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Research article

Characterization of unconventional sand-based substrates for adsorption of micropollutants in nature-based systems

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ABSTRACT

The focus of this study is the characterization of unconventional sand-based substrates used in our previous project EmiSûre, (Interreg Greater Region (German federal states Rhineland-Palatinate and Saarland, the Grand Duchy of Luxembourg, regions Wallonia and Lorraine from Belgium and France, respectively), 2017–2021). The project aimed to develop and test alternative, nature-based technologies for the elimination of micropollutants (MPs) from municipal wastewater. For the characterization, two approaches were chosen. In the first approach, adsorption kinetics with a single compound allowed a perception of the adsorption capacity of the studied substrates compared to conventional substrates (granular activated carbons). This knowledge was completed by the second approach: an implementation of the studied substrates in packed-bed columns, which treated a mixture of 27 MPs in tap water for 10 months. Additionally, all three substrates (bentonite sand, sand with 15% activated biochar and sand with 15% zeolite) were characterized for physical and chemical properties, and the microbial potential of the activated and non-activated biochar was examined. From the studies, it is clear that the sand with an admixture of activated biochar is the most efficient sorbent in terms of single compound adsorption in batch (dye) and adsorption of 27 MPs on packed-bed columns. In contrast to the two other substrates, it shows long-term stable removal efficiencies. In the packed-bed columns, 18 out of 27 compounds were removed on average with high efficiency (80–99%), which is impressive, if we consider the variety of the compounds examined (pharmaceuticals, herbicides, pesticides, etc.) and their removal in conventional treatments. Additionally, adsorption models were created for the experimental data of all compounds adsorbed on the substrate with an admixture of activated biochar resulting in the best fit with the combined Langmuir-Freundlich model. These satisfying results suggest the application of the sand-based substrate with an admixture of activated biochar for further research and possibly upscale installations with the aim to offer and prove a reasonable and efficient alternative for MPs elimination from municipal wastewater.

1. Introduction

As a result of growing population, globalization, and anthropogenic influences, the number of pollutants in water and consequently also in wastewater has grown. It is well known that conventional municipal wastewater treatment plants (WWTPs) are not designed for the removal of so-called micropollutants (MPs) (Ternes et al., 2002). These compounds are then discharged into the aquatic environment, where they are confronted with living organisms with possible negative consequences (dos Santos et al., 2021), and therefore a necessity to establish an additional treatment step needs to be considered. Among commonly known technologies for advanced treatment are membrane filtration (Zhou and Smith, 2001), advanced oxidation processes (Deng and Zhao, 2015), or constructed wetlands (CWs). A deeper investigation of the behavior of MPs in CWs with sub-surface flow configuration has previously been carried out (EmiSûre project, Interreg Greater Region (German federal states Rhineland-Palatinate and Saarland, the Grand Duchy of Luxembourg, regions Wallonia and Lorraine from Belgium and France, respectively), 2017–2021). Based on the promising results of this project, a further aim has been set up in the current research to determine the quantification of MPs' removal mechanisms, typically characterized by adsorption, phyto- and bioremediation (Lyu et al., 2018). The research started with a focus on phytoremediation (Brunhoferova et al., 2021) followed immediately by adsorption, which, contrary to the other mechanisms, has not yet been widely addressed concerning the application of unconventional substrates (i.e. activated

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biochar). Adsorption is a technology widely used for water and wastewater purification, owing to its easy applicability, efficiency, and financial availability. It is suitable for removal of a broad variety of soluble, insoluble, biodegradable, and, in general, persistent particles and it enables us to gain knowledge of different scales of the issue – from lab-scale to industrial applications in full scale.

This work aims to describe the adsorption process from two points of view; in batch experiments (kinetics with a dye) and continuous experiments (adsorption of 27 MPs on packed-bed columns). Additionally, these substrates are characterized mainly by their adsorption efficiency, followed by physical and chemical characterization and described by sorption capacities concerning common concentration ranges of MPs in real wastewater (ng/g - μg/g). The compounds studied were selected in the EmiSûre project based on various aspects: pharmaceuticals, due to their high excretion; cytostatics, due to their potential eco-toxicity; and also compounds under observation in agreement with European Commission Strategy and KomS (Kompetenzzentrum Spurenstoffe) guidelines.

For the adsorption kinetics, a single-compound approach was chosen (adsorption of one compound – dye Basovit Red 400 E) to characterize the adsorption capacity of each substrate mixture (sand-based soils) as well as commercially available granulated and regenerated activated carbons (GAC & RAC). These were chosen as comparative substrates for an evaluation of the method and to compare the different efficiencies of adsorption. Activated carbons were used as reference substrates thanks to their proven excellent adsorption capacity (Piai et al., 2020; Rattier et al., 2012) and broad usage in water treatment for over 80 years (Ali and Gupta, 2007). For substrate sterilization, it was assumed that the only removal mechanism responsible for the elimination of MPs from the liquid solution is adsorption. As the soils considered had been applied at a pilot-scale level, an entire characterization (BET (Brunauer, Emmett and Teller) specific surface area, pH, median pore diameter, porosity, mineral composition) was performed. Due to the potential use of the packed-bed columns in industry, their parameters, such as column size, dimensions, hydraulic conditions, etc., were carefully chosen and others: mass transfer zone, breakpoint, and saturation were obtained.

Sand-based substrates have already shown their successful application in sub-surface treatment wetlands and similar systems (Janzen et al., 2009). For the substrates used in our investigations, applied media sand was enriched by an admixture of biochar and zeolite. Biochar used in this study was produced from a variety of lignocellulose biomasses, not just solid wood, and was pyrolyzed under 600–800 °C and additionally activated by anaerobic fermentation. These steps imparted the biochar with advantageous features for the adsorption process, such as high porosity, large ion exchange capacity, and great stability against biodegradation. Zeolite is a substrate commonly used for different kinds of adsorption (Wang and Peng, 2010) e.g. application in drinking water purification.

The adsorbate in the performed batch experiments was a dye Basovit Red 400 E, whereas in the packed-bed columns it was a mixture of 27 previously investigated MPs, consisting of pharmaceuticals, herbicides, pesticides, corrosion inhibitors, and fluorosurfactants. However, it is important to mention that competitive group adsorption of the 27 compounds was not studied in this case, but adsorption of every single compound was separately observed, even though all the compounds were present together in one mixture. Besides the assessment of the removal rate, three well-known adsorption isotherm models (Freundlich, Langmuir-Freundlich, and Langmuir) were applied to the adsorption data to evaluate the adsorption phenomena. To this end, adsorption coefficients describing the adsorption characteristics of the studied compound were obtained. The results were demonstrated on one compound for each group of MPs (atenolol for beta-blockers, cyclophosphamide for cytostatics, benzotriazole for corrosion inhibitors, diclofenac for persistent compounds, and mecoprop (MCPP) for herbicides). These compounds were chosen for simplification and illustration.

A two-pronged approach was chosen. In the first approach, adsorption kinetics with a single compound, allowed us to gain the perception of the adsorption capacity of studied substrates compared to conventionally used substrates (granular activated carbons). This knowledge was then completed by the implementation of the substrates in packed-bed columns, which treated a mixture of 27 MPs in tap water for 10 months. The combination of these two approaches gave a complex overview of the role of the adsorption process in the removal of MPs with help of CWs from wastewater and contribute to the comprehensive characterization of the substrates studied. The significance of this research lies also in the fact that adsorption of MPs on different soil media in packed-bed columns in continuous mode can be used as a single wastewater treatment step (Meinel et al., 2015; Ronda et al., 2018).

2. Methodology and materials

2.1. Experiments

2.1.1. Adsorption kinetics (batch experiments)

The selected substrates were: 100% sand (A), 85% sand and 15% activated (C) and non-activated biochar, 85% sand and 15% zeolite (E) purchased at PalaTerra, Hengstbacherhof/Germany. As a complementary method used for determining the adsorption capacity of selected substrates, the adsorption kinetics experiment with one compound as a proxy (dye Basovit red 400 E, BASF) as an adsorbate was carried out. Experiments were performed in brown glass bottles, to avoid any possible photodegradation on a horizontal shaking table (Thermo Scientific) with a shaking intensity of 120 RPM. In all kinetic experiments, the amount of adsorbent was added as a suspension in the solution containing adsorbate at a known concentration (50 mg/l). The dye concentration in the soluble fraction was measured spectrometrically (DR 3900 VIS Spectral Photometer with RFID* technology, Hach Lange) with extinction determination. A calibration curve (R^2 = 0,99,979) is presented in Fig. 1 which clearly shows that the concentration and the extinction are fitting to linear regression, a condition necessary to fulfill the Beer-Lambert law. Within the relation given it is possible to calculate the remaining dye concentration in the liquid solution and consequently the amount of adsorbed dye. The soils used for the adsorption experiments were sterilized by heating up to 105 °C for 6 h to avoid interference of microorganisms in the adsorption process. The soils were also sieved in a sieving tower allowing just particles bigger than 0.180 mm to be present in the final mixture and so avoiding the presence of dust. Sieved soils were then stored in a cold, closed dark place. To compare

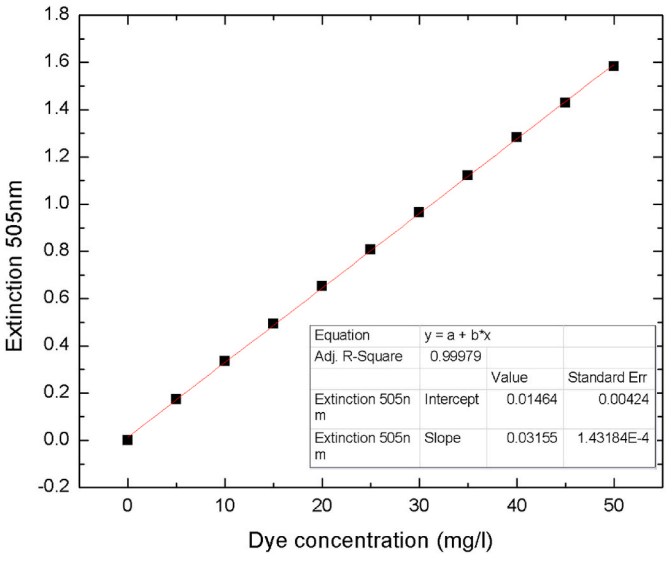

Fig. 1. Calibration curve of Basovit redE with conc. 50 mg/l.

studied sand-based substrates with well-known materials and to evaluate the reliability of the method, experiments with GAC (CarboTech AC GmbH) and RAC (NRS Carbon 0.5–2.5 type, Cabot Norit Nederland B.V.) were carried out. The physical properties of these two substrates are available in the supplementary data (Tab. S.2.1.-2.).

In the first experiment, the selected amount of GAC, as well as RAC, is 1 g/l (Suresh et al., 2011) which is left as a suspension in the solution. The 2 ml samples were taken in 20-min intervals at the beginning of the experiment, presuming that the adsorption would be most rapid at the beginning. After ca. 2 h of the experiment, the sampling period was prolonged to hourly units. The experiment was ended after the complete adsorption of the dye and reaching equilibrium. The samples were filtered through 0.45 μm filter and the absorbance was measured in the photospectrometer at the characteristic extinction value of the dye solution at 505 nm.

Next, the selected substrates A, C, E, and sand +15% non-activated biochar were studied. The non-activated biochar was included to establish the difference in terms of adsorption capacity between activated and non-activated biochar. The concentration of these substrates is 50 g/l. Such a high concentration of the substrates was chosen based on the measured adsorption capacity of the substrates during pre-experiments. As the adsorption rate was not as high as for GAC and RAC, the samples were taken on a daily, later weekly basis, in order to reach the equilibrium. To confirm the sterilization process and thus to exclude the biological potential of activated and non-activated biochar, experiments with the addition of specific nutrients were carried out. It was supposed that the bacteria, which could be present in the activated biochar, could be nourished by sources of nitrogen and carbon. With the addition of nutrients followed by the growth of bacteria, the elimination of the dye from the solution could be enhanced, because the dye is considered a potential source of carbon. In this kind of experiment, two types of nutrients (Carl Roth) were used, the first one is the Hoagland solution (components for preparation are showed in Table 1), used in our phytoremediation experiment (Brunhoferova et al., 2021). As Table 1 shows, other inorganic compounds were also present in the solution, which could be consumed by the bacteria as nourishment. The second type was a mixture of nutrients used for the formulation of synthetic wastewater according to the standard OECD 303 A (chemical components are showed in Table 2), which was used in our previous project EmiSûre. Concentrations of the used chemicals are available in supplementary data (Tab. S.1.1.-2.). The concentration of the dye and the substrates remained the same (50 mg/l and 50 g/l respectively). The 2 ml samples were taken each couple of hours, as it was presumed that the adsorption on these substrates is not very rapid. The experiments were terminated after 650 h.

Lastly, the pure kinetic experiment of the substrates (50 g/l) and the dye (50 mg/l) was performed. The goal of this experiment was to reach an adsorption equilibrium and, based on the equilibrium data, determine adsorption kinetic orders and isotherm models.

2.1.2. Packed-bed columns

The soils were packed in 3 identical plexiglass columns (height of the column 1 m, inner diameter 0.04 m, Europlex), resulting in a height of a soil bed 0.8 m and height of a gravel bed 0.08 m used as drainage. The scheme of the installation is illustrated in Fig. 2.

Table 1
Compounds for the preparation of the Hoagland solution.

Compound	CAS number
KH_2PO_4	7778-77-0
KNO_3	7757-79-1
$CaCl_2$ $2H_2O$	10,035-04-8
$Mg(SO_4)$ $7H_2O$	10,034-99-8
$NaHCO_3$	144-55-8

Table 2
Compounds for the preparation of the synthetic wastewater.

Compound	CAS number
Peptone	91,079-38-8
Meat extract	68,990-09-0
Urea	57-13-6
Potassium dihydrogen phosphate	7778-77-0

The columns were wrapped in aluminum foil to exclude the contribution of photodegradation. Next, the columns were fed from the top to the bottom with a mixture of MPs in tap water with the help of a peristaltic pump (type 530 S/R, provided by Watson-Marlow NV) whereas the influent mixture was stored in a cooling tank (4 °C, continuous stirring, Lely Center). The tap water was spiked with the mixture of 27 selected MPs (Table 3) in the range of concentrations 1–5 μg/l (Techlab, purity >99.99%). The comprehensive list presented in Table 3 relates the use of each compound with the selection criteria, identifying those of interest because of their legal obligation (i.e. clarithromycin and ciprofloxacin), consumption (i.e. atenolol), recalcitrant aspect (i.e. carbendazim) or toxicity potential (i.e. fluorosurfactants).

The first idea had been to operate the installation under continuous flow to see how this operation would influence the adsorption capacity of the studied substrates. However, the infiltration capacity decreased under continuous flow, therefore it was required to switch to an intermittent operation. This step was advantageous in terms of the hydraulic conditions. The infiltration conditions became steady with a watering cycle of 15 ml/min 3 times per day, where one cycle had a 30 min duration. After passing the columns, the mixture was then led to sampling tanks, from which the overflow was connected to the sewer. The columns were provided with the overflow configuration in case the system became clogged. The columns were operated under the conditions described for 10 months. Despite the adapted conditions, a regular backwash of columns A and C (2–3x per week) was needed. However, regular backwashing helped to regulate the thickness of generated biofilm, therefore it helped to avoid possibly occurring bioremediative processes (Fundneider et al., 2021). Samples were taken once per month and an analysis of nutrient content (Hach Lange cuvette text box), oxidation-reduction potential, conductivity, pH, and temperature was performed in-house (multi-portable parameter meters by Xylem Analytics Germany Sales GmbH & Co. KG). The samples were filtered with a 0.45 μm filter, frozen and prepared for the external analysis of MPs content.

2.1.3. Analytical methods

Concentrations of macronutrients in the adsorption kinetics batch, as well as in the packed-columns samples were measured in-house. For the kinetic, COD and TN were frequently measured, for the packed-bed columns, COD, TN, NO_3^- and NH_4^+ were measured. Further readings were taken for the pH value, the concentration of dissolved oxygen (DO), conductivity, temperature, and oxidation-reduction potential. These values are available in the supplementary data (section S.6). The samples of the MPs' content were filtered through a 0.45 μm filter and frozen at −20 °C. The concentration of MPs was analyzed externally at the Luxembourg Institute of Science and Technology (LIST). The MP samples were re-filtered and diluted with water/methanol 90/10, as preconditioning was not needed and then immediately analyzed by Liquid Chromatography (1260 Series, Agilent, Santa Clara USA) coupled to triple-quadrupole Mass Spectrometry (QTRAP 4500, AB Sciex, Framingham USA) according to the procedure described previously (Brunhoferova et al., 2021).

2.2. Calculations

2.2.1. Adsorption kinetics

For the kinetic experiments, rate constants were determined based

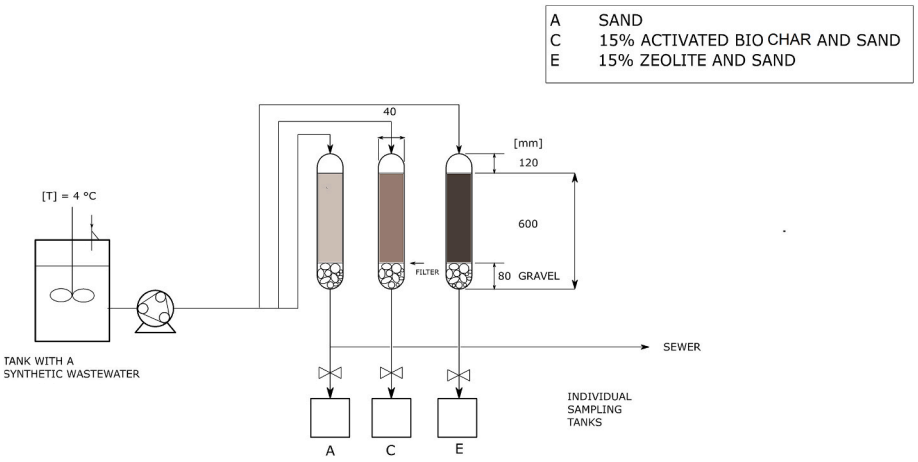

Fig. 2. Packed-bed adsorption columns installation.

Table 3
Selected MPs.

Application	Compound	CAS number	Therapeutic Group/Use	Selection criteria
Pharmaceuticals and metabolites	Atenolol	29,122-68-7	Beta Blocker	Highly prescribed.
	Bezafibrate	41,859-67-0	Lipid regulator	Highly biodegradable.
	Carbamazepine	298-46-4	Psychiatric drug	Mainly excreted as a hydroxylated metabolite. Control compound.
	Clarithromycin	81,103-11-9	Antibiotic	Present in the Watch List (EU) 2015/495 of March 20, 2015)
	Ciprofloxacin	85,721-33-1	Antibiotic	Present in the Watch List (EU) 2018/840
	Cyclophosphamide	50-18-0	Cytostatic	High eco-toxicity impact.
	Diclofenac	15,307-86-5	Analgesic/anti-inflammatories	Present in Directive (2013)/39/EU.
	Erythromycin A	114-07-8	Antibiotic	Present in the Watch List (EU) 2015/495 of March 20, 2015
	Ketoprofen	22,071-15-4	Analgesic/anti-inflammatories	Highly prescribed. Found in surface waters.
	Lidocaine	137-58-6	Anaesthetic	Highly prescribed. Found in surface waters.
	Metoprolol	51,384-51-1	Beta Blocker	Highly prescribed.
	Propranolol	525-66-6	Beta Blocker	Highly prescribed. Found in concentrations above EQS.
	N4-acetylsulfamethoxazole	21,312-10-7	Metabolite of Sulfamethoxazole	For mass balance.
	Sulfamethoxazole	723-46-6	Antibiotic	Old antibiotic, still in use. Scientific data are available.
Pesticides/Herbicides	Carbendazim	10,605-21-7	Fungicide	Very persistent.
	DEET	134-62-3	Insect repellent	Very persistent.
	Diuron	330-54-1	Herbicide	Present in Directive (2018)/105/E
	Isoproturon	34,123-59-6	Herbicide	Present in Directive (2018)/105/E
	Terbutryn	886-50-0	Herbicide	Very persistent.
	Mecoprop (MCPP)	7085-19-0	Herbicide	Found in surface waters.
	Tolyltriazole	29,385-43-1	Fertilizer	Highly used. Most abundant in WWTPs discharging in the Sûre river.
	Glyphosate	1071-83-6	Herbicide	Under discussion.
	Aminomethylphosphonic acid (AMPA)	1066-51-9	Degradation product	Under discussion.
Fluorosurfactants	Perfluorooctanesulfonic acid (PFOS)	1763-23-1	Surfactant	Priority compound.
	Perfluorooctanoic acid (PFOA)	335-67-1	Surfactant	Of political concern.
Corrosion inhibitor	Benzotriazole	95-14-7	Corrosion inhibitor/ Antiviral	Highly used. Most abundant in WWTPs discharging in the Sûre river.
Flame retardant	Tris (2-chloroisopropyl)phosphate (TCPP)	13,674-84-5	Flame retardant	Highly used. Most abundant in WWTPs discharging in the Sûre river.

on two established kinetic models; the pseudo-first-order was calculated from Eq. (1), where the integrated form of the equation is presented (Mestre et al., 2007):

$$\log(q_e - q_t) = \log\left(q_e - \left(\frac{k_1}{2.303}\right)t\right) \quad (1)$$

where q_e and q_t are the adsorbate uptake at equilibrium and at the time t

and k_1 is the pseudo-first-order rate constant. The pseudo-first-order rate constant can be obtained from the slope of the plot log ($q_e - q_t$) vs. t.

The pseudo-second-order was calculated from Eq. (2):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t \quad (2)$$

From the plot t/q_t vs. t the pseudo-second-order rate constant, k_2. can be estimated.

The adsorbed amount of dye per gram of adsorbent was calculated from Eqs. (3) and (4):

$$q_e = \frac{V(C_0 - C_e)}{M} \quad (3)$$

for batch experiments (De Carvalho et al., 2011) and

$$q_e = \frac{(C_0 - C_e)}{M} \quad (4)$$

For packed-bed experiments (Samarghandi et al., 2014), where q_e amount adsorbed of dye per gram of adsorbent, V is the volume of the solution, M is the amount of the adsorbent used and c_0 and c_e are the concentrations of the dye in the initial solution and at equilibrium.

The removal rate was calculated from Eq. (5):

$$R.r.\ (\%) = \frac{c_0 - c_e}{c_0} * 100\ \% \quad (5)$$

2.2.2. Packed-bed columns

For the optimal conditions of the adsorption in packed-bed columns, empty-bed contact time (EBCT) was calculated (Eq. (6)). As the typical value for the EBCT is 30 min, the parameters have been chosen in a way to come as close as possible to this value (in this case EBCT = 33 min).

$$EBCT = \frac{V_B}{Q_B} \quad (6)$$

where V_B is the volume of the bed and Q_B is the flow rate coming into the bed.

In order to describe the elimination of the MPs by adsorption, three commonly used models of adsorption under stable pH (Jeppu and Clement, 2012) (Langmuir, Langmuir-Freundlich and Freundlich) were created (Eqs. (7)–(9))

$$q_e = K_F T^{1/nF} \quad (7)$$

$$q_e = q_m K_{LF}(T^n) / (1 + K_{LF}(T^n)) \quad (8)$$

$$q_e = (q_m K_L T)/(1 + K_L T) \quad (9)$$

where q_e is the amount of adsorbate adsorbed on the adsorbent at equilibrium, q_m is the maximum adsorption capacity according to Langmuir and Langmuir-Freundlich models, T is reaction time, K_{LF} and K_L are parameters corresponding to adsorption intensity in Langmuir-Freundlich and Langmuir equations respectively, n is a constant corresponding to the heterogeneity of the adsorbent in Langmuir-Freundlich equation and K_F and n_F are constants defining adsorption capacity and intensity in the Freundlich model (Gómez et al., 2019).

The height of the mass transfer zone (MTZ) is calculated according to Eq. (10):

$$Height\ MTZ = h_B * 1 - \frac{q_b}{q_s} \quad (10)$$

where h_B is the height of the bed, q_b is the adsorbed amount in the break point and q_s is the adsorbed amount in the saturation point.

3. Results

3.1. Adsorption kinetics

Results of the comparative experiments among different types of activated carbon are showed in Fig. 3, where the extinction is observed during a reaction time for a given amount of carbon and related to the removal of adsorbent from the liquid fraction. 1 g/l of GAC can adsorb the dye completely in 50 h, whereas RAC requires 170 h (Fig. 3a). Under the same conditions (concentration of the adsorbent and adsorbate) the substrate C - 15% activated biochar, which proved in the past to be the most effective one, showed adsorption of the dye to a maximum of 7% over 400 h (Fig. 3b). The kinetic profiles of these experiments are available in the supplementary data (Tab. S.5.1.-2.).

Kinetic orders are determined for comparative experiments with GAC and RAC resulting in corresponding constants. Unfortunately, even with the high number of substrates studied: 50 g/l, it was not possible to reach the equilibrium and therefore to establish kinetic orders for the dye adsorption on the substrates. The values for k_1 and k_2 are calculated from the slope and intercept log (q_e-q_t) vs. t and t/q_t vs. t respectively applying equations (1)–(4). The values gained are presented in Table 4.

For GAC, the q_e calculated from kinetic models was closer to the experimental value of q_e, therefore it is likely that this reaction took place in the pseudo-first-kinetic order. On the other hand, for RAC, the experimental q_e was closer to the one from the pseudo-second-kinetic order, therefore this reaction was probably pseudo-second-kinetic order (Ho and McKay, 1998; Kusmierek et al., 2020).

The experiments for determining the microbial potential of biochars were carried out with activated and non-activated biochar in three different mixtures: a blank one (without any nutrients), in a nutrient mixture used previously in the lysimeter experiments and in a mixture containing Hoagland solution. These experiments did not confirm any presence of microbes, as no increased dye removal (Fig. 4a and b) was observed due to the presence of sources of C and N. However, decreasing concentrations of COD and TN could be observed, leading to the presumption that the nutrients are adsorbed in the adsorption centers as well. Based on these findings, it seems that the contribution of the microbial potential on the adsorption can be excluded and the appropriateness of the soil sterilization method is confirmed. The adsorption kinetics of the dye are shown in the following figures: activated biochar (c 50 g/l) a) and non-activated biochar (c 50 g/l) b).

Another kinetic experiment indicated that the 15% non-activated biochar showed lower adsorption capacity even at much higher concentrations than 15% activated biochar: the non-activated biochar in concentration 50 g/l reaches 20% removal of the dye, whereas the activated form in the same concentration removed about 50% of the adsorbate. The 15% activated biochar in 5x lower concentration than the one of 15% non-activated biochar still surpassed the non-activated form in terms of the dye removal (removal of the dye 25%). The comparison of adsorption efficiency of 15% activated biochar (10 and 50 g/l) and 15% non-activated biochar is shown in Fig. 5. These experiments demonstrate the better performance of the activated biochar over the non-activated.

The kinetic experiments of studied substrates A, C and E confirm the previous hypothesis: that substrate C (15% AB) has the highest adsorption capacity. This fact is demonstrated by removal of the dye in a total of 84%, followed by 15% zeolite with 57%, and finally by sand, reaching removal of 33% in 234 days. The kinetic profile is shown in Fig. 6. Detailed concentration profiles and the removal rates are available in the supplementary data (Tab. S.5.3.-5.).

3.2. Adsorption on packed-bed columns

3.2.1. General parameters

During the investigation, the operation mode was adapted from continuous to intermittent due to the perceiving clogging. This resulted

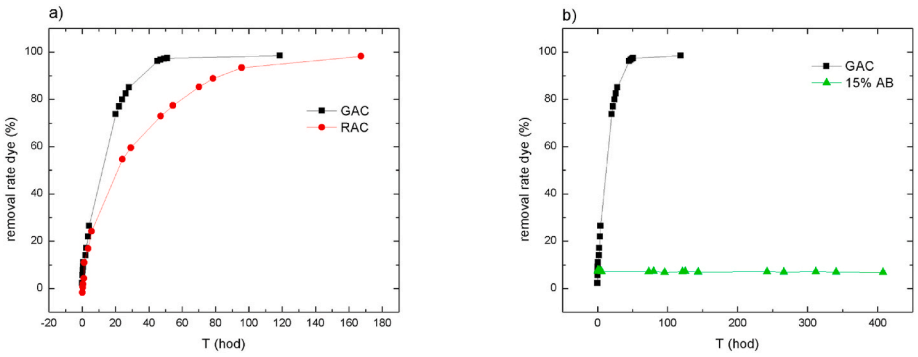

Fig. 3. Comparison of adsorption capacity of GAC and RAC (1 g/l), c dye 50 mg/l (a) and comparison of adsorption capacity of GAC and 15% activated biochar (1 g/l), c dye 50 mg/l (b).

Table 4
Kinetic constants for pseudo-first- and -second-order for substrates GAC and RAC.

adsorbent	pseudo-first-order			pseudo-second-order		
	k_1 (hod^{-1})	R^2	q_e (mg/g)	k_2 (g/mg hod^{-1})	R^2	q_e (mg/g)
GAC	0.00031	0.9854	52.747	0.00248	0.9839	53.476
RAC	6.57E-5	0.9732	43.171	0.00093	0.9799	54.644

to be advantageous, as the EBCT was prolonged and approached values typical for lab-scale constructed wetlands, which were recently investigated in our previous project (EmiSûre, Interreg Greater Region, 2017–2021). This allowed also better estimation of the adsorption's role within the wetlands and a better understanding about the role of unconventional sand-based substrates compared to common used activated carbon materials.

Stable results of effluent general parameters (e.g. pH, electrical conductivity) together with medium-high removal efficiencies of COD (on average 74% for column A, 81% for column C, and 79% for column E) suggest that the system could be efficient for stable removal of MPs (Table 5).

This fact is supported by results of the studied substrates' characterization reported in Table 6, especially for parameters like specific surface area (BET) (A 0,7 m^2/g, E 7,7 m^2/g, and C 19,9 m^2/g) and median pore volume (smallest with 69.08 mm in case of C), which support our previous estimation about the preferred candidacy of substrate C for effective removal of MPs. Other characterization parameters such as bulk density, porosity and others are included in Table 6 while results from the analysis of mineral phase using X-ray are available in the supplementary data (Tab. S4.).

3.2.2. *Removal of micropollutants*

The columns were operated under the previously mentioned conditions for 10 months. Medium-high removal efficiencies of COD (esp. in case of column C) and stable values of pH and electrical conductivity indicate stable conditions for the removal of MPs. In Fig. 7, on the example of atenolol, breakthrough of a compound according to the number of bed volumes and the volume itself is demonstrated. From this figure it is evident that the break point occurred after treatment of approx. 300 l of treated wastewater with the exhaustion after ca 600 l. From the adsorption capacity at break point (when the adsorbate leaves the column effluent (Ali and Gupta, 2007)) and saturation point (further adsorption on the substrate is not possible), the height of the mass transfer zone, i.e. the area with highest mass transfer speed (Patel, 2019) was detected, after 37 cm of the bed height (calculated according to Eq. (10)). These parameters are crucial for further scale-up of industrial packed-bed columns.

In the case of column C, 18 out of 27 compounds were removed on average with high efficiency (80–99%) including compounds known to be well absorbable, e.g. beta-blockers (Kyzas et al., 2015); antibiotics (Dutta and Mala, 2020); corrosion inhibitors (Wang et al., 2019)), but also persistent ones, e.g. diclofenac and lidocaine. Removal efficiency of column C for 27 targeted MPs is shown in Fig. 8. Some compounds, e.g. bezafibrate, carbamazepine, diuron, sulfamethoxazole, were removed with very high removal rates when exposed to vertical sub-surface flow constructed wetlands (above 99%). These compounds are known to be poorly biodegradable (Falås et al., 2016; Fundneider et al., 2021) and their successful removal through adsorption in our experiment confirms that they tend stronger to adsorption. Five compounds were removed on average with medium efficiency (40–80%): AMPA, DEET, glyphosate, MCPP and N-acetyl sulfamethoxazole; followed by compounds removed poorly (0–40%): ciprofloxacin, cyclophosphamide, PFOA, PFOS.

In cases of PFOA and PFOS, negative removal is observed in all types of substrates, confirming evidence that per-fluoroalkyl substances are likely to be desorbed in sand-based materials (Askeland et al., 2020) and

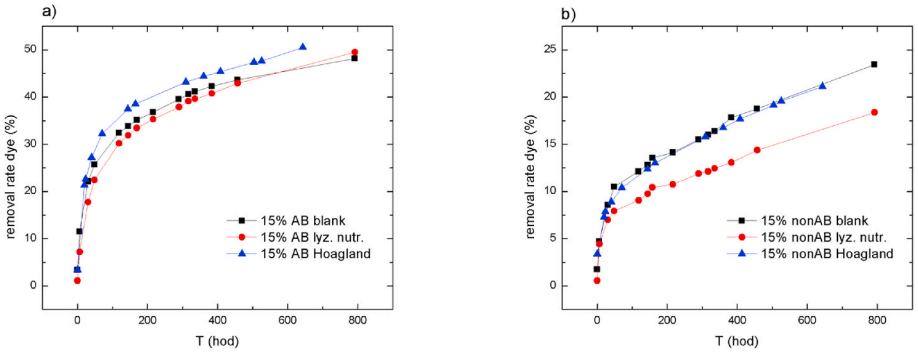

Fig. 4. Adsorption kinetics of the dye (c 50 mg/l) on 15% activated (a) and non-activated (b) biochar (c 50 g/l).

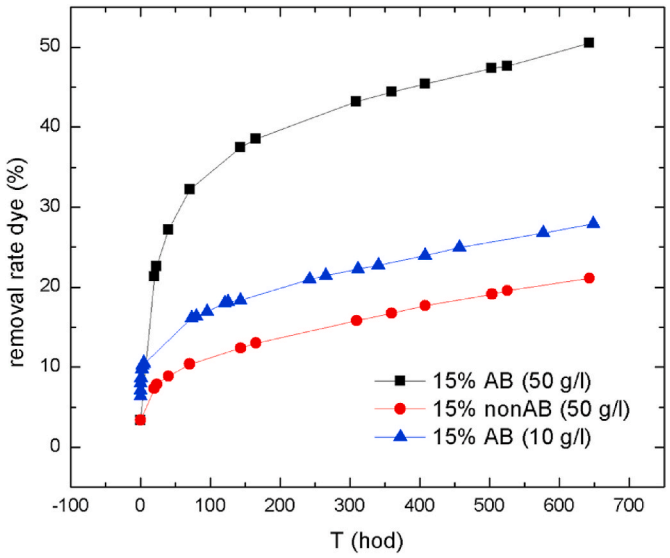

Fig. 5. Comparison of adsorption efficiency of 15% activated biochar (10 and 50 g/l) and 15% non-activated biochar, c dye 50 mg/l.

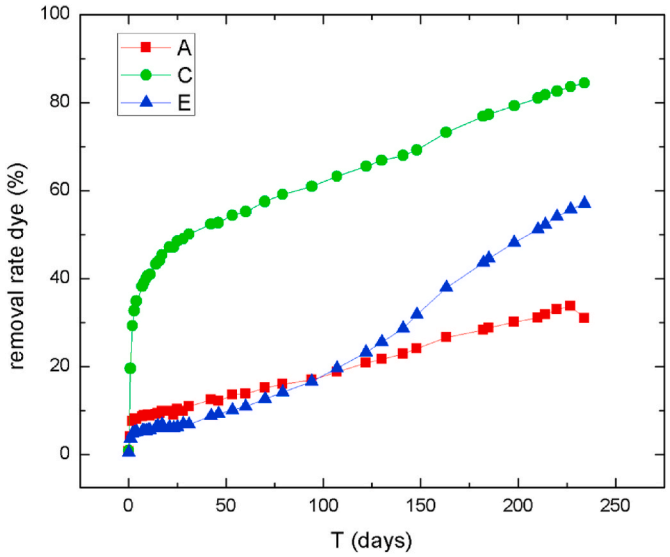

Fig. 6. Comparison of adsorption efficiency of studied sand-based substrates (50 g/l), c dye 50 mg/l.

Table 5
Influent and effluent concentrations of selected parameters ± standard deviation (N = 15).

parameter (N = 15)	influent	effluent A	effluent C	effluent E
COD (mg/l)	76.3 ± 15.8	33.7 ± 9.7	19.6 ± 6.1	32.9 ± 7.9
EC (μS/cm)	252 ± 17.5	408 ± 51.4	364 ± 44.7	395 ± 47.4
pH (mg/l)	8.25 ± 0.3	8 ± 0.3	8.16 ± 0.3	8.02 ± 0.2
E (mV)	235 ± 29.1	221 ± 29.3	229 ± 29.8	222 ± 29.6

released in the water effluent. In the case of ciprofloxacin, the analytical stability of this compound is rather poor in the influent, therefore to determine the effluent concentrations is complicated. Low and later negative elimination rates for AMPA are probably due to the fact that AMPA (a degradation product of glyphosate) tends to retransform back to its parent compound (Aparicio et al., 2013; Wang et al., 2016). Cyclophosphamide, DEET and MCPP show decreasing elimination tendency with time, suggesting that these compounds are saturated onto

Table 6
Results of characterization parameters of substrates A, C, and E.

Parameter	substrate A	substrate C	substrate E
BET (m^2/g)	0.65	19.89	7.74
pH	8.1	8.2	7.9
Bulk density by Helium pycnometer (g/cm^3)	2.73	2.62	2.59
Median pore diameter (Vol) (mm)	104.01	69.08	112.14
Bulk density by mercury intrusion porosimetry (g/cm^3)	0.65	0.68	0.83
Apparent (Skeletal) density (g/cm^3)	2.34	2.2	2.18
Porosity (Vol. %)	72.16	68.91	61.72
Cu (mg/kg)	83	84	60

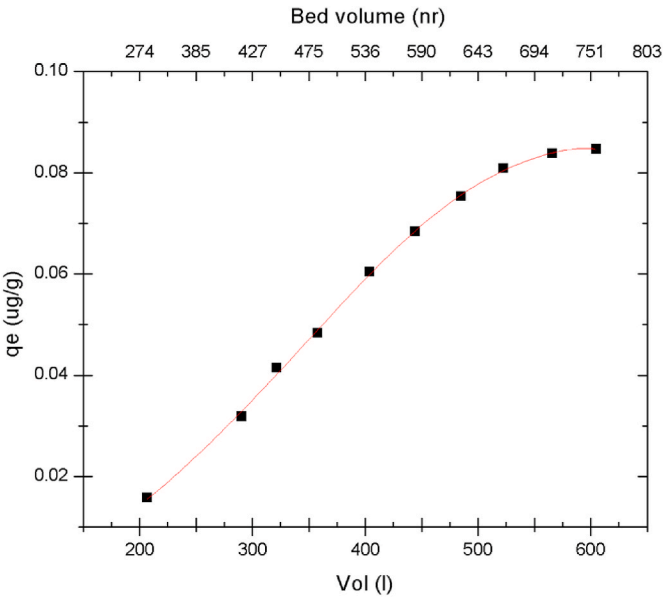

Fig. 7. Breakthrough curve of atenolol.

the substrate. The concentration profiles of the studied compounds are available in the supplementary data (Tab. S.7.). Interestingly, the addition of zeolite does not improve adsorption efficiency of the sand-based material, even though BET surface area of the substrate E is almost 12x higher and zeolite belongs to persuasive adsorbent materials. This trend was observed during our previous experiments with sand-based constructed wetlands, where the addition of zeolite did not result in higher adsorption efficiency of the substrate. Also, columns with substrates A and C are operated under similar hydraulic conditions (regular backwash 2–3x per week), whereas columns with the zeolite substrate never showed any clogging during the operation, therefore no backwash was needed. Despite these facts, when the average removal rate is compared (Fig. 9), substrate C results, with an extensive lead, in being the most efficient adsorbent among substrates used for elimination of MPs from tap water. This is probably owing to the highest BET surface area and lowest median pore diameter, which could result in better retention of the MPs in the substrate (Xiao et al., 2013; Yu et al., 2020).

3.2.3. Adsorption isotherms

For almost all of the compounds adsorbed on the substrate C, models of three adsorption isotherms (Freundlich, Langmuir-Freundlich and Langmuir) were created. The models were not created for AMPA, ciprofloxacin, glyphosate, PFOA, PFOS and Sulfamethoxazole-Acetyl because of concentration biases caused by analytical uncertainties, desorption events and occurring retransformation of some of the compounds. Table 7 shows adsorption parameters calculated according to

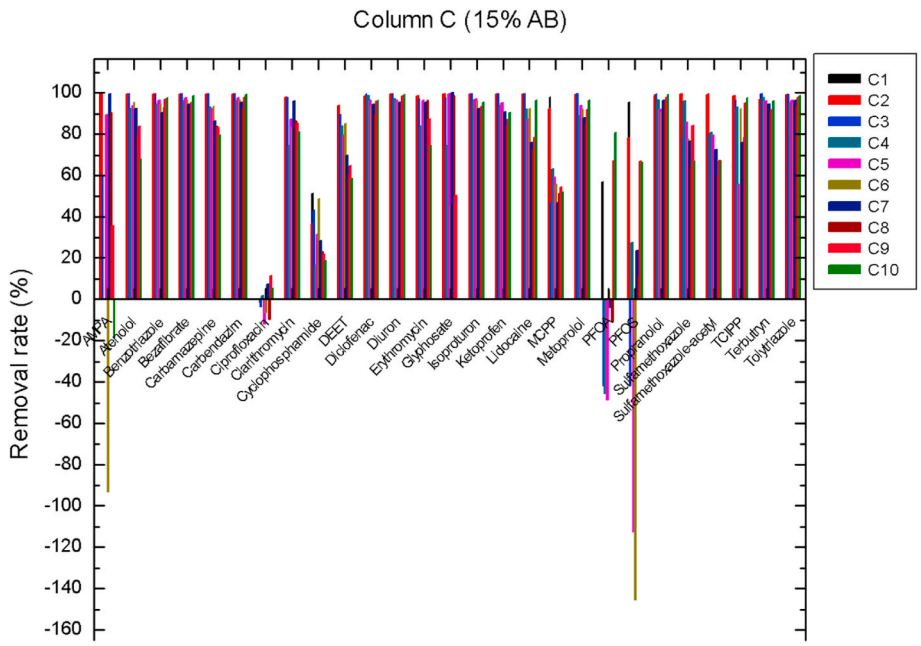

Fig. 8. Removal efficiency of column C for 27 targeted MPs, C1 – 10 are campaigns measured with an interval of one month.

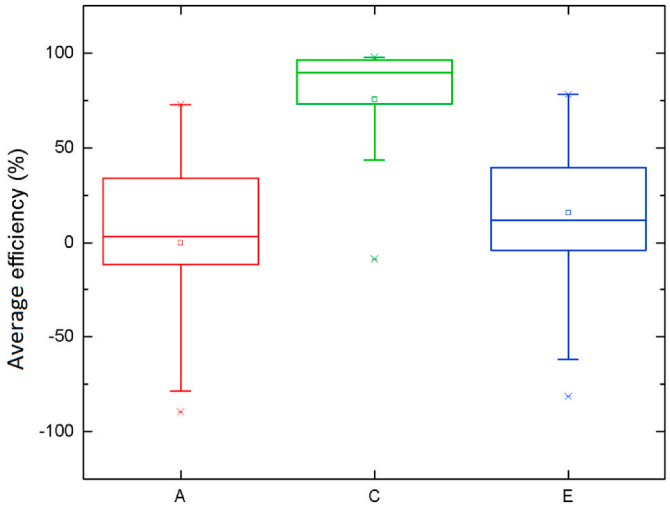

Fig. 9. Comparison of average removal rates of the studied substrates considering MPs removal from tap water.

equations (7)–(9) for a representative key member from the groups studied: atenolol for beta-blockers, cyclophosphamide for cytostatic, benzotriazole for corrosion inhibitors, diclofenac for persistent compounds and MCPP for herbicides. The parameters for all other compounds are shown in the supplementary data (Tab. S.8.).

In most of the cases, the adsorption corresponds to the Langmuir-Freundlich model, except for the antibiotics. These compounds normally fit better into the Langmuir model, e.g. in the case of sulfamethoxazole (Xu et al., 2021) or ciprofloxacin (Dutta and Mala, 2020). The Freundlich isotherm is empirical and it is suitable for multi-layer adsorption, whereas the Langmuir isotherm is a theoretical construct and accords better with monolayer adsorption (Ayawei et al., 2017; Kusmierek et al., 2020). A combination of both constitutes results in the Langmuir-Freundlich model which considers the heterogeneity of the solid surface and was the most suitable model for the removal of emerging contaminants in previous studies (Álvarez et al., 2015). This is also the case within this study, due to several factors: 1. the values of the modelled q_m parameter are closest to the experimental values of q_e of the demonstrated compounds (Chen, 2015); 2. the correlation factor R^2 is the highest for the Langmuir-Freundlich model (Mestre et al., 2007); and 3. the values of the intensity parameter n are highest in case of Langmuir-Freundlich isotherm model, suggesting that the adsorption described with this model is the strongest (Adane et al., 2015). Fig. 10 presents experimental adsorption data of atenolol and cyclophosphamide and their comparison with the previously mentioned adsorption models. The best fit of the Langmuir-Freundlich model to the experimental data in both cases confirms the discussion above. The results described help to complete the characterization of these unconventional substrates, as their adsorption capacities are substantially lower (tenths of μg/g) than adsorption capacities of other non-carbon homogenous materials, e.g. sand or zeolite, in units of μg/g (Zhang et al., 2018), or well-known sorbents, e.g. activated carbons, in mg/g.

Table 7
Adsorption coefficients of Freundlich, Langmuir-Freundlich and Langmuir isotherms for stated compounds.

Compound	Freundlich			Langmuir-Freundlich				Langmuir		
	K_F	n_F	R^{2a}	q_m[a]	K_{LF}	n	R^2	q_m[a]	K_L	R^2
atenolol	0.0014	1.3572	0.9313	0.10	8.9E-05	1.9416	0.9752	0.22	0.00234	0.9507
cyclophosphamide	6.6E-04	1.3508	0.9121	0.047	3.9E-05	2.1335	0.9633	0.11	0.0023	0.9325
benzotriazole	5.0E-04	1.0518	0.9561	0.14	7.0E-05	1.8573	0.9740	0.9	4.6E-04	0.9591
diclofenac	2.1E-04	0.9668	0.9650	0.15	2.1E-04	1.4693	0.9653	0.17	1.5E-06	0.9643
MCPP	2.2E-04	1.3293	0.9671	0.025	8.7E-04	1.3315	0.9752	0.41	0.0021	0.9748

[a] μg/g.

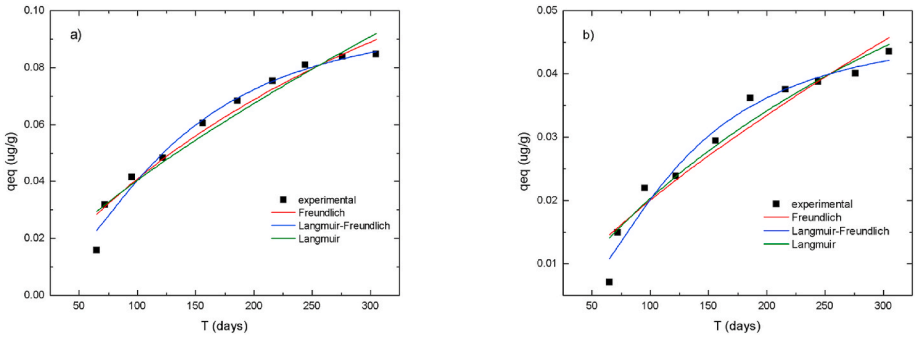

Fig. 10. Comparison of experimental adsorption data and Freundlich, Langmuir-Freundlich and Langmuir models for atenolol (a)) and cyclophosphamide (b)).

4. Conclusions

The present study has compared the adsorption capacity of the unconventional sand-based substrates previously used in pilot scale vertical flow sub-surface constructed wetlands (EmiSûre, Interreg Greater Region, 2017–2021) and the well-known sorbents (granulated activated carbons). The main results can be summarized as follows:

- •Results of one-compound adsorption with dye as a proxy lead to the conclusion that the studied substrates have substantially lower capacity than conventionally used granulated activated carbons.
- Experiments for determining the microbial potential were carried out on substrates with admixture either with activated or non-activated biochar, resulting in excluding the microbes' activity and additionally leading to an understanding that the activated biochar is more efficient in its adsorption capacity than the non-activated one.
- Among all the substrates studied, the single-compound kinetic experiments showed that the activated biochar is the most efficient substrate, followed by zeolite admixture and pure sand.
- This fact was confirmed by the results from packed-bed column experiments, where the admixture with activated biochar proved to be the most capable in terms of removal of 27 MPs compared to the zeolite admixture and pure sand. Additionally this mixture showed almost no desorption during the whole operation of 10 months in contrast to the other two substrates.
- A broad characterization of the physical and chemical properties of the studied substrates has been carried out, resulting in the fact that the highest efficiency of the activated biochar is probably caused due to its broad BET surface area and small median pore diameter.
- For the 27 MPs, adsorption models were created, and the best fitting model was evaluated for its favorable fit to experimental data and other parameters discussed above; the best model for most of the MPs is the combined Langmuir-Freundlich. This model allows a description of optimal adsorption characteristics of the substrates studied, such as maximum adsorbed capacity, heterogeneity of the surface of the substrate, which could eventually help to establish the lifetime or to design a tailored treatment.
- The parameters needed for industrial upscale of the sand-based substrate with activated biochar were specified, such as height of mass transfer zone, breakthrough and saturation point related to treated synthetic wastewater and number of bed volumes.

With the knowledge obtained from this study, we believe the characterization of the unconventional sand-based substrates used contributes significantly to understanding and consequent successful application of these substrates, especially the sand-based substrate with admixture of activated biochar, in nature-based solutions in a broad scope.

Credit author statement

Hana Brunhoferova: Writing – original draft preparation, writing – reviewing and editing, Formal analysis, Methodology, Conceptualization, Investigation, Visualization, Data curation. **Silvia Venditti**: Supervision, Funding acquisition, Project administration, writing – reviewing and editing, Formal analysis, Methodology, Conceptualization. **Joachim Hansen**: Supervision, Funding acquisition, Project administration, writing – reviewing and editing.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2022.115593.

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