Effect of Organic Materials in Water Treatment by Hybrid Module of Multi-channel Ceramic Microfiltration and Activated Carbon Adsorption

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Abstract: We investigated the effect of organic materials on membrane fouling in advanced drinking water treatment by a hybrid module packed with granular activated carbon (GAC) outside multi-channel ceramic microfiltration membrane. Synthetic water was prepared with humic acid and kaolin to simulate natural water resouces consisting of natural organic matter and inorganic particles. Kaolin concentration was fixed at 30 mg/L and humic acid was changed as 2~10 mg/L to inspect the effect of organic matters. Periodic back-flushing using permeate water was performed for 10 sec per filtration of 10 min. As a result, both resistance of membrane fouling (Rf) and permeate flux (J) were influenced highly by concentration of humic acid. It proved that NOM like humic acid could be an important factor on membrane fouling in drinking water treatment. Turbidity and UV254 absorbance were removed up to above 97.4% and 59.2% respectively.

Keywords: *hybrid module, ceramic membrane, GAC, water treatment, multi-channel*

1. Introduction

As drinking water source has been severely polluted by various organic matters, turbid materials, and pathogens, both interests and applications for advanced water treatment have increased in order to remove effectively those pollutants of undesirable source. Furthermore, researches of drinking water treatment by membrane separation have been achieved actively [1-5]. Application of membrane separation in the drinking water treatment could achieve not only superior quality of treated water, but also compact facility without limit of installation area compared with conventional water treatment technologies. In addition, quality of treated water was excellent and independent of fluctuation of water source condition because the membrane separation was physical treatment [6].

Recently a major pending problem in drinking water

treatment plant is to remove effectively NOM that has been known as a precursor of disinfection by-products (DBPs) such as trihalomethanes (THMs). However, it was difficult to remove soluble organic materials such as NOM by only microfiltration (MF) [7]. Therefore, a lot of researches for hybrid process of membrane filtration and activated carbon (AC) adsorption have been performed to remove NOM [8-11].

Additionally NOM is one of major materials to cause membrane fouling in membrane separation process applied to advanced drinking water treatment. Generally membrane fouling in drinking water treatment was made by inorganic particles (e.g. iron, silica and suspended solids) and organic compounds (e.g. humic substances, polysaccharides, proteins and microorganisms) [12-14]. And the membrane fouling caused concentration polarization [15] and gel layer formation on membrane surface [16], and adsorption and pore blockage inside membrane pores [17].

Ceramic membrane used in this study has excellent

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chemical resistance, high mechanical strength, stable characteristics at high pressure and temperature, wide available range of pH 0~14, and long lifetime compared with organic membranes. Therefore it has advantages to prevent damage and pollution, which happened frequently in organic membranes, by microorganisms and bacillus because of inorganic materials. The ceramic membrane will be dramatically applied to water treatment field, and play an important role in water treatment because it has high ripple effect on industry [18,19]. We have been continuously reported the advanced drinking water treatment by hybrid module of ceramic microfiltration and activated carbon adsorption [20-24].

However, in this study the hybrid module for advanced drinking water treatment was composed of 1.0 μm pore size multi-channel ceramic MF, which was different with them used in our previous studies [20-24], and GAC adsorption. We investigated effects of organic materials on membrane fouling and treatment efficiencies of turbidity and UV_{254} absorbance in advanced water treatment process by this hybrid module.

2. Theory

The resistance-in-series filtration model was applied to analyze experimental data for calculating filtration resistance and permeate flux (J) in this study. The model is well known in the application field of membrane separation and can be expressed by equation (1) [25].

$$J = \frac{\Delta P}{R_m + R_b + R_f} \tag{1}$$

Where J is the permeate flux through membrane, P is trans-membrane pressure (TMP), R_m is the resistance of membrane, R_b is the resistance of boundary layer, and R_f is the resistance of membrane fouling.

For filtration of pure water, R_b and R_f do not exist because of no boundary layer by concentration polari-

zation and no membrane fouling by pollutants. The equation (1) can be simplified to equation (2).

$$J = \frac{\Delta P}{R_m} \tag{2}$$

Where R_m can be calculated from the experimental data of permeate flux for pure water using equation (2). Then, the plot of $R_b + R_f$ vs. t (operation time) can be obtained from the permeate flux data using synthetic water. The intercepting value of y-axis (t = 0) in this plot using only initial 2 data is R_b because of no R_f at the initial time of filtration, and finally R_f can be calculated using equation (1).

In addition, both feed water and permeate water is analyzed in our experiment. Treatment efficiencies can be decided by following equation (3).

$$R = \frac{C_f - C_p}{C_f} \times 100 \tag{3}$$

Where R is treatment efficiency, C_f is concentration of feed water, and C_p is concentration of permeate water.

3. Materials and Methods

3.1. Multi-channel Ceramic Membrane and GAC

Multi-channel ceramic MF membrane (HC10) used in the study was coated with α-alumina on supporting layer of α-alumina, and its pore size was 1.0 μm. We purchased the membrane from Dongseo Inc. in Korea, and it had 7 channels shown in Fig. 1. Its O.D. was 20 mm, I.D. 4 mm, length 235 mm, and total surface area 206.7 cm², as arranged in Table 1.

GAC used here was coconut shell charcoal (8 × 30 mesh) for water treatment, and specification of the GAC was shown in Table 2. In order to sort uniform particle size before experiments, the GAC was separated by 9 mesh (2 mm) and then by 16 mesh (1 mm) sieves. Separated GAC particles (1~2 mm) were rinsed in distillate water and then dried at 105°C during 2 h.
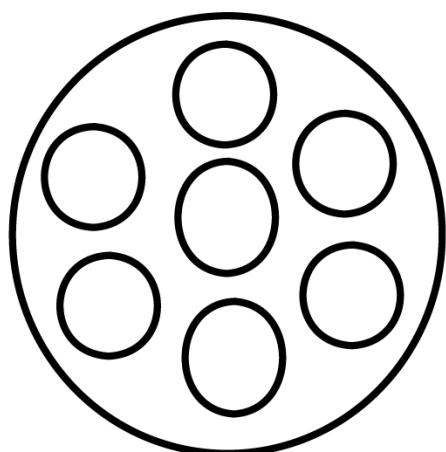
Fig. 1. Shape of multi-channel ceramic membranes [21].

Table 1. Specification of Multi-channel Ceramic Membrane used in This Study

Membrane	HC10
Pore size (μm)	1.0
No. of channels	7
Outer diameter (mm)	20
Inner diameter (mm)	4
Length (mm)	235
Surface area (cm^2)	206.7
Material	alumina coating on alumina support
Company	Dongseo Inc. (Korea)

3.2. Synthetic Water

In order to modify humic materials to be major portion of natural organic matters and fine inorganic particles such as clay to cause turbidity, a quantity of humic acid and kaolin was dissolved in distilled water. Then it was utilized as synthetic water in our experiments.

3.3. Hybrid Membrane Module

To remove turbidity and NOM, hybrid module was composed by packing GAC between module inside and outside of multi-channel ceramic membrane. In addition, 100 mesh (0.150 mm), which was extremely smaller than 1~2 mm particle size of GAC used here, was installed at outlet of the hybrid module to prevent GAC loss to treated water tank.

Table 2. Specification of GAC Employed in This Study [20].

Parameter	Average value
Mesh size	8 × 30 mesh
Moisture	2.8%
Iodine number	1,058 mg/g
Hardness	95.8%
Bulk Density	0.48 g/mL

3.4. Experimental Procedures

Advanced water treatment system using hybrid module (6) of ceramic microfiltration and GAC adsorption was shown in Fig. 2. And we performed cross-flow filtration for tubular membrane and periodic water-back-flushing using permeate water. The hybrid module (6) filled with 60 g of GAC was installed in the advanced water treatment system. And then feed tank (1) was filled with prepared 10 L of synthetic water composed of humic acid and kaolin, and temperature of feed water was constantly maintained by using constant temperature circulator (3) (Model 1146, VWR, U.S.A). Also, the synthetic feed water was continuously mixed by stirrer (4) in order to be homogeneous condition of feed water, and it was flowed into the inside of the tubular ceramic membrane by pump (2) (Procon, Standex Co., U.S.A) when solenoid valves expressed by "1" were open. Feed flow rate was measured by flowmeter (5) (NP-127, Tokyo keiso, Japan). Flow rate and pressure of feed water which was flowed into the hybrid module was constantly maintained by controlling valves (9) of both bypass pipe of pump (2) and concentrate pipe. Permeate flux treated by both ceramic membrane and GAC was measured by electric balance (11) (Ohaus, U.S.A.). Permeate water was flowed into the back-washing tank (13) when permeate flux was not 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 be constant concentration of the feed water during operation [23].

Kaolin was fixed at 30 mg/L and humic acid was varied as 2, 4, 6, 8 and 10 mg/L at experiment of organic matters effect. Then, we observed resistance of membrane fouling (R_f) and permeate flux (J) during

(1) Feed tank   (2) Feed pump   (3) Cooling system
(4) Stirrer   (5) Flow meter   (6) Membrane module
(7) GAC   (8) 100 mesh sieve   (9) Needle valve (control)
(10) Ball valve   (11) Electric balance   (12) Solenoid valve
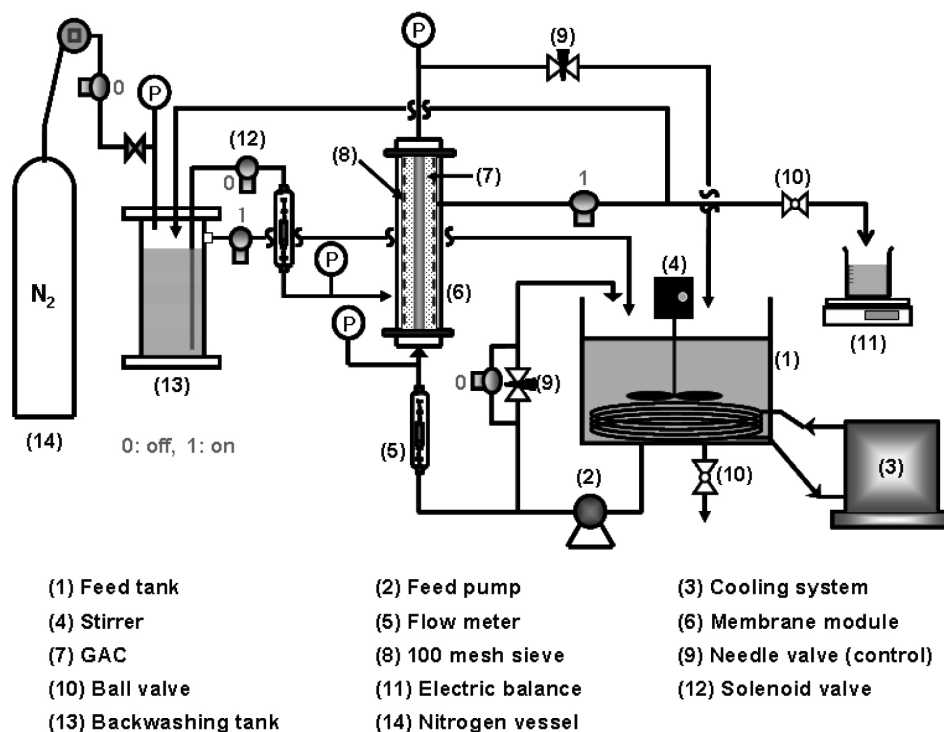(13) Backwashing tank   (14) Nitrogen vessel

Fig. 2. Apparatus of advanced water treatment system using hybrid module of multi-channel ceramic microfiltration and GAC adsorption with periodic water-back-flushing [20].

total filtration time of 180 min at each condition. At all experimental conditions, TMP was at 0.80 bar, water-back-flushing pressure at 2.50 bar, feed flow rate at 1.0 L/min, and feed water temperature at 20°C. Also, periodic water-back-flushing using permeate water was performed during 10 sec per filtration of 10 min when solenoid valves expressed by "0" were open.

Quality of feed water and treated water was analyzed in order to evaluate treatment efficiencies of turbid materials and dissolved organic matters. Turbidity was measured by turbidimeter (2100N, HACH, U.S.A.) and UV_{254} absorbance, which was directly proportional to concentration of humic acid, was analyzed by UV spectrophotometer (GENESYS 10 UV, Thermo, U.S.A.).

4. Results and Discussions

Kaolin was fixed at 30 mg/L and humic acid was changed from 2 to 10 mg/L in synthetic feed water at experiment in order to investigate effect of organic

matters. As a result, the resistance of membrane fouling (R_f) was dramatically raised as increasing concentration of humic acid from 2 mg/L to 10 mg/L as shown in Fig. 3. In particular, R_f was increased obviously when the concentration of humic acid was changed from 4 mg/L to 6 mg/L. As summarized in Table 3, the final R_f after 180 min's operation ($R_{f,180}$) at 4 mg/L and 6 mg/L were 0.534×10^{-9} and 0.668×10^{-9} kg/m^{2}s respectively. However, R_f was increased a little when the concentration of humic acid was changed from 8 mg/L to 10 mg/L, and $R_{f,180}$ values at 8 mg/L and 10 mg/L were 0.783×10^{-9} and 0.817×10^{-9} kg/m^{2}s, respectively. Finally the experimental values of $R_{f,180}$ were significantly increased according to addition of the humic acid concentration. The result was exactly same with our previous study using tubular ceramic MF membrane (NCMT-7231, pore size 0.1 μm) [23].

Fig. 4 showed a change of dimensionless permeate flux (J/J_o), which was permeate flux at given time (J) vs. initial permeate flux (J_o) during operation of water

Table 3. Filtration Factors in the Experiments for Effect of Humic Acid Concentration
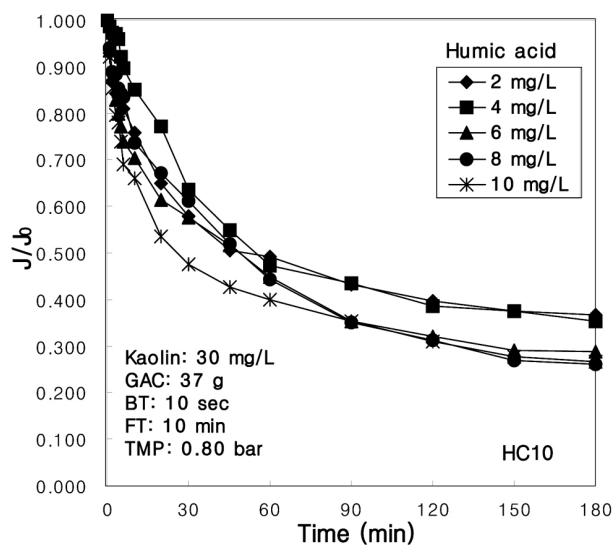
Experimental Conditions		$R_{f,180} \times 10^{-9}$ (kg/m²s)	$J_o \times 10^5$ (m/s)	$J_{180} \times 10^5$ (m/s)	J_{180}/J_o	V_T (L)
Kaolin (mg/L)	Humic acid (mg/L)					
	2	0.426	31.63	11.63	0.368	33.23
	4	0.534	26.74	9.48	0.355	29.60
30	6	0.668	28.94	8.35	0.289	26.78
	8	0.783	28.18	7.39	0.262	26.17
	10	0.817	26.53	7.05	0.266	22.97

Table 4. Water Quality and Rejection Rate of Turbidity in the Experiments Using Hybrid Module of HC10 and GAC for Effect of Humic Acid Concentration

Experimental condition		Turbidity (NTU)				Average Treatment efficiency (%)
Kaolin (mg/L)	Humic acid (mg/L)	Feed water		Treated water		
		Range	Average	Range	Average	
	2	21.10~22.50	21.82	0.15~0.18	0.16	99.25
	4	14.70~29.60	22.80	0.18~0.26	0.21	99.01
30	6	24.00~26.90	26.15	0.21~1.50	0.65	97.50
	8	27.00~29.10	27.82	0.24~1.34	0.72	97.42
	10	30.10~34.50	31.80	0.24~0.73	0.40	98.74
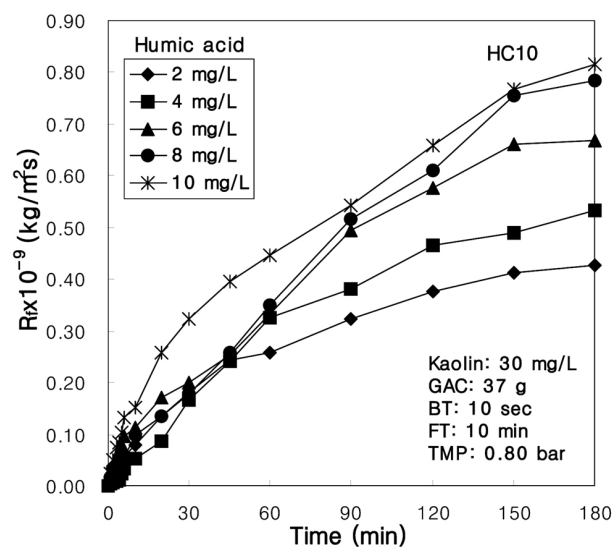
Fig. 3. Effect of humic acid concentration on resistance of membrane fouling.

Fig. 4. Effect of humic acid concentration on dimensionless permeate flux.

treatment. The values of J/J_o tended to decrease as increasing the humic acid concentration as shown in Fig. 4, because of generating membrane fouling. Thus, final value of J/J_o (J_{180}/J_o) at 2 mg/L and 10 mg/L of the humic acid concentration were 0.368 and 0.266, respectively. It proved that NOM like humic acid could

be important factor on membrane fouling in drinking water treatment.

As shown in Fig. 5, permeate flux (J) through multi-channel ceramic membrane was also decreased obviously as increasing the humic acid concentration. Final permeate flux (J_{180}) at 2 mg/L and 10 mg/L of the humic

Table 5. Water Quality and Rejection Rate of UV_{254} Absorbance in the Experiments Using Hybrid Module of HC10 and GAC for 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		
		Range	Average	Range	Average	
30	2	0.019~0.038	0.029	0.000	0.000	100.00
	4	0.071~0.116	0.092	0.015~0.018	0.017	81.06
	6	0.095~0.144	0.118	0.011~0.053	0.030	75.86
	8	0.092~0.184	0.150	0.037~0.100	0.062	59.19
	10	0.148~0.257	0.190	0.022~0.103	0.051	75.02
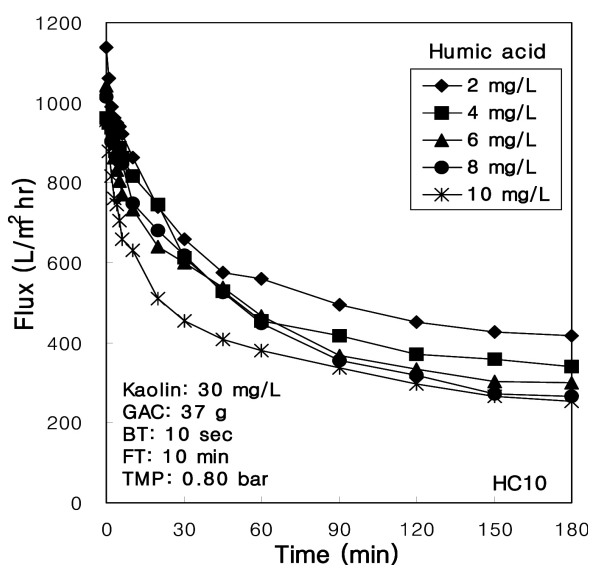
Fig. 5. Effect of humic acid concentration on permeate flux.

acid concentration were 11.63×10^{-5} and 7.05×10^{-5} m/s, respectively. Therefore, organic materials as humic acid could make severely fouling inside membrane and on the surface of membrane.

Total permeated volume (V_T) calculated using permeate flux during 180 min's operation, as shown in Table 3, was the highest value of 33.23 L at the humic acid concentration of 2 mg/L. But V_T was much low value of 22.97 at 10 mg/L of humic acid, because of severe membrane fouling by organic materials.

Then, turbidity of feed water and treated water, and average treatment efficiency was arranged in Table 4. It was high above 97.4%, and the maximum efficiency of 99.25% at 2 mg/L of humic acid. And the average

treatment efficiency of turbidity tended to decrease a little because turbidity of feed and treated water increased as increasing the concentration of humic acid, as shown in Table 4.

The average treatment efficiency of UV_{254} absorbance, which was directly proportional to concentration of humic acid, was arranged in Table 5. It was the maximum of 100% at 2 mg/L of humic acid, and the minimum of 59.19% at 8 mg/L. Therefore it tended to decrease dramatically as increasing the concentration of humic acid, because UV_{254} absorbance of feed and treated water increased as increasing the concentration of humic acid, as shown in Table 5.

5. Conclusion

In this study, we investigated the effect of organic materials on membrane fouling in advanced drinking water treatment by hybrid module packed with granular activated carbon (GAC) outside multi-channel ceramic microfiltration membrane. The experimental results of the effect of organic matters both R_f and J/J_o were highly dependent on the concentration of humic acid in the synthetic water. In particular, resistance of membrane fouling was increased obviously when the concentration of humic acid was changed from 4 mg/L to 6 mg/L. Therefore, it means that NOM like humic acid could be important factor on membrane fouling in drinking water treatment. Then, treatment efficiencies of turbidity was much high above 97.4%, but those of UV_{254} absorbance was above 59.2%.

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