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Roles of polypropylene beads and pH in hybrid water treatment of carbon fiber membrane and PP beads with water back-flushing

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Abstract. The roles of polypropylene (PP) beads and pH on membrane fouling and treatment efficiency were investigated in a hybrid advanced water treatment process of tubular carbon fiber membranes (ultrafiltration (UF) or microfiltration (MF)) and PP beads. The synthetic feed including humic acid and kaolin flowed inside the membrane, and the permeated contacted the PP beads fluidized in the space between the membrane and the module with UV irradiation and periodic water back-flushing. In the hybrid process of UF (0.05 μm) and PP beads, final resistance of membrane fouling (R_f) after 180 min increased as PP beads increased. The turbidity treatment efficiency was the maximum at 30 g/L; however, that of dissolved organic matters (DOM) showed the highest at PP beads 50 g/L. The R_f strengthened as pH of feed increased. It means that the membrane fouling could be inhibited at low alkali condition. The treatment efficiency of turbidity was almost constant independent of pH; however, that of DOM showed the maximum at pH 5. For MF (0.1 μm), the final R_f was the minimum at PP beads 40 g/L. The treatment efficiencies of turbidity and DOM were the maximum at PP beads 10 g/L.

Keywords: hybrid process; carbon fiber; membrane; polypropylene bead; pH; water back-flushing

1. Introduction

During the past few decades, membrane separation process for separation and purification has been developed dramatically. It can separate and concentrate all pollutants simultaneously in water by the retention of its microspores without secondary pollution and phase change. Additionally, its equipment is compact, easy to operate and capable of continuous operation at room temperature with the advantage of low energy consumption (Meng *et al.* 2009). However, membrane fouling due to the adsorption-precipitation of organic and inorganic compounds onto membranes leads to decrease the permeate flux, to increase membrane cleaning costs, and to reduce the membrane life. Techniques for controlling membrane fouling remain inadequate, which is the major obstacle in the successful implementation of membrane separation technology, although considerable progress has been made in membrane fouling (Liu *et al.* 2010, Yoon *et al.* 2005). Natural organic matter (NOM) is a primary component of fouling in low-pressure membrane filtration. Various preventive measures to interfere with NOM fouling have been developed and extensively tested, such as coagulation, oxidation, ion exchange, carbon adsorption, and mineral oxide adsorption (Cui and Choo 2014). In this study, the periodic water back-flushing was performed to prevent the membrane fouling.

Recently the hybrid technology of membrane separation and photo-oxidation by UV irradiation can solve the membrane fouling problem effectively (Tian *et al.* 2017). 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 other hand, the pollutants are oxidized by UV irradiation, 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 photo-oxidation efficiency and achieve excellent effluent quality. Also, effect of UV-irradiation on the nano-hybrid PES-NanoZnO membrane in term of flux and rejection efficiency has been discussed (Kusworo 2017). In addition, a comparison of the efficiency of treatment of surface water in hybrid systems coupling various advanced oxidation processes and ultrafiltration was presented (Szymański 2017). In this study, a hybrid process of ceramic membrane and pure PP beads with UV irradiation was applied for advanced water treatment.

Ceramic membranes used in this study maintain competitive prices compared with polymer membrane, and have a lot of advantages, which are mechanical, thermal and chemical resistance, and long life time. Nowadays the ceramic membranes have been applied broadly in the water or wastewater in the world (Agana *et al.* 2013, Liu *et al.* 2016, Zhang *et al.* 2013a). The influence of the characteristics of soluble algal organic matter (AOM) on the fouling of a 7-channel tubular ceramic microfiltration membrane was investigated at lab scale (Zhang *et al.* 2013b). The influence of the interaction between aquatic

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humic substances and the algal organic AOM derived from Microcystis aeruginosa on the fouling of a ceramic microfiltration (MF) membrane was studied (Zhang *et al.* 2018).

To oxidize most organic compounds, especially non-biodegradable organic contaminants, by mineralizing them to small inorganic molecules, photo-oxidation has the characteristics of high efficiency, low energy consumption and a wide range of application, and is one of excellent technologies of water pollution control. For this reason, photo-oxidation technology applied in this study has been applied broadly (Benito *et al.* 2017, Khuzwayo and Chirwa 2017, Milelli *et al.* 2017, Morgan *et al.* 2017, Semitsoglou-Tsiapou *et al.* 2016, Wu *et al.* 2009). In addition, degradation of humic acid (HA), which was contained in a synthetic solution used in this study, via photoelectrocatalysis (PEC) process and corresponding disinfection byproduct formation potential (DBPFP) were investigated, and the PEC process was found to be effective in reducing dissolved organic carbon concentration (Li *et al.* 2011).

In our research group, the results for effect of operating conditions in the hybrid water treatment process of various ceramic membranes and titanium dioxide (TiO_2) photocatalyst-coated polypropylene (PP) were published in Desal. Water Treat. (Kim and Park 2017) and Membr. J. (Park *et al.* 2016). On the other hand, roles of adsorption and photo-oxidation in hybrid water treatment process of tubular carbon fiber ultrafiltration and pure PP beads with UV irradiation and water back-flushing was reported by our group in Desal. Water Treat. (Park and Park 2017).

In this study, the effects of pure PP beads concentration and pH were investigated on membrane fouling in this hybrid water treatment process of tubular carbon fiber UF/MF membranes and PP beads with water back-flushing, which was the first research in the world. The periodic water back-flushing was performed during 10 sec per 10 min's filtration to reduce membrane fouling. A hybrid module was composed of the carbon fiber UF/MF membranes and the PP beads, which were fluidized between the gap of carbon fiber membrane and the acryl module case. The results of pH effect were compared with those of the previous study (Park and Song 2017) for the hybrid process of the tubular alumina MF (pore size: 0.1 μm) and pure PP beads with air back-flushing, to investigate the pH effect on membrane fouling and treatment efficiency depending on membrane materials.

2. Experiments

2.1 Materials

The tubular carbon fiber UF (C005) and MF (C010) membranes used in the study, were imported from Koch (U.S.A.), and their pore sizes were 0.05 and 0.10 μm, respectively. The specifications of these carbon fiber membranes were arranged in Table 1. The size of polypropylene (PP) beads employed in 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 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 acryl module by 2 UV lamps (F8T5BLB, Sankyo, Japan).

Table 1 Specifications of the tubular carbon fiber UF (C005) and MF (C010) membranes used in this study

Membrane model	C005/C010
Pore size (μm)	0.05/0.1
Outer diameter (mm)	8
Inner diameter (mm)	6
Length (mm)	250
Surface area (cm^2)	47.1
Material	Carbon fiber
Company	Koch (U.S.A)

2.2 Hybrid membrane module

The hybrid module was composed by packing the PP beads between the module inside and outside of the alumina membrane, to remove the turbidity and DOM. Additionally, to prevent the PP beads loss into the treated water tank, 100 mesh (0.150 mm) sieve, 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.

2.3 Experimental procedure

Fig. 1 is the advanced water treatment process using a hybrid module (6) of tubular carbon fiber UF/MF membrane and the pure PP beads, which was used at the previous study (Amarsanaaa *et al.* 2013). 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 acryl module case. Then, the feed tank (1) 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 (3) (Model 1146, VWR, USA). Additionally, the synthetic feed water was continuously mixed by a stirrer (4) to maintain the homogeneous condition of the feed water, and it was caused to flow into the inside of the tubular carbon fiber UF/MF membrane by a pump (2) (Procon, Standex Co., U.S.A.). The feed flow rate was measured by a flowmeter (5) (NP-127, Tokyo Keiso, Japan). The flow rate and pressure of the feed water that flowed into the hybrid module was constantly maintained by controlling valves (9) of both the bypass pipe of the pump (2) and the concentrate pipe. The permeate flux treated by both the tubular carbon fiber UF/MF membrane and the PP beads was measured by an electric balance (11) (Ohaus, U.S.A.). 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

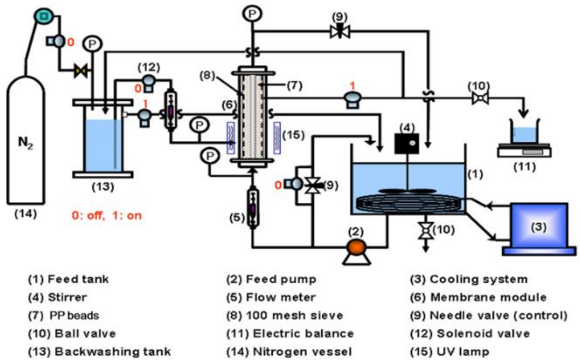


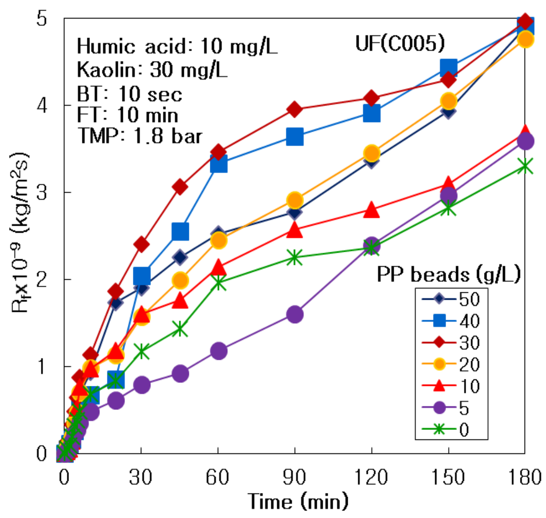
Fig. 1 Apparatus of hybrid water treatment process of tubular carbon fiber UF/MF membrane and PP beads with periodic water back-flushing (Amarsanaaa *et al.* 2013)

brush inside the tubular membrane, and the permeate flux was measured to calculate the resistances of irreversible and reversible membrane fouling.

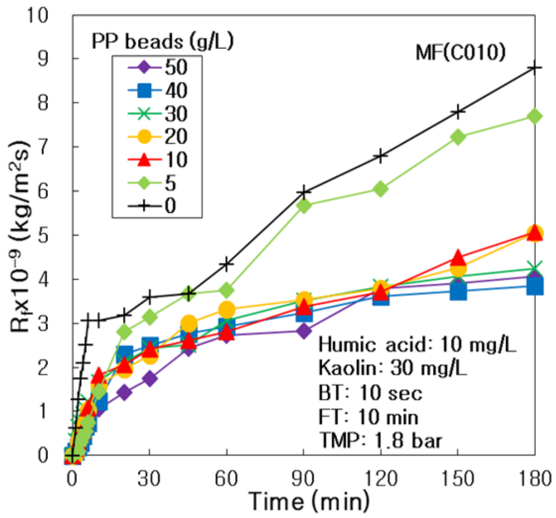
Kaolin and HA were fixed at 30 mg/L and 10 mg/L, individually in the synthetic feed water to investigate the roles of PP beads concentration and pH. The water back-flushing time (BT) and filtration time (FT) were fixed at 10 sec and 10 min, respectively. The permeate flux (J) were measured, and resistance of the membrane fouling (R_f) calculated during total operation time of 180 min under each condition. In all experiments, trans-membrane pressure (TMP) was maintained constant at 1.8 bar, the water back-flushing pressure at 2.5 bar, the feed flow rate at 1.0 L/min, and the feed water temperature at 20°C. To investigate the effect of PP beads, the PP beads concentration was changed from 0 to 50 g/L in the module. And pH was changed from 5 to 9 in the synthetic feed water to inspect pH effect.

To evaluate the treatment efficiencies of turbid materials and DOM, the quality of feed and treated water was analyzed per each experiment. To measure turbid materials and DOM, turbidity was measured by a turbidimeter (2100N, Hach, U.S.A.) and UV_{254} absorbance was analyzed by a UV spectrophotometer (Genesys 10 UV, Thermo, U.S.A). 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}) correspondingly. Before measuring UV_{254} absorbance, each sample was filtered by 0.2 μm syringe filter to remove turbid materials.

After finishing each experiment, all of the synthetic solution was 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 PP beads and the membrane were separated from the module, and the membrane was heated at 550°C in a furnace to combust fouling materials inside the membrane during 30 min. After cooling the membrane, it was immersed in a nitric acid (HNO_3) of 15% during 24 hours, and in a sodium hydroxide (NaOH) solution of 0.25 N during 3 hours for washing out organic or inorganic pollutants, and kept in distilled water during 24 hours for rinsing. Before operating a new experiment, the water permeate flux (J_w) was measured for checking the membrane recovery when a normal operation was performed with distilled water, after the recovered



(a) UF (C005)



(b) MF (C010)

Fig. 2 Effect of PP beads concentration on resistance of membrane fouling in hybrid process of tubular carbon fiber UF (C005) / MF (C010) membrane and pure PP beads

membrane was installed inside the module. The recovered membrane was used in all of the experiments to reduce the influence of membrane condition on the treatment efficiency.

3. Results and discussions

The roles of pure PP beads concentration and pH were investigated in the hybrid water treatment process of tubular carbon fiber UF/MF membrane and PP beads with periodic water back-flushing. Resistances 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 as the previous study (Amarsanaaa *et al.* 2013). Resistances of the irreversible and reversible membrane fouling (R_{if}, R_{rf}) could be found from J data after physical washing using a brush inside the membrane.

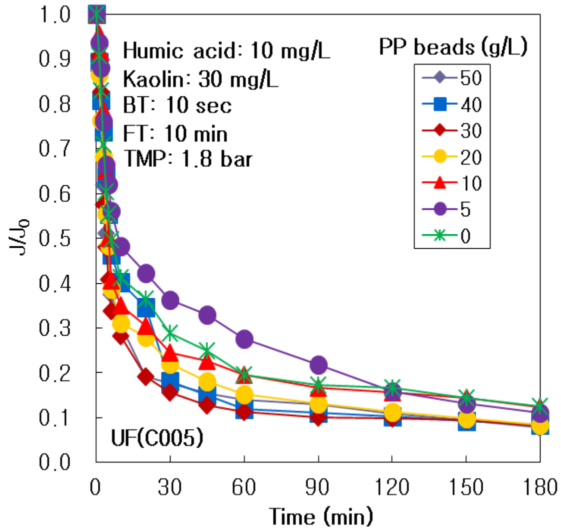
Table 2 Effect of pure PP beads on filtration factors for hybrid process of tubular carbon fiber UF/MF and PP beads with periodic water back-flushing (BT 10 sec, FT 10 min)

Membrane	PP beads (g/L)	0	5	10	20	30	40	50
UF (C005)	$R_m \times 10^{-9}$ (kg/m^{2}s)	0.413	0.409	0.409	0.411	0.403	0.405	0.403
	$R_b \times 10^{-9}$ (kg/m^{2}s)	0.062	0.043	0.119	0.031	0.042	0.048	**0.009**
	$R_{f,180} \times 10^{-9}$ (kg/m^{2}s)	**3.306**	3.596	3.683	4.767	4.967	4.918	4.892
	$R_{if} \times 10^{-9}$ (kg/m^{2}s)	0.008	0.004	0.021	0.006	0.015	0.020	**0.002**
	$R_{rf} \times 10^{-9}$ (kg/m^{2}s)	**3.298**	3.596	3.662	4.761	4.953	4.898	4.890
	J_0 (L/m^{2}hr)	1336	1407	1221	1435	1426	1401	**1543**
	J_{180} (L/m^{2}hr)	168	157	151	122	117	118	120
	J_{180}/J_0	**0.126**	0.112	0.124	0.085	0.082	0.084	0.078
	V_T (L)	4.13	**4.99**	3.54	3.35	2.73	3.16	3.29
MF (C010)	$R_m \times 10^{-9}$ (kg/m^{2}s)	0.407	0.389	0.413	0.411	0.384	0.404	0.404
	$R_b \times 10^{-9}$ (kg/m^{2}s)	0.320	0.076	0.054	0.030	**0.029**	0.111	0.157
	$R_{f,180} \times 10^{-9}$ (kg/m^{2}s)	8.805	7.700	5.062	5.051	4.249	**3.856**	4.066
	$R_{if} \times 10^{-9}$ (kg/m^{2}s)	0.364	0.080	0.102	0.055	**0.001**	0.088	0.008
	$R_{rf} \times 10^{-9}$ (kg/m^{2}s)	8.441	7.620	4.959	4.996	4.248	**3.768**	4.058
	J_0 (L/m^{2}hr)	874	1364	1359	1438	1539	1234	1132
	J_{180} (L/m^{2}hr)	69	78	115	116	136	**145**	137
	J_{180}/J_0	0.079	0.057	0.085	0.080	0.089	0.118	**0.121**
	V_T (L)	1.69	2.19	2.69	2.70	2.69	2.81	**2.94**

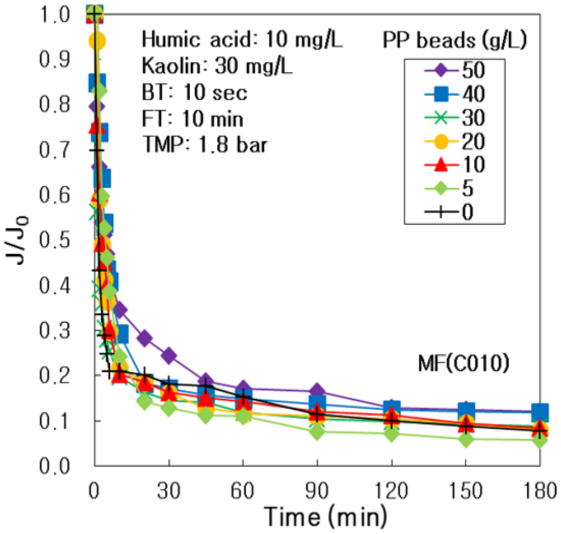
3.1 Effect of pure PP beads concentration

The previous result (Park and Park 2017) reported that the membrane fouling increased dramatically as HA increased from 2 to 10 mg/L at kaolin 30 mg/L in the same hybrid process of the carbon fiber UF membrane and PP beads with water back-flushing. Therefore, the effect of PP beads concentration was investigated at the most severe HA 10 mg/L condition at kaolin 30 mg/L and pH 7. The resistances of membrane fouling (R_f) showed the highest at 50 g/L during 180 min's operation, and the lowest at 5 g/L until 120 min and at 0 g/L of PP beads after 120 min in the hybrid water treatment process of carbon fiber UF (C005) membrane and pure PP beads, as compared in Fig. 2(a). However, R_f maintained the maximum at 0 g/L, and the minimum at 50 g/L until 120 min and at 40 g/L of PP beads after 120 min in the hybrid process of carbon fiber MF (C010) membrane and pure PP beads, as compared in Fig. 2(b). It means that the effect of PP beads concentration on membrane fouling depended on the membrane pore size in this hybrid process of carbon fiber membrane and PP beads.

As arranged in Table 2, the resistance of membrane (R_m) was controlled at constant value by combustion at a furnace and washing as acid and alkali solution. For the hybrid process of UF membrane and PP beads, the resistance of



(a) UF (C005)



(b) MF (C010)

Fig. 3 Effect of PP beads concentration on dimensionless permeate flux in hybrid process of tubular carbon fiber UF (C005) / MF (C010) membrane and pure PP beads

boundary layer (R_b), which was produced by concentration polarization on the membrane surface, was the lowest at 50 g/L of PP beads. It means that the colliding more PP beads frequently on the membrane surface could reduce the concentration polarization. The final R_f ($R_{f,180}$) after 180 min was the highest 4.892×10^9 kg/m^{2}s at 50 g/L, which was 1.48 times higher than 3.306×10^9 kg/m^{2}s of the $R_{f,180}$ at 0 g/L of PP beads. The resistance of reversible membrane fouling (R_{rf}) was the lowest at 0 g/L, and the highest at 50 g/L of PP beads; however, the resistance of irreversible membrane fouling (R_{if}) was the minimum at 50 g/L and the maximum at 10 g/L of PP beads. It means that the irreversible membrane fouling could be inhibited at 50 g/L of PP beads, because the optimal amount of PP beads captured the turbid or organic materials by adsorption.

For the hybrid process of MF membrane and PP beads, the R_b was the lowest at 30 g/L and the highest at 0 g/L. The boundary layer thickness could be reduced for the MF,

Table 3 Water quality and treatment efficiency of turbidity in the hybrid process of tubular carbon fiber UF/MF and pure PP beads for effect of the PP beads concentration with periodic water back-flushing (BT 10 sec, FT 10 min)

Membrane	PP beads (g/L)	Turbidity (NTU)				Average treatment efficiency (%)
		Feed water		Treated water		
		Range	Average	Range	Average	
UF (C005)	0	46.4~49.5	48.1	0.497~0.862	0.677	98.6
	5	37.7~43.4	39.3	0.442~0.653	0.576	98.5
	10	41.3~47.4	44.1	0.308~.0663	0.385	99.1
	20	34.1~35.7	34.6	0.498~0.941	0.720	97.9
	30	32.2~35.2	33.8	0.203~0.313	0.255	**99.3**
	40	32.7~34.8	33.6	0.292~0.564	0.445	98.7
	50	34.1~37.1	35.4	0.421~0.701	0.571	98.4
MF (C010)	0	27.8~32.1	31.3	0.167~0.429	0.292	99.1
	5	34.3~36.4	34.8	0.254~0.724	0.361	99.0
	10	47.3~54.4	49.8	0.257~0.409	0.308	**99.4**
	20	27.8~29.6	28.6	0.217~0.896	0.395	98.6
	30	29.3~31.7	31.1	0.394~0.628	0.526	98.3
	40	24.7~26.1	25.2	0.266~0.468	0.354	98.6
	50	25.2~26.6	26.0	0.248~0.456	0.347	98.7

Table 4 Water quality and treatment efficiency of DOM (UV_{254} absorbance) in the hybrid process of tubular carbon fiber UF/MF and pure PP beads for effect of the PP beads concentration with periodic water back-flushing (BT 10 sec, FT 10 min)

Membrane	PP beads (g/L)	UV_{254} absorbance (cm^{-1})				Average treatment efficiency (%)
		Feed water		Treated water		
		Range	Average	Range	Average	
UF (C005)	0	0.228~0.239	0.234	0.048~0.069	0.056	75.9
	5	0.283~0.293	0.288	0.055~0.085	0.066	77.0
	10	0.252~0.296	0.265	0.036~0.109	0.059	77.8
	20	0.322~0.346	0.333	0.041~0.072	0.056	83.2
	30	0.284~0.294	0.289	0.034~0.071	0.051	82.3
	40	0.297~0.314	0.305	0.037~0.075	0.054	82.4
	50	0.265~0.282	0.276	0.026~0.057	0.044	**84.1**
MF (C010)	0	0.345~0.406	0.377	0.109~0.202	0.161	57.3
	5	0.263~0.327	0.294	0.064~0.212	0.121	58.7
	10	0.236~0.271	0.252	0.048~0.063	0.055	**78.1**
	20	0.335~0.387	0.358	0.092~0.183	0.121	66.2
	30	0.299~0.427	0.343	0.007~0.036	0.124	63.9
	40	0.311~0.401	0.350	0.072~0.171	0.116	66.8
	50	0.316~0.375	0.342	0.127~0.257	0.183	46.6

because the higher pore size of MF passed the more HA materials through the MF membrane than the UF membrane. And the collision effect of PP beads on membrane surface to reduce the concentration polarization would be weak at high PP beads concentration for the MF. It means that the optimal PP beads concentration could be 30 g/L to control the concentration polarization. The $R_{f,180}$ and R_{rf} were the minimum at 40 g/L and the maximum at 0 g/L of PP beads; however, the R_{if} was the lowest at 30 g/L of PP beads. It is shown that the optimal PP beads condition could be 40 g/L to reduce the reversible membrane fouling; however, 30 g/L to decrease the irreversible membrane fouling.

The J/J_0, where J_0 was the initial permeate flux predicted using the initial two data by an extrapolation method, was compared to investigate a relative decline of permeate flux in Fig. 3. The J/J_0 show higher during 5-90 min at 5 g/L than those at other PP beads concentration for the carbon fiber UF process; however, a little higher at 50 g/L of PP beads and the curves were overlapped during 180 min's operation for the MF process. As arranged in Table 2, the J_0 decreased and J_{180} increased as increasing PP beads concentration for UF process, because the R_b was the minimum at 50 g/L of PP beads. Finally, the J_{180}/J_0 after 180 min's operation at 0 g/L of the PP beads was the maximum 0.126, which was 1.62 times higher than 0.078 at 50 g/L. However, the total permeated volume (V_T) was the highest 4.99 L at 5 g/L of PP beads for UF process, because J maintained higher all through the operation. For MF

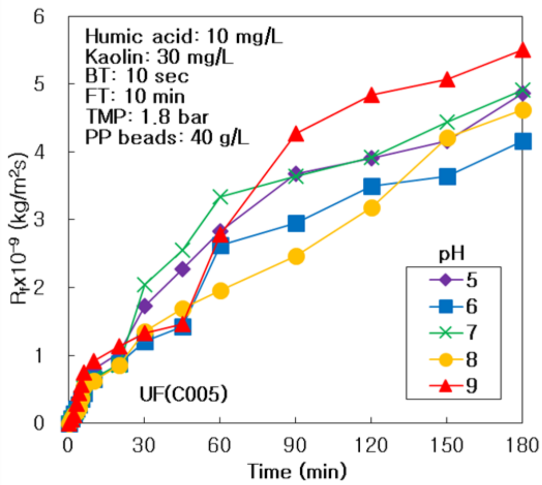


Fig. 4 Effect of pH on resistance of membrane fouling in hybrid process of tubular ceramic UF (C005) and pure PP beads

process, the J_0 was the highest at 30 g/L and the J_{180} was the maximum at 40 g/L, and the J_{180}/J_0 and V_T was the highest at 50 g/L of PP beads. It means that the more PP beads could reduce the membrane fouling by surface adsorption, and the highest permeate flux maintained during operation in the hybrid process of MF and PP beads.

As arranged in Table 3, the treatment efficiencies of turbidity were almost constant beyond 97.9% and 98.3% for

Table 5 Effect of pH on filtration factors for hybrid process of tubular carbon fiber UF (C005) and pure PP beads with periodic water back-flushing (BT 10 sec, FT 10 min)

Membrane	pH	5	6	7	8	9
Carbon fiber UF with water back-flushing	$R_m\times10^{-9}$ (kg/m^{2}s)	0.412	0.413	0.405	0.405	0.401
	$R_b\times10^{-9}$ (kg/m^{2}s)	**0.001**	0.047	0.048	0.020	0.003
	$R_{f,180}\times10^{-9}$ (kg/m^{2}s)	4.87	**4.16**	4.92	4.62	5.51
	$R_{if}\times10^{-9}$ (kg/m^{2}s)	**0.003**	0.010	0.020	0.006	0.020
	$R_{rf}\times10^{-9}$ (kg/m^{2}s)	4.865	**4.149**	4.898	4.616	5.487
	J_0 (L/m^{2}hr)	1537	1382	1401	1494	1573
	J_{180} (L/m^{2}hr)	120	**138**	118	126	107
	J_{180}/J_0	0.078	**0.099**	0.084	0.084	0.068
	V_T (L)	3.30	3.68	3.17	**3.85**	3.21
Alumina MF (pore size: 0.1 μm) with air back-flushing (Park and Song 2017)	$R_m\times10^{-9}$ (kg/m^{2}s)	0.571	0.597	0.596	0.597	0.589
	$R_b\times10^{-9}$ (kg/m^{2}s)	**0.005**	0.009	0.022	0.046	0.060
	$R_{f,180}\times10^{-9}$ (kg/m^{2}s)	**3.64**	4.10	6.55	6.97	8.74
	$R_{if}\times10^{-9}$ (kg/m^{2}s)	**0.201**	0.200	0.541	0.555	0.562
	$R_{rf}\times10^{-9}$ (kg/m^{2}s)	**3.44**	3.90	6.01	6.42	8.18
	J_0 (L/m^{2}hr)	1101	1048	1027	987	978
	J_{180} (L/m^{2}hr)	**151**	135	89	83	68
	J_{180}/J_0	**0.137**	0.129	0.086	0.084	0.069
	V_T (L)	2.93	**2.97**	1.94	1.93	1.78

UF and MF process respectively, independent of the pure PP beads concentration. However, those was the highest 99.3% at 30 g/L for UF process, and 99.4% at 10 g/L of PP beads for MF process. It means that the optimal PP beads concentration to reduce the turbid matter could depend on the pore size of membrane in this hybrid process.

As compared in Table 4, the treatment efficiency of DOM (UV_{254} absorbance) showed a trend to increase dramatically from 75.9% to 84.1% as increasing the PP beads concentration for UF process; however, that was the maximal 78.1% at 10 g/L of PP beads for MF process, and much lower 46.6-66.2% than 75.9-82.4% of UF process at other PP beads concentration. It proves that the more PP beads could adsorb the more efficiently DOM on the surface of PP beads for UF process; however, the optimal PP beads concentration was 10 g/L to remove DOM for MF process.

3.2 Effect of pH on membrane fouling and treatment efficiency

The pH of synthetic feed water was controlled by nitric acid (HNO_3) and sodium hydroxide (NaOH). As compared in Fig. 4 to investigate pH effect in UF process, the R_f showed the highest at pH 9 after 90 min and the lowest at pH 5 after 150 min, and finally have a trend to increase as increasing pH from 5 to 9. A s arranged in Table 5, the R_b

Table 6 Water quality and treatment efficiency of turbidity in the hybrid process of tubular carbon fiber UF (C005) and pure PP beads for effect of pH with periodic water back-flushing (BT 10 sec, FT 10 min)

Experimental condition			Turbidity (NTU)				Average treatment efficiency (%)	
Kaolin (mg/L)	Humic acid (mg/L)	pH	Feed water		Treated water		Carbon fiber UF with water back-flushing	Alumina MF (Park and Song 2017)
			Range	Average	Range	Average		
30	10	5	37.2~39.1	38.2	0.336~0.718	0.473	98.8	98.3
		6	37.2~39.7	38.3	0.327~0.578	0.463	98.8	98.6
		7	32.7~34.8	33.6	0.292~0.564	0.445	98.7	99.2
		8	36.1~43.7	40.7	0.323~0.468	0.424	99.0	99.3
		9	47.2~48.3	47.8	0.515~0.742	0.626	98.7	99.4

Table 7 Water quality and treatment efficiency of DOM (UV_{254} absorbance) in the hybrid process of tubular carbon fiber UF (C005) and pure PP beads for effect of pH with periodic water back-flushing (BT 10 sec, FT 10 min)

Experimental condition			UV_{254} absorbance (cm^{-1})				Average treatment efficiency (%)	
Kaolin (mg/L)	Humic acid (mg/L)	pH	Feed water		Treated water		Carbon fiber UF with water back-flushing	Alumina MF (Park and Song 2017)
			Range	Average	Range	Average		
30	10	5	0.344~0.357	0.348	0.037~0.082	0.052	**85.1**	73.6
		6	0.256~0.271	0.263	0.032~0.067	0.049	81.6	73.7
		7	0.297~0.314	0.305	0.037~0.075	0.054	82.4	74.5
		8	0.284~0.308	0.294	0.039~0.068	0.052	82.3	75.4
		9	0.391~0.425	0.402	0.055~0.088	0.074	81.7	75.7

and R_{if} were the minimum at pH 5; however, the $R_{f,180}$ and R_{rf} were the lowest at pH 6. Conclusively, the $R_{f,180}$ was the highest 5.51×10^9 kg/m^{2}s at pH 9, which was 1.32 times higher than 4.16×10^9 kg/m^{2}s at pH 6. The R_{rf} and R_{if} were the maximum at pH 9. It means that the reversible and irreversible membrane fouling, and concentration polarization could be inhibited at acid condition, because both of membrane and humic materials had a negative surface charge at acid condition below pH 7, as reported that the surface charge of ZrO_2 membrane was changed depending on pH (Zhao *et al.* 2013). The surface charge of carbon fiber membranes used in this study could be changed depending on pH, because those were the similar ceramic membranes as ZrO_2 membrane.

The optimal condition of PP beads concentration was 50 g/L; however, the previous result (Park and Song 2017) of pH effect for the hybrid process of tubular alumina MF (pore size: 0.1 μm) and PP beads with air back-flushing, which was reported at PP beads 40 g/L. It could be compared with our result for the hybrid process of carbon fiber UF membrane and PP beads with water back-flushing in Tables 5-7. The focus on comparing our result of pH effect for the carbon fiber UF membrane and the previous

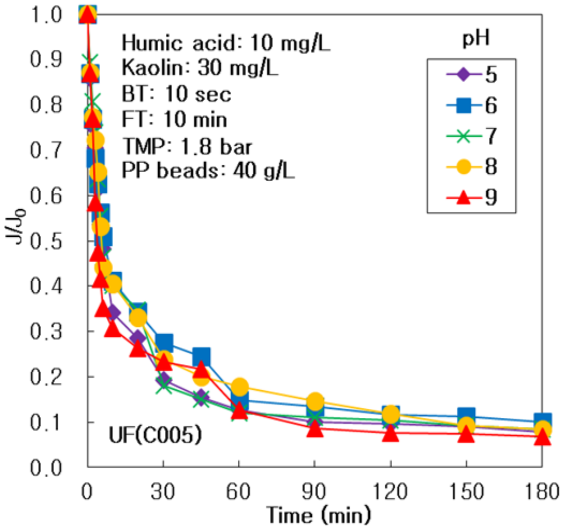


Fig. 5 Effect of pH on dimensionless permeate flux in hybrid process of tubular ceramic UF (C005) and pure PP beads

result (Park and Song 2017) for the alumina MF was to investigate the pH effect on membrane fouling and treatment efficiency depending on membrane materials, because the pore size of the carbon fiber UF and the carbon fiber UF was almost similar. In the previous work (Park and Song 2017), the R_f had a trend to increase as increasing pH for 5 to 9, and the curves of pH 5 and 6, and pH 7 and 8 were almost overlapped during 180 min of operation. The both of R_{if} and R_{rf} increased dramatically as increasing pH from 5 to 9. It means that the trends of pH effect on membrane fouling in the hybrid process using alumina MF membrane with air back-flushing agreed with this result of the hybrid process using the carbon fiber UF membrane with water back-flushing.

As compared in Fig. 5 to investigate the pH effect on relative permeate flux, the J/J_0 showed a trend to decrease a little as increasing pH from 5 to 9. The J_{180}/J_0 after 180 min of operation at pH 6 was 0.099, which was 1.46 times higher than 0.068 at pH 9, as shown in Table 5. And the J_{180} was the maximum at pH 6, and the minimum at pH 9. It means that the high permeate flux could be acquired at pH 6, because the membrane fouling was inhibited by repulsion force between the carbon fiber membrane and humic materials, which had the same negative surface charge, as reported that the surface charge of ZrO_2 membrane was changed depending on pH (Zhao *et al.* 2013). The J_{180} at pH 6 could be the higher than that at pH 5 in the same acidic range of pH 5-6, because the negative membrane charge could not decrease in absolute value with increasing pH. Finally, the V_T was the highest of 3.85 L at pH 8, because the permeate flux could maintain highly during operation. In the previous work (Park and Song 2017) with the alumina tubular MF, the J_{180}/J_0 of 0.137 after 180 min of operation at pH 5 was 1.99 times higher than 0.069 at pH 9. However, the V_T was the highest of 2.97 L at pH 6. It means that the pH effect on J/J_0 in the hybrid process using alumina MF membrane matched almost with these results of the hybrid process using the carbon fiber UF membrane, except of V_T.

As arranged in Table 6, the treatment efficiency of turbidity was almost constant above 98.7%, independent of pH. It means that pH could not affect treating the turbid matter like as kaolin for carbon fiber UF process with water back-flushing. However, in the previous work (Park and Song 2017) with the alumina tubular MF, it increased slightly from 98.3% to 99.4%, as increasing pH from 5 to 9. It means that the turbid matter could be removed more effectively at high pH condition, because the membrane fouling was more severely as increasing pH in the hybrid process using the alumina MF membrane with air back-flushing.

As compared in Table 7, the treatment efficiency of DOM was the highest at pH 5. It proves that DOM could be removed effectively at acid condition, because of repulsion force between the carbon fiber membrane and humic materials. However, in the previous work (Park and Song 2017) for the hybrid process of alumina tubular MF and PP beads with air back-flushing, it increased a little as increasing pH from 5 to 9. It means that DOM could be removed more effectively by adsorption, UV oxidation and membrane filtration, because the membrane fouling was more severely as increasing pH in in the hybrid process using the alumina MF membrane.

5. Conclusions

In this study, the effects of PP bead concentration and pH were investigated on membrane fouling and treatment efficiency of turbid matter or DOM in the hybrid process of the tubular carbon fiber UF/MF membrane and PP beads with periodic water back-flushing. The results of pH effect were compared with those of the previous study (Park and Song 2017) for the hybrid process of the tubular alumina MF and PP beads with air back-flushing. In conclusion, the following results could be extracted out from these investigation.

1) The effect of PP beads concentration on membrane fouling depended on the membrane pore size in this hybrid process of carbon fiber membrane and PP beads. For the hybrid process of UF membrane and PP beads, the colliding more PP beads frequently on the membrane surface could reduce the concentration polarization. The irreversible membrane fouling could be inhibited at 50 g/L of PP beads, because the optimal amount of PP beads captured the turbid or organic materials by adsorption. However, the optimal PP beads could be 5 g/L for the hybrid water treatment process of carbon fiber UF and PP beads, because of the maximum total permeate volume acquired during operation.

2) For the hybrid process of MF membrane and PP beads, the optimal PP beads condition could be 40 g/L to reduce the reversible membrane fouling; however, 30 g/L to decrease the irreversible membrane fouling. The more PP beads could reduce the membrane fouling by surface adsorption, and the highest permeate flux maintained during operation. However, the optimal PP beads could be 50 g/L for the hybrid process of carbon fiber MF and PP beads, because of the highest total permeate volume.

3) The optimal PP beads concentration to reduce the

turbid matter could depend on the pore size of membrane in this hybrid process. The more PP beads could adsorb the more efficiently DOM on the surface of PP beads for UF process; however, the optimal PP beads concentration was 10 g/L to remove DOM for MF process.

4) The reversible and irreversible membrane fouling, and concentration polarization could be inhibited at acid condition, because both of membrane and humic materials had a negative surface charge at acid condition below pH 7. The trends of pH effect on membrane fouling in the hybrid process using alumina MF membrane with air back-flushing agreed with this result of the hybrid process using the carbon fiber UF membrane with water back-flushing. Finally, the optimal condition could be pH 8 for the hybrid process of carbon fiber UF and PP beads with water back-flushing; however, it could be pH 6 for alumina MF with air back-flushing, because of the maximum total permeate volume.

5) The pH could not affect treating the turbid matter like as kaolin for carbon fiber UF process with water back-flushing. The DOM could be removed effectively at acid condition, because of repulsion force between the carbon fiber membrane and humic materials.

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