18th International Conference on Wetland Systems for Water Pollution Control
24 - 29 November 2024
ICWS 2024 Martinique

Study on substrates characterization and their performance for personal care products removal from light greywater in vertical-flow constructed wetlands

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Abstract
Constructed wetlands (CWs) have been employed worldwide for pollutants removal from wastewaters due to their proven efficiency at different scale levels. However, there is still room for improvements, e.g., in performance, costs, sustainability and longevity. A clear understanding of the interaction between soil-plant-microorganisms and the main removal mechanisms of target pollutants within a CW could be used to improve overall removal performance. The global pollutants removal can, for example, benefit from the choice of innovative substrates, by favoring the adsorption process, offering ideal conditions for the growth of microorganisms and, thus, promoting the biodegradation process and improving assimilation of nutrients by plants. In this study, the initial characterization of different admixtures mixed with sand (mineral zeolite, and biochar produced in a circular economy perspective from plants residues and sewage-cellulose) showed that biochar provides similar cation exchange capacity (CEC) to the substrate as zeolite, which is known as CEC booster.

Keywords
Circular biochar; innovative substrates; micropollutants removal; on-site light greywater treatment; vertical-flow constructed wetland; water recycling.

INTRODUCTION

Substrates used in constructed wetlands (CWs) for the removal of pollutants are classified according to their composition into mineral, chemical, biomass, industrial and municipal waste, as well as innovative materials. Their primary roles encompass: i) filtration of large particles; ii) adsorption of pollutants; iii) serving electron donor for different chemical reactions such as denitrification; iv) providing habitat for microorganisms; and v) offering physical support for plants (Ji et al., 2022).

Further understanding into the primary removal mechanisms of a specific admixture, such as biochar and target pollutants, as well as its behavior within the time, still needs more in-depth studies to ascertain the technology's longevity. In this context, the objective of this work is to compare the pollutants removal performance of three admixtures mixed with sand (zeolite, biochar from plants residues and biochar from sewage-cellulose) over time when employed to remove personal care products (PCPs) from light greywater (LGW) using a vertical-flow constructed wetland (VFCW). In this study, besides the initial characterization of the substrates and exploring potential modification resulting from ageing processes, microorganism development, pollutants adsorption, and other factors will be continuously monitored.

MATERIALS AND METHODS

The laboratory investigation is being carried out with six VFCWs of 71 L volume each, which are fed simultaneously and intermittently with synthetic light greywater (LSGW- wastewater from showers, baths and hand sinks) three times per day for 30 minutes. The VFCWs are planted with a mix of *Phragmites australis* and *Iris pseudacorus* and, artificially, lighted 8 hours per day.

For this study, three different substrates (S) are compared: mineral zeolite and biochar from plants residues and sewage-cellulose which were mixed with sand to find a good balance between removal efficiency of pollutants, costs and sustainability. The substrates were previously prepared and mixed by the German SME Klimafarmer as follows: S1: 85% sand + 15% zeolite, S2: 95% sand + 5% zeolite, S3: 85% sand + 15% activated biochar from plants residues, S4: 95% sand + 5% activated biochar from plants residues, S5: 85% sand + 15% activated biochar from sewage-cellulose, and S6: 95% sand + 5% activated biochar from sewage-cellulose.

For the characterization of the initial condition of the substrates, before being used to fill the VFCWs, the estimation on the relative proportion (in weight %) of labile organic matter, ash content and volatile matter were determined by performing proximate analyses (Ronsse et al., 2013 by Khan et al., 2023). The values of pH, electrical conductivity (EC), temperature (T°C) and dissolved oxygen (DO) were also measured with conventional WTW probes (Xylem, UK). The methodology of the samples preparation for the measurement of pH and electrical conductivity (EC) was adapted from Khan et al. (2023).

The sieve analysis method was used to determine the grain size distribution of the studied substrates, using a mechanical sieve shaker (Retsch AS-200) and mesh sieves from 0.063 to 2 mm, which mainly retain sand particle size (in mm): fine sand: 0.063–0.2mm, medium sand: 0.2–0.63, and coarse sand: 0.63–2.0 (ISO 14688-1:2017, 2017).

In addition, the different substrates were also externally analyzed to characterize their Brunauer–Emmett–Teller (BET) surface area by the 3P Instruments GmbH & Co. KG, and cations exchange capacity (CEC) by the AGROLAB Agrar und Umwelt GmbH.

RESULTS DISCUSSION

The results of the initial condition characterization of the substrates (S1-S6) are summarized in **Table 1** and **Figure 1**. This initial characterization will serve as basis for further comparison throughout the study duration, examining possible changes due to the pollutant sorption processes removed from LSGW, as well as the development of microbial communities capable of forming biofilm on the substrate surface, which can increase the labile organic matter (Khan et al., 2023).

Based on the proximate analyses (**Table 1**) and knowing that volatile matter is a relative proportion of biomass and organic matter, we can conclude from this first characterization that S4 and S6 presented lower amount (in weight%) of biomass (0.51 ± 0.10 and 0.69 ± 0.36, respectively) compared to the others. The S5 presented the highest amount of biomass, 2.94 ± 0.427 weight%. In the case of biochar substrates, as they were biologically activated, their lower proportion in S4 and S6 (5%) might explain why they presented lower amount of biomass when compared to S3 and S5 (both with 15% of biochar in their composition).

Concerning the labile organic matter, which is the volatile compounds adsorbed on the surface of the substrate, the S2 and S4 presented the highest values, 3.23 ± 3.15 and 2.27 ± 2.33 weight%, respectively.

Table 1. Characterization of the initial condition of the substrates: effective cation exchange capacity ($_{eff}$CEC), potential cation exchange capacity ($_{pot}$CEC), base saturation, moisture content, labile organic matter, ash content, volatile matter, electrical conductivity (EC), potential of hydrogen (pH), temperature (T) and dissolved oxygen (OD).

Substrates	Effective Cation Exchange Capacity ($_{eff}$CEC)[1a]	Potential Cation Exchange Capacity ($_{pot}$CEC)[1b]	Base saturation[1a]	CO2-BET surface area[2]	Moisture content	Proximate analyses (weight %)			Other measurements			
						Labile organic matter	Ash content	Volatile matter	EC (µS/cm)	pH	T (°C)	DO (mg/L)
	cmol+/kg		%	m²/g	%	Mean values ± Std. Dev. (n=2)						
S1	5.14	6.21	201.36	47.00	1.10	0.24 ± 0.29	98.94 ± 0.04	1.35 ± 0.46	239.35 ± 45.65	8.66 ± 0.12	20.60 ± 0.10	4.72 ± 0.06
S2	5.23	5.54	160.23	16.20	0.75	3.23 ± 3.15	99.60 ± 0.01	1.21 ± 0.16	217.50 ± 9.50	8.28 ± 0.06	20.90 ± 0.00	4.81 ± 0.00
S3	3.63	5.89	270.52	12.10	4.79	-0.19 ± 0.07	96.35 ± 0.78	1.92 ± 0.47	269.00 ± 20.00	8.68 ± 0.04	20.65 ± 0.05	4.74 ± 0.17
S4	4.93	5.61	183.98	4.04	0.60	2.27 ± 2.33	96.14 ± 0.36	0.51 ± 0.10	252.00 ± 8.00	8.67 ± 0.04	20.80 ± 0.20	4.53 ± 0.27
S5	6.01	6.19	230.45	10.50	5.95	-0.18 ± 0.37	95.64 ± 0.29	2.94 ± 0.47	358.00 ± 31.00	9.43 ± 0.01	20.45 ± 0.05	4.83 ± 0.01
S6	5.59	5.76	184.97	4.13	0.63	0.36 ± 0.04	98.82 ± 0.42	0.69 ± 0.36	294.00 ± 18.00	9.26 ± 0.09	20.60 ± 0.10	4.71 ± 0.04

S1 (85% sand + 15% zeolite), S2 (95% sand + 5% zeolite), S3 (85% sand + 15% activated biochar from plants residues), S4 (95% sand + 5% activated biochar from plants residues), S5 (85% sand + 15% activated biochar from sewage-cellulose) and S6 (95% sand + 5% activated biochar from sewage-cellulose).

1- External analysis - Agrolab company: methodologies: a) DIN ISO 11260 : 2018-11 and b) DIN ISO 13536 : 1997-04

2- External analysis - 3P company: Brunauer-Emmett-Teller (BET) method for the calculation of the specific surface area on the basis of carbon dioxide isotherm at 273K

Regarding the surface area (**Table 1**), calculated by using the Brunauer-Emmett-Teller (BET) method, the substrate with the highest value was S1 (47 m^2/g), which is the one with higher proportion of zeolite (15%). The advantage of using the zeolite in substrates is the increase of sorption or cation exchange, given its well-known higher exchange capacity than other materials used in CWs, such as a factor of more than 100 compared to gravels (Kadlec & Wallace, 2008). Another way to boost cation exchange in CWs substrates involves the addition of biochar materials (El Barkaoui et al., 2023), and this information can be confirmed in the results of potential cation exchange capacity ($_{pot}$CEC), in which the S1 presented the same value as S5 (6.2 cmol+/kg) and both, higher $_{pot}$CEC when compared to the others. In general, the substrates with higher proportion of zeolite and biochar (15%) presented higher $_{pot}$CEC.

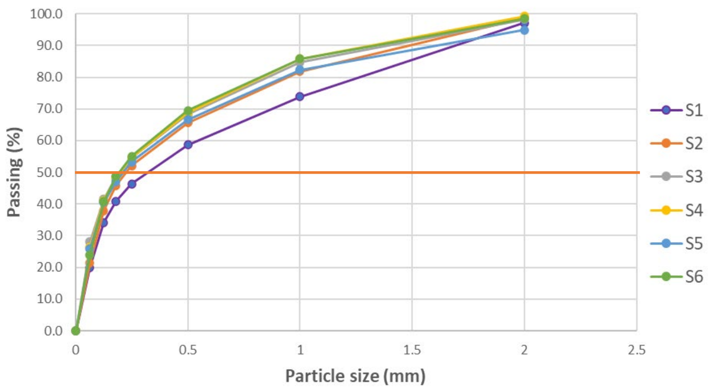

Figure 1. Sieving curves of the substrates: S1: 85% sand + 15% zeolite, S2: 95% sand + 5% zeolite, S3: 85% sand + 15% activated biochar from plants residues, S4: 95% sand + 5% activated biochar from plants residues, S5: 85% sand + 15% activated biochar from sewage-cellulose, and S6: 95% sand + 5% activated biochar from sewage-cellulose.

The results of sieve analysis which determines the grain size distribution of the studied substrates (S1-S6) are summarized in **Figure 1**. In the sieve curves, the particle size distribution (D50) shows that the majority of substrates have 50% of the particle size lower than 0.5mm so they can be classified as medium and fine sand (ISO 14688-1:2017, 2017).

The S1 presented more particles in coarse sand size. Considering physical properties only, in coarse sand soils the water is rapidly infiltrated and drained, which provide a well aerated soil (PHOGAT et al., 2015).

Since granulometry represents a basic physical property of the soils, it is expected to remain constant throughout the project duration for both mineral zeolite and sand. This might not be the case for the biochar materials, which were produced under slow pyrolysis reactions and quality studies are not conclusive yet (Ronsse et al., 2013; IBI, 2015). Therefore, further investigation would be recommended, especially towards the end of the project, to avoid disrupting the VFCWs-laboratory setup due to the substantial soil quantity required for the analysis. This information will be valuable in understanding the hydraulic dynamics and aeration process of the substrates.

NEXT STEPS AND FUTURE PERSPECTIVES

The presented results are preliminary and ongoing investigations are being carried out aiming at comparing the ageing process of these selected substrates when treating LSGW using a VFCW over six-month period. These investigations also consider possible issues that would require mitigation measures, such as clogging and iron leaching. The efficiency of removing both macropollutants and micropollutants, such as PCPs, will be also examined, as well as the final quality of treated water to ensure compliance with effluent quality standards for water reuse.

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