



## Continuous and efficient removal of THMs from river water using MF membrane combined with high dose of PAC

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### ARTICLE INFO

#### Article history:

Accepted 4 September 2008

Available online 7 October 2009

#### Keywords:

PAC-MF hybrid system  
disinfection by-products  
trihalomethanes  
biodegradation  
biofiltration

### ABSTRACT

A combination of microfiltration (MF) membrane with a high concentration (40 g/L of the reactor) of powdered activated carbon (PAC) efficiently and continuously removed trihalomethanes (THMs) and total organic carbon (TOC) from river water for a period of two months. Without PAC, the membrane reactor was able to remove less than 18% of THMs and less than 5% of TOC; with PAC, 65 to 95% of THMs and TOC were removed. Even though the THMs concentration in the influent was steadily increasing (reaching 50 µg/L), THMs concentration in the effluents from the reactors with PAC were consistently below 15 µg/L. While the MF membranes alone could not remove organics, PAC and microbial activity in the biofilm deposited on the PAC particles assured long term and continuous removal of THMs. No additional PAC was added into or removed from the reactors during the filtration period. Operational parameters such as the backwashing of the membrane, interval of the filtration cycle and biological pretreatment of the river water had a small effect on the extent of THMs removal, but they increased the filtration time prior to membrane cleaning and improved the overall performance of the reactors.

Published by Elsevier B.V.

### 1. Introduction

It is well known that strong oxidants, such as chlorine and bromine, used to disinfect drinking water, can react with natural organic materials commonly present in the source water and produce several substances collectively known as disinfection byproducts (DBPs) that pose a risk to human health. DBPs are formed from naturally occurring humic and fulvic acids reacting with chlorine and/or bromine [1] and their formation depends on the type of water treatment process and the location at which the disinfectant is added in the treatment process [2,3]. The two best known types of DBPs are the trihalomethanes (THMs) and the haloacetic acids (HAAs) [4–6]. THMs, which include chloroform (CHCl<sub>3</sub>), bromodichloromethane (CHBrCl<sub>2</sub>), dibromochloromethane (CHBr<sub>2</sub>Cl) and bromoform (CHBr<sub>3</sub>), are the best recognized DBPs. They are present in various

proportions depending on the source of raw water, its physical characteristics and chemical composition, such as the nature and concentration of the organic matter, bromide concentration, temperature, and pH [7]. The efficient and continuous removal of these constituents during water purification is often frustrating.

In order to control the formation and discharge of DBPs, the US EPA introduced a three-stage disinfectant–disinfection byproduct rule (D/DBPR). The initial stage recommended a level of 100 µg/L for total THM (TTHM). Stage 1, finalized in November of 1998, established the maximum contaminant level (MCL) at 80 µg/L for TTHM. This is followed by Stage 2 (Final Rule July 2003) of the D/DBPR, which sets a lower contaminant level at 40 µg/L for TTHM. In addition, the sum of the ratios of concentration of each to its respective guideline value as can be seen in Eq. (1) should not exceed 1.

$$\frac{C_{\text{CHCl}_3}}{GV_{\text{CHCl}_3}} + \frac{C_{\text{CHCl}_2\text{Br}}}{GV_{\text{CHCl}_2\text{Br}}} + \frac{C_{\text{CHClBr}_2}}{GV_{\text{CHClBr}_2}} + \frac{C_{\text{CHBr}_3}}{GV_{\text{CHBr}_3}} \leq 1 \quad (1)$$

A number of studies demonstrated the efficient removal of THMs using powdered activated carbon (PAC) combined with microfiltration/ultrafiltration (MF/UF); MF alone was not able to remove DBP precursors [8]. Khan et al. [9,10] treated river water using a hollow-fiber MF membrane reactor and varying the PAC dose from 0 to 50 g/L

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of the reactor and demonstrated less frequent membrane cleaning, higher adsorption of bacteria, less effect of particle size on membrane fouling and higher removal rate of polymeric substances when an optimum PAC concentration of 40 g/L of the reactor was used. Jacangelo et al. [11] used PAC-UF to remove THMs from surface waters and observed that the addition of PAC (<400 mg/L of the reactor) reduced THMs concentration significantly but the extent of this reduction varied, because PAC concentration was not sufficient to remove bromide.

Researchers mostly use PAC in the pretreatment step, prior to membrane filtration or in combination with membrane filtration in the same tank [12], which did not always provide sufficient retention time to fully utilize the capacity of the activated carbon [13–15]. In addition, the accumulation of the activated carbon on the membrane's surface separates the components of foulants from the membrane's surface and reduces the fouling potentials [16,17]. Furthermore, the PAC cake layer formed on the membrane surface can retard fouling and prevent irreversible fouling of the membrane [12,18].

Some reports indicate that using PAC may reduce the rate of membrane fouling, but the reports are not consistent. Adham et al. [19] reported that the addition of 25 mg PAC/L of the reactor to a system treating a groundwater with ~3 mg/L DOC reduced the rate of membrane fouling by approximately one-third. However, Jack and Clark [20] used PAC/UF combination to treat low quality surface water and reported that when the membrane fouling occurred unexpectedly (apparently because the water quality had changed), increasing the PAC concentration actually increased the fouling rate further.

Existing reports show a trend: increasing concentrations of PAC improves the DBP removal in PAC/MF reactors, but such important factors as for how long DBPs can be removed continuously without replacing PAC and how much PAC needs to be used are still unknown. Hypothetically, this trend can be extrapolated expecting that high concentration of PAC, higher than those reported concentrations, thus further improve the removal efficiency of DBPs using a combined PAC/MF hybrid process.

The objective of this study was to develop and evaluate the effectiveness of combining a high concentration of PAC with MF membrane filtration to remove THMs and associated compounds continuously from a relevant source of natural water – the Tama River in Tokyo Metropolitan Area. In addition, several operational parameters such as the presence of PAC, filtration-cycle time, backwashing, or biofilter pretreatment of river water were varied to examine the effects of these parameters on the removal of THMs.

## 2. Materials and methods

### 2.1. Nature of influents

This study was conducted at a water treatment plant operated by the Tokyo Metropolitan Authority and located in the southwest region of Tokyo about 15 km from the main city treating water from the Tama River. The treated water is of low quality and for industrial use only. During the winter months, more than 80% of total flow of this river consists of the treated effluent from wastewater treatment plants located upstream. As a result, the dissolved organic matter and associated DBP precursors in the river water are much higher than those expected in a typical river. In addition, the river water is contaminated with bromide from photo-processing factories and other small-scale industrial sources. It is known that brominated THMs are formed when chlorine in the form of hypochlorous acid/hypochlorite ion ( $\text{HOCl}/\text{OCl}^-$ ) oxidizes bromide in the water to hypobromous acid/hypobromite ion ( $\text{HOBr}/\text{OBr}^-$ ). This mixture of HOCl and HOBr leads to the formation of the four THMs. In winter, when the tests were conducted, the natural flow rate of the Tama River decreases so that the concentration of bromide increases, which increases the THMs concentration in the raw water above 100  $\mu\text{g}/\text{L}$ .

The bench-scale experiments on the PAC-MF system were performed to evaluate the removal efficiency of THMs from this water.

### 2.2. Influent to the reactors

In the treatment process, the river water was pumped from the intake point to a series of sedimentation ponds. The water from the secondary sedimentation pond was used as the raw water and fed to four membrane reactors. The raw water was treated again by a biofilter and the effluent of the biofilter was fed to another membrane reactor. The reactor and feed system are shown schematically in Fig. 1. The biofilter consisted of a column packed with polypropylene pellets of 5 mm length, 3 mm inner diameter and 4 mm outer diameter. The filtration velocity of this biofilter was 320 m/d. Discharge from the biofilter was stored in a 100L reservoir prior to feeding to the reactor.

### 2.3. Membrane modules and reactors

Each reactor consisted of a hollow-fiber MF membrane module operated in suction mode to maintain constant flux. The hydrophilic membrane was made of polyethylene (Mitsubishi Rayon Co. Ltd., Japan). The nominal pore size was 0.1  $\mu\text{m}$ , and the outer and inner diameters were 0.41 mm and 0.27 mm, respectively. Each membrane module had 120 mm long 320 (16  $\times$  20) fibers with combined surface area of 0.05  $\text{m}^2$ . The membrane module was submerged in a reactor made of 5 mm thick plates made of polyvinyl chloride, with an effective volume of 5 L. The membrane modules were cleaned using Milli-Q water once received and soaked in fresh Milli-Q water prior to use. The experiment was carried out under ambient conditions (20–25  $^{\circ}\text{C}$ ).

Five reactors: R1, R2, R3, R4 and R5 were operated continuously for two months. The operational conditions of each reactor are specified in Table 1. PAC (coconut shell origin, JWVA K 113 - 1985, Shirotsagi-C, Takeda Chemical Co., Japan) was used as received without pretreatment. Reactors R1, R2, R4 and R5 were operated with 40 g of PAC/L of the reactor, while reactor R3 was used as control and operated without PAC. PAC was not added to or withdrawn from the reactors during the filtration period. The filtration flux of these reactors was kept at 20.8  $\text{L}/\text{m}^2/\text{h}$ , the flow rate was 25 L/day and the residence time was 0.2 day.

Based on the results of our previous study [9], the reactors were aerated continuously at 1000  $\text{L}/\text{m}^3/\text{min}$  and the air was delivered below the fiber modules to disturb the cake formation on the membrane surface, keep the PAC and other solids in suspension, and prevent rapid flux decline. Fig. 1(A) illustrates the continuous aeration around the membrane fibers inside reactor R3. Level sensors were used to ensure a constant reactor volume, while suction through the membrane module maintained a constant flow rate. Backwashing of the membrane was performed with the stored filtrate. The backwash-water reservoirs were cleaned once a week and refilled with the fresh filtrate. Transmembrane pressures (TMP) and backwashing pressures (BWP) were recorded using a data logger. Consistent with the results of our previous study [10], the backwashing flux was twice as high as the filtration flux to ensure adequate removal of the cake layer and lower filtration pressures during operation.

### 2.4. Analytical techniques

THMs concentrations in the influents and effluents from the reactors were measured by gas chromatography using an electron capture detector (GC-ECD, GC-17A, Shimadzu Co., Japan) and following the methods developed by Lepine and Archambault [21].

To measure the total organic carbon (TOC) and dissolved organic carbon (DOC), the influents and effluents of each reactor were homogenized (Branson Sonifier 450, Yamato, Japan) for 10 min keeping the duty cycle and output control constant at 50% and 4.0,

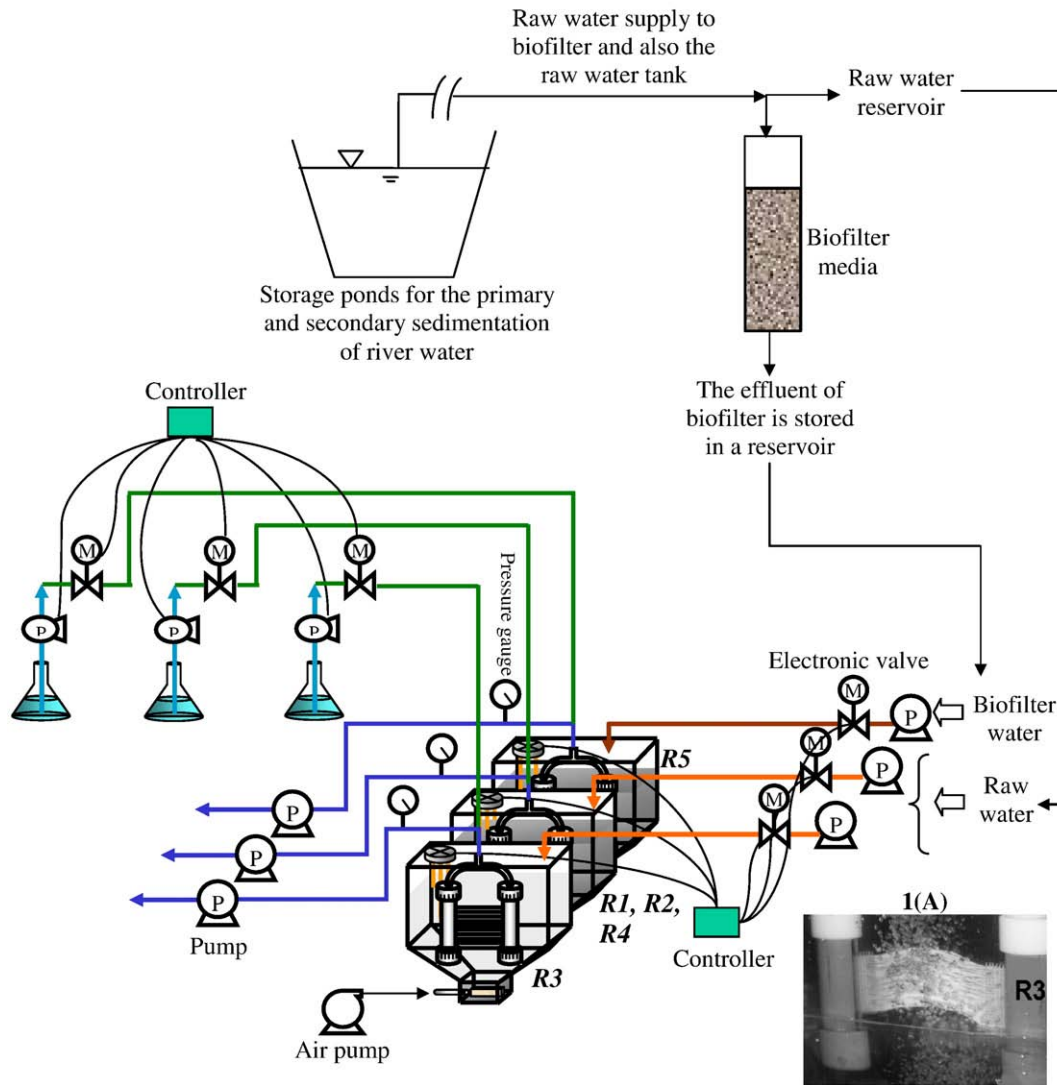


Fig. 1. Schematic diagram of the collection and pretreatment systems of the Tama River water and the PAC-MF hybrid system with backwash facilities. 1(A) shows the continuous aeration under the membrane fibers inside reactor R3 (raw without PAC).

respectively. This combination was found after several trials to produce the maximum concentrations of TOC and DOC. The homogenized samples were filtered through 0.45 μm pore size polyvinylidene fluoride (PVDF) filter for DOC measurement. Finally, 4 to 6 ml of homogenized samples (for TOC) and filtered samples after homogenization (for DOC) were treated with 50 to 60 μl of 2 M HCl and injected into a total organic carbon analyzer (TOC-5000A, Shimadzu Co., Osaka, Japan). UV<sub>260</sub> was monitored by a spectrophotometer (U-2010, Hitachi Co., Japan). The turbidity of the raw water was measured continuously by a turbidimeter (HACH 2100 N, HACH Co.).

To visualize the structure of the biofouling deposits, we used scanning electron microscope (SEM) images. At the end of the filtration period, small pieces of a representative membrane fiber with foulants from each reactor were cut off, dried at 35 °C for 1 h and then

coated with gold (50 nm thickness) by an ion coater (IB-3, EIKO Co., Japan) for 2 min. The thickness of the gold coating was varied depending on the magnification of the image. The SEM images were taken by SEM S 2400 (Hitachi Co., Japan).

### 3. Results and discussion

#### 3.1. Effects of operational parameters on filtration performance

The reactors were operated for two months. Fig. 2 shows the transmembrane pressure (TMP) records of various runs. The membrane inside reactor R3 (control – raw water without PAC) fouled first, whereas the membranes inside reactors R4 (standard operation) and R5 (biofilter treated feed with PAC) fouled later. This is consistent with

Table 1  
Operating conditions of various reactors during filtration experiment.

Reactor	Source of the influents	PAC (g/L of the reactor)	Filtration/backwashing time	Objective of operation
R1	River water	40	20 min/0 min	Control (continuous filtration without backwashing)
R2	River water	40	10 min/1 min	Short cycle time
R3	River water	0	20 min/2 min	Control (no PAC)
R4	River water	40	20 min/2 min	Standard operation (with PAC and longer filtration and backwashing)
R5	Biofiltered water	40	20 min/2 min	Biofilter treated feed

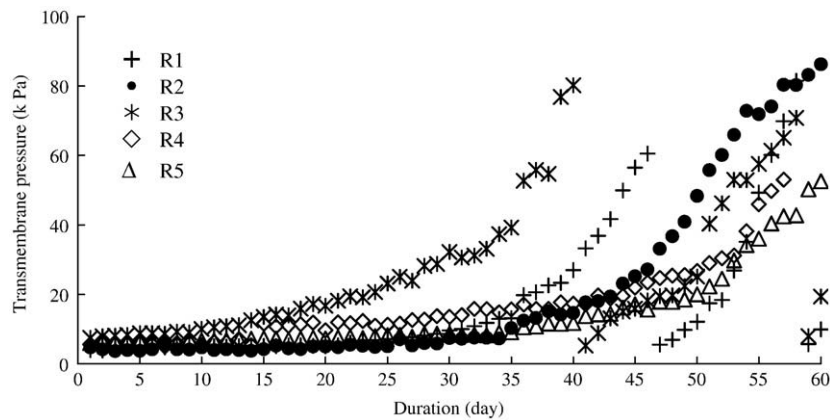


Fig. 2. The transmembrane pressure (TMP) of membranes over the experimental period. Reactor R3 was physically cleaned on days 41 and 58 and R1 was cleaned on day 46.

the results of Park et al. [22] who performed a pilot scale study with PAC-MF system to treat surface water and observed that pretreatment of river water using a biological filter removed the suspended particles and extended the filtration period of the MF membrane.

Backwashing discharged the particles entrapped in the membrane pores during filtration and effectively controlled PAC cake formation (reactors R4 vs. R1 (raw water with PAC and continuous filtration without backwashing)), even with a short filtration cycle time (reactors R2 (raw water with PAC, backwashing and short cycle time) vs. R1). Despite the absence of backwashing, the membrane module inside reactor R1 fouled slower than reactor R3, probably due to the presence of the PAC in reactor R1.

It is known and expected that frequent and longer cycles of backwashing decrease the TMP and delay fouling [10]. Moreover, optimizing backwashing frequency and time combined with high PAC concentration ensured longer operation of the membrane modules without frequent fouling. The use of biofilter (BF) treated water (reactor R5) facilitated a longer run of the membrane module, because the biofilter removed more than 80% of the suspended solids (SS), even though it could not remove more than 7–9% total organic carbon (TOC) (data not shown). Accumulation of PAC with SS can result in the formation of cake layer on the membrane, which increases membrane resistance during filtration. The concentration of the flocculated colloids on each membrane module was about 2000 mg/L, which was not high in comparison with the PAC concentration. The turbidity in the raw water was about 3NTU on the average, and 30NTU maximum.

Once TMP values reached to 90 kPa (0.9 bar), the fouled membranes from the reactors R1 and R3 were removed and washed with Milli-Q water and a soft brush to remove the cake layer. It can be seen in Fig. 2 (days 46 and 41 for reactors R1 and R3, respectively) that the TMP after this physical cleaning was comparable to that of the initial values, which indicates that the presence of PAC and backwashing in reactors R1 and R3, respectively, eliminated the irreversible fouling. In all reactors, the rate of TMP increase was slow until the TMP reached 30 kPa (0.3 bar) and then the TMP increased exponentially indicating the existence of a critical TMP after which the membranes can be fouled faster. The TMP records were similar in all reactors with PAC until the 35-day of operation.

This behavior suggests that initially PAC formed a porous cake layer on the membrane's surface, which is consistent with the data reported by Kim et al. [23]. The onset of the critical TMP can be delayed by external agitation (aeration) in front of membrane surface [24]. The turbulence caused by the aeration enhanced the removal of the cake from the membrane's surface. There was an optimum aeration rate, 1000 L/m<sup>3</sup>/min, beyond which there was no further fouling suppression [9,23], but this rate may vary depending on the geometry of the reactor. Despite this beneficial effect on TMP in the reactor without PAC, reactor R3, aeration alone did not increase the filtration period or reduce the number of membrane cleaning. The abrasion caused by the concentrated PAC particles combined with the aeration reduced the fouling of the membranes in reactors R1, R2, R4 and R5. The reactors operated with PAC showed slower fouling, which

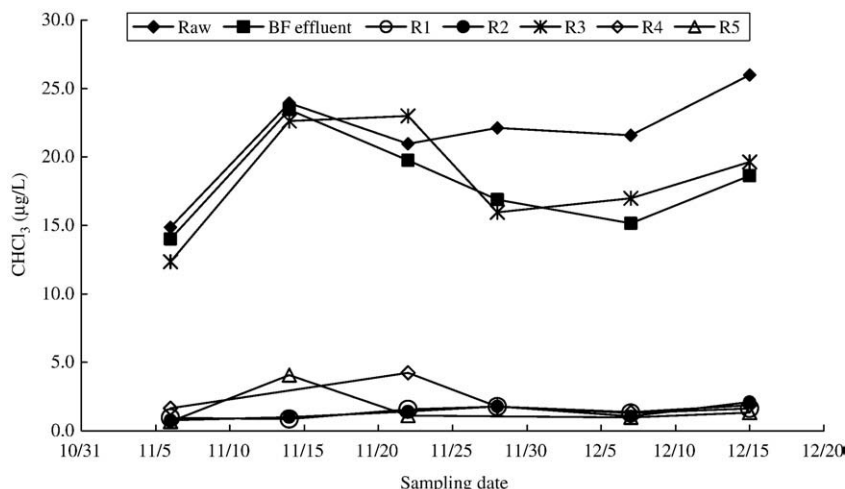


Fig. 3. The concentrations of CHCl<sub>3</sub> in the effluents and influents of different reactors.

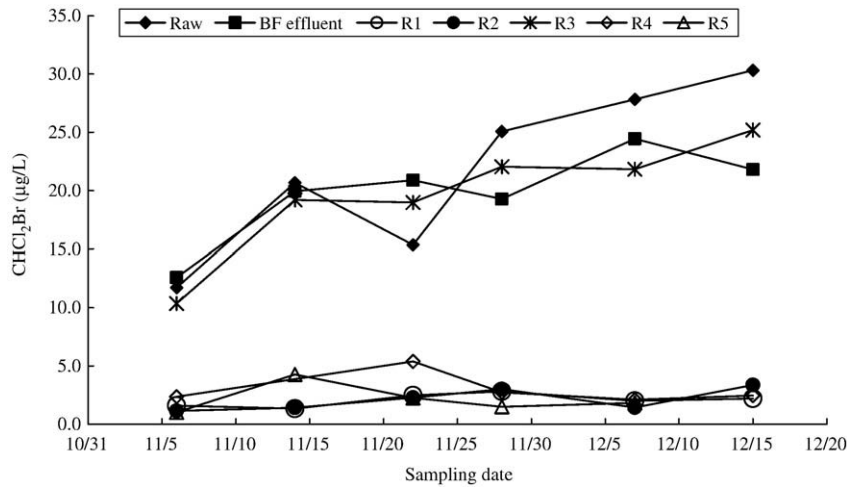


Fig. 4. The concentrations of CHCl<sub>2</sub>Br in the effluents and influents of different reactors.

could be slower even further using backwashing; reactors operated with PAC and backwashing showed the slowest fouling.

According to our estimation in which we have assumed that all PAC particles attached to the membrane surfaces during the filtration cycle were released to the bulk solution during the backwashing cycle, when 200 g of PAC was added into 5 L reactor and the reactor was operated for 60 days at the flow rate of 25 L/day, to treat 1 L of the influent the amount of PAC needed was 130 mg. It is important to see that the estimated amount of PAC needed depends on the time in which the reactor is operated, and it can be smaller if the systems is operated longer as PAC is not added into or removed from the reactors during the filtration period. The reactors with PAC were operated for 60 days without any signs that PAC needed to be exchanged. It will require additional studies to determine for how long PAC can be used before it needs to be exchanged.

### 3.2. Organic carbon removal efficiency

The average TOC concentrations were almost the same in both types of influents used, 1.65 mg/L in the raw water and 1.56 mg/L in the biofiltered water. The removal efficiencies of TOC in the reactors R1, R2, R3, R4 and R5 were 83% (± 1.7), 85% (± 2.01), 3% (± 0.6), 76% (± 1.3)

and 84% (± 1.8), respectively. The values in the parentheses indicate the standard error of mean values of three samples for the respective measurements. In reactor R5, TOC removal was calculated based on the TOC in the effluent of biofilter, while in reactors R1 through R4, it was based on the raw water TOC. The TOC removal by the reactors with PAC and receiving raw water was nearly constant during the first three weeks following the increasing removal trends (data not shown). The similar trend was observed in the reactor with PAC and receiving biofiltered water, but the TOC removal was higher in this case.

The TOC removal in reactor R4 (standard operation) was slightly lower than that in reactors R1, R2 and R5, although all reactors with PAC showed very high TOC removal (from 76% to 85%) compared to the reactor without PAC, reactor R3 (3%). In reactor R2 (raw water with PAC and short cycle time), the filtration and backwashing periods were just half of those in reactor R4. The TMP in reactor R2 increased faster than that in reactor R4, but the ultimate TOC removal in reactor R2 was slightly higher than that in reactor R4 suggesting an importance of shorter backwashing interval, which can limit the detachment of organic matter attached on the particles in front of the membrane surfaces. The shorter filtration time, no backwashing and biofiltered water as an influent enhanced the TOC removal efficiency. However, the removal efficiencies of TOC in

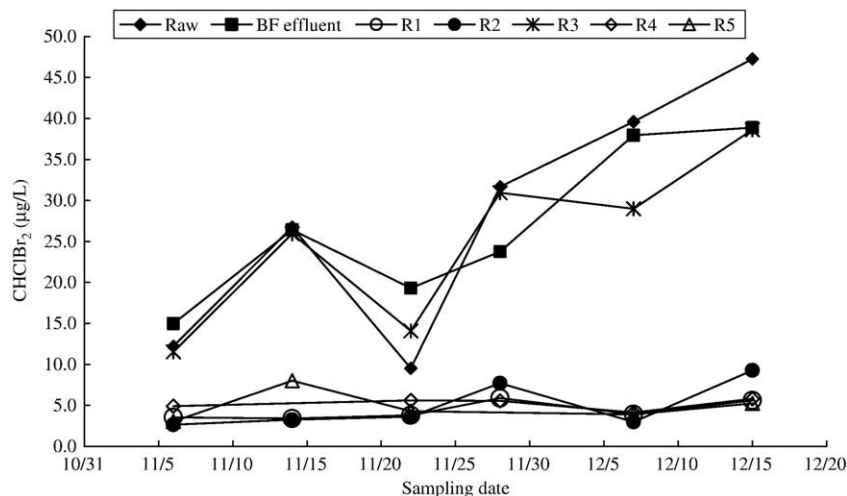


Fig. 5. The concentrations of CHClBr<sub>2</sub> in the effluents and influents of different reactors.

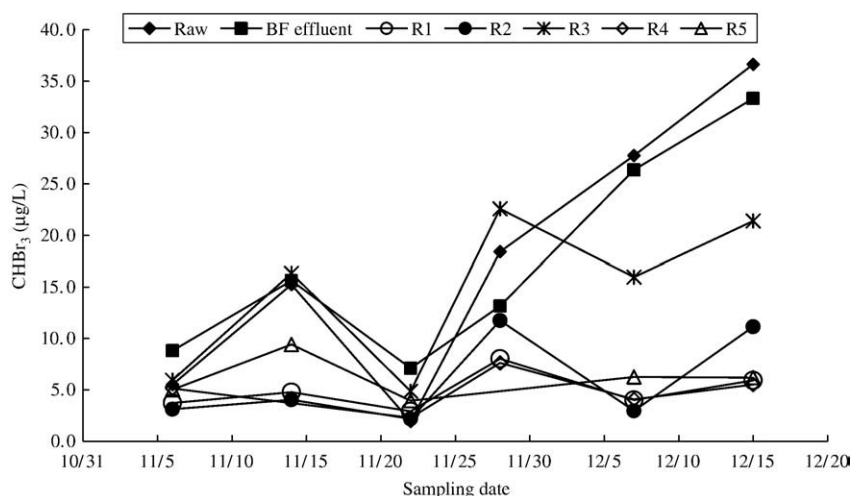


Fig. 6. The concentrations of CHBr<sub>3</sub> in the effluents and influents of different reactors.

reactors R1 and R2 were almost the same, which indicates the importance of PAC rather than filtration/backwash cycle. Similarly, Lebeau et al. [25] carried out a pilot study using a PAC-MF slurry reactor (PAC concentration 8–25 g/L) to treat river water obtained 41% of DOC removal and higher concentrations of PAC increase the TOC removal efficiency.

### 3.3. Trihalomethanes (THMs) removal efficiency

Figs. 3–6 show the concentration of each THM (CHCl<sub>3</sub>, CHCl<sub>2</sub>Br, CHClBr<sub>2</sub>, and CHBr<sub>3</sub>) in the influents and effluents of various reactors. The concentration of the bromo-THM species (CHClBr<sub>2</sub> and CHBr<sub>3</sub>) increased in the reactor influents with time. This was due to increased bromide concentration in raw water, which occurs commonly in winter, when the natural flow in the river decreases as has been explained previously. By the end of December, the total concentration of THMs (TTHM) in the raw water; the biofilter treated water; and the filtrate from reactor R3 (raw water and without PAC) exceeded the drinking water standard of 100 µg/L (US EPA September 2006). In the effluents from the reactors containing PAC (R1, R2, R4, and R5), the THMs were maintained at low levels, even for the bromo-THM species. The measurements of THMs concentrations were repeated three times for each sample.

The amounts of the chloro-THM species (CHCl<sub>3</sub> and CHCl<sub>2</sub>Br) fed with the influents, raw and biofiltered waters, to the reactors were 32 to 33 mg and 27 to 30 mg, respectively, during the operational period. The removal of these two THMs in reactors containing PAC – R1, R2, R4 and R5 varied from 80 to 95% and that in R3 varied from 10 to 15%. Similarly, the amounts of CHClBr<sub>2</sub> and CHBr<sub>3</sub> fed with the influents, raw and biofiltered waters, to the reactors were 40 to 42 mg and 25 to 29 mg, respectively. The removal of these two THMs in the reactors containing PAC varied from 65 to 85% and in the reactor without PAC, R3, varied from 10 to 18%. The standard error of mean values during the estimation of CHCl<sub>3</sub> and CHCl<sub>2</sub>Br varied from 0.21 to 0.46 µg/L and of CHClBr<sub>2</sub> and CHBr<sub>3</sub> from 0.35 to 0.51 µg/L.

It is known that MF membrane alone cannot remove THMs, but the foulants formed on the membrane surface inside reactor R3 contributed to this removal by biodegradation and/or adsorption.

The removal of the THMs was the highest in the reactor R1 (raw water with PAC and continuous filtration without backwashing), which states that during backwashing process a certain portion of THMs was discharged inside the reactors and in front of membrane surface and was available in free states in the next cycle of filtration. This trend was not observed during TOC removal in R1.

The total amount of CHClBr<sub>2</sub> and CHBr<sub>3</sub> introduced to the reactors was higher than that of CHCl<sub>3</sub> and CHCl<sub>2</sub>Br. The removal efficiency of the chloro-THM species (CHCl<sub>3</sub> and CHCl<sub>2</sub>Br) with PAC was higher

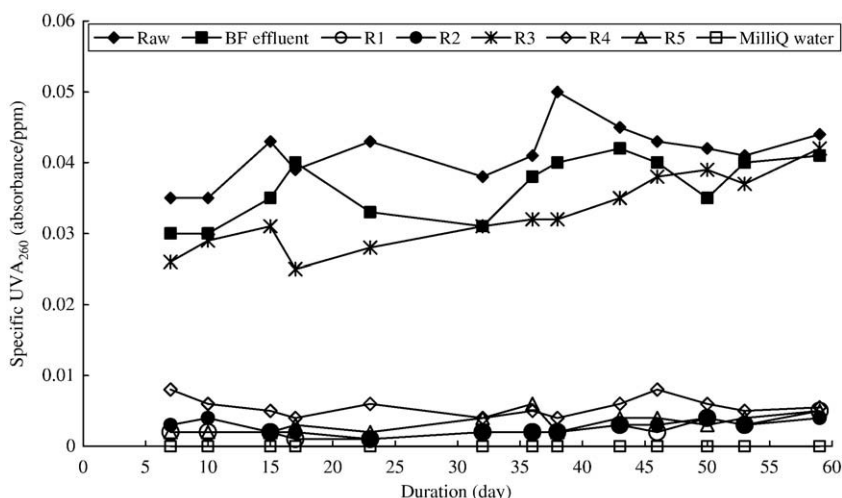


Fig. 7. SUVA<sub>260</sub> values of the effluents and influents of different reactors and Milli-Q water.

than that of the bromo-THM species ( $\text{CHClBr}_2$  and  $\text{CHBr}_3$ ), which indicates that the interaction and adsorption of each THM species with PAC are different. Furthermore, the THM concentrations in the effluents of reactors containing PAC did not vary, but TOC removal efficiencies in those reactors increased with time. There could be a competition between TOC and THMs removal with PAC after three weeks of operation. The drinking water guideline values for  $\text{CHCl}_3$ ,  $\text{CHCl}_2\text{Br}$ ,  $\text{CHClBr}_2$ , and  $\text{CHBr}_3$  concentrations are 200, 60, 100, and 100  $\mu\text{g/L}$ , respectively [26], and all were easily met in the effluent from the reactors containing PAC. The TTHM in the effluents from the reactors containing PAC was less than 40  $\mu\text{g/L}$  for 60 days, for which the maximum TTHM can be 100  $\mu\text{g/L}$  (US EPA September 2006). The sum of the ratios of concentration of THM species in the effluent of reactors containing PAC to its respective guideline values was less than 1 (Eq. (1)), but it was not satisfied in the reactor without PAC (reactor R3).

The stable and constant concentrations of THMs in the effluent from the reactors containing PAC indicate that PAC-MF systems could have been operated longer than 60 days achieving the same results. In this study, we used natural surface water as an influent, with and without pretreatment, and the THM concentrations in the effluents from the reactors with PAC were less than half of the US EPA and WHO standard guideline values, during the entire time of operation.

Fig. 7 shows the specific UV absorbance ( $\text{UVA}_{260}/\text{DOC}$ ) for various samples.  $\text{SUVA}_{260}$  represents the fraction of UV absorbing organic molecules in DOC, which typically contain aromatic groups.  $\text{SUVA}_{260}$

values are lower in the effluents from the reactors with PAC, which is consistent with high extent of the THMs removal or the components contributing to SUVA (aromatics in NOM) that are also major precursors to DBP formation. While this study was concerned primarily with direct removal of THMs, it is encouraging to note that precursors to further THMs formation were also removed reasonably and efficiently by this process.

### 3.4. Visualization of membrane foulants

The reduction or removal of TTHM in the reactors containing PAC could be caused by the adsorption of THMs on PAC and/or the microbial degradation of those species inside the reactors [27]. Fig. 8(A) shows the scanning electron microscope (SEM) image of membrane fouling deposits in reactor R2 (raw water with PAC and short cycle time). PAC particles accumulated on the membrane surface in reactor R2 with the extracellular polymeric substances (EPS). The fouling deposits on the membrane surface produced a porous cake due to the presence of PAC. The cake on the membrane surface in reactor R4 (standard operation) does not have filamentous material attached to PAC (Fig. 8(B)), and the morphology of the cake is different from that in reactor R2. As expected, the absence of PAC changed the morphology of the cake forming a dense layer on the surface of membrane (Fig. 8(C)) in reactor R3 (raw water without PAC). Even in the absence of PAC, the membrane surface was not visible because of the accumulation of foulants (Fig. 8(C)). The reactors with PAC removed TTHM below the detection limit. The

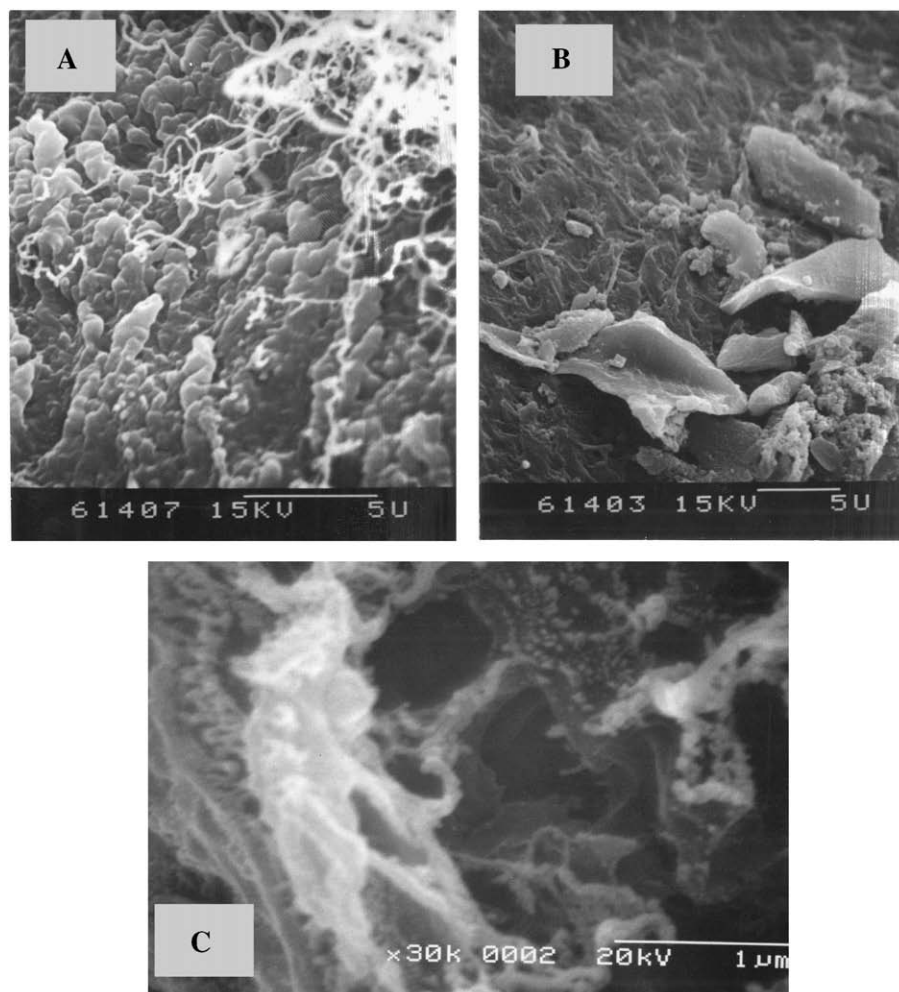


Fig. 8. Scanning electron microscope (SEM) images of (A) extracellular polymeric substances with PAC particles on the fouled membrane inside reactor R2, (B) cake layer on the membrane surface inside reactor R4 and (C) dense and disperse biofoulants on the membrane surface inside reactor R3.

formation of fouling deposits or cake layers in the absence of PAC increased the TMP (Fig. 2); however, they removed THMs up to a certain extent and PAC associated fouling deposits and cake layers helped as the final barrier to THMs (Figs. 3–6).

#### 4. Conclusions

The high PAC concentration coupled with MF membrane filtration used in this study removed the THMs from river water continuously. The submersed membrane hybrid systems are flexible tools that can be used directly for filtration or can be coupled with any conventional process such as oxidation, coagulation, adsorption, or biological treatment for the removal of both dissolved and particulate contaminants.

Biofiltration lessens fouling considerably, more than PAC addition alone. The TMP records show that PAC enhanced fouling deposits and created porous cake layers on membrane surfaces thus adsorbing or holding microorganisms, organics, and particles. Frequency of back-washing, duration of the filtration cycle, and prefiltration effectively decreased the frequency of membrane cleaning during the operational period.

The presence of PAC in reactors increased the THM removal efficiencies about six to eight times compared to the THM removal efficiency of the reactor without PAC. However, during the back-washing a certain portion of THMs was discharged in the reactors and was available in free and/or adsorbed on the particles states in the next cycle of filtration. The TOC adsorption on the PAC influenced the THMs removal after three weeks of filtration. The removal efficiencies of the chloro-THM species were higher than those of the bromo-THM species by the PAC-MF reactors, which indicates the selectivity of THMs adsorption on the PAC particles.

The high dose PAC combined with MF system extended the filtration period providing the benefits of PAC-MF hybrid system and the cost of PAC in such systems is negligible compared to the cost of the membrane systems. The frequency of PAC replacement depends on the removal rate of THMs, organics and other components of interest.

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