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Evaluation of the influence of filter medium composition on treatment performances in an open-air green wall fed with greywater

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A B S T R A C T

According to the European Research and Innovation Policy Agenda, nature-based solutions (NBSs) are key technologies to improve the sustainability of urban areas. Among NBSs, green walls have been recently studied for several applications, among the others the treatment of lowly polluted wastewater flows as greywater (GW, e.g. domestic wastewater excluding toilet flushes). This work is aimed at the evaluation of the influence of four additives (compost, biochar, granular activated carbon, polyacrylate) mixed with a base filter medium made of coconut fibre and perlite, on the performances of a green wall fed in batch mode with synthetic GW. The green wall was operated with a high hydraulic loading rate of GW (740.8 L/m^2/day) in open-air winter conditions (3.5–15 °C measured for GW) between January and April. The performances of the green wall have been assessed though the monitoring every 1–2 weeks of physicochemical and biological parameters (pH, electric conductivity, total suspended solids, dissolved oxygen, BOD_5 and COD, nitrogen and phosporus compounds, chlorides and sulphates, anionic surfactants and *E. coli*). Removal performances were excellent for BOD_5 (>95%) and *E.coli* (>98%) for all additives; compared to the base medium, biochar was the best performing additive over the highest number of parameters, achieving removals equal to 51% for COD, 47% for TKN and nitric nitrogen and 71% for anionic surfactants. Compost also achieved high removal performances, but the frequent clogging events occurred during the monitoring period do not make its use recommendable. Granular activated carbon and the combination of biochar and polyacrylate performed better than the base medium, but only about the removal of nitric nitrogen. These results demonstrated that, in the considered experimental boundaries, biochar could improve the overall treatment performances of a green wall fed by GW and operated in challenging conditions.

1. Introduction

At present over 2 billion people are living in countries experiencing high water stress (ONU, 2018). Over two-thirds of the world population, about 4 billion people, is already experiencing severe water scarcity during at least one month per year (Mekonnen and Hoekstra, 2016) and this scenario could be extended to approximately 4.8–5.7 billion people in 2050 (Burek et al., 2016). In this context, nature-based solutions (NBSs) are recommended to increase urban areas' resilience, contrast climate change effects, reduce clean water consumption and preserve natural ecosystems (European Commission, 2015). Among NBSs, green wall systems provide multiple benefits as thermal control in buildings, biodiversity protection, life quality increment and real estate valorisation (Castellar da Cunha et al., 2018; Francis and Lorimer, 2011; Seyam, 2019). Among different green wall designs (Medl et al., 2017), wall-based systems with pots have been recently proposed to treat large amounts of greywater (GW) produced in buildings (e.g., (Boano et al., 2021; Fowdar et al., 2017; Masi et al., 2016). GW is the share of household wastewater deriving from sinks, showers and laundry, exceeding 100 L/day per capita in Europe, North America and Asia (Boano et al., 2020; Ghaitidak and Yadav, 2013). "*Light*" GW excludes kitchen sinks, and it is particularly suitable for local treatment due to its

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low pollution, also allowing non-potable water reuse and clean water saving. However, wide-scale application of green walls for GW treatment is still far; one of the causes is the inadequate amount of available information on the effect of the green wall configuration on GW treatment's efficiency. The available literature is recent and relatively limited; most studies focus on filter media (Fowdar et al., 2017; Masi et al., 2016; Prodanovic et al, 2017, 2018, 2017; Svete, 2012) performances in terms of removal of nutrients and pathogens. The efficiency of GW treatment varies significantly depending on design conditions, with reported values of efficiencies in the range of 25–99%, for BOD_5, 28–97% for COD, 7–99% for TN, and 32–100% for *E. coli* (Boano et al., 2020b). These studies identified the filter medium as one of the most important elements of a green wall for GW treatment, as it plays an important role in controlling water flow and pollutant removal, while also contributing to plant well-being (Prodanovic et al., 2017). The tested filter media include sand (Fowdar et al., 2017; Masi et al., 2016), expanded clay (Masi et al., 2016; Pradhan et al., 2020; Prodanovic et al., 2017; Svete, 2012), coconut coir (Boano et al., 2021; Masi et al., 2016; Pradhan et al., 2020; Prodanovic et al., 2017), and perlite (Boano et al., 2021; Pradhan et al., 2020; Prodanovic et al., 2017). The cited studies suggested that the relatively low permeability of sand and coconut coir enhances contact time between GW and filter medium and favours GW treatment (Masi et al., 2016; Prodanovic et al., 2017). However, the high specific weight of sand can limit its application in green walls, while coconut coir is expected to degrade over time and was shown to release organic carbon (Boano et al., 2021; Masi et al., 2016). Mixing these filter media with lighter and more permeable materials (perlite, expanded clay) was employed to mitigate these issues and allowed to reach good treatment efficiencies (BOD_5: 44–97%; COD: 40–70%; TN: 30–75%; *E. coli*: 60–100%) (Boano et al., 2021; Masi et al., 2016; Prodanovic et al., 2017). Another comparison of eight different media (sand, expanded clay, vermiculite, growstone, rockwool, fyto-foam, coco coir, perlite) suggested that combining coco coir and perlite could favour contaminants' removal (COD: 55–85%, TN: 40–80% and *E. coli*: 35–90% for perlite:coir ratio below 2:1) while reducing the risk of clogging (Prodanovic et al, 2017, 2018). Recently, the use of a mixture of recycled materials (date seeds and spent coffee grounds) was shown to perform similarly to the mixture of coco coir and perlite (Pradhan et al., 2020). However, to our knowledge, there is still a strong need for studies specifically and critically exploring the influence of filter media on GW treatment efficiency, and at the same time aiming to maximize the system performances while limiting the size and complexity of the green wall. Therefore, the objective of this study is to evaluate and compare the effects of different additives mixed with a base filter medium (made of coconut fibre and perlite) in a modular green wall system for GW treatment, easily modifying the base filter media properties with minimum impact on construction time and costs. The removal efficiencies of different pollutants (e.g., suspended solids, organic substances, nutrients and *E. coli*) were determined to assess the performances of the additives. Four carbon-based additives (compost, biochar, granular activated carbon, and polyacrylate) were tested in different combinations. Synthetic GW was fed to the green wall in batch mode, and the system operated with a high Hydraulic Loading Rate (HLR) of 740.8 L/m^2/day in open-air winter conditions. The combination of low air temperature and high HLR were specifically chosen to test the performance of the green wall system in challenging conditions.

2. Materials and methods

2.1. Synthetic greywater

Domestic GW composition is highly variable, depending on commercial products, people habits and seasonal variations (Boano et al., 2020; Diaper et al., 2008; Eriksson et al., 2002; Shaikh and Ahammed, 2020). Light synthetic GW was prepared following a standard recipe (Diaper et al., 2008) adopted in previous studies (Fowdar et al., 2017; Prodanovic et al., 2017). Local brands have been used (Table S2) for GW preparation, and the resulting contaminant concentrations were measured for each sampling date. Microbiological pollutants have been introduced using *E. coli* tablets (Ielab BAControl).

2.2. Filter media

The idea behind this study is to combine a base medium suitable for plant growth and GW treatment with additive materials that are not routinely used in green walls to increase the pollutant removal capacity of the filter medium. The base medium (BM) consists of a mixture of 80% coconut fibre and 20% perlite (% in volume); its composition was optimised (Boano et al., 2020a) as reasonable balance between hydraulic conductivity and specific weight. The considered additive materials (Table 1) were: compost (CO, obtained from wastes in a dynamic composting system lasting 6 months; ANT's Compost V, Agrinewtech, Italy), biochar (BC, obtained from wood chips; Agrinewtech, Italy), granular activated carbon (GAC; SHG, Italy), and polyacrylate (PA; New PolyPlants, Italy). Compost and biochar are recycled materials used as soil amendant, renowned for the low cost and environmental benefits (Kotsiris et al., 2013; Moges et al., 2015). GAC is commonly used for wastewater treatment for its high adsorption properties (Thompson et al., 2020). PA (hydrogel) is a polymer, chosen for its high water retention capacity, supporting longer contact time for reactions in the porous medium, and its low dry weight that could reduce the transportation costs of the filter material at the installation site (Deska et al., 2020).

The performances of the BM were compared with 6 combinations with the considered additives (Table 1). Specifically, three mixtures were prepared combining 80% BM and 20% CO, BC, or PA (as alternatives, 20CO, 20BC, and 20 PA), and one mixture was made of 90% BM and 10% GAC (10GAC; a lower amount of additive was chosen due to the strong sorption potential of GAC). One additional mixture was prepared combining 60% BM with 20% BC and 20% PA (20BC20PA) to verify the effect of multiple additives. An older mixture of 80% BM and 20% PA (20 PA+) was also tested; it was part of a green wall panel installed 4 months before the others and previously employed for preliminary tests (see section 2.3). Total and effective porosity, bulk density and saturated hydraulic conductivities of are reported in Table S1. The choice of employing a relatively high fraction of BM was made with the aim of further improving the good efficiency of the mixture of coco coir and perlite. Moreover, some materials (e.g. GAC) because are not conceived as growing medium for plants and were thus considered unsuited for use in high volumetric fractions, and the amount of additives was limited to try balancing their benefits and limits.

Table 1
List of additives employed in the study and corresponding mixes (IDs are in parentheses, % in volume). The deployment date indicates when the mix was set up in the green wall and GW feeding started.

Additive	Grain size (mm)	Tested mixes (ID)	Deployment date
Granular activated carbon	1.2–2.4	90% BM + 10% GAC (10GAC)	January 2019
Compost	0.5–25	80% BM + 20% CO (20CO)	January 2019
Biochar	5–10	80% BM + 20% BC (20BC)	January 2019
Polyacrylate	1-2 (dry), 8–10 (fully hydrated)	80% BM + 20% PA (20PA and 20PA+)	September 2018 (old configuration) & January 2019
Biochar + Polyacrylate		60% BM + 20% PA + 20% BC (20BC20PA)	January 2019

2.3. Experimental setup

The experimental laboratory-scale setup, located in the Hydraulics Laboratory courtyard at Politecnico di Torino, was based on the open-air green wall system presented in (Boano et al., 2021) (Fig. 1) and summarized in the following. The green wall was made of modular panels with pots (0.18 × 0.18 × 0.22 m, 6.5 L bulk soil volume) filled with the mixtures listed in Table 1. Triplicate tests were made for each mixture using three identical columns, each one composed of three pots filled with a 0.2 m layer of the same mixture, and different ornamental plant species (from top to bottom in Fig. 1: *Carex morrowii, Hedera helix, Lonicera nitida*), chosen after a literature review (Cameron et al., 2014; Castellar da Cunha et al., 2018; Fowdar et al., 2017; Kotsia et al., 2020; Pérez et al., 2011; Rysulova et al., 2017; Serra et al., 2017) and preliminary tests (Boano et al., 2021). The columns worked independently as vertical flow systems hanged on 1 m^2 modular metallic panels, with four columns made of three pots per panel. All columns have been fed with GW prepared every two days and stored in a 1.5 m^3 HDPE tank, mixed hourly by an automatic recirculation system. GW was pumped 24 times per day for 15 min, followed by 45 min of resting time, in a pressurised feeding system of plastic pipes and drippers. Each column was fed with 1 L of GW per flush, resulting in almost 100 L/day per panel, which is coherent with the mean GW daily production per capita in developed countries (Boano et al., 2020; Ghaitidak and Yadav, 2013). In each column water flowed vertically by gravity through each pot. Plastic tubes (4 mm diameter) connected at the bottom of the lowest pots have been used to collect samples and to discharge output water in the sewer system. Daily precipitation during the sampling period ranged between 0 and 30.8 L/m^2/day, thus it was negligible compared to the high hydraulic loading rate (HLR) of system (740.8 L/m^2/day). All pots on the green wall panels were preliminarily washed with 120 L of tap water before the experiments to remove the finest particles that could clog the system (Boano et al., 2021).

2.4. Sampling and analytical procedures

Nine samples per column were collected along three months between January and April 2019, for a total of 189 outflow samples. Input GW and output water were sampled weekly during the first part of the monitoring period (January 16th-23rd-30th and February 6th-13th-27th) to better follow possible transients, and twice per month in the remainder of the period (March 6th −20th, April 2nd). The following analytical parameters were measured in all samples: temperature, pH, electric conductivity (EC), and dissolved oxygen (DO) through a WTW Multi 3320 portable 2-channels probe equipped with specific sensors/electrodes; total suspended solids (TSS) by filtering 1 L through 0.45 μm cellulose membranes; sulphate, chloride, total Kjeldhal nitrogen (TKN), nitric nitrogen, ammonia nitrogen, total phosphorus (TP), chemical oxygen demand (COD) and methylene blue active substances (MBAS, i.e. anionic surfactants) through Nanocolor™ reagent kits, a VELP COD ECO 16 thermoreactor (for TKN, TP and COD) and a AL450 Multidirect photometer. BOD_5 was analyzed through a VELP FOC 215 E incubator equipped with 24 BOD sensor systems. *E.coli* was analyzed through Colitag™ water test reagents after 24 h according to APHA standard method 9221. In the calculation of removal efficiencies, values of concentrations below the detection limit were set equal to the limit.

2.5. Statistical analysis

Two types of statistical tests were employed in this study to identify temporal trends in the data and to verify if the presence of an additive could improve the BM treatment efficiency, which was considered as reference case. For the parameters measured on site (temperature, pH, EC, DO), the tests were performed on the observed time series for GW and outflow water, while for the other parameters (COD, BOD_5, TSS, TKN, NO_3^-, TP, SO_4^{2-}, *E. coli,* MBAS) the tests were applied on the removal efficiencies, calculated comparing the values measured in GW and in the outflow, for each sampling date. For each filter medium (BM and the six mixtures), temporal trends were investigated with a two-tailed non-parametric Mann-Kendall test. A significant monotonic trend was identified when the absolute value of the test statistic |S| was larger than 17 ($p < 0.05$), the threshold value being dependent on the number of obervations over time. Furthermore, in order to compare the performance of each filter medium mixture with BM, differences between values of removal efficiency of each mixture and those of BM were calculated for each sampling date; a one-tailed Student's *t*-test was then performed to verify if the mean value of the differences was significantly higher than zero. For the considered parameters, positive test results on the removal efficiencies indicated that the tested filter medium mixture was significantly more effective ($p < 0.05$) than the BM. The test was also applied to identify differences in temperature, pH, EC, and DO between GW and outflow samples. Finally, since multiple comparisions were performed, a false discovery rate procedure (Benjamini and Hochberg, 1995) was applied on all test results to correct *p*-values and

Fig. 1. a) Overview of the green wall panels; b) Detail of a modular panel. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

avoid the inflation of Type-I error.

3. Results and discussion

Results for the tested physicochemical parameters are shown in Fig. 2. The range of GW temperature values (3.5–15.3 °C) was comparable with those observed during winter in outdoor systems (Dal Ferro et al., 2021; Prodanovic et al., 2019). Temperatures of both GW and outflow water samples significantly increased over time for all filter medium mixtures due to the increase in air temperature during the observation period (Table S3; Figure S1). In the whole monitoring period, no significant difference was found between GW temperature (7.7 ± 4.6 °C) and output water temperature in all filter medium mixtures (Fig. 2a, Table S3). For pH, no temporal trend was found for either GW or output water (Table S3; Figure S2). Output samples were on average slightly alkaline (Fig. 2b) and remained similar to GW (7.35 ± 0.31) for all mixtures (Fig. 2b, Table S3). Even though EC showed an increasing trend for GW from 400 to 712 μS/cm, no significant trend was present for the output samples (Table S3; Figure S3), suggesting that the water solution reached equilibrium with the porous medium. All mixtures (Fig. 2c, Table S3) showed higher EC values than GW, especially in the first 2 months of the monitoring period. In the whole monitoring period, no filter medium mixture exhibited significant differences in EC compared to BM (641 ± 69 μS/cm) (Fig. 2c, Table S3). DO concentration in GW strongly decreased over time from 11.7 to 1.5 mg/L (Table S3; Figure S4), suggesting that higher temperature in the last part of the monitoring period may have favoured the development of biological reactions in the storage tank with consequent DO consumption. However, average DO concentration in output samples was close to saturation for all filter medium mixtures (Fig. 2d). This indicates that oxygen exchange between soil and atmosphere produced aerobic conditions in the pots and increased DO concentrations. The compost mixture (20CO) was characterized by the lowest average DO value (10.23 ± 2.23 mg/L), possibly due to its low effective porosity (0.05 ± 0.02 Table S1) and frequently observed clogging events that may have compromised soil aeration and oxygen exchange with open air (Fig. 2d).

In GW, BOD_5 ranged between 36.2 and 71.3 mg/L, with an average value of 52.4 ± 9.0 mg/L (Fig. 3a), close to literature values for synthetic GW (65 ± 6 mg/L) (Hourlier et al., 2010) and within the range of Western European countries (20–756 mg/L) (Boano et al., 2020). All the mixtures exhibited an average removal efficiency >93% (Table 2), in line with the best literature performances for common filter media (96–99%) (Fowdar et al., 2017; Gattringer et al., 2016; Kotsia et al., 2020) and for GAC (97 ± 3%) (Dalahmeh et al., 2012). None of the tested filter medium mixtures showed any temporal trend in BOD_5 removal efficiency (Table 3, Figure S5). According to the test results, no mix performed significantly better than the BM (Table 3). Apparently, the very high removal efficiency of the BM was not altered by the additives. These results confirm the high potential of green wall application for removing BOD_5 from GW (Boano et al., 2021; Gattringer et al., 2016).

COD removal efficiency significantly increased over time for all mixtures except for 20 PA (Table 3, Figure S6). This improvement of removal efficiency may have been caused by a combination of plants growth and biofilm development and of temperature increase during the monitoring period (Boano et al., 2021). Removal efficiency varied among the mixtures between 29.6 ± 45.5% for 20CO and 50.7 ± 28.5% for 20BC (Fig. 3b, Table 2). The best removal performance was found for 20BC (50.7 ± 28.5%), which was higher than for BM (40.4 ± 25.1%) although the difference was not classified as statistically significant (corrected $p = 0.07$). (Fig. 3b, Table 3). Output COD concentration for 20BC varied between 20 mg/L and 267 mg/L (147 ± 85 mg/L on average), and its removal efficiency ranged between a slight (2.43%) release at the first sampling date to >86% removal (Figure S6). This increasing trend over the observation period led removal efficiency to gradually reach values reported in literature studies on green walls (64–98%) (Gattringer et al., 2016; Jin et al., 2018; Kotsia et al., 2020; Masi et al., 2016; Pradhan et al., 2020; Prodanovic et al., 2020). Dalahmeh et al. (2012) reported COD removal efficiency up to 94% with an unplanted GAC filter; however, this performance was obtained with a HLR value (32 $L/m^2/d$) that was about 20 times lower than in the present study. This comparison confirms previous results that increases in

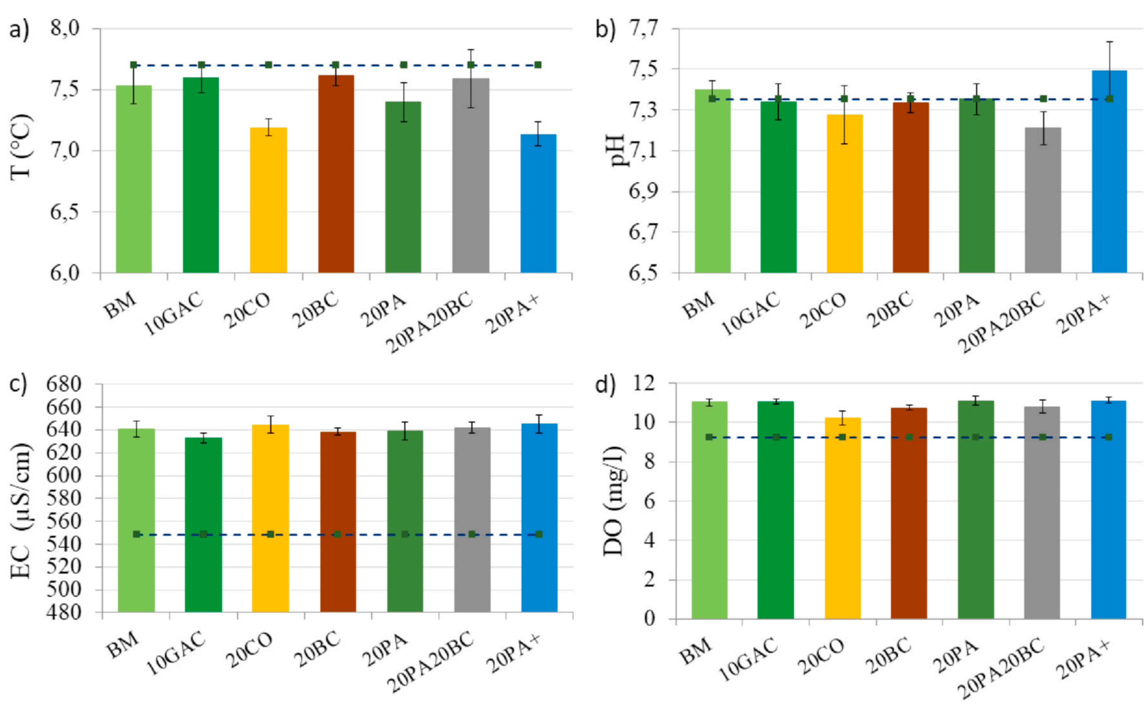

Fig. 2. Average values of a) temperature, b) pH, c) Electric Conductivity (EC) and d) Dissolved Oxygen (DO) of GW (dashed lines) and at the outlet of all filter medium mixtures (bars). Filter medium mixtures are denoted as (see text for further details) BM: base medium; 10GAC: granular activated carbon; 20CO: compost; 20BC: biochar; 20 PA: polyacrylate; 20PA20BC: polyacrylate and biochar; 20 PA+: polyacrylate (old configuration).

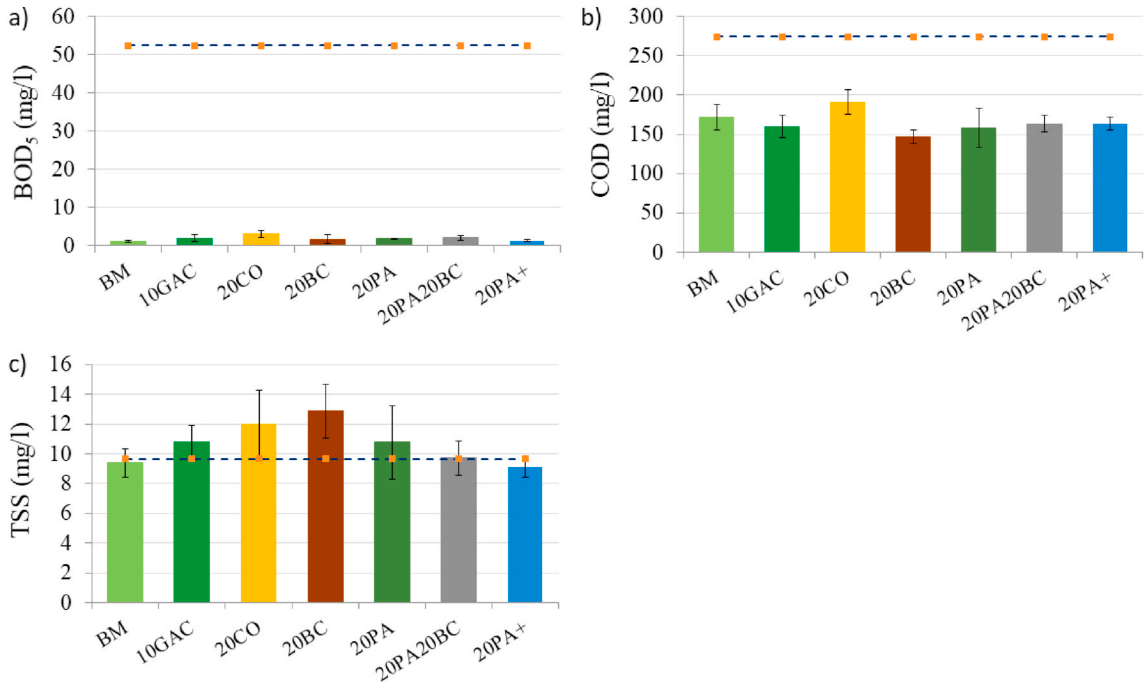

Fig. 3. Average values of concentrations of a) BOD_5, b) COD and c) TSS of input GW (dashed lines) and at the outlet of all filter media mixes (bars). Filter medium mixtures are denoted as (see text for further details) BM: base medium; 10GAC: granular activated carbon; 20CO: compost; 20BC: biochar; 20 PA: polyacrylate; 20PA20BC: polyacrylate and biochar; 20 PA+: polyacrylate (old configuration).

Table 2
Average values and standard deviations of removal efficiency over the monitoring period. Values are in expressed in percentages for all parameters except for *E. coli* (log units).

Mixture	BOD_5	COD	TSS	TKN	NO_3^--N	TP	SO_4^{2-}	*E. coli*	MBAS
BM	97.7 ± 1.3	40.4 ± 25.1	−7.4 ± 46.5	34.6 ± 29.7	25.7 ± 28.8	21.6 ± 28.7	0.9 ± 22.0	3.1 ± 1.2	63.0 ± 13.6
10GAC	95.7 ± 4.8	43.9 ± 35.1	−22.1 ± 58.1	43.6 ± 34.0	37.8 ± 27.5	21.5 ± 33.9	8.7 ± 17.6	3.2 ± 1.1	62.7 ± 27.5
20CO	93.3 ± 7.1	29.6 ± 45.5	−33.3 ± 76.9	41.3 ± 24.4	35.9 ± 26.6	16.4 ± 21.4	5.1 ± 13.9	3.1 ± 1.0	61.3 ± 22.1
20BC	96.0 ± 5.7	50.7 ± 28.5	−45.8 ± 70.7	46.8 ± 24.8	46.9 ± 21.5	16.7 ± 33.9	11.7 ± 21.5	3.1 ± 1.3	71.4 ± 21.7
20PA	96.4 ± 1.5	48.4 ± 30.1	−7.4 ± 51.3	31.7 ± 33.2	22.0 ± 27.9	31.6 ± 48.1	−5.1 ± 26.0	3.1 ± 1.1	61.5 ± 17.8
20PA20BC	95.4 ± 5.3	38.7 ± 24.2	−7.4 ± 36.8	40.2 ± 28.9	38.8 ± 22.6	29.3 ± 25.1	16.5 ± 14.1	3.2 ± 1.2	65.0 ± 20.5
20PA+	97.3 ± 1.9	45.2 ± 29.7	−4.9 ± 39.1	29.9 ± 33.9	19.6 ± 30.9	15.9 ± 24.4	12.2 ± 12.7	2.9 ± 1.2	61.3 ± 22.1

Table 3
List of *p* values of the statistical tests performed on contaminants' removal efficiencies. The Mann-Kendall test verified the presence of temporal trends (positive if not otherwise specified), and the Students' *t*-test verified if a filter medium mixture had better removal performance than the BM. Values of $p < 0.05$ are shown in bold, and asterisks denote values that were confirmed as statistically significant after applying the false discovery rate procedure.

Mixture	BOD_5	COD	TSS	TKN	NO_3^--N	TP	SO_4^{2-}	*E. coli*	MBAS
	Temporal trend								
BM	0.317	**0.001***	0.266	**0.005***	0.252	0.076	0.175	**0.019***	0.266
10GAC	0.114	**0.029***	0.902	**0.005***	0.302	**0.009**	**0.048**	**0.019***	0.174
20CO	0.602	**0.005***	0.387	**0.017***	1.000	0.118	**0.048**	**0.019***	0.536
20BC	0.094	**0.004***	1.000	**0.029***	0.602	0.076	0.348	0.108	0.902
20PA	0.916	0.108	0.387	**0.005***	0.175	0.174	0.252	**0.035***	0.536
20PA20BC	0.602	**0.029***	0.266	0.076	0.917	0.252	0.175	**0.013***	0.902
20PA+	0.917	**0.029***	0.266	**0.005***	0.348	**0.017**	**0.029**	**0.019***	0.266
	Comparison with BM								
10GAC	0.892	0.349	0.901	0.079	**0.022***	0.083	**0.041**	0.243	0.515
20CO	0.959	0.855	0.859	**0.016***	**0.019***	0.936	0.218	0.107	0.600
20BC	0.806	**0.013**	0.969	**0.006***	**0.005***	0.174	**0.001***	0.404	0.096
20PA	0.978	0.089	0.498	0.829	0.752	0.776	0.907	0.094	0.636
20PA20BC	0.887	0.592	0.500	0.103	**0.025***	0.868	**0.004***	0.233	0.378
20PA+	0.677	0.209	0.290	0.977	0.914	0.504	**0.011***	0.722	0.627

HLR up to 600–800 $L/m^2/d$ lead to relatively mild reductions in COD removal efficiency (Boano et al., 2020b).

TSS concentration in GW (9.63 ± 2.94 mg/L) was lower than usual values for synthetic GW (50–100 mg/L) (Fowdar et al., 2017; Hourlier et al., 2010; Pradhan et al., 2020), probably due to settling in the GW storage tank before the feeding system (Abed et al., 2020), but still in the range observed for real GW (e.g., 5–252 mg/L; Prodanovic et al., 2020). No significant temporal trend was detected for TSS along the monitoring period (Table 3, Figure S7). The consequence of these low concentrations are portrayed in Fig. 3c; despite a small reduction in the average output concentration for BM and PA + mixtures (9.37 ± 5.76 and 9.08 ± 5.16 mg/L, respectively) the average removal efficiency resulted in a slight TSS release for all mixes (Table 2, Fig. 3c). According to the results of the Student's *t*-test, no filter medium mixture performed significantly better than BM (Table 3). The low input TSS load hence prevented further removal by the additives.

TKN removal efficiency significantly improved over time for all filter medium mixtures except for 20BC20 PA (Table 3, Figure S8), possibly due to biofilm growth and progressive development of biological processes, as reported in previous studies (Pradhan et al., 2019). The low values of ammonia nitrogen NH_4^+-N concentrations (usually below 1 mg/L) indicate that in the present study organic nitrogen was the main component of TKN. Average TKN output concentration ranged between 2.04 ± 1.18 mg/L and 2.78 ± 1.17 mg/L (in 10GAC and 20 PA + respectively) and average removal efficiency varied between 29.9 ± 33.8% and 46.8 ± 24.8% (20 PA+ and 20BC, respectively; Fig. 4a, Table 2). These values are in line with the median TKN removal efficiencies (34–55%) observed in winter by (Dal Ferro et al., 2021) for a vertical flow system treating kitchen GW, suggesting that the low temperatures may have limited TKN removal. Both 20CO and 20BC (41.3 ± 24.4% and 46.8 ± 24.8% respectively) performed significantly better than BM (34.6 ± 29.7%) in removing TKN (Table 3).

Analysis of nitric nitrogen NO_3^--N concentrations did not reveal any significant temporal trend in removal efficiency (Table 3, Figure S9) even though GW concentration increased along time (Table S3), indicating that removal processes in the green wall were able to compensate for variations in input concentration. For all mixes, NO_3^--N concentration decreased from the GW value of 3.39 ± 1.43 mg/L to output values between 1.82 ± 1.30 mg/L and 2.61 ± 1.46 mg/L for 20BC and 20 PA+, respectively (Fig. 4b). Removal efficiencies of 20 PA and 20 PA+ were slightly (but not significantly) lower than the one of BM (25.6 ± 28.8%), while all other filter medium mixtures performed significantly better than BM (Table 3). These findings agree with the previous results reporting improvements in nitrogen removal using GAC compared to more inert filter media (Dalahmeh et al., 2012).

TP concentration (Fig. 4c) was low for most samples, both for GW (4.36 ± 6.33 mg/L) and output water (between 2.05 ± 3.77 mg/L and 3.71 ± 5.53 mg/L for 20 PA and 20CO, respectively). No significant temporal trend was identified for any filter medium mixture (Table 3, Figure S10), which may indicate the contribution of physicochemical processes (e.g., sorption) that were relatively constant over time (Pradhan et al., 2020). Net TP removal was observed for all filter medium mixtures (Fig. 4c, Table 2), and the statistical tests showed that no additive significantly improved TP removal efficiency when added to the base medium (21.6 ± 28.7%) (Table 3). In general, the average removal efficiency was coherent with studies employing ornamental plants (11–20%) (Kotsia et al., 2020), and in line with the very wide range of literature results on TP removal (Boano et al., 2020) which reflects the diverse rates of TP removal by plant uptake and microbial activity in green walls (Prodanovic et al., 2019).

Input SO_4^{2-} concentration in GW (88 ± 21 mg/L) was similar to concentrations in output samples (Fig. 4d). Average removal efficiency of BM (0.9 ± 22%) indicates that SO_4^{2-} behaved quite conservatively in the green wall, as expected for aerobic conditions (Table 2). Even though some mixtures (20BC: 11.7 ± 21.5%; 20 PA+: 12.2 ± 17.2%; 20PA20BC: 16.5 ± 14.1%) removed significatively more SO_4^{2-} than BM (Table 3), it is clear from Fig. 4d and from the removal efficiency values that this removal is minimal. As expected, a similarly conservative behaviour was also found for Cl^- (data not shown), with concentrations in GW equal to 7.0 ± 3.1 mg/L and in output water between 6.2 ± 1.4 mg/L (BM) and 7.2 ± 1.6 mg/L (20CO).

E. coli (Fig. 5a, Table 2) removal had excellent performances since the beginning of the monitoring period, and the Mann-Kendall test further identified an increasing trend in removal efficiency for all mixtures except 20BC (Table 3, Figure S12). Average removal efficiency was over 98% (>2.9 log units) for all mixtures (Table 2), and the Student's *t*-test did not find a significant improvement compared to BM (98.9 ± 1.8%, 3.1 ± 1.8 log units) (Table 3). The inclusion of additives hence did

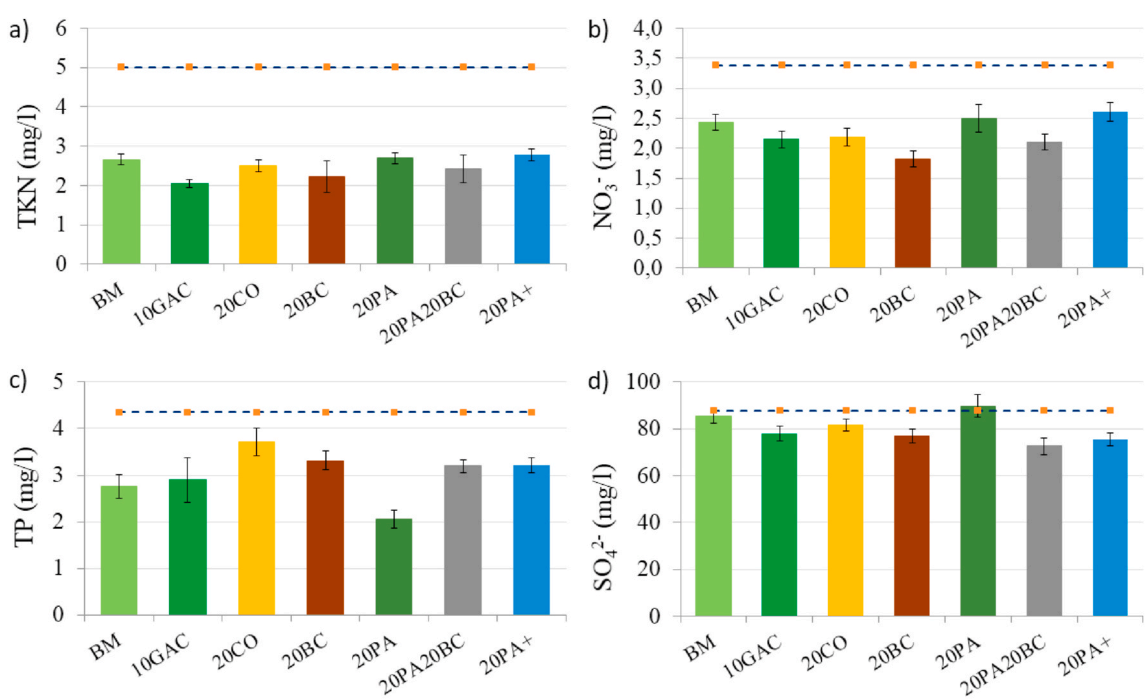

Fig. 4. Average values of concentrations of a) TKN, b) NO_3^-, c) TP and d) SO_4^{2-} of GW (dashed lines) and at the outlet of all filter medium mixtures (bars). Filter medium mixtures are denoted as (see text for further details) BM: base medium; 10GAC: granular activated carbon; 20CO: compost; 20BC: biochar; 20 PA: polyacrylate; 20PA20BC: polyacrylate and biochar; 20 PA+: polyacrylate (old configuration).

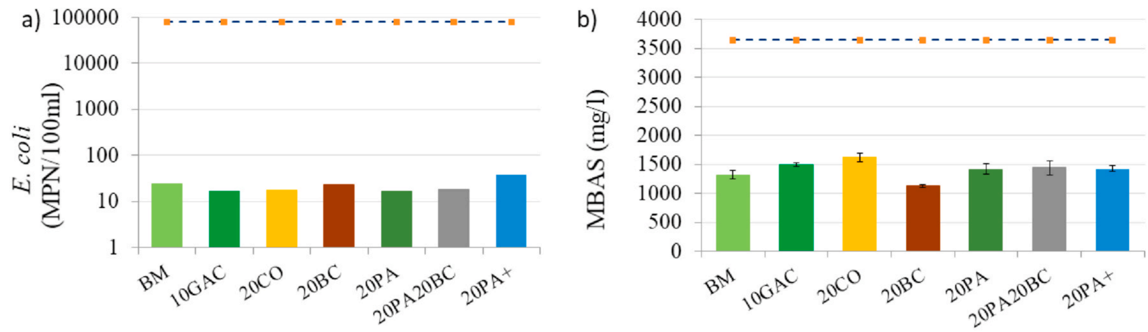

Fig. 5. Average values of concentration of a) *E. coli* and b) MBAS of input GW (dashed lines) and outlet of all filter media mixes. Filter medium mixtures are denoted as (see text for further details) BM: base medium; 10GAC: granular activated carbon; 20CO: compost; 20BC: biochar; 20 PA: polyacrylate; 20PA20BC: polyacrylate and biochar; 20 PA+: polyacrylate (old configuration).

not result in statistically significant improvements compared to the already high removal performance of the base medium mix. These performance are similar to the highest values reported in previous green wall studies for GW treatment (Bakheet et al., 2020; Boano et al., 2020; Pradhan et al., 2020; Prodanovic et al., 2020).

MBAS concentration in output water exceeded two-fold reduction for all mixtures compared to GW (Fig. 5b, Table 2), with no temporal trend during the observation period (Table 3, Figure S13). No mixture performed significantly better than BM (63.0 ± 13.6%) (Table 3), even if 20BC showed a slightly higher average removal efficiency (71.4 ± 21.7%).

4. Conclusions

This study compared the removal performances of a GW-fed green wall with pots filled with different mixtures of filter media, evaluating the contribution of additives (compost, biochar, granular activated carbon, and polyacrylate) to a base filter medium of coconut fibre and perlite. All plants showed good health conditions and similar growing rates for all filter medium mixtures during the present study. Concentrations of treated GW for the monitored parameters complied with class B/C/D requirements of the EU regulation for water reuse in agriculture (EU, 2020/741, 2020), exemplifing the applicative potential of this NBS.

The green wall showed excellent removal performances for BOD_5 (>95% for all mixtures) and *E. coli* (>98% for all mixtures); while the removal efficiencies of these contaminants were very high, the adoption of the additives resulted in no significant improvement compared to BM. Good performances were also observed for COD and nitrogen removals; biochar significantly increased removal performances for TKN (46.8 ± 24.8%) and NO_3^--N (46.9 ± 21.5%) compared to BM (TKN: 34.6 ± 29.7%, NO_3^--N: 25.7 ± 28.8%), and removal efficiency for COD (50.7 ± 28.5%) was also high but not significantly better than BM (63.0 ± 13.6%). These results demonstrate the potential benefit of using biochar as an additive in GW treatment with green walls.

Among other additives, compost performed better than BM in removing TKN and NO_3^--N, but its use is not recommended because this advantage was largely outweighted by frequent clogging issues that increased the need for maintenance of the green wall. Clogging was likely favoured by the low effective porosity of the compost mixture. Interestingly, no other clear relationship was found between removal performances and physical properties (porosity, bulk density, hydraulic conductivity) of the filter medium mixtures, suggesting that removal of contaminants is controlled by other physico-chemical properties of the materials. Significant improvements compared to BM were also observed for granular activated carbon and the combined biochar & polyacrylate mixture, but only for removal of NO_3^--N. Apparently, the combination of biochar and polyacrylate, which had the highest amount (40%) of additives, reduced the advantage provided by the addition of biochar alone, suggesting that the type of additive may be as important, if not more, as the amount of base filter medium. No evident difference was noticed between the two polyacrylate mixes, suggesting that the higher age of the old mix did not affect the removal performances.

Finally, it is important to remind that the choice of filter medium in a green wall should consider other factors beside removal efficiency. For instance, the inclusion of an additive with a slightly lower efficiency could be acceptable if it allows for substantial cost reductions. As an example, in remote areas where transportation costs are significant, dry polyacrylate could be inexpensively transported and hydrated on site to entail significant savings compared to conventional filter media. On the other hand, the use of more expensive materials with higher removal efficiency could reduce the wall size per unit volume of treated greywater (e.g., installing two-row panels) and potentially compensate their higher material cost. Further research is needed to investigate the interplay among advantages and drawbacks of different filter media, including their long-term durability, the possible leaching of compounds, and their performance in actual operating conditions.

Authors' contributions

Conceptualization, methodology and supervision: Fulvio Boano and Silvia Fiore; writing of original draft: Elisa Costamagna and Fulvio Boano; experimental activity: Elisa Costamagna, Alice Caruso and Marco Chiappero; review of the manuscript: all authors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2021.113646.

References

Abed, S.N., Almuktar, S.A., Scholz, M., 2020. Impact of storage time on characteristics of synthetic greywater for two different pollutant strengths to Be treated or recycled. Water, Air, Soil Pollut. 231 https://doi.org/10.1007/s11270-020-04602-1.
Bakheet, B., Prodanovic, V., Deletic, A., McCarthy, D., 2020. Effective treatment of greywater via green wall biofiltration and electrochemical disinfection. Water Res. 185, 116228. https://doi.org/10.1016/j.watres.2020.116228.
Benjamini, Y., Hochberg, Y., 1995. Controlling the false discovery rate: a practical and powerful approach to multiple testing. J. R. Stat. Soc. Ser. B 57, 289–300. https://doi.org/10.1111/j.2517-6161.1995.tb02031.x.
Boano, F., Caruso, A., Costamagna, E., Fiore, S., Demichelis, F., Galvão, A., Pisoeiro, J., Rizzo, A., Masi, F., 2021. Assessment of the treatment performance of an open-air green wall fed with graywater under winter conditions. ACS ES&T Water 1, 595–602. https://doi.org/10.1021/acsestwater.0c00117.
Boano, F., Caruso, A., Costamagna, E., Ridolfi, L., Fiore, S., Demichelis, F., Galvão, A., Pisoeiro, J., Rizzo, A., Masi, F., 2020. A review of nature-based solutions for greywater treatment : applications , hydraulic design , and environmental benefits. Sci. Total Environ. 711, 134731. https://doi.org/10.1016/j.scitotenv.2019.134731.
Burek, P., Satoh, Y., Fischer, G., Kahil, M.T., Scherzer, A., Tramberend, S., Nava, L.F., Wada, Y., Eisner, S., Flörke, M., Hanasaki, N., Magnuszewski, P., Cosgrove, B., Wiberg, D., 2016. Water Futures and Solution. Fast Track Initiative. International Institute for Applied Systems Analysis.
Cameron, R.W.F., Taylor, J.E., Emmett, M.R., 2014. What's "cool" in the world of green façades? How plant choice influences the cooling properties of green walls. Build. Environ. 73, 198–207. https://doi.org/10.1016/j.buildenv.2013.12.005.
Castellar da Cunha, J.A., Arias, C.A., Carvalho, P., Rysulova, M., Canals, J.M., Pérez, G., Bosch, M.G., Morató, J.F., 2018. "WETWALL" — an innovative design concept for the treatment of wastewater at an urban scale. Desalin. Water Treat. 109, 205–220. https://doi.org/10.5004/dwt.2018.22143.
Dal Ferro, N., De Mattia, C., Gandini, M.A., Maucieri, C., Stevanato, P., Squartini, A., Borin, M., 2021. Green walls to treat kitchen greywater in urban areas: performance from a pilot-scale experiment. Sci. Total Environ. 757, 144189. https://doi.org/10.1016/j.scitotenv.2020.144189.
Dalahmeh, S.S., Pell, M., Vinnerås, B., Hylander, L.D., Öborn, I., Jönsson, H., 2012. Efficiency of bark, activated charcoal, foam and sand filters in reducing pollutants from greywater. Water, Air, Soil Pollut. 223, 3657–3671. https://doi.org/10.1007/s11270-012-1139-z.
Deska, I., Mrowiec, M., Ociepa, E., Lewandowska, A., 2020. Influence of the hydrogel amendment on the water retention capacity of extensive green roof models. J. Ecol. Eng. 21, 195–204. https://doi.org/10.12911/22998993/112763.
Diaper, C., Toifl, M., Storey, M.V., 2008. Greywater Technology Testing Protocol Greywater Technology Testing Protocol, Water for a Healthy Country Flagship Report.
Eriksson, E., Auffarth, K., Henze, M., Ledin, A., 2002. Characteristics of grey wastewater 4, 85–104.
EU 2020/741, 2020. Council of 25 May 2020 on minimum requirements for water reuse.
European Commission, 2015. Towards an EU Research and Innovation Policy Agenda for Nature-Based Solutions & Re-naturing Cities. https://doi.org/10.2777/479582.
Fowdar, H.S., Hatt, B.E., Breen, P., Cook, P.L.M., Deletic, A., 2017. Designing living walls for greywater treatment. Water Res. 110, 218–232. https://doi.org/10.1016/j.watres.2016.12.018.
Francis, R.A., Lorimer, J., 2011. Urban reconciliation ecology: the potential of living roofs and walls. J. Environ. Manag. 92, 1429–1437. https://doi.org/10.1016/j.jenvman.2011.01.012.
Gattringer, H., Claret, A., Radtke, M., Kisser, J., Zraunig, A., Rodriguez-Roda, I., Buttiglieri, G., 2016. Novel vertical ecosystem for sustainable water treatment and reuse in tourist resorts. Int. J. Sustain. Dev. Plann. 11, 263–274. https://doi.org/10.2495/SDP-V11-N3-263-274.
Ghaitidak, D.M., Yadav, K.D., 2013. Characteristics and Treatment of Greywater — a Review 2795–2809. https://doi.org/10.1007/s11356-013-1533-0.
Hourlier, F., Masse, A., Jaouen, P., Lakel, A., Gerente, C., Faur, C., Le Cloirec, P., 2010. Formulation of synthetic greywater as an evaluation tool for wastewater recycling technologies. Environ. Technol. 31, 215–223. https://doi.org/10.1080/09593330903431547.
Jin, Z., Xie, X., Zhou, J., Bei, K., Zhang, Y., Huang, X., Zhao, M., Kong, H., Zheng, X., 2018. Blackwater treatment using vertical greening: efficiency and microbial community structure. Bioresour. Technol. 249, 175–181. https://doi.org/10.1016/j.biortech.2017.09.176.
Kotsia, D., Deligianni, A., Fyllas, N.M., Stasinakis, A.S., Fountoulakis, M.S., 2020. Converting treatment wetlands into "treatment gardens": use of ornamental plants for greywater treatment. Sci. Total Environ. 744, 140889. https://doi.org/10.1016/j.scitotenv.2020.140889.
Kotsiris, G., Nektarios, P.A., Ntoulas, N., Kargas, G., 2013. An adaptive approach to intensive green roofs in the Mediterranean climatic region. Urban For. Urban Green. 12, 380–392. https://doi.org/10.1016/j.ufug.2013.05.001.
Masi, F., Bresciani, R., Rizzo, A., Edathoot, A., Patwardhan, N., Panse, D., Langergraber, G., 2016. Green walls for greywater treatment and recycling in dense urban areas: a case-study in Pune. J. Water, Sanit. Hyg. Dev. 6, 342–347. https://doi.org/10.2166/washdev.2016.019.
Medl, A., Stangl, R., Florineth, F., 2017. Vertical greening systems – a review on recent technologies and research advancement. Build. Environ. 125, 227–239. https://doi.org/10.1016/j.buildenv.2017.08.054.
Mekonnen, M.M., Hoekstra, A.Y., 2016. Sustainability: four billion people facing severe water scarcity. Sci. Adv. 2, 1–7. https://doi.org/10.1126/sciadv.1500323.
Moges, M.E., Eregno, F.E., Heistad, A., 2015. Performance of biochar and filtralite as polishing step for on-site greywater treatment plant. Manag. Environ. Qual. An Int. J. 26, 607–625. https://doi.org/10.1108/MEQ-07-2014-0101.
ONU, 2018. Sustainable Development Goal 6: Synthesis Report on Water and Sanitation. United Nations. https://doi.org/10.1126/science.278.5339.827.
Pérez, G., Rincón, L., Vila, A., González, J.M., Cabeza, L.F., 2011. Behaviour of green facades in Mediterranean Continental climate. Energy Convers. Manag. 52, 1861–1867. https://doi.org/10.1016/j.enconman.2010.11.008.
Pradhan, S., Al-Ghamdi, S.G., Mackey, H.R., 2019. Greywater treatment by ornamental plants and media for an integrated green wall system. Int. Biodeterior. Biodegrad. 145, 104792. https://doi.org/10.1016/j.ibiod.2019.104792.
Pradhan, S., Helal, M.I., Al-Ghamdi, S.G., Mackey, H.R., 2020. Performance evaluation of various individual and mixed media for greywater treatment in vertical nature-based systems. Chemosphere 245, 125564. https://doi.org/10.1016/j.chemosphere.2019.125564.
Prodanovic, V., Hatt, B., Mccarthy, D., Deletic, A., 2020. Green wall height and design optimisation for effective greywater pollution treatment and reuse. J. Environ. Manag. 261, 110173. https://doi.org/10.1016/j.jenvman.2020.110173.
Prodanovic, V., Hatt, B., McCarthy, D., Zhang, K., Deletic, A., 2017. Green walls for greywater reuse: understanding the role of media on pollutant removal. Ecol. Eng. 102, 625–635. https://doi.org/10.1016/j.ecoleng.2017.02.045.
Prodanovic, V., McCarthy, D., Hatt, B., Deletic, A., 2019. Designing green walls for greywater treatment : the role of plants and operational factors on nutrient removal. Ecol. Eng. 130, 184–195. https://doi.org/10.1016/j.ecoleng.2019.02.019.
Prodanovic, V., Zhang, K., Hatt, B., McCarthy, D., Deletic, A., 2018. Optimisation of lightweight green wall media for greywater treatment and reuse. Build. Environ. 131, 99–107. https://doi.org/10.1016/j.buildenv.2018.01.015.
Rysulova, M., Kaposztasova, D., Vranayova, Z., 2017. Green Walls as an Approach in Grey Water Treatment Green Walls as an Approach in Grey Water Treatment. https://doi.org/10.1088/1757-899X/245/7/072049.
Serra, V., Bianco, L., Candelari, E., Giordano, R., Montacchini, E., Tedesco, S., Larcher, F., Schiavi, A., 2017. A novel vertical greenery module system for building envelopes: the results and outcomes of a multidisciplinary research project. Energy Build. 146, 333–352. https://doi.org/10.1016/j.enbuild.2017.04.046.
Seyam, S., 2019. The impact of greenery systems on building energy: systematic review. J. Build. Eng. 26, 100887. https://doi.org/10.1016/j.jobe.2019.100887.
Shaikh, I.N., Ahammed, M.M., 2020. Quantity and quality characteristics of greywater: a review. J. Environ. Manag. 261, 110266. https://doi.org/10.1016/j.jenvman.2020.110266.
Svete, L.E., 2012. Vegetated Greywater Treatment Walls : Design Modifications for Intermittent Media Filters. Norwegian University of Life Sciences.
Thompson, K.A., Valencia, E.W., Scott Summers, R., Cook, S.M., 2020. Sorption, coagulation, and biodegradation for graywater treatment. Water Sci. Technol. 81, 2152–2162. https://doi.org/10.2166/wst.2020.273.