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Roles of polypropylene beads and photo-oxidation in hybrid water treatment process of alumina MF and photocatalyst-coated PP beads

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ABSTRACT

The effect of titanium dioxide (TiO_2) photocatalyst-coated polypropylene (PP) beads concentration on membrane fouling and treatment efficiency was observed in a hybrid process of tubular alumina microfiltration (MF) and the PP beads with periodic air back-flushing for advanced water treatment. And the results were compared with the previous study of the hybrid process of the same MF and the photocatalyst-loaded polyethersulfone (PES) beads. The optimum concentration of PP beads could be 40 g/L in the experimental range; however, that of PES beads was 20–30 g/L in the previous work to prevent membrane fouling efficiently. The treatment efficiency of turbidity was almost constant from 99.2% to 99.5%, independent of the PP beads concentration; however, that of dissolved organic matters (DOM) was the maximal 87.6% at 40 g/L of the PP beads. Treatment portions of MF, photocatalyst adsorption, and photo-oxidation were investigated by comparing the treatment efficiencies of (MF), (MF+TiO_2), and (MF+TiO_2+UV) processes. The role of photo-oxidation by the PP beads and UV was more dominant than that of adsorption by the PP beads in the DOM treatment, which was the same trend in the previous work for the hybrid process of the same MF and the PES beads.

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

1. Introduction

By mineralizing them to small inorganic molecules, photocatalytic oxidation, which was one of new type of water pollution control technologies, 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. For this reason, photocatalytic oxidation technology has been applied widely for various water treatment fields. Among various semiconductor photocatalysts, there is a general consensus among researchers that TiO_2 is more excellent 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 applied 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 possibility 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 focusing to solve this problem [8–12].

In recent 10 years, titanium microsphere has also been suggested as a means to recover TiO_2 photocatalyst. In general, the core-shell structured TiO_2 microspheres with a mesoporous surface made of nano-TiO_2, have low density, high

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specific surface area and large size favorable for separation [13–16]. However, the preparation method and operating conditions have a great effect on particle morphology associated with photocatalysis, and many problems existing in the current preparation methods need to be solved by optimizing the process conditions or developing new ones [17].

Membrane separation process for separation and purification has been developed dramatically during the past few decades. It can separate and concentrate all pollutants in water simultaneously by retaining its microspores without secondary pollution and phase change. Additionally, with the advantage of low energy consumption, its equipment is compact, easy to operate, and possible of continuous operation at room temperature [18]. However, membrane fouling due to the adsorption-precipitation of organic and inorganic compounds onto or inside membranes leads to a decrease of 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 tubular ceramic microfiltration (MF) and polyethersulfone beads loaded with photocatalyst [23]. In addition, a few papers for effect of operating conditions in the hybrid water treatment process of various tubular ceramic membranes, and PES or PP beads in our research group have been published in Membrane Journal [24–31] in recent years.

In this study, the effect of TiO_2 photocatalyst-coated PP beads on membrane fouling was observed in a hybrid process of tubular ceramic MF and TiO_2 photocatalyst-coated PP beads with periodic air back-flushing for advanced water treatment. The application of ceramic membrane and photocatalyst-coated polymer beads to the hybrid water treatment is the first trial. A hybrid module was composed of the ceramic MF membrane and the PP beads, which were fluidized between the gap of ceramic membrane and the acryl module case. These results were compared with results using the hybrid process of the same MF membrane and photocatalyst-loaded PES beads with periodic air back-flushing. In addition, treatment portions of membrane filtration, photocatalyst adsorption, and photo-oxidation were investigated by comparing the treatment efficiencies of (MF), (MF+TiO_2), and (MF+TiO_2+UV) processes. The periodic air back-flushing was performed during 10 s per 10-min filtration to reduce membrane fouling. The results were compared with those of the previous study [31] using the hybrid process of the same MF and the PES beads.

2. Experiments

2.1. Materials

The tubular ceramic MF membrane (NCMT-7231) employed in the study was coated with α-alumina on a supporting layer of α-alumina, and its pore size was 0.1 μm. The membrane was purchased from Nano Pore Materials in Korea, and the specifications of the tubular ceramic membrane were arranged in Table 1.

The photocatalyst used was 4–6 mm PP beads coated with TiO_2 powder manufactured by Prof. Kim's group [32] using chemical vapor deposition method, which was presented in Table 2. The PES beads were prepared by loading TiO_2 powder using phase inversion method by Figoli et al. [33,34], which was shown in Table 3. Instead of natural organic matters and fine inorganic particles in natural water source, a quantity of humic acid sodium salt (Aldrich, USA)

Table 1
Specifications of the tubular ceramic MF membrane (NCMT-7231) employed in this study

Membrane	NCMT-7231
Pore size (μm)	0.1
Outer diameter (mm)	8
Inner diameter (mm)	6
Length (mm)	251
Surface area (cm^2)	47.3
Material	α-alumina coating on α-alumina support
Company	Nanopore materials in Republic of Korea

Table 2
Specification of the TiO_2-coated polypropylene beads employed 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

Table 3
Specification of the TiO_2-loaded polyethersulfone beads employed in this study [23]

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

and kaolin (Sigma-Aldrich, USA) was dissolved in distilled water. It was utilized as synthetic water in the experiment. The humic acid (HA) was selected as an organic matter representative, because it was known that HA was the major humic material of rivers or lakes. UV light with 352 nm was irradiated from outside of the acryl module by 2 UV lamps (F8T5BLB, Sankyo, Japan) having 8 W power.

2.2. Hybrid membrane module

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

2.3. Experimental procedure

The advanced water treatment system utilizing a hybrid module of the tubular ceramic MF and TiO_2 photocatalyst-coated PP beads was demonstrated in Fig. 1, which was utilized at the previous study [35] without the PP beads. The cross-flow filtration was performed inside the tubular ceramic membrane with periodic air back-flushing utilizing nitrogen gas for protecting oxygen effect on water quality. The hybrid module was supplied with the PP beads fluidizing between the gap of ceramic membrane and the acryl module case. Then, the feed tank was filled with 10 L of the synthetic water composed of HA and kaolin, and the temperature of the feed water was constantly maintained by using a constant temperature circulator (Model 1146, VWR, USA). In addition, the synthetic feed water was continuously mixed by a stirrer in order to maintain the homogeneous condition of the feed water, and it was caused to flow into the inside of the tubular ceramic MF 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, which flowed into the hybrid module, was constantly controlled by valves of both the bypass pipe of the pump and the concentrating pipe. The permeate flux treated by both the tubular ceramic MF membrane and the PP beads was measured by an electric balance (Ohaus, USA). The treated and the concentrate water were recycled to the feed tank to maintain a constant feed concentration of during operation.

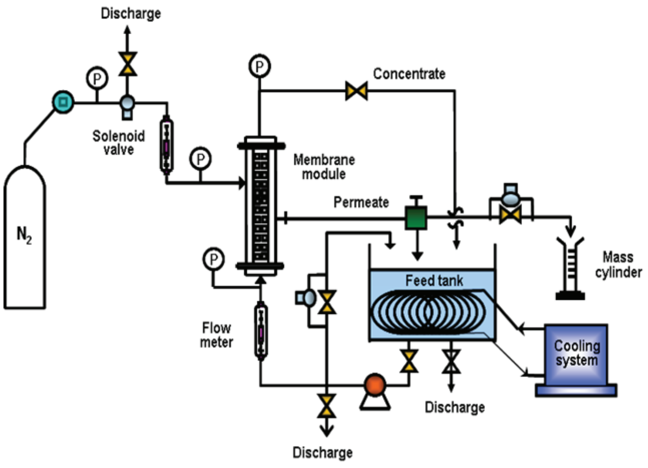

Fig. 1. Apparatus of hybrid water treatment process of ceramic microfiltration and TiO_2 photocatalyst-coated PP beads with periodic air back-flushing [35].

The concentrations of kaolin and HA were fixed at 30 mg/L and 6 mg/L, respectively. The PP beads concentration was changed from 5 to 40 g/L to investigate the effect of PP beads concentration. The air back-flushing time (BT) and filtration time (FT) were fixed at 10 s and 10 min, respectively. Only MF process without the PP beads and UV light (MF), and MF process with the PP beads (MF+TiO_2) were operated at 40 g/L of the PP beads, respectively. And the results were compared with the hybrid process of the MF and PP beads with UV (MF+TiO_2+UV) for evaluating a portion of the treatment efficiencies of MF, adsorption, and photo-oxidation.

The permeate flux (J) was monitored during total filtration time of 180 min under each condition. At all experimental conditions, trans-membrane pressure (TMP) was maintained constant at 1.8 bar, the air back-flushing 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 back-flushing was performed during 10 s per 10-min filtration.

The quality of feed and treated water was analyzed for evaluating the treatment efficiencies of turbid materials and DOM. Turbidity and UV_{254} absorbance were measured by a turbidimeter (2100N, Hach, USA) and a UV spectrophotometer (Genesys 10 UV, Thermo, USA), respectively. 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 measuring UV_{254} absorbance, the treated sample was filtered once by a 0.2-μm syringe filter to reject turbid materials.

3. Results and discussions

The effect of photocatalyst-coated PP beads concentration on membrane fouling was investigated in the hybrid process of tubular ceramic MF and TiO_2 photocatalyst-coated PP beads with periodic air back-flushing for advanced water treatment. Additionally, treatment portions by membrane filtration, photocatalyst adsorption, and photo-oxidation were evaluated by comparing the treatment efficiencies of MF (MF+TiO_2) and (MF+TiO_2+UV) processes. Resistances of membrane, boundary layer, and membrane fouling (R_m, R_b, R_f) were calculated from permeate flux (J) data using the resistance-in-series filtration equation as the same method as the previous study [35].

3.1. Effect of photocatalyst-coated PP beads concentration

The resistances of membrane fouling (R_f) decreased dramatically as increasing the photocatalyst-coated PP beads concentration from 5 g/L to 40 g/L, as compared in Fig. 2. However, in the results using the hybrid process of the same MF membrane and the photocatalyst-loaded PES beads with periodic air back-flushing, R_f showed the minimum point between 20 g/L and 30 g/L of the PP beads, as summarized in Table 4. It means that the optimum concentration of PP beads could be 40 g/L in the experimental range; however, that of

PES beads was 20–30 g/L to prevent membrane fouling efficiently on the surface and inside the ceramic membrane. The final R_f after 180-min operation ($R_{f,180}$) at 5 g/L of PP beads was 2.926 × 10^9 kg/m²s, which was 1.61 times higher than 1.813 × 10^9 kg/m²s of the $R_{f,180}$ at 40 g/L, as shown in Table 4. However, in the results of PES beads, the $R_{f,180}$ at 40 g/L of the PES beads was 1.438 × 10^9 kg/m²s, which was 1.16 times higher than 1.245 × 10^9 kg/m²s of the $R_{f,180}$ at 20 and 30 g/L. It means that too many PES beads could not prohibit membrane fouling more effectively, because the PES beads protected UV light to transport deeply inside the hybrid module for water treatment.

Fig. 3 showed the dimensionless permeate flux (J/J_0), where J_0 is the initial permeate flux which was estimated by extrapolation using initial 2 data at 1 and 2 min, to investigate a relative decline of permeate flux. The J/J_0 tended to increase as increasing the photocatalyst-coated PP beads concentration from 5 to 40 g/L, because the PP beads could reduce the membrane fouling formation effectively. The final value of J/J_0 (J_{180}/J_0) of 0.246 after 180-min operation at 40 g/L of the PP beads was 1.49 times higher than 0.165 at 5 g/L, as shown in Table 4. However, in the results with the PES beads, J_{180}/J_0 of 0.361 at 20 and 30 g/L of the PES beads was 1.09 times higher than 0.332 at 40 g/L, which was not a great difference. In addition, the total permeate volume (V_T) of 6.55 L at 40 g/L of PP beads was 1.30 times higher than 5.04 L of V_T at 5 g/L. Then, V_T of 7.06 L at 40 g/L of PES beads was 1.08 times higher than 6.56 L of V_T at 5 g/L, which was higher than that in the result with the PP beads, because the initial membrane conditions (R_m, resistance of membrane) at the result with the PES beads was the better than those with the PP beads, as compared

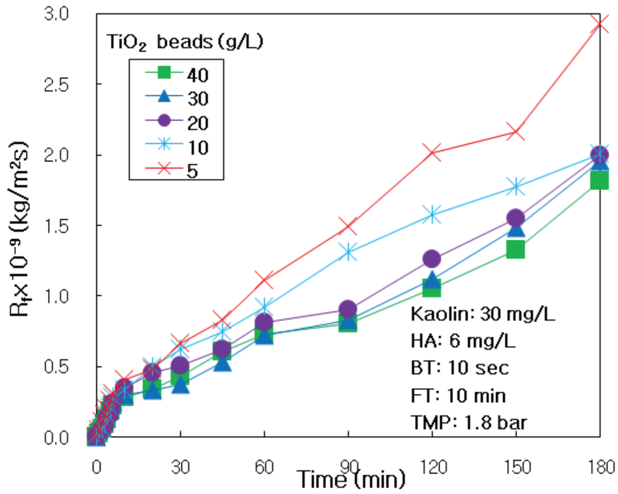

Fig. 2. Effect of photocatalyst-coated PP beads on resistance of membrane fouling in hybrid process of tubular ceramic MF and TiO_2 photocatalyst-coated PP beads.

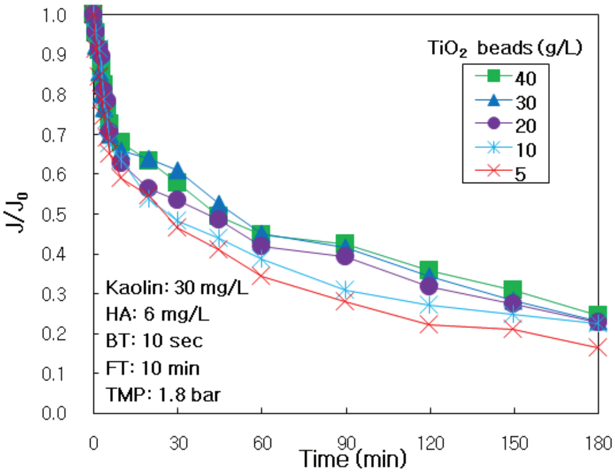

Fig. 3. Effect of photocatalyst-coated PP beads on dimensionless permeate flux in hybrid process of tubular ceramic MF and TiO_2 photocatalyst-coated PP beads.

Table 4
Effect of photocatalyst-coated PP beads on filtration factors for hybrid process of tubular ceramic MF, and TiO_2 photocatalyst-coated PP beads or photocatalyst-loaded PES beads (BT 10 s, FT 10 min)

Photocatalyst beads (g/L)		5	10	20	30	40
Polypropylene (PP)	R_m × 10^{-9} (kg/m²s)	0.570	0.551	0.549	0.559	0.553
	R_b × 10^{-9} (kg/m²s)	0.008	0.033	0.037	0.031	0.040
	$R_{f,180}$ × 10^{-9} (kg/m²s)	2.926	2.008	1.997	1.951	**1.813**
	J_0 (L/m²h)	1,100	1,086	1,083	1,078	1,071
	J_{180} (L/m²h)	181	245	246	250	**264**
	J_{180}/J_0	0.165	0.225	0.227	0.232	**0.246**
	V_T (L)	5.04	5.54	6.13	6.50	**6.55**
Polyether-sulfone (PES)	R_m × 10^{-9} (kg/m²s)	0.694	0.695	0.700	0.695	0.701
	R_b × 10^{-9} (kg/m²s)	0.021	0.007	0.003	0.008	0.016
	$R_{f,180}$ × 10^{-9} (kg/m²s)	1.367	1.251	**1.245**	**1.245**	1.438
	J_0 (L/m²h)	888	905	904	903	887
	J_{180} (L/m²h)	305	325	326	326	295
	J_{180}/J_0	0.344	0.359	**0.361**	**0.361**	0.332
	V_T (L)	6.56	6.89	6.91	6.96	**7.06**

in Table 4. It means that the PP beads could be more effective to control the membrane fouling in this hybrid process than the PES beads.

The treatment efficiency of turbidity was very high and almost constant beyond 99.2%, independent of the PP beads concentration, as shown in Table 5. It means that the PP beads could not affect the treatment of suspended particles like kaolin in this hybrid process. However, in the hybrid process of the same MF and PES beads, the treatment efficiency of turbidity increased a little from 95.7% to 98.7%, which were a little lower efficiency than those of the PP beads, as increasing the PES beads concentration from 5 g/L to 40 g/L. It means that the PP beads were the more efficient to remove the turbid materials than the PES beads in the hybrid water treatment process.

Then, the treatment efficiency of DOM, which could be analyzed by UV_{254} absorbance, increased from 62.8% to 87.6%, as increasing the PP beads concentration from 5 g/L to 40 g/L, as arranged in Table 6. The treatment efficiency of DOM in the results with the PES beads showed the same trend to increase from 70.7% to 85.6%, as increasing the PES beads concentration inside the hybrid module. The PP beads were a little more efficient to remove DOM at 40 g/L of photocatalyst beads than the PES beads; however, the PES beads were much more effective at 5 g/L than the PP beads in this hybrid water treatment process of the tubular ceramic MF and photocatalyst beads. It means that the low photocatalyst beads concentration of the PES beads like as 5 g/L could be enough to remove DOM in the hybrid water treatment process.

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

For evaluating the role of membrane filtration, adsorption, and photo-oxidation in the hybrid water treatment process of the tubular ceramic MF and the photocatalyst-coated PP beads with the periodic air back-flushing, the process with the PP beads without UV light ($MF+TiO_2$), and only MF without any PP beads and UV (MF) were performed at HA 6 mg/L, respectively. And then, they were compared with the hybrid process of MF and the PP beads with UV light ($MF+TiO_2+UV$). As shown in Fig. 4, the resistance of membrane fouling (R_f) of MF, ($MF+TiO_2$), and ($MF+TiO_2+UV$) processes at HA 6 mg/L were compared during 180-min operation. However, the MF process could be operated until 90 min, because R_f increased rapidly and the permeate flux could not be measured after 90 min. The R_f could maintain low at the ($MF+TiO_2+UV$) process during 180 min, 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 control the membrane fouling effectively in this hybrid water treatment process.

The R_f after 90-min operation ($R_{f,90}$) was the maximum 18.41×10^9 kg/m²s at MF process, which was 7.50 times higher than the R_f after 180-min operation ($R_{f,180}$) of 2.455×10^9 kg/m²s at ($MF+TiO_2+UV$) process, as arranged in Table 7. In addition, the resistance of boundary layer (R_b) was the highest at the MF process, and the membrane fouling could increase dramatically during 90-min operation. However, in the hybrid process of the same MF and the photocatalyst-loaded PES beads [31], the $R_{f,180}$ increased a little from 1.370 to 1.483, as simplifying the process from ($MF+TiO_2+UV$) to MF process.

Table 5
Water quality and treatment efficiency of turbidity in the hybrid process of tubular ceramic MF and TiO_2 photocatalyst-coated PP beads for effect of the PP beads (BT 10 s, FT 10 min)

TiO_2 photocatalyst-coated PP beads (g/L)	Turbidity (NTU)				Average treatment efficiency (%)	
	Feed water		Treated water		Photocatalyst beads	
	Range	Average	Range	Average	PP	PES
5	41.6~47.9	44.8	0.291~0.487	0.374	99.2	95.7
10	37.8~45.8	41.8	0.251~0.322	0.289	99.3	96.8
20	38.7~47.5	43.3	0.193~0.315	0.249	99.4	97.5
30	37.4~47.1	43.0	0.247~0.410	0.314	99.3	96.9
40	38.7~43.1	40.7	0.198~0.252	0.223	99.5	98.7

Table 6
Water quality and treatment efficiency of dissolved organic matters (UV_{254} absorbance) in the hybrid process of tubular ceramic MF and TiO_2 photocatalyst-coated PP beads for effect of the PP beads (BT 10 s, FT 10 min)

TiO_2 photocatalyst-coated PP beads (g/L)	UV_{254} absorbance (cm^{-1})				Average treatment efficiency (%)	
	Feed water		Treated water		Photocatalyst beads	
	Range	Average	Range	Average	PP	PES
5	0.224~0.314	0.262	0.081~0.112	0.097	62.8	70.7
10	0.189~0.254	0.230	0.052~0.091	0.076	67.1	74.3
20	0.213~0.308	0.256	0.054~0.081	0.069	72.9	78.0
30	0.122~0.166	0.139	0.020~0.031	0.026	81.3	80.3
40	0.178~0.231	0.207	0.017~0.035	0.026	87.6	85.6

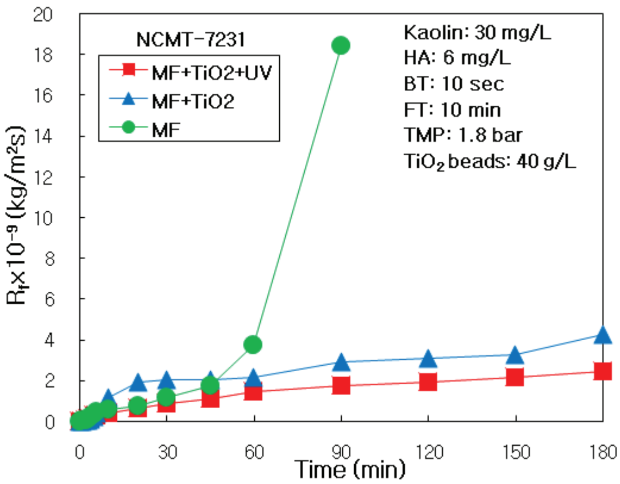

Fig. 4. Role of membrane filtration, adsorption and photo-oxidation on resistance of membrane fouling in hybrid process of tubular ceramic MF and TiO_2 photocatalyst-coated PP beads.

As shown in Fig. 5, the dimensionless permeate flux (J/J_0) could maintain the highest at the (MF+TiO_2+UV) process after 30 min, and the lowest at the MF process after 60 min. It means that the J/J_0 at the (MF+TiO_2+UV) could be the higher than those at the MF and (MF+TiO_2) processes, because the photocatalyst adsorption and photo-oxidation could control efficiently the membrane fouling. The J_{180}/J_0 after 180-min operation at the (MF+TiO_2+UV) process was the maximal 0.195, which was 5.42 times higher than 0.036 at the MF process, as summarized in Table 7. The J/J_0 could maintain the highest at (MF+TiO_2+UV) process, because the membrane fouling was reduced the more excellently by photocatalyst adsorption and photo-oxidation at (MF+TiO_2+UV) process, compared with the MF or (MF+TiO_2) processes. Additionally, the total permeate volume (V_T) could be acquired the maximal 4.62 L at the (MF+TiO_2+UV) process, and the minimal 2.00 L at the MF process. In the previous work [31] for the hybrid process of the same MF and the PES beads, the maximal J_{180}/J_0 could be acquired at (MF+TiO_2+UV) process, and decreased a little as simplifying the process from (MF+TiO_2+UV) to MF process, which was the same trend with this study. In addition, the V_T values in the result [31] could be the highest 7.61 L at the (MF+TiO_2+UV) process with the PES beads, which was the higher than 4.62 L in this study with PP beads, because the initial membrane condition (R_m, resistance of membrane) at the previous work [31] was better than that in this study, as compared in Table 7.

The turbidity treatment efficiencies decreased very little from 99.4% to 98.1%, as simplifying the process from (MF+TiO_2+UV) to MF with the PP beads; however, those decreased clearly from 99.1% to 96.6% in the result [31] with the PES beads, as shown in Table 8. Then, the treatment efficiencies of DOM (UV_{254} absorbance) decreased dramatically from 86.3% to 67.9%, as simplifying the process from (MF+TiO_2+UV) to MF with the PP beads; however, those decreased from 82.4% to 70.6% in the result [31] with the PES beads, as shown in Table 9. The portions of treatment efficiency by membrane filtration, adsorption and photo-oxidation could be calculated by reducing sequentially the turbidity or DOM treatment efficiencies of (MF+TiO_2+UV), (MF+TiO_2) and MF, which were compared with the result [31] of the PES beads in Table 10, in the hybrid water treatment process of the tubular ceramic MF and photocatalyst polymer beads.

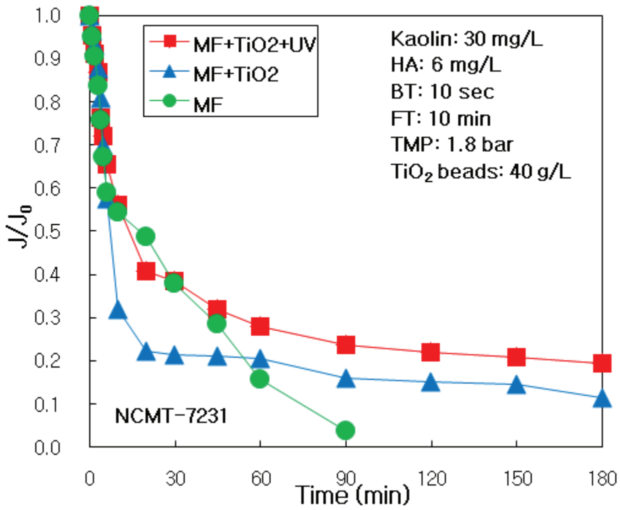

Fig. 5. Role of membrane filtration, adsorption and photo-oxidation on dimensionless permeate flux in hybrid process of tubular ceramic MF and TiO_2 photocatalyst-coated PP beads.

Table 7
Roles of membrane filtration, adsorption, and photo-oxidation on filtration factors in hybrid process of tubular ceramic MF and TiO_2 photocatalyst-coated PP beads at HA 6 mg/L

Photocatalyst beads	Process	MF + TiO_2 + UV	MF + TiO_2	MF
PP	$R_m \times 10^{-9}$ (kg/m²s)	0.567	0.550	0.563
	$R_b \times 10^{-9}$ (kg/m²s)	0.028	0.004	0.134
	$R_{f,180} \times 10^{-9}$ (kg/m²s)	2.455	4.292	18.41*
	J_0 (L/m²h)	1,067	1,147	911
	J_{180} (L/m²h)	208	131	33*
	J_{180}/J_0	0.195	0.114	0.036*
	V_T (L)	4.62	3.25	2.00*
PES [31]	$R_m \times 10^{-9}$ (kg/m²s)	0.699	0.700	0.702
	$R_b \times 10^{-9}$ (kg/m²s)	0.008	0.002	0.001
	$R_{f,180} \times 10^{-9}$ (kg/m²s)	1.370	1.440	1.483
	J_0 (L/m²h)	898	905	904
	J_{180} (L/m²h)	306	297	291
	J_{180}/J_0	0.340	0.328	0.321
	V_T (L)	7.61	7.32	7.08

*After 90 min.

In turbidity treatment efficiency, the treatment portion of membrane filtration was very high 99.4% at HA 6 mg/L. The treatment portion of adsorption by the photocatalyst-coated PP beads was very low 1.3%; however, that of photo-oxidation by the PP beads and UV light was 0.0%. In the result [31] with the PES beads, those of adsorption and photo-oxidation by

Table 8
Water quality and treatment efficiency of turbidity in the hybrid process of tubular ceramic MF and TiO_2 photocatalyst-coated PP beads for roles of membrane filtration, adsorption, and photo-oxidation at HA 6 mg/L

Experimental condition		Turbidity (NTU)				Average treatment efficiency (%)	
HA (mg/L)	Process	Feed water		Treated water		Photocatalyst beads	
		Range	Average	Range	Average	PP	PES [31]
6	MF+TiO_2+UV	32.4~40.8	35.4	0.191~0.253	0.215	99.4	99.1
	MF+TiO_2	40.6~56.7	50.3	0.171~0.474	0.278	99.4	97.1
	MF	27.6~29.1	28.3	0.237~0.825	0.540	98.1	96.6

Table 9
Water quality and treatment efficiency of dissolved organic matters (UV_{254} absorbance) in the hybrid process of tubular ceramic MF and TiO_2 photocatalyst-coated PP beads for roles of membrane filtration, adsorption, and photo-oxidation at HA 6 mg/L

Experimental condition		UV_{254} absorbance (cm^{-1})				Average treatment efficiency (%)	
HA (mg/L)	Process	Feed water		Treated water		Photocatalyst beads	
		Range	Average	Range	Average	PP	PES [31]
6	MF+TiO_2+UV	0.118~0.177	0.147	0.016~0.025	0.020	86.3	82.4
	MF+TiO_2	0.175~0.228	0.197	0.030~0.092	0.051	74.0	72.5
	MF	0.155~0.161	0.158	0.042~0.058	0.051	67.9	70.6

Table 10
Treatment efficiency portions of membrane filtration, adsorption, and photo-oxidation in the hybrid process of tubular ceramic MF and TiO_2 photocatalyst-coated PP beads at HA 6 mg/L

Portion of treatment efficiency	Turbidity		UV_{254} absorbance	
	PP	PES [31]	PP	PES [31]
Membrane filtration (%)	98.1	96.6	67.9	70.6
Adsorption (%)	1.3	0.5	6.1	1.9
Photo-oxidation (%)	0.0	2.0	12.3	9.9
Total treatment efficiency (%)	99.4	99.1	86.3	82.4

the PES beads and UV were 0.5% and 2.0%, respectively. It means that the role of adsorption by the photocatalyst-loaded PES beads [31] was the more excellent than that by the photocatalyst-coated PP beads; however, that of photo-oxidation by the PP beads and UV was the more dominant than that by the PES beads [31] for treatment of the suspended particles like kaolin in this hybrid process.

In the treatment efficiency of DOM (UV_{254} absorbance), the treatment portion of membrane filtration was still very high 67.9%; however, that of adsorption was a little 6.1% and that of photo-oxidation was high 12.3% at HA 6 mg/L. It means that the role of photo-oxidation by the photocatalyst-coated PP beads and UV light was the more dominant than that of adsorption by the PP beads for the DOM treatment in this hybrid process. The photo-oxidation by the PP beads and UV could reduce the membrane fouling effectively, because the photo-oxidation had the major role of DOM reduction in this hybrid water treatment process with the PP beads. In addition, in the previous work [31] for the hybrid process of the same MF and the PES beads, the role of photo-oxidation was the more important than that of adsorption for DOM treatment, which was the exact same trend with this study.

4. Conclusions

In this study, the effect of photocatalyst-coated PP beads on membrane fouling was observed in a hybrid process of tubular alumina MF and the PP beads with periodic air back-flushing for advanced water treatment. In addition, treatment portions by membrane filtration, photocatalyst adsorption, and photo-oxidation were investigated by comparing the treatment efficiencies of (MF), (MF+TiO_2), and (MF+TiO_2+UV) processes. The results were compared with the previous study [31] of the hybrid process of the same MF and photocatalyst-loaded PES beads. The following results could be induced finally:

(1) The optimum concentration of PP beads could be 40 g/L in the experimental range, but that of the PES beads was 20–30 g/L to prevent membrane fouling efficiently on the surface and inside the ceramic membrane. It means that too many PES beads could not prohibit membrane fouling more effectively, because the PES beads protected UV light to transport deeply inside the hybrid module. However, the total permeate volume was the maximum at 40 g/L of both the PP and PES beads.

(2) The turbidity treatment efficiency was very high and almost constant, independent of the PP beads concentration. It means that the PP beads could not affect the treatment of suspended particles like kaolin in this hybrid process. However, the treatment efficiency of DOM increased dramatically as increasing the PP beads concentration. Then, the results with PES beads showed the same trend. The low PES beads concentration like as 5 g/L could be enough to remove DOM effectively.

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

(4) The adsorption and photo-oxidation by the photocatalyst-coated PP beads could play the more dominant role to remove DOM than that of turbidity in this hybrid water treatment process. The role of photo-oxidation by the PP beads and UV was the more dominant than that of adsorption by the PP beads for the DOM treatment, which was the same trend in the previous work for the hybrid process of the same MF and the PES beads.

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