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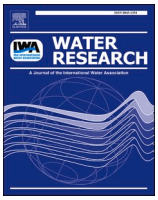

Removal of hydrophilic, hydrophobic, and charged xenobiotic organic compounds from greywater using green wall media

H.M. Abd-ur-Rehman [a,*], V. Prodanovic [a], A. Deletic [b], S.J. Khan [a], J.A. McDonald [a], K. Zhang [a]

[a] School of Civil and Environmental Engineering, University of New South Wales (UNSW), Sydney, NSW 2052, Australia
[b] School of Civil and Environmental Engineering, Faculty of Engineering, Queensland University of Technology (QUT), Brisbane, QLD 4001, Australia

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ABSTRACT

Green walls offer a novel on-site approach for greywater treatment and reuse in densely build urban environments. However, they need to be engineered for effective removal of a wide range of emerging contaminants such as xenobiotic organic compounds (XOCs), which may be present in greywater due to extensive use of personal care products and household chemicals. This study used laboratory column design and batch experiments to investigate the performance of three lightweight green wall media (coco coir, zeolite, and perlite) and their mixture in three different combinations for the removal of twelve XOCs, covering wide range of hydrophilic, hydrophobic, and charged pollutants in greywater. The experiments were designed to assess the removal of targeted XOCs under different operational condition (i.e., hydraulic loading, infiltration rate, drying) and uncover the dominant mechanisms of their removal. Results showed excellent removal (>90%) of all XOCs in coco coir and media mix columns at the start of the experiment (i.e., fresh media and initial 2 pore volume (PV) of greywater dosing). The removal of highly hydrophobic and positively charged XOCs remained high (>90%) under all operational conditions, while hydrophilic and negatively charged XOCs exhibited significant reduction in removal after 25 PV and 50 PV, possibly due to their low adsorption affinity and electrostatic repulsion from negatively charged media. The effect of infiltration rate on the removal of XOCs was not significant; however, higher removal was achieved after 2-weeks of drying in coco coir and media mix columns. The dominant removal mechanism for most XOCs was found to be adsorption, however, a few hydrophilic XOCs (i.e., acetaminophen and atrazine) exhibited both adsorption and biodegradation removal processes. While findings showed promising prospects of unvegetated media for removing XOCs from greywater, long term studies on vegetated green wall systems are needed to understand any synergetic contribution of plants and media in removing these XOCs.

1. Introduction

Rapid growth in urbanization is expected to increase global water demand between 20–30% by 2050 (The United Nations World Water Development Report, 2019). One of the potential ways to address impending water shortages is to find sustainable approaches to manage existing water resources, such as reuse of greywater. Greywater refers to non-toilet household wastewater that can be classified into high-pollutant (dark) greywater from dishwater, kitchen sinks, and laundry facilities, and low-pollutant (light) greywater from showers and basins. Contributing between 40–91% of household generated wastewater in different countries, greywater can provide a reliable on-site source of water for non-potable usage (Pradhan et al., 2019). However, greywater is a source of many xenobiotic organic compounds (XOCs; organic micropollutants from anthropogenic source), which may be derived from extensive use of household chemicals (e.g., dyes, detergents, personal care products etc.). Many of these XOCs are of serious concern due to their suspected (or known) aquatic toxicity (Glover et al., 2021), antimicrobial resistance (Alderton et al., 2021), and endocrine disrupting properties (Olaniyan et al., 2016). Therefore, the removal of XOCs may be necessary to produced suitable water quality for potential reuse (e.g., garden irrigation, on-site crop production, toilet flushing etc.).

Despite detection of many hazardous XOCs in household greywater (Donner et al., 2010), the literature on suitable methods for XOCs removal from greywater is scarce. Leal et al. (2010) reported higher removal of XOCs from greywater using aerobic sequencing batch reactor in comparison to an anaerobic reactor. However, many targeted XOCs (i.

* Corresponding author.
E-mail address: h.abd-ur-rehman@unsw.edu.au (H.M. Abd-ur-Rehman).

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e., UV-filters, preservatives, and fragrances) were still detected in treated greywater, leading to the use of ozonation and activated carbon as a post treatment step (Hernández-Leal et al., 2011). Although, adsorption on activated carbon has exhibited good removal for wide range of XOCs (Benstoem et al., 2017; Guillossou et al., 2019), its high cost and environmental concerns regarding disposal implies the need to find sustainable alternatives (Omorogie et al., 2016; Shukla et al., 2020). Nature-based solutions, such as constructed wetlands, can provide cost effective and eco-friendly alternatives for removing XOCs (Kaur et al., 2020). However, they provide centralized approach for water treatment and usually require large area for their placement, resulting in limited potential for their adoption in densely built urban environments. A vertical gardening approach, such as green walls, could be an excellent fit for urban cities due to its lower area footprints and direct attachment to building walls (Boano et al., 2020). However, the widespread adoption of green walls as a decentralized approach for greywater treatment is highly dependent on its potential to remove wide range of XOCs found in greywater.

In green walls, XOCs can be removed through a synergetic contribution of plants (i.e., phytoremediation) and growing media (i.e., adsorption and biodegradation) (Zraunig et al., 2019). However, the major contribution is offered by media (Abd-ur-Rehman et al., 2022), implying the need to find good media mixtures that can facilitate healthy growth of plants and remove wider range of XOCs (i.e., hydrophilic, hydrophobic, charged). The performance of single organic (i.e., wood fiber, coconut husk, coffee grinds, and date seeds) and inorganic media types (i.e., zeolite, perlite, pumice, and mineral wool) was tested in different literature batch studies (Abd-ur-Rehman et al., 2022; Sithamparanathan et al., 2021). Findings showed better removal potential of organic media compared to inorganic media. However, the findings were restricted to specific classes of XOCs (i.e., pharmaceutical) detected in wastewater (Sithamparanathan et al., 2021) or cover limited range of XOCs (i.e., neutral/non-ionizable) that can be found in greywater (Abd-ur-Rehman et al., 2022). Moreover, their findings indicated limited ability of a single media type to remove different categories of XOCs (i.e., hydrophilic, hydrophobic, and charged) found in greywater. Therefore, mixing different media types may provide a more effective solution. However, each media type has different hydraulic conductivity and unique adsorption kinetics for different pollutants (Abd-ur-Rehman et al., 2022), resulting in an unknown removal potential of wider range XOCs under the interaction of multiple media types in single mix.

To achieve long-term good removal of XOCs from greywater using lightweight media types, it is important to understand the impact of operational conditions in green wall systems. Although, several lightweight media types (i.e., biochar, coco coir, coffee grinds, composted fiber soil, date seeds, expanded clay, hemp fiber, lava, organic soil, perlite, and pumice) and their mixtures have been tested under various operating conditions (e.g., greywater dosing rates, pollutant inflow concentrations, prolonged drying, etc.), the focus has been limited to removal of nutrients (total nitrogen (TN) and total phosphorus (TP)), biological oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), total coliform, and *E. coli*. (Boano et al., 2022; Costamagna et al., 2022; Dal Ferro et al., 2021; Estelrich et al., 2021; Lakho et al., 2022, 2021; Martinuzzi et al., 2022; Pradhan et al., 2020; Sami et al., 2023; Satheesh et al., 2021). Few studies on green walls have reported the removal of methylene blue active substances (MBAS) as representative for anionic surfactants in greywater (Costamagna et al., 2023, 2022; Dal Ferro et al., 2021). However, these findings do not adequately elucidate the potential of green walls for removing different categories of XOCs. As each category experience different interaction with media, a change in operational conditions may have significant impacts on physicochemical and biological processes involved in the removal of these compounds. One such operational condition is the rate of hydraulic loading for which higher values could lead to biofilm washing, whereas biofilm development under low hydraulic loading could restrict intraparticle diffusion of pollutants by blocking the pore openings on media (Quispe et al., 2022). Many studies that have explored the removal of XOCs found hydraulic residence time as an important operational condition in achieving good removal (Fundneider et al., 2021; Quispe et al., 2022; Zraunig et al., 2019). Quispe et al. (2022) reported a range of 30–240 h of hydraulic residence time in existing literature on greywater treatment using a biochar-based column filtration system. However, this is not an optimal condition for a green wall system since it is typically designed with short retention time (i.e., $<$ 24 h) to treat large volumes of daily generated greywater (Boano et al., 2022; Costamagna et al., 2023, 2022; Lakho et al., 2022, 2021; Prodanovic et al., 2020).

The understanding of the mechanisms governing XOCs removal is critical for predicting long-term media performance. While it is expected that XOCs removal is primarily controlled by adsorption on media, regular dosing of greywater enriched with organic carbon and nutrients can offer favourable conditions for microbial growth (Ma et al., 2020), resulting in excretion of such enzymes that can target certain functional groups of XOCs for their potential biodegradation. The simultaneous contribution of both adsorption and biodegradation complicates the identification of limiting factors for the removal of various XOCs. Few studies found correlations between some functional groups of XOCs and their biodegradation potential, however, the findings were specific to a certain type of biological system (i.e., aquifer sediments (Patterson et al., 2011), membrane bioreactor (Tadkaew et al., 2011), and river bed filtration (Bertelkamp et al., 2014)) and cannot be directly translated to biologically active media in green walls that may experience a different microbial community due to the difference in organic matter and available nutrients (Alidina et al., 2014; Hu et al., 2012). Other limitations of existing studies were in the use of different media types (e.g., sand, river soil, agriculture soil etc.) and removal of limited XOCs from a specific class (i.e., pharmaceuticals) (Baumgarten et al., 2011; Gruenheid et al., 2008; Scheytt et al., 2006), making it difficult to translate their findings to lightweight media types for removing a wide range of XOCs from greywater. In addition, the type of water matrix (i.e., lake water, wastewater, and stormwater) in these studies offer different background contaminants (i.e., organic matter, inorganic matter, nutrients, and suspended particles) as compared to greywater, resulting in different competition for the adsorption sites.

Given the limited understanding of lightweight green wall media's role in removing wide range of XOCs from greywater under various operational conditions, this study used laboratory column design and batch experiments to answer the following research questions:

(i) What is the optimal green wall media mix that supports consistent and efficient removal of hydrophilic, hydrophobic, and charged XOCs from greywater?
(ii) How do typical green wall operational conditions (loading, drying, dosing rate) and system design (single and mix media) affect XOCs removal processes?
(iii) What are the contributions of adsorption and biodegradation in XOCs removal within selected green wall media?

The findings were used to provide design implications for green wall system focusing on XOCs removal, facilitating its use as a decentralized greywater treatment in urban landscapes.

2. Materials and methods

2.1. Selection of XOCs

Twelve XOCs were selected as representative pollutants (Table 1), covering a diversity of neutral compounds from hydrophilic to hydrophobic, as well as charged compounds including both negative and positive micropollutants. The selection process accounted for key characteristics of XOCs, such their ability to partition into the organic phase (measured by $\log K_{ow}$ value), their variable charges, and the

Table 1
Physicochemical properties of selected XOCs.

	Common use	[1]$logK_{ow}$ at pH=7	[2]Dominant functional groups	[3]H-bond Donor, Acceptor
Neutral hydrophilic				
Caffeine (CAF)	Stimulant	0.16	Amine, Amide, Aromatic	0,3
Acetaminophen (ACT)	Pain relief	0.91	Amide, hydroxyl, Aromatic	2,2
Tris(2-chloroethyl) phosphate (TCEP)	Flame retardant	1.51	Phosphate ester, Chloroalkane	0,1
Atrazine (ATZ)	Herbicide	2.20	Amine, Aromatic	2,5
Neutral hydrophobic				
N,N-Diethyl-meta-toluamide (DEET)	Insect repellent	2.50	Amide, Aromatic	0,1
Diuron (DUR)	Herbicide	2.67	Amine, Carbonyl	1,1
Bisphenol-A (BPA)	Plasticizer	3.64	Phenol, Aromatic	2,2
Triclocarban (TRC)	Antibacterial	4.90	Amide, Aromatic	2,1
Negatively charged				
Sulfamethoxazole (SMX)	Antibiotic	0.03	Sulfonamide, Amine, Aromatic	2,4
Ibuprofen (IBF)	Anti-inflammatory	1.17	Carboxylic acid, Aromatic	1,2
Positively charged				
Atenolol (ATN)	Beta blocker	−2.14	Amine, Alcohol	3,4
Trimethoprim (TRP)	Antibiotic	0.92	Amine, Aromatic	2,7

[1] $logK_{ow}$ = Octanol-water partition coefficient at pH=7 to represent pollutant hydrophobicity, value extracted from EPI Suite™-Estimation Program Interface | US EPA.
[2] Information collected from structural properties of XOCs at Chemicalize - Instant Cheminformatics Solutions.
[3] H-bond = number of hydrogen bond donner and acceptors available in XOCs structure, data extracted from Chemicalize - Instant Cheminformatics Solutions.

presence of different functional groups (e.g., alcohols, amines, esters, aromatic, etc.). These attributes contribute substantially to the reactivity, solubility, and adsorption tendencies of XOCs, thereby influencing their overall removal potential.

While the selection of XOCs was primarily dictated by distinct physio-chemical properties to cover a wide range of chemicals, their presence was confirmed at multiple greywater sampling sites (Table S1). Caffeine (CAF), commonly found in coffee grinds, caffeinated beverages, and food products, was consistently detected across various sites (Craddock et al., 2020; Delhiraja and Philip, 2020; Eriksson et al., 2003; Lalley et al., 2023; Turner et al., 2019; Zraunig et al., 2019). Among pharmaceuticals, acetaminophen (ACT) and ibuprofen (IBF), known for their analgesic and anti-inflammatory properties, were found at multiple sites, indicating their extensive use (Delhiraja and Philip, 2020; Eriksson et al., 2003; Turner et al., 2019; Zraunig et al., 2019). Atenolol (ATN), a beta blocker, along with antibiotics like sulfamethoxazole (SMX) and trimethoprim (TRM), were also identified in real greywater samples (Craddock et al., 2020; Zraunig et al., 2019). The insect repellent N, N diethyl-meta-toluamide (DEET) was confirmed at multiple locations due to its application on the skin and clothing (Lalley et al., 2023; Turner et al., 2019). However, traces of herbicides such as atrazine and diuron were also observed, despite not being commonly used in households (Craddock et al., 2020; Turner et al., 2019). The detection of Triclocarban (TRC) in greywater can be attributed to its widespread use in household and personal care items (Craddock et al., 2020). Additionally, the recurring presence of bisphenol-A, a banned plasticizer, and tri(2-chloroethyl) phosphate, a restricted flame retardant, suggests their persistent usage in consumer products (Delhiraja and Philip, 2020; Eriksson et al., 2003; Hernández-Leal et al., 2011; Zraunig et al., 2019).

2.2. Column study

2.2.1. Media characteristics

Following the recommendations from previous green wall media studies (Abd-ur-Rehman et al., 2022; Prodanovic et al., 2018), three lightweight green wall media types, coco coir, zeolite, and perlite, as well as three different combinations of their mixes were tested in this study (Table 2). Coco coir (i.e., fine media) was mixed with zeolite and/or perlite (i.e., coarse media) in volumetric ratio of 2:1 as this ratio showed a good balance between hydraulic performance and nutrient removal in green wall system (Prodanovic et al., 2019, 2018). The selected media types have low bulk density (0.09–0.63 g/cm^3), which is preferred for minimizing the green wall system's weight. Other physical parameters (i.e., surface area and hydraulic conductivity), influencing flow dynamics and pollutant removal, are presented in Table 2.

2.2.2. Experimental column design

The columns were constructed using 32 mm diameter PVC pipe with 350 mm total height, containing 300 mm media and 50 mm free gap for water detention (Fig. 1 (a)). The media depth was selected based on green wall height recommendation (300–450 mm) for effective nutrients removal (Costamagna et al., 2022; Prodanovic et al., 2020). Columns were constructed using homogenized media mix, which was added in stages (~50 mm). After each stage, columns were gently shaken and tapped to achieve even distribution of media. All columns were fitted with stainless-steel mesh (150 μm) at the bottom to avoid media leaching. A layer of washed gravel (~10 mm) was introduced at the top to avoid media floating and surface indentation due to inflow water. The single media columns (designs 1–3, Table 2) were operated in duplicate, in line with prior studies on micro pollutant removal in column experiments (Bertelkamp et al., 2015, 2014). Given their uniform composition and reduced potential for variability, two replicates were deemed sufficient for the single media columns. However, to address the inherent variability arising from the complex interactions between different media types, all media mix columns (designs 4–6, Table 2) were operated with three replicates. The utilization of higher replicates in the media mix columns was particularly important as these columns represent potentially optimal treatment designs, contrasting with the single media columns that primarily aimed to explore the interactions and contributions of different media in the mixed configuration. The columns were placed in glasshouse with natural sunlight and no rainfall.

Table 2
Physical characteristics of selected media types and their mixtures.

Column designs	Media	Volumetric ratio	[1]Average bulk density (g/cm^3)	[2]BET surface area (m^2/g)	[3]Hydraulic conductivity (cm/h)
1	Coco coir (CC)	–	0.10#,0.27^	1.39	262 (41)
2	Zeolite (Z)	–	0.63#	125	1520 (253)
3	Perlite (P)	–	0.09#	1.51	3250 (790)
4	CC : P	2 : 1	0.24^	–	444 (109)
5	CC : Z	2 : 1	0.41^	–	332 (59)
6	CC : P : Z	2 : 0.5 :0.5	0.33^	–	482 (141)

[1] Bulk density calculated using mass to volume ratio of #dry media and ^wet media.
[2] Calculated using Brunauer, Emmett and Teller (BET) surface area analyser.
[3] Calculated after packing the media into columns using constant head method. The values in brackets indicate the standard deviation among replicates.

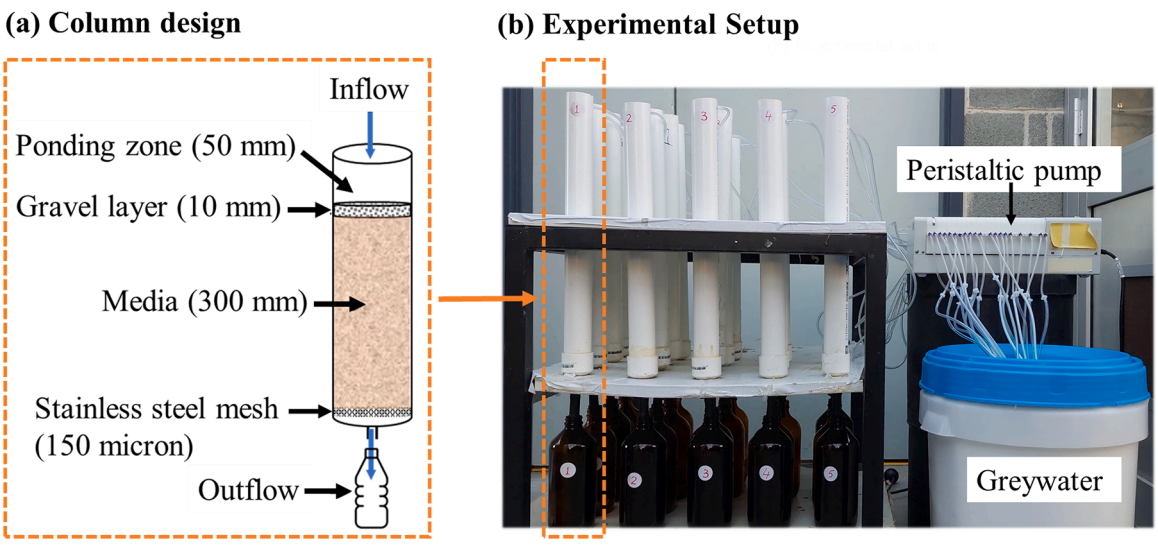

Fig. 1. (a) Column design and (b) Experimental setup.

The experiments were conducted during summer in Australia (Dec–Feb) when temperature ranged between 20–30 °C.

2.2.3. Greywater characteristics

All experiments were performed using synthetic light greywater (LGW) that mimics the household generated wastewater from showers and basins. The LGW was prepared by following the recipe (Table S2) used in previous greywater treatment studies (Abd-ur-Rehman et al., 2022; Bakheet et al., 2020; Prodanovic et al., 2017). A concentrated stock of all XOCs mix (1 g/l in methanol) was prepared with analytical grade chemicals and spiked in LGW to achieve the desired concentration of XOCs. Fresh batch of LGW was prepared every second day and quality parameters were maintained close to targeted concentrations (Table S3).

2.2.4. Operational design

All media packed columns underwent an initial one-week flush using tap water in pulses (~2 pore volume (PV), twice a day) to simulate media compaction under hydraulic loading and ensured the removal of any residual fines. Subsequently, a 10-week experimental phase was initiated, simulating various operational conditions (Table 3).

All columns were irrigated with ~2 PV of LGW daily, five days a week (resting them during the weekend) for 6 weeks. During weeks 1–5, the infiltration rate was adjusted to ~170 mm/h (standard condition) using peristaltic pump and three sampling events (S1–S3) were performed to understand the media removal performance over time. Fourth sampling event (S–4) was conducted in week 6 during which the infiltration rate was reduced to ~42.5 mm/h (4 times lower than standard), while dosing volume was kept the same (~2 PV) to understand the effect of infiltration rate on XOCs removal. Fifth sampling event (S–5) was performed right after 2-weeks of drying period using standard conditions (i.e., ~2 PV of greywater dosing, ~170 mm/h infiltration rate) to understand the effect of prolonged drying on XOCs removal. This was followed by breakthrough curve analysis under continuous greywater dosing, for which samples were collected after 0.5, 1, 1.5, 2, 4, 6, 8, 10, 12, 15, 25, 50, and 100 PV.

All samples were collected in amber glass bottles (500 ml) to avoid photodegradation. Within 3 h of sample collection, 100 ml volume for each sample was transferred to glass bottle and spiked with isotope labelled internal standards (50 µl of 1 mg/l stock) of targeted XOCs to compensate any changes that may occur during sample preparation and storage. The samples preparation involved solid phase extraction (SPE) using OASIS 500 mg hydrophilic/lipophilic balance cartridges (Waters, Millford, USA) at a rate of less than 10 ml/min. After extraction, cartridges were rinsed with 5 ml of water, eluted using methanol (3 × 2.5 ml), and evaporated under nitrogen stream to achieve clean concentrated samples. The samples were transferred to amber vials and stored at 4 °C. The XOCs concentration in samples was analysed within a week following the SPE process.

Table 3
Timeline and operational parameters during different sampling events.

Week	LGW volume	Infiltration rate	Sampling events	Event purpose
1	~2 PV/day	~170 mm/h	S1	Removal performance of fresh media.
2–5	~2 PV/day	~170 mm/h	S2 at Week 3, S3 at Week 5	Removal performance of media over time
6	~2 PV/day	~42.5 mm/h	S4	Effect of infiltration rate on XOCs removal
7–8	Drying Period	–	–	–
9	~2 PV/day	~170 mm/h	S5	Effect of prolonged drying on XOCs removal
10	Continuous dosing	~170 mm/h	0.5, 1, 1.5, 2, 4, 6, 8, 10, 12, 15, 25, 50, and 100 PV	Effect of continuous dosing on XOCs removal

2.3. Batch study

At the completion of column experiments, each column was emptied in a large container and media was gently homogenized. One half of the homogenized media was autoclaved (121°C for 30 min) to deactivate biological activities, while another half was kept in a glasshouse under same experimental environment to maintain biological activity (Piai et al., 2020). During autoclaving, a chemical indicator strip (3M™ Comply™ ISO 11,140–1:2005) was placed in media to determine if steam had completely penetrated to achieve sterilization. Moreover, autoclaving was performed for 2 consecutive days to inactivate any robust bacterial strain that may have survived during a single autoclaving cycle (Yuan et al., 2022).

The batch experiments were undertaken with two groups of aged materials: (1) biologically active media to represent combined effect of adsorption and biodegradation on the removal of XOCs; and (2) autoclaved media to represent adsorption as a sole contributor in removing

XOCs. The difference in the removal of XOCs between the two groups was used to distinguish between the removal processes of adsorption and biodegradation. For each group, batch experiments were performed using 50 ml centrifuge tubes in which media (5 ml) and LGW (20 ml) spiked with XOCs (500 μg/l in methanol) were added to attain solute to solvent volumetric ratio of 1:4 (Test No. 106: Adsorption – Desorption Using a Batch Equilibrium Method, 2000). The tubes were covered using aluminum foil to avoid photodegradation and rotated at fixed speed of 30 rpm using rotary wheel to avoid settling down of media. Based on adsorption kinetics of media to reach the equilibrium concentrations, samples were collected at 30 min and 24 h time intervals (Abd-ur-Rehman et al., 2022); whereas longer time interval (5 days) was used to differentiate between adsorption and biodegradation. For each collection, 950 μl was extracted from every tube and combined with 50 μl of isotope-labelled internal standard. The sample was centrifuged for 10 min at 4000 rpm to settle any residual particles and an aliquot (~0.5 ml) from each tube was passed through 0.22 μm polyvinylidene difluoride (PVDF) membrane filter. The filtered samples were kept at 4 °C until analyzed.

Batch experiments were run in triplicate and two types of controls, i.e., (i) autoclaved and non-autoclaved fresh media, tested in LGW spiked with XOCs to analyze the impact of autoclaving on the removal of XOCs, and (ii) LGW spiked with XOCs without media to analyze the change in XOCs concentration over time.

2.4. Quantification of XOCs concentration

The concentration of XOCs in all samples was quantified using 1200 series Agilent HPLC coupled with mass spectrometer (Sciex API 4000 triple-quadrupole). The detailed method is provided by Vanderford and Snyder (2006). Briefly, XOCs were chromatographically separated using C18 reverse phase column (5 μm particle size) in HPLC and quantified using electrospray ionization (positive and negative mode) in mass spectrometer (MS). Ammonium acetate in DI water (5 mM) and HPLC grade methanol were used as mobile phase with a flow rate of 800 μl/min. At least 5-point calibration curve was created between 0.1–500 μg/l of XOCs concentration. The linearity coefficient for all calibration curves was $\geq$0.99, indicating consistent and accurate detection of XOCs concentration. The limit of detection (LOD) and limit of quantitation (LOQ) were established by identifying the concentration of a target analyte that yielded a signal-to-noise ratio greater than 3 and 10, respectively. The established reporting limit for all targeted XOCs was 5 ng/L, except for BPA, for which it was 20 ng/L. For quality assurance, multiple blank samples (DI water) and known concentration samples were run during every batch of sample analysis. There was no detection of target analytes exceeding the LODs in blanks, and extracted analyte recoveries were within 20% of expected values, with less than 10% variation in relative standard deviations. The quantification details are provided in Table S4.

2.5. Data analysis

Data is presented as percentage removal of XOCs that was calculated as difference between inflow concentration and residual concentration in outflow, divided by inflow concentration. One of the tested XOCs (i.e., CAF) showed unexpected high concentration in both inflow and outflow samples at 54 PV due to contamination issue in analytical equipment, therefore excluded from the analysis.

The removal of each XOC by two different media types was statistically compared using simple *t*-test, whereas XOCs removal performance under two independent variables, i.e., pore volume (PV) of greywater loading and concentration of XOCs, was analyzed using 2-way ANOVA. The significance of data was analyzed at p value of 0.05.

3. Results and discussion

3.1. Media changes during experiments

The surface morphology of unused coco coir showed irregular porous structure with rough interstices (Fig. 2(a)), depicting higher availability of active sites for pollutant attachment. The fibrous structure with high porosity impeded the movement of water through coco coir, resulting in lower hydraulic conductivity (Table 2). SEM image of unused zeolite exhibits rough surface with large number of micropores (Fig. 2(b)), providing high surface area for potential adsorption of pollutants. The surface of unused perlite showed smooth glassy morphology with large pores (Fig. 2(c)), resulting in high hydraulic conductivity (Table 2) and limited opportunities to adsorb pollutants. The surface morphology of used media experienced discernible changes (Fig. 2(d–f)) with overall smoother surface as compared to unused media (Fig. 2(a–c)), indicating reduction in adsorption sites following greywater dosing. However, used coco coir (Fig. 2(d)) exhibited minimum changes in surface morphology and depicted folded structure with irregular gaps, indicating potential sites for pollutant attachment and long-term stability under greywater dosing.

3.2. Overall removal of XOCs using different media types

All XOCs, except TCEP and DEET, showed good removal (>80%) in pure coco coir column (Fig. 3), possibly due to its porous and rough surface morphology (Fig. 2(a)), offering large number of adsorptions sites (Abd-ur-Rehman et al., 2022). Moreover, the longer contact time for XOCs in coco coir column due to its lower hydraulic conductivity (Table 2) resulted in higher opportunities to attach to an active adsorption site. The low removal of TCEP (<50%) and DEET (<25%) can be attributed to lesser number of hydrogen bond donor/acceptor sites in their structure among studied XOCs (Table 1), constraining their hydrogen bonding potential with available functional groups of media (i.e., carboxyl and hydroxyl groups) (Droepenu et al., 2021; Mitra et al., 2021).

The removal of most XOCs was significantly lower in single media zeolite and perlite columns in comparison to coco coir column (p<0.05) (Fig. 3), probably due to unfavorable surface morphology with small size pores on zeolite (Fig. 2(b)) that may hinder intraparticle diffusion of XOCs; and larger pores on perlite with comparatively smooth surface (Fig. 2(c)) that may offer limited active sites for XOCs attachment. Few exceptions include good removal (>75%) of CAF, TRC, ATN, and TRP in zeolite column that can be explained based on XOCs physicochemical properties and their interaction with media. CAF, ATN, and TRP were positively charged at experimental pH, resulting in strong electrostatic attraction towards negatively charged zeolite (Bachmann et al., 2021; Martínez-Hernández et al., 2014). However, TRC remained neutral at experimental pH but experienced strong adsorption affinity for media due to its highest hydrophobicity among all studied XOCs (Table 1), resulting in lower resistance while moving from water matrix (i.e., LGW) to media surface (Jiang et al., 2020).

The overall removal of XOCs was higher in coco coir and zeolite mix column, followed by statistically similar removal by three media mix column (coco coir, perlite, and zeolite) (p>0.05) (Fig. 4). Most of the hydrophobic (i.e., DEET, BPA, and TRC) and positively charged (i.e., ATN and TRP) XOCs showed similar removal in all media mix columns (p>0.05); however, the removal for most of the hydrophilic (i.e., CAF, ACT, and ATZ) and negatively charged (i.e., SMX and IBF) XOCs was significantly higher in coco coir and zeolite mix column in comparison to coco coir and perlite mix column (p<0.05). This can be attributed to lower hydraulic conductivity of coco coir and zeolite mix column in comparison to other media mix columns (Table 2), providing longer contact time for XOCs to adhere to available adsorption sites. Moreover, higher surface area of zeolite in comparison to perlite (Table 2) may have offered increased opportunities for XOCs attachment. However, the

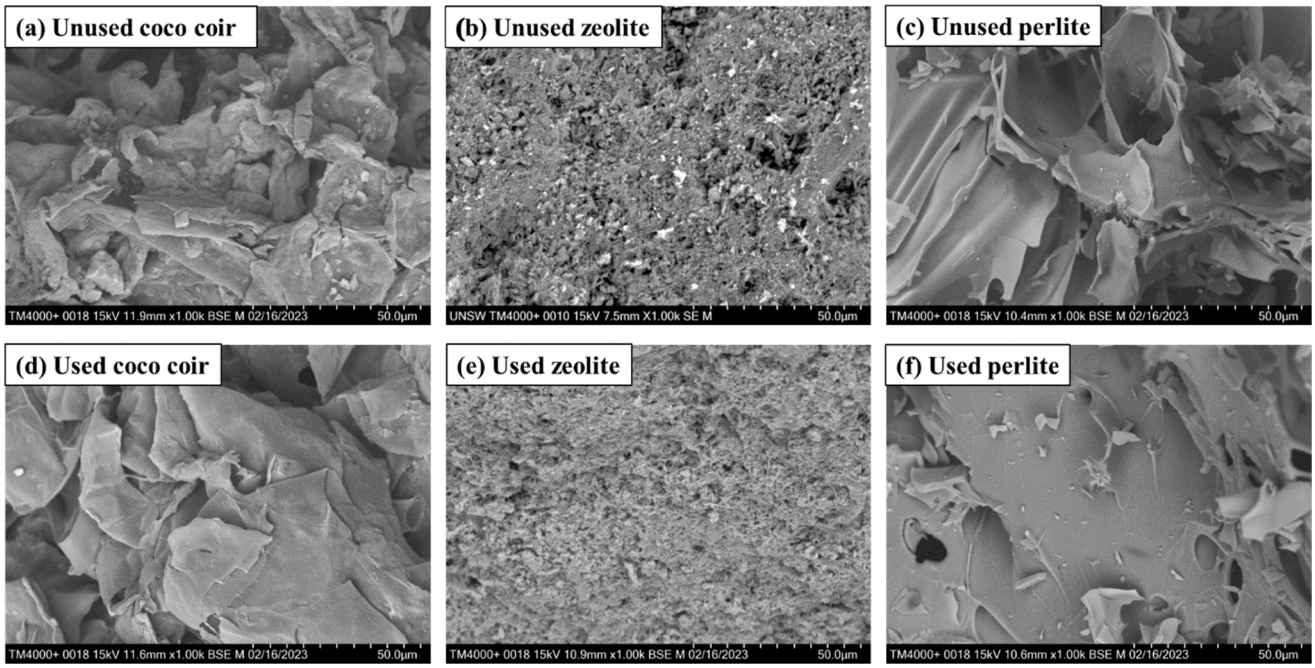

Fig. 2. SEM images of unused media (a) coco coir, (b) zeolite, (c) perlite and used media (d) coco coir, (e) zeolite, (f) perlite. The images were taken at resolution of 1000x and voltage of 15 kV.

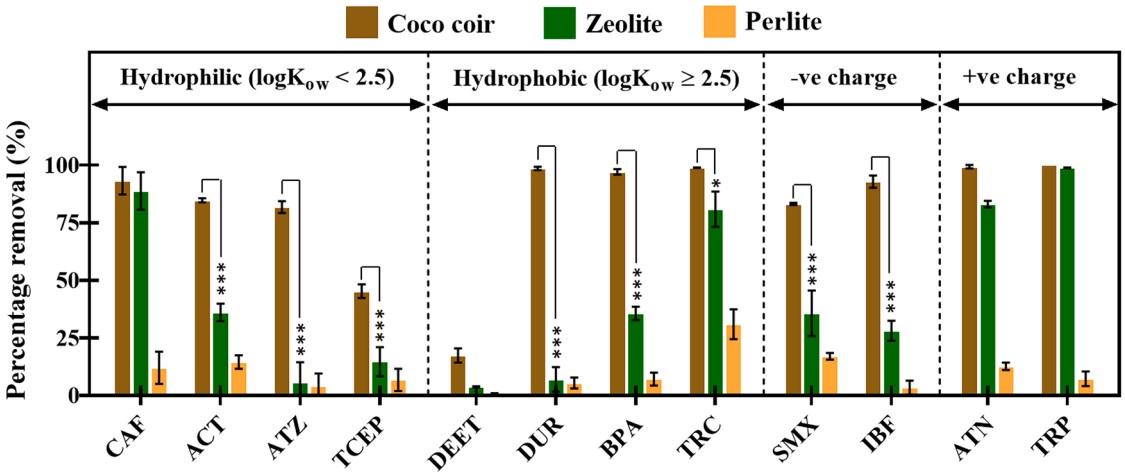

Fig. 3. Removal of XOCs using single media columns. The percentage removal is the average value of 3 sampling events under standard conditions (i.e., ~2 PV of greywater dosing and ~170 mm/h infiltration rate). The inflow concentration of each XOCs was ~10 μg/l. Coco coir showed significantly higher removal than perlite for all pollutants, whereas the statistical significance between coco coir and zeolite performance is shown with star (*), where * correspond to $p<0.05$, ** correspond to $p<0.01$, and *** correspond to $p<0.001$.

major contribution in removing XOCs was offered by coco coir as its removal performance for most of the XOCs was similar to coco coir and perlite mix column ($p>0.05$) (Fig. S1).

3.3. Effect of operational conditions and system design on XOCs removal

All XOCs showed excellent removal (>90%) at the start of the experiment (i.e., fresh media and initial 2 PV) in pure coco coir (Fig. 5 (a)) and all media mix columns (Fig. 5(b)), indicating extensive availability of active adsorption sites on fresh media surface. The removal of highly hydrophobic (TRC) and positively charged XOCs (i.e., ATN and TRP) remained highest (>90%) under all operational conditions and 54 PV loading. However, other XOCs experienced decline in removal with increasing PV (i.e., 25 and 50 PV), possibly due to the presence of background contaminants in greywater (i.e., organic matter, inorganic matter, nutrients, and suspended particles) that could compete for the adsorption sites. Similar was seen in a previous study with these light-weight media types (Abd-ur-Rehman et al., 2022). The decline in XOCs removal was lowest in coco coir column (<25%), suggesting ample availability of adsorption sites to accommodate XOCs in the presence of background contaminants (Fig. 2(d)). Few exceptions were significantly low removal of TCEP and DEET ($p>0.05$) at 25 PV that can be attributed to their limited H-bonding ability with available functional groups of media as discussed earlier (i.e., Section 3.1). Most XOCs showed a steep decline in performance (>50%) under 25 or 50 PV loading in zeolite, perlite (Fig. 5(a)), and their mix columns (Fig. 5(b)), indicating higher resistance offered by background pollutants, possibly by competing for pore diffusion or reducing the adsorption sites by covering media

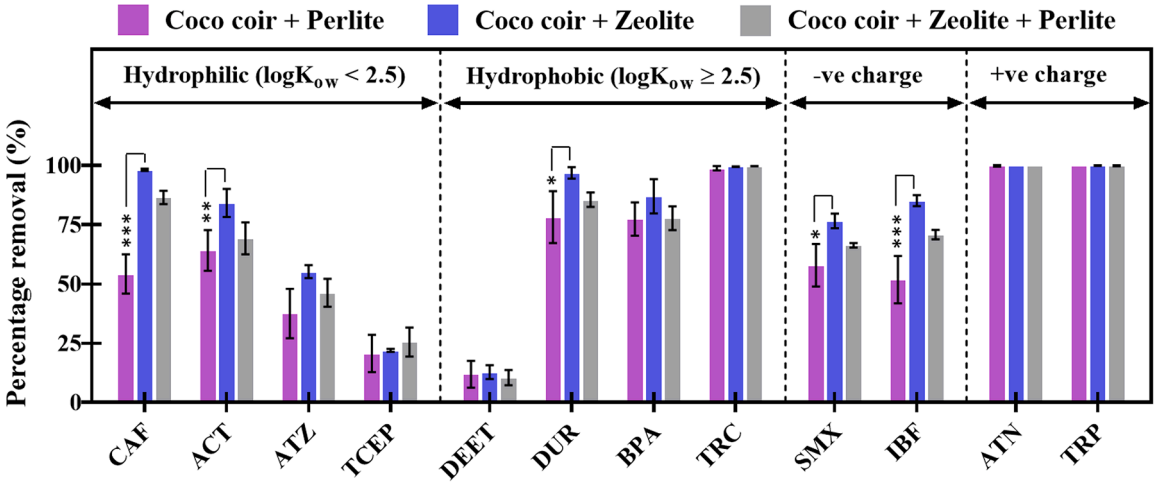

Fig. 4. Removal of XOCs using media mix columns. The percentage removal is the average value of 3 sampling events under standard conditions (i.e., 2 PV of greywater dosing and 170 mm/h infiltration rate). The inflow concentration of each XOCs was ~10 μg/l. The statistically significant groups were shown with star (*), where * correspond to $p<0.05$, ** correspond to $p<0.01$, and *** correspond to $p<0.001$.

surface (Quesada et al., 2019). The XOCs removal decline in zeolite (Fig. 5(a)) and its mix columns (i.e., CC+Z and CC+P+Z) (Fig. 5(b)) was possibly due to pore blocking (i.e., surface hinderance) on zeolite surface as major fraction of background contaminants cannot enter through small openings (Fig. 2(b)). The pore blocking was also evident on used zeolite surface morphology (Fig. 2(e)), resulting in reduced active sites for XOCs attachment. The low removal of XOCs (<50%) in perlite column (Fig. 5(a)) at the start of experiments (i.e., fresh media and initial 2 PV) can be attributed to its high hydraulic conductivity (Table 2), resulting in limited contact time for XOCs attachment. The steep decline in XOCs removal in perlite (Fig. 5(a)) and its mix columns (i.e., CC+P and CC+P+Z) (Fig. 5(b)) with increasing PV (i.e., 25) was possibly due to noticeable increase in surface smoothness of perlite with the application of greywater (Fig. 2(f)), resulting in limited availability of adsorption sites for XOCs attachment.

The effect of lower infiltration rate (i.e., 52 PV) on the removal of most XOCs was not significant ($p>0.05$) (Fig. 5). The plausible reason could be similar residence time experienced by XOCs while passing through column, resulting in an equal opportunity to grab an adsorption site irrespective of the infiltration rate. The removal of XOCs was significantly increased after 2-weeks of drying (i.e., 54 PV) ($p>0.05$) in coco coir (Fig. 5(a)) and media mix columns (Fig. 5(b)). This indicates that coco coir may have sufficient adsorption sites even after 50 PV, however, daily greywater dosing may have created a resistive water layer around media surface, limiting the access to active adsorption sites. These adsorption sites became available after drying, resulting in significantly higher removal (>50%) of XOCs. Another possibility could be the change in moisture content of media during dry period that may have resulted in favourable environment for microbial degradation of XOCs. Moreover, the dry period may have forced the heterotrophic microbes to consume XOCs as source of energy in the absence of greywater dosing that otherwise provide a primary source of organic carbon for microbial growth (Wang et al., 2022). The removal of XOCs in single media zeolite and perlite column (Fig. 5(a)) exhibited no significant change after 2-weeks of drying (i.e., 54 PV) and remained low (<50%), suggesting saturation of adsorption sites. This also implies that the significant improvement in XOCs removal after 2-weeks of drying in media mix columns (Fig. 5(b)) was offered by coco coir.

The effect of continuous greywater dosing on the removal of XOCs (Fig. 6) correlate well with pollutants hydrophobicity and charge. Hydrophilic XOCs experienced lower adsorption affinity for media and approached their inflow concentration (>80% breakthrough) during short duration of continuous greywater loading (~12 PV). The only exception was CAF, reaching ~80% breakthrough after long duration of continuous dosing (>50PV). This is because of cationic ionization of CAF, resulting in electrostatic interactions with negatively charged media. However, few studies related H-bonding and strong affinity between heterocyclic-N group on CAF and carboxyl groups on media as a dominant mechanism of adsorption rather than electrostatic interactions (Nam et al., 2014; Sotelo et al., 2012).

The high adsorption affinity for hydrophobic XOCs (i.e., DUR, BPA, TRC) and electrostatic attraction for positively charged XOCs (i.e., ATN and TRP) resulted in their slower breakthrough (>80% breakthrough after 25 PV). No breakthrough was reached for TRC (i.e., highly hydrophobic) and TRP (positively charged) during 100 PV dosing. However, DEET experienced quick breakthrough (~10 PV) and started leaching the accumulated DEET afterwards (i.e., $C_v/C_o>1$). Similar trends in XOCs removal were experienced for different media types under continuous greywater dosing (Fig. S2 (a-c)). However, most XOCs experienced quick breakthrough (~80% around 6 PV) in zeolite column (Fig. S2(b)), while no significant removal was achieved in perlite column (i.e., $C_v/C_o\sim1$) (Fig. S2(c)).

3.4. Contribution of adsorption and biodegradation in XOCs removal

The removal of XOCs using fresh media (control) was similar with and without autoclaving (Fig. S3) ($p>0.05$), indicating limited influence of autoclaving on the adsorption of XOCs on studied media types. Moreover, the concentration of most XOCs in LGW without media (control) was not significantly changed over time (i.e., 30 min, 24 h, and 5 days) ($p>0.05$) (Fig. S4), confirming minimum contribution of photodegradation or retention by background contaminants (i.e., organic matter, inorganic matter, nutrients, and suspended particles) present in LGW. The only exception was significantly higher decline in concentration of TRC ($p<0.05$), possibly due to its highly hydrophobic nature, resulting in potential retention by background contaminants or vial surface.

All XOCs showed similar removal performance using autoclaved media and biologically active media for 24 h ($p>0.05$) (Fig. 7), indicating adsorption as a dominant removal mechanism. However, hydrophilic XOCs, ACT and ATZ, showed significantly higher removal after longer contact time (i.e., 5 days) using biologically active media in comparison to autoclaved media ($p<0.05$), suggesting the contribution of both adsorption and biodegradation. The higher removal of ACT using biologically active media is in agreement with several studies (Lin et al., 2010; Sáez-Martínez et al., 2016), indicating its high biodegradation

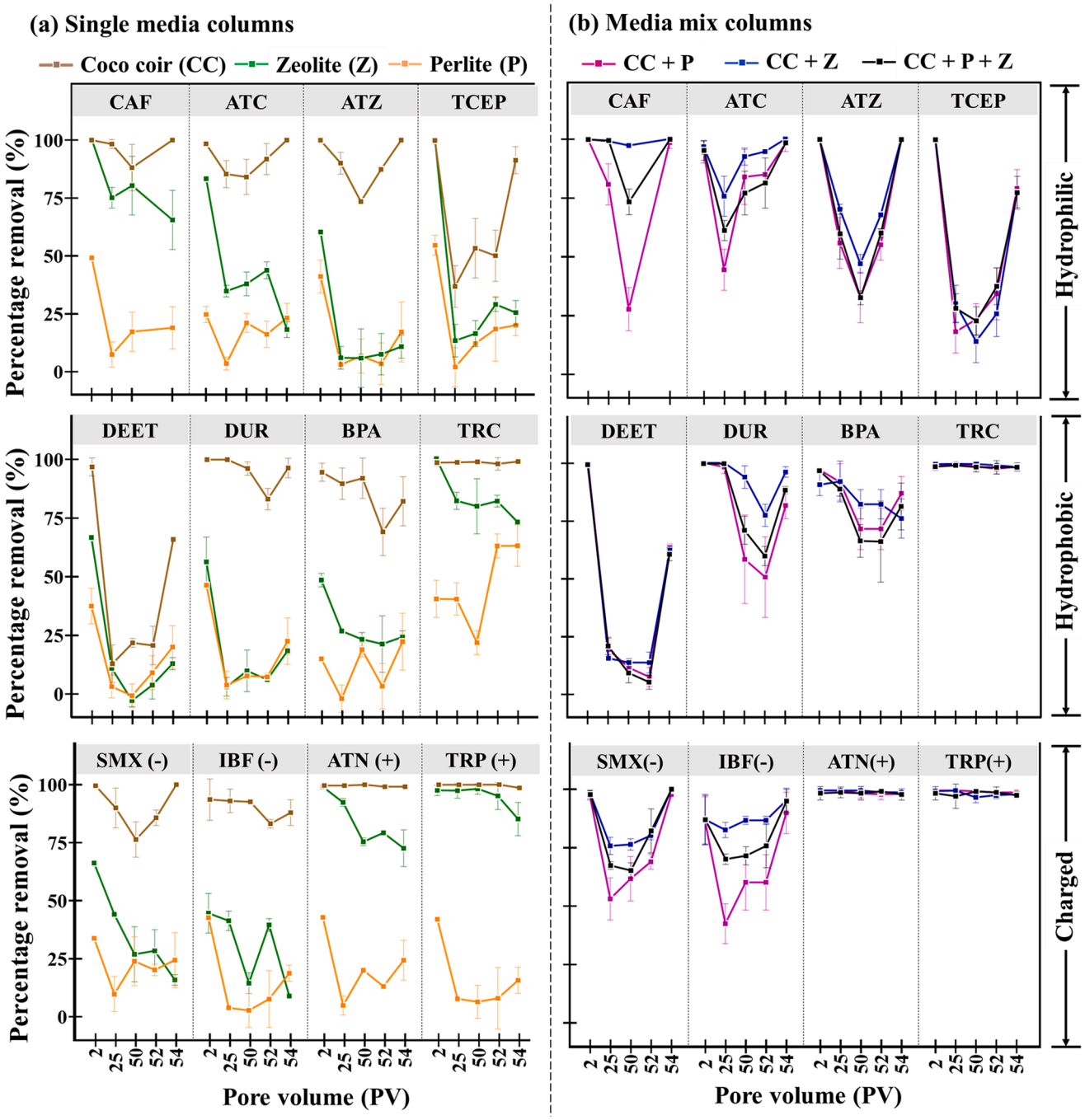

Fig. 5. Removal of XOCs under different operational conditions in (a) single media columns and (b) media mix columns. The inflow concentration of each XOCs was ~10 μg/l. The operation conditions at 2, 52, and 54 pore volume represent fresh media performance, media performance at low flowrate, and media performance after drying, respectively. The removal of CAF at 54 pore volume was excluded due to unexpected high inflow and outflow concentrations during HPLC analysis.

potential. However, ATZ showed contrasting results in biologically active media with recalcitrant behavior in riverbank filtration (Bertelkamp et al., 2016) and sand columns (Zearley and Summers, 2012); while good biodegradation in agriculture soil (Barrios et al., 2019) and bioprocessed waste (Kadian et al., 2008), possibly due to higher organic content of media with rich availability of nutrient (James et al., 2021). This indicates that bio-stimulation of organic media (i.e., coco coir) using enriched source of nutrients (i.e., greywater) in this study may have offered a favourable environment for ATZ biodegrading microorganisms (e.g., *Pseudomonas, Arthrobacter, Sinorhizobium,* etc.) (Barrios et al., 2019; Singh and Singh, 2016), however, the microbial community was not analyzed in this study.

Hydrophobic (i.e., DUR, BPA, and TRC) and positively charged (i.e., ATN and TRP) XOCs exhibited no biodegradation, possibly due to higher adsorption affinity for media, resulting in reduced mobility (and bioavailability) of XOCs (Bertelkamp et al., 2014). Negatively charged XOCs (i.e., SMX and IBF) also showed resistance to biodegradation that may be linked to their functional groups (i.e., aromatic ring structure, sulfur, and amines) that showed recalcitrant behavior towards biodegradability (Bertelkamp et al., 2016).

3.5. Practical recommendations

Coco coir was identified as best performing media for removing most

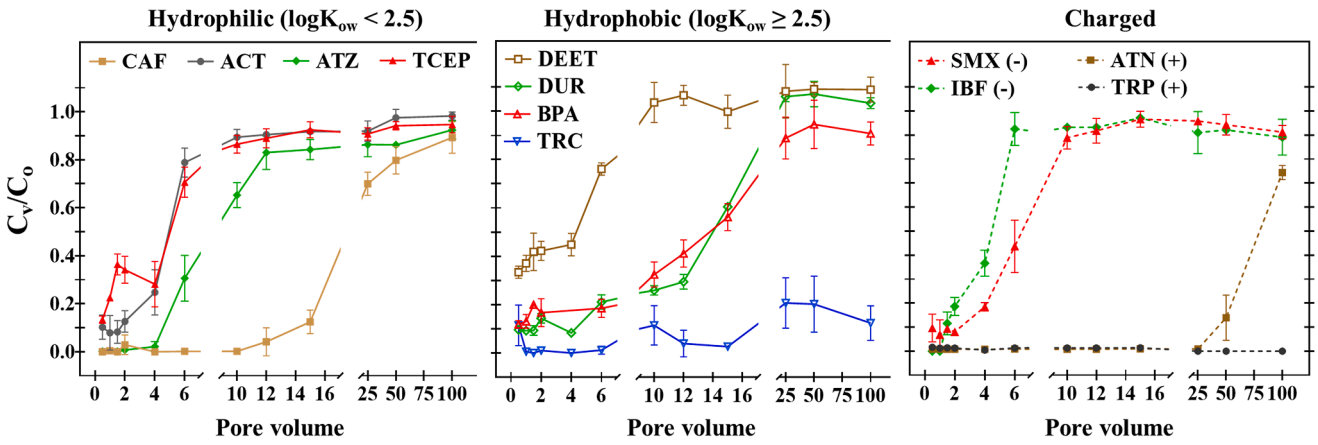

Fig. 6. Removal of XOCs in media mix column (coco coir, zeolite, and perlite) under continuous greywater loading. C_o is the inflow concentration of XOCs (~10 μg/l) while C_v represents the concentration of XOCs at different pore volumes.

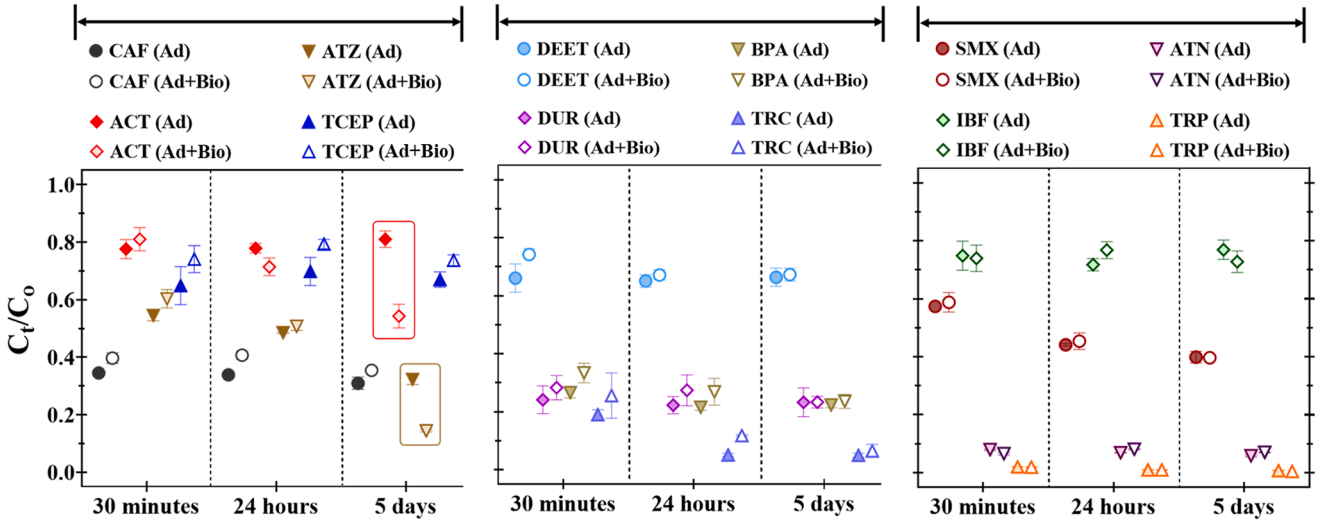

Fig. 7. Removal of XOCs using autoclaved media and biologically active media. C_o is the inflow concentration of XOCs (~500 μg/l) while C_t represents the concentration of XOCs at different time intervals. XOCs with (Ad) represent the removal of pollutants through adsorption in autoclaved media, while XOCs with (Ad+Bio) represent the removal of pollutants through the combined contribution of adsorption and biodegradation in biologically active media.

of the targeted XOCs. However, it is prone to clogging due to very fine particles, compromising the green wall potential to treat higher volume of greywater (Prodanovic et al., 2017). Hence, it is suggested to mix coco coir with zeolite and/or perlite. Among media mix designs, coco coir and zeolite mixture (2:1) showed better removal than coco coir and perlite mixture (2:1). However, zeolite is much heavier (~6 times) than perlite (Table 2), resulting in higher overall weight of green wall system and additional stress on its support structure. Moreover, there is a possibility that zeolite may settle at the bottom of the media due to its heavier weight, leading to potential clogging or compromising the uniform aeration in the system. Therefore, mixing coco coir with both zeolite and perlite (2:0.5:0.5) is recommended as it showed similar removal of XOCs as experienced using coco coir and zeolite mixture (2:1) with an added value of lower weight and uniform aeration in green wall system.

The operational conditions in green wall system (i.e., greywater volume, dosing rate, and time between dosing) should be selected based on the targeted XOCs as removal of hydrophilic and negatively charged pollutants declined quickly under continuous greywater dosing. Therefore, it is recommended to have drying period between greywater dosing events to achieve higher removal performance. However, further research needs to be done on finding an optimum length of drying period between dosing events.

The limited biodegradation of most XOCs suggests that the removal performance of media could decline over time due to saturation of adsorption sites. However, low contribution of biodegradation could be attributed to limited microbial community developed over a short period of time (~10 weeks) under stressed conditions (i.e., ~10x higher greywater dosing). During long-term field application of green wall system, the presence of rhizosphere and enriched source of nutrients (i.e., greywater) is expected to foster a robust microbial community, aiding XOCs' biodegradation. While the synergetic impact of plant uptake and microbial degradation can extend the media's lifespan, its replacement and disposal remain inevitable. Composting the exhausted media into nutrient-rich soil offers a sustainable solution for managing the media lifecycle in green wall systems. However, further research, building upon studies like the green roof disposal work of Peri et al. (2022), is required to develop a standardized, widely accepted protocol for determining the most appropriate treatments, recovery processes, or disposal methods for exhausted media in green wall systems.

4. Conclusions

This study explored the performance of three lightweight green wall media (coco coir, zeolite, and perlite) and their mixtures in three

different combinations for removing twelve XOCs, covering both neutral (hydrophilic to hydrophobic) and charged (positive and negative) pollutants in greywater. Results showed excellent removal (>90%) of highly hydrophobic and positively charged XOCs in pure coco coir column and media mix columns under all operational conditions, indicating hydrophobic and electrostatic interactions as a dominant mechanism of their removal. The removal of hydrophilic and negatively charged XOCs was significantly reduced ($p<0.05$) with increasing pore volume (i.e., 25 PV and 50 PV) of greywater dosing, possibly due the background contaminants in greywater that may compete for the adsorption sites on media surface. The effect of lower infiltration rate on the removal of most XOCs was not significant ($p>0.05$), however, the removal was increased significantly after 2-weeks of drying ($p<0.05$). The continuous greywater dosing (~10 pore volume) showed insignificant (<10%) and moderate (<40%) decline in the removal of positively charged and hydrophobic XOCs, respectively. However, similar dosing showed steep decline (>80%) in the removal of hydrophilic and negatively charged XOCs. Most XOCs experienced similar removal using autoclaved and biologically active media, indicating adsorption as a dominant mechanism of removal. However, other removal mechanisms such as biodegradation and phytoremediation may also play a vital role in removing XOCs in real green wall system. Therefore, future work should explore long-term performance of vegetated green wall system for XOCs removal from greywater.

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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Declaration of AI-assisted technologies in the writing process

During the revision of this work the author(s) used ChatGPT to improve language. After using this tool/service, the author(s) reviewed and edited the content as needed and take(s) full responsibility for the content of the publication.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2023.120290.

References

Abd-ur-Rehman, H.M., Deletic, A., Zhang, K., Prodanovic, V., 2022. The comparative performance of lightweight green wall media for the removal of xenobiotic organic compounds from domestic greywater. Water Res. 221, 118774 https://doi.org/10.1016/J.WATRES.2022.118774.

Alderton, I., Palmer, B.R., Heinemann, J.A., Pattis, I., Weaver, L., Gutiérrez-Ginés, M.J., Horswell, J., Tremblay, L.A., 2021. The role of emerging organic contaminants in the development of antimicrobial resistance. Emerg. Contam. 7, 160–171. https://doi.org/10.1016/j.emcon.2021.07.001.

Alidina, M., Li, D., Drewes, J.E., 2014. Investigating the role for adaptation of the microbial community to transform trace organic chemicals during managed aquifer recharge. Water Res. 56, 172–180. https://doi.org/10.1016/J.WATRES.2014.02.046.

Bachmann, S.A.L., Calvete, T., Féris, L.A., 2021. Caffeine removal from aqueous media by adsorption: an overview of adsorbents evolution and the kinetic, equilibrium and thermodynamic studies. Sci. Total Environ. 767, 144229 https://doi.org/10.1016/j.scitotenv.2020.144229.

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.

Barrios, R.E., Gaonkar, O., Snow, D., Li, Y., Li, X., Bartelt-Hunt, S.L., 2019. Enhanced biodegradation of atrazine at high infiltration rates in agricultural soils. Environ. Sci. Process. Impact. 21, 999–1010. https://doi.org/10.1039/C8EM00594J.

Baumgarten, B., Jährig, J., Reemtsma, T., Jekel, M., 2011. Long term laboratory column experiments to simulate bank filtration: factors controlling removal of sulfamethoxazole. Water Res. 45, 211–220. https://doi.org/10.1016/J.WATRES.2010.08.034.

Benstoem, F., Nahrstedt, A., Boehler, M., Knopp, G., Montag, D., Siegrist, H., Pinnekamp, J., 2017. Performance of granular activated carbon to remove micropollutants from municipal wastewater—A meta-analysis of pilot- and large-scale studies. Chemosphere. https://doi.org/10.1016/j.chemosphere.2017.06.118.

Bertelkamp, C., Reungoat, J., Cornelissen, E.R., Singhal, N., Reynisson, J., Cabo, A.J., van der Hoek, J.P., Verliefde, A.R.D., 2014. Sorption and biodegradation of organic micropollutants during river bank filtration: a laboratory column study. Water Res. 52, 231–241. https://doi.org/10.1016/j.watres.2013.10.068.

Bertelkamp, C., Schoutteten, K., Vanhaecke, L., Vanden Bussche, J., Callewaert, C., Boon, N., Singhal, N., van der Hoek, J.P., Verliefde, A.R.D., 2015. A laboratory-scale column study comparing organic micropollutant removal and microbial diversity for two soil types. Sci. Total Environ. 536, 632–638. https://doi.org/10.1016/J.SCITOTENV.2015.07.056.

Bertelkamp, C., Verliefde, A.R.D., Schoutteten, K., Vanhaecke, L., Vanden Bussche, J., Singhal, N., van der Hoek, J.P., 2016. The effect of redox conditions and adaptation time on organic micropollutant removal during river bank filtration: a laboratory-scale column study. Sci. Total Environ. 544, 309–318. https://doi.org/10.1016/J.SCITOTENV.2015.11.035.

Boano, F., Caruso, A., Costamagna, E., Fiore, S., Demichelis, F., Galvaõ, A., Pisoeiro, J., Rizzo, A., Masi, F., 2022. 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.

Costamagna, E., Caruso, A., Galvão, A., Rizzo, A., Masi, F., Fiore, S., Boano, F., 2023. Impact of biochar and graphene as additives on the treatment performances of a green wall fed with greywater. Water (Switzerland) 15, 1–13. https://doi.org/10.3390/w15010195.

Costamagna, E., Fiore, S., Boano, F., 2022. Influence of the number of levels and system age on greywater treatment in a green wall. Ecol. Eng. 183, 106755 https://doi.org/10.1016/j.ecoleng.2022.106755.

Craddock, H.A., Panthi, S., Rjoub, Y., Lipchin, C., Sapkota, A., Sapkota, A.R., 2020. Antibiotic and herbicide concentrations in household greywater reuse systems and pond water used for food crop irrigation: West Bank, Palestinian Territories. Sci. Total Environ. 699, 134205 https://doi.org/10.1016/j.scitotenv.2019.134205.

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.

Delhiraja, K., Philip, L., 2020. Characterization of segregated greywater from Indian households-part B: emerging contaminants. Environ. Monit. Assess. 192 https://doi.org/10.1007/S10661-020-08370-7.

Donner, E., Eriksson, E., Revitt, D.M., Scholes, L., Lützhøft, H.C.H.H., Ledin, A., 2010. Presence and fate of priority substances in domestic greywater treatment and reuse systems. Sci. Total Environ. 408, 2444–2451. https://doi.org/10.1016/j.scitotenv.2010.02.033.

Droepenu, E.K., Asare, E.A., Dampare, S.B., Adotey, D.K., Gyampoh, A.O., Kumi-Arhin, E., 2021. Laboratory and commercial synthesized zinc oxide nanoparticles adsorption onto coconut husk: characterization, isotherm, kinetic, and thermodynamic studies. Biointerface Res. Appl. Chem. 11, 7871–7889. https://doi.org/10.33263/BRIAC111.78717889.

Eriksson, E., Auffarth, K., Eilersen, A.M., Henze, M., Ledin, A., 2003. Household chemicals and personal care products as sources for xenobiotic organic compounds in grey wastewater. Water SA 29, 135–146. https://doi.org/10.4314/wsa.v29i2.4848.

Estelrich, M., Vosse, J., Comas, J., Atanasova, N., Costa, J.C., Gattringer, H., Buttiglieri, G., 2021. Feasibility of vertical ecosystem for sustainable water treatment and reuse in touristic resorts. J. Environ. Manage. 294 https://doi.org/10.1016/j.jenvman.2021.112968.

Fundneider, T., Acevedo Alonso, V., Abbt-Braun, G., Wick, A., Albrecht, D., Lackner, S., 2021. Empty bed contact time: the key for micropollutant removal in activated carbon filters. Water Res. 191, 116765 https://doi.org/10.1016/J.WATRES.2020.116765.

Glover, C.M., Liu, Y., Liu, J., 2021. Assessing the risk from trace organic contaminants released via greywater irrigation to the aquatic environment. Water Res. 205 https://doi.org/10.1016/j.watres.2021.117664.

Gruenheid, S., Huebner, U., Jekel, M., 2008. Impact of temperature on biodegradation of bulk and trace organics during soil passage in an indirect reuse system. Water Sci. Technol. 57, 987–994. https://doi.org/10.2166/WST.2008.207.

Guillossou, R., Le Roux, J., Mailler, R., Vulliet, E., Morlay, C., Nauleau, F., Gasperi, J., Rocher, V., 2019. Organic micropollutants in a large wastewater treatment plant:

what are the benefits of an advanced treatment by activated carbon adsorption in comparison to conventional treatment? Chemosphere 218, 1050–1060. https://doi.org/10.1016/j.chemosphere.2018.11.182.
Hernández-Leal, L., Temmink, H., Zeeman, G., Buisman, C.J.N., 2011. Removal of micropollutants from aerobically treated grey water via ozone and activated carbon. Water Res. 45, 2887–2896. https://doi.org/10.1016/J.WATRES.2011.03.009.
Hu, M., Wang, X., Wen, X., Xia, Y., 2012. Microbial community structures in different wastewater treatment plants as revealed by 454-pyrosequencing analysis. Bioresour. Technol. 117, 72–79. https://doi.org/10.1016/J.BIORTECH.2012.04.061.
James, T.K., Ghanizadeh, H., Harrington, K.C., Bolan, N.S., 2021. Degradation of atrazine and bromacil in two forestry waste products. Sci. Rep. 2021 111 (11), 1–12. https://doi.org/10.1038/s41598-021-83052-z.
Jiang, N., Shang, R., Heijman, S.G.J., Rietveld, L.C., 2020. Adsorption of triclosan, trichlorophenol and phenol by high-silica zeolites: adsorption efficiencies and mechanisms. Sep. Purif. Technol. 235, 1–9. https://doi.org/10.1016/j.seppur.2019.116152.
Kadian, N., Gupta, A., Satya, S., Mehta, R.K., Malik, A., 2008. Biodegradation of herbicide (atrazine) in contaminated soil using various bioprocessed materials. Bioresour. Technol. 99, 4642–4647. https://doi.org/10.1016/J.BIORTECH.2007.06.064.
Kaur, R., Talan, A., Tiwari, B., Pilli, S., Sellamuthu, B., Tyagi, R.D., 2020. Constructed wetlands for the removal of organic micro-pollutants. Curr. Dev. Biotechnol. Bioeng. 87–140. https://doi.org/10.1016/B978-0-12-819594-9.00005-X.
Lakho, F.H., Qureshi, A., Novelli, L.D.D., Depuydt, V., Depreeuw, T., Van Hulle, S.W.H., Rousseau, D.P.L., 2022. Performance of a green wall (Total Value Wall™) at high greywater loading rates and Life Cycle Impact Assessment. Sci. Total Environ. 821, 153470 https://doi.org/10.1016/j.scitotenv.2022.153470.
Lakho, F.H., Vergote, J., Ihsan-Ul-Haq Khan, H., Depuydt, V., Depreeuw, T., Van Hulle, S.W.H., Rousseau, D.P.L., 2021. Total value wall: full scale demonstration of a green wall for grey water treatment and recycling. J. Environ. Manage. 298, 113489 https://doi.org/10.1016/j.jenvman.2021.113489.
Lalley, J., Zetterholm, S.G., Waisner, S., Martinez-Guerra, E., Wamsley, M., Gurtowski, L., Wade, R., Pranger, S., Griggs, C.S., 2023. Source separated graywater: chemistry, unit operations, and criteria towards re-use. SSRN Electron. J. https://doi.org/10.2139/SSRN.4335884.
Leal, L.H., Vieno, N., Temmink, H., Zeeman, G., Buisman, C.J.N., 2010. Occurrence of xenobiotics in gray water and removal in three biological treatment systems. Environ. Sci. Technol. 44, 6835–6842. https://doi.org/10.1021/es101509e.
Lin, A.Y.C., Lin, C.A., Tung, H.H., Chary, N.S., 2010. Potential for biodegradation and sorption of acetaminophen, caffeine, propranolol and acebutolol in lab-scale aqueous environments. J. Hazard. Mater. 183, 242–250. https://doi.org/10.1016/j.jhazmat.2010.07.017.
Ma, Q., Wen, Y., Wang, D., Sun, X., Hill, P.W., Macdonald, A., Chadwick, D.R., Wu, L., Jones, D.L., 2020. Farmyard manure applications stimulate soil carbon and nitrogen cycling by boosting microbial biomass rather than changing its community composition. Soil Biol. Biochem. 144, 107760 https://doi.org/10.1016/J.SOILBIO.2020.107760.
Martínez-Hernández, V., Meffe, R., Herrera, S., Arranz, E., de Bustamante, I., 2014. Sorption/desorption of non-hydrophobic and ionisable pharmaceutical and personal care products from reclaimed water onto/from a natural sediment. Sci. Total Environ. 472, 273–281. https://doi.org/10.1016/j.scitotenv.2013.11.036.
Martinuzzi, N., Rivai, K., Rizzo, A., Masi, F., Sarnari, B., BOUSSELMI, L., 2022. Green walls for greywater treatment and reuse in Mediterranean countries. Proc. 17th Int. Conf. Environ. Sci. Technol. 17 https://doi.org/10.30955/gnc2021.00811.
Mitra, D., Zhou, C., Bin Hashim, M.H., Hang, T.M., Gin, K.Y.H., Wang, C.H., Neoh, K.G., 2021. Emerging pharmaceutical and organic contaminants removal using carbonaceous waste from oil refineries. Chemosphere 271. https://doi.org/10.1016/j.chemosphere.2021.129542.
Nam, S.W., Choi, D.J., Kim, S.K., Her, N., Zoh, K.D., 2014. Adsorption characteristics of selected hydrophilic and hydrophobic micropollutants in water using activated carbon. J. Hazard. Mater. 270, 144–152. https://doi.org/10.1016/j.jhazmat.2014.01.037.
Olaniyan, L.W.B., Mkwetshana, N., Okoh, A.I., 2016. Triclosan in water, implications for human and environmental health. Springerplus 5. https://doi.org/10.1186/s40064-016-3287-x.
Omorogie, M.O., Babalola, J.O., Unuabonah, E.I., 2016. Regeneration strategies for spent solid matrices used in adsorption of organic pollutants from surface water: a critical review. Desalin. Water Treat. 57, 518–544. https://doi.org/10.1080/19443994.2014.967726.
Patterson, B.M., Shackleton, M., Furness, A.J., Bekele, E., Pearce, J., Linge, K.L., Busetti, F., Spadek, T., Toze, S., 2011. Behaviour and fate of nine recycled water trace organics during managed aquifer recharge in an aerobic aquifer. J. Contam. Hydrol. 122, 53–62. https://doi.org/10.1016/J.JCONHYD.2010.11.003.
Peri, G., Licciardi, G.R., Matera, N., Mazzeo, D., Cirrincione, L., Scaccianoce, G., 2022. Disposal of green roofs: a contribution to identifying an "Allowed by legislation" end–of–life scenario and facilitating their environmental analysis. Build. Environ. 226, 109739 https://doi.org/10.1016/J.BUILDENV.2022.109739.
Piai, L., Blokland, M., van der Wal, A., Langenhoff, A., 2020. Biodegradation and adsorption of micropollutants by biological activated carbon from a drinking water production plant. J. Hazard. Mater. 388, 122028 https://doi.org/10.1016/J.JHAZMAT.2020.122028.
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. Manage. 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.
Quesada, H.B., Cusioli, L.F., de O Bezerra, C., Baptista, A.T.A., Nishi, L., Gomes, R.G., Bergamasco, R., 2019. Acetaminophen adsorption using a low-cost adsorbent prepared from modified residues of Moringa oleifera Lam. seed husks. J. Chem. Technol. Biotechnol. 94, 3147–3157. https://doi.org/10.1002/jctb.6121.
Quispe, J.I.B., Campos, L.C., Mašek, O., Bogush, A., 2022. Use of biochar-based column filtration systems for greywater treatment: a systematic literature review. J. Water Process Eng. 48, 102908 https://doi.org/10.1016/J.JWPE.2022.102908.
Sáez-Martínez, F.J., Lefebvre, G., Hernández, J.J., Clark, J.H., 2016. Drivers of sustainable cleaner production and sustainable energy options. J. Clean. Prod. 138, 1–7. https://doi.org/10.1016/j.jclepro.2016.08.094.
Sami, M., Hedström, A., Kvarnström, E., McCarthy, D.T., Herrmann, I., 2023. Greywater treatment in a green wall using different filter materials and hydraulic loading rates. J. Environ. Manage. 340 https://doi.org/10.1016/j.jenvman.2023.117998.
Satheesh, P.B., Oh, K.S., Tee, L.H., 2021. Life cycle assessment of various filtering media for greywater treatment using Greenwall filtration system. MATEC Web. Conf. 335, 01001. https://doi.org/10.1051/matecconf/202133501001.
Scheytt, T.J., Mersmann, P., Heberer, T., 2006. Mobility of pharmaceuticals carbamazepine, diclofenac, ibuprofen, and propyphenazone in miscible-displacement experiments. J. Contam. Hydrol. 83, 53–69. https://doi.org/10.1016/J.JCONHYD.2005.11.002.
Shukla, S.K., Al Mushaiqri, N.R.S., Al Subhi, H.M., Yoo, K., Al Sadeq, H., 2020. Low-cost activated carbon production from organic waste and its utilization for wastewater treatment. Appl. Water Sci. 10, 62. https://doi.org/10.1007/s13201-020-1145-z.
Singh, B., Singh, K., 2016. Microbial degradation of herbicides. Crit. Rev. Microbiol. 42, 245–261. https://doi.org/10.3109/1040841X.2014.929564.
Sithamparanathan, E., Kujawa-Roeleveld, K., Soedarso, J.A.R., Sutton, N.B., Grolle, K., Bruning, H., Rijnaarts, H.H.M., 2021. Sorption of micropollutants to hydroponic substrata: effects of physico-chemical properties. Environ. Adv. 4 https://doi.org/10.1016/j.envadv.2021.100049.
Sotelo, J.L., Rodríguez, A., Álvarez, S., García, J., 2012. Removal of caffeine and diclofenac on activated carbon in fixed bed column. Chem. Eng. Res. Des. 90, 967–974. https://doi.org/10.1016/j.cherd.2011.10.012.
Tadkaew, N., Hai, F.I., McDonald, J.A., Khan, S.J., Nghiem, L.D., 2011. Removal of trace organics by MBR treatment: the role of molecular properties. Water Res. 45, 2439–2451. https://doi.org/10.1016/J.WATRES.2011.01.023.
Test No. 106: Adsorption – Desorption Using a Batch Equilibrium Method, 2000. OECD Guidelines for the Testing of Chemicals, Section 1. OECD. https://doi.org/10.1787/9789264069602-en.
The United Nations World Water Development Report 2019, 2019. . United Nations World Water Dev. Rep. 10.18356/0d8fe383-en.
Turner, R.D.R., Warne, M.S.J., Dawes, L.A., Thompson, K., Will, G.D., 2019. Greywater irrigation as a source of organic micro-pollutants to shallow groundwater and nearby surface water. Sci. Total Environ. 669, 570–578. https://doi.org/10.1016/J.SCITOTENV.2019.03.073.
Vanderford, B.J., Snyder, S.A., 2006. Analysis of pharmaceuticals in water by isotope dilution liquid chromatography/tandem mass spectrometry. Environ. Sci. Technol. 40, 7312–7320. https://doi.org/10.1021/es0613198.
Wang, J., Poursat, B.A.J., Feng, J., de Ridder, D., Zhang, C., van der Wal, A., Sutton, N.B., 2022. Exploring organic micropollutant biodegradation under dynamic substrate loading in rapid sand filters. Water Res. 221, 118832 https://doi.org/10.1016/J.WATRES.2022.118832.
Yuan, J., Fox, F., Crowe, G., Mortazavian, S., Passeport, E., Hofmann, R., 2022. Is in-service granular activated carbon biologically active? An evaluation of alternative experimental methods to distinguish adsorption and biodegradation in GAC. Environ. Sci. Technol. https://doi.org/10.1021/acs.est.2c03639.
Zearley, T.L., Summers, R.S., 2012. Removal of trace organic micropollutants by drinking water biological filters. Environ. Sci. Technol. 46, 9412–9419. https://doi.org/10.1021/ES301428E/SUPPL_FILE/ES301428E_SI_001.PDF.
Zraunig, A., Estelrich, M., Gattringer, H., Kisser, J., Langergraber, G., Radtke, M., Rodriguez-Roda, I., Buttiglieri, G., 2019. Long term decentralized greywater treatment for water reuse purposes in a tourist facility by vertical ecosystem. Ecol. Eng. 138, 138–147. https://doi.org/10.1016/j.ecoleng.2019.07.003.