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Nature-based solution as an efficient wastewater pretreatment to enhance micropollutants abatement by solar photo-Fenton at natural pH

Núria López-Vinent [a,b,*], Ana Piera Santacruz [a,b], Albert Sales-Alba [a,b], Alberto Cruz-Alcalde [a], Iván Díaz Redondo [a,b], Sandra Pérez [b], Carme Sans [a]

[a] Department of Chemical Engineering and Analytical Chemistry, Faculty of Chemistry, Universitat de Barcelona, C/Martí i Franqués 1, 08028 Barcelona, Spain
[b] Department of Environmental Chemistry, IDAEA-CSIC, C/Jordi Girona 18-26, 08034 Barcelona, Spain

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ABSTRACT

This study investigated an innovative and low-cost hybrid system that couples constructed wetland (CW) and solar photo-Fenton (SPF) to enhance the elimination of 17 different micropollutants (MPs) from urban wastewater. The CW unit explored two aquatic plants (*Phragmites australis and Cyperus haspan*) and two operational modes (with and without recirculation), resulting in four different microcosms. Photo-Fenton experiments were carried out in a bench solar simulator at natural pH using the commercial fertilizer DTPA as iron catalysts. The results showed that the constructed wetlands with recirculation obtained better MPs eliminations than microcosms without recirculation, with no significant difference between the two plants. The average removal of total MPs and different cycles was 67% and 41% in the unit planted with *C. haspan*, with recirculation and no recirculation, respectively. Additionally, the removal performance of total suspended solids (TSS) and dissolved organic carbon (DOC) from water was also high, reaching about 80% and 50% for TSS and DOC, respectively in the recirculation unit with no increase in nitrites content. The CWs performance resulted in a rise yields of overall MPs abatement in photo-Fenton process, from an average removal of 73% for the single process up to almost complete removal (95%) for the hybrid system. CW with recirculation combined with SPF would let to achieve the corresponding limits according the final use/fate of the effluent in a more economical, sustainable and green way.

1. Introduction

From the 17 Sustainable Development Goals (SDGs) established by the United Nations (UN) in 2015 to accomplish the 2030 Agenda, SDG 6 aims to fully ensure the availability and sustainable management of water and sanitation for everybody [1]. However, according to data provided by the 2021 UN World Water Development Report (WWDR), the current water status is still far from the proposed target. Over 2 billion people live in countries with constant water-stressed conditions and around 4 billion people suffer severe physical water scarcity for at least one month out of the year [2]. Moreover, factors such as population growth, socioeconomic development, or consumption patterns changes are expected to increase the water demand by 50–80% in the upcoming decades [3,4]. Additionally, the accelerated climate change issue may also aggravate the situation leading to a fast global water availability reduction [5]. Given this scenario, wastewater reuse can unquestionably be viewed as a sustainable development tactic contributing to address this scarcity crisis [6]. However, wastewater must first be adequately treated, among other actions, removing all harmful elements resulting from the different continuous anthropogenic activities. Micropollutants (MPs) are a prime example of substances to be removed from aquatic bodies.

Even detected at trace levels (from ng L^{-1} to μg L^{-1}), the presence of MPs (e.g., pharmaceuticals, pesticides, personal care products, steroid hormones) in diverse aquatic environments may have detrimental impacts on organisms, ecosystems and, indirectly, on human health [7]. In this regard, conventional wastewater treatment plants (WWTPs) were not initially designed to completely remove these recalcitrant compounds [8]. Therefore, and due to their potential risk, additional treatment steps need to be implemented in WWTPs in order to clear away from water matrices. By applying approaches based on advanced treatments such as oxidation (e.g., Advanced Oxidation Processes

* Corresponding author at: Department of Chemical Engineering and Analytical Chemistry, Faculty of Chemistry, Universitat de Barcelona, C/Martí i Franqués 1, 08028 Barcelona, Spain.
E-mail address: nuria.lopez@ub.edu (N. López-Vinent).

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(AOPs)), adsorption (e.g., activated carbon) or filtration (e.g., membrane filtration), the MPs removal can be substantially enhanced [9]. Nevertheless, their implementation, procedure, and even maintenance generally entail a high cost and energy input [10].

Constructed Wetlands (CWs) are promising nature-based technologies to remove different types of MPs, in part, due to their simplicity, low investment and operation cost [11]. A wetland is defined as a flat land area that remains in flooded or waterlogged soil conditions for considerable periods of time (2–4 days for the Horizontal flow CWs (HFCWs) and 1–2 days for Vertical flow CWs (VFCWs)) [11] with the presence of hydrophilic plants that could act as water filters. CWs are a recreation of processes in which the synergy of numerous mechanisms (i.e. biodegradation, phytodegradation, photodegradation, rhizofiltration, phytovolatilization, phytoextraction and sorption) [12] makes possible the removal of heavy metals, nutrients and organics [13]. Based on this, recent studies have focused on MPs abatement through CWs [14–18].

The efficiency of MPs elimination by CWs is linked to different factors, such as the wetland configuration (i.e., surface and subsurface, horizontal and vertical) and the operation parameters (i.e., retention time or aerobic/anaerobic environment) [19]. For example, HFCWs operate under anaerobic conditions (since they work at continuous conditions) and require relatively long hydraulic retention times. On the other hand, Vertical flow CWs (VFCWs) are fed from the surface and intermittently. These facts allow a higher concentration of dissolved oxygen, which benefits plant roots, increases the rate of water infiltration and prolongs the contact between the biofilm growing on the mobile phase and the contaminants [20–23]. From several previous studies it is inferred that VFCWs present higher MPs removal efficiencies than HFCWs for a large number of compounds [16–18].

Nevertheless, CW also have disadvantages, such as long retention times and large land areas requirements. In addition, MPs removal might also be difficult to control because the performance of CWs depends on many factors, including environmental conditions and individual pollutant properties [24]. Regarding this, CWs might not achieve adequate abatement levels for certain compounds which are not affected by adsorption or biological processes, and therefore may not fulfil the requirements for water reuse [25].

To counteract these adverse effects, we propose combining constructed wetlands with a technology with broadband action against many different classes of pollutants, Advanced Oxidation Processes (AOPs). Among AOPs, solar-based systems are of greater interest because of their potential techno-economic and environmental sustainability. Since solar-based AOPs are in general affected by the presence of organic matter and suspended solids, using CW as pre-treatment may improve the efficiency of subsequent oxidation by reducing their concentration. In this study, solar photo-Fenton was used as the second step of the suggested hybrid treatment system. Commercial fertilizer DTPA-Fe was selected as the catalyst since it has been proven to provide good catalytic performance for the removal of MPs in different water matrices [26,27]. CWs were set as a first step where two types of plants (*Phragmites australis* and *Cypersus haspan*) and two operational modes (with or without recirculation) were investigated. The efficiency of the different configurations of the coupled system was explored throughout the simultaneous removal of 17 MPs at 1 μg L^{-1}, dissolved organic matter (DOM) and total suspended solids (TSS) from a WWTPs secondary effluent. Thus, the main objectives of the study were to investigate the performance of different CW configurations as a pretreatment and to evaluate the MPs removal efficiency of the hybrid system, compared to the single treatment through solar photo-Fenton at natural pH with an iron chelate acting as the catalyst.

2. Material and methods

2.1. Chemicals and reagents

The MPs used in this work (atrazine, benzotriazole, bisphenol A, carbamazepine, clofibric acid, diclofenac, fluconazole, gemfibrozil, hydrochlorothiazide, ibuprofen, iopromide, metoprolol, phenytoin, primidone, sulfamethoxazole, TCEP, venlafaxine, metronidazole and acetamiprid, see Supplementary material Table S1 for further information), catalase from bovine liver, ammonium metavanadate and 1,10-phenanthroline were purchased from Sigma-Aldrich. The iron chelated with DTPA (7% of iron) was bought from Phygenera. Chemicals used in mobile phase preparation (i.e., acetonitrile, orthophosphoric acid, ammonium fluoride, formic acid and ammonium acetate) as well as hydrogen peroxide (H_2O_2, 30% *w/v*), sodium bisulfite, methanol and ascorbic acid were acquired from Panreac Quimica.

2.2. Secondary wastewater effluent

Secondary effluent samples from the WWTP located in Gavà-Viladecans (Barcelona, Spain) were collected to perform the experiments. The secondary treatment in this facility consists of an Integrated Fixed-Film Activated Sludge (IFAS) followed by a circular clarifier. The main physicochemical parameters of the effluent sample are presented in Table 1.

2.3. Experimental setup

2.3.1. Vertical flow constructed wetlands

Four polypropylene recipients (height = 22.5 cm; diameter = 9.5 cm) were used to construct the artificial wetlands. The bottom of the container (5 cm) was filled with cobbles (particle size = 60–120 mm), this layer being set up to prevent the clogging of draining tubes. The next layer (2 cm) consisted of volcanic rocks (particle size = 25–50 mm) used to increase the porosity of the module, boost the adsorption of some compounds and allow the growth of biofilm, which could be involved in the elimination of micropollutants. A third layer (5 cm) was composed by fine gravel (particle size = 12–30 mm) which served as support of the top sand layer (10 cm, particle size= 0.5 mm). The function of that layer was serving as bed substrate and water filter. Each constructed wetland was covered with aluminium foil to minimize algae growth. The sampling point was placed at the bottom of each wetland. The aquatic plants selected to perform this study were *Cyperus haspan* and *Phragmites australis*. CWs were operated in the temperature range of 15–20 ºC and they were kept with natural day conditions (day:night regime). Before to start the experiments, each CW was acclimated for 1 month with the same secondary wastewater used in subsequent experiments. This step is necessary to allow bacterial growth and biofilm formation. Two operation modes were investigated in this study: with and without recirculation, resulting in a total of four CW (each plant was tested with two operation modes) as shown in Fig. S1.

2.3.2. Photo-Fenton reactor

A bench solar simulator (SUNTEST CPS+, Heraeus) was employed to conduct the photo-Fenton experiments. Equipped with a 1500-W Xenon lamp containing infrared and UV-C cut-off filters, the irradiance in all the trials was fixed at 500 W m^{-2}. A cylindrical Pyrex glass vessel (150 mL; inner diameter 9 cm; height 4.5 cm), used as reactor, was placed in the solar simulator over a refrigerant plate connected to a thermostatic

Table 1
Physicochemical parameters of secondary wastewater samples.

Parameters	Wastewater
pH	7.6
UV_{254} (cm^{-1})	0.3
Alkalinity (mg $CaCO_3$ L^{-1})	414
TSS (mg L^{-1})	38
DOC (mg C L^{-1})	25
Cl^{-1} (mg L^{-1})	344
NO_3 (mg L^{-1})	< 0.4
NO_2 (mg L^{-1})	< 0.4

bath (15 ºC), in order to hold the temperature of the solution steady during all the experiment (20–25 ºC). The solution was magnetically stirred (350 rpm) during experiments.

2.4. Operation of constructed wetland-photo-fenton coupled system

To perform the experiments, each CW was loaded with 1.5 L of IFAS spiked with 17 MPs at 1 μg L^{-1} each one. The selection of these compounds was performed considering its different second order reaction rate of each MP with hydroxyl radicals and its different KOW (the information could be found in additional material, Table S1). Additionally, the selection of specific micropollutants and the concentration tested were also carried out taking into account its occurrence in wastewaters [28,29]. The retention time for each CW load was 3 days. According to Zhang et al., [30] one week is commonly used as a retention time for an efficient removal of pollutants. In this work the main objective was to combine two technologies, so the authors decided operate at 3 days, in order to decrease the total treatment time of wastewater and obtaining better total removal of micropollutants. The recirculation of two CW (one planted with *P. australis* and another one with *C. haspan*) was performed with a peristaltic pump with a flow rate of 40 mL min^{-1}. At the end of the experiment (after 3 days), the water losses (evaporation and evapotranspiration) were compensated (up to 1.5 L) by the addition of deionized water. For each CW, 8 cycles of 3 days were carried out. At the beginning of each cycle, new spiked wastewater was introduced to each unit. To analyze the residual concentration of 17 MPs, samples were subjected to solid phase extraction (SPE) and then measured through Ultra Performance Liquid Chromatography (UPLC) coupled to Tandem Mass Spectrometry (MS/MS).

The effluent obtained after 3 days in each microcosm was used as an influent of solar photo-Fenton at natural pH experiments. Thus, after each CW cycle (1−8) 5 oxidation experiments (effluents from *P. australis* with recirculation (PR), *P. australis* without recirculation (P), *C. haspan* with recirculation (CR) and *C. haspan* without recirculation (C) and IFAS without pretreatment by CW (IN)) were conducted. All of them were spiked with 3 indicator MPs (metronidazole (MET), acetamiprid (ACMP) and sulfamethoxazole (SMX)). In that case, their concentrations were increased (up to 200 μg L^{-1} each one) to better monitor them during the process. The iron concentration was set at 5 mg L^{-1} and it was chelated with DTPA (selected as a catalyst since it has been proven to provide good catalytic performance for the removal of MPs in different water matrices [26,27]). The concentration of hydrogen peroxide (H_2O_2) was fixed at 50 mg L^{-1} and was added to the photoreactor just before the SUNTEST was turned on. The iron and H_2O_2 concentrations were selected according the optimization performed in Bolaños et al., [31] and the good removal performances of this pair of concentrations revealed in López-Vinent et al., work [6]. Different samples were taken from the photoreactor throughout the experiment. To quench the residual H_2O_2 in the samples, 10 μL of a 200 mg L^{-1} solution of liver bovine catalase was added to 5 mL of sample. Samples were filtered through 0.45 μm PVDF filters before analysis by High-Performance Liquid Chromatography (HPLC). Sodium bisulfite was used to quench the residual H_2O_2 for DOC analysis.

Additionally, 5 oxidation experiments were carried out with the PR, P, CR and C effluents of cycle 8 (last cycle) and IN (without CW pretreatment). In these experiments, no additional MPs were added before conducting the photo-Fenton tests. Thus, the residual concentration of 17 MPs contained in the effluent of each CW were followed in the photo-Fenton experiment. For IN matrix, 17 MPs at 1 μg L^{-1} each one were spiked. The iron and H_2O_2 concentrations, as well as the oxidation procedure were similar to the previously described. In that case, however, the residual MPs concentration was determined through SPE followed by UPLC-MS/MS.

2.5. Analytical measurements

In the present study, a HPLC (1200 Infinity Series, Agilent Technologies) was used to determine the remaining concentration of the selected target compounds spiked in the photo-Fenton experiments. The column employed was SEA18 Teknokroma (250 × 4.6 mm i.d; 5 μm particle size). The injection volume was set to 100 μL, the flow rate at 1 mL min^{-1} and an isocratic method using 80% H_2O acidified with H_3PO_4 (adjusted at pH = 3) and 20% acetonitrile were employed as mobile phases. The wavelengths to detect ACMP, SMX and MET were fixed at 250, 270 and 220 nm, respectively. The temperature was kept at 40ºC. For the constructed wetlands, the MPs concentration was measured through an Ultra Performance Liquid Chromatography (Acquity UPLC-H class, Waters) coupled to a triple quadrupole mass spectrometer Xevo TQ-S MS Detector (Waters). The column used was an Acquity Premier HSS T3 (100 × 2.1 mm i.d; 1.8 μm particle size) equipped with a VanGuard FIT precolumn (Waters). The column temperature was set at 40ºC and the flux was 0.2 mL min^{-1}. The liquids method and the mass spectrometer parameters are displayed in supplementary material Text S1 and Table S2, respectively. Solid phase extraction was performed, as a sample pretreatment, in order to concentrate the sample when 17 MPs at 1 μg L^{-1} were analyzed by UPLC- MS/MS. More information about SPE could be found in Text S2 of additional material. Additionally, the results of the recovery of 17 MPs could be seen in the Supplementary Material Fig. S2. The ultraviolet absorbance was measured using a DR6000 UV-Vis spectrophotometer by Hach (USA). For the DOC content quantification, the Standard Methods 5310B procedure [32] was followed by means of a Shimadzu 5055 TOC-VCSN analyser equipped with an ASI-V autosampler. The H_2O_2 and total iron concentration measurements were performed by the metavanadate [33] and o-phenanthroline colorimetric methods (ISO 6332) [34], respectively. The concentration of relevant anions (i.e., nitrite, nitrate, chloride, and bromide) from wastewater effluent samples were determined through ionic chromatography with conductivity and UV detectors. The flow rate was maintained at 2 mL min^{-1} and the injection volume employed was 200 μL. The column utilized was a 4.6 × 150 mm IC-PAK ANION column provided by Waters (USA). The mobile phases were mainly a mixture of borate buffer and acetonitrile, and the wavelength for the UV detector was fixed at 214 nm. The TSS was performed following the methodology of Standard Methods 2540-D [35].

3. Results and discussion

3.1. Removal efficiency in Constructed Wetlands as a function of the type of plant and operation mode

3.1.1. Micropollutants removal

The CW performance on MPs removal can be affected by photosynthesis, evapotranspiration and microbial activity [36], which in turn may be affected by different parameters such as temperature, pH, oxygen availability or ionic strength [37]. In addition, hydrophobic compounds are readily adsorbed on soil, mineral surfaces and biofilms, whereas hydrophilic compounds are mostly removed by other processes [30].

Fig. 1(a-d) displays the average MPs removal results of the 4 different evaluated microcosms of constructed wetlands for cycles 1–8.

In Fig. 1a and b, which correspond to CW vegetated with *C. haspan*, it can be observed that the removal efficiency for 17 MPs with recirculation mode was always higher than in the microcosm without recirculation. The average removal for all 17 MPs and all cycles was 67% and 41% for CR and C, respectively. Although the absolute retention time is the same in both operational modes, in the recirculation systems the contact time of MPs with the active part of the microcosm (top sand layer containing roots) is higher than without recirculation systems. This increase in contact time allows MPs to be more available for removal through sorption on biofilms, sorption by plants and biodegradation by

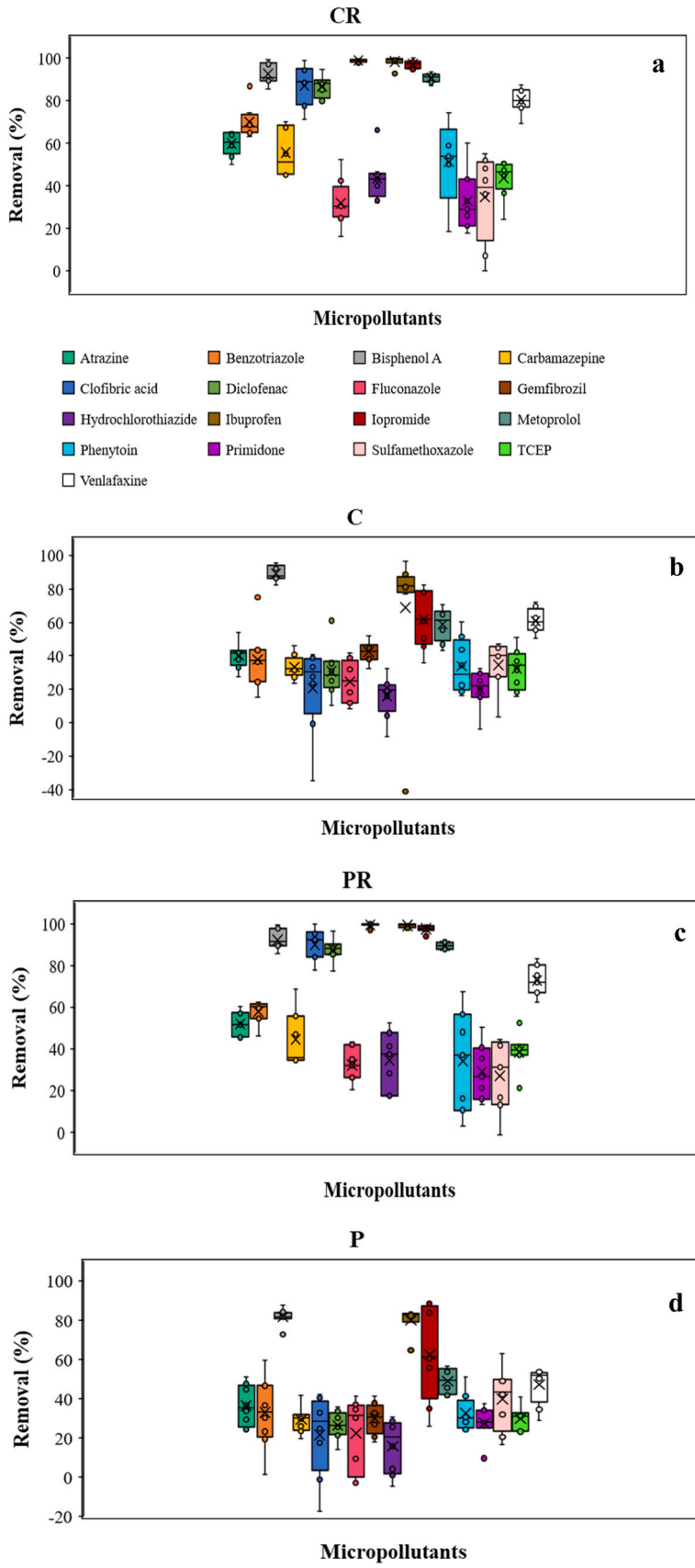

Fig. 1. Elimination of 17 micropollutants by four different types of constructed wetlands for 8 cycles, a) *C. haspan* with recirculation; b) *C. haspan* without recirculation c) *P. australis* with recirculation and d) *P. australis* without recirculation. Retention time= 3 days; $[MPs]_0 = 1\ \mu g\ L^{-1}$ each one.

bacteria. Moreover, the recirculation mode allows the constant O_2 introduction in the microcosm. As reported by Ávila et al., [38] the better removal performances achieved with high dissolved oxygen in microcosm may be indicative of biodegradation and biochemical or geochemical reactions in the filter bed. For instance, in the study of Ávila et al., it was reported that diclofenac was removed 97% in aerated systems while only 12% in the systems with no aeration. These values are according with the removal observed in this work since from Fig. 1a, b, it could be observed that diclofenac was removed about 90% and 30% for CR and C, respectively.

Concerning the elimination of micropollutants throughout vertical flow constructed wetlands with recirculation, several authors revealed similar abatements in their studies. Venditti et al., [19] reported micropollutant removals above 90% across the six different microcosms (including diclofenac, metoprolol, benzotriazole, among others). Ávila et al., [38] also studied the elimination of acetaminophen and gemfibrozil describing removals higher than 80%. However, for sulfamethoxazole the elimination was about 50% which is in accordance with the results displayed in this study (maximum removal ~ 50%, Fig. 1a). Gorito et al., [39] also reported a removal of 97–100% of clofibric acid, 83–100% of diclofenac, 100% of metoprolol, 94–100% of atrazine, 100% of venlafaxine. Again, these values are in accordance with the data represented in Fig. 1a, c.

The same pattern was observed in CWs planted with *P. australis*. In

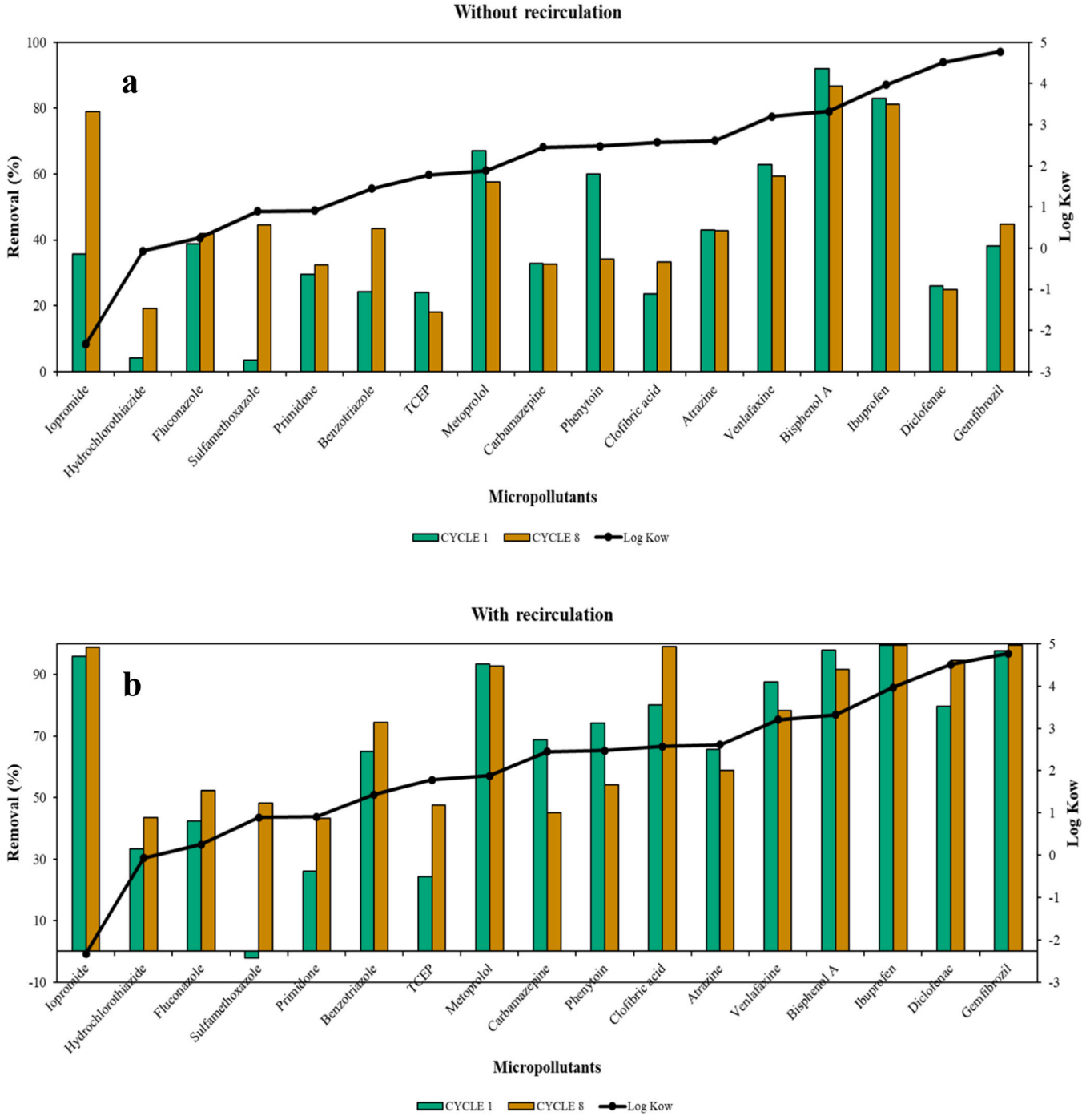

Fig. 2. Elimination of 17 micropollutants by microcosms planted with *C. haspan* a) without recirculation and b) with recirculation for cycle 1 and 8 of operation, including the corresponding values of log Kow. Retention time= 3 days; $[MPs]_0 = 1\ \mu g\ L^{-1}$ each one.

these cases, the average removal over 8 cycles was 60% and 36% for PR and P, respectively. When compared to each other, *C. haspan* CWs had higher MPs elimination than those with *P. australis*. This performance may be due to the fact that the former has a large volume of rhizomes, providing a larger specific surface area for biofilm and potentially a higher biodegradation process performance. Additionally, *C. haspan* presents high number of stems, which could increase the evapotranspiration and subsequent MPs sorption [40].

Fig. 1a-d shows different removal levels of MPs in the same microcosm depending on the target compound. In CWs with recirculation, bisphenol A, clofibric acid, diclofenac, gemfibrozil, ibuprofen, iopromide, metoprolol and venlafaxine obtained the highest removals. The average removal of these compounds for 8 cycles in CR was between 80% and 99%. While with the same plant but without recirculation (C), the highest removals were observed for bisphenol A, ibuprofen, iopromide and metoprolol. In this case, the average removal was between 59% and 89%. These differences are related to the intrinsic physical-chemical characteristics of each compound. Two of the most important is n-octanol/water partition coefficient (log Kow) since, as mentioned above, one of the mechanisms of MPs removal is its sorption on solid substrates and/or biofilm, and the biodegradability, due to the presence of microbiota in the microcosms. Fig. 2a and b displays the removal of the 17 MPs for C and CR, respectively, and the relationship with their log Kow value. The compounds were ordered from left to right from lowest to highest log Kow. As previously mentioned, the trends of CWs planted with *C. haspan* and *P. australis* were similar and therefore only the plots for *C. haspan* are shown. For further information see Fig. S3, where data for *P. australis* are presented.

As can be observed in Fig. 2, in the system with recirculation there is a strong relationship between the elimination of target MPs and the corresponding log Kow values, being higher for compounds with greater hydrophobicity.

In some cases, however, the elimination is better than expected according to its log Kow, possibly due to the influence of other removal mechanisms such as biodegradation. For example, iopromide presents the lowest log Kow, though some of the highest eliminations were observed for this chemical in both systems. Consequently, it is inferred that biodegradation and plant uptake were the major elimination mechanisms of iopromide under the studied operational conditions. These results were consistent with those by other authors. Kovalova et al. [41] reported the highest abatement of iopromide (31%), which is an iodinated X-ray contrast media (ICM), and negligible removal of other ICM in a membrane bioreactor (MBR). James et al., [42] observed the same behavior in a nitrification-denitrification (SND) system maintained in a sequencing batch reactor (SBR), obtaining almost 60% of iopromide removal of which 36% it was degraded during the aeration process. This fact would explain the greater iopromide elimination in the CW with recirculation. The same occurred with metoprolol and ibuprofen, which were two of the compounds with the highest elimination rates in both systems (Figs. 1 and 2). According to Liang and coworkers [43], the two compounds were the most rapidly removed in a moving bed biofilm reactor (MBBRs) system. Nevertheless, in this study the sorption and plant uptake could be another important mechanism since all these compounds present a relatively high value of the log Kow (1.9 and 4.0, respectively) (see Fig. 2).

On their part, clofibric acid and diclofenac present relatively high values of log Kow (2.57 and 4.51, respectively) and high removal performance in CW with recirculation (99% and 95% in cycle 8, respectively). In this case, however, the elimination of these two compounds in the system without recirculation was low (33% and 25%, in order), possibly due to the lower oxygen disposal for biodegradation. In agreement with these results, Zhang et al., [44], reported the removal of these two MPs to be significantly more efficient through membrane filtration (62% and 75%, respectively) than biodegradation (33% and 43%, in order).

3.1.2. Organic matter, TSS and NO_2^- evolution

During the investigation, the elimination efficiency of dissolved organic carbon, total suspended solids and nitrite (NO_2^-) were also measured in all the CW units. These parameters were selected since they are among the most influencing ones in the efficiency of AOPs, including the photo-Fenton process here studied as post-treatment. Organic matter reacts with hydroxyl radical (·OH) in the range of 10^8-10^9 L mol C^{-1} s^{-1}, as determined by different authors [45–50]. There is no single value for the rate constant of this reaction since different types of organic matter are present in different wastewater sources. For its part, nitrite ion presents a second order reaction rate of $1{\cdot}10^{10}$ L mol^{-1} s^{-1} [51], as well as a maximum absorption peak between 300 and 310 nm, thus competing with the species involved in the formation of ·OH and consequently decreasing the process efficiency. Finally, total suspended solids cause water turbidity, which reduces the light penetration in the solution and results also in a lower ·OH generation and subsequent decreasing in treatment efficiency.

Figs. 3–5 display averages of DOC removal, TSS elimination and NO_2^- content for the 8 cycles in PR, P, CR and C, respectively.

As can be observed in Fig. 3, DOC removal was always higher in the two constructed wetlands with recirculation. Among these, the system with *P. australis* had an average removal rate of 55% compared to 50% for *C. haspan*. In contrast, the systems without recirculation yielded lower removals of this parameter, being the corresponding averages of 35% for *P. australis* and 36% for *C. haspan.* The higher DOC abatement in the CWs with recirculation can be attributed to the fact that the plants could sorb more organic matter to carry out their vital functions as the effluent continuously circulates through the system. In addition, a higher contact time with the active part (roots) of the microcosm and the presence of more oxygen might favor an extra removal compared to the system without recirculation. The anaerobic pathways of organic matter elimination are commonly slower compared to aerobic routes [52]. These results are in accordance with other studies in which it was revealed eliminations of total organic matter about 50%. For instance, in the study of Sgroi et al., [53] it was achieved 48% of total organic carbon removal in a partially saturated vertical flow CW. In the same regard, Casierra-Martinez [54] also achieved more than 50% of DOC removal, in that case it was presented a value of 71% of removal efficiency. Additionally, in the same work of Sgroi and coworkers, they studied the removal in horizontal flow CW, where predominates the anaerobic conditions, resulting in only 32% of organic matter elimination.

Fig. 4 displays the average removal of TSS in all the studied systems during 8 cycles. As can be seen in this figure, TSS removal was quite similar in all systems, although it was slightly higher in the case of CWs with recirculation. Focusing on the results in this operational mode, it

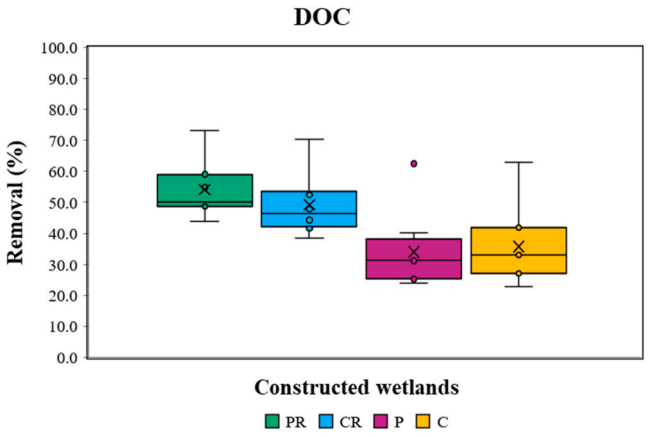

Fig. 3. Removal efficiency of Dissolved Organic Matter throughout four constructed wetlands (PR, CR, P and C) for 8 cycles. Retention time= 3 days; average $[DOC]_0$ = 22.5 mg L^{-1}.

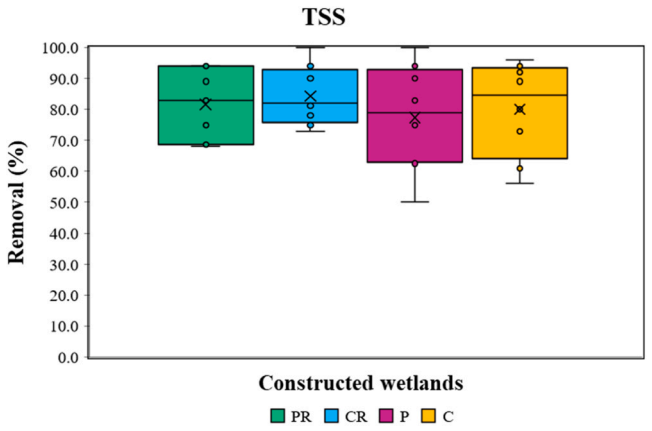

Fig. 4. Elimination efficiency of Total Suspended Solids in four constructed wetlands (PR, CR, P and C) for 8 cycles. Retention time= 3 days; average $[TSS]_0 = 29.6$ mg L^{-1}.

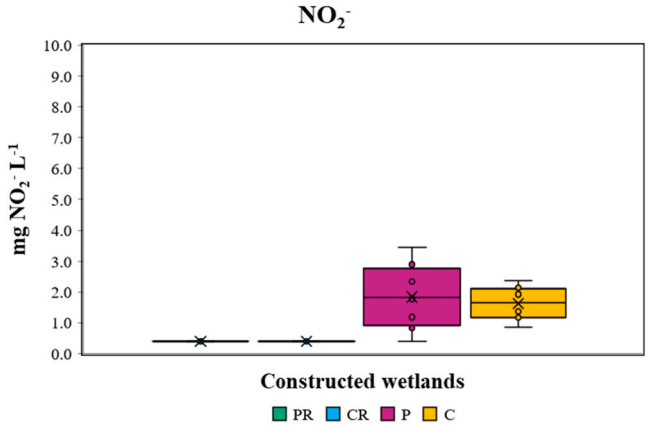

Fig. 5. Nitrite concentrations throughout four constructed wetlands (PR, CR, P and C) for 8 cycles. Retention time= 3 days, average $[NO_2^-]_0 = 0.4$ mg L^{-1}.

can be observed that the eliminations in both cases were higher than 80%. The results displayed in this figure are in accordance with the literature published. Different authors have followed the removal of TSS throughout vertical CW (aerobic conditions), such as Sgroi et al., [53] who revealed eliminations about 70% in saturated vertical flow CW. In this work, it was also evaluated the TSS content in horizontal flow CW (anaerobic conditions) and the value obtained was 72%. This poor differences between two systems (aerobic and anaerobic) removing TSS is in compliance with our results since similar eliminations were achieved in both microcosms (with and without recirculation). Additionally, in the review of Castellar et al., [55] it could be found a value more than 80%, which is an average of TSS removal of 6 research articles.

Finally, NO_2^- was also followed in each cycle and microcosm. The results are displayed in Fig. 5. The NO_2^- concentrations in wastewater without CW pretreatment were lower than 0.4 mg NO_2^- L^{-1}, which was the quantification limit. After the pretreatment in the recirculation systems, the concentration was also lower than 0.4 mg NO_2^- L^{-1}. However, in the case of the systems without recirculation, an average of 2 mg NO_2^- L^{-1} was detected in the CW effluent for *P. australis* and 1.8 mg NO_2^- L^{-1} for *C. haspan*. These differences could be related to nitrification-denitrification processes occurring in the CW microcosms. In the systems with recirculation, the presence of O_2 in the medium is higher compared to the other types of CW. Thus, the nitrifying process could occur to a greater extent in recirculated systems, transforming the NO_2^- to NO_3^-. However, in the systems without recirculation, a lower O_2 content only allows a partial nitrification (i.e., generation of NO_2^- from NH_4^+ (nitrosation), but then it is not possible to complete oxidation to NO_3^-). These results are in accordance with the literature published. For example, in the study of Ávila et al., [38] it was presented NO_2^- removal efficiencies of 93% in CW with continuous aeration while it was observed only 18% elimination in CW without aeration. Additionally, in this work it was evaluated the NH_4^+ content and it was observed that at the end of the treatment with aeration the concentration was 0.07 mg L^{-1}. However, in the system without aeration the NH_4^+ content was 6.05 mg L^{-1}, which is in compliance with our results and discussion.

3.2. Constructed Wetland as a pretreatment of solar photo-Fenton at natural pH

In this part of the study, we assessed the efficiency of a coupled system of constructed wetland followed by solar photo-Fenton treatment. The former aims to remove most of the MPs, together with the suspended solids, dissolved organic matter and nitrogen species that adversely affect the photo-Fenton process. The second step (AOP) is intended to increase the quality of the treated water by removing residual refractory compounds [56].

3.2.1. MTZ, SMX and ACMP removal in the coupled system

To study the influence of the four pre-treatment CWs on the efficiency of MPs removal in solar photo-Fenton, we spiked three target MPs: metronidazole (MTZ), sulfamethoxazole (SMX) and acetamiprid (ACMP). The selected compounds represent different kinetics of reaction with ·OH radical and photolysis (see Table 2), since both are controlling factors in the performance of photochemical transformation processes [57,58].

(a) [59]; (b) [60]; (c) [61]

Fig. 6 displays the degradation outcomes achieved for each target compound with the SPF treatment at natural pH with DTPA-Fe in a single cycle (i.e., cycle 1) for each plant type and operational mode.

From the data observed above, it is clear that irrespective of the compound type to be removed, the least favourable outcomes were achieved with the wastewater matrix without any pre-treatment. This reasoning seems obvious since no biological or physical steps were previously undertaken, hence the content of the typical parameters such as turbidity or OM (i.e., DOC, TSS, NO_2^-) were not reduced [62]. Even so, in the case of SMX, a complete degradation with SPF was successful at 90 min. A similar pattern was also presented for the MTZ scenario, achieving removal of 91% in almost 120 min. However, the most representative difference was observed for the ACMP elimination (see Fig. 6c). During the first 60 min of the SPF experiment, considerable removal occurred. But thereafter, the curve seems to reach a plateau with no further degradation beyond 47%. These results could be strongly related to the data reported in Table 1. The MTZ photolysis was roughly five times greater than SMX, while the ACMP exhibits the weakest photolysis degree value (barely above 2%). In addition, the SMX displays higher kinetics with ·OH radicals than MTZ and ACMP, for which this parameter is rather similar (2.1 and $2.8{\cdot}10^9$ M^{-1} s^{-1}). Therefore, this more than 2-fold difference in the SMX kinetics with hydroxyl radical compared to other MPs seems to be the main reason for the accelerated SMX breakdown, as also suggested by related studies

Table 2
Second-order rate constants values with ·OH radical and photolysis degree (calculated experimentally at an irradiance of 500 W m^{-2}) for the three target MPs assessed.

	MTZ	SMX	ACMP
$k_{OH\ MP}$ [M^{-1} s^{-1}]	$2.8{\cdot}10^9$ (a)	$5.5{\cdot}10^9$ (b)	$2.1{\cdot}10^9$ (c)
Photolysis degree [%]	78	16	2

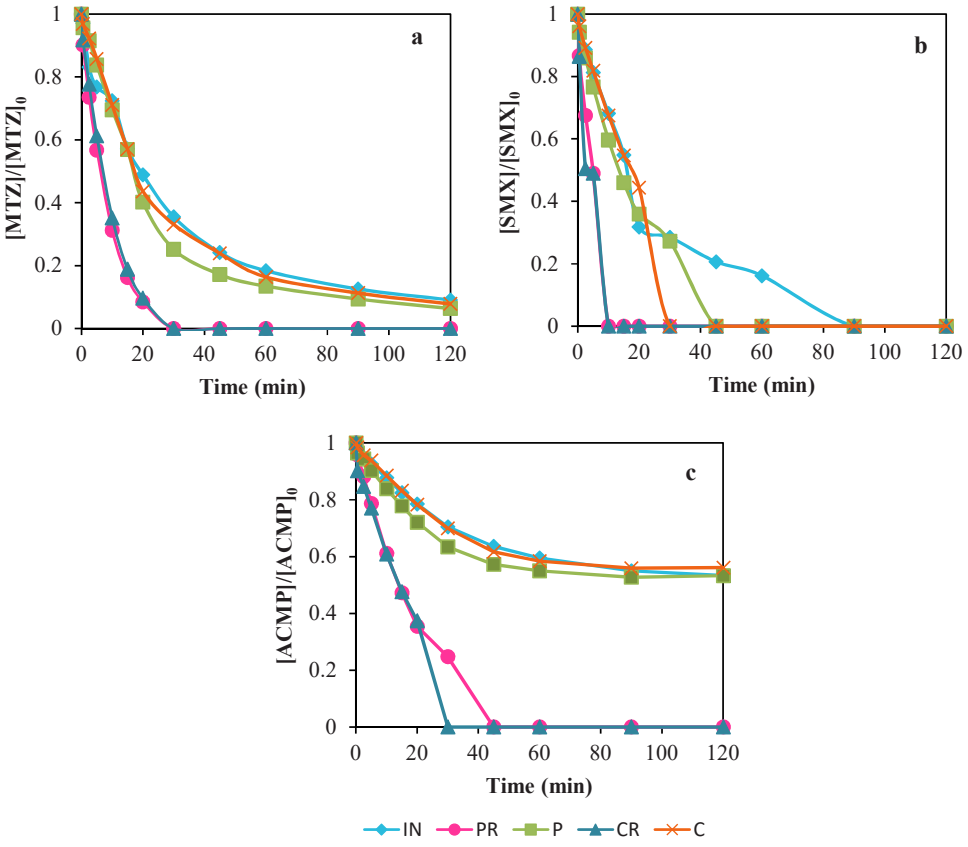

Fig. 6. Degradation of (a) MTZ, (b) SMX and (c) ACMP through SPF at natural pH with DTPA-Fe for each type of plant and operational mode used at the CWs pre-treatment with a single cycle (cycle 1). Experimental conditions: [Fe] = 5 mg L^{-1}; [H_2O_2] = 50 mg L^{-1}; $[MTZ]_0$ = $[SMX]_0$ = $[ACMP]_0$ = 0.2 mg L^{-1}; Irradiance = 500 W m^{-2}, pH= 7.6. IN: wastewater without pre-treatment; P: *P. australis* without recirculation; C: *C. haspan* without recirculation; PR: *P. australis* with recirculation; CR: *C. haspan* with recirculation.

[63]. On the other hand, the remarkably enhanced removal of MTZ over ACMP might be mostly attributable to the higher photolysis level of the former. Compounds containing such chromophore structures (i.e., aromatic rings or unsaturated functional groups) are able to selectively absorb UV light with higher intensity [64].

An additional important point to remark on the performance of the SPF system in the untreated wastewater effluent would be the stability of the iron chelate. Given the non-selective behaviour of ·OH radicals [65], the UV light effect and the large complexity of the wastewater matrix handled (since no pre-treatment was applied in this case), DTPA-Fe, which presents initially high stability with iron [57], could be broken down. This results in iron precipitation and consequently an increase in turbidity. Accordingly, it would also decrease the ·OH availability and reduce the overall MPs removal percentage [66]. Moreover, new and more stable complexes with other ions (e.g., Ca^{2+} and Mg^{2+}) and the complexing agent may also occur (as long as the stability of the resulting combination was much stronger than that with iron) [6]. In this regard, as Fig. 7 depicts, it can be noted that the amount of precipitated iron for all wastewater matrices at the end of treatments was around 80–95%. Therefore, at a certain time, it is highly likely that catalyst is no longer available for the main process reactions to occur. This affects one main source of ·OH generation. This effect is especially remarkable for more

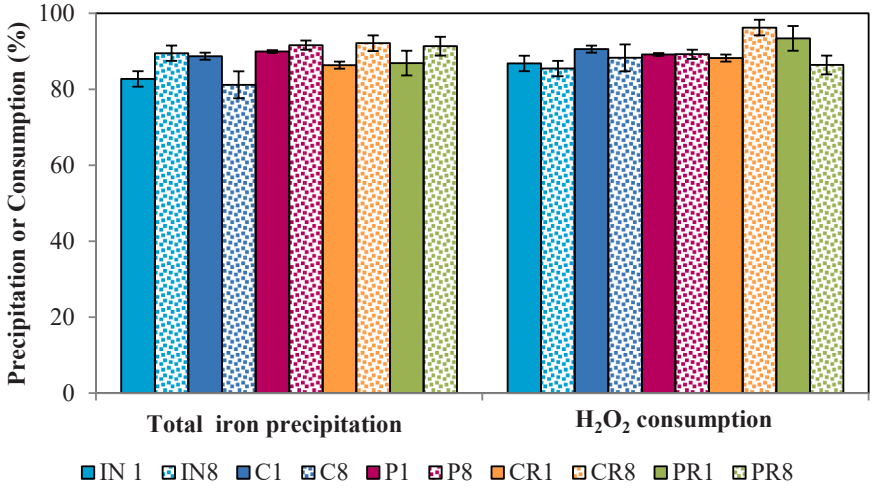

Fig. 7. Percentage of iron precipitated and H_2O_2 consumed during cycles 1 and 8 for the different types of plants and operating modes. IN: wastewater without pre-treatment; P: *P. australis* without recirculation; C: *C. haspan* without recirculation; PR: *P. australis* with recirculation; CR: *C. haspan* with recirculation. The numbers 1 or 8 in the legend correspond to the number of each cycle.

recalcitrant compounds such as ACMP [67]. This one might be in fact a plausible explanation for the observed plateau zone reached in the case of ACMP relative concentration curve before accomplishing full degradation (see Fig. 6c).

In the coupled systems and regarding the different type of plant studied in this work, there was no clear difference in the removal of MTZ, SMX and ACMP by CWs planted with *C. haspan* or *P. australis*. Both showed a similar pattern regardless of whether recirculation was applied or not. This might be partially explained by the fact that over a single cycle, variations in TSS, DOC or NO_2^- concentrations removal for both plants were fairly comparable (see point 3.1.2).

For its part, the outlet effluent recirculation was supposed to enhance organic matter and suspended solids removal, as well as to improve the efficiency of the nitrification-denitrification processes taking place in the CW [68]. Accordingly, it can be noted from Fig. 6 that recirculated WW matrix allowed to attain faster removal for all three MPs. Moreover, the elimination trend was similar to the previously indicated (SMX > MTZ > ACMP). In this case, however, it is worth emphasizing that for ACMP, the removal pattern no longer showed a plateau but a total degradation was reached.

As discussed in Section 3.1.2, the presence of dissolved organic and inorganic compounds decreased after the CW pre-treatment with recirculation. For instance, DOC content in effluents was about 1.7 times lower in recirculated systems than in the non-recirculated microcosms. The same behaviour was observed for NO_2^-, being the concentration in recirculated CW 5 times lower than in other cases. Since these are the most influencing effluent properties in the effectiveness of AOPs, it can be expected that organic compounds would degrade faster in this situation due to a lower competition of the target MPs and OM contained in the WW for ·OH radicals.

In view of the removal profiles presented in Fig. 8, it seems quite evident how the overall performance significantly improved, as the complete removal of the 3 MPs with recirculated CWs effluents took place within 30 min and, again, with almost no differences for both plant types. This could be explained by the fact that a stronger and more active biofilm is formed in the microcosm after some time, which could increase the filtration, biodegradation and adsorption of MPs and OM.

However, when compared with the untreated WW, a more noticeable dissimilarity was observed, as none of the trio of organic compounds seems to reach complete degradation (See Fig. 8 – IN), again due to the absence of a suitable WW pre-treatment. Finally, based on these data findings, it can be also inferred that no plugging emerged in either of the plants by boosting the number of cycles, given that such aquatic plants are capable to alleviate the clogging of the CWs [69].

3.2.2. *Removal efficiency of MPs at low concentration (1 μg L^{-1}) by the hybrid system*

The last part of this work deals with the assessment of the performance of the hybrid system on the removal of the 16 MPs studied in Section 3.1.1 and handling the same initial baseline concentration for each one of them (1 μg L^{-1} each). Fig. 9 displays the percentage removal for each pollutant after each treatment (i.e., directly applying the SPF without pre-treatment, working simply with a biological CW step, or employing the coupled methodology combining both CW and SPF as a "*black box*"). Since the best-preceding CWs efficiency outcomes were found to be with recirculation, this operational mode was selected to run with the CW technique for this research section. The decision was done to remark on the *C. haspan* plant type because results for both plant types were rather comparable; however, further data for *P. australis* can be found in the supplementary information (see Fig. S4).

Although the SPF process failed to phase out TCEP, with its degradation not exceeding more than 5%, biological treatment alone was able

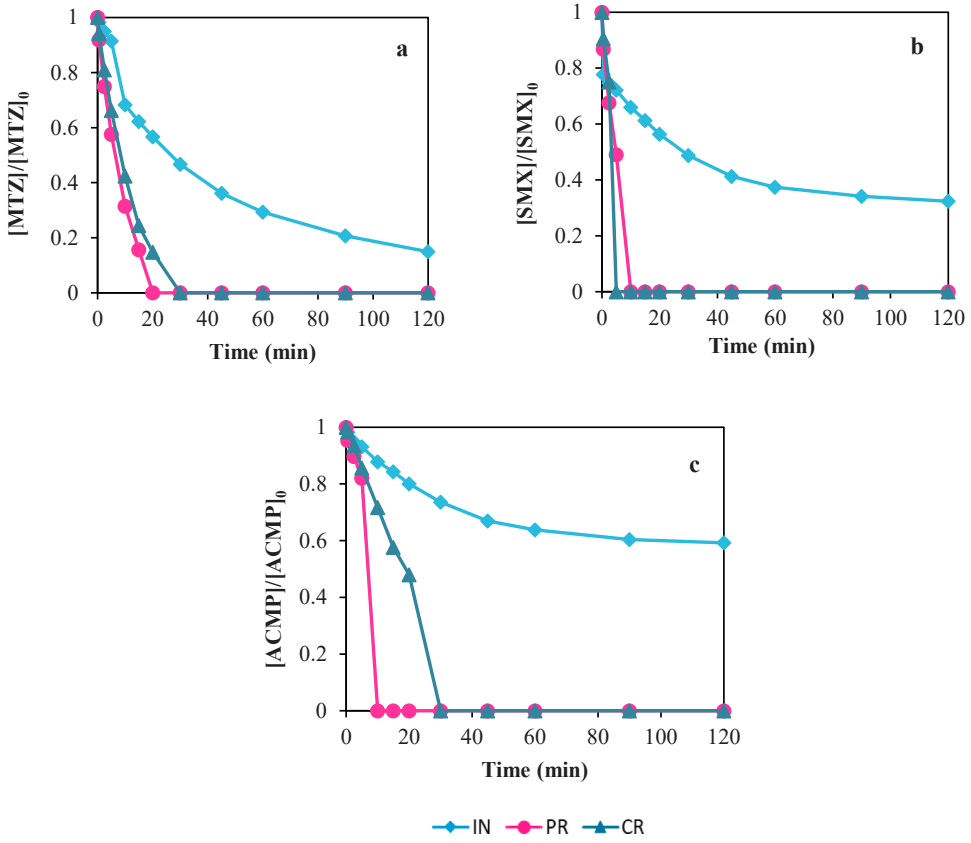

Fig. 8. Degradation of (a) MTZ, (b) SMX and (c) ACMP through SPF at natural pH with DTPA-Fe for each type of plant used at the CWs pre-treatment after performing 8 cycles. Experimental conditions: [Fe] = 5 mg L^{-1}; [H_2O_2] = 50 mg L^{-1}; [MTZ]$_0$ = [SMX]$_0$ = [ACMP]$_0$ = 0.2 mg L^{-1}; Irradiance = 500 W m^{-2}, pH= 7.6. IN: wastewater without pre-treatment; PR: *P. Australis* with recirculation; CR: *C. Haspan* with recirculation.

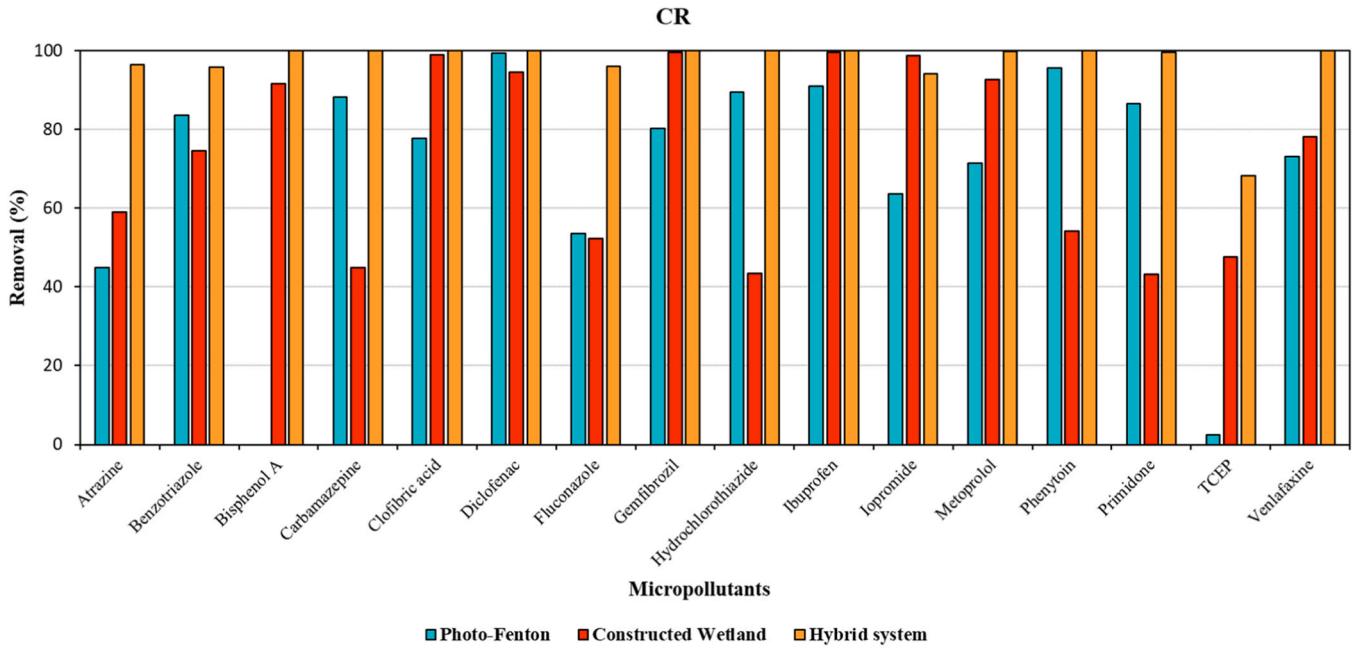

Fig. 9. Removal percentage of several target MPs after performing three different treatments (photo-Fenton, constructed wetland and hybrid system). Experimental conditions: $[Fe]_0 = 5$ mg L^{-1}; $[H_2O_2]_0 = 50$ mg L^{-1}; $[MPs]_0 = 1$ μg L^{-1}; Irradiance = 500 W m^{-2}, pH= 7.6. Photo-Fenton: solar photo-Fenton carried out with wastewater without any pre-treatment; Constructed wetland: *C. haspan* constructed wetland with recirculation mode from cycle 8; Hybrid system: effluent of CR8 treated by photo-Fenton.

to remove over 45% of TCEP. The low reactivity of TCEP, particularly owing to its symmetrical and aliphatic structure, makes it highly stable and hard to breakdown with the SPF process [70–72]. The second order kinetic of each MPs with ·OH can be found in the supplementary material (see Table S1). However, the trend for the CW being notably superior in removal efficiency than the AOP technique seems to extend to some other pollutants assessed, such as atrazine, clofibric acid, gemfibrozil, ibuprofen, iopromide, metoprolol or venlafaxine. The removal of MPs by means of CW ensues as a result of concurrent multiple mechanisms (e.g., biodegradation, sorption, hydrolysis, photodegradation, etc.) [73]. Hence, the main physicochemical features (such as log Kow, pKa, or solubility) of MPs seem to be one of the major factors to consider when discussing their removal through CWs [74]. Other parameters, such as photolysis degree or bacterial biofilms presence, should also be bear in mind since they could have a significant impact on the removal rate depending on the compound type.

On the other hand, the SPF technique attained a greater ratio of elimination than the CW process for benzotriazole, carbamazepine, diclofenac, fluconazole, hydrochlorothiazide, phenytoin, and primidone. As previously mentioned (see Section 3.2.1), the rate constant between MPs and ·OH radicals (since are the major active species during the oxidation reaction) is the principal factor contributing to the degradation occurring with the SPF process. Only in the case of diclofenac, a significant removal by photolysis was observed (i.e., > 50% after 120 min), which contributed to the high overall degradation observed during SPF. For the other micropollutants tested the photolysis was lower than 15%, being the high ·OH reactivity the principal responsible for its elevated elimination in SPF. The carbamazepine was a recalcitrant compound under the biological treatment but achieved more than twice as much degradation with SPF process. According to Sánchez et al. [75], the poor removal of carbamazepine via CW could be caused by microbial activity due to splits of the hydroxylated carbamazepine metabolite into carbamazepine or by also conversion reactions that restore the existing metabolites in the WW to the parent compound. By contrast, considering the high value of its kinetic constant with hydroxyl radicals ($k_{OH} = 8.8 \times 10^9$ M^{-1} s^{-1}) [60], the upgrade resulting from the combined effect of solar light with H_2O_2 [76] also probably the carbamazepine chemical structure, this considerable removal enhancement with SPF could be justified.

However, for all the MPs studied, the percentage removal with the "*black box*" system was reasonably upgraded than either of the two preceding approaches individually. In this regard, all pollutants were successfully removed throughout the hybrid system, except for the TCEP, benzotriazole, fluconazole and atrazine cases. Although high removal improvements were also achieved for these cases (around 70%, 94%, 95% and 96%, respectively), total removal was not achieved probably because each pollutant degrades differently when it first passed through the CW. Therefore, the second procedure (i.e., SPF) would not include all MPs at the same initial concentration, which would mean that they would not be all on an equal footing for the corresponding oxidative reaction. However, regardless of that, the most illustrative example was the fluconazole case, as with any single method (either CW or SPF), only around 50% removal was achieved. In contrast, by combining these two processes, the resulting removal ratio was increased up to 95%. These outcomes are quite consistent with similar research assessing different hybrid systems. Casierra-Martinez et al., [54] observed a removal increase up to 92% and 86% of diclofenac and carbamazepine when hybrid system (CW + photo-Fenton) was investigated since with only CW the eliminations were 56% and 40%, respectively. In the same way, Chow et al., [77] compared the removal efficiencies of BDE-209 in photocatalysis with TiO_2 alone and combining it with CW. In this case, the abatement of BDE-209 was more than 90% in hybrid system compared to photo-treatment alone presenting less than 60% of compound elimination.

In summary, since the pollutants are found collectively in the WWTP under realistic conditions, it can be inferred from the obtained outcomes that the hybrid system (CW + SPF) achieved more attractive removals for these assessed target MPs (with an average degradation of ~95%), as opposed to CW or SPF separately (with an estimated removal of 71.8% and 73%, respectively).

4. Conclusions

The results of this study demonstrate that combining constructed

wetland (CW) and solar photo-Fenton process at natural pH is a promising strategy for more economic and sustainable elimination of micropollutants contained in wastewaters with high organic matter content. The higher yields in the hybrid system were obtained by performing a pretreatment based on CW with recirculation. The average removal of 17 MPs and 7 cycles of operation was 1.6 times higher in the recirculated systems than in CWs without recirculation. Additionally, the recirculated systems obtained higher performances on the removal of dissolved organic carbon (DOC) and nitrite (NO_2^-) than CW without recirculation (1.4 and 5 times higher, respectively). The elimination of total suspended solids (TSS) was similar in both operational modes. The longer contact time of MPs with the active part of the microcosm (overall sand layer which contains the roots) and the enhanced O_2 diffusion during the trickling of the WW through the vertical bed can greatly intensify the sorption and biological processes. The observed differences on MPs elimination were related to the intrinsic characteristics of each compound, such as n-octanol/water partition coefficient and biodegradability.

The implementation of CW with recirculation as a pretreatment allowed for high reduction of DOM, TSS and NO_2^- from the effluents which improved the efficiency of MPs removal in subsequent photo-Fenton process. While the overall MPs removal of single CW and single photo-Fenton process reach 72% and 73%, the elimination was almost complete for the hybrid system (95%). This approach (combining phytoremediation and solar photo-Fenton at natural pH) offers an environmentally friendly solution for tertiary treatment in WWTP.

CRediT authorship contribution statement

Núria López-Vinent: conceptualization, data curation, writing (original draft & review and editing), visualization and project administration. **Ana Piera Santacruz:** investigation, writing (original draft & review and editing). **Albert Sales Alba:** investigation, writing (original draft & review and editing). **Alberto Cruz-Alcalde:** conceptualization, Writing (review and editing) and project administration, supervision. **Iván Díaz Redondo:** investigation, writing (original draft & review and editing). **Sandra P é rez Solsona:** Writing (review and editing), funding acquisition and project administration. **Carme Sans Mazón:** Writing (review and editing), funding acquisition and project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2023.110834.

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