Valorisation of drinking water treatment sludge as substrate in subsurface flow constructed wetlands for upgrading treated wastewater.

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ABSTRACT

Drinking water treatment sludge (DWTS) is the main waste produced in drinking water treatment plants (DWTPs). Its valorisation as substrate for constructed wetlands (CWs) aimed at upgrading treated urban wastewater is presented. Keeping a holistic approach in mind, this study looks for nutrient and organic matter removal but also contaminants of emerging concern (CECs) and pathogens. Three pilot subsurface flow CWs (1 m^2) were installed under outdoor conditions in real WWTPs. Different operation modes (sequential: S-CW and continuous saturated flow: C-CW, CC-CW), different nutrient influent concentrations (S-CW and C-CW: 0.6 mg TP/l, 12.7 mg TN/l; CC-CW: 6.5 mg TP/l, 48 mg TN/l) and high hydraulic loading rates (HLRs, 0.9-5.1 $m^3/m^2/d$) were tested. C-CW presented higher removal efficiencies than S-CW for TP (C-CW: 56-86%; S-CW: 32-66%), total nitrogen (C-CW: 23-38%; S-CW: -3-6%) and E. coli (C-CW: 94%; S-CW: 84%), while S-CW performed better for ammonium (C-CW: 29-45%; S-CW: 72-86%) and CECs removal. Among fifteen CECs monitored, most pharmaceuticals, four were significantly reduced in C-CW and nine in S-CW, which had more aerobic conditions. CC-CW reduced nutrients and organic matter by 62% (TP), 8% (TN), 23% and 40% (chemical and biochemical oxygen demands, respectively). The potential release of aluminium was negligible. Novel values for the first-order reaction coefficient of P-k-C* model are provided for the TP removal process using DWTS (0.6-1.0 h^{-1}). The main conclusion is that DWTS is a suitable substrate to significantly upgrade WWTP effluents, even at high HLRs. A hybrid system combining sequential and continuous flow modes could optimize the upgrading treatment. A proposal for the full valorisation of the sludge produced in one DWTP is presented.

Keyworks: alum sludge; treatment wetlands; emerging pollutants; upgrading treatment; phosphorus removal; pathogens removal.

1. INTRODUCTION

Constructed wetlands (CWs) constitute a nature-based solution for wastewater treatment, particularly suitable for small towns. They can efficiently remove organic matter and suspended solids, whereas specific configurations or substrates are needed when nutrients must be removed, to meet the requirements of Urban Wastewater European Directive (UWWTD) (Directive 91/271/EEC).

According to the Redfield ratio, the discharge limits fixed in UWWTD for phosphorus (1-2 mg TP/l) are not enough to prevent eutrophication when WWTP effluents represent a high percentage of the water inputs to a water body, especially in case of lentic aquatic ecosystems, such as natural wetlands or lakes. Accordingly, Jucar River Basin Plan has lowered the discharge limit to 0.6 mg TP/l for WWTPs whose receiving water body is the Lake Albufera (RD 1/2016), a shallow hypereutrophic lagoon located in Valencia (Spain). Although this is an important step to recover the good status of the lake, according to the Water Framework Directive, earlier water quality modelling studies reported that it would be necessary a maximum of 0.1 mg/l for all the influents to the lake, for achieving this goal (Martin et al. 2013). However, it is difficult to achieve such low concentration in conventional WWTP since the biological treatment could be negatively affected because of nutrient limitation or bulking problems (Jenkins et al. 2004). At this point, CWs can play a key role in further phosphorus removal by using adsorbent substrates, especially in small WWTPs, where other kind of treatments for nutrient removal complicates its management.

Drinking water treatment sludge (DWTS) is the residual of potable water treatment process, not harmful and without toxic elements such as heavy metals (Zhao et al. 2020). Moreover, it has a high retention capacity of phosphorus, as well as other pollutants such as metals and semimetals, thus representing a low-cost adsorbent material (Zhao et al. 2020).

To the best of our knowledge, only few studies have focused on the potential reuse of DWTS for treating wastewater with low phosphorus concentrations (Gao et al. 2020). Regarding to contaminants of emerging concern (CECs), few studies have dealt with the potential of DWTS as substrate for removing pesticides (Hu et al. 2011; Zhao et al. 2013), surfactants (Jangkorn et al. 2011), tetracyclines or dyes (Devi and Saroha, 2017). A recent review (Wang et al. 2020), did not report any study regarding pharmaceuticals nor faecal indicator removal using DWTS. Accordingly, no study has addressed the role of DWTS as substrate in CWs for removing pharmaceuticals, thus it is interesting to cover this knowledge gap. Previous studies have demonstrated that CW are able to remove CECs, at least as efficient as conventional activated sludge, because of their higher sludge retention time and the coexistence of aerobic, anoxic and anaerobic microenvironments (Dotro et al. 2017).

In the present study, pilot-scale CWs were tested under outdoor weather conditions and treating real wastewater coming from two different secondary treatments. The objective of the study was to assess the ability of DWTS-based CWs to upgrade the quality of secondary effluents, from a holistic point of view, looking at organic matter and nutrient removal, but also emerging pollutants and faecal indicators.

The following hypothesis were put forward: (1) secondary effluents from WWTPs with nutrient removal can be substantially upgraded using CWs with DWTS as reactive substrate; (2) total phosphorus concentrations around 0.1 mg/l can be reached working at high hydraulic loading rates using these intensified CWs; (3) other pollutants like CECs and faecal coliforms can be significantly reduced in this upgrading treatment.

2. MATERIALS AND METHODS

2.1. Pilot plant and monitoring description

Three pilot CWs were installed in two WWTPs in Valencia (Spain). Two of them, called S-CW and C-CW (Fig. S1), were placed in a large WWTP (129000 PE) which has conventional activated sludge followed by tertiary treatment, with nutrient removal and disinfection. The influent to these CWs was the effluent from secondary treatment. The third pilot wetland (CC-CW) was placed in the WWTP of a small town (100 PE), which consists of two Imhoff tanks in series followed by two horizontal subsurface flow CWs in series. The pilot systems consisted of containers with a surface 1 m^2, filled with DWTS from "La Presa" DWTP (Valencia) (37 cm depth; 0.83-19.0 mm grain size), and two layers of coarse gravel (10-11 mm grain size) at bottom (10 cm depth) and surface (5 cm depth). Common reed (*Phragmites australis*) was planted with an initial density of 10 stems/m^2 in C-CW and S-CW, and 3 stems/m^2 in CC-CW. Two operation modes were tested: continuously saturated flow (C-CW and CC-CW) and sequential operation (S-CW). The sequential operation consisted of loading-contact period-draining batches. The draining operation was controlled by a solenoid valve. Three different hydraulic loading rates (HLR) in different periods were tested in S-CW and C-CW (Table 1). The performance of pilot CWs was monitored for one year and a half. Grab samples (2 l) of the influent and the effluent from each pilot CW were collected for physical-chemical analysis. Dissolved oxygen (DO) was measured in situ, with a Hach HQ40D portable multiparameter. Electrical conductivity and pH were measured with a Hach440d multiparameter. The samples were transported to the laboratory in an icebox and kept in refrigerator (4ºC) until chemical analysis, within 24 h.

2.2. Chemical analyses

Water quality (WQ) variables analysed, and methods (in parenthesis), were: turbidity (TN100 Eutech turbidity-meter), total suspended solids (TSS) (UNE-EN 872, UNE 77034), chemical oxygen demand (COD) (Hach test: ISO 6060), biochemical oxygen demand (BOD_5) (respirometry test through OxiTop® control system), total nitrogen (TN) (Hach test: ISO 11905-1+photometry), ammonium ($N\text{-}NH_4^+$) (Hach test: ISO 7150-1), nitrites ($N\text{-}NO_2^-$) (Hach test: ISO 26777), nitrates ($N\text{-}NO_3^-$) (Hach test: ISO 7890-1-2), total phosphorus (TP) (Hach test: digestion + ISO 6878), orthophosphates ($P\text{-}PO_4^{3-}$) (Hach test: ISO 6878), aluminium (Al) (ultraviolet–visible spectrophotometry). The analyses frequency was 3 times a week for the physicochemical parameters and soluble compounds, and one a week for total compounds. *Escherichia coli* (ISO 9308-1) was monitored weekly from Apr to Sep 2019 and monthly afterwards (n=24). Intestinal nematode eggs (modified Bailinger's Method) were evaluated once a month.

A total of 15 CECs, belonging to different therapeutic classes, were monitored monthly. The CECs were selected because of their widespread use and high frequency in urban wastewater. Chemical analyses were performed by an accredited laboratory, which used the following methods: CSN EN ISO 18857-2 for Bisphenol A; DIN 38407-35 for caffeine, ibuprofen, salicylic acid and triclosan; US EPA 1694 for atenolol, metoprolol, diclofenac, naproxen, paracetamol, carbamazepine, sulfamethoxazole, trimethoprim, gemfibrozil, and furosemide.

DWTS was analysed using standard methods for TP, Al and other metals (ISO 11885), organic matter (loss on ignition according to UNE EN 15169) and total organic carbon (TOC) (EN 15936).

2.3. Statistical analyses

Statistical analyses were performed using Statgraphics XVII centurion. Three different periods were established according to HLR. Influent and effluents (S-CW and C-CW) were compared for WQ variables, assuming that samples were related because were taken on the same dates. For this, t-student test was used if normality was satisfied and a non-parametric test (W de Mann-Whitney (Wilcoxon)) otherwise. Correlation coefficients were calculated to assess the influence of some variables on the performance of the pilot CWs. Multiple linear regression models (MLRM) were estimated using the stepwise method. Statistical significance was indicated by a probability of type I error < 5 % ($p<0.05$).

2.4 Mathematical modelling

The mathematical model P-k-C*, based on a tanks-in-series model (Dotro et al. 2017), has been calibrated for TP. The objective was to provide suitable values of the constant rates to be used for designing intensified treatment wetlands aimed at phosphorus removal. The calibration was focused on the saturated systems (C-CW and CC-CW) because the hydraulic model of tanks-in-series is suited only for them (Dotro et al. 2017). The P-k-C* approach has the following equation:

$$C_{ef} = C^* + \frac{C_{in} - C^*}{(1 + k \cdot \frac{\tau}{P})^P} \qquad (Eq. 1)$$

Where C_{ef} is the effluent concentration (mg P/l) to be achieved, C_{in} the influent concentration (mg P/l), C* is the background concentration, k is the first-order reaction coefficient (h^{-1}), τ is the theoretical retention time (h), and P is the apparent number of tanks-in-series (dimensionless). For its calibration, data were divided into groups with the following ranges of C_{in}: <1, 1-2, 2-3.5, 3.5-9 mg P/l. The C_{in} ranges below 3.5 mg P/l correspond to C-CW and the range 3.5-9 mg P/l correspond to CC-CW system. Then the data of C_{ef} were fitted to Ec. 1 by varying the value of k, seeking for the minimum root-mean-square error (RMSE) between the simulated and experimental data. The value of P was fixed in constant values (P = 3) and C* was set in 0.015 mg P/l, the half of the lowest value measured in the full study period.

3. RESULTS AND DISCUSSION

3.1. Performance as upgrading treatment system.

3.1.1. Organic matter, total suspended solids, pH, dissolved oxygen and nitrogen.

COD was significantly reduced in the three pilot systems ($p<0.05$). It decreased from values between 26 and 38 mg/l to values around 20 mg/l (Table 2) for S-CW and C-CW, and from a mean value of 40 mg/l to an average of 31 mg/l in CC-CW (Table 3). All systems contributed to a further reduction of BOD_5 as well ($p<0.05$). The effluents presented very low values, around 4 mg/l, which is very beneficial for the receiving water bodies. TSS were also significantly improved by systems S-CW and C-CW ($p<0.05$), producing an effluent with less than 5 mg/l and high transparency. Conversely, CC-CW did not achieve a further decrease of TSS, as they reached 5 mg/l in the influent.

The second period presented a lower efficiency than the others, likely due to the extremely high HLR. Contrariwise to other parameters discussed later, non-significant differences were found between the operation modes for COD, BOD_5 or TSS ($p>0.05$). In the case of organic matter, the more aerobic conditions in S-CW could have compensated the shorter HRT, thus achieving removal efficiencies like those of C-CW. For TSS, the filtration process would have been equally efficient in both systems due to the same characteristics of the filter media. Interestingly, the effluents generally presented less standard deviation than the influent (Tables 2 and 3), highlighting the buffer capacity of CWs.

The pH did not vary significantly from the influent to effluent (Table 2), in contrast to other adsorbent materials that cause significant pH rises (Dotro et al., 2017). Dissolved oxygen (DO) in the effluent from C-CW was significantly lower than the influent and S-CW effluent ($p<0.05$) (Table 2), because of the lower reaeration of C-CW.

The ammonium concentration was significantly reduced in systems S-CW and C-CW ($p<0.05$), from influent values around 4 mg N/l to average effluent concentrations of 0.8 and 2.6 mg N/l in S-CW and C-CW, respectively (Table 2), which is very beneficial for the receiving aquatic environment, especially in areas under water stress and droughts. The removal efficiency was significantly higher in the S-CW, because of its more aerobic conditions (Table 2). Conversely, total nitrogen and nitrates were only significantly reduced in system C-CW ($p<0.05$). In this system, aerobic and anoxic environments coexisted, allowing nitrification and denitrification processes, while in S-CW the denitrification could have been inhibited due to higher DO concentrations. Based on these results, a combination of both operation modes to create a two-stage system or a partially saturated system would allow the optimization of nitrogen removal.

In the case of CC-CW, the low removal efficiencies reached could be related with the much lower vegetation development in comparison to C-CW.

3.1.2. Phosphorus removal efficiencies and saturation degree.

All three pilot CWs significantly reduced the concentration of total phosphorus ($p<0.05$) (Fig. 1 and Table 3). The CWs treating low concentrations of TP reached average effluent concentrations ranging from 0.18 to 0.44 mg P/l in S-CW and from 0.08 to 0.25 mg P/l in C-CW. C-CW removed TP more efficiently than the S-CW in all three periods ($p<0.05$). The best performances were found during period 1, when efficiency mean values of 66% and 86% for the S-CW and C-CW were reached, working at very high HLR (around 3 $m^3/m^2/d$).

After these good results, it was decided to raise the HLR (5 $m^3/m^2/d$) to test the boundaries of the pilot systems. However, in this second period both CWs decreased their efficiencies, with average values of 32% (S-CW) and 56% (C-CW). Probably HLR was too high and, consequently, HRT was too short to achieve a good efficiency of the sorption process. In addition, the influent concentration was lower than in the other periods, which could also have contributed to the lower efficiency, because lower influent concentration implies lower efficiency (Martin et al. 2013). In fact, the influent concentration (C_{in}) influenced positively on mass removal rate (Fig. S4). Temperature can also influence the efficiency of the process; however, it was not significantly different among the periods.

During the third period, the HLR was reduced to 1 $m^3/m^2/d$, giving rise to an enhancement of the efficiencies, 45% for S-CW and 69% for C-CW. However, these efficiencies were lower than those registered in the first period, despite the HLR reduction. A possible reason could be the accumulation of organic matter inside the systems. On several occasions, surface clogging symptoms were observed after cleaning operations of the secondary clarifiers of the WWTP. This organic matter could have released phosphorus during its biodegradation. Moreover, it could have hindered the diffusion of phosphorus to the sorbent surface.

In general, orthophosphates presented a trend similar to TP. For both variables, C-CW presented higher efficiencies in all periods. Despite working at relatively similar HLR, the HRT was significantly lower in the S-CW because the draining stage spends time, which is only partially considered as HRT. Overall, the C-CW was more resilient to HLR and C_{in} changes. Regarding the buffer capacity, the variability of influent is reduced in the upgrading treatment in the pilot CWs. During the third period some peak concentrations in the influent were indeed substantially reduced in both pilot systems (Fig. 1), with removal efficiencies around 65%.

The CW prototype treating higher phosphorus concentration (CC-CW) presented a mean removal efficiency of 62%, significantly reducing the TP concentration from 6.15 to 2.36 mg/l ($p<0.05$) (Table 3). More interestingly, just with 1 m^2, CC-CW treated 17% of the total WWTP's flow, and had a noticeable effect on its final effluent, which decreased from 6.12 mg/l of TP (average of 18 months before) to an average of 5.2 mg/l during the research period. Thus, the full-scale CW that receives the effluent of the CC-CW increased its TP removal efficiency from 8% to 16%.

The results obtained in this study agree with earlier research. Babatunde et al. (2010) found very high removal efficiencies in the first of a four-stage treatment, but lower efficiencies in the subsequent treatment stages. Under a HLR 1.27 $m^3/m^2/d$ and an influent concentration of 21 mg P/l (SRP), the treatment reached a removal efficiency of 89% and an effluent concentration of 2.3 mg P/l in the first stage, and subsequent reductions to 1.2 mg P/l (48%), 0.86 mg P/l (28%) and 0.47 mg P/l (45%) in the second, third and fourth stages, respectively. Mass removal rates (MRR) varied between -0.17 and 5.0 $g/m^2/d$ in the systems treating low concentrations. On average, the mass loading rate (MLR) was reduced by 59% in S-CW and by 69% in C-CW (Fig. S2). The obtained multiple linear regression models (MLRM) showed that MRR depended on C_{in}, HLR and temperature (Figures S4 and S5).

CC-CW reached a removal rate of 14.7 $g/m^2/d$ when the HLR was 3.3 $m^3/m^2/d$, on average the MLR was removed by 58%.

The cumulative phosphorus removed during the whole study period, 285, 396 and 3013 g/m^2 in S-CW, C-CW and CC-CW respectively, was estimated by interpolating linearly for the periods between samplings (Fig. S3). These data represent a 7, 10 and 111% of the sludge adsorption capacity, respectively, calculated from the mass of DWTS inside the pilot systems and its maximum sorption capacity, which was calculated experimentally applying the Langmuir model (Table S1). Phosphorus can be bound to the DWTS through adsorption, chemical precipitation with iron, aluminium, or calcium, and coprecipitation with calcium carbonate (Babatunde and Zhao, 2009). Considering the average removal rates of 0.53 and 0.73 $g/m^2/d$ (S-CW and C-CW respectively), they could keep working for more than ten years. Remarkably, CC-CW exceeded the maximum adsorption capacity and, even though the efficiency has decreased to 32% in the last three samplings, it continues removing phosphorus. Zhao et al. (2008) also noticed that the mass of P immobilized exceeded the maximum adsorption capacity.

Compared with other materials, the efficiencies achieved in the present study can be considered high, considering the high HLR tested. Martin et al. (2013) obtained a mean efficiency of 75% for TP in a full-scale vertical flow CW filled with a mixture of sand and iron oxides but working with HRT of 24 hours and Vera et al. (2014) obtained a removal efficiency around 70% using zeolites with HRT of 3-4 days. If non-reactive materials, such as gravel, are used, typical efficiencies of 10-20% are obtained (Dotro et al. 2017).

In summary, the results obtained indicate that it is possible to work with high HLR without giving up the system efficiency. This allows upgrading large flows with relatively small areas. The efficiency can be enhanced enlarging the depth of DWTS, to increase the HRT, or working in multi-stage systems.

3.1.3. Aluminium

The concentration of aluminium in DWTS is very high, because of the coagulant used in the water treatment. In this study the content of Al in the DWTS was on average 34.8% (Table S2). Other authors measured Al contents varying between 6.1 and 44.05 % (Hou et al. 2018). Looking at the values compiled by those authors, it appears to exist a certain positive correlation between Al content and maximum adsorption capacity.

Given this aluminium high content, it is important to check that it is not leached from the substrate to the treated water. During the whole study period, the Al concentration in the effluent was below 0.2 mg/l, value established for human consumption (Directive 98/83/EC). Indeed, it was mostly below the detection limit (0.05 mg/l). These results agree with previous studies and corroborates that DWTS can be safely used as reactive media in CWs (Zhao et al. 2008; Babatunde et al. 2011). Moreover, the aluminium content in reed was measured in a previous microcosm experiment where two substrates were compared (gravel and DWTS). The results showed that reed growing on DWTS presented an Al content (48 and 11 mg/kg dry weigh (d.w.) in dead and fresh stems respectively) similar to reed growing on gravel (52 and 34 mg/kg d.w. respectively) (Naranjo-Ríos et al. 2018).

3.1.4. Contaminants of emerging concern (CECs)

In this study, the concentrations of CECs in the influent are low because it comes from the secondary treatment of the WWTP. Most CECs were below 1 µg/l, except bisphenol A, which reached a mean concentration of 1.301 µg/l (Table 4). These low concentrations were further reduced in the pilot systems for most CECs. A significant decrease was achieved in the S-CW for seven of the CECs analysed, while four CECs were significantly removed in the C-CW ($p<0.05$). Hence, the results indicate that the more aerobic conditions in the S-CW favoured a more efficient removal of CECs, with significant removal efficiencies varying between 11% (carbamazepine) and 85% (bisphenol A). This positive effect of aerobic conditions agrees with previous studies (Kahl et al. 2017; Ilyas and van Hullebusch, 2020).

Matamoros et al. (2008) measured similar levels of analgesics in a secondary treatment effluent, which were further reduced in a surface flow CW with moderate to high efficiencies (carbamazepine: 0.37 µg/l, 30-47%; ibuprofen: 0.04 µg/l, 95-96%; naproxen: 0.34 µg/l, 52-92%; diclofenac: 1.25 µg/l, 73-96%). Their efficiencies were considerably higher than those found in this study, probably due to higher HRT (1 month). In addition, the photooxidation process, feasible in surface flow CW, is not active in subsurface flow CW. In this sense, removal efficiencies are highly variable among different studies. For instance, Ilyas and van Hullebusch (2020) compiled mean efficiencies of 53, 39 and 63% for the analgesics ibuprofen, diclofenac and naproxen, respectively, with relative standard deviations varying between 40 and 60%. In this study, paracetamol was under the detection limit in most cases, both in influent and effluents. It usually presents very high removal efficiencies, indeed Verlicchi et al. (2012) reported an average removal efficiency of 93% in conventional activated sludge, so it was probably removed in the previous treatment.

Regarding the studied antibiotics, trimethoprim was reduced in both wetland systems, more significantly in S-CW (43%). The efficiencies are within the range of variation reported by Ilyas and van Hullebusch (2020). In contrast, sulfamethoxazole increased significantly, about a 42% ($p<0.05$). Previous studies have also reported variable and mainly poor, even negative, removal efficiency for sulfamethoxazole (Auvinen et al. 2017). They hypothesized that it could be due to the potential retransformation of the metabolite to the parent compound.

Among beta-blockers, metoprolol was undetectable neither in the influent nor in the effluents. Whereas, atenolol was significantly reduced in both pilot systems ($p<0.05$), reaching similar mean concentrations of 0.122 µg/l (S-CW) and 0.108 µg/l (C-CW). Sorption is recognized as the dominant removal mechanism for this CEC (Table 4). This could explain the fact that both pilot systems achieved efficiencies statistically non different ($p>0.05$).

The diuretic furosemide presented negative removal efficiencies. The removal efficiency reported in literature is widely variable, from values of 35% (Verlicchi et al. 2013) to 80-96% (Chen et al. 2016) or -10.5-98.8% (Vymazal et al. 2017). Hydrolysis and photolysis are usually considered the major removal pathways in water environment, and hydrolysis in subsurface flow CWs (Chen et al. 2016; Vymazal et al. 2017). Olvera-Vargas et al. (2016) demonstrated microbial transformation of furosemide and identified three different metabolites, two of which exhibited higher toxicity than furosemide. Nevertheless, CECs with chlorine in their molecular structure are considered recalcitrant and their removal efficiency is inversely proportional to the molecular weight (Ilyas et al. 2020). Furosemide has a high molecular weight (330.7 g/mol), which could explain the low removal efficiencies. Other authors obtained good removal efficiencies in adsorption experiments using light expanded clay aggregates (LECA) and cork granulates as sorbent materials (Machado et al. 2017). It is difficult to explain the increase observed in the pilot CWs, feasible hypotheses could be the retransformation of metabolites to the parent compound or desorption of previously adsorbed contaminant, if the substrate was rapidly saturated. The monitoring of CECs started two months after the operation onset and the substrate could have been saturated during this period. In this sense, the valorisation of exhausted activated carbon, which is another waste produced in DWTPs, to generate a mixed reactive media (DWS + activated carbon) would enhance the removal efficiency of this and other CECs. Indeed, Ataki et al. (2021) also suggest the mixture of multiple substrates, with complementary properties, to target multiple contaminants and improve the performance of CWs.

Carbamazepine was reduced with a low but significant percentage yield in both systems (16% in C-CW; 11% in S-CW) ($p<0.05$). The recalcitrance of this compound is well documented (Kahl et al. 2017; Delgado et al. 2020; Ilyas and van Hullebusch, 2020) and Delgado et al. (2020) found that its removal was mainly linked to plant absorption.

The concentration of the lipid regulator gemfibrozil decreased a 35% in S-CW and 3% in C-CW. It agrees with previous studies where the removal is mainly attributed to aerobic degradation (Ilyas and van Hullebusch, 2020).

Salicylic acid was substantially reduced in both pilot systems ($p<0.05$), from 0.452 µg/l in the influent to 0.271 µg/l in the effluent of S-CW and 0.187 µg/l in C-CW, which achieved a more significant decrease ($p<0.05$). The main removal pathway reported in the literature is aerobic biodegradation (Table 4). Plant uptake could be also possible because of its low molecular weight joined to its high-water solubility and hydrophilic nature (Ilyas et al. 2020). In this study, it could be more efficiently removed in the C-CW due to its higher HRT.

Caffeine was reduced in both pilot CWs with similar and high efficiencies (56% in C-CW and 58% in S-CW), in line with other studies where caffeine is described as a readily biodegradable compound (Ilyas and van Hullebusch, 2020).

The antiseptic triclosan was below the detection limit in all samples. It could have been removed in the previous activated sludge process, as high removal efficiencies are usually found (Verlicchi et al. 2012). Ávila et al. (2015) reported an average removal efficiency of 61% in a full-scale vertical flow CW, attributing the high efficiency to the prevailing aerobic conditions, which was further increased to 79% in subsequent wetlands (horizontal flow + free water surface flow), decreasing the concentration from 0.15 to 0.03 µg/l. These authors also demonstrated a decrease of the treatment performance when HLR was increased (Ávila et al. 2014).

Bisphenol A was efficiently reduced in both pilot CWs, more significantly in S-CW (85%) (Table 4). High removal efficiencies have been found for this CEC, especially in aerobic conditions, and not dependent on HLR by Ávila et al. (2014, 2015). This high biodegradability would explain the good efficiencies obtained in this study despite the high HLR applied to the pilot systems. Interestingly, it was observed that CEC concentrations in influent and effluents were negatively correlated with temperature (Table S3). This correlation can be explained because most processes implied in CEC removal depend on temperature (biodegradation, adsorption, photolysis, hydrolysis). Additionally, another influencing factor could be the consume pattern (Chen et al. 2016), as it seems reasonable that some of the pharmaceuticals are more consumed in winter. In this sense, the monitoring for periods of one year, or longer, are essential to allow a robust evaluation of the dependence of removal performance on operational conditions (Kahl et al. 2017). These authors also found a dependence of removal efficiencies on temperature.

Finally, the environmental risk was assessed through the calculation of the risk quotient (Fig. 2), according to Chen et al. (2016). In general, CECs levels presented low environmental risk in the influent. For eleven of the monitored CECs the Risk Quotient (RQ) was below 0.1, indicating low environmental risk. Three CECs (gemfibrozil, salicylic acid, and bisphenol A) presented a medium environmental risk in the secondary treatment effluent (RQ between 0.1 and 1), which was considerably reduced in the wetland pilot systems. Only sulfamethoxazole presented a high-risk level (RQ >1), despite its concentration was relatively low (0.1 µg/l), but the predicted no-effect concentration (PNEC) is even much lower (0.027 µg/l). This highlights the importance of bearing in mind the toxicity and non-toxicity levels of each substance, to evaluate the risk posed by their presence in treated wastewater.

3.1.5. Microbiological indicators

The main microbiological indicators considered in Spanish and European regulation on water reuse, *Escherichia coli* and helminth eggs, were monitored. Helminth eggs were not detected neither in the influent nor the effluents, in any sampling campaign.

Regarding *E. coli*, a significant decrease was obtained in both pilot systems (Fig. 3), from an average concentration of $2.2 \cdot 10^5$ CFU/100 ml to $3.9 \cdot 10^4$ and $1.6 \cdot 10^4$ CFU/100 ml in S-CW and C-CW, respectively. The mean efficiencies were 84.4% (S-CW) and 94.1% (C-CW). Such difference could be related with the higher retention time in C-CW or the operation mode, maybe more predator organisms can develop inside the continuously saturated CW. Other studies have also reported better efficiencies in horizontal flow CWs (99.7%) respect to vertical flow CWs (82.0%) (Ávila et al. 2015). Although it should be mentioned that the studies are not directly comparable because in that study the CWs worked in series (VFCW+HFCW) and their HLR was much lower.

C-CW efficiency presented a strong correlation with temperature ($r = 0.59$, $p<0.05$) and HLR ($r = -0.62$, $p<0.05$), so high temperatures and low HLR favoured the removal of E. coli. In contrast, S-CW efficiency did not correlate with these variables ($r = 0.25$, $p>0.05$ for T; $r = 0.07$, $p>0.05$ for HLR). For both systems, the influent concentration strongly influenced the effluent concentration ($r = 0.78$, $p<0.05$ for C-CW; $r = 0.73$, $p<0.05$ for S-CW). The relation between *E. coli* and TSS was also evaluated to assess if TSS could be used as indicator of faecal contamination, but the correlation was very weak.

On an average basis the effluents would not meet the requirements for any use foreseen in the European Regulation on water reuse (REGULATION (EU) 2020/741). Nevertheless, it should be noted that in most cases (81% of samples) the effluent from the C-CW accomplished the requirements for the use called D (crop category: industrial, energy and seeded crops). The compliance rate in case of S-CW was lower (43%), which could be enhanced by decreasing HLR. The addition of a subsequent free-water surface CWs would help to further reduce the concentration of E. coli and could provide an effluent suitable for several irrigation uses (Ávila et al. 2015).

3.2. Design criteria for phosphorus removal and water quality upgrading.

The P-k-C* model has been calibrated as a tool for wetland design. This model was selected because the influence of the HRT was observed, so that the hypothesis is that the sorption of phosphorus on this material follows a first-order kinetics (Fig. 4).

The values obtained for k were 1.0, 0.8, 0.6 and 0.6 h^{-1} for the ranges <1, 1-2, 2-3.5, 3.5-9 respectively, thus the value of k decreases as the C_{in} increases. This trend was also reported for BOD_5 (Dotro et al. 2017), which means that when C_{in} is high more HRT is needed for reaching the same C_{ef}. The RMSE values obtained are shown in Table S4. The k values resulted far higher than those listed by Rousseau et al. (2004) (0.14-0.28 d^{-1}) for gravel beds, because of the greater adsorption capacity of DWTS, and also higher than those obtained for other sorbent materials (0.26 h^{-1}, Delgado et al. 2021).

Once obtained the k values, the equation for estimating the necessary area is:

$$A = \frac{P \cdot Q}{k \cdot \phi \cdot h}\left(\left(\frac{C_{in} - C^*}{C_{ef} - C^*}\right)^{1/P} - 1\right) \qquad (Eq. 2)$$

Where A is the area (m^2) and ϕ is the porosity (Dotro et al. 2017). By way of example, for a town with a population of approximately 1000 inhabitants, with an average daily flow of 150 m^3/d and a C_{in} equal to 6 mg P/l, the necessary area to reach a C_{ef} equal to 0.5 mg P/l would be 234 m^2. A wetland water depth of 0.5 m, a porosity of 0.35, P equal to 3, C* equal to 0.015 mg P/l and the k corresponding to this C_{in} (0.6 h^{-1}) have been assumed. Additionally, from a management point of view, the lifespan of the intensified CW should be estimated. For this, the quantity of DWTS inside the CW can be calculated as follows. The density of the material is around 750 kg dw/m^3. The total volume of the CW would be 117 m^3, thus the mass of DWTS would be 82 tons. Multiplying the mass per the maximum adsorption capacity (14.5 g P/kg DWTS), the total quantity of TP to be removed is 1188 kg P. Applying a safeguard of 25% because the efficiency decreases as the DWTS becomes saturated, the mass of P would be 890 kg P. This would allow treating the flow for approximately 3 years. In addition, as the efficiency decreases as the material becomes saturated, it is advisable to propose a design based on a sequence of cells in series, in order to make maximum use of the sorption capacity of the DWTS and renew them as they become completely saturated.

3.3 Proposal for the full valorisation of sludge produced at “La Presa” DWTP.

“La Presa” DWTP (Manises, Valencia), with a production capacity of 0.15 Hm^3/d, supplies drinking water to a population of 0.8 million inhabitants. The purification process produces between 3 and 4 m^3/d of sludge cake, which is equivalent to approximately 1,670 tons/year, with an average content of 26% of dry matter. This dryness must be increased to 90% to proceed with grinding. In the grinding process to obtain the desired granulometry, there were losses of 15% of the processed material, because the size was too fine or too coarse. Considering these losses, a production of 370 tons/year of dry granulated sludge is estimated. Assuming that the annual production could be stored, a selection of towns near the DWTP has been made with the aim of proposing a full valorisation of the sludge annually generated. The following criteria have been applied: population less than 2000 inhabitants, WWTP without phosphorus removal, distance from DWTP less than 100 km, proximity between towns, and discharge of their treated effluents in the Turia river basin. This last criterion has been considered since upgrading the wastewater discharged in the Turia river basin will contribute to improve its water quality, which in turn can benefit the purification process, since it is an important water source for the DWTP.

Another variable to be fixed is the lifespan of the upgrading CWs. As a premise, it was set for at least 5 years. Further considering aspects such as transport costs and associated emissions, it was concluded that 7 years provided the best combination of groups and individual municipalities to valorise the annual production of dry granulated sludge, so that every 7 years they would have to change the sludge-based substrate in the upgrading CWs (Figure S6). The necessary mass of sludge to satisfy this life span was calculated from the maximum adsorption capacity determined and the phosphorus emitted by the towns proposed. This group of municipalities has a total population near 10000 inhabitants and produces a total wastewater flow of 4800 m^3/d. Therefore, a relation between drinking water produced and treated wastewater to be upgraded can be estimated, giving a ratio of 32 litres upgraded wastewater per cubic meter of drinking water produced.

Once exhausted, the sludge could be used in agriculture as it meets the requirements set out in the European Directive on the protection of the environment and soil, when sewage sludge is used in agriculture (86/278/EEC) (Table S2).

4. CONCLUSIONS

The main conclusions are:

- DWTS is a good substrate for upgrading treated urban wastewater, being able to produce a significant enhancement of the effluent even under high hydraulic loading rates.
- Effluent concentration depends on operation conditions. A level of TP around 0.1 mg/l is achievable working with a continuous flow and 3 $m^3/m^2/d$ if influent concentration is around 0.5 mg/l. When the influent concentration is around 6 mg P/l, an effluent concentration of 0.5 mg/l can be reached working at 0.8 $m^3/m^2/d$.
- Novel values for the first-order reaction coefficient are provided for TP removal.
- Continuous flow operation performs better for TP, nitrates, TN and pathogens, whereas a sequential setup is more efficient for ammonium and CECs removal. Therefore, a hybrid system, consisting of a sequential layer on the top and a continuously saturated bottom layer, could optimize the upgrading treatment.
- The combination of DWTS with exhausted activated carbon, another waste produced in DWTPs, could enhance the efficiency for CECs removal.
- Our results confirm previous literature statements, DWTS is presented as a low-cost adsorbent substrate with good efficiencies despite the variability in its composition, usually found in waste materials. Therefore, it should be valorised whenever possible to

integrate the principles of circular economy in the urban water cycle. A widespread implementation of systems for upgrading treated wastewater, based on wetlands with reactive media, can contribute to significantly improve the water quality of the receiving environments, thus helping to meet the objectives of the Water Framework Directive, and making them more resilient to the effects of climate change. This is especially important for removing emerging pollutants such as those evaluated in this study, but also other like microplastics or organic UV filters.

- These low cost, effective and environmentally friendly technologies are highly recommended for upgrading treatments.

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TABLES AND FIGURES

Table 1. Mean ± standard deviations are indicated for HLR (hydraulic loading rate) and HRT (hydraulic retention time), and range of variation for temperature (T) for different study periods. N is the number of data for each period, for small WWTP the monitoring period was extended only for TP, which N is in parenthesis.

WWTP	Large						Small
Variable	Period 1 (Apr – Aug 2019)		Period 2 (Sep – Dec 2019)		Period 3 (Dec 2019 – Sep 2020)		(Nov 2019 – Feb 2021)
Abbreviature	S-CW	C-CW	S-CW	C-CW	S-CW	C-CW	CC-CW
HLR ($m^3/m^2/d$)	3.4 ± 0.3	2.8 ± 0.7	5.1 ± 0.8	4.7 ± 1.6	0.9 ± 0.1	1.3 ± 0.6	2.6 ± 1.5
HRT (h)	0.9 ± 0.1	1.8 ± 0.7	0.5 ± 0.1	1.3 ± 1.3	2.4 ± 0.0	4.6 ± 3.0	2.3 ± 1.3
T (ºC) range	17.6–28.9	17.1–28.7	16.8–27.8	15.6–26.0	11.6–29.5	14.4–30.0	5.7 –25.9
N	56	52	23	21	37	32	8 (12)

Table 2. Mean concentration (mg/l) ± standard deviation and removal efficiencies (%) of S-CW and C-CW for each study period. N and P forms in mg N/l and mg P/l, respectively. Inf: influent, Ef: effluent.

	Period 1			Period 2			Period 3		
	Inf.	Ef. S-CW	Ef. C-CW	Inf.	Ef. S-CW	Ef. C-CW	Inf.	Ef. S-CW	Ef. C-CW
TN	8.90±3.04	8.70±2.73 (2%)	5.95±2.23 (33%)	10.82±2.07	10.44±2.05 (4%)	8.29±2.40 (23%)	13.77±8.04	13.57±6.73 (1%)	8.56±6.95 (38%)
NH_4^+	3.28±2.43	0.29±0.45 (91%)	2.38±1.60 (27%)	4.44±3.64	1.33±2.69 (70%)	2.66±3.24 (40%)	4.93±4.57	0.87±1.43 (82%)	2.71±4.00 (45%)
NO_3^-	3.89±1.34	8.11±2.68 (-108%)	2.66±1.54 (32%)	5.42±2.46	10.60±4.33 (-96%)	4.99±2.39 (8%)	4.05±2.30	9.39±4.44 (-132%)	2.49±2.53 (39%)
COD	32.59±8.30	20.91±4.52 (36%)	20.81±4.49 (36%)	26.06±3.79	18.94±4.46 (27%)	19.20±3.38 (26%)	37.67±10.41	21.90±4.61 (42%)	23.42±6.43 (38%)
BOD_5	10.70±3.97	5.21±2.97 (51%)	5.21±2.53 (51%)	7.88±1.46	4.57±1.27 (42%)	4.43±1.13 (44%)	11.59±4.54	4.88±1.83 (58%)	3.47±1.55 (70%)
TSS	7.26±5.85	2.72±1.50 (63%)	2.27±1.29 (69%)	4.28±1.27	3.11±6.52 (27%)	1.76±0.90 (59%)	11.86±4.99	8.27±10.74 (30%)	4.11±2.58 (65%)
DO	2.54±0.75	3.20±1.38	1.89±0.47	3.21±1.29	3.06±1.22	1.57±0.30	4.17±1.47	3.48±1.11	2.71±1.20
pH	7.5±0.2	7.4±0.2	7.5±0.2	7.4±0.2	7.4±0.2	7.4±0.2	7.4±0.3	7.4±0.2	7.4±0.2

Table 3. Mean concentration (mg/l) ± standard deviation and removal efficiency (R.E.) of the pilot CC- for the full period. N and P forms in mg N/l and mg P/l.

	Influent	Effluent	R.E. (%)
TP	6.15 ± 2.77	2.36 ± 1.21	62%
PO_4^{3-}	5.89 ± 2.58	2.12 ± 1.07	62%
TN	48.06 ± 19.02	44.06 ± 13.41	8%
NH_4^+	37.34 ± 15.45	34.19 ± 16.23	8%
NO_2^-	0.21 ± 0.53	0.36 ± 0.38	-68%
NO_3^-	1.17 ± 2.59	2.47 ± 3.33	-111%
COD	40 ± 11	31 ± 6	23%
BOD_5	6 ± 9	3 ± 6	40%
TSS	5.38 ± 1.99	5.75 ± 2.91	-7%

Table 4. Mean concentrations (± standard deviation) of CECs (µg/l) in influent and effluent of CW pilot systems, from June 2019 to June 2020 (N = 12). RE: removal efficiency. The arrows indicate the direction of the variation, double arrows in bold indicate significant variation (p <0.05). The detection limit is assigned when the concentration is below it. [1]Based on Ilyas and van Hullebusch (2020); [2](Chen et al. 2016; Vymazal et al. 2017); [3]Olvera-Vargas et al. (2016); [4]Machado et al. (2017); [5]Ávila et al. (2014, 2015).

Therapeutic class	CEC	Influent	S-CW effluent	RE (%)		C-CW effluent	RE (%)		Main removal mechanism
Analgesical / anti-inflammatories	Ibuprofen	0.176 ± 0.072	**0.126 ± 0.038**	**28%**	**↓↓**	0.153 ± 0.056	13%	↓	Biodegradation (aerobic)[1]
	Diclofenac	0.529 ± 0.359	**0.342 ± 0.221**	**35%**	**↓↓**	0.514 ± 0.333	3%	↓	Biodegradation (aerobic)[1]
	Naproxen	0.205 ± 0.102	**0.110 ± 0.029**	**46%**	**↓↓**	**0.144 ± 0.062**	**30%**	**↓↓**	Biodegradation (aerobic) and photodegradation[1]
	Paracetamol	0.102 ± 0.007	<0.10			<0.10			Biodegradation and sorption[2]
Antibiotics	Sulfamethoxazole	0.083 ± 0.029	**0.120 ± 0.052**	**-45%**	**↑↑**	**0.118 ± 0.050**	**-43%**	**↑↑**	Biodegradation (aerobic, anaerobic)[1]
	Trimethoprim	0.090 ± 0.055	0.051 ± 0.004	43%	↓↓	0.064 ± 0.045	29%	↓	Biodegradation (anaerobic)[1]
Beta-blockers	Atenolol	0.193 ± 0.057	**0.122 ± 0.026**	**37%**	**↓↓**	**0.108 ± 0.023**	**44%**	**↓↓**	Sorption[1]
	Metoprolol	<0.05	<0.05			<0.05			Biodegradation (aerobic)[1]
Diuretics	Furosemide	0.540 ± 0.457	0.953 ± 1.314	-76%	↑	0.648 ± 0.339	-20%	↑	Hydrolisis, photolysis[2] Biodegradation[3], Adsorption[4]
Psychiatric drug	Carbamazepine	0.105 ± 0.016	**0.093 ± 0.021**	**11%**	**↓↓**	**0.088 ± 0.024**	**16%**	**↓↓**	Adsorption, sorption, plant uptake[1]
Lipid regulators	Gemfibrozil	0.233 ± 0.167	0.151 ± 0.095	35%	↓	0.226 ± 0.134	3%	↓	Biodegradation (aerobic)[1]
Keratolytic	Salicylic acid	0.452 ± 0.632	**0.271 ± 0.411**	**40%**	**↓↓**	**0.187 ± 0.271**	**59%**	**↓↓**	Biodegradation (aerobic)[1]
Stimulant drug	Caffeine	0.291 ± 0.438	0.123 ± 0.048	56%	↓	0.127 ± 0.113	58%	↓	Biodegradation (aerobic), Plant uptake[1]
Antiseptics	Triclosan	<0.40	<0.40			<0.40		↓	Biodegradation[5]
Endocrine disrupter	Bisphenol A	1.301 ± 3.656	**0.195 ± 0.161**	**85%**	**↓↓**	0.483 ± 0.759	63%	↓	Biodegradation[5]

Figure 1. Box-and-whisker plot of TP (left) and ortophosphates (right) in the three studied periods. C_{in} is the influent concentration, C_{ef_S} and C_{ef_C} are the effluent concentrations from the sequential and continuous flow CWs. [a]indicates significant difference between C_{in} and C_{ef}, [b]means significant difference between C_{ef_S} and C_{ef_C}.

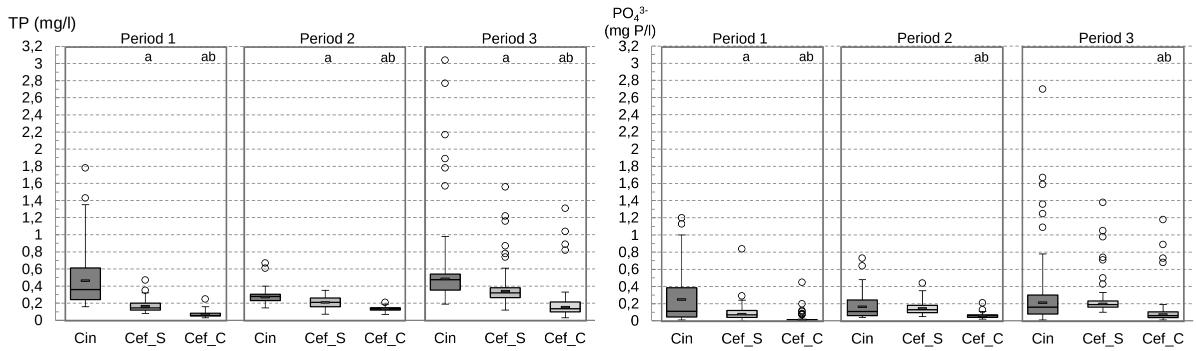

Figure 2. Environmental risk assessment by CECs monitored. Risk quotient (RQ) is the ratio between the measured concentration in each site and the predicted no-effect concentration (PNEC). PNEC values have been taken from Ilyas et al. 2020, Isidori et al. (2006) and ECHA website.

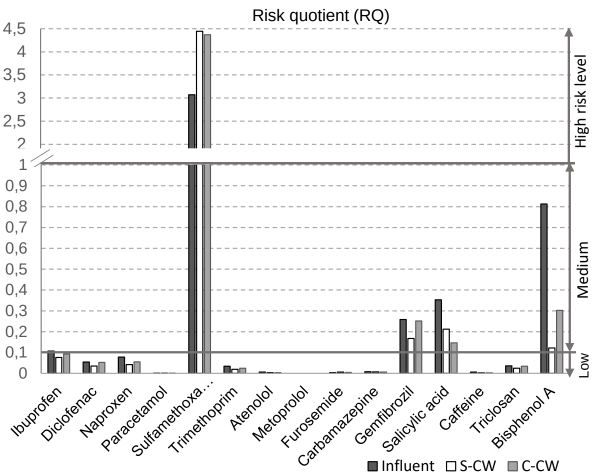

Figure 3. Escherichia coli (log CFU/100 ml) measured in the influent and effluents of the CW pilot systems. Temperature is displayed in the secondary y-axis.

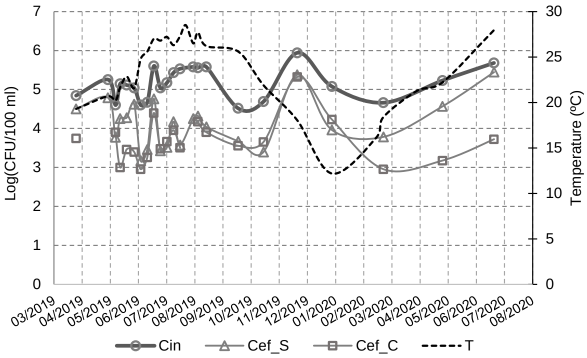

Figure 4. Calibration of the P-k-C* model for total phosphorus.