Effect of low dosages of powdered activated carbon on membrane bioreactor performance
Maxime Remy, Hardy Temmink and Wim Rulkens

ABSTRACT
Previous research has demonstrated that powdered activated carbon (PAC), when applied at very low dosages and long SRTs, reduces membrane fouling in membrane bioreactors (MBRs). This effect was related to the formation of stronger sludge flocs, which are less sensitive to shear. In this contribution the long-term effect of PAC addition was studied by running two parallel MBRs on sewage. To one of these, PAC was dosed and a lower fouling tendency of the sludge was verified, with a 70% longer sustainable filtration time. Low PAC dosages showed additional advantages with regard to oxygen transfer and dewaterability, which may provide savings on operational costs.

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Key words | filterability, membrane bioreactor, membrane fouling, powdered activated carbon, sludge characteristics

INTRODUCTION
Membrane bioreactors (MBRs) have a 30–50% higher energy consumption than conventional wastewater treatment plants employing secondary settlers. This is mainly caused by the necessity to prevent excessive membrane fouling. In the case of sewage treatment this is the main bottleneck for a more widespread application of MBR technology, even though this technology offers advantages such as smaller footprint, improved effluent quality and better possibilities to reuse the effluent (Judd 2006).

Research to reduce membrane fouling mainly focuses on optimizing membrane materials (e.g. van der Marel et al. 2010), improving membrane module design and membrane operation (Meng et al. 2009), and, to a lower extent, on enhancing the filterability of the feed sludge by additives such as organic and inorganic flocculants and powdered activated carbon (PAC) (e.g. Ying & Ping 2006; Koseoglu et al. 2008). For example, in short-term experiments, Remy et al. (2009) demonstrated that very low PAC dosages of 0.5 g L$^{-1}$ of sludge, corresponding to 4 mg PAC L$^{-1}$ of wastewater, can already significantly improve sludge filterability. The critical flux in the presence of PAC was found to be 102 L m$^{-2}$ h$^{-1}$, which was 11% higher than a critical flux of 92 L m$^{-2}$ h$^{-1}$ in the absence of PAC. Also, much longer periods could be sustained without significant fouling. Further research by Remy et al. (2010) strongly indicated that this positive effect of PAC could be attributed to the formation of stronger sludge flocs, as was demonstrated under conditions of enhanced shear by a lower release of potential membrane foulants from the sludge flocs and a smaller decrease of the floc size compared to sludge without PAC.

In this paper, the effect of similar low PAC dosages on long-term fouling behavior and on sewage treatment performance was studied in a pilot-scale MBR during a period of almost a year. This effect was compared to a reference MBR without PAC addition. Because PAC changes the structure of the sludge flocs, it was expected that also other important performance parameters such as oxygen transfer efficiency and sludge dewaterability could be affected. Both are important parameters for the energy efficiency of wastewater treatment plants. Therefore, these parameters were also compared for sludges taken from the two MBR systems. Finally, an important topic for the near future with respect to receiving surface water quality is the removal of organic micropollutants. To investigate a potential additional advantage of PAC addition on this removal, both MBRs were spiked with a number of selected micropollutants.

MATERIAL AND METHODS
Pilot-scale MBRs and operation
Two identical pilot-scale MBRs, each with a total working volume of 85 L, were operated in parallel and fed with...
sewage. Figure 1 is a schematic representation of the two pilot-scale MBRs. The total hydraulic retention time (HRT) was 10 h, with 4.1 h anoxic retention time to accommodate denitrification, 4.1 h aerobic retention time and 1.8 h retention time in the membrane tank. Both MBRs were operated at a sludge retention time (SRT) of 50 days. The dissolved oxygen concentration in the aerobic tank was maintained at 1.5 mg L\(^{-1}\) using a fine-bubble diffuser (ITT Flygt, Sani-taire 9\(^{\text{®}}\) membrane). Further details about the pilot-scale MBRs can be found in Remy \textit{et al.} (2012).

The membrane tanks were equipped with homemade double-sided submerged PVDF flat sheet membranes with a nominal pore size of 0.1 \(\mu\)m and a surface area of 0.1 m\(^2\) each. The channel width between the membranes was 6 mm. Coarse bubble aerators located below the membrane sheets provided a specific aeration of 1.8 m\(^3\) m\(^{-2}\) h\(^{-1}\). Trans-membrane pressure (TMP) was monitored on-line and registered continuously (Endress + Hauser, Cerebar M PMC 41). Membrane cleaning was performed as soon as the TMP exceeded 75 mbar. The cleaning procedure consisted of gentle rinsing with permeate using a nozzle to remove gel layer deposition, rinsing with demineralized water, soaking in 3,000 ppm sodium hypochlorite for 2 h followed by 1 h in 1% oxalic acid and once more rinsing with demineralized water. Initially, the membrane flux was set at 43.5 L m\(^{-2}\) h\(^{-1}\), later on, the flux was increased to 58 and 87 L m\(^{-2}\) h\(^{-1}\). Those fluxes were respectively used for periods of 280, 35 and 5 days. To avoid changes in the HRT, increase of flux was accomplished by taking out membrane sheets, keeping the flow over the reactor stable.

The MBRs were fed with sewage for a total period of 320 days. The sewage passed a 5 mm sieve, followed by a grit removal unit. The average sewage composition, based on weekly samples, was 353 ± 190 mg COD L\(^{-1}\) and 54 ± 14 mg NH\(_4^+\)-N L\(^{-1}\). The COD consisted of 70% suspended solids, 12% colloidal material and 18% soluble material. Daily, 0.8 g of mesoporous PAC (Norit SAE Super) was added to the anoxic tank of one of the two MBRs to compensate for the amount of PAC that was wasted with the excess sludge. This corresponds to a concentration of 0.5 g PAC L\(^{-1}\) of sludge and a dosage of 4 mg PAC L\(^{-1}\) of wastewater. More background information on the PAC characteristics can be found in Schouten \textit{et al.} (2007).

Seven different organic micropollutants (Table 1) were continuously dosed to the wastewater to reach a concentration of 5 \(\mu\)g L\(^{-1}\) of sewage during a period of 100 h, i.e. 10 times the HRT. A stock solution containing 2.175 mg L\(^{-1}\) of each micro-pollutant and 10 ppm methanol in demineralized water was used for this purpose. More background information on these micro-pollutants can be found in the work by Hernández (2010).

### Sampling and chemical analyses

Grab samples of wastewater, supernatant fractions from the membrane tank mixed liquor and of permeate were taken on a weekly basis. Supernatant from the membrane tank

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbreviation</th>
<th>Application</th>
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<tbody>
<tr>
<td>2-phenyl-5-benzimidazolesulfonic acid</td>
<td>PBSA</td>
<td>UV filter</td>
</tr>
<tr>
<td>Caffeine</td>
<td>–</td>
<td>Stimulant</td>
</tr>
<tr>
<td>Bisphenol A diglycidyl ether</td>
<td>BADGE</td>
<td>Plasticizer</td>
</tr>
<tr>
<td>Bisphenol F diglycidyl ether</td>
<td>BFDGE</td>
<td>Plasticizer</td>
</tr>
<tr>
<td>Benzalkonium chloride</td>
<td>BaCl</td>
<td>Surfactant</td>
</tr>
<tr>
<td>Benzophenone-3</td>
<td>BP-3</td>
<td>UV filter</td>
</tr>
<tr>
<td>Butyl methoxydibenzoylmethane</td>
<td>Avobenzone</td>
<td>UV filter</td>
</tr>
</tbody>
</table>

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Table 1 | Spiked organic micro-pollutants
mixed liquor was obtained with a centrifuge (Sigma, 2–16), operated for 15 min at 3,000 rpm, corresponding to 1,500 g. The supernatant was sequentially paper filtered (Whatman Black Ribbon 589/1) and filtered with a PTFE 0.45 μm pore size membrane filter (Cronus). The difference between paper and membrane filtrate is referred to as the colloidal fraction of the supernatant, and the membrane filtrate as the soluble fraction. COD as well as total suspended solids (TSS) and volatile suspended solids (VSS) of sludge samples were all determined according to standard methods (APHA-AWWA-WEF 1998). Micro-pollutant concentrations in the permeate were determined according to analytical methods described by Hernández et al. (2010).

Concentrations of polysaccharides and proteins were determined according to the methods of Dubois et al. (1956) using glucose as the standard and Bradford (1976) using immunoglobulin as the standard, respectively. Extracellular polymeric substances (EPS) bound to the sludge flocs were extracted by mixing the sludge with cation exchange resin, using a method adapted from Frølund et al. (1996). To remove similar EPS compounds from bulk water, first a washing step was performed on the sludge. The sludge was centrifuged at 2,000 g for 15 min. Sludge pellets were resuspended to their original volume using a buffer consisting of 2 mmol/L Na₃PO₄, 4 mmol/L NaH₂PO₄, 9 mmol/L NaCl and 1 mmol/L KCl at pH 7. The EPS extraction was performed as follows: 300 mL sludge was transferred to a beaker and the cation exchange resin (DOWEX® Marathon®, Ca⁺ form, with 70 g g⁻¹ VS⁻¹) was added. The suspension was stirred at 900 rpm for 4 h at 4 °C. The extracted EPSs were harvested by centrifugation following the fractionation method presented above, after which, COD, polysaccharides and proteins were determined. Dissolved organic carbons (DOC) from the permeates were measured with LC-OCD (Liquid Chromatography-Organic Carbon Detection) by D.O.C Labor (Germany).

Sludge parameters

Dynamic viscosity of sludge samples was assessed at 20 °C, with a HAAKE rotary viscotester 6 L using spindle L1 at different rotational speeds (0–200 rpm). Settled supernatant of sludge samples, expressed as the sludge volume index (SVI) was measured according to standard methods (APHA-AWWA-WEF 1998) after diluting the sludge four times in permeate. Particle size distribution of the sludge was measured with an Eyetech particle size analyzer, with a range from 5 to 600 μm, and using video measurements coupled with an Ankersmid liquid flow controller LFC-101. Oxygen transfer parameters ($k_{L}a$ and respiration rate) from sludge samples were determined in non-steady-state batch tests under endogenous respiration conditions, following the method described by WEF & ASCE (2001). Three litre beakers were used and several air flow rates were applied. The beakers were mixed with a Heidolph overhead mixer at 400 rpm. The temperature of the sludge was kept constant at 20 °C. During those tests, the dry solids concentrations were 9.8 and 10.3 g L⁻¹ respectively for the sludge samples without and with PAC. Dissolved oxygen concentration was followed in time by a HACH handheld DO meter.

RESULTS

Membrane fouling

Membrane cleaning was performed as soon as a TMP exceeded 75 mbar. Long-term operation at the initial flux of 43.5 L m⁻² h⁻¹ showed that for the MBR with PAC addition, a much lower cleaning frequency was required than for the MBR without PAC addition. The average sustainable filtration time, i.e. the average operational period between two cleanings, was 55 days for the system with PAC and 32 days for the system without PAC. This represents an increase of sustainable filtration time of over 70%. Remarkably, during periods of low sewage temperatures, typically below 12 °C, sludge foaming, associated with membrane fouling by You & Sue (2009), was frequently detected in the MBR without PAC addition, whereas foaming did not occur in the MBR with PAC.

Figure 2 illustrates for three representative periods the effect of the different membrane fluxes on the TMP development in the two MBR systems. At a flux of 43.5 L m⁻² h⁻¹, even after 10 days after the last cleaning procedure, neither MBR exhibited significant fouling. A higher flux of 58 L m⁻² h⁻¹ in the MBR without PAC addition resulted in a severe increase in TMP and required frequent cleaning actions (Figure 2). At the same flux, in the MBR with PAC addition, the TMP increase was below 5 mbar for the 10 days. At the highest flux of 87 L m⁻² h⁻¹, severe fouling was detected in both MBRs, although the required cleaning frequency was rather significantly lower for the MBR with PAC addition.

Visible gel deposition on the membrane surface took place in both MBRs. However, the gel layer in the MBR with PAC addition was much easier to remove, as indicated by the distance between the nozzle and the membrane.
surface required for rinsing, i.e. 15 cm compared with 7 cm for the gel that deposited in the system without PAC addition. On one occasion, gel deposition was investigated after running new membranes for 12 h at 90 L m\(^{-2}\) h\(^{-1}\). The TMP for sludge without PAC was 600 mbar and that for sludge with PAC was 300 mbar. The gels were harvested and homogenized by sonication and their COD, polysaccharide and protein composition was determined (Table 2). Clearly, the gels from the MBR with PAC addition contained much lower amounts of organic material than the gels which were harvested from the MBR without PAC addition. Also, the protein to polysaccharide ratio of the gel was lower (0.72) than in the MBR with PAC (0.82).

### Treatment performance

Average COD, polysaccharide and protein concentrations in the membrane tank supernatant and permeate over a period of 320 days are given in Table 3. Average COD removal efficiencies were 88 and 89% for the MBR without and with PAC, respectively. LC-OCD measurements of the permeate showed that the DOC in the permeate of both reactors consisted mostly of poorly biodegradable humic substances, probably already present in the sewage that was treated (Huck 1999). Although the differences were small and exhibited considerable variation in time, for all three mentioned parameters the concentrations in the supernatant of the membrane tank and in the permeate were consistently lower in the MBR system with PAC than in the MBR system without PAC. For over 90% of the simultaneous samplings, the permeate from the reactor with PAC showed lower concentrations when compared with that from the reactor without PAC. Membrane rejection with respect to

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**Table 2** Composition of the gel layer harvested from the membranes after operating during 12 h at a flux of 90 L m\(^{-2}\) h\(^{-1}\)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MBR without PAC g m(^{-2})</th>
<th>MBR with PAC g m(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>409</td>
<td>191</td>
</tr>
<tr>
<td>Polysaccharides</td>
<td>93</td>
<td>32</td>
</tr>
<tr>
<td>Proteins</td>
<td>67</td>
<td>26</td>
</tr>
<tr>
<td>Ratio proteins/ polysaccharides</td>
<td>0.72</td>
<td>0.82</td>
</tr>
</tbody>
</table>

**Table 3** Average membrane tank supernatant and permeate concentrations of COD, polysaccharides and proteins and membrane rejection of these compounds (concentrations all in mg L\(^{-1}\) and rejection in %)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MBR without PAC</th>
<th>MBR with PAC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Supernatant</td>
<td>Permeate</td>
</tr>
<tr>
<td>COD</td>
<td>43</td>
<td>33.3</td>
</tr>
<tr>
<td>Polysaccharides</td>
<td>8.7</td>
<td>7.2</td>
</tr>
<tr>
<td>Proteins ratio proteins/polysaccharides</td>
<td>4.8</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>0.55</td>
<td>0.55</td>
</tr>
</tbody>
</table>
COD, polysaccharides and proteins are also presented in Table 3. These were similar for the two MBRs, apart from the polysaccharide rejection of 11% in the MBR with PAC, which was considerably lower than the polysaccharide rejection of 18% in the system without PAC. This corresponds with the higher protein to polysaccharide ratio in the gel layer, which deposited on the membrane surface in the MBR with PAC (Table 2).

Figure 3 compares the removal efficiencies of the selected organic micropollutants for the two MBR systems. They were all removed with a decreasing efficiency in the order: caffeine > BP-3 > BADGE > avobenzone > BFDGE > BaCl > PBSA. Removal efficiencies were in the same range as that observed by Hernández et al. (2010) in an aerobic biological grey water treatment reactor, and can be explained by biodegradation (caffeine, BADGE, BFDGE) or adsorption to the biological sludge (BP-3, avobenzone, BaCl). However, in the study by Hernández (2010) PBSA was not removed biologically but could be removed by adsorption to PAC. For all compounds, apart from caffeine, which in both MBRs was completely removed, the removal efficiency in the system with PAC was slightly higher than in the MBR without PAC, indicating an enhanced adsorption capacity caused by the sludge with PAC particles. For PBSA the difference in removal efficiency between the two MBRs was more substantial than for the other compounds.

**Sludge properties**

Average suspended solids concentration in the MBR systems without and with PAC were $9.6 \pm 0.9$ and $10.1 \pm 1.3 \text{ g L}^{-1}$ respectively, with volatile fractions of 76 and 78%. These differences can be completely attributed to the presence of PAC. Concentrations of extracellular polymers extracted from sludge samples are presented in Table 4. Based on COD, the amount of extracted extracellular polymers was significantly higher in the MBR without PAC. Differences between the two MBR systems in extracted polysaccharides and proteins are small, but the ratios of extracted proteins to extracted polysaccharides (0.73 and 0.84 respectively for the MBR sludge without PAC and the MBR sludge with PAC) correspond very well with the protein to polysaccharides ratios that were found in the gel layers that deposited on the membrane surfaces (Table 2).

The average equivalent area diameter of the particles respectively was 65.1 and 72.2 $\mu$m for sludge taken from the MBR without PAC and the MBR with PAC. The particle size distribution (data not shown) did not exhibit a peak at 15 $\mu$m, which is the average size of the PAC particles. This implies that the PAC particles were incorporated in the sludge flocs, which was also confirmed by microscopic sludge observations (data not shown).

Because the PAC amended sludge had a slightly higher suspended solids concentrations than the sludge without

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MBR without PAC</th>
<th>MBR with PAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>164</td>
<td>127</td>
</tr>
<tr>
<td>Polysaccharides</td>
<td>31</td>
<td>27</td>
</tr>
<tr>
<td>Proteins</td>
<td>23</td>
<td>22</td>
</tr>
<tr>
<td>Ratio proteins/</td>
<td>0.73</td>
<td>0.84</td>
</tr>
<tr>
<td>polysaccharides</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
PAC (10.1 compared to 9.6 g L\(^{-1}\)), a higher (apparent) dynamic viscosity was expected (e.g. Seyssiecq et al. 2008). However, Figure 4 clearly demonstrates that at the lower shear speed (rpm), the sludge with PAC is less viscous than the sludge without PAC. In addition, the PAC amended sludge is less shear-thinning, which indicates it is more resistant to shear.

The oxygen transfer efficiency \(k_{1a}\) of both sludges was determined at four different air flow rates. On average, the \(k_{1a}\) of the sludge with PAC was found to be consistently higher than of the sludge without PAC, with an average difference of 11\%, while no difference could be found in the respiration rate. Probably the differences in \(k_{1a}\) are related to the lower dynamic viscosity of the sludge with PAC than the sludge without PAC (Figure 4) (Germain & Stephenson 2005).

Although not directly relevant for MBRs, the sludge volume index (SVI) as a measurement of settleability of the MBR sludges was determined as an indication of their dewaterability (Li & Yang 2007). The SVI of the sludge without PAC was 150 ml g\(^{-1}\) while the SVI of the sludge with PAC was 45\% lower, i.e. 80 ml g\(^{-1}\).

DISCUSSION

Short-term filtration experiments with PAC amended sludge had demonstrated that PAC already at very low dosages reduces the membrane fouling potential of the sludge mixture (Remy et al. 2009). Further investigations strongly indicated this lower fouling potential is not caused by an enhanced scouring of the membrane surface with PAC particles or by adsorption of potential membrane foulants such as polysaccharides and proteins, but most likely is caused by the formation of stronger activated sludge flocs, which have a higher resistance to shear (Remy et al. 2010). In this study the positive effect of low concentrations of PAC was confirmed during long-term operation of a MBR. Supernatant composition in the membrane tank mixed-liquor was not very different from the composition in the reference MBR without PAC addition. However, some differences were observed. Less organic material deposited as a gel layer on the membrane surface in the MBR where PAC was dosed, the ratio between proteins and polysaccharides in the gel layer that formed with PAC amended sludge was higher than in the MBR without PAC addition, and in both MBRs this ratio corresponded very well with the protein to polysaccharide ratio of the extracellular polymers that could be extracted from the sludge. Possibly, due to the enhanced shear in the vicinity of the membrane surface, in the case of sludge without PAC addition more of the bound extracellular polymers are loosen from the floc structure and become membrane foulants. This in particular applies to polysaccharides, which, also by others, have been reported to be the most important membrane foulants (e.g. Rosenberger et al. 2006; Drews et al. 2008; Yigit et al. 2008).

Long-term MBR operation at different fluxes showed that a low dosage of PAC makes it possible to operate MBRs at significantly higher fluxes. In our experiments it was possible to increase the flux from 43.5 to 58 L m\(^{-2}\) h\(^{-1}\) without any fouling problems, whereas in the system without PAC addition this resulted in a dramatic increase of the cleaning frequency. Such a 53\% increase of the sustainable flux has a large impact on the energy consumption of MBR systems because it implies that less membrane surface area can be installed with a lower energy consumption to scour this membrane surface.

Another observation was an 11\% higher \(k_{1a}\) of the PAC amended sludge. Because, together with air scouring of the membranes, oxygen transfer in MBRs is the biggest energy consuming process, this further contributes to a lower overall energy consumption of MBRs.

Treatment performance of the MBR with PAC addition was not very different from the MBR which was operated without PAC, although consistently lower effluent concentrations were observed with respect to COD. A number of selected organic micropollutants were removed at a slightly higher efficiency, probably due to additional adsorption to the PAC particles. But, apart from the additional removal of the UV filter PBSA, the differences were not large enough to justify the addition of PAC. Apparently the dosage of 4 mg PAC L\(^{-1}\) of wastewater (0.5 g PAC L\(^{-1}\) of sludge) was too low to accommodate a complete removal of the selected organic micropollutants, even though
Hernández (2010) showed that this objective can be achieved by activated carbon treatment.

The MBR sludge with PAC exhibited a much better settleability than MBR sludge without PAC: SVI values of 80 compared to 150 mL g⁻¹. Although not directly related, a better settleability is an indication of a higher sludge dewaterability (Li & Yang 2007), which may have important implications for the sludge treatment equipment and costs. A similar positive effect of PAC on sludge dewaterability was also reported by Çeçen et al. (2005) and, according to Yang & Li (2009) may be caused by the lower amount of (loosely) bound extracellular polymers in the PAC enriched sludge (Table 4).

Considering the low costs of PAC addition of less than 0.01 € m⁻² of permeate, and the large potential advantages this gives with respect to fouling, energy consumption and dewaterability, as outlined above, PAC addition is a good strategy for sewage treatment by MBRs.

CONCLUSIONS

The effect of PAC was investigated over a period of 320 days in two pilot-scale MBRs treating municipal wastewater. It was shown that the combination of a low PAC dosage (0.5 g L⁻¹ of sludge) combined with a relatively long SRT of 50 days resulted in:

- an improvement of the sustainable filtration time of 70%,
- a possibility to increase the sustainable flux by at least 30%,
- a slight but consistent improvement of the permeate quality,
- an increase of the oxygen transfer by 11%,
- a probable increase of the dewaterability as indicated by a 45% lower SVI,
- an increased efficiency regarding the removal of organic micro-pollutants.

ACKNOWLEDGEMENTS

This work was performed in the TTIW-cooperation framework of Wetsus, Centre of Excellence for Sustainable Water Technology (www.wetsus.nl). Wetsus is funded by the Dutch Ministry of Economic Affairs, the European Regional Development Fund, the Province of Fryslân, the City of Leeuwarden and the ERZ/Kompas programme of the ‘Samenwerkingsverband Noord-Nederland’. The authors would like to thank the participants of the MBR research theme for their financial support.

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First received 26 July 2011; accepted in revised form 31 October 2011.