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Hybrid water treatment process of carbon fiber microfiltration and photocatalyst-coated polypropylene beads: roles of humic acid, photo-oxidation, and adsorption

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ABSTRACT

The effect of organic matters on membrane fouling was observed in a hybrid process of tubular carbon fiber microfiltration (MF) and polypropylene (PP) beads coated with TiO_2 photocatalyst with periodic water back-flushing for advanced water treatment. Also, the 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 filtration to reduce membrane fouling. As results, the organic matter, such as humic acid (HA), could be one of the main factors affecting membrane fouling, because the resistance of membrane fouling (R_f) increased significantly as increasing HA concentration. The treatment efficiencies of turbidity increased a little; however, those of dissolved organic matters (DOM) increased dramatically as increasing HA. As a result of investigating the roles 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. It means that the photo-oxidation and adsorption could control the membrane fouling in this hybrid water treatment process. In DOM treatment efficiency, the proportion of MF was still very high as 70.5%; however, those of adsorption and photo-oxidation were 4.8 and 2.3%, respectively. It means that the role of adsorption was dominant than that of photo-oxidation to remove DOM in this hybrid water treatment process.

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

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 a superior photocatalyst 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 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]. Our previous result published recently about effect of water back-flushing in a hybrid water treatment process of multi-channel ceramic MF and polyethersulfone (PES) beads loaded with photocatalyst [23]. A lot of papers for the hybrid water treatment process of tubular membranes and PES or polypropylene (PP) beads in our research group were published in Membrane Journal [24–31] recently.

In this study, the effect of organic matters on membrane fouling was observed in a hybrid process of tubular carbon fiber microfiltration (MF) and PP beads coated with TiO_2 photocatalyst with periodic water back-flushing for advanced water treatment. A hybrid module case was composed of ceramic MF membrane and the PP beads fluidized between the gap of ceramic membrane and module case. 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. The periodic water 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 [32] using the hybrid process of the seven channels alumina MF membrane (HC10) and photocatalyst-coated PP beads with water back-flushing.

2. Experiments

2.1. Materials

The tubular ceramic MF membrane (C010) with pore size of 0.1 μm was imported from Koch in USA, and it was manufactured with carbon fiber. The specifications of the carbon fiber MF membrane are arranged in Table 1.

The photocatalyst used was 4 to 6 mm PP beads coated with TiO_2 powder made by other research group [33] using chemical vapor deposition method, which is presented in Table 2. Instead of natural

Table 1
Specifications of the tubular carbon fiber microfiltration (C010) used in this study

Membrane	C010
Pore size (μm)	0.1
Outer diameter (mm)	8
Inner diameter (mm)	6
Length (mm)	249
Surface area (cm^2)	46.9
Material	Carbon fiber
Company	Koch in USA

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

organic matters (NOM) and fine inorganic particles in natural water source, a quantity of humic acid (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 tubular carbon fiber 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 were extremely smaller than 4–6 mm particle size of the PP beads utilized here, were installed at the outlet of the hybrid module to prevent the PP beads loss into the treated water tank.

2.3. Experimental procedure

The advanced water treatment system utilizing a hybrid module (6) of tubular carbon fiber MF and PP beads coated with TiO_2 photocatalyst is demonstrated in Fig. 1, which was utilized at our previous study [32]. We performed cross-flow filtration for the tubular carbon fiber membrane and periodic water back-flushing utilizing permeated water. The hybrid module (6) was filled up with 40 g/L of PP beads coated with TiO_2 photocatalyst 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 (1) was filled with 10 L of prepared synthetic water composed of HA and kaolin, and the temperature of the feed water was constantly maintained using a constant temperature circulator (3) (Model 1146, VWR, USA). Also, 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 tubular carbon fiber membrane by a pump (2) (Procon, Standex Co., USA). The feed flow rate was measured by a flow meter (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 tubular carbon fiber membrane and PP beads coated with photocatalyst was measured by an electric balance (11) (Ohaus, USA). The permeate water flowed into the back-washing tank (13) when the permeate flux had not been measured. After the treated water was over a certain level in the back-washing tank (13), it recycled to the feed tank (1) to maintain a constant concentration of the feed water during operation.

The water 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 tubular carbon fiber 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 conditions, trans-membrane pressure (TMP) was maintained constant at 1.8 bar, the water back-flushing pressure at 2.5 bar, the feed flow rate at 1.0 L/min, and the feed water temperature at 20˚C. Periodic

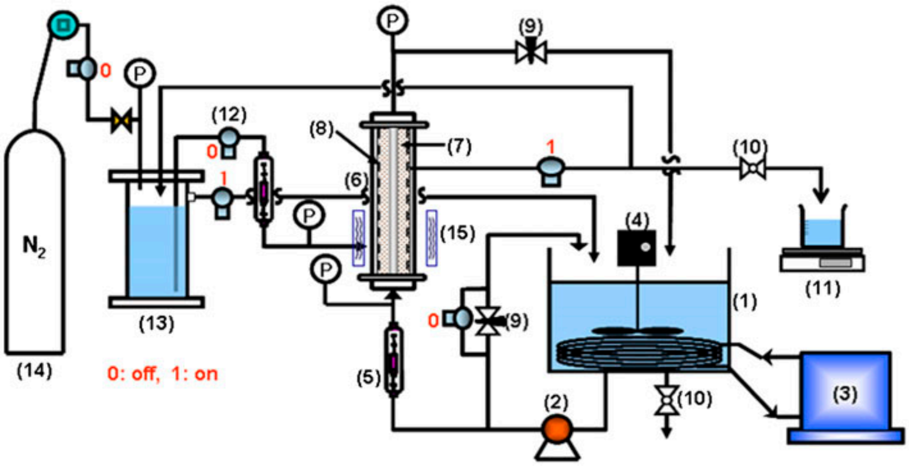

Fig. 1. Apparatus of hybrid water treatment process of tubular carbon fiber microfiltration and TiO_2 photocatalyst-coated PP beads with periodic water back-flushing [32].
Notes: (1) feed tank, (2) feed pump, (3) colong system, (4) stirrer, (5) flow meter, (6) membrane module, (7) TiO_2, (8) 100 mesh sieve, (9) needle valve (control), (10) ball valve, (11) electric balance, (12) solenoid valve, (13) backwashing tank, (14) nitrongen vessel, (15) UV lamp.

water 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 (2100N, 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 –0.1–3.0 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 discussions

The effect of organic matters on membrane fouling was investigated in the hybrid process of tubular carbon fiber MF and TiO_2 photocatalyst-coated PP beads with periodic water back-flushing for advanced water treatment. Also, treatment portions by membrane filtration, photocatalyst adsorption, and photo-oxidation could be calculated 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, and R_f) were extracted from permeate flux (J) data using the resistance-in-series filtration Eq. (1) as the same method as our previous study [34].

$$J = \Delta P/(R_m + R_b + R_f) \tag{1}$$

3.1. Effect of humic acid (HA) concentration

As shown in Fig. 2, the resistances of membrane fouling (R_f) were effectively influenced by HA concentration, and R_f increased dramatically as increasing HA concentration from 2 to 10 mg/L. It means that the organic matter such as HA could formulate the

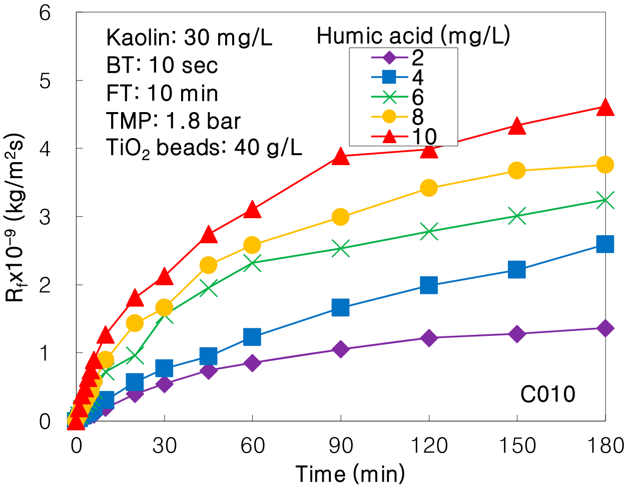

Fig. 2. Effect of HA on resistance of membrane fouling in hybrid process of tubular carbon fiber MF and TiO_2 photocatalyst-coated PP beads.

membrane fouling more effectively on the surface and inside the ceramic membrane as increasing HA concentration. However, R_f increased a little in our previous study [32] utilizing the same hybrid process of seven channels alumina MF (HC10) membrane and the photocatalyst-coated PP beads with periodic water back-flushing, because HC10 had the larger pore size 1.0 μm, and TMP condition was the lower 0.8 bar than this hybrid process. The final R_f ($R_{f,180}$) after 180-min operation at 10 mg/L of HA was 4.614×10^9 kg/m^2 s, which was 3.38 times higher than 1.365×10^9 kg/m^2 s of the $R_{f,180}$ at 2 mg/L as summarized in Table 3. However, in the previous study [32], the $R_{f,180}$ at 10 mg/L of HA was 0.825×10^9 kg/m^2 s, which was 1.34 times higher than 0.616×10^9 kg/m^2 s of the $R_{f,180}$ at 2 mg/L. It means that the larger pore size membrane and the lower TMP condition in the previous study [32] could control the membrane fouling more effectively than this result with the smaller pore size membrane and the higher TMP in the hybrid water treatment process.

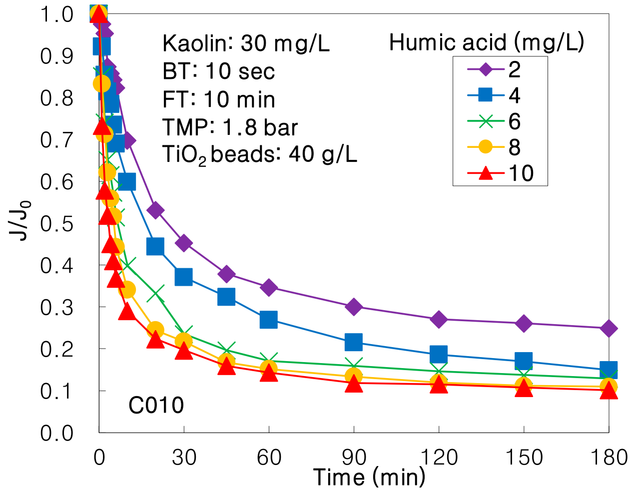

Fig. 3. Effect of HA on dimensionless permeate flux in hybrid process of tubular carbon fiber MF and TiO_2 photocatalyst-coated PP beads.

Fig. 3 shows 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 1–2 min, which can be used to investigate the relative trends of permeate flux. The flux declined dramatically during initial 45 min; however, it was almost constant and reached to the pseudo-steady state flux after 120 min. Its trends were generally shown in the previous study of our research group [23,32]. Effect of water back-flushing was investigated in the previous work [31] in the same hybrid water process. As the result, the maximal flux was acquired at FT (back-flushing period) 2 min and BT 10 s; however, FT 10 min and BT 10 s were selected to evaluate the roles of HA, photooxidation, and adsorption at the proper membrane fouling condition and to compare the previous study [32] at the same FT and BT condition. The J/J_0 tended to decrease rapidly as increasing HA concentration from 2 to 10 mg/L, because the membrane fouling could be formed more effectively by more organic matters. Thus, the final J/J_0 value (J_{180}/J_0) of 0.249 after 180-min operation at HA 2 mg/L was 2.47 times higher than 0.101 at HA 10 mg/L as shown in Table 3. However, in the study [32], J_{180}/J_0 of 0.386 at HA

Table 3

Effect of humic acid on filtration factors for hybrid process of tubular carbon fiber MF and TiO_2 photocatalyst-coated PP beads (BT 10 s, FT 10 min)

Membrane	Humic acid (mg/L)	2	4	6	8	10
Tubular carbon fiber (C010)	$R_m \times 10^{-9}$ (kg/m^2 s)	0.427	0.427	0.424	0.423	0.437
	$R_b \times 10^{-9}$ (kg/m^2 s)	0.025	0.028	0.055	0.040	0.083
	$R_{f,180} \times 10^{-9}$ (kg/m^2 s)	1.365	2.593	3.243	3.759	4.614
	J_0 (L/m^2 h)	1,404	1,395	1,327	1,373	1,220
	J_{180} (L/m^2 h)	349	208	171	150	124
	J_{180}/J_0	0.249	0.149	0.129	0.110	0.101
	V_T (L)	7.03	5.35	3.69	3.26	2.64
Seven channels alumina (HC10) [32]	$R_m \times 10^{-9}$ (kg/m^2 s)	0.374	0.369	0.370	0.369	0.368
	$R_b \times 10^{-9}$ (kg/m^2 s)	0.008	0.006	0.005	0.013	0.021
	$R_{f,180} \times 10^{-9}$ (kg/m^2 s)	0.616	0.688	0.738	0.789	0.825
	J_0 (L/m^2 h)	740	753	754	738	741
	J_{180} (L/m^2 h)	285	266	254	241	234
	J_{180}/J_0	0.386	0.353	0.337	0.326	0.316
	V_T (L)	26.5	23.8	22.4	20.7	19.4

2 mg/L was 1.22 times higher than 0.316 at HA 10 mg/L. Furthermore, the total permeate volume (V_T) of 7.03 L at HA 2 mg/L was 2.66 times higher than 2.64 L of V_T at HA 10 mg/L, but in the study [32,] V_T of 26.5 L at HA 2 mg/L was 1.37 times higher than 19.4 L of V_T at HA 10 mg/L. It means that the larger pore size membrane and the lower TMP condition in the previous study [32] could be the more effective to prohibit the membrane fouling as increasing HA concentration in this hybrid process than this study. Finally, DOM concentration, such as HA, should be one of the main factors affecting the membrane fouling in the hybrid process of tubular carbon fiber MF membrane and TiO_2 photocatalyst-coated PP beads.

As shown in Table 4, the treatment efficiency of turbidity increased slightly from 98.0 to 98.7% as rising HA concentration. It means that the organic matters could affect a little the treatment of suspended particles such as kaolin in the hybrid process. However, in the previous study [32], the treatment efficiency of turbidity was almost constant between 96.6 and 96.9% independent of HA concentration. In the other previous work [31] with the same hybrid water process, the treatment efficiency of turbidity was almost constant above 99.2% independent of FT. It means that the water back-flushing could not effect on the treatment of suspended particles.

Then, the treatment efficiency of DOM, which could be analyzed by UV_{254} absorbance, increased dramatically from 63.1 to 85.5% as increasing HA concentration from 2 to 10 mg/L, as shown in Table 5. It means that the organic matters could affect severely the treatment of DOM such as HA in this hybrid process. However, the treatment efficiency of DOM in the previous work [32] with seven channels alumina MF (HC10) membrane was the maximum 65.4% at HA 6 mg/L, as shown in Table 5. The treated water quality of organic matters increased the less slowly than the feed water quality from 2 to 6 mg/L of HA, because most of HA could be adsorbed on fouling materials inside the membrane or rejected by cake layer on the membrane, and the remained things passed through the membrane adsorbed or oxidized by photocatalyst-coated PP beads. However, the treated water quality of organic matters increased more rapidly than the feed water quality above 6 mg/L of HA, because most of the organic matters passed through the membrane and could not be captured by adsorption or photo-oxidation by photocatalyst-coated PP beads. In the previous work [31] with the same hybrid water process, the treatment efficiency of DOM was the minimum 65.6% at NBF, and increased as decreasing FT, because the shorter FT was effective to clean the photocatalyst surface, and the adsorption and photo-oxidation of DOM could increase by the recovered photocatalyst-coated PP beads.

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

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 HA 6 mg/L, and compared with the hybrid process of MF and PP beads with UV light ($MF + TiO_2 + UV$). And then, the role of membrane filtration, adsorption, and photo-oxidation could be evaluated in the hybrid process of tubular carbon fiber MF and photocatalyst-coated PP beads. The resistance of membrane fouling (R_f) values of ($MF + TiO_2 + UV$), ($MF + TiO_2$), and only MF process at HA 6 mg/L are compared in Fig. 4 during 180-min operation. The R_f could maintain low at the ($MF + TiO_2 + UV$) process, and increased dramatically as simplifying the process from ($MF + TiO_2 + UV$) to

Table 4
Water quality and treatment efficiency of turbidity in the hybrid process of tubular carbon fiber MF and TiO_2 photocatalyst-coated PP beads for effect of humic acid (BT 10 s, FT 10 min)

Experimental condition		Turbidity (NTU)				Average treatment efficiency (%)	
		Feed water		Treated water		Membrane	
Kaolin (mg/L)	Humic acid (mg/L)	Range	Average	Range	Average	C010	HC10 [32]
30	2	17.0–21.9	19.4	0.358–0.395	0.378	98.0	96.9
	4	19.0–21.7	20.4	0.249–0.365	0.296	98.5	96.8
	6	23.3–26.0	24.6	0.320–0.384	0.349	98.6	96.7
	8	26.0–26.7	26.3	0.305–0.500	0.375	98.6	96.6
	10	27.4–28.7	27.9	0.277–0.737	0.376	98.7	96.8

Table 5
Water quality and treatment efficiency of dissolved organic matters (UV_{254} absorbance) in the hybrid process of tubular carbon fiber MF and TiO_2 photocatalyst-coated PP beads for effect of humic acid (BT 10 s, FT 10 min)

Experimental condition		UV_{254} absorbance (cm^{-1})				Average treatment efficiency (%)	
		Feed water		Treated water		Membrane	
Kaolin (mg/L)	Humic acid (mg/L)	Range	Average	Range	Average	C010	HC10 [32]
30	2	0.037–0.068	0.051	0.009–0.031	0.019	63.1	61.8
	4	0.085–0.108	0.094	0.025–0.052	0.035	62.3	63.6
	6	0.095–0.137	0.115	0.013–0.046	0.026	77.6	65.4
	8	0.132–0.184	0.153	0.010–0.053	0.026	83.0	61.4
	10	0.222–0.250	0.236	0.018–0.063	0.034	85.5	52.1

MF. It means that the photocatalyst adsorption and photo-oxidation by the PP beads and UV irradiation could reduce powerfully the membrane fouling in this hybrid water treatment process. The $R_{f,180}$ after 180-min operation was the highest 4.349×10^9 kg/m^2 s at MF process, which was 1.34 times higher than 3.243×10^9 kg/m^2 s at (MF + TiO_2 + UV) process, as summarized in Table 6. The $R_{f,180}$ was 1.153 × 109 kg/m^2 s at MF process, which was 1.06 times higher than 1.088 × 109 kg/m^2 s at (MF + TiO_2 + UV) process in the previous result [32] with seven channels alumina MF membrane (HC10). It means that the smaller pore size membrane and the higher TMP condition in this study could control the membrane fouling more effectively by the photocatalyst adsorption and photo-oxidation by the PP beads and UV irradiation than the previous study [32]. However, as shown in Table 6, the total permeate volume (V_T) was much greater in the previous study [32] than that of this study, because seven channels alumina MF membrane (HC10) had the larger surface membrane area than the tubular carbon fiber MF membrane (C010) in this study in spite of the higher TMP operation.

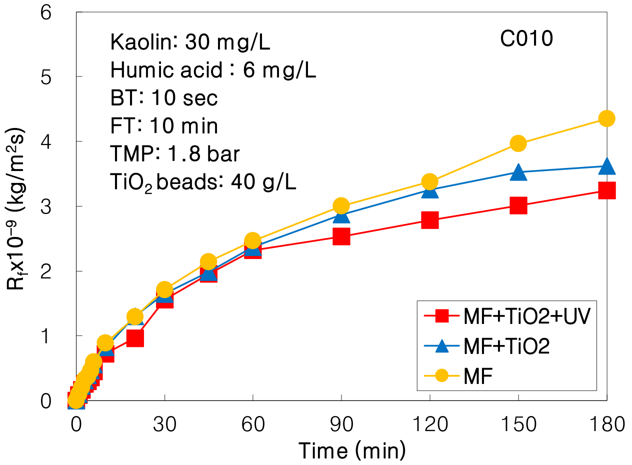

Fig. 4. Role of membrane filtration, adsorption, and photo-oxidation on resistance of membrane fouling in hybrid process of tubular carbon fiber MF and TiO_2 photocatalyst-coated PP beads.

The J/J_0 values could maintain the highest at the (MF + TiO_2 + UV) process and the lowest at MF process, as shown in Fig. 5. It means that the J/J_0 at the (MF + TiO_2 + UV) could be the higher than those at only MF and the (MF + TiO_2) processes, because the photocatalyst adsorption and photo-oxidation could reduce the membrane fouling, efficiently. The J_{180}/J_0 after 180-min operation was the maximal, 0.129, at (MF + TiO_2 + UV) process, which was 1.30 times higher than 0.099 at MF process, as summarized in Table 6. The highest J/J_0 could be maintained, because the membrane fouling could be 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 the previous work [32] for the same hybrid process with seven channels alumina MF membrane (HC10), the maximal J_{180} could be acquired at (MF + TiO_2 + UV) process, which was the same trend with this study, in spite of the larger pore size membrane and the lower TMP operation than this study.

As shown in Tables 7 and 8, the treatment efficiencies of turbidity and DOM (UV_{254} absorbance) decreased as simplifying the process from (MF + TiO_2 + UV) to MF, except treatment efficiencies of turbidity from (MF + TiO_2 + UV) to (MF + TiO_2), which was the same trend with the previous result [32] of seven channels alumina MF membrane (HC10). The portions of treatment efficiency, which were performed by the membrane filtration, adsorption, and photo-oxidation, respectively, in this hybrid

Table 6
Roles of membrane filtration, adsorption, and photo-oxidation on filtration factors in hybrid process of tubular carbon fiber MF and TiO_2 photocatalyst-coated PP beads at humic acid 6 mg/L

Membrane	Process	MF + TiO_2 + UV	MF + TiO_2	MF
Tubular carbon fiber (C010)	$R_m \times 10^{-9}$ (kg/m^2 s)	0.424	0.453	0.458
	$R_b \times 10^{-9}$ (kg/m^2 s)	0.055	0.002	0.019
	$R_{f,180} \times 10^{-9}$ (kg/m^2 s)	3.243	3.621	4.349
	J_0 (L/m^2 h)	1,327	1,396	1,333
	J_{180} (L/m^2 h)	171	156	132
	J_{180}/J_0	0.129	0.112	0.099
	V_T (L)	3.77	3.48	3.29
Seven channels alumina (HC10) [32]	$R_m \times 10^{-9}$ (kg/m^2 s)	0.351	0.369	0.379
	$R_b \times 10^{-9}$ (kg/m^2 s)	0.061	0.046	0.015
	$R_{f,180} \times 10^{-9}$ (kg/m^2 s)	1.088	1.184	1.153
	J_0 (L/m^2 h)	684	681	716
	J_{180} (L/m^2 h)	188	177	182
	J_{180}/J_0	0.275	0.259	0.255
	V_T (L)	17.1	17.2	16.9

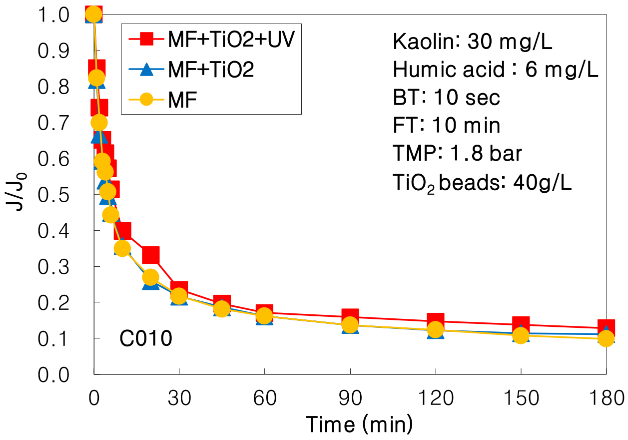

Fig. 5. Role of membrane filtration, adsorption, and photo-oxidation on dimensionless permeate flux in hybrid process of tubular carbon fiber MF and TiO_2 photocatalyst-coated PP beads.

process, could be calculated by reducing sequentially the turbidity or DOM treatment efficiencies of (MF + TiO_2 + UV), (MF + TiO_2), and MF, and those were compared with the result [32] of seven channels alumina MF membrane (HC10) in Table 9. In turbidity treatment efficiency, the treatment portion of membrane filtration was very high 98.1% at HA 6 mg/L. The treatment portion of adsorption by the photocatalyst-coated PP beads was very low 0.5% and that of photo-oxidation by the PP beads and UV light was 0.0%. However, those of adsorption by the photocatalyst-coated PP beads and photo-oxidation by the PP beads and UV light were 0.0–0.6%, respectively, in the result [32] with seven channels alumina MF membrane (HC10). It means that the roles of adsorption and photo-oxidation by the photocatalyst-coated PP beads and UV were not important for the treatment of the suspended particles such as kaolin in this hybrid process, independent of membrane classification. Kaolin could not be removed effectively by the adsorption and photo-oxidation by the photocatalyst-coated PP beads, because kaolin was inorganic and did not have electric charge.

As shown in Table 9, in the treatment efficiency of DOM (UV_{254} absorbance), the treatment portion of the membrane filtration was still very high 70.5%; however, that of the adsorption was a little high 4.8% and that of photo-oxidation was low 2.3% at HA 6 mg/L. It means that the role of the adsorption by the photocatalyst-coated PP beads was dominant than that of the photo-oxidation by the PP beads for the DOM treatment in this hybrid process. The adsorption by the PP beads could reduce the membrane fouling powerfully, because the adsorption had the major role of DOM reduction in this hybrid water treatment process. However, in the previous work [32] with the same hybrid process of seven channels alumina MF membrane (HC10), the role of the photo-oxidation was a little more important (3.2%) than that of the adsorption (0.5%) for the DOM treatment. It means that the photo-oxidation was the more effective for reducing the membrane fouling than the adsorption, because the photo-oxidation was dominant to treat DOM in the hybrid process with seven channels alumina MF membrane (HC10), which had the larger pore size and the lower TMP operation than this study.

Table 7
Water quality and treatment efficiency of turbidity in the hybrid process of tubular carbon fiber MF and TiO_2 photocatalyst-coated PP beads for roles of membrane filtration, adsorption, and photo-oxidation at humic acid 6 mg/L

Experimental condition		Turbidity (NTU)				Average treatment efficiency (%)	
		Feed water		Treated water		Membrane	
Humic acid (mg/L)	Process	Range	Average	Range	Average	C010	HC10 [32]
6	MF + TiO_2 + UV	23.3–26.0	24.6	0.320–0.384	0.349	98.6	98.5
	MF + TiO_2	22.0–23.4	22.9	0.289–0.385	0.326	98.6	98.5
	MF	22.6–23.5	23.2	0.293–0.839	0.440	98.1	97.9

Table 8
Water quality and treatment efficiency of dissolved organic matters (UV_{254} absorbance) in the hybrid process of tubular carbon fiber MF and TiO_2 photocatalyst-coated PP beads for roles of membrane filtration, adsorption, and photo-oxidation at humic acid 6 mg/L

Experimental condition		UV_{254} absorbance (cm^{-1})				Average treatment efficiency (%)	
		Feed water		Treated water		Membrane	
Humic acid (mg/L)	Process	Range	Average	Range	Average	C010	HC10 [32]
6	MF + TiO_2 + UV	0.095–0.137	0.115	0.013–0.046	0.026	77.6	48.3
	MF + TiO_2	0.093–0.145	0.111	0.023–0.035	0.027	75.3	45.1
	MF	0.090–0.136	0.114	0.020–0.069	0.034	70.5	44.6

Table 9
Treatment efficiency portions of membrane filtration, adsorption, and photo-oxidation in the hybrid process of tubular carbon fiber MF and TiO_2 photocatalyst-coated PP beads at humic acid 6 mg/L

	Membrane			
	Turbidity		UV_{254} absorbance	
Portion of treatment efficiency (%)	C010	HC10 [32]	C010	HC10 [32]
Membrane filtration	98.1	97.9	70.5	44.6
Adsorption	0.5	0.0	4.8	0.5
Photo-oxidation	0.0	0.6	2.3	3.2
Total treatment efficiency	98.6	98.5	77.6	48.3

4. Conclusions

The effect of organic matters on membrane fouling was observed in the hybrid process of tubular carbon fiber MF and photocatalyst-coated PP beads with water back-flushing for advanced water treatment in this study. Also, treatment portions by the 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 [32] of the same hybrid process with seven channels alumina MF membrane (HC10).

(1) The organic matter, such as HA, could be one of the main factors affecting the membrane fouling, because the final resistance of membrane fouling ($R_{f,180}$) increased dramatically as increasing HA concentration from 2 to 10 mg/L. It was exactly the same result with the previous study [32] with seven channels

alumina MF membrane (HC10); however, R_f increased the less than that in the previous study [32]. It means that the larger pore size membrane and the lower TMP condition in the study [32] could control membrane fouling more effectively than this result in the hybrid water treatment process.

(2) The treatment efficiencies of turbidity increased slightly as increasing HA concentration. It means that the organic matters could affect a little the treatment of suspended particles such as kaolin in this hybrid process. Then, the DOM treatment efficiencies increased dramatically as increasing HA concentration from 2 to 10 mg/L. It means that the organic matters could affect severely the DOM treatment in this hybrid process. However, the DOM treatment efficiencies in the previous work [32] were the maximum at HA 6 mg/L. The treated water quality of DOM increased less slowly than the feed water quality when increasing HA from 2 to 6 mg/L.

(3) As a result of investigating the role of membrane filtration, adsorption, and photo-oxidation, the membrane fouling resistance was the minimum, and the resistance of membrane fouling (R_f) could maintain low at the (MF + TiO_2 + UV) process and increased dramatically as simplifying the process to MF. It means that the photocatalyst adsorption and photo-oxidation by the PP beads and UV irradiation could reduce the membrane fouling powerfully in this hybrid water treatment process.

(4) In turbidity treatment efficiency, the treatment portion of membrane filtration was very high 98.1%; however, those of adsorption and photo-oxidation by the PP beads and UV light were very low 0.5 and 0.0%, respectively. The trends were the same with the result [32] of seven channels alumina MF membrane (HC10). It means that the roles of adsorption and photo-oxidation by the PP beads and UV were not important for the treatment of the suspended particles such as kaolin in this hybrid process, independent of membrane classification. In the DOM treatment efficiency, the treatment portion of membrane filtration was still very high 70.5%; however, that of adsorption was a little high 4.8% and that of photo-oxidation was low 2.3% at 6 mg/L of HA. It means that the role of adsorption by photocatalyst-coated PP beads was dominant than that of photo-oxidation by the PP beads for the DOM treatment in this hybrid process.

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