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Membrane fouling due to dynamic particle size changes in the aerated hybrid PAC–MF system

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ABSTRACT

To quantify the effect of dynamic particle size changes and degradation and accumulation of suspended solids (SS) in influents to reactors on membrane fouling frequency in hybrid powder-activated carbon (PAC)–microfiltration (MF) reactors, we operated a PAC–MF system (hollow-fiber module) for more than five months to purify river water before and after pretreatment by a biofilter. The transmembrane pressure, backwashing pressure, resistance to filtration, and SS accumulation and degradation during these dynamic changes were evaluated. The initial dose of PAC was 40 g/L of the reactor and no additional PAC was added during this continuous operational period. The presence of PAC reduced the membrane resistance to filtration even at the end of filtration period when the number of particles in the smallest range (>1.0–3.6 μm) was the highest measured by the flow cytometer and microscopy image analysis. This resistance was reduced further when the river water was biofiltered prior to membrane filtration. This real-time study demonstrates that over time PAC and other particles coming into the reactors through the influents degrade and/or become smaller because of the turbulence caused by continuous aeration below the MF membrane fibers. The number of particles in the reactors with diameters less than 10 μm increased with time, increasing the fouling frequency; however, the presence of PAC further reduced the particle enhanced fouling. The presence of PAC also increased SS degradation by up to 10%. The increased number of bacteria inside the PAC–MF systems did not contribute to the number of membrane fouling. Even though the particle sizes inside the reactors became smaller with time, the gradual increase in net accumulation of SS was also an important factor controlling the performance of the PAC–MF system.

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1. Introduction

During the past decades, the microfiltration (MF) membranes emerged as one of the most reliable, cost-effective and sustainable units for surface water treatment separating macromolecules, bacteria and discrete particles [1–6]. When surface waters are treated using MF membranes, suspended solids (SS) carrying organic materials and different types and sizes of particles cause a rapid flux decline [7–10]. It has been demonstrated that particle sizes change during the filtration process: for high cross-flow velocity and in the presence of aeration, large particles break down into smaller ones [11]. These small particles then cause pore blocking of MF membranes during filtration [12–14] and increase transmembrane pressure (TMP).

If the natural organic matter and microorganism load can be reduced at upstream of the membranes, the extended membrane filtration period can be achieved [15]. This may be accomplished by optimizing the adsorption of organics and microorganisms by powdered activated carbon (PAC) and/or by the use of biological filtration. There have been several discussions about whether PAC itself fouls membranes attenuating membrane permeability/productivity reduction [16,17]. Several reports indicated that the addition of PAC in the membrane process decreased the rate of flux decline [2,18,19]. The addition of PAC sometimes fouls the membrane, depending on the PAC–membrane interaction and the characteristics of the PAC cake layer [3,20,21]. Moreover, it is not

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entirely clear how the dynamic particle size changes in a PAC–MF hybrid system affect the rate of membrane fouling or TMP during surface water treatment.

To the best of our knowledge there have been no studies or published reports on the dynamic effects of particle size changes in the presence of PAC on increase in TMP or fouling of MF membranes during long-term treatment of real surface water with variable water quality parameters. The models demonstrating particle-enhanced fouling that have been developed were tested in controlled laboratory environments using particles of unique shapes or even having the same mean particle sizes [22–24], which did not change their sizes during filtration and using unique influent qualities.

Several studies used PAC in the pretreatment step, prior to membrane filtration [21,25–28], or in combination with membrane filtration in the same tank [29,30] to demonstrate the membrane fouling mitigation mechanisms. PAC was combined with MF membrane forming a hybrid system to remove organic compounds [8,17,30–32], 17β-estradiol (an endocrine disrupting compound) [33], disinfection byproducts [30], atrazine [34], and microorganisms like *Norovirus* (27–40 nm in diameter) [35]. However, the performance of the PAC–MF process depends on several factors.

In addition, such questions as how the size changes of PAC and other particles entering the membrane reactor continuously affect the membrane fouling in real filtration systems using real surface water; whether the presence of PAC affects the degradation of SS in influents and reduce their effects on membrane fouling; and how TMP and resistance to filtration change in the presence or absence of biofiltration of the river water are still unanswered. In our previous studies [5,14] on PAC–MF systems for surface water treatment, in which the PAC dose was varied from 0 to 50 g/L of the reactor, we observed that at 40 g of PAC per liter of the reactor, the membrane fouling frequency was the lowest and the removal rate of dissolved organic carbon (DOC) was more than 80%. For this study, we hypothesized that PAC and other particles entering the reactors would be smaller with time because of the aeration under the membrane modules and the presence of PAC would lessen the effect of particle and bacterial enhanced foulings. Moreover, pretreatment of the river water would provide additional benefits. We also expected that the presence of PAC would affect the degradation of SS.

In this study we used the flow cytometer (FCM) to count and distinguish the particles and bacteria in different samples. Cluster composition in aggregation processes of multiple particle species can be dynamically determined using the novel FCM analysis [36,37].

A better understanding of the interactions among the various factors, such as pretreatment of influent, particle size changes and the role of SS in the influents to the reactors on the dynamics of TMP changes, is needed to optimize the performance of hybrid PAC–MF reactors. To provide insight on these interactions, the objectives of this study were to: (1) quantify the combined effect of PAC and pretreatment of influent on MF membrane fouling and the dynamic particle size changes in the reactors, and (2) estimate the accumulation and degradation of SS in the influents to membrane bioreactors.

2. Materials and methods

2.1. Site location and influents to the reactors

This study was conducted at a water treatment plant operated by the Tokyo Metropolitan Authority. The plant is located in the southwest region of Tokyo, about 15 km from the main city, and treats water from the Tama River. The details of this river water quality are mentioned elsewhere [30]. A bench-scale study of the PAC–MF system was performed in this treatment plant using the river water.

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 into two membrane reactors. The raw water was treated with a biofilter, and the effluent of the biofilter was fed into another membrane reactor. The biofilter consisted of a column packed with polypropylene pellets with a length of 5 mm, an inner diameter of 3 mm and an outer diameter of 4 mm. The filtration velocity and residence time of this biofilter were 320 m/d and ~10 min, respectively. Discharges from the biofilter and raw water were stored separately in two 100-L reservoirs and stirred continuously prior to being fed into the reactors.

2.2. Experimental design and operational conditions of the reactors

We operated three reactors (R1, R2, and R3) continuously for 151 days in this study. Each reactor consisted of a hollow-fiber MF membrane module operated in suction mode to maintain constant flux. The polyethylene hydrophilic membrane was made by Mitsubishi Rayon Co., Ltd., Japan. The nominal pore size was 0.1 μm, and the outer and inner diameters were 0.41 mm and 0.27 mm, respectively. Each membrane module had 320 (16 × 20) 120-mm-long fibers, with a combined surface area of 0.05 m^2. The reactors were made of 5-mm-thick polyvinyl chloride plates, and each had an effective volume of 5 L. The membrane modules were cleaned with Milli-Q water when received and soaked in fresh Milli-Q water prior to use. The experiment was carried out under ambient conditions (17–28 °C). The raw water was fed as an influent into reactors R1 and R2, and the effluent from the biofilter (BF) was fed into reactor R3. Fig. 1 shows the entire system and specifies the operational protocol for each reactor.

PAC (coconut shell origin, JWWA K 113-1985, Shirosagi-C, Takeda Chemical Co., Japan) was used as received and the dose was 40 g of PAC per liter of the reactor added into reactors R2 and R3 at the beginning of the operation. Reactor R1 was operated without PAC as a control. The filtration flux was kept at 20.8 L/m^2/h, the flow rate was 25 L/day, and the residence time was 0.2 day. All membrane modules were equipped with a backwash mechanism, which was controlled by electronic valves and timers, providing 2 min of backwashing after 20 min of filtration. Level sensors were used to ensure a constant reactor volume, while suction through the membrane module maintained a constant flow rate. Fresh filtrates were used for backwashing of the membrane modules. The backwash-water reservoirs were cleaned once a week and refilled with fresh filtrate, and the backwashing flux (41.6 L/m^2/h) was twice as high as the filtration flux. The reactors were aerated continuously at 1000 L/m^3/min (5 L/min), and the air was delivered below the fiber modules. Transmembrane pressures (TMP) and backwashing pressures (BWP) were recorded using a data logger.

Once TMP values reached to 50 kPa (0.5 bar), the fouled membrane modules from the reactors were removed and washed with Milli-Q water and a soft brush to remove the foulants from the membrane's surfaces. The resistance to filtration and pure water flux were measured right after physical cleaning of the membrane modules and prior to starting the next cycle of filtration. At the end of the study (on Day-151), the membrane surfaces were chemically cleaned by soaking in 20 mM EDTA and 4% NaOH solutions for 2 h and finally being rinsed with Milli-Q water. The resistance to filtration and pure water flux were also measured after this chemical cleaning of the membrane modules.

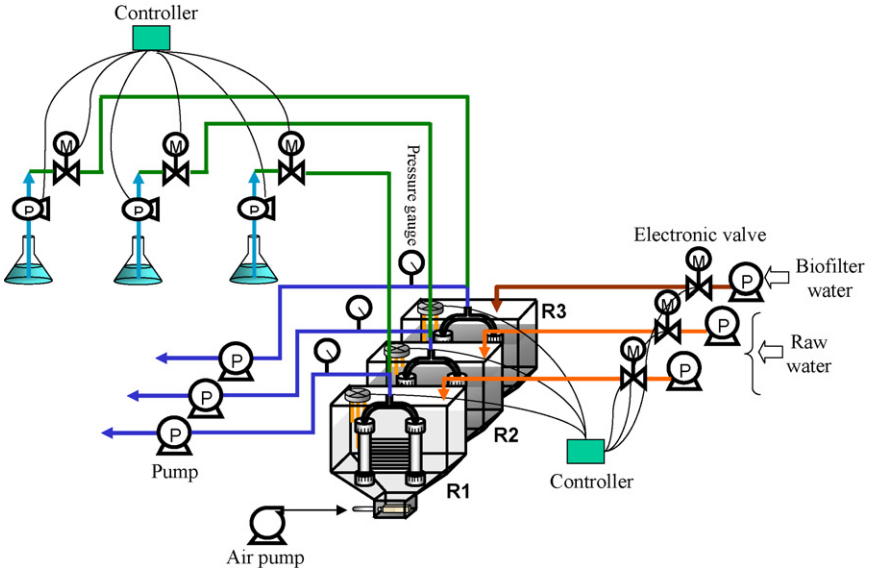

Fig. 1. Reactor R1, the control, treated raw water and was operated without PAC; R2 treated raw water and was operated with PAC; and R3 treated water pretreated in a biofilter, BF, and was operated with PAC.

2.3. Resistance to filtration

The total resistance to filtration was evaluated from Darcy's law:

$$J = \frac{Q}{A} = \frac{\Delta P}{\mu R_T} \quad (1)$$

where J is the membrane flux, A is the membrane filtration surface area, Q is the volumetric flow rate through the membrane, μ is the dynamic viscosity, R_T is the total resistance to filtration, and ΔP is the transmembrane pressure.

The total membrane resistance is modeled as the sum of the resistances to filtration through the membrane (R_m) and through the cake layer (R_c). Further, the resistance to filtration through the cake layer has two components: pore blocking (R_p), primarily due to particles of the same size range as the membrane pores, and adsorption (R_a), which alters the membrane pore size through micro/nano-scale interactions with the pore openings and walls. In addition, in a system without bulk fluid agitation, an additional resistance to filtration, due to concentration polarization, R_{cp}, arises. We minimized this component by placing aeration below the membrane fibers. Fang and Shi [38] showed that the cake layer could not be thoroughly removed, so that R_a and R_p cannot be separated accurately. Based on the above, Eq. (1) can be modified as:

$$J = \frac{Q}{A} = \frac{\Delta p}{\mu} \cdot \frac{1}{(R_m + R_c)} \quad (2)$$

2.4. Analytical techniques

2.4.1. Particle counting using flow cytometer

We used the Coulter EPICS ALTRA Flow Cytometer (Coulter Corporation, Miami, FL) to count particles inside the reactors at three- to four-day intervals and also in the influents to the reactors twice a week. Particles with diameters between 1 and 20 μm were counted, as particles within this range were the most likely to obstruct the pores of the membrane. The cut-off size (nozzle diameter) for the application of the flow cytometer (FCM) was 20 μm.

To cover the spectrum of particle sizes, four standard particles from Coulter Corporation were used for particle counting and size distribution:

(1) N4 size control L1000 (mean size 1088.6 ± 65.3 nm, polystyrene latex beads),
(2) Flow-set fluorospheres (mean size 3.6 μm, fluorescent microspheres),
(3) Flow-check fluorospheres (mean size 10 μm, fluorescent microspheres), and
(4) CC size standard L20 (mean size 20.09 μm, polystyrene latex beads).

When these four standard particles were mixed in equal proportions and injected into the FCM, four distinct histograms were generated for particle counting based on the standard particles (1.0, 3.6, 10 and 20 μm). These provided the three interim regions (particle sizes >1.0 to <3.6 μm, >3.6 to <10 μm, and >10 to <20 μm) to cover the spectrum of particles in the range from 1 μm to 20 μm. Finally, the combined display of histograms for the four standard particles and their interim regions, or the combined protocol, was used to find the numbers and size distributions of the particles in the reactors. The reproducibility of these measurements exceeded 98% and paticles in each sample were measured 2–3 times.

2.4.2. Particle size distribution measurements using a microscope

The numbers and size distributions of particles of virgin PAC and of samples from reactors R2 (raw water with PAC) and R3 (BF water with PAC) at the end of the filtration experiment, on Day-151, were also determined using microscopic observation. To obtain a countable concentration, 2 ml of virgin PAC from stock PAC solution (40 g of PAC dissolved in 1 L of Milli-Q water) was diluted with Milli-Q water at 1:100. The same dilution procedure was applied to the samples from reactors R2 and R3. Prior to particle counting, the particles in the reactors and influents were observed under a microscope before and after the dilutions. The particles in reactor R1 (raw water without PAC) were found to be a fragile nature (breakable easily during sample preparation or agitation) before dilution and even more fragile nature after dilution compared to other samples. Therefore, the particle size distribution of the samples in R1 could not be determined using this technique.

A 30-μl of diluted sample was placed on a glass slide and observed under the microscope (Olympus DP71, Japan). Paticles in each sample were measured in duplicates and 15 images for each sample were captured using a 20× objective. The effective

area of each particle and their consecutive numbers of particles from all images were calculated using a LEICA QWIN image processing and analysis software system (Leica Imaging Systems, Ltd., Cambridge, UK). The weighted average mean values of these data from 15 images were calculated to compensate for the effect of different-sized particle counts.

2.4.3. Bacteria enumeration using flow cytometer

To differentiate bacteria from inert particles, the FCM was used to count the total number of bacteria in the influents to the reactors and in the bulk phase of the reactors. Five different protocols were developed with these samples. The standard particle, Flow-count fluorospheres R 2-99 (mean size 10 μm, COULTER Corporation, Miami, FL), and a specific dye, SYTO 9 (LIVE/DEAD BacLight™ Bacterial Viability Kits L-7007, Molecular Probe, Oregon) were used. Based on different trials for the highest quantification and intensity in the histograms, PMT 5 log and PMT 2 log (excitation wavelength at 525 nm) were used for bacterial counting. The voltage for forward scatter (FS) was fixed to 600 mV in all five protocols. The reproducibility of each protocol was more than 92%. The numbers of bacteria in each sample were counted 2–3 times.

To ensure efficient separation of attached cells, the reactor samples and influents to the reactors were homogenized (by Branson Sonifier 450, Yamato, Japan) for 5 and 2 min, respectively. This protocol was optimized by varying the homogenization time at which the number of total bacteria was the highest. Immediately after homogenization, the sample was filtered through a 1.0 μm sterilized glass fiber filter (Millipore, USA). 30 μl SYTO 9 dye was added to 1 ml filtered sample and kept in the dark for 20 min before injecting to the FCM using the specific protocol for respective sample.

2.4.4. Suspended solids

The periodic SS concentrations of the samples in the reactors, the raw water and the BF effluent were measured using a glass fiber filter with a 1-μm pore size and a 47-mm diameter following a standard method of analysis (Method VI-1-12, Japanese Standard Methods for Water Analysis, 2001). The volume of bulk solution withdrawn for SS sampling was accounted for in the mass balances of solids in the reactors.

3. Results and discussion

3.1. Quantifying the combined effect of PAC and pretreatment of influent on MF membrane fouling and the dynamic particle size changes in reactors

3.1.1. Filtration performance

The transmembrane pressure (TMP) and backwashing pressure (BWP) records of the membrane modules are shown in Fig. 2 and Supplementary Figure S1, respectively. A few TMP and BWP data points are missing because of an electromechanical problem with the data logger. Moreover, during the first filtration cycle of R2 (raw water with PAC), the air pump was malfunctioning which resulted an earlier TMP increase of membrane module in this reactor than that of other reactors. The TMP of the membrane increased faster in R1 (raw water without PAC) than in the other two systems with PAC. The membrane in R1 required five cycles of physical cleaning during the filtration period. In contrast, the membrane in R2 required three cycles of cleaning and that in R3 (BF water with PAC) required only two cycles. The use of BF-treated water (reactor R3) facilitated a longer run of the membrane module, because the biofilter removed more than 80% of the suspended solids (SS), even though it did not remove more than 7–9% of the total organic carbon (TOC) [5]. Similar trends were observed in the backwash pressure (Supplementary Figure S1), although with somewhat less clarity

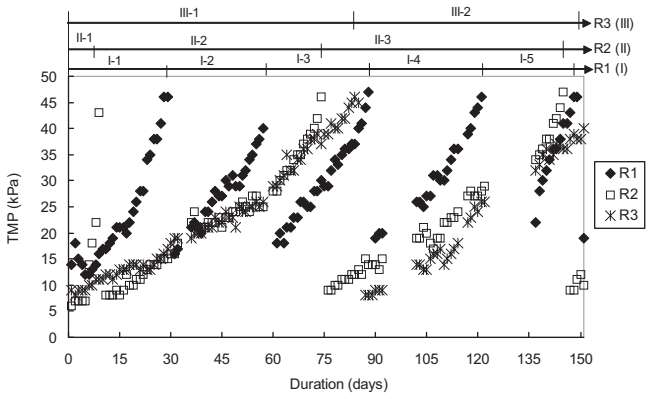

Fig. 2. Transmembrane pressure record for the membrane modules in the reactors. One kPa = 0.01 bar. The roman numerals at the top of the figure indicate the type of reactor (I, II, and III correspond to R1, R2, and R3, respectively), and the arabic numerals beside them represent the number of cleanings for each module.

because of the irregular particle removal from the membrane surface which occurred during backwashing. It has been shown by other studies that periodic backwashing reduces the number of membrane foulings [14,39]. Adham et al. [2] reported that addition of 25 mg/L PAC to systems treating a groundwater with ~3 mg/L DOC reduced the rate of membrane fouling by approximately one-third.

It can be seen in Fig. 2 (reactors R2 and R3) that the TMP after the physical cleaning of fouled membrane modules was comparable to that of the initial values, which indicates that the presence of PAC in reactors R2 and R3 kept the foulants away from the membrane pores and that the particles attached to membrane surfaces and pores during filtration were released into the bulk solution after backwashing. At the end of each filtration cycle, irregular and somewhat thicker cake layers formed at both ends of the membrane fibers, where the aeration was not effective and the fibers were stagnant; however, only very thin cake layers were observed on the fibers between the supports. To treat 1 L of influent we used 53 mg of PAC when 200 g of PAC was added into a 5-L reactor operated for 151 days at the flow rate of 25 L/day.

Performance of the PAC–MF process depends on various factors; however, operating mode, carbon dose, carbon adsorptive characteristics and influent characteristics are the major factors [33]. In a submerged membrane bioreactor (MBR), the deposition of foulants on the membranes is predominantly engendered by the hydrodynamic forces encountered in the filtration processes [40] and an optimum quantity of air bubbles can prevent the deposition of foulants on the membrane surfaces and particle sedimentation inside the reactor [1]. Aeration also increased the particle abrasion of the membrane surfaces, which contributed significantly to the removal of cake layers from the membrane surfaces. There was an optimum aeration rate, 1000 L/m^3/min (5 L/min), beyond which there was no further effect on fouling suppression. However, aeration by itself did not reduce the frequency of fouling (R1 vs. R2). Thus, the continuous abrasion of the membrane surfaces by a high concentration of particles (PAC and solids entered into the reactors through influents) associated with other components in the presence of aeration was responsible for the hydrodynamic disruption of the cake layers [30], reducing the number of membrane fouling in reactors R2 and R3.

Resistance to filtration caused by pore blocking is the dominant factor during the initial period of filtration, but cake resistance to filtration begins to dominate following the initial pore blocking [41]. Physical cleaning of the fouled membranes decreased the membrane resistance to filtration by 80%. Moreover, chemical cleaning followed by the physical cleaning at the end of the study (on Day-

Table 1
The average numbers of particles in size ranges from 1.0 to 20 μm in the influents and reactors R1, R2, and R3 during the operation period, 151 days, measured with the flow cytometer.

Particle size (μm) range	Average number of particles in influents and the reactor (#/ml)				
	Raw	Biofilter	R1	R2	R3
>1.0 to <3.6	59	48	1880	5981	3050
>3.6 to <10.0	176	94	3070	2103	3451
>10.0 to <20.0	121	36	445	102	118
20.0	185	14	196	31	44

151) reduced the TMP further by 15–20%. This trend proved that the deposits, including very small particles, organic matter, microorganisms and other components, could not be completely removed by physical cleaning.

The resistance of the membranes in reactors R1, R2 and R3 due to filtration varied from 2.3×10^{12} to 7.85×10^{12} m^{-1}, 1.1×10^{12} to 7.3×10^{12} m^{-1}, and 0.90×10^{12} to 7.1×10^{12} m^{-1}, respectively, and that due to backwashing varied from 1.4×10^{12} to 5.24×10^{12} m^{-1}, 0.7×10^{12} to 5.1×10^{12} m^{-1}, and 0.50×10^{12} to 5.0×10^{12} m^{-1}, respectively. The increasing rates of the resistance to filtration were more pronounced than those of TMP and BWP for the respective membrane modules (data not shown). Moreover, the resistance to filtration of the membrane in R1 increased the most rapidly, followed by those of R2 and then R3. Reactors R2 and R3 had more particles than reactor R1 because of the presence of PAC. The addition of PAC reduced the membrane resistance to filtration (R1 vs. R2), which was reduced further in the presence of a biofilter as a pretreatment (R2 vs. R3). This supports the hypothesis that the addition of PAC effectively slows the increase of membrane resistance to filtration and also biofiltration of river water added an extra benefit.

3.1.2. Changes in particle size distribution

In this report, PAC and particulate materials in the influents to the reactors are referred to as particles. The statistical analyses of particle counting using the flow cytometry and microscopy show that $p < 0.05$ as calculated using two-tailed Student's t-test.

The particle size distributions of samples in the bulk phases of the reactors and in influents were monitored using the FCM. Table 1 gives the average number of particles in each size range in influents and each reactor during the study period. The biofiltration reduced the number of particles in all size ranges from the raw water. The removal of larger particulate material (larger than 20 μm) by a biofilter with 3–5 mm porous media was expected because of the irregular orientation of the media, depth of the biofilter, retention time and activity of the biofilm in the biofilter.

Once particles in influents entered in the reactors, they broke into different sizes and accumulated and/or degraded in the reactors and MF membrane retained these particles inside the reactors. Furthermore, Zabawa [42] and Droppo and Ongley [43] reported that particulate material occurs mainly as aggregates of much smaller particles. The number of particles in reactors R2 and R3 in the range >1.0 to <3.6 μm were much higher than that in R1, which indicates that PAC particles were reduced and/or degraded into the smallest size range. The abundance of bigger flocks (>10.0–20 μm) was the highest in R1, which could be because of the absence of PAC in this system. This FCM observation (Table 1) indicates that the PAC particles broke the incoming solids through the influents to the smallest sizes (20 μm size particles in raw vs. R1 and R2); however, the bulk solution of R3 was different from that of R2 because of the different influents to these reactors, so in R3 the numbers of 20 μm particles was a little higher than that in biofilter water.

The FCM analysis data of particles in reactors as time series are shown in Fig. 3. The normalized data show the number of particles of each size range on a specific day divided by the average number of particles of that size range during the study period ("events/average"). The relative number of particles from 1 to 3.6 μm was the highest at the end of the filtration period (Fig. 3).

Because of the continuous agitation by aeration, simultaneous particle degradations and interactions among particles, membrane surfaces and reactor walls, particles in the reactors were reduced to smaller sizes. There could be other reasons of the particle size reductions. The normalized data (Fig. 3) show that the relative number of particles in the size range of less than 10 μm increased with time in all three reactors, while the number of particles larger than 10 μm decreased with time in reactor R1 (raw water without PAC). The steady decline in 20-μm particles in reactor R1 was likely due to physical disruption into smaller particles. Moreover, the particles inside R1 were fragile and once they came in contact with the membrane surface because of the aeration; they also broke into smaller sizes. In reactors R2 and R3, particle counts were dominated initially by PAC. Since PAC was the primary source of particles larger than 20 μm, the abrasion and fracture of these particles produced first a peak at this size and then a decline as particles continued to abrade (Fig. 3D).

The FCM could detect the particles in between 1 and 20 μm, so the particle size distribution was monitored in the reactors, raw water and effluent from the biofilter (BF) using microscopy and image analysis. The arithmetic mean diameter, mode, 90th percentile of the particle size (d_{90}) and median (d_{50}) of the particles in the raw water were 102.0, 94.0, 108.4 and 83.2 μm, respectively, and those in the BF effluent were 11.9, 6.0, 15.3, and 5.5 μm, respectively. The particles in the BF effluent water (influent to reactor R3) were much smaller than those in the raw water (influents to reactors R1 and R2), which corroborates to the FCM observations (Table 1). The mean diameter of the particles in the BF effluent was ~10% of that in the raw water.

Fig. 4A shows the representative particle size distribution of virgin PAC measured with microscopy. The particles in Fig. 4 were binned for every 2 μm size interval. For example, particle sizes more than 0–2 μm and more than 2–4 μm were binned in 2 μm and 4 μm, respectively, and so on. The median size is 25 μm, and only about 30% of the particles are smaller than 20 μm, which was the maximum size detected with the FCM. In contrast, the samples in reactors R2 and R3 at the end of the filtration period consisted of particles smaller than 20 μm (Fig. 4B and C, respectively), which corroborates the trends observed with the FCM analyses (Fig. 3). The PAC particle sizes were also reduced over time breaking down the particles entering the reactors with the influents (Figs. 3 vs. 4).

The mean diameter, mode and d_{50} of the particles in reactor R2 (raw water with PAC) were smaller than those for reactor R3 (BF water with PAC); however, the d_{90} value of the particles in reactor R2 was greater than that for reactor R3. This may be due to the continuous influx of larger particles with the raw water into reactor R2. In contrast, the particles entering reactor R3 (BF water with PAC) from the BF effluent were almost constant in size. Figs. 3 and 4B and D indicate that the number of particles smaller than 20 μm increased with time. The lowest size of particles measured using FCM and microscopic measurements were 1 μm; however, the pore size of the membrane was 0.1 μm. It was not possible to measure

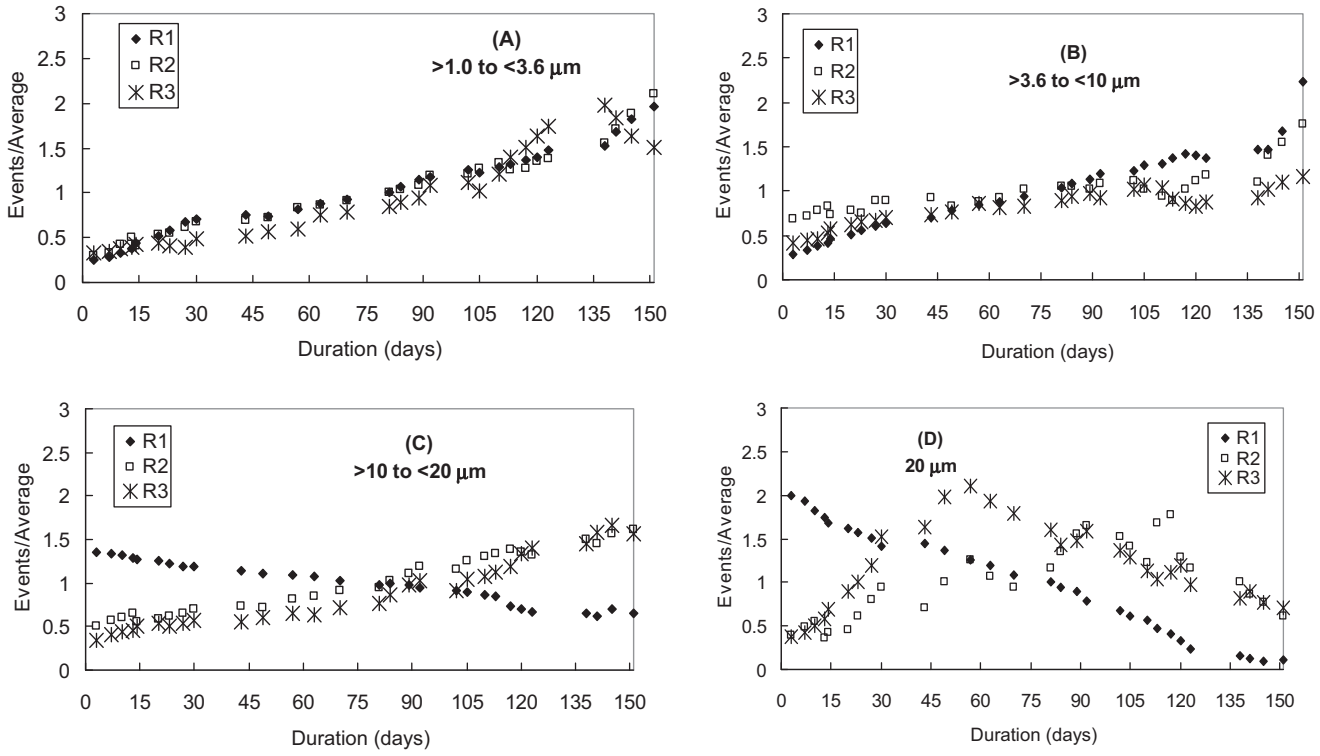

Fig. 3. Relative numbers of particles of sizes (A) >1.0 to <3.6 μm, (B) >3.6 to <10 μm, (C) >10 to <20 μm, and (D) 20 μm in the reactors over the duration of the study, measured with the flow cytometer.

the particle size less than 1 μm; however, the trends in Table 1 and Figs. 3 and 4 show that there could be higher number of particles less than 1 μm size, which potentially enhanced the particle fouling with time.

The average SS concentration of the raw water fed into reactors R1 and R2 was about 25.8 mg/L, while that of the biofilter water fed into reactor R3 was about 2.0 mg/L. The amount of SS fed over the entire 151-day period into reactors R1 and R2 was 98 g each, and that fed into reactor R3 was 8 g. Thus, it is to be expected (especially toward the end of the filtration period) that fragmentation products from PAC should dominate the particle size distribution in reactors R2 and R3.

Comparing these trends with the particle size distribution data, the performance of reactor R1 was increasingly dominated by the presence of smaller particles, to a greater extent than the performances of reactors R2 and R3 were, although all three reactors accumulated the smallest particles at about the same relative rate (Fig. 3A). Fang and Shi [38] and Choi et al. [12] observed that frag-

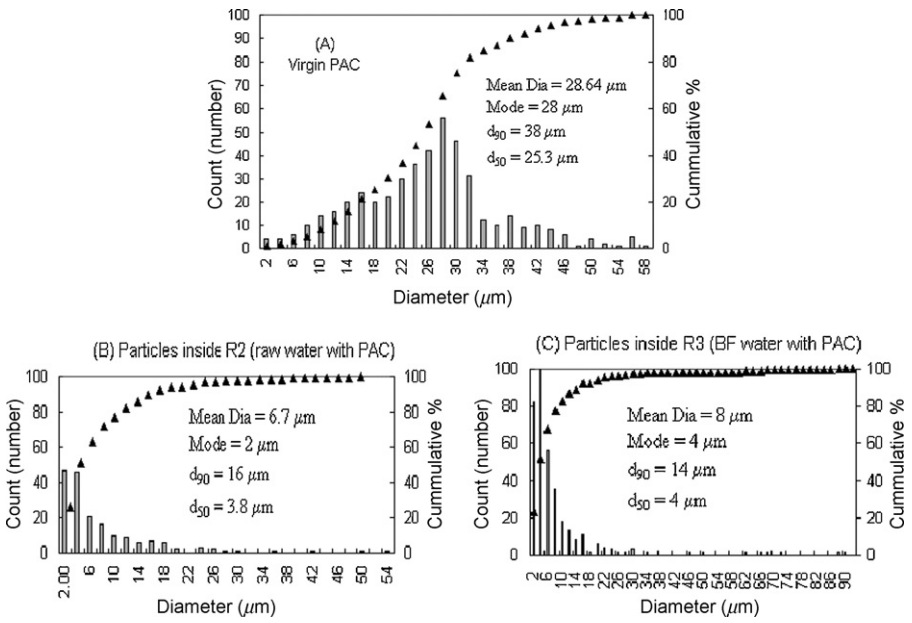

Fig. 4. Particle size distribution of (A) virgin PAC and samples in (B) reactor R2 (raw water with PAC) and (C) reactor R3 (BF, water with PAC) on Day-151, at the end of the filtration experiment, measured with microscopy. The numbers of particles in individual bin sizes are shown on the left ordinate, while the cumulative percentage is shown on the right.

mented small particles may cause rapid flux decline or a high TMP compared to larger-sized particles. These observations were performed in the absence of PAC, which is also demonstrated in this study for R1. Moreover, the average numbers of particles smaller than 3.6 μm (Table 1) were higher in reactors contained PAC (R2 and R3) than in R1.

With aeration, the PAC particle sizes not only were reduced but also broke particles coming into reactors R2 and R3 and these two reactors had less fouling, which indicates that the presence of PAC lessened smaller particle enhanced fouling and created higher porous cake layers on the membrane surfaces during filtration (R1 vs. R2 and R3), therefore, reduced the TMP [19,30]. Although the porosity of the cake formed on the MF surfaces in three reactors was not measured in this study, our speculations here are supported by Madaeni [44], who observed variable porosities inside cakes on MF membrane using wide ranges of particle sizes and correlated the flux decline. Moreover, the drag forces due to suspension flow, permeate flow, and air bubble flow play the major role in determining the particle stability and cake porosity on the membrane surfaces [40,45].

3.2. Estimation of the accumulation and degradation of SS in the influents to membrane bioreactors

3.2.1. Accumulation and degradation of SS

In this report, SS refers to the solids in the influents that entered to the reactors. During three time periods of the 151 days of operation, the influents and the contents of the reactors were sampled at three-day intervals. These samples were used to perform a mass balance of SS through the reactors as follows:

$$V\frac{dS}{dt} = Q(S_{in} - S_{out}) - \frac{m_{sampled}}{\Delta t} - Vr_S \quad (3)$$

where V is the volume of the reactor (5 L); S, the SS concentration in the reactor; Q, the flow through the reactor (25 L/day); S_{in} and S_{out}, the concentrations of SS in the influent (measured) and effluent (assumed zero) of the reactor, respectively; $m_{sampled}$, the collected sample volume times the concentration (to account for spent solids from the reactors during sampling) in period Δt; and r_S, the SS degradation rate in the system. The time derivative was computed from the slope of a SS versus time plot (data not shown), and other parameters were measured so that r_S could be computed from Eq. (3).

The degradation rates, input and accumulation of SS during the three time periods are shown in Fig. 5. The SS in the raw and in the biofiltered water varied from 10 to 65 mg/L and from 1 to 3 mg/L, repectively. The rate of degradation of suspended solids in reactors R1 (raw water without PAC), R2 (raw water with PAC) and R3 (BF water with PAC) varied from 45 to 150 mg/L/day, from 73 to 170 mg/L/day, and from 0 to 8 mg/L/day, respectively, through Day-151. Overall, for the last half of the study period (82–151 days), reactor R1 degraded 54% of the influent SS, R2 degraded 63%, and R3 (with 10-fold less incoming solids) degraded only 24%. As the SS load increased and MF membrane retained these SS inside the reactors, the amount of SS degradation decreased, which suggests a possibly finite capacity for SS degradation in the reactors.

In reactor R3, the accumulation rate was minimal during certain periods of operation, because it was receiving biofilter-treated river water. Over the entire 151-day period, SS entered in R3 was 10–20% of that in R1 and R2, the SS accumulation increased in all reactors (Fig. 5). The biofiltration of raw water reduced the SS load on R3. The low degradation rate of the SS in reactor R3 resulted from the prior degradation of the biodegradable portions of the SS in the biofilter. All three reactors received aeration below the membrane modules. There was consistently a higher SS degradation rate in reactor R2 than in R1. The mean diameter of particles in the raw

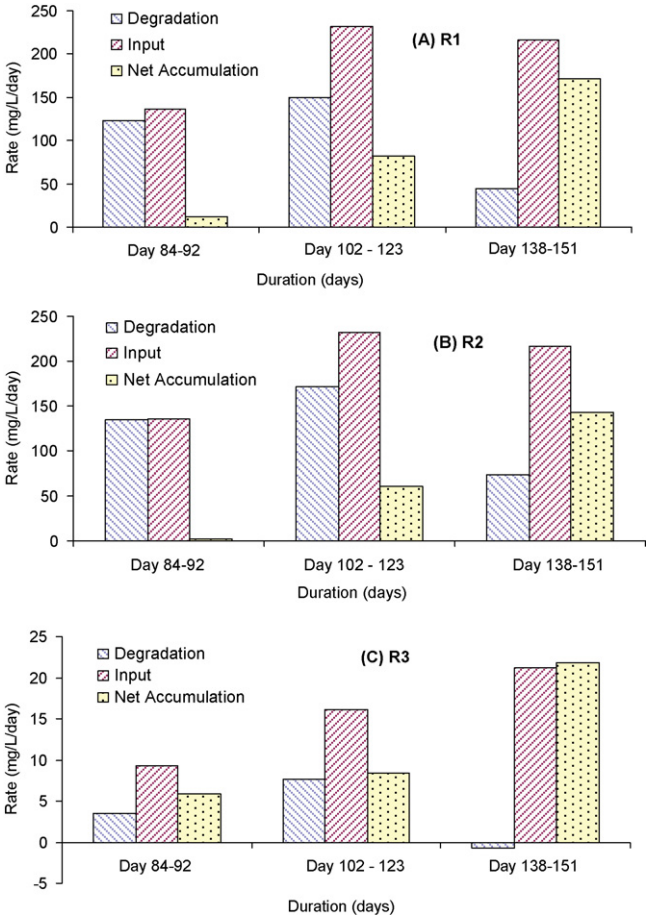

Fig. 5. Degradation, input and net accumulation rates of suspended solids (SS) during three time periods in reactors (A) R1 (raw water without PAC), (B) R2 (raw water with PAC) and (C) R3 (BF water with PAC). The losses of SS due to sampling were included in the accumulation data.

water was 102 μm measured using microscopy and Fig. 4(B) shows that at the end of operation, on Day-151, most of the particles inside R2 were less 20 μm and the maximum size of the particles in R2 was 54 μm. This indicates that the PAC in R2 enhanced the disintegration of SS in the raw water, the influent to this reactor, and also played an important role in higher SS degradation (~9% more than that in R1). The particles larger than 20 μm in R2, which was not possible to measure using the FCM, on Day-151 (Fig. 4B), could be broken/disintegrated SS, degraded PAC and/or the flocks of PAC and SS.

The overall accumulation of SS in reactor R1 was not significantly higher than that in reactor R2 (Fig. 5), but the membrane in reactor R1 experienced almost twice as much fouling as that in R2. Possibly the accumulated SS in R2 was not adsorbed in the way as they did on the membranes in R1 because of the presence of PAC, which lowered the resistance to filtration, delayed the TMP increase and extended the filtration cycle. In addition, Madaeni [44] and Hwang and Chen [45] demonstrated that higher resistance to filtration was caused by a less porous cake layer on the membrane. Therefore, the presence of PAC in R2 possibly altered the cake properties on the MF surface in a way that made the cake more favorable to filtration than that cake on the MF surface in R1, which was without PAC.

3.2.2. Role of bacteria on MF fouling

The concentrations of bacteria inside the reactors, the raw water and the biofilter effluent were enumerated every three days interval using the FCM. The average numbers of bacteria during the

filtration period in the raw water and the biofilter effluent were $55.9 \pm 1.1 \times 10^3$ and $78.7 \pm 7.7 \times 10^3$ cells/ml, respectively. The statistical analyses of bacterial count using the flow cytometry show that $p < 0.05$ as calculated using two-tailed Student's *t*-test. The number of bacteria entered in reactor R3 was more than that in reactors R1 and R2. However, the numbers of bacteria inside the reactors R1, R2 and R3: 94.5×10^3 (on day-3) to 238.1×10^3 cells/ml (on day-151); 163.9×10^3 (on day-3) to 502.3×10^3 cells/ml (on day-151) and 188.1×10^3 (on day-3) to 412.2×10^3 cells/ml (on day-151), respectively, increased with time. The number of total bacteria inside reactors R2 (raw water with PAC) and R3 (BF water with PAC) was always higher than those in reactor R1 (raw water without PAC), but that inside R3 was lower than R2, but more than R1.

The SS entered in reactors R1 and R2 was more than that in R3, which carried also more bacteria with it to reactors R1 and R2. Particulate matter has the ability to adsorb dissolved organic matter (DOM), ions or cell debris, thus leading to a micro-spatial accumulation of nutrients [46] and some (but not all) of the organics are degradable by the microorganisms in the reactors. Higher bacterial counts in R2 and R3 correspond to higher degradation rates of suspended solids, suggesting that the presence of PAC helped enhanced decomposition of SS. Reactor R3 received the effluent from the biofilter, which would expect to contain less biodegradable organics than the raw water. Thus, less bacterial growth would be expected in reactor R3 than in reactor R2. Bacteria sloughed from the biofilter could contribute potentially to increase the bacterial concentration inside reactor R3. The number of bacteria increased steadily with time and with nearly indentical counts in reactors R2 and R3, which suggests a constant rate of accumulation of bacteria due to the presence of PAC.

Since reactors R2 and R3 had less fouling than reactor R1, the increased number of bacteria did not contribute to the number of membrane fouling. In reactors containing PAC, the bacteria were likely adsorbed on PAC rather than being available for binding to the membrane surfaces [47]. However, there is no clear evidence that links the number of organisms in the bulk phase with the level of microbial fouling [5].

It has been shown that bacteria can convert dissolved and particulate organic matter into bacterial biomass and inorganic carbon [15,48,49]. In our previous study [30], we observed that PAC has continuous and high adsorption capacity of organic carbon in the presence of other competitive organic compounds. Therefore, the bacteria inside reactor R1 were mostly in contact with the membrane surface and produced more biomass, thus, reduced the cake porosity and increased the number of fouling. On the other hand, in R2 and R3, PAC adsorbed a significant portion of organic carbon and bacteria inside these reactors produced less biomass and thus, caused lower number of membrane fouling than in R1.

4. Conclusions

PAC–MF hybrid technologies are entering the mainstream for drinking water treatment because of the increased stringency of water quality standards, increasingly restricted water sources and supplies, and their more competitive cost. The lifetime of the PAC in terms of size and respective effect of PAC on the membrane fouling was about five months in these systems, but it was not clear how the quality of the raw water affected the lifetime of the PAC and how long the PAC could be used in the similar system, which will be examined in our next study. This novel study explored the dynamics of real-time particle size changes, SS accumulation and degradation, and MF membrane fouling in the presence and absence of PAC and the biofiltration of river water.

PAC reduced the effects of membrane fouling even after the larger particles had abraded to much smaller sizes, causing higher TMP and increasing the fouling frequency. In the presence of PAC, smaller particles did not play an important role in membrane fouling. Biofiltration lessens fouling considerably, more than the addition of PAC alone. Moreover, continuous air scrubbing reduced the formation of cake on the MF surfaces. Higher accumulations of SS and the gradual incremental accumulation of finer particles were observed in the system without PAC. PAC particles in the reactors enhanced the disaggregation of SS. The biofiltration of raw water reduced SS significantly, and a substantial amount of degradation of the biodegradable portions of the SS took place in the biofilter, which caused a low SS degradation rate in the reactor receiving BF-treated water and containing PAC. The gradual increase in the net accumulation of SS was an important factor controlling the performance of the PAC–MF system. The increased number of bacteria in the PAC–MF systems did not contribute to the number of membrane fouling.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.memsci.2011.01.017.

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