Comparative performance of different green wall media for the removal of xenobiotic organic compounds from greywater

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Highlights

- Removal of XOCs increases with the increase in pollutant hydrophobicity.
- Coco coir and coffee grinds can effectively remove the hydrophobic XOCs with short retention time.
- Zeolite is more effective in removing polar hydrophilic XOCs with long retention time.

Introduction

The sustainable management of existing water resources such as greywater treatment and its reuse can help to tackle the water crises. Greywater may account for daily volume of up to 120 litters per person in developed countries and represents up to 75% of household wastewater (Ghaitidak and Yadav, 2013). The treatment of such large volume of greywater can provide a reliable source of non-potable water with an additional advantage of reducing the strain on existing sewage system by decreasing the wastewater volume. The treatment of greywater can be accomplished by nature-based systems such as constructed wetlands, green roofs, and green walls. While all these nature-based treatment systems offer multiple environmental benefits, the green walls provide an added value of lower area footprints in densely built urban environment. The existing literature have limited studies on exploring the potential of green wall systems for greywater treatment and these studies are focused on the removal of limited greywater pollutants such as nutrients (total nitrogen and total phosphorus), chemical oxygen demand, and *Escherichia coli* (*E. coli*) (Pradhan et al., 2019; Prodanovic et al., 2020). However, it is not clear if green wall system can treat high-risk contaminants such as xenobiotic organic compounds (XOCs) that persist in household greywater due to extensive use of personal care products, dyes, and detergents (Eriksson et al., 2003). XOCs (also known as organic micropollutants and emerging contaminants) are of serious concerns due to their acute toxicity and endocrine disrupting properties. The lack of understanding about the removal of these XOCs through green wall systems is impending their widespread adoption in urban environment. As green wall media is the major contributor in removing the pollutants from greywater, this study is aimed to analyse the performance of different green wall media types for the removal of XOCs. The specific objectives of this study are to (i) quantify the adsorption potential of different media types for XOCs, (ii) analyse the role of contact time between different media types and XOCs using adsorption kinetics, (iii) determine the adsorption capacity of different media types for XOCs using adsorption isotherms, and (iv) analyse the impact of complex greywater matrix on the removal inhibition of XOCs.

Methodology

Three potential green wall media types including one mineral (zeolite) and two carbonaceous materials (coffee grinds and coco coir) were tested in batch study to find their adsorption potential for four XOCs that cover both hydrophobic and hydrophilic range of pollutants in greywater. These XOCs are acetaminophen (ACT), diethyltoluamide (DEET), bisphenol A (BPA), and nonylphenol (NP). The physio-chemical properties of XOCs along with their household usage, concentration range, and health hazards are summarized in Table 1.

The media was washed with DI water and oven dried at 105˚C for two days before being used for experiments. Experiments were performed on two types of water matrix (i) XOCs spiked DI water (DI_{XOC}) and (ii) XOCs spiked synthetic greywater (SGW_{XOC}) under varying initial concentrations (1 µg/l – 250 µg/l) of XOCs. All experiments were conducted using 40 ml amber vials in which 0.5 g of each media type was added in 25 ml water matrix. The vials were rotated at 30 rpm using rotary wheel and 0.5 ml samples were taken at 8

min, 15 min, 30 min, 90 min, and 1440 min. All experiments were run in triplicate and two types of controls, i.e., (i) DI_{XOC} and SGW_{XOC} without media to test the decline in XOCs concentration with time, and (ii) media in DI water without XOCs to test the leaching of pollutants by different media types.

Table 1. Physiochemical properties of selected XOCs along with their usage, concentration range, and hazards.

XOCs	household use	[1]Concentration range (µg/l)	[2]Log Kow	[2]WS mg/ml	[3]Projection radius (Å)	Health Hazards
ACT	Analgesic	0.09 - 1.5	0.46	11.12	3.49	Skin/Eye irritant
DEET	Insect repellents	0 - 1.5	2.18	0.266	4.40	Skin irritant, respiratory damage
BPA	Plasticizer	0.42 - 1.2	3.32	0.150	4.53	Endocrine disruptor
NP	Surfactant	0.56 - 38	5.76	0	3.65	Endocrine disruptor

[1](Donner et al., 2009; Eriksson et al., 2003, 2002)

[2]Kow=octanol-water partition coefficient, WS = water solubility @ PH=7, Data extracted from EPI Suite™-Estimation Program Interface | Predictive Models and Tools for Assessing Chemicals under the Toxic Substances Control Act (TSCA) | US EPA.

[3]Data extracted using Chemicalize online platform, developed by ChemAxon (http://www.chemaxon.com)

The concentration of XOCs in DI_{XOC} was analysed using high performance liquid chromatography tandem mass spectroscopy (HPLC-MS). The calibration curve was created using at least five relative response ratios of XOCs between concentration range of 1-100 µg/L. The experimental data was fitted to pseudo-first order, pseudo-second order, intraparticle diffusion, and Freundlich isotherm equations. The goodness-of-fit for experimental data was accessed using r^2 values.

Results and discussion

The overall removal of studied XOCs from DI_{XOC} using carbonaceous media types (coffee grinds and coco coir) followed the following order: ACT < DEET < BPA < NP (Figure 1). This removal order can be well explained through log Kow values of XOCs (Table 1). As the log Kow value increase, the XOCs become more hydrophobic and their adsorption affinity for media increases. ACT is the most hydrophilic pollutants (log Kow = 0.46) among the analysed XOCs and therefore showed lowest removal (< 20%) from DI_{XOC} using carbonaceous media types. However, ACT was well removed (> 90%) from DI_{XOC} using zeolite (Figure 1(a)). The high removal of ACT using zeolite can be explained through hydrophilic surfaces within porous structure of zeolite that offers high affinity for polar molecules such as ACT. Moreover, ACT has the lowest value of minimum projection radius (Table 1) that fits well in the heulandite framework of the zeolite used in this study (Ambrozova et al., 2017). The removal of ACT from DI_{XOC} is slow and kept on increasing with time indicating that higher removal of ACT can be achieved by using zeolite with longer retention time.

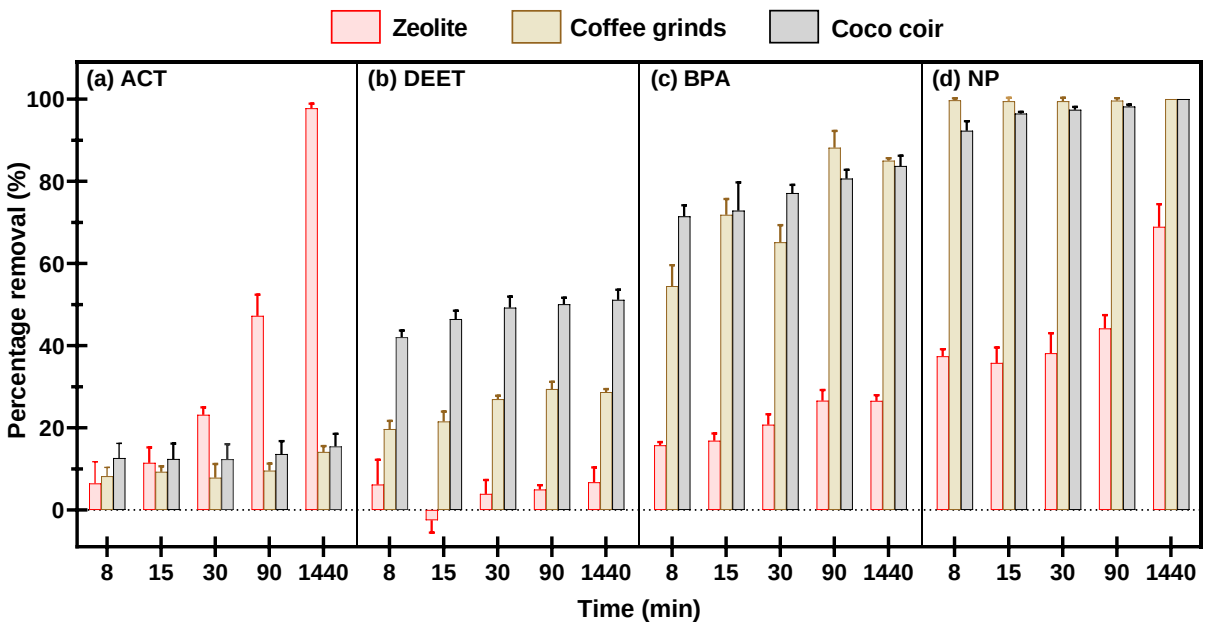

Figure 1. The removal rate of (a) ACT, (b) DEET, (c) BPA, and (d) NP from DI_{XOC} by using different media types. Results are presented for the removal of XOCs with initial concentration of 10 µg/l.

The removal of DEET (Figure 1(b)) from DI_{XOC} using coffee grinds and coco coir was better than ACT as DEET has more adsorption affinity for carbonaceous media types due to higher hydrophobicity (log Kow = 2.18) in comparison to ACT. However, no media type was able to remove more than 50% DEET from DI_{XOC} with maximum removal achieved by coco coir (50%) during initial 30 minutes. No considerable change in removal was observed between 30 to 1440 minutes, indicating quick attachment of DEET (< 30 min) on the limited favourable adsorption sites of coco coir. BPA removal (Figure 1(c)) from DI_{XOC} using carbonaceous media types was better than ACT and DEET due to higher log Kow value. The removal process was quick with 70% and 75% removal from DI_{XOC} was achieved within 30 minutes by using coffee grinds and coco coir, respectively. NP showed highest removal from DI_{XOC} using carbonaceous media types due to its highly hydrophobic nature (log kow = 5.76). The removal process was quick with more than 95 % removal achieved using spent coffee grinds and coco coir within 30 minutes (Figure 1(d)). This indicate that both coco coir and spent coffee grinds have large number of highly favourable adsorptions sites for the quick removal of NP.

The adsorption kinetics data for all XOCs showed goodness-of-fit for both pseudo first and second order rate equations (r^2 > 0.94). This indicate that simultaneous contribution of multiple interactions (physical or chemical) could be involved in the adsorption process. As the adsorption process was fast for all XOCs except for ACT, it is expected that XOCs may adsorb instantaneously on carbonaceous media types via hydrophobic interactions. ACT removal using zeolite showed multilinear data fitting using intraparticle diffusion model suggesting more than one rate limiting steps such as film diffusion and intraparticle diffusion may be involved in the adsorption process. Adsorption isotherm (Freundlich) indicated linear increase in adsorption capacity of carbonaceous media types with the increase in equilibrium concentration of XOCs. However, ACT adsorption on zeolite showed that saturation level of the adsorbent was reached at higher equilibrium value.

The removal rate of ACT, DEET, BPA, and NP from SGW_{XOC} was lower than DI_{XOC} for all media types due to the presence of background organic matter that offered hinderance by covering the media surface. However, the overall removal potential of carbonaceous media types was not disturbed due to the availability of large number of adsorption sites.

Conclusions and future work

- The overall removal of tested XOCs using carbonaceous media (coffee grinds and coco coir) increased with the increase in XOCs hydrophobicity.
- Coco coir and coffee grinds completely removed the NP (hydrophobic XOC) with more than 90% removal was achieved within 15 minutes.
- The favourable dimension of zeolite structure channel and its high affinity for polar molecules resulted in higher removal of ACT.
- In future study, the mixture of zeolite and coco coir will be tested in non-vegetated and vegetated columns to explore the combined potential of plant and media for the removal of XOCs from greywater.

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