Water Research 84 (2015) 58–65

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Integrating organic micropollutant removal into tertiary filtration: Combining PAC adsorption with advanced phosphorus removal

Johannes Altmann [a, *], Alexander Sperlich [b], Martin Jekel [a]

[a] *Technische Universität Berlin, Chair of Water Quality Control, Str. des 17. Juni 135, 10623 Berlin, Germany*
[b] *Berliner Wasserbetriebe, Cicerostr. 24, 10709 Berlin, Germany*

ARTICLE INFO

Article history:
Received 30 April 2015
Received in revised form
7 July 2015
Accepted 14 July 2015
Available online 20 July 2015

Keywords:
Organic micropollutants
Powdered activated carbon (PAC)
Adsorption
Deep-bed filtration
Wastewater treatment

ABSTRACT

Direct addition of powdered activated carbon (PAC) to a deep-bed filter was investigated at pilot-scale as a single advanced treatment stage for simultaneous removal of organic micropollutants (OMPs) and phosphorus from secondary effluent. PAC doses of 10–50 mg/L were assessed with regard to their impacts on filter performance and removal of 15 selected OMPs over a period of 18 months. The PAC was effectively retained by the filter and had no negative effect on filter head loss. Filter runtime until particle breakthrough depended mainly on coagulant dose and did not decrease significantly due to the additional PAC load. Removal of suspended solids and phosphorus by coagulation was effective independent of the PAC dose. A PAC dose of 35 mg/L PAC was suitable to remove well-adsorbing OMPs (e.g. carbamazepine, diclofenac) by >80% and medium adsorbing OMPs (e.g. primidone, sulfamethoxazole) by 50–80%. Median removals were 50–80% for well-adsorbing and 30–50% for medium adsorbing OMPs with 20 mg/L PAC. Abatement of all OMPs was low (<50%) with 10 mg/L PAC, possibly because of the high effluent organic matter content (median dissolved organic carbon (DOC) concentrations of 11.2 mg/L). In addition to adsorptive removal, relevant concentration decreases of certain OMPs (e.g. 4-formylaminoantipyrine) were attributed to biological transformation in the filter. Adsorption onto accumulating PAC in the top layer of the filter bed led to improved OMP adsorption with increasing filter runtime. The comparison of OMP removal in the pilot filter with laboratory adsorption tests demonstrates that batch test results can be applied to estimate adsorptive OMP removal in real applications.

1. Introduction

Because many organic micropollutants (OMPs) are not effectively removed by conventional wastewater treatment plants (WWTPs), they are frequently found in receiving waters and can thus affect drinking water resources (Luo et al., 2014; Michael et al., 2013). While the number of pharmaceuticals, personal care products and industrial chemicals detected in the aquatic environment increases constantly (Loos et al., 2013; Wode et al., 2015), impacts on aquatic life and humans are still being investigated (Leusch et al., 2014; Magdeburg et al., 2014). As studies increasingly report negative effects of individual compounds (Liang et al., 2014; Melnyk-Lamont et al., 2014) or complex mixtures at environmentally relevant concentrations (Pomati et al., 2006; Vasquez et al., 2014), upgrading WWTPs with additional treatment stages is currently being discussed as a precautionary measure (Eggen et al., 2014). The most promising treatment options include oxidation with ozone or adsorption onto activated carbon, either in powdered or granular form (Altmann et al., 2014; Hollender et al., 2009; Kennedy et al., 2015).

Powdered activated carbon (PAC) is typically applied in a separate adsorption stage followed by sedimentation/filtration (Kovalova et al., 2013; Löwenberg et al., 2014; Margot et al., 2013). In order to improve PAC utilization, the PAC is sometimes recirculated or embedded into fluidized flocs to increase its residence time (Mailler et al., 2015; Serpa et al., 2004). Instead of a separate treatment stage, addition of PAC into the biological stage has been proposed as a less expensive alternative (Böhler et al., 2012). However, increased PAC demands were reported and attributed to the high content of dissolved organic matter (DOM). Another less energy- and space consuming alternative is the direct dosing of PAC into the influent of a deep-bed filter. In this process combination, the adsorption of OMPs occurs primarily in the filter supernatant. Because the adsorption capacity of the PAC is typically not

---

* Corresponding author.
E-mail address: johannes.altmann@tu-berlin.de (J. Altmann).

http://dx.doi.org/10.1016/j.watres.2015.07.023
0043-1354/

exhausted before separation, further adsorption onto embedded PAC may increase the PAC efficiency (Altmann et al., 2015). In combination with coagulation, this process scheme is suitable to simultaneously reduce phosphorus and OMP concentrations. For WWTPs already employing tertiary filtration, this process represents an inexpensive alternative to a separate adsorption stage. Additionally, stringent legislation limiting nutrient concentrations may necessitate upgrading of conventional WWTPs with tertiary filtration, opening up the possibility for simultaneous OMP removal.

Because the PAC is not separated by sedimentation before filtration, the solids load on the filter increases considerably compared to coagulation/filtration and may negatively affect the filter runtime. Furthermore, reliable retention of small PAC particles needs to be ensured. Böhler et al. (2012) reported slight increases in filter effluent solids concentrations with PAC addition. Likewise, Margot et al. (2013) observed good PAC separation by sand filtration but assumed releases of loaded PAC into the effluent. Besides those coarse evaluations, the impact of the additional PAC load on filter runtime and particle retention in coagulation/filtration has not yet been investigated systematically. Additionally, very few reliable data are available presenting OMP removals at pilot-scale with multiple PAC doses.

This study investigates the feasibility of direct PAC addition to a deep-bed filter as a single advanced treatment stage for simultaneous OMP and phosphorus removal from secondary effluent. The impact of PAC dosing on filter resistance, backwash intervals and particle retention was investigated. Furthermore, the achievable OMP removal by direct PAC dosing and filtration was determined and compared to lab-scale adsorption batch tests.

2. Materials and methods

2.1. Pilot experiments

The experiments were conducted at municipal WWTP Münchehofe (Berlin, Germany) over a consecutive period of 18 months. The wastewater treatment includes primary sedimentation, conventional activated sludge treatment with chemical precipitation and secondary clarification. The pilot plant consists of a dual-layer rapid filter with a filter area of 1.13 m^2 and 1.2 m anthracite (1.4–2.5 mm) and 0.6 m quartz sand (0.7–1.25 mm) as filter material. The filter is fed with secondary effluent at a filtration rate of 7.5 m/h (corresponding to 8.5 m^3/h). Influent characteristics during the experimental period are given in Table 1. PAC was supplied from Donau Carbon (Germany). Carbopal AP ($d_{70} < 40$ μm, B.E.T. surface >1300 m^2/g according to the manufacturer) is prepared as a slurry with tap water (6–30 g/L) and added to the influent by inline dosing with 15 L/h for PAC doses of 10, 20, 35 and 50 mg/L. Following PAC dosing, ferric chloride (50 g/L Fe) is added to a static mixer in proportion to the orthophosphate load (as determined by an online probe) with 4.4 mol Fe/mol reactive phosphorus, resulting in a median dose of 4.8 mg/L Fe (see Fig. S1 in supporting information for cumulative frequency of coagulant dose). The hydraulic residence time (HRT) for adsorption and floc formation in the filter supernatant is 15 min, with an additional maximum HRT of 7 min in the filter bed. The filter is backwashed time-controlled after 12 or 24 h by air and water scouring with influent water.

Table 1
Characteristics of the secondary effluent used as influent to the PAC filter (22 h composite samples).

Parameter		Median (25th–75th percentile), n = number of measurements
Total suspended solids	[mg L^{-1}]	4.6 (3.8–5.1), n = 174
DOC	[mg L^{-1}]	11.2 (10.4–12.2), n = 75
COD	[mg L^{-1}]	35.3 (33.3–39.7), n = 51
UVA_{254}	[1/m]	25.8 (24.1–27.4), n = 85
Total phosphorus	[mg L^{-1}]	0.72 (0.65–0.80), n = 124
pH	[–]	7.0 (6.8–7.0), n = 89
Temperature	[°C]	17.3 (13.8–20.0), n = 89

Influent and effluent samples were collected as 22 h composite samples using automated samplers. The first 1.5 h of filtration were not sampled to exclude residual backwash water. In large-scale operation, backwashing is typically performed with filtrate instead of untreated influent. Additionally, corresponding grab samples of the influent were taken from sampling points before and after PAC addition (before coagulant dosing point) for PAC dose verification at each sampling date. Grab samples were also taken from sampling points at different filter media depths and in the supernatant to measure concentration profiles a total of ten times during the experimental period.

2.2. Batch experiments

For adsorption batch experiments, PAC slurry was taken from the pilot storage tank and added to glass flasks with 100 mL influent composite samples taken on the same day. Following PAC addition to achieve doses of 10, 20, 35 and 50 mg/L, the flasks were agitated on a horizontal shaker for 2 min–48 h. The PAC was subsequently separated by 0.45 μm membrane filters (regenerated cellulose, Macherey–Nagel, Germany). Control samples without PAC were also treated in identical fashion.

2.3. Analytical methods

For analyses of dissolved parameters, the samples were filtered through 0.45 μm membrane filters (regenerated cellulose, Macherey–Nagel, Germany). 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). Furthermore, the samples were analyzed for total phosphorus (TP), soluble phosphorus (sP), soluble reactive phosphorus (srP), chemical oxygen demand (COD) and sCOD by Hach Lange cuvette tests using a Hach Lange photometer (DR 3800). The gravimetric determination of total suspended solids (TSS) was performed using glass fiber filters (0.3–1.0 μm, Macherey–Nagel, Germany). Similarly, PAC concentrations of the pilot filter influent (differential measurement before and after PAC addition to discount for influent TSS) and the PAC slurry for batch experiments were also determined gravimetrically using glass fiber filters. The effluent turbidity (Solitax probe, Hach-Lange, Germany) and head loss of the filter were monitored continuously.

OMPs were quantified by HPLC-MS/MS using a XSelect HSS T3 column (2.5 μm, 50 × 2.1 mm, Waters, USA) for separation and a TSQ Vantage (Thermo Scientific, USA) for analysis. Direct injection of 25 μL sample and a linear gradient were used 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. Mass fragments were chosen according to the DAIOS database and deuterated internal standards were used for quantification (DAIOS, 2014). The OMPs were selected based on their permanent occurrence in elevated concentrations in Berlin wastewater effluents, their status as priority or indicator substances and because of their varying adsorbabilities onto PAC. Additional information on the areas of application and the limits of quantification of each OMP are given in Table S1.