agitation processes, as well as with the different sludge treatment
57 stages. PCE, in particular, is widely used as model target pollutant due to its toxicity
58 and carcinogenic potential to humans.

59 Since the pioneer work by Fujishima and Honda in 1972 [2], the interest on
60 photocatalytic processes applied to environmental issues has been growing every year,
61 not only regarding photocatalytic processes (PCO) for water/wastewater treatment
62 applications, but also for air purification [3-10]. The degradation of air pollutants by
63 PCO is an attractive and efficient route when compared to other conventional
64 techniques, such as adsorption on activated carbon, since the photocatalytic
65 semiconductors are able to mineralize the pollutants, instead of a simple and more
66 common phase transfer.

67 Semiconductors as metal oxides (*e.g.* TiO₂, ZnO, WO₃, Si, SnO₂, Fe₂O₃) or
68 metal chalcogenides (*e.g.*, CdS, ZnS, WSe₂) are often employed as photocatalysts, pure
69 or modified by metal and non-metal ions doping, metal deposition, coupling with other
70 semiconductors or sensitising with organic dyes [11-17]. Nevertheless, not all the
71 semiconductors abide by the following requirements: (i) prone for UV/Vis activation,
72 (ii) biologically and chemically inert while maintaining their resistance to chemical and
73 mechanical attacks, (iii) insoluble in water, non-toxic (or at least with low toxicity) and,
74 at the same time, (iv) commercially attractive. From these reasons, TiO₂ (also known as

75 titania) stands out as one of the most photoactive semiconductor based catalysts [18].

76 A number of commercial photocatalytic TiO₂ powders are available on the
77 market, but TiO₂ Aeroxide P25 from Evonik® is the most commonly employed [19-22].
78 This material is composed of 80 % anatase and 20 % rutile, with a specific surface area
79 (SSA) of around 50 m² g⁻¹ and an average particle size of 21 nm [23]. It is generally
80 accepted that the high activity of P25 comes from the formation of heterojunctions
81 between the two types of crystalline phases, anatase and rutile, which may also explain
82 the low activity of P25 under visible light in some particular cases [24]. Specifically,
83 rutile, owing to its lower conduction band, may absorb some light in the visible range
84 (blue) and thus serve as a photosensitizer of the anatase phase. The respective positions
85 and the difference between the higher energy levels of the conduction bands of the two
86 phases may cause a transfer of electrons from anatase towards rutile, preventing at the
87 same time charge recombination [25].

88 Although the actuating mechanism of pure anatase is well established, as regards
89 P25 it has been over the years a matter of debate [26-28]. In a study conducted by
90 Hajaghazadeh *et al.* [29], PC500 (consisting of 100 % anatase) yielded a higher reaction
91 rate than P25 in the degradation of gaseous methylethylketone under UVA light. The
92 superior photocatalytic activity of PC500 was attributed to its higher SSA. Taranto *et al.*
93 [30] also reported a slight higher photocatalytic activity of P25 over PC500 PCO in the
94 degradation of methanol and *n*-octane as gas-phase model pollutants. The higher
95 photoactivity of PC500 in comparison with P25 towards the degradation of
96 acetaldehyde was also reported by Verbruggen *et al.* [31].

97 In another study conducted by Águia *et al.* [21], ten distinct commercially
98 available photocatalysts were incorporated into a water-based exterior paint aiming NO
99 photoabatement. The highest yields were obtained with the catalysts consisting of 100%

100 anatase, such as PC500.

101 Reactor geometry is also a key factor in gas-phase photocatalysis due to its
102 influence on optimizing the catalyst exposure to both radiation and reactants [32, 33].
103 The most common photoreactors (found in scientific publications and patents) are
104 tubular, annular and flat plate types [34-36]. Regarding the photocatalyst structural
105 configuration, thin-film powder layer and/or fluidized bed [34, 37], coated wall-parallel
106 [38, 39] and honeycomb/foam monolithic reactors [40-44] are probably the most
107 representative.

108 This paper presents the results from a study on gas-phase solar photo-oxidation
109 of VOCs present in relatively high concentrations in industrial indoor environments:
110 *n*-decane and PCE. Two different commercially available TiO₂ photocatalysts (P25
111 from Evonik[®] and PC500 from Cristal[®]) were selected to prepare photocatalytic films
112 and compared in terms of photocatalytic conversions using a lab-scale single-pass
113 continuous-flow annular photoreactor equipped with a compound parabolic collector
114 (CPC). This configuration allows the illumination of the whole reactor perimeter and
115 catalytic bed, enhancing therefore the photonic efficiency [45, 46]. Besides, the
116 presence of an internal quartz cylinder allows the use of a UVA light lamp which
117 enables photocatalysis at low or even none external irradiance conditions [47, 48]. The
118 photocatalysts were deposited onto the surface of a monolithic and transparent structure
119 of cellulose acetate. Applying such structure into the annular reactor permits to take
120 advantage of the low pressure drop and the high surface-area-to-volume ratio, typical of
121 honeycomb reactors [49].

122 The PCO of *n*-decane and PCE over PC500 and P25 films were studied for
123 different operating conditions, namely the feed flow rate (Q_{feed}), feed VOC
124 concentration ($C_{\text{dec, feed}}$ or $C_{\text{PCE, feed}}$), and incident irradiance (I). The influence of relative

125 humidity (RH), and the presence or absence of oxygen, in the photodegradation of such
126 compounds was also assessed using PC500 film. To the best of our knowledge, few
127 papers have compared the efficiency of PC500 and P25 films in the gas-phase PCO of
128 VOCs.

129

130 **2. Experimental**

131 *2.1. Materials and methods*

132 P25 and PC500 powders were supplied by Evonik[®] (formerly Degussa) and
133 Cristal[®] (formerly Millennium), respectively, and used as delivered, without further
134 modification or purification. Some characteristics of PC500 and P25 powders provided
135 by the suppliers are given in Table 1. Cellulose acetate monolithic structures (TIMax
136 CA50-9/S – $L_C = 80$ mm, $d_{ch}^2 = 9$ mm $\times$ 9 mm, $e_{w,ch} = 0.1$ mm; Wacotech GmbH & Co.
137 KG.) were used as substrate to affix the powders.

138 *n*-Decane (≥ 94 %; CAS no. 124-18-5; Merck), PCE (≥ 99.5 %; CAS no.
139 127-18-4; Panreac Química S.A.U.) and deionized water were used for the generation of
140 contaminated and humidified air streams. Helium N50 and nitrogen N50 (purity $\geq$
141 99.999 %), and synthetic air N50 (O_2 : 20 ± 1 %; H_2O : < 3 ppm; C_nH_m : < 0.1 ppm; CO_2 :
142 < 1 ppm; CO : < 1 ppm) were provided by Air Liquide.

143 Monolithic cellulose acetate structures were evenly coated using aqueous
144 suspensions of P25 and PC500 by the dip-coating method (Dip-Coater RDC21-K,
145 Bungard Elektronik GmbH & Co. KG.) [50]. Before coating, the honeycomb structures
146 were soaked for 1 h with distilled water and alkaline detergent (Derquim LM 01,
147 Panreac Química, S.A.U.), subsequently washed with Milli-Q water, and dried at 323 K.
148 The photocatalysts aqueous suspensions (2 % wt.) were sonicated for 10 min at 50 kHz
149 in order to better disperse the particles. Based on Lopes *et al.* [51] work, where the

influence of the number of layers upon the PCE photocatalytic conversion was assessed, nine layers of P25 or PC500 powder were deposited at a withdrawal rate of 0.8 mm s^{-1} assuring a thin and uniform film on each substrate surface (samples were dried at 323 K for 30 min between each layer deposition). Finally, the TiO_2 -coated monolithic structures were assembled into the annular photocatalytic reactor (see section 2.2) for the PCO study of *n*-decane and PCE. The catalytic bed properties are also detailed in Table 1.

2.2. *Experimental setup and photocatalytic experiments*

The schematic representation of the experimental setup is illustrated in Fig. 2 which is already carefully described in our previous work [52]. Briefly, humidified air stream contaminated with PCE or *n*-decane was generated by flowing air with 21 % oxygen through different Woulff bottles (Normax, Lda.), one containing PCE or *n*-decane and another filled with deionized water (Fig. 2a). The flows were controlled by three mass flow controllers (MFC, El-Flow, Bronkhorst High-Tech B.V.). Oxygen-free experiments were performed by replacing the flowing air by nitrogen and removing dissolved oxygen in water by replacing deionized water by a $10 \text{ g L}^{-1} \text{ Na}_2\text{SO}_3$ solution in the Woulff bottle. The photocatalytic system entails three main parts (Fig. 2b): i) a solar light simulator (Atlas, model Suntest XLS+) with 0.110 m^2 of working area illuminated by a 1700 W air-cooled Xenon arc lamp and an infrared coated quartz glass daylight filter reproducing the solar light spectrum within $300 < \lambda < 800 \text{ nm}$; ii) an electropolished anodized aluminium CPC with 0.023 m^2 of irradiated area able to use both direct and diffuse UV radiation [53, 54]; iii) an annular photoreactor (the outer tube made of soda-lime glass, Duran borosilicate glass 3.3, cut-off at 280 nm, Schott-Rorhglas GmbH; and the inner tube made of quartz, Quarzglas-Rohr Quarzglasstechnik,

GmbH & Co.). Table 1 summarizes the tube dimensions of the photoreactor and Fig. 2b₁ and b₂ schematically represent the side and frontal views of annular photoreactor, respectively. The feed and exit tubing are made of PTFE minimizing the adsorption of VOCs.

Gas-phase PCE and *n*-decane concentration histories were monitored using a gas chromatograph (MGC Fast GC, Dani Instruments S.p.A.) equipped with a flame ionisation detector (FID) and a Volcol capillary column (20 m × 0.18 mm × 1.00 μm; Supelco, Sigma-Aldrich Co. LLC.), represented in Fig. 2c. The experimental setup was connected to a computer and controlled using a data acquisition board system and an in-house program developed routine written in Labview environment (NI Corporation). All connections are of 1/16" stainless steel tubing to reduce dead volumes. Additionally, the CO₂ concentration of the photoreactor feed/exit stream was monitored online using an Indoor Air IAQ-Calculator™ quality meter 7545 (TSI, Inc.).

All experiments were carried out inside the chamber of the solar light simulator (Fig. 2b), being the incident irradiance measured by a broadband UV radiometer (CUV 5, Kipp & Zonen B.V.), placed outside the outer tube and at the same height, within a spectral range of 280 – 400 nm corresponding to the UV fraction of the solar radiation.

The efficiency of the PCO process of both TiO₂ photocatalytic films toward *n*-decane and PCE degradation were compared in similar operational conditions and calculated as follows:

$$\text{Conversion (\%)} = \left(1 - \frac{C_{\text{VOC, exit}}}{C_{\text{VOC, feed}}} \right) \times 100 \quad (\text{eq. 1})$$

At steady-state, VOC photodegradation fractions ($C_{\text{VOC, exit}} / C_{\text{VOC, feed}}$, where $C_{\text{VOC, feed}}$ and $C_{\text{VOC, exit}}$ are the pollutant concentration in the feed and exit gas streams, respectively, expressed in ppm) were studied for different experimental conditions: Q_{feed} (75 – 300 cm³ min⁻¹, measured at 1 bar and 298 K), $C_{\text{VOC, feed}}$ ($C_{\text{dec, feed}} = 71 - 283$ ppm

and $C_{\text{PCE, feed}} = 548 - 2738$ ppm), RH of the feed gas stream both in the presence and absence of oxygen (3 – 40 %, measured at 1 bar and 298 K), and I (18.9 - 38.4 $\text{W}_{\text{UV}} \text{m}^{-2}$, measured in the spectral range 280 - 400 nm: UV fraction of the incident sunlight).

The mineralization yield of n -decane and PCE due to PCO was also evaluated and calculated as follows:

$$\text{Mineralization (\%)} = \left(\frac{C_{\text{CO}_2, \text{exit}}}{C_{\text{VOC, feed}}} \times \frac{1}{n} \right) \times 100 \quad (\text{eq. 2})$$

where n is the number of carbons present in each pollutant molecular structure and $C_{\text{CO}_2, \text{exit}}$ is the CO_2 exit stream concentration.

Before turning on the solar simulator, the catalytic bed was continuously fed and several exit stream samples were measured until reaching a constant VOC concentration. Finally, at steady state conditions, the VOC conversion was determined for each experiment.

3. Results and discussion

3.1. VOCs photolysis

Blank experiments (*i.e.* photoreactor without TiO_2 -photocatalytic film) were performed with three different incident irradiances, *i.e.*, 18.9, 29.1, and 38.4 $\text{W}_{\text{UV}} \text{m}^{-2}$ (reference values to the sunlight UV fraction on the 280 – 400 nm range) in order to establish the effect of direct photolysis on the conversion of n -decane and PCE. No degradation of n -decane or PCE was observed for the range of irradiances tested (data not shown).

3.2. Catalytic film performance

3.2.1. Influence of the feed flow rate and VOC concentration

Fig. 3 illustrates the effect of the feed flow rate (Q_{feed}) on the n -decane (Fig. 3a)

225 and PCE (Fig. 3c) conversion over PC500 (full coloured columns) and P25 (columns
 226 with patterns) films. Fig. 3a and 2c show that increasing Q_{feed} , the photocatalytic
 227 conversion of *n*-decane and PCE reduces regardless the employed irradiance (*i.e.* 18.9,
 228 29.1, and 38.4 $\text{W}_{\text{UV}} \text{m}^{-2}$) or even the type of catalytic film. More than 99 % of the initial
 229 *n*-decane ($C_{\text{dec, feed}} = 71 \text{ ppm}$) and PCE ($C_{\text{PCE, feed}} = 1095 \text{ ppm}$) were converted over
 230 PC500 under $I = 38.4 \text{ W m}^{-2}$ when the feed flow rates of $75 \text{ cm}^3 \text{ min}^{-1}$ and
 231 $150 \text{ cm}^3 \text{ min}^{-1}$ were set. Over P25 film, 93 % of *n*-decane conversion was attained only
 232 when $Q_{\text{feed}} = 75 \text{ cm}^3 \text{ min}^{-1}$ whereas 86 % of *n*-decane was converted when
 233 $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$, in both cases for $C_{\text{dec, feed}} = 71 \text{ ppm}$ and $I = 38.4 \text{ W}_{\text{UV}} \text{m}^{-2}$.
 234 Nevertheless, P25 film also promoted 99 % of PCE conversion (Fig. 3c) for the same
 235 experimental conditions, *i.e.*, $Q_{\text{feed}} = 75 - 150 \text{ cm}^3 \text{ min}^{-1}$ and $C_{\text{PCE, feed}} = 1095 \text{ ppm}$ under
 236 $I = 38.4 \text{ W}_{\text{UV}} \text{m}^{-2}$. Increasing Q_{feed} to $300 \text{ cm}^3 \text{ min}^{-1}$, *n*-decane conversion reached
 237 approximately 65 and 91 % while PCE conversion reached 67 % and 92 % respectively
 238 over P25 and PC500 films, under $I = 38.4 \text{ W}_{\text{UV}} \text{m}^{-2}$.

239 In order to better understand the extent of the catalytic film activity toward the
 240 conversion of *n*-decane and PCE, the effect of Q_{feed} on the pollutant consumption by
 241 PCO (expressed in mol min^{-1} , *i.e.*, number of moles consumed per unit of time, and
 242 normalized by the corresponding mass of TiO_2 employed) was also assessed at steady-
 243 state conditions as shown in Fig. 3b and 2d, respectively. The upmost values of
 244 *n*-decane consumption over PC500 (full coloured columns) and P25 (columns with
 245 patterns) films – $3.14 \times 10^{-4} \text{ mol min}^{-1} \text{ g}_{\text{PC500}}^{-1}$ and $1.56 \times 10^{-4} \text{ mol min}^{-1} \text{ g}_{\text{P25}}^{-1}$, respectively
 246 – were attained when using the highest Q_{feed} ($300 \text{ cm}^3 \text{ min}^{-1}$) followed by
 247 $1.71 \times 10^{-4} \text{ mol min}^{-1} \text{ g}_{\text{PC500}}^{-1}$ and $1.03 \times 10^{-4} \text{ mol min}^{-1} \text{ g}_{\text{P25}}^{-1}$ for $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$, in
 248 both cases under $I = 38.4 \text{ W m}^{-2}$ (Fig. 3b). Although the highest conversion was attained
 249 at $Q_{\text{feed}} = 75 \text{ cm}^3 \text{ min}^{-1}$ and $I = 38.4 \text{ W m}^{-2}$ (conversion of > 99 % over PC500 and P25

250 films), the *n*-decane consumption was the lowest ($8.47 \times 10^{-5} \text{ mol min}^{-1} \text{ g}_{\text{PC500}}^{-1}$ and
 251 $5.55 \times 10^{-5} \text{ mol min}^{-1} \text{ g}_{\text{P25}}^{-1}$). Fig. 3c and Fig. 3d respectively show the PCE conversion
 252 and consumption over PC500 and P25 films. As seen before for *n*-decane, higher Q_{feed}
 253 ($300 \text{ cm}^3 \text{ min}^{-1}$) also promote higher consumptions of PCE ($6.22 \times 10^{-3} \text{ mol min}^{-1} \text{ g}_{\text{PC500}}^{-1}$
 254 and $1.56 \times 10^{-4} \text{ mol min}^{-3} \text{ g}_{\text{P25}}^{-1}$) under $I = 38.4 \text{ W m}^{-2}$; on the other hand, the PCE
 255 conversions attained under the same conditions were the lowest (92 and 67 % over
 256 PC500 and P25). Setting $Q_{\text{feed}} = 75 \text{ cm}^3 \text{ min}^{-1}$ and $I = 38.4 \text{ W m}^{-2}$ both TiO_2
 257 photocatalytic films promoted the highest PCE conversion (99 %) and, at the same time,
 258 the lowest PCE consumption ($1.68 \times 10^{-3} \text{ mol min}^{-1} \text{ g}_{\text{PC500}}^{-1}$ and $5.92 \times 10^{-4} \text{ mol min}^{-3} \text{ g}_{\text{P25}}^{-1}$
 259 respectively for PC500 and P25).

260 In both cases, the results suggest a fostering in the mass transfer between the
 261 pollutant molecules and the catalytic film surface as Q_{feed} increases, mainly due to a
 262 higher organic load which also increases the moles consumption; however, together
 263 with a 4-fold increase in Q_{feed} (from $75 \text{ cm}^3 \text{ min}^{-1}$ to $300 \text{ cm}^3 \text{ min}^{-1}$) a reduction in the
 264 same order is observed in the residence time (from 176 s to 44 s). In this sense, for
 265 higher feed flow rates (*i.e.* $300 \text{ cm}^3 \text{ min}^{-1}$) the residence time inside the photoreactor is
 266 probably not enough to convert pollutant molecules in the same proportion as for
 267 $Q_{\text{feed}} = 75 \text{ cm}^3 \text{ min}^{-1}$ explaining why higher Q_{feed} impairs the photocatalytic process.

268 Regarding the efficiency of both catalytic films, it is worth noting that P25 film
 269 promoted much less consumption of organics than PC500 film in the PCO of *n*-decane
 270 and PCE: P25 film promoted 35 to 58 % less consumption of *n*-decane than PC500 film
 271 depending on I and Q_{feed} as well as, the differences in consumptions between both
 272 catalytic films become greater as the Q_{feed} increases and I decreases. For example,
 273 fixing Q_{feed} at $75 \text{ cm}^3 \text{ min}^{-1}$ the PCO of *n*-decane over P25 film consumes 35 %, 36 %

274 and 39 % less *n*-decane respectively under 38.4 W m^{-2} , 29.1 W m^{-2} and 18.9 W m^{-2}
 275 whereas for $Q_{\text{feed}} = 300 \text{ cm}^3 \text{ min}^{-1}$ P25 film promotes 50, 54 and 58 % less *n*-decane
 276 consumption than PC500 film under the same irradiances. The same trend can be
 277 observed for the PCO of PCE but, in this case, P25 film promotes 65 up to 76 % lower
 278 consumptions of PCE than PC500 film employing the above described experimental
 279 conditions.

280 Fig. 4 shows the influence of the feed concentration of *n*-decane ($C_{\text{dec, feed}}$) and
 281 PCE ($C_{\text{PCE, feed}}$) on the conversion and consumption of *n*-decane and PCE. For the same
 282 residence time in the photoreactor ($\tau = 88 \text{ s}$; $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$) the conversion of *n*-
 283 decane (Fig. 4a) and PCE (Fig. 4c) decreases as the feed concentration increases,
 284 regardless the catalytic film used.

285 Employing PC500 film more than 98 % of *n*-decane conversion was attained for
 286 the three irradiances employed (*i.e.* 18.9, 29.1, and $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$) when the initial *n*-
 287 decane concentration was 71 ppm, whereas P25 film yielded 74 up to 86 % conversion,
 288 depending on the irradiance (Fig. 4a). Also, increasing *n*-decane feed concentration
 289 ($C_{\text{dec, feed}} = 142 \text{ ppm}$), the conversion of *n*-decane over PC500 film decreased in the
 290 range of 5 – 25 % as I decreased from 38.4 W m^{-2} to 18.9 W m^{-2} while over P25 film
 291 the reduction was around 20 -30 % for the same irradiance reduction. It is interesting to
 292 note that, at this concentration and fixing $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$ and $RH = 40 \%$, the
 293 *n*-decane conversion over P25 film is closer to that found when the photoreactor was
 294 packed with PC500 film and fed with twice the *n*-decane feed concentration (*i.e.*
 295 283 ppm). In particular P25 film converted 50, 62 and 69 % of the initial *n*-decane
 296 ($C_{\text{dec, feed}} = 142 \text{ ppm}$), respectively under $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$, $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ and
 297 $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$, whereas PC500 yielded 37, 51 and 62 % for the $C_{\text{dec, feed}} = 283 \text{ ppm}$.

298 The behaviour of the activity of both photocatalysts towards PCE conversion as
 299 a function of the PCE feed concentration ($C_{\text{PCE, feed}}$) is shown in Fig. 4c. As seen before
 300 for *n*-decane conversion over P25 and PC500 films, PCE conversion follows the same
 301 trend, *i.e.*, the efficiency of the process decreases as the PCE feed concentration
 302 increases. PC500 film yields more than 98 % for the PCE feed concentrations in the
 303 range of 549 – 2190 ppm under higher irradiances ($29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ and $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$).
 304 On the other hand, increasing $C_{\text{PCE, feed}}$ from 542 ppm to 2190 ppm a reduction in the
 305 conversion of 20 % (from 99 to 79 %) can be observed (Fig. 4c) when using PC500 film
 306 under $I = 18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$. Increasing the PCE feed concentration even further
 307 (2738 ppm), conversion efficiency losses of 4 and 42 % respectively under $29.1 \text{ W}_{\text{UV}}$
 308 m^{-2} and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ were observed whereas under higher irradiance ($38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$)
 309 no efficiency loss was observed. Although P25 film allows to achieve conversions of
 310 approximately 99 % of the feed PCE concentration ($Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$, $C_{\text{PCE,}}$
 311 $\text{feed} = 1095 \text{ ppm}$ and $RH = 40 \%$) under $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$, it is under lower irradiances that
 312 the differences between both catalyst activities become greater: *i.e.* 87 and 75 % of PCE
 313 conversion are attained under $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ of irradiance with P25
 314 film, while PC500 film converted 98 and 97 % under the same operational conditions.
 315 Increasing the PCE feed concentration from 1095 ppm to 1643 ppm, the P25 film
 316 efficiency is impaired, decreasing the PCE conversion in 12 , 16 and 25 % respectively
 317 under $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$, $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$, in comparison to the conversions
 318 attained when $C_{\text{PCE, feed}} = 1095 \text{ ppm}$.

319 A similar approach regarding the consumption of pollutant per unit of time
 320 (normalized by the mass of catalyst) was plotted in Fig. 4b and 3d: in these cases, for
 321 the three incident irradiances employed ($38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$, $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ and
 322 $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$) and over PC500 and P25 films the consumption of *n*-decane and PCE

increases as the feed concentration increases. In other words, higher $C_{\text{dec, feed}}$ and $C_{\text{PCE, feed}}$ for a same flow rate ($Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$), enhances the mass transfer between the feed gas stream and the catalyst surface, increasing the consumption of the pollutant.

The results above described show that P25 film provides lower pollutant consumptions in comparison to PC500 film. The former promotes 40 up to 53 % less *n*-decane consumptions than the latter depending on $C_{\text{dec, feed}}$ and I : for example, fixing $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$, $C_{\text{dec, feed}} = 142 \text{ ppm}$ and $I = 38.4 \text{ W m}^{-2}$ the *n*-decane moles consumed over P25 and PC500 films were respectively $3.04 \times 10^{-4} \text{ mol min}^{-1} \text{ g}_{\text{P25}}^{-1}$ and $6.49 \times 10^{-4} \text{ mol min}^{-1} \text{ g}_{\text{PC500}}^{-1}$. The PCO of PCE over PC500 film also revealed higher consumptions values than over P25 film as the latter promotes PCE consumptions 65 % up to 79 % lower than over PC500 in the range of PCE feed concentration tested (1095 ppm and 1643 ppm) depending on the incident irradiance.

For a given gas-phase pollutant feed concentration and/or feed flow rate, the consumption of that pollutant by PCO is dependent on the number of oxidant species formed at the surface of the catalytic film. Likewise, the number of oxidant species depends on the photon flux whereby an increase in the irradiance is followed by an increase in the number of generated photons, which form an equivalent number of electro-hole pairs (and subsequently others oxidizing species) ultimately resulting in VOCs conversion gains. In this scenario, an increase in the irradiance from 18.9 to $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ will increase the conversion (and mineralization) or the consumption of that pollutant. From Fig. 2 and Fig. 3 it is possible to see that the consumption of *n*-decane (Fig. 2b and Fig. 4d) and PCE (Fig. 2d and Fig. 4d) over PC500 and P25 films as a function of Q_{feed} or $C_{\text{VOC, feed}}$ becomes more dependent on the incident irradiation as the organic load increases (higher Q_{feed} or $C_{\text{VOC, feed}}$): for low organic loads the incident

irradiance has almost no effect on the consumption of the VOC whereas for higher organic loads the consumption is nearly proportional to the irradiance employed, within the range $I = 18.9 - 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$. This phenomenon is related to the number of organic molecules entering the reactor and the number of photons available: at low organic loads the photons are in excess under the three irradiances, consuming all or almost all available molecules; at high organic loads the number of molecules to be converted is higher and the photons are no longer in excess requiring higher irradiances (higher number of photons) to achieve similar conversion values. In other words, higher organic loads make a better use of the photons converting more molecules as the irradiance increases. However, as it was seen, the conversion of a given pollutant is impaired.

The mineralization of *n*-decane and PCE over PC500 and P25 photocatalytic films is represented in Fig. 4. Although the mineralization of PCE over both photocatalytic films provided similar values for each corresponding irradiance (*ca.* 39, 31 and 24 % for $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$, $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$, respectively) the results clearly show that PC500 film was able to yield higher mineralization of *n*-decane: 100 % of converted *n*-decane ($C_{\text{dec, feed}} = 71 \text{ ppm}$) was fully mineralized (100 %) into CO_2 and water whereas over P25 film only 69 % out of 86 % of converted *n*-decane was, in fact, mineralized under $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$. Decreasing the irradiance, the mineralization of *n*-decane also decreased: under $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$, PC500 film was able to mineralize 83 and 73 % while P25 film only mineralized 54 and 40 %, respectively.

From the study on the influence of the pollutants feed concentration or the feed flow rate on their conversion and consumption, it seems clear that PC500 film promotes higher conversions and higher consumptions of *n*-decane and PCE than P25 film even considering that the produced PC500 film has lower mass of PC500 photocatalyst.

373 However, it is a challenging task to explain why PC500 film promoted higher
374 photocatalytic conversions than P25 film in gas-phase experiments. For the last decades,
375 several research works have been focused on the structure of P25 craving to understand
376 the generally accepted superior activity of P25 over other commercially available
377 photocatalysts mainly in liquid-phase studies [24, 25, 55-57]. Bickley *et al.* [25]
378 attributed high photocatalytic activity of P25 to the presence of rutile and anatase
379 phases. Admitting that each photocatalyst particle consists of an anatase core and a thin
380 rutile cover layer, photogenerated holes of the anatase core would be effectively
381 transferred to the rutile layer. However, Ohno *et al.* [55] stated that P25 powder
382 consists, in fact, of relatively large rutile particles and very small anatase particles,
383 which independently form agglomerates before mixing. They also stated that the
384 superior activity of P25 was due to the proper band bending in rutile particles, which are
385 in contact to anatase particles. Hurum *et al.* [24] concluded that the higher activity of
386 mixed-phase TiO₂ was due to a more stable charge separation by electron transfer from
387 rutile to lower energy anatase lattice trapping sites.

388 On the other hand, Sun *et al.* [56] proposed that, in aqueous phase, the contact
389 between anatase and rutile phases and a subsequently band bending between the two
390 phases promotes a good charge-carrier separation. But such synergistic effect of anatase
391 and rutile in aqueous phase is not exclusive to P25. Ohno *et al.* [57] reported the
392 enhanced efficiency for mixed anatase and rutile at different ratios as well as thermally
393 treated anatase yielding the two phases. It is worth noting that rutile phase can be
394 formed in anatase samples by heat treatment [58] changing the crystallinity and the size
395 of TiO₂ particles which can affect the photocatalytic activity [24, 59-61].

396 In gas-phase photocatalytic reactions, the contact between the two P25 phases
397 may not be so effective and, thus, the synergistic effect may not be observed. An

insufficient band bending will impair the contact between the two phases resulting in poor charge-carrier separation and, subsequently, in a loss of photocatalytic efficiency of mixed-phases TiO_2 . In the absence of any synergistic effect between the anatase and rutile mixed TiO_2 phases, it is accepted that anatase is much more active than rutile in the PCO of organic compounds in water and air [62]. Even considering that the smaller crystal size of PC500 (Table 1) may foresee higher density in surface defects [30, 63, 64] reducing the electron-hole recombination time, which ultimately results in lower photocatalytic efficiencies, the larger surface area of PC500 in comparison to P25 may justify the superior activity of PC500 [62].

407

3.2.2. *Effect of the relative humidity on PCO of n-decane and PCE over PC500 film*

The effect of the water content on the conversion of *n*-decane (Fig. 6a) and PCE (Fig. 6b) over PC500 film was evaluated for three *RH* conditions (3, 20, and 40 %). Fig. 6a presents the conversion of *n*-decane attained under each *RH* condition for three given $C_{\text{dec, feed}}$. Fixing $C_{\text{dec, feed}}$ at 71 ppm ($2.87 \times 10^{-3} \text{ mol m}^{-3}$), a negligible decrease of 1.4 % was observed as the water content decreases from 40 to 3 % ($3.61 \times 10^{-1} \text{ mol m}^{-3}$ to $2.71 \times 10^{-2} \text{ mol m}^{-3}$ of water; water/*n*-decane molar ratio of 125.8 and 9.4, respectively). The effect of *RH* on the *n*-decane conversion became clearer as the initial concentration of *n*-decane increases. Setting the *n*-decane feed concentration four times higher ($C_{\text{dec, feed}} = 284 \text{ ppm}$ or $1.15 \times 10^{-2} \text{ mol m}^{-3}$), it was observed that when *RH* was reduced from 20 % ($1.81 \times 10^{-1} \text{ mol m}^{-3}$ of water) to 3 % the *n*-decane conversion also decreased (from 69 to 54 %). The water/*n*-decane molar ratio is approximately 2.4 and 15.7 for *RH* of 3% to 20%. This indicates that water/*n*-decane molar ratios higher than 2.4 and lower than 9.4 are required to produce the necessary number of hydroxyl radicals for the pollutant degradation. On the other hand, at higher *RH* (40 %) no improvement in the

423 *n*-decane conversion was observed most likely due to competitive adsorption of
424 *n*-decane and water molecules on the photocatalytic film surface. The same behaviour
425 was observed for a $C_{\text{dec, feed}} = 142$ ppm, but in this case, the differences are less evident,
426 probably due to the high conversions of *n*-decane hiding the real effect of the water
427 content variation.

428 Fig. 6b shows the effect of *RH* on the conversion of PCE over PC500 film, but
429 instead of varying the feed concentration of the pollutant, two feed flow rates were
430 tested ($150 \text{ cm}^3 \text{ min}^{-1}$ and $300 \text{ cm}^3 \text{ min}^{-1}$) for the same $C_{\text{PCE, feed}}$ (1095 ppm). For
431 $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$, no effect owed to the variation of *RH* was observed on the PCE
432 conversion. However, doubling the total flow rate to $300 \text{ cm}^3 \text{ min}^{-1}$, it becomes clear
433 that *RH* has the same impact on the PCE conversion, in comparison with that described
434 before for *n*-decane (Fig. 6a). The conversion of PCE reached its highest value (98 %)
435 when *RH* was set to 20 %, while only 92 and 89 % of the initial PCE were converted at
436 40 and 3 % *RH*, respectively. It is important to note that at *RH* = 3 % the concentration
437 of water is lower than that of PCE ($C_{\text{H}_2\text{O, feed}} = 2.71 \times 10^{-2} \text{ mol m}^{-3}$ and
438 $C_{\text{PCE, feed}} = 4.43 \times 10^{-2} \text{ mol m}^{-3}$) which would foresee a drastic reduction of PCE
439 conversion regardless Q_{feed} . However such reduction was not observed which may
440 indicate further mechanisms in the photodegradation of PCE besides the classical attack
441 of hydroxyl radicals. Chlorine radicals chain propagation reactions have been a matter
442 of discussion by several research groups in an attempt to explain the PCO mechanism of
443 chlorinated compounds [65-68].

444 The opposing effect of the water content has already been discussed in several
445 research works and even so it still is a matter of debate [69-78]. Several authors reported
446 that the absence of water vapour will seriously retard the conversion of several
447 chemicals and their mineralization to CO_2 may become incomplete, but excessive water

vapour may inhibit the degradation by competitive adsorption on the photocatalyst surface [69, 70, 78]. For instance, Obee and Brown [71] demonstrated that the oxidation rates of formaldehyde, toluene, and 1,3-butadiene (sub-ppmv concentrations) increase as the humidity decreases (for water content above *ca.* 1000 ppm). They suggested that the influence of humidity and trace contaminant concentrations on the oxidation rates on TiO₂ surface is due to the competitive adsorption on the available hydroxyl adsorption sites and to changes in hydroxyl radical population levels.

The effect of water content on PCO of 1-butene ($1.12 \times 10^{-4} \text{ mol m}^{-3}$) over TiO₂ and SnO₂ was also investigated by Cao *et al.* [73]. These authors observed high photoactivity of SnO₂ at low water vapour contents ($< 1000 \text{ ppm}$ or $4.09 \times 10^{-2} \text{ mol m}^{-3}$) and a drastic reduction of photoactivity after increasing the water content above 2000 ppm ($8.18 \times 10^{-2} \text{ mol m}^{-3}$). TiO₂ films showed stable performance for water concentrations between 0 and 3000 ppm ($1.12 \times 10^{-1} \text{ mol m}^{-3}$). Pengyi *et al.* [74] showed that the photocatalytic conversion of trace toluene concentrations ($4.09 \times 10^{-5} - 8.18 \times 10^{-4} \text{ mol m}^{-3}$) by O₃/UV, TiO₂/UV and O₃/TiO₂/UV processes was slightly affected by the relative humidity in the range 20 - 55 % ($2.04 \times 10^{-1} - 7.77 \times 10^{-1} \text{ mol m}^{-3}$) being the optimal humidity around 35 % ($4.82 \times 10^{-1} \text{ mol m}^{-3}$). In a similar study, Zhang and Liu [79] reported that the relative humidity played a significant role in reducing? trace hexane concentrations ($5.73 \times 10^{-5} - 3.12 \times 10^{-4} \text{ mol m}^{-3}$) by TiO₂/UV and O₃/TiO₂/UV processes. The authors found that little humidity improved the decomposition of hexane whereas relative humidity above 45 % ($1.96 \times 10^{-1} \text{ mol m}^{-3}$) would depress the decomposition. Jo and Park [75] revealed that photo-oxidation of benzene, ethyl benzene, and *o*-, *m*-, *p*-xylenes, trichloroethylene, and perchloroethylene in trace levels was independent of humidity in the range 10 – 100 % ($0.10 - 1.03 \text{ mol m}^{-3}$).

473

474 3.2.3. Effect of oxygen on *n*-decane and PCE PCO over PC500 film

475 The effect of the gas-phase molecular oxygen absence on the pollutants
476 conversion over PC500 film under different water content conditions is depicted in Fig.
477 7 (columns with patterns). Fig. 7a shows a drastic reduction on the *n*-decane conversion
478 after removing the oxygen feed gas stream from the reaction: only 16 % of *n*-decane
479 was converted at $RH = 40\%$ against more than 99 % conversion when 21 % of oxygen
480 was present, under the highest irradiance used in this study ($I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$).
481 Reducing RH from 40 to 3 % the conversion of *n*-decane decreased by 36 %, *i.e.* from
482 16 % to 10 % under the same irradiance. Reducing the irradiance to $I = 29 \text{ W}_{\text{UV}} \text{ m}^{-2}$ so
483 does the *n*-decane conversion. For instance, 14 % of *n*-decane was converted at
484 $RH = 40\%$, while only 1 % of *n*-decane was converted at $RH = 3\%$. For the lowest
485 irradiance applied ($I = 18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$), no *n*-decane conversion was observed for both
486 RH conditions in the absence of oxygen. A similar trend may be perceived from Fig. 7b,
487 which represents PCE photocatalytic conversion experiments. Under 40 % of RH the
488 initial PCE was converted by 15 and 6 % for $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ and $I = 29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$,
489 respectively, whereas under 3 % of RH no PCE conversion was detected. In addition, no
490 PCE conversion was observed for $I = 18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ irrespective of the RH value in the
491 gas stream.

492 The presence of oxygen has been reported as essential for the photoreaction and
493 increasing the oxygen concentration so does the pollutant decomposition rate [45, 80-
494 84]. Yet, the mechanism of action is not clear. Larson *et al.* [45] found that the complete
495 oxidation of 2-propanol by UV/TiO₂ was dependent on the presence of oxygen: the
496 conversion of acetone increased from 20 to 70 % after 6 min of UV radiation as the
497 oxygen content increased from 0 % to 5 % (v/v). They also observed that in the absence

498 of gas-phase oxygen the photo-oxidation of propanol could still take place through TiO_2
499 lattice oxygen atoms and that oxygen was needed only to replenish the produced oxygen
500 vacancies on the TiO_2 lattice. Muggli *et al.* [81-83] reported the photo-oxidation of
501 acetic and formic acids over TiO_2 lattice oxygen and found that gas-phase oxygen
502 replenishes the lattice oxygen vacancies even in the dark. On the other hand, they
503 observed that when gas-phase oxygen was present the oxidation rate of formic acid was
504 greatly improved, suggesting the important role of adsorbed oxygen. Likewise, El-
505 Maazawi *et al.* [84] proposed that the photocatalytic reaction could take place in the
506 absence of oxygen due to the TiO_2 lattice oxygen. The oxygen from TiO_2 lattice is
507 depleted during the conversion of gaseous acetone being replenished by the oxygen
508 from the feed gas stream.

509 Considering that the conversion of the two pollutants (*n*-decane and PCE) was
510 drastically hindered after removing the gas-phase molecular oxygen from the gas
511 stream, two oxygen-related mechanisms may be involved in their photocatalytic
512 conversion [45, 80-84]. The first is based on the photodissociation of gas-phase
513 molecular oxygen from the feed stream at the TiO_2 surface into $\text{O}^\cdot$, which spontaneously
514 reacts with O_2 forming $\text{O}_3^\cdot$. These species may greatly contribute to the conversion of
515 pollutants being at the same time the limiting step of the photocatalytic reaction. The
516 second mechanism, where no gas-phase oxygen is present, may be related to the oxygen
517 existing in the TiO_2 lattice. Assuming the limited availability of surface lattice oxygen,
518 it would be expected that the photocatalysis would be considerably impaired, as it was,
519 in fact, observed (see Fig. 7). Regardless of the presence or absence of gas-phase
520 molecular oxygen and the surface density of TiO_2 on the substrate, it is possible to
521 observe in both Figs. 5 and 6 that increasing the *RH* the conversion of the pollutants
522 also increases as it was already previously discussed. The contribution of the classic

523 photocatalytic mechanism where $\text{HO}^\bullet$ radicals initiate the photocatalytic process
524 certainly explain such behavior. Another hypothesis for the role of $\text{HO}^\bullet$ radicals is based
525 on the ability of such species to act as effective traps for the holes preventing electron-
526 hole recombination [85, 86]. In this way the reduced titanium centers (produced by
527 reductive reaction between $e_{\text{CB}}^- (\text{TiO}_2)$ and Ti^{4+} center of the TiO_2) will enhance the
528 space charge layer resulting in a longer lifetime, which ultimately promotes the
529 oxidation of more gas-phase molecular oxygen [85, 86].

530 Several authors have followed another meaningful approach to clarify the
531 mechanism of PCE degradation by PCO [65-67, 69, 87-89]. However, agreement is yet
532 to be found. On one hand, different authors [65-67] claimed that $\text{Cl}^\bullet$ radical addition to
533 PCE occurs several times faster than $\text{HO}^\bullet$ radical addition, neglecting therefore the role
534 of $\text{HO}^\bullet$ radical. Such conclusion was further substantiated by Lu et al. [88] and Fan and
535 Yates [89] after finding that the surface hydroxyl groups were inactive in the oxidation
536 of methyl chloride and trichloroethylene. On the other hand, Yamazaki *et al.* [69, 87],
537 for example, stated that the PCO of PCE could occur via $\text{HO}^\bullet$ radical or $\text{Cl}^\bullet$ radical, but
538 they concluded that $\text{Cl}^\bullet$ radical initial reaction rarely occurs on the catalyst surface since
539 the reaction with $\text{HO}^\bullet$ radical is thermodynamically favourable.

540

541 **4. Conclusions**

542 Different photocatalytic oxidation (PCO) reactions under simulated solar
543 radiation showed that films using the commercial TiO_2 photocatalyst PC500 provide
544 higher conversions of PCE and *n*-decane than those obtained with standard P25. It was
545 also found that PC500 film provides higher mineralization of *n*-decane than P25 film.
546 Although the smaller crystallite size suggests the possibility of higher density in surface
547 defects impairing the charge carriers and, therefore the photocatalytic efficiency, the

548 higher surface area of PC500 catalyst may justify its superior performance towards the
549 conversion of *n*-decane and PCE in comparison to P25 catalyst under steady state
550 conditions.

551 Regarding PC500 film, it was evidenced the effect of the relative humidity (*RH*)
552 on the photocatalytic conversion of both pollutants. The results suggest that for *RH* in
553 the range 3 - 20 %, the competitive adsorption between water and pollutant molecules is
554 unlikely to occur since the pollutants conversion increases with *RH*. On the other hand,
555 at 40 % of *RH* the pollutant conversion over of PC500 film decreases, which means
556 competitive adsorption between the above-mentioned molecules. The conversion of
557 *n*-decane and PCE by PCO was drastically impaired or even no observable in the
558 absence of gas-phase molecular oxygen, which indicates the key role of oxygen in
559 photocatalysis. Three major mechanisms may be implicit in the effect of the oxygen
560 content. One is the formation of reactive species from the adsorbed gas-phase molecular
561 oxygen, which will oxidize the pollutants. The second involves the action of the oxygen
562 from the lattice of TiO₂. The third mechanism involves the classical hydroxyl radical
563 formation on the TiO₂ surface. Acting directly over the pollutant molecules or as a trap
564 for holes, delaying the charge recombination and therefore promoting the formation of
565 other oxidant species, HO[•] radicals cannot be excluded from the reaction. Chlorine
566 radicals chain propagation reactions may also be involved in the PCO reaction
567 mechanism of chlorinated compounds such as PCE.

568

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725 **Table captions**

726 **Table 1.** Catalysts, catalytic bed properties and dimensions of the photoreactor
727 employed in the PCO of *n*-decane and PCE under simulated solar radiation.

728

729 Figures captions

730 **Fig. 1.** Schematic representation of the experimental set-up and the continuous-flow
 731 photoreactor: a) lab-scale unit used for the generation of air streams containing *n*-decane
 732 and water vapour; b) sunlight simulator containing the photoreactor: b₁) side view and
 733 b₂) frontal view; c) master gas chromatograph analytic system used for the analysis of
 734 the photoreactor feed and exit gas streams. Adapted with permission from Lopes *et al.*
 735 [52]. Copyright © 2012, Elsevier.

736 **Fig. 2.** Effect of feed flow rate [Q_{feed}^*] on the conversion of *n*-decane (a) and PCE (c)
 737 and on their consumption ((b) and (d), respectively). Experimental points for incident
 738 irradiances of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,▨), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,▩), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (□,▢),
 739 measured within the spectral range of 280 – 400 nm, at steady-state conditions;
 740 $C_{\text{dec, feed}} = 71 \text{ ppm}$ $C_{\text{PCE, feed}} = 1095 \text{ ppm}$, $RH^* = 40 \%$ and 21 % oxygen. Full coloured
 741 columns represent PC500 (■,▩,□) and columns with patterns P25 (▨,▩,▢) films.
 742 * measured at 298 K and 1 bar.

743 **Fig. 3.** Effect of VOC feed concentration ($C_{\text{dec, feed}}$, and $C_{\text{PCE, feed}}$) on the conversion of
 744 *n*-decane (a) and PCE (c) and on their consumption ((b) and (d), respectively).
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 746), and $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (□,▢) measured within the spectral range of 280 - 400 nm, at
 747 steady-state conditions; $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$, $RH^* = 40 \%$ and 21 % oxygen; Full
 748 coloured columns represent PC500 (■,▩,□) and columns with patterns P25 (▨,▩,▢)
 749 films. * measured at 298 K and 1 bar.

750 **Fig. 1.** Mineralization yields of PCE and *n*-decane due to PCO over PC500 and P25
 751 films. Experimental points for incident irradiances of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,▨), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$
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754 $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$, $RH^* = 40 \%$ and 21 % oxygen; Full coloured columns represent
 755 PC500 (■,■,□) and columns with patterns P25 (▨,▨,□) films. * measured at 298 K and
 756 1 bar.

757 **Fig. 5.** Effect of water content [RH^*] on the conversion over PC500 film of: (a)
 758 *n*-decane, at steady-state conditions, for $C_{\text{dec, feed}} = 71 \text{ ppm}$ (■), $C_{\text{dec, feed}} = 142 \text{ ppm}$ (■),
 759 $C_{\text{dec, feed}} = 284 \text{ ppm}$ (□), and $Q_{\text{feed}} = 150 \text{ cm}^3 \text{ min}^{-1}$; (b) PCE ($C_{\text{PCE, feed}} = 1095 \text{ ppm}$), at
 760 steady-state, for $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$ (■) and $Q_{\text{feed}}^* = 300 \text{ cm}^3 \text{ min}^{-1}$ (□); 21 % oxygen
 761 and $I = 38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$, measured within the spectral range of 280 - 400 nm. * measured
 762 at 298 K and 1 bar.

763 **Fig. 6.** Effect of water content [RH^*] on the conversion over PC500 film: (a) *n*-decane
 764 conversion at steady-state conditions for $C_{\text{dec, feed}} = 71 \text{ ppm}$; (b) PCE conversion at
 765 steady-state conditions for $C_{\text{PCE, feed}} = 1095 \text{ ppm}$; Full coloured columns (■,■,□) and
 766 columns with patterns (▨,▨,□) represent the presence of oxygen (21 %) and its absence,
 767 respectively; $Q_{\text{feed}}^* = 150 \text{ cm}^3 \text{ min}^{-1}$, I of $38.4 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,▨), $29.1 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (■,▨), and
 768 $18.9 \text{ W}_{\text{UV}} \text{ m}^{-2}$ (□,□) were measured within the spectral range of 280 – 400 nm.
 769 * measured at 298 K and 1 bar.

770

Table 1. Catalysts, catalytic bed properties and dimensions of the photoreactor employed in the PCO of *n*-decane and PCE under simulated solar radiation.

TiO₂ Catalysts		
PC500 (Cristal [®])		
	PCO of <i>n</i> -decane	PCO of PCE
Crystal structure	> 99 % Anatase	
Crystal size [nm]	5-10	
Surface area [m ² g ⁻¹]	345	
<i>m</i> _{PC500} [mg]	52.3	35.3
<i>ρ</i> _{A, PC500} [mg cm ⁻²]	6.48×10^{-2}	4.38×10^{-2}
P25 (Evonik [®])		
	PCO of <i>n</i> -decane	PCO of PCE
Crystal structure	80 % Anatase, 20 % Rutile	
Crystal size [nm]	25	
Surface area [m ² g ⁻¹]	50	
<i>m</i> _{P25} [mg]	74.7	100.4
<i>ρ</i> _{A, P25} [mg cm ⁻²]	9.26×10^{-2}	1.24×10^{-1}
Photoreactor		
Outer tube	<i>d</i> _{ot,e} [cm]	5.00
(Pyrex-glass)	<i>d</i> _{ot,i} [cm]	4.64
Inner tube	<i>d</i> _{in,e} [cm]	2.00
(quartz)	<i>d</i> _{in,i} [cm]	1.64
Photoreactor	Lenght, <i>L_R</i> [cm]	16.0
	Volume, <i>V_R</i> [cm ³]	220

Fig. 1. Schematic representation of the experimental set-up and the continuous-flow photoreactor: a) lab-scale unit used for the generation of air streams containing *n*-decane and water vapour; b) sunlight simulator containing the photoreactor: b₁) from a side point of view and b₂) from a frontal point of view; c) master gas chromatograph analytic system used for the analysis of the photoreactor feed and exit gas streams. Adapted with permission from Lopes *et al.* [52]. Copyright © 2012, Elsevier.

783

784 **Fig. 2.** Effect of feed flow rate [Q_{feed}^*] on the conversion of *n*-decane (a) and PCE (c)
 785 and on their consumption ((b) and (d), respectively). Experimental points for incident
 786 irradiances of 38.4 $\text{W}_{\text{UV}} \text{m}^{-2}$ (■,▣), 29.1 $\text{W}_{\text{UV}} \text{m}^{-2}$ (■,▣), and 18.9 $\text{W}_{\text{UV}} \text{m}^{-2}$ (□,▣),
 787 measured within the spectral range of 280 – 400 nm, at steady-state conditions;
 788 $C_{\text{dec, feed}} = 71 \text{ ppm}$ $C_{\text{PCE, feed}} = 1095 \text{ ppm}$, $RH^* = 40 \%$ and 21 % oxygen. Full coloured
 789 columns represent PC500 (■,▣,□) and columns with patterns P25 (▣,▣,▣) films.
 790 * measured at 298 K and 1 bar.

791

Fig. 3. Effect of VOC feed concentration ($C_{dec,feed}$ and $C_{PCE,feed}$) on the conversion of (*n*-decane (a) and PCE (c) and on their consumption ((b) and (d), respectively). Experimental points for incident irradiances of 38.4 $W_{UV} m^{-2}$ (■,▨), 29.1 $W_{UV} m^{-2}$ (▤,▥), and 18.9 $W_{UV} m^{-2}$ (□,◻) measured within the spectral range of 280 - 400 nm, at steady-state conditions; $Q_{feed}^* = 150 cm^3 min^{-1}$, $RH^* = 40\%$ and 21 % oxygen; Full coloured columns represent PC500 (■,▤,□) and columns with patterns P25 (▨,▥,◻) films. * measured at 298 K and 1 bar.

801

802 **Fig. 4.** Mineralization yields of PCE and *n*-decane over PC500 and P25 films.

803 Experimental points for incident irradiances of $38.4 W_{UV} m^{-2}$ (■,▨), $29.1 W_{UV} m^{-2}$ (■,▨)

804), and $18.9 W_{UV} m^{-2}$ (□,▣) measured within the spectral range of 280 - 400 nm, at

805 steady-state conditions; $C_{PCE, feed}^* = 1095$ ppm, $C_{dec, feed}^* = 71$ ppm

806 $Q_{feed}^* = 150 cm^3 min^{-1}$, $RH^* = 40$ % and 21 % oxygen; Full coloured columns represent

807 PC500 (■,▨,□) and columns with patterns P25 (▨,▣,▣). * measured at 298 K and 1 bar.

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825 $18.9 \text{ W}_{UV} \text{ m}^{-2}$ (□, ▨) were measured within the spectral range of 280 – 400 nm.
826 * measured at 298 K and 1 bar.

- Gas-phase PCO of PCE and *n*-decane in a fixed bed annular photoreactor.
- Photocatalytic films produced from PC500 and P25 commercial TiO₂ powders.
- Films with PC500 provide higher conversions than with P25 under solar radiation.
- Films with PC500 mineralize the converted *n*-decane up to 100 %.
- Gas-phase molecular oxygen and Cl[•] radicals have an important role in PCO of PCE.