Removal of emerging pollutants by a 3-step system: Hybrid digester, vertical flow constructed wetland and photodegradation post-treatments

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HIGHLIGHTS

- The removal of nine persistent pollutants was evaluated using a 3-step system.
- Over 99 % removal of four drugs and caffeine was done in biological steps.
- Photodegradation was effective for some biologically refractory compounds.
- Photodegradation with sunlight and TiO_2 resulted in a promising post-treatment.
- Bisphenol A removal was 80 % in biological steps but not completed by photodegradation.

GRAPHICAL ABSTRACT
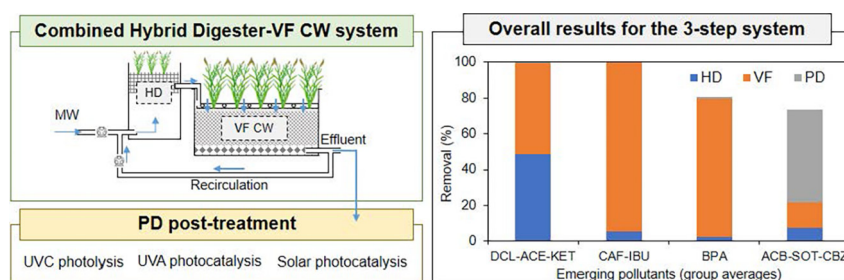
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ABSTRACT

The removal of emerging pollutants from municipal wastewater was studied for the first time using a three-step pilot-scale system: 1) hybrid digester (HD) as first step, 2) subsurface vertical flow constructed wetland (VF) as second step, and 3) photodegradation (PD) unit as third step or post-treatment. The HD and VF units were built and operated in series with effluent recirculation at pilot scale. For the PD post-treatment, three alternatives were studied at lab-scale, i) UVC irradiation at 254 nm (0.5 h exposure time), ii) UVA irradiation at 365 nm using a TiO_2-based photocatalyst and iii) sunlight irradiation using a TiO_2-based photocatalyst, the last two for 1 and 2 h. Alternative iii) was also tested at pilot-scale. Degradation of nine compounds was evaluated: acetaminophen (ACE), caffeine (CAF), carbamazepine (CBZ), ketoprofen (KET), ibuprofen (IBU), diclofenac (DCL), clofibric acid (ACB), bisphenol A (BPA), and sotalol (SOT). Overall, the HD-VF-UVC system completely removed (>99.5 %) ACE, CAF, KET, IBU, DCL and ACB, and to a lesser extent SOT (98 %), BPA (83 %) and CBZ (51 %). On the other hand, the HD-VF-UVA/TiO_2 system (at 2 h) achieved >99.5 % removal of ACE, CAF, KET, IBU and DCL while ACB, BPA, CBZ and SOT were degraded by 83 %, 81 %, 78 % and 68 %, respectively. Working also at 2 h of exposure time, in summer conditions, the HD-VF-Sol/TiO_2 system achieved >99.5 % removal of ACE, CAF, KET, IBU, DCL and ACB, and to a minor extent BPA (80 %), SOT (74 %) and CBZ (69 %). Similar results, although slightly lower for SOT (60 %) and CBZ (59 %), were obtained in the pilot sunlight plus TiO_2 catalyst unit. However, the use of sunlight irradiation with a TiO_2-based photocatalyst clearly showed lower removal efficiency in autumn conditions (i.e., 47 % SOT, 31 % CBZ).

1. Introduction

Nowadays there is widespread concern about the occurrence and bioaccumulation of new substances known as emerging pollutants (EP). EP were defined as those chemical compounds that are currently not included in routine monitoring programmes at EU level but appear as a potential threat to human health and the environment, and for which there is no regulation yet (EP&C, 2013). The presence of EP in the environment is due to its direct emission by the population (like most pharmaceuticals) or by its emission from various human activities (agriculture, livestock, industry, waste treatment facilities, etc.). In addition, the concentrations reached of some EPs

are also conditioned by their potentially persistent character. Conventional wastewater treatment plants (WWTP) are not designed to remove these substances, most EP pass through them with little or no transformation and they are eventually discharged into the aquatic environment (Luo et al., 2014; Tran et al., 2018). EP concentration levels depend on the source of pollution (cities, agriculture, livestock, industry, hospitals), site constituents such as sediments and vegetation, and on the environmental conditions (physicochemical conditions, weather conditions, etc.) (Gogoi et al., 2018). EP may be classified into different groups, such as hormones, pesticides, surfactants, endocrine disruptors, pharmaceutically active compounds and personal care products, and industrial additives, among others.

In recent years, the removal of EP from municipal wastewater (MW) has been studied using a wide variety of technologies. However, no single working technology has yet been found that can effectively remove the many different EP that wastewater may contain, so hybrid systems must be used (Dhangar and Kumar, 2020). Conventional WWTP may combine biological treatment (such as activated sludge) with a tertiary oxidation treatment such as ozonation or UV light radiation, or adsorption (usually with activated charcoal) for EP removal (Saidulu et al., 2021; Taoufik et al., 2020). However, design, installation and maintenance of such infrastructure is not economically viable for the poorest countries, nor it is for decentralized treatment in areas of scattered population. Therefore, nature-based solutions have emerged as an alternative, among them, constructed wetlands (CW), which have become an eco-viable treatment under these premises (Kataki et al., 2021). Similar EP removal performance has been obtained in both CW and WWTP. Diverse microenvironments coexist in CW, whereas WWTP are based on a smaller number of degradation pathways (Ávila et al., 2010). On the other hand, CW have some disadvantages such as clogging or the requirement of a large surface area. In this regard, anaerobic/anoxic digesters (AD) have been used as CW pre-treatment with the aim of reducing the suspended solid and organic load rate, thus decreasing the required footprint (Álvarez et al., 2008; De la Varga et al., 2013; Gonzalo et al., 2017b). On the other hand, the presence of the AD may contribute to the elimination of EP that degrade better under anaerobic conditions or that require a low redox potential environment (Reyes-Contreras et al., 2011).

EP removal mechanisms in CW are complex and simultaneous. Whether some processes predominate over others depends mainly on CW design (Ilyas and van Hullebusch, 2020; Luo et al., 2014). The main removal mechanisms reported were sorption and biodegradation in subsurface flow (SSF) CW and photodegradation (PD) in surface flow (SF) CW (Saidulu et al., 2021). Recent literature shows the removal efficiencies of different EP through CW. For example, an effective removal of endocrine disrupting compounds, such as for bisphenol A (between 75 and 100 % removal), was reported. Removal of pesticides was more effective in SF while removal of personal care products predominated in horizontal SSF (HF) rather than in vertical SSF (VF) CW. With respect to pharmaceutically active compounds, the trend in analgesic removal efficiency followed the order SF > HF > VF, while the trend in antibiotic removal was in the order HF > SF > VF (Dhangar and Kumar, 2020).

Although CW have a high capacity to degrade certain EP, simultaneous removal of different EP requires effective technological solutions under different operating conditions (Mohapatra and Kirpalani, 2019). For this purpose, the implementation of Advanced Oxidation Processes (AOP) as a post-treatment to CW emerges as an interesting combination. This group of chemical-oxidative processes is characterised by the generation of hydroxyl radicals (HO•) (Ma et al., 2021). HO• is the strongest possible oxidant in water and unselectively oxidises and mineralises almost all organic molecules into CO_2 and inorganic ions, at reaction rates that are close to the diffusion-control limit. In particular, heterogeneous photocatalysis is an AOP in which a metal oxide semiconductor, immersed in water and irradiated with near UV light (at $\lambda < 385$ nm), leads to the formation of HO•. Titanium dioxide (TiO_2) is the most widely used catalyst due to its photostability, non-toxicity, low cost, and insolubility in water under most environmental conditions. In addition, TiO_2 has a great ability to absorb UV–Vis light, such as sunlight, which is abundant and free (Canle

et al., 2017). Heterogeneous photocatalysis may be appropriate as a post-treatment step to the combined AD-CW system, with the aim of removing the most recalcitrant EP.

Combining CW and TiO_2-based photocatalysis is a new approach. The literature on the combined CW-TiO_2 system is scarce and limited to laboratory-scale studies. Even for most of the pollutants in this study, no publications were found. Cardoso-Vera et al. (2021) highlighted the combination of CW with photocatalysis post-treatment for the removal of recalcitrant compounds such as carbamazepine as a novel, environmentally friendly and effective strategy. Overall, the implementation of TiO_2-based photocatalysis as a post-treatment of CW effluent has resulted in higher effluent water quality (Liu et al., 2015). Nguyen et al. (2019) reported a successful reduction of organic matter and tetracycline through a surface flow CW system along with a photocatalytic system composed of TiO_2/α-Al_2O_3 catalyst and UVA radiation. Felis et al. (2016) concluded that the coupling a VF with TiO_2-photocatalysis induced by artificial sunlight could be a promising system to increase the removal efficiency of benzotriazole and benzothiazole. Therefore, there is a need for research on the combined photocatalysis system based on CW-TiO_2 and its potential for field-scale application.

Therefore, the aim of this study was the investigation of the removal of several EP present in MW by a three-step hybrid system at pilot scale: biological treatment in a combined AD-CW system, followed by heterogeneous photocatalysis post-treatment. The efficiency and possible removal mechanisms were assessed at each step according to the different physicochemical conditions. In addition, for the post-treatment step, the performance of heterogeneous photocatalysis with sunlight was compared with the results of photocatalysis with UVA light (at $\lambda = 365$ nm) and photolysis with UVC light (at $\lambda = 254$ nm).

2. Material and methods

2.1. Selected EP for system monitoring

The three-step system was evaluated by monitoring a set of nine selected EP. Two main criteria were followed to select the EP to be monitored: i) to include EP that are hardly removed by CW according to previous literature, and ii) to use EP that require different physicochemical conditions for their degradation. First, a list of compounds that presumably met some of the indicated criteria was elaborated after a literature review. Finally, after a discussion of the various practical aspects by the research team, the following pollutants were selected: acetaminophen (ACE), caffeine (CAF), carbamazepine (CBZ), ketoprofen (KET), ibuprofen (IBU), diclofenac (DCL), clofibric acid (ACB), bisphenol A (BPA) and sotalol (SOT). The chemical structure and physicochemical properties of the selected EP are summarised in the supplementary information (Fig. S1).

2.2. Description and operational parameters of the combined (HD-VF)$_R$ system

The two-stage biological system, which consists of a hybrid (HD) digester followed by a VF, and was provided with recirculation (R) of the VF effluent to the HD inlet, was labeled as (HD-VF)$_R$. (Fig. 1). The combined (HD-VF)$_R$ system at pilot plant scale was placed close to the Faculty of Sciences (A Coruña, Spain). The design of the HD consists of an up-flow sludge bed anaerobic zone at the bottom and an anaerobic-aerobic planted filter at the top. The sludge bed zone at the bottom always remains flooded while the planted filter was flooded during the operating period and drained during the resting period, following the flow regime of the subsequent VF unit. The HD had a diameter of 0.7 m and a height of 0.65 m, being the overall active volume of 0.222 m^3 and surface area of 0.385 m^2. The granular medium of HD was gravel with a particle size between 0.5 and 16 mm (d_{60} 8.5 mm, Cu 1.8). The anaerobic filter was planted with *Phragmites australis*.

Different type and particle size of materials were used in the VF (surface area of 3 m^2): coarse gravel of 20 mm in the bottom (drainage layer, 10 cm height), coarse sand of 1–3 mm in the main filter layer (80 cm height) and
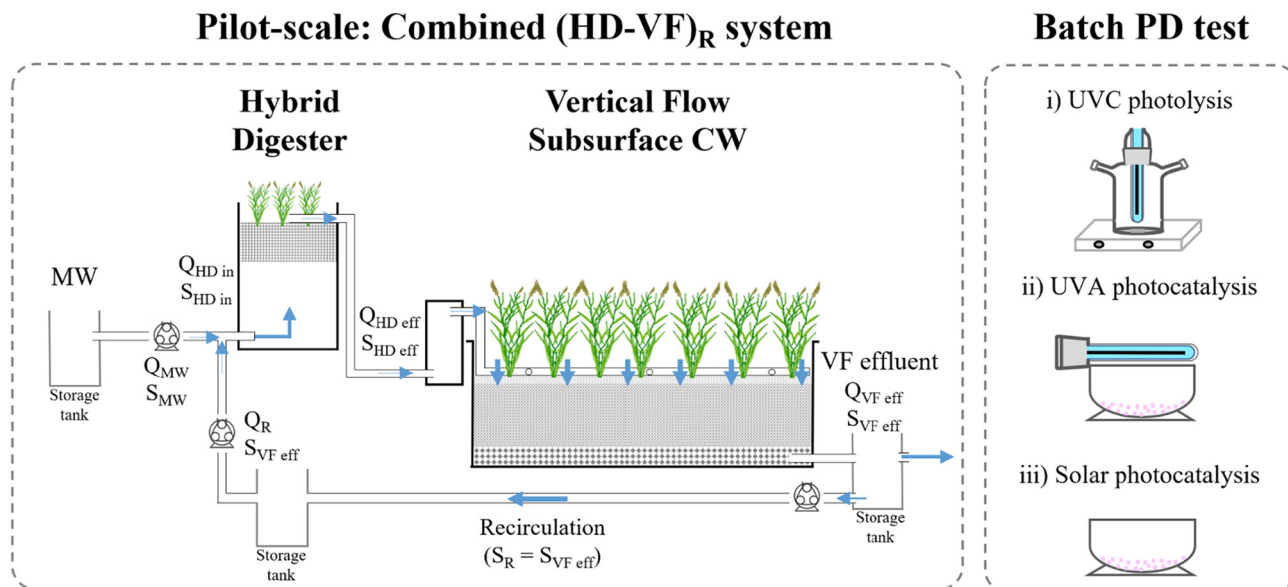
Pilot-scale: Combined (HD-VF)$_R$ system   ## Batch PD test

Fig. 1. Scheme of the combined (HD-VF)$_R$ system at pilot scale and different photodegradation post-treatments.

fine sand of 0.5–2 mm in the upper surface layer (10 cm height). The aim of the fine sand layer at the top of the bed was to increase the treatment efficiency, as demonstrated by previous studies (Torrijos et al., 2016; Carballeira et al., 2021). Carballeira et al. (2021) found that adding that layer of fine sand resulted in a significant improvement in removal efficiency, doubling the water retention time and increasing removal rates while infiltration rates remained high enough for an operation without clogging. The VF unit was also planted with *Phragmites australis*. Other characteristics of the VF pilot plant have been given previously (Carballeira et al., 2021).

The MW was pumped from the storage tank to the HD and the HD effluent was introduced by gravity and intermittently by a self-priming siphon, being spread over the surface of the VF. In addition, part of the final VF effluent was recirculated to the HD inlet where it joined the influent MW. The feeding strategy followed a weekly routine consisting of 4 days of feeding and 3 days of rest. This combined biological system, had been in operation for 182 days, treating MW consisting of a mixture of wastewater from a nearby faculty, stormwater, and runoff water. 77 days corresponded to the start-up. Fortification of MW with EP was carried out from day 78 (after the start-up period) and was maintained until the end of the study. Sampling began two weeks after the start of EP fortification.

Table 1 shows the main characteristics applied in the three operational campaigns. Other characteristics (pH, temperature, dissolved oxygen and oxidation-reduction potential for the influent and effluent of each unit) are available in the supplementary information (Table S1). Each campaign was defined according to the MW flow treated and the recirculation ratio. Thus, during campaign I, a daily flow of 554 ± 68 L/day was treated with a recirculation ratio of 0.86; in campaign II, the combined system

received the highest MW flow (790 ± 8 L/day) and recirculation ratio of 0.67, while during campaign III the lowest daily flow (342 ± 36 L/day) with the highest recirculation ratio (1.49) was treated. The HD operated at hydraulic retention time (HRT) between 6.7 and 15.6 h. The unsaturated VF received the HD effluent intermittently, from 6 to 12 pulses per day, operating at a hydraulic loading rate (HLR) between 114 and 263 mm/day (Table 1). The surface loading rate ranged from 52 to 123 g COD/m^2·day for the overall system, being clearly lower for the VF unit.

2.3. Characteristics of the photodegradation post-treatments applied

After biological treatment, samples of the VF effluent were post-treated by photodegradation. Batch tests were carried out at lab-scale following three alternatives: i) photolysis with UVC light, ii) heterogeneous photocatalysis with UVA light, and iii) heterogeneous photocatalysis with sunlight. Photolysis (UVC) took place in a glass photoreactor of 8 cm diameter and 500 mL active volume. A quartz-jacketed irradiation UVC (Heraeus TNN 15/32 low-pressure Hg-vapor lamp, with $\lambda_{max} = 254$ nm) was immersed in the reactor, which was kept under stirring during the treatment. Direct photolysis was only performed with UVC, since this radiation typically provides a much faster removal of organic pollutants than UVA photolysis (Celeiro et al., 2017). Heterogeneous photocatalysis experiments were performed in borosilicate vessels with a flat round bottom (14 cm diameter), where 20 g of a TiO$_2$-based photocatalyst pellets were placed at the beginning of the experiment, and the VF effluent (500 mL) was added to reach a total height of 2.5 cm. Photocatalytic pellets (2 mm diameter, 5–15 mm long cylinders, with density ca. 4.0 g/mL) were prepared according to our patent application PCT/ES2021/070940, using 10 % a local clay (42 % illite, 28 % kaolinite, 20 % quartz, 10 % 2:1–2:1:1), obtained from *Cerámicas El Progreso* (Malpica de Bergantiños, A Coruña, Spain) without further treatment, and 90 % Degussa Aeroxide P25 TiO$_2$. A second irradiation lamp (Heraeus TQ 150 medium-pressure Hg-vapor lamp, with $\lambda_{max} = 365$ nm) was placed horizontally above the catalyst for the photocatalysis post-treatment (UVA/TiO$_2$), while in lab-scale solar photocatalysis (Sol/TiO$_2$) experiments, this reactor was directly exposed to sunlight radiation. In the case of heterogeneous photocatalysis, together with solar radiation, the UVA lamp option was chosen taking into consideration the absorption properties of P25 TiO$_2$. This photocatalyst shows a band gap around 3.20–3.25 eV (Fonseca-Cervantes et al., 2020). An exposure time of 0.5 h was applied for UVC treatment, while times of 1.0 and 2.0 h were applied for UVA/TiO$_2$ and Sol/TiO$_2$ treatments.

Table 1
Operational parameters for the combined (HD-VF)$_R$ system.

Campaign	I	II	III
Operation time (days)	34	25	46
Combined (HD-VF)$_R$ system			
Q_{MW} (L/day)	554 ± 68	790 ± 8	342 ± 36
Recirculation ratio (Q_R/Q_{MW})	0.85	0.67	1.49
HLR (mm/day)	163.5	233.5	100.9
Surface loading rate (g COD/m^2·day)	73.7	123.1	51.5
Hybrid digester			
HRT$_{HD}$ (hours)	9.5	6.7	15.6
Vertical SSF CW			
HLR (mm/day)	184.5	263.4	113.9
Surface loading rate (g COD/m^2·day)	41.4	35.3	19.8

Heterogeneous photocatalysis with sunlight was also tested at pilot plant scale, by using a methacrylate pond with a surface area of 1 m^2 and water layer depth of 5 cm (i.e., a volume of 50 L). Two kilograms of TiO$_2$-based photocatalyst were placed at the bottom of the pond, which was exposed to sunlight. The pilot post-treatment unit with sunlight (p. Sol/TiO$_2$) was designed and scaled with the aim of fitting to the combined system (HD-VF)$_R$ of the pilot plant, which had a capacity for 3–4 equivalent inhabitants (EI) and a reference flow of 600 L/day. Based on the lab-scale results and establishing a maximum water depth of 5 cm and a daily reference campaign of 12 h of sunlight, it was estimated that an area of 1 m^2 was required to treat the effluent of the HD-VF installation (600 L/day). This results in a retention time in the range of 1.0 h. With this in mind, the evolution of the performance was determined by applying exposure times of 0.5, 1.0 and 2.0 h.

All solar experiments (both Sol/TiO$_2$ and p.Sol/TiO$_2$) were performed during the daily peak of maximum radiation (13.30–15.30 GMT) at A Coruña, Spain (43°19′36″ N, 8°24′33″ W). Sol/TiO$_2$ experiments were conducted in June, July and autumn (from late September to mid-October), corresponding to campaigns I, II and III, respectively, while p. Sol/TiO$_2$ experiments were carried out on the same days but only for campaigns II and III. Solar radiation was high and uniform in summer conditions (June and July, campaigns I and II, with an average of 7492 ± 844 W/m^2) but low and variable in autumn conditions (campaign III, 2825 ± 2173 W/m^2).

2.4. Sampling and analysis of EP

To ensure that the samples correspond to steady state, sampling campaigns began after at least one week of applying the change of conditions to the new campaign of operation and was extended for the next two weeks. Daily grab samples of the influent and effluents of each biological unit of the combined (HD-VF)$_R$ system were taken (4 per week, corresponding with the 4 days of each feeding cycle) and were integrated in a unique weekly sample. In this way, two integrated samples per operational campaign were obtained for analysis.

Aliquots (500 mL) from the weekly integrated sample of the VF effluent were taken to test each different PD post-treatment in the laboratory. On the other hand, batches of 50 L of VF effluent were used for the p.Sol/TiO$_2$ treatment on a pilot scale. Samples for EP analysis were obtained after each exposure time.

Following these procedures, a total of 64 samples were collected for EP analysis. This included 18 samples from (HD-VF)$_R$ system, 30 samples from the laboratory PD tests (duplicate sampling for 3 campaigns in each system and exposure time), and 16 samples from the p.Sol/TiO$_2$ system (duplicate sampling for 2 campaigns and 4 exposure times each).

All samples were immediately filtered (0.7 μm pore size glass microfibre filter) and stored at −20 °C until EP analysis. At the time of analysis, samples were previously defrosted and again filtered through a 0.2 μm hydrophilic Teflon filter. The determination of EP was carried out by HPLC/HRMS (Thermo Scientific LTQ Orbitrap) with detection by high resolution mass spectrometry after chromatographic separation. HPLC conditions were as follows: Column Kinetex 2.6 μm XB-C18 100A 100 mm × 2.10 mm, column temperature 40 °C, injection volume 100 μL, flow rate 200 μL/min, mobile phase A: aqueous solution 1 mM ammonium acetate plus 0,1 % HCOOH, mobile phase C: acetonitrile 0,1 % HCOOH. HRMS detection conditions were: capillary voltage 4500 V (ESI positive) and −3500 V (ESI negative), scan range: 100–800 amu, capillary temperature: 300 °C. Samples were diluted 1:1 with mobile phase. Compounds were identified by their retention time, the presence of a qualifier ion and a quantifier ion. The resolution was higher than 30,000 and the mass accuracy lower than 1 pp. The limit of quantification (LOQ) was below 0.11 μg/L, with the following individual values (μg/L): ACE, 0.09; CAF, 0.07; CBZ, 0.11; KET, 0.07; IBU, 0.07; DCL, 0.06; ACB, 0.10; BPA, 0.10; SOT, 0.07.

Validation of the method was performed with pattern overloads on stream water samples. Overloads were performed at 3 concentration levels (0.10, 1, 200 μg/L) and a minimum of 10 times each level. The average accuracy of the method expressed as recovery was 87–98 % and the reproducibility ranged between 8 and 10 % as relative standard deviation.

As a quality control, low-level and high-level concentration controls were run into each sample batch. The accepted accuracy values for a set of analysis to be considered correct must be between 80 and 120 %. For the control of procedures and equipment, the laboratory is ISO 9001: 2008 certified.

2.5. EP concentration in raw wastewater and fortification

Table 2 shows the average concentration of selected EP in raw MW that reached the pilot plant on campus, corresponding to three samples obtained during the study. The major EP found were ACE (between 8 and 222 μg/L), CAF (86–377 μg/L) and IBU (48–53 μg/L) and in minor proportion BPA (0.9–4.1 μg/L). The rest of EP (CBZ, KET, DCL, ACF and SOT) were not detected. However, in previous studies with MW from a conventional municipal WWTP (Gonzalo et al., 2017a), it was observed that all the selected EP were presented in quantifiable quantities, due to the contribution from a much higher population. This suggests that the wastewater generated on campus has a very different EP content profile from that of an urban effluent from the nearby city, probably due to the, on average, younger university population, with lower medical drug consumption apart from some over-the-counter pain relievers. In particular, it is characterised by undetectable amounts of various EP that would be present in the city's wastewater. Thus, in order to ensure the presence of all EP selected for research, during the study period a supplementary amount of each EP was added to the raw MW. The fortification procedure consisted of spiking the target compounds previously dissolved in methanol in a 25 L bottle of tap water with a concentration of 1 mg/L for each compound freshly prepared weekly. Some of the compounds (ACE (100 mg/mL oral solution, *Apiretal* by ERN), CBZ (200 mg tablets, by Normon), KET (50 mg/mL injectable solution, *Orudis* by Sanofi), DCL (25 mg/mL injectable solution, *Voltaren* by Novartis), IBU (40 mg/mL oral suspension, *Dalsy* by Mylan), and SOT (80 mg tablets, *Sotapor* by Bristol-Myers Squibb)) were sourced from commercial pharmaceutical products while others (CAF (>99 %, Merck), BPA (≥ 99 %, Sigma-Aldrich), and ACB (97 %, Sigma-Aldrich)) were purchased as chemical standards. From this stock solution, the necessary volume (i.e.: 5 mL per L of MW, or 0.5 % vol.) was taken and added to obtain a final concentration of 5 μg/L of each compound in the MW storage tank. Approximately 4 mg/L of methanol was added to the MW using this procedure. Finally, the actual EP influent concentration was obtained by analysing the composite samples taken after fortification and homogenisation by agitation.

Therefore, the average concentration of each EP in the influent to the pilot plant is shown in Table 2. CAF, ACE and IBU were the compounds with the highest overall mean concentrations (>40 μg/L) while KET, BPA, SOT and CBZ were in 5–20 μg/L concentration range. The influent concentration of DCL was lower than theoretical dosage (<5 μg/L), possibly due to the dispersion behaviour of the drug used or its adsorption on the organic matter sedimented in the feed tank. The mean concentrations for the whole period study were maintained with coefficients of variation below

Table 2

Mean concentration (± SD) of selected EP present in raw MW and fortified MW.

Selected EP	Raw MW (μg/L)	Fortified MW (μg/L)
ACE	117.2 ± 107.1	93.8 ± 23.9
CAF	185.1 ± 165.9	147.5 ± 50.0
CBZ	<LOQ	5.9 ± 1.9
KET	<LOQ	13.3 ± 8.9
IBU	50.1 ± 2.7	44.6 ± 1.3
DCL	<LOQ	2.4 ± 0.9
ACB	<LOQ	4.4 ± 0.8
BPA	2.9 ± 1.8	14.2 ± 3.7
SOT	<LOQ	9.3 ± 3.1
Number of samples[a]	6	6

[a] Corresponding to 2 integrated samples of each operational campaign.

60 % for each compound (30.1 % on average), indicating that, in terms of EP content, the influent composition was quite similar throughout the study.

2.6. Data analysis and calculations

The equations below were used to obtain the percentage removal efficiency (RE) for each unit and for the overall system. Calculations for the biological treatment units with recirculation were obtained from mass balances making use of recirculation flow as variable.

Combined $(HD-VF)_R$ system:

$$\%RE_{(HD-VF)R} = \frac{S_{MW} - S_{VF\,eff}}{S_{MW}} \cdot 100$$

Hybrid Digester:

$$\%RE_{HD} = \frac{Q_{HD\,in} \cdot (S_{HD\,in} - S_{HD\,eff})}{Q_{MW} \cdot S_{MW}} \cdot 100$$

where $Q_{HD\,in} = Q_{MW} + Q_R$

$$S_{HD\,in} = \frac{(Q_{MW} \cdot S_{MW} + Q_R \cdot S_R)}{Q_{MW} + Q_R}$$

Vertical Flow CW:

$$\%RE_{VF} = \%RE_{overall} - \%RE_{HD}$$

Photodegradation post-treatments:

$$\%RE_{PD} = \frac{S_{VF\,eff} - S_{PD}}{S_{VF\,eff}} \cdot 100$$

Overall three-step system:

$$\%RE_{overall} = \%RE_{(HD-VF)R} + \left(100 - \%RE_{(HD-VF)R}\right) \cdot \frac{\%RE_{PD}}{100}$$

where Q_{MW} = volumetric flow of MW; Q_R = volumetric flow of recirculation; $Q_{HD\,in}$ = combined MW and recirculation flow rate; S_{MW} = MW concentration; $S_{VF\,eff}$ = VF effluent concentration; S_R = concentration in recirculation stream ($S_R = S_{VF\,eff}$); $S_{HD\,in}$ = influent concentration to HD; $S_{HD\,eff}$ = HD effluent concentration; S_{PD} = PD effluent concentration in any UVC, UVA/TiO$_2$ and Sol/TiO$_2$ treatment.

The %RE was obtained for each sampling week by applying the above equations. From these weekly removal percentage values, the mean per campaign ($n = 2$) was obtained as well as the mean per step for both each campaign ($n = 2$) and for the entire study ($n = 6$).

3. Results and discussion

3.1. Removal efficiency of EP by the combined $(HD-VF)_R$ system

The removal efficiency of each EP was obtained from the influent and effluent concentration to the biological treatment units of the $(HD-VF)_R$ treatment system (Table S2) after the application of equations in Section 2.6. The overall results are shown in Fig. 2. For the overall (HD-
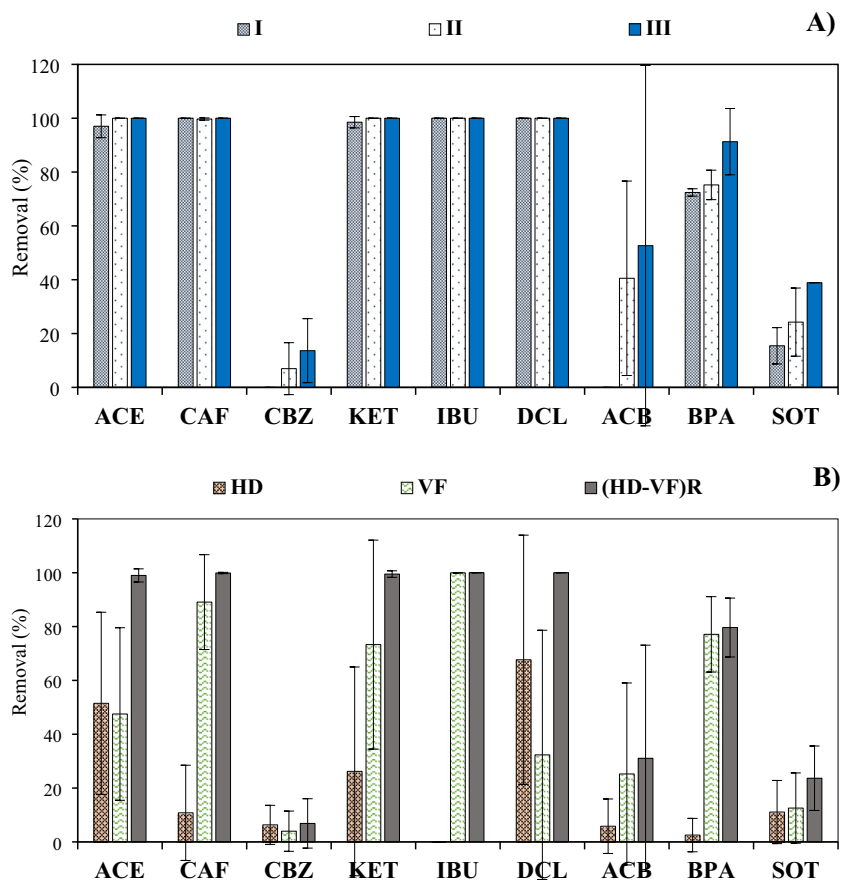

Fig. 2. Concentration removal efficiency of EP by the combined $(HD-VF)_R$ system: A) mean cumulative removal during campaigns I, II and III ($n = 2$); B) overall mean removal at each step and the whole system ($n = 6$).

VF)$_R$ system, the removal of ACE, CAF, KET, IBU and DCL achieved the highest values (above 99 %), while BPA was removed in moderately high percentages (80 %). ACB and SOT were eliminated at about 31 % and 24 % respectively, and CBZ was the compound with the lowest removal (7 %) (Fig. 2B).

As indicated, the parameters that defined each operating campaign were the influent flow and the recirculation ratio (Table 1). Nevertheless, these parameters had a reduced effect on the removal of selected EP (Fig. 2A). The increase in HLR from 164 mm/d (campaign I) to 234 mm/d (campaign II) slightly enhanced the removal of ACE, KET, BPA, CBZ and SOT (between 1 and 9 %) while the increase in ACB removal was remarkable (41 %). However, these differences were not significant due to the large variation of the samples analysed in each campaign. For the rest of the compounds no variation was observed (Table S2).

The best overall removal for ACB, BPA and SOT was achieved during campaign III, when the recirculation ratio doubled and the HLR was halved (Table 1). Due to the small number of samples per campaign, the strong variation between the analysed samples and the change of several operational variables, only a qualitative analysis of these results can be performed. Increasing the recirculation ratio could have a positive effect on EP removal, since recirculation has been shown to increase carbon and nitrogen removal efficiency (Torrijos et al., 2016). However, Gonzalo et al. (2017a) reported that increasing the recirculation ratio from 1 to 2 did not improve the EP removal efficiency operating at HLR of 68 mm/d in a HF-VF system at lab-scale. On the other hand, the difference in temperature values between campaigns was reduced, so it was not considered a determining parameter. Thus, the data analysis suggest that that the slightly higher removal efficiency of some EP (i.e., CBZ, ACB, SOT, BPA) observed during campaign III could be due to lower HLR.

The percentage reduction of concentration achieved in each biological unit throughout the study (average of the three campaigns) for each selected EP was also evaluated (Fig. 2B). The HD achieved the best removal for ACE (51.5 ± 33.8 %) and DCL (67.7 ± 46.3 %) while KET showed intermediate removal (26.2 ± 38.8 %). The removal of the rest of compounds in the HD unit was also highly variable but usually low, showing average values of about 11 % (CAF and SOT) or even below 6 % removal (CBZ, ACB, BPA and IBU). On the other hand, the VF received the selected EP that were not degraded in the HD. Thus, the VF unit contributed to the removal of ACE (47.5 ± 32.1 %), CAF (89.1 ± 17.6 %), KET (73.3 ± 38.8 %), IBU (100 ± 0.1 %), DCL (32.3 ± 46.3 %) and BPA (77.1 ± 14.0 %). In fact, for all these compounds, with the exception of BPA, the VF unit eliminated virtually 100 % of the received concentration. However, ACB, SOT and CBZ showed very low removal (below 25 %) in the VF unit.

3.2. Behaviour of each EP during combined (HD-VF)$_R$ treatment

Fig. 3 shows the percentage reduction of concentration for each of the selected compounds by operating campaigns for each step of the system. The behaviour of each individual compound is analysed below.

3.2.1. Acetaminophen

ACE was removed in both biological units (Fig. 3). In campaign I, the HD degraded moderately ACE (34 %) while in campaign II and III this percentage increased to 68 % to decrease again to 53 % in campaign III. Physicochemical properties of ACE (n-octanol-water distribution coefficient = 0.26 and biodegradation kinetic constant = 58–240 L/gSS·d according to Joss et al. (2006)) indicated its low probability of sorption onto sludge and its high biodegradability. In all campaigns, the VF unit contributed effectively to the removal of ACE, obtaining an overall removal of 99 % by the combined (HD-VF)$_R$ system. The fact that ACE was eliminated in both biological units is consistent with the premise that its degradation can happen in both anaerobic and aerobic environments (Chen et al., 2016; Yu et al., 2006). From the literature, ACE has been defined as a compound that is easily removed in WWTP (Kosma et al., 2010), so

the main mechanism of ACE removal can be attributed to biodegradation (Vo et al., 2019).

3.2.2. Caffeine

The VF was the main step where CAF was removed for all campaigns (Fig. 3). A little contribution was observed for the HD except in campaign II, where the removal efficiency was 23 %. According to Froehner et al. (2011), CAF is an easily degradable compound under both anaerobic and aerobic conditions. However, the poor contribution of the HD in CAF removal was also observed by Reyes-Contreras et al. (2011), who worked with an up flow anaerobic sludge bed digester and removed CAF by only 10–35 %. On the other hand, Carranza-Diaz et al. (2014) reported a percentage of 66 % of CAF removal and also Chen et al. (2016), He et al. (2018), Hijosa-Valsero et al. (2016) and Kahl et al. (2017) achieved >80 % CAF removal in HF (i.e., with predominantly anaerobic conditions). Furthermore, Nivala et al. (2019) noted that use of intensified CW with artificial aeration, partial saturation and subsequent filtration with unsaturated sand showed a higher removal efficiency than CW with anaerobic/anoxic environments (>70 %). Kahl et al. (2017) reported that aerobic conditions and low amounts of readily available carbon resulted in high removal of moderately to low biodegradable pollutants, such as CAF. These conditions probably exist in the present VF due to advanced hydrolysis in the anaerobic pre-treatment step (Álvarez et al., 2003). Furthermore, Hijosa-Valsero et al. (2016) studied the removal of several EP, including CAF, in seven different CW and concluded that adsorption on macrophyte roots could be an effective mechanism for its removal.

The predominant aerobic environment in VF appears to be the reason for removing practically all CAF. The high removal efficiencies (between 77 and 97 %) could be enhanced by particle size of filter media. Thus, in VF, Matamoros and Bayona (2006) reported that CAF was the compound with a removal efficiency of >80 % using gravel (0–4 mm) as filter material while de Oliveira et al. (2019) used fine sand (0–1 mm) and CAF removal efficiency improved to 97 %. In the present VF, sand (1–3 mm) was used as the main filter material, while fine sand of 0.5–2 mm was used in the upper surface layer. In addition, the high water solubility of CAF leads to the assumption that degradation, both by microbial action and plant uptake, would be faster in summer than in winter (Zhang et al., 2014). In the present study, the temperature ranged 18 °C to 22 °C (Table S1), which is consistent with the high CAF removal efficiency observed.

3.2.3. Ketoprofen

The KET elimination has always been 100 % in the two-stage biological system. In campaigns I and III it was produced almost exclusively in VF, while in campaign II, approximately 64 % of the KET was eliminated by HD (Fig. 3). The irregular behaviour in HD unit did not seem to be related to the operating conditions, which can be considered similar in campaigns I and II but with higher loading rates in campaign II (Table 1). However, as discussed below, absorption may have contributed to the removal of KET in the HD unit during campaigns I and II.

In the case of VF, HF or hybrid CW, the main removal pathway for KET is biodegradation, according to the literature (Chen et al., 2016; Francini et al., 2018; Zhang et al., 2012a, 2018). Zhang et al. (2018) reported higher removals in SF than in SFF since KET is easily photodegraded. However, these authors observed a negative correlation between KET and dissolved oxygen, ammonium, and COD, thus suggesting that anaerobic biodegradation could be another removal process in CW. Reyes-Contreras et al. (2011) reported that an up flow anaerobic sludge bed digester was more efficient in winter than in summer for the removal of KET (not exceeding 30 % removal in both seasons). Although anaerobic digestion is more efficient at higher temperatures, these authors found that adsorption on biomass was the main removal mechanisms in winter. Literature on the behaviour of KET in VF is scarce. Gonzalo et al. (2017a) reported a KET removal of 43 % in a lab-scale VF. According to Urase and Kikuta (2005), the removal of acidic pharmaceutically active compounds (such as IBU and KET) was strongly affected by pH, where these authors obtained the highest removal efficiencies in acidic environments at pH between 5 and 6. In the present
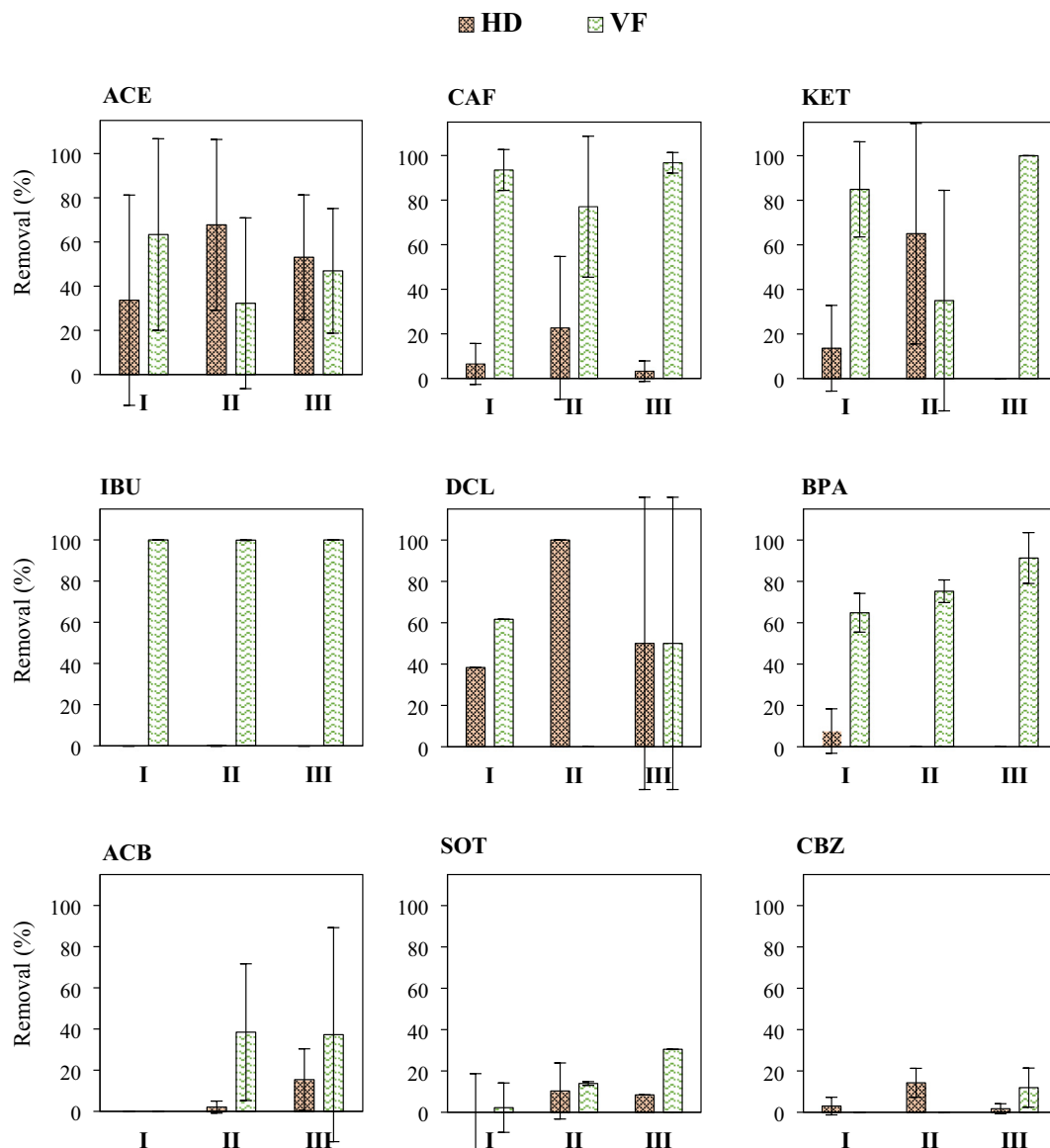
Fig. 3. Contribution of each biological unit to EP concentration removal ($n = 2$ per campaign I, II and III; HD: hybrid digester, VF: vertical flow CW).

study, the pH in the VF was acidic (values between 5.5 and 6.6 during the three campaigns) as a consequence of the nitrification processes (see Table S1), a factor that may have contributed to the high efficiency observed.

3.2.4. Ibuprofen

As shown in Fig. 3, IBU was completely removed from the VF unit. This occurred in all campaigns. The non-contribution of the HD in its degradation can be attributed to the fact that IBU is a biodegradable compound but only under aerobic conditions (Hijosa-Valsero et al., 2011, 2010; Quintana et al., 2005). Alvarino et al. (2014) reported a recalcitrant behaviour of IBU (removal efficiency <15 %) in an up flow anaerobic sludge bed digester operating at HRT of 1 day. In addition, Nivala et al. (2019) observed that while in a conventional HF, which operated at 3 ± 2 mg O_2/ L and -220 ± 41 mV, IBU was removed by 85 %, in other intensified CW, which operated at values higher than 5 mg O_2/L and 88 mV, was removed by 96–99 %. Besides microbial degradation, the removal of IBU could also be attributed to plant uptake (Zhang et al., 2017). Zhang et al. (2018) treated synthetic wastewater in a lab-scale VF and demonstrated that the increase in IBU degradation kinetics was influenced by the presence of plants, reaching high yields (between 82 and 97 % of IBU removed).

Thus, Ilyas and van Hullebusch (2020) concluded that the highest performance in terms of IBU removal was found in VF (mean efficiencies of 79 ± 24 %) compared to HF (53 ± 27 %) as aerobic biodegradation is the main removal process.

3.2.5. Diclofenac

Irregular behaviour was observed in the elimination of DCL (Fig. 3). The HD was responsible for 38 %, 100 % and 50 % removal in campaigns I, II and III, respectively. On the other hand, the VF was able to remove the remaining DCL in all campaigns, so the combined system $(HD\text{-}VF)_R$ always achieved the complete removal of DCL.

Several authors have indicated that sorption processes may play an important role in the observed elimination of EP during primary and secondary treatment in WWTP (Rout et al., 2021; Tran et al., 2018). This could be the case for DCL, which shows middle values for the n-octanol-water distribution coefficient (1.17) and water distribution coefficient (up to 321 L/kg SS) (Rout et al., 2021). According to Tran et al. (2018), DCL also shows low to moderate biodegradability rates (<10 L/g SS·L). In the present study, in addition to progressive adaptation to biodegradation, absorption may have contributed to DCL elimination in the HD unit during campaigns I and II. Accumulation during these campaigns I and II could lead to

saturation of the absorption capacity, and the reduction of the flow during the campaign III could lead to favourable conditions for desorption, which would explain the lower percentages of elimination during campaign III in the HD unit.

According to the review by Ilyas and van Hullebusch (2020), the removal efficiency of DCL was low to moderate in VF (50 ± 17 %), HF (39 ± 24 %) and hybrid CW (56 ± 32 %). Kimura et al. (2005) demonstrated that the presence of chlorine in DCL structure cased its persistence under biological treatment. Ilyas and van Hullebusch (2020) found studies in which a high redox potential could promote DCL removal by aerobic biodegradation (Hijosa-Valsero et al., 2011, 2010) while other research suggests that anaerobic/anoxic conditions could favour its removal (Zwiener and Frimmel, 2003). Thus, the slightly higher removal efficiency obtained through hybrid CW could be explained by the coexistence of anaerobic and aerobic environments (Ávila et al., 2015; Kahl et al., 2017; Nivala et al., 2019). Hence, our results showed that the combination of the HD and the VF resulted in high removal efficiencies.

3.2.6. Bisphenol A

The VF was responsible for the observed removal of BPA, which reached removal efficiencies ranging from 65 to 91 %. BPA elimination rates were highest during campaign III, in which the highest recirculation ratio and the lowest loading rate occurred. According to literature, aerobic biodegradation is the main mechanism of BPA removal (Ávila et al., 2015, 2014, 2013), in agreement with the observations of the present study. However, Ávila et al. (2015) obtained a 44 % removal in a VF and a 19 % removal in a HF. Thus, these authors indicated that multiple mechanisms could be related to BPA degradation, which would vary significantly over time (Ávila et al., 2010).

In addition, the high removal efficiency obtained in the present study could be related to the particle size used in the filtering media (fine sand 0.5–3 mm). This hypothesis is in agreement with Ávila et al. (2014), who reported that a larger particle size in the VF bed (4–8 mm) resulted in lower removal efficiencies compared to the use of a smaller particle size (1–3 mm). Gonzalo et al. (2017a) also reported reduced BPA removal using sand of 1–4 mm particle size.

3.2.7. Refractory compounds to biological degradation: ACB, SOT and CBZ

After biological treatment, ACB, SOT and CBZ behaved as recalcitrant compounds (Fig. 3). Thus, ACB was hardly removed by the HD and VF units in this study. Considering the overall average removal of ACB, the HD removed 5.8 % while the VF responded with a removal of 25.2 % (Fig. 3). Although highly variable, the observed removals for ACB were low, which is consistent with the literature regarding its non-biodegradable and refractory nature (Dordio et al., 2010; Matamoros

et al., 2008; Zhang et al., 2012b, 2012a). Zhang et al. (2012a) concluded that the presence of plants in CW significantly improved the degree of ACB removal. This could be the reason for the greater elimination observed in the present study during campaigns II and III compared to campaign I. On the other hand, Cardinal et al. (2014) found that photolytic processes occurring in a SF were the mechanisms responsible for ACB removal.

If behaviour of SOT is analysed, it has also observed in Fig. 3 how SOT showed a low removal efficiency in the combined (HD-VF)$_R$ system (removal efficiencies between 16 and 39 % in all three campaigns). The unit that contributed most to its elimination was the VF. According to Li et al. (2014), SOT appeared as a low removal compound in hybrid CW (around 30 %) and in conventional WWTP (between 26 and 48 %). Furthermore, Mathon et al. (2019) classified SOT as a medium photodegradable compound. Thus, the removal of SOT was mainly achieved under PD processes, which are evaluated in the following Section 3.3.

Finally, neither the HD nor the VF were effective in CBZ removal (Fig. 3). According to the literature, CBZ is persistent in aerobic environments while reductive transformation seems to be possible to some extent (König et al., 2016). In typical biological treatment in WWTP, the gradual release of adsorbed CBZ in sludge can lead to an increase in CBZ concentration at the discharge (Jelic et al., 2011). Nivala et al. (2019) found that in conventional WWTP only 12 % of CBZ was removed while the percentage given by Tran et al. (2018) in their review was below 20 %. The low observed value of biodegradation kinetic constant during activated sludge processes (0.005–0.389 L/gSS·d according to Tran et al. (2018)) classified CBZ as a recalcitrant compound to biodegradation processes and therefore its low removal in the HD and VF was to be expected. Verlicchi and Zambello (2014) concluded that CW operating as secondary treatment, CBZ showed low removal efficiencies in SSF and SF although performance was slightly better in SF (i.e., 36 % in SF versus 23–25 % in SSF).

3.3. Photodegradation of remaining EP after biological treatment

3.3.1. Lab-scale experiments

As indicated, CBZ, ACB and SOT were the most recalcitrant compounds during treatment in the combined (HD-VF)$_R$ system. In addition, BPA in the (HD-VF)$_R$ system was also partially eliminated in all campaigns. Thus, these compounds were available at concentrations well above the LOQ for the treatment monitoring in subsequent PD steps. Fig. 4 represents the removal percentage of each compound in laboratory-scale PD experiments.

Sol/TiO$_2$ post-treatment experiments included in Fig. 4 were limited to those performed during campaigns I and II (n = 4). Experiments conducted during campaign III (autumn, n = 2) yielded very poor results without removal of ACB and SOT and 27 % reduction in CBZ removal compared to campaigns I (June) and II (July). It should be noted that photocatalysis
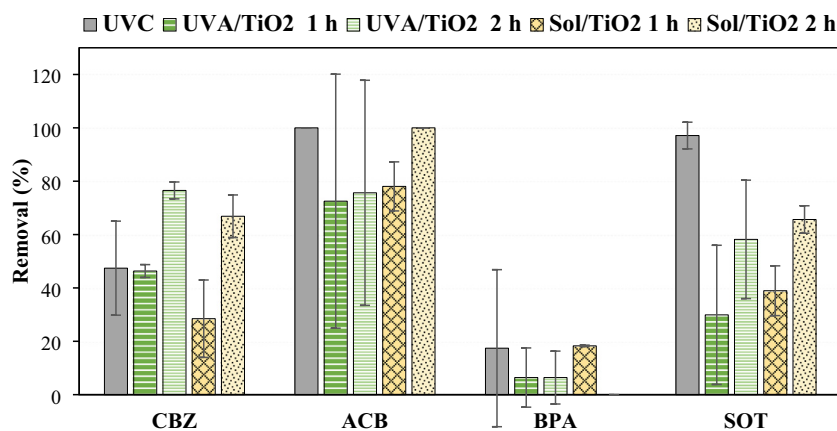

Fig. 4. Removal efficiency of biologically recalcitrant EP in photodegradation experiments at lab-scale. (UVC and UVA/TiO$_2$: autumn campaign included, n = 6; Sol/TiO$_2$: autumn campaign excluded, n = 4).

process depends on several factors such as irradiation intensity (W/m^2), catalyst dosage, initial concentration and nature of EP, pH of the medium and the water matrix (Tufail et al., 2021). So, the behaviour found in campaign III may be due to the variation in the intensity of sunlight, which anticipates a very low effectiveness of Sol/TiO$_2$ post-treatment in the winter months when using the current formulation of the catalyst.

Given these considerations, Fig. 4 allows one to compare the effectiveness of the three photodegradation post-treatment alternatives. The UVC lamp achieved high eliminations for ACB and SOT with percentages of 100 % and 97.1 % respectively. UVC photolysis had a moderate efficiency for CBZ, removing 47.4 %, while it had a low and variable removal of BPA (17.4 %). The high removal efficiency of ACB and SOT was also reported in some studies during WWTP effluent treatment by UV radiation at 254 nm (De la Cruz et al., 2012; Li et al., 2010). The complete elimination of ACB due to UVC radiation at 254 nm was consistent with the results obtained by Wang et al. (2019) at a pH range of 2–10, which could be explained because ACB has two peaks of maximum absorption at 230 and 278 nm. Therefore, direct photolysis was considered the main removal mechanism for ACB. On the other hand, CBZ demonstrated poor absorbance of light at 254 nm with removals <25 % (Alharbi et al., 2017; De la Cruz et al., 2012; Hollman et al., 2021; Im et al., 2012). The low effectiveness of UV radiation in BPA removal had already been observed by Sharma et al. (2015). These authors studied the extent of degradation of BPA in an aqueous solution under UV radiation with different oxidants but during the experiment without oxidant, an insignificant removal of BPA was obtained. Sharma et al. (2015) argue that 254 nm irradiation could not induce electron state transitions that can convert BPA since its maximum absorption is at 276 nm.

Photodegradation by UVA/TiO$_2$ was moderately effective for CBZ, ACB and SOT at 2 h of treatment. Eliminations were clearly lower after 1 h of exposure for CBZ and SOT (Fig. 4). Although very little differences were observed in terms of exposure time for ACB and BPA, the large variation observed precludes conclusion in this regard. CBZ was removed more efficiently by UVA/TiO$_2$ than by UVC, the opposite of what happens to the other compounds (ACB, BPA and SOT). The behaviour of CBZ was consistent with the analysis by Im et al. (2012), who investigated the degradation of CBZ in deionised water by photolysis and photocatalysis using UVC (254 nm) and UVA (365 nm) radiation and TiO$_2$ catalyst. Im et al. (2012) observed no elimination of CBZ under UVC radiation within 60 min while TiO$_2$ photocatalysis with UVC or UVA completely removed CBZ after 30 min and 60 min of exposure, respectively. This suggests that direct photolysis did not degrade CBZ since its amide bond could resist degradation (Kim and Tanaka, 2009) meanwhile indirect photolysis due to wastewater matrix could enhance its degradation. Moreover, the presence of TiO$_2$ could promote a higher generation of HO•, improving the removal efficiency during photocatalytic treatment (Alharbi et al., 2017; Capodaglio

et al., 2018; Tufail et al., 2021). Mean removals after 2 h of exposure for UVA/TiO$_2$ photodegradation were 76.5 %, 75.6 %, 58.2 % for CBZ, ACB and SOT, respectively (Fig. 4). On the other hand, the effect on BPA was considered negligible. Some studies obtained lower removal efficiencies of BPA when treating WWTP effluents under UVC and UVA/TiO$_2$, which was justified due to the presence of organic compounds and ions (Goulart et al., 2021; Mehrabani-Zeinabad et al., 2016). However, other studies found that the extent of BPA degradation depended strongly on the photocatalyst used (Canle et al., 2017; Kaplan et al., 2015).

Regarding heterogeneous photocatalysis with sunlight in summer conditions, the obtained results were at least comparable to those obtained for UVA/TiO$_2$. The removal of all compounds in Sol/TiO$_2$ increased with time, being clearly better at 2 h than at 1 h of treatment (Fig. 4). Mean removals after 2 h of exposure for Sol/TiO$_2$ photodegradation in summer conditions were 66.9 %, 100 %, 65.6 % for CBZ, ACB and SOT, respectively. However, as pointed out above, this post-treatment in autumn conditions was the least effective compared to UVC or UVA/TiO$_2$. The high removal efficiency of ACB by heterogeneous photocatalysis has already been reported (Li et al., 2012, 2011). Nevertheless, Li et al. (2011) observed a lower elimination of ACB when treating WWTP effluents than in Milli-Q water. This was attributed to the presence of dissolved organic matter and inorganic species that could act as hydroxyl radical scavengers. On the other hand, according to Piram et al. (2008), some β-blockers (such as SOT) only absorb in the UVC range (i.e., λ < 280 nm). So, direct photolysis of SOT cannot take place under common environmental conditions. The complete removal of SOT during UVC treatment found in this study is in line with the explanations given by Piram et al. (2008). However, the UVA/TiO$_2$ and Sol/TiO$_2$ experiments were also able to remove SOT in the range of 58–66 %, indicating the important role of the TiO$_2$ catalyst under these conditions.

3.3.2. Pilot-scale photocatalysis pond

Results on the efficiency of the p.Sol/TiO$_2$ or photocatalysis pond as a post-treatment step to the combined (HD-VF)$_R$ system at pilot scale are shown in Fig. 5. The three compounds ACB, SOT and CBZ showed a regular degradation during treatment in summer conditions, in which percentage removal after 1 h of exposure reached 68.4 %, 33.3 % and 28.6 % for ACB, SOT and CBZ, respectively. Removals still increased to 100 % (ACB), 48.0 % (SOT) and 56.2 % (CBZ) after 2 h of exposure. However, during autumn conditions, percentage removals were limited to 15–25 % after both 1 h and 2 h of exposure (Fig. 5B).

Meanwhile, BPA remained the most resistant compound to be photodegraded in both summer and autumn conditions, with registered removals of 4.9 % in July campaign and −9.4 % in October campaign. The obtained results for heterogeneous photocatalysis with sunlight were similar at both lab (Sol/TiO$_2$) and pilot scale (p.Sol/TiO$_2$) experiments. In
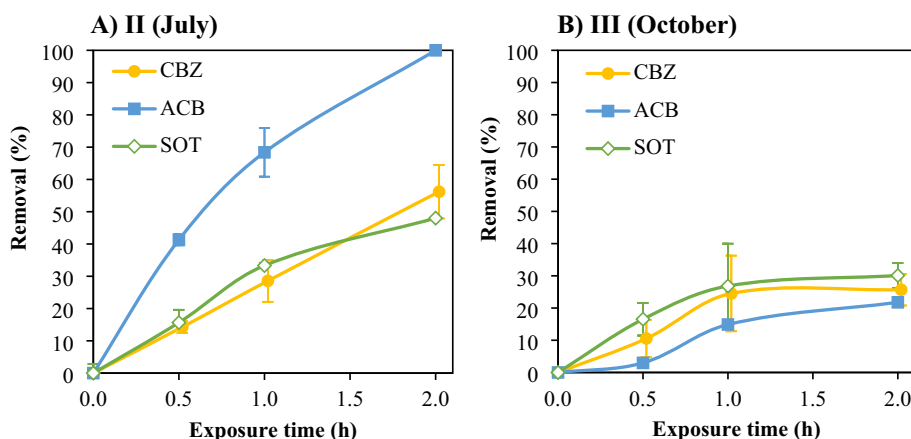

Fig. 5. Time evolution of EP removal in the pilot-scale solar photocatalysis pond (p.Sol/TiO$_2$): A) Summer experiments (*n* = 2), B) Autumn experiments (n = 2).

summer conditions, photodegradation was high for ACB, medium for CBZ and SOT and null for BPA. On the other hand, in autumn conditions, low or even null removals were obtained for all these compounds, meaning that the developed catalyst needs improvement to work in conditions of less intense sunlight radiation.

3.4. EP removal efficiency by the three-step system and overall assessment

The overall effect of the three-step system on EP removal was obtained by adding the removals obtained in the considered post-treatment step to those achieved by the biological treatment system. The results are shown in Fig. 6. Easily biodegradable compounds were virtually removed in the biological (HD-VF)$_R$ system due to the contribution of both anaerobic/anoxic and aerobic steps. However, the role of the VF unit, which showed predominant aerobic conditions, prevailed over the role of the HD. In fact, the VF unit had the ability to remove all the remaining amount of ACE, CAF, KET, IBU and DCL, suggesting that the anaerobic step could be not necessary in terms of EP removal.

BPA did not show biodegradation in the anaerobic step but reached a high although partial removal (about 80 %) in the VF unit. However, none of the different PD post-treatments was able to complete the removal of BPA, thus the overall removal in the three-step system remained in the range of 80–83 %. Biodegradation of three compounds, ACB, SOT and CBZ, appeared to be very limited, as indicated by the low removals observed in the (HD-VF)$_R$ system (Fig. 6). All PD post-treatments clearly increased the removal of these biologically refractory compounds. Degradation rates generally followed the same trend, decreasing in the following order: ACB > SOT > CBZ. UVC post-treatment showed the strongest effect in a shorter time (0.5 h), while methods incorporating TiO$_2$ catalysis required 2 h of exposure and summer sunlight conditions to be effective. Considering these light and exposure conditions, the removal ranges were 83–100 % (ACB), 60–100 % (SOT) and 51–78 % (CBZ), as shown in Fig. 6.

3.5. Integration and potential full-scale application of combined CW and TiO$_2$ catalysis systems

As shown in Fig. 6, all three technologies contributed significantly to the elimination of different EP that require suitable conditions for the processes of aerobic and anaerobic biodegradation as well as photodegradation. HD is an essential pretreatment step for the retention and hydrolysis of particulate organic matter, denitrification and prevention of VF unit clogging (Gonzalo et al., 2017b). The VF unit carries out nitrification and the

elimination of residual organic matter and of more difficult biodegradation. Thus, VF also plays the most important role in the removal of many EPs. This 2-stage system with recirculation (HD-VF)$_R$ is sufficient for the conventional tertiary treatment of raw wastewater. However, photodegradation processes are virtually excluded from these first two stages and many EP that require photodegradation would remain in the VF effluent. One option is to include a surface flow CW stage, but this option necessarily increases the surface area of the system. Therefore, the present solution seeks the combination with intensive photodegradation systems, in particular photocatalysis with TiO$_2$, which contributes to the configuration of a very compact hybrid system.

The three-stage system (HD-VF-p.Sol/TiO$_2$) configured in the pilot plant is a compact system with a high treatment capacity. According to the loading rates indicated in Table 1, the required area of the VF unit is 1–2 m^2/EI. In fact, it is equivalent to 1 m^2/EI during period II of operation. The VF unit is the largest and most basic element of the system, while the HD adds an area of approximately 13 % (see Section 2.2), and the p.Sol/TiO$_2$ unit (currently with 1 m^2 compared to 3 m^2 of VF), contributes an additional 33 %, in percentages referred to the surface of VF. The 3-stage system, taken as a whole, requires an area in the range of 1.7 to 3.5 m^2/EI. The per capita surface of this small pilot-scale plant can be optimized for plants serving a higher number of EI.

However, in the current state of development of the HD-VF-p.Sol/TiO$_2$ system, there are still outstanding issues that require further research as well as the resolution of aspects related to the configuration of the combined system on a field scale. Among these aspects is the need for greater catalyst efficiency for the photodegradation of recalcitrant EP. An improvement of the design of the photodegradation unit containing the catalyst is also necessary to facilitate its coupling with the other units. This may optionally include the photodegradation unit within the effluent recirculation loop, now limited to the two HD and VF units.

The results clearly indicated that the TiO$_2$ catalyst needs improvement to increase its effectiveness when combined with solar lighting. Firstly, the effective exposure time in summer conditions should be 2 h or more. Because the combination of immobilised TiO$_2$ catalyst and solar radiation require very shallow water layers (we used 5 cm in the pilot pond), the surface area required for EP degradation post-treatment would be high. With the current catalyst formulation and pond design, and considering up to 12 h/day of viable lighting campaign in summer conditions, an area of 0.5 m^2/inhabitant would be required (for a reference flow of 150 L/inhabitant). This surface is at least half (and not 33 % as initially estimated, due to the need for 2 h of exposure better than 1 h, Fig. 5) that required
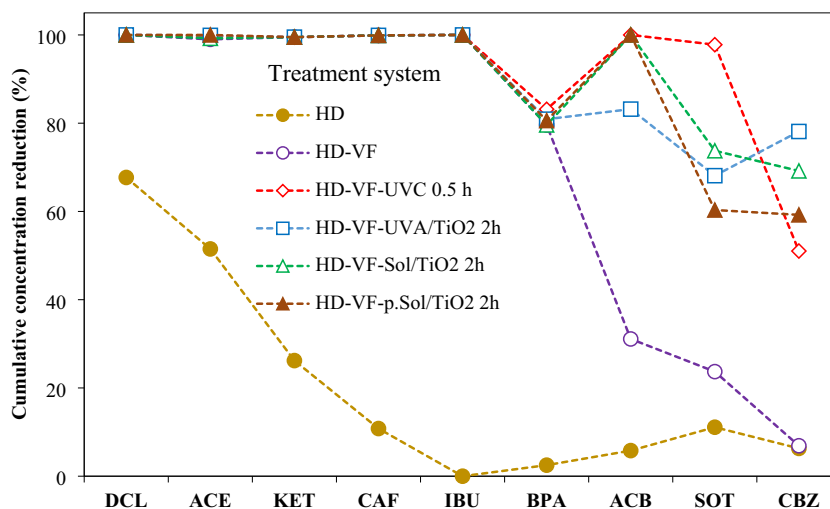

Fig. 6. Percentage reduction of concentration achieved by the hybrid digester and the combined two and three-step systems (data for solar systems correspond to only summer conditions). Note: Although without specific significance in this study, dashed lines are useful for visually identifying the efficiency of each technology combination and comparing them.

by intensified CW for BOD and nitrogen removal and would make the three-step system hardly feasible. Of course, innovative spatial configurations for the Sol/TiO$_2$ treatment could help overcome this limitation.

Secondly, the results showed a clear decrease in photodegradation efficiency in the autumn campaigns (last days of September and mid-October), even when the central hours of the day (13.30 pm–15.30 pm GTM) were chosen for the experiments. In addition, the effective lighting campaign is shorter during the winter. All this would limit the feasibility of the current catalyst formulation to the summer campaign at this latitude. Even so, the efficiency of EP photodegradation could be improved in several different ways (Belekbir et al., 2020; Canle et al., 2013). The intensity and time of illumination can be increased by using of artificial light obtained from renewable energy sources such as photovoltaics, with the option of on-site production. Enlarging the pool surface area increases the total solar radiation received, allows a higher photocatalyst load and a longer retention time, and reduces the height of water layer of both. The use of mirrors, as in more frequent but complex compound parabolic collectors, also helps, by increasing the incident radiation. The photocatalyst has been prepared with a more sustainable local clay, but other materials have, since then, shown better catalytic activities. Finally, addition of co-oxidants (such as H$_2$O$_2$ or S$_2$O$_8^{2-}$) or impregnation of the photocatalyst with certain transition metal cations might improve the effectivity of the process. The best option for any particular case may be chosen considering ground availability, initial installation cost, specific latitude and weather conditions, etc.

Different studies have shown that PD, provided enough time is given, leads eventually (with some exceptions) to complete photomineralisation (Burrows et al., 2002). However, different intermediates or by-products, which are formed during the phototransformation, might show relevant toxicities or chemical risk (Canle et al., 2012). For this reason, further research is needed to expand knowledge on PD pathways and photoproducts.

In systems without recirculation, the order of treatment is critical and can affect overall efficiency and the elimination of degradation by-products. Optimal configurations can vary according to the nature of the contaminants (Lazar et al., 2012). These authors found higher degradation rates for the combined CW-PD treatment in comparison with the combined PD-CW treatment. They also observed that some of the intermediates generated during TiO$_2$ photocatalysis were not biodegradable (Lazar et al., 2012). However, several authors indicated that in the PD-CW scheme, the generated intermediates could be further degraded in the subsequent CW step (Chow et al., 2017; Escolà Casas and Matamoros, 2020).

Systems with recirculation have achieved greater efficiency, particularly for nitrogen removal (Torrijos et al., 2016). When the CW stages show very different conditions in terms of oxygenation and redox potential, high effluent recirculation rates (e.g., 200–400 %) are required to ensure a high total nitrogen removal. These high recirculation rates increase the hydraulic load per step in each unit, an aspect that must be taken into account in the CW design criteria. The inclusion of the PD stage in the recirculation loop will raise similar requirements on the design of that stage. The way the catalyst is immobilised and its stability in the face of the presence of high flows can condition the design and size of these units. However, in CW-PD sequences, recirculation would favour the potential elimination of photodegradation by-products as a consequence of their return to the previous biological unit. Although Gonzalo et al. (2017a) indicated that increasing recirculation from 100 % to 200 % from the final PD unit to the inlet of the CW did not show an impact on the overall EP removal efficiency, this aspect also requires additional research, particularly regarding the mineralization of by-products.

4. Conclusions

A hybrid system consisting of a combination of HD, VF and PD processes operating in series at pilot-scale, achieved advanced MW treatment for a selected set of EP. Different PD post-treatments were studied to treat the effluent from combined (HD-VF)$_R$ system, varying the external energy sources (UVC, UVA or solar light), the use of catalyst (TiO$_2$), and the treatment time (from 0.5 h to 2 h).

As remarkable results, the biological treatment carried out by the combined (HD-VF)$_R$ system was able to remove >99 % of DCL, ACE, CAF, KET and IBU while BPA was largely removed by 80 %. On the other hand, low removal efficiencies were obtained in the (HD-VF)$_R$ system for ACB, SOT and CBZ, confirming its recalcitrant behaviour through biological treatment. In terms of removal mechanisms by steps, CAF, KET, IBU and BPA were mainly removed by aerobic biodegradation in the VF. DCL and ACE were removed in both HD and VF, so they degraded in both anaerobic and aerobic environments.

All PD post-treatments were effective to varying degrees in removing the remaining ACB (76–100 % removal respect to the (HD-VF)$_R$ system effluent), SOT (48–97 %) and CBZ (47–77 %). However, no post-treatment was effective in the removal of BPA (<30 % removal). It should be noted that better CBZ removal performances were found with heterogeneous photocatalysis (both UVA and sunlight) than with UVC. However, the efficiency of sunlight plus TiO$_2$ catalyst was still poor in autumn conditions.

Therefore, this 3-step HD-VF-PD system showed a high capacity to remove the selected EP. PD with sunlight and TiO$_2$ catalyst resulted in a promising post-treatment for the removal of EP recalcitrant to biological treatment. Nevertheless, further research is needed to improve the catalyst performance as well as on the integration of solar photocatalysis in continuous CW systems.

CRediT authorship contribution statement

M. Sánchez: Data curation; Formal analysis; Investigation; Methodology; Visualization; Writing - original draft; Writing - review & editing. **D. R. Ramos**: Data curation; Formal analysis; Methodology; Validation; Writing - review & editing. **M. I. Fernández**: Formal analysis; Methodology; Supervision; Validation. **S. Aguilar**: Data curation; Formal analysis; Validation. **I. Ruiz**: Conceptualization; Data curation; Investigation; Supervision; Validation; Roles/Writing - original draft; **M. Canle**: Conceptualization; Formal analysis; Methodology; Supervision; Funding acquisition; Project administration; Resources; Writing - review & editing. **M. Soto**: Conceptualization; Formal analysis; Methodology; Supervision; Visualization; Writing - review & editing.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.156750.

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