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Effect of humic acid, photo-oxidation, and adsorption at air back-flushing in hybrid water treatment of multi-channel alumina MF and photocatalyst-coated PP beads

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ABSTRACT

The effect of humic acid (HA) on membrane fouling and treatment efficiency was observed in a hybrid process of seven channel alumina microfiltration (MF) and TiO_2 photocatalyst-coated polypropylene (PP) beads with air back-flushing for advanced water treatment, and compared with the previous study with water back-flushing. As a result, the organic matter could be one of the main factors affecting membrane fouling because the final membrane fouling resistance decreased significantly as reducing HA concentration. The turbidity treatment efficiencies were very high as 95.5–98.3% independent of HA, but that of dissolved organic matters (DOM) was the maximal 80.1% at HA 8 mg/L. However, in the result with water back-flushing, the DOM treatment efficiency was almost constant between 78.9 and 81.8% independent of HA. Treatment portions of MF, photocatalyst adsorption, and photo-oxidation were investigated by comparing the treatment efficiencies of (MF), (MF + TiO_2), and (MF + TiO_2 + UV) processes. The membrane fouling resistance was the minimum at (MF + TiO_2 + UV) process. It means that the photo-oxidation and adsorption could control membrane fouling in the hybrid water treatment process. The role of adsorption was more important than that of photo-oxidation in the hybrid process with air back-flushing; but, the role of photo-oxidation was a little more important than that of adsorption in the result with water back-flushing for DOM treatment.

Keywords: Microfiltration; Photocatalyst; Hybrid process; Ceramic membrane; Water treatment; Photo-oxidation

1. Introduction

Photocatalytic oxidation, a new type of water pollution control technology, with the characteristics of high efficiency, low energy consumption, and a wide range of application, can oxidize most organic compounds, especially non-biodegradable organic contaminants, by mineralizing them to small inorganic molecules. For this reason, photocatalytic oxidation technology has broad prospects for application. Among various semiconductor photocatalysts, there is

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a general consensus among researchers that TiO_2 is more superior because of its high activity, large stability to light illumination, and low price [1–4]. In photocatalytic degradation, two modes of TiO_2 application are adopted: (1) TiO_2 immobilized on support materials, and (2) TiO_2 suspended in aqueous medium [5,6]. Application of TiO_2 in suspension instead of immobilizing the TiO_2 on solid carriers has shown an improvement in organic degradation efficiencies due to the uniform distribution and large specific surface area. However, classical solid–liquid separation processes such as sedimentation, centrifugation, and coagulation used for separation of the fine TiO_2 particles (typically less than 1 μm), are not effective [7]. In addition to the low reutilization rate, there is also a chance of secondary pollution caused by fine TiO_2 particles in the effluent. Therefore, the recovery of the photocatalysts is one of the main concerns that affect its engineering application on a large scale. A lot of investigations have been conducted aiming at solving this problem [8–12].

In recent years, titanium microsphere has also been proposed as a means to recover TiO_2 photocatalyst. Generally, the core-shell structured TiO_2 microspheres with a mesoporous surface made of nano-TiO_2 have low density, high specific surface area, and large size favorable for separation [13–16]. But, the preparation method and operating conditions have great effect on particle morphology associated with photocatalysis, and many problems existing in the current preparation methods need to be solved by optimizing the process conditions or developing new ones [17].

Membrane separation process for separation and purification has been developed rapidly during the past few decades. It can simultaneously separate and concentrate all pollutants in water by the retention of its microspores without secondary pollution and phase change. In addition, with the advantage of low energy consumption, its equipments are compact, easy to operate, and capable of continuous operation at room temperature [18]. However, membrane fouling due to the adsorption–precipitation of organic and inorganic compounds onto membranes leads to a decrease in the permeate flux, an increase in membrane cleaning costs, and a reduction of the life of the membrane. Although considerable progress has been made in membrane fouling [19,20], techniques for controlling membrane fouling remain inadequate, which is the major obstacle in the successful implementation of membrane separation technology. The TiO_2 photocatalysis membrane separation coupling technology emerged recently can solve the two problems mentioned above effectively [21]. The coupling technology not only keeps the characteristics and capacity of the two technologies, but also produces some synergistic effects to overcome the drawbacks of the single technology. On the one hand, the pollutants are oxidized by the photocatalysis, and the selected membranes show the capability not only to retain the photocatalyst, but also to reject partially organic species by controlling the residence time in the reacting system. In other words, the membrane is also a selective barrier for the molecules to be degraded; thus, the coupling technology could enhance the photocatalytic efficiency and achieve excellent effluent quality. On the other hand, the coupling of photocatalysis and membrane separation could solve or alleviate the problem of flux decline associated with membrane fouling [22]. Our previous result published recently about effect of water back-flushing in a hybrid water treatment process of multi-channel ceramic MF and polyethersulfone beads loaded with photocatalyst [23].

In this study, the effect of humic acid (HA) on membrane fouling was observed in a hybrid process of seven channel alumina MF and TiO_2 photocatalyst-coated PP beads with periodic air back-flushing for advanced water treatment. The one hybrid module of ceramic MF membrane and the PP beads fluidized between the gap of ceramic membrane and the acryl module case was the first trial in the hybrid water treatment process field of MF and photocatalyst. Also, treatment portions of membrane filtration, photocatalyst adsorption, and photo-oxidation were investigated by comparing the treatment efficiencies of (MF), (MF + TiO_2), and (MF + TiO_2 + UV) processes. Periodic air back-flushing was performed during 10 s per 10 min filtration to reduce membrane fouling. The results were compared with those of the previous study [24] using the hybrid process of the same MF membrane and photocatalyst-coated PP beads except water back-flushing. This hybrid process could be applied as pretreatment before desalination reverse osmosis (RO) plant if the treated water quality were satisfied as the feed water of RO.

2. Experiments

2.1. Materials

The multi-channel ceramic MF membrane (HC04) used in the study was coated with α-alumina on a supporting layer of α-alumina, and its pore size was 0.4 μm. We purchased the membrane from Dongseo Inc. in Korea, and the specifications of the seven-channel ceramic membrane were arranged in Table 1.

The photocatalyst used was 4–6 mm PP beads coated with TiO_2 powder made by Prof. Kim's group [25] using chemical vapor deposition method, which

Table 1
Specifications of the multi-channel ceramic microfiltration (HC04) used in this study

Membrane	HC04
Pore size (μm)	0.4
No. of channels	7
Outer diameter (mm)	20
Inner diameter (mm)	4
Length (mm)	241
Surface area (cm^2)	212
Material	α-Alumina coating on α-alumina support
Company	Dongseo Industry in Republic of Korea

was presented in Table 2. Instead of natural organic matters (NOM) and fine inorganic particles in natural water source, a quantity of HA sodium salt (Aldrich) and kaolin (Sigma–Aldrich) was dissolved in distilled water. It was then utilized as synthetic water in our experiment. The HA was selected as an organic matter representative because it was known that HA was the major humic material of river or lake. Kaolin concentration was fixed at 30 mg/L and HA concentration was changed from 2 to 10 mg/L in the synthetic feed water to investigate the effect of organic matters. The HA concentration was fixed at 6 mg/L for researching a portion of the treatment efficiencies of multi-channel ceramic MF, adsorption, and photo-oxidation. UV light with 352 nm was radiated from outside of the acryl module by two UV lamps (F8T5BLB, Sankyo, Japan) having 8 W power.

2.2. Hybrid membrane module

For eliminating the turbidity and NOM, the hybrid module was constructed by packing PP beads coated with TiO_2 powder between the module inside and outside of a ceramic membrane. In addition, 100 meshes (0.150 mm), which was extremely smaller than 4–6 mm particle size of the PP beads utilized here, was installed at the outlet of the hybrid module to prevent the PP beads loss into the treated water tank.

Table 2
Specification of the TiO_2-coated polypropylene beads used in this study

Material of the beads	Polypropylene (PP)
TiO_2 coating method	Chemical vapor deposition
Diameter (mm)	4–6
Weight (mg)	21.8–48.3
Average weight (mg)	39.9

2.3. Experimental procedure

The advanced water treatment system utilizing a hybrid module of multi-channel ceramic microfiltration and TiO_2 photocatalyst-coated PP beads was demonstrated in Fig. 1, which was utilized at our previous study without the PP beads [26]. We performed cross-flow filtration for the multi-channel ceramic membrane and periodic air back-flushing utilizing nitrogen gas for protecting oxygen effect on water quality. The hybrid module filled up with 40 g/L of TiO_2 photocatalyst-coated PP beads between the gap of ceramic membrane and the acryl module case, and it was installed in the advanced hybrid water treatment system. Then, the feed tank was filled with 10 L of prepared synthetic water composed of HA and kaolin, and the temperature of the feed water was constantly maintained by using a constant temperature circulator (Model 1146, VWR, USA). Also, the synthetic feed water was continuously mixed by a stirrer in order to maintain the homogeneous condition of the feed water, and it was caused to flow into the inside of the multi-channel ceramic membrane by a pump (Procon, Standex Co., USA). The feed flow rate was measured by a flow meter (NP-127, Tokyo Keiso, Japan). The flow rate and pressure of the feed water that flowed into the hybrid module was constantly maintained by controlling valves of both the bypass pipe of the pump and the concentrate pipe. The permeate flux treated by both the multi-channel ceramic membrane and the PP beads was measured by an electric balance (Ohaus, USA). The treated and the concentrate water recycled to the feed tank to maintain a constant concentration of the feed water during operation.

Kaolin was fixed at 30 mg/L and HA was changed from 2 to 10 mg/L in the synthetic feed water to investigate the effect of organic matters. The air back-flushing time (BT) and filtration time (FT) were fixed at 10 s and 10 min, respectively. Only MF process without PP beads coated with TiO_2 photocatalyst and UV light (MF), and MF process with PP beads ($MF + TiO_2$) were, respectively, operated at 6 mg/L of HA and compared with the hybrid process of MF and PP beads with UV ($MF + TiO_2 + UV$) for researching a portion of the treatment efficiencies of multi-channel ceramic MF, adsorption, and photo-oxidation.

We observed the resistance of the membrane fouling (R_f) and permeate flux (J) during a total FT of 180 min under each condition. Under all experimental

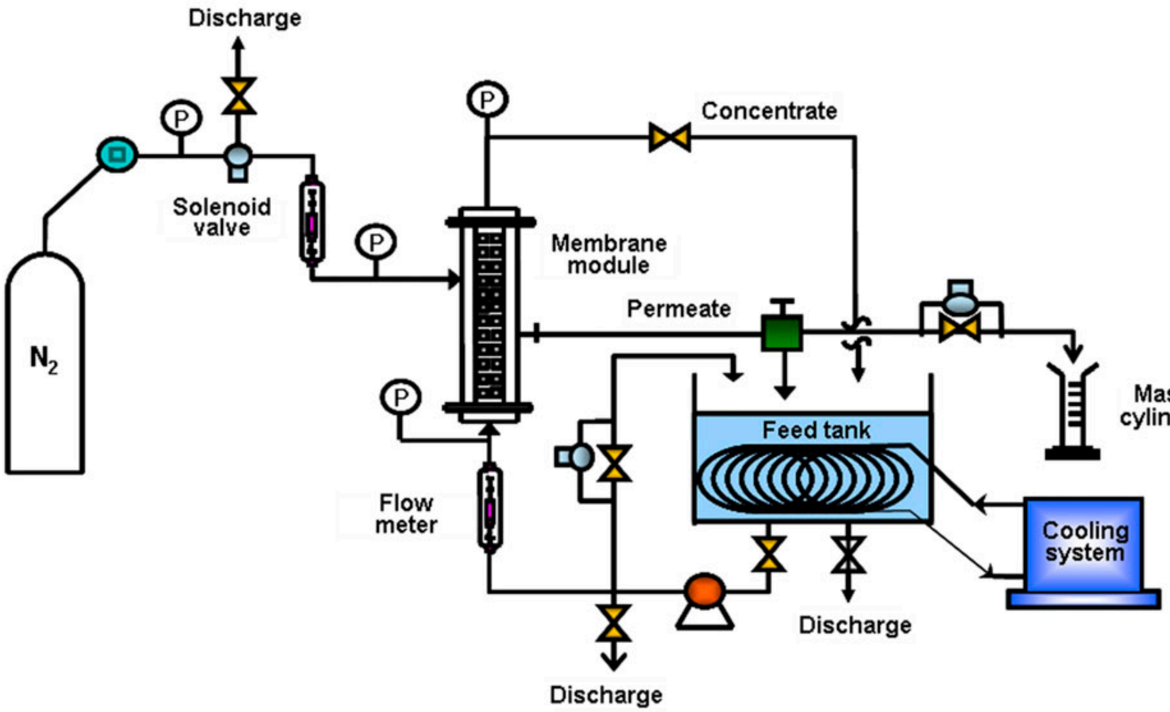

Fig. 1. Apparatus of hybrid water treatment process of ceramic microfiltration and TiO_2 photocatalyst-coated PP beads with periodic air back-flushing [26].

conditions, trans-membrane pressure was maintained constant at 0.8 bar, the air back-flushing pressure at 1.0 bar, the feed flow rate at 1.0 L/min, and the feed water temperature at 20°C. Periodic air back-flushing using permeate water was performed during 10 s per 10 min filtration.

The quality of feed water and treated water was analyzed in order to evaluate the treatment efficiencies of turbid materials and dissolved organic matters (DOM). Turbidity was measured by a turbidimeter (2100 N, Hach, USA) and UV_{254} absorbance was analyzed by a UV spectrophotometer (Genesys 10 UV, Thermo, USA). The detection limits of turbidimeter and UV spectrophotometer were 0–4,000 NTU (±0.001 NTU) and -0.1 to 3.0 cm^{-1} (±0.001 cm^{-1}). Before the measurement of UV_{254} absorbance, the sample was filtered by 0.2 μm syringe filter to remove turbid materials.

3. Results and discussion

The effect of organic matters on membrane fouling was investigated in the hybrid process of multi-channel ceramic MF and TiO_2 photocatalyst-coated PP beads with periodic air back-flushing for advanced water treatment. Also, treatment portions by membrane filtration, photocatalyst adsorption, and photo-oxidation were investigated by comparing the treatment efficiencies of MF, (MF + TiO_2), and (MF + TiO_2 + UV) processes. Resistances of membrane, boundary layer, and membrane fouling (R_m, R_b, R_f) were calculated from permeate flux (J) data using the resistance-in-series filtration equation as the same method as our previous study [26].

3.1. Effect of HA concentration

As shown in Fig. 2, the resistances of membrane fouling (R_f) were highly influenced by HA concentration, and R_f increased as rising HA concentration from 2 to 10 mg/L. However, R_f increased more dramatically in our previous study [24] using the same hybrid process of HC04 membrane and the photocatalyst-coated PP beads with periodic water membrane and the photocatalyst-coated PP beads. It means that the organic matter as HA could make membrane fouling more severely on the surface and inside the ceramic membrane as increasing the HA concentration in water. The final R_f ($R_{f,180}$) after 180 min operation at 10 mg/L of HA was 2.446×10^9 kg/m^2s, which was 1.89 times higher than 1.293×10^9 kg/m^2s of the $R_{f,180}$ at 2 mg/L as summarized in Table 3. But, in the

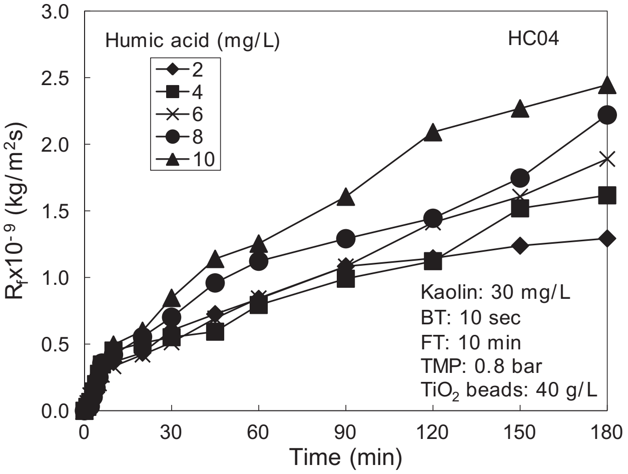

Fig. 2. Effect of HA on resistance of membrane fouling in hybrid process of multi-channel ceramic MF and TiO_2 photocatalyst-coated PP beads.

previous study [24], the $R_{f,180}$ at 10 mg/L of HA was 1.422×10^9 kg/m^{2}s, which was 2.77 times higher than 0.513×10^9 kg/m^{2}s of the $R_{f,180}$ at 2 mg/L. It means that air back-flushing could prohibit membrane fouling more effectively than water back-flushing [24] in the hybrid water treatment process.

To investigate a relative decline of permeate flux, Fig. 3 showed the dimensionless permeate flux (J/J_0), where J_0 is the initial permeate flux which was estimated by extrapolation using initial 2 data at 1 and 2 min. The J/J_0 tended to decrease a little as increasing HA concentration from 2 to 10 mg/L because of the membrane fouling formation by more organic macromolecules. Thus, the final value of J/J_0 (J_{180}/J_0) of 0.412 after 180 min operation at 2 mg/L of HA was 1.34 times higher than 0.306 at 10 mg/L as shown in Table 3; but, in the study [24] J_{180}/J_0 of 0.571 at 2 mg/L of HA was 1.66 times higher than 0.344 at 10 mg/L. Furthermore, the total permeate volume (V_T) of 9.84 L at 2 mg/L of HA was 1.38 times higher than 7.10 L of V_T at 10 mg/L; but, in the study [24] V_T of 15.5 L at 2 mg/L of HA was 1.62 times higher than 9.59 L of V_T at 10 mg/L. It means that air back-flushing could be more effective to control the membrane fouling in this hybrid process than water back-flushing [24]. Finally, NOM concentration, like HA, should be one of the main factors affecting membrane fouling in the hybrid process of multi-channel ceramic MF membrane and TiO_2 photocatalyst-coated PP beads with air back-flushing.

As arranged in Table 4, the treatment efficiency of turbidity was almost constant between 95.5 and 98.3% independent of HA concentration. It means that the organic matters could not affect the treatment of suspended particles like kaolin in our hybrid process. However, in the study [24], the treatment efficiency of turbidity declined a little from 98.8 to 96.4% as increasing the HA concentration. However, the treatment efficiency of DOM, which can be analyzed by UV_{254} absorbance, was found to be maximal as 80.1% at 8 mg/L of HA concentration, and minimal as 65.0% at 2 mg/L as shown in Table 5. The treated water quality of DOM increased less slowly than the feed water quality from 2 to 8 mg/L of HA because most of the HA could be adsorbed on fouling materials inside the membrane or retained by cake layer on the membrane, and the remaining things passed through

Table 3
Effect of HA on filtration factors for hybrid process of multi-channel ceramic MF and TiO_2 photocatalyst-coated PP beads (BT 10 s, FT 10 min)

Back-flushing	Humic acid (mg/L)	2	4	6	8	10
Air	$R_m \times 10^{-9}$ (kg/m^{2}s)	0.860	0.895	0.879	0.839	0.837
	$R_b \times 10^{-9}$ (kg/m^{2}s)	0.058	0.059	0.086	0.232	0.256
	$R_{f,180} \times 10^{-9}$ (kg/m^{2}s)	1.293	1.617	1.890	2.220	2.446
	J_0 (L/m^2 h)	307	296	293	263	258
	J_{180} (L/m^2 h)	127	109	98.3	85.0	79.1
	J_{180}/J_0	0.412	0.368	0.336	0.323	0.306
	V_T (L)	9.84	9.56	9.19	8.02	7.10
Water [24]	$R_m \times 10^{-9}$ (kg/m^{2}s)	0.568	0.670	0.663	0.657	0.683
	$R_b \times 10^{-9}$ (kg/m^{2}s)	0.115	0.050	0.046	0.064	0.064
	$R_{f,180} \times 10^{-9}$ (kg/m^{2}s)	0.513	0.842	1.015	1.247	1.422
	J_0 (L/m^2 h)	413	392	398	391	378
	J_{180} (L/m^2 h)	236	181	164	143	130
	J_{180}/J_0	0.571	0.461	0.411	0.366	0.344
	V_T (L)	15.5	12.2	11.5	10.5	9.59

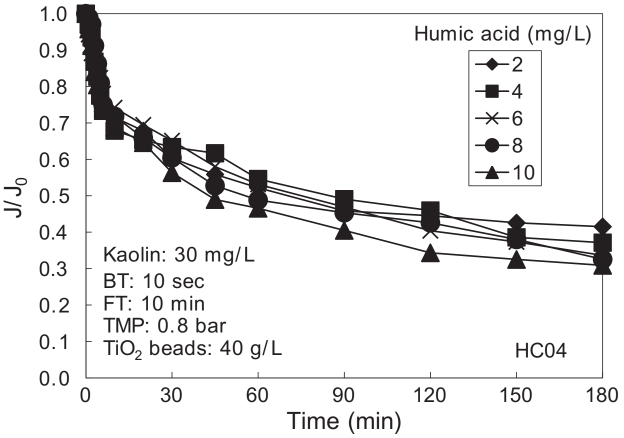

Fig. 3. Effect of HA on dimensionless permeate flux in hybrid process of multi-channel ceramic MF and TiO_2 photocatalyst-coated PP beads.

the membrane adsorbed or oxidized by TiO_2 photocatalyst-coated PP beads. But, the treated water quality of DOM increased more rapidly than the feed water quality above 8 mg/L of HA because most of organic matters passed through the membrane and could not be treated by adsorption or photo-oxidation by photocatalyst-coated PP beads. However, the treatment efficiency of DOM in our previous work [24] with water back-flushing was almost constant between 78.9 and 81.8% independent of HA concentration. The treated water quality of DOM increased at the same rate as increasing HA concentration as shown in Table 5 because the more severe membrane fouling ($R_{f,180}$) at the higher HA concentration with water back-flushing [24] as arranged in Table 3 could reject DOM more effectively in the hybrid process with water back-flushing [24] than air back-flushing.

3.2. Role of membrane filtration, adsorption, and photo-oxidation

To evaluate the role of membrane filtration, adsorption, and photo-oxidation in the hybrid process of multi-channel ceramic MF and photocatalyst-coated PP beads with air back-flushing, the process with PP beads without UV light ($MF + TiO_2$) and only MF without any PP beads and UV (MF) were performed, respectively, at 6 mg/L of HA, and compared with the hybrid process of MF and PP beads with UV light ($MF + TiO_2 + UV$). In Fig. 4, the R_f values of ($MF + TiO_2 + UV$), ($MF + TiO_2$) and only MF process at 6 mg/L of HA were compared during 180 min operation. The R_f could maintain low at the ($MF + TiO_2 + UV$) process and increased dramatically as simplifying the process to MF. It means that photocatalyst adsorption by the PP beads and photo-oxidation by UV irradiation could reduce the membrane fouling strongly in this hybrid water treatment process. The $R_{f,180}$ after 180 min operation was the highest at MF process, but the minimal 1.890×10^9 kg/m^2s at ($MF + TiO_2 + UV$) process as summarized in Table 6. The $R_{f,180}$ trend was the same with the result [24] with water back-flushing.

The J/J_0 values could maintain the highest at the ($MF + TiO_2 + UV$) process and the lowest at MF process, but the final value of J/J_0 (J_{180}/J_0) after 180 min operation converged to a similar value as shown in Fig. 5. It means that the J/J_0 at the ($MF + TiO_2 + UV$) could be higher than that at only MF and the ($MF + TiO_2$) processes because the photocatalyst adsorption and photo-oxidation could reduce the membrane fouling effectively. The J_{180}/J_0 after 180 min operation was the maximal 0.336 at ($MF + TiO_2 + UV$) process, which was almost the same with the minimal 0.330 at ($MF + TiO_2$) process as summarized in Table 6. The highest permeate flux could be maintained

Table 4
Water quality and treatment efficiency of turbidity in the hybrid process of multi-channel ceramic MF and TiO_2 photocatalyst-coated PP beads for effect of HA (BT 10 s, FT 10 min)

Experimental condition		Turbidity (NTU)				Average treatment efficiency (%) Back-flushing	
		Feed water		Treated water			
Kaolin (mg/L)	Humic acid (mg/L)	Range	Average	Range	Average	Air	Water [24]
30	2	28.4–42.7	34.8	0.908–1.64	1.180	96.6	98.8
	4	45.2–50.3	48.2	0.583–1.13	0.795	98.3	98.3
	6	43.1–51.5	47.0	0.686–2.71	1.414	97.0	98.1
	8	36.6–39.8	38.4	0.589–0.720	0.656	98.3	97.9
	10	38.0–45.7	40.8	1.11–2.87	1.850	95.5	96.4

Table 5
Water quality and treatment efficiency of DOM (UV_{254} absorbance) in the hybrid process of multi-channel ceramic MF and TiO_2 photocatalyst-coated PP beads for effect of HA (BT 10 s, FT 10 min)

Experimental condition		UV_{254} absorbance (cm^{-1})				Average treatment efficiency (%) Back-flushing	
		Feed water		Treated water			
Kaolin (mg/L)	Humic acid (mg/L)	Range	Average	Range	Average	Air	Water [24]
30	2	0.054–0.074	0.067	0.018–0.033	0.024	65.0	81.4
	4	0.155–0.185	0.171	0.027–0.071	0.047	72.4	81.8
	6	0.102–0.166	0.137	0.016–0.049	0.036	74.0	79.8
	8	0.170–0.226	0.204	0.031–0.058	0.041	80.1	80.0
	10	0.188–0.291	0.224	0.067–0.084	0.077	65.4	78.9

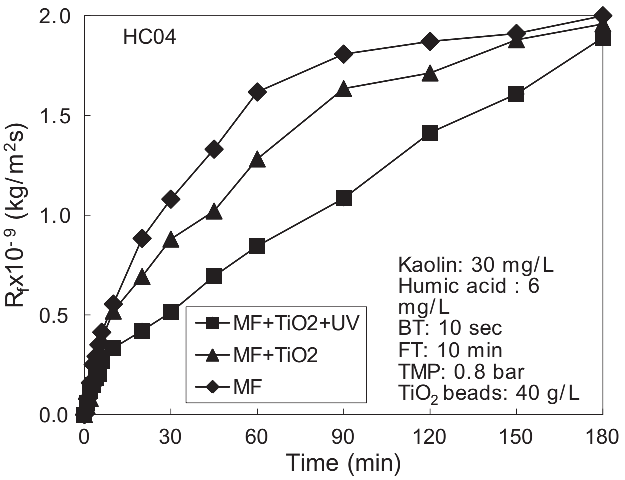

Fig. 4. Role of membrane filtration, adsorption, and photo-oxidation on resistance of membrane fouling in hybrid process of multi-channel ceramic MF and TiO_2 photocatalyst-coated PP beads.

because the membrane fouling was controlled more effectively by photocatalyst adsorption and photo-oxidation at ($MF + TiO_2 + UV$) process than at only MF or ($MF + TiO_2$) processes. In our previous work [24], for the same hybrid process with water back-flushing, the maximal J_{180} could be acquired at ($MF + TiO_2 + UV$) process, which was the same trend with this study.

The treatment efficiencies of turbidity and DOM (UV_{254} absorbance) decreased as simplifying the process from ($MF + TiO_2 + UV$) to MF with air back-flushing as shown Tables 7 and 8, which was the same trend with the result [24] with water back-flushing. The portions of treatment efficiency performed by membrane filtration, adsorption and photo-oxidation, respectively, in our hybrid process with air back-flushing could be calculated by reducing sequentially the

Table 6
Roles of membrane filtration, adsorption, and photo-oxidation on filtration factors in hybrid process of multi-channel ceramic MF and TiO_2 photocatalyst-coated PP beads at HA 6 mg/L

Process	$MF + TiO_2 + UV$	$MF + TiO_2$	MF
$R_m \times 10^{-9}$ (kg/m^{2}s)	0.872	0.831	0.830
$R_b \times 10^{-9}$ (kg/m^{2}s)	0.085	0.134	0.173
$R_{f,180} \times 10^{-9}$ (kg/m^{2}s)	1.890	1.959	2.000
J_0 (L/m^2 h)	295	292	282
J_{180} (L/m^2 h)	99.1	96.5	94.0
J_{180}/J_0	0.336	0.330	0.334
V_T (L)	9.23	7.87	7.21

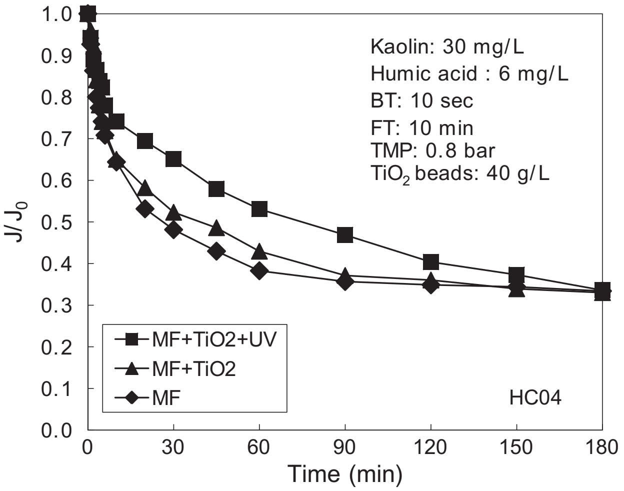

Fig. 5. Role of membrane filtration, adsorption, and photo-oxidation on dimensionless permeate flux in hybrid process of multi-channel ceramic MF and TiO_2 photocatalyst-coated PP beads.

Table 7
Water quality and treatment efficiency of turbidity in the hybrid process of multi-channel ceramic MF and TiO_2 photocatalyst-coated PP beads for roles of membrane filtration, adsorption, and photo-oxidation at HA 6 mg/L

Experimental condition		Turbidity (NTU)				Average treatment efficiency (%)	
		Feed water		Treated water		Back-flushing	
Humic acid (mg/L)	Process	Range	Average	Range	Average	Air	Water [24]
6	MF + TiO_2 + UV	43.1–51.5	47.0	0.686–2.71	1.41	97.0	98.1
	MF + TiO_2	38.6–48.0	44.6	1.19–2.11	1.54	96.5	96.7
	MF	31.4–39.4	35.1	0.474–3.31	1.52	95.7	93.7

Table 8
Water quality and treatment efficiency of DOM (UV_{254} absorbance) in the hybrid process of multi-channel ceramic MF and TiO_2 photocatalyst-coated PP beads for roles of membrane filtration, adsorption, and photo-oxidation at HA 6 mg/L

Experimental condition		UV_{254} absorbance (cm^{-1})				Average treatment efficiency (%)	
		Feed water		Treated water		Back-flushing	
Humic acid (mg/L)	Process	Range	Average	Range	Average	Air	Water [24]
6	MF + TiO_2 + UV	0.102–0.166	0.137	0.016–0.049	0.036	74.0	79.8
	MF + TiO_2	0.138–0.164	0.153	0.029–0.055	0.043	72.2	68.9
	MF	0.138–0.173	0.153	0.052–0.071	0.062	59.6	60.8

Table 9
Treatment efficiency portions of membrane filtration, adsorption, and photo-oxidation in the hybrid process of multi-channel ceramic MF and TiO_2 photocatalyst-coated PP beads at HA 6 mg/L

	Turbidity		UV_{254} absorbance	
	Back-flushing			
Portion of treatment efficiency (%)	Air	Water [24]	Air	Water [24]
Membrane filtration	95.7	93.7	59.6	60.8
Adsorption	0.8	3.0	12.6	8.1
Photo-oxidation	0.5	1.4	1.8	10.9
Total treatment efficiency	97.0	98.1	74.0	79.8

turbidity or organic matter treatment efficiencies of (MF + TiO_2 + UV), (MF + TiO_2), and MF, which were compared with the result [24] with water back-flushing in Table 9. In turbidity treatment efficiency, the treatment portion of membrane filtration was very high (95.7%) at 6 mg/L of HA. The treatment portions of adsorption by photocatalyst-coated PP beads and photo-oxidation by PP beads and UV light were—very low—0.8 and 0.5%, respectively, which was lower than the result [24] with water back-flushing. It means that the role of adsorption and photo-oxidation by photocatalyst-coated PP beads and UV was not important for treatment of the suspended particles like kaolin in our hybrid process. Kaolin could not be removed effectively by the adsorption and photo-oxidation by photocatalyst-coated PP beads because kaolin was inorganic and did not have electric charge. In the treatment efficiency of DOM (UV_{254} absorbance), the treatment portion of membrane filtration was still very high (59.6%), but that of adsorption was high (12.6%) and that of photo-oxidation was low (1.8%) at 6 mg/L of HA. It proved that the role of adsorption by photocatalyst-coated PP beads was more important than that of photo-oxidation by PP beads for the DOM treatment in our hybrid process. The adsorption by PP beads could reduce the membrane fouling strongly because the adsorption had the major role of DOM reduction in this hybrid water treatment process with air back-flushing. However, in our previous work [24], for the same hybrid process with water back-flushing, the role of photo-oxidation was a little more important than that of adsorption for DOM treatment. It was thought that the photo-oxidation could be more effective for reducing membrane fouling because the photo-oxidation had a more important role to treat DOM in the hybrid process with water back-flushing than the adsorption.

4. Conclusions

In this study, the effect of organic matters on membrane fouling was observed in a hybrid process of seven-channel alumina microfiltration (MF) and photocatalyst-coated polypropylene (PP) beads with air back-flushing for advanced water treatment. Also, treatment portions by membrane filtration, photocatalyst adsorption, and photo-oxidation were investigated by comparing the treatment efficiencies of (MF), ($MF + TiO_2$), and ($MF + TiO_2 + UV$) processes. The results were compared with the previous study [24] of the same hybrid process with water back-flushing. Finally, we could find out the following results.

(1) The organic matter, like HA, could be one of the main factors affecting membrane fouling because the final resistance of membrane fouling ($R_{f,180}$) value decreased significantly as reducing the HA concentration. However, R_f increased more dramatically in our previous study [24] with periodic water back-flushing.

(2) The treatment efficiencies of turbidity were very high at 95.5–98.3% independent of HA concentration, but that of DOM was the maximal 80.1% at HA 8 mg/L. However, in the result [24] with water back-flushing, the treatment efficiency of DOM was almost constant between 78.9 and 81.8% independent of HA concentration. It proved that water back-flushing was more effective to treat DOM than air back-flushing in this hybrid process of alumina microfiltration (MF) and photocatalyst-coated polypropylene (PP) beads. This hybrid process could be applied as pretreatment before desalination RO plant if the treated water quality were satisfied as the feed water of RO.

(3) As a result of investigating the role of membrane filtration, adsorption, and photo-oxidation, the membrane fouling resistance was the minimum, and the final permeate flux was the maximum at ($MF + TiO_2 + UV$) process. This result proved that photocatalyst adsorption and photo-oxidation could control membrane fouling in our hybrid water treatment process. The trend was the same with the result [24] with water back-flushing.

(4) The adsorption and photo-oxidation by the photocatalyst-coated PP beads could play a much greater role in the removal of DOM than that of turbidity in our hybrid water treatment process. Kaolin could not be removed effectively by the adsorption and photo-oxidation because kaolin was inorganic and did not have electric charge. The role of adsorption was more important than that of photo-oxidation in our hybrid process with air back-flushing, but the role of photo-oxidation was a little more important than that of adsorption in the result [24] with water back-flushing for DOM treatment. It concluded that the role of adsorption and photo-oxidation was dependent on the back-flushing media in this hybrid process of alumina MF and photocatalyst-coated PP beads.

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