



Sorption of micropollutants on selected constructed wetland support matrices

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HIGHLIGHTS

- Selecting a suitable support matrix predicts adsorption of micropollutants in a CW.
- Combining support materials is advised.
- A combination of bark and biochar has potential to remove micropollutants in a CW.

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ABSTRACT

Micropollutants (MPs) are organic chemicals that are present in the environment at low concentrations (ng/L–μg/L), for example pharmaceuticals. A constructed wetland (CW) is a promising post-treatment technique to remove MPs from wastewater effluent. Selecting a suitable material for support matrix is important when designing such a CW. Nine materials were studied as potential support matrices: Light Expanded Clay Aggregates (LECA), compost, bark, granulated activated carbon (GAC), biochar, granulated cork, lava rock, sand and gravel. Batch experiments were conducted to study MP removal by nine materials in phosphate buffer with 5 or 50 μg/L MPs, or wastewater effluent with 50 μg/L of MPs. GAC and biochar removed almost all MPs in both phosphate buffer and wastewater effluent, followed by bark, compost, granulated cork. Sand, gravel, LECA and lava rock removed less than 30% of most MPs in both matrixes. Based on set criteria (e.g. removal efficiency), biochar, bark, compost, LECA and sand were selected, and used in combinations in column studies to test their overall performance. A combination of bark and biochar performed the best on MP removal, as 4 MPs were highly (70%–100%) removed, 4 MPs were moderately (30%–70%) removed while only 3 MPs were hardly removed. The main flow regime of this combination was both plug flow and dispersive flow. Moreover, we hypothesized to apply bark and biochar in a CW. Based on the assumptions and calculations, some benefits are expected, such as increasing MP removal and extending operation time.

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1. Introduction

In recent years, the presence of organic micropollutants (MPs) in water and soil has gained increasing attention. MPs include various types of chemicals, such as pharmaceuticals, personal care products, natural and synthetic hormones, pesticides, and by-products of disinfection such as trihalomethanes and haloacetic acid (Ojajuni et al., 2015). MPs have been detected in the aquatic environment, such as wastewater, surface water, groundwater and drinking water (Luo et al., 2014). Although these chemicals are

generally present in the environment at low concentrations (ng/L–μg/L), their direct or accumulative toxicity and associated long-term exposure may lead to potential risks for the health of ecosystems and humans.

The discharge of MPs in treated municipal wastewater is a major source of these chemicals in surface water (Kasprzyk-Hordern et al., 2009). Although current wastewater treatment plants (WWTPs) can eliminate some substances efficiently (e.g. nitrogen and phosphorus), the removal of many MPs is limited. The occurrence of MPs in various countries/regions (e.g. Austria, China, and EU-wide) has been reported to be 0.1–10 μg/L and 0.001–1 μg/L in WWTP influent and effluent, respectively (Luo et al., 2014). This incomplete removal can be explained as conventional WWTPs are not designed for MP removal, consequently the unremoved chemicals are

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discharged with wastewater into the surface water (Gorito et al., 2017).

Constructed wetlands (CWs) are engineered systems, designed and constructed to use natural wetland processes to treat wastewater effluent under a more controlled environment (Vymazal, 2011). CWs can be used to treat primary, secondary, or tertiary effluents and have the ability to remove MPs from wastewater (Hijosa-Valsero et al., 2010; Verlicchi and Zambello, 2014; Zhang et al., 2014). For example, Verlicchi and Zambello (2014) reported that in CWs that were used to treat influent of tertiary treatments, 52% naproxen was removed by surface flow CWs (SF CWs), 42% in vertical subsurface flow CWs (VSSF CWs) and 14% in horizontal subsurface flow CWs (HSSF CWs); HSSF CWs eliminated 60% carbamazepine, followed by 25% in SF CWs and 26% in VSSF CWs. VSSF CWs removed diclofenac more efficiently (79%) than other types of CWs (i.e. 58 % in SF CWs and 7.5% in HSSF CWs), and ibuprofen was removed better in VSSF CWs (69%) compared than 60% in SF CWs and 48% in HSSF CWs. Different types of CWs present varying abilities to remove MPs from wastewater.

Support matrix (or substrate, media or filling material) is one of the major components in CWs (Yang et al., 2018). It plays an important role in the sorption of contaminants, the permeability of the system to provide adequate flow of water in CWs, the support for rooting of plants, a matrix for microorganisms to adhere to, and the retention of suspended solids (Li et al., 2014; Wang et al., 2010; Wu et al., 2015). The material selection is based on hydraulic permeability and the adsorption capacity of contaminants (Wu et al., 2015). The support matrix used in CWs can be classified into traditional and newly emerged materials (Yang et al., 2018). Traditional materials mainly include soil, sand and gravel (Yang et al., 2018). However, using sand and/or gravel in systems may cause some non-negligible problems, for example difficulties of plant settlement, low adsorption efficiency, and clogging (Wang et al., 2010). To improve MP removal and the effectiveness of the system, some newly emerged materials are gradually getting more attention (e.g., biochar, activated carbon, Light Expanded Clay Aggregates (LECA), cork granulates and pine bark) (Ahmed, 2017; Bras et al., 1999; Domingues et al., 2007; Dordio et al., 2017; Jung et al., 2013, 2015a, 2015b; Kim et al., 2016; Kovalova et al., 2013; Machado et al., 2017; Mansour et al., 2018; Nam et al., 2014; Quinlivan et al., 2005; Shimabuku et al., 2016; Solanki and Boyer, 2017). However, the potential application of these materials in CWs is still unclear, considering the properties needed: a high MP removal capacity and a suitable particle size that is large enough to prevent clogging and small enough to have a water holding capacity to sustain microbial activities.

The aim of this study is to select individual support matrix materials or combinations with batch or column experiments that will result in an optimal MP adsorption. Sand and gravel were used as two traditional materials, and seven new materials were investigated; LECA, compost, bark, granulated activated carbon, biochar, granulated cork and lava rock. Batch experiments were performed to explore the adsorption capacity of these nine matrix materials for 11 MPs; mecoprop, sulfamethoxazole, trimethoprim, diclofenac, carbamazepine, benzotriazole, caffeine, furosemide, metoprolol, propranolol and irbesartan. These chemicals are frequently detected in wastewater effluent, e.g. Margot et al. (2015) and Tran et al. (2018). Column experiments were carried out to study MP removal of selected material combinations and to identify the optimal combination for application in CWs. Moreover, a tracer residence time distribution experiment was conducted to investigate the hydraulic characteristics of the columns: hydraulic retention time (HRT) and flow dispersion regime.

2. Materials and methods

2.1. Materials

Properties of sand, gravel, Light expanded clay aggregate (LECA), compost, bark, lava rock, granulated activated carbon F400 (GAC), biochar made from cow manure and granulated cork are summarized in Table 1. All studied matrix materials were rinsed with deionized water (tap water treated by reversed osmoses technique and purified with regenerated deionization cartridges, Veolia Water technologies, the Netherlands) for 1 h to eliminate impurities. After rinsing, GAC and biochar were dried in an oven at 105 °C overnight as performed by Behera et al. (2010) and Shimabuku et al. (2016), to completely remove the water remaining in the porous structure of GAC and biochar. After that, GAC and biochar were stored in Schott bottles at room temperature. The other matrix materials were dried at room temperature and stored similarly.

2.2. Chemicals and reagents

Micropollutants (MPs) were purchased from Sigma- Aldrich (U.S) and included mecoprop (MCP), sulfamethoxazole (SMZ), trimethoprim (TRM), diclofenac (DFC), carbamazepine (CBZ), benzotriazole (BTA), caffeine (CAF), furosemide (FRS), metoprolol (MET) and propranolol (PRO). Irbesartan (IBT) was purchased from TOKYO CHEMICAL INDUSTRY (Japan). Details of the physicochemical properties of MPs are given in Appendix C. Methanol, acetonitrile, ultrapure water and formic acid were bought from ACTUAL CHEMICALS (the Netherlands). All other chemicals used were of analytical grade. All solutions in this study were prepared in ultrapure water (resistivity ~ 18.2 MΩ cm at 25 °C), which was tap water treated by a MilliQ system (Merck Millipore, Germany).

2.3. Wastewater effluent

Wastewater effluent used in this experiment originated from the municipal wastewater treatment plant in Bennekom, the Netherlands. Average pH and conductivity of the wastewater effluent were 7.1 and 196.3 μS/cm, respectively. Average total organic carbon (TOC), average total nitrogen (TN) and average total phosphorous (TP) of wastewater effluent were 12.1 TOC mg/L, 5.7 mg TN/L and 0.3 mg TP/L, respectively.

2.4. Experimental set-up

2.4.1. Batch experiments

Batch experiments were conducted to compare MP removal by different matrix materials and to study the influence of different MP concentrations and wastewater effluent on their removal performance. Details of the experimental set-ups are given in Appendix D.

A mixed MP stock solution of 500 mg/L of each MP was prepared in methanol and diluted to 1 mg/L in ultrapure water as working solution. Phosphate buffer Na₂HPO₄/NaH₂PO₄ (P-buffer) was prepared in ultrapure water with a concentration of 0.01 mol/L and pH 7.1, which was used to mimic pH of the wastewater effluent. Matrix materials (2 g) were mixed with 100 mL 0.01 mol/L phosphate buffer, and spiked with 5 μg/L MPs, 1.3 g/L NaN₃ and small amounts of 58.4 g/L NaCl in a 250 mL Schott bottle with a screw cap (Appendix D). Concentrations of 5 μg/L MPs were used in this study, as this concentration represents the concentration of MPs in wastewater effluent from the WWTP in Bennekom, the Netherlands (Appendix E). NaN₃ solution of 65 g/L was prepared in ultrapure water and spiked to batches to inhibit microbial processes. Small amounts of 58.4 g/L NaCl were used to adjust the

Table 1
Properties of the used matrix materials.

Materials	Sand	Gravel	LECA ^a	Compost	Bark	Lava rock	GAC ^b	Biochar	Ganulated cork
Average particle size (mm)	0.2	8–12	8–15	N.A.	5–25	5–25	1	0.5–5	4–12
Density (kg/m ³)	1984.9 ± 113 ^c	1600 ^d	859.9 ± 46.1 ^c	1269.5 ± 84.1 ^c	515.6 ± 53.3 ^c	2180.4 ± 109.1 ^c	1200 ^e	1730.3 ± 147.6 ^c	120 ^f
pH in ultrapure water ^g	7.3 ± 0.1	7.6	6.2 ± 0.1	6.7	6.8 ± 0.2	6.8	8.5 ± 0.1	10.1	6.3
Supplier	GAMMA, the Netherlands	WELKOOP, the Netherlands				CAMPINGAZ, France	Chemviron Carbon, the Netherlands	MAVITEC, the Netherlands	KORK-DEKO, Germany

N.A.: not available.

^a LECA=Light expanded clay aggregate.

^b GAC=granulatedactivated carbon F400.

^c Values were measured in this experiment and details are given in Appendix A. Data are mean ± standard deviation (n=2).

^d Data from: <https://www.grind.be/siersplit/mediterranee-split>.

^e Data from: <https://www.chemviron.eu/applications/municipal-water-treatment/municipal-drinking-water/>.

^f Data from: <https://www.kork-deko.de/magazin/daemmen-mit-korkgranulat-die-oekologische-isolation-im-hausinneren>.

^g pH of ultrapure water was 8 ± 0.1. All values were measured in this experiment and details are given in Appendix B. Data are mean ± standard deviation (n = 2).

conductivity in all batches to 3.9 mS/cm, the highest measured conductivity after biochar addition (Appendix F). A similar set-up was used for controls without MP addition (control 1), and controls without matrix materials (control 2). All conditions were performed in duplicate. The batches were incubated in the dark at 20 °C on a shaker at 120 rpm for 3 days. Liquid samples of 1 mL were taken from all batches at 0, 0.5, 4, 8, 24, 48 and 72 h for analyses. pH and conductivity were measured in all batches by a HQ40d multi meter (Hach, USA) at each sampling time.

A higher MP concentration 50 µg/L was used to study the influence of different MP concentrations on their removal in the matrix materials (Appendix D). All set-ups and sampling strategies were the same as described above. To study the influence of wastewater effluent on MP removal in the matrix materials, matrix materials (2 g) was mixed with 100 mL wastewater effluent spiked with 50 µg/L MPs and 1.3 g/L NaN₃ in a 250 mL Schott bottle with a screw cap (Appendix D). The wastewater effluent was centrifuged at 10,000 rpm for 15 min at 4 °C, and the supernatant was used in this experiment. All set-ups and sampling strategies were as described above.

The selection of the studied matrix materials was based on several characteristics: removal efficiencies of MPs in wastewater effluent, particle size, environment friendly, cost, stabilization of support matrix, providing extra nutrients for plants and microorganisms in CWs and availability. Each of these characteristics were given quantitative criteria and a relative weight in an overall evaluation (Appendix G), which were based on discussions with scientists and a coworker at a waterboard.

2.4.2. Column experiments

Column experiments were carried out in five continuous-fed up-flow cylindrical glass columns (34 cm height, 10 cm diameter). All columns were packed with selected matrix materials based on the results from 2.4.1. The selected matrix materials were homogeneously mixed with a mixer in a volume ratio, namely (1) bark and biochar (9:1, wet v: wet v), (2) LECA and biochar (9:1, wet v: wet v), (3) sand and biochar (9:1, wet v: wet v), (4) bark and biochar (9:1, wet v: wet v) and (5) only sand. The columns were packed with 5 layers from bottom to top: gravel layer 4 cm, glass beads layer 3 cm (7 mm diameter, VWR, the Netherlands), layer with a mixture of the selected matrix materials 22 cm, gravel layer 2 cm and effluent water layer 2 cm. Gravel and glass beads were used at the bottom to avoid clogging in the inlet and to distribute the liquid equally over the width of the column. Gravel was used on the top layer to maintain the column structure. The column was fed upwards, as upward flow reduced the preferential pathways of

influent and therefor a preferred operation mode in the column setups. The flow rate was 0.35 mL/min per column. A schematic drawing of the column setup is shown in Fig. 1.

The column experiment lasted for 67 days. The columns were first stabilized with deionized water during 3 days onwards, followed by 1.3 g/L NaN₃ in deionized water for 3 days and 1.3 g/L NaN₃ in wastewater effluent for 9 days. After stabilization, no leakages happened in the column setups and stable pH and conductivity values were observed in the effluent of each column. This was followed by the determination of the hydraulic retention time (HRT) during 9 days, whereafter the columns were continuously fed with 1.3 g/L NaN₃ in wastewater effluent for 13 days to inhibit microbial processes prior the adsorption experiment. Lastly, the adsorption experiment was performed for 30 days.

Hydraulic retention time (HRT) and identifying hydraulic flow type. HRT was calculated based on retention time distribution (RTD) of a tracer, and the RTD was identified according to the method of Headly and Kadlec (2007) with a pulse injection of NaCl as a tracer. 10.5 mL of a 25 mg/L NaCl solution was prepared in wastewater effluent and injected to each column. The determination of NaCl dosage is shown in Appendix H. After injection of the tracer, the columns were continuously fed with 1.3 g/L NaN₃ in wastewater effluent. The conductivity of the effluent was measured every 15 min during 9 days by a Datalogger (Consort D230, Belgium) with conductivity electrode (Prosense QC212x, Netherlands). Detailed analysis of HRT measurement is shown in Appendix I. The hydraulic flow type of columns was assessed by studying the flow regime of tracer in the columns, see also Appendix I.

Adsorption of MPs. To observe adsorption breakthrough of most MPs in the columns in one month, column experiments were conducted by continuously feeding wastewater effluent that was spiked with a mixture of 11 MPs (25 mg/L each) and 1.3 g/L NaN₃. The influent concentration of MPs (25 mg/L each) was based on the results of batch experiments, flow rate and operation time of the columns. This concentration was diluted from a stock solution of MPs (600 mg/L) prepared in a mixture of methanol and acetonitrile (v:v, 1:1). Consequently, the influent contained 4% of this mixed organic solvent. This small amount of organic solvent (4%) had no significant influence on the absorption of MPs in all material combinations, as tested in a separate experiment (Appendix J).

The sampling frequency of influent and effluent in the columns was determined by the actual HRT (also called as mean HRT or tracer HRT), which was calculated based on the HRT test. Influent and effluent (1 mL each) of the columns were collected before and after each actual HRT for chemical analyses. pH was measured in

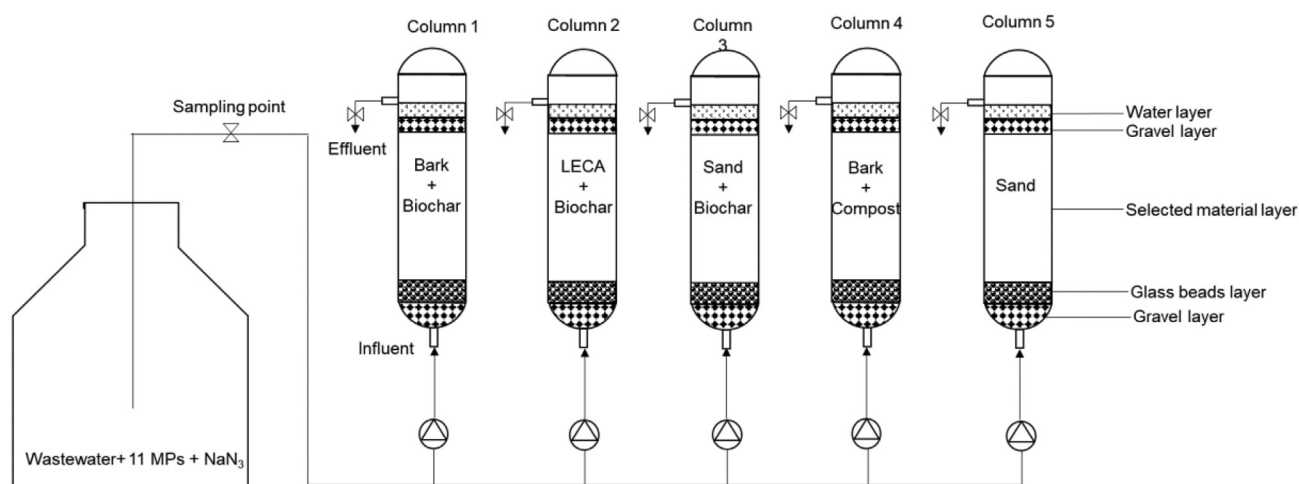


Fig. 1. Set-up of the column experiments.

influent and effluent by an HQ40d multi meter (Hach, USA), the conductivity was monitored by a Datalogger (Consort D230, Belgium) with conductivity electrode (Prosense QC212x, Netherlands). The volume of effluent was calculated based on its weight measured by a scale (Sartorius, Germany).

2.5. Chemical analyses

Liquid samples were centrifuged at 15,000 rpm for 10 min (Eppendorf, Germany). The supernatant was collected and stored at -20°C prior to analysis. Analysis took place by injecting 50 μL of the sample in an UHPLC Dionex Ultimate 3000 system (Thermo Fisher Scientific, US). This system was completed with a pump, an autosampler and a temperature controllable column compartment. This system was equipped with the orbitrap mass spectrometer Q-Executive (QEx) (Thermo Fisher Scientific, US) for MP analysis. The analytical column was the Acuity UHPLC CSH Phenyl-Hexyl (1.7 μm 2.1*150 mm inline filter) (Waters, US) equipped with a guard column (Waters, US) with the same phase. The composition of the mobile phases, the gradient elution and flow rate were the same as the used by He et al. (2016). The chemicals were detected and quantified by the exact mass of their molecular ion, which can be found in Appendix K. The detect range of this technique was in a range between 50 ng/L up to 900 ng/L. The calibration standards of MPs showed a good linearity ($R^2 > 0.99$) after detection except for CAF ($R^2 > 0.96$).

MPs in a higher concentration range (0.1 mg/L – 1 mg/L) were detected with an UHPLC Dionex ultimate 3000 (Thermo Fisher Scientific, US) with a diode array detector (DAD) as described in detail by He et al. (2016). Target MPs were detected and quantified, as shown in Appendix L. The calibration standards showed a good linearity ($R^2 > 0.99$) after detection. The retention times of target MPs in QEx and UHPLC- DAD are shown in Appendix M.

3. Results and discussion

3.1. Batch experiments

3.1.1. MP adsorption by various materials

All batches showed a stable pH and conductivity (Appendix N). Different removal efficiencies were observed for 11 MPs and 9 tested matrix materials in three liquid phases (Fig. 2). When comparing the removal efficiencies using 5 $\mu\text{g/L}$ MPs, granulated activated carbon (GAC) and biochar achieved the highest removal of

all tested MPs (close to 100%). This high adsorption of MPs can be attributed to their high surface area and high micropore structure, as well as their surface chemical properties, which are suitable for high adsorption (Ahmad et al., 2014; Delgado et al., 2012).

Bark, compost and granulated cork showed a high removal efficiency ($>85\%$) for a few MPs, such as PRO and TRM, and a moderate removal efficiency (30%–85%) for most of the other tested MPs. These different removal efficiencies appear to be related to the various properties of MPs. For example, PRO shows a high adsorption, due to its hydrophobicity and positive charge, which is also described in a previous CW study (He et al., 2018). TRM was also highly removed by these three materials, indicating that adsorption is an important removal pathway of TRM. This is in line with findings from a study that TRM was removed through adsorption to activated sludge (Li and Zhang, 2010).

Lava rock, sand, gravel and LECA showed a removal efficiency below 45% for all MPs. Lava rock removed SMZ, IBT, FRS, MCP and DFC in a range of 33%–43% and poorly removed all other MPs ($<30\%$). Despite its porous structure and large surface area like GAC and biochar, the removal performance of lava rock is limited. The used sand and gravel are also natural geomaterials like lava rock, but showed a lower MP removal efficiency than lava rock. This may be explained by the lack of large extended surface area of sand and gravel. LECA hardly removed any MPs in this study. However, a good removal was found with LECA for some MPs in previous studies, for example FRS, gemfibrozil, mefenamic acid and naproxen (Dordio et al., 2017; Machado et al., 2017). These different results are most likely due to the difference in raw materials and manufacturing techniques used for LECA production.

The influence of initial MP concentrations was determined by comparing the removal efficiencies when using 5 $\mu\text{g/L}$ and 50 $\mu\text{g/L}$ MPs (Fig. 2). GAC and biochar achieved the highest removal (close to 100%) of all MPs at both concentrations. This means that the tested initial concentrations of MPs do not influence the removal performance of GAC and biochar in this concentration range. With increasing the initial concentration from 5 $\mu\text{g/L}$ to 50 $\mu\text{g/L}$, the removal efficiencies slightly increased in LECA (from min. 0% to 17%) and decreased in sand, gravel, lava rock, compost, bark and granulated cork (from max. 83%–0%). However, for LECA, it is difficult to explain these increasing removal efficiencies in this study because of a lack of information on the adsorption mechanisms of this LECA product. The removal efficiencies with a decreasing trend means that the adsorption sites of matrix materials are not fully occupied at low MP initial concentration and the

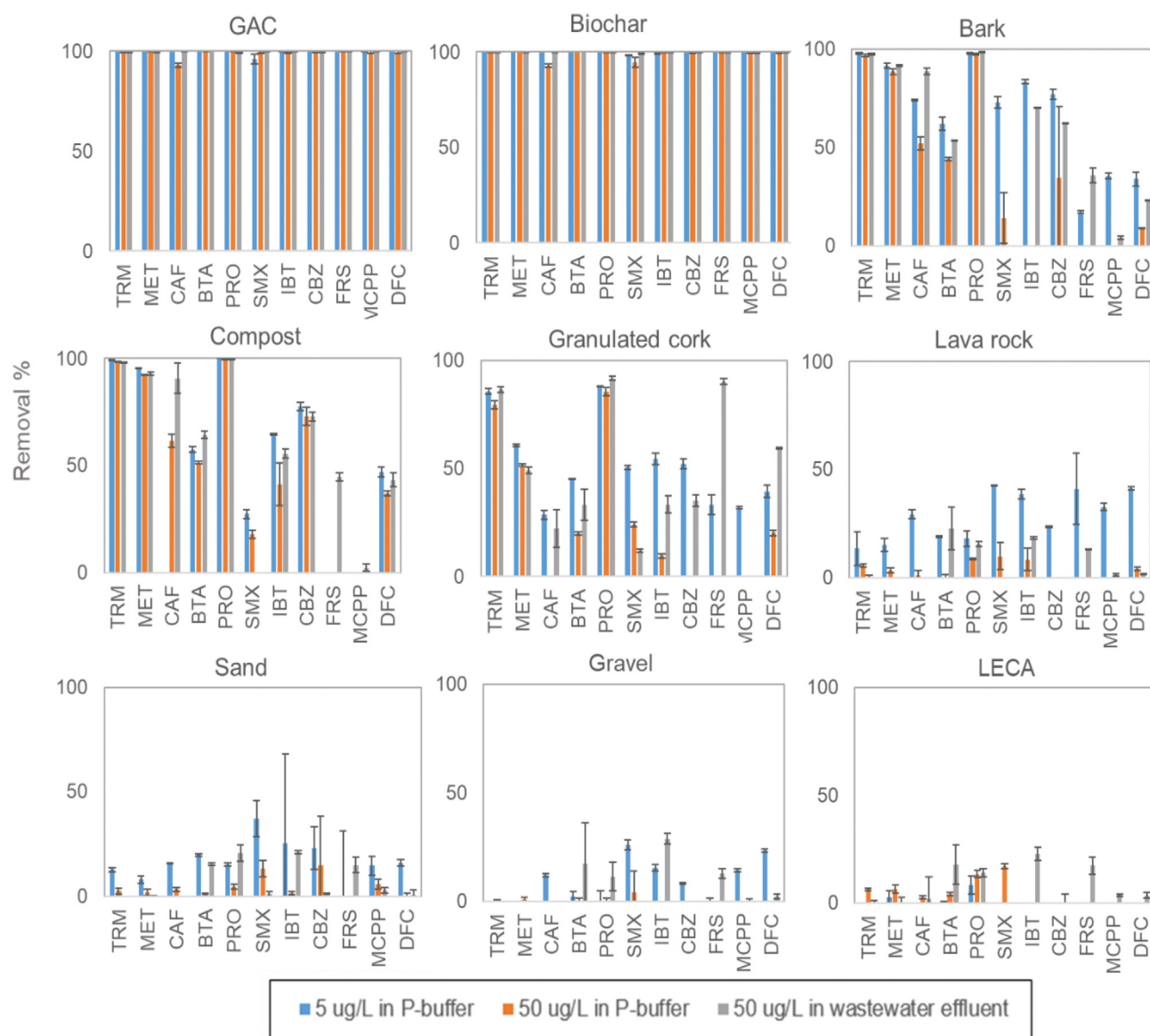


Fig. 2. Removal of 11 MPs by 9 matrix materials in phosphate buffer with two concentrations (5 µg/L with blue and 50 µg/L with orange) and wastewater effluent with 50 µg/L (grey). Data are mean value ± standard deviation (n = 2). All negative removal efficiencies were set to zero. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

high initial concentrations of MPs lead to the adsorption saturation of materials.

The influence of wastewater was studied by comparing the removal of 50 µg/L MPs in phosphate buffer and wastewater effluent (Fig. 2). Compared to phosphate buffer, wastewater effluent contains many forms of organic matter (OM), which competes with MPs for the adsorption sites of the matrix materials, or even block or constrict micropores in the matrix materials (Margot et al., 2013; Delgado et al., 2012). As a result, these phenomena may limit MP adsorption. The results show that using a wastewater effluent matrix had no significant influence on the removal performance with GAC, biochar, sand, gravel, LECA and lava rock. This indicates that OM presence does not affect the adsorption of all target MPs on these matrix materials under the tested conditions. GAC and biochar showed almost 100% removal of all chemicals in both phosphate buffer and wastewater effluent. The removal of TRM, MET and PRO by bark, compost and granulated cork was similar in both phosphate buffer and wastewater in a

range of 49%–100%, while the removal of other tested MPs was slightly influenced by the wastewater effluent. Sand, gravel, LECA and lava rock poorly removed all chemicals in both phosphate buffer and wastewater effluent (<30%).

3.1.2. Selection of matrix materials

Based on the overall evaluation, biochar, bark and compost received a high final grade (Appendix G), and were chosen for further study in packed columns. Sand and LECA were also selected for further study. Sand was used as a control, as it is one of the most widely used material in CWs (Yang et al., 2018). LECA has been used successfully in some CW studies Dordio et al. (2010), Dordio et al. (2009) and Auvinen et al. (2017), and was therefore also taken along, in contrast to other unselected materials (i.e. lava rock and granulated cork). Moreover, LECA has a larger particle size (8–15 mm) compared to e.g. GAC, and therefore suitable in combination with other selected materials with smaller particle size, to achieve adequate hydraulic permeability of its combined use.

After selection, these five matrix materials were tested in a mixed matrix, based on the two most important characteristics for application in a MP removing CW: removal efficiencies of MPs and particle size. Each material of a combination represents either good removal or adequate hydraulic permeability. In study, five combinations were selected and tested, namely 1) bark and biochar, 2) LECA and biochar, 3) sand and biochar, 4) bark and compost, 5) sand as a control.

3.2. Column experiments

3.2.1. Hydraulic retention time and hydraulic flow type

The tracer study of the columns provided information about the flow behavior through each unique column, including the time of flow movement (i.e. hydraulic retention time (HRT)) and the movement pathway of flow (i.e. flow dispersion regime). The actual HRT in column 1 to 5 were 3.4 days, 3.4 days, 2.7 days, 3.3 days and 2.6 days, respectively (Appendix I). The theoretical HRTs were 2.5 days, 2.2 days, 2.0 days, 2.3 days and 2.0 days in column 1 to 5, which were defined as the estimated water volume in columns divided by the flow rate (Appendix O). The estimated water volume was calculated based on separate experiments in cylinders (Appendix O). The actual HRTs were higher than the theoretical HRTs, which is a result of a difference in water volume due to the packing status of the bed medium in the columns. Over time, the bed medium of the columns became more compacted after continuously feeding influent, whereas the estimated HRT with the cylinder tests simulated the operation of a fresh packed column.

A similar actual HRT was observed in column 1, 2 and 4 or in column 3 and 5. To further understand the influence of different material combinations on the formation of the actual HRTs, the dominant flow regime of five columns was studied by analyzing the dispersion pattern of the added tracer in the columns. According to the shape of the tracer curves, the mixing degree in the columns was considered as a combination of plug flow resulting in a time delay, and dispersive flow resulting in a broadened peak (Appendix I). Moreover, the plug flow breakthrough happened earlier in the columns than that of the dispersive flow. To further distinguish the procedure of plug flow and dispersive flow in the columns, the tracer curves were validated by modelling (Appendix I). The main parameters of this modelling are present in Table 2: the time of plug flow (t_p) and dispersive flow (t_d), and the relative importance of plug flow (RI_p) or dispersive flow (RI_d) in the actual HRT. Detailed modelling information is shown in Appendix I.

The times of plug flow (t_p) and dispersive flow (t_d) are comprised of the actual HRT and the sum of RI_p and RI_d is 1. In column 1, both plug flow and dispersive flow are the main flow types, as RI_p and RI_d are 0.5 (Table 2). In column 3, 4 and 5, the plug flow is the main flow type, as RI_p values are higher than RI_d values (Table 2). Furthermore, the time of plug flow (t_p) was similar in these three columns (close to 1.9 days). By contrast, their time of dispersive flow (t_d) was different. This is due to various actual HRTs

and the particle size of the material combinations. Column 4 had a longer actual HRT than column 3 and 5, as the bed matrix had a larger particle size (i.e. mainly bark with particle size 5–25 mm) and therefore the water filled pore volume was larger than in column 3 and 5. Apparently, the mixed bark and compost in column 4 influenced the microscale flow regime in the pores in a way that dispersion was enhanced (i.e. by compost particles clogging pores and thus enhancing channeling, or other phenomena) leading to a longer t_d than column 3 and 5.

Unlike other columns, the main flow type of column 2 was dispersive flow, as its RI_d is nine times higher than RI_p (Table 2). Although column 2 had a similar actual HRT as column 1 and 4, its time of dispersive flow (t_d) was about two times longer than that in these two columns, which must be due to the shape and surface characteristics of the LECA (e.g. its surface roughness and inner pores in the LECA), and not the particle size. This is because the columns packed with mainly bark (1 and 4) with a similar particle sizes as LECA (Table 1) do not show the dispersive flow as the main flow type. The regular sphered shape of LECA distributes influent in a column more dispersive than the other matrix shapes: the water is completely mixed, typically for highly dispersive flow with a longer time of dispersive flow.

3.2.2. Removal of MPs in columns

All columns showed a stable pH and conductivity of influent and effluent after MP addition during 30 days (Appendix P). Breakthrough curves of MPs in the columns are shown in Appendix Q. The concentration of MPs in the effluent increased immediately after day 0 and was detected from day 3 onwards. When the concentration of MPs in the effluent was almost equal to that in the influent in a certain time period (i.e. average $C_e/C_0 = 1 \pm 0.05$, with deviations of $C_e/C_0 \leq 3\%$), these MPs were reaching their maximum adsorption in the columns (i.e. resulting in their full breakthrough in the columns). For example, MCPP achieved its maximum adsorption in all columns during 30 days; CAF, SMZ and CBZ reached this situation in column 2 (LECA and biochar), column 3 (sand and biochar) and column 5 (sand) (Table 3). This indicates that these chemicals have a low sorption affinity with the studied material combinations. Thus, adsorption of these chemicals may be limited when CWs with these material combinations are used. Other processes, such as biodegradation or plant uptake, need to remove these chemicals, otherwise such a CW is not effective.

A high number of target MPs did not show a full breakthrough in the columns after 30 days, but showed a levelling off curve with average $C_e/C_0 < 1 \pm 0.05$ in a certain time period and deviations of $C_e/C_0 \leq 3\%$ (Appendix Q). This means MPs reached a slow and continued adsorption in the columns and their full breakthrough $C_e/C_0 = 1 \pm 0.05$ would take more time. To define the column effectivity, the sorption affinity was pragmatically characterized in this study on the basis of the averaged C_e/C_0 reached for the MPs: $0.5 \leq \text{average } C_e/C_0 < 1$, moderate sorption affinity and $0 < \text{average } C_e/C_0 < 0.5$, high sorption affinity, which were classified respectively

Table 2

Main parameters from the modelling analysis of 5 columns (t_p , t_d , RI_p and RI_d), and a summary of dominant flow regime in the columns (plug flow and/or dispersive flow). t_p and t_d are comprised of the actual HRT. The sum of RI_p and RI_d is 1.

Parameters		Column 1	Column 2	Column 3	Column 4	Column 5
Plug flow	RI_p	0.5	0.1	0.7	0.6	0.65
	t_p (day)	1.8	0.3	1.9	2.0	1.7
Dispersive flow	RI_d	0.5	0.9	0.3	0.4	0.35
	t_d (day)	1.6	3.1	0.8	1.3	0.9
Dominant flow Regime		P ^a + D ^b	D	P	P	P

^a Plug flow (P).

^b Dispersive flow (D).

Table 3

MP adsorption capacity of five columns after 30 days was pragmatically characterized on C_e/C_0 concentration reached: C_e/C_0 kept an increasing trend and no breakthrough occurred (green, average $C_e/C_0 < 1 \pm 0.05$, deviations of $C_e/C_0 > 3\%$); C_e reached plateau level: high sorption affinity (yellow, $0 < \text{average } C_e/C_0 < 0.5 \pm 0.05$, deviations of $C_e/C_0 \leq 3\%$) and moderate sorption affinity (orange, $0.5 \pm 0.05 \leq \text{average } C_e/C_0 < 1 \pm 0.05$, deviations of $C_e/C_0 \leq 3\%$); full breakthrough occurred (red, average $C_e/C_0 = 1 \pm 0.05$, deviations of $C_e/C_0 \leq 3\%$). The specific values of average C_e/C_0 and their run time when reaching the four statuses are presented in [Appendix R](#).

	TRM	MET	CAF	BTA	PRO	SMZ	IBT	CBZ	FRS	MCPP	DFC
Column 1: bark + biochar	Green	Yellow	Green	Green	Green	Yellow	Yellow	Yellow	Yellow	Red	Yellow
Column 2: LECA + biochar	Yellow	Green	Red	Green	Green	Red	Yellow	Red	Yellow	Red	Red
Column 3: sand + biochar	Green	Green	Red	Green	Green	Red	Yellow	Red	Yellow	Red	Yellow
Column 4: bark + compost	Green	Green	Yellow	Yellow	Green	Yellow	Yellow	Yellow	Yellow	Red	Yellow
Column 5: sand	Green	Red	Red	Red	Green	Red	Yellow	Yellow	Yellow	Red	Yellow

■ No breakthrough and adsorption increasing over time, with very high sorption affinity
■ Levelling off adsorption, with high sorption affinity
■ Levelling off adsorption, with moderate sorption affinity
■ Full breakthrough occurred, with low sorption affinity

(in classifying ± 0.05 error range was considered). Most MPs had the moderate sorption affinity with the material combinations chosen, except for MET with high sorption affinity in column 1 (bark and biochar) ([Table 3](#)). This indicates that sorption process is an important removal pathway of these MPs, especially for MPs with high sorption affinity. But other removal processes in CWs are still needed when considering completely removing these MPs.

A few target MPs did not reach either their maximum adsorption or a levelling off adsorption in the columns after 30 days, but showed an increasing trend of C_e/C_0 over time (i.e. average $C_e/C_0 < 1 \pm 0.05$ and deviations of $C_e/C_0 > 3\%$) ([Appendix Q](#)), for example PRO in all columns and TRM in column 1 (bark and biochar), column 3 (sand and biochar), column 4 (bark and compost) and column 5 (sand) ([Table 3](#)). This means that more sorption of these MPs can occur in the columns after 30 days and sorption could be the main removal pathway of these MPs, especially MPs with C_e/C_0 far below 1 after 30 days. Thus, the adsorption breakthrough of these MPs in CWs is expected for a longer time than other MPs mentioned above.

The total removal efficiencies of target MPs after 30 days are shown in [Table 4](#). Column 1 (bark and biochar) and column 4 (bark and compost) showed a high or moderate removal for most MPs after 30 days while other columns showed a moderate or poor removal for most MPs. More specific, 4 MPs (i.e. TRM, MET, BTA and PRO) were highly removed by column 1 (bark and biochar) and 3 MPs (i.e. TRM, MET and PRO) were highly removed by column 4 (bark and compost). This indicates that the combination of bark and biochar had a better performance on MP removal than bark and compost, which is due to a high adsorption capacity for MPs. Moreover, compared to the traditional matrix material sand in column 5, bark and biochar in column 1 significantly improved the removal ($>20\%$) of most MPs, especially BTA, MET and TRM.

Among the 11 target MPs, PRO presented the highest total

removal efficiency from 36% to 91% in all columns, showing its high affinity to the tested matrix materials and ability to compete successfully with other tested MPs and compounds in the wastewater effluent, e.g. organic matter ([Margot et al., 2013](#)), for the adsorbent sites. It has been demonstrated before that sorption is the main removal pathway for PRO in CWs with sediment and sand as matrix ([He et al., 2018](#)). Poor removal of SMZ, MCPP and DFC was observed in all columns. Especially MCPP showed poorest removal efficiencies, ranging from 7% to 15% in all columns. This is due to its physicochemical properties, e.g. a high-water solubility (850 mg/L), a low $\log K_{ow}$ 1.41 and a pK_a of 3.9 ([Harrison et al., 2003](#)). This shows that MCPP exists mainly in anionic form and does not tend to sorb to soil constituents at a typical groundwater pH between 5 and 9 ([Harrison et al., 2003](#)). As the pH in our column experiments was around 7.3 in the influent and 8.1 to 8.5 in the effluent ([Appendix P](#)), this also explains the poor MCPP removal in the columns.

3.2.3. Implication for practice

Bark and biochar are the most suitable material combination as a support matrix for further testing in CWs. This is due to that they have shown a better adsorption capacity of MPs than other tested material combinations. To further assess the application of this combination in practice, several assumptions and calculations were made to predict a column length needed to achieve a decrease in MP concentration from 5 $\mu\text{g/L}$ to 10 ng/L in wastewater effluent ([Appendix S](#)). Hypothetical clean-bed columns were used for the calculations, two with bark and biochar, and one control with sand. The lengths of the clean-bed columns were calculated based on the set MP removal aim from 5 $\mu\text{g/L}$ to 10 ng/L, which shows the potential removal capacity of the columns in practical situations ([Table 5](#)). In the example presented, PRO, TRM, MET and BTA could be removed by bark and biochar in a shorter column (≤ 3 m) compared to the other MPs. This indicates that these four chemicals

Table 4

Total removal efficiency of MPs in columns after 30 days. Green is 'High removal', orange is 'Moderate removal', and red is 'Poor removal'.

	TRM	MET	CAF	BTA	PRO	SMZ	IBT	CBZ	FRS	MCPP	DFC
Column 1: bark + biochar	77	78	58	75	88	24	47	53	35	15	26
Column 2: LECA + biochar	35	49	31	63	72	15	52	21	44	14	19
Column 3: sand + biochar	21	54	29	69	91	12	50	18	49	11	15
Column 4: bark + compost	78	77	55	49	88	27	48	56	31	13	29
Column 5: sand	17	15	9	8	36	8	27	8	10	7	9

■ High removal: 70 % ~ 100 %
 ■ Moderate removal: 30 % ~ 70 %
 ■ Poor removal: 0 % ~ 30 %

Table 5
Length of the calculated clean-bed columns and CWs.

	Length of clean-bed column m		Length of clean-bed CW m	
	Bark + biochar	Sand	Bark + biochar	Sand
PRO	1.1	18.3	10.0	170.9
TRM	1.5	26.9	14.2	251.5
MET	1.8	N.A	17.1	N.A
BTA	2.1	N.A	19.7	N.A
CAF	4.4	N.A	40.9	N.A
CBZ	5.0	N.A	46.6	N.A
IBT	5.1	6.7	48.0	62.4
FRS	10.7	N.A	100.1	N.A
DFC	17.3	N.A	161.7	N.A
SMZ	19.1	N.A	178.4	N.A
MCPP	N.A	N.A	N.A	N.A

N.A.: not available.

are expected to be sufficiently removed by bark and biochar. Regarding the other seven MPs, sorption processes may not be sufficient to remove them in a column with a relatively short length (≤ 3 m) and other removal processes are needed, such as biodegradation. Compared to the control with only sand, bark and biochar can be applied in a shorter column, especially for PRO and TRM removal (i.e. 1.1 m and 1.5 m in bark and biochar and 18.3 m and 26.9 m in sand). This shows that using bark and biochar to remove MPs is more suitable for applications than a bed with only sand.

To further compare the potential application of bark and biochar in a CW, a horizontal flow CW with a clean bed was used as an example. A CW was assumed with 5000 m² of surface area, 1 m of depth and a flow rate of 3000 m³/day. The calculated clean-bed length of this CW for MP removal was based on the calculations of the clean-bed columns above (Table 5). Details of assumptions and calculations are presented in Appendix S. The results show applying bark and biochar in a CW uses less length to achieve MP removal from 5 µg/L to 10 ng/L than a CW with only sand. This means that in a same designed CW bark and biochar are able to remove MPs more sufficiently and have a higher overall adsorption capacity for MPs than sand. Thus, in application, due to the high adsorption capacity of bark and biochar, a CW filled with this material combination can use less matrix material and the land use footprint to achieve a same removal aim than sand. Moreover, a CW with bark and biochar can maintain its clean-bed status as other processes are also able to remove MPs, such as phytodegradation and biodegradation. Thus, the operation time of the adsorption functioning of a CW in MP removal is likely to be extended. All these assumptions and speculations needs to be further studied in field-scale test applications with a long-term (months to years) operation.

4. Conclusions

This study investigated the use of nine widely available materials as potential support matrix to remove MPs via adsorption. Batch experiments show that GAC and biochar achieved the highest removal of MPs in both phosphate buffer and wastewater effluent, followed by bark, compost and granulated cork. Sand, gravel, LECA and lava rock showed a poor removal of most MPs in both phosphate buffer and wastewater effluent. Biochar, bark, compost, LECA and sand were selected to study their overall performance on MP removal in combinations. Bark and biochar showed the best MP removal and this combination showed both plug flow and dispersive flow regime in the column. Moreover, applying this combination as support matrix in a CW has various benefits in practical application compared to the traditional support matrix of sand, a

higher removal of MPs, less matrix material is needed in the CW bed, the needed surface area can be smaller and the CW will have a longer operation time.

In summary, this study gives insight in the design of CWs, by enhancing MP removal via adsorption. This study innovatively proposes a material combination as support matrix in CWs instead of a single traditional matrix material (e.g. sand). The results from this study contribute to the implementation of CWs as an effective post-treatment technique for MP removal.

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

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