



## Sorption of micropollutants to hydroponic substrata: Effects of physico-chemical properties

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### ARTICLE INFO

#### Keywords:

Hydroponic substrata  
Micropollutant  
Sorption  
Organic matter  
Sorption isotherm  
Constructed wetland

### ABSTRACT

Constructed wetlands could be improved with novel substrata to enhance the removal efficiency of micropollutants from wastewater and reduce the spatial footprint. Use of hydroponic substrata like mineral wool, pumice, wood - and coconut fibre is both novel for wastewater treatment, and potentially suitable, due to their hydraulic compatible texture. Since sorption is a key removal process for pollutants in constructed wetlands, this study investigates sorption to novel substrata by six priority micropollutants, caffeine, carbamazepine, ibuprofen, naproxen, sulfamethoxazole and trimethoprim, with diverse Log  $K_{ow}$  and pKa values. We found that higher sorption was positively related to substrata's organic matter content. Organic substrata, namely wood - and coconut fibre, demonstrated higher sorption affinity compared with the inorganic substrata mineral wool and pumice, notably regardless of the micropollutants' Log  $K_{ow}$ . Carbamazepine efficiently and rapidly sorbed onto organic substrata, which is particularly noteworthy considering the recalcitrance of carbamazepine in conventional treatment plants. The sorption isotherms were best described by the Freundlich model rather than Langmuir or linear models. We determined that using wood fibre in constructed wetlands would require around 35–66% less area to remove the selected micropollutants, compared to soil as matrix. Thus our results show the potential of using hydroponic substrata such as wood - and coconut fibre to both remove micropollutants in, and reduce the footprint of constructed wetlands.

### Introduction

Constructed wetlands (CWs) are commonly applied secondary or tertiary wastewater treatment systems (Zhang et al., 2017a). CWs exploit natural processes to remove pollutants via substrata, vegetation and microorganisms (Vymazal, 2007). CWs were traditionally employed to remove traditional pollutants, but are recently being used to remove micropollutants from wastewater.

Numerous studies reported the adverse effects of micropollutants on human and environmental health (Luo et al., 2014). Effects include feminization of fish, short and long-term toxicity to biota, and the development of antibiotic resistance among natural and anthropogenic microbiomes (Kodešová et al., 2015; Li et al., 2014). Currently, physico-chemical technologies, such as ozonation, and membrane and activated carbon filters are implemented as tertiary treatment to remove micropollutants (Luo et al., 2014). However, such high-tech, expensive methods are less suitable in many emerging and developing economies (Luo et al., 2014; Srinivasan et al., 2013b). CWs are an attractive alternative: CWs are cost effective, eco-friendly and easy to operate and

maintain (Meng et al., 2014). However, a key limitation in application of CWs is their high land area requirements, typically termed a land footprint.

The CW substratum plays the key role in determining the size of a CW. Substrata remove various pollutants directly by sorption, precipitation, filtration and biodegradation (Meng et al., 2014; Wu et al., 2015). In addition, the substratum supports plant and microbial growth. Initially, soil was used as substratum. Recently, sand and gravel have been selected for their high hydraulic conductivity, resulting in improved performance of CWs. However, the application of these materials has limitations due to low removal of nitrogen and phosphorous, and more recently for micropollutants (Meng et al., 2014; Wu et al., 2015). Considering the importance of substrata for CW performance, selection of proper substrata could both reduce CW footprint while also removing micropollutants.

Hydroponic substrata are good candidates for use in CWs. Developed for hydroponic plant growth in horticulture, hydroponic substrata have attractive properties, such as higher oxygen and water holding capacity, large surface area and retain nutrients (Gurbuz and Codd, 2008;

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### Nomenclature

C	concentration of solute in aqueous phase at given time, mg/L
$C_e$	concentration of solute in aqueous phase at equilibrium, mg/L
$C_o$	initial concentration of solute in aqueous phase, mg/L
$K_d$	distribution coefficient, L/g
$K_F$	Freundlich constant, (mg/g)/(mg/L) <sup>n</sup>
$K_L$	Langmuir constant, L/mg
Log	$K_{ow}$ n-octanol/water partition coefficient
n	Freundlich intensity parameter
pKa	dissociation constant
$q_e$	mass of a sorbate sorbed per unit mass of a sorbent at equilibrium, mg/g
$q_t$	mass of a sorbate adsorbed per unit mass of a sorbent at given time, mg/g
R	correlation coefficient
$R^2$	coefficient of determination
X	amount of the sorbent, g/L
$Q_{max}^o$	maximum sorption capacity, mg/g
$\chi^2$	chi-squared

Wanko et al., 2016). In this study, the use of four commonly used hydroponic substrata were compared: mineral wool, pumice, wood fibre and coconut fibre. To date, a limited number of studies were conducted on their usability in CWs and on their potential to remove micropollutants from wastewater (Gurbuz and Codd, 2008; Wanko et al., 2016). Yang et al. (2018) reviewed the studies which focused on the use of emerged substrata (e.g. organic rich materials) in CWs to remove conventional pollutants. However, suitability of the emerged substrata to remove micropollutants was not reported. Furthermore, Wang et al. (2020) articulated that there is a lack of comprehensive studies available on the suitability of hydroponic CW substrata (e.g. coconut dust and cocopeat) to remove various pollutants. Therefore, there is an urgent need to study the potential of the four substrata to remove micropollutants in CWs.

Generally, sorption is one of the initial removal processes of a pollutant in the filter bed of CW. Sorption is an umbrella term covering both absorption (solid phase bulk inclusion) and adsorption (surface interaction mediated) processes, and is especially used when these two mechanisms cannot be distinguished (Kouksou et al., 2014; Tran et al., 2017; Wang et al., 2009). Isotherm models, such as Freundlich and Langmuir models can be used to unravel the sorption mechanisms from experimental data to distinguish surface related or absorption related mechanisms (Tran et al., 2017).

Sorption behaviour of a sorbate (pollutant) to a sorbent (substratum) is governed by many factors. These include physico-chemical properties of a sorbent and sorbate, such as acidity ( $pK_a$ ) and hydrophobicity (Log  $K_{ow}$ ) of a pollutant, and organic matter content of a substratum (Zhang et al., 2017b). These factors influence the affinity between a sorbent and sorbate and transport of the sorbates from bulk solution to sorption sites, influencing extent and kinetics of sorption. Thus, understanding sorption mechanisms is crucial for successful applications of a substratum in CWs treating micropollutant-containing wastewater.

This study aims to investigate the applicability of four hydroponic substrata for efficient removal of micropollutants from wastewater. We determine sorption affinities and kinetics, and interpret this data using isotherm models and physico-chemical properties of substrata and micropollutants. These results are used to assess the suitability of the substrata in CWs, both for micropollutant removal and for reducing CW footprint.

## Materials and methods

### Substrata

Four hydroponic substrata were used in batch experiments (Fig. S11), namely mineral wool from Drainblock BV, the Netherlands, and pumice, wood fibre and coconut fibre from Greenyard Horticulture Belgium NV. The properties of the substrata were assessed in order to better interpret the sorption behaviour of the different substrata. Organic matter content, natural pH and Cation Exchange Capacity (CEC) of the substrata were determined (SIA5). The surface characteristics of the substrata were studied employing two models: Brunauer, Emmett, Teller (BET) (surface area) and t-plot (micropore area and micropore volume) (SIA6).

### Micropollutants

Six pharmaceuticals: caffeine, carbamazepine (>98 % purity), ibuprofen, naproxen (98% purity), sulfamethoxazole and trimethoprim (>99% purity), all purchased from Sigma Aldrich Chemie NV. Zwijndrecht, the Netherlands, were selected as representative pharmaceuticals (Table 1). These compounds are frequently detected in wastewater treatment plants and have diverse physio-chemical properties, such as  $pK_a$  and Log  $K_{ow}$ , and different sorption potentials (Luo et al., 2014). Carbamazepine is specifically selected since it is poorly removed in traditional wastewater treatment processes. For each compound, a primary stock solution of 3 g/L in methanol was prepared. From the primary stock solutions, a secondary stock solution was prepared with a mixture of all six compounds in Milli-Q water with a final concentration of 100 mg/L per compound. This secondary stock was used for batch preparation.

### Batch sorption experiment

Sorption experiments were carried out using 250 mL micropollutant working solution and 100 mL substratum in 500 mL Scott bottles at 20°C. All four substrata were sieved to keep the particle size larger than 4 mm and a detailed description on the preparation of the substrata is available in SIA1. The solid to liquid (volume/volume) ratio was 0.4, well above the minimum ratio of 0.25 suggested to achieve a consistent sorption distribution coefficient ( $K_d$ ) in batch experiments (Wang et al., 2009).

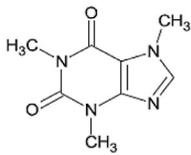
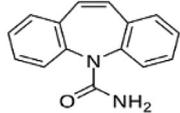
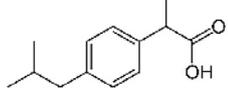
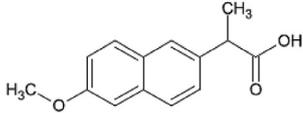
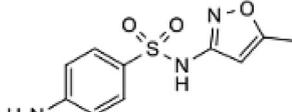
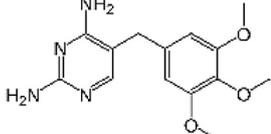
Batches were prepared by diluting the secondary stock of 100 mg/L in Milli-Q water to obtain for each compound five different initial concentrations: 0.5, 1, 2.5, 5 and 10 mg/L. The experiments were conducted at a range of concentrations to cover the nonlinear shape of sorption isotherm, similar to the other batch sorption experiments in literature (Doretto et al., 2014; Kodešová et al., 2015). The ionic strength of the working solution was controlled at 0.01 M by using NaCl. The pH of the working solution was maintained at 7.2 using 10 mM phosphate buffer.

All the prepared batches were capped, covered with aluminium foil to prevent photodegradation of the micropollutants and kept in the shaker for 72 hours, at 100 rpm at 20°C. Control batches were run without substratum to quantify and correct for any adsorption to the wall of the Scott bottle and cap, contamination of the samples or degradation of the compounds. All batches were run in duplicate.

From each batch, 5 mL supernatant was taken at 0, 0.25, 2, 6, 24, 30, 48, 72 h. The samples were stored at -20°C. Prior to the analysis, all the samples were centrifuged at 10000 rpm for 5 minutes, filtered with 0.20  $\mu$ m Polyethersulfone (PES) syringe filter and transferred into 1.5 ml vials for Liquid Chromatography with PhotoDiode Array Detection (LC-DAD) measurement. More details on LC-DAD analysis and the quality control tests for the sample preparation method is available in the SIA2 and SIA3.

Sorption kinetics were obtained by monitoring the concentrations of the micropollutants in the liquid phase over time for the four substrata.

**Table 1**  
The properties of the selected micropollutants investigated in this study; the data were retrieved from the database PubChem (PubChem, 2020)

Micropollutants	Use	pK <sub>a</sub>	Log K <sub>ow</sub>	Chemical structure
Caffeine	Stimulant	10.4	-0.07	
Carbamazepine	Antiepileptic	13.9	2.45	
Ibuprofen	Non-steroidal anti-inflammatory drug	4.91	3.97	
Naproxen	Non-steroidal anti-inflammatory drug	4.15	3.18	
Sulfamethoxazole	Antibiotic	6	0.89	
Trimethoprim	Antibiotic	7.12	0.91	

### Data analysis and sorption models

The sorption (%) of the micropollutants onto the substrata over time was calculated using Eq. (1) (Nanta et al., 2018).

$$\text{Sorption (\%)} = (1 - C/C_0) * 100\% \quad (1)$$

where C<sub>0</sub> (mg/L) is the initial micropollutant concentration in the liquid phase of a batch and C (mg/L) is the micropollutant concentration in the liquid phase of a batch at given time. The mass of a sorbate sorbed per unit mass of a sorbent at equilibrium q<sub>e</sub> (mg/g) was determined by analysing the concentrations before and after the incubation using Eq. (2) (Tran et al., 2017).

$$q_e = (C_0 - C_e)/X \quad (2)$$

X (g/L) is the amount of the sorbent.

The experimental data was fitted with sorption isotherms plotting q<sub>e</sub> against C<sub>e</sub> to elucidate the sorption behaviour of the substrata for the investigated micropollutants. Furthermore, the kinetic data was fitted using the pseudo-first and second-order models and the experimental sorption equilibrium data was fitted with Freundlich, Langmuir and linear models (SLA4) (Tran et al., 2017).

### Statistical analysis

Simple correlation study between the properties of the substrata and Freundlich constant K<sub>F</sub> was conducted using IBM SPSS Statistics 25.0. Pearson correlation coefficient (bivariate correlation) values were obtained and used to understand the effect of different properties of substrata on their sorption towards the micropollutants. Additionally, P-values were also tested to evaluate the statistical significance of the obtained correlations.

## Results

### Properties of the substrata

Prior to sorption experiments, substrata were characterized for their physico-chemical properties. Organic matter content of wood fibre and coconut fibre is above 90% and categorized as organic substrata whereas the substrata, pumice and mineral wool, were categorized as inorganic substrata with less than 3% of organic matter (Greenyard Horticulture Belgium NV and Drainblock BV). The organic substrata had a higher CEC than the inorganic substrata. The pH was acidic for the organic substrata and neutral for the inorganic substrata (Table 2A).

Substrata surfaces were quantified using BET and t-plot models (Table 2A). All substrata can be characterized as having mesopores (Hu and Srinivasan, 1999; Leofanti et al., 1998; Scherdel et al., 2010). Specifically, substrata' BET surface area is mainly comprised of t-plot external surface area more than t-plot micropore area. Additionally, it was found that the average pore-width of all four substrata lie between 7.2-8.7 nm, indicating that all the substrata primarily have mesopores (Leofanti et al., 1998). Among the substrata, wood fibre had the highest surface area, followed by pumice, coconut fibre and mineral wool (Table 2A).

### Sorption affinities

Sorption experiments were performed to determine the affinity of substrata to sorb the six micropollutants. The affinities were thus experimentally determined by quantifying sorption (%) over the contact time (hour) (Fig. 1). In general the organic substrata had a higher micropollutant sorption affinity than the inorganic substrata. The affinities of the organic substrata wood fibre and coconut fibre followed the order:

**Table 2A**

Properties of the substrata: pH in water, organic matter content, Cation Exchange Capacity (CEC), The European Committee for Standardization (CEN) density, Brunauer, Emmett, Teller (BET) surface area, t-Plot external surface area, t-Plot micropore area and adsorption average pore width. The data regarding pH, organic matter and CEN were provided by Greenyard Horticulture Belgium NV and Drainblock BV (Greenyard Horticulture Belgium NV, 2011; Drainblock BV, 2018). The remaining properties were measured following the standard protocols (SLA5; SLA6). The values are presented with their standard deviations calculated for triplicates.

Substratum	pH in water	Organic matter <sup>a</sup> (% (m/m))	CEC (cmol <sub>c</sub> /kg)	CEN density (kg/m <sup>3</sup> )	BET surface area (m <sup>2</sup> /g)	t-Plot external surface area (m <sup>2</sup> /g)	t-Plot micro pore area (m <sup>2</sup> /g)	Adsorption average pore width (4V/A by BET) (nm)
Wood fibre	5.5	97	5715 ± 838	270	2.7 ± 0.8	2.0 ± 0.7	0.7 ± 0.2	8.0 ± 2.6
Coconut fibre	6	90-100	6873 ± 25	30-70	1.8 ± 0.7	1.1 ± 0.4	0.8 ± 0.5	7.3 ± 2.6
Mineral wool	7.7	3	258 ± 22	80	0.5 ± 0.5	0.4 ± 0.3	0.4 ± 0.0	8.7 ± 3.5
Pumice	7	<1	1755 ± 23	900	2.4 ± 0.1	2.3 ± 0.1	0.1 ± 0.02	7.7 ± 0.5

<sup>a</sup>The percentage organic matter was calculated by dividing mass organic matter by total dry mass of the substratum.

trimethoprim>carbamazepine>caffeine>sulfamethoxazole>ibuprofen=naproxen. Sorption of trimethoprim, caffeine and sulfamethoxazole was observed for pumice, but only after an initial incubation period of 6 h. Essentially no sorption by any micropollutant occurred to mineral wool (Fig. 1).

#### Sorption kinetics

Sorption kinetics were studied using the sorption (%) of the micropollutants into the substrata over the contact time (Fig. 1). Fast initial sorption to organic substrata was observed for most of the studied micropollutants during the first 6 h, followed by a slower sorption phase. This suggests diffusion into internal substratum was limiting: rapid sorption to the outer layer of the substrata is followed by slower diffusion in an apparent first order process. Naproxen and ibuprofen exhibited distinctly slower kinetics during sorption to the organic substrata. For inorganic substrata, even slower kinetics were observed for the studied micropollutants (Fig. 1). A thorough and further mechanistic interpretation of the sorption kinetic data using pseudo-first and second-order models was not possible due to insufficient R<sup>2</sup> values resulting from fitting data with these models (Table S16).

The profile of the sorption kinetics (Fig. 1) was used to identify equilibrium. The sorption curves levelled off between 24 and 72 h, indicating that sorption reached a status of equilibrium. Based on this, the concentration obtained at 72 h was taken as an estimate of the equilibrium concentration C<sub>e</sub>.

#### Sorption isotherms

Sorption isotherms were used to gain insight into the type of interaction between sorbates and sorbents (Fig. 2). Isotherms were further used to identify the suitable isotherm models allowing comparison of the sorption behaviour, and providing insight into possible sorption mechanisms. Subsequently, sorption equilibrium data was fitted with Freundlich, Langmuir and linear sorption models (Table 3) (Table S17). Higher R<sup>2</sup> and smaller  $\chi^2$  indicated better fitting of the data (Tran et al., 2017).

The sorption behaviour of wood fibre may not be explained by any of the models included in this study. The observed upward convex shape (n>1) might be explained by multilayer adsorption as in the BET-model (Fig. 2). This implies that adsorption of compounds onto the sorbent makes additional sorption more favourable, and may even lead to pore condensation as suggested by Leofanti et al. (1998) for other systems at high concentrations. Equilibrium data for the other organic substratum, coconut fibre, could be better explained by the Langmuir model, as coconut fibre clearly exhibited a saturation type of sorption (Fig. 2). Surface saturation in the pores may have controlled the sorption process.

Minimal sorption was observed for the two inorganic substrata, mineral wool and pumice. The equilibrium data of mineral wool could not be fit to any models due to the low sorption affinity for all the compounds. Therefore, no further interpretation was made based on this

data. While pumice also exhibited low sorption, experimental data could be described by either Freundlich or Langmuir models. The result indicates a surface saturation type of sorption (Fig. 2).

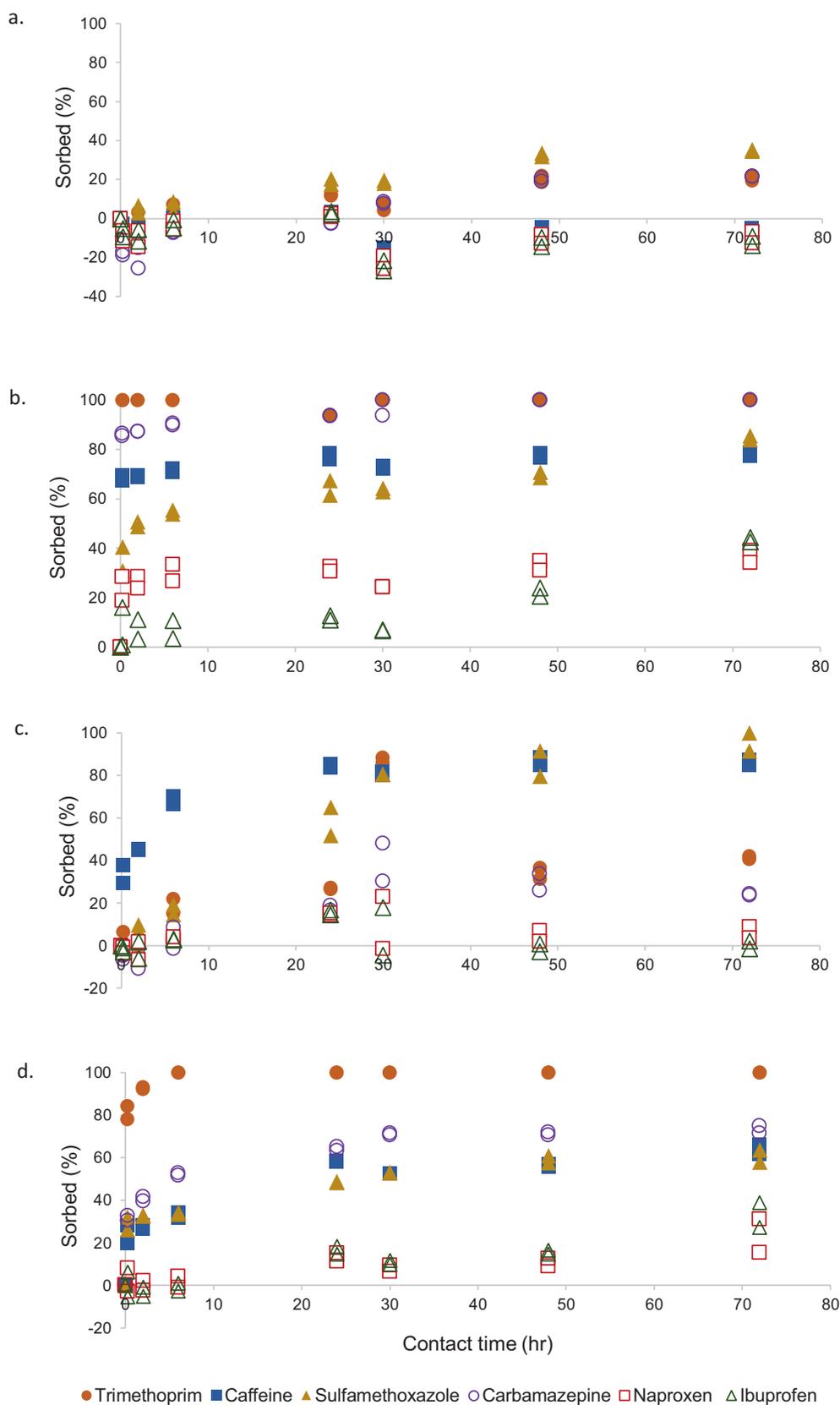
Freundlich model can better explain our data. Among the three models studied, linear model is more simple and useful considering its one adjustable constant K<sub>d</sub> with better R<sup>2</sup> and  $\chi^2$  values (Table 3). Further, the interest of this study lies in the low concentration ranges where the Langmuir model also approaches linearity but requires two (K<sub>L</sub> / Q<sub>max</sub>) parameters and the linear model requires only one (K<sub>d</sub>) parameter to characterize the sorption affinity, favouring the linear model and K<sub>d</sub>. However, the linear model does not accommodate curved sorption isotherms occurring for complex, heterogeneous systems even at low concentrations whereas the Freundlich model does. Furthermore, for curved isotherms, K<sub>F</sub> is also a better indicator of the actual distribution coefficient value at low concentrations. Therefore, K<sub>F</sub> values of R<sup>2</sup> > 0.500 were selected for further interpretation of the sorption behaviour of the substrata for the different micropollutants studied.

#### The effect of the substrata properties on sorption

In this study, K<sub>F</sub> was selected as the most appropriate indicator of sorption affinity. Therefore, bivariate correlations between K<sub>F</sub> and the properties of the substrata were determined in order to further understand the sorption behaviour of the substrata.

The K<sub>F</sub> of all the investigated micropollutants was negatively correlated to the pH of the substrata (Table 2B). This is explained by both the properties of the substrata and the micropollutants under the experimental pH. The organic substrata have a pH between 5 and 6, indicating an acidic pH<sub>PZC</sub> (point of zero charge) (Bakatula et al., 2018). Wood fibre (pH=5.5) and coconut fibre (pH=6.0), containing lignin and hemicellulose polymers, can lose the protons from their carboxyl (-COOH) or hydroxyl (-OH) groups. This creates negatively charged surface (Kodešová et al., 2015; Qin et al., 2017). Inorganic substrata mineral wool (pH=7.7) and pumice (pH=7) have a neutral pH, indicating dissociation is limited and no active charged groups are expected at their surface. At neutral pH, naproxen (pKa = 4.15), ibuprofen (pKa = 4.91) and sulfamethoxazole (pKa = 1.83 and 5.57) would deprotonate, forming anionic species. Thus, electrostatic repulsion between the anionic species and negatively charged surface could explain the observed negative correlation between the micropollutants and substrata pH.

Organic matter was positively correlated with K<sub>F</sub> (Table 2B). This to some extent conflicts with our observation of electrostatic repulsion between the anionic species and predominantly negatively charged organic matter surface. However, we found a positive correlation from the statistical analysis, indicating that other processes also occur at the surface. For example, complexation between anionic species and the hydrous oxides of aluminium and iron on surface may occur (Martínez-Hernández et al., 2014). Similarly, the positive effect of organic matter on sorption could be explained by molecular interactions between the aromatic part of the compounds and the lignin matrix (wood fibre



**Fig. 1.** The sorption (%) of the micropollutants onto mineral wool (a), wood fibre (b), pumice (c) and coconut fibre (d) over time (at initial concentrations of 0.5 mg/L). Similar results were observed for other initial concentrations: 1, 2.5, 5, 10 mg/L (SI. B1) (in supplementary information file B). The samples from the duplicate batches were presented as single samples.

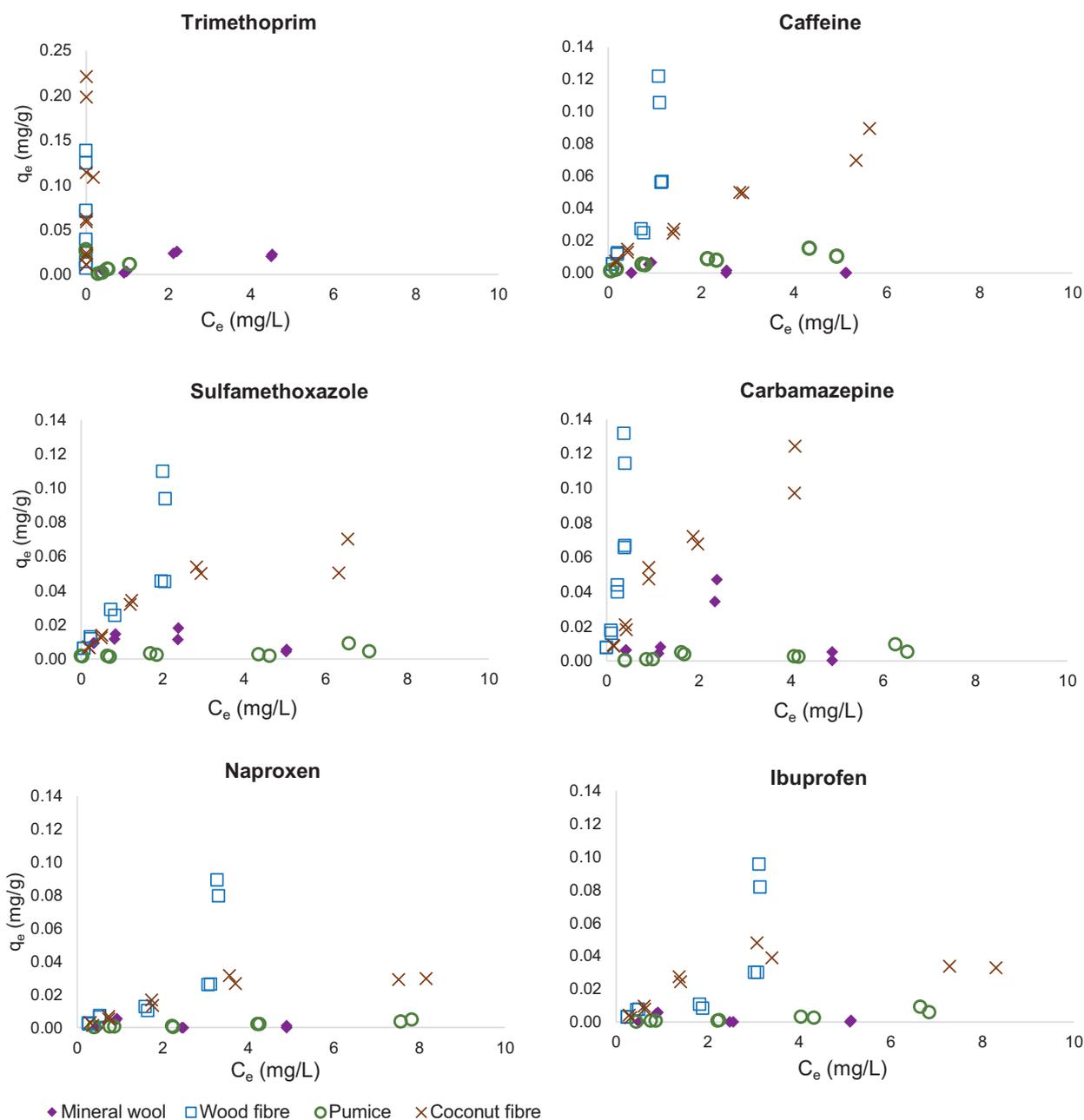


Fig. 2. Sorption isotherms obtained from the experimental equilibrium data;  $C_e$  (mg/L) is the sorbate concentration at equilibrium and  $q_e$  (mg/g) is the mass of sorbate adsorbed per unit mass of sorbent. The samples from the duplicate batches are presented as single samples.

and coconut fibre) or hydrophobic interactions pushing the compounds out of the water phase into the organic matrix (Kodešová et al., 2015; Qin et al., 2017; Srinivasan et al., 2013a). Based on these observations, it can be stated that organic matter content of substrata is an important parameter for improving micropollutant sorption.

CEC of the substrata was positively correlated with  $K_F$  (Table 2B). Among the four substrata, coconut fibre had the highest CEC, followed by wood fibre, pumice and mineral wool (Table 2A). We expected that anionic species would show coulombic attraction to the exchangeable cations on the surface of high CEC substrata, known as cation bridging (Vasudevan et al., 2009). However, experimental results showed that anionic species, e.g. ibuprofen and naproxen, did not have a good sorption affinity to the organic substrata (Figs. 1 and 2) suggesting that strong electrostatic repulsion of these anionic species makes sorption less favourable. Apparently, the repulsion is too strong to be overcome by an attractive cationic bridging (Wu et al., 2002).

Other substrata properties generally showed insignificant correlation with  $K_F$  (Table 2B). Therefore, no further data interpretation was made from these statistical analysis.

#### The effect of the micropollutant properties on sorption

To further understand the use of substrata for micropollutant removal, the effect of micropollutant properties on sorption was investigated. Bivariate correlations among  $K_F$  and  $pK_a$  and  $\log K_{ow}$  of the micropollutants were determined. However, the obtained R values were generally low, indicating the dataset is insufficient for such an assessment; therefore, we only qualitatively assess the role of micropollutant properties on sorption.

As described above,  $pK_a$  is an important property of a compound influencing its charge and thus sorption affinity. At the neutral pH used in this experiment, micropollutants were in some cases charged or un-

**Table 2B**

The correlation coefficient (R) describing relationships between Freundlich constant  $K_F$  (mg/g)/(mg/L)<sup>n</sup> and the properties of substrata: natural pH, organic matter (% (m/m)), Cation Exchange Capacity CEC (cmol<sub>c</sub>/kg), Brunauer, Emmett, Teller (BET) surface area (m<sup>2</sup>/g), t-Plot external surface area (m<sup>2</sup>/g) and adsorption average pore width (nm)

	Substrata Properties					
	Natural pH	Organic matter	CEC	BET surface area	t-Plot external surface area	Adsorption average pore width
Caffeine- $K_F$	-0.905 <sup>c</sup>	0.728 <sup>d</sup>	0.548	0.561	nc	0.618
Sulfamethoxazole- $K_F$	-1.000 <sup>**c</sup>	1.000 <sup>**c</sup>	1.000 <sup>**c</sup>	1.000 <sup>**c</sup>	1.000 <sup>**c</sup>	1.000 <sup>**c</sup>
Carbamazepine - $K_F$	-0.830 <sup>d</sup>	0.616	nc	0.680	nc	0.730 <sup>d</sup>
Naproxen - $K_F$	-0.949 <sup>c</sup>	1.000 <sup>**c</sup>	0.973 <sup>c</sup>	nc	-0.650	nc
Ibuprofen - $K_F$	-0.823 <sup>d</sup>	0.959 <sup>c</sup>	0.999 <sup>c</sup>	nc	-0.837 <sup>d</sup>	nc

\*Correlation is significant at the 0.05 level (2-tailed).

\*\*Correlation is significant at the 0.01 level (2-tailed)

<sup>c</sup>Strong correlation (R>0.900)

<sup>d</sup>Moderate correlation (0.700<R<0.900)

Weak correlation (0.500<R<0.700)

nc: No correlation (R<0.500; data not shown)

**Table 3**

Calculated Freundlich and linear sorption parameters:  $K_F$  (mg/g)/(mg/L)<sup>n</sup> is the Freundlich constant; n is a dimensionless Freundlich intensity parameter;  $K_d$  (L/g) is the distribution coefficient; R<sup>2</sup> is the coefficient of determination and  $\chi^2$  represents the value from chi-squared test. The detailed Freundlich and linear sorption model analysis can be found in SI. B2 and SI. B4 respectively (in supplementary information file B).

Substratum	Compound	Freundlich				Linear		
		$K_F$	n	R <sup>2</sup>	$\chi^2$	$K_d$	R <sup>2</sup>	$\chi^2$
Wood fibre	Trimethoprim	nd	nd	nd	nd	nd	nd	nd
	Caffeine	0.064	1.8	0.698	0.142	0.067	0.662	0.080
	Sulfamethoxazole	0.042	0.9	0.711 <sup>b</sup>	0.048	0.036	0.719 <sup>b</sup>	0.057
	Carbamazepine	0.338	1.4	0.778 <sup>b</sup>	0.043	0.229	0.753 <sup>b</sup>	0.052
	Naproxen	0.011	1.4	0.651	0.064	0.017	0.602	0.080
	Ibuprofen	0.013	1.3	0.579	0.088	0.017	0.551	0.101
Coconut fibre	Trimethoprim	nd	nd	nd	nd	nd	nd	nd
	Caffeine	0.022	0.8	0.976 <sup>a</sup>	0.004	0.015	0.943 <sup>a</sup>	0.037
	Sulfamethoxazole	0.026	0.5	0.890 <sup>b</sup>	0.015	0.011	0.536	0.123
	Carbamazepine	0.046	0.6	0.952 <sup>a</sup>	0.013	0.030	0.835 <sup>b</sup>	0.073
	Naproxen	0.011	0.5	0.843 <sup>b</sup>	0.014	0.005	0.586	0.040
	Ibuprofen	0.018	0.4	0.624	0.039	nf	nf	nf
Mineral wool	Trimethoprim	0.009	1.0	0.599	0.086	0.009	0.599	0.085
	Caffeine	nf	nf	nf	nf	nf	nf	nf
	Sulfamethoxazole	nf	nf	nf	nf	nf	nf	nf
	Carbamazepine	nf	nf	nf	nf	nf	nf	nf
	Naproxen	nf	nf	nf	nf	nf	nf	nf
	Ibuprofen	nf	nf	nf	nf	nf	nf	nf
Pumice	Trimethoprim	nd	nd	nd	nd	nd	nd	nd
	Caffeine	0.006	0.5	0.895 <sup>b</sup>	0.002	0.003	0.681	0.036
	Sulfamethoxazole	nf	nf	nf	nf	nf	nf	nf
	Carbamazepine	0.002	0.8	0.582	0.009	0.001	0.562	0.011
	Naproxen	0.000	1.4	0.959 <sup>a</sup>	0.002	0.000	0.920 <sup>a</sup>	0.001
	Ibuprofen	0.000	1.7	0.891 <sup>b</sup>	0.003	0.001	0.802 <sup>b</sup>	0.005

<sup>a</sup> Good fit (R<sup>2</sup>>0.900)

<sup>b</sup> Moderate fit (0.700<R<sup>2</sup><0.900)

Weak fit (0.500<R<sup>2</sup><0.700)

nf: No fit (R<sup>2</sup><0.500; data not shown)

nd: Not determined: aqueous equilibrium concentration was below the lower limit of detection

charged. For example, trimethoprim with pKa of 7.12 was predominantly neutral at the experimental pH (Kodešová et al., 2015), and thus sorbed more easily to negatively charged wood fibre and coconut fibre, as observed in Fig. 1. On the other hand, caffeine with a pKa of 10.4, is protonated at neutral pH and thus, may have a coulombic attraction to the organic fraction (Vasudevan et al., 2009). Sulfamethoxazole has two pKa values 1.83 and 5.57, indicating the species would predominantly exist as anions at neutral pH (Srinivasan et al., 2013a). Thus, poor sorption of sulfamethoxazole to the organic substrata could be explained by the electrostatic repulsion between the anionic species and negatively charged organic matter (Srinivasan et al., 2013a). Similarly, ibuprofen (pKa=4.91) and naproxen (pKa=4.15) would mainly exist in

their anionic forms at neutral pH (Zhang et al., 2017b), explaining the low sorption affinity for the negatively charged surfaces of the substrata (Fig. 1).

Hydrophobicity, as expressed by Log K<sub>ow</sub>, is another important property of a compound affecting its sorption behaviour. The hydrophobic compounds naproxen and ibuprofen showed slower sorption kinetics during the first 6 h of contact time; rather, their sorption (%) on wood fibre and coco fibre started increasing with the increasing contact time (Fig. 1). Electrostatic repulsion between the negatively charged surface area and these anionic species could possibly explain this slow sorption during the initial contact time (Tülp et al., 2009). However, hydrophobicity of these negatively charged compounds appears to favour a con-

tinued sorption to the negatively charged surface over longer contact times, i.e. via a slow mass transfer most likely pore diffusion of these species from the outer to the inner parts of these substrata. Overall, hydrophobicity of the negatively charged compounds positively affected the sorption.

## General discussion

### *Effect of physico-chemical properties on sorption*

Organic substrata wood fibre and coconut fibre sorbed micropollutants more than the inorganic substrata mineral wool and pumice (Fig. 1). The observed sorption affinity of the organic substrata with the micropollutants followed the order: trimethoprim>carbamazepine>caffeine>sulfamethoxazole>ibuprofen= naproxen (Fig. 1). A similar order of sorption affinity for trimethoprim, carbamazepine and sulfamethoxazole was found for soils by Kodešová et al. (2015). Ibuprofen and naproxen, containing -COOH groups, and sulfamethoxazole, containing -SO<sub>2</sub>-NH moieties, have acidic protons which can dissociate and form anionic species (Table 1). Subsequently, a strong repulsion occurs between these anionic species and negatively charged surface of the organic substrata. Although sulfamethoxazole has a basic NH<sub>2</sub> group (amino group), it has acidic protons due to the presence of an acidic -NH- and an electron-withdrawing -SO<sub>2</sub>- in the vicinity. The presence of two basic NH<sub>2</sub> groups in trimethoprim explains its highest sorption affinity. Carbamazepine has one amido group and the basicity of an amido group is lower than of an amino group. This could explain the sorption order: trimethoprim is followed by carbamazepine. Caffeine has a lone pair of electrons at the non-methylated N site (Table 1). Therefore, caffeine acts as a proton-acceptor, basic, so it is positively charged and attracted to the negatively charged surface. Caffeine is hydrophilic whereas carbamazepine is hydrophobic due to its dibenzoazepine structure (Table 1). The hydrophobicity positively affects the sorption (Tülp et al., 2009). Therefore, carbamazepine is followed by caffeine in the sorption order.

The sorption of micropollutants on organic rich materials appears to be a trade-off between electrostatic interaction and hydrophobic interactions between the organic matrices and the micropollutants. This is further depicted in a four quadrant matrix (Fig. SI2). In the high pK<sub>a</sub> and high Log K<sub>ow</sub> quadrant, both electrostatic interactions and hydrophobicity positively affect the sorption, as indicated by high K<sub>F</sub> values for carbamazepine on the organic substrata (Table 3) (Tülp et al., 2009; Vasudevan et al., 2009). For the low pK<sub>a</sub> and high Log K<sub>ow</sub> quadrant, the positive effect of hydrophobicity of ibuprofen and naproxen appears to be largely counteracted by strong electrostatic repulsion due to deprotonation (Tülp et al., 2009). At the quadrant of high pK<sub>a</sub> and low Log K<sub>ow</sub>, an intermediate sorption on the organic substrata was observed for caffeine and sulfamethoxazole. In this study, no compounds falling into the low pK<sub>a</sub> and low Log K<sub>ow</sub> quadrant were investigated. We speculate based on our results, that even lower sorption is to be expected for compounds in this quadrant on our selected substrata.

Inorganic substrata mineral wool and pumice generally exhibited much lower sorption and slower sorption kinetics towards the studied micropollutants. Mineral wool is a non-reactive neutral material. Therefore, unlike wood fibre and coconut fibre, mineral wool has no extensive net negative surface charge. Furthermore, mineral wool has the lowest surface area among all the substrata (Table 2A). These properties together explain the low sorption (%) of the micropollutants. Similar to mineral wool, pumice is also a neutral material containing less than 1% organic matter. Thus, it showed minimal sorption affinity to most of the studied compounds during the initial contact time. Caffeine is a notable exception. We speculate that caffeine's low molecular mass allowed high mass transfer into pumice's large number of pores.

Some limitations to this study are apparent, and limit a complete mechanistic interpretation due to lack of statistical significance in some kinetic and sorption equilibrium data. In order to obtain mass balances and insights in reversibility of ad- and desorption, we suggest to identify

suitable elution agents for these novel substrata to conduct desorption experiments. Furthermore, this study did not specifically investigate the effect of phosphate buffer on sorption. Previous studies report that phosphate sorption is inhibited on adsorption sites due to surface complexation with metals and repulsion of phosphate ions by negatively charged organic matter (Hunt et al., 2007). However, specific adsorption of phosphate could also occur by ligand exchange with surface hydroxyl groups. Also, cation bridges may also increase phosphate sorption sites and may result in competitive interaction for sorption sites between phosphate and micropollutants (Hunt et al., 2007). Further study is required to get more insights into this.

### *Applying hydroponic substrata in CWs treating wastewater*

Selection of suitable substrata is important when designing CWs like systems. Substrata with a high sorption capacity efficiently remove a variety of pollutants, including micropollutants. Generally, higher K<sub>d</sub> values for the six selected compounds were obtained on the organic substrata (Table 3). These values were compared with the available literature data for natural sorbents, like soil (Table SI8). K<sub>d</sub> values of wood fibre and coconut fibre for the selected compounds were mostly 5-20 times higher than that of soil. High K<sub>d</sub> values suggest a larger partitioning of the micropollutants onto the organic matter. When compounds can accumulate on- and into the substrata, they would have a strongly retarded mobility in the solid-liquid matrix of a filter bed (Barron et al., 2009; Xu et al., 2009). This characteristic of the organic substrata illustrates the suitability of organic hydroponic substrata for use in wastewater treatment technologies. For example, CWs could be amended with such a substrata filter to mitigate the emissions of micropollutants to the environment.

Wood fibre is particularly suited for application in CWs. To illustrate this, we compared two generic CWs with either wood fibre or soil as a filter bed and determined the theoretical removal of carbamazepine and trimethoprim from wastewater (Table SI9; Table SI10). These compounds were selected considering carbamazepine's recalcitrance in conventional wastewater treatment plants and presence of trimethoprim residues in wastewater may lead to the development of antibiotic resistance, affecting human health and environment.

Based on the calculations, hydroponic substrata like wood fibre have a great potential to remove micropollutants by sorption, which could reduce the size of a CW. A wetland constructed with wood fibre requires significantly less surface area to achieve the same micropollutant removal as a wetland using soil. A wood fibre wetland requires only 35% and 66% of the surface area of a traditional CW to remove trimethoprim and carbamazepine respectively from the wastewater (SLA7; Table SI9; Table SI10). It is important to mention that under natural conditions, there are multiple compounds competing for available sorption sites on a substratum. Also, additional removal mechanisms, like biodegradation and phytodegradation would play a role in the removal of these compounds. Therefore, it is recommended to study the sorption behaviour of the substrata and micropollutants at trace concentrations taking into account the natural conditions that may restrict sorption, and other additional removal mechanisms that may support micropollutant removal. Additionally, to optimize the treatment performance of the envisioned CWs, further studies on the operational parameters, for example, hydraulic loading rate, hydraulic retention time and plant types, are recommended (Rahman et al., 2020).

## Conclusion

Our study aimed at determining the suitability of four hydroponic substrata for use in wastewater treatment. We thus determined the sorption behaviour of these hydroponic substrata towards six micropollutants frequently detected in wastewater, namely trimethoprim, caffeine, carbamazepine, sulfamethoxazole, ibuprofen and naproxen. The

Freundlich isotherm is the most appropriate model to describe the experimental sorption data for these heterogeneous sorbents. The sorption appears to be dominated by attractive and repulsive forces between micropollutants and substrata and depends on physico-chemical characteristics, such as pKa and hydrophobicity of both components. Organic substrata wood fibre and coconut fibre had significantly higher sorption affinity to the investigated micropollutants than inorganic substrata mineral wool and pumice. Therefore, organic matter was the most important factor governing sorption in this study. The rapid and high sorption of recalcitrant carbamazepine onto wood fibre and coconut fibre was observed. The estimated  $K_d$  values of wood fibre and coconut fibre were 5-20 times higher than of soil, suggesting the suitability of these hydroponic substrata to be employed in CWs to efficiently remove micropollutants and to reduce CW footprints.

## Consent to Publish

This work is original and has not been published elsewhere.

## 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.

## CRedit authorship contribution statement

**Elackiya Sithamparamanathan:** Conceptualization, Methodology, Formal analysis, Writing - original draft, Writing - review & editing, Visualization. **Katarzyna Kujawa-Roeleveld:** Conceptualization, Methodology, Writing - review & editing, Visualization, Supervision. **Jill A.R. Soedarso:** Methodology, Formal analysis, Writing - review & editing. **Nora B. Sutton:** Conceptualization, Writing - review & editing, Visualization, Supervision. **Katja Grölle:** Methodology, Writing - review & editing. **Harry Bruning:** Methodology, Writing - review & editing. **Huib H.M. Rijnaarts:** Conceptualization, Writing - review & editing, Supervision.

## Acknowledgments

This research is a part of the LOTUS-HR project which is an Indian-Dutch consortium, funded by the TTW (Toegepaste en Technische Wetenschappen)-NWO (Netherlands Organisation for Scientific Research), the Netherlands. The authors appreciate the support provided by the LOTUS-HR project partners. The authors would also like to thank Livio Carlucci from Environmental Technology department, Wageningen University and Research, and Jelmer Dijkstra from Wetsus, the Netherlands for their assistance in the laboratory analysis.

## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.envadv.2021.100049](https://doi.org/10.1016/j.envadv.2021.100049).

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