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Roles of ultrafiltration, photo-oxidation, and adsorption in hybrid water treatment process of tubular alumina UF and photocatalyst-coated PP beads with air backflushing

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ABSTRACT

The effect of humic acid (HA) concentration on membrane fouling and treatment efficiency was investigated in a hybrid process of tubular alumina ultrafiltration (UF) and TiO_2 photocatalyst-coated polypropylene (PP) beads with air backflushing for advanced water treatment, and compared with the previous study with water backflushing. With increasing HA concentration in water, membrane fouling occurred severely on the surface and inside the ceramic membrane. The treatment efficiencies of turbidity and dissolved organic matters (DOM) were maximal as 99.3 and 89.9% at HA 8 mg/L, respectively. DOM could be treated effectively until higher HA concentration in the hybrid process with air backflushing than that with water backflushing. Treatment portions of UF, photocatalyst adsorption, and photo-oxidation were evaluated by comparing the treatment efficiencies of (UF), (UF + TiO_2), and (UF + TiO_2 + UV) processes. The membrane fouling resistance was minimal at (UF + TiO_2 + UV) process. It proved that the photo-oxidation and adsorption could control membrane fouling in the hybrid water treatment process. The adsorption and photo-oxidation were more excellent to treat DOM in the same hybrid process with water backflushing than that with air backflushing.

Keywords: Ultrafiltration; Air backflushing; Photocatalyst; Hybrid process; Ceramic membrane; Water treatment

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1. Introduction

As a new type of water pollution control technology, photocatalytic oxidation has been widely researched over the world because of the characteristics of high efficiency, low-energy consumption, and a wide range of application. And it 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. There is

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a general consensus among researchers that TiO_2 is more superior among various semiconductor photocatalysts because of its high activity, large stability to light illumination, and low price [1–4]. Two modes of TiO_2 application are adopted in photocatalytic degradation: (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, it was proved that 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 photocatalysts recovery is one of the main concerns that affect its large-scale application. A lot of researches have been conducted aiming to solve this problem [8–12].

Recently, titanium microsphere has also been proposed as a means to recover TiO_2 photocatalyst. The core–shell structured TiO_2 microspheres with a mesoporous surface made of nano-TiO_2, generally have many advantages like as 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 a lot of problems existing in the current preparation methods need to be solved by optimizing the process conditions or developing new ones [17].

During the past few decades, membrane separation process for separation and purification has been developed rapidly. It can simultaneously separate and concentrate all pollutants in water by the retention of its microspores without secondary pollution and phase change. Additionally, its equipment has a lot of advantage of low energy consumption 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 in 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 hybrid technology can solve the two problems mentioned above effectively [21]. The hybrid 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 hybrid technology could enhance the photocatalytic efficiency and achieve excellent effluent quality. On the other hand, the hybrid 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 the effect of water backflushing in a hybrid water treatment process of multi-channel ceramic MF and polyethersulfone microsphere beads loaded with TiO_2 photocatalyst [23]. In addition, roles of photo-oxidation and adsorption at water backflushing were investigated in hybrid water treatment of multi-channels alumina MF and polypropylene (PP) beads coated with photocatalyst in our group [24].

In this study, the effect of humic acid (HA) on membrane fouling was observed in a hybrid process of tubular alumina ultrafiltration (UF) and TiO_2 photocatalyst-coated PP beads with periodic air backflushing for advanced water treatment. A hybrid module of ceramic UF membrane and the PP beads fluidized between the gap of ceramic membrane and the acryl module case was the first trial in the hybrid water treatment process field of UF and photocatalyst. Additionally, treatment portions of membrane filtration, photocatalyst adsorption, and photo-oxidation were investigated by comparing the treatment efficiencies of (UF), (UF + TiO_2), and (UF + TiO_2 + UV) processes. The periodic air backflushing was performed during 10 s per 10 min filtration to reduce membrane fouling. The results were compared with those of the previous study [25] using the hybrid process of the same membrane having larger diameter (OD 10 mm) and the same photocatalyst-coated PP beads with periodic water backflushing. This hybrid process could be applied as pretreatment before desalination reverse osmosis (RO) plant if the treated water satisfied as the feed water quality of RO.

2. Experiments

2.1. Materials

The tubular ceramic UF membrane (NCMT-5231) used in the study was coated with α-alumina on a supporting layer of α-alumina, and its pore size was

0.05 μm. The membrane was purchased from Nano Pore Materials in Korea, and the specifications of the membrane are arranged in Table 1.

The photocatalyst utilized in this study was 4–6 mm PP beads coated with TiO_2 powder made by Prof. Kim's group [26] using chemical vapor deposition method, of which the characteristics are summarized in Table 2. Instead of natural organic matters (NOM) and fine inorganic particles in natural water source, a quantity of HA sodium salt (Aldrich) and kaolin (Sigma-Aldrich) was dissolved in distilled water. It was then utilized as a synthetic solution in this research. The HA was selected as a NOM representative because it was known that HA was the major humic material of river or lake. 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 UF membrane. In addition, 100 meshes (0.150 mm), which were extremely smaller than 4–6 mm particle size of the PP beads utilized in this research, were installed at the outlet of the hybrid module to prevent the PP beads loss into the treated water flow.

2.3. Experimental procedure

The advanced water treatment system utilizing a hybrid module of tubular ceramic UF and TiO_2 photocatalyst-coated PP beads was demonstrated in Fig. 1, which was utilized at our previous study [27] without the PP beads. Cross-flow filtration was performed in and out using the tubular ceramic UF membrane, and the periodic air backflushing utilized nitrogen gas for protecting oxygen effect on water quality. The hybrid module filled up with 40 g/L of the TiO_2 photocatalyst-coated PP beads between the gap of ceramic UF membrane and the acryl module case, and it was applied for the advanced hybrid water treatment. After that, the feed tank was filled with 10 L of the prepared synthetic water composed of HA and kaolin, and the temperature of the feed water was constantly maintained using a constant temperature circulator (Model 1146, VWR, USA). In addition, the synthetic feed water was continuously mixed by a stirrer in order to maintain homogeneous condition of the feed water, and it was caused to flow inside the tubular ceramic UF membrane by a pump (Procon, Standex Co., USA). The feed flow rate was measured by a flow meter (NP-127, Tokyo Keiso, Japan). The flow rate and pressure of the feed water that flowed into the hybrid module were constantly maintained by controlling valves of both the bypass pipe of the pump and the concentrate pipe. The permeate flux through the tubular membrane contacted the PP beads, and it was measured by an electric balance (Ohaus, USA). The treated and the concentrate water recycled to the feed tank to maintain a constant concentration of the feed water during operation.

Table 1
Specifications of the tubular ceramic UF membrane (NCMT-5231) used in this study

Membrane	NCMT-5231
Pore size (μm)	0.05
Outer diameter (mm)	8
Inner diameter (mm)	6
Length (mm)	250
Surface area (cm^2)	47.1
Material	α-alumina coating on α-alumina support
Company	Nano Pore Materials in Republic of Korea

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

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

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 HA concentration. The air backflushing time (BT) and filtration time (FT) were fixed at 10 s and 10 min, respectively. Only UF process without the TiO_2 photocatalyst- coated PP beads and UV light UF, and UF process with the PP beads (UF + TiO_2) were, respectively, operated at HA of 6 mg/L, and compared with the hybrid process of UF and PP beads with UV (UF + TiO_2 + UV) for evaluating the treatment efficiency portions of tubular ceramic UF, adsorption, and photo-oxidation.

The resistances of the membrane fouling (R_f) and permeate flux (J) were investigated during total FT of 180 min under each condition. In all experiments,

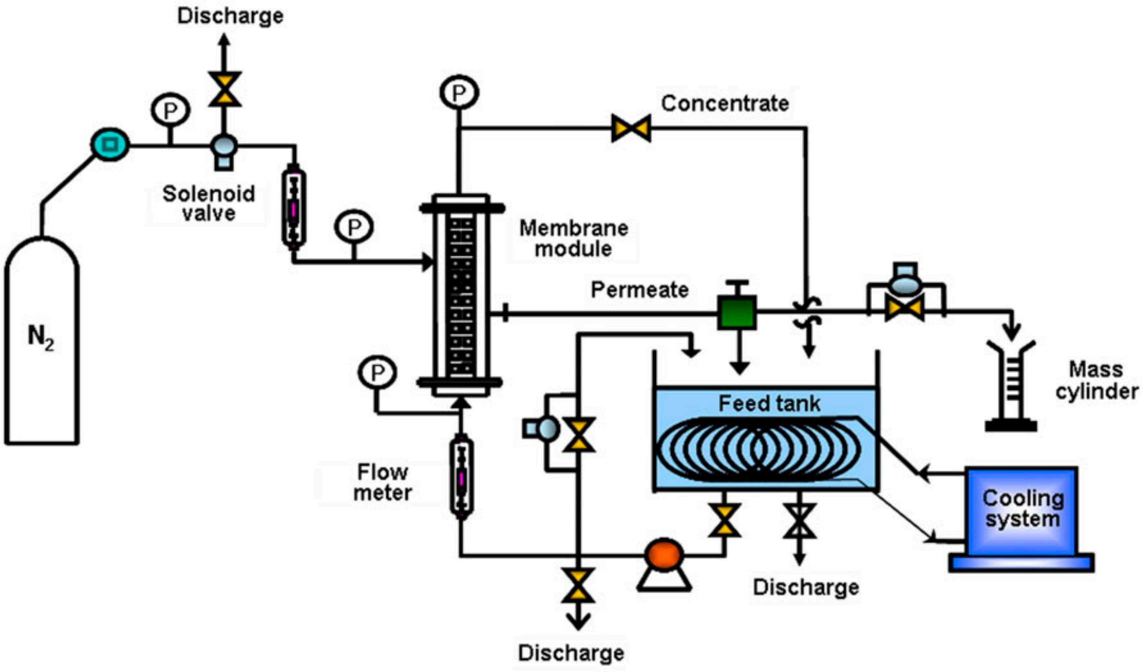

Fig. 1. Apparatus of hybrid water treatment process of tubular ceramic UF and TiO_2 photocatalyst-coated PP beads with periodic air backflushing [27].

transmembrane pressure was maintained constant at 1.8 bar, the air backflushing pressure at 2.5 bar, the feed flow rate at 1.0 L/min, and the feed water temperature at 20˚C. The periodic air backflushing was performed during 10 s per filtration of 10 min.

The quality of feed and treated water was analyzed in order to evaluate the treatment efficiencies of turbid materials and dissolved organic matters (DOM). Turbidity was measured by a turbidimeter (2100 N, Hach, USA) and UV_{254} absorbance was analyzed by a UV spectrophotometer (Genesys 10 UV, Thermo, USA) to measure turbid materials and DOM. 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), respectively. Before the measurement of UV_{254} absorbance, the sample was filtered by 0.2 μm syringe filter to remove turbid materials.

After finishing each experiment, all of the synthetic solutions were discharged from the hybrid water treatment system, and distilled water was circulated in the line of the system for cleaning the ceramic membrane and apparatus during 15 min. After that, the TiO_2 photocatalyst-coated PP beads and the membrane were separated from the module, and the membrane was heated at 550˚C in a furnace for combusting fouling materials inside the membrane during 30 min. After cooling the membrane, it was chemically washed in a nitric acid (HNO_3) of 15% during 24 h, and in a sodium hydroxide (NaOH) solution of 0.25 N during 3 h, and kept in distilled water. Before operating at a new experimental condition, the recovering membrane was installed inside the module, and the water permeate flux (J_w) was measured for checking the membrane recovery when a normal operation was performed with distilled water.

3. Results and discussion

The effect of organic matters on membrane fouling was investigated in the hybrid process of tubular ceramic UF and TiO_2 photocatalyst-coated PP beads with periodic air backflushing for advanced water treatment. Additionally, treatment portions of membrane filtration, photocatalyst adsorption, and photo-oxidation were evaluated by comparing the treatment efficiencies of UF, (UF + TiO_2), and (UF + TiO_2 + UV) processes. Resistances of membrane, boundary layer, and membrane fouling (R_m, R_b, and R_f) were calculated from permeate flux (J) data using the resistance-in-series filtration equation as the same method as our previous study [27].

3.1. Effect of HA concentration

The resistances of membrane fouling (R_f) were highly influenced by HA concentration, and R_f increased dramatically as rising HA concentration from 2 to 10 mg/L, as shown in Fig. 2. In addition, the membrane fouling was very severe at HA concentration of 6, 8, and 10 mg/L, and this hybrid water treatment process could operate until 60, 45, and 30 min, respectively. It means that the organic matter as HA could make membrane fouling more severely on the surface and inside the ceramic membrane as increasing the HA concentration in water. However, as compared in Table 3, the hybrid water treatment process could operated well during 180 min, and R_f increased less in our previous study [25] using the hybrid process of the same membrane having larger diameter (OD 10 mm) and the photocatalyst-coated PP beads with water backflushing than this result with air backflushing. The final R_f ($R_{f,180}$) after 30 min's operation at HA of 10 mg/L was 7.484×10^9 kg/m^{2}s, which was 2.59 times higher than the $R_{f,180}$ of 2.895×10^9 kg/m^{2}s at HA of 2 mg/L, as summarized in Table 3. However, in the previous study [25] the $R_{f,180}$ at HA of 10 mg/L was 3.485×10^9 kg/m^{2}s, which was 3.03 times higher than the $R_{f,180}$ of 1.152×10^9 kg/m^{2}s at HA of 2 mg/L. It proved that the air backflushing for smaller diameter (OD 8 mm) membrane could prohibit membrane fouling more efficiently than the water backflushing [25] for larger diameter (OD 10 mm) membrane in this hybrid water treatment process. It was strange that the final resistance of membrane fouling ($R_{f,45}$) at HA of 8 mg/L in Table 3 and Fig. 2 was higher than that ($R_{f,30}$) at 10 mg/L. The final resistance of membrane fouling at HA of 10 mg/L should be higher between 30 and 45 min than that ($R_{f,45}$) at 8 mg/L, however it could not be measured because the measuring period of permeate flux was 15 min.

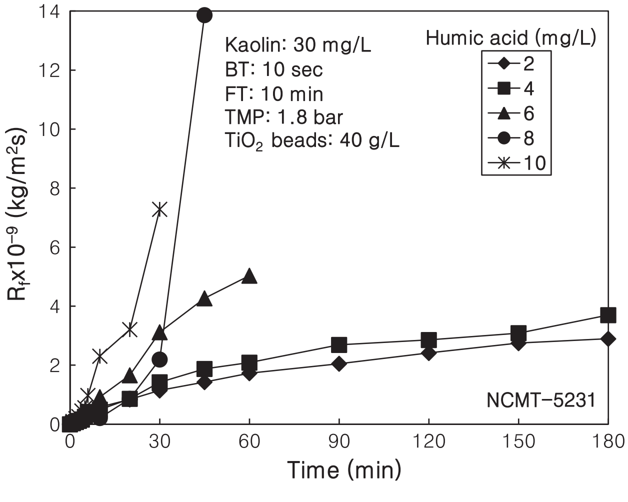

Fig. 2. Effect of HA on resistance of membrane fouling in hybrid process of tubular ceramic UF and TiO_2 photocatalyst-coated PP beads.

The water backflushing could reduce more effectively the resistance of boundary layer (R_b), which produced by concentration polarization, than the air backflushing as the values of R_b were 0.000–0.024×10^9 kg/m^{2}s and 0.031–0.528×10^9 kg/m^{2}s for water and air backflushing in Table 3, respectively. Specially, the difference of R_b between air and water backflushing was dramatically outstanding at high HA concentration beyond 4 mg/L. The higher R_b at the air backflushing could formulate severely the irreversible inner membrane fouling and cake layer on the membrane surface than water backflushing, and the operation time was limited until 60, 45, and 30 min at HA concentration of 6, 8, and 10 mg/L with air backflushing, respectively. However, the resistance of membrane (R_m) could be controlled similarly by the furnace combustion, and chemical cleaning of acid and alkali solution mentioned in the experimental procedure of Section 2.3.

The dimensionless permeate flux (J/J_0), where J_0 is the initial permeate flux which was estimated by extrapolation using initial two data at 1 and 2 min, was compared in Fig. 3 to investigate a relative decline of permeate flux. As the results of HA at 8 mg/L is shown in Fig. 3, the J/J_0 at 10 min increased suddenly because the air backflushing at 10 min could eliminate the large part of cake layer on the membrane surface, and the decreasing trend in J/J_0 at HAHA of 8 mg/L was much different with other results. The J_0 at air backflushing was much lower than that at water backflushing especially in the higher HA concentration beyond 6 mg/L because of high R_b as presented in Table 3. The J/J_0 tended to decrease dramatically as increasing HA concentration from 2 to 10 mg/L because of the membrane fouling formation by more organic macromolecules. Thus, as shown in Table 3, the final value of J/J_0 (J_{180}/J_0) of 0.163 after 180 min operation at HA of 2 mg/L was 1.77 times higher than 0.092 after 30 min operation at 10 mg/L. However, in the study [25] J_{180}/J_0 of 0.268 at HA of 2 mg/L was 2.39 times higher than J_{180}/J_0 of 0.112 at 10 mg/L. Furthermore, the total permeate volume (V_T) of 4.09 L at HA of 2 mg/L was 6.29 times higher than V_T of 0.65 L at 10 mg/L, but in the study [25] V_T of 11.87 L at HA of 2 mg/L was 2.88 times higher than 4.12 L at 10 mg/L. However, the absolute value of V_T at air backflushing was much lower than that at water backflushing in the same

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

Backflushing	HA (mg/L)	2	4	6	8	10
Air	$R_m \times 10^{-9}$ (kg/m^{2}s)	0.558	0.536	0.561	0.532	0.543
	$R_b \times 10^{-9}$ (kg/m^{2}s)	0.004	0.031	0.083	0.528	0.199
	$R_{f,180} \times 10^{-9}$ (kg/m^{2}s)	2.895	3.697	5.034[a]	13.87[b]	7.484[c]
	J_0 (L/m^{2}hr)	1,130	1,120	987	599	856
	J_{180} (L/m^{2}hr)	184	149	112[a]	43[b]	79[c]
	J_{180}/J_0	0.163	0.133	0.113[a]	0.071[b]	0.092[c]
	V_T (L)	4.09	3.67	1.40	1.08	0.65
Water [25]*	$R_m \times 10^{-9}$ (kg/m^{2}s)	0.416	0.416	0.430	0.417	0.415
	$R_b \times 10^{-9}$ (kg/m^{2}s)	0.005	0.000	0.000	0.004	0.024
	$R_{f,180} \times 10^{-9}$ (kg/m^{2}s)	1.152	1.818	2.110	3.044	3.485
	J_0 (L/m^{2}hr)	1,508	1,524	1,474	1,510	1,448
	J_{180} (L/m^{2}hr)	404	284	250	183	162
	J_{180}/J_0	0.268	0.186	0.170	0.121	0.112
	V_T (L)	11.87	8.65	7.17	5.48	4.12

[a] After 60 min operation.
[b] After 45 min operation.
[c] After 30 min operation.
*OD of ceramic membrane = 10 mm.

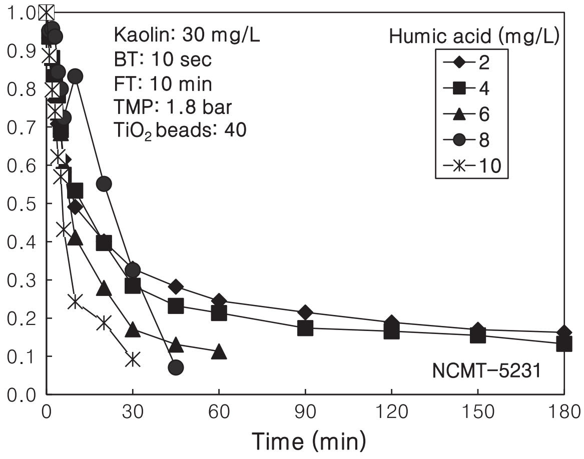

Fig. 3. Effect of HA on dimensionless permeate flux in hybrid process of tubular ceramic UF and TiO_2 photocatalyst-coated PP beads.

HA concentration. It proved that the air backflushing for smaller diameter (OD 8 mm) membrane could be more effective to control the membrane fouling in this hybrid process than the water backflushing [25] for larger diameter (OD 10 mm) membrane as increasing the HA concentration; however, the water backflushing could be more efficient than the air backflushing in the same HA concentration. Finally it was found that NOM, like HA, should be one of the main factors affecting membrane fouling in the hybrid process of tubular ceramic UF membrane and TiO_2 photocatalyst-coated PP beads with air or water backflushing.

The treatment efficiency of turbidity was found to be maximal as 99.3% at HA concentration of 8 mg/L, however the difference was a little from 93.9 to 99.3%, as arranged in Table 4. It was found that NOM could not affect the treatment of suspended particles like kaolin in this hybrid process with air backflushing. However, in the hybrid process with water backflushing [25] the treatment efficiency of turbidity declined dramatically from 99.1 to 89.5% as increasing the HA concentration. It proved that the turbid matter as kaolin was efficiently treated by adsorption of photocatalyst-coated PP beads at low HA concentration, but could not at high concentration. However, the treatment efficiency of UV_{254} absorbance, which means the concentration of DOM, was found to be maximal as 89.9% at HA concentration of 8 mg/L, as shown in Table 5. The treated water quality of DOM increased less slowly than HA increasing rate in feed water from 2 to 8 mg/L. The reason is that most of DOM could be retained by cake layer on the membrane or absorbed on fouling materials inside the membrane, and the remained DOM passed through the membrane could be adsorbed or oxidized by the TiO_2 photocatalyst-coated PP beads. Then, DOM of the treated water increased more rapidly than that of the feed water above HA of 8 mg/L, because most of DOM passed through the membrane and could not treated by

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

Experimental condition		Turbidity (NTU) Feed water		Treated water		Average treatment efficiency (%) Backflushing	
Kaolin (mg/L)	HA (mg/L)	Range	Average	Range	Average	Air	Water [25]*
30	2	30.1–32.1	31.3	0.438–0.477	0.486	98.4	99.1
	4	36.7–38.4	37.1	0.374–0.434	0.409	98.9	99.0
	6	37.9–38.7	38.4	0.287–0.294	0.238	99.2	98.6
	8	40.2	40.2	0.267	0.267	99.3	91.8
	10	39.6	39.6	2.400	2.400	93.9	89.2

*OD of ceramic membrane = 10 mm.

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

Experimental condition		UV_{254} absorbance (cm^{-1}) Feed water		Treated water		Average treatment efficiency (%) Backflushing	
Kaolin (mg/L)	HA (mg/L)	Range	Average	Range	Average	Air	Water [25]*
30	2	0.075–0.099	0.093	0.021–0.027	0.024	73.9	89.4
	4	0.129–0.139	0.135	0.029–0.038	0.034	74.5	94.9
	6	0.144–0.148	0.146	0.035–0.037	0.036	75.3	84.5
	8	0.207	0.207	0.021	0.021	89.9	79.3
	10	0.271	0.271	0.070	0.070	75.7	75.1

*OD of ceramic membrane = 10 mm.

adsorption or photo-oxidation of the photocatalyst-coated PP beads. In addition, in the hybrid process with water backflushing [25], the treatment efficiency of DOM was found to be maximal as 89.9% at HA concentration of 4 mg/L, which was lower concentration than 8 mg/L with air backflushing, as shown in Table 5. It proved that DOM could be treated effectively until higher HA concentration in the hybrid process with air backflushing than that with water backflushing [25].

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

The process with PP beads without UV light (UF + TiO_2) and only MF without any PP beads and UV (UF) were performed, respectively, at 6 mg/L of HA, and compared with the hybrid process of UF and PP beads with UV light (UF + TiO_2 + UV). After that, the roles of membrane filtration, adsorption, and photo-oxidation were evaluated in the hybrid process of tubular ceramic UF and photocatalyst-coated PP beads with air backflushing. Because the permeate flux could be measured at HA concentration of 6 mg/L until 60 min, and the membrane fouling was produced enough in the experiment of HA concentration effect, this 6 mg/L condition was selected to investigate the roles of membrane filtration, adsorption, and photo-oxidation. As shown in Fig. 4, the R_f values of (UF + TiO_2 + UV), (UF + TiO_2), and only UF processes at HA of 6 mg/L were compared during 60 min's operation, because the treated water could be acquired until 60 min in the treatment processes. The R_f could maintain low at the (UF + TiO_2 + UV) process and increased a little as simplifying the process from (UF + TiO_2 + UV) to UF. As summarized in Table 6, the $R_{f,60}$ of 5.715×10^9 kg/m^{2}s after 60 min's operation at UF process was 1.14 times higher than 5.034×10^9 kg/m^{2}s at (UF + TiO_2 + UV) process. Then, in the hybrid process with water backflushing [25], the $R_{f,180}$ of 1.994×10^9 kg/m^{2}s after 180 min's operation at UF process was 1.73 times higher than 1.152×10^9 kg/m^{2}s at (UF + TiO_2 + UV) process. It was found that photocatalyst adsorption and photo-oxidation by the PP beads and UV irradiation could reduce the membrane fouling in this hybrid water

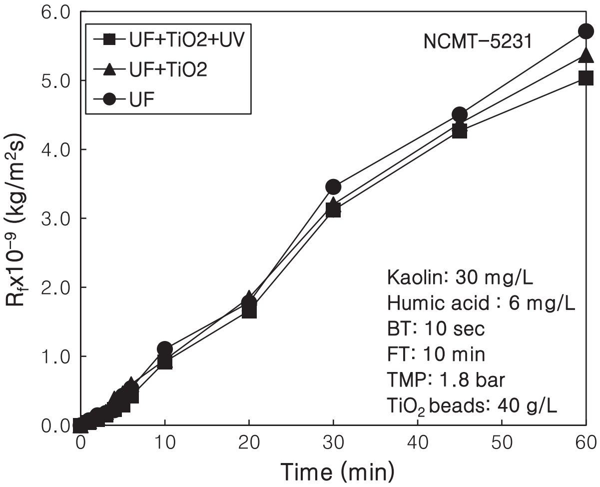

Fig. 4. Roles of membrane filtration, adsorption, and photo-oxidation on resistance of membrane fouling in hybrid process of tubular ceramic UF and TiO_2 photocatalyst-coated PP beads.

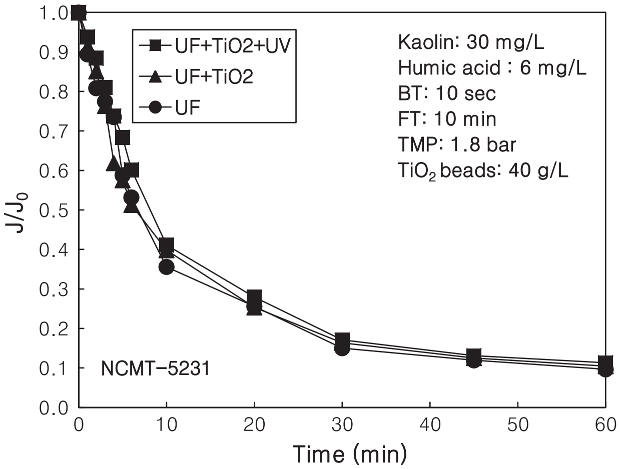

Fig. 5. Roles of membrane filtration, adsorption, and photo-oxidation on dimensionless permeate flux in hybrid process of tubular ceramic UF and TiO_2 photocatalyst-coated PP beads.

treatment process with air or water backflushing, and effect of water backflushing was more efficient to reduce the membrane fouling than that of air backflushing.

As shown in Table 6, the values of R_b at air backflushing were much higher than those at water backflushing, although the HA concentration was almost similar 4 and 6 mg/L at water and air backflushing, respectively, in the (UF + TiO_2 + UV), (UF + TiO_2), and only UF processes. Finally, the higher resistance of boundary layer at air back-flushing should formulate the membrane fouling severely, and the final permeate flux and the total permeate volume (V_T) were much lower than those at water backflushing.

As compared in Fig. 5, the J/J_0 values could maintain the highest at the (UF + TiO_2 + UV) process and the lowest at UF process. However, the final value of J/J_0 (J_{60}/J_0) after 60 min's operation converged to a similar value. It proved that the J/J_0 at the (UF + TiO_2 + UV) could be higher than that at UF and the (UF + TiO_2) processes, because the photocatalyst

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

Backflushing	Process	UF + TiO_2 + UV	UF + TiO_2	UF
Air	$R_m \times 10^{-9}$ (kg/m^{2}s)	0.561	0.555	0.573
	$R_b \times 10^{-9}$ (kg/m^{2}s)	0.083	0.085	0.039
	$R_{f,60} \times 10^{-9}$ (kg/m^{2}s)	5.034	5.359	5.715
	J_0 (L/m^{2}hr)	987	993	1,038
	J_{60} (L/m^{2}hr)	112	106	100
	J_{60}/J_0	0.113	0.107	0.097
	V_T (L)	1.42	1.35	1.34
Water [25]*	$R_m \times 10^{-9}$ (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}hr)	1,508	1,522	1,477
	J_{180} (L/m^{2}hr)	404	315	262
	J_{180}/J_0	0.268	0.207	0.177
	V_T (L)	11.87	7.93	6.97

*HA 4 mg/L, OD of ceramic membrane = 10 mm.

adsorption and photo-oxidation could reduce the membrane fouling efficiently. As summarized in Table 6, the J_{60}/J_0 after 60 min operation was found to be maximal as 0.113 at ($UF + TiO_2 + UV$) process, which was 1.16 times higher than 0.097 at UF process. The highest permeate flux could be maintained at ($UF + TiO_2 + UV$) process, because the membrane fouling was more effectively prohibited by photocatalyst adsorption and photo-oxidation at ($UF + TiO_2 + UV$) process than UF or ($UF + TiO_2$) processes. In our previous work [25] using the hybrid process of the same membrane having larger diameter (OD 10 mm) and the photocatalyst-coated PP beads with water backflushing, 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 study. It was found that effect of photocatalyst adsorption and photo-oxidation on membrane fouling reduction with water backflushing was more excellent than that with air backflushing.

As arranged in Tables 7 and 8, the treatment efficiencies of turbidity and DOM (UV_{254} absorbance) decreased as simplifying the process from ($UF + TiO_2 + UV$) to UF with air backflushing, which was the same trend with the result [25] with water backflushing. The portions of treatment efficiency performed by membrane filtration, adsorption, and photo-oxidation in this hybrid process with air back-flushing could be calculated by subtracting sequentially 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 result [25] of the same hybrid process with water backflushing in Table 9. The turbidity treatment portion of membrane filtration was very high 98.1% at HA concentration of 6 mg/L. However, the turbidity treatment portions of adsorption by the photocatalyst-coated PP beads and photo-oxidation by the PP beads and UV light were very low 0.8 and 0.3%, respectively. Then, the turbidity treatment portions of adsorption and photo-oxidation were 24.1 and 3.0% in the result [25] with water backflushing. It proved that the roles of adsorption and photo-oxidation by the photocatalyst-coated PP beads and UV were not important in the hybrid process with air backflushing, but the role of adsorption was dominant in the hybrid process with water backflushing for treatment of the suspended particles like kaolin. The DOM (UV_{254} absorbance) treatment portion of membrane filtration was still very high 60.1%; however, those of

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

Experimental condition		Turbidity (NTU) Feed water		Treated water		Average treatment efficiency (%) Backflushing	
Humic acid (mg/L)	Process	Range	Average	Range	Average	Air	Water [25]*
6	$UF + TiO_2 + UV$	37.9–38.7	38.4	0.287–0.294	0.238	99.2	99.0
	$UF + TiO_2$	36.8–38.7	37.8	0.363–0.434	0.399	98.9	96.0
	UF	36.2–37.4	36.8	0.605–0.707	0.691	98.1	71.9

*HA of 4 mg/L, OD of ceramic membrane = 10 mm.

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

Experimental condition		UV_{254} absorbance (cm^{-1}) Feed water		Treated water		Average treatment efficiency (%) Backflushing	
Humic acid (mg/L)	Process	Range	Average	Range	Average	Air	Water[25]*
6	$UF + TiO_2 + UV$	0.144–0.148	0.146	0.035–0.037	0.036	75.3	94.9
	$UF + TiO_2$	0.140–0.155	0.148	0.047–0.048	0.048	67.8	81.6
	UF	0.146-0.152	0.149	0.052–0.067	0.060	60.1	55.2

*HA of 4 mg/L, OD of ceramic membrane = 10 mm.

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

	Backflushing			
	Turbidity		UV_{254} absorbance	
Portion of treatment efficiency (%)	Air	Water [25]*	Air	Water [25]*
Membrane filtration	98.1	71.9	60.1	55.2
Adsorption	0.8	24.1	7.7	26.4
Photo-oxidation	0.3	3.0	7.5	13.3
Total treatment efficiency	99.2	99.0	75.3	94.9

*HA of 4 mg/L, OD of ceramic membrane = 10 mm.

adsorption and photo-oxidation were high 7.7 and 7.5%, respectively at HA of 6 mg/L. It was found that the roles of adsorption and photo-oxidation by the photocatalyst-coated PP beads and UV were important for the DOM treatment in this hybrid process with air backflushing. It proved that the adsorption and photo-oxidation by the photocatalyst-coated PP beads and UV could reduce the membrane fouling strongly, because the adsorption and photo-oxidation had the major role of DOM reduction in this hybrid water treatment process with air backflushing. Then, in our previous work [25] for the same hybrid process with water backflushing, the DOM treatment portions of adsorption and photo-oxidation were 26.4 and 13.2%, which were much higher than 7.7 and 7.5% with air backflushing, as shown in Table 9. It proved that the roles of adsorption and photo-oxidation were more dominant to treat DOM in the same hybrid process with water backflushing than that with air backflushing, because air bubbles could reflect UV radiation and prohibit the adsorption on PP beads, and backflushing media were important to treat DOM in water.

4. Conclusions

The effect of HA concentration on membrane fouling was investigated in a hybrid process of tubular alumina UF and photocatalyst-coated PP beads with air backflushing for advanced water treatment. In addition, treatment portions of membrane filtration, photocatalyst adsorption, and photo-oxidation were evaluated by comparing the treatment efficiencies of (UF), (UF + TiO_2), and (UF + TiO_2 + UV) processes. The results were compared with the previous study [25] using the hybrid process of the same membrane having larger diameter (OD 10 mm) and the photocatalyst-coated PP beads with periodic water backflushing. Finally, the following results could be found out from this research.

(1) The organic matter as HA made membrane fouling more severely on the surface and inside the ceramic membrane, as increasing the HA concentration in water. The air backflushing for smaller diameter (OD 8 mm) membrane could be more effective to control the membrane fouling in this hybrid process than the water backflushing [25] for larger diameter (OD 10 mm) membrane as increasing the HA concentration; however, the water backflushing could be more efficient than the air backflushing in the same HA concentration. NOM, like HA, should be one of the main factors affecting membrane fouling in the hybrid process with air or water backflushing.

(2) The turbid matter as kaolin was efficiently treated by adsorption of the photocatalyst-coated PP beads at low HA concentration, but could not at high concentration. Most of DOM could be retained by cake layer on the membrane or absorbed on fouling materials inside the membrane, and the remained DOM passed through the membrane could be adsorbed or oxidized by the TiO_2 photocatalyst-coated PP beads. DOM could be treated effectively until higher HA concentration in the hybrid process with air backflushing than that with water backflushing [25].

(3) 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 (UF + TiO_2 + UV) process. It proved that photocatalyst adsorption and

photo-oxidation by the PP beads and UV irradiation could reduce the membrane fouling in this hybrid water treatment process with air or water backflushing, and effect of water backflushing on membrane fouling reduction was more efficient than that of air backflushing.

(4) The roles of adsorption and photo-oxidation by photocatalyst-coated PP beads and UV were not important in the hybrid process with air backflushing, but role of adsorption was dominant in the hybrid process with water backflushing for treatment of the suspended particles like kaolin. However, the roles of adsorption and photo-oxidation were important for the DOM treatment in this hybrid process with air backflushing. The roles of adsorption and photo-oxidation were more dominant to treat DOM in the same hybrid process with water backflushing than that with air backflushing, because air bubbles could reflect UV radiation and prohibit the adsorption on PP beads. Finally, the hybrid water treatment system of UF and photocatalyst-coated PP beads was very compact comparing with the conventional advanced water treatment process, and could remove effectively DOM, which was difficult to be rejected by the UF membrane only.

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