

Removal of organics and viruses using hybrid ceramic MF system without draining PAC

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Abstract

Ceramic microfiltration combined with powdered activated carbon adsorption (PAC-MF) was tested for organic and microbial control using river water laden with sewerage effluents. The PAC-MF was compactly configured with PAC adsorption and MF filtration zones in one reactor. It was operated with PAC addition of 20 g/L at the beginning without PAC drain. Organic matter was largely removed in the adsorption zone and then additional removal was obtained in the filtration zone. Selective adsorption of hydrophobic organic compounds onto PAC resulted in greater UV₂₆₀ removal of $90.3 \pm 3.2\%$ than DOC removal of $80.2 \pm 8.6\%$. Efficient organic control of the PAC-MF considerably decreased chlorine consumption to less than 0.5 ± 0.08 mg/L, and thus THMFP was brought down to less than 8.8 ± 2.2 µg/L in permeate. Furthermore, adsorption or attraction potential of microorganisms by PAC addition as well as virus capture in the PAC cake layer also assisted ceramic MF to remove viruses to less than detection limit after 60 days of operation. Therefore, the hybrid PAC-MF is a prospective advanced water treatment process that is capable of simultaneous organic and microbial removal by adsorption and filtration mechanisms.

Keywords: Ceramic membrane; Chlorine demand; Natural organic matter; Powdered activated carbon; Viruses

1. Introduction

Many researches for advanced water production using microfiltration (MF) and ultrafiltration (UF) membrane technology have been actively conducted. The produced water by an advanced

water treatment process should be safe from microbial pathogens, contain low concentration of synthetic organic compounds or small amount of disinfection by-products (DBP) precursor, and have no harmful heavy metals. Hybrid membrane system with addition of powdered activated carbon (PAC), in which membranes work as a final barrier against PAC particles and microbial

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contaminants, has been demonstrated to be capable of improving low organic removal of UF and MF, as well as controlling chronic membrane fouling. Various studies on the hybrid adsorption-membrane have been carried out to meet the specific requirements: characteristics of carbon [granular activated carbon (GAC) or PAC, carbon material, particle size, surface chemistry of carbon]; dosing method of carbon (step dose, pulse dose, carbon concentration, adsorbent contact time); membrane type (UF or MF, membrane material, module type); pressurized or submerged membrane configuration [1–4]. Thus, they showed small or enormous improvement of pollutant removal. However, conflicting observations in flux improvement were reported due to differences in water chemistry, membrane characteristics and applied carbons [5]. PAC-membrane processes with continuous dose of PAC were designed to remove taste and odor as well as synthetic organic compounds from drinking water treatment but PAC dose was not high enough to remove a significant fraction of dissolved organic matter. In addition, clear criteria in the combination of PAC and membranes have not yet been proposed, because selection of this system is very site specific. Therefore, accumulation of reliable data through long-term operation of pilot-scale PAC-membrane is required to promote practical use of the hybrid membrane in water treatment.

Ceramic membrane modules can withstand elevated temperatures, extremes of pH, and high operating pressure up to 10 bar without concern of membrane compaction, lamination and swelling. Ceramic membrane pore size covers the MF, UF and tight UF ranges from 5 μm down to 1000 Daltons of molecular weight cut-off [6]. This unique thermal, chemical and mechanical properties of ceramic membranes have significant advantages over polymeric membranes in many applications. In addition, ceramic membranes have been also reported to have a narrow pore size distribution compared to the polymeric

membranes. Nevertheless, it is rare for them to be used in water treatment compared to usage of polymeric membranes. Ceramic membranes can be significantly resistant to membrane deterioration by microbes and surface abrasion by coarse particles circulation, especially in the combination between PAC adsorption and membrane filtration. Thus, they are expected to have great benefits to combine with PAC adsorption for controlling membrane fouling and improving removal rates.

MF membranes, typically with pore sizes larger than 0.1 μm have showed lower removal of virus, and in some cases, could not at all act as a physical barrier to viruses [7]. Virus sizes with 0.005–0.1 μm generally correspond to the entire range of UF and the smallest pore size of MF. Among the viruses, *Norovirus* with two genotypes of NV-G1 and NV-G2 is the most common ecological agent for gastroenteritis outbreaks in all ages and has a significant public health impact worldwide. Most outbreaks of NV gastroenteritis have a distinct seasonality linked to the winter season [8]. NV of single strand of RNA generally has a diameter of 27–40 nm, which is smaller than the pore size of MF membranes. Meanwhile, enteric adenovirus (AdV) has a diameter of 70–100 nm and is usually detected in summer season. It is also not comparable to the pore size of MF. Thus, both viruses with different size and seasonality were selected to be monitored in this study. Virus removal could be enhanced through mechanical sieving by membrane or adsorption onto the membrane, as well as by cake layer during MF filtration [9]. Hence a hybrid membrane system using coagulation or adsorption is required to enhance virus removal of MF membrane alone [10].

This study focused on the organic and virus control using the pilot-scale PAC-MF system. In addition, chlorine demand and THM formation potential (THMFP) in the PAC-MF were compared with other conventional and advanced water treatment processes to confirm the efficiency of organic control by the PAC-MF.

2. Materials and methods

2.1. Experimental set-up of membrane pilot plants

Two trains of PAC-MF were installed as shown in Fig. 1. Each of them had PAC adsorption zone (PAZ) and submerged MF filtration zone (MFZ) in one reactor. Different types of MF module (Kubota Co., Japan) with a nominal pore size of $0.1\ \mu\text{m}$ was installed in each membrane reactor. One of the modules (denoted hereafter as R1) had 120 ceramic tubes with an outer diameter of 3.3 mm and the other module (denoted hereafter as R2) had 11 ceramic tubes with 13 mm in an outer diameter. About 20 g/L of PAC with a mean diameter of $151.2\ \mu\text{m}$ (Shirasagi S1, Japan Environmental Chemicals Co., Japan) was put into the PAZ at the beginning of the operation. Carbon concentration was naturally balanced between PAZ and MFZ since PAC in MFZ settled down and moved back to the PAZ during the filtration cycle when no aeration was done in MFZ. This system with no PAC drain can supply high buffering capacity to the fluctuation of micropollutant load. Fluxes of R1 and R2 were 1.99 and 2.61 m/day, respectively. Hydraulic retention times (HRT) were 67 and 53 min, respectively in PAZ and MFZ of R1 and HRTs of PAZ and MFZ in R2 were 60 and 48 min, respectively. Aeration rate of PAZ was 60 L/min throughout the MF filtration and 50 L/min of aeration rate was applied only during backwash operation.

2.2. Measurements of THMFP and chlorine consumption

The DBP formation potential of water samples was assessed on the basis of 1-day and 7-day THMFP. The pH of water samples was adjusted at 7.0 ± 0.2 with 0.5 M phosphate buffer, followed by chlorination. The dose of buffered sodium hypochlorite was determined so as to ensure a residual chlorine of more than 1 mg/L at the end of the incubation at $25 \pm 0.5^\circ\text{C}$. Excess chlorine in the sample was quenched with Na_2SO_3 , followed by THM analysis using a gas chromatograph (HP6890, USA) equipped with capillary column (HP-5, Agilent, USA) and an electron capture detector. The residual chlorine at the required chlorination time was determined by DPD method with a portable spectrophotometer (DR/700, Hach, USA).

2.3. Microbial assay

About 2 L of samples was concentrated by the following method as described by Katayama et al. [8]. A sample mixed with 2.5 mM MgCl_2 was passed through an HA filter (Nihon Millipore, Japan) with a $0.45\text{-}\mu\text{m}$ pore size, which was then rinsed with 200 mL of 0.5 mM H_2SO_4 (pH 3.0), followed by elution of viruses with 10 mL of 1 mM NaOH (pH 10.8). The filtrate was neutralized upon recovery, followed by reconcentration using a Centriprep YM-50 (Millipore) to obtain

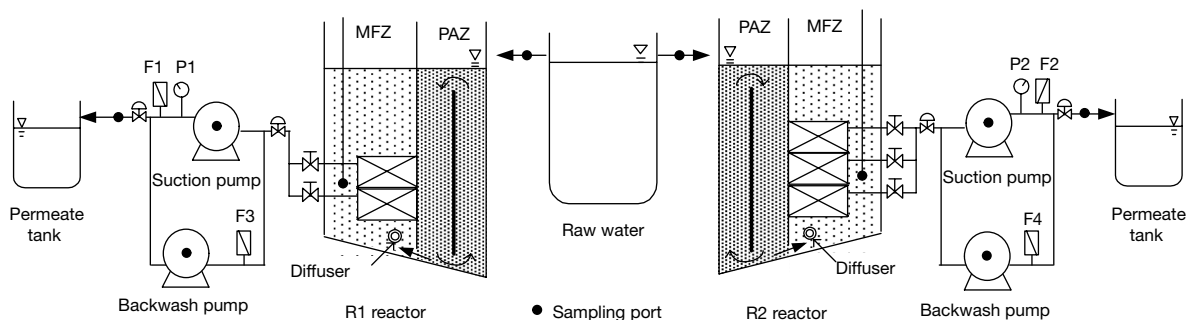


Fig. 1. Schematic diagram of the PAC-MF using two different kinds of ceramic module tubes.

a final volume of 700 μ L. Final eluate was applied for viral RNA extraction (NV-G1 and NV-G2) and DNA extraction (AdV) by using a QIAamp viral RNA/DNA mini kit (QIAGEN, Tokyo, Japan), followed by quantification by the TaqMan PCR technique with the ABI PRISM 7000 (Applied Biosystems, Tokyo, Japan). Virus concentration was calculated as PCR detection unit (PDU/mL) from the result of the end point dilution of detection limit of the positive control. Total coliforms (TCs) and *E. coli* were determined as colony forming unit (CFU/mL) using Coliform Agar, Chromocult[®].

2.4. Organic matter analysis and surface charge measurement

Turbidity was measured by a turbidimeter (2100N, Hach, USA) at the sampling site. Water samples treated by 0.45 μ m filter were used to analyze dissolved organic carbon (DOC) (TOC 5000A, Shimadzu Co., Japan) and UV absorbance at 260 nm (U-2010, Hitachi, Japan). Surface charge of PAC was measured by potentiometric acid–base titration method by adding various amount of HCl or NaOH into PAC suspension in Milli-Q water, and then measuring pH after 24-h equilibration.

3. Results and discussion

3.1. Organic removal

For the evaluation of organic removal using the PAC-MF, raw water, MFZ water and membrane filtrate were sampled for DOC and UV₂₆₀ analysis. Permeate DOC of both PAC-MF was 0.28 ± 0.12 (mean \pm std. dev.) mg/L, which was 0.74 ± 0.17 mg/L of sand filter and 0.63 ± 0.14 mg/L of O₃+ GAC (BAC) as shown in Fig. 2. Natural organic matter (NOM) was mainly removed by carbon adsorption in the first PAZ, and then additional removal of 10–20% was obtained by MF filtration and adsorption onto accumulated PAC in the MFZs. R2 reactor

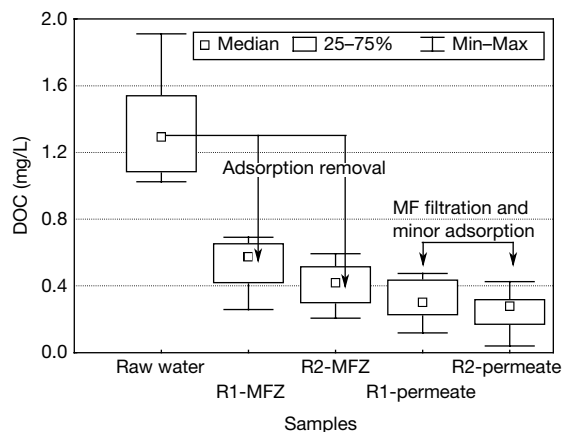


Fig. 2. DOC removal in the PAC-MF.

showed higher DOC removal than R1 reactor, even though both reactors had the same pore size of ceramic membranes. R1 module with fine 120 tubes caused poor carbon circulation between PAZ and MFZ and decreased carbon concentration of PAZ during the course of filtration cycles, resulting in slight decrease of DOC removal through carbon adsorption.

Fig. 3 shows the resulting UV₂₆₀ removal through the PAC-MF membrane. UV₂₆₀ was removed up to 65 and 68% in R1-PAZ and R2-PAZ, respectively, by adsorption of aromatic

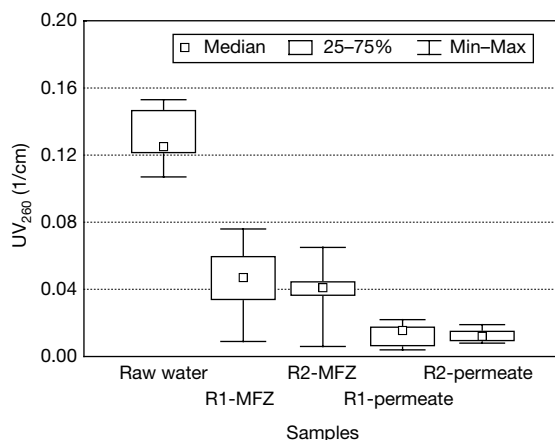


Fig. 3. UV₂₆₀ removal through the PAC-MF.

organic compounds on PAC. Filtration by MF as well as minor adsorption by suspended and attached PAC in R1-MFZ and R2-MFZ further reduced UV_{260} by 25 and 31%, respectively. It could be assumed that NOM was mainly removed in the PAZ, due to carbon adsorption of lower molecular weight and hydrophobic organic compounds, and additionally reduced in the MFZ due to major size exclusion of higher MW organic compounds. Overall UV_{260} removal of $90.3 \pm 3.2\%$ was higher than DOC removal rate of $80.2 \pm 8.6\%$ because of selective adsorption of hydrophobic organic fraction on activated carbon. Consequently, the PAC-MF demonstrated enough adsorption capacity of organics even after 60 days of operation, and was expected to produce safer drinking water with low contents of DBP precursors.

3.2. THMFP removal and chlorine consumption

Concurrently with the PAC-MF pilot experiments, Tokyo Metropolitan Waterworks (TMW) operated a pilot plant for advanced water treatment, which had a treatment train with coagulation, sand filtration, ozonation and granular (biological) activated carbon (BAC). Sand filtrate (rapid sand filter after coagulation with ferric-silicate coagulant) and effluent of $O_3 + BAC$ (0.48 mg/L of ozone dose rate in the three-stage counter-current flow reactor; GAC column with 13.3 m/h of filtration velocity) were sampled from the TMW's pilot unit to compare the THMPF and chlorine demand with the PAC-MF process.

Chlorine consumption of the PAC-MF was characterized in Fig. 4 and compared with that of sand filter. Chlorine reaction with organic matter was fast and initial chlorine was consumed by almost 40% after 1 h of chlorination and 70–80% after 1-day chlorination. Chlorine consumption of raw water was 2.58 mg/L after 7 days of incubation. 7-day chlorine consumption was lower than 1 mg/L after PAC adsorption, and final water from R1 and R2 reactors showed chlorine

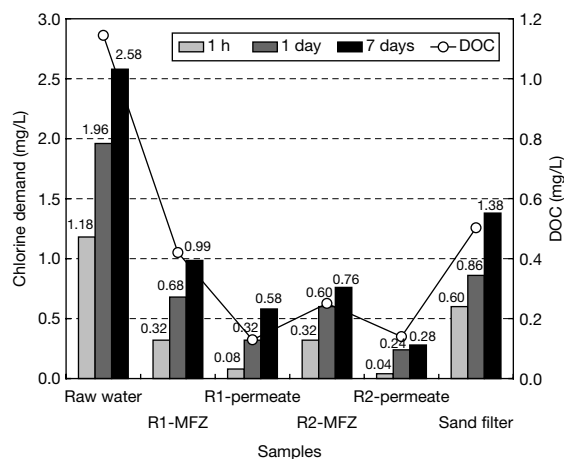


Fig. 4. Chlorine consumption via chlorination time.

consumption by 0.58 and 0.28 mg/L , respectively. It was significantly lower than the chlorine consumption of 1.38 mg/L in the filtrate from the sand filter. In Fig. 5, 1-day chlorine consumption through various water treatment processes using the same raw water was also investigated to compare with the PAC-MF. Chlorine consumption of the PAC-MF was 0.5 ± 0.08 (mean \pm std. dev.) mg/L , which was lower than $0.77 \pm 0.21 \text{ mg/L}$ of BAC and $1.29 \pm 0.23 \text{ mg/L}$ of sand filter. It was demonstrated that the

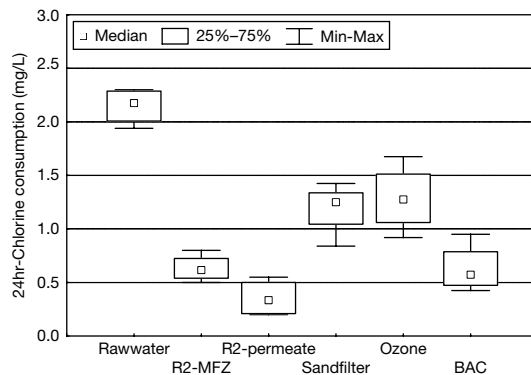


Fig. 5. Comparison of chlorine consumption.

PAC-MF could significantly reduce chlorine demand for disinfection and decrease formation of DBP. Therefore, decrease in NOM and chlorine demand by the PAC-MF contributes considerably to control THMs as well as other DBPs.

As shown in Fig. 6, the PAC-MF showed higher removal of 7-day THMFP (up to 81–89%) than 50% of sand filter and 73% of BAC, resulting in 8.8 ± 2.2 $\mu\text{g/L}$ of THMFP in permeate. The different design of ceramic membrane module in the same reactor caused different PAC behavior, such as carbon concentration and carbon retention time in each reactor zone, resulting in a small difference in THMFP removal rates as the removal of DOC. 1-day THMFP of the whole water samples was almost 40–60% of 7-day THMFP, which corresponded to the resulting chlorine consumption as shown in Fig. 4.

Fig. 6 also shows composition of THMFP through various water treatment processes. Chloroform has been generally known to be more than 50% of THM. In Tama River Water, however, bromated THM was more than 60% of total THMs and CHCl_3 was only 10–20% of total

THMs. Tokyo Metropolitan Waterworks reported that bromide concentration of Tama River ranged from 22 to 370 $\mu\text{g/L}$ in 2002 and 2003. Higher concentration of bromide was observed between May and September and lower concentration was observed between December and April because of seasonal fluctuation of water flow in Tama River. The PAC-MF was very efficient in producing treated water with low THM concentration compared with other treatments, e.g., conventional rapid sand filtration or O_3 + BAC process. Furthermore PAC-MF could be a better option than O_3 + BAC treatment if an elevated concentration of bromide is detected in raw water, which may promote formation of hypobromite, bromate and bromated DBPs after ozonation.

Fig. 7 depicts a linear relationship between the initial UV_{260} before chlorination and THM formation potential of each sample, as well as the correlation between the initial UV_{260} and chlorine consumption of each sample. As shown in Fig. 7, UV_{260} reduction after 24 h of chlorination (ΔUV_{260}) also showed good linearity with THMFP and chlorine consumption. Thus UV_{260} could be a useful indicator to predict

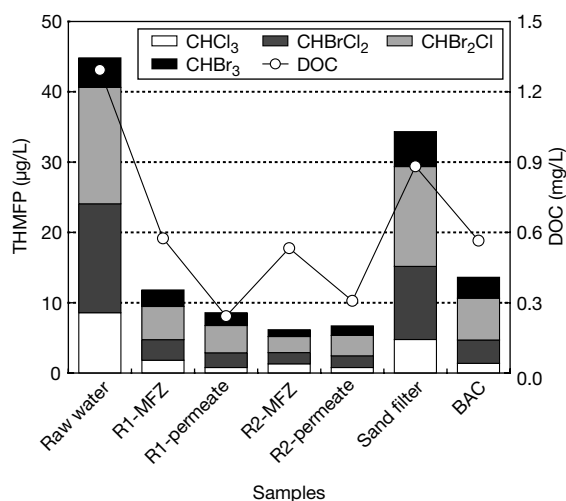


Fig. 6. Removal of THMFP and composition.

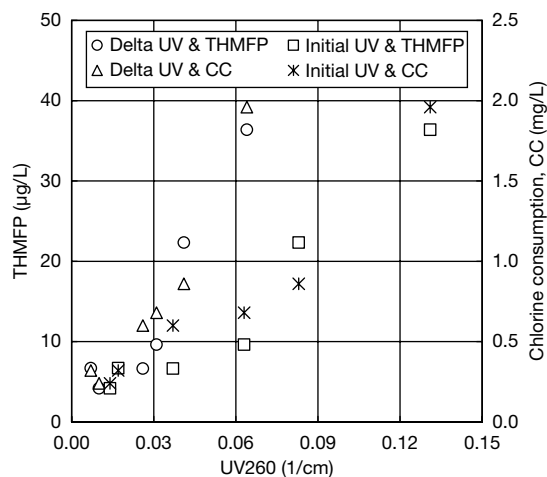


Fig. 7. Relationships among UV_{260} , THMFP and chlorine consumption.

THM formation potential and to estimate chlorine demand.

3.3. Removal of bacteria and viruses

Bacteria and viruses concentrations in raw water and effluents from PAC-MF, sand filtration and O₃ + BAC were analyzed two times during the winter season in 2004 and the results of microbial tests were summarized in Table 1. *E. coli* was detected in the sand filtrate, but could be removed to below detection limit by the following O₃ + BAC. *E. coli* and TCs were removed to below the detection limit by size exclusion of MF as expected. Since the bacterial tests were conducted by natural bacterial concentration, the PAC-MF showed lower log removals of *E. coli* and TCs by 1.10–1.54 and 2.10–2.51 log, respectively, than the seeded bacteria challenge studies [7].

Sizes of the tested virus (27 ± 40 nm of NV, 70 ± 100 nm of AdV) were much smaller than the MF pore size of 100 nm, however the PAC-MF exhibited virus removal to less than detection limits after 60 days operation. The PAC-MF could remove NV-G2 and AdV by 1.54–2.67 and 2.07–2.57 log, respectively, showing no detection in permeate. However NV-G1 from permeate of PAC-MF was detected by 0.29 PDU/100 mL in

one case of virus analysis as shown in Table 1. Sand filter showed poor removal of all the test viruses, however viruses from the O₃ + BAC were not at all detected in this study.

The elapsed operating time after a backwash or chemical cleaning event could significantly impact virus removal due to the formation of a cake layer on the membrane surface. As the cake layer thickened and compressed through a filtration cycle, it was reported that the removal of viruses by membranes could be improved [9]. In this study, PAC addition before the ceramic membrane filtration might contribute to the virus removal by adsorption or attraction on suspended PAC with enough adsorption potential, virus capture in the PAC cake layer and virus clogging in the constricted membrane pore including membrane physical sieving. The virgin PAC used for this PAC-MF was measured to have positive charge at neutral pH, having an isoelectric point of pH 9.52. Thus negatively charged virus at neutral pH could bound or attach on PAC by electrical attractive interaction in the bulk solution of PAZ and MFZ, followed by MF filtration of carbon or particles. However, the virgin carbon would be neutralized by other negative contaminants like organics and the surface area of carbon would be fouled by colloids and NOM, resulting in loss of positive charge of

Table 1
Results of bacteria and viruses removals

Samples	Bacteria (CFU/mL)				Viruses (PDU/100 mL)					
	<i>E. coli</i>		TCs		NV-G1		NV-G2		AdV	
	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
Raw water	0.5	0.7	10	13	1.0	9.36	34.7	465	116	371
PAC-MF	ND*		ND		ND	0.29	ND	ND		ND
Sand filter	0.1	0.2	ND		0.20	9.36	ND	5.78	ND	3.75
O ₃ + BAC	ND		ND		ND		ND	ND		ND

*ND: not detected.

PAC surface via operation time. Detection result of NV-G1 in permeate of PAC-MF explained that many potential mechanisms of virus removal in the PAC-MF could not completely reject viruses, especially small size of virus like NV-G1. Therefore, the removal mechanism of viruses by adsorption onto suspended carbon, capture in the carbon cake layer and MF filtration including competition of adsorption sites should be further investigated in relation with carbon usage or filtration time in the PAC-MF process.

4. Conclusions

The organic and microbial control using pilot-scale ceramic microfiltration combined with powdered activated carbon adsorption was investigated for surface water treatment. Different module types with 120 and 11 tubes were used for submerged membrane reactors and 20 g/L of PAC was added one time at the start of membrane operation. Selective adsorption of hydrophobic organic compounds by PAC addition resulted in greater UV_{260} removal of $90.3 \pm 3.2\%$ than DOC removal of $80.2 \pm 8.6\%$. NOM was largely removed in the adsorption zone and then additional removal was obtained by MF filtration and minor adsorption of accumulated carbon in the MF filtration zone. This efficient organic control by the PAC-MF could reduce chlorine consumption to 0.5 ± 0.08 mg/L and THMFP of permeate to 8.8 ± 2.2 μ g/L. Removal efficiency of NOM and THM precursors and reduction of chlorine consumption by the PAC-MF was greater than $O_3 + GAC$ process. Furthermore, adsorption or attraction potential of microorganisms by PAC addition as well as virus capture in the PAC cake layer also assisted ceramic MF to remove viruses to less than detection limit. Therefore, this hybrid system is a prospective advanced water treatment process that makes use of both adsorption and filtration mechanisms.

References

- [1] T. Suzuki, Y. Watanabe, G. Ozawa and S. Ikeda, Removal of soluble organics and manganese by a hybrid MF hollow fiber membrane system, *Desalination*, 117 (1998) 119–130.
- [2] C. Campos, L. Schimmoller, B.J. Marinās, V.L. Snoeyink, I. Baudin and J.M. Lainé, Adding PAC to remove DOC, *J. AWWA*, 92 (8) (2001) 69–83.
- [3] Y. Matsui, A. Yuasa and F. Colas, Effect of operational modes on the removal of synthetic organic chemical by powdered activated carbon during ultrafiltration, *Water Sci. Technol.: Water Supply*, 1 (5/6) (2001) 39–47.
- [4] S.G. Yiantsios and A.J. Karabelas, An experimental study of humid acid and powdered activated carbon deposition on UF membranes and their removal by backwashing, *Desalination*, 140 (2001) 195–209.
- [5] C.F. Lin, Y.J. Huang and O.J. Hao, Ultrafiltration processes for removing humic substances: effect of molecular weight fractions and PAC treatment, *Water Res.*, 33 (1999) 1252–1264.
- [6] R. Sondhi, R. Bhave and G. Jung, Applications and benefits of ceramic membranes, *Membr. Technol.*, (2003) 5–8.
- [7] US EPA, Low-pressure membrane filtration for pathogen removal: application, implementation, and regulatory issues, Report EPA 815-C-01-001, Office of water, USA, 2001, pp. 119–130.
- [8] H. Katayama, A. Shimasaki and S. Ohgaki, Development of a virus concentration method and its application to detection of enterovirus and Norwalk virus from coastal seawater, *Appl. Environ. Microbiol.*, 68 (3) (2002) 1033–1039.
- [9] J.G. Jacangelo, S.S. Adham and J.M. Lainé, Mechanism of *Cryptosporidium*, *Giardia*, and MS2 virus removal by MF and UF, *J. AWWA*, 87 (9) (1995) 107–121.
- [10] T. Matsushita, Y. Matsui, N. Shirasaki and Y. Kato, Effect of membrane pore size, coagulation time, and coagulant dose on virus removal by a coagulation–ceramic microfiltration hybrid system, *Proc. EDS Conf. on MDIW Production*, L’aquila, Italy, 2004, pp. 15–17.