

Roles of adsorption and photo-oxidation in hybrid water treatment process of tubular carbon fiber ultrafiltration and PP beads with UV irradiation and water back-flushing

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ABSTRACT

Roles of ultrafiltration, adsorption and photo-oxidation on membrane fouling and treatment efficiency were observed in a hybrid water treatment process of tubular carbon fiber ultrafiltration (UF) and polypropylene (PP) beads with UV irradiation and water back-flushing. The synthetic feed was prepared with humic acid (HA) and kaolin. The synthetic feed flowed inside the UF membrane, and the permeate contacted the PP beads fluidized in the gap of the membrane and the acryl module case. The membrane fouling resistance of (UF+PP) process showed the minimum, and increased dramatically from (UF+UV) to UF process. The portions of UF and photo-oxidation by the PP beads and UV for turbidity treatment were 99.5% and 0.2%, respectively; however, the portions of UF and adsorption for dissolved organic matters (DOM) treatment were 57.1% and 5.4%. It means that UF was dominant for turbid matter treatment, and UF and adsorption had important roles for DOM treatment. The membrane fouling resistance increased dramatically as increasing HA concentration, and the maximum total permeated volume was acquired at HA 2 mg/L. The treatment efficiency of turbidity was almost constant, independent of HA concentration; however, that of DOM showed the maximal 69.3% at HA 6 mg/L. It proved that DOM could play a dominant role for membrane fouling.

Keywords: Adsorption; Photo-oxidation; Polypropylene bead; Ultrafiltration; Water back-flushing; Organic matter

1. Introduction

Photo-oxidation, which is one of excellent technologies of water pollution control, with the characteristics of high efficiency, low energy consumption and a wide range of applications, can oxidize most organic compounds, especially non-biodegradable organic contaminants, by mineralizing them to small inorganic molecules. For this reason, photo-oxidation technology has broad prospects for applications [1–4].

Membrane separation process for separation and purification has been developed dramatically during the past few decades. It can simultaneously separate and concentrate all

pollutants in water by the retention of its microspores without secondary pollution and phase change. In addition, with the advantage of low energy consumption, its equipment is compact, easy to operate and capable of continuous operation at room temperature [5]. However, membrane fouling due to the adsorption-precipitation of organic and inorganic compounds onto membranes leads to a decrease in the permeate flux, an increase in membrane cleaning costs and a reduction of the life of the membrane. Although considerable progress has been made in membrane fouling [6,7], techniques for controlling membrane fouling remain inadequate, which is the major obstacle in the successful implementation of membrane separation technology. The TiO₂ photocatalysis-membrane separation coupling technology emerged recently can solve

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the two problems mentioned above effectively [8]. 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 other 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 [9]. In addition, a few papers for effect of operating conditions in the hybrid water treatment process of various tubular ceramic membranes, and TiO₂ photocatalyst-contained PES or PP beads in our research group have been published in Membrane Journal [10–18] in recent years.

In this study, treatment portions of membrane filtration, adsorption, and photo-oxidation with the PP beads were investigated by comparing the treatment efficiencies of (UF), (UF+UV), (UF+PP) and (UF+PP+UV) processes in the hybrid process of tubular carbon fiber UF and PP beads with periodic water back-flushing. The PP beads did not contain any photocatalyst. A hybrid module was composed of the ceramic UF membrane and the PP beads, which were fluidized between the gap of carbon fiber membrane and the acrylic module case. In addition, the effect of dissolved organic matters (DOM) was investigated on membrane fouling in this hybrid water treatment process. The periodic water back-flushing was performed during 10 s per 10 min filtration to reduce membrane fouling. The results were compared with those of the previous study [19,20] using the hybrid process of the same tubular carbon fiber UF and the TiO₂ photocatalyst-coated PP beads with periodic water back-flushing to investigate the effect with or without photocatalyst.

2. Materials and methods

2.1. Materials

The tubular carbon fiber UF membrane (C005) used in the study, was imported from Koch (USA), and its pore size was 0.4 μm. The specifications of the carbon fiber membrane were shown in Table 1. The size of PP beads employed in

Table 1
Specifications of the tubular carbon fiber ultrafiltration (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)

this study was 4–6 mm, which of the average weight was 39.9 mg. Instead of natural organic matters and fine inorganic particles in natural water source, a quantity of humic acid (HA) and kaolin was dissolved in distilled water. It was then utilized as synthetic water in this experiment. UV with 352 nm was irradiated from outside of the acrylic module by 2 UV lamps (F8T5BLB, Sankyo, Japan).

2.2. Hybrid membrane module

To remove the turbidity and DOM, the hybrid module was composed by packing the PP beads between the module inside and outside of the carbon fiber membrane. In addition, 100 mesh (0.150 mm), which was extremely smaller than 4–6 mm particle size of the PP beads used here, was installed at the outlet of the hybrid module to prevent the PP beads loss into the treated water tank.

2.3. Experimental procedure

The advanced water treatment system using a hybrid Module (6) of tubular carbon fiber UF and the PP beads were shown in Fig. 1, which was used in previous study [10]. Cross-flow filtration was performed for the tubular carbon fiber UF membrane with periodic water back-flushing using permeated water. The hybrid Module (6) was supplied with the PP beads fluidizing between the gap of carbon fiber membrane and the acrylic module case. Then, the feed tank (1) was filled with 10 L of the synthetic water composed of humic acid and kaolin. And the temperature of the feed water was constantly maintained by using a constant temperature circulator (3) (Model 1146, VWR, USA). In addition, the synthetic feed water was continuously mixed by a stirrer (4) in order to maintain the homogeneous condition of the feed water, and it was caused to flow into the inside of the tubular carbon fiber UF membrane by a pump (2) (Procon, Standex Co., USA). The feed flow rate was measured by a flow meter (5) (NP-127, Tokyo Keiso, Japan). The flow rate and pressure of the feed water that flowed into the hybrid module was constantly maintained by controlling

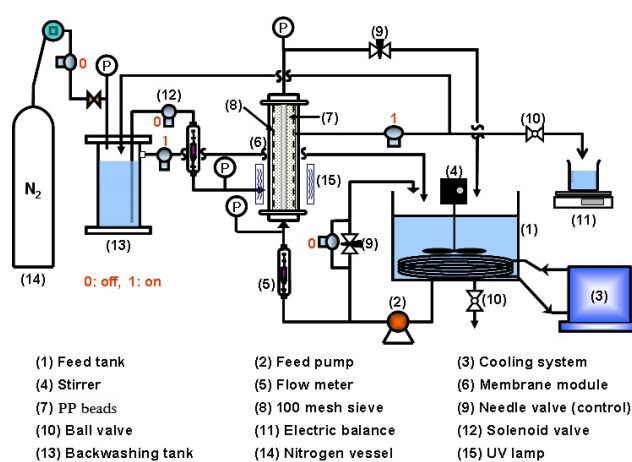


Fig. 1. Apparatus of hybrid water treatment process of tubular carbon fiber ultrafiltration and the PP beads with periodic water back-flushing [10].

valves (9) of both the bypass pipe of the pump (2) and the concentrate pipe. The permeate flux treated by both the tubular carbon fiber UF membrane and the PP beads were measured by an electric balance (11) (Ohaus, USA.). The permeate water flowed into the back-washing tank (13) if the permeate flux had not been measured. After the treated water was over a certain level in the back-washing tank (13), it was recycled to the feed tank (1) to maintain a constant concentration of the feed water during operation. After each operation, physical washing was performed by a brush inside the tubular membrane, and the permeate flux was measured to calculate the resistance of irreversible and reversible membrane fouling.

Only UF process without the PP beads and UV light (UF), UF process with UV irradiation (UF+UV), and UF process with the PP beads (UF+PP) were operated at 6 mg/L of HA, respectively. And the results were compared with the hybrid process of the UF and PP beads with UV (UF+PP+UV) for evaluating a portion of the treatment efficiencies of UF, adsorption, and photo-oxidation with or without the PP beads. Kaolin was fixed at 30 mg/L and humic acid was changed from 2 to 10 mg/L in the synthetic feed water, to investigate the effect of DOM. The water back-flushing time (BT) and filtration time (FT) were fixed at 10 s and 10 min, respectively.

The resistance of membrane fouling (R_f), dimensionless permeate flux (J/J_0) and permeate flux (J) during total filtration time of 180 min were observed under each condition. Under all experimental conditions, the TMP (trans-membrane pressure) was maintained at 1.80 bar, the water back-flushing pressure at 2.5 bar, the feed flow rate at 1.0 L min⁻¹, and the feed water temperature at 20°C.

The quality of feed water and treated water was analyzed in order to evaluate the treatment efficiencies of turbid materials and DOM. Turbidity was measured by a turbidimeter (2100N, HACH, USA), and UV₂₅₄ absorbance, which represented DOM, was analyzed by a UV spectrophotometer (GENESYS 10 UV, Thermo, USA). The detection limits of turbidimeter and UV spectrophotometer were 0–4,000 NTU (± 0.001 NTU) and $-0.1 \sim 3.0$ cm⁻¹ (± 0.001 cm⁻¹). Before measuring UV₂₅₄ absorbance, the treated sample was filtered once by a 0.2 μ m syringe filter to reject turbid materials.

3. Results and discussion

Treatment portions by membrane filtration, adsorption and photo-oxidation with or without the PP beads were evaluated by comparing the treatment efficiencies of UF, (UF+UV), (UF+PP) and (UF+PP+UV) processes. In addition, the effect of DOM such as HA was investigated in the hybrid water treatment process of tubular carbon fiber UF and PP beads with periodic water back-flushing. The results were compared with the previous study [19,20] using the hybrid process of the same tubular carbon fiber UF and the TiO₂ photocatalyst-coated PP beads to investigate the effect with or without photocatalyst. Resistance of the membrane, boundary layer, membrane fouling 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 in the previous study [10]. Resistance of the irreversible and reversible membrane fouling (R_{ir} , R_{re}) could be

evaluated from J data after physical washing using a brush inside the membrane.

3.1. Role of UF, adsorption, and photo-oxidation with/without the PP beads

To investigate UF, adsorption, and photo-oxidation with or without the PP beads in the hybrid process of tubular carbon fiber UF and the PP beads, the UF process without the PP beads with UV (UF+UV), the process with the PP beads without UV irradiation (UF+PP), and only UF without the PP beads and UV (UF) were performed at 6 mg/L of HA respectively. And the results were compared with the hybrid process of UF and the PP beads with UV light (UF+PP+UV). The R_f values of (UF+PP+UV), (UF+UV), (UF+PP) and only UF processes at HA 6 mg/L were compared during 180 min operation, as shown in Fig. 2. The R_f values maintained the lowest values at the UF process until 30 min operation; however, those were the lowest at the (UF+PP) process after 45 min. It means that the adsorption by the PP beads did not activate initially until 30 min; however, it could reduce the membrane fouling strongly after 45 min. In addition, the R_f maintained the highest values at the (UF+PP) process until 20 min operation; however, it was the highest at the (UF+PP+UV) process after 30 min. It was found that the photo-oxidation with the PP beads by UV irradiation could reduce the membrane fouling until 20 min; however, it did not activate after 30 min.

The filtration factors in this hybrid water treatment process were summarized in Table 2. The final R_f after 180 min operation ($R_{f,180}$) was the minimum at (UF+PP) process, and increased dramatically from (UF+UV) to UF process. And $R_{f,180}$ at UF process was 4.590×10^9 kg m⁻² s⁻¹, which was 1.81 times higher than 2.529×10^9 kg m⁻² s⁻¹ at (UF+PP) process. The resistances of the irreversible and reversible membrane fouling (R_{ir} , R_{re}) was the maximum at UF process, and the R_{re} was the minimum at (UF+PP) process. It means that the

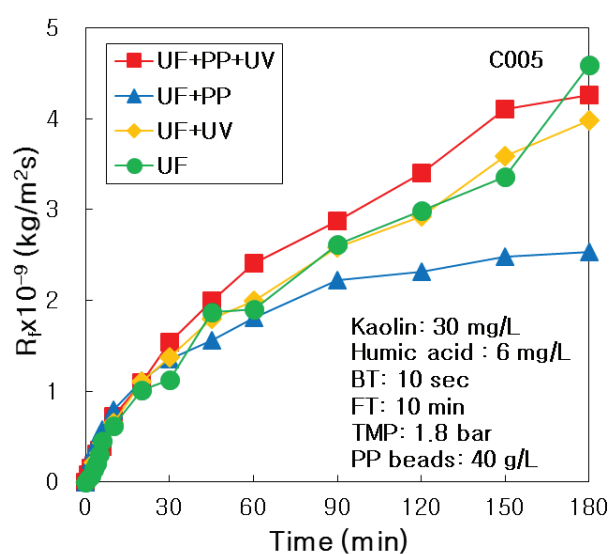


Fig. 2. Role of membrane filtration, adsorption and photo-oxidation on resistance of membrane fouling in hybrid process of tubular carbon fiber UF and PP beads at humic acid 6 mg/L.

Table 2

Roles of membrane filtration, adsorption, and photo-oxidation on filtration factors in hybrid process of tubular carbon fiber UF (C005) and PP beads at humic acid 6 mg/L

Adsorption media	Process	UF + PP + UV	UF + PP	UF + UV	UF
PP beads	$R_m \times 10^{-9}$ (kg m ⁻² s ⁻¹)	0.425	0.429	0.411	0.432
	$R_b \times 10^{-9}$ (kg m ⁻² s ⁻¹)	0.007	0.104	0.092	0.091
	$R_{f180} \times 10^{-9}$ (kg m ⁻² s ⁻¹)	4.262	2.529	3.979	4.590
	$R_{if} \times 10^{-9}$ (kg m ⁻² s ⁻¹)	0.063	0.055	0.024	0.174
	$R_{rf} \times 10^{-9}$ (kg m ⁻² s ⁻¹)	4.199	2.474	3.955	4.415
	J_0 (L m ⁻² h ⁻¹)	1470	1191	1261	1213
	J_{180} (L m ⁻² h ⁻¹)	135	207	142	124
	J_{180}/J_0	0.092	0.174	0.112	0.102
	V_T (L)	3.52	3.92	3.66	3.70
TiO ₂ photocatalyst-coated	Process	UF + TiO ₂ + UV	UF + TiO ₂	UF	
PP beads [19]	$R_m \times 10^{-9}$ (kg m ⁻² s ⁻¹)	0.812	0.803	0.836	
	$R_b \times 10^{-9}$ (kg m ⁻² s ⁻¹)	0.059	0.084	0.041	
	$R_{f180} \times 10^{-9}$ (kg m ⁻² s ⁻¹)	1.974	2.203	2.593	
	J_0 (L m ⁻² h ⁻¹)	324	318	322	
	J_{180} (L m ⁻² h ⁻¹)	99	91	81	
	J_{180}/J_0	0.306	0.287	0.253	
	V_T (L)	8.05	7.97	7.44	

adsorption by the PP beads could control effectively the membrane fouling, and the effect of photo-oxidation by UV irradiation on the membrane fouling, especially the reversible membrane fouling, was lower than that of the adsorption by the PP beads. In the previous work [19] using the hybrid process of the same tubular carbon fiber UF and the TiO₂ photocatalyst-coated PP beads, the R_{f180} at UF process was 2.593×10^9 kg m⁻² s⁻¹, which was 1.31 times higher than 1.974×10^9 kg m⁻² s at (UF+TiO₂+UV) process. However, the R_{f180} at (UF+TiO₂+UV) process was higher than that at (UF+PP) process. It means that the adsorption and photo-oxidation by the photocatalyst-coated PP beads and UV irradiation in the result [19] could control the membrane fouling more efficiently than the adsorption by the PP beads in this study.

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, maintained the highest in UF process until 30 min operation; however, those were the highest at (UF+PP) after 45 min, as compared in Fig. 3. It means that the J/J_0 at the (UF+PP) process could be higher than those at only UF process after 45 min, because the adsorption by the PP beads did not activate until 30 min; however, it reduced effectively the membrane fouling after 45 min.

As summarized in Table 2, the final J/J_0 after 180 min operation (J_{180}/J_0) at the (UF+PP) process was 0.174, which was 1.71 times higher than 0.102 at the UF process, and it was 0.112 at the (UF+UV) process. Finally, the maximal total permeate volume (V_T) could be acquired at the (UF+PP) process. It means that the J_{180}/J_0 increased from UF to (UF+UV), and (UF+PP) process, because the reduction effect of membrane fouling by the adsorption of PP beads was more excellent than that by photo-oxidation of UV

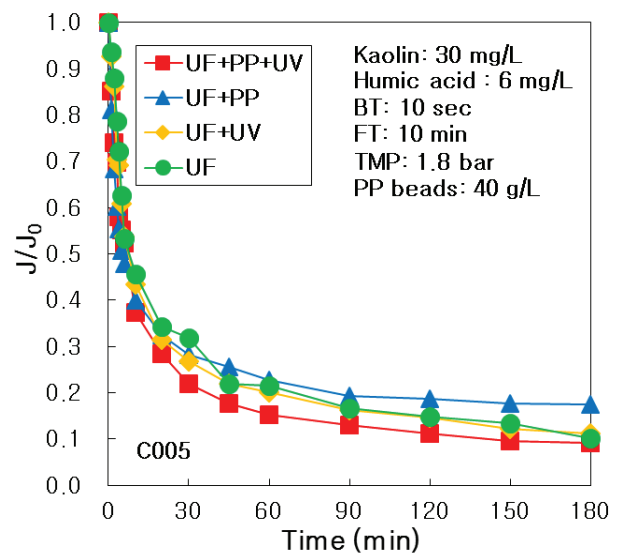


Fig. 3. Role of membrane filtration, adsorption and photo-oxidation on dimensionless permeate flux in hybrid process of tubular carbon fiber UF and PP beads at humic acid 6 mg/L.

irradiation. In the result [19] using the hybrid process of the same tubular carbon fiber UF and the photocatalyst-coated PP beads, the J_{180}/J_0 value decreased dramatically as simplifying from (UF+TiO₂+UV) to UF, and the maximal V_T could be acquired at the (UF+TiO₂+UV) process. It was found that the high permeate flux could be maintained, because the adsorption and photo-oxidation by the photocatalyst-coated PP beads and UV irradiation prohibited the membrane fouling, effectively.

As compared in Table 3, the turbidity treatment efficiencies was a little higher 99.7% at the (UF+PP+UV) process than 99.5% at the others processes. It means that the turbidity treatment efficiencies could be affected a little by the photo-oxidation and adsorption of the PP beads and UV irradiation, when simplifying the process from (UF+P+UV) to (UF+PP) and (UF+UV). However, in the result [19] using the hybrid process of the same tubular carbon fiber UF and the photocatalyst-coated PP beads, those decreased a little from 99.3% to 98.7%, as simplifying the process from (UF+TiO₂+UV) to UF. It was found that the turbid materials could be treated a little by the photo-oxidation and adsorption of the photocatalyst-coated PP beads and UV irradiation.

As shown in Table 4, the treatment efficiencies of DOM (UV₂₅₄ absorbance) decreased a little from 63.2% to 57.1%, as simplifying the process from (UF+PP+UV) to UF. It means that the organic matters could be treated a little by the photo-oxidation and adsorption of the PP beads and UV irradiation; however, in the result [19] using the hybrid process of the same tubular carbon fiber UF and the photocatalyst-coated PP beads, those decreased dramatically from 66.6% to 53.0%, as simplifying the process from (UF+TiO₂+UV) to UF. It was found that the organic matters could be treated efficiently by the photo-oxidation and adsorption of the photocatalyst-coated PP beads and UV irradiation, in sequence.

As summarized in Table 5, the treatment efficiency portions of membrane filtration, adsorption, UV photo-oxidation, and photo-oxidation with the PP beads in this hybrid process could be calculated by subtracting sequentially the turbidity or DOM treatment efficiencies of (UF+P+UV), (UF+PP), (UF+UV) and UF. In turbidity treatment efficiency, the treatment portion of membrane filtration was very high 99.5% at 6 mg/L of HA. The treatment portions of adsorption by the PP beads and UV photo-oxidation without the PP beads were 0.0%. In addition, that of photo-oxidation by the PP beads and UV light was very low 0.2%; however, in the results [19] using the hybrid process of the same tubular carbon fiber UF and the photocatalyst-coated PP beads, those of adsorption and photo-oxidation were 0.5% and 0.1% at HA 6 mg/L, respectively. It means that the roles of adsorption and photo-oxidation by the PP beads and UV were not important for the turbid matter treatment, in the hybrid process of the PP beads or the photocatalyst-coated PP beads. Kaolin could not be removed effectively by the adsorption and photo-oxidation by the PP beads and UV irradiation, because kaolin was inorganic and did not have electric charge.

As shown in Table 5, in the treatment efficiency of DOM, the treatment portion of membrane filtration was still very high 57.1% at HA 6 mg/L. And that of adsorption was high 5.4%; however, those of UV

Table 3

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

Adsorption media	Process	Turbidity (NTU)				Average treatment efficiency (%)
		Feed water		Treated water		
		Range	Average	Range	Average	
PP beads	UF + PP+UV	32.7~34.7	33.8	0.160~0.222	0.101	99.7
	UF + PP	29.3~30.5	29.9	0.103~0.180	0.149	99.5
	UF + UV	28.8~30.0	29.6	0.107~0.172	0.148	99.5
	UF	38.5~41.2	39.4	0.172~0.227	0.197	99.5
TiO ₂ -coated	UF + TiO ₂ + UV	21.2~28.2	25.5	0.150~0.234	0.191	99.3
PP beads [19]	UF + TiO ₂	24.4~28.9	26.8	0.155~0.332	0.208	99.2
	UF	24.4~28.7	26.0	0.247~0.430	0.335	98.7

Table 4

Water quality and treatment efficiency of dissolved organic matters (UV₂₅₄ absorbance) in the hybrid process of tubular carbon fiber UF and PP beads for roles of membrane filtration, adsorption, and photo-oxidation

Adsorption media	Process	UV ₂₅₄ absorbance (cm ⁻¹)				Average treatment efficiency (%)
		Feed water		Treated water		
		Range	Average	Range	Average	
PP beads	UF + PP + UV	0.146~0.194	0.165	0.053~0.074	0.061	63.2
	UF + PP	0.146~0.163	0.154	0.038~0.078	0.058	62.5
	UF + UV	0.087~0.113	0.099	0.033~0.051	0.042	57.8
	UF	0.076~0.196	0.159	0.010~0.104	0.068	57.1
TiO ₂ -coated	UF + TiO ₂ + UV	0.145~0.163	0.158	0.036~0.069	0.053	66.6
PP beads [19]	UF + TiO ₂	0.098~0.218	0.141	0.020~0.109	0.062	56.2
	UF	0.149~0.168	0.156	0.052~0.098	0.073	53.0

Table 5

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

Portion of treatment efficiency	Turbidity		UV ₂₅₄ absorbance	
	PP beads	TiO ₂ -coated PP beads [19]	PP beads	TiO ₂ -coated PP beads [19]
Membrane filtration (%)	99.5	98.7	57.1	53.0
Adsorption (%)	0.0	0.5	5.4	3.2
UV photo-oxidation (%)	0.0	—	0.7	—
Photo-oxidation with PP beads (%)	0.2	0.1	0.7	10.4
Total treatment efficiency (%)	99.7	99.3	63.2	66.6

photo-oxidation and photo-oxidation with the PP beads were very low 0.7%. By the way, in the results [19] using the hybrid process of the same tubular carbon fiber UF and the photocatalyst-coated PP beads, those of adsorption and photo-oxidation were low 3.2% and very high 10.4% at HA 6 mg/L. It was found that the role of adsorption by the PP beads was more important than those of UV photo-oxidation and photo-oxidation with the PP beads; however, that of photo-oxidation by the photocatalyst-coated PP beads was more dominant than the adsorption, in the DOM treatment. The adsorption could reduce the membrane fouling effectively in the hybrid process with the PP beads, because of the dominant role for organic matter treatment; however, the photo-oxidation could reduce the membrane fouling strongly, because the photo-oxidation had the major role of organic matters reduction in the hybrid water treatment process with the photocatalyst-coated PP beads. The PP beads were made by pure polymer, and they could be recycling after melting them. There could be no damage to PP beads by the photo-oxidation, because the treatment efficiency of DOM did not decrease during 180 min operation.

3.2. Effect of DOM

The resistance of membrane fouling (R_f) was highly influenced by HA, which was one of major natural organic matters (NOM) in lakes or rivers, and R_f increased dramatically as increasing concentration of HA from 2 mg/L to 10 mg/L, as compared in Fig. 4. The increasing rate of R_f was very high when HA increased from 6 mg/L to 10 mg/L, particularly. It means that DOM like as HA could drive membrane fouling more severely on the surface and inside the carbon fiber membrane, as increasing HA concentration in water, and specifically at high HA concentration. As summarized in Table 6, the $R_{f,180}$ value after 180 min operation at HA 10 mg/L was $6.998 \times 10^9 \text{ kg m}^{-2} \text{ s}^{-1}$, which was 3.94 times higher than $1.775 \times 10^9 \text{ kg m}^{-2} \text{ s}^{-1}$ of the $R_{f,180}$

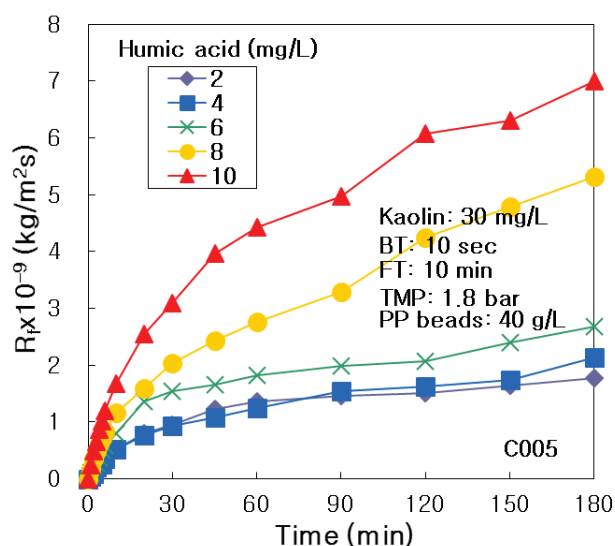


Fig. 4. Effect of HA on resistance of membrane fouling in hybrid water treatment process of tubular carbon fiber UF and PP beads.

value at HA 2 mg/L. In the previous study [20] for the hybrid water treatment process of the same tubular carbon fiber UF and the photocatalyst-coated PP beads, $R_{f,180}$ at HA 10 mg/L was $4.443 \times 10^9 \text{ kg m}^{-2} \text{ s}^{-1}$, which was 1.90 times higher than $2.338 \times 10^9 \text{ kg m}^{-2} \text{ s}^{-1}$ of the $R_{f,180}$ value at HA 2 mg/L. The $R_{f,180}$ increasing rate of the previous result [20] was lower than that of this study, because the photocatalyst-coated PP beads could control more excellently the membrane fouling, which was affected less severely by DOM, than that in this hybrid process with the PP beads not including photocatalyst. The resistance of irreversible membrane fouling (R_{if}) did not show the clear trend as increasing HA; however, it was the maximum at HA 10 mg/L. By the way, the resistance of reversible membrane fouling (R_{rf}) increased dramatically as increasing HA, as shown in Table 6. It means that the high DOM concentration could affect primarily the reversible membrane fouling in this hybrid water treatment process of the carbon fiber UF and PP beads.

As compared in Fig. 5, the dimensionless permeate flux (J/J_0) was plotted according to HA concentration. The J/J_0 tended to decrease as increasing HA concentration from 2 to 10 mg/L, specifically from 6 to 8 mg/L, because of the membrane fouling development by the more DOM. As arranged in Table 6, the final J/J_0 after 180 min operation (J_{180}/J_0) was 0.241 at HA 2 mg/L, which was 2.84 times higher than 0.085 at HA 10 mg/L. In the previous work [20] of the photocatalyst-coated PP beads, the J_{180}/J_0 was 0.312 at HA 2 mg/L, which was 1.34 times higher than 0.232 at HA 10 mg/L. It means that the photocatalyst-coated PP beads could prohibit more successfully the membrane fouling by HA, and maintained higher flux in the hybrid water treatment process than the PP beads. Finally, the DOM could affect less severely on the flux reduction in the hybrid process with the photocatalyst-coated PP beads than that with the PP beads.

Table 6

Effect of humic acid concentration on filtration factors in the hybrid process of tubular carbon fiber UF and PP beads and TiO₂-coated PP beads

Adsorption media	Humic acid (mg/L)	2	4	6	8	10
PP beads	$R_m \times 10^{-9}$ (kg m ⁻² s ⁻¹)	0.429	0.397	0.418	0.418	0.415
	$R_b \times 10^{-9}$ (kg m ⁻² s ⁻¹)	0.133	0.185	0.174	0.174	0.237
	$R_{f,180} \times 10^{-9}$ (kg m ⁻² s ⁻¹)	1.775	2.135	2.676	5.311	6.998
	$R_{f_j} \times 10^{-9}$ (kg m ⁻² s ⁻¹)	0.389	0.016	0.215	0.194	0.768
	$R_{f_f} \times 10^{-9}$ (kg m ⁻² s ⁻¹)	1.386	2.119	2.461	5.118	6.230
	J_0 (L m ⁻² h ⁻¹)	1129	1092	1073	1072	974
	J_{180} (L m ⁻² h ⁻¹)	272	234	194	108	83
	J_{180}/J_0	0.241	0.214	0.181	0.100	0.085
	V_T (L)	4.98	4.89	3.83	2.67	1.92
	TiO ₂ -coated PP beads [20]	$R_m \times 10^{-9}$ (kg m ⁻² s ⁻¹)	1.008	1.049	1.043	1.021
$R_b \times 10^{-9}$ (kg m ⁻² s ⁻¹)		0.000	0.229	0.134	0.029	0.295
$R_{f,180} \times 10^{-9}$ (kg m ⁻² s ⁻¹)		2.338	2.723	3.430	4.429	4.443
J_0 (L m ⁻² h ⁻¹)		600	497	539	605	474
J_{180} (L m ⁻² h ⁻¹)		187	159	138	116	110
J_{180}/J_0		0.312	0.319	0.256	0.192	0.232
V_T (L)		3.54	3.20	2.80	2.55	2.15

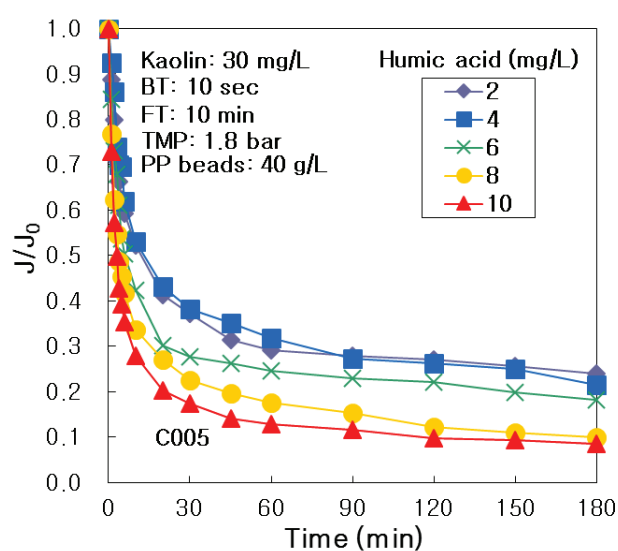


Fig. 5. Effect of HA on dimensionless permeate flux in hybrid water treatment process of tubular carbon fiber UF and PP beads.

In addition, the total permeate volume (V_T) of 4.98 L at HA 2 mg/L was 2.59 times higher than 1.92 L of V_T at HA 10 mg/L, as shown in Table 6. In the result [20] of the photocatalyst-coated PP beads, V_T at HA 2 mg/L was 3.54 L, which was 1.65 times higher than 2.15 L of V_T at HA 10 mg/L. The effect of HA on V_T was a little higher in the hybrid process with the PP beads than that with the photocatalyst-coated PP, because the photocatalyst-coated PP could control more efficiently the flux declining than

the PP beads; however, the V_T values at the PP beads were lower than those at the photocatalyst-coated PP, because the membrane resistances (R_m) at the PP beads were higher than those at the photocatalyst-coated PP beads. Finally, it could be found out that DOM, like HA, should be one of the main factors affecting membrane fouling in this hybrid process of the carbon fiber UF membrane and the PP beads.

As seen in Table 7, the treatment efficiency of turbidity was almost constant, independent of HA concentration. In addition, in the result [20] with the photocatalyst-coated PP, the treatment efficiency of turbidity was almost constant, too. It means that the organic matters could not affect the treatment of suspended particles like kaolin in the hybrid process of the tubular carbon fiber membrane and the PP beads or the photocatalyst-coated PP beads.

As compared in Table 8, the treatment efficiency of UV₂₅₄ absorbance, which means the concentration of DOM, was the maximum 69.3% at HA 6 mg/L. The treated water quality of HA increased less slowly than the feed water quality from 2 mg/L to 6 mg/L of HA, because most of DOM could be adsorbed on fouling materials inside the membrane or retained by cake layer on the membrane, and the remained things passed through the membrane adsorbed or oxidized by the PP beads and UV. However, the treated water quality of HA increased more rapidly than the feed water quality above 6 mg/L of HA, because most of DOM passed through the membrane and could not be treated by adsorption or photo-oxidation by the PP beads and UV. In the previous work [20] for the hybrid process of the same tubular carbon fiber MF membrane and the photocatalyst-coated PP beads, the treatment efficiency of DOM was the maximum 77.1% at HA 8 mg/L. The treated water quality of HA increased less slowly than the feed water quality from 2 mg/L to

Table 7

Water quality and treatment efficiency of turbidity in the hybrid process of tubular carbon fiber UF and PP beads for the effect of humic acid concentration

Experimental condition		Turbidity (NTU)				Average treatment efficiency (%)	
Kaolin (mg/L)	Humic acid (mg/L)	Feed water		Treated water		Adsorption media	
		Range	Average	Range	Average	PP beads	TiO ₂ -coated PP beads [20]
30	2	27.6~31.5	29.4	0.239~0.279	0.256	99.1	97.1
	4	21.0~23.2	21.8	0.356~0.611	0.434	98.0	98.1
	6	33.3~38.9	36.2	0.323~0.493	0.413	98.9	98.1
	8	23.1~32.8	30.3	0.392~0.837	0.599	98.0	97.2
	10	35.3~37.3	36.2	0.274~0.486	0.355	99.0	98.3

Table 8

Water quality and treatment efficiency of UV₂₅₄ absorbance in the hybrid process of tubular carbon fiber UF and PP beads for the effect of humic acid concentration

Experimental condition		UV ₂₅₄ absorbance (cm ⁻¹)				Average treatment efficiency (%)	
Kaolin (mg/L)	Humic acid (mg/L)	Feed water		Treated water		Adsorption media	
		Range	Average	Range	Average	PP beads	TiO ₂ -coated PP beads [20]
30	2	0.035~0.042	0.039	0.009~0.019	0.039	67.2	72.0
	4	0.077~0.086	0.083	0.014~0.046	0.028	65.9	79.0
	6	0.118~0.154	0.138	0.019~0.076	0.043	69.3	74.2
	8	0.205~0.220	0.213	0.058~0.116	0.087	59.3	77.1
	10	0.248~0.266	0.255	0.063~0.144	0.100	60.9	76.9

8 mg/L of HA, because the remained DOM passed through the membrane adsorbed or oxidized more efficiently by the photocatalyst-coated PP beads and UV than this study with the PP beads.

4. Conclusions

In this study, treatment portions of membrane filtration, photocatalyst adsorption, and photo-oxidation with/without the PP beads were investigated by comparing the treatment efficiencies of (UF), (UF+UV), (UF+PP) and (UF+PP+UV) processes in the hybrid process of the tubular carbon fiber UF and PP beads with periodic water back-flushing. The PP beads did not contain any photocatalyst. In addition, the effect of DOM was investigated on membrane fouling in this hybrid water treatment process. The results were compared with those of the previous study [19,20] using the hybrid process of the same tubular carbon fiber MF and the photocatalyst-coated PP beads. In conclusion, the following results could be found out.

- (1) The adsorption by the PP beads could control effectively the membrane fouling, and the effect of photo-oxidation by UV irradiation on the membrane fouling, especially the reversible membrane fouling, was lower than that of the adsorption by the PP

beads. The adsorption and photo-oxidation by the photocatalyst-coated PP beads and UV irradiation in the result [19] could control the membrane fouling more efficiently than the adsorption by the PP beads in this study.

- (2) The roles of adsorption and photo-oxidation by the PP beads and UV were not important for the turbid matter treatment, in the hybrid process of the PP beads or the photocatalyst-coated PP beads. Kaolin could not be removed effectively by the adsorption and photo-oxidation by the PP beads and UV. Then, the role of adsorption by the PP beads was more important than those of UV photo-oxidation and photo-oxidation with the PP beads; however, that of photo-oxidation by the photocatalyst-coated PP beads was more dominant than the adsorption, in the DOM treatment.
- (3) DOM like as HA could drive membrane fouling more severely on the surface and inside the carbon fiber membrane as increasing HA concentration. The high DOM concentration could affect primarily the reversible membrane fouling in this hybrid water treatment process of the carbon fiber UF and PP beads. The photocatalyst-coated PP beads could control the membrane fouling more excellently than that in this hybrid process with the PP beads not including photocatalyst.

- (4) The organic matters could not affect the turbid matter treatment in the hybrid process of the carbon fiber UF and the PP beads with or without photocatalyst. The DOM treatment efficiency was the maximum at HA 6 mg/L. The treated water quality of HA increased less slowly than the feed water quality from 2 mg/L to 6 mg/L of HA, because most of DOM could be adsorbed or retained by the membrane, and the remained things passed through the membrane adsorbed or oxidized by the PP beads and UV; however, above 6 mg/L of HA, most of DOM passed through the membrane could not treated by adsorption or photo-oxidation.

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