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Roles of organic matters, photo-oxidation and adsorption in the hybrid water treatment process of multi-channel ceramic MF and photocatalyst-loaded PES beads

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ABSTRACT

The effect of natural organic matters (NOM) concentration on membrane fouling was investigated in a hybrid water process treatment of multi-channel ceramic microfiltration (MF) and titanium dioxide (TiO_2) photocatalyst-loaded polyethersulfone (PES) beads with periodic water back-flushing. The PES beads were fluidized in the space between the outside of a 7-channel ceramic membrane (0.4 μm average pore size) and the module inside. Kaolin was fixed at 30 mg/L and humic acid (HA) was varied from 2 to 10 mg/L to investigate effect of NOM. The resistance membrane fouling (R_f) increased dramatically as increasing HA. Finally, the highest total permeated volume (V_T) was acquired at HA 2 mg/L after 180 min operation. The treatment efficiencies of turbidity and UV_{254} absorbance were outstanding at 96.7%~98.3% and 80.2%~85.0%, respectively. The treatment efficiency proportions of UV_{254} absorbance were 70.8% for MF, 0.2% for TiO_2 bead adsorption, and 10.1% for photo-oxidation for 4 mg/L of HA; however, those of turbidity were 97.5% for MF, but only 0.1% for adsorption and 0.4% for photo-oxidation. The role of photo-oxidation by the PES beads was the more important at low HA concentration; however, that of adsorption was the more dominant at high HA, for the organic matters treatment.

Keywords: Microfiltration; Photocatalyst; Hybrid process; Ceramic membrane; Water treatment; Organic matter

1. Introduction

Photocatalytic oxidation, which is one of remarkable technologies of water pollution control, 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 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, 2 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].

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In recent 10 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 dramatically 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 equipment is 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]. In addition, a few papers for effect of operating conditions in the hybrid water treatment process of various tubular ceramic membranes, and PES or PP beads in our research group have been published in Membrane Journal [23–31] in recent years.

In this study the effect of natural organic matters (NOM) was investigated on membrane fouling in the hybrid process of multi-channel ceramic MF and photocatalyst-loaded PES beads with periodic water back-flushing. A hybrid module was composed of the ceramic MF membrane and the PES beads, which were fluidized between the gap of ceramic membrane and the acryl module case. In addition, 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. The periodic water back-flushing was performed during 10 s per 10 min's filtration to reduce membrane fouling. The results were compared with those of the previous study [29] using the hybrid process of the tubular ceramic MF and the PES beads with periodic water back-flushing.

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. The membrane was purchased from Nano Pore Materials in Korea, and the specifications of the multi-channel ceramic membrane were arranged in Table 1.

The photocatalyst employed in this study was 1.4–1.8 mm polyethersulfone (PES) beads loaded with TiO_2 powder made by Figoli et al. [32,33], which is shown in Table 2. Instead of NOM and fine inorganic particles in natural water source, a quantity of humic acid sodium salt (Aldrich) and kaolin (Sigma-Aldrich) was dissolved in distilled water. It was then utilized as synthetic water in this experiment. UV with 352 nm was irradiated from outside of the acryl module by 2 UV lamps (F8T5BLB, Sankyo, Japan).

2.2. Hybrid membrane module

To remove the turbidity and NOM, the hybrid module was composed by packing the photocatalyst-loaded PES beads between the module inside and outside of a ceramic membrane. In addition, 100 mesh (0.150 mm), which was extremely smaller than 1.4–1.8 mm particle size of the photocatalyst beads used here, was installed at the outlet of the hybrid module to prevent the PES beads loss into the treated water tank.

2.3. Experimental procedure

The advanced water treatment system using a hybrid module (6) of multi-channel ceramic microfiltration and the

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)	235
Surface area (cm^2)	206.7
Material	α-alumina coating on α-alumina support
Company	Dongseo Inc. in Republic of Korea

Table 2
Specification of the TiO_2 photocatalyst-loaded beads polyethersulfone employed in this study

Material of the beads	Polyethersulfone (PES)
TiO_2 coating method	Phase inversion
Diameter (mm)	1.4–1.8
Weight (mg)	1.3–1.8
Average weight (mg)	1.5

photocatalyst-loaded PES beads was shown in Fig. 1, which was used at the previous study [23]. Cross-flow filtration was performed for the multi-channel ceramic membrane with periodic water back-flushing using permeated water. The hybrid module (6) was supplied with the PES beads fluidizing between the gap of ceramic membrane and the acryl module case. Then, the feed tank (1) was filled with 10 L of the synthetic water composed of humic acid (HA) and kaolin. And the temperature of the feed water was constantly maintained by using a constant temperature circulator (3) (Model 1146, VWR, USA). In addition, the synthetic feed water was continuously mixed by a stirrer (4) 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 (2) (Procon, Standex Co., U.S.A.). The feed flow rate was measured by a flowmeter (5) (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 (9) of both the bypass pipe of the pump (2) and the concentrate pipe. The permeate flux treated by both the multi-channel ceramic membrane and the PES beads was measured by an electric balance (11) (Ohaus, U.S.A.). The permeate water flowed into the back-washing tank (13) if the permeate flux had not been measured. After the treated water was over a certain level in the back-washing tank (13), it was recycled to the feed tank (1) 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 NOM. The water back-flushing time (BT) and filtration time (FT) were fixed at 10 s and 10 min, respectively. Only MF process without the PES beads and UV light (MF), and MF process with the PES beads (MF + TiO_2) were operated at 4 and 6 mg/L of HA, respectively. And the results were compared with the hybrid process of the MF and PES beads with UV (MF + TiO_2+UV) for evaluating a portion of the treatment efficiencies of MF, adsorption, and photo-oxidation.

The resistance of membrane fouling (R_f), dimensionless permeate flux (J/J_0) and permeate flux (J) during total filtration time of 180 min were observed under each condition. Under all experimental conditions, the TMP (trans-membrane pressure) was maintained at 0.81 bar, the water back-flushing pressure at 1.0 bar, the feed flow rate at 1.0 L/min, and the feed water temperature at 20°C.

The quality of feed water and treated water was analyzed in order to evaluate the treatment efficiencies of turbid materials and dissolved organic matters. Turbidity was measured by a turbidimeter (2100N, HACH, U.S.A.) and UV_{254} absorbance was analyzed by a UV spectrophotometer (GENESYS 10 UV, Thermo, U.S.A). The detection limits of turbidimeter

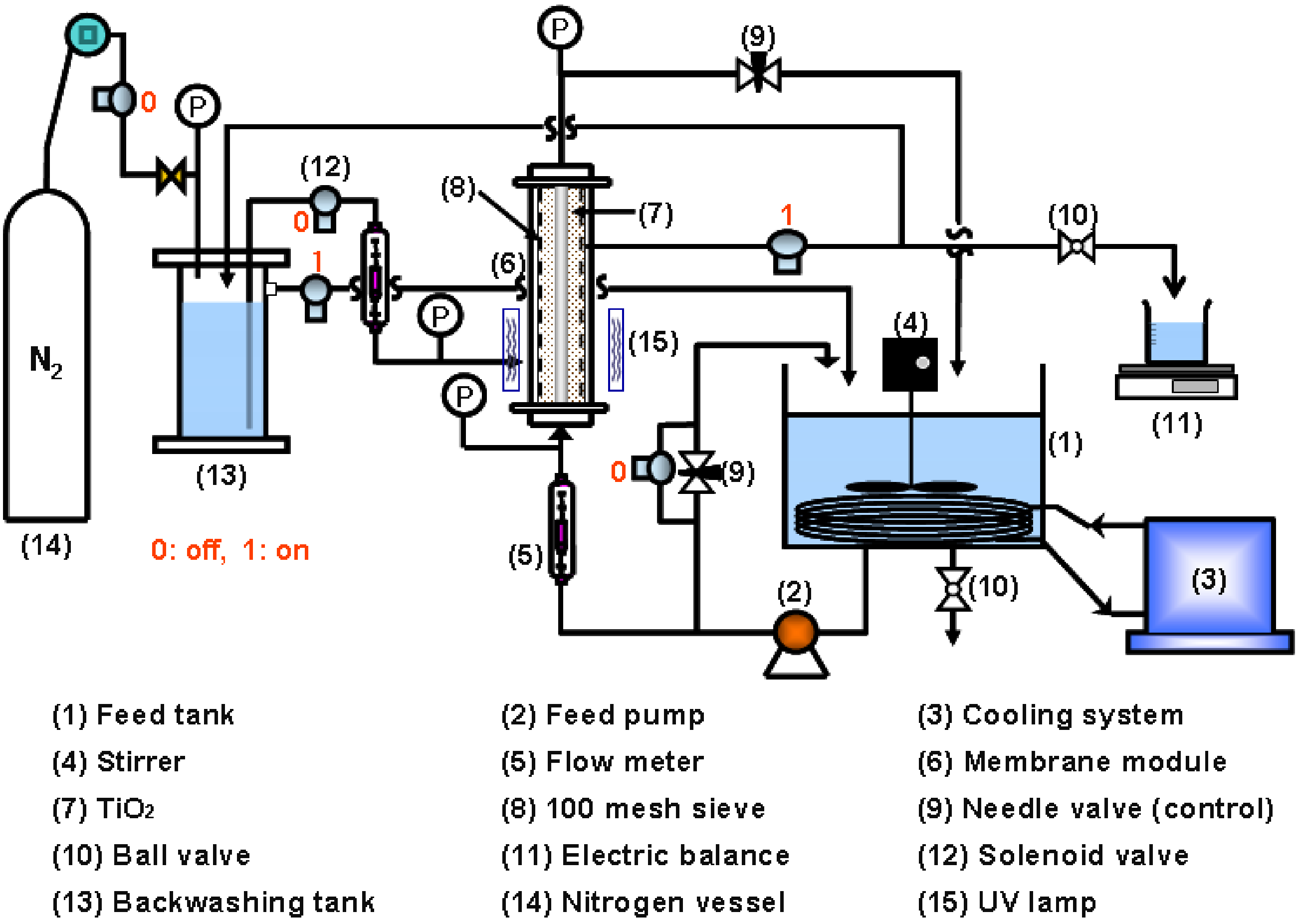

Fig. 1. Apparatus of hybrid water treatment process of multi-channel ceramic microfiltration and the photocatalyst-loaded PES beads with periodic water back-flushing [23].

and UV spectrophotometer were 0~4,000 NTU (± 0.001 NTU) and –0.1~3.0 cm^{-1} (± 0.001 cm^{-1}). Before measuring UV$_{254}$ absorbance, the treated sample was filtered once by a 0.2 µm syringe filter to reject turbid materials.

3. Results and discussions

The effects of NOM like as HA was investigated in the hybrid water treatment process of multi-channel ceramic MF and TiO$_2$ photocatalyst-loaded PES with periodic water back-flushing. In addition, treatment portions by membrane filtration, photocatalyst adsorption, and photo-oxidation were evaluated by comparing the treatment efficiencies of MF, (MF + TiO$_2$) and (MF + TiO$_2$ + UV) processes. The results were compared with those of the previous study [29] using the hybrid process of the tubular ceramic MF and the PES beads. Resistances of the 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 the previous study [23].

3.1. Effect of natural organic matters (NOM)

As compared in Fig. 2, the resistances of membrane fouling (R_f) were highly influenced by HA, which was one of major NOM in lakes or rivers, and R_f increased dramatically as increasing concentration of HA from 2 to 10 mg/L. Specially, the increasing rate of R_f was very high when HA increased from 6 to 10 mg/L. It means that NOM like as HA could drive membrane fouling more severely on the surface and inside the ceramic membrane as increasing HA concentration in water. As summarized in Table 3, the $R_{f,180}$ value after 180 min' operation at HA 10 mg/L was 3.869 × 10^9 kg/m^{2}s, which was 3.10 times higher than 1.247 × 10^9 kg/m^{2}s of the $R_{f,180}$ value at HA 2 mg/L. In the previous study [29] for the hybrid water treatment process of the tubular ceramic MF (NCMT-7231, pore size 0.1 µm) and the same PES beads with periodic water back-flushing, $R_{f,180}$ at HA 10 mg/L was 5.345 × 10^9 kg/m^{2}s, which was 1.92 times higher than 2.789 × 10^9 kg/m^{2}s of the $R_{f,180}$ value at HA 2 mg/L. The $R_{f,180}$ increasing rate of the previous result [29] was the lower than that of this study, because the membrane fouling mechanism could be different by the smaller pore size of the membrane.

As shown in Fig. 3, 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, was compared as HA concentration. The J/J_0 tended to decrease rapidly as increasing HA concentration from 2 to 10 mg/L, especially from 6 to 8 mg/L, because of the membrane fouling development by the more organic macromolecules, that could be a very complex combination process involving the macromolecules adsorption to the membrane surface and within the membrane pores, and formation of a gel cake layer on the membrane surface. As compared in Table 3, the final J/J_0 after 180 min's operation (J_{180}/J_0) was 0.381 at HA 2 mg/L, which was 2.20 times higher than 0.173 at HA 10 mg/L. In the previous work [29] of NCMT-7231, the J_{180}/J_0 was 0.147 at HA 2 mg/L, which was 1.67 times higher than 0.088 at HA 10 mg/L. It means that the larger pore size HC04 membrane with 7 channels could be influenced the more severely by NOM than the smaller pore size NCMT-7231 membrane, which was the tubular type, in the hybrid water treatment process of MF and the PES beads.

Furthermore, the total permeate volume (V_T) of 10.45 L at HA 2 mg/L was 1.56 times higher than 6.69 L of V_T at HA 10 mg/L. In the result [29] of NCMT-7231, V_T at HA 2 mg/L was 4.79 L, which was 1.72 times higher than 2.79 L of V_T at HA 10 mg/L. The effect of HA on V_T was a little higher at NCMT-7231 than that at HC04, because of pore size difference. Finally, it could be found out that NOM, like HA, should be one of the main factors affecting membrane fouling in this hybrid process of the ceramic MF membrane and the TiO$_2$ photocatalyst-loaded PES beads.

As arranged in Table 4, the treatment efficiency of turbidity decreased a little from 98.3% to 96.7% as increasing HA concentration. It means that the organic matters could

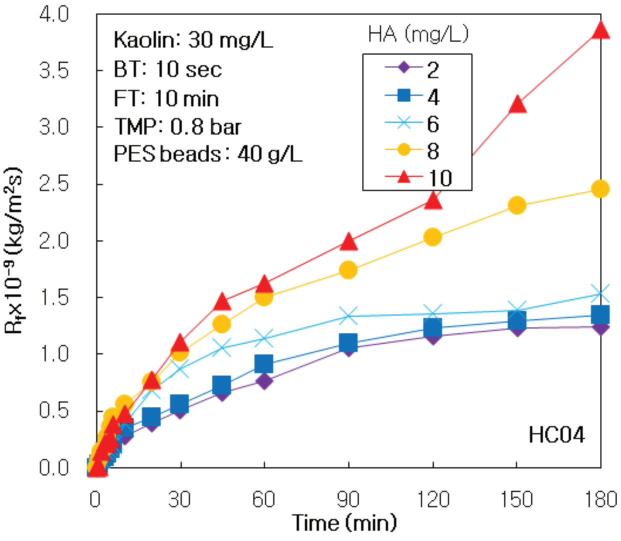

Fig. 2. Effect of HA on resistance of membrane fouling in hybrid water treatment process of multi-channel ceramic MF and photocatalyst-loaded PES beads.

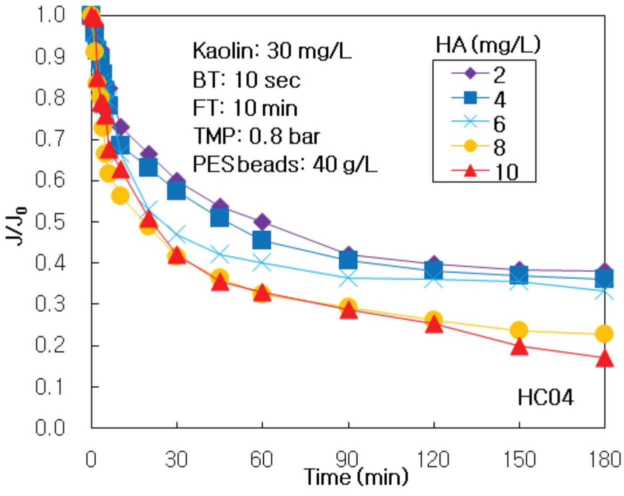

Fig. 3. Effect of HA on dimensionless permeate flux in hybrid water treatment process of multi-channel ceramic MF and photocatalyst-loaded PES beads.

affect the treatment of suspended particles like kaolin in this hybrid process of the 7 channels MF membrane and the PES beads, because the treatment efficiency of turbid materials was a little low at high HA concentration. However, in the result [29] of NCMT-7231, the treatment efficiency of turbidity was almost constant independent of HA concentration. It means that the organic matters could not affect the treatment of suspended particles like kaolin in the hybrid process of the tubular ceramic membrane and the PES beads.

As arranged in Table 5, the treatment efficiency of UV_{254} absorbance, which means the concentration of organic matters, was the maximum 85.0% at 2 mg/L of HA, and decreased as increasing HA concentration. The treated water quality of HA increased the more dramatically than the feed water quality from 2 to 10 mg/L of HA concentration, because most of HA passed through the HC04 MF membrane (pore size: 0.4 μm), and could not treated by adsorption or photo-oxidation by the TiO_2 photocatalyst-loaded PES beads and UV. In the previous work [29] for the hybrid process of the tubular ceramic MF membrane (pore size: 0.1 μm) and the PES beads, which was the same PES beads used in this study, the treatment efficiency of HA was the maximum 81.7% at HA 6 mg/L. The treated water quality of HA increased the less slowly than the feed water quality from 2 to 6 mg/L of HA, because most of organic matters could be adsorbed on fouling materials inside the membrane or retained by cake layer on the membrane, and the remained things passed through the membrane adsorbed or oxidized by the PES beads and UV. However, the treated water quality of HA increased the more rapidly than the feed water quality above 6 mg/L of HA, because most of organic matters passed through the membrane and could not treated by adsorption or photo-oxidation by the PES beads and UV.

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

For the investigate of the role of membrane filtration, adsorption, and photo-oxidation in the hybrid process of multi-channel ceramic MF and the TiO_2 photocatalyst-loaded PES beads, the process with the PES beads without UV light

Table 3
Effect of HA concentration on filtration factors in the hybrid process of multi-channel ceramic MF and photocatalyst-loaded PES beads

Membrane	HA (mg/L)	2	4	6	8	10
HC04 (0.4 μm)	$R_m \times 10^{-9}$ (kg/m²s)	0.682	0.676	0.687	0.718	0.728
	$R_b \times 10^{-9}$ (kg/m²s)	0.087	0.081	0.081	0.005	0.079
	$R_{f,180} \times 10^{-9}$ (kg/m²s)	1.247	1.346	1.536	2.454	3.869
	J_0 (L/m²h)	367	373	368	391	350
	J_{180} (L/m²h)	140	134	123	89	60
	J_{180}/J_0	0.381	0.360	0.333	0.227	0.173
	V_T (L)	10.45	10.10	9.03	7.63	6.69
NCMT-7231 [29] (0.1 μm)	$R_m \times 10^{-9}$ (kg/m²s)	0.479	0.476	0.473	0.476	0.480
	$R_b \times 10^{-9}$ (kg/m²s)	0.001	0.013	0.001	0.007	0.037
	$R_{f,180} \times 10^{-9}$ (kg/m²s)	2.789	3.152	3.258	4.473	5.345
	J_0 (L/m²h)	1322	1299	1399	1315	1230
	J_{180} (L/m²h)	194	174	170	128	108
	J_{180}/J_0	0.147	0.134	0.127	0.097	0.088
	V_T (L)	4.79	4.02	3.62	3.39	2.79

Table 4
Water quality and treatment efficiency of turbidity in the hybrid process of multi-channel ceramic MF and photocatalyst-loaded PES beads for the effect of HA concentration

Experimental condition		Turbidity (NTU)				Average treatment efficiency (%)	
Kaolin (mg/L)	HA (mg/L)	Feed water		Treated water		Membrane	
		Range	Average	Range	Average	HC04	NCMT-7231 [29]
30	2	20.7~27.7	23.8	0.310~0.501	0.395	98.3	97.8
	4	22.2~29.1	25.8	0.418~0.605	0.503	98.0	97.6
	6	25.5~30.6	27.2	0.534~0.736	0.643	97.6	98.1
	8	27.4~32.4	29.8	0.731~1.085	0.911	96.9	97.7
	10	30.3~35.0	32.3	0.640~1.300	1.059	96.7	97.9

Table 5
Water quality and treatment efficiency of UV_{254} absorbance in the hybrid process of multi-channel ceramic MF and photocatalyst-loaded PES beads for the effect of HA concentration

Experimental condition		UV_{254} absorbance (cm^{-1})				Average treatment efficiency (%)	
Kaolin (mg/L)	HA (mg/L)	Feed water		Treated water		Membrane	
		Range	Average	Range	Average	HC04	NCMT-7231 [29]
30	2	0.022~0.048	0.033	0.002~0.010	0.005	85.0	80.2
	4	0.038~0.086	0.061	0.008~0.014	0.012	81.1	77.6
	6	0.060~0.115	0.082	0.010~0.022	0.016	80.4	81.7
	8	0.086~0.142	0.108	0.014~0.029	0.021	80.2	79.0
	10	0.112~0.191	0.147	0.016~0.048	0.029	80.2	71.4

(MF + TiO_2) and only MF without the PES beads and UV (MF) were performed at 4 and 6 mg/L of HA, respectively. And the results were compared with the hybrid process of MF and the PES beads with UV light (MF + TiO_2 + UV). The R_f values of (MF + TiO_2 + UV), (MF + TiO_2) and only MF processes at 4 and 6 mg/L of HA were compared during 180 min's operation, as shown in Figs. 4(a) and (b). The R_f increased dramatically as simplifying the process from (MF + TiO_2 + UV) to MF process. It means that the adsorption and photo-oxidation by the photocatalyst-loaded PES beads and UV irradiation could reduce the membrane fouling strongly. In addition, the R_f values at HA 6 mg/L increased the more rapidly than those at HA 4 mg/L, as compared in Figs. 4(a) and (b). It means that the high HA concentration could form the membrane fouling the more dramatically than the low HA concentration in all of MF, (MF + TiO_2) and (MF + TiO_2 + UV) processes.

As summarized in Table 6, the final R_f after 180 min's operation ($R_{f,180}$) increased as simplifying the process from (MF + TiO_2 + UV) to MF process. And $R_{f,180}$ at HA 4 mg/L in MF process was 2.041 × 10^9 kg/m²s, which was 1.52 times higher than 1.346 × 10^9 kg/m²s in (MF + TiO_2 + UV) process. However, $R_{f,180}$ at HA 6 mg/L in MF process was 2.593 × 10^9 kg/m²s, which was 1.31 times higher than 1.974 × 10^9 kg/m²s in (MF + TiO_2 + UV) process. It means that the membrane fouling at high HA concentration could be the more severe than that at low HA; however, the increasing rate of membrane fouling at the high HA was the lower at the high HA than that at the low HA, when simplifying the process from (MF + TiO_2 + UV) to MF process. In the previous work [29] with NCMT-5231 membrane at HA 6 mg/L, $R_{f,180}$ in MF process was 4.448 × 10^9 kg/m²s, which was 1.37 times higher than 3.258 × 10^9 kg/m²s in (MF + TiO_2 + UV) process. The increasing rate of $R_{f,180}$ was a similar value with 1.31 at HA 6 mg/L in this study.

The dimensionless permeate flux (J/J_0) values increased a little as simplifying the process from (MF + TiO_2 + UV) to MF at both 4 and 6 mg/L of HA, as compared in Figs. 5(a) and (b). It means that the J/J_0 at the (MF + TiO_2 + UV) process could be the higher than that at only MF and the (MF + TiO_2) processes, because the adsorption and photo-oxidation by the PES beads and UV reduced effectively the membrane fouling. As summarized in Table 6, the final J/J_0 after 180 min's operation (J_{180}/J_0) was the maximum 0.360 at HA 4 mg/L in (MF + TiO_2 + UV) process, which was 1.18 times higher than the minimum 0.305 at HA 4 mg/L in MF process. Then, the J_{180}/J_0 was 0.306 at HA 6 mg/L in (MF + TiO_2 + UV) process, which was 1.21 times higher than 0.253 at HA 6 mg/L in MF process. It means that the increasing rate of J_{180}/J_0 at high HA was a little higher than that at low HA when complicating the process from MF to (MF + TiO_2 + UV) process, because the reduction effect of membrane fouling by the adsorption and photo-oxidation was a little more excellent at the high HA than that at the low HA. In the result

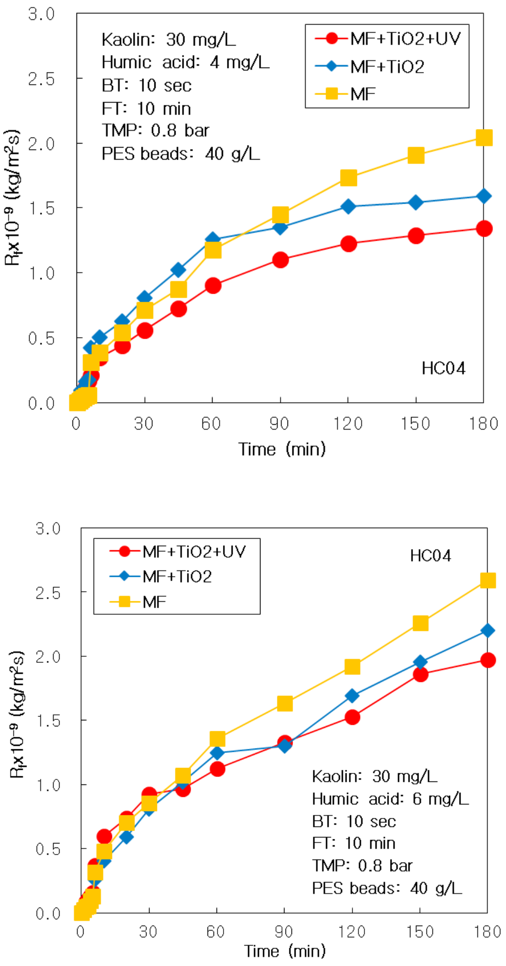

Fig. 4. Role of membrane filtration, adsorption and photo-oxidation on resistance of membrane fouling in hybrid process of multi-channel ceramic MF and photocatalyst-loaded PES beads; (a) HA 4 mg/L, (b) HA 6 mg/L.

Table 6
Roles of membrane filtration, adsorption, and photo-oxidation on filtration factors in hybrid process of multi-channel ceramic MF and photocatalyst-loaded PES beads at different HA concentration

Membrane	HA (mg/L)	Process	MF + TiO_2 + UV	MF + TiO_2	MF
HC04	4	$R_m \times 10^{-9}$ (kg/m^{2}s)	0.676	0.843	0.832
		$R_b \times 10^{-9}$ (kg/m^{2}s)	0.081	0.029	0.062
		$R_{f,180} \times 10^{-9}$ (kg/m^{2}s)	1.346	1.590	2.041
		J_0 (L/m^{2}h)	373	324	316
		J_{180} (L/m^{2}h)	134	115	96
		J_{180}/J_0	0.360	0.354	0.305
		V_T (L)	10.10	8.25	8.05
HC04	6	$R_m \times 10^{-9}$ (kg/m^{2}s)	0.812	0.803	0.836
		$R_b \times 10^{-9}$ (kg/m^{2}s)	0.059	0.084	0.041
		$R_{f,180} \times 10^{-9}$ (kg/m^{2}s)	1.974	2.203	2.593
		J_0 (L/m^{2}h)	324	318	322
		J_{180} (L/m^{2}h)	99	91	81
		J_{180}/J_0	0.306	0.287	0.253
		V_T (L)	8.05	7.97	7.44
NCMT-7231 [29]	6	$R_m \times 10^{-9}$ (kg/m^{2}s)	0.473	0.490	0.473
		$R_b \times 10^{-9}$ (kg/m^{2}s)	0.001	0.018	0.002
		$R_{f,180} \times 10^{-9}$ (kg/m^{2}s)	3.258	4.092	4.448
		J_0 (L/m^{2}h)	1339	1250	1339
		J_{180} (L/m^{2}h)	170	138	129
		J_{180}/J_0	0.127	0.110	0.096
		V_T (L)	3.62	3.40	3.12

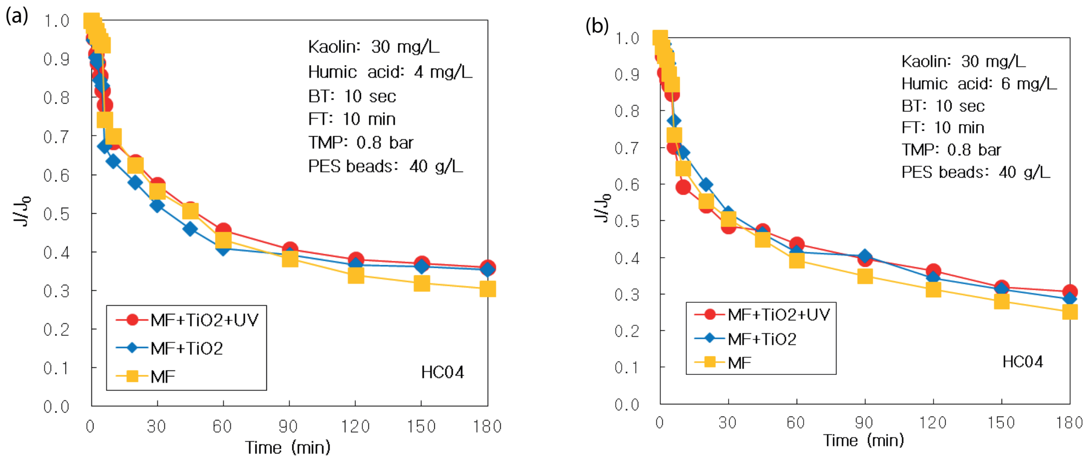

Fig. 5. Role of membrane filtration, adsorption and photo-oxidation on dimensionless permeate flux in hybrid process of multi-channel ceramic MF and photocatalyst-loaded PES beads; (a) HA 4 mg/L, (b) HA 6 mg/L.

[29] for the hybrid process of the tubular ceramic MF (pore size: 0.1 μm) and the PES beads, the J_{180}/J_0 in (MF + TiO_2 + UV) process was 0.127, which was 1.32 times higher than the minimum 0.096 in MF process, those were the lower than those of this results; however, the exactly same trend with this study.

The turbidity treatment efficiencies decreased a little from 98.0% to 97.5% at HA 4 mg/L, and very little from 97.8% to 97.5% at HA 6 mg/L, as simplifying the process from (MF + TiO_2 + UV) to MF with the HC04 (0.4 μm). In addition, those decreased a little from 98.1% to 97.8% at HA 6 mg/L in the result [29] with the NCMT-7231 (0.1 μm). It means that the turbidity treatment efficiencies could not be affected by HA concentration and membrane pore size, when simplifying the process from (MF + TiO_2 + UV) to MF.

The treatment efficiencies of organic matters (UV_{254} absorbance) decreased dramatically from 81.1% to 70.8% at HA 4 mg/L, and a little lower from 81.1% to 73.9% at HA 6 mg/L, as simplifying the process from (MF + TiO_2 + UV) to

MF with the HC04. Additionally, those decreased the lower from 81.7% to 76.0% at HA 6 mg/L in the result [29] with the NCMT-7231 than those in this study. It means that the effects of adsorption and photo-oxidation at low HA concentration was the greater than those at high HA, and those at the larger pore size was the greater than those at the smaller one, when simplifying the process from (MF + TiO_2 + UV) to MF.

As summarized in Table 7, the treatment efficiency portions of membrane filtration, adsorption and photo-oxidation in this hybrid process could be calculated by subtracting sequentially the turbidity or NOM treatment efficiencies of (MF + TiO_2 + UV), (MF + TiO_2) and MF. In turbidity treatment efficiency, the treatment portion of membrane filtration was very high 97.5% at both 4 and 6 mg/L of HA. The treatment portions of adsorption by the TiO_2 photocatalyst-loaded PES beads were very low 0.1% and 0.2% at 4 and 6 mg/L of HA, respectively. In addition, those of photo-oxidation by the PES beads and UV light were very low 0.4% and 0.1%, respectively. Also, in the results [29] with NCMT-7231, those of adsorption and photo-oxidation were 0.3% and 0.0% at HA 6 mg/L. It means that the roles of adsorption and photo-oxidation by the PES beads and UV were not important, independent of HA concentration and membrane pore size for treatment of the suspended particles like kaolin in the hybrid process. Kaolin could not be removed efficiently by the adsorption and photo-oxidation by the PES beads and UV, because kaolin was inorganic and did not have electric charge.

As shown in Table 7, in the treatment efficiency of organic matter, the treatment portion of membrane filtration was still very high 70.8% and 73.9% at 4 and 6 mg/L of HA, respectively. However, those of adsorption were very low 0.2% and high 6.1%, and those of photo-oxidation were high 10.1% and low 1.1% at 4 and 6 mg/L of HA, respectively. However, in the results [29] with NCMT-7231, those of adsorption and photo-oxidation were low 3.7% and 2.0% at HA 6 mg/L. It means that the role of photo-oxidation by the photocatalyst-loaded PES beads was the more important at low HA concentration; however, that of adsorption was the more dominant at high HA, for the organic matters treatment in this hybrid process with the HC04 membrane. The photo-oxidation by the PES beads and UV irradiation could reduce the membrane fouling strongly at low HA concentration, because the photo-oxidation had the major role of organic matters reduction in this hybrid water treatment process. Additionally, it proved that the role of adsorption was the greater at the larger pore size membrane than that of photo-oxidation. It thought that the particle size through the larger pore size HC04 membrane was much larger than those through NCMT-7231, and the larger particles could be adsorbed easily by the PES beads.

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 TiO_2 photocatalyst-loaded polyethersulfone (PES) beads for advanced water treatment. In addition, 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 those of the previous study [29] using the hybrid process of the tubular ceramic MF and the same PES beads. The following results could be found out finally.

(1) NOM like as HA could drive membrane fouling more severely on the surface and inside the ceramic membrane as increasing HA concentration in water. The increasing rate of final resistance of membrane fouling in the previous result [29] was the lower than that of this study, because the membrane fouling mechanism could be different by the smaller pore size.

(2) The organic matters could affect the treatment of suspended particles like kaolin in this hybrid process of the 7 channels MF membrane and the PES beads, because the treatment efficiency of turbid materials was a little low at high HA concentration. The treatment efficiency of organic matters was the maximum at 2 mg/L of HA, and decreased as increasing HA concentration. The treated water quality of HA increased the more dramatically than the feed water quality from 2 to 10 mg/L of HA, because most of HA passed through the membrane, and could not treated by adsorption or photo-oxidation by the PES beads and UV.

(3) As a result of investigating the role of membrane filtration, adsorption, and photo-oxidation, the high HA concentration could form the membrane fouling the more dramatically than the low HA concentration in all of MF, (MF + TiO_2) and (MF + TiO_2 + UV) processes. However, the increasing rate

Table 7
Treatment efficiency portions of membrane filtration, adsorption, and photo-oxidation in the hybrid process of multi-channel ceramic MF and photocatalyst-loaded PES beads at HA 6 mg/L

Portion of treatment efficiency	Turbidity			UV_{254} absorbance		
	HC04		NCMT-7231 [29]	HC04		NCMT-7231 [29]
	HA (mg/L)					
	4	6	6	4	6	6
Membrane filtration (%)	97.5	97.5	97.8	70.8	73.9	76.0
Adsorption (%)	0.1	0.2	0.3	0.2	6.1	3.7
Photo-oxidation (%)	0.4	0.1	0.0	10.1	1.1	2.0
Total treatment efficiency (%)	98.0	97.8	98.1	81.1	81.1	81.7

of membrane fouling was the lower at the high HA than the low HA, when simplifying the process from (MF + TiO_2 + UV) to MF process.

(4) The role of photo-oxidation by the PES beads was the more important at low HA concentration; however, that of adsorption was the more dominant at high HA, for the organic matters treatment in this hybrid process with the HC04 membrane. The role of adsorption was the greater at the larger pore size membrane than that of photo-oxidation. It thought that the particle size through the larger pore size HC04 membrane was much larger than those through NCMT-7231, and the larger particles could be adsorbed easily by the PES beads.

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