Research article

Bioremediation of emerging micropollutants in irrigation water. The alternative of microalgae-based treatments

The corrections made in this section will be reviewed and approved by a journal production editor.

Lucas Vassalle[a,b], Adrià Sunyer Caldú[c], Enrica Uggetti[b], Rubén Díez-Montero[b], M. Silvia Díaz-Cruz[c], Joan García[b], Ma Jesús García-Galán[b,*][Instruction: It would be necessary to change the membership. Since the research leader is GEMMA - UPC Being: a - GEMMA - Group of Environmental Engineering and Microbiology, Department of Civil and Environmental Engineering, Universitat Politècnica de Catalunya-BarcelonaTech, C / Jordi Girona 1-3, Building D1, E-08034, Barcelona, Spain b - Department of Sanitary and Environmental Engineering, Federal University of Minas Gerais (UFMG), Av. Antônio Carlos, 6627, Belo Horizonte, MG, Brazil c - ENFOCHEM-Water, Environmental and Food Chemistry Unit, Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research (IDAEA-CSIC), C / Jordi Girona 18-26, 08034, Barcelona, Spain The authors: LucasVassalle ab Adrià Sunyer Caldú c Enrica Uggetti a RubénDíez-Montero a M. SilviaDíaz-Cruz c Joan García a Ma Jesús García-Galán a*]

chus.garcia@upc.edu

[a]Department of Sanitary and Environmental Engineering, Universidade Federal de Minas Gerais (UFMG), Av. Antônio Carlos, 6627, Belo Horizonte, MG, Brazil

[b]GEMMA – Group of Environmental Engineering and Microbiology, Department of Civil and Environmental Engineering, Universitat Politècnica de Catalunya-BarcelonaTech, C/Jordi Girona 1-3, Building D1, E-08034, Barcelona, Spain

[c]ENFOCHEM-Water, Environmental and Food Chemistry Unit, Department of Environmental Chemistry, Institute of Environmental Assessment and Water Research (IDAEA-CSIC), C/Jordi Girona 18-26, 08034, Barcelona, Spain

*Corresponding author.

Abstract

The present study evaluated the efficiency of a closed horizontal tubular photobioreactor (PBR) at demonstrative scale to remove a total of 35 target compounds, including benzotriazoles, benzophenones, antibiotics and anti-inflammatories (amongst others) present in irrigation water in a peri-urban rural area. This water run through an open channel and was a mixture of reclaimed wastewater from a nearby wastewater treatment plant (WWTP) and run-off from the different agricultural fields in the area. Most of the compounds studied are usually not fully eliminated during conventional wastewater treatment, which justifies the need to investigate alternative treatment strategies. A total of 21 of these compounds were detected in the irrigation water. Benzotriazoles were only partially removed after the microalgae treatment, with elimination rates similar to those of conventional WWTPs. The UV filter benzophenone-3 (BP3) showed variable removals, ranging from no elimination to 51%, whereas 4-methylbenzilidenecamphor (4MBC) was completely eliminated. Regarding pharmaceuticals, average removals were better, in the range of 60–100%, with the exception of the antibiotics sulfamethoxazole (46%) and sulfapyridine, which was not removed. Despite the low biomass productivity of the PBR, parameters such as the size of the reactors, the specific mixed cultures developed and the high temperatures and pH in the closed system may account for these good results, The efficiency and sustainability of these systems make them a solid, feasible treatment choice.

Keywords: Organic micropollutants; Pharmaceuticals; Sunscreens; Metabolites; Green treatment; Photobioreactors

1 Introduction

Pharmaceuticals and personal care products (PPCPs) have become an integral part of our daily life. Their frequent consumption and usage have led to their regular entrance into the environment, being the aquatic ecosystems the most vulnerable. Indeed, they are constantly receiving these inputs from both point sources such as wastewater treatment plant (WWTP) effluents (urban, rural or industrial) (García-Galán et al., 2011; Molins-Delgado et al., 2015; Verlicchi et al., 2010) or from non-point sources such as urban or agricultural run-off waters, intensive cattle farming or biosolids application from WWTPs (Dolliver and Gupta, 2008; Sabourin et al., 2009). In rural areas (including also peri-urban crops), irrigation or strong precipitation events can lead to the loss of different pollutants from the crop soils such as pesticides, inorganic fertilizers or residues of different organic micropollutants, such as pharmaceuticals, contained in the applied biosolids. Drainage and open irrigation channels can receive a large amount of this rural run-off, but they usually discharge into rivers and not in other main collectors towards WWTPs. In consequence, a huge variety of organic micropollutants eventually reach surface waters and groundwater bodies, and may indirectly affect to different non-target organisms and the ecological status of the receiving aquatic ecosystems (Langdon et al., 2010; Postigo et al., 2016; Proia et al., 2013).

During the last two decades, intensive monitoring campaigns on the occurrence of PPCPs have been carried out, demonstrating the inefficient removal for most of them during conventional wastewater activated sludge wastewater treatment (CAS), and their ubiquity in basically all type of environmental matrices, including tap water (Díaz-Cruz et al., 2012; Dolar et al., 2012; Gros et al., 2012; Serra-Roig et al., 2016). Apart from pharmaceuticals, personal care products (PCPs) comprise a wide group of chemicals of daily use such as soaps and detergents, toothpastes, sunscreens, cosmetics, biocides, fragrances and insect repellents amongst others. Their continuous release into the environment has led to their classification as *pseudo*-persistent contaminants (Tolls et al., 2009) and understanding their fate and behaviour in the aquatic ecosystems shoud be a priority, considering their potential to bioaccumulate and biomagnify through the trophic chain, and their subsequent negative impact on the receiving ecosystems (Fent et al., 2010). Nevertheless, and despitethe lack of ecotoxicity data for many sunscreen agents, available toxicity data indicated for instance that two metabolites of benzophenone-3 (BP3), 2,4-dihydroxybenzophenone (BP1) and 4-hydroxybenzophenone (4HB) showed a high estrogenicity against rainbow trout (Kunz et al., 2006; Kunz and Fent, 2009).

Similarly, benzotriazoles are high production volume chemicals which have become crucial in many industrial processes as UV blockers or stabilizers of different plastic products, corrosion inhibitors in detergents, antifreezing or antifogging agents in photography or airplane fluids (Asimakopoulos et al., 2013; Gatidou et al., 2019; Liu et al., 2012, 2011a). 1H-benzotriazole (BZT, also found as BTri) and 5-methyl-1H-benzotriazole (5-MeBZT, also found as TTri) are the two UV blockers most frequently detected in environmental samples, as they are poorly volatile and only partially removed during CAS treatment due to their high polarity and low biodegradability (Asimakopoulos et al., 2013; Molins-Delgado et al., 2015; Reemtsma et al., 2010). Some studies have shown that benzotriazoles can ultimately accumulate in humans, being detected in human adipose tissues, urine and amniotic fluid samples (Li et al., 2018; Wang et al., 2015). Regarding their ecotoxicity, there are only a few studies and yet all have evidenced that these chemicals have endocrine disrupting properties, impairing oxidative stress, hepatotoxicity and neurotoxicity in freshwater and marine fish (Liang et al., 2017, 2016; 2014; Tangtian et al., 2012).

Regarding pharmaceuticals, thousands of tons of different classes are consumed regularly in both human and veterinary medicine. It is estimated that pharmaceuticals usage will reach 4.5 trillion doses per day in adults worldwide by 2020 (Patel et al., 2019). After usage and excretion, both the metabolites and the remnants of the original drug are released into the environment where they may resist biodegradation and bioaccumulate, depending on their physical and chemical properties (Daughton, 2013). In these cases, they could also pose a toxicological risk to different non-target organisms, altering the ecosystem dynamics, as is the case of antibiotics and the development of antibiotic resistant bacteria and genes (including pathogens) (Kümmerer, 2009, 2004; Rodriguez-Mozaz et al., 2015). Antibiotics consumption alone reached 34.8 billion daily doses worldwide in 2015 (Klein et al., 2018).

Taking all this information into account, the need to find alternative and more efficient treatments is evident. Nature-based, low-cost treatment systems such as microalgae-based systems or constructed wetlands are currently being intensively investigated and, so far, with promising results regarding PPCPs removal (Ávila et al., 2014; García-Galán et al., 2018; Matamoros et al., 2015; Vassalle et al., 2020b). In particular, microalgae-based treatments, despite having been operative since the 50's, are recently gaining a renewed popularity due to their high efficiency removing nutrients and organic matter within a much more sustainable frame than conventional treatments. Indeed, these systems can operate maintaining low operation and maintenance (O&M) costs, as they do not require external aeration due to photosynthesis, or any chemical input (García et al., 2006; Muñoz and Guieysse, 2006). Microalgae biomass grows fixating CO_2 and assimilating the nutrients (mostly nitrogen (N) and phosphorus (P)) present in the influent wastewater. Through photosynthesis, microalgae generate the oxygen needed by heterotrophic bacteria to aerobically degrade the organic matter present in the water (including organic micropollutants). These systems have the dual advantage of treating wastewater efficiently and, simultaneously, producing microalgae biomass which, after an appropriate harvesting/separation technique from the aqueous phase, can be further profited to produce bioenergy (biogas) or other added-value products such as pigments, biofertilizers or even bioplastics (Arashiro et al., 2018; Rueda et al., 2020; Vassalle et al., 2020a). If managed sustainably (with proper use), the waste generated in this overall process is considerably reduced, as well as the energy requirement for this system, when compared to conventional systems. For microalgae bioremediation, there are two basic types of systems: open and closed systems. Open systems or high rate algal ponds (HRAPs) have already been used for decades not only for wastewater treatment but in industrial microalgae production (Chisti, 2013; Oswald, 1995). HRAPs are the most frequently used systems, mainly due to their lower energy requirements, as well as O&M costs, but cultures can be easily contaminated and the control of the different growth and environmental parameters (temperature, sunlight) is worse than that of closed systems (Park and Craggs, 2010). Closed systems usually yield higher biomass productions, microalgae cultures are more protected against external contamination and the control of the different parameters is better than in HRAPs. However, the costs of O&M are higher (higher energy requirements for mixing), dissolved oxygen may accumulate to toxic levels and biofouling may appear in the inner walls. It seems consistent that a new design of a hybrid PBR, combining the advantages and avoiding the shortcomings of both open and closed systems, could yield the highest efficiencies in biomass yield and wastewater bioremediation. Regarding their efficiency in PPCPs removal, studies on open systems are predominant, but yet scarce. In recent studies, removal efficiencies (RE%) between 40% and >90% have been reported in HRAPs treating sewage (García-Galán et al., 2020; Vassalle et al., 2020b). Regarding closed or semi-closed systems, to the authors knowledge only one study by the same authors evaluated PPCPs removal in water from the same irrigation channel by microalgae semi-closed systems (García-Galán et al., 2018), and a second one by Hom-Diaz et al. (2017) evaluated the fate of 17 pharmaceuticals in a closed tubular reactor treating wastewater.

The present study aims to evaluate the removal capacity of a hybrid, horizontal tubular PBR for 35 different PPCPs, including UV-filters and parabens (10), benzotriazoles (4), antibiotics (15) and other pharmaceuticals (6), in a mixed water from an irrigation channel To the best of the author's knowledge, it is the first time that a hybrid, (open/close) PBR is investigated regarding the removal of a UV filters in this type of water matrix.

2 Materials and methods

2.1 Microalgae-based treatment system description and operation

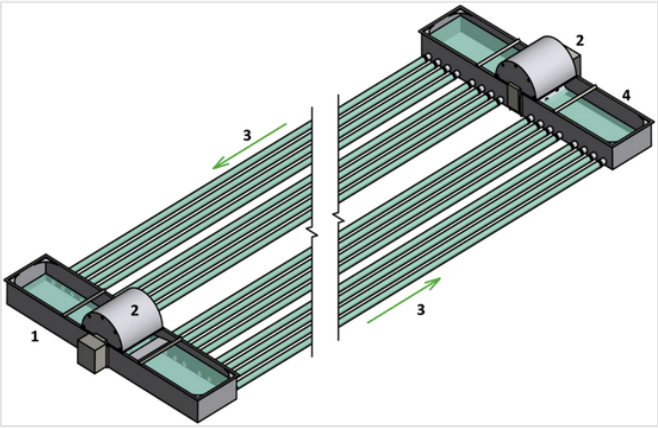
2.1.1 Hybrid tubular horizontal photobioreactor (PBR)

The sampling campaign was carried out in one of the three PBRs designed, built and operated by the Environmental Engineering and Microbiology research group (GEMMA, (Universitat Politècnica de Catalunya-BarcelonaTech) in collaboration with Disoltech S.L. (Tarragona, Spain), within the framework of the H2020 EU project INCOVER “Innovative Eco-technologies for Resource Recovery from Wastewater” (http://incover-project.eu/GA 689242). These PBRs were the core of a more complex pilot plant at demonstrative scale, which main objective was to use wastewater as a valuable resource to produce different added-value products within the biorefinery concept and circular economy paradigm. A detailed description of the PBRs can be found elsewhere (García et al., 2018; Uggetti et al., 2018). Briefly, each PBR consisted of two open tanks of polypropylene connected by 16 horizontal tubes (Fig. 1). The useful volume of each PBR was 11.7 m^3. Eight-blade paddlewheels were installed in the middle of each open tank to ensure and favor the homogeneous distribution and mixing of the liquor and also the release of the excess dissolved oxygen (DO) accumulated along the closed tubes. Paddle wheels also contributed to create a water level difference (0.2 m) which made the mixed liquor flow by gravity from one tank to the other. The PBRs were inoculated in April with a mixed culture of microalgae and bacteria grown in urban wastewater and operating since then (Uggetti et al., 2018). Irrigation water derived from a drainage-irrigation channel near the facilities, containing a mix of agricultural run-off and reclaimed wastewater from a WWTP nearby, was fed to the PBR daily, under a HRT regime of 5 d (2.3 m^3 d^{-1} approximately). Previously, this water was mixed with urban wastewater from a septic tank (7:1, v:v) (to provide nutrients for the biomass growth) in a homogenization tank with constant stirring, right before the feeding operation (it was filled up anew every day). Online sensors of pH (Hach Lange Spain S.L.), dissolved oxygen

(Neurtek, Spain) and temperature (Campbell Scientific Inc., USA) were installed in one of the two open tanks of each PBR.

alt-text: Fig. 1

Fig. 1



Scheme of the hybrid tubular closed photobioreactor used in this study. 1:inflow from the homogenization tank; 2: paddle wheel; 3: direction of the flow within the tubes; 4: outflow to the storage tanks. Samples were taken in 1 and 4.

2.2 Sampling strategy

The PBR was already in operation for two full months before the sampling campaign in July, and had already reached the steady state (for complete-mix reactors, from 3 to 5 HRTs are needed to reach this steady state). Sampling was carried out during two weeks in July, three days per week. Influent samples were taken from the homogenization tank and effluent samples were taken from one of the open tanks (as mixed liquor) (n = 12 samples). The PBR was treated as a complete-mix reactor, so the HRT was not considered when taking the influent and effluent samples. For chemical characterization of the water, samples were taken in PVC bottles and directly analyzed in the laboratory on the same day. For the analysis of environmental levels of PPCPs, samples were collected and immediately filtered through 0.45 µm PVDF membrane filters (Millipore, USA) and frozen upon arrival to the laboratory (amber glass bottles).

2.3 Chemicals and reagents

High purity standards (>99%) for 4 benzotriazoles (1H-benzotriazole (BZT), its two metabolites 5-methyl-1-H-benzotriazole (MeBZT) and 5,6-dimethyl-1H-benzotriazole (DMBZT), and 2-(2′-hydroxy-5′-methylphenyl)benzotriazol (UVP), 6 benzophenones (benzophenone-1 (BP1), benzophenone-2 (BP2), benzophenone-3 (BP3), two metabolites of BPR, 4-hydroxybenzophenone (4HB) and 4,4 –dihydroxybenzophenone (4DHB), and 2,2′-dihydroxy-4-methoxybenzophenone (DHMB)), 1 camphor derivative (4-methylbenzilidenecamphor (4MBC)), 1 cinnamate derivative (ethylhexyl methoxycinnamate (EHMC)), 2 *p*-aminobenzoic acid derivatives (benzocaine (EtPABA), and ethylhexyl-4-(dimethylamino)benzoate (ODPABA)) and their corresponding isotopically labelled compounds were purchased from were purchased from Sigma Aldrich (Augsburg, Germany) and Merck (Darmstadt, Germany). Regarding pharmaceuticals, 2 macrolides (clarithromycin and tylosin), 2 fluoroquinolone (flumequine and ofloxacine), 1 quinolone (oxolinic acid), 9 sulfonamides, trimethoprim, 3 anti-inflammatories (ketoprofen, naproxen and mefenamic acid), the lipid regulator gemfibrozil, the β-blocking agent atenolol and the stimulant caffeine, and their corresponding isotopically labelled compounds were purchased from Sigma-Aldrich (St. Louis, MO, USA) and TRC (Toronto Research Chemicals Inc., Ontario, Canada). Detailed information for all the studied compounds is given in Table S1 of the Supplementary Information (SI). Standard solutions of the mixtures of all compounds were made at appropriate concentrations and used to prepare the aqueous calibration curve and also to perform the recovery studies. Similarly, stock standard solutions for the internal standards were prepared. Aqueous standard solutions always contained <0.1% of methanol (MeOH).

2.4 Analytical methodologies and statistical analysis

2.4.1 Samples characterization

Both influent and effluent samples were analyzed on the following conventional wastewater quality parameters: dissolved oxygen (DO) and temperature (EcoScan DO 6, ThermoFisher Scientific, USA) and pH (portable pH-meter 506, Crison Instruments, Spain). These parameters were also measured on-site in the mixed liquor of the PBR by means of online sensors submerged in one of the open tanks and connected to a Multimeter 44 (Crison Instruments, Spain); turbidity (Hanna HI 93703, USA); total suspended solids (TSS), volatile suspended solids (VSS), alkalinity, chemical oxygen demand (COD), following Standard Methods (APHA-AWWA-WEF, 2012); Ammonium (NH_4^+-N) according to Solórzano method (Solórzano, 1969). The ions nitrite (NO_2^--N), nitrate (NO_3^--N) and phosphate (PO_4^{3-}P) were measured by ion chromatography (ICS-1000, Dionex Corporation, USA). Total carbon (TC), total phosphorus (TP) and total nitrogen (TN) were measured by a TOC analyzer (multi N/C 2100 S, Analytik Jena, Germany). All the analyses were done in triplicate and results are given as average values. Mixed liquor samples were examined under bright light microscope (Motic, China) equipped with a camera (Fi2, Nikon, Japan) for qualitative evaluation of microalgae populations, employing taxonomic books and databases for their identification (Komárek J. & Hauer T, 2013; Streble and Krauter, 2018).

Average biomass productivity (gVSS $m^{-2}\cdot d^{-1}$) in the PBR was calculated based on the VSS concentration in the mixed liquor of both systems, using equation (1):

$$Biomass\ productivity = \frac{VSS\ (Q - Q_E + Q_P)}{A} \quad (1)$$

where VSS is the volatile suspended solids concentration of the PBR mixed liquor (g VSS L^{-1}); Q is the wastewater flow rate (L d^{-1}); Q_E is the evaporation rate (L d^{-1}); Q_P is the precipitation rate (L d^{-1}); and A is the surface area of the system (for the PBR, it was calculated including both tanks surfaces and half of the surface of the 16 tubes). The evaporation rate was calculated using equation (2):

$$Q_E = E_p\, A \quad (2)$$

where E_p is the potential evaporation (mm d^{-1}), calculated using equation (3) (Fisher and Pringle, 2013).

$$E_p = a\, \frac{T_a}{(T_a + 15)}\, (R + 50) \quad (3)$$

where a is a dimensionless coefficient which varies depending on the sampling frequency (0.0133 for daily samples); R is the average solar radiation in a day (MJ m^{-2}), and T_a is the average air temperature (°C). Meteorological data (solar radiation, temperature and precipitation) were obtained from the network of local weather stations in the metropolitan area of Barcelona (www.meteo.cat), and are given in Table S2 in SI.

2.4.2 Online-SPE-HPLC-MS/MS analysis of the target compounds

The target analytes were analyzed using a methodology adapted from Gago-Ferrero et al. (2013) and García-Galán et al. (2010). Briefly, pre-concentration and chromatographic separation was performed by automated on-line solid phase extraction coupled to liquid chromatography (SPE–LC), by means of a Symbiosis™ Pico instrument from Spark Holland (Emmen, The Netherlands). On-line SPE pre-concentration of all samples, including the calibration curve (5 mL volume), were performed using PLRP-s cartridges (Agilent, St. Clara, CA, US). HPLC-MS/MS analyses were performed using a 4000 Q TRAP™ MS/MS system (Applied Biosystems-Sciex (Foster City, CA, US). MS/MS detection was performed in both positive and negative ionization modes, under the selected reaction monitoring (SRM) mode. Table S3 summarizes the HPLC-MS/MS conditions for the targeted compounds. Linearity and limits of detection (LOD) of the methodology are given in Table S4.

2.4.3 Statistical analysis

The Mann-Whitney U-Statistical test was used for independent samples to confirm the statistical difference between the concentration I influent and effluent samples, regarding both physical-chemical parameters and to PPCPs. Statistica 10.0® software was used, using a significance level for all tests of 95%.

3 Results

3.1 Conventional water quality parameters and PBR performance

The physical-chemical properties of the feed water (irrigation water from the open channel) and the PBR effluent are summarized in Table 1. Point and continuous measurements of temperature are given in more detail in SI (Figure S1). The VSS/TSS ratio in the PBR mixed liquor was 74%. In these systems, pH values > 8 promote precipitation of inorganic salts of different nature, leading to an increase of the VSS/TSS ratio (Gutiérrez et al., 2016). Average COD was 92 mg L^{-1} in the irrigation water, with no removal but an increase of 16% in the PBR. This increase has been also observed in previous works on closed systems (Arbib et al., 2013; García-Galán et al., 2018; García et al., 2006) and can be related to the microalgae biomass produced in the system releasing a fraction of the carbon fixed during photosynthesis as dissolved organic carbon (DOC). It has been demonstrated that 5–30% of the carbon photosynthetically fixed is released during microalgae growth as dissolved organic matter or carbon (DOC) (Arbib et al., 2013). In the present study, using the relation given by Dubber and Gray (2010) [4] to convert COD into total organic carbon (TOC, and in consequence DOC), we would obtain an increase of 18% in the PBR.

$$COD = 7.25 + 2.99 \times TOC \quad (4)$$

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Table 1

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Physical-chemical characterization of the feed water (PBR inf) and PBR effluent (mixed liquor).

Parameters	Sample type	
	PBR_{inf}	**PBR_{eff}**
	Mean ± SD	**Mean ± SD**
TSS (mg L^{-1})	73.70 ± 58.81	291.18 ± 200.91
VSS (mg L^{-1})	20.43 ± 13.85	215.35 ± 124.95
COD (mgO_2 L^{-1})	92.50 ± 50.06	107.64 ± 81.06
pH	8.3 ± 0.3	9.1 ± 1.0
DO (mg L^{-1})	–	8.97 ± 0.86
Temperature (ºC)	24.18 ± 2.1	24.87 ± 1.6
$N–NH^{4+}$ (mg L^{-1})	4.4 ± 1.5	0.3 ± 0.5
TN (mg L^{-1})	23.8 ± 2.7	23.8 ± 1.9
TIN (mg L^{-1})	14.4 ± 8.9	6.6 ± 5.3
TC (mg L^{-1})	162.0 ± 19.9	246.3 ± 34.4
$N–NO_2^-$ (mg L^{-1})	1.1 ± 1.0	2.2 ± 3.4
$N–NO_3^-$ (mg L^{-1})	9.3 ± 1.8	4.3 ± 5.3
$P-PO_4^{3-}$ (mg L^{-1})	1.6 ± 1.0	0.0 ± 0.0
$S–SO_4^{2-}$ (mg L^{-1})	79.5 ± 18.8	63.9 ± 17.9

TSS – Total Suspended Solids; VSS – Volatile Suspended Solids; COD – Chemical oxygen demand; DO – Dissolved Oxygen; TN – Total Nitrogen; $N–NH_4^+$ - Ammonium - TN – Total Nitrogen – TC – Total Carbon.

Furthermore, indicative of carbon fixation is the increase of the total carbon (TC) on the effluent, from 162 mg L^{-1} to 246 mg L^{-1}. In addition, there is also an increase in VSS (from 20 mg L^{-1} to 215 mg L^{-1}) indicating the growth of biomass in the system. On the other hand, the higher COD values in the effluent from PBR may be related to the low organic matter biodegradability of the feed water and consequently, to carbon limitation that affected the algal growth. The same was observed in the work by Arbib et al. (2013). The Mann-Whitney U statistical test applied not showed significant statistical difference for temperature and TN parameters.

The average concentration of $N–NH_4^+$ in the irrigation water was 4.4 mg [$N–NH_4^+$] L^{-1}, which was removed up to 83%. Microalgae biomass assimilation is the main removal pathway of $N–NH4^+$ in algae systems, but nitrification and volatilization (in the open tanks of the reactor) as secondary routes should also be considered (García et al., 2006).

3.1.1 Biomass productivity

The average biomass productivity in the PBR was 61.18 ± 6 mg VSS L^{-1} d^{-1}, (equivalent to 6.88 g VSS m^{-2} d^{-1}) Similar results, ranging from 4.4 g m^{-2} d^{-1}–8.26 g m^{-2} d^{-1}, were reported by Arbib et al. (2013) in a small scale PBR (380 L) and also by Park and Craggs (2010), with an an average volumetric productivity ranging from 53 to 69 mgVSS·L^{-1}·d^{-1} treating domestic wastewater in an open system. However, values between 20 and 40 g m^{-2} d^{-1} are considered typical in closed systems (García-Galán et al., 2018). As expected, the concentration of total inorganic nitrogen (TIN) and total phosphorus (P-PO_4^{3-}) in the feed water were low, explaining the overall low productivity. Higher productivities (55–79 mg $_{dcw}$ L^{-1}·d^{-1}), were obtained in previous studies using pure cultures and synthetic culture medium (Troschl et al., 2018). The BG-11 medium used In this study contained 65.8 mg L^{-1} of TIN, whereas the average concentration in the water feedstock of the present study was 15 mg L^{-1} of TIN. Furthermore, biomass development involves the assimilation of NH_4^+ (Arashiro et al., 2019), and indeed nearly all the available NH_4^+ was assimilated by microalgae, but again the input in the PBR influent was low. Last of all, despite the good maintenance of the PBR system during the experiment, the development of biofilm was unavoidable. Its attachment to the inner walls of the tubes probably hindered partially the penetration of sunlight within the tubes and the mixed liquor, affecting to the full growth of microalgae. Nevertheless, its detachment due to the shearing stress produced by the turbulent flow within the tubes together with its regular maintenance aided to keep a correct operation of the PBR.

Regarding the different microalgae species present in the PBR, the cyanobacteria *Synechocystis* sp. Was the most abundant (Fig. 2). Arias et al. (2018) reported the same cyanobacteria species in a lab-scale PBR system, and explained its predominance in terms of the nutrients concentrations in the liquor. These authors showed that in PBR systems operating with 4 days of HRT and with TN concentration <11.72 mg N L d^{-1}, cyanobacteria predominated. These conditions are similar to the PBR system of this work.

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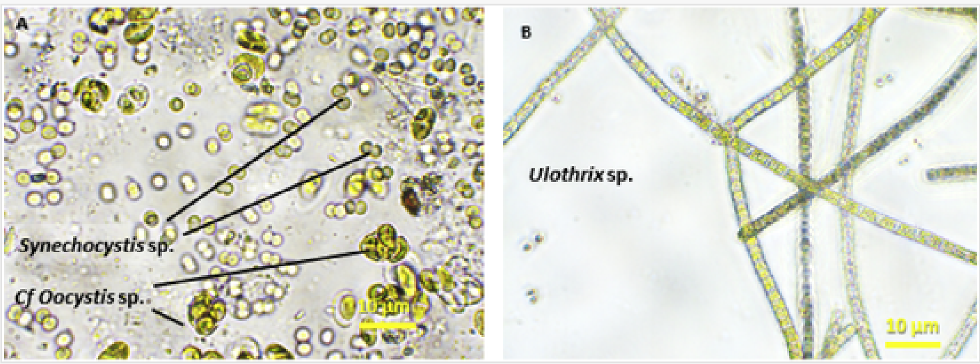
Fig. 2



Microscope images of mixed liquor of the hybrid PBR (A–B), observed in bright light microscopy (x1000).

3.2 Occurrence of PPCPs in irrigation/agricultural run-off water

3.2.1 UV-filters and benzotriazoles

Out of the 14 UV filters and benzotriazoles (UV blockers) targeted, 6 were detected in the feedwater to the PBR. For the 10 UV filters evaluated, none of the *p*-aminobenzoic acid and cinnamate derivatives were detected. The benzophenone BP3 was detected in all the influent samples of the PBR at concentrations ranging from 7 ng L^{-1} to 75 ng L^{-1}. Its metabolites 4DHB and DHMB were not present, and 4HB was only detected in one sample. The camphor derivative 4MBC was found in 3 of the 6 samples analyzed (21 ng L^{-1}-86 ng L^{-1}). To the best of the authors' knowledge, there is no previous data on the presence of these compounds in agricultural run-off, nor irrigation water.

Regarding the 4 benzotriazoles targeted, BZT and MeBZT were the two compounds detected at the highest concentration (1098 ng L^{-1}-2003 ng L^{-1} for BZT and 220 ng L^{-1}-1982 ng L^{-1} for MeBZT, respectively) (see Fig. 3). DMBZT was detected in the 50% of the samples and at lower concentrations (45 ng L^{-1}-77 ng L^{-1}). In a previous campaign on the same site, BZT was also one of the contaminants of emerging concern detected at the highest concentration in the irrigation water, despite at lower levels (420 ng L^{-1}) (García-Galán et al., 2018).

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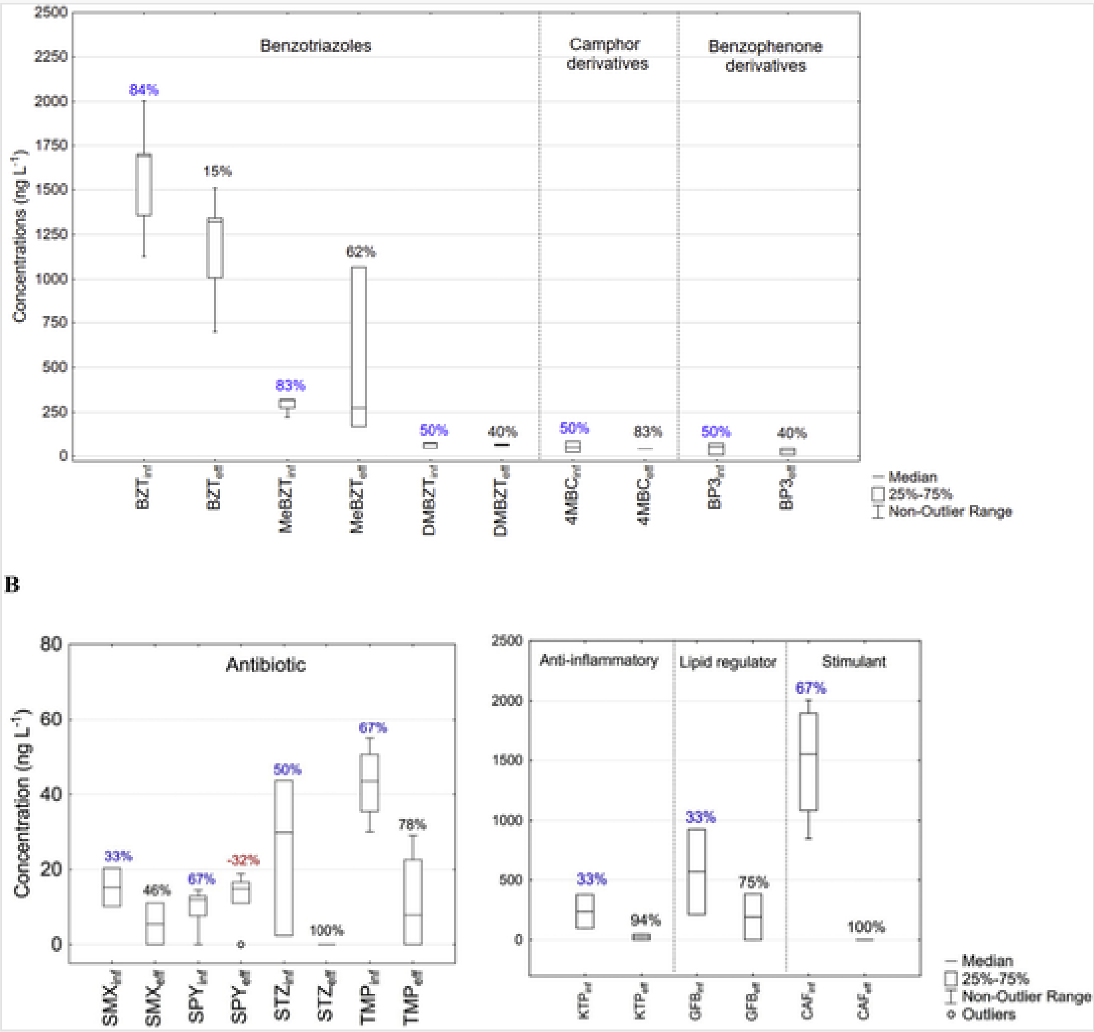
Fig. 3



Concentrations of benzotriazoles and UV-filters (A) and pharmaceuticals (B) detected in the PBR system. For practical purposes, only compounds with frequencies of detection (F%) ≥ 30% (2 samples out of 6) are represented. The percentage value placed on top of the influent box-plots refers to the frequency of detection in the influent water of the PBR; the percentage value placed on top of the effluent box-plots corresponds to the average removal observed (RE%). For pharmaceuticals: SPY: sulfapyridine; STZ: sulfathiazole; TMP: trimethoprim; KTP: ketoprofen; GFB: gemfibrozil.

3.2.2 Pharmaceuticals

Thirteen out of the 21 PhACs targeted were also detected in the feed water of the PBR (Fig. 3). For antibiotics, only sulfonamides and trimethoprim were detected. Caffeine was detected in 5 of the 6 samples and at the highest concentrations, ranging from 850 ng L^{-1} to 2008 ng L^{-1}. These levels are higher than those detected in the same location and season in a previous study (150 ng L^{-1}) (García-Galán et al., 2018). Median concentrations of 384 ng L^{-1} and up to 29,300 ng L^{-1} were detected in agricultural run-off in Singapore (Tran et al., 2019) and up to 5200 ng L^{-1} in storm water run-off in Australia (Sidhu et al., 2013), with frequencies of detection near or 100% in both cases. High concentrations were observed also for gemfibrozil (214 ng L^{-1} and 925 ng L^{-1}), and naproxen (774 ng L^{-1}), although they were detected only in 2 and 1 samples, respectively. Similar levels of gemfibrozil were reported in agricultural run-off from effluent-irrigated crop fields in Southern California, ranging from 190 ng L^{-1} to 790 ng L^{-1} (Pedersen et al., 2005). Ketoprofen was found in 50% of the samples, at levels ranging from 98 ng L^{-1} to 379 ng L^{-1}, similar to those detected by Moeder et al. (2017) in agricultural run-off in Mexico (18 ng L^{-1}-230 ng L^{-1}). Regarding antibiotics, sulfapyridine and trimethoprim were detected with the highest frequencies and average values of 43 ng L^{-1} and 15 ng L^{-1}, respectively, followed by sulfathiazole. Sulfamethoxazole was present only 2 out of the 6 days of sampling, at concentrations between 10 ng L^{-1}-20 ng L^{-1}. Similar results were obtained by Bailey et al. (2015), who also obtained average concentrations of 22 ng L^{-1} for sulfapyridine in agricultural run-off. These authors pointed out the use of sulfonamides as fertilizers in agriculture, which justifies their presence in the run-off. The β-blocker atenolol was not detected in any sample.

3.3 Removal of PPCPs in microalgae-based systems

Aqueous phase removal in the PBR was calculated according to equation (5):

$$RE\% = 100x\left(1 - \frac{C_{eff}}{C_{inf}}\right) \quad (5)$$

where C_{inf} and C_{eff} are the concentrations (ng L^{-1}) in the influent and effluent waters, respectively.

3.3.1 Removal efficiency of PBRs

3.3.1.1 Benzotriazoles and UV filters

Fig. 3A and B shows the influent and effluent concentrations of the different compounds evaluated, indicating also their frequency of detection and removal after the treatment in the PBR. Removal of BZT in the PBR ranged from 3% to 25%. To the author's knowledge, only García-Galán et al. (2018) had previously studied the removal of BZT in closed (semi-closed) systems. These authors obtained a 50% elimination in a PBR of smaller capacity, and in the same location. But as mentioned in the previous section, the concentrations detected in the influent water of the PBR were much lower than those obtained in the present study. Matamoros et al. (2015) also studied the removal of BZT in microalgae-based treatments, specifically in an open system. The authors obtained eliminations in the range of 33–74% working under an HRT of 4 d during summer in the city of Barcelona, but again the concentrations at the influent were lower. Regarding RE% of BZT in different conventional WWTPs, results are highly variable and can range from negative values up to 99% (Molins-Delgado et al., 2017); for instance, Liu et al. (2012) obtained a RE% of 7%, Asimakopoulos et al. (2013) RE% in the range of 25–37%, and Reemtsma et al. (2010) observed eliminations of 20–59%. Nevertheless, the frequent presence of BZT in different aquatic ecosystems (Molins-Delgado et al., 2017; Serra-Roig et al., 2016) reinforces the predominance of low removals in conventional WWTPs. Photodegradation, which is usually enhanced in microalgae-based treatment systems (García-Galán et al., 2020; Matamoros et al., 2015), was not significant for BZT. Yet, its photodegradability was demonstrated by Liu et al. (2012, 2011b), who obtained removals in stabilization ponds of 47% but only after long HRTs (27 d). BZT is highly soluble and with a low log K_{ow}, which together with its high ionization tendency (high pk_a, see Table S1), indicates a poor retention/sorption tendency on the microalgae biomass and a low biodegradability. Elimination of MeBZT was more efficient, ranging from 15% to 48%, and the second metabolite DMBZT was barely removed, with variable RE% from 3% to 17%, but also 100% elimination one of the sampling days (average RE% of 40%) (Fig. 3A). Comparing these RE% to those obtained in conventional WWTPs, a high variability is again observed for these two compounds, with removals in the range of 0–72% for MeBZT and 0–16% for DMBZT (Asimakopoulos et al., 2013; Molins-Delgado et al., 2015; Reemtsma et al., 2010). The presence of other benzotriazole derivatives in the irrigation water (not included in the scope of the present study) that could biotransform into BZT or MeBZT, could also explain the low removals obtained for these compounds. For instance, xylyltriazole demethylates are known to release both MeBZT and BZT as transformation products, and 5-chloro-benzotriazole can lose the chlorine moiety to transform back into BZT (Liu et al., 2011a).

Regarding benzophenone derivatives, BP3 was eliminated up to a 43% (39.9% in average). These results are similar to those obtained by Díaz-Garduño et al. (2017) in an open microalgae system. The authors used an HRAP as tertiary treatment for WWTPs effluents, with RE% ranging from −50% to 70%. Removal rates found in the literature after conventional wastewater treatments are also variable and in the range of 58%–91% for BP3 (Molins-Delgado et al., 2017). As expected, due to its nature and end use, the resilience of BP3 to photodegradation has been demonstrated (Gago-Ferrero et al., 2012). The metabolite 4HB was detected only once in the inlet of the PBR and was 100% removed (Figure S2); its removal in WWTPs is also efficient, and has been detected in sewage sludge at concentrations of 0.15 $\mu g\ g^{-1}$ (Gago-Ferrero et al., 2011). The other two metabolites evaluated, 4DHB and 4DHMB, were not detected in the inlet. Regarding the camphor derivative 4MBC, it was efficiently removed in the PBR system (50–100%). 4MBC is a highly lipophilic compound, and due to its low solubility and high log K_{ow}, biosorption to microalgae biomass seems to be the main removal pathway in the pond. Its removal in conventional WWTPs is also usually high, being frequently detected in the sewage sludge (Gago-Ferrero et al., 2011). To the author's knowledge, this is the first study evaluating the fate of benzothiazoles in closed microalgae-based systems.

The Mann-Whitney U statistical test applied showed significant statistical difference for all benzotriazoles and UV filters found in the analyzed matrix.

3.3.1.2 Pharmaceuticals

Efficient removals were obtained for sulfathiazole (100%) and trimethoprim (78%). Sulfapyridine was poorly removed (−32% average). The higher pK_a of sulfapyridine compared to the other two antibiotics could explain that difference, meaning a lower adsorption tendency to the microalgae biomass and lower bioavailability (see Table S1). Moreover, previous studies have demonstrated that the acetylated metabolite of this compound, N^4-acetylsulfapyridine (out of the scope of this study) can revert back into the parent compound during wastewater treatment (García-Galán et al., 2012); this back-transformation could explained the frequent higher concentrations of sulfapyridine found in the effluent wastewaters of different reactors and incomplete removals in CAS WWTPs (García-Galán et al., 2012, 2011). Lower removals were obtained also for sulfamethoxazole, ranging from no elimination (−8%) to 100% removal. The PBR showed a good performance in the elimination of the anti-inflammatory ketoprofen (88%–100%) and also for naproxen, which was fully removed. Lower elimination rates for ketoprofen (36%–85%) and naproxen (10%–70%) were obtained by Hom-Diaz et al. (2017) in a smaller PBR used to treat urban wastewater. These differences are probably due to the different season of the year in that study (autumn), with lower solar irradiation and fewer light hours. Temperature may also have a relevant role in the treatment efficiency of these systems; the high temperatures in the PBR (see Figure S1), especially inside the tubes, could enhance not only biodegradation and bioassimilation routes in the mixed liquor, but could also alter the structure and stability of the compound itself (Cirja et al., 2008).

Regarding the lipid regulator gemfibrozil, an average elimination of 75% was observed. The log K_{ow} of this drug, 4.77, indicates its high tendency to adsorb onto the biomass and probably accounts for these results, as it is generally only moderately biodegradable. Lower eliminations for gemfibrozil are usually obtained during conventional wastewater treatment, and may be related to a competition for adsorption sites with the humic substances (Maeng et al. 2011). A greater availability of active sites in the microalgae biomass could also be responsible for this high removal rates (Vassalle et al., 2020b). Nevertheless, worse removals (20.6%) were reported in a PBR operating under controlled conditions with artificial light and a HRT of 4 days (Kang et al., 2018). Last of all, caffeine was fully eliminated in the PBR. These results contrast with RE% values previously obtained in the same location (<50%) (García-Galán et al., 2018), indicating an enhanced efficiency of the studied PBR. The Mann-Whitney U statistical test applied showed significant statistical difference for all pharmaceuticals found in the analyzed matrix.

Considering these results, it should be noted that PBRs are biological, complex systems. In consequence, different mixed cultures can grow under different reactors configurations and/or conditions, leading to different elimination routes and pathways in the systems. Indeed, different publications on the elimination of a single compound using different microalgae cultures have yielded dissimilar results (de Wilt et al., 2016; Matamoros et al., 2016; Xiong et al., 2016). Biomass production in the reactors can also be determinant in terms of bioadsorption. In our case, however, despite the low biomass productivity in the PBR, its removal efficiency was high. The scale of the reactor studied may also influence the outcome. High temperature within the tubes of the PBR (Figure S1) may have led to faster biodegradation processes and removal routes. It has been observed in different studies in WWTPs that seasonal variations in the temperature do influence the removal efficiency for different contaminants (Matamoros et al., 2015). Other factors such as the transparency of the tubes in the closed system (and indirectly the material) or its roughness regarding biofouling can also be determinant (Harris et al., 2013). The control of pH could also aid to the removal via bioadsorption of the target analytes by changing their protonation state. Taking all this into consideration, further studies should be conducted, including the analysis of biomass to make a complete mass balance of the evaluated compounds and thus, better clarify the main removal routes in systems similar evaluated in this study.

4 Conclusions

The efficiency of a hybrid, tubular horizontal PBR to treat a mix of agricultural run-off and reclaimed wastewater used for irrigation was evaluated, focusing on their capacity to remove different PPCPs, including benzotriazoles, benzothiazoles and pharmaceuticals amongst others. BZT and BP3 were detected in all the influent samples investigated, and MeBZT in all except one. The PBR was not efficient in removing BZT and MeBZT, with average elimination not better than those obtained in conventional WWTPs. The limited photodegradability and low sorption to biomass tendency of these compounds could account for this lack of improvement, with elimination rates only attributable to biodegradation. The removal of BP3 was better than that of the benzotriazoles, but yet not higher than 40%. On the other hand, pharmaceuticals were efficiently removed, with full elimination in most cases. The sulfonamide antibiotic sulfapyridine was the exception, with no removal and negative eliminations in all cases, probably to metabolite deconjugation. High temperatures and pH could be determinant parameters in the elimination rates observed. Nevertheless, further studies should be developed to confirm this hypothesis, including biomass analysis in order to establish complete mass balances. Factors potentially affecting PPCP removals in this systems, such as the presence of heavy metals, should also be considered, as well as potential biomass growth hindering by other microorganisms present in the mixed liquor, such as protozoa. Overall, data on the removal capacity of microalgae-based systems under real conditions is still scarce, especially in closed systems, with most of the studies developed under laboratory controlled conditions and not considering the concentration in the biomass, which would help to understand the main removal mechanisms and predominant routes within these systems.

CRediT authorship contribution statement

Lucas Vassalle: Investigation, Writing - original draft, Writing - review & editing, Supervision. **Adrià Sunyer Caldú:** Methodology, Formal analysis. **Enrica Uggetti:** Resources, Writing - review & editing. **Rubén Díez-Montero:** Writing - review & editing. **M. Silvia Díaz-Cruz:** Methodology, Resources, Writing - review & editing, Funding acquisition, Visualization. **Joan García:** Project administration, Funding acquisition, Visualization. **Ma Jesús García-Galán:** Conceptualization, Investigation, Resources, Writing - original draft, Writing - review & editing, Visualization, Supervision.

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.

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Appendix A Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2020.111081.

Uncited references

Bourrelly, 1990, Palmer, 1962, Santiago et al., 2017.

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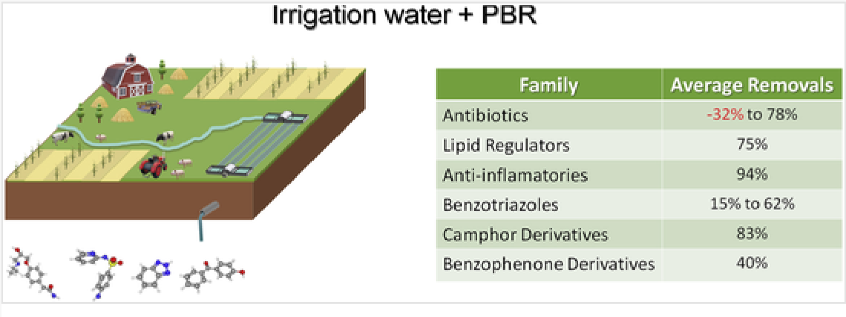
Graphical abstract

alt-text: Image 1



Highlights

- Treatment of irrigation water by microalgae in a semi-closed PBR was investigated.
- The semi-closed PBR at real scale removed efficiently very different contaminants.
- Removals were similar or better than those obtained in conventional treatments.
- Biodegradation, adsorption and photodegradation were the main removal mechanisms.

Appendix A Supplementary data

The following is the Supplementary data to this article:

Multimedia Component 1

Multimedia component 1

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