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# Evaluation of solid waste stratified mixtures as constructed wetland fillers under different operation modes

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## Abstract

Based on the strategy that all processes can and should be modified to contribute to a circular economy, this work evaluates the recovery of waste solids as filler material in Constructed Wetlands (CWs) used for wastewater treatment. Five sets of lab-scale CWs were assembled with mixtures of five waste solids and operated to evaluate the removal of chemical oxygen demand (COD) and nutrients from urban and industrial-types of wastewater. The adaptation and growth of the macrophyte *Phragmites australis* in the mixed-filler CWs was also monitored. Although all evaluated waste solids showed to be acceptable substrates for macrophyte development and wastewater treatment, CWs assembled with mixtures of limestone waste and coal slag showed the best plant growth indicators and wastewater treatment efficiencies. The CWs assembled with mixtures of limestone waste and clay brick fragments or cork granulates showed to be suitable alternatives. With exception for CWs filled with mixtures of limestone and snail shells, pollutant removal efficiencies up to 95%, 86% and 83% were obtained respectively for COD, total phosphorous and total nitrogen, depending on the type of wastewater and mode of operation. Removal efficiencies were not significantly affected by increased hydraulic rate. The CWs can be operated to a hydraulic loading rate of 0.056 m/d, which corresponds to a retention time of 1.5 days. The valorisation of solid waste as a filler can contribute to CWs closely participating in the creation of circular flows for the reuse of waste solids.

Keywords: coal slag, cork granulates, limestone waste, wastewater, waste recovery

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## 1. Introduction

The effective and widespread implementation of a circular economy can contribute to ensuring healthy and sustainable growth or even survival of societies. Although the fundamentals of circular economy are not recent, related concepts and strategies are currently relevant topics and are interrelated with sustainability principles and objectives (Korhonen et al., 2018; Pieroni et al., 2019).

Circular economy knowledge and tools are evolving, but only a few cases of materials and energy flows can be converted completely into closed circuits. However, all processes can be included as an incremental part of a larger loop, such as the recycling and recovery of packaging materials (Civancik-Uslu et al., 2019), household waste plastics (Huysveld et al., 2019) and, particularly, the reuse of treated wastewater (Akhoundi and Nazif, 2018) or sludge originated in wastewater treatment facilities (de Azevedo et al., 2018).

Constructed Wetlands (CWs) of subsurface flow type, although an example of an eco-efficient and cleaner technology for wastewater treatment, require a granular filling medium as the main construction material which usually represents the major fraction of capital expenditure (Yang et al., 2018). In order to improve the wastewater treatment, special manmade or modified natural materials can be used, which represents high energy and raw material consumption. Examples of these kind of materials are light expanded clay aggregates (Mateus and Pinho, 2010) and calcium silicate hydrate (Li et al., 2015). Alternative low-cost materials, including solid waste, were the subject of intense research in recent years. Examples of alternative materials are broken bricks and oyster shells (Wang et al., 2013), dewatered alum sludge (Zhao et al., 2011), limestone rock waste (Mateus et al., 2012), rice straw and ceramsite (Cao et al., 2016) and rubber tyre chips (Chyan et al., 2013).

The reuse of waste materials allows CWs to be included as part of a recovery cycle of these materials, preventing them from being sent to landfills. The recovery and valorisation of treated water and the valorisation of the produced biomass (macrophytes) can also contribute to integrate the CWs in the circular reuse of water and bioeconomic resources (Avellán and Gremillion, 2019; Masi et al., 2018).

Although there are many studies evaluating the potential of using waste materials at bench-scale in wastewater treatment applications, there are still few studies that demonstrate their effective use in CWs, both in terms of confirmation of their quality as filler and contribution to wastewater treatment as well as its quality to ensure the healthy growth of macrophytes, which represent an essential component of CWs.

The present study was conducted to assess the performance of five waste materials as CWs fillers, both in terms of pollutant removal efficiency from urban and industrial wastewaters under different operating conditions and macrophyte adaptation to the waste materials. The evaluated residual materials included solid residues whose recovery is usually little explored, as is the case of coal burning slags and granulates resulting from cork transformation. The use of coal for energy generation is still very representative on a world scale, and even if in the future it will be reduced or even eliminated, the slag generated will continue to be deposited in landfills (Ryabov et al., 2019). Similarly, the cork industry is very representative worldwide, but particularly in Portugal, with large quantities of cork waste being generated (Sepúlveda et al., 2018).

Considering that previous bench-scale studies have shown that waste materials can contribute in a differentiated way to the removal of pollutants from wastewater (Mateus and Pinho, 2018), the simultaneous use of different fillers could allow CWs to adapt to specific types of wastewater to be treated and contribute to the valorisation of a wider range of solid waste. This is the first study to evaluate the reuse of mixtures of limestone waste with one of the following solid wastes: clay brick fragments, coal slags, cork granulates and snail shells. Therefore, the present work has three main goals: (i) evaluate an innovative combination of stratified-mixtures of waste solids as filling media for constructed wetlands; ii) evaluate the capabilities of those mixtures to guarantee the healthy growth of the macrophyte plants; iii) evaluate the stratified-mixture constructed wetlands robustness to variations in the operation conditions.

## 2. Materials and Methods

### *2.1 Wastewater*

In this study two types of wastewater were used: a synthetic low strength urban-type wastewater and an industrial pre-treated effluent. Table 1 shows the average composition of both types of wastewater over the trial period. The synthetic wastewater was prepared with tap water, phosphorus, nitrogen and potassium salts, and with glucose as a source of carbon. The industrial effluent was collected from the drained outlet of a winery byproduct distillery industry after secondary treatment by anaerobic digestion. The collected wastewater was transported to the experimental site and was stored during the trial period of phases 4 and 5 (section 2.4) in feeding tanks, at an average temperature of 15 ºC in the absence of light and analysed before being dosed into the wetland systems.

**Table 1**

Characteristics of wastewater (mean values ± 95% Confidence Interval; n>12 for urban wastewater type and n>5 for industrial waste water): Electrical conductivity (EC), chemical oxygen demand (COD), biochemical oxygen demand ($BOD_5$), total nitrogen (TN), total phosphorus (TP), total suspended solids (TSS).

| Type of wastewater | pH | EC µS/cm | Colour PCU | COD mg/L | $BOD_5$ mg/L | TN mg/L | TP mg/L | TSS mg/L |
|---|---|---|---|---|---|---|---|---|
| Urban | 7.4±0.5 | 220±60 | 32±16 | 258±23 | 176±5 | 18.1±0.2 | 2.24±0.06 | 48±19 |
| Industrial | 8.62±0.08 | 3140±20 | 201±9 | 80±5 | 24±9 | 72±5 | 2.0±0.1 | 28±6 |
| NEQS[1] | NG | NG | NG | 125 | 25 | 10 | 1 | 35 |

[1] NEQS = Portuguese National Effluent Quality Standards for urban wastewater treatment plants (NG = not given).

## 2.2 Building of the constructed wetland prototypes

In order to evaluate the potential of various combinations of waste materials to treat wastewater, duplicates of five sets of lab-scale vertical flow (VF) CWs were built. CWs systems consisted of truncated cone pots in black opaque PVC plastic with 35.0 cm × 31.5 cm × 39.0 cm in height, lower and upper diameter. A schematic diagram and a picture of the experimental wetland units are provided in Fig. 1.

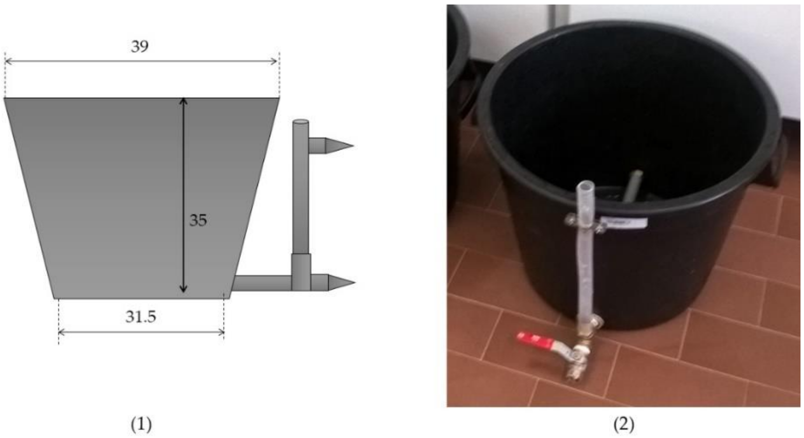

**Fig. 1.** Lab-scale constructed wetlands: (1) schematics (pot's inner dimensions, in cm); (2) picture of pot without filler.

Combinations of five solid wastes were employed as filling materials for the CWs: cork granulates resulting from the cork industry; snail shells resulting from the food and catering industries; coal slag resulting from coal power plants; clay brick fragments and limestone rock fragments, both resulting from construction activities.

A reference set was filled with limestone fragments only, already shown to be a good CW substrate (Mateus et al., 2012). The remaining four sets were filled with three layers, 7 cm bottom and top layers of limestone fragments and a 15 cm inner layer of the evaluated waste material. Total volume occupied by the filling media is 28 L. The area at the surface of the filling was 0,116 m$^2$. Fig. 2 presents a photograph of the materials and a scheme representing the three-layers assembly.

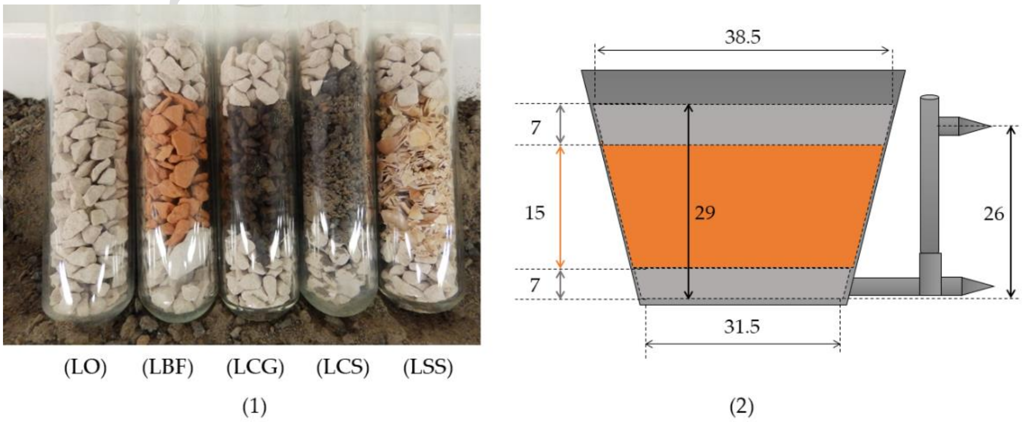

**Fig. 2.** Solid waste evaluated as filler materials: (1) picture of material combinations and respective nomenclature according to table 2; (2) schematics of the three-layer assembly (dimensions in cm).

Physical properties, i.e. particle size distribution, true density, loose bulk density and voids, of the five materials tested had already been determined in a previous study (Mateus and Pinho, 2018). The working bulk porosity of the CWs was evaluated by measuring the required water volume to flood the pots filled with the different waste material combinations. The three-layer combinations and the mixed-filler working porosity of the five lab-scale CW sets are reported in Table 2.

**Table 2**

Nomenclature and working porosity of the lab-scale mixed-filler CWs.

| CWs | Bottom layer | Middle layer | Top layer | Working porosity |
|---|---|---|---|---|
| LO | Limestone | Limestone | Limestone | 0.388 ± 0.007 |
| LBF | Limestone | Brick fragments | Limestone | 0.37 ± 0.01 |
| LCG | Limestone | Cork granulates | Limestone | 0.404 ± 0.006 |
| LCS | Limestone | Coal slags | Limestone | 0.186 ± 0.008 |
| LSS | Limestone | Snail shells | Limestone | 0.44 ± 0.02 |

Each CW was equipped with two discharge valves at different depths, approximately 2.6 and 12.0 cm below the surface of the top layer, to allow working at two flooding ratios, respectively 89% and 54%, which consist in the wastewater volume to total void volume of the filling.

### *2.3. Cultivation details and plant growth monitoring*

The five sets of CW prototypes were kept indoors, exposed to daylight through glass walls. Average, minimum and maximum room temperature for the period of the experiment was 21.6 ± 3.2 ºC, 20.5 ± 3.0 ºC, 22.4 ± 3.5 ºC, respectively.

The CWs systems were fed with wastewater between January and November 2018. Different operating conditions were tested in five experimental phases. These will be elaborated on below, in section 2.4.

In January, CWs were planted with two shoots of the *Phragmites australis* reed, which was approximating equivalent to 17 shoots per square meter. The reeds were monitored every two weeks for the height of the shoots and the number of new shoots. For the primary shoots (those that sprouted up to mid-March, about 2 months after planting) average rates of stem elongation were obtained through linear regression of stalk height plotted against time.

In November, at the autumnal end of the first growing season and approximately 10 months after planting, the above-ground biomass was harvested, and its fresh weight measured. Representative samples of the stem and leaves of the plants were finely chopped using a cutter-grinder. Sub-samples were dried at 60 °C to constant weight and dry weight (dw) was determined. The results were used to determine reed biomass productivity for the first plants growth cycle per CW area. In addition, the chlorophyll pigment content of representative samples of the harvested leaves was measured. Firstly, approximately 50 mg of leaves were extracted with 1 mL 80% acetone and total chlorophyll, as well as chlorophyll-a and chlorophyll-b, was determined by a spectrophotometer assay method (Gechev et al., 2013). Absorbance was read at both 663.6 and 646.6 nm in a spectrophotometer (CADAS100 DRLANGE, Germany). Quantification of the pigment content was performed using equations (1) to (3) for chlorophyll concentrations in μg/ml (Porra et al., 1989):

$$Chl_a = 12.25Abs_{663.6} - 2.55Abs_{646.6} \quad (1)$$

$$Chl_b = 20.31Abs_{646.6} - 4.91Abs_{663.6} \quad (2)$$

$$Chl_{a+b} = 17.76Abs_{646.6} + 7.34Abs_{663.6} \quad (3)$$

Finally, the calculated values were then converted to a per fresh weight basis (μg/$gf_w$).

## 2.4. Wastewater treatment experiments

The wastewater treatment experiments performed in the CWs were divided in five phases based on the two types of wastewater studied and the different operation conditions evaluated.

**Phase 1** corresponded to the first two weeks after planting, consisting of a period of acclimatization to allow the establishment of biological activity. The CWs were operated

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in a discontinuous mode for two successive fill-and-drain cycles using effluent from a pilot-scale tertiary-treatment CW in operation for 8 years. The wastewater was dosed manually into the CWs on Mondays and left without circulation. Afterwards, the water was drained on Fridays and the systems remained dry over the weekend.

**Phase 2 and 3** occurred in the following 3 months, February, March and April, when the CWs were fed with the urban wastewater. Phase 2 investigates the effect of the contact time, i.e. hydraulic retention time (HRT). The CWs were operated in a discontinuous mode for successive fill-and-drain cycles, with one dry day, HRTs of 0.5, 1, 2, 4, 6 and 8 days, which correspond to 12, 24, 48, 96, 144 and 192 hours respectively, and with an 89% flooding ratio. In phase 3 the effect of the flooding ratio was investigated. Therefore, the CWs were operated in continuous mode with vertical flow towards the bottom. First, they were operated at an 89% flood rate for about three weeks until they reached a pseudo steady state, then the flood rate was changed to 54% and the CWs continued to operate until the new steady state was reached. The flow was monitored regularly by weight-based measurement (Mettler Toledo PB8001-L) and was kept constant at $6.46\times10^{-3} \pm 0.12\times10^{-3}$ $m^3 day^{-1}$ by peristaltic pumps with four channels (323S/D, Watson-Marlow Inc, Wilmington, USA), corresponding to a hydraulic loading rate (HLR) of $5.55\times10^{-2} \pm 1.45\times10^{-3}$ m/d. The mean HRT was of 1.52 ± 0.09 days, corresponding to 37 ± 2 hours, excluding the LCS set. The lower porosity of the LCS CWs resulted in an HRT of approximately half this value (0.76 ± 0.01 days, corresponding to 18.2 ± 0.2 hours). In order to obtain comparable results, two LCS CWs were operated in a sequential cascade arrangement.

**Phases 4 and 5** occurred during the month of May, when the CWs were fed with the industrial wastewater. Phase 4 was carried out to investigate the effect of the contact time. As above, CWs were operated in discontinuous mode with a flooding of 89%. HRTs studied were 1 day, 2 days, and, for the last batch, a total of 4 days comprising a refeeding back the effluents into the respective systems after two 2 days, separated by a resting period of 4 hours. In Phase 5 the effect of the addition of an external biodegradable carbon source was investigated. CWs were operated with the optimized HRT from phase 4 and 0.15 grams of glucose were added per litre of fresh industrial wastewater.

## *2.5 Sampling and analysis*

In the discontinuous operation mode, the samples were collected from a feedwater container immediately before contacting the filling of the CWs. After completing the selected HRT the water content of each CW was drained into receiving containers. Representative water samples were collected from each receiving container after mixing.

In the continuous flow experiments, the samples were collected at the inlet and outlet of each CW unit, two and three weeks after the start of the continuous operation in each set of tested operative conditions. The average of the measurements in these two sampling moments is reported.

Collected samples were analysed immediately for the environmental parameters temperature, pH, dissolved oxygen (DO) and conductivity with an HI-98194 multiparameter meter and respective probes supplied by Hanna Instruments. The analysis of TN, TP, TSS, COD and water colour was carried out using an HI-83399 spectrophotometer and an HI-839800 reactor block, both supplied by Hanna Instruments. Standard procedures were used, as highlighted by the supplier. The 5-day biochemical oxygen demand ($BOD_5$) determination was carried out according to the standard methods for the examination of water and wastewater (Rice et al., 2017). At least two replicates were made of all assays and measurements.

### 2.6. Data analysis

Statistical tests were performed using IBM SPSS® software, version 24. One-way ANOVA, Kruskal-Wallis test, T-test and Post Hoc tests were performed at a significance level of 95% ($p=0.05$).

All numerical confidence intervals were computed from the standard deviation assuming a 95% confidence level.

## 3. Results

### 3.1. Macrophyte growth evaluation

To evaluate the adaptation of macrophytes to the waste solids combinations, the growth of the plants was monitored during a growing season, after which the plants were harvested to assess the dry biomass yield. Figures S1 to S6 (Supplementary material) show pictures of the lab-scale CWs set-up and the growth of the *Phragmites australis* plants.

Fig. 3 presents the average height of the plants primary-shoots in the five lab-scale CWs sets during the experiments. All plants showed an approximate linear growth, apparently not affected by the changes in the operation mode but dependent on the kind of filling material. Table 3 presents the average growth rate calculated from linear fitting to Fig. 3 data. The highest average plant height was observed for CWs LCG and LCS, whose values are significantly different from the other CWs.

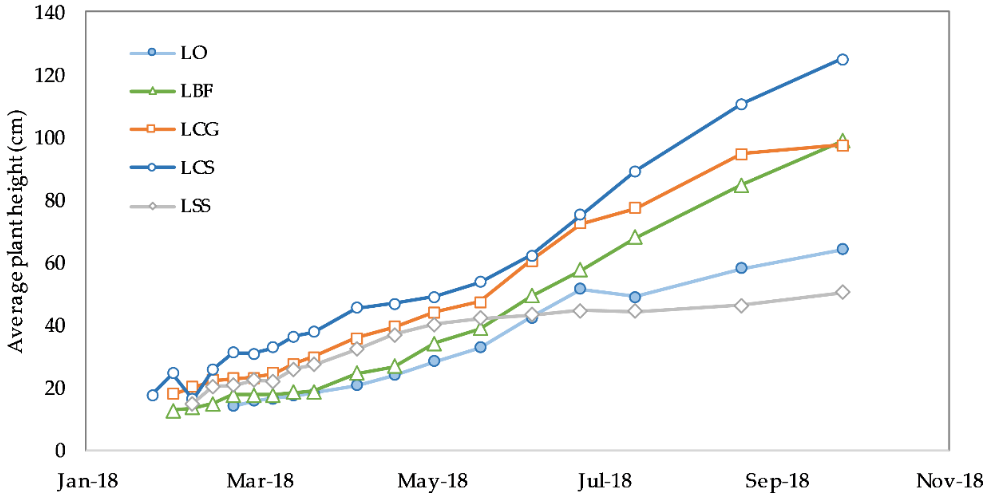

**Fig. 3.** Average height of macrophyte primary shoots during the lab-scale CWs operation.

**Table 3**

Macrophyte growth indicators for the five lab-scale CWs sets.

| CWs | Number of primary shoots | Total number of shoots | Average height$^{1,2}$ (cm) | Biomass productivity$^{3}$ (g/m$^{2}$year) | Growth rate$^{1,2}$ (cm/day) | r$^{2}$ | Photosynthetic pigments$^{1}$ (µg/g$_{fw}$)<br>Chl-a<br>Chl-b |
|---|---|---|---|---|---|---|---|
| LO | 3 | 14 | 44 ± 10 $^{a}$ | 46.4 | 0.26 ± 0.03 $^{a}$ | 0.971 | 272 ± 82<br>120 ± 3 |
| LBF | 3 | 33 | 50 ± 9 $^{a}$ | 147.1 | 0.38 ± 0.04 $^{b}$ | 0.966 | 434 ± 230<br>270 ± 90 |
| LCG | 4 | 44 | 65 ± 10 $^{b}$ | 117.0 | 0.38 ± 0.03 $^{b}$ | 0.979 | 358 ± 82<br>158 ± 47 |
| LCS | 2 | 36 | 69 ± 10 $^{b}$ | 148.3 | 0.43 ± 0.04 $^{c}$ | 0.970 | 427 ± 82<br>243 ± 44 |
| LSS | 6 | 28 | 31 ± 5 $^{c}$ | 46.8 | 0.17 ± 0.03 $^{d}$ | 0.880 | 201 ± 107<br>86 ± 30 |

[1] The average height was determined with the total number of shoots; The growth rate was determined with a minimum of 14 data points; The photosynthetic pigments content was evaluated with a minimum of 4 replicates.

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[2] Values marked with different letters in the same column are significantly different under a statistical level of 0.05.

[3] Total biomass productivity was estimated in dry weight basis for the first plants growth cycle of 10 months.

Growth rates were highest for plants grown in LCS, LBF and LCG CWs by that order, and all were higher than for growth rate of plants grown in the reference LO CW. Otherwise, the macrophyte plants showed the lowest growth rate in the LSS CW, which value is statistically different from the remaining CWs. Despite the highest number of primary shoots, the LSS filling figures the worst growth indicators. The leaves of the plants grown in LSS CW showed the lower chlorophylls contents, which justify the lower biomass productivity due to minor rates of photosynthesis. However, due to the dispersion of the results obtained, the ANOVA performed does not present statistical significance in the mean values for each type of pigment.

LCG and LCS filling combinations showed to be favourable substrate to plant growth with outstanding growth indicators when compared to the LO filling. All growth indicators are significantly different when LCG and LCS results are directly compared with the LO results ($p<0.05$).

### *3.2. Batch mode operation with urban-type wastewater (phase 2)*

COD and nutrient removal efficiencies for the batch experiments using synthetic urban-type wastewater are presented in Fig. 4.

The COD removal from the wastewater was always greater than 70% and not significantly affected by the HRT (Tables A1 and A2 in the Appendix A). All mixed-filling CW showed high performances with removal efficiencies better than the reference LO CW. The average COD removal rate was significantly higher at CWs LCG and LCS (Table A1). The LCS CW showed the best removal efficiencies even for the lowest HRT.

The LSS CW showed the lowest TP and TN removal efficiencies. Moreover, this CW showed an unexpected trend as the increase in HRT causes a decrease in nutrient removal efficiency, the reason of which is unclear.

TP removal efficiencies are not significantly different for the CWs LO, LBF and LCG (Table A1). TP removal efficiencies of LCG CW were comparable to the LO efficiencies. LCS CW showed the highest TP removal efficiencies and significatively higher than those observed with the LO CW. It should be pointed that the LO filling was already confirmed as a good substrate for CWs designed for phosphorous removal from wastewaters (Mateus et al., 2012). Although the CW LBF had lower TP removal efficiencies than the CW LO, the results obtained are nonetheless acceptable and without significant difference. The efficiencies of TP removal by the LO, LBF, LCG and LCS CWs were not significantly affected by the HRT (Fig. 4 and Table A2). For these three filling combinations TP removal efficiencies were near 80% even for a HRT of one day.

All but the LSS CW showed TN removal efficiencies higher than the LO CW efficiencies. LBF and LCS CWs showed the highest TN removal efficiencies, which increase slightly but not significantly with the HRT increase. It was observed that the variation of HRT between 1 and 8 days affects significantly only the removal of nutrients by the LSS CW.

Considering the objective of simultaneously removal of COD, TP and TN source compounds from the wastewater, the LCG and LCS CWs consisted in the best systems when operated in a batch mode. The HRT can be kept as low as 1 day without a significant effect on the pollutants removal efficiency. Lower HRT corresponds to higher HLR and higher usability of the CWs systems.

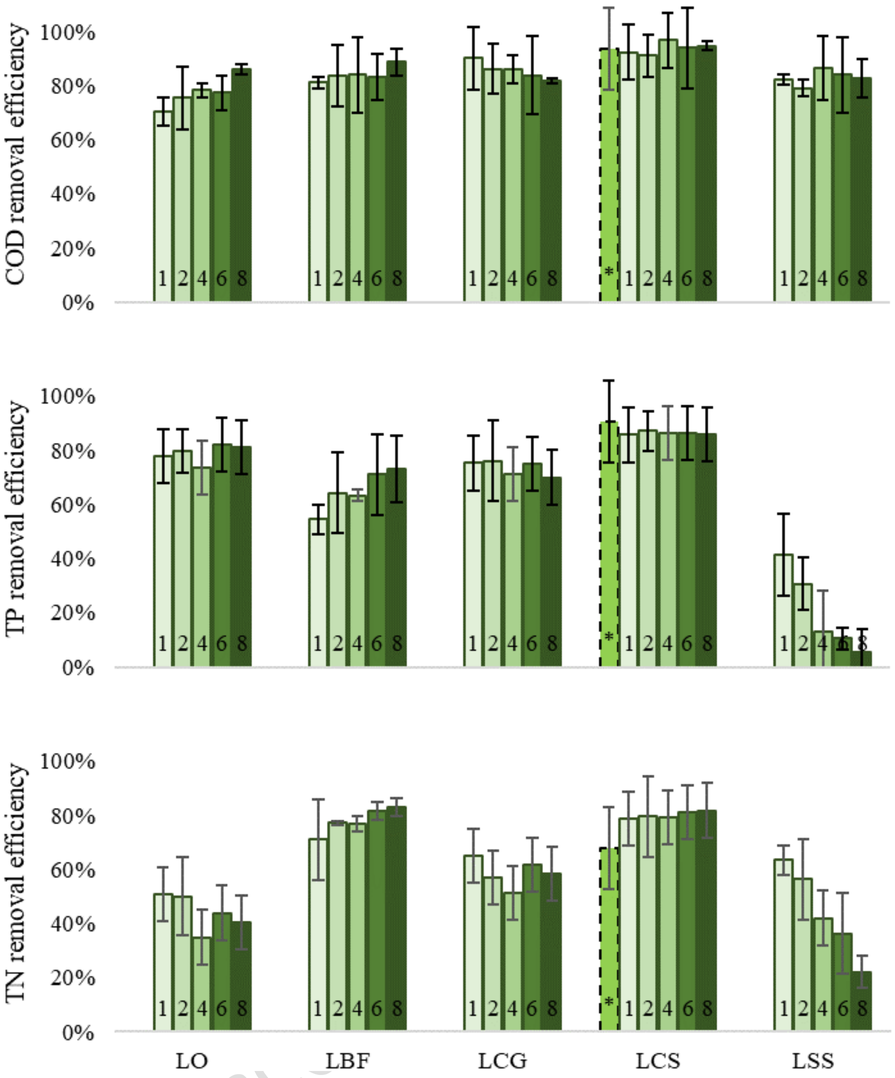

**Fig. 4.** COD and nutrients removal efficiency of the five lab-scale CWs. for batch mode operation with urban-type wastewater during phase 2. Numbers inside bars represent HRT (days). HRT for the line dotted bar with “*” mark was 0.5 days. The values and the error bars represent the means ± confidence interval (n=4).

### *3.3. Continuous mode operation with urban-type wastewater (phase 3)*

The capability for the mixed-filled CWs to operate in continuous mode was evaluated for a HLR of $5.55\times10^{-2} \pm 1.45\times10^{-3}$ m/d, which corresponds to an average HRT of 1.52 ± 0.09 days when the LCS CW set is excluded. As already mentioned in section 2.4, the lower porosity of the LCS CWs resulted in an HRT of 0.76 ± 0.01 days. A similar overall retention time was obtained through sequential operation of two LCS CWs.

The continuous mode of operation was tested with a flooding ratio of 89% and in a partial percolating setup (54% flooding), where only half height of the porous filling was flooded. The obtained average COD and nutrient removal efficiencies are presented in Fig. 5, which contains the results for both flooding ratios and the interpolated results obtained in batch mode (section 3.2) equivalent to the continuous average HRT (1.52 days). Table A3 contains the statistical analysis of the data presented in Fig. 5.

COD removal from the urban-type wastewater was not significantly affected by the operation mode, nor by the lower water level in the percolating mode. The LCS CW showed the highest COD removal efficiencies but all CWs performed above 60% of removal efficiency.

Otherwise, all but the LCS CW performed worse in continuous mode than in batch mode concerning TP removal from the urban-type wastewater. Although it was not a clear trend, the percolating mode improves the TP removal efficiencies. The LCS CW showed to be a stable system as the TP removal was higher than 80%. Both batch and percolating modes have in common the characteristic of allowing the particle bed aeration, which may have potentiated the degradation of phosphorus compounds by aerobic processes.

As for TP removal, TN removal efficiencies were slightly negatively affected by the continuous operation mode in comparison with the batch mode. The relative trend was similar to the batch mode trend: LCG and LSS CWs performed in a similar way as the reference LO CW; LBF and LCS CWs performed better than the LO CW. The percolating mode improved all the five lab-scale CWs concerning TN removal. As for TP removal, aerobic processes may have contributed to the TN removal, improving the nitrification/denitrification steps associated to the removal of nitrogen compounds from wastewater.

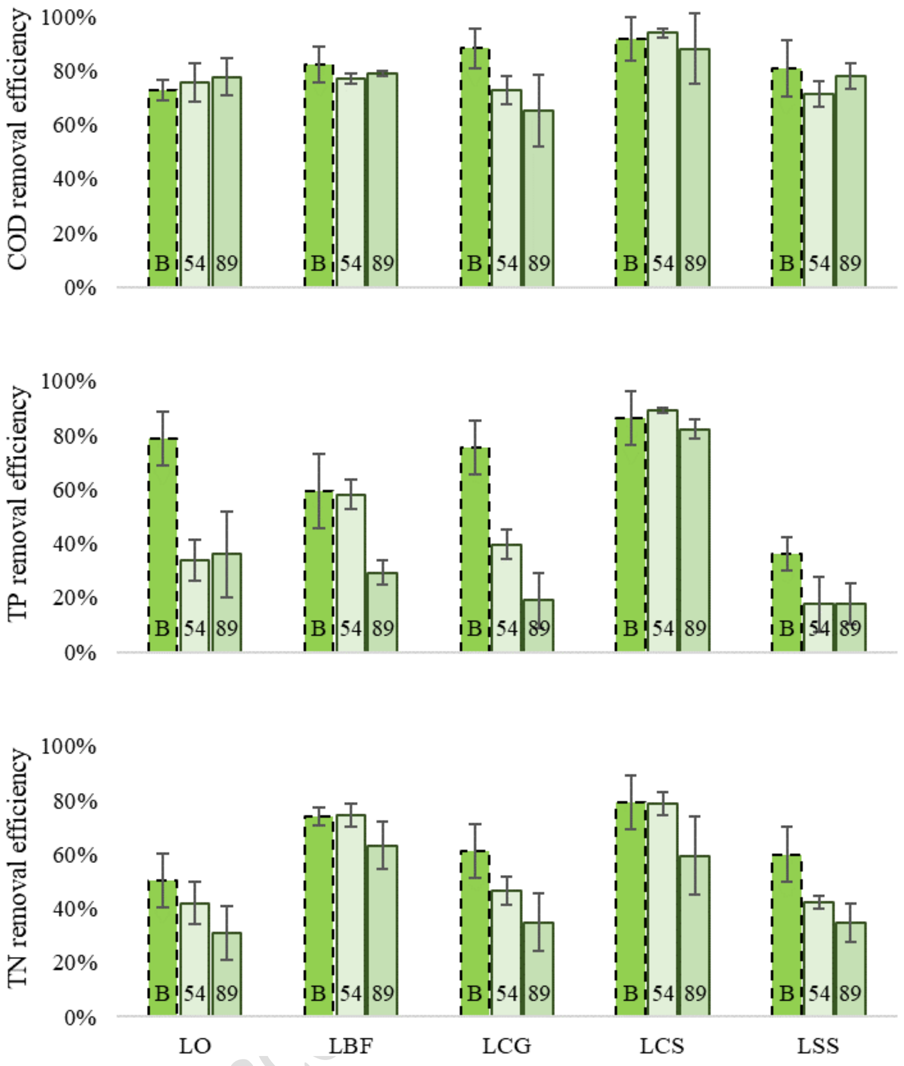

**Fig. 5.** COD and nutrients removal efficiency of the five lab-scale CWs for continuous mode operation with urban-type wastewater (phase 3) and HRT of 1.5 days. Notation inside bars represents batch mode efficiencies for comparison (B) and the flooding ratio (54 and 89%). The error bars represent the confidence interval (n=4).

## *3.4. Experiments with industrial wastewater (Phases 4 and 5)*

During experimental phases 4 and 5, the five sets of lab-scale CWs were used for treatment of wastewater from a distillery after aerobic and anaerobic treatments in the industrial facility. The wastewater fulfils the quality requirements concerning COD, $BOD_5$ and TSS, but fails the required limits concerning TP and, mainly, TN. The situation is typical for most Portuguese industrial and urban wastewater treatment facilities not equipped with tertiary nor advanced treatment systems, being the removal of nutrients the utmost challenge. For this particular case, the ratios C:N:P (COD:TN:TP) (41:37:1), presents an additional difficulty because they are very different from the recommended ratios for biological denitrification process. The denitrification potential of wastewater is primarily a function of the available organic carbon, which is usually expressed as the COD:N or the $BOD_5$:N ratios. Available studies report a wide range of COD:N ratios required for satisfactory denitrification processes, which can be between 4 and 15 (Metcalf & Eddy et al., 2014; Peng et al., 2007). If the proportion of biodegradable carbon is low the efficiency of the denitrification process is impaired, and an external carbon source is required (Liwarska-Bizukojć et al., 2018; Swinarski et al., 2012; Wang et al., 2019). In addition, the biological removal of nitrogen compounds from wastewater is attained through both nitrification and denitrification processes which require, respectively, aerobic and anaerobic environments (Kadlec and Wallace, 2009; Metcalf & Eddy et al., 2014). The anaerobic environments are guaranteed by the deep-water levels in the CWs. A partial aerobic environment is provided by the oxygen transport from reeds roots to their surroundings (Bezbaruah and Zhang, 2005; Colmer, 2003). A more enhanced aerobic environment can be provided by operating CWs in a tidal-flow mode, with alternated fill and drain periods (Chang et al., 2014). Aiming to study the potential of nitrification enhancement through aeration of the CWs' filler matrix, a set of assays were carried out in phase 4 in tidal-flow operating mode. The effects of the addition of an external carbon source was evaluated in phase 5.

### *3.4.1 Residence time and tidal-flow effects evaluation (phase 4)*

Fig. 6 presents the COD and nutrient removal efficiencies of the five lab-scale CWs treating the distillery wastewater in batch mode. Tables A4 and A5, in the Appendix A, include the statistical analysis of the data in Fig. 6. The increase in the HRT did not affect significantly any of the observed removal efficiencies, neither did the tidal-flow operation mode contribute to improve the removal processes. The results indicate that the increase in oxygen availability did not favour nutrient removal processes in the distillery wastewater, as the observed differences fail within the typical variation-range in CW systems (Mateus and Pinho, 2010).

The results also indicated that retention time increase did not contribute to increase the COD and nutrient removal efficiencies, which means that one day contact is enough to obtain the maximum removal efficiencies. However, the observed removal efficiencies were lower than the efficiencies obtained when the CWs treated the synthetic urban-type wastewater. The worse performance for the CWs treating industrial wastewater can be justified by the relative higher content of nitrogen compounds in industrial wastewater than in the urban-type wastewater. The lower ratio $BOD_5$/COD in the industrial wastewater compared to the same ratio in the urban type wastewater may also have contributed to the observed lower CWs performances when treating the industrial wastewater.

All but TP removal efficiencies by LSS CW were higher than COD and nutrient removal performances by the LO CW. LCS CW showed the best removal efficiencies, near 80% removal for both COD and TP and near 40% for TN removal from wastewater.

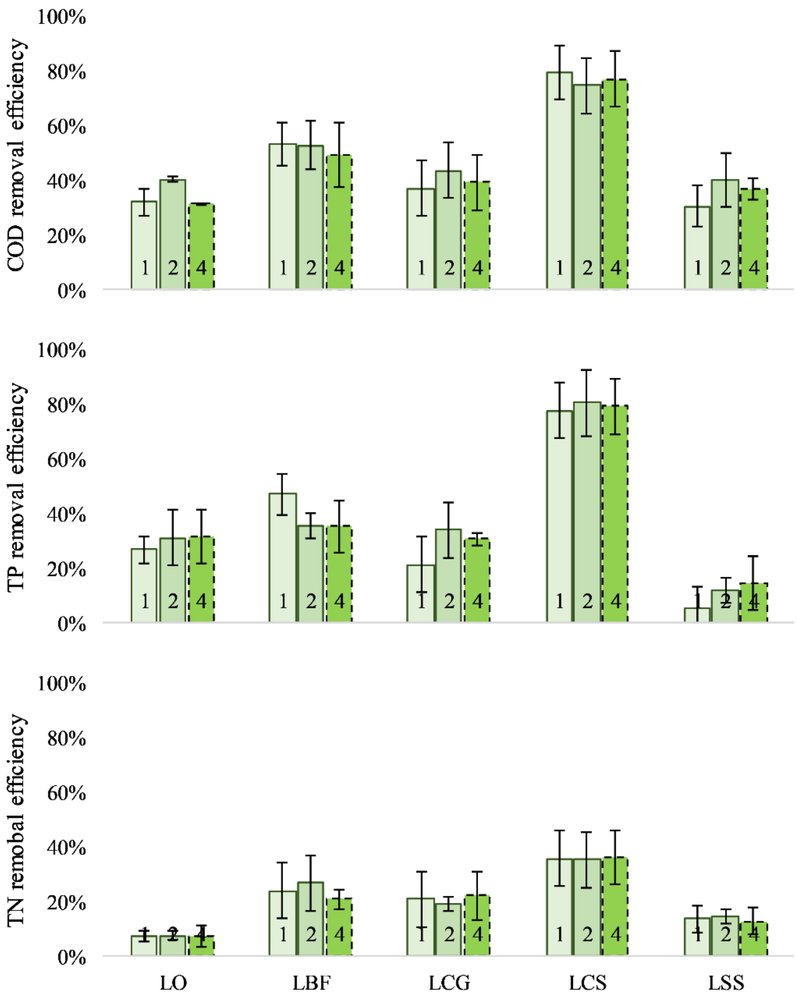

**Fig. 6.** COD and nutrient removal efficiency of the five lab-scale CWs for batch mode treating industrial wastewater. Numbers inside bars represent HRT (days). The dotted-line bars represent tidal-flow operation mode. The error bars represent the confidence interval (n=4).

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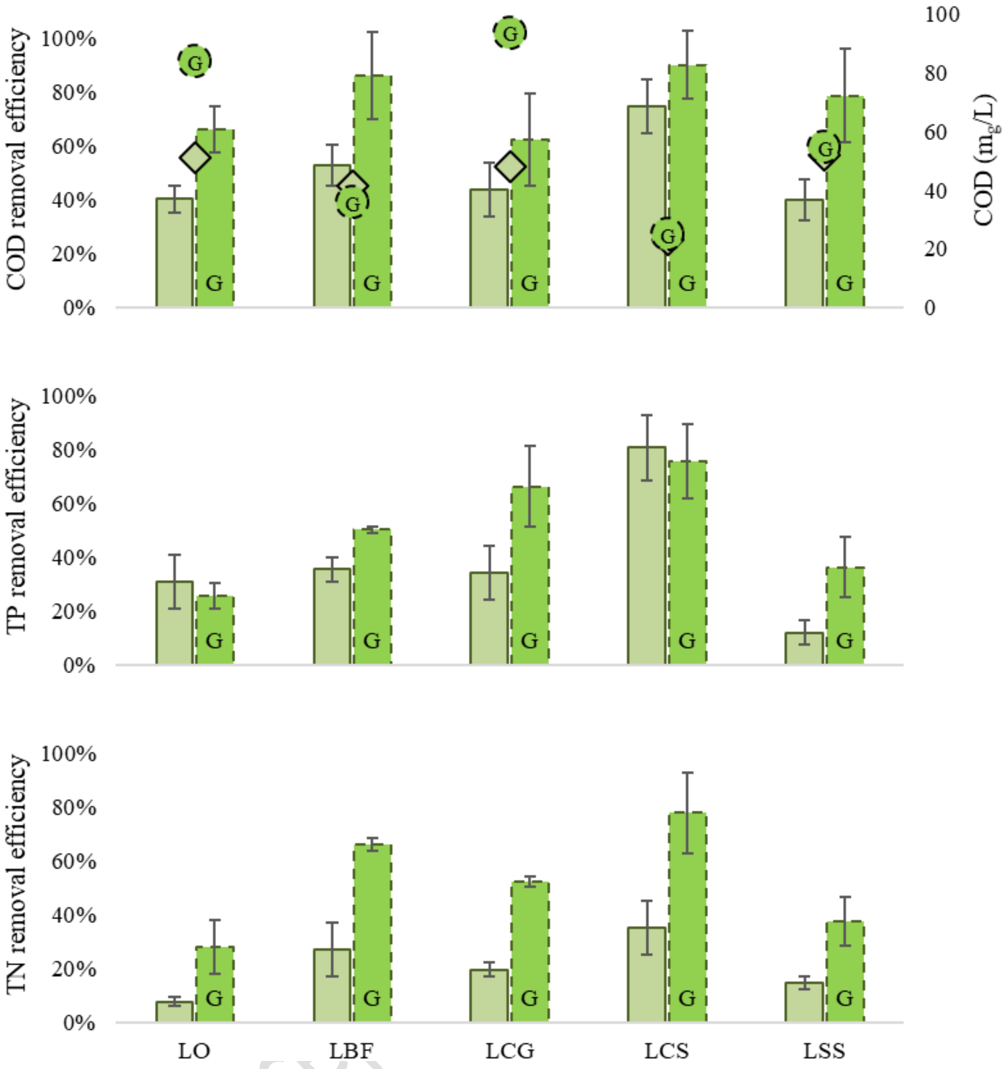
### *3.4.2 Evaluation of the effectd of adding an external carbon source (phase 5)*

In order to evaluate the enhancement in nutrient removal efficiency by the increase in the COD:TN ratio, glucose was added to the industrial wastewater. The addition of glucose increased the COD:TN:TP ratios from 41:37:1 to 112:37:1.

Fig. 7 contains the COD and nutrient removal efficiencies of the five lab-scale CWs treating the distillery wastewater after glucose addition. The bars marked with “G” represent the efficiencies in the assays where glucose was added to the wastewater. Circles and diamonds in the COD removal chart represent the COD concentration at CWs outflow respectively for wastewater with added glucose and wastewater without glucose addition. Table A6, in the Appendix A, contains the statistical analysis of the data in Fig. 7.

COD removal efficiencies have shown an increase when glucose was added. However, glucose addition did not contribute to a net effect in the COD removal, as the COD concentration did not decrease below the outflow concentrations observed without glucose addition. The glucose was effectively biodegraded without improving the removal of the originally present oxidable compounds. In the other hand, the glucose addition contributed to improve the TP removal capabilities of CWs LCG, LSS and LBF, and contributed to improve the TN removal of all CWs.

When comparing CWs observed performance differences, it was found that all mixed-filled CWs performed better than the LO CW, with exception for the TP removal efficiency of LSS CW. LCS CW showed the higher removal efficiencies for all three classes of monitored pollutants. The LCG and LBF CWs showed to be acceptable alternative systems concerning this kind of wastewater.



438 **Fig. 7.** COD and nutrient removal efficiency of the five lab-scale CWs for batch mode
439 (HRT of 2 days) and industrial wastewater. Assays with glucose addition were identified
440 as "G". The top chart includes outflow COD concentration after glucose addition (circle
441 with "G") and without glucose addition (diamond symbol). The error bars represent the
442 confidence interval (n=4).

Table 4 contains a summary of the COD and nutrients removal efficiency results obtained in this work and a comparison with results presented in the literature. The range of COD and nutrient removal rates depend on the type of CW system, mode of operation and type of wastewater. The highest pollutants removal rates are usually observed for CWs designed with expensive fillings, hybrid systems or multistage modules, which present higher capital and operation costs.

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**Table 4**

Summary of pollutant removal performances in subsurface flow constructed wetland systems with common and alternative filling media.

| Ref | CW type[1] | Wastewater type | Filling media | Removal performance (%) | | |
|---|---|---|---|---|---|---|
| | | | | COD | TP | TN |
| This work | Lab-scale tidal VFCW | Synthetic urban | LO (Limestone fragments) | 70-86 | 73-82 | 35-51 |
| | | | LBF (Limestone + Clay brick fragments) | 81-89 | 55-73 | 71-83 |
| | | | LCG (Limestone + Cork granulates) | 82-90 | 70-76 | 51-65 |
| | | | LCS (Limestone + Coal slags) | 91-97 | 86-91 | 68-82 |
| | | | LSS (Limestone + Snail shells) | 79-86 | 6-41 | 22-63 |
| | Lab-scale VFCW | Synthetic urban | LO (Limestone fragments) | 72-83 | 19-51 | 19-42 |
| | | | LBF (Limestone + Clay brick fragments) | 76-79 | 28-61 | 56-77 |
| | | | LCG (Limestone + Cork granulates) | 56-76 | 11-42 | 25-49 |
| | | | LCS (Limestone + Coal slags) | 81-95 | 78-90 | 52-89 |
| | | | LSS (Limestone + Snail shells) | 67-82 | 10-23 | 29-43 |
| | Lab-scale tidal VFCW | Industrial Anaerobic digested | LO (Limestone fragments) | 32-66 | 26-32 | 7-28 |
| | | | LBF (Limestone + Clay brick fragments) | 53-86 | 35-50 | 24-66 |
| | | | LCG (Limestone + Cork granulates) | 37-62 | 21-66 | 19-52 |
| | | | LCS (Limestone + Coal slags) | 75-90 | 76-81 | 35-78 |
| | | | LSS (Limestone + Snail shells) | 30-79 | 6-36 | 13-37 |
| (García-Pérez et al., 2015) | Pilot-scale HFCW | Bakery | Tyre chips | >92 | 65 | 56 |
| (Kizito et al., 2017) | Lab-scale tidal VFCW | Anaerobic digested | Corn biochar | 54-79 | 33-90 | 62-74 |
| | | | Wood biochar | 57-92 | 42-97 | 73-87 |
| | | | Gravel[2] | 43-63 | 20-84 | 45-63 |
| (Konnerup et al., 2009) | Pilot-scale HFCW | Domestic | Gravel[2] | 42-83 | 6-35 | 4-37 |
| (Lu et al., 2016) | Pilot-scale upward-flow VFCW | Rural household sewage | Maifanite | 81 | 79 | 79 |
| | | | Steel slag | 80 | 84 | 74 |
| | | | Bamboo charcoal | 68 | 69 | 69 |
| | | | Limestone | 74 | 55 | 50 |
| (Mateus and Pinho, 2010) | Pilot-scale VFCW | Synthetic urban | Lightweight expanded clay (Filtralite® MR)[2] | 32-69 | 43-93 | 50-87 |
| | | | Lightweight expanded clay (Filtralite® NR)[2] | 53-71 | 29-79 | 48-70 |
| (Mateus et al., 2016) | Pilot-scale HFCW | Synthetic urban | Clay brick fragments | 58-66 | 69-77 | 55-60 |
| | | | Fragmented Moleanos limestone | 64-77 | 58-68 | 51-58 |
| (Saeed et al., 2018) | Lab-scale two stage VFCW/HFCW hybrid system | Mixed industrial | Recycled bricks | 83 | 89 | 80 |
| | | | Sugarcane bagasse | 67 | 64 | 68 |
| (Saraiva et al., 2018) | Pilot-scale HFCW | Dairy industry | Gravel[2] | 88-93 | 20-27 | 30-38 |
| | | | Crushed PET bottles | 86-92 | 23-29 | 21-43 |
| (Wang et al., 2013) | Lab-scale VFCW | Livestock anaerobic | Oyster shells | | | 88-96 |
| (Zhao et al., 2011) | Pilot-scale four stage tidal VFCW | Livestock | Alum sludge | 36-84 | 75-94 | 11-78 |
| | | | Summary of this work | 30-97 | 6-91 | 7-89 |
| | | | Summary of common filling media | 42-93 | 6-93 | 4-87 |
| | | | Summary of alternative filling media | 43-92 | 23-97 | 21-87 |

[1] VFCW vertical flow constructed wetlands; HFCW horizontal flow constructed wetlands.

[2] Common filling media.

The removal rates of the referred works in table 4 range from 42 to 93%, 6 to 97% and 4 to 87%, for COD, TP and TN removal, respectively. The lowest removal rates in this work were obtained for the LSS CWs, filled with a mixture of limestone and snail shells from the food industry. That lowest rates are 30%, 6% and 13%, for COD, TP and TN removal, respectively. Except for the lowest value of COD removal obtained, all results of present work fill within the literature range or are even higher.

CWs filled with a stratified mixture of limestone, from construction stones industry, and coal slag, from coal power plants (LCS CWs), showed to be the best system, whose removal rates range from 75 to 97%, 76 to 91% and 35 to 89%, for COD, TP and TN removal, respectively. The highest removal rates were obtained with the batch operation mode at a hydraulic retention time of about 1.5 days. However, a continuous operation mode at the same equivalent retention time is an adequate alternative. The continuous operation with a partial flooding of the filler media can slightly improve the pollutants removal efficiencies. In spite of this, the verified efficiencies were lower than the obtained in batch mode. In addition, the results show that LCS CWs performed significantly better ($p<0.05$) than the reference LO CWs for all operation modes, which can be interpreted as an evidence of CW improvement by using a mixed-filler of waste solids when compared to traditional single-filling CWs.

Mix-filled CWs with limestone and clay brick fragments, also from construction activities (CBF CWs), and CWs with limestone and cork granulates, a solid waste from the cork industry (LCG CWs), showed performances similar to, or generally better than, the reference single-filling LO CW and can be also acceptable solutions that enable the recovery of waste solids for the treatment of wastewater by constructed wetlands.

## 4. Conclusions

Reusing solid waste as filler media represents a way to avoid disposal in landfills while reducing investment costs in the implementation of constructed wetland for wastewater treatment. In addition, some materials can improve CWs treatment capabilities by directly intervening in the pollutant removal processes from the wastewater.

The feasibility of using mixtures of different solid wastes as filler media was evaluated through a set of lab-scale CWs planted with *Phragmites australis*.

The obtained results showed that:

(i) The macrophyte plants adapted well to all but the CW whose filler consisted in a mixture of limestone fragments and snail shell wastes;

(ii) Although all CWs prototypes filled with mixtures of waste solids can be satisfactory solutions to treat urban-type wastewater and the tested distillery wastewater, the combination of limestone fragments and coal slags (LCS) presented the highest pollutants removal efficiencies and best macrophyte growth indicators;

(iii) The combination of limestone fragments and clay brick fragments (LBF) or cork granulates (LCG) are also acceptable alternatives as CWs fillers;

(iv) In the evaluated operation conditions, the CWs filled with the mixtures of waste solids were not significantly favoured by the increase in the hydraulic retention time, which can be set as 1.5 days corresponding to a hydraulic loading rate of 0.056 m/d;

(v) Depending on the type of wastewater and operation conditions, the CWs filled with most promising combinations of waste solids operated in a hydraulic retention time of 1.5 days presented removal efficiencies between 75-95% COD, 76-86% TP and 35-82% TN, for the LCS CW, 53-88% COD, 28-73% TP and 24-83% TN, for the LBF CW, and 37-84% COD, 21-75% TP and 19-62% TN, for the LCG CW.

While traditional Constructed Wetlands represent a clean and green technology for wastewater treatment, recovery of solid waste as a filler can contribute to these systems closely participating in the creation of circular flows for the reuse of waste materials.

CWs designed with mixtures of waste solids can benefit from the contribution of the different materials for removing specific pollutants, improving the CWs robustness to fluctuations in wastewater composition and flow rate.

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# Appendix A

## Table A1

Effect of filler type on pollutants mean removal rate for the batch experiments with urban type wastewater[1].

| | LO | LBF | LCG | LCS | LSS |
|---|---|---|---|---|---|
| COD | 77 ± 7% [a] | 84 ± 3% [a b] | 86 ± 4% [b] | 94 ± 3% [c] | 85 ± 3% [a b] |
| TP | 79 ± 4% [a b] | 65 ± 9% [a] | 74 ± 3% [a b] | 86 ± 1% [c] | 20 ± 18% [d] |
| TN | 44 ± 8% [a] | 78 ± 6% [b] | 59 ± 7% [a] | 80 ± 2% [b] | 44 ± 20% [a] |

[1] Values marked with the same letter in the same row are not significantly different under a statistical level of 0.05.

## Table A2

Effect of hydraulic retention time on pollutants mean removal rate for the batch experiments with urban type wastewater. Negative signs represent no significant effect and the positive signs represent a significant effect at a 0.05 statistical level. The numbers represent the p-values of one-way ANOVA.

| | LO | LBF | LCG | LCS | LSS |
|---|---|---|---|---|---|
| COD | – (0.126) | – (0.892) | – (0.858) | – (0.963) | – (0.900) |
| TP | – (0.813) | – (0.347) | – (0.944) | – (0.999) | + (0.014) |
| TN | – (0.417) | – (0.334) | – (0.541) | – (0.996) | + (0.007) |

## Table A3

Effect of operation mode on pollutants mean removal rate for the batch and continuous experiments with urban type wastewater. Negative signs represent no significant effect and the positive signs represent a significant effect at a 0.05 statistical level. The numbers represent the p-values of one-way ANOVA.

| | LO | LBF | LCG | LCS | LSS |
|---|---|---|---|---|---|
| COD | – (0.641) | – (0.337) | – (0.057) | – (0.719) | – (0.334) |
| TP | + (0.005) | + (0.010) | + (0.001) | – (0.427) | – (0.051) |
| TN | – (0.110) | – (0.103) | + (0.031) | – (0.101) | + (0.015) |

**Table A4**

Effect of filler type on pollutants mean removal rate for the batch experiments with industrial wastewater[1].

| | LO | LBF | LCG | LCS | LSS |
|---|---|---|---|---|---|
| COD | 35 ± 4% $^{a}$ | 52 ± 7% $^{b}$ | 40 ± 7% $^{a}$ | 77 ± 7% $^{c}$ | 36 ± 6% $^{a}$ |
| TP | 30 ± 6% $^{a}$ | 39 ± 7% $^{a}$ | 29 ± 7% $^{a}$ | 79 ± 7% $^{b}$ | 11 ± 6% $^{c}$ |
| TN | 7 ± 2% $^{a}$ | 24 ± 6% $^{b}$ | 21 ± 5% $^{b\ c}$ | 36 ± 7% $^{d}$ | 14 ± 3% $^{a\ c}$ |

[1] Values marked with the same letter in the same row are not significantly different under a statistical level of 0.05.

**Table A5**

Effect of hydraulic retention time on pollutants mean removal rate for the batch experiments with industrial wastewater. Negative signs represent no significant effect at a 0.05 statistical level. The numbers represent the p-values of one-way ANOVA.

| | LO | LBF | LCG | LCS | LSS |
|---|---|---|---|---|---|
| COD | – (0.177) | – (0.878) | – (0.727) | – (0.846) | – (0.356) |
| TP | – (0.774) | – (0.175) | – (0.232) | – (0.943) | – (0.439) |
| TN | – (0.977) | – (0.705) | – (0.911) | – (0.996) | – (0.879) |

**Table A6**

Effect of glucose addition on pollutants mean removal rate for the batch experiments with industrial wastewater. Negative signs represent no significant effect and positive signs represent a significant effect at a 0.05 statistical level. The numbers represent the p-values of unpaired T-test.

| | LO | LBF | LCG | LCS | LSS |
|---|---|---|---|---|---|
| COD | + (0.007) | + (0.036) | – (0.180) | – (0.169) | + (0.029) |
| TP | – (0.446) | + (0.005) | + (0.036) | – (0.667) | + (0.039) |
| TN | – (0.075) | + (0.003) | + (<0.001) | + (0.015) | + (0.013) |

## Appendix B

Supplementary data.

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