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Advanced water treatment of high turbid source by hybrid module of ceramic microfiltration and activated carbon adsorption: Effect of organic/inorganic materials

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Abstract−We investigated the effect of organic or inorganic materials on membrane fouling in advanced drinking water treatment by hybrid module packed with granular activated carbon (GAC) outside a tubular ceramic microfiltration membrane. Instead of natural organic matters (NOM) and fine inorganic particles in the natural water source, synthetic water was prepared with humic acid and kaolin. Concentrations of kaolin or humic acid were changed to see effects of inorganic or organic matter. And periodic water-back-flushing using permeate water was performed during 10 sec per filtration of 10 min. As a result, both the resistance of membrane fouling (R_f) and permeate flux (J) were influenced higher by concentration of humic acid rather than kaolin. It was proved that NOM like humic acid could be a more important factor on membrane fouling in drinking water treatment than fine inorganic particles. Treatment efficiencies of turbidity and UV_{254} absorbance were very high above 97.4% and 92.0%, respectively.

Key words: Hybrid Module, Ceramic Membrane, GAC, Microfiltration, Water Treatment

INTRODUCTION

As drinking water sources have been severely polluted by various organic or inorganic matters, turbid materials and pathogens, the interest in 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 pursued actively [1-5]. Application of membrane separation in the drinking water treatment not only achieves superior quality of treated water, but also requires only a compact facility without limit of installation area compared with conventional water treatment technologies. In addition, the quality of treated water is excellent and independent of fluctuation of water source condition because the membrane separation is physical treatment [6].

Recently, a major pending problem in drinking water treatment plants is to effectively remove NOM that has been known as a precursor of disinfection by-products (DBPs) such as trihalomethanes (THMs). However, it has been difficult to remove soluble organic materials such as NOM by only microfiltration (MF) [7]. Therefore, a large number 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 the major materials that cause membrane fouling in membrane separation process applied to advanced drinking water treatment. Generally, membrane fouling in drinking water treatment occurs from 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 causes 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 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. It also has the advantage of preventing damage and pollution, which happen frequently in organic membranes, by microorganisms and bacillus because of inorganic materials. The ceramic membrane will be dramatically applied to the water treatment field, and play an important role in water treatment because it has a high ripple effect on industry [18,19].

The hybrid module for advanced drinking water treatment in this study was composed of a ceramic MF for turbidity removal and GAC adsorption for NOM removal. We investigated the effects of organic or inorganic materials on membrane fouling and treatment efficiencies of turbidity and UV_{254} absorbance in advanced water treatment process by this hybrid module.

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 could be expressed by Eq. (1) [20].

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

Where J is the permeate flux through membrane, P is trans-mem-

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[‡] This article is dedicated to Professor Chang Kyun Choi for celebrating his retirement from the School of Chemical and Biological Engineering, Seoul National University.

brane 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 polarization and no membrane fouling by pollutants. Eq. (1) could be simplified to Eq. (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 by using Eq. (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 intercept value of y-axis (t=0) in this plot using only initial 2 data was R_b because of no R_f at the initial time of filtration, and finally R_f could be calculated by Eq. (1).

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

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

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

Table 1. Specification of GAC employed in this study

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

EXPERIMENTS

1. Ceramic Membrane and GAC

Tubular ceramic MF membrane (NCMT-7231) used in the study was coated with α-alumina on supporting layer of α-alumina. We purchased the membrane from Nano Pore Materials Co. in Korea, and its surface area was 47.5 cm^2, pore size 0.1 μm, O.D. 8 mm, I.D. 6 mm and length 252 mm. GAC used here was coconut shell charcoal (8×30 mesh) for water treatment, and specification of the GAC is shown in Table 1. 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 distilled water and then dried at 105 °C during 2 hours.

2. Synthetic Water

To modify humic materials to be a 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 used as synthetic water in our experiments.

3. Hybrid Membrane Module

To remove turbidity and NOM, the hybrid module was composed by packing GAC between module inside and outside of 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 the outlet of the hybrid module to prevent GAC loss to treated water tank.

4. Experimental Procedures

The advanced water treatment system using q hybrid module (6) of ceramic microfiltration and GAC adsorption is shown in Fig. 1. We performed cross-flow filtration for the 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. Then the feed tank (1) was filled with prepared

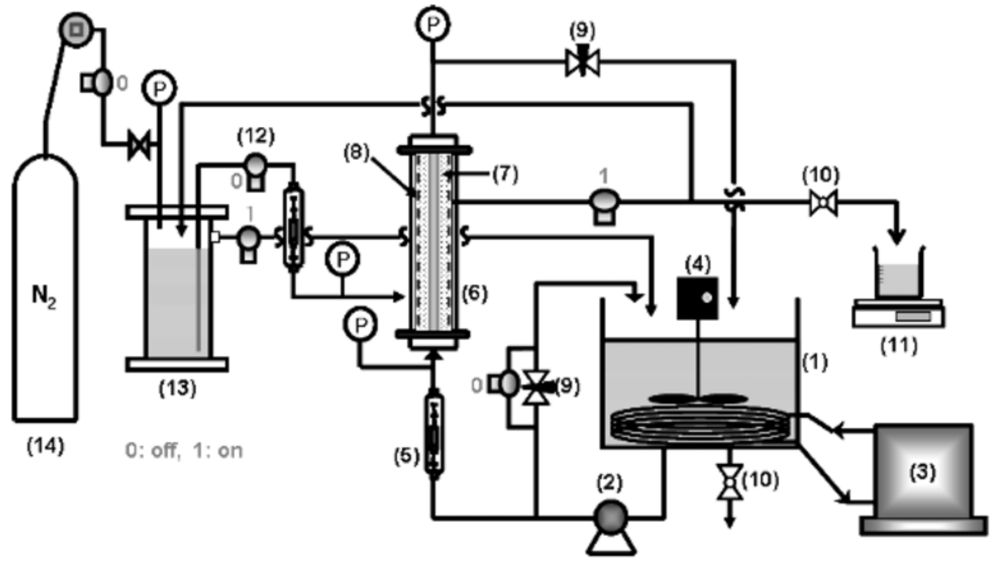

Fig. 1. Apparatus of advanced water treatment system using hybrid module of ceramic microfiltration and GAC adsorption with periodic water-back-flushing.

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

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 maintain 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.) Feed flow rate was measured by flowmeter (5) (NP-127, Tokyo Keiso, Japan) Flow rate and pressure of feed water which flows 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 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 maintain a constant concentration of the feed water during operation.

Humic acid was fixed at 10 mg/L and kaolin was changed as 10, 20, 30, 40 and 50 mg/L in the synthetic feed water to study the effect of inorganic particles. Also, kaolin was fixed at 30 mg/L and humic acid was varied as 2, 4, 6, 8 and 10 mg/L in the experiment for effect of organic matters. We observed the resistance of membrane fouling (R_f) and permeate flux (J) during total filtration time of 180 min at each condition. At all experimental conditions, TMP was maintained at 1.77 bar, water-back-flushing pressure at 2.50 bar, feed flow rate at 1.0 L/min, and feed water temperature at 20 °C. Periodic water-back-flushing using permeate water was performed during 10 sec per filtration of 10 min.

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 was analyzed by UV spectrophotometer (GENESYS 10 UV, Thermo, U.S.A).

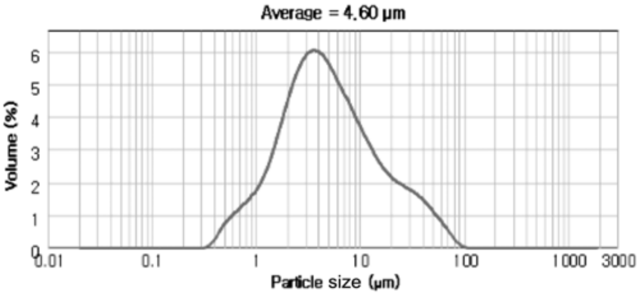

Fig. 2. Size distribution of kaolin solution.

RESULTS AND DISCUSSION

1. Effect of Kaolin Concentration

To see particle size distribution of kaolin used here, kaolin was analyzed by using a laser particle size analyzer (Mastersizer 2000, Malvern, UK) as shown in Fig. 2. Distribution of kaolin was approximately a normal distribution and the average particle size was 4.60 µm.

The concentration of humic acid was fixed at 10 mg/L and that of kaolin was changed from 10 to 50 mg/L in synthetic feed water to determine the effect of inorganic particles on membrane fouling. As a result, R_f during operation time tended to be slightly increased with increment of kaolin concentration as shown in Fig. 3, but the effect of kaolin concentration was little on membrane fouling. Actually, the final R_f after 180 min's operation was almost the same in the range of 4.89×10^{-9}-5.15×10^{-9} kg/m^2·s as summarized in Table 2. A cake layer could be formed on the membrane surface because the particle size (4.60 µm) of kaolin was larger than the pore size of ceramic membrane (0.1 µm). However, cross flow inside the module and periodic water-back-flushing could restrain kaolin particles from forming a cake layer on the membrane surface, or remove the cake layer formed. Therefore, most of the membrane fouling would be developed more actively by humic acid than kaolin.

Fig. 4 shows the change of dimensionless permeate flux (J/J_o), which was the permeate flux at given time (J) vs. initial permeate flux (J_o) during operation of water treatment. The curves of J/J_o almost

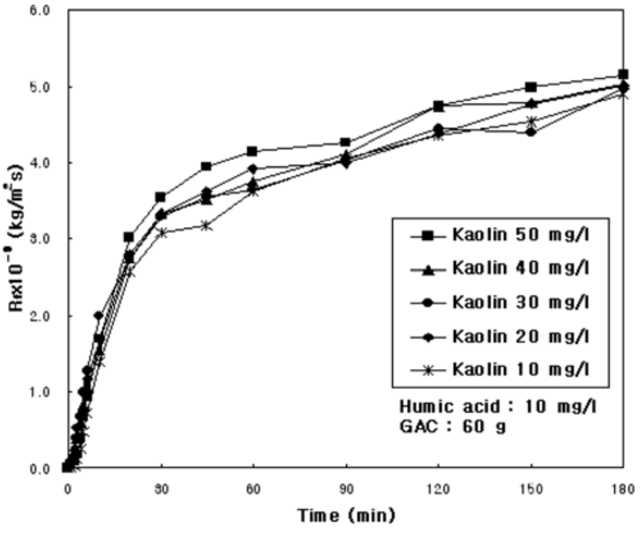

Fig. 3. Effect of kaolin concentration on resistance of membrane fouling.

Table 2. Filtration factors in the experiments for effect of kaolin concentration

Experimental conditions		$R_{f,180}$ (kg/m^{2}s)$\times10^{-9}$	J_o (m/s)$\times10^5$	J_{180} (m/s)$\times10^5$	J_{180}/J_o	V_T (L)
Kaolin (mg/l)	Humic acid (mg/l)					
10		4.89	33.21	3.26	0.098	2.545
20		5.02	34.72	3.19	0.092	2.331
30	10	4.96	34.76	3.22	0.093	2.379
40		5.02	34.67	3.19	0.092	2.353
50		5.15	33.60	3.11	0.093	2.302

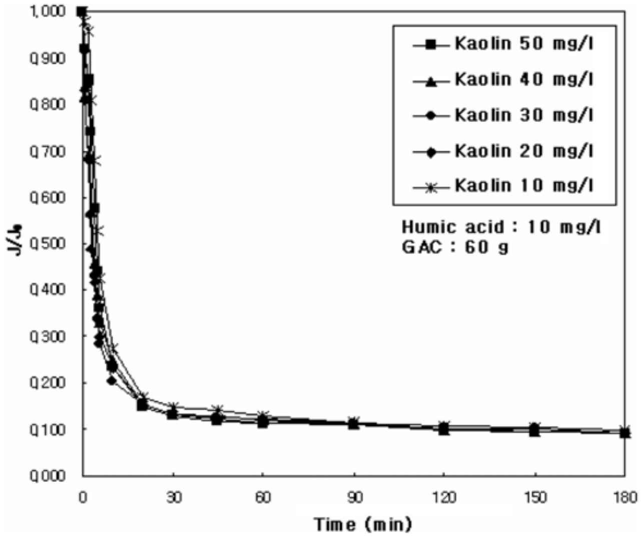

Fig. 4. Effect of kaolin concentration on dimensionless permeate flux.

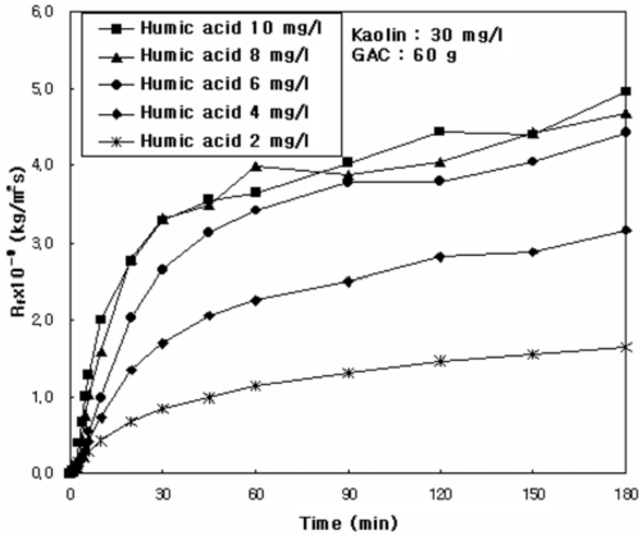

Fig. 5. Effect of humic acid concentration on resistance of membrane fouling.

overlapped independent of kaolin concentration. In addition, J/J_o was dramatically decreased since membrane fouling was processed within initial 30 minutes of operation. Then, treatment efficiency of turbidity and UV_{254} absorbance was analyzed as 97.95-99.54% and 95.79-98.53% respectively.

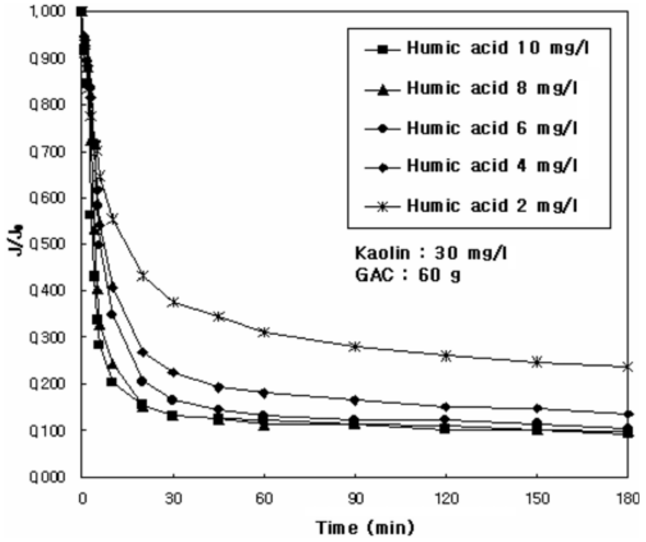

Fig. 6. Effect of humic acid concentration on dimensionless permeate flux.

2. Effect of Humic Acid Concentration

Kaolin was fixed at 30 mg/L and humic acid was changed from 2 to 10 mg/L in synthetic feed water in the experiment in order to investigate the effect of organic matters. As a result, R_f was dramatically dropped with decreasing concentration of humic acid from 10 mg/L to 2 mg/L as shown in Fig. 5. In particular, R_f clearly decreased when the concentration of humic acid was changed from 4 mg/L to 2 mg/L. As summarized in Table 3, $R_{f,180}$ values at 4 mg/L and 2 mg/L were 3.16×10^{-9} and 1.65×10^{-9} kg/m²·s, respectively. These $R_{f,180}$ values should be much smaller than the $R_{f,180}$ value of 4.96×10^{-9} kg/m²·s at the humic acid concentration of 10 mg/L. Finally, the experimental values of $R_{f,180}$ were significantly decreased according to reduction of the humic acid concentration.

The values of J/J_o tended to be increased with decreasing the humic acid concentration as shown in Fig. 6, because of reducing membrane fouling. Thus, the J/J_o value at 2 mg/L of the humic acid concentration was about 2.6 higher than J/J_o value at 10 mg/L of humic acid. It proved that NOM like humic acid could be a more important factor on membrane fouling in drinking water treatment than fine inorganic particles. Then, treatment efficiencies of turbidity and UV_{254} absorbance were very outstanding at 99.39-99.68% and 97.26-98.50%, respectively.

CONCLUSIONS

We investigated the effect of organic or inorganic materials on

Table 3. Filtration factors in the experiments for effect of humic acid concentration

Experimental conditions		$R_{f,180}$ (kg/m²s)×10^{-9}	J_o (m/s)×10^5	J_{180} (m/s)×10^5	J_{180}/J_o	V_T (L)
Kaolin (mg/l)	Humic acid (mg/l)					
30	2	1.65	34.29	8.17	0.238	5.608
	4	3.16	35.65	4.82	0.135	3.694
	6	4.44	33.46	3.55	0.106	2.791
	8	4.69	34.86	3.40	0.097	2.478
	10	4.96	34.76	3.22	0.093	2.379

membrane fouling in advanced drinking water treatment by hybrid module packed with granular activated carbon (GAC) outside a tubular ceramic microfiltration membrane. The experimental results of the effect of inorganic particles showed that R_f, which was the resistance of membrane fouling, for various concentrations of kaolin would be mostly similar and independent of kaolin concentration in the synthetic water. Also, the curves of J/J_o, which was dimensionless permeate flux, were almost overlapped and independent of kaolin concentration. Then, in 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, permeate flux was clearly increased when the concentration of humic acid was changed from 4 mg/L to 2 mg/L. Therefore, NOM like humic acid could be a more important factor on membrane fouling in drinking water treatment than fine inorganic particles.

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REFERENCES

1. A. R. Costa and M. N. Pinho, *Desalination*, **196**, 55 (2006).
2. L. Fiksdal and T. O. Leiknes, *J. Membr. Sci.*, **279**, 364 (2006).
3. Y. T. Lee and J. K. Oh, *Membrane Journal*, **9**, 193 (1999).
4. T. Leiknes, H. Ødegaard and H. Myklebust, *J. Membr. Sci.*, **242**, 47 (2004).
5. J. I. Oh and S. H. Lee, *J. Membr. Sci.*, **254**, 39 (2005).
6. M. H. Kim and J. Y. Park, *Membrane Journal*, **11**, 190 (2001).
7. M. H. Cho, C. H. Lee and S. H. Lee, *Desalination*, **191**, 386 (2006).
8. S. Gur-Reznik, I. Katz and C. G. Dosoretz, *Water Res.*, **42**, 1595 (2008).
9. H. S. Kim, S. Takizawa and S. Ohgaki, *Desalination*, **202**, 271 (2007).
10. S. Mozia and M. Tomaszewska, *Desalination*, **162**, 23 (2004).
11. H. K. Oh, S. Takizawa, S. Ohgaki, H. Katayama, K. Oguma and M. J. Yu, *Desalination*, **202**, 191 (2007).
12. Y. T. Lee and J. K. Oh, *Membrane Journal*, **13**, 219 (2003).
13. D. B. Mosqueda-Jimenez and P. M. Huck, *Desalination*, **198**, 173 (2006).
14. W. Yuan, A. Kocic and A. L. Zydney, *J. Membr. Sci.*, **198**, 51 (2002).
15. M. Heran and S. Elmaleh, *J. Membr. Sci.*, **188**, 181 (2001).
16. S. K. Karode, *J. Membr. Sci.*, **188**, 9 (2001).
17. P. Rai, C. Rai, G. C. Majumdara, S. D. Gupta and S. De, *J. Membr. Sci.*, **283**, 116 (2006).
18. E. O. Kim, *Membrane Journal*, **3**, 12 (1993).
19. Y. T. Lee and M. H. Song, *Membrane Journal*, **14**, 192 (2004).
20. M. Cheryan, Technomic Publishing Company, Lancaster, Pennsylvania (1984).