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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 TiO_2 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.

1. Introduction

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

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

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

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

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

In this context, it is necessary to learn how to fully master the solar oxidation treatment in order to partially or totally eliminate (by mineralization) the pollutants present in complex effluents. The community has identified two main obstacles: the characteristics of the solar resource and the complexity and diversity of the effluents. Works have been done on the integration of the specificities of the solar resource [45,46]. Indeed, the irradiation conditions depend on the meteorological conditions (and particularly clouds), but also on the daily and seasonal cycles which significantly modify the available resource [23,26,47,48]. Generally, to account for the performance of solar photoreactors, degradation rates or capacities are expressed as a function of the amount of energy received [23,46]. This approach to compare the performance of solar photoreactors will also be adopted in this work. The other critical point is due to the diversity of effluents. As the oxidation process is notoriously very multifactorial, it depends on the physic-chemical conditions (pH, alkalinity, salinity, O_2) [49–52], the nature of the effluent (industrial, agricultural, domestic) [46,53], its composition (biocides, pharmaceutical residues, phytosanitary products, etc.) [50,51] and the concentration of pollutants [26,47,54]. As an example, the matrix (raw wastewater, effluent) containing the pollutants [55,56] can strongly influence the efficiency of the oxidation treatment through inhibition or competition effects (the organic compounds contained in the effluent are also oxidized). The pollutant cocktail effect [57,58] makes the evaluation of the capacity of an oxidation treatment a complex task as it depends both on the composition of the cocktail (type and number of pollutants) and on the potential inhibition and competition between pollutants. Currently, the literature proposes numerous studies related to the evaluation of advanced oxidation processes on complex effluents in order to identify the effects of effluent characteristics[55,57–59]. In view of the diversity of effluents and their variability and many issues, the community is currently unable to universally evaluate and model the capabilities of oxidation processes to treat effluents. Thus, certain key factors deserve to be studied in greater depth and in particular, the phenomena of competition between pollutants (the cocktail effect), and the effect of the matrix on the degradation process. One question is to know to what extent the matrix and its composition (screen and cocktail effect) affect the photodegradation capacity of the pollutants.

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

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

Second, a solar oxidative set-up (storage volume ≈ 0.5 m^3, irradiance surface of ≈ 3 m^2) was designed. Like in the first step, outdoor experiments were run mainly on wastewater treatment plant effluent. The objectives were to strengthen the experimental results obtained under controlled irradiances and to evaluate the transferability of performances obtained at lab scale under artificial irradiance to natural solar irradiance, in the case of complex effluents.

2. Material and Methods

2.1. Pharmaceutical compounds and water matrix

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

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

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

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

2.2. Catalyst and pilots

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

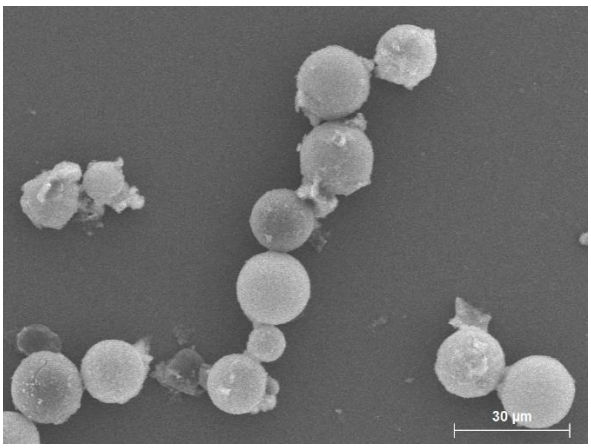

Figure 1. Photography of photospheres under Field Emission Gun Scanning Electron Microscopy FEG SEM Hitachi S-4500. Images were acquired with a secondary electron detector and a 15 kV electron beam at a working distance of 14 mm.

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

The water was homogenized by pressurized airflow pumped into the bed of the tank via five holes evenly spaced across the width. Irradiance source was an artificial LED UV panel of the same surface area as the tank in order to achieve uniform irradiance. This LED UV panel was placed 2 cm from the PMMA surface. Irradiance was delivered in a very narrow range of wavelength centered around 365 nm. After calibration with a UV sensor (Apogee Instruments MU-200), the radiant flux density at the reactor surface was controlled and adjustable between 5 and 85 W/m².

The outdoor set-up (**Fig. 2**, right side) was composed of a 300 L cylindrical stainless-steel tank connected to the solar reactor with a closed-loop fluid circuit. Two stainless-steel ramps delivered the feed influent (at the inlet) and collected the treated effluent (at the outlet) via a series of 1.55 m-long and 32 mm-outer diameter borosilicate glass tubes harvesting the natural light from the sun. Water passed from the cylindrical tank through the reactor from bottom to top and was recirculated by a volumetric pump (Pompes Guinard XENAJET 3000). Homogenization was ensured by the fast-circulating flow and the fact that recirculated water fell into the 300 L tank from around 40 cm in height. Tubes were oriented southwards and tilted at an angle of about 42°. Solar flux density was recorded through each experiment via a UV radiometer (UVA-Sensor CT-UVA 3) fixed to the top of the tube-carrying frame.

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

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

Table 1: Detailed characteristics of both pilots.

	External pilot	**Internat pilot**
UV light type	Solar	Artificial
Flux density (W/m²)	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 (m²)	2.9	0.1

3. Results and Discussion

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

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

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

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

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

$$\boldsymbol{\frac{dC}{dt} = -\frac{S}{V_t}.(\alpha.I(t)).C} \qquad \textit{eq.2}$$

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

$$\boldsymbol{C(t) = C_0.e^{-\alpha.Q_{UV}(t)}} \qquad \textit{eq.3}$$

3.1. Experiments under controlled conditions

3.1.1. Matrix effect

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

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

On the one hand, this is much faster than another study conducted on fixed TiO_2 and pharmaceuticals initial concentrations of 5 mg/L which needed 50 and 70 h for the complete removal of DCF in wastewater effluent and deionized water, while did not fully degrade CBZ and even IBU, in both waters, after 100 h of experiment [24]. On the other hand, this is much slower than the 30 min observed in distilled water with P25 Aeroxide TiO_2 and 30 mg/L DCF initial concentration [84] but his study used a very powerful MP 500W mercury lamp.

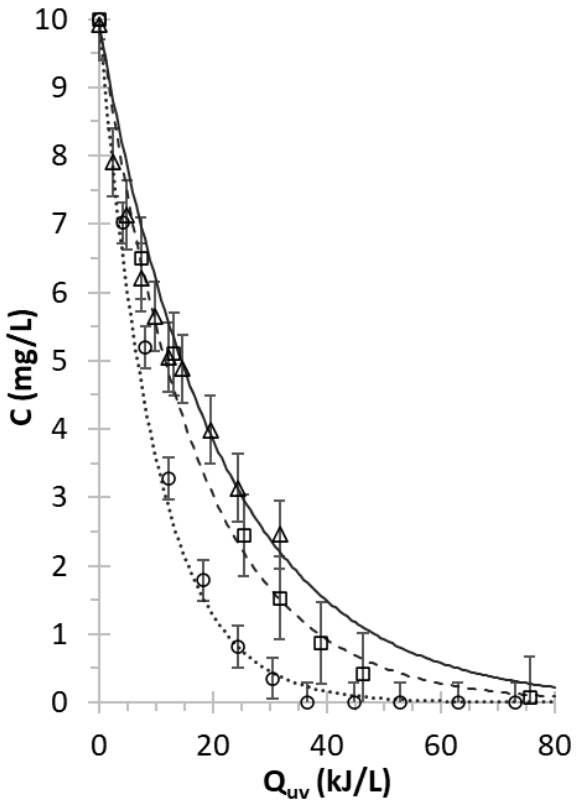

Figure 3: Measured and calculated (*eq. 3*) concentrations of carbamazepine (CBZ) [Δ,—], diclofenac (DCF) [○,·] and ibuprofen (IBU) [□,-] at 85 W/m² flux density in tap water.

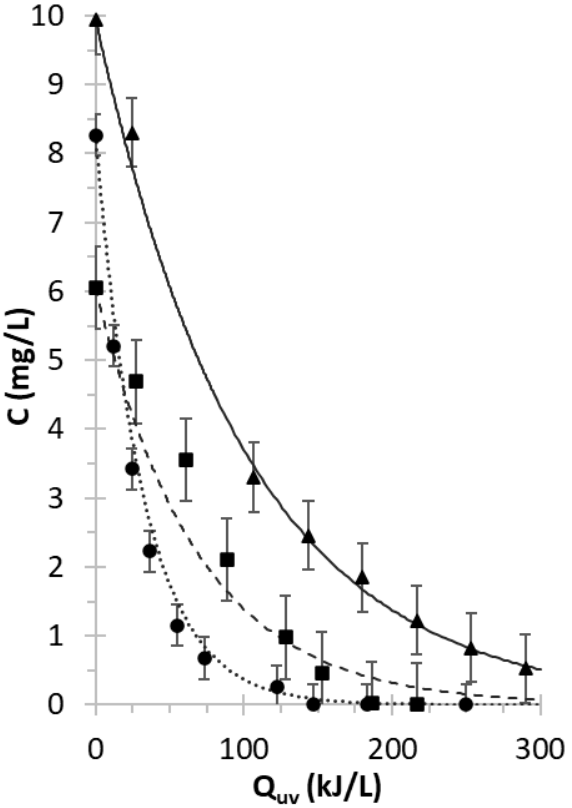

Figure 4: Measured and calculated (*eq. 3*) concentrations of CBZ, DCF and IBU at 85 W/m² flux density in treated wastewater (TWW) [▲,— / ●,· / ■,-].

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

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

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

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

Table 2: Kinetic coefficients α (L/kJ) for each molecule (in dark color) as well as their ratios Tap water /Treated wastewater (in light color) for laboratory high concentrations. R^2 of the linear regressions used 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

3.1.2. Cocktail effect

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

molecules were also present in the water. The cocktail effect thus had a clear negative impact on degradation rates, but the matrix effect still appeared to prevail.

To further refine these results, **Table 3** reports the *α* kinetic coefficients calculated for the cocktail effect in order to complete **Table 2**. In each case scenario (each molecule in each matrix), degradation rate was higher for the molecule alone than mixed with the two others, thus showing that the cocktail effect hampers degradation. DCF was still the easiest molecule to degrade while CBZ and IBU showed similar degradation rates, but the cocktail effect tended to narrow the gap between the *α* values. Interestingly, the cocktail effect had more impact on TWW with an average ratio of 3.3 against only 2.5 in tap water.

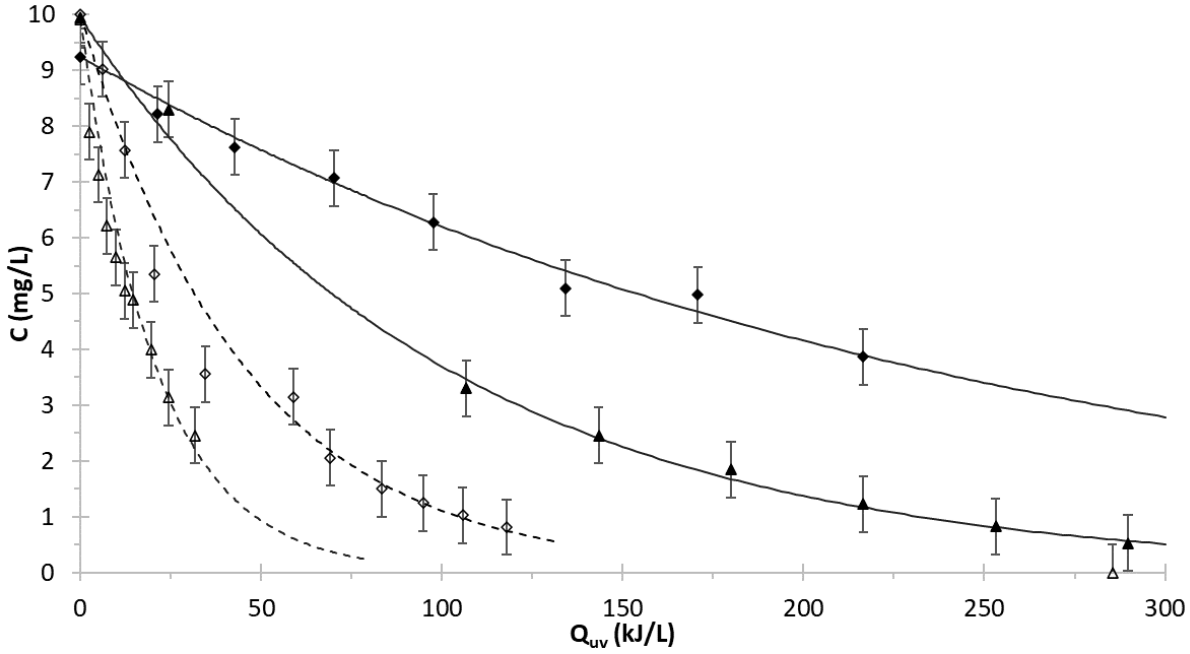

Figure 5: Measured and calculated (*eq. 3*) concentrations of CBZ at 85 W/m² flux density, alone in tap water [Δ,-], alone in TWW [▲,—], mixed in tap water [◇,-] and mixed in TWW [◆,—].

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

Table 3: Kinetic coefficients α (L/kJ) in each case scenario for each molecule (in dark color) as well as their ratios tap water / treated wastewater (TWW) and alone / mixed (in light color). R^2 of the linear regressions used to determine the kinetic coefficients α of the molecules mixed are between 0.9817 and 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

3.1.3. Concentration effect

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

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

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

Kinetic coefficients were determined for these lower concentrations in the same way as previously for the high concentrations (**Table 4**). Results showed the same effects and tendencies at low initial concentrations as at high initial concentrations. Degradation rates were molecule-dependent, but at lower concentrations, DCF was globally still easier to degrade than IBU, which was easier to degrade than CBZ.

The matrix effect still occurred, as previously found elsewhere [34], but it was less pronounced with lower concentrations. Indeed, an average α tap water to α TWW ratio of 4.1 was found for the compounds alone at high concentrations (**Table 3**) but only 2.6 for lower concentrations (**Table 4**).

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

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

3.2. Experiments under solar conditions

The final goal of this study was to evaluate the capacity of solar photo-oxidation process to treat the target molecules. Only filtered TWW was used, and it was only spiked with low initial concentrations (50 µg/L CBZ and DCF but 400 µg/L IBU).

Experiments were conducted over full days until target molecules were considered totally degraded. In total, four experiments were conducted for 6 to 7 h per day on sunny spring days (May 15 and 16 and then May 21 and 22, 2019). As the molecules were tested at different initial concentrations, **Figures 6** & **7** report the results as dimensionless concentrations C/C_0. The figures also give the UV flux densities coming from the sun on two sample days, which follow classical daily curves that increase in the morning to peak at around 45 W/m² at noon and then decrease in the afternoon. Only a few clouds passed during these days (the steep point-decreases), allowing a total Q_{UV} of around 10 kJ/L for each experiment.

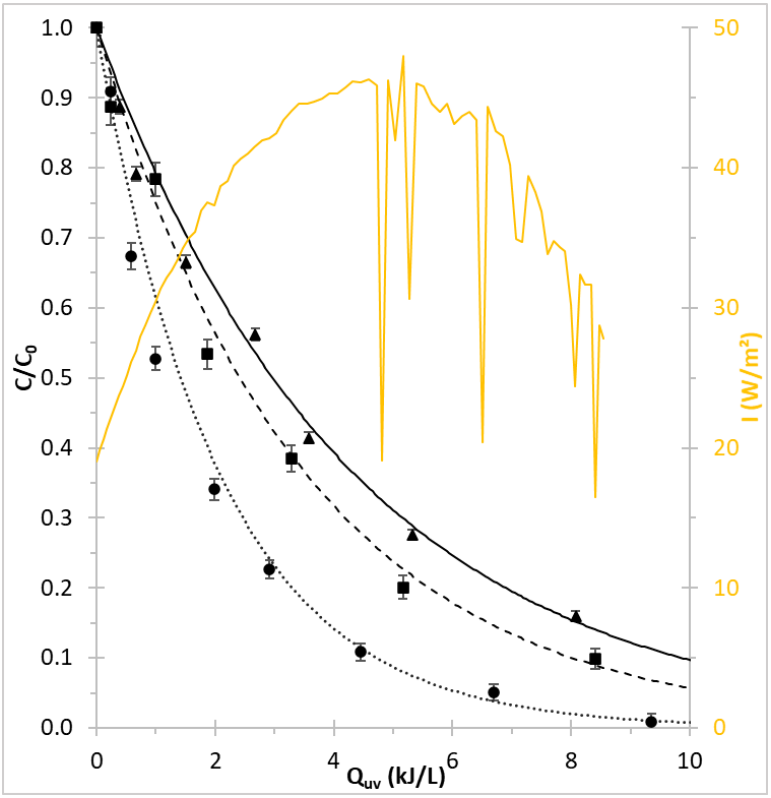

Figure 6: Measured and calculated (*eq. 3*) concentrations of CBZ [▲ / —], DCF [● / ·] and IBU [■ & -] alone in treated wastewater during spring days. The measured flux density of the "IBU alone experiment" (22/05/2019) is also reported.

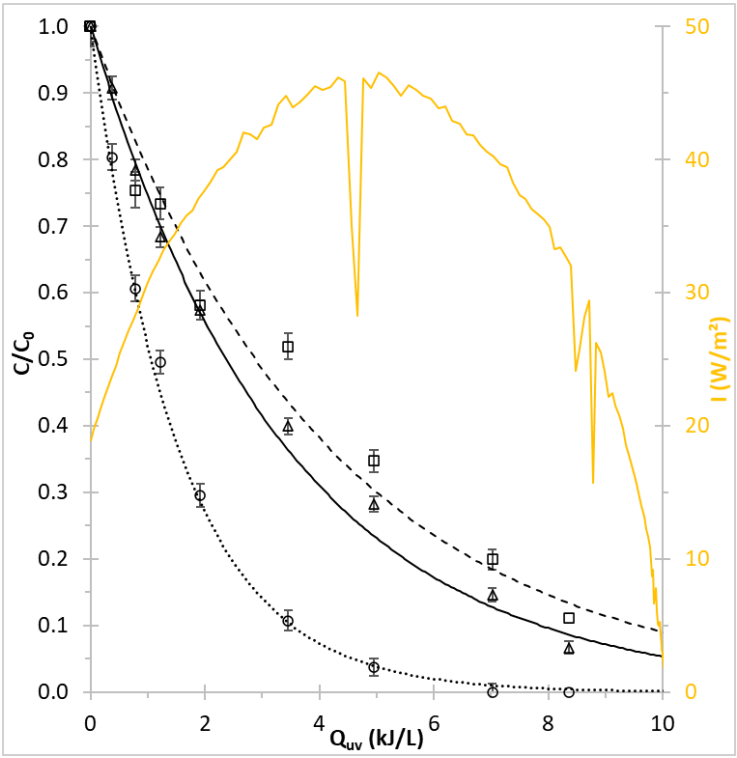

Figure 7: Measured and calculated (*eq. 3*) concentrations of CBZ [Δ / —], DCF [○ / ·] and IBU [□ / -] mixed together in treated wastewater during spring days. The measured flux density of the "DCF alone experiment" (21/05/2019) is also reported.

Four experimental campaigns were thus been conducted under solar irradiance. The first three campaigns aimed to understand the degradation of each of the three target molecules alone (**Fig. 6**), while the fourth campaign aimed to clarify what would happen when the three target molecules were mixed together (**Fig. 7**). Here the three molecules were nearly totally removed after a full day of treatment, highlighting the great performance of the process using TiO_2 Photospheres considering the TWW matrix in comparison with the literature. Indeed, for TiO_2 Degussa P25, 4.5 h of solar irradiation degraded 75 % of CBZ mixed with other pharmaceuticals using [89] which is totally in accordance with the results here: 4.5 h corresponded to a Q_{UV} of 5.7 kJ/L, thus 80 % of degradation for CBZ (**Fig. 7**). For P25 Aeroxide TiO_2, 6 h of solar exposure was needed to achieve the total removal of DCF alone (at 30 mg/L initial concentration) in distilled water [84]. For DCF, another study found that only 50 min were necessary to completely remove this compound in treated wastewater but contrary to this present paper, it was filtered through 0.45 µm Millipore filters and stored at 4 °C prior to use [31].

Tendencies observed in controlled conditions were valid in outdoor conditions and at the solar photoreactor scale, as the degradation profiles respected the same ranking. When each compound was alone, DCF was the easiest to degrade, followed by IBU and then CBZ (**Fig. 6**) ; whereas when in mixture together, DCF was still the easiest to degrade, but CBZ was the next easiest, followed by IBU (**Fig. 7**). Other study on solar driven oxidation process based on Nitrogen-doped TiO_2 (N-TiO_2) also found that DCF was easier to degrade than CBZ, and both in distilled water and wastewater [33].

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

Table 5: Kinetic coefficients α (L/kJ) for each molecule (in dark color) as well as their ratios alone / mixed (in light color) for low concentrations and solar photocatalysis. R^2 of the linear regressions used to 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

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

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

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

4. Conclusions

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

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

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