Characterizing solids retention, headloss development and micropollutant removal in the case of direct powdered activated carbon dosage upstream of deep bed filtration

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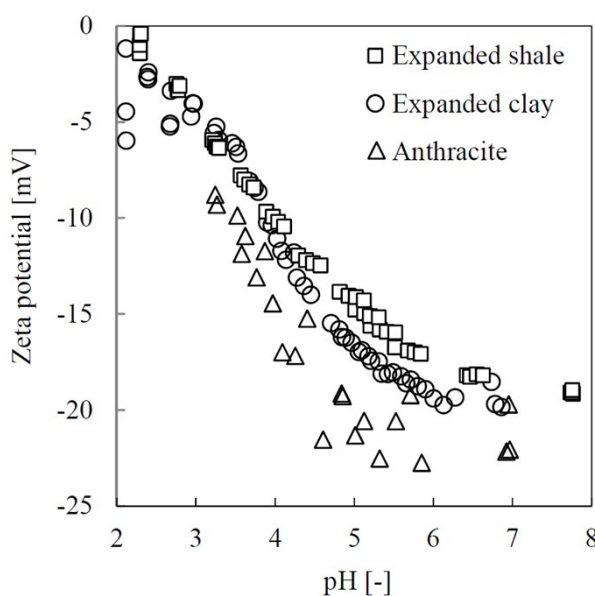
ESI: Additional figures

Figure S1: Zeta potential of the different filter media measured at different pH values
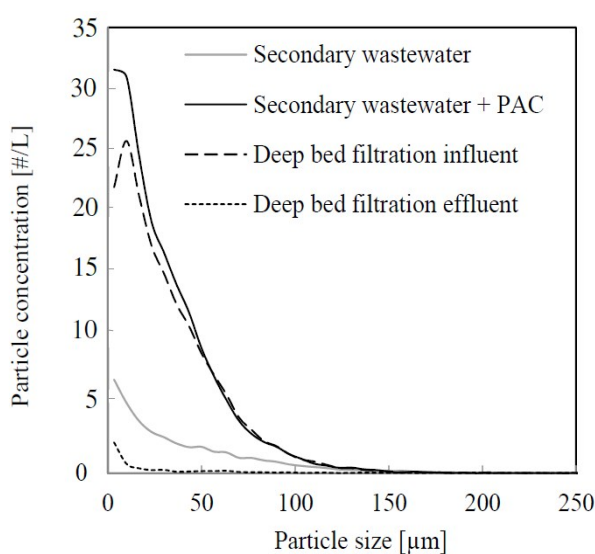

Figure S2: Particle concentration measured in grab water samples from different sampling points along the PAC process (measuring campaign 1)
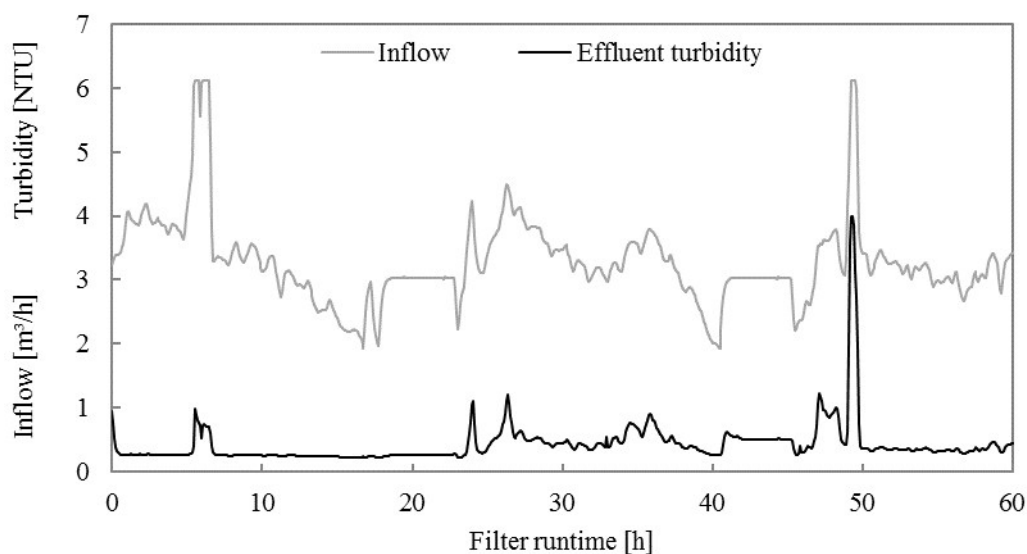
Figure S3: Correlation between pilot unit inflow volume and effluent turbidity (measuring campaign 3)

ESI: Analytical methods

Micropollutant analysis

Samples of each 500 mL were taken as 48-h volume proportional composite samples and stored at 10°C on site in a refrigerator. Sample flasks were cindered at 500 °C for 5 h before use. Before preparation by solid-phase extraction as described by Hummel et al. (2006) the samples were stored at 4°C in a cooling room. Samples were conditioned to a pH of 7.5 and methanol was used as extraction medium for manual extraction using Oasis HLB 6 cc (Waters, Ireland).

A liquid chromatography-mass spectrometry system consisting of an Agilent (Waldbronn, Germany) 1260 Infinity HPLC system (binary pump, degasser, auto sampler) coupled to a 6420 Triple Quad LC/MS equipped with an electrospray ionization (Agilent, Waldbronn, Germany) was used for detection and quantification of micropollutants. The chromatographic separation was conducted using a Zorbax SB-C8 Rapid Resolution HT column (50 mm x 2.1 mm, 1.8 µm particle size) from Agilent Technologies (Wilmington, DE, USA) at a column temperature of 40°C.

For the analysis in both negative and positive ion mode during the same run a binary gradient mixture consisting of 0.1% (v/v) acetic acid and 5% acetonitrile in HPLC grade water (eluent A) and 0.1% (v/v) acetic acid and 5% HPLC grade water in acetonitrile (eluent B) was used at a flow rate of 0.6 mL/min. The elution gradient started with a mixture of 98% of eluent A and 2% of eluent B. Isocratic conditions were held for 1.5 min and then eluent B increased to 15% within 15 min. Afterwards the system was set back to initial conditions within 6 min. The sample injection volume was set to 10 µL. By direct injection of stock solutions with a concentration of 10 µg/mL fragmentor voltage and collision energy were optimized (Table S1). Protonated ([M+H]+) or deprotonated ([M-H]-) molecular ions were selected for all analytes as precursor ions. Two transitions per analyte were selected, whereby the intense product ion of each analyte was used for quantification and the secondary product ion was used as qualifier. As scan type dynamic multiple reaction monitoring (MRM) was used. Source parameters were set to 3.5 kV in positive mode and to -2.5 kV in negative mode for capillary voltage, desolvation gas temperature was set to 350°C, desolvation gas flow to 10 L/min and the nebulizer pressure to 50 psi.

To determine the lowest concentration of micropollutants which are detected in presence of possible matrix effects, wastewater samples (n = 7) spiked with analytes were prepared and measured as described generating a method detection limit (MDL). The MDLs for the investigated micropollutants are listed in Table S 2. The linearity of the eleven point calibration curve in the range of 0.05-51.2 ng/L was also calculated and high correlation coefficients (R^2) of 0.9984 or better were achieved (Table S2).

Table S1: Parent compounds and their transformation products, substance specific MS/MS parameters: precursor ion, main product ions (quantifier), secondary product ions (qualifier), collision energy [CE], fragmentor voltage, precursor ion (+/-).

Analyte	Precursor ion	Quantifier	Qualifier	CE	Fragmentor voltage	polarity
Benzotriazole	120	65	39	25	120	+
Sulfamethoxazole	254	156	92	14	100	+
Carbamazepine	237	194	179	18	100	+
Mecoprop	213	141	71	8	69	-
Diclofenac	296	250	215	10	80	+
Amisulpride	370.2	242.1	196.1	27	150	+
Metoprolol	268.2	116.1	72.1	16	131	+
Venlafaxin	278	260	58.2	10	100	+
Citalopram	325.2	262.1	109.2	15	150	+
Clarithromycin	748.4	590.4	158.2	17	165	+
Irbesartan	429.3	207.2	195.3	26	120	+
Hydrochlorothiazide	295.95	268.9	78.1	17	145	-

Table S2: Method detection limits (MDL) and linearity of analytes (range 0.05-51.2 ng/L)

Analyte	Linearity correlation factor (R^2)	Method detection limit [ng/L]
Benzotriazol	0.9994	0.2
Sulfamethoxazole	0.9990	0.1
Carbamazepine	0.9995	0.05
Mecoprop	0.9989	0.4
Diclofenac	0.9984	0.2
Amisulpride	0.9985	0.04
Metoprolol	0.9994	0.05
Venlafaxin	0.9994	0.06
Citalopram	0.9988	0.8
Clarithromycin	0.9983	0.003
Irbesartan	0.9993	0.005
Hydrochlorothiazide	0.9991	0.3

Thermogravimetric PAC quantification

PAC quantification was done with a thermogravimetric analyser (TGA 4000, Perkin Elmer, measuring accuracy 0.2%). The sample mass during thermogravimetric analysis was assessed with a TGA software (Pyris Software, Version 2009, Perkin Elmer). A specific heating method was applied to identify specific solid sample fractions (Table S3). At temperatures <150 °C, filter humidity evaporates. Then, wastewater background matrix is degraded at 200-400 °C under nitrogen and at 300-600 °C under oxygen atmosphere.

Table S3: TGA heating method consisting of a drying step (0), and two measuring steps under N_2 (steps 1–3) and O_2 (steps 4–6)

Method step	Temperature	Atmosphere
0	Heat from 30 °C to 100 °C at 40 °C/min and hold at 100 °C for 60 min	20 mL/min N_2
1	Heat from 30 °C resp. 100 °C to 350 °C at 5 °C/min	20 mL/min N_2
2	Hold at 350 °C for 300 min	20 mL/min N_2
3	Cool to 30 °C	20 mL/min N_2
4	Hold at 30 °C for 300 min	20 mL/min O_2
5	Heat from 30 °C to 900 °C at 5 °C/min	20 mL/min O_2
6	Cool to 30 °C	20 mL/min O_2

The solid fractions were determined by integrating the mass loss rate in clearly identifiable characteristic peaks under N_2 and O_2. The PAC concentration C_{PAC} was calculated as described in a previously published study [1], using a linear correlation of the form:

$$C_{PAC} = F_{Degr} \cdot TSS \cdot \left[(1 + F_{Matrix}) \cdot F_{TGA} - F_{Matrix} \right]$$

where F_{TGA} is an indicator for the sample's PAC content derived from the TGA curve, TSS is the concentration of total suspended solids in the water sample and F_{Degr} and F_{Matrix} are parameters for the specific degradation behavior.

Particle size analysis

For each particle measurement, a 800 mL water sample was filled in a reactor (Mettler Toledo, OptiMax Synthesis Workstation) with online temperature and pH sensors (Mettler Toledo, InPro 32501) to perform particle analysis under well reproducible conditions. The reactor was constantly cooled to 10±1 °C and mixed with a pitch-blade stirrer (4 blades, 30 mm diameter). The stirring intensity maintained at 150 rpm, corresponding to a mean velocity gradient of 35/s.

The particle size distribution in the reactor was continuously monitored using a Focused Beam Reflectance Measurement (FBRM) probe (Mettler Toledo, ParticleTrack G400). FBRM allows for the measurement of flock size distributions in real time [2-4]. The FBRM functioning principle is based on a highly focused laser beam that is scanned across a suspension, and the duration of light backscattering from suspended particles [5]. As preliminary experiments and previous studies showed that the FBRM chord length corresponds well to the actual particle diameter [4, 6], both values were considered equivalent in this study. The FBRM measuring data is expressed in particle counts per measurement interval and directly relates to a volume specific particle concentration, because a constant measurement interval of 2 seconds was maintained.

References

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