Removal of nitrogen, phosphorus and other priority (hazardous) substances from WWTP effluent

Water Science & Technology Vol 54 No 8 pp 189–195 © IWA Publishing 2006

V. Miska*, H.W.H. Menkveld, L. Kuijer**, M. Boersen*** and J.H.J.M. van der Graaf***

*Department of Sanitary Engineering, Faculty of Civil Engineering and Geoscience, Delft University of Technology, PO Box 5048, 2600 GA Delft, The Netherlands (E-mail: *V.miska@citg.tudelft.nl*)

**Witteveen + Bos, Consulting Engineers, PO Box 233, 7400 AE Deventer, The Netherlands

***Water Board de Stichtse Rijnlanden, PO Box 550, 3990 GJ Houten, The Netherlands

Abstract More stringent effluent criteria will be required in the near future for the so-called priority substances listed in the Annex of the European Water Framework Directive (WFD) 2000/60/EC. This includes heavy metals, volatile and semi-volatile organic substances, pesticides and polychlorinated biphenyls. The Fraunhofer Institute suggested FHI values for these substances in water. National Dutch legislation, the Vierde Nota WaterHuishouding (NWH) introduced in 1998 'maximum tolerable risk concentrations' (MTR). These include requirements for nutrients: $P_{tot} < 0.15$ mg/l and $N_{tot} < 2.2$ mg/l. The MTR values are being used until the FHI values become effective. Investigation into possible effluent polishing techniques is required in order to reach these objectives. During pilot research with tertiary denitrifying multi-media and biological activated carbon filtration at the WWTP Utrecht in the Netherlands, simultaneous nutrient removal to MTR quality was observed. Furthermore, simultaneous removal of heavy metals, 17β-estradiol, bisphenol A and nonylphenols to extreme low concentrations by denitrifying activated carbon filtrated is achieved.

Keywords Biological activated carbon filtration; effluent polishing; European Water Framework Directive; multi-media filtration; nutrient removal

Introduction

An increasing demand by citizens and environmental organisations for cleaner surface water bodies led to the first step of the strategy within the European Water Framework Directive 2000/60/EC (WFD), the establishment of a list of priority substances as an annex of the directive.

The European Commission identified 33 substances including heavy metals, volatile and semi-volatile organic substances, pesticides and polychlorinated biphenyls. The Fraunhofer Institute (FHI) suggests concentration limits for these substances (Beek and Oudendijk, 2003). This led to objectives for nitrogen, phosphate and priority (hazardous) substances in water, implemented as Maximum Tolerable Risk concentrations (MTR) in the Dutch legislation, introduced by the 4th Nota WaterHuishouding (NWH) (van der Beesen, 1998).

Until now those objectives are hardly reached. Therefore, additional measures should be taken to reach the WFD objectives. The starting point for these measures is the single-point emissions of Water Treatment Plants (WWTPs) which, compared to non-localised nutrient emissions caused by widespread agriculture and farming, can be easily controlled. Besides removal of nutrients to MTR concentrations ($P_{tot} = 0.15$ mg/l; $N_{tot} = 2.2$ mg/l) the elimination of priority (hazardous) substances is a major issue.

Based on these interests a pilot scale project has been originated as part of a cooperation project between Witteveen + Bos Consulting Engineers, Delft University of Technology and Water Board De Stichtse Rijnlanden. The research took place at the WWTP in Utrecht (Netherlands), from January to July 2004. The common objective was to reach MTR concentrations for phosphorus and nitrogen by applying several filtration techniques, such as flocculation filtration with simultaneous nutrient removal in a multi-media filter and biological activated carbon filtration. The results are presented in this article.

Nutrient removal is investigated during multi-media filtration as a single process. The process performance of biological activated carbon filtration is evaluated in regard to nutrient removal and some selected components, like 17β-estradiol, bisphenol A and nonylphenol. Important research questions are:

- to what extent is further removal of P and N possible with conventional filtration techniques?
- which minimal empty bed contact time is necessary for biological activated carbon filtration?
- is it possible to remove endocrine disruptors (tracer 17β-estradiol) simultaneous to NO_3-N removal under denitrifying conditions?

Based on the positive results the research has continued together with Water Management and Sewage Service Amsterdam (DWR) since March 2005 for several years. The investigation on removal of nitrogen, phosphorus, suspended solids, heavy metals and other selected priority substances with multi-media filtration and other filtration techniques for polishing of WWTP-effluent takes place at the WWTP Horstermeer, in The Netherlands (Miska *et al.*, 2006).

Methods

Pilot plant

Figure 1 shows the configuration of the pilot plant with the measuring points for online analysers and dosing points for chemicals.

The pilot plant consists of a multi-media filter and two biological activated carbon filters. The WWTP-effluent has passed a sieve (450 μm) and is collected in

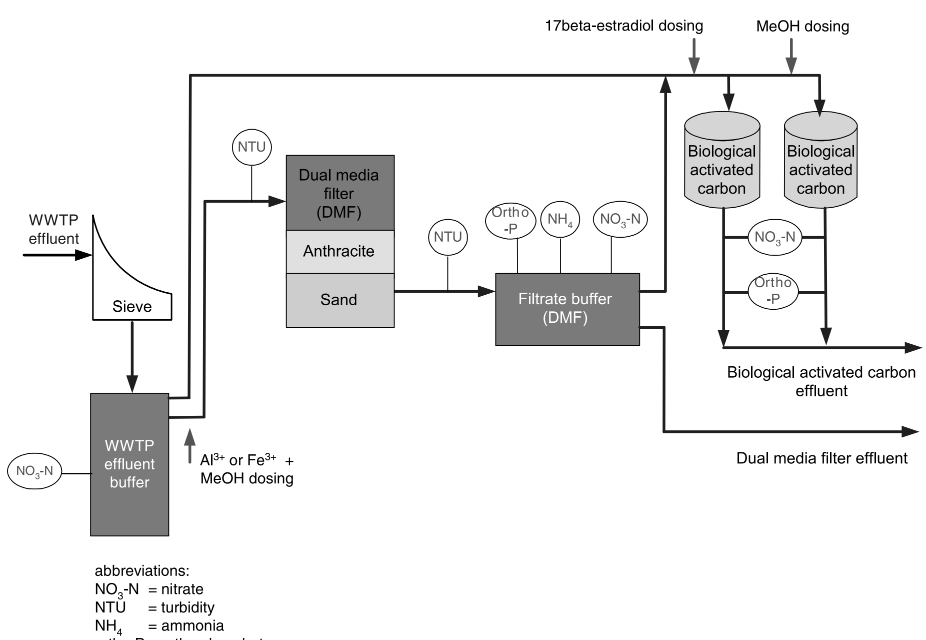

Figure 1 Schematic overview of pilot installations

the WWTP-effluent buffer. The filtrate of the multi-media filter is collected in the filtrate buffer. From these two buffer tanks, water is distributed to the installations.

Turbidity is analysed on-line in the process influent and in the filtrate of the multi-media filter. Other on-line measurements (Menkveld *et al.*, 2004) are:

- NO_3-N in the effluent buffer (in a later period also PO_4-P);
- NO_3-N, NH_4-N and PO_4-P in the filtrate buffer; and
- NO_3-N and PO_4-P in the filtrate of the biological activated carbon filters.

Multimedia filtration

For pilot scale investigation a downward discontinuous filtration installation (inner diameter 80 cm; lower layer: quartz sand Ø 1.5–2.25 mm, 40 cm height; upper layer: anthracite Ø 2.0–4.0 mm, 80 cm height) is applied. The filter installation is preceded by a dosing of polyaluminiumchloride (PACl, dosing of 1–2.5 mg Al/l) or iron(III)chloride ($FeCl_3$, dosing of 1–3 mg Fe/l) for removal of suspended solids and phosphorus. Methanol is used as carbon source for denitrification with a dosing ratio of 4.2 g methanol per g NO_3-N. This is inclusive of an overdose of 40% for the removal of free oxygen present in the WWTP effluent. During simultaneous denitrifying flocculation filtration a constant flow rate of 5 m^3/h (filtration rate 6.3 m/h; bed contact time 13 minutes) is applied.

Before the on-line PO_4-P analyser was installed, manual measurements of orthophosphate took place in the effluent buffer on samples pre-filtered over a 0.45 μm cellulose acetate filter. A constant filtration rate of 6.3 m/h is applied during operation with simultaneous denitrifying flocculation filtration. For the experiments with single flocculation filtration the installation is operated with filtration rates of 6.4, 10.2, 12.7 and 17.2 m/h (Menkveld *et al.*, 2004).

Biological activated carbon filtration

The pilot scale biological activated carbon installation contains two separate columns, for parallel or serial use, each filled with 60 l activated carbon (Norit GAC 830P) with a bed height of 1.2 m. Both columns (BACF 1 and BACF 2) are fed by the filtrate from the multi-media filter. While BACF 2 is kept as a reference, the feed water for BACF 1 is conditioned with methanol to achieve denitrifying conditions. Dosing rates of 2.2–2.5 g CH_3OH per g NO_3-N are used. Empty bed contact times (EBCTs) of 60, 40, 20 and 10 minutes are applied resulting in filtration rates of 1.2–7.6 m/h (Table 1). Backflush occurred manually every 2–4 days with a flow between 1,100–1,400 l/h for 10–20 minutes with filtrate of the BACF installation and tap water. For the adsorption tests a solution of 17β-estradiol is dosed resulting in a concentration of 1 μg/l in the process influent (van Oene, 2004).

Table 1 Applied EBCT and flows during biological activated carbon filtration (van Oene, 2004)

Period	EBCT (min)	Flow (l/h)
27-02-04–22-03-04	60	59
22-03-04–24-03-04	40	88
24-03-04–13-04-04	20	177
13-04-04–11-05-04	10	355
11-05-04–25-05-04	20	177
23-05-04–02-06-04	10	355

Results and discussion

Multi-media filtration

In preliminary jar tests polyaluminiumchloride (PACl) showed higher efficiency for phosphorus removal than iron(III)chloride ($FeCl_3$) probably due to the relatively low average pH of 6.9 in the WWTP effluent. As a consequence, PACl was mainly used in the pilot scale experiments for coagulation/flocculation and chemical phosphorus precipitation.

Although only a few manual measurements of PO_4-P in WWTP effluent have been conducted, the trend for good removal is shown in Figure 2. Low concentrations in the process filtrate of 0.04 mg PO_4-P/l are achieved during simultaneous flocculation filtration. This is reached with both a dosing of 1.5 mg Al/l and a dosing of 1.0 mgFe/l at a filtration rate of 6.3 m/h. The MTR quality for $P_{tot} < 0.15$ mg/l was reached with an average concentration of 0.1 mg/l of organic phosphorus in the filtrate. The biological phosphorus removal due to denitrifcation is calculated to a maximum of 0.2 mg/l during the whole research period.

Weekly Kjeldahl nitrogen measurements of around <2.0 mg/l in the filtrate, together with the nitrate measurements in Figure 2, show that MTR quality for $N_{tot} < 2.2$ mg/l in the filtrate is possible. A stable low NO_3-N concentration in the filtrate can be reached during proper methanol dosing.

In Figure 3, results for phosphorus measurements are shown for filtration tests with high filtration rates of 8, 12.5 and 17 m/h. High filtration rates and varying orthophosphate (PO_4-P) concentrations in the WWTP effluent have no negative influence on the removal. An average PO_4-P concentration below 0.1 mg/l was measured (Menkveld *et al.*, 2004).

During the whole research period, while applying different filtration rates, the turbidity of the multi-media filtrate is always below 2 NTU and is thereby independent of the incoming turbidity of the WWTP effluent.

It appears that progressive phosphate removal to <0.1 mg/l PO_4-P has no negative effect on the denitrification rate nor on the nitrate removal. This is in contrast to continuous sand filtration where some researchers show that phosphate removal leads to a significantly lower denitrification efficiency. A possible cause could be that contrary to sand, anthracite sustains the biomass better in the system and thus requires less growth of denitrifying biomass and consequently requires less phosphate for its growth. This should be further investigated.

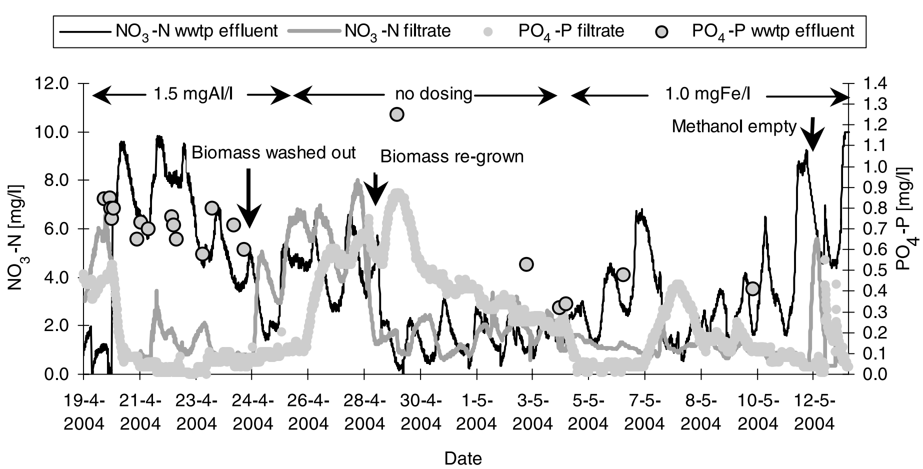

Figure 2 Nitrogen and phosphorus removal during simultaneous denitrifying multi-media filtration

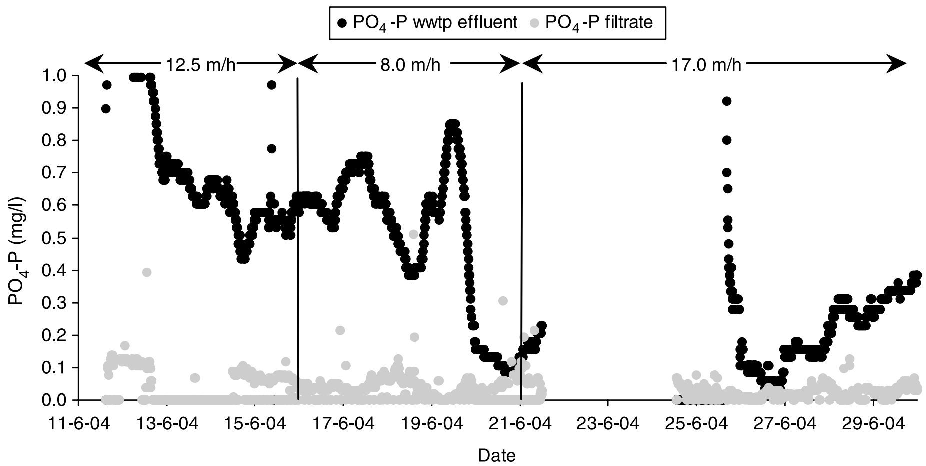

Figure 3 Phosphorus removal during simultaneous denitrifying multi-media filtration (dosing of 1.5 $mgAl^{3+}/l$)

Knowledge is required on the relation between orthophosphate and organic bonded phosphate in the WWTP effluent.

The coagulant dosing should be controlled by the fraction of orthophosphate because at a dosing based on P-total an overdose of coagulant can occur (Menkveld *et al.*, 2004; Menkveld and Miska, 2005).

Biological activated carbon filtration

In Figure 4 the on-line measurement for NO_3-N in the feed water and filtrate of the biological activated carbon filter (BACF 1 enhanced with CH_3OH) is displayed. In the beginning of the research WWTP effluent is used as feed water. Later, the BACF 1 is fed with the filtrate from the multi-media filter (MMFI).

The concentrations of NO_3-N measured in the filtrate of BACF 1 are below 2 mg/l and are independent of the concentration in the feed water and the empty bed contact time (Figure 4).

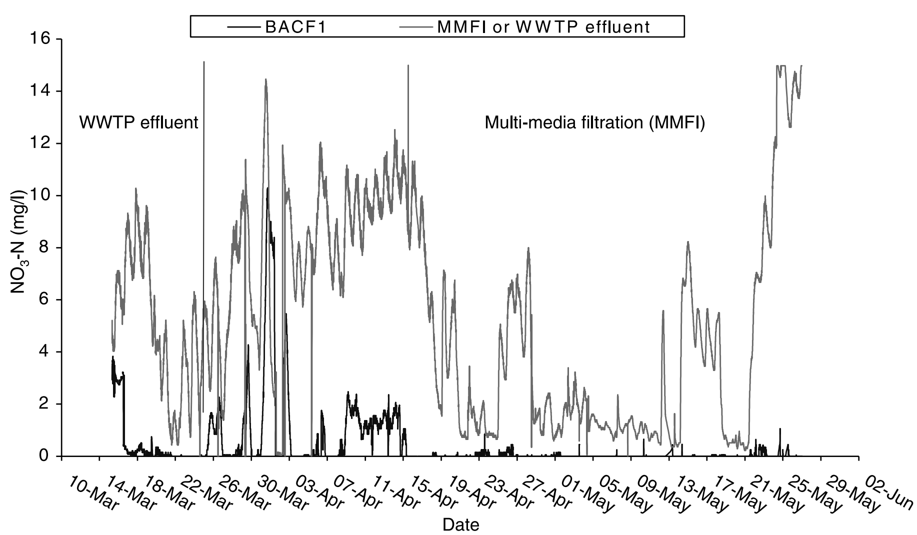

Figure 4 NO_3-N concentrations for biological activated carbon (van Oene, 2004)

Table 2 Removal of 17β-estradiol in activated carbon filters under denitrifying conditions (van Oene, 2004)

Sampling	EBCT (min)	Influent (ng/l)	BACF1 (ng/l)	Removal (%)
13-05-04	20	1,200	<0.4	99.9
19-05-04	20	710	<0.4	99.9

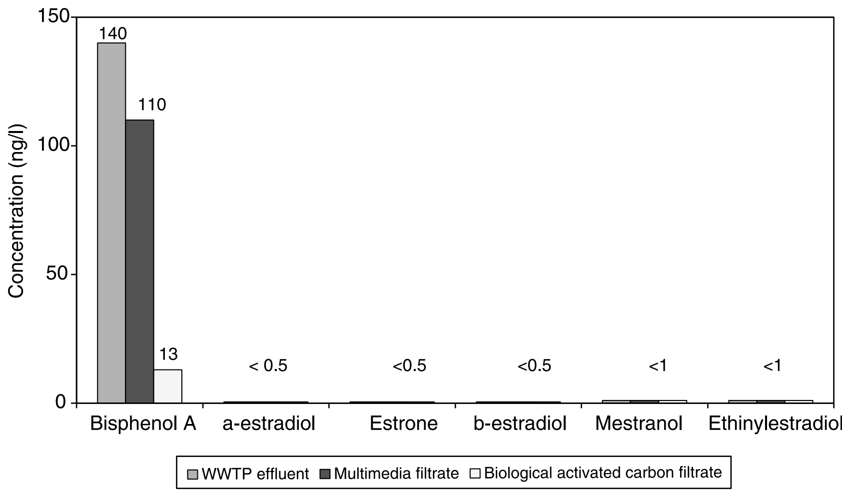

Figure 5 Removal efficiency for biological activated carbon (Menkveld, 2004)

The results for the adsorption experiments with 17β-estradiol (in Table 2) show a removal efficiency of 99.9%. The sampling is conducted after 5,500 bed volumes at an empty contact time (EBCT) of 20 minutes. The existing biomass on the activated carbon has no negative effect on the removal efficiency of 17β-oestradiol (van Oene, 2004).

The removal of bisphenol A and nonylphenol during biological activated carbon filtration is also investigated. Bisphenol A is present in the WWTP effluent with a concentration of 140 ng/l. During denitrifying flocculation filtration only 30 ng/l is removed while biological activated carbon filtration reduced the concentration to 13 ng/l. The concentration of nonylphenol of 3.1 μg/l measured in the WWTP effluent is removed to a concentration <0.1 μg/l measured in the filtrate of the BACF, which is below the FHI norm of 0.25 μg/l, as shown in Figure 5 (Menkveld, 2004).

Table 3 shows heavy metal analyses conducted at two different sampling days (3 May 04 and 10 May 04). Reduction of copper, nickel and zinc in the BACF installation is observed. MTR for heavy metals for all sample points (WWTP effluent, filtrate MMFI and filtrate BACF) are reached.

Table 3 Heavy metal measurements at different installations on 3 May and 10 May 2004 (van Oene, 2004)

Heavy metal	WWTP-effluent (μg/l)	Filtrate MMFI (μg/l)	Filtrate BACF (μg/l)	Removal BACF (%)	MTR (μg/l)
Arsenic	2/2	2/2	2/2	0/0	32
Cadmium	0.05/0.05	0.05/0.05	0.05/0.05	0/0	2
Chromium	2/2	2/2	2/2	0/0	84
Copper	3/2	2/3	1/1	50.0/66.7	3.8
Nickel	3/3	4/5	3/2	25.0/60.0	6.3
Lead	1/1	1/1	1/1	0/0	220
Zinc	13/19	16/24	13/11	18.8/54.2	40

Conclusions

Multi-media filtration

Simultaneous denitrifying flocculation filtration in a multi-media filter seems applicable for typical effluent characteristics of wastewater treatment plants in The Netherlands. The MTR-quality for $P_{tot} < 0.15$ mg/l and $N_{tot} < 2.2$ mg/l can be reached. MTR for $P_{tot} < 0.15$ mg/l can be reached with an average concentration of 0.1 mg/l of organic phosphorus in the filtrate. Even at high filtration rates (17 m/h) with a dosing of 2.0–2.5 mgAl^{3+}/l (10.1–12.6 mol Al^{3+}/ mol PO_4-P).

For total nitrogen, MTR is achievable with a PACl dosing of 1.0 mg Al^{3+}/l (4.6 mol Al^{3+}/mol PO_4-P) and a methanol dosing of 4.2 kg CH_3OH / kgNO_3-N. The dosage of PACl and methanol for simultaneous denitrification and chemical phosphorus precipitation seems to be appropriate. No negative influence of methanol on floc forming during coagulation and flocculation processes is observed (Menkveld, 2004).

Biological activated carbon filtration

Biological activated carbon filtration seems applicable for nitrate removal in effluent polishing. Fluctuating NO_3-N loads and low empty bed contact times (e.g. 10 minutes) have no negative influence on the process performance. Furthermore, simultaneous removal of NO_3-N and 17β-estradiol is possible. Also, significant removal of bisphenol A and nonylphenol is observed.

MTR for total nitrogen (2.2 mgN_{tot}/l) can be reached with BACF at an EBCT of 10 minutes and an average methanol ratio of 2.5 kg CH_3OH / kg NO_3-N. Nitrate removal with BACF is not sensitive to variations of NO_3-N concentrations measured in the process influent (between 1–15 mg/l). A nitrate load of 1.5–3 kg NO_3-N /m^3 bedvolume* day is possible. Methanol dosing can be regulated properly by on-line measured NO_3-N concentration. Phosphate removal with BACF is low and is caused by phosphate consumption in the biomass. Removal of 17β-estradiol (99.9%) is possible with denitrifying BACF after approximately 5,500 bed volumes and an EBCT of 20 minutes. The present biomass in the activated carbon filter has no negative influence on the removal efficiency (Menkveld *et al.*, 2004).

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