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Photo-oxidation of three major pharmaceuticals in urban wastewater under artificial and solar irradiations.

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Abstract

The conditions of wastewater treatment by photo-oxidation are addressed in this work with the aim of highlighting the importance of the matrix, concentration and cocktail effects of pharmaceutical pollutants very present in wastewater treatment plant. The idea is to operate under real conditions, i.e. effluent from the WWTP, representative concentrations and natural irradiation. Photospheres are micrometric glass spheres coated with TiO₂ which have the particularity to float and therefore be much easier to separate from treated water during photocatalysis. Three pharmaceutical target molecules were chosen: carbamazepine (CBZ), diclofenac (DCF) and ibuprofen (IBU) to evaluate, in a controlled 2 L artificial UV photoreactor, the individual and coupled effects of three strategic points: i) the matrix effect (tap water vs filtered treated wastewater), ii) the cocktail effect (one molecule vs the three mixed together) and iii) the initial concentration level effect (µg/L vs mg/L). A 300 L solar photoreactor was also designed for this study to evaluate the transferability of performances. Experiments conducted under controlled conditions highlighted that i) the molecule removal was most negatively impacted by the matrix effect, ii) the cocktail effect, even if still negative, appeared to decrease the difference between the degradation rates and iii) initial low concentrations were easier to degrade than higher laboratory concentrations. Transposition to the larger scale solar photoreactor confirmed the order of molecule degradation: DCF > IBU > DCF when alone and DCF > CBZ > IBU when mixed together but also showed that this set up was actually more efficient in the degradation of these molecules than the artificial photoreactor.

Keywords: pharmaceuticals in wastewater, photooxidation, solar irradiation, cocktail effect, matrix effect, concentration effect.

43

44 **1. Introduction**

45 There is mounting economic, societal, and especially environmental pressure to meet
46 the challenges of prevention and protection for natural environments, which makes it
47 strategically important to manage pollution from water or sludge matrices and the reuse
48 of treated water. The Water Framework Directive [1] policy instrument for
49 environmental and health protection cemented toxic pollution as a major challenge by
50 setting two set-deadline objectives to achieve 'good status' for all waters and decrease
51 or even eliminate discharges of certain substances. European Union directive
52 2013/39/EU then prescribed monitoring of pollutants classified as 'priority substances'
53 [2]. Measurement campaigns carried out around the world have highlighted diffuse but
54 persistent pollution of surface waters by a number of contaminants [3,4], partly due to
55 emerging organic pollutants, suspected carcinogens and endocrine disruptors found
56 in trace amounts (ng/L to µg/L) at wastewater treatment outlets as they are resistant
57 to conventional biological treatments [5]. Among these pollutants, drug residues from
58 pharmaceuticals that are increasingly used in our modern and aging societies [6] also
59 end up in wastewaters. As they are not effectively degraded by classical activated
60 sludge treatments, a significant percentage of these pharmaceuticals gets released
61 directly into the environment [7–10].

62 One attractive strategy to improve the global efficiency of wastewater treatment and
63 address the wider problem of environmental pollution is to supplement these biological
64 treatments with tertiary processes [11–13]. Membrane separation[14,15], carbon
65 adsorption processes [16,17] and ozonation [18–20] are known to be effective tertiary
66 water treatment processes, but they also come with drawbacks, including high
67 equipment and operating costs and negative environmental impacts [8,13]. Innovative
68 advanced oxidation processes such as photocatalysis offer a more promising option
69 as they carry the added advantage of non-selective pollutant destruction [18,19,21,22].
70 Among these processes, solar photo-oxidation is a self-powered off-grid process that
71 is both environmentally and economically efficient [23–25]. Meeting dual technical–
72 economic imperatives is integral to successful development of any innovative water
73 treatment processes.

74 Recent research has provided concrete evidence that solar oxidation can significantly
75 reduce the toxicity of complex effluents. Studies have followed the degradation of
76 different mixtures of pesticide pollutants [26–28], pharmaceutical pollutants [29–33],
77 and even both combined [34]. Studies have also been conducted on complex matrixes
78 such as vinasse from a sugarcane ethanol plant [35], surface waters [36,37], municipal
79 wastewater treatment plant effluents [37,38], and even mixtures of pharmaceuticals in
80 treated wastewater [24,31,39,40].

81 The scientific community has recently turned more attention to combining an advanced
82 oxidation process with a biological treatment as a particularly complementary and
83 relevant way to increase the global efficiency of wastewater treatment plants [41]. The
84 biological process is designed to degrade 'biodegradable' organic compounds while
85 the oxidation process is designed to mineralize 'biorecalcitrant' compounds [21,39,42–
86 44]. An oxidation process can be positioned as a pre-treatment upstream of the

87 biological process but it is mainly considered as a post-treatment to reduce non-
88 biodegraded residues immediately downstream of biological treatment [12,35,41]].
89 Among these approaches, some research [35] tends to show that it is necessary to not
90 totally mineralize the pollutants as conventionally proposed in the literature, but to
91 partially oxidize the compounds to make them biodegradable and therefore more
92 amenable to removal by the biological process. The latest results confirm the relevance
93 of this coupling by showing that the partial oxidation of a biorecalcitrant effluent actually
94 makes this effluent biodegradable by the biological treatment [12,37,41].

95 In this context, it is necessary to learn how to fully master the solar oxidation treatment
96 in order to partially or totally eliminate (by mineralization) the pollutants present in
97 complex effluents. The community has identified two main obstacles: the
98 characteristics of the solar resource and the complexity and diversity of the effluents.
99 Works have been done on the integration of the specificities of the solar resource
100 [45,46]. Indeed, the irradiation conditions depend on the meteorological conditions
101 (and particularly clouds), but also on the daily and seasonal cycles which significantly
102 modify the available resource [23,26,47,48]. Generally, to account for the performance
103 of solar photoreactors, degradation rates or capacities are expressed as a function of
104 the amount of energy received [23,46]. This approach to compare the performance of
105 solar photoreactors will also be adopted in this work. The other critical point is due to
106 the diversity of effluents. As the oxidation process is notoriously very multifactorial, it
107 depends on the physic-chemical conditions (pH, alkalinity, salinity, O₂) [49–52], the
108 nature of the effluent (industrial, agricultural, domestic) [46,53], its composition
109 (biocides, pharmaceutical residues, phytosanitary products, etc.) [50,51] and the
110 concentration of pollutants [26,47,54]. As an example, the matrix (raw wastewater,
111 effluent) containing the pollutants [55,56] can strongly influence the efficiency of the
112 oxidation treatment through inhibition or competition effects (the organic compounds
113 contained in the effluent are also oxidized). The pollutant cocktail effect [57,58] makes
114 the evaluation of the capacity of an oxidation treatment a complex task as it depends
115 both on the composition of the cocktail (type and number of pollutants) and on the
116 potential inhibition and competition between pollutants. Currently, the literature
117 proposes numerous studies related to the evaluation of advanced oxidation processes
118 on complex effluents in order to identify the effects of effluent characteristics [55,57–
119 59]. In view of the diversity of effluents and their variability and many issues, the
120 community is currently unable to universally evaluate and model the capabilities of
121 oxidation processes to treat effluents. Thus, certain key factors deserve to be studied
122 in greater depth and in particular, the phenomena of competition between pollutants
123 (the cocktail effect), and the effect of the matrix on the degradation process. One
124 question is to know to what extent the matrix and its composition (screen and cocktail
125 effect) affect the photodegradation capacity of the pollutants.

126 Thus, in this paper, it is proposed to contribute to this problem by conducting
127 experiments on WWTP effluents, complex by definition because of their composition,
128 matrices and variability. The general idea is to determine how to transpose the work
129 generally conducted in the laboratory to solar pilots. The aim is to facilitate the scaling
130 up of solar installations by targeting the key variables that influence and differentiate

131 the performances obtained with photoreactors operating under controlled conditions
132 (tap water, high concentrations, artificial and constant irradiation) and pilot installations
133 on a representative scale operating under real conditions (m³ capacity, WWTP effluent,
134 low concentrations) and dynamics (variable solar irradiation). Thus, this work is divided
135 into two complementary parts in terms of information. First, a set of experiments was
136 carried out with a specific laboratory set-up working under controlled artificial UV
137 irradiation in order to evaluate the separate and coupled effects of three strategic
138 factors: (1) effect of the wastewater matrix (tap water and filtered effluent discharged
139 from a wastewater treatment plant), (2) effect of a cocktail of pollutants, and (3) effect
140 of different initial concentration levels on the degradation rates of the three target
141 molecules.

142 Second, a solar oxidative set-up (storage volume \approx 0.5 m³, irradiance surface of \approx 3
143 m²) was designed. Like in the first step, outdoor experiments were run mainly on
144 wastewater treatment plant effluent. The objectives were to strengthen the
145 experimental results obtained under controlled irradiances and to evaluate the
146 transferability of performances obtained at lab scale under artificial irradiance to natural
147 solar irradiance, in the case of complex effluents.

148
149

150 **2. Material and Methods**

151 **2.1. Pharmaceutical compounds and water matrix**

152 This study used carbamazepine (CBZ), diclofenac (DCF) and ibuprofen (IBU) (100%
153 purity; Sigma-Aldrich, MO). These three pharmaceutical molecules were chosen as
154 they are widely encountered in freshwaters [60–63] and have different features of
155 toxicity and different biodegradability levels [64–68]. Numerous studies on titanium
156 dioxide photocatalysis for pharmaceutical wastewater treatment have worked on these
157 same molecules for the same reasons [24,30,34].

158 Two initial concentration ranges for CBZ, DCF and IBU were considered. High initial
159 concentrations in the range of a microgram per liter (mg/L) were used for all three
160 pharmaceuticals, and their concentration profiles were followed throughout the
161 experiment using a HPLC analyzer (Ultimate 3000 Thermo Fischer) equipped with a
162 diode array detector (DAD) at 220 nm. Analytes were separated with a mixture of
163 ultrapure water/acetonitrile with 0.1% formic acid (70/30, v/v) at a flowrate of
164 0.5 mL/min in isocratic elution mode. Column (EC 100/3 Nucleoshell RP18 Plus
165 2.7 μ m) temperature was set at 35 °C. Injection volume was 25 μ L. Limits of detection
166 of this equipment hosted at the Promes lab were 0.1 mg/L for DCF and 0.2 mg/L for
167 CBZ and IBU. Limits of quantification were 0.3 mg/L for DCF, 0.5 mg/L for CBZ, and
168 0.6 mg/L for IBU.

169 Low initial concentrations in the range of a microgram per liter (μ g/L) were followed by
170 liquid chromatography–tandem mass spectrometry (LC-MS/MS) at the COFRAC-
171 accredited Carso lab. Limits of detection were 0.012 μ g/L for CBZ and DCF and 0.160
172 μ g/L for IBU. Limits of quantification were 0.4 μ g/L for CBZ, 0.5 μ g/L for DCF, and
173 4.0 μ g/L for IBU.

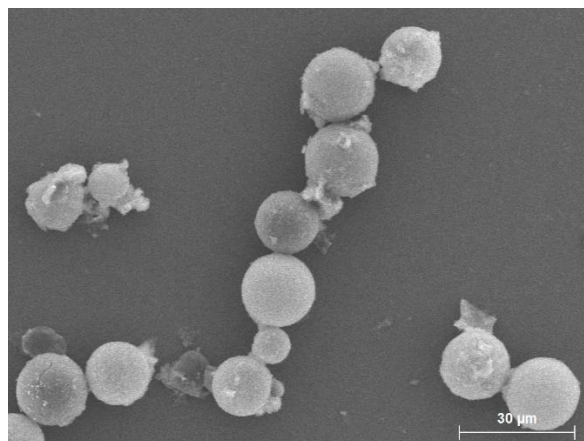
174 Tap water was chosen as the 'reference matrix' to oppose to a very complex matrix.
175 Indeed, treated effluent from the outlet of Perpignan city wastewater treatment plant
176 (classical activated sludge process without tertiary treatment) was used as a far more
177 complex matrix for comparison (pH = 7.4, COD = 28.1 mg/L, TOC = 12.2 mg/L,
178 N = 9.2 mg/L, TKN = 7 mg/L, SO_4^{2-} = 195 mg/L). This treated wastewater (TWW) had
179 been run through a sand filter to afford 'clear water' to make it easier to photo-oxidize
180 with 'only' 8.5 g/L total suspended solids. However, it still contained a lot of other
181 compounds, especially micropollutants poorly degraded by classical WWTP, which
182 could create a cocktail effect by interacting with each other and competing with the
183 three target molecules for degradation.

184
185

186 2.2. Catalyst and pilots

187 Titanium dioxide (TiO_2) was used as one of the most attractive catalysts for
188 environmental remediation [69–71]. Most studies classically use TiO_2 in its Degussa
189 P25 form [72]. The novelty of this work is the use of TiO_2 in its photosphere form, i.e.
190 45 μm (range: 5 μm –85 μm) TiO_2 -coated glass microspheres (**Fig. 1**) which has the
191 advantage of floating (0.22 g/L density) and is therefore much easier to separate from
192 treated water. The optimal photocatalyst concentration corresponds to the total
193 absorption of the radiation inducing the fastest kinetics [47]. Preliminary tests (data not
194 shown) to vary the concentrations of the photospheres in a lab-scale pilot photoreactor
195 (**Fig. 2**) concluded that 5 g/L of photospheres maximized the pollutant degradations
196 kinetics. Even if the outdoor solar photoreactor is slightly different in terms of optical
197 thickness and geometric configuration, the catalyst concentration was kept identical.
198 For both pilots, the catalyst was new at the start of the first experiment but not renewed
199 between each experiment.

200



201
202 Figure 1. Photography of photospheres under Field Emission Gun Scanning Electron Microscopy FEG
203 SEM Hitachi S-4500. Images were acquired with a secondary electron detector and a 15 kV electron
204 beam at a working distance of 14 mm.

205

206 The lab-scale photoreactor (**Fig. 2**, left side) was composed of a single closed 2 L flat-
207 panel reactor (25 x 45 x 2 cm) with a parallelepiped shape. It had a stainless-steel base
208 and was covered in front by a UV-transparent (91% UV transmission) PMMA plate.

209 The water was homogenized by pressurized airflow pumped into the bed of the tank
 210 via five holes evenly spaced across the width. Irradiance source was an artificial LED
 211 UV panel of the same surface area as the tank in order to achieve uniform irradiance.
 212 This LED UV panel was placed 2 cm from the PMMA surface. Irradiance was delivered
 213 in a very narrow range of wavelength centered around 365 nm. After calibration with a
 214 UV sensor (Apogee Instruments MU-200), the radiant flux density at the reactor
 215 surface was controlled and adjustable between 5 and 85 W/m².
 216 The outdoor set-up (**Fig. 2**, right side) was composed of a 300 L cylindrical stainless-
 217 steel tank connected to the solar reactor with a closed-loop fluid circuit. Two stainless-
 218 steel ramps delivered the feed influent (at the inlet) and collected the treated effluent
 219 (at the outlet) via a series of 1.55 m-long and 32 mm-outer diameter borosilicate glass
 220 tubes harvesting the natural light from the sun. Water passed from the cylindrical tank
 221 through the reactor from bottom to top and was recirculated by a volumetric pump
 222 (Pompes Guinard XENAJET 3000). Homogenization was ensured by the fast-
 223 circulating flow and the fact that recirculated water fell into the 300 L tank from around
 224 40 cm in height. Tubes were oriented southwards and tilted at an angle of about 42°.
 225 Solar flux density was recorded through each experiment via a UV radiometer (UVA-
 226 Sensor CT-UVA 3) fixed to the top of the tube-carrying frame.



227
 228 Figure 2: Experimental set up of the artificial light photoreactor (left) & the natural sunlight one (right).
 229

230 Both systems were operated in batch mode, and their main characteristics are
 231 summarized in **Table 1**. The lab-scale photoreactor allowed to precisely set and test
 232 different parameters (light flux density, catalyst concentration, treatment duration, and
 233 so on) in controlled conditions before scaling up the process to assess its
 234 performances at larger scale and in outdoor conditions.

235
 236

Table 1: Detailed characteristics of both pilots.

	External pilot	Internat pilot
UV light type	Solar	Artificial
Flux density (W/m ²)	0-60	0-85
Total volume V _t (L)	400	2

Irradiated volume V_i (L)	70	2
Ratio V_t/V_i	5.7	1
Irradiated shapes	Tubes	Cuboid
Irradiated projected surface (m ²)	2.9	0.1

237

238 3. Results and Discussion

239 The impact of the photocatalysis [48,73–76] on the degradation of target
 240 pharmaceuticals has been studied. The three molecules (CBZ, DCF and IBU) were
 241 tested independently and all together in both tap water and filtered treated wastewater
 242 in the artificial photoreactor, but only in filtered wastewater in the solar photoreactor.

243 Sunlight as a resource poses specific challenges, such as a low flux density in the
 244 spectral range useful for photo-oxidation (ultraviolet), geographic variability and very
 245 strong discontinuities. Solar irradiation conditions depend on daily and seasonal cycles
 246 but also on local weather conditions. This variability makes it a complex task to conduct
 247 experiments under the same experimental conditions over time but also to compare
 248 performances between 'natural' outdoor experiments and 'artificial' indoor experiments
 249 that use controlled and mainly uniform irradiance conditions. A well-known and efficient
 250 way to standardize the experimental results is to analyze the concentration-profile data
 251 not as a function of time but of the amount of irradiance energy received [26,77], i.e.
 252 as a function of the accumulated UV energy received by the reactor surface per volume
 253 of solution to be treated: Q_{UV} (J/m³). This accumulated UV energy can be defined as:

$$254 \quad Q_{UV}(t) = \frac{S}{V_t} \int_0^t I(t) dt \quad eq.1$$

255 where S is surface area of the collector (m²), V_t is total volume of solution treated (m³),
 256 and I is incident light flux density (W/m²) over time t (s).

257 The objective of this mainly experimental work was not to develop a theoretical kinetics
 258 study but to compare, via a simple but quantitative criterion, the performance of the
 259 photocatalytic process under extremely different conditions. For this reason, the
 260 simplest kinetic formalism was retained. Data were exploited according to a pseudo-
 261 first-order kinetic model with an effective constant (α in m³/J) directly proportional to
 262 the irradiance measured at the surface of the reactor (eq. 2):

$$263 \quad \frac{dC}{dt} = -\frac{S}{V_t} \cdot (\alpha \cdot I(t)) \cdot C \quad eq.2$$

264 Combined with eq. 1, this leads to an expression of the concentration profiles as a
 265 function of Q_{uv} given by [24,34]:

$$266 \quad C(t) = C_0 \cdot e^{-\alpha \cdot Q_{UV}(t)} \quad eq.3$$

267

268

269 3.1. Experiments under controlled conditions

270 3.1.1. Matrix effect

271 Photo-oxidation processes implemented in wastewater treatment plants as a tertiary
 272 or quaternary water treatment will have more complex effluents to deal with. These
 273 treated wastewaters (TWW) come from upstream treatments unable to eliminate
 274 micropollutants such as pharmaceuticals [8,78,79], metals [80,81] or pesticides
 275 [82,83].

276 The first goal of this study was to quantify how much the use of a real treated effluent
 277 would impact the photo-oxidation-driven degradation rates of the three target
 278 molecules in comparison to tap water. To do so, a set of experiments was conducted
 279 with the artificial-UV-light photoreactor at a maximum light flux density of 85 W/m², at
 280 high initial concentrations (10 mg/L) and in both tap water (**Fig. 3**) and TWW (**Fig. 4**)
 281 The experiments were continued until the target molecules were almost completely
 282 degraded, which corresponded to maximum oxidation times of 2.5 h in tap water and
 283 6 h in TWW.

284 On the one hand, this is much faster than another study conducted on fixed TiO₂ and
 285 pharmaceuticals initial concentrations of 5 mg/L which needed 50 and 70 h for the
 286 complete removal of DCF in wastewater effluent and deionized water, while did not
 287 fully degrade CBZ and even IBU, in both waters, after 100 h of experiment [24]. On the
 288 other hand, this is much slower than the 30 min observed in distilled water with P25
 289 Aeroxide TiO₂ and 30 mg/L DCF initial concentration [84] but his study used a very
 290 powerful MP 500W mercury lamp.
 291

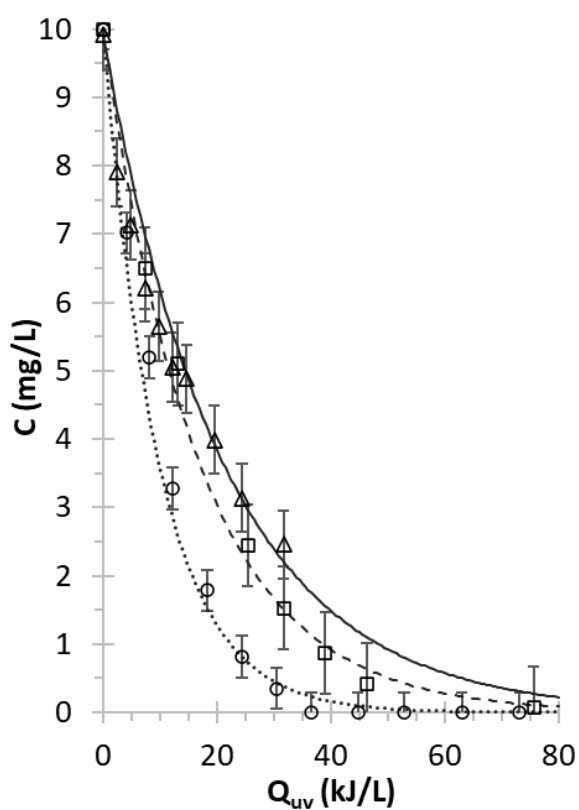


Figure 3: Measured and calculated (eq. 3) concentrations of carbamazepine (CBZ) [Δ ,—], diclofenac (DCF) [\circ ,·] and ibuprofen (IBU) [\square ,-] at 85 W/m² flux density in tap water.

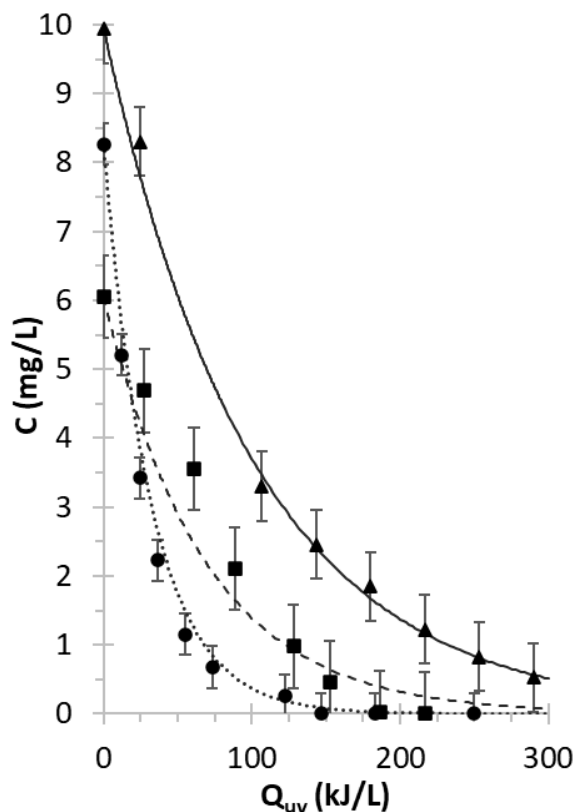


Figure 4: Measured and calculated (eq. 3) concentrations of CBZ, DCF and IBU at 85 W/m² flux density in treated wastewater (TWW) [\blacktriangle ,— / \bullet ,· / \blacksquare ,-].

292
 293 The degradation profiles were similar in both waters, showing the same global behavior
 294 and mechanisms in action, which seemed independent of the matrix containing the
 295 target molecules. These observations suggest that the processus of photo-oxidation,
 296 photo-excitation and recombination were little affected by the catalyst environment,
 297 therefore those processus were the same whatever the matrix. DCF degraded fastest,
 298 followed by IBU and then CBZ, in accordance with recent literature [24]. DCF was
 299 easily oxidized whereas CBZ was very hard to degrade, which underlines the major
 300 disparities between target molecules, as previously reported [85].

301 Thus, despite its simplicity, the pseudo-first-order kinetic model was able to accurately
 302 depict, for both waters, the time–course changes in target-molecule concentration as
 303 a function of amount of energy received. The kinetic rate constant α , in liters of water
 304 treated per kilojoule of received radiation (L/kJ) for easier reading and comparison,
 305 was determined by linear regressions for each molecule in both tap water and TWW
 306 (**Table 2**). These coefficients are an efficient way to quantify the degradation rates,
 307 where higher values correspond to faster degradation.

308 The previously-stated order of degradability (DCF>IBU>CBZ) was of course reflected
 309 in the α rates. DCF had the highest α values, at around two times higher than for IBU
 310 and CBZ, and in both waters. DCF was therefore an easier pharmaceutical compound
 311 to treat by photocatalysis, as already shown elsewhere [39,42].

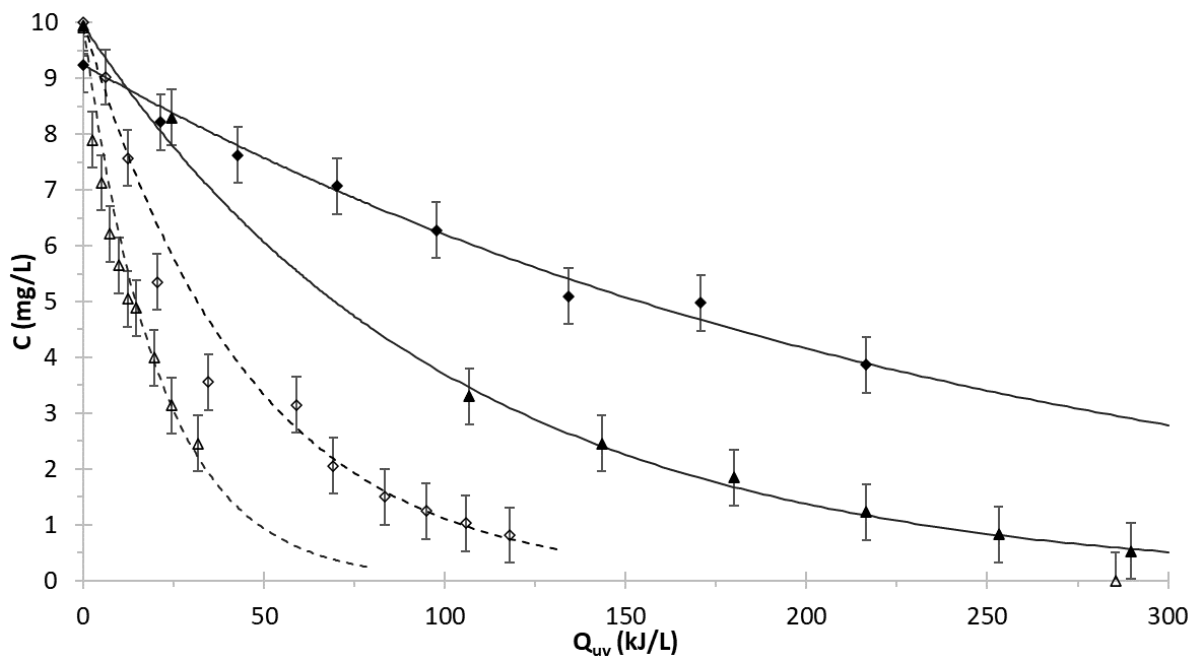
312 The ratios between the kinetic coefficients of tap water and TWW was also calculated
 313 through linear regressions (**Table 2**). On average, it took 4.1 times more accumulated
 314 energy Q_{UV} to degrade the three molecules in TWW than in tap water. This result
 315 confirms a negative impact of the matrix effect on their photocatalytic degradability
 316 [84,86]. This negative impact has mostly been attributed to the competitive inhibition
 317 of photocatalysts by OH° scavenging from organic matter [37,85,86], but other
 318 explanations could be active site coverage [40,86] or adsorption and light attenuation
 319 due to suspended solids [24,86].

320
 321 Table 2: Kinetic coefficients α (L/kJ) for each molecule (in dark color) as well as their ratios Tap water
 322 /Treated wastewater (in light color) for laboratory high concentrations. R^2 of the linear regressions used
 323 to determine the kinetic coefficients α are between 0.9703 and 0.9991.

	CBZ	DCF	IBU
Tap water	0.047	0.103	0.060
TWW	0.010	0.031	0.015
Ratio Tap Water / TWW	4.8	3.3	4.1

324
 325 **3.1.2. Cocktail effect**
 326 Treatment of all three molecules in mixture in the water matrices highlighted the
 327 competition that spontaneously occurred during degradation. **Figure 5** shows that CBZ
 328 was always (in each matrix) harder to degrade in mixture than alone. DCF and IBU
 329 also followed this same pattern: degradation was always slower when the other

330 molecules were also present in the water. The cocktail effect thus had a clear negative
 331 impact on degradation rates, but the matrix effect still appeared to prevail.
 332 To further refine these results, **Table 3** reports the α kinetic coefficients calculated for
 333 the cocktail effect in order to complete **Table 2**. In each case scenario (each molecule
 334 in each matrix), degradation rate was higher for the molecule alone than mixed with
 335 the two others, thus showing that the cocktail effect hampers degradation. DCF was
 336 still the easiest molecule to degrade while CBZ and IBU showed similar degradation
 337 rates, but the cocktail effect tended to narrow the gap between the α values.
 338 Interestingly, the cocktail effect had more impact on TWW with an average ratio of 3.3
 339 against only 2.5 in tap water.
 340



341
 342 Figure 5: Measured and calculated (eq. 3) concentrations of CBZ at 85 W/m² flux density, alone in tap
 343 water [Δ , -], alone in TWW [\blacktriangle , —], mixed in tap water [\diamond , -] and mixed in TWW [\blacklozenge , —].
 344

345 The kinetic coefficients (**Table 3**) also demonstrated that the matrix effect still
 346 prevailed. On average, it was 2.9-times harder to treat a molecule in mixture than
 347 alone, and it was 4.6-times harder to treat the molecule in TWW than in tap water.
 348 Taken together, these results on both matrix and cocktail effects showed that each
 349 effect impacted the degradation of the target molecules in a non-linear way, but also
 350 in a synergistic way that further manifested the observed phenomena.
 351

352 Table 3: Kinetic coefficients α (L/kJ) in each case scenario for each molecule (in dark color) as well as
 353 their ratios tap water / treated wastewater (TWW) and alone / mixed (in light color). R² of the linear
 354 regressions used to determine the kinetic coefficients α of the molecules mixed are between 0.9817 and
 355 0.9968.

	Alone			Mixed			Ratio Alone / Mixed		
	CBZ	DCF	IBU	CBZ	DCF	IBU	CBZ	DCF	IBU
Tap water	0.047	0.103	0.060	0.022	0.037	0.023	2.2	2.8	2.6
TWW	0.010	0.031	0.015	0.004	0.009	0.004	2.5	3.4	3.9

Ratio Tap Water / TWW	4.8	3.3	4.1	5.5	4.1	6.0
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356

357 3.1.3. Concentration effect

358 The third step of this study was to test the influence of initial concentrations. Thus, in
 359 addition to the high 10 mg/L concentrations, low concentrations of 50 µg/L for CBZ and
 360 DCF, and 400 µg/L for IBU were tested. In European Union countries, maximum
 361 wastewater treatment plant inlet and outlet concentrations are similar between CBZ
 362 and DCF but much higher for IBU [79].

363 All other operating conditions were kept constant, and the three molecules were
 364 considered almost totally degraded by photooxidation in less than 3 h. Other studies
 365 conducted on these molecules at initial low concentrations also found high degradation
 366 rates in relative short times. Miranda-Garcia et al. [42] worked at initial concentrations
 367 of 100 µg/L and found that 90% of each molecule was degraded within 1h15min.
 368 Fernandez et al. [34] worked with initial concentrations of around 500 ng/L and found
 369 that 95% of each molecule was degraded within 2h45min.

370

371 Table 4: Kinetic coefficients α (L/kJ) for each molecule (in dark color) as well as their ratios tap water /
 372 TWW (in light color) for low concentrations. R^2 of the linear regressions used to determine the kinetic
 373 coefficients α are between 0.9300 and 0.9995.

	Alone			Mixed			Ratio Alone / Mixed		
	CBZ	DCF	IBU	CBZ	DCF	IBU	CBZ	DCF	IBU
Tap water	0.235	0.525	0.363	0.316	0.244	0.302	0.7	2.2	1.2
TWW	0.072	0.213	0.186	0.102	0.134	0.087	0.7	1.6	2.2
Ratio Tap Water / TWW	3.3	2.5	1.9	3.1	1.8	3.5			

374

375 Kinetic coefficients were determined for these lower concentrations in the same way
 376 as previously for the high concentrations (**Table 4**). Results showed the same effects
 377 and tendencies at low initial concentrations as at high initial concentrations.
 378 Degradation rates were molecule-dependent, but at lower concentrations, DCF was
 379 globally still easier to degrade than IBU, which was easier to degrade than CBZ.
 380 The matrix effect still occurred, as previously found elsewhere [34], but it was less
 381 pronounced with lower concentrations. Indeed, an average α tap water to α TWW ratio
 382 of 4.1 was found for the compounds alone at high concentrations (**Table 3**) but only
 383 2.6 for lower concentrations (**Table 4**).

384 The cocktail effect also appeared to be largely attenuated at low concentrations.
 385 Indeed, average ratios between α for molecules alone and α for molecules in mixture
 386 were 2.5 for tap water and 3.3 for TWW at high concentrations but only 1.4 for tap
 387 water and 1.5 for TWW at low initial concentrations. Furthermore, variations were not
 388 homogeneous and were molecule-dependent: for instance, CBZ appeared to degrade
 389 much better when mixed at low initial concentrations.

390 Comparison of these results (**Table 4**) against the high initial concentrations in the in-
391 lab experiment (**Table 3**) showed that, as expected, degradation of the molecules was
392 not of a first-order kinetics as a function of concentration. The general trends observed
393 showed that direct-proportionality kinetics strongly overestimated the influence of initial
394 concentrations. α values should only be considered as a way to provide a quantitative
395 comparison of kinetics for different experimental conditions. Either way, ratios between
396 initial concentrations of 200 for CBZ and DCF (between 10 mg/L and 50 $\mu\text{g/L}$) while
397 only 25 for IBU (between 10 mg/L and 400 $\mu\text{g/L}$), led to 10-fold-smaller α coefficients
398 for high concentrations. Even though this ratio was dependent on the conditions (matrix
399 and cocktail effects), it nevertheless showed that these molecules were easier to
400 degrade at lower concentrations. Previous studies arrived at similar conclusions
401 [47,54,87,88] but gave different explanations, most of which were directly linked to the
402 process of heterogenous photodegradation. For instance, TiO_2 can saturate at higher
403 pollutant concentrations, as photocatalysis needs a sorption stage on the catalyst,
404 which limits the degradation kinetics. The presence of more recalcitrant by-products at
405 high initial concentrations can also limit degradation, especially at the end of the
406 mineralization process.

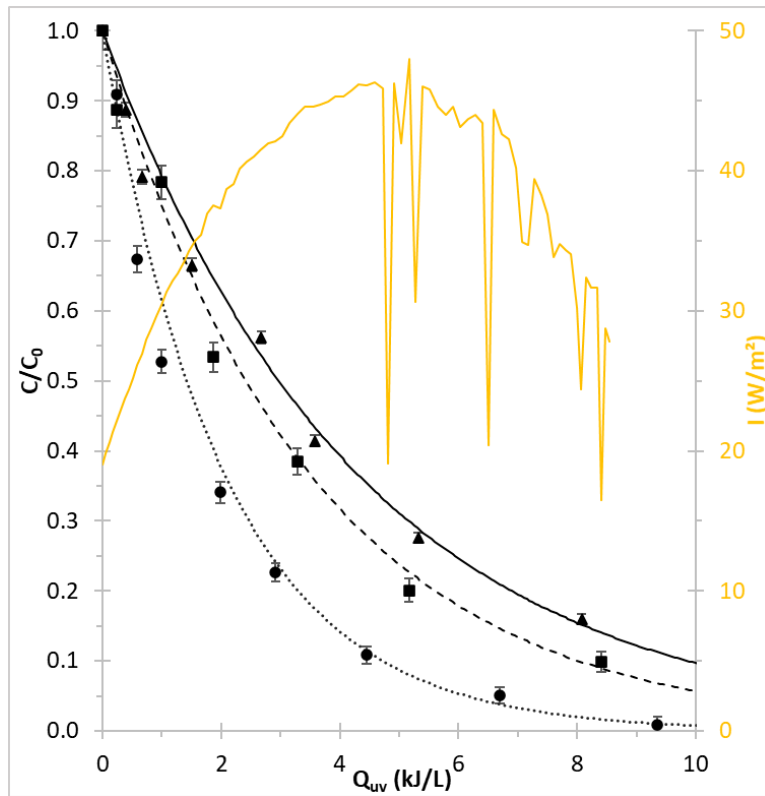
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408

409 **3.2. Experiments under solar conditions**

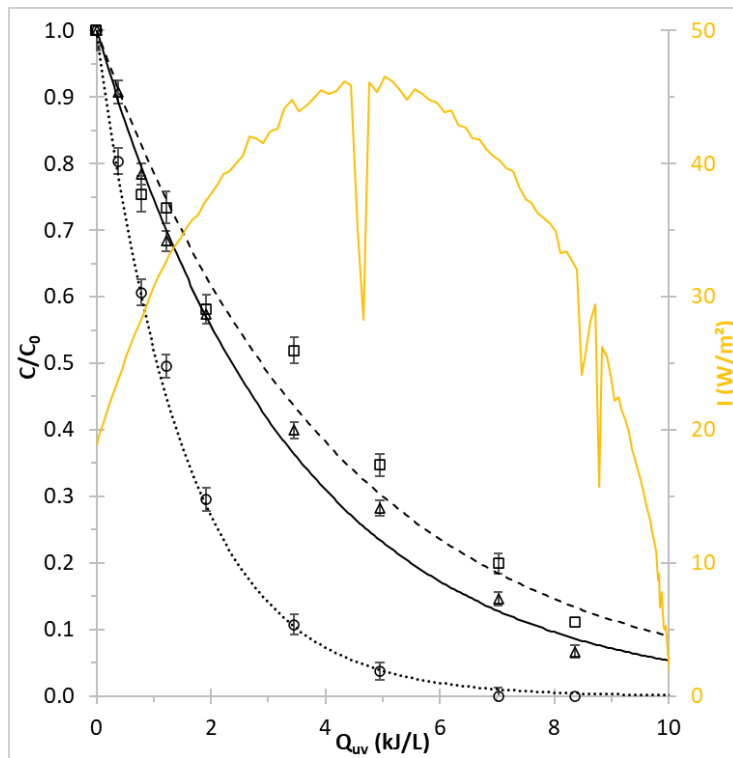
410 The final goal of this study was to evaluate the capacity of solar photo-oxidation
411 process to treat the target molecules. Only filtered TWW was used, and it was only
412 spiked with low initial concentrations (50 $\mu\text{g/L}$ CBZ and DCF but 400 $\mu\text{g/L}$ IBU).

413 Experiments were conducted over full days until target molecules were considered
414 totally degraded. In total, four experiments were conducted for 6 to 7 h per day on
415 sunny spring days (May 15 and 16 and then May 21 and 22, 2019). As the molecules
416 were tested at different initial concentrations, **Figures 6 & 7** report the results as
417 dimensionless concentrations C/C_0 . The figures also give the UV flux densities coming
418 from the sun on two sample days, which follow classical daily curves that increase in
419 the morning to peak at around 45 W/m^2 at noon and then decrease in the afternoon.
420 Only a few clouds passed during these days (the steep point-decreases), allowing a
421 total Q_{UV} of around 10 kJ/L for each experiment.



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Figure 6: Measured and calculated (eq. 3) concentrations of CBZ [▲ / —], DCF [● / ·] and IBU [■ & -] alone in treated wastewater during spring days. The measured flux density of the “IBU alone experiment” (22/05/2019) is also reported.



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Figure 7: Measured and calculated (eq. 3) concentrations of CBZ [Δ / —], DCF [○ / ·] and IBU [□ / -] mixed together in treated wastewater during spring days. The measured flux density of the “DCF alone experiment” (21/05/2019) is also reported.

432 Four experimental campaigns were thus been conducted under solar irradiance. The
 433 first three campaigns aimed to understand the degradation of each of the three target
 434 molecules alone (**Fig. 6**), while the fourth campaign aimed to clarify what would happen
 435 when the three target molecules were mixed together (**Fig. 7**). Here the three
 436 molecules were nearly totally removed after a full day of treatment, highlighting the
 437 great performance of the process using TiO₂ Photospheres considering the TWW
 438 matrix in comparison with the literature. Indeed, for TiO₂ Degussa P25, 4.5 h of solar
 439 irradiation degraded 75 % of CBZ mixed with other pharmaceuticals using [89] which
 440 is totally in accordance with the results here: 4.5 h corresponded to a Q_{UV} of 5.7 kJ/L,
 441 thus 80 % of degradation for CBZ (**Fig. 7**). For P25 Aeroxide TiO₂, 6 h of solar exposure
 442 was needed to achieve the total removal of DCF alone (at 30 mg/L initial concentration)
 443 in distilled water [84]. For DCF, another study found that only 50 min were necessary
 444 to completely remove this compound in treated wastewater but contrary to this present
 445 paper, it was filtered through 0.45 μm Millipore filters and stored at 4 °C prior to use
 446 [31].

447 Tendencies observed in controlled conditions were valid in outdoor conditions and at
 448 the solar photoreactor scale, as the degradation profiles respected the same ranking.
 449 When each compound was alone, DCF was the easiest to degrade, followed by IBU
 450 and then CBZ (**Fig. 6**) ; whereas when in mixture together, DCF was still the easiest to
 451 degrade, but CBZ was the next easiest, followed by IBU (**Fig. 7**). Other study on solar
 452 driven oxidation process based on Nitrogen-doped TiO₂ (N-TiO₂) also found that DCF
 453 was easier to degrade than CBZ, and both in distilled water and wastewater [33].

454 The corresponding normalized concentrations were fitted in **Figures 6 & 7** according
 455 to the pseudo-first-order kinetic model (eq .3). Here again, this simple model sharply
 456 depicted the target-molecule degradations as a function of amount of received energy,
 457 even with natural solar light instead of artificial LED light. The normalized
 458 concentrations were calculated after first determining α kinetic coefficients for each
 459 case scenario (**Table 5**).

460

461 Table 5: Kinetic coefficients α (L/kJ) for each molecule (in dark color) as well as their ratios alone / mixed
 462 (in light color) for low concentrations and solar photocatalysis. R² of the linear regressions used to
 463 determine the kinetic coefficients α are between 0.9888 and 0.9992.

	Alone			Mixed			Ratio Alone / Mixed		
	CBZ	DCF	IBU	CBZ	DCF	IBU	CBZ	DCF	IBU
TWW	0.233	0.488	0.287	0.293	0.654	0.241	0.8	0.7	1.2

464

465 Comparison of these α coefficients against the α coefficients under artificial irradiance
 466 (TWW row in **Table 4**) highlighted that degradation of the target molecules was on
 467 average 2.9-times more efficient under sunlight. The artificial and solar photoreactors
 468 were used under equivalent conditions in terms of target compounds (low initial
 469 concentrations), TWW matrix (the same pH and chemical composition) and catalyst
 470 (photospheres at 5 g/L). Basically, experimental data from eq. 3 were used to account
 471 for the huge difference in terms of surfaces irradiated and volumes treated, but it was
 472 harder to compare the photoreactors in terms of radiative transfer with cylindrical tubes

473 in one configuration and a flat surface in the other configuration. Characteristic optical
474 path lengths are clearly defined for the artificial set-up but more difficult to estimate
475 with the solar set-up due to the trajectory of the sun.

476 Nonetheless, the photoreactors did differ in some photo-chemical properties, which
477 could explain the better degradations observed in the solar photoreactor. First, natural
478 sunlight has a wider UV spectrum than artificial UV light, and a wider spectrum is
479 known to increase the efficiency of photocatalysis [90–93]. Another major difference
480 between the two reactors was the continuous substantial oxygenation of the artificial
481 reactor due to the flowing air bubbles used to homogenize the photospheres. Studies
482 have shown the importance of dioxygen in photocatalytic treatments [49,94,95], and
483 the absence of dissolved oxygen has been shown to improve the photodegradation of
484 CBZ [96] as well as IBU [97], which were the two molecules most impacted here.

485

486

487 **4. Conclusions**

488 This study showed that the three target compounds CBZ, DCF and IBU can be
489 effectively degraded by photocatalysis based on a new photosphere-format catalyst
490 allowing separation by flotation. Under artificial controlled conditions, the matrix effect
491 always had the most negative impact on molecule removal. The cocktail effect also
492 had a negative impact on degradation rates but tended to attenuate the degradation
493 rate differential between the compounds. The concentration effect consequently
494 gained importance, as it was easier to treat low concentrations ($\mu\text{g/L}$) than higher
495 laboratory concentrations (mg/L).

496 The solar photoreactor proved scalable to near-real-world conditions (with wastewater
497 treatment plant effluent and compound concentrations at $\mu\text{g/L}$ magnitude) with very
498 good removal efficiencies. This transposition also showed that DCF was always the
499 easiest compound to degrade (alone or mixed with CBZ and IBU), and that the target
500 compounds held the same rank order of degradation between the two photoreactors:
501 DCF > IBU > DCF when alone and DCF > CBZ > IBU when mixed together. While both
502 photoreactors produced these same general qualitative behaviors, the solar
503 photoreactor was actually more efficient than the artificial-UV photoreactor.

504

505

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512 SOLSTICE.

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