Combination of granular activated carbon adsorption and deep-bed filtration as a single advanced wastewater treatment step for organic micropollutant and phosphorus removal

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ABSTRACT

Adsorption onto granular activated carbon (GAC) is an established technology in water and advanced wastewater treatment for the removal of organic substances from the liquid phase. Besides adsorption, the removal of particulate matter by filtration and biodegradation of organic substances in GAC contactors has frequently been reported. The application of GAC as both adsorbent for organic micropollutant (OMP) removal and filter medium for solids retention in tertiary wastewater filtration represents an energy- and space saving option, but has rarely been considered because high dissolved organic carbon (DOC) and suspended solids concentrations in the influent of the GAC adsorber put a significant burden on this integrated treatment step and might result in frequent backwashing and unsatisfactory filtration efficiency. This pilot-scale study investigates the combination of GAC adsorption and deep-bed filtration with coagulation as a single advanced treatment step for simultaneous removal of OMPs and phosphorus from secondary effluent. GAC was assessed as upper filter layer in dual-media downflow filtration and as mono-media upflow filter with regard to filtration performance and OMP removal. Both filtration concepts effectively removed suspended solids and phosphorus, achieving effluent concentrations of 0.1 mg/L TP and 1 mg/L TSS, respectively. Analysis of grain size distribution and head loss within the filter bed showed that considerable head loss occurred in the topmost filter layer in downflow filtration, indicating that most particles do not penetrate deeply into the filter bed. Upflow filtration exhibited substantially lower head loss and effective utilization of the whole filter bed. Well-adsorbing OMPs (e.g. benzotriazole, carbamazepine) were removed by >80% up to throughputs of 8000–10,000 bed volumes (BV), whereas weakly to medium adsorbing OMPs (e.g. primidone, sulfamethoxazole) showed removals <80% at <5,000 BV. In addition, breakthrough behavior was also determined for gabapentin, an anticonvulsant drug recently detected in drinking water resources for which suitable removal technologies are still largely unknown. Gabapentin showed poor adsorptive removal, resulting in rapid concentration increases. Whereas previous studies classified gabapentin as not readily biodegradable, sustained removal was observed after prolonged operation and points at biological elimination of gabapentin within the GAC filter. The application of GAC as filter medium was compared to direct addition of powdered activated carbon (PAC) to deep-bed filtration as a direct process alternative. Both options yielded comparable OMP removals for most compounds at similar carbon usage rates, but GAC achieved considerably higher removals for biodegradable OMPs. Based on the results, the application of GAC in combination with coagulation/filtration represents a promising alternative to powdered activated carbon and ozone for advanced wastewater treatment.

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1. Introduction

The occurrence of personal care products, pharmaceuticals and industrial chemicals in freshwater sources is closely monitored worldwide (Luo et al., 2014; Nam et al., 2014; Putschew et al.,

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2000). While the impacts of these organic micropollutants (OMPs) on the environment and humans are still not clear to date (Pomati et al., 2006; Vasquez et al., 2014), precautionary measures to avoid potential negative ecological effects by OMPs are currently being discussed (Eggen et al., 2014). As regulating the admission of relevant substances to the market appears unrealistic in the near future, an end-of-pipe approach utilizing technical measures is seen as a possible solution. Upgrading conventional wastewater treatment plants (WWTPs), which currently do not represent an effective barrier for many OMPs (Loos et al., 2013; Michael et al., 2013), can reduce OMP discharges into the aquatic environment. Alternatively, advanced drinking water treatment can be used as a final barrier to prevent OMP occurrence in finished drinking waters.

Oxidation with ozone and adsorption onto activated carbon are the most commonly used treatment options for OMP mitigation (Kovalova et al., 2013; Margot et al., 2013). Powdered activated carbon (PAC) is often seen as a viable alternative in advanced wastewater treatment (Böhler et al., 2012; Löwenberg et al., 2014), whereas granular activated carbon (GAC) has long been applied as adsorbent for treatment of drinking water with low to moderate content of organic matter (dissolved organic carbon (DOC) concentrations of 1–5 mg/L) and very low particle concentrations (Kennedy et al., 2015; Paune et al., 1998) or as biological activated carbon for advanced wastewater treatment (Reungoat et al., 2011). However, the dual use of GAC as both adsorbent and filter medium for solids retention in advanced wastewater treatment is a novel concept and has not been investigated sufficiently to date. While GAC has previously been applied for adsorptive removal of OMPs from wastewater (Ho et al., 2011), high DOC concentrations are usually seen as unfavorable for adsorption onto GAC because of long-term carbon fouling reducing the adsorption capacity and leading to accelerated breakthrough (Wang and Alben, 1998).

The integration of GAC adsorption into coagulation/filtration represents an energy- and space saving alternative to more complex treatment options, but it is generally assumed that high suspended solids concentrations result in unsatisfactory filtration efficiency and negatively impact OMP adsorption. Furthermore, OMP removal and effective solids retention combine partially conflicting requirements with regard to GAC grain size. On the one hand, adsorption kinetics improve with decreasing GAC grain size (Corwin and Summers, 2010). However, utilizing fine GAC fractions as filter medium may increase head losses and lead to short backwash intervals or blocking of the filter. In a study employing comparably coarse-grained GAC as top layer in dual-media filtration, Meinel et al. (2015) observed good particle retention but poor OMP adsorption. Similarly, Benstöm et al. (2014) tested different GAC grain sizes at large-scale and experienced either rapid OMP breakthrough (coarse-grained GAC) or short backwash intervals due to increasing head loss (fine-grained GAC). Therefore, those studies call the applicability of GAC for advanced wastewater treatment into question because high OMP removals and effective particle retention might not be met simultaneously.

As an alternative to common dual-media filtration, upflow filtration utilizing GAC as mono-media has been tested in tertiary wastewater without coagulation (Nahrstedt et al., 2014). It is assumed that this process scheme leads to better depth utilization of the filter bed with regard to particle retention.

This study investigates the integration of GAC adsorption into deep-bed filtration for the combined removal of phosphorus and OMPs. Pilot-scale testing included GAC as upper filter layer in dual-media filtration and as mono-media upflow filter. The objectives were to 1) assess the feasibility of utilizing GAC in deep-bed filtration and its impacts on particle retention, head loss and phosphorus removal, 2) determine the breakthrough behavior of 15

relevant OMPs in wastewater with a high organic matter content and 3) evaluate the OMP removal efficiency using GAC for advanced wastewater treatment in comparison with direct PAC addition as an alternative treatment option.

2. Materials and methods

2.1. Pilot GAC filter

The GAC pilot study was conducted at the municipal wastewater treatment plant Muenchehofe (Berlin, Germany) over a consecutive period of ten months. The WWTP treats up to 42,500 m^3/d by primary sedimentation, biological activated sludge treatment with chemical precipitation and secondary clarification. Characteristics of the secondary effluent during the experimental period are given in Table 1. The pilot plant consists of two identical filter columns, each with a diameter of 0.15 m and a height of 4 m. One filter is operated as dual-media downflow filter, whereas the other filter uses only GAC as filter material and is fed in upflow direction. GAC Epibon A 8 × 30 mesh was supplied by Donau Carbon, Germany. Upon filling the filter columns, the GAC was wetted for two days and backwashed several times to remove undersized particles. The dual-media filter uses 1.4 m GAC and 0.6 m quartz sand (0.7–1.1 mm) as filter material. The GAC bed in the upflow filter initially had a height of 2.0 m, but decreased to 1.9 m during operation, possibly due to slight material discharges during improper backwash. The filter bottom of the upflow filter is designed as a perforated plate with openings of 2.6 mm in diameter for uniform distribution of the influent water. Gravel (3.0–5.6 mm) is used as supporting material to prevent the GAC particles from entering the perforated plate. The downflow filter is equipped with a filter nozzle as underdrain system to collect the filtrate and distribute backwash water.

The flow scheme of both filters is given in Fig. 1. The filters are fed with secondary effluent at a constant filtration rate of 6 m/h, corresponding to a flow rate of 105 L/h. The resulting GAC empty bed contact time (EBCT) is 19 min in the mono-media and 14 min in the dual-media filter, respectively. The downflow filter operates by gravity after initial lifting of the influent, whereas a peristaltic pump is used to operate the upflow filter. Ferric chloride is added to the influents of both filters by inline dosing into a static mixer at doses of 4–5 mg/L Fe. The coagulant dose was chosen to achieve a ratio of 4–5 mol Fe/mol reactive phosphorus, which has shown to effectively remove phosphorus by inline-coagulation (Altmann et al., 2015, Sperlich et al., 2012). Following coagulant addition, a flocculation tank (downflow filter) and a tube flocculator (upflow filter) with a hydraulic retention time (HRT) of 6 min each serve to promote floc growth. The filters are backwashed manually after 23 h of operation by air scouring and water flushing with tap water. The backwash procedures were optimized separately for each filter to achieve optimum bed fluidization and are listed in Table S1 in the

Table 1
Characteristics of the secondary effluent used as influent to the GAC pilot filters.

Parameter		Median (25th–75th percentile), n = number of measurements
DOC	[mg/L]	11.4 (10.6–12.5), n = 80
UVA$_{254}$	[1/m]	24.8 (23.6–25.6), n = 80
Total phosphorus	[mg/L]	0.54 (0.49–0.62), n = 47
Ammonium	[mg N/L]	0.07 (0.05–0.22), n = 54
Nitrate	[mg N/L]	11.9 (10.9–12.8), n = 54
Total suspended solids	[mg/L]	2.6 (2.3–2.9), n = 45
Dissolved oxygen	[mg/L]	6.8 (5.5–8.9), n = 78
Temperature	[°C]	15.0 (13.6–15.8), n = 78
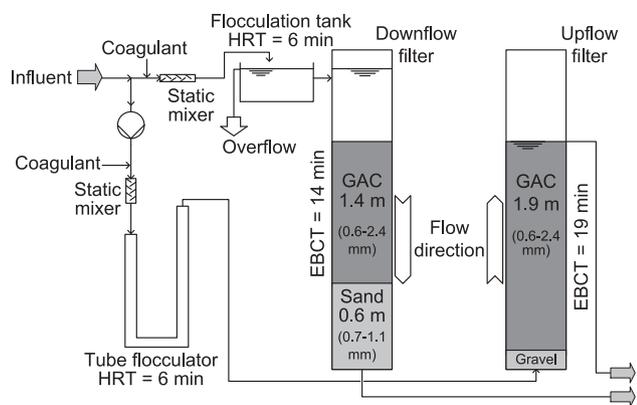
Fig. 1. Flow scheme of the pilot plant with dual-media downflow and mono-media upflow GAC filtration.

supporting information. The backwash intervals were chosen based on previous results, which indicated that solids breakthrough might be expected with longer filtration intervals and also for practical reasons. Influent and effluent samples were collected as 22 h composite samples for chemical analysis. The first 1 h of filtration was not sampled to exclude residual backwash water. In large-scale operation, backwashing is typically performed with filtrate, which was not feasible in the pilot testing and tap water was used instead. Additionally, corresponding grab samples of the influent and both effluents were taken at the end of each filter run for suspended solids determination.

Sampling points along the filter bed are connected to vertical transparent pipes, which are open to the atmosphere at the top. As the fluid level in each pipe corresponds to the pressure in the respective filter layer, this method can be used to determine the head loss in the filter bed. The sampling points are equipped with three-way valves to disconnect and empty out the pipes after each measurement.

At the end of the experimental period, the bed material of both pilot filters was completely removed in layers of 0.2–0.4 m thickness in order to determine the GAC grain size distribution. The GAC was dried at 105 °C and sieved manually using mesh seizes from 0.63 to 2.5 mm.

2.2. Analytical methods

The samples were analyzed for total phosphorus (TP) using Hach Lange cuvette tests and a Hach Lange photometer (DR 3800). Concentrations of total suspended solids (TSS) were determined gravimetrically after filtration of 2.5 L influent sample and up to 10 L effluent sample through glass fiber filters (0.3–1.0 μm, Macherey–Nagel, Germany). Quantification of dissolved parameters was preceded by sample filtration using 0.45 μm membrane filters (regenerated cellulose, Macherey–Nagel, Germany). Dissolved organic carbon (DOC) concentrations were measured with a Vario TOC cube (Elementar Analysensysteme, Germany). UV absorbance at 254 nm (UVA_{254}) was determined on a Lambda 12 UV–VIS photometer (Perkin Elmer, Germany).

OMP concentrations were quantified by direct injection of 25 μL sample into a HPLC-MS/MS system. For separation, a XSelect HSS T3 column (2.5 μm, 50 × 2.1 mm, Waters, USA) was used and a linear gradient was applied with (A) water with 5% methanol (HPLC gradient grade, J.T. Baker) and 0.5% formic acid (HPLC grade, Fluka) and (B) methanol as eluents. MS analysis was performed with a TSQ Vantage (Thermo Scientific, USA). Mass fragments were chosen according to the DAIOS database and deuterated internal standards

were used for quantification (DAIOS, 2014). A group of 15 OMPs was selected for analysis because of their permanent occurrence in Berlin wastewater effluents, their relevance as priority or indicator substances and due to their varying adsorbabilities onto activated carbon. An overview of the OMPs that were quantified, their typical areas of application, method reporting limits, molecular mass, log D values and pilot influent concentrations are given in SI2.

3. Results and discussion

3.1. GAC as filter material in deep-bed filtration

3.1.1. Grain size distribution

Deep-bed filters are backwashed periodically to remove retained particles. As a result, the filter grains are stratified according to their density and size. Assuming a constant material density within a filter layer (e.g. the GAC layer), the smallest grains accumulate near the top of the bed whereas larger grains collect mostly near the bottom. Fig. 2 presents the grain size distributions of the GAC material in six layers of the (A) downflow and (B) upflow filter, respectively, and the calculated overall distribution in each filter column. Additionally, the size distribution of the fresh GAC material is also given. The fine-grained GAC fraction ($d_p < 1$ mm)
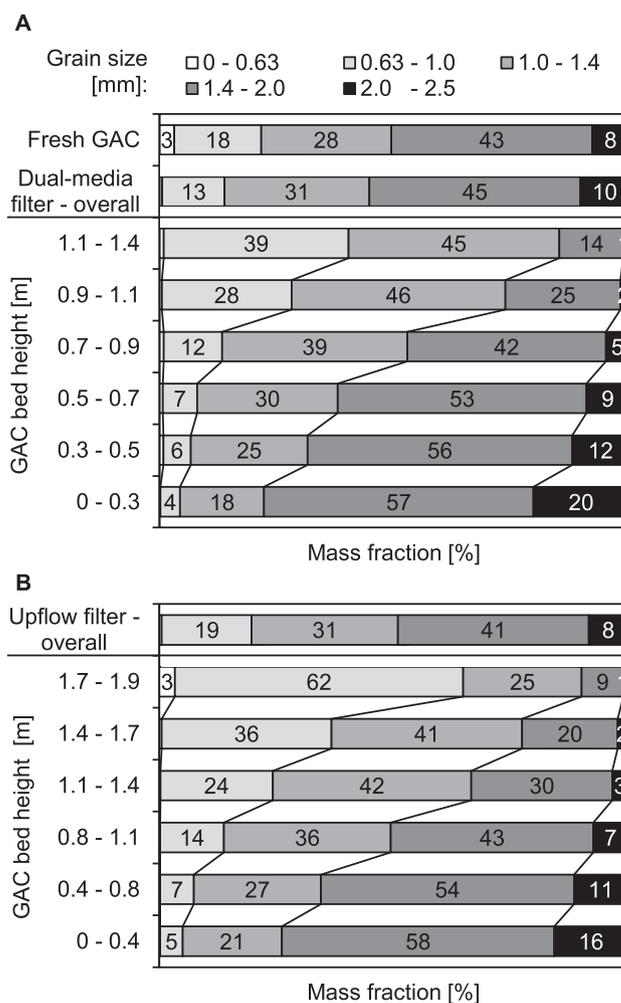
Fig. 2. GAC grain size distribution of (A) the downflow dual-media filter and (B) the upflow filter after 10 months of operation. Bed height = 0 refers to the bottom of the GAC bed, corresponding to the top of the lower sand layer in the dual-media filter and the bottom of the filter column in the mono-media filter.

constitutes approx. 21 mass-% of the overall raw material, but accounts for ~40% in the top GAC layer of the dual-media filter and ~65% in the upflow filter. At the same time, the top filter layers contain only 1% of coarse-grained GAC (2—2.5 mm), respectively, compared to 8% in the raw material. Accordingly, the share of coarse material is highest in the lowest GAC layer of each filter, whereas GAC grains <1 mm account for only 5%. Even though the raw GAC contains about 3 mass-% of very fine material (d_p < 0.63 mm), the fraction could only be quantified to a comparatively small degree in each top filter layer. Thus, the very fine-grained GAC particles are probably flushed out during frequent backwashing. This could be more relevant in the dual-media filter, as the overall share of grains with d_p = 0.63—1.0 mm in the used material is smaller than in the raw GAC. Apart from that, abrasion of coarse grains does not appear to be of major relevance, as the fresh raw material shows a similar overall composition as the GAC in both filter columns after 10 months of operation.

3.1.2. Head loss

Determination of the head loss at multiple sections within the filter bed provides information about the local distribution of retained particles. Fig. 3 shows head loss profiles for (A) the dual-media downflow filter and (B) the upflow filter at filter runtimes of 0, 4 and 22 h after backwash. The profiles were taken after ~22,000 bed volumes (BV) treated in the downflow filter and ~18,000 BV in the upflow filter. At the beginning of filtration, the clean bed head loss increases steadily with increasing filter depth for both filters. Increasing filter runtime leads to increased head loss due to particle attachment. In dual-media filtration utilizing GAC as upper filter medium, the head loss occurs mainly in the topmost filter layer, indicating that most particles are retained by the comparably fine GAC grains and do not penetrate deeply into the bed. The considerable head loss in a thin layer can lead to filter blocking, which occurred towards the end of some filter runs. The lower filter medium in a dual-media filter typically serves the purpose of retaining finer particles that are not removed in the coarse filter medium. As shown above, the GAC grains at the top of the filter bed have a similar or smaller diameter as the quartz sand (d_p = 0.7—1.1 mm). As a result, the head loss increases only marginally at the interface of the GAC and sand layers, suggesting that the sand layer is not used effectively. Coarser GAC material could be suitable to improve depth filtration in dual-media GAC filtration.

The key benefit of upflow filtration with regard to optimum filter depth utilization is based on the fact that the flow direction matches the stratification of the filter material from coarse to fine grains. Therefore, particles penetrate deeper into the filter bed, as evidenced by a steady increase in head loss with increasing bed depth (Fig. 3B). While the head loss still increases the most in the lowest filter layer, the results indicate that particle retention also occurs in deeper filter layers. The first 30 cm of the filter bed cause about 75% of the total head loss in downflow filtration, whereas the first layer induces only ~30% of the overall head loss in the upflow filter. A comparison of relative head loss in both filter columns is given in SI3.

Upflow filtration caused significantly lower head loss, resulting in a median total head loss of 90 mbar after filtration intervals of 23 h, compared to 200 mbar in the dual-media filter. The improved operation can be attributed to better depth utilization and the absence of a sand layer in upflow filtration, which leads to increased head loss due to decreasing void space. Additionally, the operating mode of an upflow filter limits the maximum head loss. Particle attachment leads to a decrease in bed porosity, increasing the actual flow velocity in the filter bed (and thus the head loss). If the flow velocity is sufficiently high, the filter medium gets fluidized and attached particles are released to a certain extent, leading to a decrease in flow velocity (and head loss) and settling of the filter medium. In contrast, head loss in downflow gravity filtration is limited by the height of the filter supernatant. As a result, excessive head loss leads to filter blocking rather than particle breakthrough.

3.1.3. TSS and phosphorus removal

Initial operation of the upflow filter yielded poor particle retention, possibly due to insufficient floc formation or because of floc destruction in the filter inlet. Therefore, the hydraulic conditions in the feed piping were improved by increasing the cross-sectional openings of the perforated plate used as filter bottom and extending the HRT in the tube flocculator. As a result, both the dual-media downflow filter and the GAC upflow filter achieve effluent concentrations of 0.1—0.2 mg/L TSS in the filtrate, which is distinctly below the treatment goal of 1 mg/L (Fig. 4A). While the influent TSS concentrations of on average 2.6 mg/L are comparably low, coagulation with 4—5 mg/L Fe leads to total solid concentrations of 12—15 mg/L that need to be retained by the filters.

Efficient removal of phosphorus is not affected by employing GAC as filter medium in dual-media filtration, achieving effluent TP concentrations <0.1 mg/L TP (Fig. 4B). Similar removals are also reached in upflow filtration, indicating effective floc formation in the filter inlet and subsequent retention in the filter bed. Comparable effluent concentrations of TSS and phosphorus have been reported for conventional tertiary wastewater filtration utilizing anthracite and sand as filter media (Sperlich et al., 2012) and for dual-media filtration with GAC as top filter medium (Meinel et al., 2015).

Median TSS and TP concentrations are slightly lower in dual-
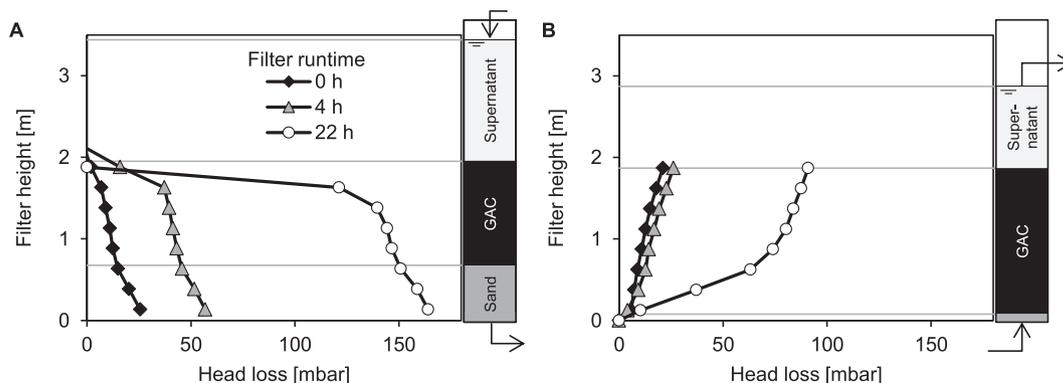
Fig. 3. Head loss profiles in the filter bed of (A) the dual-media downflow filter, (B) the upflow filter.
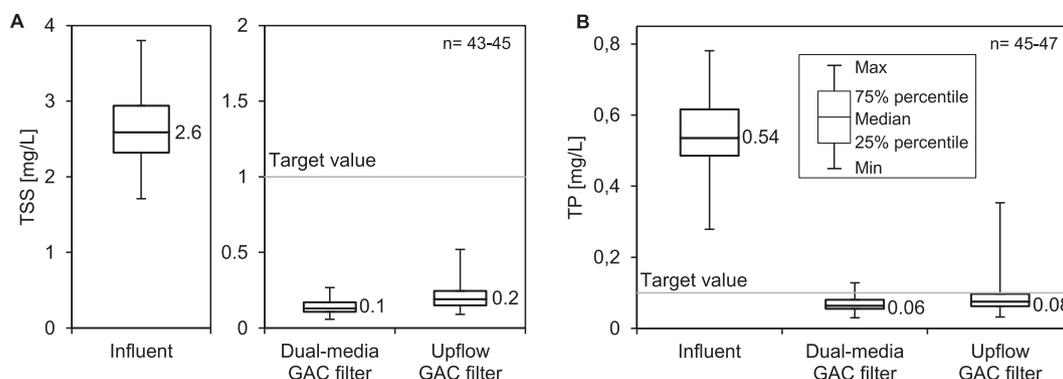
Fig. 4. Concentrations of (A) TSS and (B) TP in the influent and effluents of the tertiary GAC filters, composite samples of 22 h filter runs.

media filtration compared to mono-media upflow filtration. While the differences are within the margin of error of both analytical methods, filter breakthrough has been observed in some cases in upflow filtration, leading to considerably higher effluent concentrations. As described above, excessive head loss in upflow filtration may lead to filter bed expansion and detachment of particles, whereas filter overloading in the downflow filter typically caused filter blocking instead of particle breakthrough. Additionally, hydraulic conditions for floc formation are more favorable in downflow filtration because the gentle mixing conditions in the filter supernatant assist floc growth. Meanwhile, flocs in the upflow filter may be partially destroyed when passing the filter bottom due to increased shear stress.

3.2. DOC and micropollutant removal

DOC breakthrough curves related to throughput in bed volumes for both pilot filters are shown in Fig. 5. Immediate DOC breakthrough is caused by partly non-adsorbable dissolved organic matter (DOM) fractions and generally poor adsorption of DOM. The DOC concentrations increase steadily and reach a relative breakthrough of 50% at around 3,000 BV. Relative DOC concentrations assume almost constant values at approx. 10,000 BV, indicating that the adsorption capacity for compounds determined as DOC is largely exhausted. The sustained removal of about 20% DOC can be attributed in part to precipitation due to coagulant addition. Previous trials at the same pilot plant under similar conditions achieved at maximum 10% DOC removal with coagulation/filtration (Altmann et al., 2014). Therefore, it can be assumed that the GAC filter layer also operates as an biological activated carbon (BAC) system and supports additional 10% biological DOC degradation,

which has also been reported in water purification and advanced wastewater treatment applications (Reungoat et al., 2011; Simpson, 2008).

The breakthrough curves of benzotriazole, carbamazepine and primidone as exemplary non-biodegradable OMPs are given in Fig. 6. The breakthrough curves for all 15 OMPs related to throughput and operating time in days, as well as influent and effluent concentrations are shown in SI4. All OMPs are completely retained at the beginning of GAC filtration. The normalized concentrations subsequently increase depending on the adsorbability of each compound. Medium adsorbing primidone exhibits

Fig. 5. Normalized DOC breakthrough in the pilot GAC filters.
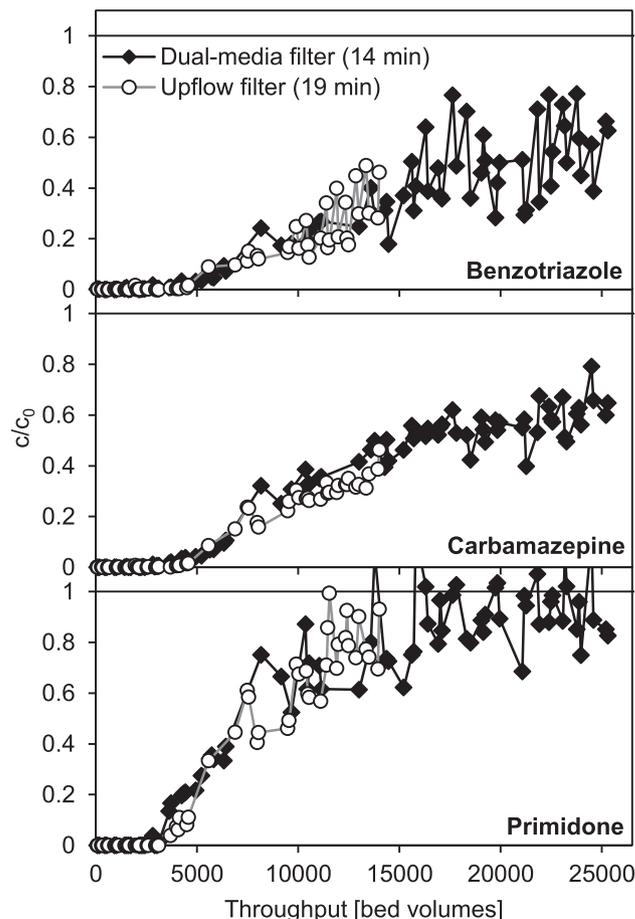
Fig. 6. Breakthrough curves of OMPs benzotriazole, carbamazepine and primidone related to normalized throughput.

complete breakthrough ($c/c_0 = 1$) after approx. 16,000 BV. Well-adsorbing compounds, such as carbamazepine, are still removed by around 40% after 25,000 BV, corresponding to 250 days of operation. Very weakly adsorbing OMPs, such as acesulfame and diatrizoic acid, experience complete breakthrough after <5,000 BV (Figures S2, S4). Moreover, effluent concentrations of diatrizoic acid and acesulfame increase to almost 1.5 times the influent concentration, pointing at desorption of previously adsorbed substances. This might be caused by competition with well-adsorbing compounds leading to desorption after complete breakthrough or by changes of the influent concentrations. Influent concentrations of acesulfame decrease after around 50 days of operation, which might result in the establishment of a lower adsorption equilibrium loading on the GAC surface and may lead to desorption of adsorbed acesulfame. However, influent and effluent concentrations of acesulfame return to being similar during further operation despite significant changes of the influent concentrations. This shows that competition with other OMPs is a major factor in determining a compounds breakthrough behavior instead of only the influent concentration of the target OMP. Similarly, Corwin and Summers (2011) showed that desorption after intermittent loading only occurs at low levels and over a long period of time. Therefore, it is assumed that displacement by well-adsorbing OMPs after complete breakthrough is the main cause for acesulfame desorption. Conversely, relevant concentration increases of diatrizoic acid and gabapentin in the influent result in higher equilibrium capacity, allowing for increased OMP loadings onto the GAC surface and a temporary decrease of relative effluent concentrations.

The effluent concentration of medium adsorbing sulfamethoxazole (Figure S8) also exceeds the influent concentration after complete breakthrough at approx. 8,000 BV, but subsequently remains at $c/c_0 = 1.5–2$ during the entire experimental period. This may be explained by the formation of sulfamethoxazole in the GAC filter due to backtransformation of metabolites (Bonvin et al., 2012). As influent concentrations of sulfamethoxazole decreased from 0.4 µg/L to 0.15 µg/L at the same time, desorption might also be possible. In general, the breakthrough behavior of each OMP depends on its chemical properties, such as hydrophobicity (expressed by the octanol–water distribution coefficient log D), aromaticity, molecular size, and on the competition with other OMPs and organic matter. Substances with high log D values (high hydrophobicity) and aromatic structures (e.g. carbamazepine and diclofenac) typically adsorb better onto the activated carbon surface than more hydrophilic compounds (e.g. sulfamethoxazole) (Kovalova et al., 2013). Of the substances investigated, acesulfame (log D = −2.77), Iomeprol (−2.61) and diatrizoic acid (−2.53) have the lowest log D values and also show poor adsorptive removal (log D values are given in SI2). Conversely, carbamazepine (2.28), methylbenzotriazole (1.74) and benzotriazole (1.50) have the highest log D values and are well adsorbed.

Overall, both GAC filter columns show a similar throughput-related breakthrough behavior with regard to most OMPs and the DOC, indicating that the increase of EBCT from 14 min (dual-media filter) to 19 min (upflow filter) does not have a relevant influence on adsorptive removal.

As indicated by DOC breakthrough behavior, an intensified biological activity within the GAC filter bed can be assumed and is supported by a dissolved oxygen depletion of ~6 mg/L in both filters (see SI5). As a result, biodegradable OMPs experienced significantly delayed breakthrough. Fig. 7 shows the normalized concentrations of 4-formylaminoantipyrine, gabapentin and iopromide related to operating time. For those OMPs, the concentrations initially increase with operating time, with a faster increase in the dual-media filter due to a higher normalized throughput (bed volumes per day) compared to the upflow filter. Especially the weakly adsorbing
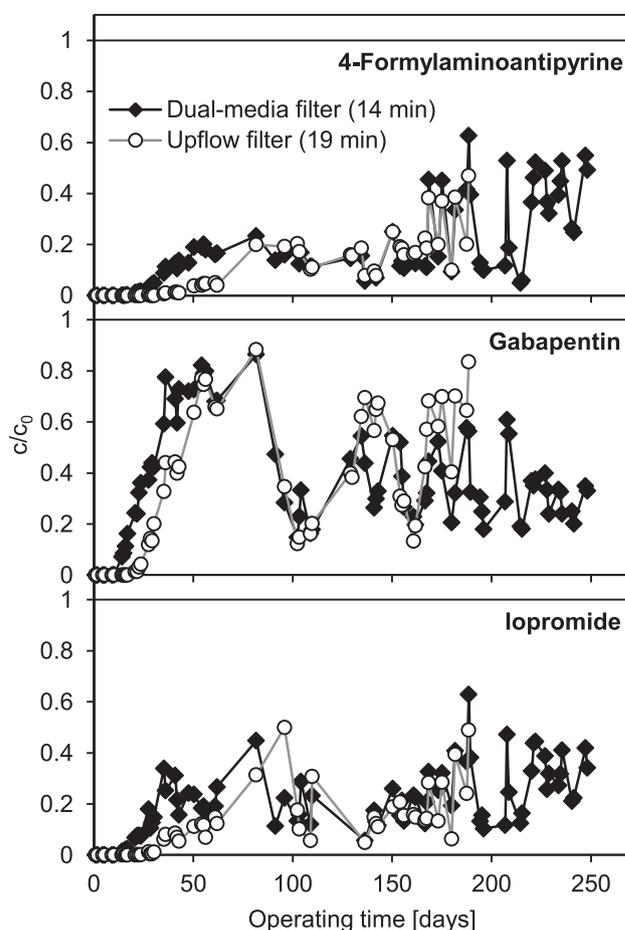
Fig. 7. Breakthrough curves of degradable OMPs 4-formylaminoantipyrine, gabapentin and iopromide related to operating time.

compound gabapentin shows a rapid concentration increase within the first 100 days of operation, corresponding to almost complete breakthrough at around 5,000 BV (see also Figure S5). The effluent concentrations subsequently decrease simultaneously in both GAC filter columns and achieve sustained gabapentin removals of at least 40% ($c/c_0 = 0.6$). Similarly, the concentrations of medium adsorbing compounds 4-formylaminoantipyrine and iopromide increase only slowly over the entire experimental period, indicating relevant concentration reductions due to biological transformation in addition to adsorptive removal. Therefore, a significant and sustainable removal of those OMPs can be expected even after prolonged operation. Because operating time is the critical factor for initiation of biological degradation, both GAC columns show similar concentration profiles when related to operating time, whereas OMPs that are primarily removed by adsorption are better comparable at similar normalized throughputs (see Figures S2–S9). Interestingly, the onset of gabapentin reduction coincides with a comparably rapid increase of influent concentrations from 4 µg/L to approx. 16 µg/L, indicating that a certain concentration might be necessary for biological gabapentin degradation. Gabapentin has recently been found in waste-, surface and drinking waters (Kasprzyk-Hordern et al., 2009; Reungoat et al., 2010), but only few data are available on its fate during advanced wastewater treatment, indicating poor removal by ozonation and activated carbon adsorption (Kovalova et al., 2013; Margot et al., 2013). Hermann et al. (2015) assessed the biodegradability of gabapentin in a closed bottle test and classified the substance as not readily

biodegradable, whereas the results of this study clearly indicate biotransformation of gabapentin, although factors affecting biological gabapentin removal still need to be investigated. Low temperatures led to seasonally varying nitrification in the conventional activated sludge treatment stage, resulting in occasional ammonium peaks of up to 4 mg NH_4–N/L in the filter influent beginning after 150 days of operation. Influent nitrate concentrations varied between 9 and 15 mg/L but showed no seasonal trend. Overall, median influent ammonium concentrations were <0.1 mg NH_4–N/L during the experimental period (also shown in SI5). Recent research suggests that nitrifying bacteria are relevant for the biodegradation of certain OMPs (Rattier et al., 2014). However, the data show no clear correlation with dissolved nitrogen concentrations, although GAC breakthrough curves of gabapentin, 4-fromylaminoantipyrine and iopromide indicate biodegradation of these substances.

Fig. 8 shows the respective throughputs in the dual-media filter at which each OMP reaches relative effluent concentrations of 20% and 50%. Carbon usage rate is also given for comparison. Biological degradation that resulted in meeting the removal goals at longer operating times is not considered. Weakly to medium adsorbing OMPs experience relative breakthrough of 20% after <5,000 BV, which corresponds to operating times of <50 days. For weakly adsorbing and non-biodegradable OMPs, the throughput until 50% breakthrough does not increase significantly. Meanwhile, biodegradation leads to relevant removal of valsartan, 4-formylaminoantipyrine (4-FAA), iomeprol and iopromide before reaching 50% breakthrough, resulting in considerable extensions of operating times. As a result, the generally medium adsorbing X-ray contrast media iomeprol and iopromide are removed by >50% even after 25,000 BV (250 days of operation). Degradation of gabapentin does not become relevant until after 50% breakthrough, leading to very low throughput until breakthrough because of poor adsorptive removal. Well-adsorbing OMPs bezafibrate, benzotriazole and carbamazepine reach 20% breakthrough at 8,000–10,000 BV and 50% breakthrough at 12,000–15,000 BV, the latter corresponding to a carbon usage rate of approx. 20 mg/L. The results can largely be transferred to the mono-media upflow filter due to similar breakthrough behavior for most OMPs.

3.3. Comparison with direct PAC addition

Besides the option of utilizing GAC as filter medium in tertiary filtration, direct addition of PAC to deep-bed filtration represents another alternative for the combined removal of micropollutants and phosphorus in a single advanced treatment stage. This process has been recently evaluated at the same WWTP (Altmann et al., 2015). Both studies were conducted during the same time period, resulting in similar secondary effluent DOC and UVA_{254} values of 11.2 mg/L and 25.8 1/m in the PAC study compared to 11.4 mg/L and 24.8 1/m, respectively, in this study. Furthermore, the same activated carbon type was used in both cases. Therefore, the data allow for a direct comparison of both treatment options with regard to OMP removal efficiency. Fig. 9 compares the OMP removal in GAC filtration with direct PAC addition at similar activated carbon usage rates of 20 mg/L and 35 mg/L, corresponding to throughputs of 14,250 BV and 8,140 BV, respectively, in the GAC filter. In the following section, carbon usage rate is used mutually for both applications and is synonymous to the activated carbon dose for PAC.

Generally, OMP removal is comparable in both activated carbon applications at similar carbon usage rates. Well-adsorbing OMPs, such as benzotriazole, diclofenac and carbamazepine are removed to a high degree in both applications, whereas the removal of weakly adsorbing compounds diatrizoic acid and acesulfame is very limited in either case. Meanwhile, degradable OMPs, such as valsartan, 4-formylaminoantipyrine and iopromide, show significantly higher removals in GAC filtration compared to application of PAC at carbon usage rates of 20 mg/L. This highlights the relevance of biological degradation, which is more pronounced in the GAC filter compared to dual-media filtration utilizing anthracite as top filter layer. The effect is stronger at 20 mg/L compared to 35 mg/L because the lower carbon usage rate corresponds to a higher throughput in the GAC filter, enabling improved biological activity with longer operating time. In the case of gabapentin, this results in higher removal in GAC filtration at the lower carbon usage rate because improved biodegradation outweighs the decline in adsorptive removal.

As discussed above, removal of sulfamethoxazole was poor in the GAC filter, which also stands out in comparison to the removal with PAC. Again, this might be attributed to backtransformation or desorption effects.

While the OMP removal is approx. constant with a certain PAC dose, GAC filtration leads to gradual breakthrough of OMPs. Therefore, the OMP removal is usually higher than the presented values up until the considered carbon usage rate (throughput) in the GAC filter. Still, comparing the data in this way seems reasonable if certain removal goals need to be met. Exceeding those limits will require replacing the GAC material in spite of better removals during previous operating time. Typically, exhausted GAC is regenerated instead of a complete renewal, with a makeup of ~10% due to losses during thermal regeneration. Therefore, the actual carbon consumption in a GAC application might be even lower. In terms of PAC efficiency, it has to be noted that more complex PAC applications, such as addition to a contact stage with PAC recycling, typically achieve higher OMP removals than single stage PAC application (Meinel et al., 2016). Further relevant aspects regarding the application of PAC or GAC in advanced wastewater treatment are the effects on the existing WWTP process, such as sludge treatment. Whereas GAC is replaced after exhaustion and does not affect the original treatment process, backwash water containing loaded PAC is typically recirculated into the treatment process, ultimately leading to PAC particles in the excess sludge that needs to be treated accordingly.

An additional advantage of GAC filtration is the possibility of combining multiple filter units to achieve higher throughputs until
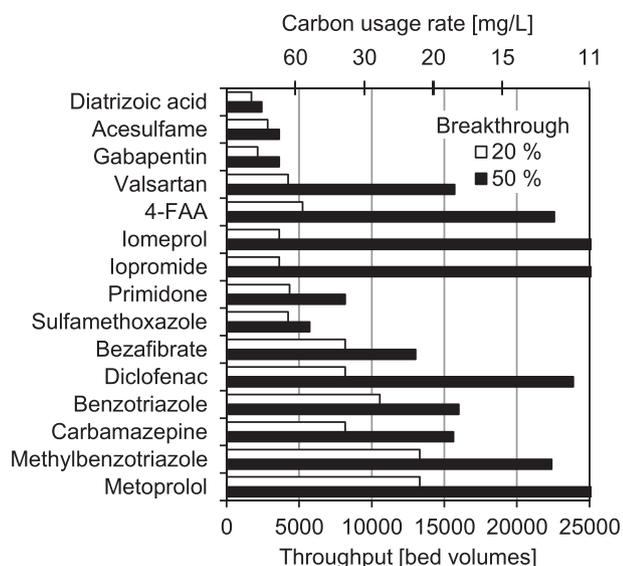
Fig. 8. Throughput at 20% and 50% OMP breakthrough in the dual-media GAC filter. Note that possible biological degradation resulting in meeting the removal goals at longer operating times is not considered.
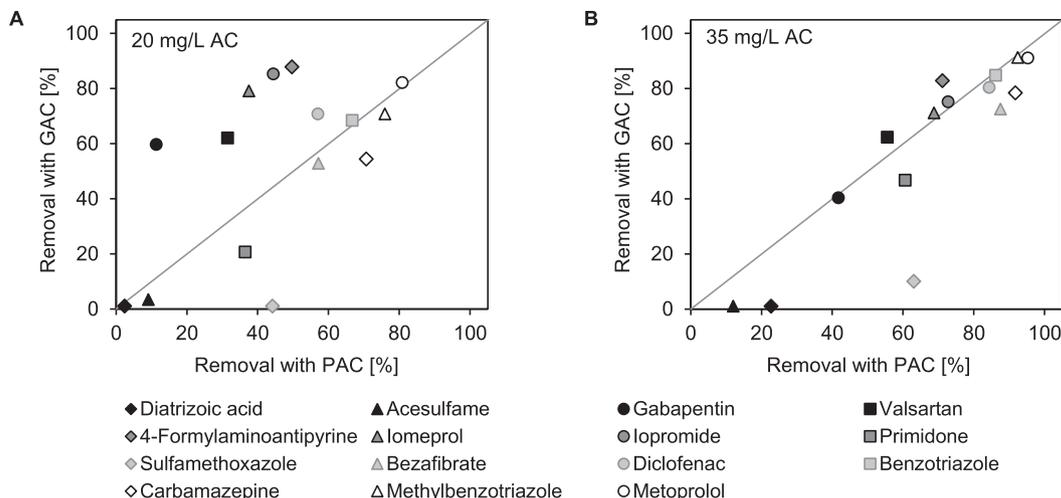
Fig. 9. Comparison of OMP removal in GAC filtration with direct PAC addition to deep-bed filtration at similar GAC carbon usage rates and PAC doses, respectively: (A) 20 mg/L PAC related to 14,250 BV, (B) 35 mg/L PAC related to 8,140 BV, PAC results taken from Altmann et al. (2015). The experiments were conducted at the same wastewater treatment site.

the GAC needs to be replaced. Because the OMP concentrations are generally lower than the desired treatment objective up until the time of breakthrough, it is possible to blend filter effluents exceeding the concentration limits with effluents of filters with lower concentrations, if the start of operation of the filters in parallel is adjusted accordingly. Additionally, it is also possible to operate two or more filter columns in series, allowing for higher exhaustion of the GAC in the first filter and thus increasing overall GAC utilization. Based on the pilot test results, throughputs of up to 20 filters in parallel and two filters in series have been calculated (methods and basic assumptions are described in SI6). Combination of two filters in parallel increases filter runtime until 20% breakthrough by around 30% for primidone and around 50% for carbamazepine compared to a single GAC filter (Table S3). The GAC replacement intervals further increase with a higher number of filter units operated in parallel and almost double with the use of up to 20 filter units (see Figure S12). Operation of two beds in series is suitable to prolong the runtime until replacement of GAC by 50–70%, depending on the OMP considered. Because large WWTPs typically already require several filter units for treatment of large water flows, the operation of multiple GAC filters in parallel does not necessarily require more expenses. Meanwhile, operating two or more filters in series necessitates additional filter units.

4. Conclusions

- Micropollutant removal by GAC adsorption can be integrated into deep-bed filtration for advanced phosphorus removal. Dual-media downflow filtration and mono-media GAC upflow filtration in combination with inline coagulation are capable of meeting treatment goals of 0.1 mg/L TP and 1 mg/L TSS.
- Frequent backwashing leads to stratification of GAC material according to its grain size and density with small grains near the top and large grains near the bottom of the filter column. Therefore, retention of particles in the topmost filter layer may lead to excessive head loss in downflow filtration and can cause filter blocking. Meanwhile, upflow filtration leads to significantly lower overall head loss and better depth utilization but is more prone to particle breakthrough at longer backwash intervals.
- OMP breakthrough behavior varies strongly depending on the substance considered. Very weakly adsorbing OMPs acesulfame and diatrizoic acid experience complete breakthrough after

<5,000 BV treated, whereas the influent concentrations of well-adsorbing compounds, such as carbamazepine and benzotriazole, are still reduced by almost 40% at 25,000 BV. Biological activity in the GAC filter bed leads to degradation of 4-formylaminoantipyrine and iopromide, among others, resulting in lasting concentration decreases of those OMPs even after prolonged operation. An increase in EBCT from 14 min to 19 min did not show a relevant influence on breakthrough behavior of most OMPs.

- Gabapentin, an anticonvulsant drug recently detected in drinking water resources, shows poor adsorptive removal but concentration decreases within the GAC filter indicate biological degradation after prolonged operation. Previously, gabapentin has been thought to be not biodegradable.
- At similar carbon usage rates, the application of GAC as filter medium achieves similar OMP removals as direct addition of PAC to deep-bed filtration. However, degradable OMPs show significantly higher removals in GAC filtration compared to application of PAC, emphasizing the relevance of GAC as filter material to promote biological OMP reduction. Furthermore, operation of multiple GAC filter units in parallel or in series can extend the intervals for GAC replacement substantially without worsening effluent quality.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.watres.2016.01.051.

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