Hybrid membrane process: Performance evaluation of biological PAC

Ara Markarian, Annie Carrière, Pierre-Olivier Dallaire, Pierre Servais and Benoit Barbeau

ABSTRACT

This study investigated the use of biological powdered activated carbon (PAC) for the removal of natural organic matter (NOM) and ammonia from drinking water. The impact of solids retention time (SRT), hydraulic retention time (HRT), PAC diameter and PAC concentration on the process efficiency was evaluated. Five bioreactors were filled with a slurry using two PAC concentrations (5 or 25 g l^{-1}), two PAC mean diameters (25 or 200 μm) and two SRTs (30 or 100–160 days). The bioreactors were operated during 161 days using post-ozonated water as influent. It was determined that the PAC concentration in the bioreactors was a key parameter for the improvement of biological removal. The higher PAC concentration (25 g l^{-1}) was more efficient for the removal of ammonia, dissolved organic carbon (DOC) and biodegradable dissolved organic carbon (BDOC). Full nitrification was observed after 90 days in bioreactors with 25 g l^{-} of PAC. The PAC diameter (25 vs. 200 μm) did not significantly influence BDOC, DOC and N-NH_4 removals under stable conditions, although nitrification was initiated faster using a 25-μm diameter PAC. Increasing HRT from 15 to 30 minutes improved NOM and ammonia removals. Reducing SRT from 100–161 to 30 days improved DOC removals but reduced BDOC and ammonia removals. The overall performances observed during this study demonstrate the efficiency of biological PAC. Its combination with ultrafiltration in a hybrid membrane process appears promising but the feasibility from an operational standpoint still has to be demonstrated

Key words | BDOC, biological treatment, bioreactor, hybrid membrane process, nitrification, PAC

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INTRODUCTION

Over the last two decades, many utilities relying on conventional treatment were upgraded to meet increasingly stringent drinking water regulations. The combined use of ozone and biological activated carbon filtration (BAC) has emerged as an attractive alternative to achieve a higher level of disinfection and reduced concentrations of chlorinated disinfection by-products. In addition to the benefit of reducing bacterial regrowth in the distribution system, this treatment train also lowers taste and odours (Elhadi *et al.* 2006). These objectives are achieved through the reduction of ammonia, microbial metabolites (such as MIB and geosmin) and biodegradable organic carbon (BDOC).

Although BAC remains efficient for the removal of natural organic matter, some contaminants such as saxitoxin are more effectively removed by adsorption than biodegradation (Newcombe & Nicholson 2002). Granular activated carbon (GAC) filters can be operated under adsorption mode by regenerating the media regularly; however, this solution is costly and labour intensive.

Low-pressure membranes have emerged as an attractive alternative to conventional treatment, mainly due to their superior performance with respect to particulate contaminants and some pathogens such as *Cryptosporidium*. However, their limited ability to address dissolved

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contaminants such as organic matter and trace contaminants (Lee *et al.* 2005; Huang *et al.* 2009) requires combination with other technologies, when necessary, based on feed water quality. Adding post-ozonation and GAC or BAC filtration represents one possibility. Alternatively, injecting powdered activated carbon (PAC) ahead of vacuum membrane results in a high concentration slurry within the membrane basin. This process has often been referred to as the hybrid membrane process (HMP) (Watanabe *et al.* 2000; Saravia *et al.* 2006; Song *et al.* 2009) or as the powdered activated carbon–membrane bioreactor (HCPAC-MBR) (Seo *et al.* 2004). The former term will be used in this text.

Research on HMP for the production of drinking water treatment has multiplied in recent years. It mainly targeted conditions under which PAC is operated under adsorption mode (Tomaszewska & Mozia 2002; Zhang *et al.* 2003; Xia *et al.* 2007). One interesting characteristic of the HMP would be the possibility to operate under biological mode. This objective is accomplished by simply increasing the PAC residence time (defined hereafter in the text as solids retention time or SRT) within the bioreactor, achieved via the reduction of the daily volume of purge. This process presents several similarities to the membrane bioreactors (MBR) used in wastewater treatment, the main difference being that the mixed liquor (also called activated sludge) is replaced by the PAC slurry.

Some studies used PAC in combined biological and adsorption modes (no PAC replacement) to remove dissolved contaminants. It has been demonstrated that over 80% total organic carbon (TOC) removals could be achieved (Kim *et al.* 2007; Oh *et al.* 2007). According to Seo *et al.* (2002), dissolved organic carbon (DOC) removal decreases gradually (from 80% to 30–40%) as biodegradation overtakes adsorption. This result is consistent with Lebeau *et al.* (1998) who measured between 40 and 69% of DOC removals with SRT of 30 and 60 days. Aside from organic matter, trace contaminants such as atrazine could be lowered by 92% (Lebeau *et al.* 1999) and ammonia could be nitrified almost entirely even under cold water conditions (Seo *et al.* 2002).

However, many questions remained unanswered concerning the use of PAC mainly in biological mode. For one, operating with various PAC concentrations within the HMP has only been evaluated regarding its impacts on adsorption performances (Seo *et al.* 2004; Kim *et al.* 2007). The influences of PAC diameter (Zhao *et al.* 2005) and HRT (Vigneswaran *et al.* 2007) were evaluated only in regard to their contribution to membrane fouling. Hence, these design and operational parameters were not evaluated for a PAC operated under biological mode. The complexity of the respective contribution of adsorption and biodegradation was assessed within a membrane bioreactor (Sagbo *et al.* 2008; Tian *et al.* 2008). However, PAC was used in adsorption mode (as a complement to the biological removal from a mixed liquor) rather than solely as a support for biomass growth. In addition, the experimental conditions, similarly to most published literature to date, involved the use of polluted surface water.

Lebeau *et al.* (1998) used an immersed PAC-UF (ultrafiltration) bioreactor fed by clarified water and observed moderate BDOC removals (25%). When the feed water was switched to raw water, BDOC removals increased to 86%, most likely because of the higher initial BDOC concentration (1.2 vs. 0.4 $mg\,l^{-1}$) in the feed water. The use of a hybrid process for the treatment of ozonated surface water was investigated by Williams & Pirbazari (2007). Although the objective was to work under biological mode, their operating conditions (low SRT and 5 $mg\,l^{-1}$ PAC dosage) suggest that adsorption was partly responsible for the observed performance. The work of Seo *et al.* (2004) involved a two-year operation of a PAC-MBR without PAC renewal (i.e. operating conditions normally leading to bacterial colonization of PAC). Complete nitrification and about 40% DOC removal were achieved once the adsorption capacity of the PAC was exhausted. However, neither assimilable organic carbon (AOC) nor BDOC were measured during this study.

The current project aimed to study the performance of a bioreactor fed with pretreated surface water (from the Pont-Viau drinking water treatment plant, Laval, Quebec) including conventional treatment and post-ozonation. These assays were intended to help in the selection of study conditions for a hybrid membrane process to be tested in an upcoming larger-scale pilot plant study.

The originality of this project relies on: (i) the operating conditions mainly targeted biodegradation (no PAC replacement); (ii) the good quality of influent water; and

(iii) the comparison of two different PAC mean diameters. In theory, a smaller PAC diameter should offer increased surface area for bacterial colonization and higher adsorption capacity. However, a larger PAC would be easier to separate from the process stream if ever the bioreactor was to be dissociated from the membrane process (as would be done using pressurized UF membranes, for example).

MATERIALS AND METHODS

Experimental set-up

Five PAC reactors, called bioreactor hereafter, were constructed for this project. Figure 1 presents a schematic of the small-scale pressurized bioreactors that were used during this study, while Figure 2 presents a picture of the reactor(s). The bioreactors are made of clear PVC plastic and have a volume of 1 l. Influent water is admitted at a flow rate of 4 litres per hour (HRT = 15 min) by the side of the bioreactor in which a blade stirrer (65 rpm) prevents PAC settling. Effluent water exits by the top of the bioreactor by passing through a 10-μm nylon sieve, acting as a solid–liquid barrier. Near the end of the project, the impact of HRT was tested by increasing its value to 60 min (by lowering the flow rates of the five pilots from 4 to 1 l h^{-1}) and leaving it to stabilize overnight. The following morning, effluent samples were collected and the flow rates were progressively increased to yield a HRT of 30 and 15 min. Between each increment, bioreactors were left to stabilize for the equivalent of 3 HRTs before sampling.

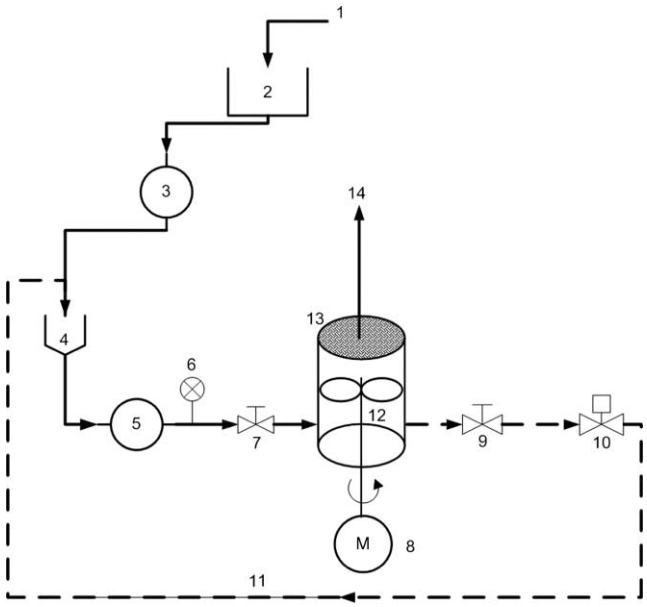

Figure 1 | Schematic of the experimental set-up. 1: Influent post-ozonated water; 2: 20-l tank used to strip residual dissolved ozone; 3 and 5: peristaltic pumps; 4: accumulation funnel for ozonated water and sludge recirculation; 6: pressure gauge; 7: normally open entry valve; 8: variable speed motor; 9: normally closed sludge discharge valve; 10: normally closed solenoid valve; 11: sludge recirculation line; 12: bioreactor; 13: 10 μm sieve; 14: bioreactor effluent water.

The influent water, post-ozonated water from the Pont-Viau filtration water treatment plant (Laval, Quebec), had an ozone residual of 0.34 ± 0.15 ppm. The characteristics of the feed water are summarized in Table 1. The influent water had undergone a conventional treatment (alum + sludge blanket clarifiers + dual media granular filtration) and exhibited low turbidity, pH and alkalinity and low nutrient concentrations. A 20-l reservoir (48 minutes retention time) was installed ahead of the bioreactors in order to reduce the ozone residual below 0.1 ppm. However, this set-up increased the water temperature, which explains why the influent water did not reach temperatures below 6.3°C while water temperatures as low as 0.5°C are usually reached during winter at this location.

Two backup bioreactors (20 g l^{-1} of each PAC size) consisting of 16-litre reservoirs completely mixed and aerated were installed in the lab. These reservoirs were used as a source of colonized PAC in case of losses on the online bioreactors. After a start-up period of bacterial enrichment using treated wastewater, the reactors were supplemented weekly with an autoclaved yeast solution to provide a similar DOC concentration as the online reactors. A yeast solution was chosen instead of glucose as it is a more complex source of carbon and it also implicitly contains nitrogen, phosphorus and other trace nutrients.

Operating conditions

The bioreactors were operated continuously for 161 days. They were initially filled with virgin (uncolonized) PAC. The internal pressure and the temperature were monitored on a routine basis. The bioreactors were designed to withstand pressures up to 140 kPa (20.3 psi). Once the bioreactor's internal pressure reached 70 kPa (at an average frequency of 5 days of continuous operation), it was manually

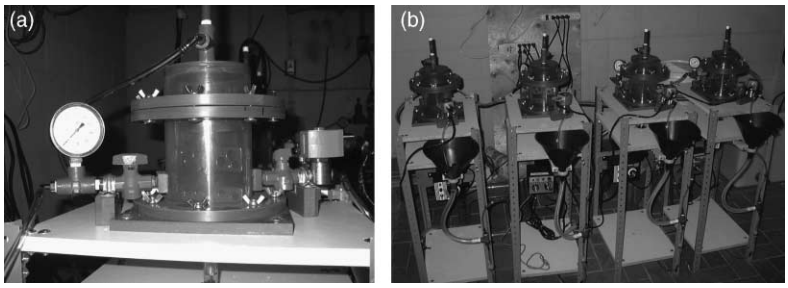

Figure 2 | (a) Side view of one of the bioreactors; (b) four of the five bioreactors shown side by side.

depressurized by opening a valve located on its lower side (item 10 in Figure 1). This operation reduced the build-up head losses by destabilizing the cake layer accumulated on the 10-μm sieve. By doing so, a portion of the PAC slurry was extracted from the bioreactor and reinjected in the influent water by passing in the solids recirculation line (Figure 1). However, this procedure did not completely eliminate head loss accumulation. On average, the sieves were replaced four times with new ones over the 161 days of operation.

Experimental design

Table 2 summarizes the five conditions tested in the different bioreactors. Four of these five bioreactors were operated without PAC renewal. Two independent variables, PAC concentration (5 vs. 25 $g\,l^{-1}$) and PAC mean diameter (25 vs. 200 μm) were compared. The last bioreactor (BR5) served as a reference for which a 30-day SRT was targeted. The actual SRT, based on dry weight measurement of extracted PAC, varied from 30 to 37 days. After the first month of operation, 25% of the PAC within the BR5 bioreactor was replaced with fresh PAC on a weekly basis (equivalent to a PAC dose of 8.5 $mg\,l^{-1}$ or a 3% solid wasting). Except for the diameter, the tested PAC was identical for all five bioreactors: a wood-based material, PicaHydro®, provided by *Pica*®. The 200-μm PAC (PicaHydro® L30-260) was specifically ground by *Pica*® for this project (median diameter between 210 and 260 μm) while the 25-μm is PicaHydro® LP39 (mean diameter of 24.0 μm and median 18.7 μm). This PAC is microporous and macroporous.

Analytical methods

The influent and effluent water quality of the bioreactors was monitored routinely over the course of the study. The sampling frequency varied from weekly to monthly for total numbers of samples ranging from 9 to 14 for each parameter.

DOC and BDOC analysis were performed using a TOC-meter (Sievers 5310 C) on 100 ml samples that had previously been filtered on prewashed (with 1 litre of ultrapure water), 0.45-μm pore-size filters (PALL

Table 1 | Characteristics of the feed water

Parameters	Average ± SD	N	Unit
Dissolved organic carbon (DOC)	2.93 ± 0.20	14	$mg\,C\,l^{-1}$
Biodegradable organic carbon (BDOC)	0.43 ± 0.16	9	$mg\,C\,l^{-1}$
UV_{254}	0.032 ± 0.009	14	cm^{-1}
Ammonia ($N\text{-}NH_4$)	61.9 ± 11.6	9	$\mu g\,N\text{-}NH_4\,l^{-1}$
Alkalinity	31	1	$mg\,CaCO_3\,l^{-1}$
Turbidity	0.10 ± 0.05	14	NTU
pH	6.67 ± 0.07	9	

SD: standard deviation.

Table 2 | Summary of the experimental design

Bioreactors	PAC concentration ($g\,l^{-1}$)	PAC diameter (μm)	SRT* (days)
BR1	5	25	Variable†
BR2	5	200	Variable†
BR3	25	25	Variable†
BR4	25	200	Variable†
BR5	25	200	30

*Solid retention time.
†Increasing progressively from 0 to 161 days due to the absence of PAC renewal.

Supor450® PES). BDOC was measured using a slightly modified version of the method developed by Servais *et al.* (1989). Briefly, the assay consisted of measuring the DOC concentration decrease following a 30-day incubation in the dark in the presence of excess nutrients ($10\,\mu g\,l^{-1}$ P as KH_2PO_4, $200\,\mu g\,l^{-1}$ N as $(NH_4)_2SO_4$) and a small, 1-ml raw water seed (1% in volume) prefiltered on $2.7\,\mu m$ filter (WHATMAN GF/D fibreglass, to remove micro-zooplankton) in order to provide some biomass. Ammonia nitrogen (NH_3 and NH_4^+ measured as N) was measured using the indophenol colorimetric method (AFNOR 1990). This method has an excellent accuracy ($\pm 3\,\mu g\,l^{-1}$) and a low detection limit ($5\,\mu g\,l^{-1}$). Table 3 summarizes the experimental methods used to evaluate process performance.

Monitoring of PAC colonization

PAC colonization was assessed at the end of the study using a respirometric assay adapted from an existing methodology for BAC filters (Urfer & Huck 2001). The assay consists of measuring the total mass of oxygen consumed in 5 hours by a given mass of activated carbon in the presence of substrate. While a mixture of aldehydes was used by Urfer & Huck (2001), yeast extract was used as substrate during this project because of concerns related to the toxic effect that aldehydes (e.g. formaldehyde) may induce at the concentration needed to reach saturation condition.

A total of 9.0 g of PAC (wet weight) was recovered from each bioreactor using an 8-μm filter (Whatman 40, 11 cm, Fisher Scientific). This mass was divided in triplicate bottles containing 600 ml sterile saline (0.85%) water, 30 ml of a 2% (W/V) yeast extract solution (Bacto™ Yeast Extract from BD) and 0.16 g of nitrification inhibitor (2-chloro-6-(trichloromethyl) pyridine). Bottles were transferred in a respirometer (Challenge AER-200) where the oxygen uptake rate was monitored over a 5-h period. Agitation (400 rpm) and temperature (20°C) were kept constant during the procedure. Control samples and blank samples consisted of adding autoclaved PAC or no PAC in the bottles. Final results are expressed as mg $O_{2(5\,h)}$/g PAC (dry weight). The dry weight/wet weight ratios were, respectively, 0.38 and 0.33 for the 25-μm and 200-μm PAC. The average coefficient of variation of this method was calculated as 6.9% amongst triplicate bottles.

Impact of PAC colonization on its settleability

At the end of the project, approximately 0.3 g (wet weight) of colonized or virgin PAC were added to Imhoff cones in

Table 3 | Summary of analytical methods

Parameters	Description	N*	References
$N\text{-}NH_4$	Indophenol colorimetric method	9	AFNOR 1990 NF T 90–015
DOC	UV/Persulfate oxidation method. Sample prefiltered through a prewashed 0.45-μm filter (PALL Supor450® PES)	14	*Standard Methods* 2005, 5310C
BDOC	DOC sample amended with nutrient, seeded with prefiltered raw water and incubated for 30 days in the dark	9	Servais *et al.* 1989
UVA_{254}	Spectrometer lecture of sample prefiltered through a 0.45-μm filter (PALL Supor450® PES)	14	*Standard Methods* 2005, 5910B
Alkalinity	Titration method	2	*Standard Methods* 2005, 2320B
Turbidity	Nephelometric method, hach turbidimeter, model 2100 An	12	*Standard Methods* 2005, 2130B
O_3 residual	Indigo trisulfonate colorimetric method	13	*Standard Methods* 2005, 4500B

*Number of weeks for which analyses were conducted.

order to evaluate whether the colonization had increased the settling rate of PAC particles. Arbitrarily, the total volume of settled PAC was recorded after 45 min and was used as a basis of comparison.

RESULTS

The operation of the bench-scale bioreactors started on 27 October 2008, when the influent water was still relatively warm (≈16°C). During the entire operation period, the average temperatures entering and exiting the bioreactors were 10.3°C and 12.3°C, respectively. The two backup bioreactors with colonized PAC were needed four times during the study (BR1 on days 39 and 81, BR4 on day 87 and BR5 on day 74). Each time the sieve was damaged and some PAC was lost. Note that the dates of PAC losses and replacements are circled in Figure 3. As no official method exists to measure biomass on PAC, colonization of the PAC in the backup reactors was verified visually using Baclight™ analysis. Although colonized PAC was certainly different, it was hypothesized that it was a better alternative than replacing with virgin PAC or having a lower PAC concentration. As will be seen later, these PAC replacements did not appear to have had an impact on performance.

Removal of organic matter

Figure 3 presents the removals of DOC, BDOC, UVA_{254} and $N\text{-}NH_4$ during the 161-day study period. DOC removals rapidly declined in the first weeks of operation because of the exhaustion of PAC adsorption capacity. For the $5\,g\,l^{-1}$ reactors, removals decreased from 10 to 0% in three weeks while for the $20\,g\,l^{-1}$ reactors, they decreased from 20–25% to about 10% in the same period. After 30

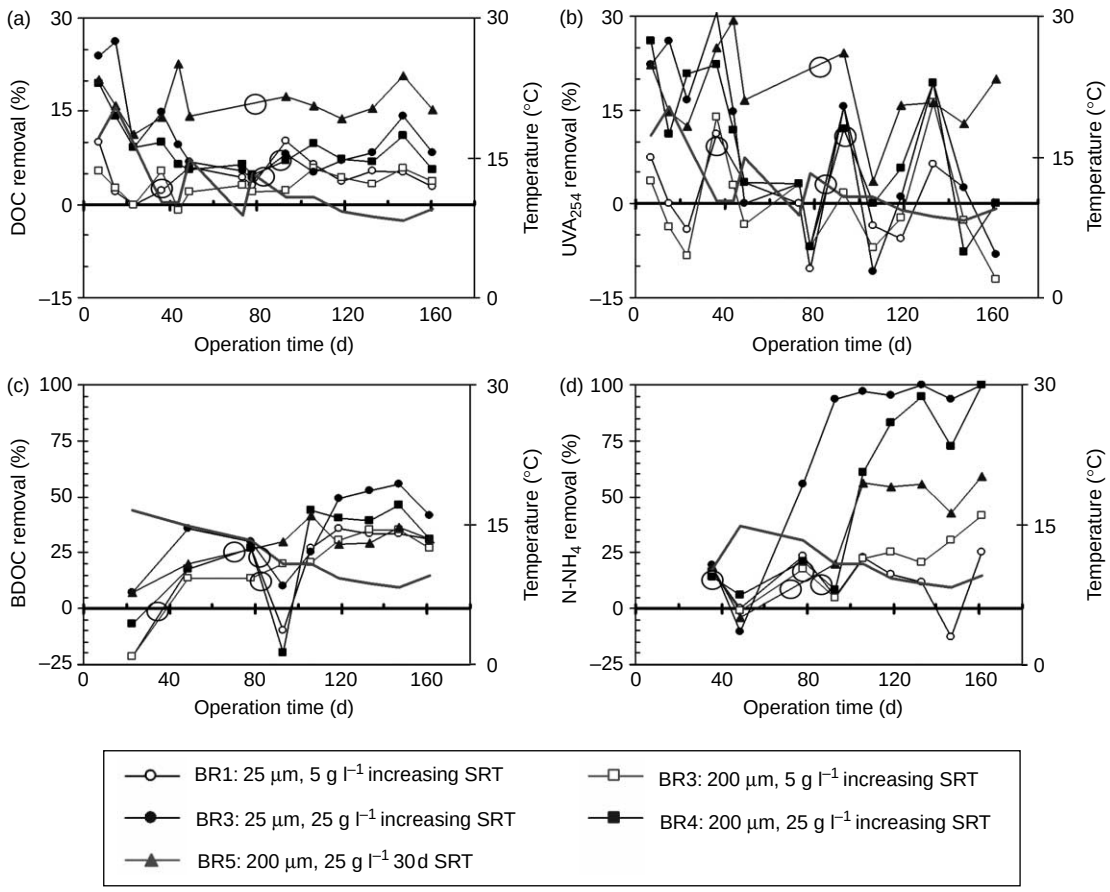

Figure 3 | Removal of: (a) DOC, (b) BDOC, (c) UVA_{254} and (d) $N\text{-}NH_3$. *Note*: PAC loss and replacement events are presented by circles.

days, fresh PAC was added to the BR5 reactor maintaining some adsorption capacity, which explains the higher average DOC removal of 17% observed in this reactor. DOC removals were averaging 7.4% during that period for the other 25 g l^{-1} reactors (BR3 and BR4).

As for UVA_{254}, the ozonated feed water measure was already low (0.032 cm^{-1} on average). The precision of the method is limited by the relative standard deviation (which is estimated at 6% or higher for low DOC waters) (*Standard Methods* 2005). The UVA_{254} removals or increases in the order of 8% calculated are therefore within the precision of the method for the UVA_{254} range measured. No significant removals could thus be calculated.

On average, BDOC represented 15.2 ± 5.8% of the DOC in the influent. On one occasion, this fraction was lowered to only 3% due to a one-week routine shutdown of the ozonation process for operation and maintenance. This event had important impact on the BDOC removals for BR1, BR3 and BR4, as seen on Figure 3(b) at $t = 90$ days. BR2 (5 g l^{-1}, 200 μm) was able to maintain a 20% removal; however the BDOC standard deviation was unusually high (17%). When ozonation resumed, BDOC removals returned to the values observed before this event for BR1 to BR4. BR5 (adsorption mode) maintained a good performance of 30% BDOC removal during this event. However, a sieve failure had resulted in the addition of colonized back-up PAC one week before, a situation that may have provided increased stability to the process. Globally, BDOC removals increased through time even for BR5, which would be expected for biological processes. It is important to mention that, although adsorption is favoured in the 30-day SRT reactor, biological activity also occurs.

Figure 4 summarizes the average performance once the bioreactors reached stable performance; that is, after 100 days of operation (or the last five sampling campaigns). Stable performance was defined relative to ammonia removal, the parameter that took the longest period to stabilize.

As expected, the bioreactor with a constant SRT of roughly 30 days (BR5), maintained a statistically higher performance than the other four biological bioreactors for DOC removals. Under stable conditions, average DOC removals varied from 5 to 9% in BR1 to BR4 and were slightly higher in BR5 (16%). UVA_{254} removals (not shown) were negligible (<3%) for BR1 to BR4, reaching 14% for

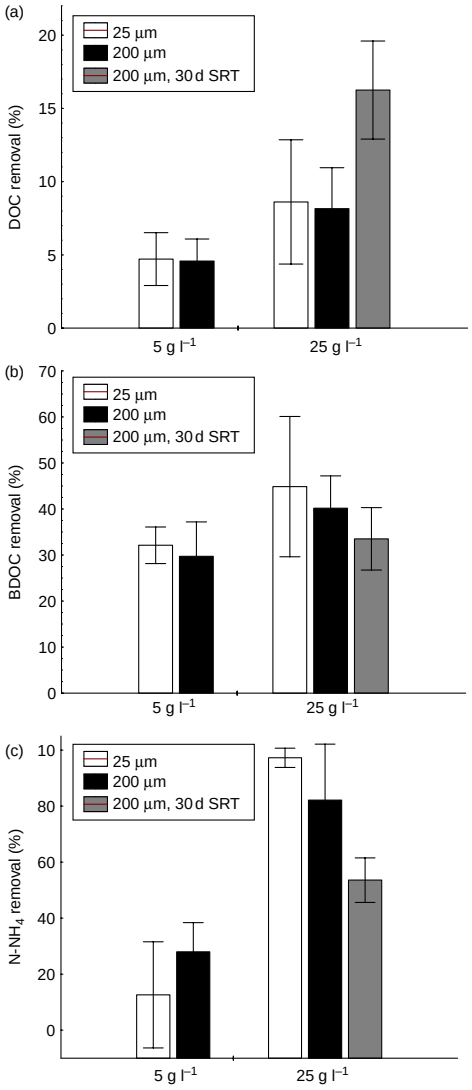

Figure 4 | Average removal under stable conditions (after 100 days of operation) for: (a) DOC, (b) BDOC and (c) $N\text{-}NH_4$. Error bars denote 95th confidence intervals. Abscissa represents PAC concentration.

BR5. Although the difference is not statistically significant, it could be explained by the fact that UVA_{254} is preferentially removed through adsorption rather than biodegradation. Indeed, the aromaticity of hydrophobic organic matter has been shown to be closely related to the UVA_{254} (McKnight *et al.* 1997). Preferential removal of UV over DOC was observed using PAC adsorption (Oh *et al.* 2007).

Under stable conditions, the bioreactors performing in biodegradation mode using 25 g l^{-1} of PAC were more efficient (40–45% removals) for removing BDOC than the bioreactor with a 30-d SRT (34%), suggesting that longer

SRT improved BDOC removal. The observed difference is statistically significant when comparing the two 200 μm PAC (BR4 and BR5). The bioreactors with 5 g l^{-1} of PAC offered good BDOC removals (30–32%) considering the fivefold lower PAC concentration.

Ammonia removal

Initially, ammonia removal was generally low for all bioreactors (Figure 3(d)). However, the performance of the 25 g l^{-1} and > 100-day SRT bioreactors reached 82–97% under stable conditions (Figure 4(c)). Nitrification started more rapidly in the bioreactor with the smallest PAC (25 g l^{-1}, 25 μm). It is hypothesized that the 25 μm PAC initially offered more surface area for biomass colonization. Full nitrification was achieved after three months of operation for the 25-μm PAC while it took four months for the 200-μm PAC (Figure 3(d)). Under stable conditions (Figure 4(c)), the bioreactor with PAC renewal (BR5) showed a lower performance (54%) although this was still superior to BR1 and BR2 (13–28%), the two bioreactors with 5 g l^{-1} of PAC. Once more, BR5 shows a mixture of adsorption and biodegradation. Nitrification performance appeared more sensitive to the PAC concentration than did BDOC with removals significantly lower for the 5 g l^{-1} bioreactors.

Impact of PAC diameter, concentration and SRT on process performance

A repeated measure ANOVA (Statistica 7.0, Statsoft, USA) was performed using data under stable conditions in order to test whether the influence of PAC diameter, concentration and SRT significantly affected the process performance. The PAC diameter had no significant impact ($p > 0.05$) on the removal of BDOC, UVA_{254}, DOC and N-NH_4. However, a higher PAC concentration significantly ($p < 0.01$) improved process performance for N-NH_4, BDOC and DOC removals. Finally, maintaining a 30-day SRT improved the stable performance of DOC removal while it negatively influenced N-NH_4 and BDOC removals ($p < 0.01$). UVA_{254} removal was superior in the 30-day SRT bioreactor (14 vs. 4%), but this difference was not statistically significant ($p = 0.09$).

Impact of hydraulic residence time (HRT) on process performance

In order to evaluate the influence of HRT, it was increased from its initial value of 15 to 30 and finally 60 min on 23 March 2009. Figure 5 illustrates this impact on the average removal of ammonia and BDOC. Considering that the diameter had no significant impact on the tested removals (as stated above), only the PAC concentrations (5 vs. 25 g l^{-1}) were used as a comparison parameter to determine the HRT impact (average BR1-BR2 vs. BR3-BR4, 1 sample per reactor in duplicate for ammonia and triplicate for BDOC). It is worth noting that, when the HRT was increased, the temperature of the effluent water increased slightly as well (8.3°C for a 15-min HRT, 9.5°C for a 30-min HRT and 12.2°C for a 60-min HRT).

Globally, increasing HRT improved the removal of ammonia and BDOC. The largest impact was observed when increasing HRT from 15 min to 30 min. BDOC removals increased from 34 to 42% (5 g l^{-1}) and 51 to 57% (25 g l^{-1}) ($p < 0.01$), while ammonia removals increased from 5 to 54% (5 g l^{-1}) and 83 to 94% (25 g l^{-1}) ($p < 0.01$). The removals observed at 60 min were not statistically different from those at 30 min ($p > 0.05$). Ammonia removal also appears more sensitive to HRT than BDOC, especially at a lower concentration of PAC (5 g l^{-1}). The lower efficiency of the 5 g l^{-1} bioreactors for ammonia removal presented in Figure 4 could be partly mitigated by increasing contact time as shown in Figure 5, although the performance does not equate that of the

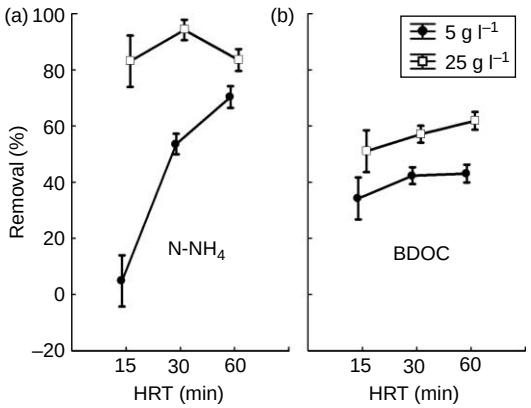

Figure 5 | Influence of HRT on the removal of: (a) ammonia and (b) BDOC. Results present the average of BR1–BR2 (5 g l^{-1}) and BR3–BR4 (25 g l^{-1}). Error bars denote 95th confidence intervals.

$25\,g\,l^{-1}$ bioreactors. Finally, the impact of HRT on BR5 (SRT = 30 d) was not statistically different from BR4 (SRT variable) (data not shown).

Evaluation of PAC colonization using respirometry

At the end of the study period, the five bioreactors were opened and the PAC was recovered to perform a respirometric assay. Figure 6 summarizes the results of the specific oxygen consumption test ($mg\,O_{2(5\,h)}/g\,PAC$) and compares them to the average normalized BDOC removals (% BDOC/g PAC) under stable operating conditions.

Specific O_2 consumption over a 5 h period varied from 1.2 to 5.0 $mg\,O_{2(5\,h)}/g\,PAC$. The PAC diameter did not influence O_2 consumption ($p > 0.05$). The lowest value was obtained on the bioreactor with a constant SRT of 30 days, a result in agreement with the lower biological PAC colonization expected under this condition. Interestingly, it was observed that the bioreactors with the lowest PAC concentration exhibited a significantly higher specific O_2 consumption (4.7–5.8 vs. 2.3 $mg\,O_{2(5\,h)}/g\,PAC$) than the ones at high concentration. We suggest that the substrate (BDOC) availability is higher for the bacterial biomass in the low PAC bioreactors, a situation that favours the development of a more active biomass. This hypothesis is supported by the correlation established in Figure 6, which indicates that the specific BDOC removals (% removal/g PAC) increased with higher biomass activity ($mg\,O_{2(5\,h)}/g$ PAC). In fact, the specific BDOC removal was actually four times higher in the lowest PAC concentration bioreactors. These results explain why the BDOC removals, although significantly impacted by the PAC concentration within the bioreactor, were still acceptable at the lowest PAC concentration. When comparing the total oxygen consumption between the $25\,g\,l^{-1}$ 30-day SRT reactor ($25\,g\,l^{-1} \times 1.2\,mg\,O_2/g\,PAC = 30\,mg\,O_2\,l^{-1}$) and the $5\,g\,l^{-1}$ reactors ($5\,g\,l^{-1} \times 5.2\,mg\,O_2/g\,PAC = 26\,mg\,O_2\,l^{-1}$), it is very similar and consistent with the BDOC removal presented in Figure 4. It is proposed that specific O_2 consumption could be used to monitor heterotrophic biomass activity within hybrid membrane processes.

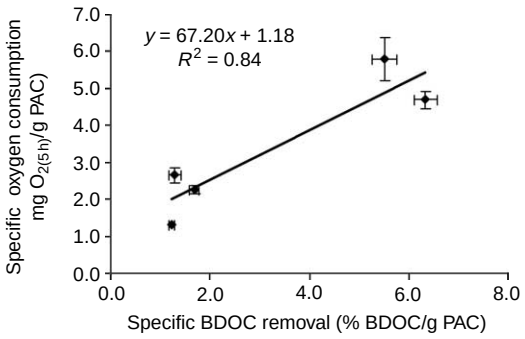

Figure 6 | Correlation between specific oxygen consumption ($mg\,O_{2(5\,h)}/g\,PAC$) and BDOC removal per gram of PAC. Error bars denote 95th confidence intervals.

Impact of PAC colonization on its settleability

The most striking difference in PAC settleability was observed by comparing the 25-μm virgin and colonized PAC. In order to assess this impact, the ratios between the volumes of solids settled after 45 min divided by the mass of PAC initially added were calculated for both PAC. This ratio was $4.5\,ml\,g^{-1}$ for colonized PAC and less than $2.0\,ml\,g^{-1}$ (detection limit) for virgin PAC. For the 200-μm, the ratios also increased from 4.3 to $6.8\,ml\,g^{-1}$ for virgin and colonized PAC, respectively. These results indicate that PAC colonization will lead to improve settleability characteristics, an issue which should be accounted for in the design of full-scale hybrid membrane processes. Particle counts were also performed to compare the PAC size distribution for virgin and colonized PAC using a Brightwell DPA4000 particle counter. This analysis confirmed an increase in particle size distribution: the volume fraction of particles less than 10 μm decreased from 19% for virgin PAC to 13% for colonized PAC.

DISCUSSION

The hybrid membrane process has mainly been studied under conditions where adsorption on PAC is the dominant mechanism of organic matter removal. In this study, our objective was to work under conditions where PAC can support an active heterotrophic biomass for BDOC removal and nitrifying biomass for nitrification. Our results indicate that complete nitrification, 30–50% BDOC and 5–10% DOC removals may be achieved under a biological PAC mode of operation.

Lebeau *et al.* (1998) conducted a similar research using clarified surface water. Using a 30-day SRT and a 43 min HRT, they observed somewhat similar results: complete nitrification, 25% BDOC and 41% DOC removals at water temperatures of 1–15°C. As the SRT was maintained at 30 days, these performances represent a combination of adsorption and biodegradation. The fact that the DOC removal is actually higher than the BDOC removal suggests that adsorption also played a role in the performance during their study.

Williams & Pirbazari (2007) operated a mini pilot-scale hybrid process (SRT lower than 20 days, HRT unknown) with $3\,g\,l^{-1}$ of acclimated PAC fed with ozonated surface water (DOC = $2.9\,mg\,C\,l^{-1}$). They observed DOC removals of 15–30% and AOC removals around 90% at 20°C. AOC removal is not directly comparable to BDOC removal and the former is expected to be higher than the latter since AOC mostly reflects the easily assimilable organic compounds (Prévost *et al.* 2005). In addition, the fairly short SRT suggests that adsorption was also playing a role, as pointed out by Williams & Pirbazari (2007).

Finally, Seo *et al.* (2004) performed a two-year evaluation of a $40\,g\,l^{-1}$ PAC-MBR hybrid process fed by conventionally treated surface water. As PAC was not replaced, DOC removal progressively decreased from > 80% to about 40%. Similarly to previous results from Seo *et al.* (2002), complete nitrification was also observed under 10°C even though feed water was spiked with high concentrations of ammonia ($1–7\,mg\,N\text{-}NH_4\,l^{-1}$). A few months were necessary to allow for the development of a nitrifying biomass. These authors also observed the adverse impact of low pH (<6.0) on nitrification performance.

In summary, evidence has shown that operating a HMP under mostly biological mode will lead to reduced DOC removal but improved nitrification and slightly improved BDOC removal. For example, during this project, operating the bioreactors with an extended SRT (100–160 days), compared with 30 day, decreased DOC removal from 16 to 8% but increased nitrification and BDOC removals from 54 to 84% and from 33 to 40%, respectively. BDOC removal is known to be an important factor to achieve biostability (Laurent *et al.* 1997). One attractive characteristic of this process concerns the possibility to vary the SRT in order to respond to seasonal fluctuations of water quality. The hybrid-process could be operated with lower SRT during periods where adsorption is needed (for pesticide, taste and odours or DBP precursors). Operating with lower SRT does, however, imply higher operating costs due to the increased PAC replenishment needed.

The feed water used in this study was of higher quality (low BDOC, low $N\text{-}NH_4$) than other pilot studies, which most likely explains the slightly lower performance observed under stable conditions than in previous pilot studies. Our study demonstrates the impact of HRT as increasing it from 15 to 30 min led to higher performance. In comparison, Lebeau *et al.* (1998) were using a 43-min HRT. The role of HRT on process performance is coherent with current knowledge on biological filtration on BAC which has shown that empty bed contact time was a dominant parameter (Urfer *et al.* 1997).

Under adsorption mode, it has already been demonstrated that a higher PAC concentration (40 vs. $4\,g\,l^{-1}$) improves DOC removal (Kim *et al.* 2007). Under biological mode, the PAC concentration should influence the quantity of biomass available in the bioreactor for biodegradation. Our results clearly indicate that a high PAC concentration should also be targeted for biodegradation, although a compromise has to be made in relation to the impact of PAC on membrane fouling. Nevertheless, Seo *et al.* (2004) has shown that long-term operation was possible with as much as $40\,g\,l^{-1}$. Interestingly, our respirometry assays indicate that increasing PAC concentration from 5 to $25\,g\,l^{-1}$ will not lead to a fivefold increase in heterotrophic active biomass, probably reflecting the lower food/biomass ratio while operating at higher PAC concentration.

As for the diameter impact, a higher adsorption is expected while using a finer PAC (Matsui *et al.* 2007). In theory, a higher surface area will also be available for biomass colonization with a finer PAC while operating under biological mode. While nitrification started more rapidly on a 25-μm PAC, minimal differences in performances were observed between the two PAC under stable conditions. Respirometry confirmed the absence of difference between the two PAC mean diameters with respect to heterotrophic biomass colonization, although a difference may exist with respect to the nitrifying biomass. After 161

days of operation, we observed that the PAC settleability was greatly improved, indicating that PAC diameter may not be an adequate indicator of surface area available for colonization. The improved settleability indicates a certain level of aggregation between PAC particles. Assuming that aggregation was limited by the shear forces in the reactor, the two PAC could have ended up with similar aggregate size, which could explain the lack of differences between the two PAC diameters. This topic warrants additional studies for two reasons. First, this observation suggests that attention should be given to maintain the PAC in suspension within the bioreactors. Second, the increased settleability of the PAC suspension would allow an easier separation of the bioreactors from the membranes in order to allow the use of pressurized membranes that do not tolerate such high solids loadings as immersed membranes.

CONCLUSIONS

Five PAC bioreactors were operated for 161 days to evaluate the impacts of SRT, PAC diameter and concentration on NOM removal and nitrification.

The following conclusions were derived from these assays:

- The concentration of PAC in the bioreactors is a key process parameter. The bioreactors with high PAC concentration ($25\,g\,l^{-1}$) were more efficient for nitrification, DOC and BDOC removals. However, full nitrification was only observed after 90 days in bioreactors with $25\,g\,l^{-1}$ of PAC.
- The PAC mean diameter (25 vs. 200 μm) did not significantly affect BDOC, DOC and N-NH_4 removals under stable conditions, although nitrification was initiated more rapidly using a 25-μm PAC. Colonization of the PAC resulted in particle aggregation which affected the settling properties. This phenomenon may have contributed to the absence of difference between PAC diameters on process performance.
- Increasing hydraulic residence time from 15 to 30 minutes improved BDOC and N-NH_4 removals, with greatest improvements for the low PAC concentration ($5\,g\,l^{-1}$) reactors. However, no additional significant gain in performance was obtained by increasing HRT from 30 to 60 min.
- Reducing the SRT from 100–161 to 30 days improved DOC and UVA_{254} removals but reduced BDOC and ammonia removals.

The overall performance observed during this study supports the concept that a PAC-MF hybrid process could be operated under biological mode from a water quality standpoint. Further studies should address the issue of PAC colonization on its settleability characteristics as this could have an important impact on the design of full-scale bioreactors. Impacts of colonized PAC on membrane operation should also be studied in detail in order to evaluate the real potential of this technology.

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REFERENCES

AFNOR (Association Française de Normalisation) 1990 *Eaux Méthodes d'Essai, Ammonia Dosage by Indophenol Colorimetric Method, Method # T90-015*, 4th edn. AFNOR, Paris.

Elhadi, S. L. N., Huck, P. M. & Slawson, R. M. 2006 Factors affecting the removal of geosmin and MIB in drinking water biofilters. *J. Am. Water Works Assoc.* **98**(8), 108–119.

Huang, H., Schwab, K. & Jacangelo, J. G. 2009 Pretreatment for low pressure membranes in water treatment: a review. *Environ. Sci. Technol.* **43**(9), 3011–3019.

Kim, H.-S., Takizawa, S. & Ohgaki, S. 2007 Application of microfiltration systems coupled with powdered activated carbon to river water treatment. *Desalination* **202**(1–3), 271–277.

Laurent, P., Servais, P., Prévost, M., Gatel, D. & Clément, B. 1997 Testing the SANCHO model on distribution systems. *J. Am. Water Works Assoc.* **89**(7), 92–103.

Lebeau, T., Lelièvre, C., Buisson, H., Cléret, D., Van de Venter, L. W. & Côté, P. 1998 Immersed membrane filtration for the production of drinking water: combination with PAC for NOM and SOCs removal. *Desalination* **117**, 219–231.

Lebeau, T., Lelièvre, C., Wolbert, D., Laplanche, A., Prados, M. & Côté, P. 1999 Effect of natural organic matter loading on the atrazine adsorption capacity of an aging powdered activated carbon slurry. *Water Res.* **33**(7), 1695–1705.

Lee, N., Amy, G., Croue, J. P. & Buisson, H. 2005 Morphological analyses of natural organic matter (NOM) fouling of low-pressure membranes (MF/UF). *J. Membr. Sci.* **261**(1–2), 7–16.

Matsui, Y., Yamagishi, T., Terada, Y., Matsushita, T. & Inoue, T. 2007 Suspended particles and their characteristics in water mains: developments of sampling methods. *J. Water Suppl. Res. Technol.–AQUA* **56**(1), 13–24.

McKnight, D. M., Harnish, R., Wershaw, R. L., Baron, J. S. & Schiff, S. 1997 Chemical characteristics of particulate, colloidal, and dissolved organic material in Loch Vale Watershed, Rocky Mountain National Park. *Biogeochemistry* **36**(1), 99–124.

Newcombe, G. & Nicholson, B. 2002 Treatment options for the saxitoxin class of cyanotoxins. *J. Water Sci. Technol. Water Supply* **2**(5–6), 271–275.

Oh, H. K., Takizawa, S., Ohgaki, S., Katayama, H., Oguma, K. & Yu, M. J. 2007 Removal of organics and viruses using hybrid ceramic MF system without draining PAC. *Desalination* **202**(1–3), 191–198.

Prévost, M., Laurent, P., Servais, P. & Joret, J.-C. 2005 *Biodegradable Organic Matter in Drinking Water Treatment and Distribution*, 1st edition. American Water Works Association, Denver, CO.

Sagbo, O., Sun, Y., Hao, A. & Gu, P. 2008 Effect of PAC addition on MBR process for drinking water treatment. *Sep. Purif. Technol.* **58**(3), 320–327.

Saravia, F., Naab, P. & Frimmel, F. H. 2006 Influence of particle size and particle size distribution on membrane-adsorption hybrid systems. *Desalination* **200**(1–3), 446–448.

Seo, G., Takizawa, S. & Ohgaki, S. 2002 Ammonia oxidation at low temperature in a high concentration powdered activated carbon membrane bioreactor. *Water Sci. Technol. Water Supply* **2**(2), 169–176.

Seo, G. T., Moon, C. D., Chang, S. W. & Lee, S. H. 2004 Long term operation of high concentration powdered activated carbon membrane bio-reactor for advanced water treatment. *Water Sci. Technol.* **50**(8), 81–87.

Servais, P., Anzil, A. & Ventresque, C. 1989 Simple method for determination of biodegradable dissolved organic carbon in water. *Appl. Environ. Microbiol.* **55**(10), 2732–2734.

Song, K.-Y., Park, P.-K., Kim, J.-H., Lee, C.-H. & Lee, S. 2009 Coupling effect of 17β-estradiol and natural organic matter on the performance of a PAC adsorption/membrane filtration hybrid system. *Desalination* **237**(1–3), 392–399.

Standard Methods for the Examination of Water and Wastewater 2005 21st edition, American Public Health Association/ American Water Works Association/Water Environment Federation, Washington, DC.

Tian, J., Liang, H., Yang, Y., Tian, S. & Li, G. 2008 Membrane adsorption bioreactor (MABR) for treating slightly polluted surface water supplies: as compared to membrane bioreactor (MBR). *J. Membr. Sci.* **325**(1), 262–270.

Tomaszewska, M. & Mozia, S. 2002 Removal of organic matter from water by PAC/UF system. *Water Res.* **36**(16), 4137–4143.

Urfer, D. & Huck, P. M. 2001 Measurement of biomass activity in drinking water biofilters using a respirometric method. *Water Res.* **35**(6), 1469–1477.

Urfer, D., Huck, P. M., Booth, S. D. J. & Coffey, B. M. 1997 Biological filtration for BOM and particle removal: a critical review. *J. Am. Water Works Assoc.* **89**(12), 83–98.

Vigneswaran, S., Guo, W. S., Smith, P. & Ngo, H. H. 2007 Submerged membrane adsorption hybrid system (SMAHS): process control and optimization of operating parameters. *Desalination* **202**(1–3), 392–399.

Watanabe, Y., Kimura, K. & Suzuki, T. 2000 Membrane application to water purification process in Japan: development of hybrid membrane system. *Water Sci. Technol.* **41**(10–11), 9–16.

Williams, M. D. & Pirbazari, M. 2007 Membrane bioreactor process for removing biodegradable organic matter from water. *Water Res.* **41**(17), 3880–3893.

Xia, S., Liu, Y., Li, X. & Yao, J. 2007 Drinking water production by ultrafiltration of Songhuajiang River with PAC adsorption. *J. Environ. Sci.* **19**(5), 536–539.

Zhang, M. M., Li, C., Benjamin, M. M. & Chang, Y. J. 2003 Fouling and natural organic matter removal in adsorbent/membrane systems for drinking water treatment. *Environ. Sci. Technol.* **37**(8), 1663–1669.

Zhao, P., Takizawa, S., Katayama, H. & Ohgaki, S. 2005 Factors causing PAC cake fouling in PAC-MF (powdered activated carbon-microfiltration) water treatment systems. *Water Sci. Technol.* **51**(6–7), 231–240.

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