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Integrating powdered activated carbon into wastewater tertiary filter for micro-pollutant removal

Jingyi Hu ^{a, b}, Annelies Aarts ^b, Ran Shang ^b, Bas Heijman ^b, Luuk Rietveld ^b

^a *Department of Municipal Engineering, School of Civil Engineering and Architecture, Wuhan University of Technology, Wuhan, China*

^b *Department of Water Management, Faculty of Civil Engineering and Geoscience, Delft University of Technology, P.O. Box 5048, 2600 GA, Delft, The Netherlands*

* Corresponding authors.

Email address: j.hu-1@tudelft.nl (J. Hu), r.shang@tudelft.nl (R. Shang).

Abstract:

Integrating powdered activated carbon (PAC) into wastewater tertiary treatment is a promising technology to reduce organic micro-pollutant (OMP) discharge into receiving waters. To take advantage of the existing tertiary filter, PAC was pre-embedded inside the filter bed acting as a fixed-bed adsorber. The pre-embedding (i.e. immobilization) of PAC was realized by direct dosing a PAC solution on the filter top, which was then promoted to penetrate into the filter media by a down-flow of tap water. In order to examine the effectiveness of this PAC pre-embedded filter towards OMP removal, batch adsorption tests, representing PAC contact reactor (with the same PAC mass-to-treated water volume ratio as in the PAC pre-embedded filter) were performed as references. Moreover, as a conventional dosing option, PAC was dosed continuously with the filter influent (i.e. the wastewater secondary effluent with the investigated OMPs). Comparative results confirmed a higher OMP removal efficiency associated with the PAC pre-embedded filter, as compared to the batch system with a practical PAC residence time. Furthermore, over a filtration period of 10 hours (approximating a realistic filtration cycle for tertiary filters), the continuous dosing approach resulted in less OMP removal. Therefore, It was concluded that the pre-embedding approach can be preferentially considered when integrating PAC into the wastewater tertiary treatment for OMP elimination.

Keywords: Powdered activated carbon; Organic micro-pollutants; Secondary effluent; Tertiary filter; Pre-embedding.

1. Introduction

Organic micro-pollutants (OMPs) are emerging as a threat to the aquatic ecosystems and to human health as they can possibly threaten our drinking water quality (Boehler et al., 2012; Zietzschmann et al., 2014). The effluent of conventional wastewater treatment plant (WWTP) represents a major source of OMPs (Rosi-Marshall and Royer, 2012; Sun et al., 2014), because many OMPs were found to pass the wastewater treatment process without sufficient removal (Grover et al., 2011; Reemtsma et al., 2006). It was reported that the conventional WWTPs were not sufficient in degrading persistent OMPs (e.g. some pharmaceutical compounds, macrolide antibiotics and beta blockers etc.), with elimination rates between 20 and 80% (Loos et al., 2013). After an efficient biological treatment with complete nitrification, on average, only 50% removal of the OMPs (out of 70 potentially problematic compounds) was achieved (Margot et al., 2013). Besides, the consumption of pharmaceuticals, will even rise in the near future due to a demographic aging problem (Zietzschmann et al., 2014). To date, the effects of long-term exposure to the trace-level OMPs remain to be fully understood for human body. It is therefore of great necessity to implement additional treatment steps to eliminate OMP loads in the WWTP effluent, which is sometimes adopted for artificial groundwater recharge and reused for potable water supply supplement (Ternes et al., 1999; Yu and Chu, 2009).

Powdered activated carbon (PAC) has been successfully applied at full-scale WWTPs for reduction of OMPs and ecotoxicity in the receiving waters (Boehler et al., 2012; Margot et al., 2013). The addition of PAC is preferably located at the tertiary treatment step, because there is a lower competition of the effluent organic matter (EfOM) with the target OMPs for adsorption sites on activated carbon (Hu, 2015). PAC is normally implemented in combination with other technologies for a better exploitation of the adsorption capacity and an easier separation of the waste PAC, e.g. in the flocculation-sedimentation process before the tertiary filter (Boehler et al., 2012), or in a pressurized or submerged ultrafiltration system (Löwenberg et al., 2014). Alternatively, initially immobilizing (pre-embedding) the PAC in an existing tertiary filter can be a cost-effective option, as no extra footprint and constructional change are required in this case. Besides, the original filter packing materials are expected to retain the PAC particles for subsequent OMP adsorption, allowing for utilizing PAC in a fixed bed adsorber mode. Moreover, as compared to the granular activated carbon (GAC), PAC with

particle size up to two orders of magnitudes smaller would be advantageous, due to the correspondingly faster adsorption kinetics.

The OMP removal characteristics in a fixed bed adsorber are associated with the OMP adsorption capacity (i.e. as determined by the adsorption isotherm), the transport mechanism in the adsorbent particles and the filter operating conditions (Kim et al., 2010). OMP adsorption capacity depends on the availability of carbon micropores which can admit both OMP and the competing bulk organic matter (e.g. EfOM) with comparable molecular size (Hu et al., 2014). While, the simultaneously favourable adsorption and mass transfer of OMPs has been attributed to a combination of both micropores and mesopores (Pelekani and Snoeyink, 2001; Redding and Cannon, 2014), suggesting the suitability of a broad pore-size-distributed carbon for the dynamic fixed-bed application. In the perspective of adsorption competition, the pre-adsorbed bulk organic matter (e.g. EfOM) inevitably results in pore blockage, which hinders the transport of target OMPs into the appropriate adsorption sites. Previous finding demonstrated that the pore blockage impact is dependent on the carbon particle size (Corwin and Summers, 2010), it is expected that PAC with smaller particle size would exhibit much less pore blockage impact if applied in a fixed-bed adsorber system (Meinel et al., 2015).

To effectively attenuate OMPs from WWTP secondary effluent and to make a full use of the existing tertiary filter (i.e. the anthracite-sand dual media filter), PAC with a proper pore structure was selected and was pre-embedded inside the tertiary filter, which was propelled by a down-flow of tap water before the filtration of secondary effluent started. The effectiveness of this PAC pre-embedded filter towards OMP removal was evaluated in comparison with the related batch test and with the continuous PAC dosing approach (an alternative option of dosing PAC into the filter). Additionally, the PAC distribution profile inside the filter bed was characterized as a function of the pre-embedding down-flow velocity, and the influence of the PAC distribution profiles on OMP breakthrough was investigated.

2. Materials and methods

2.1. Powdered activated carbon (PAC)

The commercially available PAC Norit SAE SUPER (Norit B.V., The Netherlands) was selected, as it is manufactured to have abundant micro- and mesopores, and is widely used for WWTP tertiary treatment (Boehler et al., 2012; Margot et al., 2013; Zietzschmann et al., 2014). The detailed parameters of the PAC is given in Table 1. Before each experiment, PAC

was conditioned with demineralized water (a predetermined amount of PAC in 500 mL demineralized water), which was then shaken for full wetting at a speed of 130 rpm for more than 12 hours in an incubator (Innova 44, Eppendorf, USA).

2.2. *Target OMPs and water quality*

Six OMPs (purchased from Sigma Aldrich, the Netherlands) was chosen due to their general occurrences in the WWTP effluents (Hollender et al., 2009; Margot et al., 2013) and the popularity of consumption (e.g. paracetamol), their physicochemical properties are listed in Table S1 (the supporting information). The OMP stock solution was 1.5 g/L per OMP in methanol (analytical grade, Sigma Aldrich, the Netherlands). For each experiment, the spiked OMP stock solution was far below 0.1% (v/v) of the working solution to minimize the co-solvent effect.

Wastewater secondary effluent was collected from a conventional WWTP (HHSK, Rotterdam City, The Netherlands) on each experimental day at around 8:00 a.m. using a 1000 L polyethylene portable tank. After its arrival in the lab, OMP stock solution was spiked to reach a nominal concentration of 5 µg/L per OMP (on top of the background OMP concentration in the collected secondary effluent) in the feed water. This spiking was meant to offset the difference of OMP background concentrations, and relate the OMP removal (during the adsorption experiments) more to its molecular properties. To facilitate OMP spiking, a 10 L Duran glass bottle was used to transport the prepared OMP solution into the 1000 L feed tank. A submersible pump (Elite 200, AFEC Pump, Taiwan) was placed at the bottom of the tank to circulate the feed water, which was designed to avoid sedimentation of the particulate matter and maintain a homogeneous water quality. In addition, a peristaltic pump (D-4923 extertal, Lenze, Germany) was used to supply the feed water to the top of the filter continuously.

2.3. *Batch adsorption tests*

The feed water for the filter operations was also used for the batch tests. To determine the OMP removal as a function of PAC dose at the adsorption equilibrium, a prepared PAC slurry (2.5 g/L) was pipetted into 7×250 mL Erlenmeyer glass bottles to achieve a varying dosage ranging from 2.5 mg/L to 50 mg/L, after 48 h contact time at a stirring speed of 150 rpm under ambient temperature (20±2 °C), the supernatants were collected and filtered through 0.45 µm regenerated cellulose membrane discs (Sartorius, Germany) for OMP analysis. The batch adsorption kinetic experiment was carried out at PAC dosage of 10 and 20

mg/L over a period of 48 h, respectively; supernatants were sampled at fixed time intervals. The experimental condition was kept the same as in the batch equilibrium adsorption test. During each experiment, a blank bottle without PAC addition was running simultaneously, and the supernatant was filtered through the same 0.45 μm membrane disc, the measured OMP concentrations were served as the initial OMP concentrations.

2.4. *Filter design and operations*

The pilot installation is a perspex column with an internal diameter of 67 mm (surface area of 35 cm^2) and a height of ~ 2 m. The filtration media inside the column consisted of anthracite (on the top) with grain size of 0.8–1.6 mm and sand with grain size of 0.8–1.25 mm. For each filtration cycle, new media were replaced into the column with the same weight and compacted to the same height with both an equal anthracite layer and an equal sand layer. The depth of a fully packed filter bed was 36 cm (896 g) for anthracite and 25.5 cm (1310.7 g) for sand. During filtration, the flow velocity was controlled by a flow meter at the down-stream of the filter bed, water level in the filter was kept constant at the top (i.e. the influent point). The schematic diagram of the setup is illustrated in Figure 1.

OMP breakthrough from the PAC pre-embedded filter was determined, in which, the directly dosed PAC amount was calculated based on the PAC mass-to-treated water volume ratio (10 and 20 mg/L) as in the batch tests, and a filtration velocity of 10 m/h (equals to ~ 35 L/h) along with a filtration period of 10 h. Specifically, ~ 3.5 g (and ~ 7 g) PAC slurry in ~ 500 mL demineralized water was driven downwards through the filter bed using tap water (Delft City, The Netherlands) at a velocity (pre-embedding velocity) of 10 m/h for ~ 15 min, then filtration of the feed water started in the PAC pre-embedded filter at a velocity (filtration velocity) of 10 m/h for ~ 10 h. As another dosing approach, PAC was continuously added with the feed water to the influent point using an extra peristaltic pump (520U, Watson-marlow, UK). The average PAC dose for this continuous dosing in one filtration cycle (~ 10 h) was ~ 20 mg/L with the total PAC mass (~ 7 g) equal to the pre-embedding experiment, filtration velocity was kept at 10 m/h. Each experiment was performed in duplicate and the average data point was adopted. The filter effluents in each experiment were periodically sampled and filtered by 0.45 μm membrane discs. Prior to analysis; the PAC particles which were likely to leak from the filter were captured on the 0.45 μm membrane disc for observation. In addition, a control column test with no PAC dosing was performed to assess any removal of the investigated OMPs by the original filter materials.

2.5. *PAC distribution in the filter*

To characterize PAC distribution over the filter bed, a series of layer-by-layer PAC breakthrough experiments were designed: by increasing the medium depth from the top 5.5 cm to 21 cm, 36 cm (anthracite layer) and further to 41.5 cm, 51.5 cm, 61.5 cm (sand layer). For each of the six experiments, PAC slurry (~3.5 g or ~7 g PAC in 500 mL demineralized water) was added initially on top of the filter, by controlling the outflow valve, different pre-embedding velocities were achieved (i.e. 5, 10 and 15 m/h, respectively), expecting to cause an impact on the PAC distribution profiles. The filter effluents were sampled at fixed time intervals, and the PAC concentration in the effluent sample was then determined via turbidity measurement according to a pre-established calibration curve between turbidity and PAC concentration (supporting information Figure S1). The filter bed was backwashed with tap water after each experiment, which was lasting for a sufficient period of time to ensure the PAC particles to be completely flushed out.

To examine the influence of PAC distribution on OMP removal, filtration of the feed water was initiated following the PAC immobilization. To avoid redistribution of the PAC particles during the filtration process, filtration velocity was kept either equal to or lower than the pre-embedding velocity. The following combinations were applied for the pre-embedding and filtration velocities, respectively: 15+5 m/h, 10+5 m/h and 5+5 m/h. Sulfamethoxazole (SMX) was selected as an indicator compound for these sets of experiments. The SMX stock solution (1.5 g/L SMX in methanol) was spiked in the WWTP secondary effluent to obtain ~5 µg/L SMX in the feed tank (on top of the background SMX concentration). After one filtration cycle (~8 h under the filtration velocity of 5 m/h), the filter was replaced with new packing materials, which were pre-soaked in the tap water overnight to remove fines and avoid bubble formation in the next filtration cycle.

2.6. *Analytical methods*

The quantification of SMX follows an Enzyme-linked immunoassay measurement (Abraxis LLC, USA), the detection limit ranged from 0.025 to 1.0 µg/L, samples with SMX concentration exceeding 1.0 µg/L were diluted and re-measured at least in triplicate for accuracy. Also, a control solution with SMX concentration of 0.2 µg/L was tested each run to check the constructed standard curve. The quantification of samples with a cocktail of OMPs was executed using UHPLC-HR-Orbitrap-MS (Benchtop Exactive Orbitrap mass-spectrometer, Thermo Fisher Scientific). Specifically, 100 ml OMP samples were spiked with 100 µL of a

mixture of the matching labelled internal standards with determined concentrations, afterwards, they were concentrated by a factor of 80 (from 100 to 1.25 mL) using the hydrophilic-lipophilic solid phase extraction (SPE) Oasis HLB cartridges (6 cm³, 200 mg sorbent, Waters, Ireland), which were previously conditioned with 3 mL LC-MS grade methanol. After the loading of OMPs, 2x2.5 mL ultrapure water were applied to wash the cartridges, and a 10 min continuous vacuum was used to dry these cartridges. The OMP samples were subsequently eluted by 2x4mL LC-MS grade methanol, and were further treated with a nitrogen gas evaporator. Ultimately, a reference vial was used to correct the sample volume to 1.25 mL, before their injections into the instrument. The analysis details are described in the supporting information of Vanoppen et al. (Vanoppen et al., 2015), and the UHPLC-HR-Orbitrap-MS output were interpreted by the Xcalibur 2.1.0.1140 software (Thermo Scientific, USA). The detection limit of this instrument for each OMP (without SPE) is listed in Table S1.

The dissolved organic matter (DOC) was determined by a TOC analyser (TOC-VCPH, Shimadzu, Japan) and UV₂₅₄ was determined by an UV-vis spectrophotometer (Thermo Scientific, Germany). Turbidity was measured using a turbidimeter (2100N, Hach, USA) and the particle size distribution of the applied PAC was analysed by a particle counter (Model 3000, Pacific Scientific, the Netherlands).

2.7. Data analysis

The pseudo-second-order kinetic model was used to describe the batch kinetic data for all the investigated OMPs, due to its good presentation of the experimental data for most of the adsorbent-adsorbate systems (Ghaedi et al., 2015; Ho and McKay, 1999; Hu et al., 2015; Roosta et al., 2015; Yu et al., 2012), the expression is:

$$\frac{t}{q_t} = \frac{1}{k_p q_{eq}^2} + \frac{t}{q_{eq}} \quad (1)$$

Where, q_t (mg/g) and q_{eq} (mg/g) are the adsorbate solid phase concentrations at time t (h) and at equilibrium; k_p (g·mg⁻¹·h⁻¹) is the pseudo-second-order adsorption rate constant.

OMP breakthrough from the filter with PAC pre-embedding was described by an analytical expression combining the pseudo-second-order kinetic model with the adsorbate mass balance equation, the final equation is shown as (Skrip et al., 2013):

$$\frac{c}{c_0} = 1 - \left(\frac{1+n_{BT}Da_2}{1+nDa_2} \right)^2 \quad (2)$$

Where c_0 and c are OMP concentrations in the filter influent and in the effluent at filtration time t , respectively. Da_2 is the dimensionless second-order rate constant and n_{BT} is the assumed bed volume at breakthrough; while the only variable n is the bed volume at time t .

Whereas, OMP breakthrough from the filter with PAC continuous dosing was approximated according to the shape of the breakthrough curves: polynomial functions were applied for all the investigated OMPs. This practical method was employed for estimating the OMP breakthrough from GAC filters (Altmann et al., 2016), and allows for calculating the cumulative OMP breakthrough within the investigated filtration period.

3. Results and discussion

3.1. *Water characteristics of WWTP secondary effluent*

The studied WWTP secondary effluent contained an average DOC concentration of ~12 mg/L, and a SUVA value of 2.57 (Table 2). The background OMP concentrations in the secondary effluent ranged from less than 0.05 µg/L for clofibric acid to almost 2 µg/L for hydrochlorothiazide. As compared to other studies, the average concentrations of metoprolol, SMX and carbamazepine generally agreed with what were detected in Swiss 'Micropoll Project', i.e. 0.166, 0.238 and 0.482 µg/L, respectively (supporting information in (Loos et al., 2013)); and that of SMX corresponded well to the average value (0.142 µg/L) reported in (Loos et al., 2013) monitoring 90 European WWTP effluents; also, the obtained data for clofibric acid was comparable to the maximum value (0.03 µg/L) found in seven WWTPs located along a river basin of Spain (Gros et al., 2010). The variation in water quality during the experimental period was not obvious as evident from the respective relative standard deviation listed in Table 2.

3.2. *OMP removals in batch test*

OMP removal from the feed water (i.e. 5 µg/L spiked OMPs in the background of WWTP secondary effluent) as a function of PAC dose is shown in Figure 2. The required minimum PAC dose for e.g. 80% OMP removal differed considerably, from ~5 mg/L for metoprolol and carbamazepine to almost 35 mg/L for SMX and clofibric acid. At a PAC dose of 10 mg/L, metoprolol, carbamazepine and hydrochlorothiazole were well adsorbed at above

80%, while paracetamol, clofibric acid and SMX were moderately adsorbed at 30-40%. With 20 mg/L PAC, all OMPs were abated up to 60%. The results agree well with a previous finding based on a pilot-scale PAC-ultrafiltration membrane system with PAC dosage between 10 to 20 mg/L, and the solid (PAC) retention time between 2-17 days (Margot et al., 2013). 10 and 20 mg/L PAC were considered as appropriate doses for an overall OMP elimination from the secondary effluent and served as references for the subsequent investigation of the PAC pre-embedded filter.

Figure 3(a) and 3(b) present the OMP removal kinetics in the batch system at PAC dose of 10 and 20 mg/L, respectively, the fitted pseudo-second-order kinetic parameters are provided in Table S2. Specially, the calculated q_e (i.e. $q_{e,cal}$) based on the curve fitting was compared with the experimental $q_{e,exp}$ for each OMP, the relative standard deviations in TableS2 demonstrate the consistency between q_e and $q_{e,exp}$, verifying the modelling. It is observed that the time for OMP adsorption equilibrium was independent of the PAC dose and that most of OMPs reached adsorption equilibrium after 12 h (720 min). However, in practice, the retention time of PAC in a single-stage adsorption system (e.g. the sequencing batch reactor) is in the magnitude of minutes (Ruhl et al., 2014; Zoschke et al., 2011), which is much less than the observed 12 h to ensure the maximum adsorption capacity. Immobilizing PAC in the tertiary filter, in this sense, can guarantee a sufficient PAC retention time.

3.3. OMP breakthrough in PAC pre-embedded filter

OMP breakthrough under PAC amount of ~3.5 and ~7 g in the pre-embedded filter (corresponding to 10 and 20 mg/L PAC in the batch kinetic tests, respectively) are depicted in Figure 4(a) and 4(b), respectively, and the fitted parameters of equation (2) were provided in Table S3. The blank filter running without PAC addition showed an immediate breakthrough of OMP (i.e. SMX) from the filter (Figure S2), indicating that the obtained OMP removal was substantially attributed to the dosed PAC, rather than the filter materials, e.g. anthracite, sand and the filter walls. To compare the OMP removal efficiency in the PAC pre-embedded filter and in the batch system, the cumulative OMP breakthrough (C/C_0) over the investigated 10 h in PAC pre-embedded filter was calculated based on the curve fitting of the OMP breakthrough data. Next, this cumulative C/C_0 was interpolated into the fitted batch kinetic curve (Figure 2) to calculate the contact time required for the same OMP removal objective.

Table 3 lists the required contact time in the batch system for an equivalent OMP removal as in the PAC pre-embedded filter, the values varied considerably depending on the

specific OMP. Except for metoprolol which showed ~30 min, the other OMPs exhibited much longer time exceeding 1 h, making it practically inapplicable for the single-stage contact reactor where PAC is usually used. It has to be mentioned that, the cumulative OMP removal in the PAC pre-embedded filter was less than the respective equilibrium OMP removal in the batch system, reflecting a non-complete usage of the PAC capacity in the pre-embedded filter. This is most likely due to the short contact time between PAC and the OMPs, i.e. the residence time of feed water in the filter is ~2 min. However, unlike the batch system with decreasing OMP concentration along the adsorption process, the constant initial OMP concentration occurring in the PAC pre-embedded filter provided a 'multi-stage' adsorption condition (Zhao et al., 2012), which, enabled a reasonable exploitation of the PAC adsorption capacity. Nonetheless, this positive effect appears to be less obvious with an increase in the PAC dose (Table 3).

3.4. *OMP removal in the filter with continuous PAC dosing*

OMP breakthrough under continuous PAC dosing is given in Figure 5. This adsorption process consists of a primary adsorption onto the freshly dosed PAC in the filter supernatant, and an additional adsorption onto the retained PAC in the filter bed (Altmann et al., 2014; Altmann et al., 2015). In this study, however, only 7 min contact time was available during PAC transport in the filter supernatant, explaining the low OMP removal (less than 25% except for metoprolol) in the initial filtration stage. Whereas, as the filtration progressed, a steady decrease in the relative OMP concentration was observed, which emphasizes the importance of the retained PAC for OMP removal: the more PAC was accumulated, the better OMPs were adsorbed. However, the observed OMP removal trend deviates from what was found by (Altmann et al., 2015), where OMP removal stabilized after certain period of filtration (i.e. 4 h). This can be explained by the higher PAC dose in the present study (20 versus ~7.2 mg/L), which resulted in more unexhausted PAC in the studied filter bed.

To compare OMP removal between continuous PAC dosing and the pre-embedding, the cumulative OMP breakthrough (C/C_0) in Figure 5 was estimated over the same filtration time of 10 h as in the PAC pre-embedded filter, the comparative results are shown in Table 4. It is clear that PAC pre-embedded filter exhibited less OMP breakthrough than the continuous dosing in the given period, regardless of the type of OMP. However, the continuous dosing offered a better OMP removal in the latter filtration period, while the pre-embedding offered a better OMP removal in the initial filtration period. In this case, an equal cumulative OMP

removal could be expected after a prolonged filtration run, considering the same total amount of PAC added. However, Table 4 reflects that, except for SMX and clofibric acid which are less hydrophobic (with lower log D values), the other four OMPs had cumulative breakthrough less than or close to 20% after 10 h running of the ~7 g PAC pre-embedded filter, demonstrating an effectiveness of this PAC pre-embedded filter towards such OMPs.

From the experiments it was found that PAC constantly leaked through the filter under the continuous dosing; while this leakage was indiscernible in the effluent of the pre-embedded filter (Figure S3). It can partly be attributed to the much higher PAC input concentration under pre-embedding, which enabled PAC particles to occupy the attachment sites of the filter media more rapidly, and hindered the downward transport of the subsequent PAC (Sun et al., 2015), thus enhancing their retention inside the filter.

3.5. *PAC distribution in pre-embedded filter and the influence on OMP breakthrough*

In consideration of an easy implementation and an effective OMP removal (during ~10h operation), the PAC pre-embedding approach was preferred in this study. From the particle size distribution analysis, it is shown that the employed PAC has a dominant size less than 5 μm (Figure S4). Furthermore, the PAC distribution profile expressed by the cumulative mass percentage along the filter height is illustrated in Figure 6(a) and 6(b), with the direct PAC dose of ~3.5 and ~7 g, respectively.

Apparently, the PAC particles penetrated more downwards to the filter end with an increase in the pre-embedding velocity, and a more heterogeneous PAC distribution was created in a consequence. It is found in Figure 6(a) that, ~80 wt% PAC was retained in the first 5.5 cm anthracite layer under a flow of 5 m/h as compared to ~54 and ~36 wt% under 10 m/h and 15 m/h, respectively; the latter two even drove PAC deeper down to the sand layer (~4 wt%). This phenomenon recurred in the filter when the PAC dose was doubled (Figure 6(b)). However, a less scattered PAC distribution was observed with an increase in the dosed PAC amount under the respective pre-embedding velocities. For instance, when ~7 g PAC was added, the mass percentage in the first 5.5 cm anthracite layer were ~90, ~65 and ~56 wt% under flow of 5, 10 and 15 m/h, respectively, all higher than the corresponding values in the ~3.5 g PAC-added filter. This dose-dependent distribution behaviour appears to comply with the finding of Section 3.4, and confirms that a higher PAC input concentration was able to increase the potential for PAC retention on the filter top. Moreover, after passing through 10 L

tap water, a negligible amount of PAC (< 1 wt%) was present in the effluent, indicating the immobilization of PAC particles in the filter bed.

Due to the poorly adsorbing character, SMX was selected as a first breakthrough indicator to test the influence of PAC distribution on OMP breakthrough. SMX breakthrough as a function of the specific throughput (the treated effluent volume divided by the dosed PAC mass) are depicted in Figure 6(c) and 6(d), with the filter pre-embedding conditions corresponding to Figure 6(a) and 6(b), respectively. The results show that, a retarded SMX breakthrough was associated with a higher pre-embedding velocity, although SMX breakthrough overlapped somehow at pre-embedding velocity of 10 and 15 m/h under PAC dose of ~3.5 g, and at 5 and 10 m/h under PAC dose of ~7 g. For example, to achieve 80% SMX removal (i.e. 20% SMX breakthrough), the specific throughput increased by a factor of 2, from ~5 L/g at 5 m/h pre-embedding velocity to ~9 L/g at 15 m/h pre-embedding velocity (Figure 6(c)). The same increase rate occurred in the case of ~7 g PAC pre-embedded filter, from ~6 L/g at 5 m/h pre-embedding velocity to ~11 L/g at 15m/h pre-embedding velocity (Figure 6(d)). The extension of OMP breakthrough by higher pre-embedding velocity can be correlated to a more homogeneous distribution of the PAC particles, allowing for a better contact between PAC and the target compound, and thus better adsorption kinetics.

Given a complex EfOM background in the secondary effluent, the OMP removal was inevitably subjected to an adsorption competition effect, which explains the 9 times less specific throughput for 20% breakthrough of SMX than the reported values in the study of Altmann et al.(2015), in which tap water was used as a background. However, a similar increase rate (i.e. two times) of the specific throughput for 20% breakthrough of SMX was found in this study and in (Altmann et al., 2015), where a much more homogenous PAC distribution was established by an up-flow pre-embedding in the backwashing direction. This implies that a homogeneous PAC distribution might be more beneficial for OMP removal with a complex organic matter background where adsorption competition is involved.

4. Conclusion

In this study, PAC was integrated into a tertiary dual media filter for OMP removal from the WWTP secondary effluent. As an economic approach, direct dosing PAC on top of the filter to immobilize PAC inside the filter bed was exercised. OMP adsorption in batch tests were performed as a reference to evaluate the effectiveness of the PAC pre-embedded filter.

Comparative results confirmed a higher OMP removal efficiency in the PAC pre-embedded filter than the batch system, which employed an equal PAC mass-to-treated water volume ratio (i.e. 10 and 20 mg/L) and a practical PAC residence time (e.g. in the magnitude of minutes). As another dosing approach, continuous dosing PAC caused a constant leakage of the PAC particles from the filter bed. Additionally, in comparison to the PAC retained in the filter bed, the suspended PAC in the filter supernatant contributed less to the OMP adsorption. The pre-embedding approach was preferred, considering its simple implementation and the relatively efficient OMP removal throughout the filtration period of e.g. 10 h, which represents a realistic running time for tertiary filters. Furthermore, the distribution profile of the embedded PAC was identified as an important factor governing OMP removal rate, that a more homogeneous PAC distribution created by a higher pre-embedding velocity was able to prolong the OMP (i.e. SMX) breakthrough from the filter.

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Figures

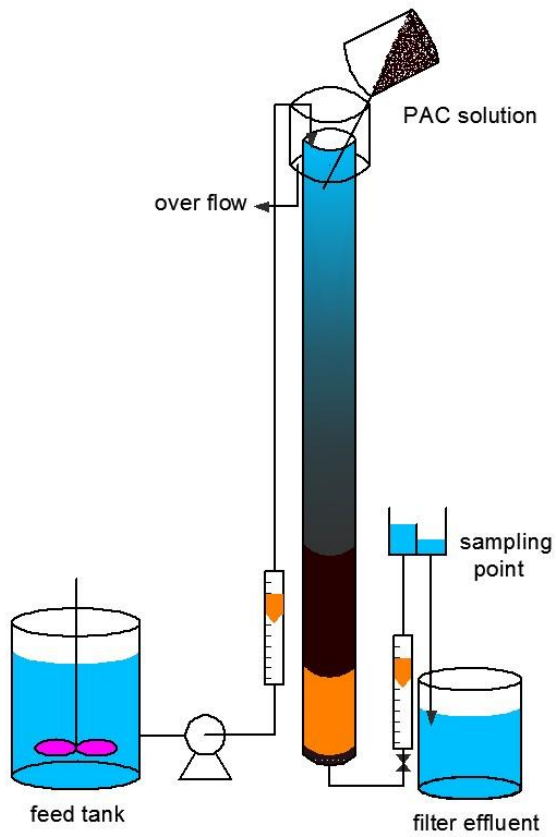


Figure 1. Schematic diagram of the pilot-scale filter with PAC pre-embedding.

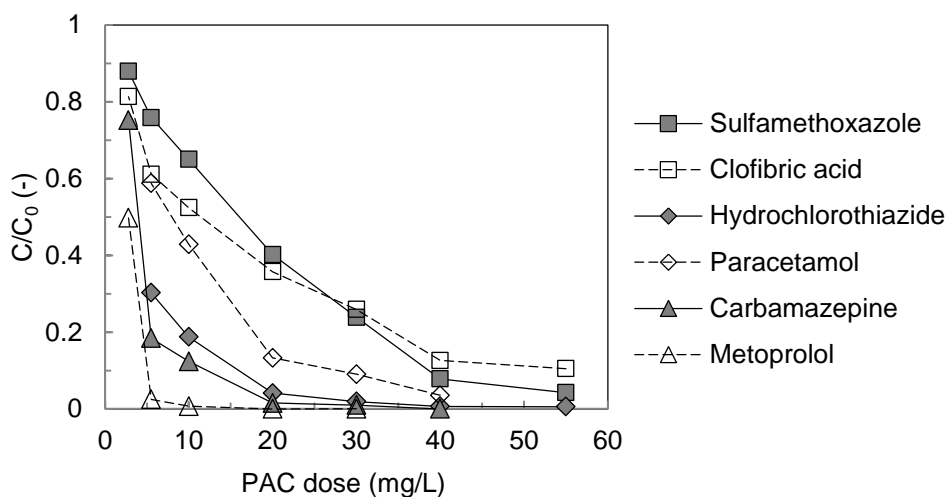


Figure 2. The batch OMP removal (relative OMP concentration) at equilibrium as a function of the PAC dose.

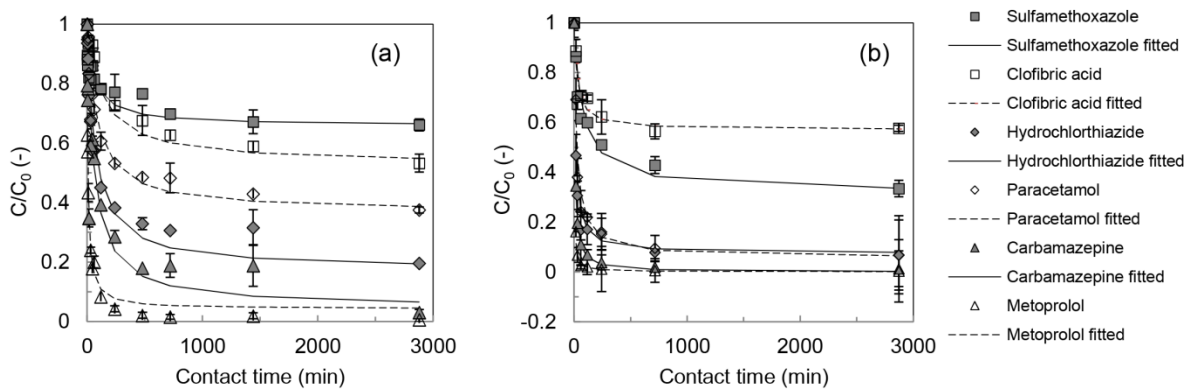


Figure 3. The batch OMP removal (relative OMP concentration) as a function of the contact time at PAC doses of: (a) 10 mg/L and (b) 20 mg/L.

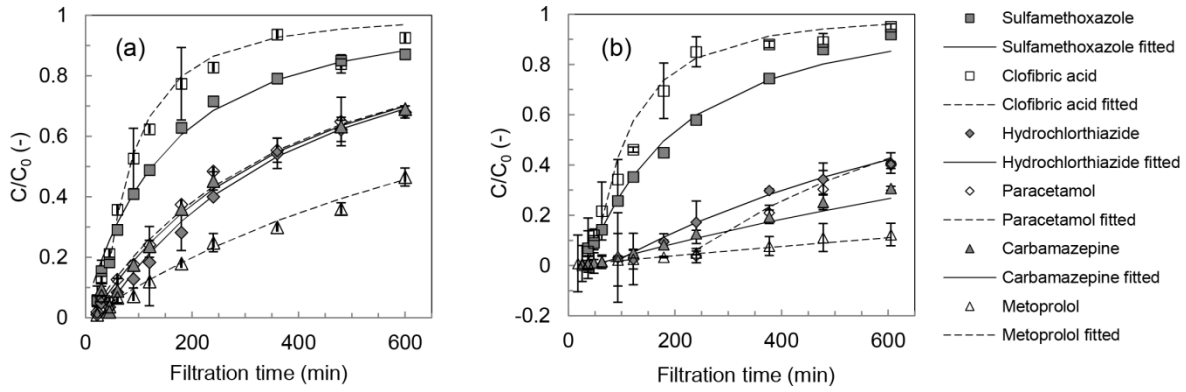


Figure 4. The OMP breakthrough (relative OMP concentration) from the PAC pre-embedded filter as a function of filtration time under PAC amount of: (a) ~3.5 g and (b) ~7 g.

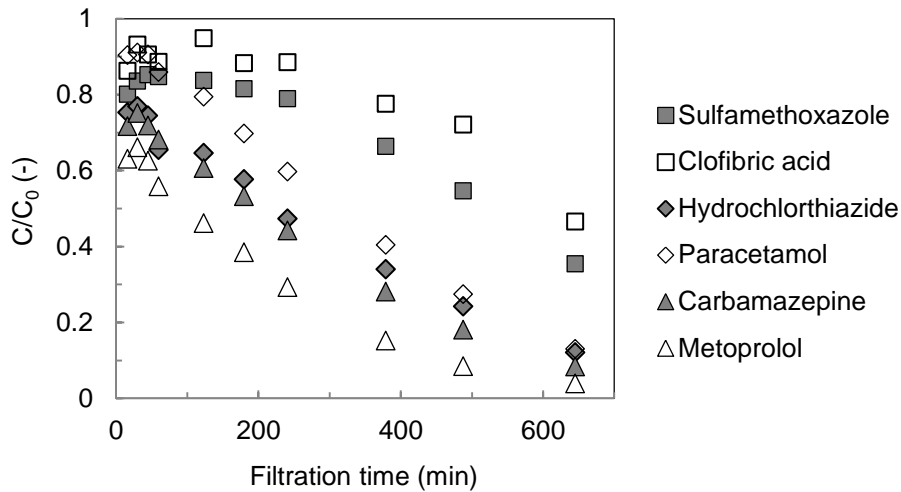


Figure 5. The OMP breakthrough (relative OMP concentration) from PAC continuous dosing filter. PAC dose: 20 mg/L; filtration period: ~10.75 h, filtration velocity: 10 m/h.

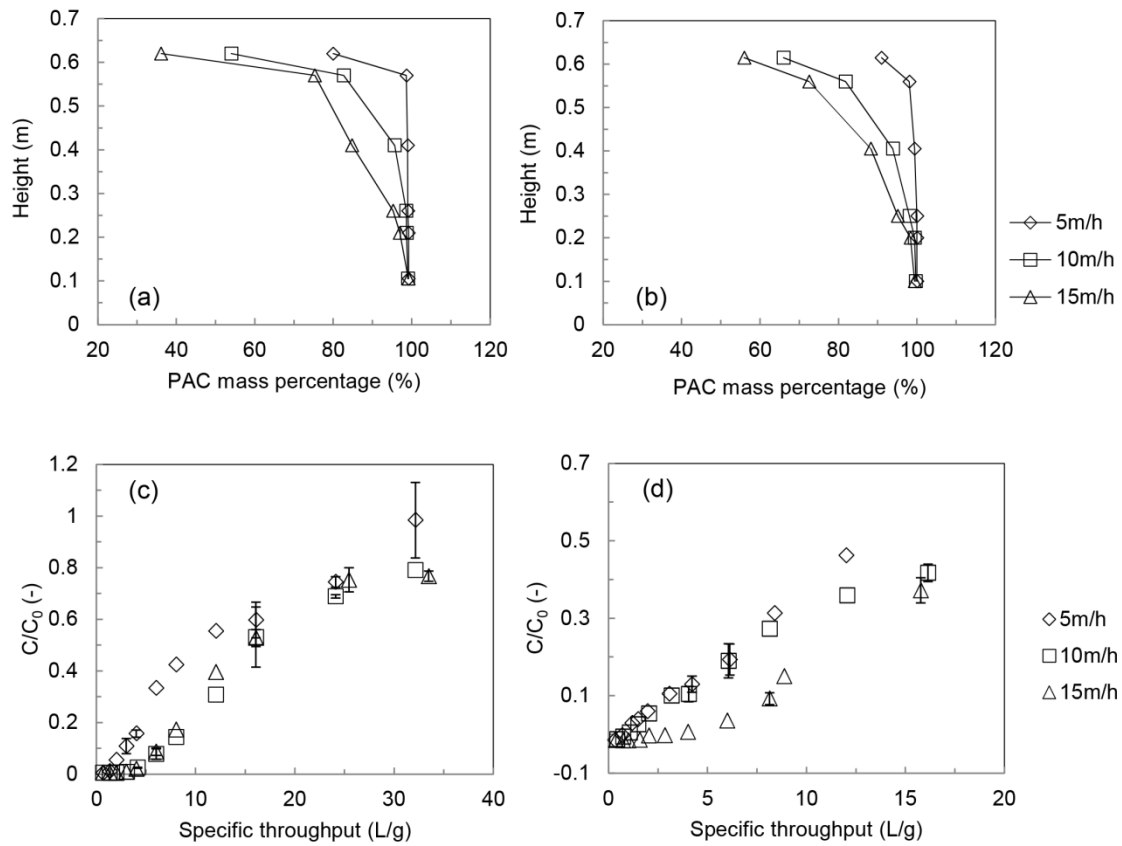


Figure 6. The cumulative PAC mass percentage along the filter height under different pre-embedding velocities, with the PAC dose amount of (a) ~3.5 g and (b) ~7 g. The corresponding relative concentration of SMX in the filter effluent under a fixed filtration velocity of 5 m/h, with the PAC dose amount of (c) ~3.5 g and (d) ~7 g.

Tables

Table 1.Characterization of the used PAC.

PAC	Raw material	Bulk density (kg/m ³)	Grain size d50 (μm)	BET surface area (m ² /g)	pH _{pzc} ¹
Norit SAE SUPER	Peat/wood	425	15	1150	9.8 ²

¹: point of zero charge of the PAC;

²: data obtained from (Kovalova, 2009).

Table 2. Water characteristics of the studied WWTP secondary effluent.

Parameter	Unit	Average concentration	Relative standard deviation
DOC	mg/L	12.23	± 4.2%
UV ₂₅₄	cm ⁻¹	0.315	± 6.5%
SUVA	L/mg·m	2.57	-
Turbidity	NTU	1.91	± 12.3 %
pH	-	7.2	-
Paracetamol	μg/L	ND (n ¹ =6)	ND ²
Hydrochlorothiazide	μg/L	1.80 (n=6)	±17.4%
Metoprolol	μg/L	0.45 (n=6)	±5.9%
Sulfamethoxazole	μg/L	0.15 (n=6)	±26.5%
Carbamazepine	μg/L	0.37 (n=6)	±23.4%
Clofibric acid	μg/L	0.014 (n=6)	±8.5%

¹: the number of quantifications/campaigns;

²: not detected.

Table 3. Comparing OMP removal between the PAC pre-embedded filter and the batch system.

OMPs	Calculated cumulative breakthrough (C/C ₀) within 10 h in PAC pre-embedded filter (%)		Required contact time for the same C/C ₀ in batch kinetic test (min)	
	10 mg/L PAC	20 mg/L PAC	10 mg/L PAC	20 mg/L PAC
	Sulfamethoxazole	66.5	57.6	5789.5

Clofibric acid	76	69.3	135.4	67.5
Hydrochlorothiazide	42	20.5	165.6	85.7
Paracetamol	45.1	10.2	567.4	459.4
Carbamazepine	44.2	13.2	84.4	48.2
Metoprolol	26.1	5.7	29.8	35.1

Table 4. Comparing OMP removal between PAC continuous dosing and pre-embedding over the filtration time of 10 h at an equivalent PAC dose of 20 mg/L.

OMPs	Calculated cumulative breakthrough (C/C_0) under PAC continuous dosing	Calculated cumulative breakthrough (C/C_0) under PAC pre-embedding
	(%)	(%)
Sulfamethoxazole	70.0	57.6
Clofibric acid	80.7	69.3
Hydrochlorothiazide	43.6	20.5
Paracetamol	53.0	10.2
Carbamazepine	39.4	13.2
Metoprolol	27.2	5.7