

PAC membrane bioreactor as an alternative to biological activated carbon filters for drinking water treatment

Simon Leveille, Annie Carriere, Sebastien Charest and Benoit Barbeau

ABSTRACT

A high concentration powdered activated carbon (PAC) membrane bioreactor (MBR) was fed by clarified-ozonated surface water. As a control, a MBR without PAC was run in parallel. Water quality was also compared with a full-scale biological activated carbon (BAC) filter. Biological PAC inside the MBR caused a higher fouling rate as compared to the MBR without PAC, although it was still possible to maintain operation for about 3 months at $25 \text{ L m}^{-2} \text{ h}^{-1}$ before a chemical cleaning was needed. The fouling rate inside the MBR with PAC increased as the PAC age increased from 0 to 60 d. Full nitrification was achieved in the PAC-MBR down to 7°C . Preozonation had no significant impact on dissolved organic carbon removal. Although the PAC-MBR globally provided superior removal of natural organic matter, haloacetic acid precursors and UV absorption at 254 nm (UVA_{254}), its removal of trihalomethane (THM) precursors was inferior compared to the BAC filter. This effect was shown to be caused by the accumulation of suspended solids inside the bioreactor.

Key words | activated carbon, biological treatment, drinking water, hybrid membrane process, THM, ultrafiltration

Simon Leveille (corresponding author)
Annie Carriere
Sebastien Charest
Benoit Barbeau
NSERC Industrial Chair in Drinking Water Treatment,
Civil, Geological and Mining Department,
Ecole Polytechnique de Montréal,
C.P. 6079,
succ. Centre-ville,
Montréal (Québec),
Canada H3C 3A7
E-mail: simon.levaille@polymtl.ca

INTRODUCTION

Low-pressure membranes (i.e., ultrafiltration and microfiltration (UF/MF), referred to hereafter as LPM) have gained popularity in the drinking water industry due to their efficiency in reducing suspended solids, including protozoan parasites such as *Giardia* and *Cryptosporidium*. However, UF/MF processes demonstrate a limited ability to handle dissolved contaminants. Combination of powdered activated carbon (PAC) with LPM has been proposed as a means to achieve higher performance. Under this configuration, LPM membranes act as a physical barrier that retains not only particulate contaminants present in the influent but also the PAC injected ahead of the membrane.

Many investigators (Lebeau *et al.* 1998; Seo *et al.* 2004; Kim *et al.* 2007; Tian *et al.* 2008; Treguer *et al.* 2008) have evaluated the possibility of adding PAC in the membrane tank in order to maintain a high PAC concentration (1–40 g/L) using an outside-in membrane configuration. The presence of PAC inside a carbon contactor coupled with low pressure membrane (CC-LPM) process brings an additional challenge

regarding fouling: PAC gradually accumulates on the membranes and forms what is referred to as a PAC cake layer. Although a portion of natural organic matter (NOM) fouling is prevented due to the cake layer acting as a filter (Yan *et al.* 2010), its presence may also cause additional resistance to filtration. Within the reactor, biofilm progressively grows on ageing PAC leading to an increased development of the cake layer (Seo *et al.* 2005). For instance, these authors observed that 29% of an initial PAC concentration of 40 g/L was found in the cake layer after a few months of operation. Although fresh PAC has been shown to prevent membrane fouling (Campinas & Rosa 2010), additional work is needed to define the operating conditions that minimize PAC cake layer formation. Aeration, backpulse conditions, flux, and PAC concentration inside the reactor are among many operating conditions that need to be optimized in order to minimize fouling inside a CC-LPM reactor.

Minimizing fouling must be done while considering process performance, as many process variables impact both

simultaneously. Treatment performance of the CC-LPM is highly defined by the PAC age and, to a lower extent, by the hydraulic residence time (HRT) in the case of biodegradable compounds such as biodegradable dissolved organic carbon (BDOC) and NH_4^+ (Markarian *et al.* 2010) and by the PAC concentration in the case of adsorbable compounds (Treguer *et al.* 2010). The performance can be quite high when the PAC age is low (<10 d) and acts mostly in adsorption. For instance, 80% dissolved organic carbon (DOC) removal was observed for the first month of operation of a 20 g/L CC-LPM using settled-filtered water (Seo *et al.* 2004). DOC removal progressively diminished to 20%, a residual performance which was attributed to biological activity (Seo *et al.* 2004). Reduction of disinfection by-products (DBP) precursors can also be significant, as Tian *et al.* (2009) measured 34% trihalomethanes formation potential (THMFP) and 25% halogenated acetic acids formation potential (HAAFP) removals while operating at a PAC concentration of 1.5 g/L and at a PAC age over 80 d (i.e., essentially in biological mode). In this study, a parallel biological activated carbon (BAC) filter obtained 36% THMFP and 37% HAAFP reductions. However, the work of Tian *et al.* (2009) was using an influent composed of simulated surface water made by mixing wastewater and tap water. In addition, no pretreatment (coagulation or ozonation) was performed on this water. Additional research is therefore needed to evaluate the role of coagulation and ozonation as a pretreatment to CC-LPM. Coagulation is expected to increase removal of NOM and suspended solids. However, it may favour the development of the PAC cake layer. Ozonation could help reduce fouling and increase the performance of the process under biological mode due to the formation of BDOC.

The global objective of this work is to develop an alternative treatment to biological filtration that is economical, compact and flexible. To our knowledge, long-term operation and performance demonstration of a CC-LPM using natural water and aged PAC has not yet been published. The specific objectives of this project were to evaluate the fouling and performance of a CC-LPM process operated at 10 g/L of PAC. An industrial pilot process (50 m³/d) was fed with settled-ozonated surface water. The impact of ozonating the settled water prior to the CC-LPM was investigated. In addition, the impact of PAC age on

membrane fouling and cleaning efficacy was tested. In parallel, process performance was evaluated with respect to ammonia, NOM and DBP precursor removals and was compared with a full-scale BAC filter.

MATERIAL AND METHODS

Source water characteristics and Ste. Rose water treatment plant

The pilot study was conducted at the Ste. Rose water treatment plant in Laval (Canada). The raw water, drawn from the Mille Iles River, has a high organic load (DOC: 4–8 mg C L⁻¹), low alkalinity (between 20 and 50 mg CaCO₃ L⁻¹), moderate ammonia concentration (50–200 µg N L⁻¹) and a poor bacteriological quality (100–1,000 *Escherichia coli*/100 mL). The water is subject to important seasonal fluctuations in temperature (1–28 °C).

The treatment plant has a nominal capacity of 110,000 m³ d⁻¹ and is composed of sludge blanket clarifiers (26–122 mg/L of alum +1.5–2.8 mg/L of activated silica), rapid sand/anthracite filtration, ozonation, BAC filtration, pH adjustment and chlorination. Average full-scale ozone dosage was 2.3 mg/L. The BAC filters are composed of dual media: sand ($D_{10} = 0.45$ mm, $H = 15$ cm) and wood-base BAC ($D_{10} = 0.81$ mm, $H = 156$ cm). The empty bed contact time in the BAC ranges from 9.4 to 18.8 min, depending on water demand.

Membrane bioreactors' description

Two parallel CC-LPM pilots were operated for 210 d (May to December 2010) while being fed with clarified water from the water treatment plant. The membranes were nearly new, as they were immersed only 105 d prior to the project to test different operating conditions. Settled water was ozonated (1.1 ± 0.3 mg/L O₃) at pilot-scale up to the 60th day. On the 167th day, the short-term impacts of ozone dosage were also evaluated by progressively increasing applied ozone from 0 to 3.6 mg O₃ L⁻¹. Figure 1 presents a schematic of the pilot plant while Table 1 summarizes the operational conditions.

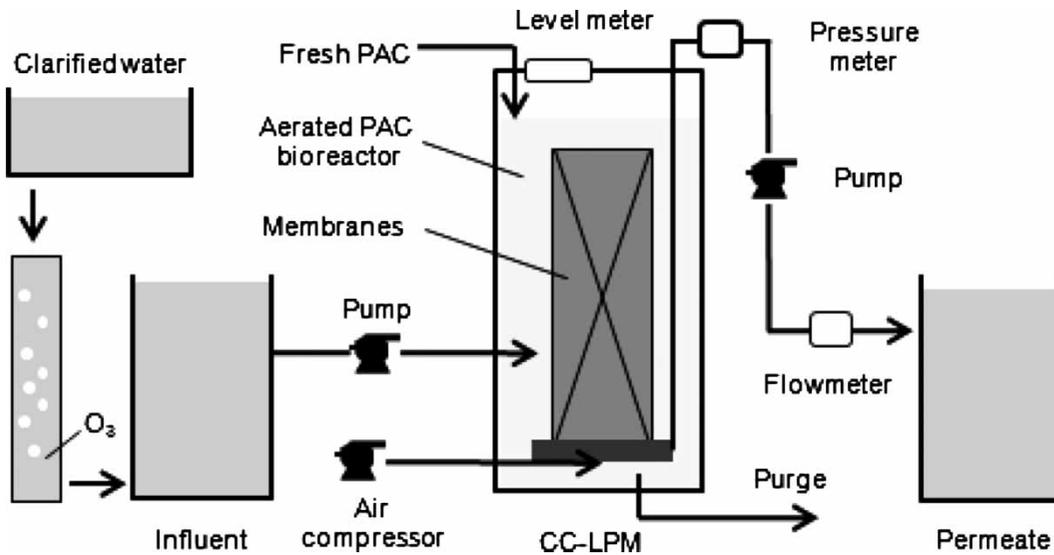


Figure 1 | Flow diagram and schematic of the CC-LPM. MBR without PAC is identical.

Table 1 | Operational characteristics of the two MBRs

Parameters	Values
<i>Bioreactor</i>	
PAC concentration	Reactor 1: 0 g/L Reactor 2: 10 g/L
PAC age	0–60 d
Bioreactor volume	173 L
Aeration rate	37 L/min
Diameter/height	0.35 m/2.1 m
Residence time at a flux of 25 LMH	67 min
<i>Powdered activated carbon</i>	
Type	Picahydro LP39
Material	Wood-base
Iodine number	1,000
Diameter	$D_{10} = 3.2 \mu\text{m}$ $D_{50} = 18.8 \mu\text{m}$ $D_{90} = 52.8 \mu\text{m}$
<i>Membrane</i>	
Flux	15–25 LMH
Membrane area	10 m ²
Membrane type	PES hollow fibre UF from Puron
Porosity ^a	0.05 μm

^aAccording to the supplier.

Both membrane reactors were operated under identical conditions, except that one reactor contained 10 g/L of fresh PAC (see Table 1 for PAC characteristics) while the other one did not include any PAC. A wood-base PAC was selected for its macroporous structure favourable to biological activity (Prévost *et al.* 1992). After 30 d of operation, PAC age was maintained constant, first at 30 d then at 60 d. This was accomplished by purging daily a specific volume of water which had 10 g/L of old PAC and replacing it by an equivalent mass of fresh PAC. The selected PAC ages (30 and 60 d) are equivalent to PAC dosages of 16 and 8 mg/L, respectively. Purges were also performed on the membrane bioreactor (MBR) without PAC in order to limit suspended solids accumulation to the same levels as in the PAC contactor.

UF membranes were operated at fluxes ranging from 15 to 25 L m⁻² h⁻¹. Transmembrane pressure (TMP) was monitored and standardized at 20 °C using a correction factor for water viscosity (United States Environmental Protection Agency (USEPA) 2005). At a flux of 25 L m⁻² h⁻¹, the theoretical HRT is 67 min. The filtration cycles consisted of 5 min of filtration followed by a 1 min backpulse at 30 L m⁻² h⁻¹. UF membrane cleaning was performed in three steps: (i) transfer PAC or sludge into a stand-by tank; (ii) move the membranes into a basin to conduct physical cleaning using a pressurized water jet in order to detach the PAC

cake layer accumulating on the membrane; (iii) reinstall the membranes back into the empty reactor in order to conduct chemical cleaning, which consisted of 1 h contact time with NaOCl + NaOH (1.2 g Cl₂/L, pH = 11 at 35 °C) and 1 h contact time with citric acid (0.9 g/L, pH = 2.5 at 35 °C). Three chemical cleanings were conducted, including one that was performed on day 0.

Analytical methods

Raw, clarified, ozonated and CC-LPM-treated effluents were collected routinely from May 2010 to December 2010. In parallel, water treatment plant samples were collected after ozonation and after BAC filtration. Table 2 lists analytical methods used to characterize performance.

DOC and BDOC analysis were performed using a total organic carbon (TOC)-meter (Sievers 5310C) on 100 mL samples that had previously been filtered on prewashed (with 1 L of ultrapure water) 0.45 mm pore-size filters (PALL Supor 450w PES). BDOC technique is described in greater detail in Markarian *et al.* (2010). BDOC analysis precision was evaluated to 4.6% (based on the coefficient of variation of 96 duplicate samples). Ammonia was measured using the indophenol colorimetric method (Association Française de Normalisation (AFNOR) 1990). This method has an excellent accuracy (3 µg/L) and a low detection limit (5 µg/L). The removal of DBP precursors was assessed on buffered

samples (pH 8.0) using the uniform formation conditions technique (Summers *et al.* 1996).

RESULTS

Performances with respect to water quality

Trends in the rate of fouling

Temperature-corrected TMP (at 20 °C) are presented in Figure 2. The operating flux was 22–25 L m⁻² h⁻¹ for most of the study, apart from a short period of operation at 15 L m⁻² h⁻¹. Biological PAC at 10 g/L caused significant fouling of the membranes. The fouling rate, defined here as the slope of TMP increase vs. time, was roughly 13 times higher in the reactor with PAC than without PAC. Nevertheless, it was possible to operate the CC-LPM for over 90 d before reaching the maximum TMP recommended by the manufacturer (62 kPa).

The drops in TMP observed on the 50th, 75th, 118th, 124th and 176th days were caused by unintended short-term (8–30 h) shutdowns of the process, while the TMP drop observed on the 142nd day was caused by a voluntary flux reduction from 25 to 15 L m⁻² h⁻¹. Short-term shutdowns caused a relaxation of the hollow fibres that helped recover permeability, an observation that was also noted

Table 2 | Summary of analytical methods

Parameters	Description/materials	References
UV absorbance	Spectrophotometer Biochrome 3100, at 254 nm	5910B, Standard Methods (2005)
Ammonia (N-NH ₄ ⁺)	Indophenol blue colorimetric method	NF T 90-015, AFNOR (1990)
Free chlorine	DPD colorimetric method	4500G, Standard Methods (2005)
DOC	Sievers 5310C carbon analyser	5310C, Standard Methods (2005)
BDOC	Sievers 5310C carbon analyser (inoculum: raw water from Mille-Ile River)	Servais <i>et al.</i> (1987)
Ozone residual	Indigo colorimetric method	4500-O ₃ , Standard Methods (2005)
THM _{UFC} and HAA5 _{UFC} ^a	<i>Incubation</i> Dosage sufficient to maintain 1.0 ± 0.5 mg Cl ₂ /L CL ₂ after 24 h, pH = 8.0, T = 22 °C <i>Analysis</i> Gas chromatography and electron capture detection	5710C, Standard Methods (2005)

^aUFC: Uniform formation conditions.

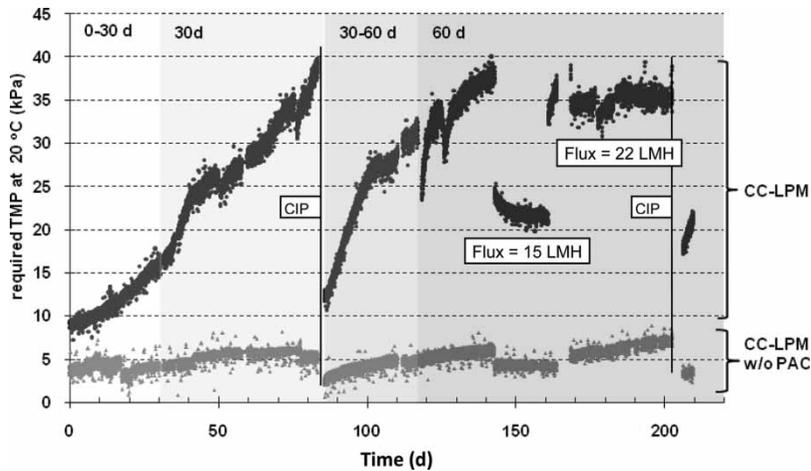


Figure 2 | TMP corrected at 20 °C for the CC-LPM and the MBR without PAC. (CIP: chemical cleaning.) TMP values presented are negative as the system is operated in vacuum. PAC/sludge age is specified in the shading. Concentration of PAC is 10 g/L. Flux = 25 LMH ($L m^{-2} h^{-1}$) unless specified.

by Treguer *et al.* (2008). However, this impact was not durable as the TMP trend went back to its original value after a few days. The largest TMP drop observed on the 118th day also coincided with an integrity loss. The integrity loss was immediately detected as the turbidity rose from 0.025 UTN to over 0.2 UTN due to PAC particles. This observation suggests that it might be more useful to perform direct integrity test on a CC-LPM process using online turbidity or particle counts rather than offline pressure decay tests. Finally, as expected, reducing flux from 25 to 15 $L m^{-2} h^{-1}$ had a large impact on TMP. During the 18 d of operation at the lower flux, TMP actually declined. We suggest that the lower flux reduced advective transport of PAC on the membrane and allowed increased back transport of the cake layer in the bulk solution. This statement implies that a fraction of the cake layer accumulating on the membrane can be re-suspended in bulk solution under favourable conditions. A follow-up study conducted after this project (data not shown) confirmed that the sustainable flux was in the range of 15 rather than 25 $L m^{-2} h^{-1}$.

Impact of PAC age on fouling

Critical flux tests were conducted on the CC-LPM reactor on the new membranes and after each chemical cleaning: (i) before adding PAC, (ii) with 10 $g L^{-1}$ of fresh PAC and (iii) with 10 $g L^{-1}$ of 30, 60 or 200 d old PAC. Results of critical flux tests are presented in Figure 3. Critical fluxes

were determined on the same LPM both in the absence of PAC and with PAC in order to clearly delineate the effect of ageing PAC vs. membrane fouling. The test followed the flux stepping method as described in Bacchin *et al.* (2006) using flux steps lasting 12 min composed of two filtration cycles (5 min filtration followed by 1 min backwash). Conducting tests with settled, tap or ozonated-settled water did not make any difference to critical flux results (data not shown).

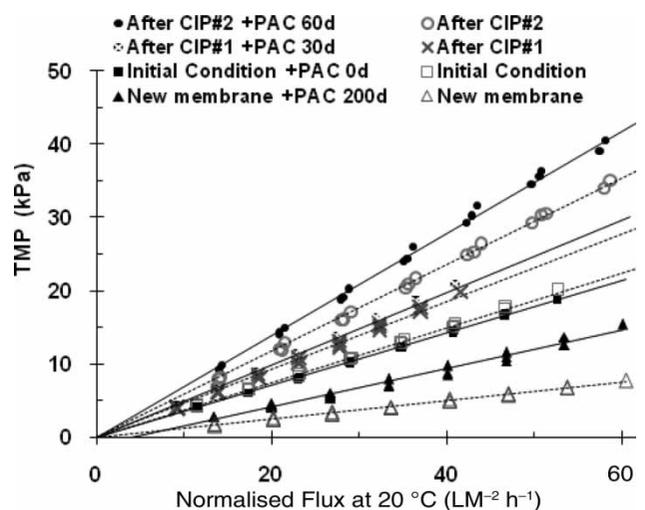


Figure 3 | Critical flux assays for the CC-LPM at the start of the project (initial conditions) and after each chemical cleaning (CIP #1 and #2) with or without PAC inside the reactor. The 200-d PAC was tested on the new membranes prior to the start of this project. Tests on new membrane were made 105 d prior to the project (see Material and methods section).

Adding 10 g/L of fresh PAC did not significantly impact permeability (+5%). On the other hand, older PAC had an adverse impact. The permeability was reduced by 6% when the 30-d-old PAC was reintroduced in the CC-LPM. Furthermore, when the 60-d-old PAC was reintroduced in the CC-LPM following the second CIP, the permeability was reduced by 18% and this number increased to 47% for the 200-d-old PAC.

Efficacy of membrane cleaning

Efficacy of membrane cleaning was evaluated by calculating the recovery of membrane permeability following a CIP procedure and using the initial permeability without PAC as a reference. The membranes were not new at the start of the project. The CC-LPM had been in operation for 105 d and had seen its initial permeability reduced from 810 to 282 LMH/bar at 20 °C. During the current project, two CIP procedures were completed: a first one after 88 d and a second one after 207 d (cf. Figure 2). Permeabilities were reduced to 203 (CIP #1) and 144 LMH/bar (CIP #2) or respectively 72 and 51% of the initial permeability (282 LMH/bar). CIP performances were equivalent (71–72%) when calculated with respect to the permeability before initiating the cleaning procedure. On one occasion, a physical cleaning was conducted alone. However, permeability recovery was minimal, leading to a TMP gain of about 2.0 kPa (0.3 psi). Consequently, significant irreversible fouling was observed during the test period. In comparison, the control MBR without PAC did not suffer any decrease in

permeability. The permeabilities fluctuated in a range of 800–1,015 LMH/bar without any distinguishable trend.

Performance with respect to water quality

Effluents were compared between the two membrane reactors (with or without PAC) as well as with the effluent of a full-scale BAC filter. Table 3 summarizes the influent water characteristics as well as the raw water quality. The following sections present these results in greater detail.

Ammonia removal

Figure 4 illustrates the ammonia removal results for both MBR and the BAC filter effluents. Full nitrification started during the fourth week of operation of the CC-LPM. This lag phase corresponds to the time needed to establish a consistent nitrifying biomass on PAC (Ma et al. 2010). Full nitrification was maintained in the CC-LPM until the 167th day of operation. At this time, a drop of performance was noted after a flux increase from 15 to 25 L m⁻² h⁻¹, which reduced the available contact time within the CC-LPM from 141 to 67 min. About 10 d later, full nitrification resumed within the CC-LPM and was maintained with water temperatures as low as 7 °C.

Interestingly, the MBR without PAC also allowed full nitrification in summer. However, it took a longer time for the nitrifying biomass to develop and nitrification was negligible below a temperature of about 11 °C. Although free of PAC, this MBR accumulated total suspended solids

Table 3 | Raw water from Mille-Ile River, MBR influent (settled water or settled + ozonated water) and biological filter influent (settled + filtered + ozonated)

Parameters	Units	Raw	Settled	Settled + O ₃	BAC influent
DOC	mg C L ⁻¹	6.3 ± 0.2	2.9 ± 0.2	2.8 ± 0.2	2.6 ± 0.2
BDOC	mg C L ⁻¹	0.68 ± 0.17	0.29 ± 0.07	0.63 ± 0.12	0.66 ± 0.07
N-NH ₄ ⁺	µg N L ⁻¹	142 ± 43	139 ± 44	NA	126 ± 42
UV ₂₅₄	cm ⁻¹	0.180	0.051	0.029	0.018
Alkalinity	mg CaCO ₃ L ⁻¹	<60	NA	NA	NA
pH	–	7.1 ± 0.2	6.0 ± 0.2	6.1 ± 0.2	NA
THM-UFC	µg L ⁻¹	NA	49 ± 4 n = 5	36 ± 2 n = 11	30 ± 4 n = 11
HAA-UFC	µg L ⁻¹	NA	48 ± 6 n = 3	26 ± 4 n = 11	21 ± 7 n = 9
Turbidity	NTU	3.1 ± 2.7	0.53 ± 0.16	NA	NA

NA: Not available; n: number of samplings.

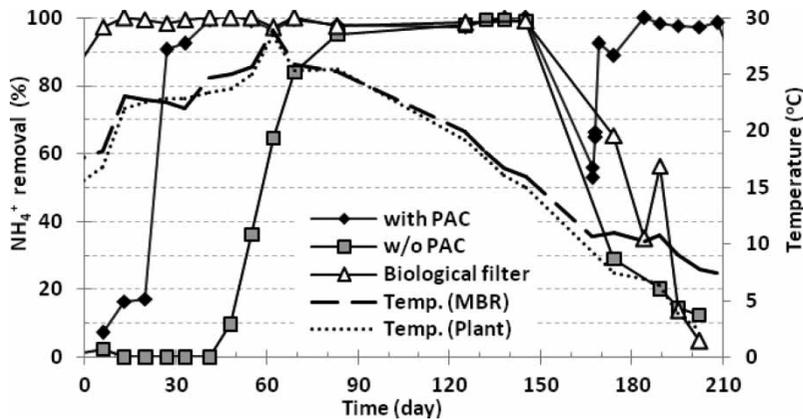


Figure 4 | Ammonia removal for the CC-LPM, MBR without PAC and the full-scale biological activated carbon filters. Influent ammonia concentration is provided in Table 3. Effluent temperatures are provided for the pilot and the full-scale plant.

originating from settled water. Concentrations as high as 400–1,600 mg L⁻¹ were measured within the reactor, depending on the selected solid residence time. These solids probably promoted the growth of an active nitrifying population. Nevertheless, this process was less robust in the absence of PAC, as evidenced by the longer lag phase and the fastest loss of nitrification under adverse water temperature.

The BAC filter from the plant achieved full nitrification in warm water. Nitrification performance decreased with lower temperature and was found to be marginal below 4 °C. The CC-LPM exceeded the full-scale BAC filter performance in cold water. The higher residence time in the

CC-LPM contributed in part to this improved performance. However, the slower drop in water temperature at pilot-scale than at full-scale (a 4–6 °C temperature difference was observed even though the CC-LPM was insulated) could also have offered more favourable conditions for prolonged nitrification in cold water.

Biodegradable dissolved organic carbon removal

BDOC removals are presented in Figure 5 for both MBRs and the full-scale BAC filter. For the CC-LPM, BDOC removal averaged 48% during the first week, due to the

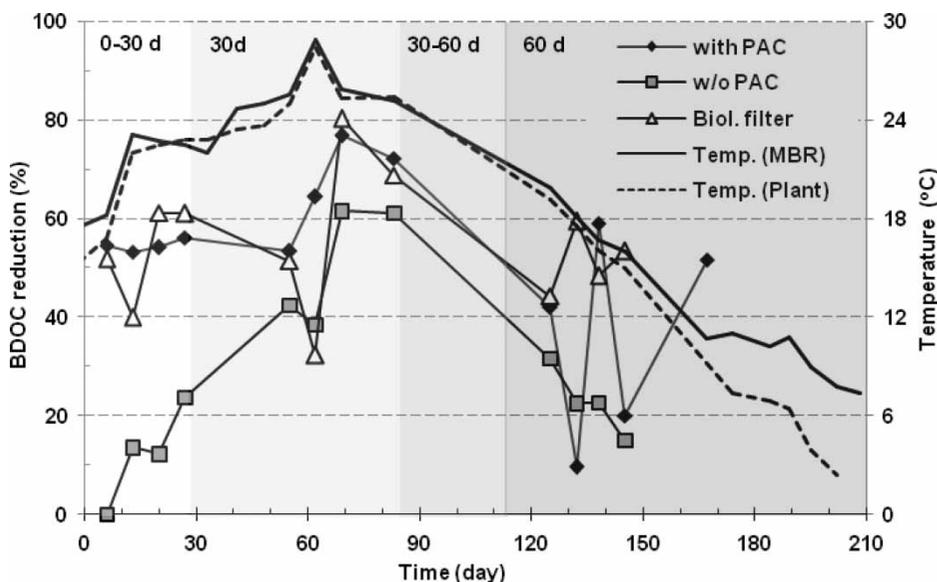


Figure 5 | Biodegradable dissolved organic carbon (BDOC) removals for the CC-LPM, the MBR without PAC and the full-scale biological activated carbon filter. PAC/sludge age for both MBRs is specified in the shading. Influent concentrations are specified in Table 3.

high adsorption of BDOC on PAC (Treguer *et al.* 2010). BDOC removal stayed high (50–80%) and then declined when water temperature diminished. Without PAC, BDOC removal is much lower, especially during the first months of operation. Once again, this is explained by the long period needed to develop a biomass inside the LPM without PAC. The decline in BDOC removal due to lower water temperature is also more pronounced for this reactor.

The CC-LPM with PAC ages of 30 or 60 d offered similar BDOC removals to the BAC filter (paired *t*-test $p_{\text{value}} = 0.63$). Overall, the BAC filter, the CC-LPM and the MBR achieved 54, 51 and 29% BDOC removals over the course of this project. The MBR performance without PAC was 15% lower on average when excluding the period of biomass acclimatization (60 d). Therefore, the accumulation of suspended solids in the MBR without PAC promoted biological activity as evidenced by the temperature-dependent removal of BDOC. However, this performance was insufficient to compete with a BAC filter or a CC-LPM.

Natural organic matter removal

DOC and UVA₂₅₄ removals by the MBR processes and the BAC filter are presented in Figures 6(a) (DOC) and 6(b) (UVA₂₅₄). For both MBRs (with and without PAC), performance data were stratified according to the solid residence time (30 or 60 d) and the absence/presence of ozonation ahead of the reactors.

The DOC removal in the 30 d CC-LPM (33%) was found to be higher than the one achieved by the biological filters (24%) and not impacted by the use of ozonation ahead of the contactor. For the higher PAC age of 60 d, removals were not statistically different (20–22%) between the BAC filter and the CC-LPM. In addition, ozonation did not improve DOC removal on the 60-d CC-LPM. On the other hand, in the absence of PAC inside the MBR, ozonation was found to improve DOC removals from 6 to 16%. Although ozonation improved DOC removals, the overall performance of this configuration was significantly lower than for the CC-LPM. As expected, the presence of PAC inside the MBR favours

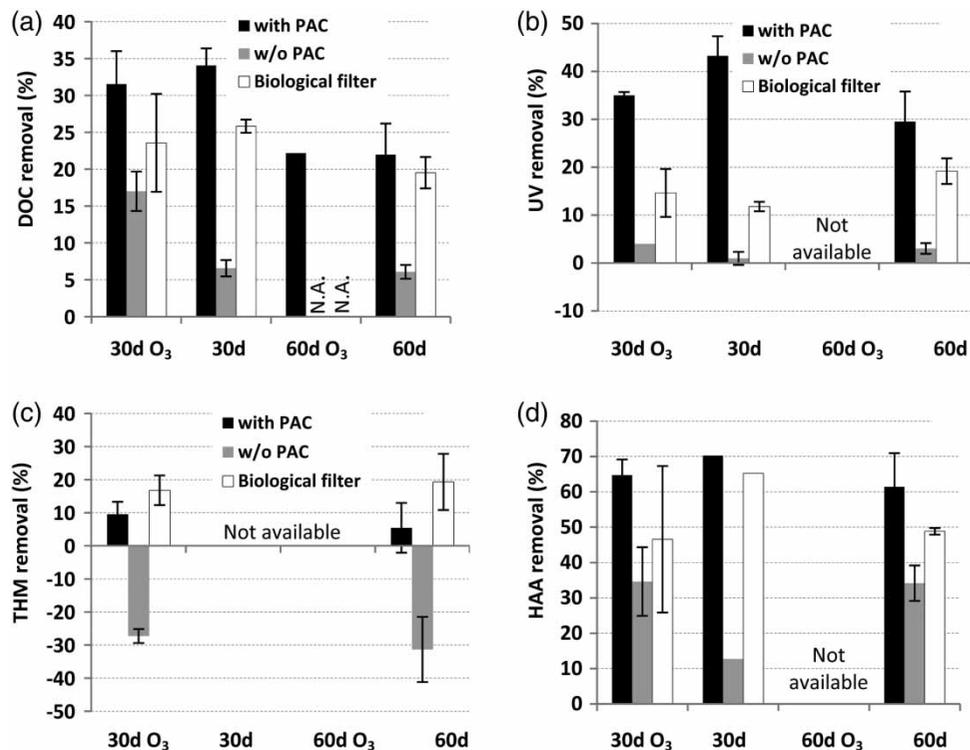


Figure 6 | Performances achieved by the CC-LPM, the MBR without PAC and the BAC filter for DOC (a), UVA₂₅₄ (b), THM-UFC (c) and HAA-UFC (d). Removals are compared for four conditions: (i) PAC aged 30 d (30 d), (ii) PAC aged 30 d with ozonation (30 d O₃), (iii) PAC aged 60 d (60 d) and (iv) PAC aged 60 d with ozonation (60 d O₃). Influent concentrations are specified in Table 3. Ozonation was always online for the biological filter; 30 d and 60 d for the biological filter refer to the data sampled at the same time as the CC-LPM.

additional removal of DOC. This additional performance is sufficient to match the one of a BAC filter for high PAC age (60 d) or even surpass it for a lower PAC age (30 d).

UV removals were highest (30–43%) for the CC-LPM, a clear indication that adsorption is taking place under this operational mode. The BAC filter reduced UVA_{254} by 10–20% depending on the time of the year while the MBR without PAC had only a marginal impact on UVA_{254} (<4%). Logically, the performance was also higher for the 30-d PAC (43%) than the 60-d PAC (30%).

THM and HAA precursor removal

The removal of chlorinated DBP precursors was assessed by performing haloacetic acid (HAA)-UFC and trihalomethane (THM)-UFC analysis. Results are presented in Figures 6(c) (THM) and 6(d) (HAA). The performance of the BAC filter for THM averaged 18% during the project. On the other hand, the MBR without PAC was not only unable to remove THM precursors; it even increased their formation by 20–30%. The CC-LPM allowed a THM removal of 10 and 5% for PAC ages of 30 or 60 d, respectively. The impact of PAC on THM precursors can be assessed by calculating the difference between the two MBR configurations. Such analysis reveals that the presence of PAC roughly reduced THM precursors by 36–37% (for PAC ages of 30 or 60 d). Clearly, the PAC inside the reactor is more effective than the BAC filter (36 vs. 18%). However, the process appears to suffer from the accumulation of suspended solids within the reactor. This issue will be discussed later in greater detail.

Results describing the removal of HAA precursors (Figure 6(d)) provide quite a different picture from the ones for THM. The HAA precursors were best removed by the CC-LPM, which consistently achieved 60–70% removal. This high performance was driven by the presence of PAC, since the MBR without PAC reduced HAA by only 13–34%. This performance was also higher than for the BAC filter, which achieved a 46–65% reduction depending on the period of investigation.

Impact of ozonation on NOM removal

A short-term ozonation assay was conducted on the CC-LPM in order to evaluate if increased ozone dosage would yield

improved performance due to increased BDOC formation. In order to better understand the impact of ozonation on DOC and BDOC removals, removal of refractory dissolved organic carbon (RDOC) was also calculated. RDOC concentration is calculated by subtracting BDOC concentration from DOC concentration. Ozone dosages were increased from 0 to 3 mg/L by increments and the process was then left to stabilize for 12 h before each sampling. Ozone residuals of 0.3 and 0.7 mg/L were measured in the influent for the two highest ozone dosages (1.5 and 3.0 mg/L).

Figure 7 presents the removals of BDOC, RDOC and DOC as a function of ozone dosages. In the absence of ozone, the removal of DOC (0.86 mg/L) was essentially the result of RDOC removal (0.81 mg/L). As ozone dosage was increased, RDOC removal progressively decreased down to negligible levels (0.05 mg/L at 3 mg O_3 /L). BDOC removal increased due to the use of ozone. However, this removal rapidly reached a plateau of 0.30 mg/L, as only a fraction of DOC is converted to BDOC by ozone. Consequently, the overall performance of the process for DOC was observed to be negatively impacted by the use of ozone.

DISCUSSION

The operation of a high (10 g/L) concentration CC-LPM presented significant challenges with respect to fouling. Most of

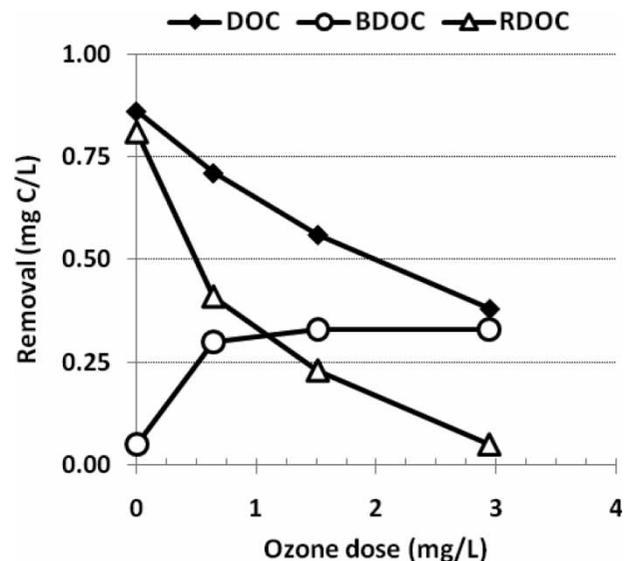


Figure 7 | Absolute removals (in mg C/L) of DOC, BDOC and refractory dissolved organic carbon (RDOC) for increased ozone dosages.

the study was conducted at a flux of $25 \text{ L m}^{-2} \text{ h}^{-1}$. However, the sustainable flux is most likely lower and probably in the vicinity of $15 \text{ L m}^{-2} \text{ h}^{-1}$. Such flux is lower than what is typically used in drinking water applications but in line with wastewater MBR conditions (Gander *et al.* 2000).

The irreversible fouling observed for the CC-LPM could be explained by either the presence of a cake layer or the pre-clogging due to small PAC particles. The PAC cake layer, which acts as an additional filter (Yan *et al.* 2010), was not observed to be significant, as demonstrated by the poor TMP recovery after an isolated physical cleaning (0.3 psi). This is a probable consequence of the important aeration occurring inside the CC-LPM in order to prevent PAC settling. Performing a physical cleaning of the membranes also led to minimal permeability recovery and chemical cleaning was not very efficient in dislodging these foulants. Considering these observations, it is possible that pore plugging may have been the principal cause of the observed irreversible fouling. Saravia *et al.* (2006) have suggested that the ratio of PAC diameter over membrane pore size should be 100-fold or higher. In the current project, this ratio was 64 ($d_{10} = 3.2 \mu\text{m}$ vs. $d_{ps} = 0.05 \mu\text{m}$ according to the supplier). However, bubble point tests performed on these membranes indicated a low value (17–20 kPa), an observation suggesting that the membrane pore size could well be higher than the value of $0.05 \mu\text{m}$ stated by the manufacturer, thus lowering the ratio.

The PAC age also had an important impact on fouling. PAC diameter inside the reactor is expected to change over time. While some authors observed smaller particles over time (Khan *et al.* 2002), it was found that PAC particles in the current study were larger over time and tended to form aggregates. As opposed to the work of Khan *et al.* (2002), the PAC reactor was fed with settled water, which most likely favours aggregation of PAC particles due to the presence of residual coagulants. In addition, since we were working with aged PAC, the formation of an extended biofilm at the surface of the PAC favoured the aggregation of PAC particles by increasing their stickiness. PAC aggregation was also noted for other projects performed by our group using the same aged PAC with pretreated waters (Markarian *et al.* 2010). Markarian *et al.* (2010) also noted that biological PAC settled faster than fresh PAC. Lebeau *et al.* (1998), who worked with biological PAC and fed their reactor with

coagulated-settled water, also obtained larger particles after 62 d of operation. Although larger particles will often lead to reduced membrane fouling (Park *et al.* 2006), the cohesive nature of the aggregated PAC particles increased fouling under the current operating conditions and suggests that maintaining a lower PAC age would be beneficial to reduce fouling. Preliminary tests (thermogravimetric analysis, viscosity measurement, backlight observations) confirmed the biological nature of the biofilm development at the surface of the aged PAC and provided additional insights to explain the increased fouling. Further work on PAC is ongoing.

With respect to water quality, it has already been reported that CC-LPM can achieve high ammonia removal in warm water ($>15^\circ\text{C}$) (Lebeau *et al.* 1998; Suzuki *et al.* 1998; Watanabe *et al.* 2000; Seo *et al.* 2002, 2004) and even under adverse temperature conditions (Suzuki *et al.* 1998; Seo *et al.* 2002). Ammonia removals of 60–70% were achieved at 5°C in 10–15 min of contact time with a PAC of approximately 30 d (Suzuki *et al.* 1998). During the current project, full nitrification was observed at temperatures as low as 7°C . Ammonia removal in the CC-LPM was found to be efficient for a longer period of time in the presence of PAC than in the reactor without PAC. The reactor without PAC allowed the accumulation of suspended matter and thus nitrifying biomass accumulation. However, in the absence of PAC acting as a support for biofilm growth, ammonia removal could not be maintained while temperature was decreasing. Indeed, studies demonstrated that adsorbed biofilms were better protected from changes in their environment than suspended biofilms (Simpson 2008). Nitrification in the CC-LPM was also noted to be more efficient than in the BAC filter. The nitrifying biomass activity inside the BAC filter was submitted to faster drops of temperature as well as to lower temperatures. Moreover, the contact time applied in the CC-LPM (i.e., 67 min) was 3.5 to 7 times higher than in the BAC filter, depending on the water demand. This difference is significant, since Markarian *et al.* (2010) demonstrated that achieving good nitrification ($>80\%$) in their CC-LPM process required a contact time superior to 30 min under cold water conditions.

Surprisingly, the MBR without PAC led to an increase of THM as high as 30% despite DOC removal of 6–16% across the process. This difference in performance can only be explained by PAC, since both MBRs were under the same

operating conditions. We propose that the NOM present in the MBR effluents had a higher propensity to form THM (i.e., a higher reactivity). Such a phenomenon is not seen on the BAC filter since the latter is backwashed on a regular basis. Suspended solids concentrations inside the MBR reactor without PAC were in the range of 400–1,600 mg/L and mostly composed of alum microflocs on which NOM is adsorbed. We propose that the microbial activity within the MBR, favoured by a significant organic carbon accumulation, increased THM formation. Increased biological activity has been shown to increase DBP yield for reservoir water (Hoehn *et al.* 1984). In the area of wastewater treatment, soluble microbial products (SMPs) have been identified as DBP precursors (Galapate *et al.* 1999). It was also shown that biological wastewater treatment increases DBP yield even though NOM is globally decreased by such a process (Liu & Li 2010). These authors also attributed this effect to the release of SMPs in the effluent water. Future research should confirm this hypothesis and try to understand why this phenomenon was observed only for THM and not HAA formation.

On a final note, the impact of ozonation as a pre-treatment was of particular interest. Ozonation led to a decrease in DOC removal. This observation suggests that ozonation reduced NOM adsorbability, a phenomenon which has also been observed by Treguer *et al.* (2010) and which was attributed to the increased hydrophilicity of ozone-treated NOM. These authors concluded that combining pre-ozonation with a CC-LPM had a minor impact on NOM removal. While ozonation increases the biodegradability of organic matter, it also affects its adsorbability, making it more or less adsorbable according to the ozone dose (Treguer *et al.* 2010). Consequently, the use of ozone might not be essential for an optimized operation of the CC-LPM, although it may be useful to achieve other treatment needs such as DBP reductions and to increase the overall treatment robustness.

CONCLUSIONS

The operation and the water quality delivered by a high concentration (10 g/L) CC-LPM were studied for a period of 210 d. The treatment performance of the CC-LPM was

superior to an equivalent MBR without PAC and a full-scale biological activated carbon filter, the exception being THM formation, which was shown to be more important in MBR effluents. It was suggested that the increased THM yield was caused by the microbial activity within the MBR. Ozonation prior to the CC-LPM did not significantly increase NOM removal across the process.

Biological PAC caused a higher fouling rate compared to a MBR without PAC, although it was possible to maintain operation for about 3 months at 25 LMH, at which point a chemical cleaning was required. Permeability recoveries after each chemical cleaning (71%) were too low to permit long-term operation of the process.

Strategies to limit fouling of the CC-LPM need to be further developed. Optimization of filtration cycles, chemical cleanings, operating flux, PAC concentration and PAC age are examples of potential alternatives to limit fouling. Future research should also attempt to document and limit the impacts on the process of suspended solids accumulating inside the bioreactor.

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