Removal of micropollutants in WWTP effluent by biological assisted membrane carbon filtration (BioMAC)

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ABSTRACT

In the frame of the European FP6 project Neptune, a combination of biological activated carbon with ultrafiltration (BioMAC) was investigated for micropollutant, pathogen and ecotoxicity removal. One pilot scale set-up and two lab-scale set-ups, of which in one set-up the granular activated carbon (GAC) was replaced by sand, were followed up during a period of 11 months.

It was found that a combination of GAC and ultrafiltration led to an almost complete removal of antibiotics and a high removal (>80%) of most of the investigated acidic pharmaceuticals and iodinated contrast media. The duration of the tests did however not allow to conclude that the biological activation was able to extend the lifetime of the GAC. Furthermore, a significant decrease in estrogenic and anti-androgenic activity could be illustrated. The set-up in which GAC was replaced by sand showed a considerably lower removal efficiency for micropollutants, especially for antibiotics but no influence on steroid activity.

Key words | ICM, GAC, micropollutants, pharmaceuticals, ultrafiltration, WWTP effluent

INTRODUCTION

Wastewater treatment plants (WWTPs) have been designed and optimized for the removal of organic matter and nutrients. Recently, concern is rising on the potential threats of other chemicals and compounds which are discharged at low concentrations but which can have high environmental effects, such as endocrine disrupting compounds, pharmaceutical residues and personal care products (PCPs).

Wastewater treatment plants are a point source of many anthropogenic micropollutants. Although there are not any limiting consents yet on the discharge of pharmaceutical compounds, the removal of those substances poses a challenge to WWTP operators. The occurrence of endocrine disrupting compounds (EDCs) in surface waters has become a major concern due to the increasing evidence by which exposure to EDCs was linked to reproductive effects on aquatic organisms (Oehlmann et al. 2007). Moreover, several pharmaceuticals (e.g. X-ray contrast media) have been detected in drinking water resources (Schulz et al. 2008).

Although a conventional WWTP is not designed for the removal of pharmaceuticals and PCPs, some substances can be transformed in the nitrification tank in conventional activated sludge plants at elevated sludge retention times (Wick et al. 2009). Since all WWTPs in Flanders >2000 IE are designed for nutrient removal and consequently have high SRTs, there is already a partial removal of pharmaceuticals (Figure 1).

However, several compounds are known to be detrimental even at concentrations of ng/L level. Therefore, advanced tertiary treatment is inevitable if the ecotoxicological effects of effluent discharge or re-use are to be minimized.

Ozonation or activated carbon have the potential to drastically reduce the load of micropollutants to the environment. Ozonation has the additional advantage of achieving partial disinfection (Joss et al. 2008). However, there is some concern on the formation of by-products and their ecotoxicity formed during ozonation (Stalter et al. 2010a).

This study presents the results of advanced effluent treatment with the patented BioMAC concept (patent no. EP 1270513).

The concept couples an in-situ regenerative biological activated carbon filter with a filtration device for enhanced treatment of (municipal) wastewater. It has been tested on
laboratory scale for the treatment of WWTP effluent (Van Hege et al. 2002) and on pilot scale for the treatment of brines resulting from RO-treatment of effluent from a municipal WWTP (De Wilde et al. 2007).

In this study, the BioMAC concept was evaluated for advanced treatment of municipal WWTP effluent with the aim of reducing micropollutants, microbiological parameters and ecotoxicity. The work was carried out in the frame of the European FP6 project Neptune (Contract-No. 036845).

**MATERIALS AND METHODS**

All experiments were carried out with effluent from the WWTP of Aartselaar (Belgium), a 60,000 PE municipal WWTP treating the wastewater of the city of Aartselaar, together with industrial wastewater (beverage industry) and hospital wastewater. The WWTP is an extended aeration plant with N-DN and biological phosphorus removal.

**Pilot scale set-up: pilot BioMAC**

A pilot scale BioMAC was constructed in a previous project (De Wilde et al. 2007) and optimized within this study. The principle is outlined in Figure 2. An activated carbon tank of 430 L was filled with 135 kg GAC and fed at a rate of 900 L/h (downflow), providing an empty bed contact time (EBCT) of 13 minutes. The GAC bed was followed by a Zeeweed 500c ultrafiltration unit (Zenon) consisting of hollow fibre membranes with nominal pore size of 0,04 m and total membrane surface area of 60 m². Coarse bubble aeration was applied for membrane scouring.

Permeate was produced at a rate of 900 L/h and was collected for analyses. The retentate (450 L/h) was recirculated to the top of the GAC bed.

The GAC bed was backwashed every 2 hours in order to remove solids accumulating on the top layer of the filter with a regular purge of the backwash water to the entrance of the WWTP.

The GAC bed operated under aerobic conditions because the recirculation flow was oxygen saturated as a result of the coarse bubble aeration in the MF compartment.

The adsorbent used was Organosorb 10-mb GAC supplied by the company Desotec in Roeselare, Belgium. Main characteristics are a density of 460 g/L, specific surface area of 1020 m²/g and a mesh size of 0.6–2.36 mm.

The BioMAC pilot had been operated for a period of 9 months in the European FP6 project Reclaim Water. Although the GAC bed had already shown DOC breakthrough, the removal efficiencies for micropollutants showed...
good removal at the end of the experiment within Reclaim Water (single monitoring campaign, De Wilde et al. 2007). In order to assess the lifetime of the GAC, it was decided not to renew the GAC for the experiments in Neptune.

**Lab scale set-ups: lab scale GAC-UF and lab scale sand-UF**

Parallel to the pilot BioMAC, two lab scale set-ups were operated for a period of one year to assess the different mechanisms in pollutant removal.

Lab scale tests were performed in PVC columns with a diameter of 9.7 and a height of 22.5 cm. In one set-up the column was filled with 270 g of activated carbon (600 mL) (lab scale GAC-UF). In the second set-up the column was filled with sand instead of activated carbon, grain size 1.2–2 mm (lab scale sand-UF).

Each of the columns was fed at a rate of 900 mL/h with effluent from the WWTP of Aartselaar and was followed by a crossflow hollow fibre ultrafiltration. The permeate was collected for analyses. The retentate was recirculated to the inlet of the lab scale GAC-UF resp. lab scale sand-UF at a rate of 450 mL/h, resulting in an EBCT of 26 min.

**Analytical methods**

24 h composite samples were analyzed every week or every two weeks for standard parameters, micropolllutants, bacteriological parameters and (anti-) estrogenic and (anti-) androgenic activity.

**Sample preparation and extraction for micropollutant parameters**: All samples were filtrated through glass fibre filters (GF6, <1 m, diameter 55 mm from Schleicher und Schuell, Dassel, Germany). 200 mL of each sample was spiked with the internal standards and the solid phase extraction (SPE) was performed as described by Ternes & Joss (2006).

**LC-MS analyses**: The samples extracts (10–50 L) were injected into the LC system (Agilent 1100 with degasser, quaternary pump and autosampler, Agilent Technologies, Waldbronn, Germany). Chromatographic separation was achieved at ambient temperature using columns and mobile phases as described by Ternes & Joss (2006).

The tandem mass spectrometer (API 4000 with turbo/electrospray ionization; Applied Biosystems, Foster City, CA, USA) was operated in multiple reaction monitoring (MRM) for all measurements.

**Microbiological parameters**: The wastewater samples were transported cooled (4°C) and dark in presterilized water bottles to the laboratory and were processed within 24 h.

For identification and enumeration of microbial indicators and pathogens, test procedures according to EN ISO standards were adapted to whole effluents of WWTP. The detection of *E. coli* and coliform bacteria were performed by membrane filtration technique according to EN ISO 9308-2:2000, of intestinal enterococci according to EN ISO 7899-2:2000. The somatic coliphages that served as viral indicator organisms were detected by a double-layer technique according to EN ISO 10705-2:2001. More details on the procedure can be found in Lachmund et al. (2007). The methodological
limit of quantification (LOQ) of all bacterial indicators is < 1 colony forming unit (cfu) /100 mL wastewater, for somatic coliphages <1 plaque forming unit (pfu) /1 mL wastewater.

(Anti-) estrogenic and (anti-) androgenic activity: The extracts of ten samples of each sampling point (0.5 L per sample acidified on pH 2 with 25% HCl, enriched with Oasis HLB 200 and eluted with 6 mL MTBE and MEOH) were analyzed. The estrogenic and androgenic activity was measured with the yeast estrogen screen and yeast androgen screen according to Routledge & Sumpter (1996) with modifications according to Wagner & Oehlmann (2009). For analysis of the anti-estrogenic activity hydroxytamoxifen was used as positive control and 17-β-estradiol for background estrogenicity. For the anti-androgenic activity flutamide served as positive control and testosterone as background androgenic substance. The toxic equivalents were determined as described in Wagner & Oehlmann (2009).

RESULTS AND DISCUSSION

As a result of the ultrafiltration, suspended solids were absent in the treated effluent in all three set-ups, which was also reflected in the decreased total COD and TOC concentrations (Table 1). Heavy metals (results not shown) were already below the limit of detection in the effluent of the WWTP.

The results in Table 1 also show a further 75–85% reduction of effluent NH₄-N, and 40–50% reduction of total phosphorus.

Soluble compounds were removed to a higher extent in the lab scale GAC-UF compared to the pilot BioMAC and the lab scale sand-UF.

This was attributed to the higher sorption capacity of the GAC in the lab scale GAC-UF compared to the GAC of the pilot BioMAC that had been used in a previous project. Already from the start of the experiments, the pilot BioMAC showed higher DOC concentrations in the effluent compared to the lab scale GAC-UF (Figure 3). Towards the end of the test, the GAC in the lab scale GAC-UF also seemed to show DOC breakthrough. Figure 4 shows the mean removal efficiencies of all measured pharmaceuticals.

The (fresh) activated carbon in the lab scale GAC-UF led to an almost complete removal of antibiotics, whereas the pilot BioMAC and the lab scale sand-UF showed a low to moderate removal efficiency for these compounds. The efficient adsorption of several antibiotics and of carbamazepine was documented by Snyder et al. (2007). This was confirmed by Ternes & Joss (2006), who also noted that sulfamethoxazole was less adsorbable whereas ionic contrast media were the most difficult to remove with activated carbon.

Indeed, sulfamethoxazole, together with clarithromycin were the only antibiotics present in the effluent of the lab scale GAC-UF at concentrations above the LOQ. However, the concentrations of clarithromycin and sulfamethoxazole, showed no increase in the effluent of the lab scale GAC-UF during the course of the experiments (Figure 5), despite the apparent DOC-breakthrough.

Ibuprofen, naproxen, iopromide, iohexol and iomeprol are removed 4–80% in both lab scale set-ups with sand and activated carbon. Okuda et al. (2008), Lishman et al. (2006) and Yu et al. (2006) demonstrated that ibuprofen and naproxen are readily biodegradable. Ternes & Joss (2006) illustrated that also iopromide could be removed to the extent

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Influent (WWTP effluent)</th>
<th>Effluent pilot BioMAC</th>
<th>Effluent lab scale sand-UF</th>
<th>Effluent lab scale GAC-UF</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD</td>
<td>1.9 ± 3.1</td>
<td>0.0 ± 0.0</td>
<td>0.3 ± 1.3</td>
<td>0.6 ± 3.4</td>
</tr>
<tr>
<td>COD</td>
<td>29.4 ± 7.7</td>
<td>18.6 ± 2.8</td>
<td>18.9 ± 3.1</td>
<td>9.2 ± 9.9</td>
</tr>
<tr>
<td>COD filtered</td>
<td>26.2 ± 13.5</td>
<td>18.6 ± 5.2</td>
<td>18.6 ± 5.7</td>
<td>7.9 ± 9.6</td>
</tr>
<tr>
<td>SS</td>
<td>6.1 ± 8.5</td>
<td>0.0 ± 0.0</td>
<td>0.1 ± 0.8</td>
<td>0.3 ± 1.3</td>
</tr>
<tr>
<td>TOC</td>
<td>9.6 ± 4.3</td>
<td>7.0 ± 3.8</td>
<td>7.5 ± 4.5</td>
<td>4.4 ± 4.4</td>
</tr>
<tr>
<td>DOC</td>
<td>9.4 ± 4.5</td>
<td>7.4 ± 4.8</td>
<td>8.0 ± 4.8</td>
<td>4.9 ± 4.5</td>
</tr>
<tr>
<td>P tot</td>
<td>0.13 ± 0.33</td>
<td>0.07 ± 0.35</td>
<td>0.05 ± 0.19</td>
<td>0.08 ± 0.24</td>
</tr>
<tr>
<td>N tot</td>
<td>7.3 ± 2.9</td>
<td>7.1 ± 2.0</td>
<td>6.8 ± 1.9</td>
<td>5.8 ± 2.2</td>
</tr>
<tr>
<td>NH₄-N</td>
<td>1.16 ± 1.89</td>
<td>0.46 ± 1.12</td>
<td>0.25 ± 0.72</td>
<td>0.18 ± 0.51</td>
</tr>
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</table>
of 95% by biological transformation. These results suggest biological activity in the two lab scale set-ups.

The pilot BioMAC showed slight/moderate lower removal efficiencies for these compounds, indicating lower biological activity in the pilot BioMAC.

This could be explained on the one hand by lower temperatures in the pilot BioMAC because this plant was located outside and the monitoring campaign was mainly performed during the winter months. Although Göbel et al. (2007) questioned the temperature dependency of the biological transformation of micropollutants, lower removal efficiencies for several pharmaceuticals in full scale WWTPs in winter time were illustrated by Castiglioni et al. (2006).

On the other hand, the activated carbon in the pilot plant was regularly backwashed with discharge of the backwash water, possibly leading to a waste of the biofilm and consequently lower SRTs. The influence of the SRT on the removal efficiency of pharmaceuticals was described by Clara et al.
who determined a critical SRT of at least 10 days for removal of ibuprofen, bezafibrate and natural estrogens. These findings were confirmed by Wick et al. (2009) for beta blockers and psychoactive drugs.

The running time of 11 months resulted in an activated carbon load in the lab scale GAC-UF of 22 L/g GAC, corresponding to 45 mg GAC/L. Literature data on the use of (powdered) activated carbon suggest carbon dosages of 10–20 mg/L for an efficient removal of micropollutants in natural water with a DOC contents up to 3.7 mg/L (Ternes & Joss, 2006; Yu et al. 2008).

Although the DOC content of the investigated WWTP effluent is higher, the running time was not sufficient to conclude that the biological activity in the lab scale GAC-UF could lead to an increased lifetime of the activated carbon. Further tests should indicate whether the combined approach of activated carbon adsorption and biological filtration with complete retention of the biomass shows an added value over conventional GAC treatment.

The results of the microbiological analyses are shown in Table 2. The ultrafiltration unit in the pilot BioMAC establishes an almost complete removal of bacteria as well as virus indicators. The number of total coliforms in the effluent of the lab scale GAC-UF was higher than expected after ultrafiltration. However this set-up used a sample pretreatment filter to mimic the ultrafiltration step, a device which is less reliable than a pilot or full scale ultrafiltration unit.

The results of the ecotoxicity tests (Figure 6) showed a considerable better reduction in ecotoxicity for the pilot BioMAC and the lab scale GAC-UF: estrogenic activity (estriadiol equivalents, EEQ) as well as anti-androgenic activity (flutamide equivalents, FEQ) is significantly reduced after the BioMAC treatment and after the treatment in the lab scale GAC-UF. Androgen activity (TEQ) is not affected significantly and anti-estrogenic activity (OHT, 4-hydroxytamoxifen equivalents) remains on the same level apart from the lab scale sand-UF where there is a significant increase in anti-estrogenic activity.

These results suggest that activated carbon is essential in the removal of substances responsible for endocrine disrupting activity. This might be environmentally relevant as both estrogenic and anti-androgenic activities are supposed to contribute to an impairment of the endocrine system of wild fish populations (Jobling et al. 2009).

An effective removal of estrogenic compounds and consequently a decrease of estrogenicity of WWTP effluent treated by activated carbon was confirmed by Reungoat et al. (2010) as well as by Stalter et al. (2010b).

**Table 2** Microbiological parameters in the effluent of the conventional WWTP, the pilot BioMAC and the lab scale GAC-UF and sand-UF.

<table>
<thead>
<tr>
<th></th>
<th>CFU/100 mL</th>
<th>CFU/100 mL</th>
<th>CFU/100 mL</th>
<th>CFU/100 mL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total coliforms</td>
<td>E. coli</td>
<td>Enterococci</td>
<td>Somatic coliphages</td>
</tr>
<tr>
<td>WWTP effluent</td>
<td>6800–270000</td>
<td>3500–84300</td>
<td>193–10200</td>
<td>31–79</td>
</tr>
<tr>
<td>pilot BioMAC</td>
<td>0–56</td>
<td>0–22</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Lab scale GAC-UF</td>
<td>0–1600</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Lab scale sand-UF</td>
<td>0–6</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</table>
CONCLUSIONS

To evaluate the efficiency of a combined approach of biological activated carbon and ultrafiltration (BioMAC) for micropollutant removal in WWTP effluent, three set-ups were studied. A pilot BioMAC with highly loaded activated carbon was compared to two lab scale set-ups, one similar to the pilot BioMAC (lab scale GAC-UF) and one with sand instead of activated carbon (lab scale sand-UF).

The results illustrated the following:

- The combination of biological activated carbon with ultrafiltration was able to remove antibiotics and acidic pharmaceuticals to a high extent. The lab scale GAC-UF showed a consistent removal for the tested pharmaceuticals for a period over 11 months (18,000 bed volumes).
- The concept could remove most of the iodinated contrast media over 80%, which is a considerable advantage over ozonation.
- Part of the removal was due to biological activity. However, the duration of the tests was not long enough to conclude that there was also an increased lifetime of the GAC as a result of biological activity.
- Pathogens were almost completely removed as a result of the ultrafiltration.
- There was a significant decrease in estrogenic and anti-androgenic activity in both set-ups with GAC (pilot BioMAC and lab scale GAC-UF), whereas the set-up in which the GAC was substituted by sand (lab scale sand-UF) showed no significant removal.
- Although the combination of sand filtration followed by ultrafiltration showed a good removal of biodegradable micropollutants, active carbon was shown to be inevitable for the removal of antibiotics, and for a decrease in estrogenic and anti-androgenic activity.
- Further research should focus on the added value of the biological activity and on the lifetime of the GAC.
ACKNOWLEDGEMENTS

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