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The application of GAC sandwich slow sand filtration to remove pharmaceutical and personal care products

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Abstract

Lab-scale GAC sandwich slow sand filters with different GAC layer depths were evaluated for the first time on removing selected pharmaceutical and personal care products (PPCPs) (i.e. DEET, paracetamol, caffeine and triclosan, 25 μg/L). Coarse sand (effective grain size of 0.6 mm) was used instead of conventional fine sand. In addition to single sand and GAC filters, GAC sandwich filters were assessed at three filtration rates (i.e. 5 cm/h, 10 cm/h and 20 cm/h) to compare removals. Sandwich filter with 20 cm GAC achieved the best average PPCP removal (98.2%) at 10 cm/h rate. No significant difference of average PPCP removal was found between 10 and 20 cm/h filtration rates for the three GAC sandwich filters ($p > 0.05$). Among the selected PPCPs, DEET, the recalcitrant compound, was most effectively removed by the GAC sandwich filters. The addition of the GAC layers in the slow sand filters significantly enhanced the removal of the target PPCP compounds ($p < 0.05$), demonstrating that both adsorption and biodegradation contributed to the removals. Furthermore, pseudo-second-order equation (Type 1) could best represent the adsorption kinetics of the four target PPCP compounds onto GAC. In relation to other quality parameters, sandwich filter with 20 cm of GAC also showed good average removals of chemical oxygen demand (COD) at 65.8% and total organic carbon (TOC) at 90.3%, but occurrence of ammonium up to 0.76 mg/L concentration indicated inapplicability of filtration rate of 5 cm/h. No significant difference was found between 10 cm/h and 20 cm/h filtration rates for nitrogen and phosphate removals

($p>0.05$). Results of this lab-scale investigation show that GAC sandwich slow sand filter is potentially an effective process for removing PPCPs from tertiary wastewater.

Keywords: GAC sandwich slow sand filtration; PPCPs; Removal; Adsorption kinetics

1. Introduction

PPCPs are emerging environmental pollutants which have increasingly drawn attention of researchers over the last few decades (Suarez et al., 2010; Xia et al., 2005; Zhu et al., 2013). Compared with conventional contaminants (e.g. NH_4-N, COD, TSS), PPCP concentrations usually lie within a low range (ng/L~μg/L) (Cheng et al., 2016; Dougherty et al., 2010). Studies with conventional wastewater treatment processes for removal of PPCPs (e.g. biological anoxic/anaerobic/oxic, ultraviolet treatment, advanced oxidation treatment) have been conducted (Carballa et al., 2004; Kim and Tanaka, 2009; J. Li et al., 2016; W. Li et al., 2016; Suarez et al., 2010; Sui et al., 2011), but generally these systems demonstrate to be ineffective for PPCP removal (Hirsch et al., 1999; Matamoros et al., 2009; Xia et al., 2005).

Slow sand filtration (SSF) is one of the earliest water treatment processes which has a continuous flow and non-backwash mode of operation (Campos et al., 2002; Haig et al., 2011). Over the last three decades, SSF has gained more attention than before mainly due to the fact that it does not require chemical coagulation and has low operational costs due to low energy use, and simplicity in operation and maintenance. In addition, it is an efficient single-stage treatment for water with turbidity below than 10 NTU and can be applied as a tertiary stage in wastewater treatment (Haig et al., 2014). Usually, the sand grain for SSF has an effective size of 0.1~0.3 mm (Huisman and Wood, 1974) but coarser sand has been also used in SSF (Matamoros et al., 2007; Rizzo et al., 2015; Young-Rojanschi and Madramootoo, 2014).

Previous studies investigated the removals of various PPCPs using SSF processes and found removals varying considerably (generally below 80%), indicating a potential technology but not sufficient by itself alone (Escolà Casas and Bester, 2015; Nakada et al., 2007; Pompei et al., 2016). Among tertiary treatment technology, adsorption by activated carbon is one of the most cost-effective techniques. Compared to 15~2500 USD by other techniques, adsorption only costs 50-150 USD per one million litres of treated water (Gupta et al., 2012). However, GAC (granular activated carbon) adsorption is still considered an expensive process due to its regeneration costs (Weng and Hsu, 2008). The combination of GAC with other low-cost filter media could reduce the total capital and operational costs of adsorption systems. In practice, sand is the commonest low-cost filter medium used in water purification and cheaper than adsorbents (e.g. GAC, graphene). Therefore, GAC sandwich SSF seems an attractive solution for tertiary wastewater treatment.

GAC sandwich SSF was first studied by Bauer et al. (1996) to remove pesticides. Compared to single medium filters, the GAC sandwich SSF is multi-functional: the upper layer of sand ensures the biological treatment process and host on its top a biolayer called *schmutzdecke* which plays an important role in water purification. The middle GAC layer acts as a non-backwashed adsorbent which can remove contaminants that cannot be biodegraded within the *schmutzdecke*. In addition, the lower sand layer minimises the potential of biological particles and GAC fines entering the filtrate (Bauer et al., 1996). Other advantages include the longer GAC life cycle (2~4 years) and relatively low overall costs than GAC contactors (Bauer et al., 1996). These aspects make GAC sandwich SSF a promising process for PPCP removal by tertiary treatment.

Bauer et al. (1996) used only fine sand (effective size of 0.3 mm) in sandwich SSF but coarser sand has not been tried before. To decrease headloss, reduce medium clogging and prolong service life of the filters, a coarse sand was used in the present study (Robeck et al. 1962). To our best knowledge, the performance of removing PPCPs by slow sand filtration with different GAC layer depths and coarse sand was not investigated before. In the present research, three GAC sandwich SSFs with coarse sand (effective size of 0.6 mm) were constructed with different GAC layer depths and assessed at three filtration rates. In order to compare GAC sandwich filter performance with conventional filters, single medium filters with sand and GAC were also built. The effectiveness in removing four widely-used PPCPs, i.e. DEET, paracetamol (PAR), caffeine (CAF) and triclosan (TCS), was studied at different filtration rates. The adsorption kinetics of DEET, PAR, CAF and TCS at 25 μg/L onto GAC were determined to give a deeper insight into GAC adsorption mechanisms.

2. Materials and methods

2.1 Chemicals and materials

Standards and chemicals of DEET, PAR CAF and TCS were purchased from Sigma-Aldrich (UK), and their properties are shown in Table S1. Methanol and acetonitrile (HPLC grade) were purchased from Fisher Scientific (UK).

Synthetic wastewater was prepared using dechlorinated tap water with 40 mg/L COD, 7.43 mg/L NH_4Cl and 6 mg/L KH_2PO_4. Abundance of 1×10^6 CFU/100 mL of *E.coli* (ATCC11775, Sigma-Aldrich, UK) was also added into the synthetic wastewater as indicator of microbes (Ávila et al., 2015). Mixed PPCP solution (1 mg/mL) was added into the wastewater to reach a final concentration of 25 μg/L (J. Li et al., 2017). Fresh synthetic wastewater was prepared every day.

Acrylic columns (internal diameter of 54 mm) were purchased from Plastic Shop (UK) for constructing the filters. Filter sand was purchased from Mineral Marketing (UK) and had an effective size of 0.6 mm and a uniform coefficient of 1.4. GAC with particle size of 0.4~1.7 mm was purchased from Chemviron Carbon (UK). GAC particle was characterised by Brunauer–Emmett–Teller (BET, Quantachrome autosorb-iQ_2) and Scanning Electron Microscopy (SEM, JSM-6700F). The surface area of GAC was about 556 m^2/g with microporous (<2 nm), mesoporous (2~50 nm) and macroporous (>50 nm) accounting for 80.0%, 10.4% and 9.6% of the total pores, respectively (Fig. S1). Infrared spectra analysis showed no specific functional groups existed on surface of GAC. Both sand and GAC were washed by tap water and rinsed 5 times with deionized water, then dried at 105 ℃ overnight and left cooling before use. Gravels (2~5 mm) used as supporting media were also washed before use.

2.2 Filtration system and experiment design

A schematic representation of the experimental arrangement is shown in Fig. 1. Five columns were built, having each filter a total height of 65 cm with 3 cm of gravels and filter medium depth of 50 cm. Overflow pipe was installed 5 cm above the filter medium and effluent pipe was located 1 cm from the bottom. The effluent pipe had one valve to control the filtration rate. Filters were marked as number 1 to 5, which contained different media as respectively: 50 cm sand; 10 cm sand/10 cm GAC/30 cm sand; 10 cm sand/20 cm GAC/20 cm sand; 10 cm sand/30 cm GAC/10 cm sand; and 50 cm GAC (Fig. 1). Peristaltic pump was used to deliver synthetic wastewater into the filters. Influent tank was cleaned, and sample storage bottles were sterilized by 70% alcohol every day.

This study was carried out in the Environmental Engineering Laboratory at the University College London (UCL). Lake water from Regent's Park (London, UK) which had on average turbidity < 2 NTU and coliform and *E.coli* abundance around 7.6×10^3 and 1×10^2 CFU/100 mL, respectively, was collected and left in room temperature (around 23 ℃), and used for filter maturation before tests started. To evaluate the maturation period of the filters, effluent samples were initially collected on Mondays, Wednesdays and Fridays for the turbidity and total coliforms and *E.coli* abundance determinations. Slow sand filters reach maturation when turbidity of effluent is less than 1 NTU and removals of both total coliforms and *E.coli* are higher than 99% (Tebbutt, 1997). When the filters were matured, synthetic wastewater contaminated with target PPCP compounds was filtered through the five filters. Three filtration rates, i.e. 5 cm/h, 10 cm/h and 20 cm/h, were tested successively without the need of media cleaning. Although SSF filtration rate is usually between 10 cm/h to 30 cm/h (Campos et al., 2002), 5 cm/h was also tested to explore whether target PPCP compounds could be removed maximally at lower filtration rate. Filtration rates of all filters were monitored twice a day and adjusted if needed. Supernatant water level was maintained at 5 cm above media, and duration of each filtration run was 3 weeks for all filtration rates. Water temperature was around 23 ℃ constantly.

Replicate effluent samples were collected twice a week, on Tuesdays and Fridays, for quantification of the target PPCP compounds, NO_2^-, NO_3^-, NH_4^+ and PO_4^{3-}. Also, pH, conductivity and redox potential were measured along with the effluent samples. COD and TOC were determined once a week.

2.3 GAC adsorption kinetics

As adsorption is the one of main mechanisms for removal of organics from wastewater (Cooney, 1998), adsorption kinetics of the four target PPCP compounds on GAC were determined to further explain the adsorption mechanisms. 0.500g GAC was placed in nine 500 mL glass bottles, respectively. Each glass bottle was filled with 500 mL synthetic wastewater. Mixed target compound solution was added into the wastewater to reach the final concentration of 25 μg/L. Bottles were placed in a rotary mixer (designed and manufactured in-house) at the speed of 30 rpm. They were taken off from the mixer at 5 min, 10 min, 20 min, 30 min, 60 min, 120 min, 180 min, 300 min, 420 min and 660 min adapted from Cao et al. (2013) and Kumar (2006a). Replicate samples preparation followed the analytical procedures (Section 2.4).

2.4 Analytical procedures for PPCPs determination

Solid phase extraction (SPE) technique was used to extract target PPCPs from water samples. Final treated samples were analysed by Gas Chromatography-Mass Spectrometer (GC-MS, PerkinElmer Company, Clarus 500). Details can be found in J. Li et al. (2017).

2.5 Analysis of general parameters

M-ColiBlue24® method was employed to determine total coliforms and *E.coli* abundance (method 10029, USEPA). COD and TOC concentrations of water samples were determined by using Hach COD TNT digestion solution (0-1500 mg/L, HACH Company, UK) and Shimadzu TOC-L machine (UK), following manufacture procedures. Ion chromatography (IC, Dionex ICS 1100, US) method was employed to measure the concentrations of NO_2^-, NO_3^-, NH_4^+ and PO_4^{3-}. pH, conductivity and redox potential were measured using standard methods (APHA 9221).

2.6 Statistical analysis

ANOVA tests were carried out to assess the difference significance between sample concentrations and *p*-value < 0.05 was considered statistically significant. OriginPro 9.1 was used to develop all graphs. The data processing was conducted by Microsoft Excel 2013.

3. Results and discussion

3.1 Overview of target PPCP removals

Average removals of DEET, PAR, CAF and TCS are summarized in Table 1. The comparisons of corresponding dynamic concentration changes are illustrated in Fig. 2. The concentrations of DEET, PAR, CAF and TCS in the effluents of the five filters at each sampling day are shown in Table S2.

As shown in Table 1, total average removals of the four target compounds during whole operation were 51.9%, 97.6%, 97.9%, 96.2% and 95.7% for Filters 1-5, respectively. GAC sandwich filters (Filters 2-4) achieved considerably higher removals than conventional slow sand filter (Filter 1) and total average removals of each compound were all higher than 90%. DEET removal has been significantly improved compared with authors' previous work using greater duckweed-based constructed wetland. Removals of PAR, CAF and TCS were higher than 90% but DEET removal was much lower (<45%) (J. Li et al., 2017). Monsalvo et al. (2014) conducted a study removing trace organics using anaerobic membrane bioreactors, finding removals of DEET, CAF, PAR and TCS at 1.4%, 76.9%, 58.1% and 90.2%, respectively. In addition, except for CAF, removals of DEET, PAR and TCS were found all below 25% in activated sludge tank-plate and frame/hollow-fibre membrane system (Kim et al., 2007). Good removal results found in our study indicate the applicability of GAC sandwich SSF for removing the target PPCPs. Details and discussion of individual compound are presented below.

3.2 Comparison of filter performance on target PPCPs' removal

3.2.1 DEET

Highest DEET effluent concentrations were found in Filter 1 (sand only), ranging from14.14 to 21.91 μg/L (Table S2, removals between 14.4% to 43.4%). In contrast, the effluent concentrations of DEET from the other four filters were all below 2.00 μg/L (removal higher than 94%), achieving significantly better removal than that in Filter 1 ($p<0.05$). ANOVA test showed Filter 3 (10 cm sand/20 cm GAC/20 cm sand) presented the best performance for DEET removal compared to the other four filters ($p<0.05$). DEET is usually regarded as a recalcitrant (Ávila et al., 2017; Zhu and Chen, 2014) and hydrophobic compound, but it can be biodegraded theoretically (Verlicchi and Zambello, 2014). However, the low DEET removal in Filter 1 (sand only) indicates biodegradation in the sand filter and *schmutzdecke* was not effective even for low filtration rate of 5 cm/h. High removals of DEET by Filters 2 to 5 confirm that GAC can effectively remove DEET as indicated by Lin et al. (2016) who found 100% DEET removal in GAC contactors.

3.2.2 Paracetamol

GAC-associated filters achieved significantly higher removal than Filter 1 ($p<0.05$) but no significant difference was found among the three sandwich filters ($p>0.05$). PAR was not detected in the Filter 2 effluent during the whole experimental period and it was only detected in the effluents of Filter 3 and Filter 4 during the first few days after maturation (Table S2). However, in Filter 5, PAR was found in the first 16 days while it disappeared from day 17, even when filtration rate was increased. Nevertheless, PAR was detected in Filter 1 (only sand) at day 2, then no detection occurred for a while, and from day 26, it was detected again until the end of the run, fluctuating from 5.46 (78.2% removal) to 8.09 μg/L (67.6% removal) (Table S2). These values are slightly greater than the findings (65.2% highest removal) of Pompei et al. (2016) who used a finer sand grain with effective size of 0.210 mm to remove a small PAR concentration of 2 μg/L from natural lake water by household SSF. In the present work, it can be suggested that PAR elimination can occur by both biodegradation and GAC adsorption as demonstrated by Filter 1 and Filter 5, respectively. Zhao et al. (2015) treated 60 μg/L triclosan by constructed wetland and found triclosan-biodegradation bacteria abundance increased 9.36~31.37%. Thus, it can be speculated that during the first few days of filtration process, PAR-preference microbes within SSF may thrive with contact of PAR and accelerate PAR elimination, as shown by Filters 1, 3 and 4. However, this should be further investigated.

3.2.3 Caffeine

No significant CAF removal difference was found between the four GAC-associated filters ($p>0.05$) but it was significantly higher than the sand alone Filter 1 ($p<0.05$). CAF was not found in the effluent of Filter 3 during the whole experiment. But CAF in the effluents was observed in one sampling day (Day 23) of Fiter 2 and two sampling days in Filter 4 and Filter 5 (Days 23 and 26), all below 0.50 μg/L (Table S2). The sudden occurrence of CAF in the effluents may be attributed to the change of filtration rate, which is discussed in Section 3.3. Rizzo et al. (2015) investigated the removal of CAF by conventional sand filtration coupling with graphene adsorption reactor (GAR, 890 m^2/g surface area) at flow rate of 4.4~5.3 mL/min and found 98.2% of removal, having GAR adsorption played the most important role. More than 80% removal of CAF using biological activated carbon filter (surface area not specified) was also found by Reungoat et al. (2012). Although CAF is regarded easily biodegraded (Lin et al., 2010; Zhang et al., 2013), it was detected in all treated water samples of Filter 1 (only sand) with concentrations fluctuating between 14.46 to 22.92 μg/L (Table S2, removal from 8.3% to 42.2%). Results also confirm that CAF can be adsorbed (Filters 2-5), having the Filter 3 presented the highest efficiency.

3. 2.4 Triclosan

Compared with other three compounds, TCS behaved more recalcitrant. It was detected in all effluent samples of Filter 1 with concentrations ranging from 2.21 to 15.12 μg/L (Table S2, removals from 91.3% to 39.5%). From day 23, TCS was detected in effluent samples of Filter 2 until the end of the filtration run. It was also detected in majority of the other three filters: 13 out of 18 sampling days of Filter 3, and 17 out of 18 sampling days of Filters 4 and 5. Rossner et al. (2009) found 99.5 % TCS removal using coconut-shell-based GAC CC-602 with surface area of 1160 m^2/g which is double than the GAC used in our work (i.e. 556 m^2/g). Although TCS removals in the GAC-associated filters varied, the overall TCS removal of Filters 2, 3, 4 and 5 showed no significant difference ($p>0.05$), but it was significantly different from Filter 1 ($p<0.05$). Generally, photo-degradation is recognised as an important TCS elimination mechanism and biodegradation of TCS has been reported elsewhere (Aranami and

Readman, 2007; Taştan and Dönmez, 2015). In the present filtration systems, visible light was directly affecting the supernatant water layer and surrounding the filtration columns which were transparent. This may indicate that the removal of TCS in Filter 1 may have been by photo-biodegradation in the supernatant layer (Campos et al., 2006), and it should be further investigated. However, relatively low TCS concentrations in GAC-associated filter effluents indicated this compound may also be adsorbed.

In the present study, Filter 3 achieved overall best removal and the use of GAC significantly ($p<0.05$) enhanced removal performance compared with traditional SSF (Filter 1). Under same filtration rate, more GAC volume ensures more adsorption time between GAC and contaminants. However, removals of the target compounds using GAC sandwich filters were not proportional to the GAC volume. Our results agree well with Feng et al. (2012) who also found no direct proportion between contaminant removal and adsorption time. Also, Paredes et al. (2016) used GAC contactors to remove PPCPs at different empty bed contact time but no direct correlations were found between organic pollutants and contact time, and influence of other factors including biological activity and loading rates were suggested as the main cause.

3.3 Target PPCP removals at different filtration rates

From Fig. 2, DEET effluent concentrations in all five filters increased when filtration rate rose from 5 cm/h to 10 cm/h as expected (Zearley and Summers, 2012). When filtration rate rose to 20 cm/h, effluent concentrations of DEET continued increasing in Filters 4 and 5, but dropped in Filters 1, 2 and 3. However, despite the increased effluent concentration when switching to faster filtration rates, DEET concentrations did not increase drastically.

PAR was not detected for filtration rates of 10 cm/h and 20 m/h in all GAC-associated filters. However, at 10 cm/h, PAR was detected in Filter 1 at average concentration of 5.98 μg/L and rose to 7.43 μg/L when filtration rate increased to 20 cm/h, which demonstrated that Filter 1 (sand only) was not capable of efficiently removing 25 μg/L PAR at filtration rate faster than 10 cm/h, while GAC helped improving the filter efficiency considerably ($p<0.05$).

CAF was present in all effluent samples of Filter 1 and its concentration increased from 18.20 µg/L (day 19, 5 cm/h) to 20.76 µg/L (day 23, 10 cm/h) but interestingly it did not increase when filtration rate rose to 20 cm/h (day 44). Also, CAF concentration in Filter 1 fluctuated with increased filtration rate, but it was kept on average 17~20 µg/L. However, in the other filters, CAF only appeared when filtration rates were increased, then declined to zero again, which may be attributed to release/desorption effect when hydraulic pressure suddenly changed (Rizzo et al., 2015).

Compared with the other three compounds, TCS showed more resistance. It was found in all effluent samples of Filter 1 (only sand) and Filter 5 (only GAC) at filtration rate of 5 cm/h, but the use of combination of sand and GAC showed a better TCS removal performance ($p<0.05$). When filtration rate changed to 10 cm/h, TCS effluent concentrations increased first (except in Filter 5 with only GAC) and decreased quickly again. No significant TCS removal difference ($p>0.05$) was found between 10 cm/h and 20 cm/h, although Filter 3 and Filter 5 achieved the highest average removal at these filtration rates (94.8% and 92.2%, respectively).

From the results, it can be assumed that in GAC sandwich SSF system, the removal of target PPCPs may be due to both adsorption by the GAC layer (as shown by Filter 5) and biodegradation within the *schmutzdecke* and upper sand layer (as shown by Filter 1), and these are in accordance with Escolà Casas and Bester (2015). Apart from biodegradation, bio-sorption process such as electrostatic attraction and adhesion may also contribute to the removal of target compounds (Huisman and Wood, 1974). During the first few weeks, microbes within the *schmutzdecke* and upper sand layer may thrive gradually (Campos et al., 2002), favouring the target PPCPs elimination. When the filtration rate increased, the decline of PPCP removal by Filter 1 (sand only) may be attributed to the short contact time (Campos and Outhwaite, 2014) and release/desorption effect (Rizzo et al., 2015). But the subsequent decrease of PPCP concentrations within several days in GAC-associated filters suggests a fast system adaption to filtration rate changes (Table S2).

At 5 cm/h, Filter 2 achieved the highest average removal at 99.5%, but the average PPCP removals in the other four filters at 5 cm/h were lower than at larger filtration rates (Table 1).

Filter 3 achieved the highest average PPCP removal (i.e. 98.2%) at 10 cm/h, but no significant difference was found between filtration rates of 10 and 20 cm/h for the three GAC sandwich filters ($p>0.05$). In addition, the fluctuation of PPCP and high concentrations in the effluent of Filter 1 indicates that the filter with sand only (effective size of 0.6 mm) was not effective enough to remove PPCP (25 μg/L) in the present study. Reungoat et al. (2011) studied pilot-scale WWTP filters and found that biosand filters showed limited PPCP removal and that biological activated carbon (BAC, 1,146 m^2/g surface area) removed 90% of PPCP concentration. In the present study, GAC improved the PPCP compound removals but the average PPCP removal in Filter 5 (95.7%, only GAC) was lower than that in Filters 2 (97.6%), 3 (97.7%) and 4 (96.2%) (Table 1). Thus, our results suggest that biological activities within the *schmutzdecke* and upper sand layer of the sandwich filters have played an important role for the target PPCP removals. Also, it can be suggested that the use of GAC sandwich SSF could compensate the ineffectiveness of both single sand and GAC filters.

3.4 General parameters during filtration

The COD and TOC concentrations of the effluents in each filter are shown in Table S3. The average removals of COD for the five filters were 62.2%, 63.9%, 65.8%, 62.9% and 50.8%, respectively for Filters 1 to 5. TOC average removals were 84.5%, 81.4%, 90.3%, 76.2% and 68.3%, respectively, for Filters 1 to 5. As for the target PPCPs, Filter 3 (10 cm sand/20 cm GAC/20 cm sand) had the best average removals for both COD and TOC. TOC removal was found to be around 50% using GAC contactors (Velten et al., 2011). Bauer et al. (1996) found TOC removal from surface water in large scale GAC sandwich SSF around 30~40 % and on average 20 % in control slow sand filter. As glucose was used as carbon source to prepare the synthetic wastewater in the present study, higher TOC removal could be due to the fact that it is more degradable than other organics in real natural water (Zeng et al., 2007).

The concentrations of nitrite, nitrate, phosphate and ammonium are shown in Table S4. Effluent pH was around 7.5~8.5, which lay within the range of discharge standards (6.5~8.5) reported by WHO-EM/CEH/142/E. Other general water parameters are shown in Table S5. Total headloss of all filters were below 2.0 cm during the whole experiment. No nitrite was detected except only a few days. During the whole test, average removals of 97.7%, 97.4%, 99.7%, 100% and 99.9% for nitrate and 92.5%, 93.8%, 95.1%, 94.1% and 94.5% for ammonium were achieved in Filters 1 to 5, respectively, indicating very good nitrate and ammonium removals by all filters. Ammonium was just detected at 5 cm/h and during the first few days at 10 cm/h. The highest concentration reached to 0.76 mg/L and exceeded 0.5 mg/L limit suggested by EU Drinking Water Directive (98/83/EC). Nitrification and denitrification can occur simultaneous in sand filtration and higher dissolved oxygen (DO) transferred into the sand bed with faster filtration rates enhance nitrification process (Nakhla and Farooq, 2003). So, it can be suggested that higher filtration rates (10 and 20 cm/h) promoted nitrification process transforming ammonium to nitrate. Denitrification microbes could therefore denitrify nitrate to nitrite, then to nitrogen (Holman and Wareham, 2005). Hence, apart from relatively low efficiency, the presence of ammonium at slow filtration rates in the present study suggests inapplicability of filtration rate of 5 cm/h.

Phosphate removals were 13.3%, 12.6%, 11.4%, 7.2% and 7.9% for Filters 1 to 5, respectively. Without any chemical dosing, up to 35% total phosphorus removal was achieved using biological aerated filters by Clark et al. (1997). Altmann et al. (2016) found 80% removal of phosphorus by a GAC-sand filter (GAC upper layer with surface area not specified, and sand lower layer) for secondary effluent treatment but ferric chloride was added into the influent as coagulant.

Overall, no significant difference was found between filtration rates of 10 cm/h and 20 cm/h for N and P removals ($p > 0.05$).

3.5 Kinetics of target PPCP compounds adsorption onto GAC

From Table 1, it can be seen that adsorption played an important role in the removal of the target PPCPs investigated in this study. Thus, to further understand the removal mechanisms, adsorption kinetics of the four target PPCP compounds at 25 μg/L onto GAC was investigated. Fig. 3 shows the adsorption capacity (μg/mg) of the four target compounds by GAC within 660 min.

Adsorption of PAR and TCS reached equilibrium at around 120 min while DEET and CAF reached equilibrium at about 300 min (Fig. 3). Maximum adsorption capacity was 0.025 μg/mg for all compounds. From Fig. 3, experimental adsorption capacity (q_e, Exp) of DEET, PAR, CAF and TCS were about 0.0243, 0.0249, 0.0249 and 0.0242 μg/mg, respectively. Further kinetic modelling of the adsorption process of all target PPCP compounds onto GAC were carried out using Lagergren pseudo-first-order, pseudo-second-order and Elovich equations. These three models have been widely applied to describe the adsorption of pollutants from water onto adsorbents (Cao et al., 2013; Leng et al., 2015; Z. Li et al., 2017; Yan and Viraraghavan, 2003).

For Lagergren pseudo-first-order equation:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_{p1}(q_e - q_t) \qquad \text{Eq. (1)}$$

Which can be rearranged to:

$$\log(q_e - q_t) = \log q_e - \frac{k_{p1}}{2.303}t \qquad \text{Eq. (2)}$$

Where qe and qt (μg/mg) are the adsorption capacities at equilibrium and time t (min), respectively. k_{p1} (min^{-1}) is the pseudo-first-order constant for this kinetic model.

For pseudo-second-order equation:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_{p2}(q_e - q_t)^2 \qquad \text{Eq. (3)}$$

Where qe and qt (μg/mg) are the adsorption capacities at equilibrium and time t (min), respectively. k_{p2} (mg/μg·min) is the pseudo-second-order constant for the kinetic model. V_0 ($k_{p2}q_e^2$, μg/mg·min) means the initial adsorption rate (Ho and McKay, 1998). Pseudo-second-order equation has different variations and based on the study of Kumar (2006b), five linear forms were chosen and are shown in Table 2.

For Elovich equation (Low, 1960):

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = ae^{-\alpha q_t} \qquad \text{Eq. (9)}$$

Which can be rearranged to:

$$q_t = \alpha \ln(a\alpha) + \alpha \ln t \qquad \text{Eq. (10)}$$

Where q_t represents the amount of pollutants adsorbed at time t, a is the desorption constant (μg/mg.min), and α is the initial adsorption rate (mg/μg) (Al-Meshragi et al., 2008; Cao et al., 2013).

Table S6 summarizes the fitted parameters of kinetic models of Lagergren pseudo-first-order and Elovich equations for adsorption of DEET, PAR, CAF and TCS onto GAC. The correlation coefficients (R^2) for the fitted Lagergren pseudo-first-order equation were 0.9511, 0.8652, 0.9459 and 0.5594 for DEET, PAR, CAF and TCS, respectively (Table S6). Calculated q_e were 0.0207, 0.7752, 0.0154 and 0.0037 μg/mg for DEET, PAR, CAF and TCS, respectively, comparing to the experimental q_e at 0.0243, 0.0249, 0.0249 and 0.0242 μg/mg (Fig. 3). For Elovich equation, the R^2 of the fitted models for DEET, PAR CAF and TCS were 0.9796, 0.8542, 0.9582 and 0.8642, respectively. These two equations usually describe diffusion and chemical adsorption models (Li et al., 1999; Wu et al., 2009). In the present study, data did not fit the Lagergren pseudo-first-order and Elovich equations very well as the calculated q_e and R^2 varied significantly.

Parameters of the kinetic models of pseudo-second-order equation for adsorption of DEET, PAR, CAF and TCS on GAC are shown in Table 2. Among the five models, model Type 1 gave the best fitting level as R^2 values for DEET, PAR, CAF and TCS were 0.9983, 0.9994, 0.9990 and 0.9994, with corresponding calculated q_e of 0.0261, 0.0254, 0.0264 and 0.0247 μg/mg, respectively, which were much closer to the experimental q_e values than Lagergren pseudo-first-order fitted models. Calculated q_e of DEET and CAF by model Type 5 was negative, which indicates this linearization technique was not suitable in the present study. Based on the claculation, the pseudo-second-order fitted the data, suggesting the direct adsorption mechinism for the proposed system (Plazinski et al., 2009). Similarly, Lu et al. (2014) studied the adsorption kinetics of oxidized sulphur compounds onto GAC and found that it was well fitted to the pseudo-second-order model ($R^2 > 0.99$).

At the end of the filtration process, no PAR and CAF were found in the treated water by the GAC-associated filters, while DEET and TCS removals by GAC adsorption were less effective. Kinetic results showed that TCS had the lowest equilibrium capacity (0.0242 μg/mg), followed by DEET, which had the equilibrium capacity of 0.0243 μg/mg. This agreed well with the results found above (Sections 3.2.1 and 3.2.4). As TCS has larger molecular weight than other three compounds (Table S1) and the GAC used in the present study has 80% of the pores comprised by microporous, it might be that TCS molecule was larger to enter the GAC pores than other PPCP molecules, resulting in relatively lower removals (Yang et al., 2011; Zhang et al., 2010). Besides, DEET is usually regarded as a compound resistant to biodegradation (Zhu and Chen, 2014) and removal of DEET in Filter 1(sand only) was lower than the other three compounds at 10 and 20 cm/h. Thus, the good removal of DEET by GAC-associated filters indicated effective adsorption, which may be attributed to hydrophobic property and interactions of both GAC and DEET molecules (Li et al., 2002; Moreno-Castilla, 2004; Reeder et al., 2001). In addition, the π–π dispersion, existence of hydrogen bonds, release/desorption effect and electron distribution may have influenced the adsorption performance and led to the fluctuations of the treated water concentration (Li et al., 2002; Liu et al., 2010; Moreno-Castilla, 2004; Rizzo et al., 2015). It is worth noting that, as shown by the filter 1 (sand only), removal of the target PPCP compounds also demonstrate that biodegradation processes were present in the filter. Hence, deeper biodegradation process and molecular-level adsorption mechanisms during GAC sandwich SSF filtration process can be further investigated.

4. Conclusions

The main conclusions drawn from this work are:

- The target PPCP compounds were significantly (p<0.05) removed by using GAC sandwich SSF than sand alone. Filter 2 (10 cm sand/10 cm GAC/30 cm sand) at 5 cm/h had 99.5% average removal for the target PPCP compounds, but 5 cm/h led to slower filtration and ammonium was not effectively removed. Filter 3 (10 cm sand/20 cm

GAC/20 cm sand) achieved the overall optimal average target PPCP removal (98.2%) at 10 cm/h filtration rate.

- No significant difference of average PPCP removals was found between 10 cm/h and 20 cm/h filtration rates for the three GAC sandwich filters (p>0.05).
- Filter 3 (10 cm sand/20 cm GAC/20 cm sand) also showed better average removals of COD (65.8%) and TOC (90.3%), compared with the other filters. Nitrogen could be effectively removed by the GAC sandwich SSFs. No significant difference was found between 10 cm/h and 20 cm/h for nitrogen and phosphate removals (p>0.05).
- Type 1 pseudo-second-order model fitted best the adsorption kinetics of the target PPCP compounds onto GAC.
- Results of this lab-scale test show that GAC sandwich slow sand filter was an effective process for removing the target PPCPs from synthetic wastewater. This suggests that PPCPs may be effectively removed from wastewater by using a combination of sand with reduced GAC layer depth at tertiary treatment, potentially reducing operational costs.

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Table 1: Summary of average removals for individual and total compounds during the filtration process

Compound	Filtration rate*	Filter 1	Filter 2	Filter 3	Filter 4	Filter 5

DEET	5 cm/h	Average removal (%)	36.0	97.9	97.7	98.1	98.3
	10 cm/h	Average removal (%)	23.3	95.6	98.0	97.5	97.1
	20 cm/h	Average removal (%)	18.8	97.9	99.4	98.2	98.3
	Total average DEET (%)		25.7	97.2	98.4	98.0	97.9
PAR	5 cm/h	Average removal (%)	98.2	100	97.0	89.6	84.7
	10 cm/h	Average removal (%)	77.6	100	100	100	100
	20 cm/h	Average removal (%)	70.3	100	100	100	100
	Total average PAR (%)		81.4	100	99.1	96.7	95.2
CAF	5 cm/h	Average removal (%)	19.8	100	100	100	99.8
	10 cm/h	Average removal (%)	29.7	99.8	100	99.6	99.7
	20 cm/h	Average removal (%)	26.4	100	100	100	100
	Total average CAF (%)		25.3	99.9	100	99.9	99.8
TCS	5 cm/h	Average removal (%)	57.1	100	94.3	89.0	83.9
	10 cm/h	Average removal (%)	85.2	88.6	94.8	89.2	94.2
	20 cm/h	Average removal (%)	80.3	91.1	90.6	92.1	92.2
	Total average TCS (%)		74.2	93.2	93.2	90.1	90.1
Total average PPCPs at 5 cm/h (%)			52.8	99.5	97.3	94.2	91.7
Total average PPCPs at 10 cm/h (%)			53.9	96.0	98.2	96.6	97.8
Total average PPCPs at 20 cm/h (%)			48.9	97.3	97.5	97.6	97.6
Total average PPCPs for whole tests (%)			51.9	97.6	97.7	96.2	95.7

* Operation period for each filtration rate was three weeks.

Table 2 Types and parameters of kinetic models of pseudo-second-order equation for adsorption of DEET, PAR, CAF and TCS on GAC

	DEET				PAR			
Type	q_e, Cal (μg/mg)	k_{p2} (mg/μg·min)	V_0 (μg/mg·min)	R^2	q_e, Cal (μg/mg)	k_{p2} (mg/μg·min)	V_0 (μg/mg·min)	R^2
1 $\frac{t}{q_t} = \frac{1}{k_{p2}q_e^2} + \frac{1}{q_e}t$	0.0261	0.9338	6.361E-04	0.9983	0.0254	4.3645	2.816E-03	0.9994
2 $\frac{1}{q_t} = \left(\frac{1}{k_{p2}q_e^2}\right)\frac{1}{t} + \frac{1}{q_e}$	0.0220	1.8149	8.784E-04	0.9806	0.0233	6.6209	3.594E-03	0.8061
3 $\frac{1}{t} = \frac{k_{p2}q_e^2}{q_t} - \frac{k_{p2}q_e^2}{q_e}$	0.0223	1.6410	8.985E-04	0.9806	0.0249	4.6707	2.896E-03	0.8061
4 $\frac{q_t}{t} = k_{p2}q_e^2 - \frac{k_{p2}q_e^2 q_t}{q_e}$	0.0236	1.2585	7.009E-04	0.8961	0.0261	3.8167	2.600E-03	0.7377
5 $\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_{p2}t$	-0.0002	82.701	3.308E-06	0.8005	0.0001	106.32	1.063E-06	0.5715
	CAF				TCS			
Type	q_e, Cal (μg/mg)	k_{p2} (mg/μg·min)	V_0 (μg/mg·min)	R^2	q_e, Cal (μg/mg)	k_{p2} (mg/μg·min)	V_0 (μg/mg·min)	R^2
1 $\frac{t}{q_t} = \frac{1}{k_{p2}q_e^2} + \frac{1}{q_e}t$	0.0264	1.2081	8.420E-04	0.9990	0.0247	4.0913	2.496E-03	0.9994
2 $\frac{1}{q_t} = \left(\frac{1}{k_{p2}q_e^2}\right)\frac{1}{t} + \frac{1}{q_e}$	0.0253	1.3310	8.520E-04	0.9833	0.0219	7.1407	3.425E-03	0.7892
3 $\frac{1}{t} = \frac{k_{p2}q_e^2}{q_t} - \frac{k_{p2}q_e^2}{q_e}$	0.0246	1.3211	7.995E-04	0.9833	0.0238	4.7731	2.704E-03	0.7892
4 $\frac{q_t}{t} = k_{p2}q_e^2 - \frac{k_{p2}q_e^2 q_t}{q_e}$	0.0268	1.1119	7.986E-04	0.9282	0.0247	3.7652	2.297E-03	0.7005

5 $\frac{1}{(q_e-q_t)} = \frac{1}{q_e} + k_{p2}t$	-4.41E-05	45.163	8.763E-08	0.8466	0.0004	15.732	2.676E-06	0.4276

q_e, Exp (µg/mg) of DEET, PAR, CAF and TCS are 0.0243, 0.0249, 0.0249 and 0.0242 µg/mg, respectively

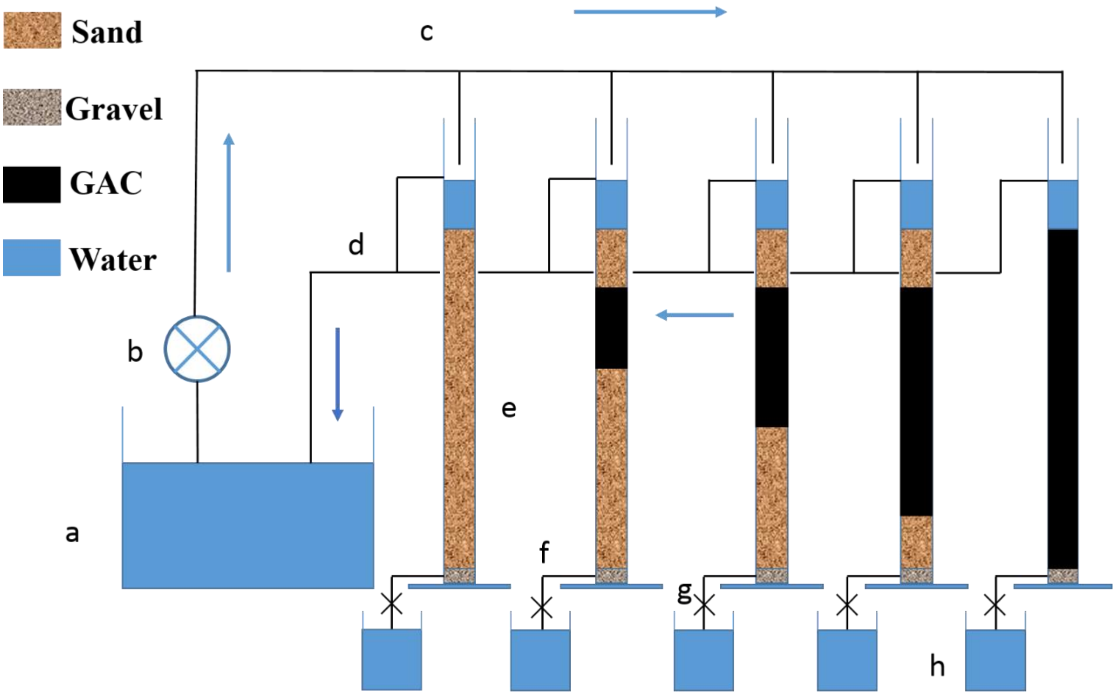

Fig 1: Schematic representation for GAC sandwich SSF experiment.

(a) influent tank; (b) peristaltic pump; (c) influent pipe; (d) overflow pipe; (e)filter; (f) effluent pipe; (g) effluent valve; (h) effluent bottle.

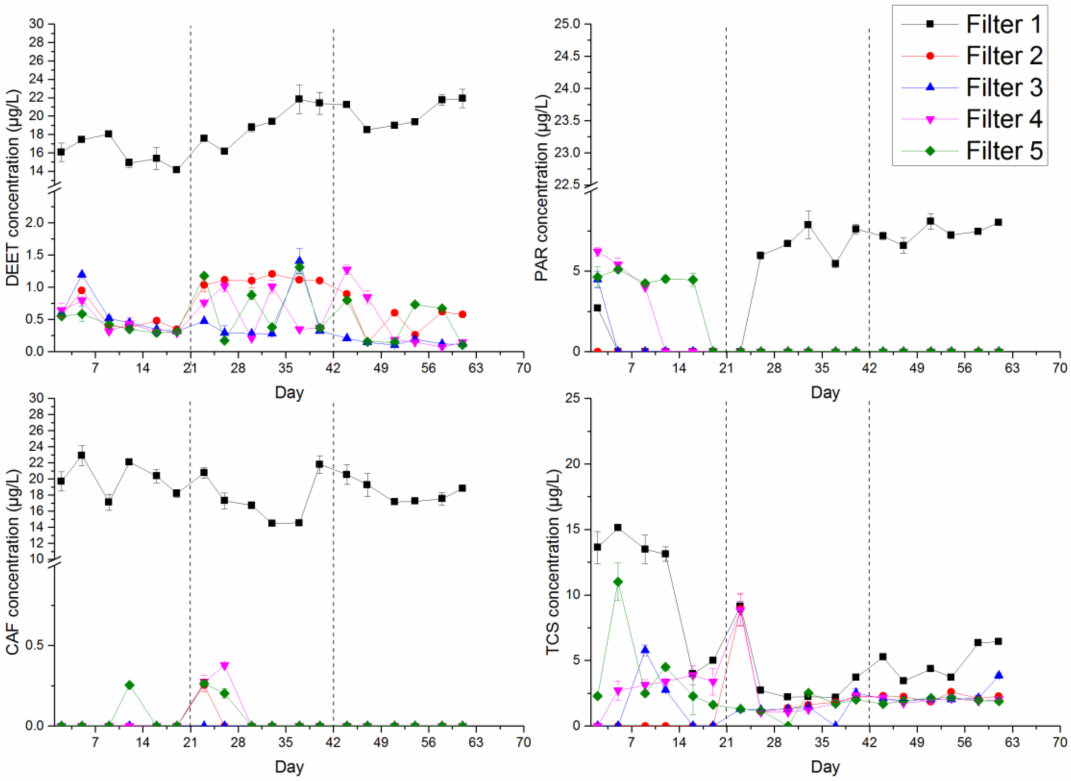

Fig 2: Comparisons of dynamic concentration changes of DEET, PAR, CAF and TCS during filtration process.

(Day 1 to Day 21, filtration rate at 5 cm/h; Day 22 to day 42, filtration rate at 10 cm/h; Day 43 to Day 63, filtration rate at 20 cm/h)

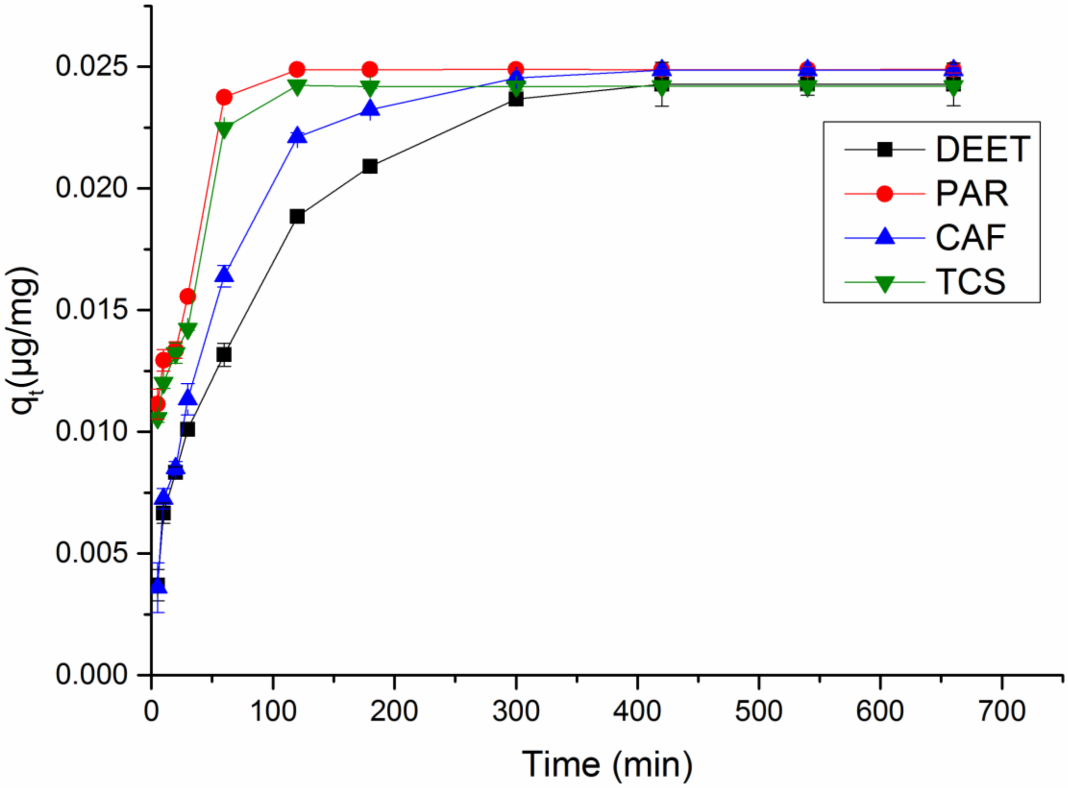

Fig 3: Adsorption kinetic plots of DEET, PAR, CAF and TCS on GAC. (Adsorption conditions: water temperature = 23 °C; initial DEET, PAR, CAF and TCS concentration = 25 µg/L; GAC dose = 1 g/L)

Supplementary Data

For

The Application of GAC Sandwich Slow Sand Filtration to Remove Pharmaceutical and Personal Care Products

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List of supporting information:

Figure S1 Scanning electron microscopy of GAC

Table S1 Target PPCPs and relevant information

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Table S3 COD and TOC concentrations in the effluent during the filtration tests

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Table S5 pH, conductivity and redox potential in the effluents during the filtration tests

Table S6 Parameters for the kinetic models of Lagergren pseudo-first-order and Elovich equations for adsorption of DEET, PAR, CAF and TCS on GAC

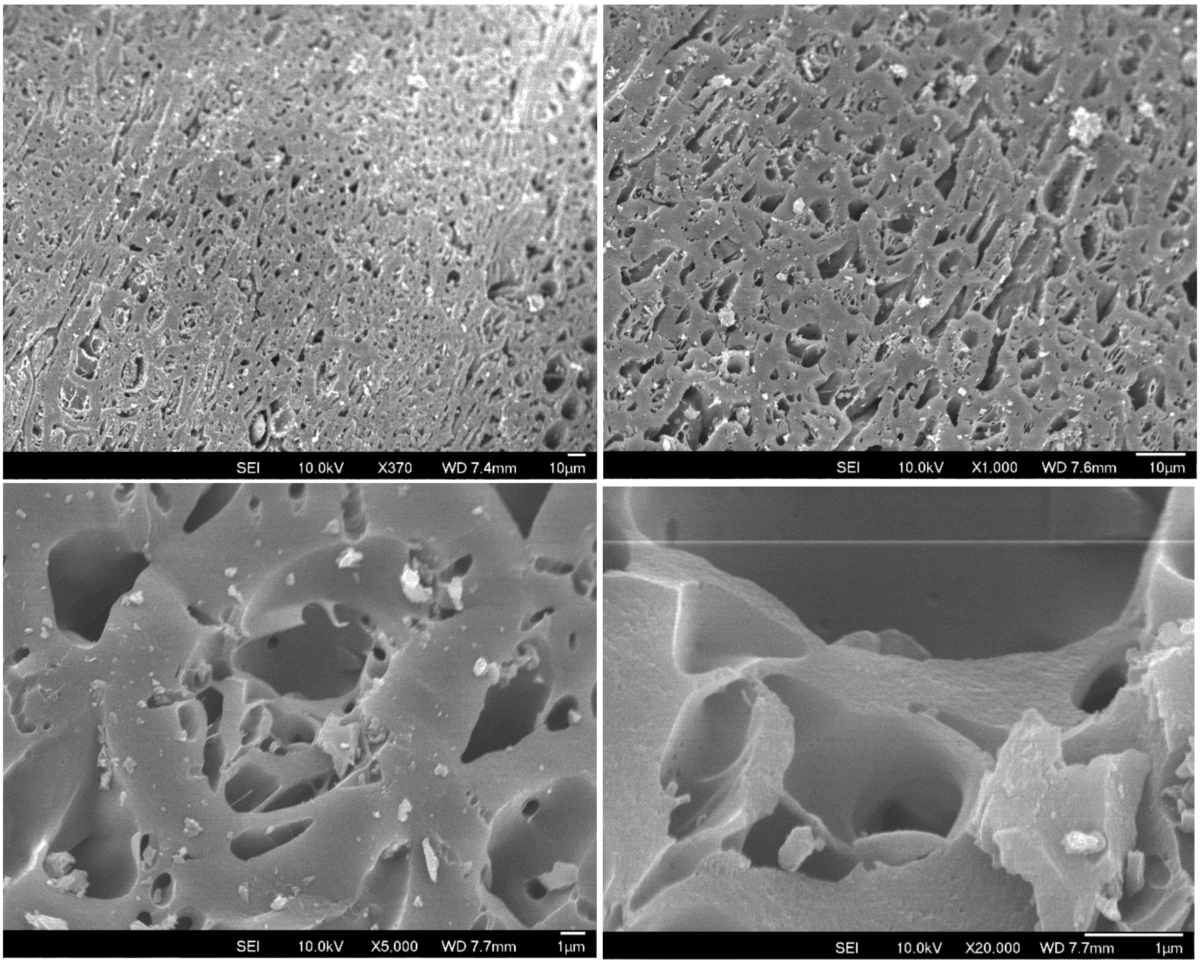


Figure S1 Scanning electron microscopy of GAC

Table S1 Target PPCPs and relevant information

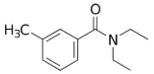
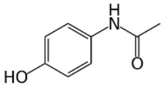
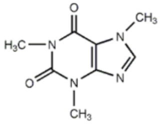
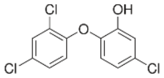
Compounds	Abbreviation	Molecular formula	Molecular weight	CAS No.	Category	Structure
Diethyltoluamide	DEET	$C_{12}H_{17}NO$	191.27	134-62-3	repellent	
Paracetamol	PAR	$C_8H_9NO_2$	151.16	103-90-2	analgesic	
Caffeine	CAF	$C_8H_{10}N_4O_2$	194.19	58-28-2	stimulant	
Triclosan	TCS	$C_{12}H_7Cl_3O_2$	289.54	3380-34-5	antibacterial	

Table S2 Concentrations of DEET, PAR, CAF and TCS in the effluents during the filtration process

Filtration rate		Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
	day	DEET (μg/L)	RSD*	DEET (μg/L)	RSD	DEET (μg/L)	RSD	DEET (μg/L)	RSD	DEET (μg/L)	RSD
5 cm/h	2	16.07	1.01	0.56	0.01	0.60	0.01	0.64	0.11	0.55	0.01
	5	17.42	0.24	0.95	0.02	1.20	0.02	0.80	0.04	0.59	0.12
	9	18.04	0.15	0.40	0.01	0.52	0.04	0.32	0.03	0.42	0.02
	12	14.90	0.46	0.38	0.00	0.45	0.08	0.43	0.10	0.35	0.03
	16	15.38	1.21	0.48	0.04	0.35	0.09	0.31	0.02	0.29	0.04
	19	14.14	0.15	0.35	0.03	0.32	0.00	0.29	0.01	0.31	0.01
	Average	15.99	0.54	0.52	0.02	0.57	0.04	0.47	0.05	0.42	0.04
10 cm/h	23	17.56	0.26	1.04	0.10	0.47	0.00	0.76	0.04	1.18	0.01
	26	16.13	0.24	1.11	0.01	0.29	0.11	1.02	0.08	0.17	0.02
	30	18.76	0.45	1.10	0.11	0.28	0.02	0.21	0.00	0.88	0.07
	33	19.38	0.17	1.21	0.01	0.28	0.03	1.01	0.10	0.38	0.02
	37	21.82	1.56	1.11	0.00	1.41	0.20	0.35	0.00	1.32	0.10
	40	21.39	1.21	1.10	0.00	0.32	0.00	0.37	0.01	0.37	0.01
	Average	19.17	0.65	1.11	0.04	0.51	0.06	0.62	0.04	0.72	0.04
20 cm/h	44	21.23	0.12	0.90	0.02	0.21	0.00	1.28	0.08	0.80	0.02
	47	18.52	0.23	0.15	0.00	0.14	0.01	0.85	0.10	0.16	0.04
	51	18.99	0.24	0.60	0.04	0.10	0.01	0.18	0.00	0.15	0.01
	54	19.36	0.12	0.26	0.00	0.19	0.01	0.15	0.01	0.73	0.02
	58	21.75	0.56	0.62	0.01	0.12	0.02	0.07	0.00	0.67	0.03
	61	21.91	0.99	0.58	0.02	0.11	0.01	0.14	0.00	0.11	0.01
	Average	20.29	0.38	0.52	0.02	0.15	0.01	0.45	0.03	0.44	0.02
Total average DEET		18.49	0.52	0.72	0.02	0.41	0.04	0.51	0.04	0.52	0.03
Filtration rate		Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
	day	PARn (μg/L)	RSD	PAR (μg/L)	RSD	PAR (μg/L)	RSD	PAR (μg/L)	RSD	PAR (μg/L)	RSD
5 cm/h	2	2.71	0.11	n.d.	n.a.	4.50	0.51	6.22	0.25	4.64	0.63
	5	n.d.**	n.a.***	n.d.	n.a.	n.d.	n.a.	5.42	0.42	5.11	0.12
	9	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	4.02	0.12	4.25	0.07
	12	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	4.52	0.23
	16	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	4.47	0.41
	19	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	Average	0.45	0.02	n.d.	n.a.	0.75	0.09	2.61	0.13	3.83	0.24
10 cm/h	23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	26	5.98	0.23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	30	6.70	0.14	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	33	7.88	0.86	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	37	5.46	0.23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	40	7.61	0.31	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	Average	5.61	0.30	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
20 cm/h	44	7.19	0.22	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	47	6.58	0.47	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	51	8.09	0.48	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.

	54	7.25	0.23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	58	7.46	0.11	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	61	8.03	0.03	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	Average	7.43	0.26	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
Total average PAR		4.50	0.19	n.d.	n.a.	0.25	0.03	0.87	0.04	1.28	0.08

Filtration rate		Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
	day	CAF (μg/L)	RSD	CAF (μg/L)	RSD	CAF (μg/L)	RSD	CAF (μg/L)	RSD	CAF (μg/L)	RSD
5 cm/h	2	19.70	1.21	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	5	22.92	1.23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	9	17.11	1.01	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	12	22.10	0.23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	0.25	0.01
	16	20.35	0.85	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	19	18.20	0.47	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	Average	20.06	0.83	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	0.04	0.00
10 cm/h	23	20.76	0.66	0.25	0.04	n.d.	n.a.	0.27	0.04	0.26	0.02
	26	17.28	0.97	n.d.	n.a.	n.d.	n.a.	0.38	0.01	0.20	0.03
	30	16.72	0.41	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	33	14.46	0.21	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	37	14.53	0.23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	40	21.80	1.11	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	Average	17.59	0.60	n.d.	n.a.	n.d.	n.a.	0.11	0.01	0.08	0.01
20 cm/h	44	20.54	1.23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	47	19.25	1.45	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	51	17.15	0.11	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	54	17.23	0.03	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	58	17.52	0.78	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	61	18.79	0.01	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
	Average	18.41	0.60	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
Total average CAF		18.69	0.68	0.01	0.00	n.d.	n.a.	0.04	0.00	0.04	0.00

Filtration rate		Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
	day	TCS (μg/L)	RSD	TCS (μg/L)	RSD	TCS (μg/L)	RSD	TCS (μg/L)	RSD	TCS (μg/L)	RSD
5 cm/h	2	13.62	1.22	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	2.30	0.20
	5	15.12	0.14	n.d.	n.a.	n.d.	n.a.	2.71	0.74	11.01	1.45
	9	13.49	1.10	n.d.	n.a.	5.77	0.41	3.13	0.43	2.50	0.03
	12	13.12	0.56	n.d.	n.a.	2.76	0.21	3.38	0.23	4.49	0.23
	16	3.98	0.11	n.d.	n.a.	n.d.	n.a.	3.88	0.74	2.28	1.41
	19	5.00	0.11	n.d.	n.a.	n.d.	n.a.	3.38	1.01	1.63	0.03
	Average	10.72	0.54	n.d.	n.a.	1.42	0.10	2.75	0.53	4.04	0.56
10 cm/h	23	9.13	0.41	8.92	1.21	1.29	0.03	8.83	1.20	1.31	0.02
	26	2.72	0.06	1.10	0.01	1.24	0.09	1.06	0.03	1.16	0.14
	30	2.21	0.07	1.37	0.01	1.28	0.10	1.06	0.01	n.d.	n.a.
	33	2.24	0.12	1.62	0.04	1.46	0.01	1.26	0.00	2.54	0.02
	37	2.18	0.02	1.82	0.01	n.d.	n.a.	1.72	0.00	1.72	0.15

	40	3.70	0.04	2.21	0.11	2.51	0.31	2.32	0.04	2.01	0.11
	Average	3.70	0.12	2.84	0.23	1.30	0.09	2.71	0.21	1.46	0.07
	44	5.27	0.06	2.30	0.14	2.08	0.04	2.15	0.02	1.70	0.02
	47	3.44	0.21	2.24	0.21	1.97	0.01	1.73	0.01	1.92	0.01
	51	4.36	0.18	1.85	0.07	2.04	0.18	1.95	0.01	2.12	0.14
20 cm/h	54	3.71	0.04	2.60	0.09	2.03	0.11	2.10	0.21	2.16	0.17
	58	6.34	0.01	2.10	0.13	2.13	0.21	1.90	0.07	1.96	0.03
	61	6.44	0.07	2.28	0.11	3.84	0.22	2.02	0.02	1.91	0.04
	Average	4.93	0.10	2.23	0.13	2.35	0.13	1.98	0.06	1.96	0.07
Total average TCS		6.45	0.25	1.69	0.12	1.69	0.11	2.48	0.27	2.48	0.23

* RSD. relative standard deviation ** n.d. not detected *** n.a. not available

Table S3 COD and TOC concentrations in the effluent during the filtration tests

	Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
	COD (mg/L)	TOC (mg/L)	COD (mg/L)	TOC (mg/L)	COD (mg/L)	TOC (mg/L)	COD (mg/L)	TOC (mg/L)	COD (mg/L)	TOC (mg/L)
week 1	10	5.6	8	4.5	8	2.0	9	3.4	25	7.9
week 2	22	4.7	20	7.3	20	3.3	22	5.0	24	15.1
week 3	21	5.1	14	2.3	18	0.3	21	1.9	26	9.3
week 4	16	6.0	17	3.4	15	2.0	19	4.3	19	6.4
week 5	12	4.8	12	5.9	11	1.3	15	5.5	17	5.4
week 6	15	1.5	13	3.6	10	1.0	14	4.7	15	0.6
week 7	12	1.0	15	4.3	13	0.9	13	6.1	16	4.8
week 8	15	0.7	16	3.8	15	0.1	12	4.2	17	2.1
week 9	13	1.4	15	0.4	13	0.4	12	3.7	18	5.4

Table S4 Nitrite, nitrate, phosphate and ammonium concentrations in the effluents during the filtration tests

Nitrite	Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
Day	Con (mg/L)*	RSD**	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD
2	n.d.**	n.a.****	1.18	0.24	n.d.	n.a.	n.d.	n.a.	1.50	0.31
5	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
9	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
12	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
16	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
19	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
26	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
30	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	0.20	0.02
33	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
37	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
40	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
44	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
47	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
51	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
54	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
58	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
61	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	0.08	0.02

Nitrate	Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
Day	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD
2	10.25	0.39	11.26	0.22	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
5	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
9	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
12	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
16	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
19	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
23	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.

26	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
30	n.d.	n.a.	n.d.	n.a.	0.25	0.08	n.d.	n.a.	n.d.	n.a.
33	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
37	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
40	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
44	0.86	0.10	n.d.	n.a.	0.30	0.01	0.07	0.01	0.67	0.03
47	n.d.	n.a.	n.d.	n.a.	0.86	0.11	n.d.	n.a.	n.d.	n.a.
51	2.00	0.48	2.16	0.01	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
54	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
58	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
61	n.d.	n.a.	1.14	0.09	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.

Phosphate	Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
Day	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD
2	5.43	0.08	6.21	0.06	5.04	0.18	6.20	0.11	4.59	0.00
5	4.76	0.34	6.55	0.47	7.07	0.47	6.76	0.67	5.55	0.20
9	6.22	0.88	6.23	0.52	5.65	0.32	6.65	0.34	6.18	0.12
12	6.43	0.84	5.98	0.43	6.61	0.35	6.65	0.13	6.72	0.39
16	4.81	0.29	5.85	0.69	6.27	0.40	5.17	0.73	4.62	0.00
19	7.53	0.52	7.19	0.68	6.96	0.00	7.34	0.79	7.44	0.84
23	7.68	0.00	6.89	0.00	6.00	0.07	7.26	0.00	6.96	0.00
26	6.50	0.19	6.95	0.03	7.00	0.08	7.09	0.08	7.30	0.41
30	5.51	0.22	4.70	0.05	6.41	0.06	6.89	0.11	6.72	0.04
33	6.41	0.14	6.29	0.16	6.48	0.02	6.98	0.11	6.98	0.00
37	6.26	0.07	6.04	0.26	6.17	0.18	6.54	0.24	7.03	0.05
40	6.46	0.05	6.33	0.20	6.20	0.15	6.53	0.08	6.99	0.12
44	7.04	0.47	6.94	0.47	5.75	0.17	7.41	0.00	7.55	0.33
47	6.73	0.12	6.44	0.69	6.66	0.11	6.82	0.39	6.62	0.24
51	5.94	0.69	6.17	0.43	6.66	0.23	6.29	0.19	6.27	0.31
54	6.48	1.09	6.01	0.06	6.92	0.11	5.91	0.55	7.04	0.09
58	6.08	0.01	6.30	0.39	6.61	0.19	7.31	0.07	8.41	0.25
61	6.05	0.33	6.22	0.31	6.41	0.23	6.45	0.25	6.41	0.19

Ammonium	Filter 1		Filter 2		Filter 3		Filter 4		Filter 5	
Day	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD	Con (mg/L)	RSD
2	0.43	0.01	1.00	0.02	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
5	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	0.76	0.02	0.22	0.02
9	0.31	0.04	0.43	0.11	0.39	0.04	0.42	0.01	0.27	0.05
12	0.42	0.01	n.d.	n.a.	0.23	0.02	0.34	0.05	0.51	0.02
16	0.37	0.14	0.40	0.16	0.51	0.03	0.37	0.04	0.53	0.01
19	0.49	0.04	0.41	0.05	0.49	0.01	0.21	0.01	0.32	0.01
23	0.32	0.03	0.55	0.10	0.58	0.06	0.58	0.09	0.57	0.02
26	0.28	0.08	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
30	0.35	0.01	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
33	0.43	0.11	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
37	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
40	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	0.04	0.01
44	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
47	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
51	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
54	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
58	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.
61	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.	n.d.	n.a.

*Con. concentration

** RSD. relative standard deviation

*** n.d. not detected

**** n.a. not available

Table S5 pH, conductivity and redox potential in the effluents during the filtration tests

	Filter 1			Filter 2			Filter 3			Filter 4			Filter 5		
Day	pH	Conductivity (μS/cm)	Redox potential (mv)	pH	Conductivity (μS/cm)	Redox potential (mv)	pH	Conductivity (μS/cm)	Redox potential (mv)	pH	Conductivity (μS/cm)	Redox potential (mv)	pH	Conductivity (μS/cm)	Redox potential (mv)
2	8.01	649	70.1	8.09	634	57.9	8.05	610	58.9	8.00	600	59.1	7.84	584	55.2
5	8.17	624	60.5	8.20	652	64.9	8.13	654	69.1	8.05	637	52.0	7.80	673	59.0
9	7.94	630	33.0	8.12	673	35.0	8.23	664	35.6	8.06	645	37.4	8.12	645	31.5
12	7.83	643	32.2	8.07	639	31.4	8.10	643	33.1	8.09	630	27.3	8.17	646	28.1
16	7.93	587	38.6	8.04	620	38.6	8.12	611	33.0	8.09	634	34.5	8.02	626	33.1
19	7.81	604	42.6	7.97	622	46.0	7.99	614	46.8	8.08	628	47.5	8.12	623	38.0
23	7.76	610	27.2	7.68	615	33.4	7.95	631	30.0	7.99	613	30.3	7.92	602	27.8
26	7.81	608	37.0	7.78	612	39.6	7.88	609	32.7	8.00	609	37.9	8.03	611	45.3
30	7.59	610	64.1	7.65	607	67.4	7.80	610	66.0	7.85	613	35.9	7.85	614	36.5
33	7.82	598	76.1	7.75	595	74.9	7.72	594	72.4	7.80	608	67.1	7.92	610	59.8
37	7.55	610	68.6	7.62	617	74.2	7.64	612	72.4	7.67	617	69.2	7.78	626	65.6

40	7.41	602	61.5	7.50	606	61.2	7.61	601	59.1	7.52	600	57.1	7.72	620	53.8
44	7.58	604	64.8	7.55	597	63.3	7.66	592	62.4	7.58	599	55.5	7.85	612	53.3
47	7.66	619	60.5	7.70	603	67.3	7.74	623	68.2	7.75	611	63.2	7.80	622	63.2
51	7.78	686	62.2	8.00	685	50.3	7.86	679	51.4	7.87	688	54.9	7.86	681	60.3
54	7.59	688	55.7	7.68	690	46.9	7.69	690	45.5	7.71	684	61.2	7.74	683	66.4
58	7.83	682	51.3	7.83	689	61.6	7.91	690	50.9	7.80	692	52.6	7.69	688	49.3
61	7.67	682	39.8	7.72	678	28.9	7.70	674	30.4	7.66	682	44.5	7.82	682	42.9

Table S6 Parameters for the kinetic models of Lagergren pseudo-first-order and Elovich equations for adsorption of DEET, PAR, CAF and TCS on GAC

	Pseudo-first order equation				Elovich equation		
Compound	q_e, Exp (μg/mg)	q_e, Cal (μg/mg)	k_{p1} (min^{-1})	R^2	a (μg/mg·min)	α (mg/μg)	R^2
DEET	0.0243	0.0207	0.0122	0.9511	78.27	0.0047	0.9796
PAR	0.0249	0.7752	1.7966	0.8652	2196.18	0.0032	0.8542
CAF	0.0249	0.0154	0.0111	0.9459	90.54	0.0048	0.9582
TCS	0.0242	0.0037	0.0076	0.5594	1689.36	0.0032	0.8642