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Hybrid water treatment process of tubular carbon fiber ultrafiltration and photocatalyst-coated PP beads: treatment mechanisms and effects of water back-flushing time

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ABSTRACT

The effect of water back-flushing time (BT) on membrane fouling and treatment efficiency was investigated in a hybrid process of tubular carbon fiber ultrafiltration (UF) and titanium dioxide photocatalyst-coated polypropylene beads for advanced water treatment, and compared with the previous study utilizing alumina or carbon UF membranes. The resistances of membrane fouling (R_f) were highly affected by BT, and R_f decreased significantly as increasing BT. The water back-flushing prohibited membrane fouling more efficiently for the carbon fiber UF than the alumina UF. The BT did not affect the turbidity treatment in this hybrid process; however, the turbidity treatment efficiency was maximal at no back-flushing, and increased dramatically as increasing BT in the hybrid process utilizing alumina UF. The treatment efficiency of dissolved organic matters (DOM) was maximal at BT of 30 s, and increased dramatically as increasing BT. The adsorption and photo-oxidation by the PP beads and UV could not play important roles in turbid matters treatment of the hybrid process utilizing the carbon fiber or carbon UF membranes; however, the role of adsorption was significantly dominant in the hybrid process utilizing the alumina UF. Additionally, the adsorption and photo-oxidation could play more dominant roles in the DOM treatment of the hybrid process utilizing the alumina UF than those utilizing the carbon fiber or carbon UF.

Keywords: Ultrafiltration; Water back-flushing; Photocatalyst; Hybrid process; Carbon fiber; Water treatment

1. Introduction

As one of new types of water pollution-control technologies, photocatalytic oxidation has been researched worldwide because of the characteristics of high effectiveness, low energy consumption, and a wide range of application. In addition, it can oxidize most organic compounds, particularly non-biodegradable organic pollutants, by mineralizing them to small

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inorganic molecules. Therefore, photocatalytic oxidation technology has extensive forecast for application. There is a general agreement among researchers that titanium dioxide is greater among various semiconductor photocatalysts because of its high activity, large stability to light illumination, and low price [1–4]. Two modes of titanium dioxide application are adopted in photocatalytic degradation: (1) titanium dioxide immobilized on support materials and (2) titanium dioxide suspended in aqueous medium [5,6]. Application of titanium dioxide in suspension instead of immobilizing the titanium dioxide on solid carriers has shown an enhancement in organic degradation efficiencies due to the uniform distribution and large specific surface area. However, it proved that classical solid−liquid separation processes such as sedimentation, centrifugation, and coagulation used for separation of the fine titanium dioxide particles (typically less than 1 μm) were not efficient [7]. Additionally, to the low reutilization rate, there is also an opportunity of secondary pollution caused by fine titanium dioxide particles in the effluent. Consequently, the photocatalysts recovery is one of the main issues that affect its large scale application. A lot of researches have been performed focusing to solve this problem [8–12].

In recent times, titanium microsphere has also been proposed as a means to recover titanium dioxide photocatalyst. The core-shell structured titanium dioxide microspheres with a mesoporous surface prepared of nano-titanium dioxide, commonly have many advantages like as low density, high specific surface area, and large size encouraging for separation [13–16]. On the other hand, the preparation method and operating conditions have a great effect on particle morphology related with photocatalysis, and numerous problems existing in the present 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 concurrently separate and concentrate all pollutants in water by the retention of its microspores without secondary pollution and phase change. In addition, its apparatus has a lot of benefits of low energy consumption, compact, easy to operate, and capable of incessant operation at room temperature [18]. However, membrane fouling due to the adsorption–precipitation of organic and inorganic compounds inside or on the surface of membranes leads to a decrease in the permeate flux, an increase in membrane recovery costs, and a decline of the membrane life. Techniques for controlling membrane fouling remain insufficient, which is the major obstruction in the successful accomplishment of membrane separation technology in the field of water treatment, although significant improvement has been made in membrane fouling [19,20]. The titanium dioxide photocatalysis-membrane separation hybrid technology can solve the two problems mentioned above successfully [21]. The hybrid technology not only keeps the characteristics and capacity of the two technologies, but also produces some synergistic effects to conquer the drawbacks of the single technology. On the one hand, the pollutants are oxidized by the photocatalysis, and the chosen membranes demonstrate the potential not only to preserve the photocatalyst, but also to eliminate partially organic species by controlling the retention time in the reacting system. In other words, the membrane is also a selective barrier for the molecules to be degraded, thus the hybrid technology could improve the photocatalytic effectiveness and accomplish outstanding effluent quality. Alternatively, the hybrid of photocatalysis and membrane separation could solve or assuage the problem of flux decrease related with membrane fouling [22]. Our previous result published in recent times about roles of photooxidation and adsorption at water back-flushing in hybrid water treatment of multi-channels alumina MF and photocatalyst-coated PP beads [23]. In addition, optimum operating conditions were investigated in a hybrid water treatment process of multi-channel ceramic MF and photocatalyst-loaded polyethersulfone microsphere beads [24].

In this research, the effect of water back-flushing time (BT) on membrane fouling and treatment efficiency was investigated in a hybrid process of tubular carbon fiber UF and TiO_2 photocatalyst-coated PP beads for advanced water treatment. A hybrid module of carbon fiber, which was a kind of ceramic, UF membrane, and the PP beads fluidized at the gap between the tubular membrane and the acryl module case, was the first trial in the hybrid water treatment process field of UF and photocatalyst. On the one hand, treatment portions of UF, photocatalyst adsorption, and photo-oxidation were examined by evaluating the treatment efficiencies of UF, UF + TiO_2, and UF + TiO_2 + UV processes. Periodic water back-flushing was executed during 10 s per 10 min's filtration to inhibit membrane fouling. The results were evaluated with those of the previous study for the hybrid process of a tubular alumina membrane (NCMT-5231) [25,26] having the same pore size of 0.05 μm, or a tubular carbon membrane (M8) [27] having molecular weight cut-off (MWCO) of 150,000 Dalton, and the same photocatalyst-coated PP beads with periodic water back-flushing. The alumina and carbon utilized in the previous researches [25–27] were a kind of ceramic material.

2. Experiments

2.1. Materials

In the research, the tubular ceramic UF membrane (C005) with pore size of 0.05 μm was imported from Koch in USA, and it was manufactured with carbon fiber. The specifications of the tubular carbon fiber membrane were summarized in Table 1.

The photocatalyst employed in this study was the same PP beads with those of the previous studies [25–27], which was coated with titanium dioxide powder made by Prof. Kim's group [28] utilizing chemical vapor deposition method, as arranged in Table 2. A quantity of humic acid sodium salt (Aldrich) and kaolin (Sigma-Aldrich) was dissolved in distilled water in place of natural organic matters (NOM) and fine inorganic particles in natural water source. Subsequently, it was utilized as synthetic water in this research. Because it was known that humic acid was the major humic material of river or lake, it was selected as a NOM representative. Two UV lamps (F8T5BLB, Sankyo, Japan) having 8 W power radiated UV light with 352 nm from outside of the acryl module. The UV light with 352 nm was utilized in this research because the sun puts 0.2–0.3 mol photons/m^2 h with a typical UV-flux near the surface of the earth of 20–30 W/m^2 in the 300–400 nm range at the process disposal. It was known that principally these photons are suitable for destroying water pollutants in photocatalytic reactors [29].

2.2. Hybrid membrane module

The hybrid module was assembled by packing the PP beads coated with titanium dioxide powder at the gap between the module inside and outside of the carbon fiber UF membrane for eliminating the turbidity and NOM flourished from kaolin and humic acid. Additionally, to prevent the PP beads loss into the treated water tank, 100 meshes (0.150 mm), which were tremendously smaller than 4–6 mm particle size of the PP beads applied in this research, were mounted at the outlet of the hybrid module.

Table 1
Specifications of the tubular carbon fiber ultrafiltration membrane (C005) used in this study

Membrane	C005
Pore size (μm)	0.05
Outer diameter (mm)	8
Inner diameter (mm)	6
Length (mm)	250
Surface area (cm^2)	47.1
Material	Carbon fiber
Company	Koch (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

2.3. Experimental procedure

Fig. 1 demonstrates the advanced water treatment system utilizing a hybrid module of the tubular carbon fiber UF and the titanium dioxide photocatalyst-coated PP beads, which was applied at our previous study [25]. Cross-flow filtration and periodic water back-flushing utilizing the treated water were performed to suppress fouling of the tubular carbon fiber UF membrane. The hybrid module was filled up with 40 g/L of the photocatalyst-coated PP beads at the gap between the UF membrane and the module case, and it was utilized for the advanced hybrid water treatment. Subsequently, the feed tank was filled with the synthetic water of 10 L constituted of humic acid and kaolin, and temperature of the feedwater was continuously sustained by utilizing a constant temperature circulator (Model 1146, VWR, USA). Furthermore, the synthetic feedwater was incessantly stirred by an agitator in order to maintain homogeneous, and it was caused to flow into the inside of the tubular UF membrane by a pump (Procon, Standex Co., USA). The feed flow rate was gauged by a flow meter (NP-127, Tokyo Keiso, Japan). The flow rate and pressure of the feedwater that flowed into the hybrid module were maintained continuously by regulating valves of both the bypass pipe of the pump and the concentrate pipe. The permeate flux through the tubular UF membrane approached the PP beads, and the treated water was gauged by an electric balance (Ohaus, USA). To sustain a constant concentration of the feedwater during procedure, the treated and the concentrate water recycled to the feed tank.

The kaolin and humic acid concentrations were, respectively, fixed at 30 and 10 mg/L in the synthetic feedwater, the filtration time (FT) at 10 min, however only BT was changed from 6 to 30 s to investigate the effect of water BT. Only UF process without any photocatalyst-coated PP beads and UV radiation (UF), and UF process with PP beads (UF + TiO_2) were operated at 6 mg/L of humic acid, correspondingly.

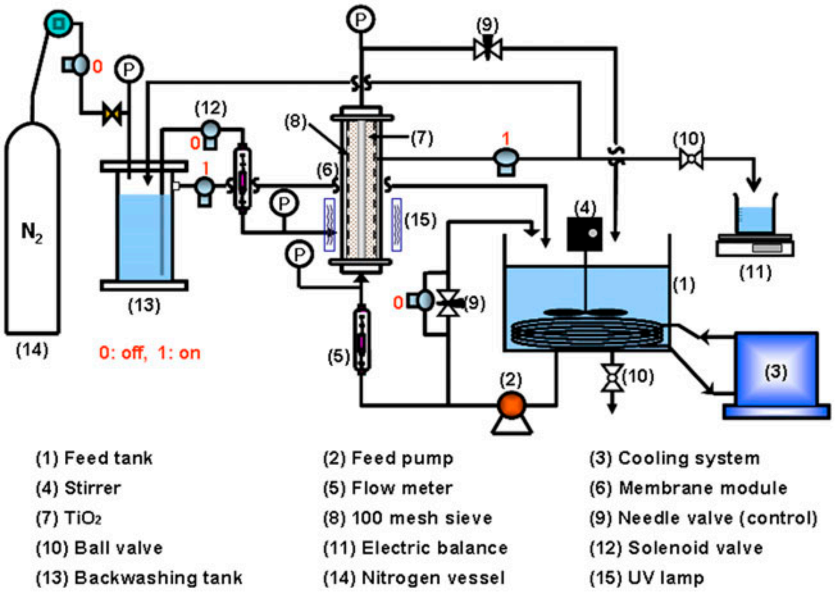

Fig. 1. Apparatus of hybrid water treatment process of tubular carbon fiber ultrafiltration and TiO_2 photocatalyst-coated PP beads with periodic water back-flushing [25].

The resistance of the membrane fouling (R_f) and permeate flux (J) were investigated during total FT of 180 min under each condition. Under all experimental conditions, trans-membrane pressure (TMP) was maintained steady at 1.8 bar, the water back-flushing pressure at 2.5 bar, the feed flow rate at 1.0 L/min, and the feedwater temperature at 20˚C. The periodic water back-flushing utilizing permeate water was performed during 10 s per 10 min's filtration for evaluating a portion of the treatment efficiencies of UF, adsorption, and photo-oxidation.

The quality of feed and treated water was analyzed in order to estimate the treatment efficiencies of turbid materials and dissolved organic matters (DOM). For measuring turbid materials and DOM, turbidity was gauged by a turbidimeter (2100 N, Hach, USA) and UV_{254} absorbance was examined 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 (±0.001/cm) correspondingly. To eliminate turbid materials, the sample was filtered by 0.2 μm syringe filter prior to the measurement of UV_{254} absorbance.

3. Results and discussions

The effect of water BT on membrane fouling was examined in the hybrid process of tubular carbon fiber UF and titanium dioxide photocatalyst-coated PP beads for advanced water treatment. In addition, treatment portions by membrane filtration, photocatalyst adsorption, and photo-oxidation were evaluated by subtracting in sequence the treatment efficiencies of UF, ($UF + TiO_2$) and ($UF + TiO_2 + UV$) processes. Utilizing the resistance-in-series filtration equation as the same method as our previous study [30], resistances of membrane, boundary layer, and membrane fouling (R_m, R_b, R_f) were calculated from permeate flux (J) data. The results of BT effect were compared with our previous study [25] of the hybrid process of alumina (NCMT-5231) UF membrane with the same pore size of 0.05 μm and the same PP beads. Then, the roles of UF, adsorption, and photo-oxidation were evaluated with our previous result [26] utilizing the same PP beads, and alumina (NCMT-5231) UF, and our other previous research [27] using carbon (M8) UF membrane.

3.1. Effect of water BT

As shown in Fig. 2, the resistances of membrane fouling (R_f) were highly influenced by BT, and R_f decreased significantly as increasing BT from no back-flushing (NBF) to 30 s. Furthermore, the membrane fouling was very serious at NBF and BT of 6 s. It means that the water back-flushing could reduce efficiently the membrane fouling on the surface and inside the carbon fiber UF membrane. On the other hand, as arranged in Table 3, the hybrid water

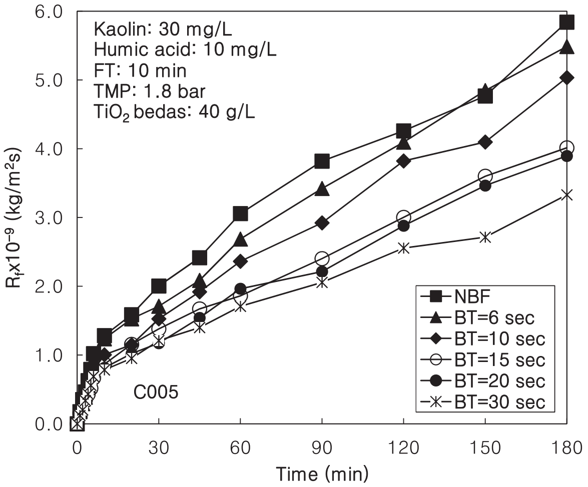

Fig. 2. Effect of water BT on resistance of membrane fouling in hybrid process of tubular carbon fiber UF and TiO_2 photocatalyst-coated PP beads.

treatment process of carbon fiber UF membrane and the photocatalyst-coated PP beads in this research could operate well during 180 min. However, in our previous study [25], the hybrid process of alumina UF membrane with the same pore size of 0.05 μm and the same PP beads could be performed until 60 and 150 min at NBF and BT of 6 s, respectively, because of severe membrane fouling. The final R_f ($R_{f,180}$) after 60 min's operation at NBF was 5.049×10^9 kg/m^{2}s, which was 1.56 times higher than the $R_{f,180}$ of 3.241×10^9 kg/m^{2}s at BT of 30 s in the previous study [25]. However, in this research the $R_{f,180}$ at NBF was 5.841×10^9 kg/m^{2}s, which was 1.76 times higher than the $R_{f,180}$ of 3.328×10^9 kg/m^{2}s at BT of 30 s. It proved that the water back-flushing could prohibit membrane fouling more efficiently for the carbon fiber membrane than the alumina membrane [25] in this hybrid water treatment process of UF and photocatalyst-coated PP beads. In addition, the resistance of irreversible membrane fouling (R_{if}) could be calculated from the permeate flux recovered by physical washing of brush inside the tubular membrane after 180 h's operation. Subsequently, the resistance of reversible membrane fouling (R_{rf}) could be acquired utilizing the equation of $R_f = R_{if} + R_{rf}$. As compared in Table 3, R_{if} was almost constant independent of BT; however, R_{rf} decreased dramatically as increasing BT from NBT to 30 s. It was found that the reversible membrane fouling could be effectively inhibited by more frequent water back-flushing.

To investigate a relative decline of permeate flux, the dimensionless permeate flux (J/J_0), where J_0 is the initial permeate flux which was predicated by extrapolation utilizing initial two data at 1 and 2 min, was compared in Fig. 3. The J/J_0 tended to increase

Table 3
Effect of water BT on filtration factors for hybrid process of tubular carbon fiber or alumina UF and TiO_2 photocatalyst-coated PP beads at humic acid of 10 mg/L and kaolin of 30 mg/L (FT 10 min)

Membrane	BT (sec)	NBF[a]	6	10	15	20	30
C005	$R_m \times 10^{-9}$ (kg/m^{2}s)	0.990	1.003	1.017	1.016	1.017	1.011
	$R_b \times 10^{-9}$ (kg/m^{2}s)	0.026	0.079	0.111	0.078	0.114	0.143
	$R_{f,180} \times 10^{-9}$ (kg/m^{2}s)	5.841	5.487	5.034	4.013	3.895	3.328
	$R_{if} \times 10^{-9}$ (kg/m^{2}s)	0.830	0.825	–	–	0.785	0.900
	$R_{rf} \times 10^{-9}$ (kg/m^{2}s)	5.011	4.662	–	–	3.110	2.429
	J_0 (L/m^{2}h)	625	587	563	580	562	551
	J_{180} (L/m^{2}h)	93	97	103	124	126	142
	J_{180}/J_0	0.148	0.165	0.183	0.214	0.246	0.257
	V_t (L)	2.25	2.30	2.47	2.78	2.83	3.00
NCMT-5231 (0.05 μm) [25]	$R_m \times 10^{-9}$ (kg/m^{2}s)	0.417	0.417	0.415	0.411	0.412	0.416
	$R_b \times 10^{-9}$ (kg/m^{2}s)	0.007	0.000	0.024	0.021	0.014	0.000
	$R_{f,180} \times 10^{-9}$ (kg/m^{2}s)	5.049[b]	4.263[c]	3.485	3.430	3.318	3.241
	J_0 (L/m^{2}h)	1,499	1,523	1,448	1,471	1,491	1,525
	J_{180} (L/m^{2}h)	116[b]	136[c]	162	164	170	174
	J_{180}/J_0	0.077[b]	0.089[c]	0.112	0.112	0.114	0.114
	V_T (L)	1.78[b]	3.74[c]	4.12	4.13	4.32	4.64

[a] No back-flushing.

[b] After 60 min' operation.

[c] After 150 min' operation.

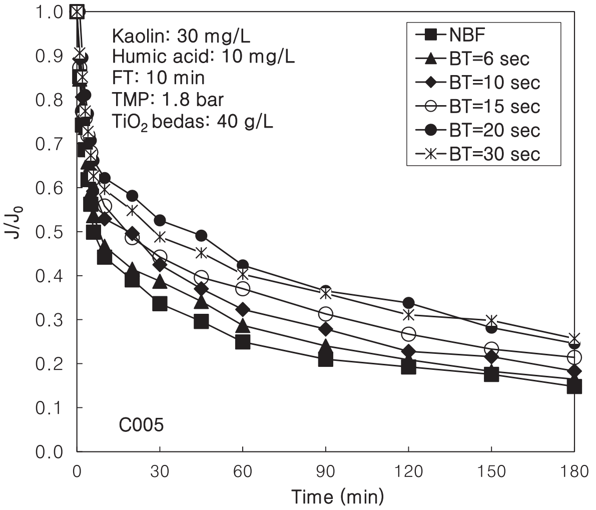

Fig. 3. Effect of water BT on dimensionless permeate flux in hybrid process of carbon fiber ceramic UF and TiO_2 photocatalyst-coated PP beads.

significantly as increasing BT from NBF to 30 s, because more frequent water back-flushing should restrain the cake accumulation on membrane surface and the fouling inside membrane. On the other hand, in the study [25] the final value of J/J_0 (J_{180}/J_0) of 0.114 after 180 min's operation at BT of 30 s was 1.48 times higher than 0.077 after 60 min's operation at NBF, as shown in Table 3. Nevertheless, in this research the J_{180}/J_0 of 0.257 at BT of 30 s was 1.74 times higher than J_{180}/J_0 of 0.148 at NBF. It confirmed that the water back-flushing could be more effective to control the membrane fouling for the carbon fiber membrane than the alumina membrane [25] in the hybrid water treatment process of UF and the photocatalyst-coated PP beads. However, the total permeate volume (V_T) of 3.00 L at BT of 30 s was 1.33 times higher than V_T of 2.25 L at NBF, but in the study [25] V_T of 4.64 L at BT of 30 s was 2.61 times higher than 1.78 L at NBF, as shown in Table 3. It happened that the hybrid water treatment utilizing alumina UF membrane in the previous research [25] could be operated until 60 and 150 min, respectively, at NBF and BT of 6 s because of severe membrane fouling, and therefore, the low V_T was acquired at NBF and BT of 6 s.

As arranged in Table 4, the treatment efficiency of turbidity was found to maintain almost same as 99.2–99.5% independent of water BT. It proved that the water BT could not affect the treatment of suspended particles like kaolin in the hybrid process of carbon fiber UF membrane and photocatalyst-coated PP beads. On the other hand, the treatment efficiency of turbidity was found to be maximal as 98.2% at NBF, and increase dramatically from 88.9 to 94.3% as increasing BT from NBF to 30 s in the hybrid process of alumina UF membrane [25]. It confirmed that the turbid matter as kaolin could be efficiently captured by cake layer accumulated on the membrane surface at NBF in the hybrid process of alumina UF [25], because the turbidity treatment efficiency was maximal at NBF condition in this hybrid process. Subsequently, the photocatalyst-coated PP beads could be cleaned successfully by water back-flushing as increasing BT from NBF to 30 s (namely "cleaning effect"), and finally the turbid matter was effectively adsorbed by the PP beads. However, as shown in Table 5, the treatment efficiency of UV_{254} absorbance, which means the concentration of DOM, was found to be maximal as 67.3% at BT of 30 s, and increased dramatically as increasing BT from NBF to 30 s. It proved that the photocatalyst-coated PP beads were cleaned effectively by water back-flushing as increasing BT from NBF to

Table 4
Water quality and treatment efficiency of turbidity in the hybrid process of tubular carbon fiber or alumina UF and TiO_2 photocatalyst-coated PP beads for effect of BT (FT 10 min)

Experimental condition			Turbidity (NTU)				Average treatment efficiency (%)	
			Feedwater		Treated water			
Kaolin (mg/L)	Humic acid (mg/L)	BT (sec)	Range	Average	Range	Average	C005	NCMT-5231 [25]
30	10	NBF[a]	15.5–28.5	22.1	0.153–0.186	0.172	99.2	98.2
		6	19.4–35.5	26.8	0.141–0.257	0.198	99.3	88.9
		10	21.7–30.3	25.8	0.138–0.204	0.164	99.4	89.2
		15	23.6–36.5	28.0	0.094–0.254	0.177	99.4	91.3
		20	25.1–35.1	30.2	0.063–0.262	0.165	99.5	92.1
		30	20.8–32.7	25.2	0.021–0.201	0.116	99.5	94.3
Average			–	26.4	–	0.165	99.4	92.3

[a] No back-flushing.

Table 5
Water quality and treatment efficiency of DOM (UV_{254} absorbance) in the hybrid process of tubular carbon fiber or alumina UF and TiO_2 photocatalyst-coated PP beads for effect of BT (FT 10 min)

Experimental condition			UV_{254} absorbance (cm^{-1})				Average treatment efficiency (%)	
			Feed water		Treated water			
Kaolin (mg/L)	Humic acid (mg/L)	BT (sec)	Range	Average	Range	Average	C005	NCMT-5231[25]
30	10	NBF[a]	0.334–0.402	0.374	0.156–0.197	0.181	51.7	95.6
		6	0.408–0.485	0.431	0.186–0.237	0.205	52.5	73.7
		10	0.316–0.407	0.365	0.144–0.201	0.170	53.3	75.1
		15	0.274–0.338	0.317	0.116–0.156	0.136	56.9	78.8
		20	0.108–0.237	0.191	0.025–0.131	0.076	60.3	80.4
		30	0.083–0.324	0.203	0.132–0.021	0.066	67.3	84.9
Average			–	0.314	–	0.139	57.0	81.4

[a] No back-flushing.

30 s, and finally the DOM could be photo-oxidized or adsorbed effectively by the PP beads and UV radiation. On the other hand, as arranged in Table 5, in the hybrid process of alumina UF [25] the treatment efficiency of DOM was found to be maximal as 95.6% at NBF because of the severe membrane fouling, and increased dramatically as increasing BT from 6 to 30 s by the cleaning effect of PP beads. It proved that the trend of DOM treatment depended on membrane materials in the hybrid water treatment process. Additionally, the UV_{254} absorbance was only used to evaluate the variation of DOM. This method can evaluate only the C=C molecule; however, after the oxidation process the molecule organic can change to the other smaller organic molecule or mineralization to carbon dioxide that can change, or still remain the total organic carbon in the aqueous solution.

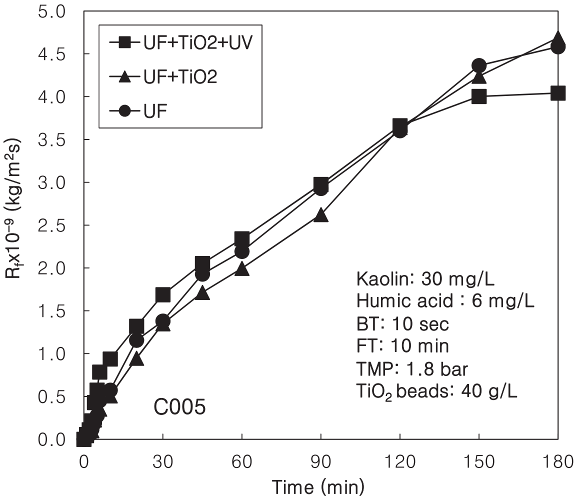

Fig. 4. Roles of ultrafiltration, adsorption, and photo-oxidation on resistance of membrane fouling in hybrid process of tubular carbon fiber UF and TiO_2 photocatalyst-coated PP beads.

3.2. *Roles of ultrafiltration (UF), adsorption, and photo-oxidation*

The UF + TiO_2 process with PP beads without UV radiation, and UF process without any PP beads and UV were performed, respectively, at 6 mg/L of humic acid, and compared with the UF + TiO_2 + UV hybrid process of UF and PP beads with UV radiation. Subsequently, the roles of UF, adsorption, and photo-oxidation were estimated in the hybrid process of tubular carbon fiber UF and photocatalyst-coated PP beads with periodic water back-flushing of FT 10 min and BT 10 s. It was the optimized condition proved in the previous research [25] utilizing alumina UF membrane. The R_f values of UF + TiO_2 + UV, UF + TiO_2 and UF processes at humic acid of 6 mg/L were compared during 180 min's operation, as plotted in Fig. 4. The R_f of the UF + TiO_2 + UV hybrid process was a little higher than those of the UF+TiO_2 and UF processes before 120 min, after that it increased very gradually and finally was much lower than those of the UF + TiO_2 and UF processes. It proved that the photocatalyst adsorption by the PP beads and photo-oxidation by the PP beads and UV irradiation could prohibit the membrane fouling in this hybrid water treatment process regardless of utilizing any carbon fiber, alumina, or carbon UF membranes. The $R_{f,180}$ of 4.583×10^9 kg/m^2s at UF process was 1.13 times higher than 4.041×10^9 kg/m^2s at UF + TiO_2 + UV process, as summarized in Table 6. On the other hand, the $R_{f,180}$ of 1.994×10^9 kg/m^2s at UF process was 1.73 times higher than 1.152×10^9 kg/m^2s at UF + TiO_2 + UV process in the previous study [26] utilizing alumina (NCMT-5231) UF membrane. By the way, the $R_{f,180}$ of 5.642×10^9 kg/m^2s at UF process was 1.14 times higher than 4.952×10^9 kg/m^2s at

Table 6
Roles of membrane filtration, adsorption, and photo-oxidation on filtration factors in hybrid process of tubular carbon fiber or alumina UF and TiO_2 photocatalyst-coated PP beads at humic acid of 6 mg/L, FT of 10 min and BT of 10 s

Membrane	Process	UF + TiO_2 + UV	UF + TiO_2	UF
C005	$R_m \times 10^{-9}$ (kg/m^{2}s)	0.998	1.013	0.991
	$R_b \times 10^{-9}$ (kg/m^{2}s)	0.219	0.024	0.053
	$R_{f,180} \times 10^{-9}$ (kg/m^{2}s)	4.041	4.687	4.583
	J_0 (L/m^{2}h)	522	612	608
	J_{180} (L/m^{2}h)	121	111	113
	J_{180}/J_0	0.232	0.181	0.186
	V_T (L)	2.42	2.80	2.68
NCMT-5231 [26][a]	$R_m \times 10^{-9}$ (kg/m^{2}s)	0.416	0.414	0.421
	$R_b \times 10^{-9}$ (kg/m^{2}s)	0.005	0.003	0.009
	$R_{f,180} \times 10^{-9}$ (kg/m^{2}s)	1.152	1.599	1.994
	J_0 (L/m^{2}h)	1,508	1,522	1,477
	J_{180} (L/m^{2}h)	404	315	262
	J_{180}/J_0	0.268	0.207	0.177
	V_T (L)	11.87	7.93	6.97
M8 [27]	$R_m \times 10^{-9}$ (kg/m^{2}s)	2.434	2.431	2.436
	$R_b \times 10^{-9}$ (kg/m^{2}s)	0.379	0.044	0.067
	$R_{f,180} \times 10^{-9}$ (kg/m^{2}s)	4.952	5.553	5.642
	J_0 (L/m^{2}h)	226	257	254
	J_{180} (L/m^{2}h)	82	79	78
	J_{180}/J_0	0.362	0.308	0.307
	V_T (L)	1.55	1.50	1.49

[a] Humic acid of 4 mg/L.

UF + TiO_2 + UV process in the other previous research [27] utilizing carbon (M8) UF membrane, as shown in Table 6. It was found that the effect of adsorption and photo-oxidation by the PP beads and UV irradiation was more efficient to reduce the membrane fouling in the hybrid process utilizing alumina UF membrane than carbon fiber or carbon UF membranes.

As plotted in Fig. 5, the J/J_0 values of the UF + TiO_2 + UV hybrid process were a little lower than those of the UF + TiO_2 and UF processes before 30 min, after that it decreased very gradually, and finally was higher than those of the UF + TiO_2 and UF processes. On the other hand, the final value of J/J_0 (J_{180}/J_0) after 180 min's operation at the UF + TiO_2 and UF processes converged to a similar value. It was found that the J/J_0 at the UF + TiO_2 + UV was higher than that at UF or the UF + TiO_2 processes, because the adsorption and photo-oxidation by the PP beads and UV irradiation could forbid competently the fouling inside or outside the UF membranes. The J_{180}/J_0 after 180 min's operation was found to be maximal as 0.232 at UF + TiO_2 + UV process, which was 1.25 times higher than 0.186 at UF process, as summarized in Table 6. It confirmed that the highest permeate flux could be maintained at UF + TiO_2 + UV process, because the membrane fouling was inhibited more successfully by the adsorption and photo-oxidation at UF + TiO_2 + UV process than at UF or UF + TiO_2 processes. Additionally, in the previous study utilizing

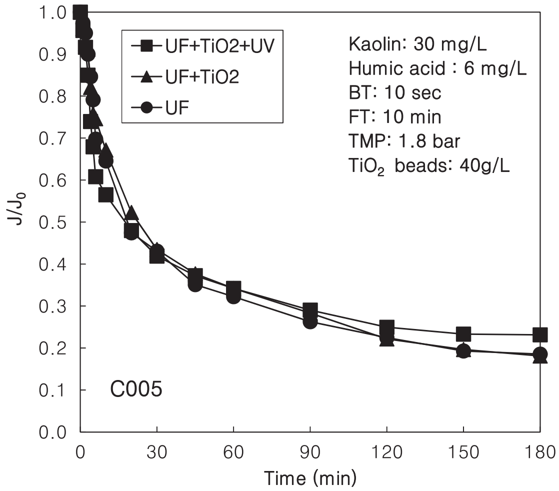

Fig. 5. Roles of ultrafiltration, adsorption, and photo-oxidation on dimensionless permeate flux in hybrid process of tubular carbon fiber UF and TiO_2 photocatalyst-coated PP beads.

alumina (NCMT-5231) UF membrane [26], the maximal J_{180}/J_0 of 0.268 at UF + TiO_2 + UV process was 1.51 times higher than 0.177 at UF, which was the same trend with this research result. By the way, the maximal J_{180}/J_0 of 0.362 at UF + TiO_2 + UV process was 1.18 times higher than 0.307 at UF in the other study utilizing carbon (M8) UF membrane [27]. It was found that in the viewpoint of J_{180}/J_0, the effect of adsorption and photo-oxidation on membrane fouling reduction increased gradually in the hybrid water treatment process utilizing carbon (M8), carbon fiber (C005), and alumina (NCMT-5231) UF membranes in sequence, because J_{180}/J_0 ratios of UF + TiO_2 + UV vs. UF process were 1.18, 1.25, and 1.51, respectively.

As compared in Table 7, the treatment efficiency of turbidity in this research utilizing carbon fiber UF (C005) decreased gradually as simplifying the process from UF + TiO_2 + UV to UF, which was the same trend with the previous result [27] utilizing carbon (M8) UF membrane. However, the treatment efficiency of turbidity reduced dramatically as simplifying the process in the hybrid water treatment process utilizing alumina (NCMT-5231) UF membrane [26]. By the way, as shown in Table 8, treatment efficiency of DOM (UV_{254} absorbance) decreased dramatically as simplifying the process from UF + TiO_2 + UV to UF in the hybrid process utilizing carbon fiber (C005), alumina (NCMT-5231) [26], or carbon (M8) [27] UF membranes. As arranged in Table 9, the treatment efficiency portions of UF, adsorption, and photo-oxidation in this hybrid process utilizing the carbon fiber UF (C005) could be evaluated by deducting in sequent the turbidity or DOM treatment efficiencies of UF + TiO_2 and UF from those of UF + TiO_2 + UV, and those were compared with the previous results utilizing alumina (NCMT-5231) [26], or carbon (M8) [27] UF membranes. The turbidity treatment portion of UF at this research utilizing the carbon fiber UF membrane (C005) was very high as 98.7% at humic acid concentration of 6 mg/L. On the other hand, the turbidity treatment portions of adsorption by the photocatalyst-coated PP beads and photo-oxidation by PP beads and UV irradiation presented very low values of 0.5 and 0.1%, correspondingly, because the turbid matters like kaolin was inorganic, and could not be decomposed by photo-oxidation. By the way, the turbidity treatment portions of the adsorption and photo-oxidation showed lofty values of 24.1 and 3.0% in the previous result [26] utilizing the alumina UF membrane (NCMT-5231) at low humic acid concentration of 4 mg/L; however, those were very low values of 0.2 and 0.1% in the other result [27] utilizing the carbon UF (M8). It confirmed that the adsorption and photo-oxidation by the photocatalyst-coated PP beads and UV irradiation at turbid matters treatment like kaolin could not play an important role in the hybrid process utilizing the carbon fiber (C005) or carbon (M8) [27] UF membranes; however, the role of adsorption was significantly dominant in the hybrid process utilizing the alumina (NCMT-5231) UF [26] at lower humic acid concentration of 4 mg/L. By the way, the DOM (UV_{254} absorbance) treatment portion of UF presented still a very high value of 53.0%; nevertheless, those of adsorption and photo-oxidation showed higher values as 3.2 and 10.4% than those of turbidity treatment portions, respectively. It proved that the adsorption and photo-oxidation by the photocatalyst-coated PP beads and UV radiation could play a significant role for the DOM treatment in this hybrid process utilizing the carbon fiber UF (C005). In addition, it confirmed that the adsorption and photo-oxidation by the photocatalyst-coated PP beads and UV could decrease powerfully the membrane fouling, because the adsorption and photo-oxidation played a major role in the DOM treatment in this hybrid process utilizing the carbon fiber UF. On the other hand, as summarized in Table 9, the DOM treatment portions of adsorption and photo-oxidation presented high values of 26.4 and 13.2%, respectively, in the previous work [26] utilizing the alumina UF (NCMT-5231), which were much higher values than 3.2 and 10.4% in this

Table 7

Water quality and treatment efficiency of turbidity in the hybrid process of tubular carbon fiber, alumina, or carbon UF and TiO_2 photocatalyst-coated PP beads for roles of membrane filtration, adsorption, and photo-oxidation at humic acid of 6 mg/L (FT 10 min, BT 10 s)

Experimental condition		Turbidity (NTU)						
		Feedwater		Treated water		Average treatment efficiency (%)		
Humic acid (mg/L)	Process	Range	Average	Range	Average	C005	NCMT-5231 [26][a]	M8 [27]
6	UF + TiO_2 + UV	21.2–28.2	25.5	0.150–0.234	0.191	99.3	99.1	99.5
	UF + TiO_2	24.4–28.9	26.8	0.155–0.332	0.208	99.2	95.6	99.4
	UF	24.4–28.7	26.0	0.247–0.430	0.335	98.7	85.3	99.2

[a] Humic acid of 4 mg/L.

Table 8

Water quality and treatment efficiency of dissolved organic matters (UV_{254} absorbance) in the hybrid process of tubular carbon fiber, alumina, or carbon UF and TiO_2 photocatalyst-coated PP beads for roles of membrane filtration, adsorption, and photo-oxidation at humic acid of 6 mg/L (FT 10 min, BT 10 s)

Experimental condition		UV_{254} absorbance (cm^{-1})						
		Feedwater		Treated water		Average treatment efficiency (%)		
Humic acid (mg/L)	Process	Range	Ave.	Range	Ave.	C005	NCMT-5231 [26][a]	M8 [27]
6	UF + TiO_2 + UV	0.145–0.163	0.158	0.036–0.069	0.053	66.6	89.4	96.0
	UF + TiO_2	0.098–0.218	0.141	0.020–0.109	0.062	56.2	71.0	83.7
	UF	0.149–0.168	0.156	0.052–0.098	0.073	53.0	59.2	81.2

[a] Humic acid of 4 mg/L.

Table 9

Treatment efficiency portions of ultrafiltration, adsorption, and photo-oxidation in the hybrid process of tubular carbon fiber, alumina, or carbon UF and TiO_2 photocatalyst-coated PP beads at humic acid of 6 mg/L (FT 10 min, BT 10 s)

Membrane	C005		NCMT-5231 [26][a]		M8 [27]	
Portion of treatment efficiency	Turbidity	UV_{254} absorbance	Turbidity	UV_{254} absorbance	Turbidity	UV_{254} absorbance
Ultrafiltration (%)	98.7	53.0	71.9	55.2	99.2	81.2
Adsorption (%)	0.5	3.2	24.1	26.4	0.2	2.5
Photo-oxidation (%)	0.1	10.4	3.0	13.3	0.1	12.3
Total treatment efficiency (%)	99.3	66.6	99.0	94.9	99.5	96.0

[a] Humic acid of 4 mg/L.

hybrid process utilizing the carbon fiber UF (C005). Additionally, those were 2.5 and 12.3% correspondingly in the other research [27] utilizing the carbon UF (M8), which were similar values of this results utilizing C005. It confirmed that the adsorption and photo-oxidation could play more dominant role in the DOM treatment in the hybrid process utilizing the alumina UF than those utilizing the carbon fiber or carbon UF membranes, and finally the DOM treatment depended significantly on the membrane materials utilized in this hybrid water treatment process. Finally, in all of the hybrid water treatment processes the turbidity was removed by UF with the certain amount of DOM, whereas the most portion of DOM was removed by photo-oxidation. Normally, it was known that the feedwater which contained turbidity could cause significant effect to the photo-oxidation efficiency. However, in this research the exactly same amount of kaolin was added in the feedwater, and the turbidity effect on the photo-oxidation efficiency was almost same at each experiment.

4. Conclusions

In this research, the effect of water BT on membrane fouling was examined in a hybrid process of the tubular carbon fiber UF and photocatalyst-coated PP beads for advanced water treatment. In addition, the treatment portions of UF, photocatalyst adsorption, and photo-oxidation were estimated by comparing the treatment efficiencies of UF, UF + TiO_2, and UF + TiO_2 + UV processes. The results were evaluated with the previous study of the hybrid water treatment utilizing the alumina [26] or carbon [27] UF membranes, and the PP beads same with that of this research. Ultimately, the following conclusions could be leaded out from the results.

(1) The resistances of membrane fouling (R_f) were highly influenced by BT, and R_f decreased significantly as increasing BT from NBF to 30 s. The water back-flushing prohibited membrane fouling more efficiently for the carbon fiber UF membrane than the alumina UF [25] in this hybrid water treatment process of UF and photocatalyst-coated PP beads. Additionally, the reversible membrane fouling was effectively prohibited by more frequent water back-flushing.

(2) The water BT could not affect severely the turbidity treatment in the hybrid process of carbon fiber UF and photocatalyst-coated PP

beads. On the other hand, the turbidity treatment efficiency was maximal at NBF, and increase dramatically as increasing BT in the hybrid process of alumina UF [25], because the turbid matter was efficiently captured by cake layer on the membrane surface at NBF. The treatment efficiency of DOM was maximal at BT of 30 s, and increased dramatically as increasing BT. The reason is that the PP beads were cleaned effectively by water back-flushing as increasing BT, and finally DOM was photo-oxidized or adsorbed effectively by the PP beads. However, in the study [25] the DOM treatment efficiency was maximal at NBF because of the severe membrane fouling, and increased dramatically as increasing BT by the cleaning effect of PP beads.

(3) It was found that the adsorption and photo-oxidation by the PP beads and UV irradiation reduced the membrane fouling in this hybrid process in spite of utilizing any carbon fiber, alumina, or carbon UF membranes. On the other hand, the effect of adsorption and photo-oxidation was more efficient to reduce the membrane fouling in the hybrid process utilizing alumina UF membrane than carbon fiber or carbon UF. In the viewpoint of the dimensionless permeate flux (J/J_0), the effect of adsorption and photo-oxidation on membrane fouling reduction increased gradually in the hybrid water treatment process utilizing carbon, carbon fiber, and alumina UF membranes in sequence.

(4) The adsorption and photo-oxidation by the photocatalyst-coated PP beads and UV could not play important role in turbid matters treatment of the hybrid process utilizing the carbon fiber or carbon [27] UF membranes; however, the role of adsorption was significantly dominant in the hybrid process utilizing the alumina [26] UF. Additionally, the adsorption and photo-oxidation could play more dominant role in the DOM treatment in the hybrid process utilizing the alumina UF than those utilizing the carbon fiber or carbon UF membranes, and it depended significantly on the membrane materials utilized in this hybrid water treatment process.

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