Green approach for micropollutants removal: study of constructed wetlands as pretreatment of solar photo-Fenton catalyzed by organic fertilizers

Núria López-Vinent, Alberto Cruz-Alcalde*, Ana Piera Santacruz, Carme Sans

Department of Chemical Engineering and Analytical Chemistry, Faculty of Chemistry, Universitat de Barcelona, C/Martí i Franqués 1, 08028 - Barcelona, Spain. Tel: +34934021293. Fax: +34934021291

*Corresponding Author: *alberto.cruz@ub.edu*

ABSTRACT

This study proposes a combination of vertical-flow constructed wetlands and solar photo-Fenton catalyzed by Fe-EDTA/DTPA as a greener approach to enhance micropollutant removal from simulated polluted water. In this research, two planted microcosms, one featuring *Cyperus haspan* and the other *Phragmites australis*, were examined for their effectiveness in eliminating 5 different micropollutants over varying retention times (2, 4, 7, and 14 days). The goal was to identify the most suitable conditions for an integrated treatment approach. The findings revealed that in all cases the hybrid system provided better removals than the individual treatments, above all for the more recalcitrant compounds. Notably, the combined use of *C. haspan* and 2 days retention time in the CW, followed by photo-Fenton applying 5 mg L^{-1} of iron, 50 mg L^{-1} of H_2O_2 and 20 minutes of irradiation achieved total removal of the micropollutants. In contrast, using only the photo-Fenton process, it needed 60 minutes to remove just 60% of acetamiprid, which is the most resilient of the studied substances. Constructed wetlands, however, required a longer period of contact, up to 14 days, to completely eliminate this

pharmaceutical. Ultimately, this hybrid system offers a practical and adaptable solution to meet regulatory limits, tailored to the intended use or destination of the effluent. It combines cost-effectiveness, environmental friendliness, and sustainability.

KEYWORDS

Advanced Oxidation Processes, Combined technologies, Contaminants of emerging concern, Hybrid system, Organic fertilizers

1. Introduction

Water is an essential resource for life on Earth, presenting an immeasurable value on economic, social and environmental sector. However, as a consequence of the continuous growth in water demand joined to Climate Change, the water scarcity is the principal problem to be confront by the World in the 21st century. Moreover, according to predictions presented by United Nations, the population will keep increasing from 7700 million to between 9400 and 10200 million by 2050 [1], resulting in a rise between 20% and 30% of water demand [2]. Associated to that fact, as a consequence of human activities, there is the continuous generation of wastewater, which must be appropriately treated before pouring them into the aquatic compartments. Ensuring safe, quality and readily available water is essential for environmental and human health. In the last two decades, the presence of micropollutants (MPs) into the aquatic environments has increased the attention of researchers due to the negative effects it could present on human health and ecosystems [3-5]. A multitude of sources collectively contribute to the introduction of MPs into the environment. Aquaculture facilities are also recognized as potential contributors to the presence of MPs in aquatic environments [6, 7]. The utilization of artificial feed, veterinary drugs, disinfectants and antifoulants (commonly employed to enhance the survival rates of cultivated organisms and manage pathogens)

within this industry has the potential to introduce MPs into aquaculture discharge. Additionally, the water sources harnessed for these activities may also contain MPs. Absolutely, the aquaculture industry is currently responsible for almost half of the global fish consumption, and there's an expected production growth of over 60% in the upcoming years according to FAO [8]. Consequently, it is imperative the adoption of appropriate treatment methods capable of efficiently removing MPs to safeguard the environment.

Advanced Oxidation Processes (AOP) have demonstrated their effectiveness in removing a wide range of MPs according to references [9-11]. Nevertheless, it's worth noting that these technologies come with high energy demands and associated costs for implementation and maintenance [12].

In light of this, Nature-based Solutions (NbS), such as constructed wetlands (CW), have been explored for wastewater treatment due to their potential to eliminate MPs and their recognized advantages. CW is among the technologies known for their eco-friendliness, cost-effectiveness in terms of operation and maintenance, and simplicity [13]. Additionally, CW have proven effective in removing organic matter, total suspended solids, nutrients, and metals [14]. However, it's essential to consider that the need for a larger land area could constrain the practical application of CW, particularly in urban areas with limited available land [15, 16]. Furthermore, using only NbS for effluent treatment might not meet the minimum requirements for water reuse concerning the removal of MPs or bacterial inactivation [17].

In this context, hybrid CW-AOP system could constitute an appropriate option to solve the individual limitations of using CW or AOPs individually. The principal advantages of coupling CW-AOPs are: the reduction of land footprint [13, 18, 19], diminution in

energy and maintenance costs [13, 20, 21] and facilitate the water reuse since it could be enhanced the bacterial inactivation and MPs removal [13, 22-25]. Typically, the most convenient hybrid system consists of CW as a first step, followed by AOP. CW serves as a pretreatment, eliminating organic matter and suspended solids to the influent of the AOP system and AOP works to polish the effluent to ensure the water reuse in different sectors [13]. However, few investigations have been carried out in this field [26-28]. In this sense, according to Casierra-Martinez and coworkers [26], the hybrid system performed by CW and solar photo-Fenton could reduce the discharge of MPs into the aquatic environments by reaching high removal rates at low cost. For instance, in this study [26] the use of a hybrid system resulted in carbamazepine removal exceeding 85% at the end of the treatment, while only 46% removal was achieved in a single CW unit. However, to the best of author's knowledge, there are no studies testing the CW-photo-Fenton hybrid approach afor removing the typical MPs found in aquaculture waters.

This study aimed to investigate the potential of a hybrid system consisting of CWs-solar photo-Fenton at natural pH, for the removal of MPs. To this scope, the efficiency of the coupled technology was investigated by the simultaneous elimination of five MPs found in aquaculture farms, namely acetamiprid (ACMP), sulfamethoxazole (SMX), metronidazole (MET), ciprofloxacin (CIPR), and estradiol (E2), in a river matrix, and using two different aquatic plants (*Cypersus haspan* and *Phragmites australis*). The main objectives of this study were to: i) investigate the potential efficiency of vertical flow constructed wetland (VFCW) in the removal of different MPs, ii) determine the best efficiency on MPs elimination in VFCW in terms of plants and RT, and iii) evaluate the effectiveness of VFCW coupled to photo-Fenton by comparing its efficiency with the sole treatments.

2. Material and methods

98 *2.1. Chemicals and reagents*

99 Most of target compounds used in this work (sulfamethoxazole, acetamiprid, estradiol
100 and metronidazole), ammonium metavanadate and liver bovine catalase from bovine liver
101 were purchased from Sigma-Aldrich. Target micropollutant ciprofloxacin, was acquired
102 from Riedel-de Haën. The iron complexes DTPA-Fe (7% (wt) of iron (III)) and EDTA-
103 Fe (13.3% (wt) of iron (III)) were bought from Phygenera, Germany. Methanol,
104 acetonitrile, orthophosphoric acid, hydrogen peroxide (H_2O_2, 30% *w/v*) and ascorbic acid
105 were purchased from Panreac Quimica.

106 *2.2. Water matrix*

107 The water samples used in the CW and photo-Fenton experiments were collected from
108 Llobregat River in Sant Vicenç dels Horts, Barcelona (Spain). The sampling was carried
109 out during October-December 2021. River water was selected in this study to simulate
110 influents from aquaculture facilities, *since aquaculture farms commonly extract water*
111 *from rivers to serve as the primary source for their aquatic environments (this river water*
112 *is utilized to fill ponds, tanks, or other enclosures where fish, crustaceans, or other*
113 *aquatic organisms are raised)*. The physicochemical characteristics are depicted in Table
114 1.

115 **Table 1.** Physic-chemical parameters of wastewater (DOC: Dissolved Organic
116 Carbon).

Parameters	**River water**
pH	8.1
UV_{254} (m^{-1})	11.4
DOC (mg C L^{-1})	5.8
Cl^{-1} (mg L^{-1})	210.0
SO_4^{2-} (mg L^{-1})	118.6

$N\text{-}NO_2^-$ (mg L^{-1})	0.4
$N\text{-}NO_3^-$ (mg L^{-1})	6.6

117

118 *2.3. Constructed wetland-photo-Fenton coupled system*

119 *2.3.1. Constructed wetland unit*

120 The microcosms were made using polypropylene container (H=22.5 cm; d= 9.5 cm) filled
121 with first layer of cobbles (5cm, Ø=60-120 mm), a second layer of volcanic rocks (2cm,
122 Ø= 25-50 mm), a third layer of fine gravel (5cm, Ø= 12-30 mm) and, finally, a layer of
123 sand (10cm, Ø= 0.5 mm) (see supplementary material Figure S1). Similar to Gorito and
124 coworkers [7], gravel was placed at the bottom to prevent clogging of draining tubes. A
125 layer of lava rock was placed in the middle to rise the porosity of the system, promoting
126 the retention of some micropollutants and the development of biofilm, which could be
127 involved in the elimination of organic compounds. Fine gravel was applied at the top to
128 aid further filtration, which begins in the layers with lower porosity. Finally, sand was
129 used as a bed substrate. Two microcosms were planted, one with *Cyperus haspan* and the
130 other one with *Phragmites australis.* Additionally, one microcosm was left unplanted to
131 serve as a control of substrate adsorption. *P. australis* was selected due to its recognized
132 potential eliminating diverse type of MPs [7, 13, 29], while *C. haspan* was not widely
133 investigated. Additionally, the former has large roots but short and few stems
134 (approximately 50 cm and about 20 stems per plant), while *C. haspan* presents large roots
135 but higher and grater stems (approximately 85 cm and about 90 stems per plant). The
136 containers were covered with aluminium foil to prevent the photodegradation of MPs.
137 The outlet of each CW was located at the bottom of the container, which served for
138 sampling and daily manual recirculation of the water to prevent anoxic areas [7]. The
139 constructed wetlands were kept in the laboratory with natural day conditions: solar light

and day: night regime. The temperature was maintained constant between 15 ºC and 20 ºC. Before the experiments, each microcosm was acclimated for one month with river water used in the experiments, allowing bacterial growth and biofilm formation. Finally, each CW was filled with 1.5 L of river water spiked with five MPs.

2.3.2. Photo-Fenton photoreactor

The photo-Fenton experiments were carried out in a bench solar simulator (SUNTEST CPS+, Hereaus) equipped with a 1500-W Xenon lamp with infrared and UV-C cut off-filters. The irradiance was set at 500 W m^{-2}. To perform the experiments 150 mL cylindrical Pyrex glass reactors (D=9.0 cm h=4.5 cm) were used under a constant stirring (200 rpm). The photoreactor was placed over a refrigerant plate, which was connected to a thermostatic bath to maintain the temperature of the solution constant during the experiments (20-25ºC). The schematic set up of SUNTEST is displayed in Figure S1 of supplementary material.

2.4. Experimental procedure and operation

Five VFCW were assembled at laboratory scale each one treating 1.5 L of spiked river water containing 200 µg L^{-1} of each MP (ACMP, SMX, CIPR, E2 and MET). The first two compounds were selected due to its occurrence in aquatic bodies [30-32] (which it could serve as an influent of aquaculture facilities). Additionally, SMX is also used as an antibiotic in this sector. The other three MPs were chosen since they are used in aquaculture sector as an antibiotic (CIPR and MET), hormone (E2) and antiprotozoal (MET) [13]. The concentration of the different compounds was selected to ensure the proper analysis of each micropollutant, while simultaneously maintaining the lowest possible concentration. Two microcosms planted with *P. australis* served as a duplicate, in the same way than *C. haspan*. One system was unplanted, serving as a control, as aforementioned. The treating volume was fixed in order to maintain the total saturation

of the substrate, and the total volume was manually recirculated every day to avoid the presence of anoxic zones. Each day, water losses due to evaporation and evapotranspiration, which concentrates the MPs into solution, were compensated by adding deionized water until 1.5 L, equalizing the initial volume for a proper analysis. This study measured total water losses due to evaporation and evapotranspiration by accounting for the initial water added (1.5 L) and the water quantified at the treatment's end. The discrepancy between these volumes accounts for the evaporative and evapotranspiration losses. To accurately quantify the volume before adding the initial 1.5 L, the wetland, particularly the sand, needs to be moist. This precaution is necessary because, at the treatment's end, the wetland retains moisture. Without pre-moistening, water loss would be overestimated. After adding the spiked water into the CW, the retention times were fixed at 2, 4, 7 and 14 days, resulting in a 4 separately cycles. At the beginning of each cycle, new spiked water was added into each CW. Since the different cycles were performed in the same microcosm, the concentration of MPs at 2, 4, 7 and 14 days in each cycle was followed to ensure that the differences between cycles were due to the effect of retention time and not the formation of biofilm during cycle after cycle, which it could be involved in the elimination of MPs.

To perform the sole photo-Fenton experiments, spiked river water with 200 $\mu g\ L^{-1}$ of each MP and 2.5 or 5 $mg\ L^{-1}$ of iron was added into the photoreactor. The iron used was a pre-chelated iron with 50% EDTA and 50% DTPA according to our previous studies [33, 34]. The use of pre-chelated iron prevents in situ iron chelation, avoiding the difficulties and time this may entail. An appropriate amount of each iron chelate was added to the solution considering the percentage of chelated iron in both cases to obtain the concentration of iron aforementioned. Finally, the hydrogen peroxide (25 or 50 $mg\ L^{-1}$, when corresponding) was added to the photoreactor just before the reaction started.

Immediately, the SUNTEST was turned on. Samples were periodically withdrawn from the photoreactor throughout the entire experiment, and bovine liver catalase was added in each sample (10 µl of a 200 mg L^{-1} solution of catalase in 5 mL of sample) to quench the residual H_2O_2. HPLC samples were filtered with 0.45 µm PVDF filter to avoid any interference in the analysis. The samples used to analyze the E2 compound were previously mixed with acetonitrile (1:1) and then filtered to prevent it adsorption into the filter. Samples used to analyze the total iron content were previously filtered with 0.2 µm PVDF filter to guarantee a good analysis of soluble iron.

To carry out the photocatalytic experiments in the hybrid system, the same procedure as explained above was followed, using the effluent of CW to perform the tests.'

2.5. Analytical measurements

The concentration of selected target compounds was measured by High Performance Liquid Chromatography (HPLC Infinity Series, Agilent Technologies) using a C-18 Tecknokroma column (250 x 4.6 mm i.d; 5 µm particle size). MET, SMX, ACMP and CIPR were detected with the same conditions: 80% H_2O acidified with H_3PO_4 (pH = 3) and 20% acetonitrile, 1 mL min^{-1} of flow rate and 100 µL of injection volume. Four wavelengths were fixed depending on the compound: 220, 270, 250 and 280 nm for MET, SMX, ACMP and CIPR, respectively. E2 was analyzed separately, using 50% H_2O acidified with H_3PO_4 (pH = 3) and 50% acetonitrile, 1 mL min^{-1} of flow rate, 100 µL of injection volume and the wavelength was fixed at 200 nm. The quantification of DOC content was performed following the Standard Methods 5310B procedure [35] and employing a 5055 TOC-VCSN analyzer equipped with an ASI-V autosampler, both by Shimadzu. The ultraviolet absorbance was evaluated through a spectrophotometer DR6000 UV-Vis by Hach (USA). The concentration of relevant anions (i.e., nitrite and nitrate) in effluent samples was determined by ionic chromatography through a high-

performance liquid chromatograph coupled to conductivity and UV detectors connected in series. A 4.6x150 mm IC-PAK ANION column by Waters (USA) was used for separation. The mobile-phase was mainly mixtures of borate buffer and acetonitrile, the flow-rate was set at 2 mL min^{-1}, the injection volume was 200 µL and the detection wavelength (in the case of UV detector) was 214 nm. Total iron content was determined by complexation with 1,10-phenanthroline according to ISO 6332 [36]. The consumption of H_2O_2 was evaluated following the metavanadate colorimetric method [37].

3. Results and discussion

3.1. Efficiency of CW microcosms on MPs removal

Constructed wetlands are controlled environments aiming to recreate the conditions and processes occurring in natural wetlands. Biotic and abiotic processes take place in the system since they are constituted by water, substrate, plants and microorganisms [13], participating in the removal of different variety of compounds. According to Lin and coworkers [38], microbial degradation and plant uptake are the principal biotic mechanisms removing contaminants contained in water, while sedimentation, adsorption into substrate, volatilization and photodegradation are the main abiotic processes. Nevertheless, the occurrence of these processes in CW systems depends on diverse factors, such as the environmental and operational conditions and characteristics of pollutant [39]. Among operational conditions, retention time is one of the most important parameters to consider. The selection of the type of plant is also an important factor in order to eliminate specific types of pollutants. For these reasons, in this work, the effect of these two parameters was studied in the elimination of five target compounds.

238 *3.1.1. Effect of retention time*

239 Figure 1 displays the removal of MET, CIPR, ACMP, SMX and E2 in a constructed
240 wetland planted with *P. australis* in function of retention time: 2, 4, 7 and 14 days before
241 conducting the experiments, a control test of MPs adsorption onto a plastic container was
242 carried out to avoid overestimating the MPs elimination in the system. In this case, a
243 solution of MPs mix (200 μg L^{-1} of each one) was placed into the plastic container without
244 substrates or plants for 14 days. The results revealed that less than 5% of MPs adsorption
245 was observed after 14 days of operation.

246 From Figure 1, it can be observed that the removal of target compounds varies for the
247 same retention time. E2 and CIPR presented the best removals, achieving 100% and 94%,
248 respectively, in only 2 days. On the other hand, ACMP and SMX displayed low
249 eliminations: 32% and 25%, respectively, at the same retention time. For its part, MET
250 achieved 54% of removal. These differences are related to the different characteristics of
251 micropollutants, as mentioned before. Hydrophobic compounds are handily adsorbed
252 onto soil and biofilm, while hydrophilic ones are mainly eliminated by other mechanisms
253 [40]. In this sense, E2 has the highest partition coefficient between n-Octanol and water
254 (k_{ow}) being $\log k_{ow}$ 4.01. Thus, its total removal in only 2 days was not unexpected.
255 Additionally, this result was corroborated with the CW unplanted (see Figure 2), which
256 achieved the same result, confirming the adsorption of E2 onto soil or biofilm. Regarding
257 CIPR, the removal results in both systems, planted and unplanted, are not consistent with
258 its log Kow, since it is 0.28. CIPR has a hydrophilic character, so it should not be adsorbed
259 by soil. However, CIPR is readily biodegradable in activated sludge [41], so it could be
260 degraded by microorganisms forming biofilm, which could be present in both systems.
261 Additionally, a photolysis experiment was conducted in SUNTEST resulting in a CIPR
262 reduction of 97% after 1h. Thus, a part of CIPR removal in the microcosms could be due

263 to the photodegradation since the layer of water above of CW is directly exposed to
264 sunlight. For its part, MET has a log Kow of -0.02. This value indicates that it is a
265 hydrophilic compound. In this way, low removal it be expected in microcosms. However,
266 as can see in Figure 1, after 2 days of retention time in two microcosms (planted and
267 unplanted), good removals were observed: 54 and 40%, respectively. Compared to CIPR,
268 MET was degraded by 78% in a photolysis test, so the photodegradation could be
269 involved in its removal on CW. Additionally, observing Figure 2 and 3, 15% more MET
270 removal was observed with planted microcosm, revealing the possible degradation of
271 MET by bacteria on roots or sorption by plant. For instance, according to Lyman [42],
272 MET biodegradation in sandy soil-manure slurry was between 9.7 and 14.7 days,
273 revealing significant biodegradation in soil. On the other hand, ACMP and SMX are
274 characterized by their hydrophilic character, presenting n-Octanol partition coefficients
275 of 0.80 and 0.89, respectively. This fact is evidenced by their low removal in both
276 constructed wetlands, planted and unplanted, at 2 days. Additionally, sulfonamide
277 antimicrobials, like SMX, are not readily biodegraded in soils [43]. Nevertheless, studies
278 reported that half-lives of ACMP in aerobic soils range from less than 1 day to 8.2 days,
279 suggesting its possible biodegradation in CW [44].

280 Regarding the effects of different retention times, the highest retention time of 14 days
281 displayed the greatest elimination of MPs. At this time, total removal was observed for
282 MET, CIPR and E2 and 76 and 75% for ACMP and SMX, respectively. Decreasing the
283 retention time from 14 to 7 days, reduced the elimination by 1.2 times for ACMP and
284 SMX, resulting in removals of 64 and 61% at 7 days, respectively. The removal of ACMP
285 and SMX for 4 days of retention time were similar to those obtained by 7 days, being 59
286 and 55% at 4 days, respectively. These values represent only a 1.1 times greater
287 elimination in 7 days than in 4 days for ACMP and SMX. In the case of MET, the

difference was higher: 69% was removed in 4 days in front of 94% observed in 7 days, representing 1.35 times more. However, observing Figure 1, the differences in MPs elimination from 2 to 4 days of retention time for ACMP and SMX were greater than those observed increasing RT from 4 to 7 days. In that case, the elimination of ACMP and SMX was 1.8 and 2.2 times more, respectively, treating water for 4 days compared to 2 days. In the case of MET, the differences from 2 to 4 days and from 4 to 7 days were very close. These differences between MPs are probably related to the different mechanisms involved in the elimination of MPs from water matrix (adsorption, biodegradation, photodegradation and plant uptake) and the time required for each process. The same reasons explain the differences between different retention times. High retention times allows high contact of sunlight, soil and bacterial community with MPs, which can result in a greater elimination rate. Nevertheless, biotic mechanisms are usually slower than abiotic. For instance, E2 and major part of CIPR were removed in only 2 days, since the adsorption and photodegradation are the main processes. However, MPs such as ACMP and SMX, presented low elimination rate since biotic processes probably were the principal mechanisms involved.

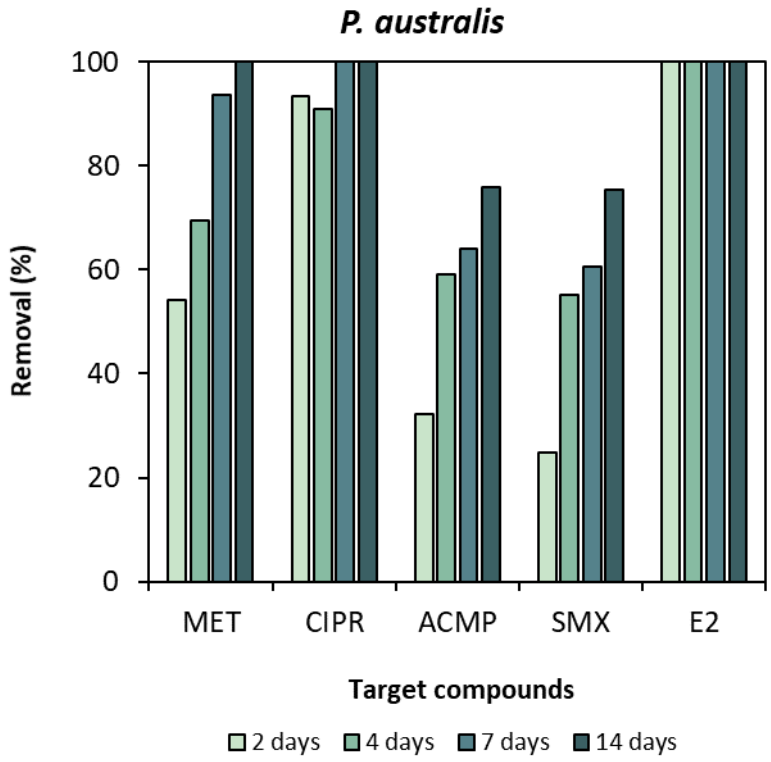


Figure 1. Target compounds removal (MET, CIPR, ACMP, SMX and E2) in VFCW planted with *Phragmites australis* in function of retention time (2, 4, 7 and 14 days).

Finally, Figure 2 displays the elimination of 5 MPs in an unplanted microcosm. Observing the two figures (Figure 1 and 2), it can be observed the role of the plant in the MPs removal. Poor differences in MPs removal were seen in unplanted microcosm (Figure 2) for different retention times, indicating the benefits of plants in these systems. Plants could improve the elimination of MPs by uptake them by sorption, MPs adsorption into the roots, increasing the bacterial community which could biodegrade the MPs and supplying O_2, which plays an important role in the activity and type of microorganisms in the root zone [45]. The results obtained are in accordance with this fact. For instance, for 4 days of retention time, the elimination of MET and ACMP was two times higher in planted (Figure 1) than in unplanted system (Figure 2).

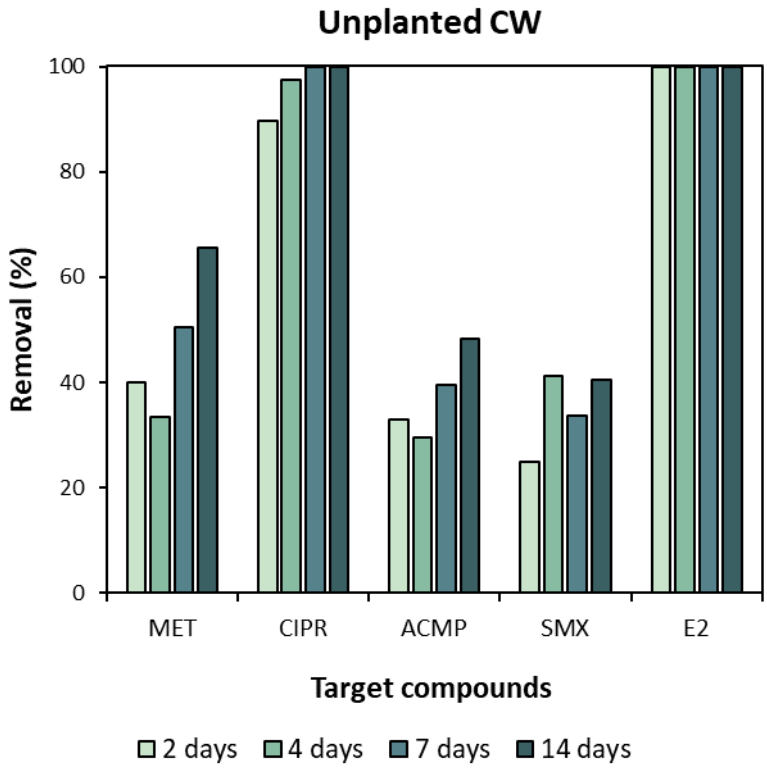


Figure 2. Target compounds removal (MET, CIPR, ACMP, SMX and E2) in VFCW unplanted in function of retention time (2, 4, 7 and 14 days).

3.1.2. Effect of type of plants: comparison between P. australis and C. haspan

The role of plants in the removal of conventional pollutants and micropollutants was a controversial issue since some researchers suggested that plants did not contribute significantly to the removal of MPs in surface flow CW systems [46]. However, there is scientific evidence from laboratory and pilot scale wetland systems that micropollutant removal efficiencies in CWs are much higher than in unplanted wetlands, as described in this study in the above section. Additionally, the selection of plant species is important to eliminate certain groups of micropollutants, since several biotic and abiotic processes occur in CW and depending on the main removal mechanism to which the MPs is subjected.

In this work, the efficiency of *P. australis* and *C. haspan* was investigated in the removal of different MPs. Figure 3 displays the removal of MET, CIPR, ACMP, SMX and E2 in a constructed wetland planted with two plant species for different retention times.

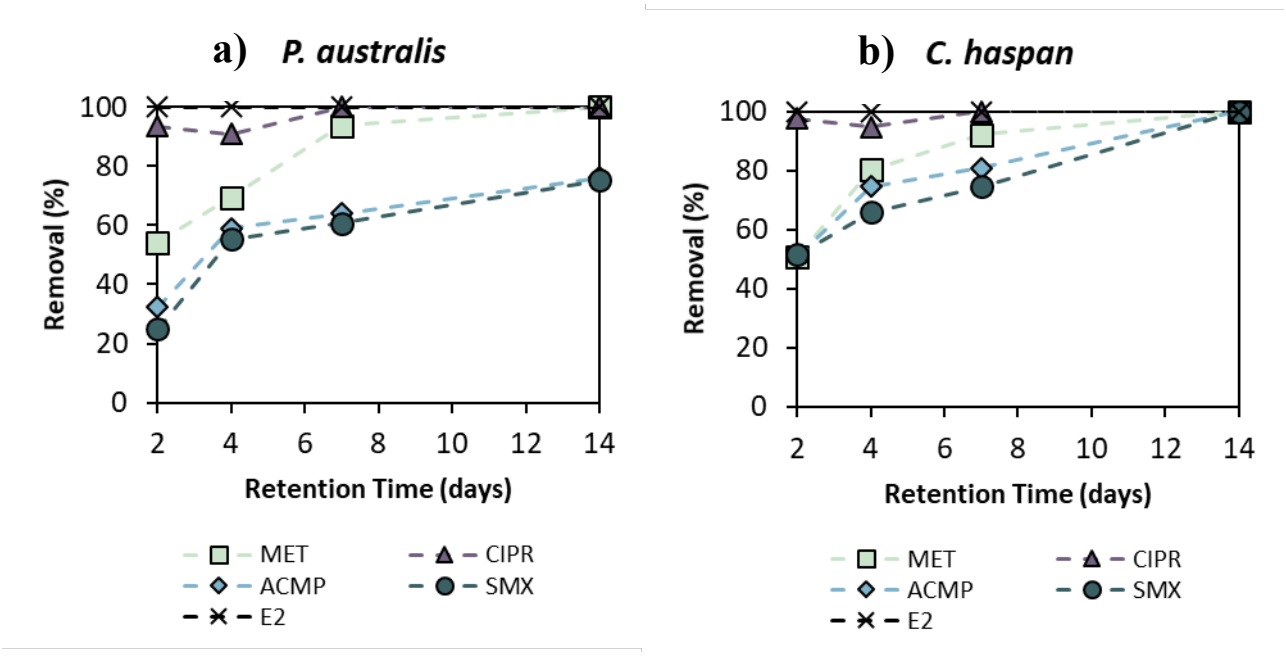


Figure 3. Removal efficiencies of constructed wetlands planted with a) *P. australis* (filled columns) and b) *C. haspan* (striped columns) in the elimination of MET, CIPR, ACMP, SMX and E2 in a function of retention days: 2, 4, 7 and 14 days.

In Figure 3, it can be observed that the CW planted with *C. haspan* presented higher MPs removal than *P. australis* for all of them and for all the retention times investigated. The biggest differences were observed in the removal of MET, ACMP and SMX, evidencing the previously discussed: the removal mechanisms of CIPR and E2 did not depend on the plants (*i.e.* adsorption onto substrate and photolysis). For instance, at 14 days of retention time, total MET, ACMP and SMX were removed from wastewater in CW planted with *C. haspan* while less than 80% of ACMP and SMX were eliminated in *P. australis*. ACMP and SMX removal for other retention times (2, 4 and 7 days) was lower than 80% in both microcosms *C. haspan* and *P. australis.* ACMP showed removals of 51, 75 and 80% in CW planted with *C. haspan* for 2, 4 and 7 days, respectively, while in P. *australis*

unit, the ACMP abatements were 32, 59 and 64%, respectively. The results correspond to 1.6, 1.3 and 1.2 times higher removal in CW planted with *C. haspan* than *P. australis* for 2, 4 and 7 days of RT. For SMX the highest difference was also found at 2 days since the removal in *C. haspan* unit was double than in *P. australis* (25 and 52%, respectively). This performance could be attributed to the fact that the *C. haspan* possesses an extensive quantity of rhizomes, resulting in a greater specific surface area for biofilm formation and, potentially, a more effective biodegradation process. Furthermore, the former exhibits a substantial number of stems, which may lead to increased evapotranspiration and, consequently, enhanced sorption of MPs [47].

3.1.3. Monitoring of DOC, TSS and ions

The efficiency of removing dissolved organic carbon, total suspended solids, nitrite and nitrate was also assessed in all conditions for two types of constructed wetlands (*P. australis* and *C. haspan*). These parameters were chosen because they significantly impact the effectiveness of Advanced Oxidation Processes, including the solar photo-Fenton process being studied here as a post-treatment method. As reported by various researchers, the organic matter reacts with hydroxyl radicals (HO·) at the rate ranging from 10^8 to 10^9 L $molC^{-1}$ s^{-1} [48-53]. Furthermore, TSS contribute to water turbidity, diminishing light penetration in the solution, and consequently leading to a decreased generation of HO· and subsequent reduction in treatment efficiency. Lastly, nitrite ions exhibit a second-order reaction rate of 10^{10} L mol^{-1} s^{-1} [54] and adsorb light maximally between 300 and 310 nm, thus competing with the species involved in HO· formation, ultimately reducing process efficiency. Figure 4 display the evolution of the concentration of the different parameter's evolution over time.

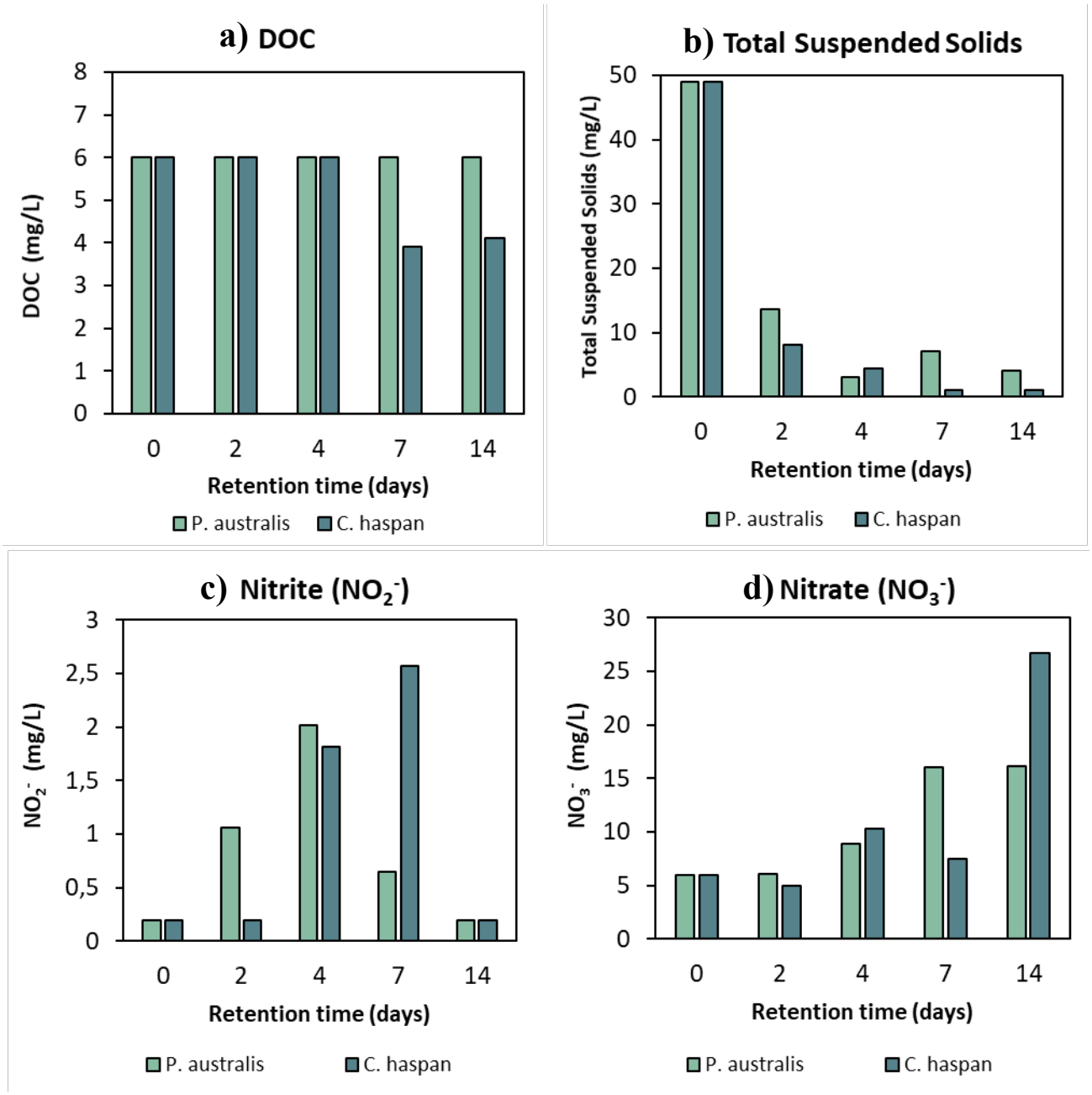


Figure 4. Evolution of a) dissolved organic carbon, b) total suspended solids, c) nitrite and d) nitrate for different retention times in constructed wetlands in *P. australis* and *C. haspan* microcosms.

As shown in Figure 4a, DOC elimination was not observed for the first 4 days in both microcosms planted with *P. australis* and *C. haspan.* In the case of *P. australis,* the same behavior was seen for 7 and 14 days. Nevertheless, in *C. haspan* unit a reduction about 30% was monitored for the last two operating conditions. The diminished effectiveness may be linked to the fact that although microbial communities and plants can employ

427 organic carbon for cellular respiration and biomass expansion, it is crucial to recognize
428 that DOC can be discharged into the water as it traverses CW systems, prompted by the
429 growth, demise, and decomposition of plants and bacteria, as noted by Scholz [55].
430 Additionally, the elimination of organic matter through anaerobic pathways is typically
431 slower when compared to aerobic processes (since no recirculation was added in this
432 study).

433 A limited studies have been published concerning the variation of DOC during the
434 treatment process in CWs and they show highly divergent outcomes. For example, our
435 findings align with those of Gorito and colleagues [7], where the DOC content remained
436 stable, staying consistent with the initial value of 10 mg L^{-1} throughout the 7-day duration
437 of the experiment in microcosms planted with *P. australis*, even being in aerobic
438 conditions (with recirculation). However, in the work of Sgroi and coworkers [56], it was
439 observed a DOC reduction of 32% (anaerobic conditions, ($[DOC]_0$ = 46 mg L^{-1}) in only
440 12 hours. These diverse findings could be attributed to the initial content of DOC. Same
441 results of DOC removal were observed compared to the study of Gorito in which the
442 initial DOC content was 10 mg L^{-1}. Furthermore, the authors investigated the evolution
443 of DOC within the same microcosm, altering the initial water matrix ($[DOC]_0$=22.5
444 instead of 6 mg L^{-1}). This alteration led to a remarkable 35% reduction in DOC levels
445 under anaerobic conditions, achieved in just 3 days [57].

446 Figure 4b displays the evolution of total suspended solids in two microcosms over time.
447 In this case, it was observed an important removal in all conditions. The findings
448 presented in this figure align with existing literature. Various authors have examined the
449 removal of TSS in vertical constructed wetlands under aerobic conditions. For instance,
450 Sgroi et al. [56] reported TSS removal rates of approximately 70% in fully saturated
451 vertical flow constructed wetlands. Furthermore, in a review by Castellar et al. [14], an

452 average TSS removal rate of over 80% was observed, which is based on the collective
453 findings from six different research articles.

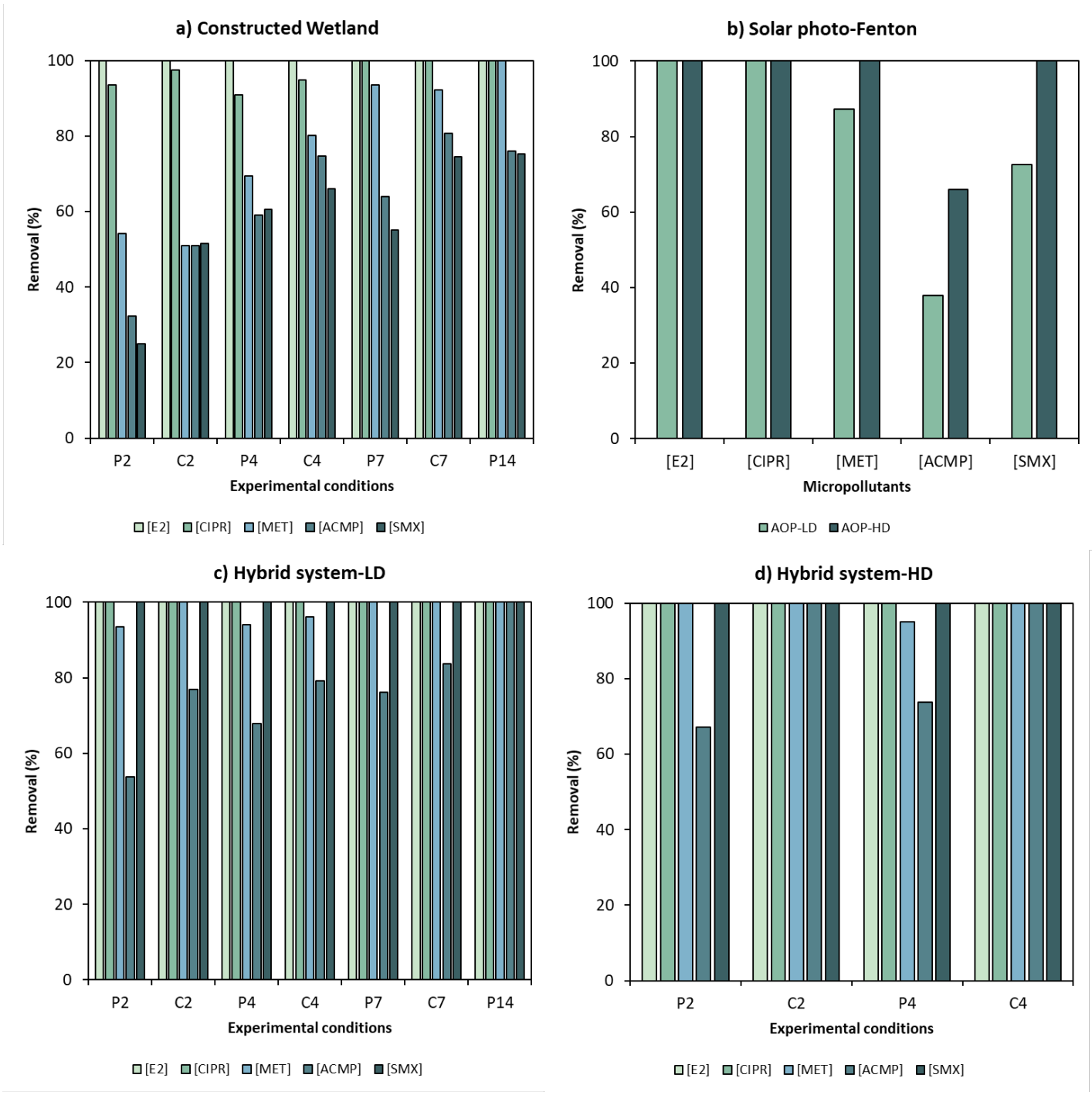
454 Finally, Figure 4c and 4d represent the evolution of nitrites and nitrates in the CW. As
455 can be observed in Figure 4c, the nitrites content increased over time until 7 first days and
456 then decreased until it was equal to the starting levels. These results are not unexpected
457 since the nitrification is a biotic process which depends on several factors such as the
458 retention time and vegetation type [13]. Additionally, it seems that the nitrification
459 process was faster in *P. australis* than *C. haspan*, probably due to the high O_2 content in
460 the microcosm (caused by differences in plant type) which boosts the conversion of
461 nitrites to nitrates [27]. For its part, Figure 5d demonstrated that nitrates raised in all
462 conditions over time due to the nitrification process and low denitrification pathway.

463 *3.2. Effect of the retention time on constructed wetlands in the micropollutant removal in*
464 *the hybrid system*

465 In this section of the study, it was conducted an evaluation of a comprehensive system
466 that integrates a constructed wetland followed by solar photo-Fenton treatment. The
467 primary aim of the initial phase is to eliminate a substantial portion of MPs, along with
468 suspended solids, dissolved organic matter, and nitrogen species, all of which have the
469 potential to compromise the effectiveness of the subsequent photo-Fenton process. The
470 ensuing advanced oxidation process is tailored to elevate the water quality by selectively
471 targeting the removal of any remaining recalcitrant compounds. Nevertheless, the quality
472 of the effluent coming from the first stage (constructed wetland) is a key factor to achieve
473 a synergistic effect in a subsequent photo-Fenton process. For this reason, in the hybrid
474 system, effluents from constructed wetlands were tested for different retention times (2,
475 4, 7 and 14 days). This testing was conducted because a different performance was

476 observed in terms of MPs and DOC elimination, as well as the evolution of nitrites, as
477 aforementioned in previous section (see Figure 3 and 4).

478 Figure 5 displays the removal of the 5 MPs tested in this study by sole constructed
479 wetlands, sole photo-Fenton and the combination of the two treatments. In the photo-
480 Fenton experiments, two pairs of Fe/H_2O_2 concentrations were used: low dose (LD): 2.5
481 mg L^{-1} Fe chelated with EDTA-DTPA and 25 mg L^{-1} of H_2O_2 and high dose (HD): 5 mg
482 L^{-1} Fe chelated with EDTA-DTPA and 50 mg L^{-1} of H_2O_2. The last pair of concentrations
483 was chosen based on the optimization carried out in Bolaños et al., [58], and considering
484 the effective removal demonstrated by this concentration pair in the studies conducted by
485 López-Vinent et al. [33,34]. The low dose Fenton's reagents was used on a comparative
486 purpose.



487

488 **Figure 5.** Removal of E2, ciprofloxacin, metronidazole, acetamiprid and sulfamethoxazole throughout a)
489 constructed wetlands; b) solar photo-Fenton; c) hybrid system using low dose (LD) of Fe and H_2O_2 and d)
490 hybrid system using high dose (HD) of Fe and H_2O_2. Experimental conditions: "P" refers to *P. australis* and
491 "C" refers to *C. haspan*. The numbers after each letter refer to the retention time in constructed wetland (2,
492 4, 7 and 14 days). "LD" refers to low dose of Fe and H_2O_2 used in photo-Fenton process (2.5 mg L^{-1} of Fe
493 chelated with (50-50% (w/w) EDTA-DTPA) and 25 mg L^{-1} of H_2O_2) and "HD" refers to high dose of Fe
494 and H_2O_2 used in photo-Fenton process (5 mg L^{-1} of Fe chelated with (50-50% (w/w) EDTA-DTPA) and
495 50 mg L^{-1} of H_2O_2), $MET]_0 = [CIPR]_0 = [ACMP]_0 = [SMX]_0 = [E2]_0 = 0.2$ mg L^{-1}; Irradiance in photo-
496 Fenton process = 500 W m^{-2}, pH= 8.1.

Observing the Figures 5a and 5b it can be noted that E2 and CIPR presented high removals in the sole treatments. E2 was totally eliminated in all assayed conditions of constructed wetland and also shown a total removal in photo-Fenton process even at low reactants dose. The high performance in photo-Fenton process is due to these compounds have an elevated second order reaction rate with HO· ($1.41 \cdot 10^{10}$ and $6.22 \cdot 10^{9}$ M^{-1} s^{-1} for E2 and CIPR, respectively [57]). The time required to eliminate E2 was 60 and 10 minutes for LD and HD of Fenton' reagents. For its part, CIPR was removed in 20 and 10 minutes in the same conditions (the degradation profiles can be seen in supplementary material Figure S3a and S4a). Although the second order kinetic rate of E2 is higher than CIPR, the latter presented a 97% removal by photolysis in 60 minutes while E2 only displayed a 20% abatement (supplementary material Table S1). Furthermore, the differences were more accentuated in photo-Fenton using low doses of Fe and H_2O_2 due to the slower HO· generation, giving more prominence to the effect of the light. Although both treatments alone demonstrated high yields in the reduction of E2 and CIPR, the hybrid system presents the advantage of eliminating the compounds in a shorter time in the photo-Fenton process (see Table 1). For instance, the time required to eliminate 90% of CIPR was 10 min. in photo-Fenton (HD) while only 30 seconds were needed in a hybrid system (*C. haspan* 2 and 4 days of RT + photo-Fenton-HD). Additionally, in the hybrid system treatment time was also reduced even using low dose of Fenton' reagents, meaning a reduction in the photo-Fenton treatment cost since the reagents are one of the highest costs in the process [12].

MET showed removals higher than 90% in the constructed wetlands with retention times of 7 and 14 days. However, for 2 and 4 days of retention times the eliminations were about 50 and 70%, respectively, indicating the requirement of additional treatment to achieve the total elimination, ensuring the quality of the treated effluent. For its part, 90%

522 and total MET was degraded in 60 min by using LD and HD of Fenton's reagents,
523 respectively. Although MET has a lower second order reaction rate with HO· than CIPR
524 and E2 ($k_{HO\cdot,\,MET}$= $2.8\cdot10^9$ M^{-1} s^{-1}) [57] and lower photolysis degradation than CIPR (78%
525 in 60 minutes), the hybrid system presented the advantage of reducing the treatment time
526 in the second stage of the combined process. MET depicted a removal higher than 90 and
527 100% in all conditions using low dose and high dose Fenton's reagents, respectively (see
528 Figures 5c and 5d). Additionally, as seen in Table 1, the treatment time was reduced by
529 half (to obtain 90% elimination) when effluents from *C. haspan* with 2 days of retention
530 time were combined with photo-Fenton (LD and HD). Even treating the wastewater by
531 hybrid system using low dose of Fe and H_2O_2 it was required the same treatment time in
532 photo-Fenton (30 min) than if the photo-Fenton alone is performed but employing double
533 of Fenton's reagents.

534 Focusing on the most recalcitrant compounds (SMX and, above all, ACMP) it can be
535 observed that the hybrid system depicted an enormous advantage in their elimination. As
536 can be observed in Figure 5a and 5b, these two compounds were not removed efficiently
537 by constructed wetlands or in photo-Fenton process. The maximum elimination in
538 constructed wetland of these two compounds was about 80% with high retention times (7
539 and 14 days). For its part, SMX was totally eliminated by photo-Fenton process only
540 with high doses of Fenton's reagents and in 20 min of treatment. SMX has a second order
541 kinetic with HO· similar to CIPR ($k_{HO\cdot,\,SMX}$= $5.5\cdot10^9$ M^{-1} s^{-1}) [57] but the contribution of
542 photolysis was significantly lower (only 16% for SMX in front of 97% for CIPR).
543 However, when LD of Fe and H_2O_2 were employed, SMX depicted a similar degradation
544 profile than MET and lower than CIPR, because of the important contribution on the
545 photolytic process.

546 Regarding ACMP the scenario was more critical since the total elimination was not
547 accomplished in an any case. The removals obtained in 60 min of treatment were 38 and
548 66% for LD and HD, respectively. This fact was not unexpected since ACMP has the
549 lowest second order reaction rate with HO· ($2.1 \cdot 10^9$ M^{-1} s^{-1}) [59] and photolysis (2%). In
550 this context, as depicted in Figure 5c and 5d, it becomes evident that the combination of
551 two processes delivers a substantial enhancement in the removal of two specific
552 compounds. Thus, SMX was totally removed in all experimental conditions of the two
553 hybrid systems (with LD and HD) while with sole photo-Fenton SMX degradation was
554 lower than 90%. Additionally, just as it happened with the other MPs, the required times
555 to achieve 90% of sulfamethoxazole elimination in photo-Fenton process (hybrid system)
556 was decreased compared to the individual treatment. Taking a look at Table 1, it can be
557 observed that in a combined system-LD the time required were 5 and 14.5 min in C2 and
558 C4, respectively while with sole photo-Fenton 90% of sulfamethoxazole degradation was
559 not achieved.

560 Concerning ACMP, which is the most recalcitrant compound, the use of combined system
561 was the only way to achieve its total removal. Observing Figure 5c (hybrid system-LD)
562 it can be noted that the ACMP elimination in all experimental conditions was higher than
563 the removal in individual treatments (Figure 5a and 5b). For example, in the hybrid
564 system-LD its elimination was 77% for *C. haspan* with 2 days of retention time while in
565 individual treatments its elimination was lower 51 and 38% for constructed wetland and
566 photo-Fenton, respectively. Moreover, as depicted in Figure 5d, the hybrid system-HD
567 allows to reach the total ACMP removal in the microcosms planted with *C. haspan*.
568 Looking at Table 1, the combined system offers the possibility to achieve 90% of the
569 most recalcitrant compound tested in this study in only 15 minutes employing the effluent
570 C2 and HD of Fenton's reagents. This means that hybrid system offers a practical and

adaptable solution to meet regulatory limits, tailored to the intended use or destination of the effluent, combining cost-effectiveness, environmental friendliness, and sustainability.

Table 1. Time required in solar photo-Fenton process to achieve 90% elimination of E2, ciprofloxacin, metronidazole, acetamiprid and sulfamethoxazole. AOP: sole photo-Fenton; Hybrid system: C2, C4 ("C" refers to *C. haspan* and "2 and 4" refer to retention time in constructed wetlands; LD: low dose in photo-Fenton and HD: high dose in photo-Fenton; "n.a": 90% not achieved in 60 minutes; "0": 90% achieved in constructed wetland.

	Time (min) required to achieve 90% MP elimination					
	LD			**HD**		
	AOP	**C2**	**C4**	**AOP**	**C2**	**C4**
E2	20	0	0	6	0	0
CIPR	15	5	0.5	10	0.5	0.5
MET	60	30	n.a	30	12.5	53
ACMP	n.a	n.a	n.a	n.a	15	54
SMX	n.a	5	14.5	15	2.5	0.5

Nevertheless, although the hybrid system presented the highest elimination in all conditions for the five micropollutants tested in this study, the degradation rates in the second stage (photo-Fenton) were affected by DOC, TSS and nitrites content in the influent of the photo-Fenton process. In Figure S3, illustrating the photo-Fenton process with a low dose of Fenton's reagents, it's noticeable that the combined removal of SMX and MET was as fast as or even quicker than in the individual photo-Fenton process. However, for ACMP (having the slowest reaction rate with HO·), its elimination rate was lower in specific conditions of the hybrid system. Only in C2 and P14 did it achieve a higher removal rate. This improved performance, such as in C2, might be linked to reduced TSS and other MPs after passing through the constructed wetland. Lower TSS decreased light scattering, boosting MET's photolysis elimination (total removal at 45 min, 15 min faster than the individual photo-Fenton process) and HO· generation. Additionally, lower MP concentrations reduced their competition for HO·, making more available for the highly resistant compound, ACMP.

593 Conversely, in C4, ACMP removal was inferior compared to C2 or the individual
594 treatment. This might be associated with a ninefold increase in nitrite concentration,
595 potentially acting as a HO· scavenger.

596 P14 displayed the swiftest ACMP removal, degrading in just 20 min. P14's effluent
597 contained only ACMP and SMX, reducing the HO· competition compared to the
598 individual or C2 processes. Furthermore, this hybrid system had lower TSS compared to
599 the individual process, with consistent nitrite levels.

600 Observing Figure S4, referred to photo-Fenton process with high doses of Fenton's
601 reagents, it could be seen that the behavior was similar than Figure S3 (photo-Fenton LD).
602 In this case, the hybrid system C2 achieved the total elimination of ACMP in only 20
603 min, which means an enormous improvement in the MP removal since only 70% of
604 ACMP was achieved with the individual treatment in 1 h. Finally, with high doses of
605 Fenton's reagents it was reached a total ACMP degradation in 1 h in the hybrid system
606 C4. The removal kinetic was lower than C2, but it was an enhancement compared to
607 individual treatment. The difference compared to the process using LD could be attributed
608 to the fact that a greater generation of HO· causes the effect of nitrites to decrease.

609 In summary, the hybrid system exhibited enhanced removal efficiencies in comparison to
610 the individual treatment methods, particularly for the more recalcitrant compounds. The
611 superior performance of the hybrid system is primarily ascribed to its preliminary
612 treatment phase characterized by shorter retention times, which serve to augment removal
613 kinetics in the subsequent stage of the integrated system. The constructed wetland pre-
614 treatment likely reduced contaminant concentrations, allowing Fenton's process to better
615 target and elimination of remaining pollutants, possibly boosting removal rates.
616 Additionally, the CW might have assisted in removing interfering substances, indirectly

617 improving Fenton's process efficiency. However, the interaction between CW pre-
618 treatment and Fenton's process is intricate and can affect removal rates differently based
619 on contaminants and their properties.

620 **4. Conclusions**

621 Aquaculture farms are potential sources of micropollutants into aquatic ecosystems.
622 Therefore, it is of paramount importance to adopt appropriate technologies for the
623 removal of these contaminants before reusing or releasing water into the environment.
624 Building upon the established efficacy of the solar photo-Fenton process and constructed
625 wetlands in mitigating a wide range of these substances, this study proposes a hybrid
626 system combining both (CW + photo-Fenton) to address the specific limitations
627 associated with each technology. This study demonstrated that the integrated approach
628 significantly enhances the removal of micropollutants. The findings revealed that in all
629 cases the hybrid system provided better removals than the individual treatments, above
630 all for the more recalcitrant compounds. For the operational conditions studied, the hybrid
631 system's superior performance is notably attributed to a preliminary treatment phase
632 featuring shorter retention times, specifically 2 days in the microcosm planted with *C.*
633 *haspan*. During this 2-day treatment period, the reduction in total suspended solids and
634 the partial removal of micropollutants significantly improved the subsequent efficiency
635 of the photo-Fenton process, which reached total MPs removal in 20 minutes treatment,
636 using 5 mg L^{-1} of iron and 50 mg L^{-1} of H_2O_2. In contrast, longer retention times (4 and
637 7 days) in CW led to increased nitrite levels in the microcosm, which adversely affected
638 the photo-Fenton treatment's efficacy.

639 The extension of the retention times of constructed wetlands planted with *C. haspan* up
640 to 14 days achieved the removal of all compounds without the need for a secondary
641 treatment. However, this prolonged treatment duration is a drawback that the hybrid

system aims to overcome. Moreover, it would be necessary to verify that the eliminations of the micropollutants are maintained for long periods of operation due to the possible desorption of these substances. On the other hand, the standalone use of the photo-Fenton process managed to eliminate only 60% of ACMP, notably the most recalcitrant compound, and extending the treatment time up to 60 minutes.

This innovative hybrid approach, combining constructed wetlands with solar photo-Fenton, offers a practical and adaptable solution to meet regulatory limits, tailored to the intended use or destination of the effluent. It excels in cost-effectiveness, environmental sustainability, and overall efficiency. However, it is essential to consider that the interaction between the CW pre-treatment and the subsequent Fenton's process can be complex and multifaceted, impacting the removal rates or kinetic constants in varied ways depending on the contaminants and their specific properties such as recalcitrance and Kow.

Acknowledgments

This Special Issue is dedicated to honor the retirement of Prof. Santiago Esplugas at the Universitat de Barcelona (UB, Spain), a key figure in the area of Catalytic Advanced Oxidation Processes.

To Santi, whose knowledge, kindness and generosity has left an imprint on the minds and hearts of those of us who were fortunate enough to work under his leadership. His work and vision on ozone and advanced oxidation will remain forever as an inestimable reference.

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