DEVELOPMENT OF HYBRID ULTRAFILTRATION COMBINED WITH BOTH FLOCCULATION AND ADSORPTION TREATMENTS FOR ADVANCED REMOVAL OF HUMIC SUBSTANCES

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Introduction

Currently with the progression of the pollution in water sources, considerable attention has been given to the application of membrane filtration technology using microfiltration or ultrafiltration membranes to the surface water treatment as an alternative to conventional coagulation sedimentation and sand filtration. The microfiltration and ultrafiltration membranes are appropriate for complete removal of suspended solids or bacteria, but cannot completely remove such dissolved organic matter as the humic substances due to their small molecular size. The humic substances, which have become a problem as a trihalomethane precursor in the process of surface water treatment, mainly consist of humic acids of relatively high molecular weight (more than ca 1,500) and fulvic acids of relatively low molecular weight (less than ca 1,500) [1], and it is believed that it would be difficult to completely remove the humic substances by such single treatment as flocculation and adsorption because they have so broad molecular weight distribution. Moreover, the humic substances often cause the membrane fouling in the membrane filtration process, and therefore many researches on membrane filtration of humic acids of the high molecular weight fractions have been reported recently [1-8]. Also, the pretreatment by flocculation or adsorption and the combination with ozone treatment have been developed to reduce the membrane fouling [9-15].

In this study, hybrid ultrafiltration combined with both treatments of flocculation effective for humic acids and adsorption effective for fulvic acids is developed for removing humic substances. The validity of this method is verified from the standpoint of both filtration rate and rejection of solutes by conducting hybrid ultrafiltration of humic acids, fulvic acids and humic substances, respectively.

Experimental Method and Materials

Humic acids obtained by refining commercial humic acids, fulvic acids extracted from commercial leaf soils, and humic substances prepared by mixing humic and fulvic acids were used as the sample materials. Humic acids were prepared by dissolving commercial humic acids (Wako Pure Chemical Ind. Corp., Japan) with alkaline solution, adjusting the solution pH to 5 after removing insoluble contents by filter papers, and filtering it by 0.5 μm microfiltration membranes. Fulvic acids were prepared by filtering alkali-extracted commercial leaf soils by 0.5 μm microfiltration membranes, taking the supernatant solution after adjusting the filtrate pH to 1 for the removal of humic acids, and filtering it by 0.5 μm microfiltration membranes after adjusting its pH to 5. The obtained humic and fulvic acid solutions were used singly as the sample fluid, and furthermore the mixtures of equal amount of both solutions were used as the humic substance solutions. The concentrations of humic acids, fulvic acids and humic substances were evaluated by the absorbance at a wavelength of 260 nm, E260, usually used in the field of the surface water treatment. Poly aluminum chloride (PACl) was used as a flocculant and powdered activated carbon (PAC) was used as an adsorbent. The PACl dosage was expressed by the aluminium concentration in the sample fluid, mg-Al/l. PAC used in this study had a surface mean diameter of 2.67 μm, a BET specific surface area of 954 m^2/g and a mean pore size of 1.83 nm. Hollow fiber (cellulose acetate) ultrafiltration membranes (FUC1582, Daicel Chem. Ind. Corp., Japan) were employed for ultrafiltration experiments. Membranes had an effective length of 35 cm, an inside diameter of 0.8 mm, an outside diameter of 1.3 mm and a molecular weight cut-off of 150,000 Da.

In flocculation experiment, after a given amount of PACl was added to the sample solution and the flocs were formed by 3 min rapid agitation (120 rpm) and 10 min slow agitation (50 rpm), the absorbance E260 of the filtrate obtained through a 0.45 μm microfiltration membrane was measured to obtain the solute concentration in the supernatant. In adsorption experiment, after a given amount of PAC was added to the sample solution and it was shook at a speed of 120 rpm at a given time, the absorbance E260 of the filtrate obtained through a 0.45 μm microfiltration membrane was measured to obtain the concentration of the solutes which were not adsorbed. Furthermore, combination experiment of flocculation and adsorption was also performed by adding both PACl and PAC.

A schematic drawing of the membrane filtration apparatus is shown in Fig. 1. After given amounts of PACl and PAC were added to the feed solution in the agitated vessel with the agitation of 120 rpm, the feed solution was flowed into one hollow fiber ultrafiltration membrane at a single-pass mode by a peristaltic pump, and then ultrafiltration experiment was conducted under the constant pressure condition of 98 kPa controlled by a reducing valve by applying compressed nitrogen gas. The filtrate weight was measured using an electronic balance, and the solute concentration in the filtrate was measured by reading the absorbance E260.

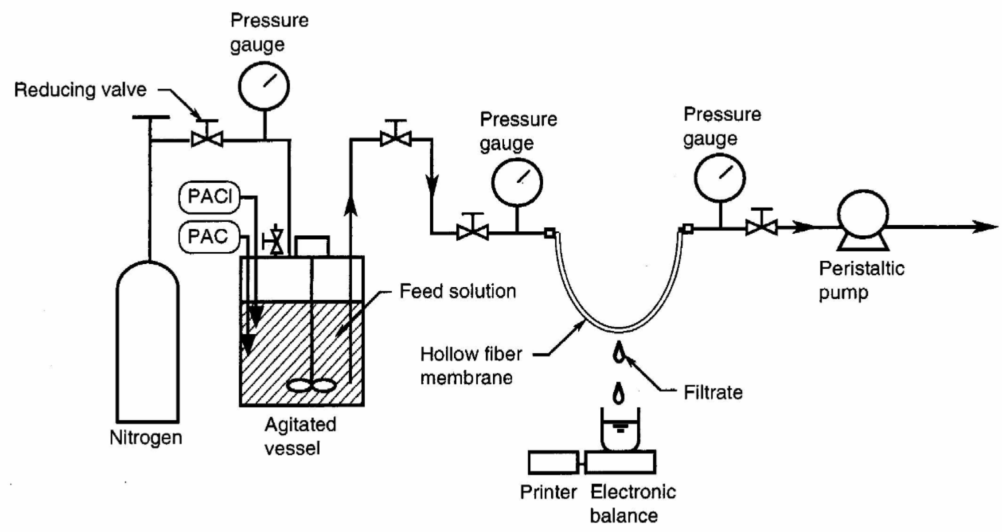

Fig. 1 Schematic diagram of experimental hybrid ultrafiltration apparatus

Results and Discussion

Flocculation properties by addition of PACl

In Fig. 2, E260 of the supernatant after flocculation by addition of PACl divided by $(E260)_0$ of the solution before flocculation is plotted against the aluminium concentration c_p in the sample fluid for various conditions of pH. All plots of E260 have a tendency to decrease as c_p increases and increase sharply above certain aluminium concentrations. This is because the negatively-charged humic substances are flocculated due to charge neutralization caused by the positive aluminium ions under the lesser dosage of PACl, while under excessive amounts of PACl the humic substances are positively charged and redispersed due to adsorption of aluminium ions.

In Fig. 3, the flocculation properties of each of humic and fulvic acids at pH 5 where the humic substances are flocculated effectively are shown and compared with those of humic substances. The figure shows the humic acid is flocculated more effectively than the fulvic acid. This is because the fulvic acid does not form so large flocs due to the flocculation pattern that the fulvic acid with a low molecular weight adheres to the surface of aluminium particles [13]. In order to investigate a correlation between the results for each of single components and the humic substances, the rejection of humic substances calculated based on the additivity of that of each single component is shown with a dotted line in Fig. 3. The calculated result is similar to the measured one but underestimates it slightly. This may be attributed to the fact that the removal of fulvic acids is slightly improved by the existence of humic acids since the fulvic acids are involved in the flocs of humic acids.

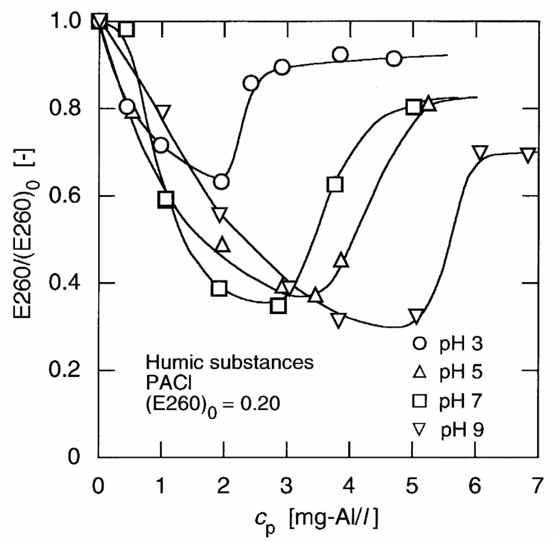

Fig. 2 Flocculation properties of humic substances

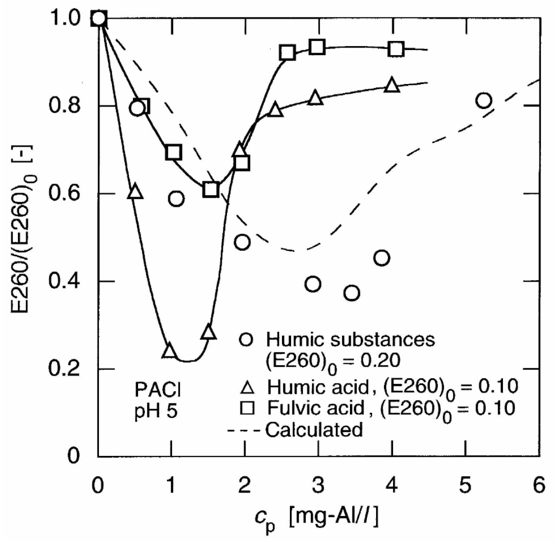

Fig. 3 Flocculation properties of fulvic acid and humic acid

Adsorption properties by addition of PAC

In Fig. 4, E260 of the sample solution after adsorption by addition of PAC divided by $(E260)_0$ of the solution before adsorption is plotted against the PAC dosage c_c for various conditions of pH. The adsorption time was set at 2 hours at which the amount of adsorption comes to equilibrium. The value of $E260/(E260)_0$ has a tendency to decrease dramatically and subsequently show a gentle decrease as c_c increases. Also, the plots show that the adsorption performance is improved with a decrease of pH since the electrostatic repulsive interactions are diminished by the decrease of the negative charges of both humic substances and PAC [16].

In Fig. 5, the adsorption properties of each of humic and fulvic acids at pH 5 are shown and compared with those of humic substances. The figure shows the adsorption performance of the humic acid is higher than that of the fulvic acid, and therefore PAC used in this study is also effective to adsorption of the humic acid with relatively high molecular weight. Furthermore, the adsorption by PAC is more effective in removing the fulvic acid than the flocculation by PACl as shown in Figs. 3 and 5, while in removing the humic acid, both adsorption by PAC and flocculation by PACl are useful very well. In conclusion, it is considered most reasonable to remove poorly flocculated fulvic acid by PAC, the humic acid by PACl which is cheaper and more manageable than PAC, and the humic substances consisting of humic and fulvic acids by a combination of PACl and PAC. The dotted line drawn in Fig. 5 is the rejection of humic substances calculated based on the additivity of measured results for each of humic and fulvic acids. The calculated result is approximately in agreement with the measured one, which verifies the validity of the additivity. In addition, the amount of adsorption in equilibrium of humic acid, fulvic acid and humic substances measured in this study can be described by Freundlich equation, as reported in other literature [16].

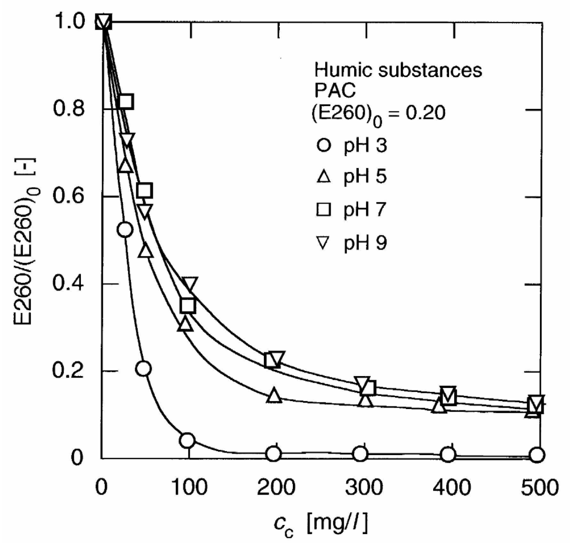

Fig. 4 Adsorption properties of humic substances

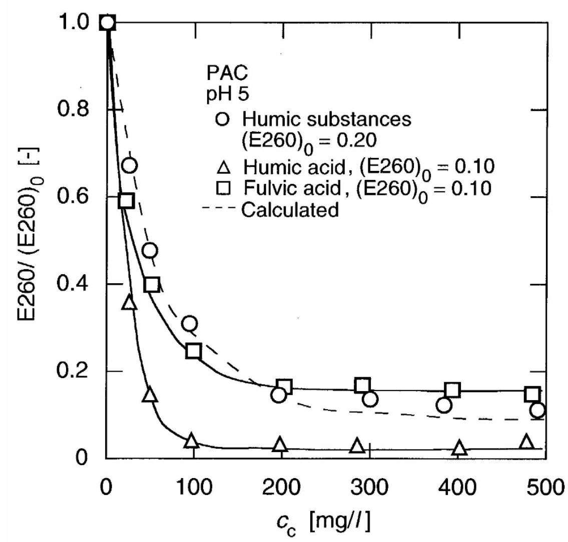

Fig. 5 Adsorption properties of fulvic acid and humic acid

Combinational effect of flocculation by PACl and adsorption by PAC

In Fig. 6, the rejection of the humic substances by a combination of flocculation by PACl and adsorption by PAC in c_p of 1 mg-Al/l and c_c of 100 mg/l is shown and compared with that by each single treatment. The combination of PACl and PAC can improve the rejection of the humic substances significantly compared with each single treatment except the condition of pH 3, because the humic acids with high molecular weight are removed by the flocculation treatment and unflocculated fulvic acids with low molecular weight are removed by the adsorption treatment. Also, the simultaneous addition of PACl and PAC is compared with the sequential addition of them in Fig. 6. When adding PAC first or both simultaneously at higher pH, the rejection of the humic substances becomes a little lower, because the fulvic acids with low molecular weight are prevented from getting inside PAC due to the blockage of pores of PAC by the humic acids with high molecular weight [17]. At less than pH 5, however, this trend is not so significant.

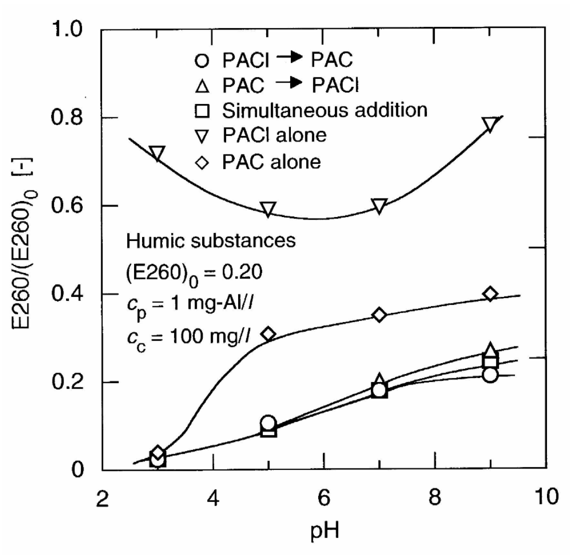

Fig. 6 Combined properties of flocculation and adsorption of humic substances at dosage of 1 mg-Al/l

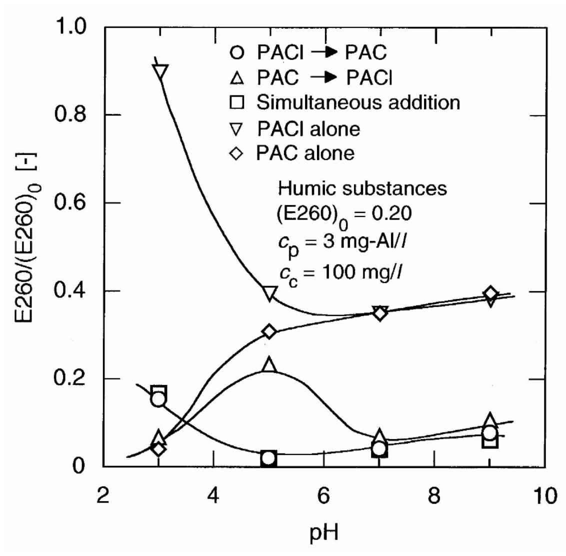

Fig. 7 Combined properties of flocculation and adsorption of humic substances at dosage of 3 mg-Al/l

In Fig. 7, the experimental results in c_p of 3 mg-Al/l are shown. This figure demonstrates that the rejection of the humic substances at pH 3 becomes lower when adding PAC first or both simultaneously. Also at pH 5, the removal performance becomes lower when PAC is added first, but the decrease in removal performance in the simultaneous addition as shown at pH 3 does not occur.

Ultrafiltration combined with flocculation by PACl and adsorption by PAC

In Fig. 8, the experimental results in crossflow ultrafiltration (u_c = 0.11 m/s) of humic substance solutions are plotted in the form of the reciprocal filtration rate (dq/dv) and the rejection R of the humic substances defined as $\{(E260)_0–E260\}/(E260)_0$ against the filtrate volume v per unit effective membrane area. This figure shows the experimental data for four types of ultrafiltration operation (with flocculation and adsorption treatments, with only flocculation treatment, with only adsorption treatment, without both treatments). The rejection in the mode of membrane alone without treatments is extremely low (ca 0.05) because most of untreated humic substances are smaller than a molecular weight cut-off (150,000) of the membrane used. The rejection increases to 60% by combined with flocculation treatment, and increases progressively from 40% to 80% by combined with adsorption treatment. Moreover, the mode of membrane filtration combined with flocculation and adsorption treatments provides a quite high rejection of ca 0.95 from the initial stage of filtration, and maintains comparatively high filtration rate close to data in the mode of membrane alone. It is also demonstrated that PAC particles cause the growth of the filter cake with high

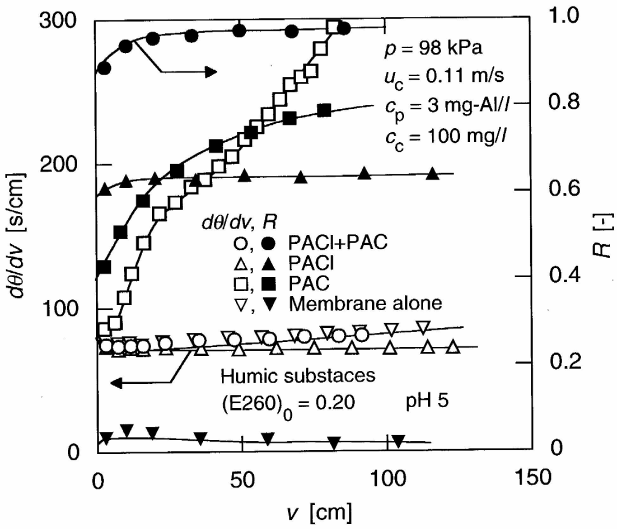

Fig. 8 Effect of operation method on filtration rate and rejection in hybrid ultrafiltration of humic substances

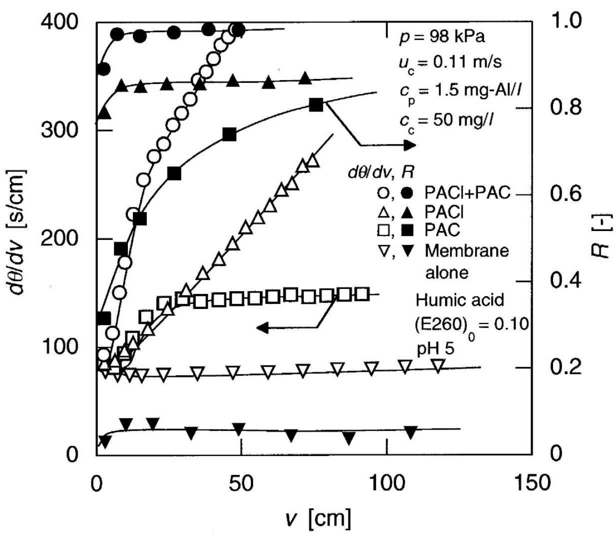

Fig. 9 Effect of operation method on filtration rate and rejection in hybrid ultrafiltration of humic acid

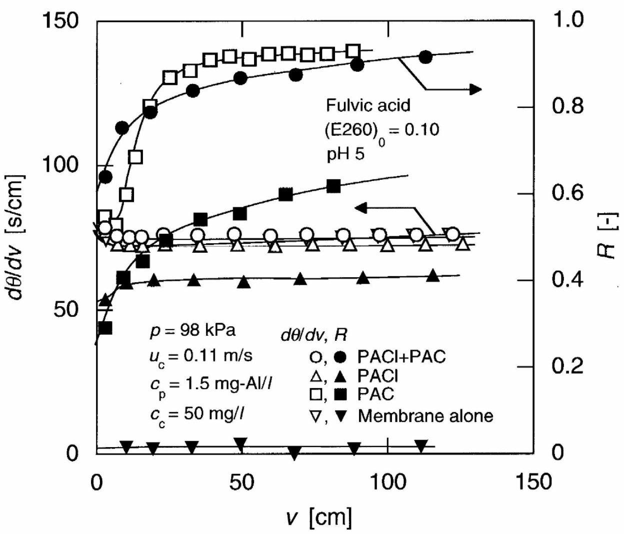

Fig.10 Effect of operation method on filtration rate and rejection in hybrid ultrafiltration of fulvic acid

filtration resistance but the flocs of PAC formed by the addition of PACl are easily swept away by a shear rate on the membrane. Thus, it is concluded that hybrid ultrafiltration combined with both flocculation and adsorption treatments is the best method for obtaining both high rejection of humic substances and high filtration rate.

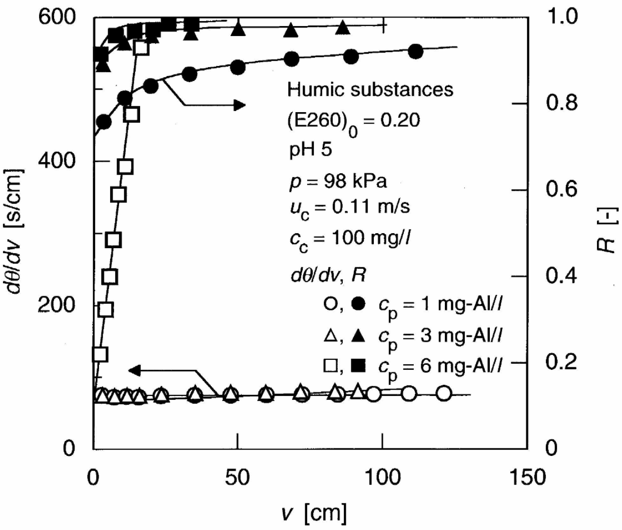

Fig.11 Effect of concentration of PACl on filtration rate and rejection in hybrid ultrafiltration of humic substances

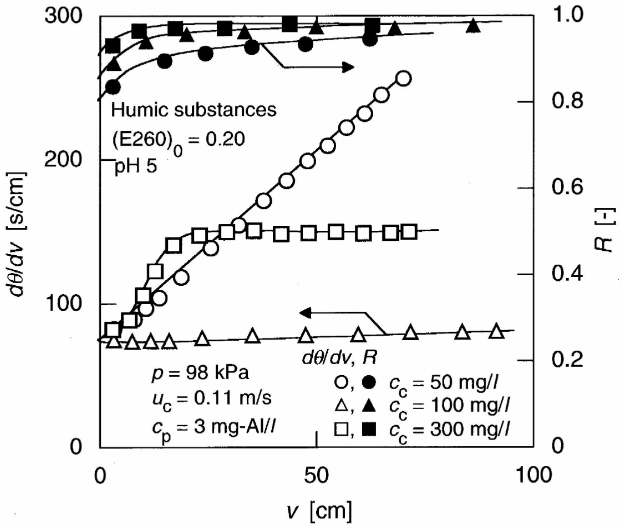

Fig.12 Effect of concentration of PAC on filtration rate and rejection in hybrid ultrafiltration of humic substances

In Figs. 9 and 10, the results of the same ultrafiltration experiments are plotted for the humic acids and fulvic acids, respectively. Also for humic acids, the high rejection is obtained by a combination of flocculation and adsorption. However, the filtration rate decreases markedly due to the growth of filter cake when adding PACl and/or PAC. The combination of both treatments leads to higher rejection also in case of fulvic acids. The filtration rate observed for fulvic acids has a tendency to decrease due to the cake growth when only PAC is added, but the decline in filtration rate is suppressed by the addition of both PACl and PAC since the flocs of PAC formed by PACl are easily swept away. In addition, the flocs of fulvic acids are also easily swept away as expected from the result of filtration rate in the addition of only PACl. These results indicate that the suppression of decline in filtration rate in hybrid ultrafiltration combined with both PACl and PAC observed in Fig. 8 is closely related to the presence of flocs of fulvic acids in feed solutions.

In Fig. 11, the results of the hybrid ultrafiltration experiments in fixed c_c of 100 mg/l are plotted for various PACl dosages c_p. A marked decrease in filtration rate and extremely high rejection of 0.96 are observed in c_p of 6 mg-Al/l. This may be attributed to the blockage of membrane pores by the dispersed microflocs of humic substances. On the other hand, the results of the hybrid ultrafiltration experiments in fixed c_p of 3 mg-Al/l are plotted for various PAC dosages c_c in Fig.12. The rejection has a tendency to

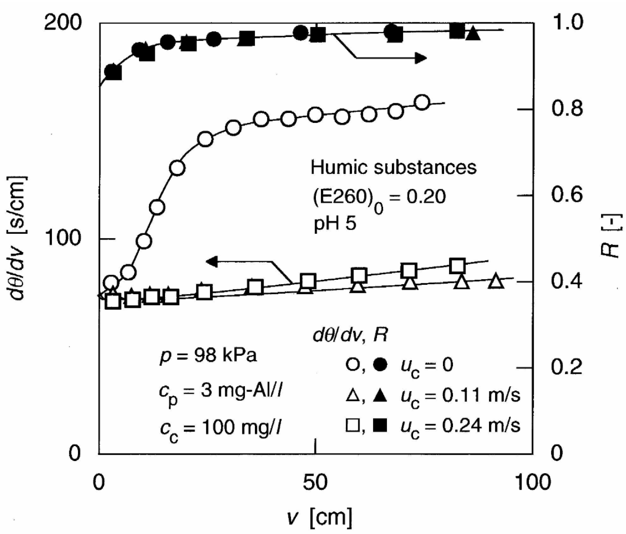

Fig.13 Effect of crossflow velocity on filtration rate and rejection in hybrid ultrafiltration of humic substances

increase with an increase of PAC dosage, while the filtration rate becomes the highest at c_c of 100 mg/l. These figures suggest that there exist the optimum dosages of PACl and PAC.

In Fig. 13, the effects of the average crossflow velocity u_c flowing inside of a hollow fiber membrane on the properties of hybrid ultrafiltration are shown. It is clearly demonstrated that the substantially high filtration rate can be maintained by the crossflow effect, just like crossflow ultrafiltration of proteins or nanoparticles [18]. On the other hand, the rejection is little affected by the crossflow velocity.

Conclusions

A method has been developed for removing humic substances by hybrid ultrafiltration combined with both flocculation and adsorption treatments. Flocculation by use of PACl was specially effective for the removal of humic acids referred to the relatively high molecular weight fractions of humic substances, whereas adsorption by use of PAC was able to remove fulvic acids of relatively low molecular weight effectively which could not be fully flocculated by PACl. Consequently, the combined operation of flocculation and adsorption was extremely effective for the treatment of humic substances. It was shown that both flocculation and adsorption characteristics of humic substances were strongly influenced by the solution pH. Hybrid ultrafiltration in combination with flocculation and adsorption treatments exhibited high permeate flux with high permeate quality. It was appeared that the dosages of both PACl and PAC exerts large effect on the filtration performance, and that there exist the optimum dosages of PACl and PAC.

Acknowledgments

This work has been supported in part by the Future Program of Japan Society for the Promotion of Science. The authors wish to acknowledge with gratitude the generous financial support for this study.

Nomenclature

c_c	=	concentration of PAC added to solution	[mg/l]
c_p	=	concentration of Al in PACl added to solution	[mg-Al/l]
E260	=	absorbance of solution at 260 nm	[-]
$(E260)_0$	=	absorbance of solution at 260 nm before treatment	[-]
p	=	applied filtration pressure	[Pa]
R	=	rejection of solute	[-]
u_c	=	average crossflow velocity flowing inside of hollow fiber membrane	[m/s]
v	=	filtrate volume per unit membrane area	[m]

Greek letters

q	=	time	[s]

References

1. Bian, R., Y. Watanabe, G. Ozawa and N. Tambo (1998), “Membrane Fouling of Ultrafiltration – Evaluation of Fouling for Treating River Water with Batch Test,” *J. Japan Water Works Assoc.*, **67**(1), pp. 16-24.
2. Jucker, C. and M. M. Clark (1994), “Adsorption of Aquatic Humic Substances on Hydrophobic Ultrafiltration Membranes,” *J. Membrane Sci.*, **97**, pp. 37-52.

3. Li, D., K. Urano, N. Kamiko, T. Ase and S. Nakatsuka (1996), "Cardinal Performance of New Hollow Fiber Ultrafiltration Membrane Made of Cellulose Diacetate for Water Treatment," *J. Japan Water Works Assoc*., **65**(4), pp. 31-39.
4. Clark, M. M. and P. Lucas (1998), "Diffusion and Partitioning of Humic Acid in a Porous Ultrafiltration Membrane," *J. Membrane Sci.*, **143**, pp. 13-25.
5. Takata, K., K. Yamamoto, R. Bian and Y. Watanabe (1998), "Removal of Humic Substances with Vibratory Shear Enhanced Processing Membrane Filtration," *Desalination*, **117**, pp. 273-282.
6. Combe, C., E. Molis, P. Lucas, R. Riley and M. M. Clark (1999), "The Effect of CA Membrane Properties on Adsorption Fouling by Humic Acid," *J. Membrane Sci.*, **154**, pp. 73-87.
7. Yuan, W. and A. L. Zydney (1999), "Humic Acid Fouling during Microfiltration," *J. Membrane Sci.*, **157**, pp. 1-12.
8. Ruohomäki, K. and M. Nyström (2000), "Fouling of Ceramic Capillary Filters in Vacuum Filtration of Humic Acid," *Filtration & Separation*, **37**(1), pp. 51-57.
9. Turcaud, V. L., M. R. Wiesner, J. Y. Bottero and J. Mallevialle (1990), "Coagulation Pretreatment for Ultrafiltration of a Surface Water," *J. Am. Water Works Assoc.*, **82**, pp. 76-81.
10. Adham, S. S., V. L. Snoeyink, M. M. Clark and J.-L. Bersillon (1991), "Predicting and Verifying Organics Removal by PAC in an UF system," *J. Am. Water Works Assoc.*, **83**, pp. 81-91.
11. Jacangelo, J. G., J.- M. Laine, E. W. Cummings and S. S. Adham (1995), "UF with Pretreatment for DBP Precursors," *J. Am. Water Works Assoc.*, **87**(3), pp. 100-112.
12. Kamei, T., Y. Matsui, T. Nakanori, N. Tambo and H. Takeda (1995), "Color Removal by Ceramic Membrane Filtration," *J. Japan Water Works Assoc*., **64**(7), pp. 34-40.
13. Bian, R., Y. Watanabe, G. Ozawa and N. Tambo (1998), "Membrane Fouling of Ultrafiltration – Evaluation of Influences of Pretreatment with Batch Test," *J. Japan Water Works Assoc*., **67**(3), pp. 11-19.
14. Lin, C.-F., Y.-J. Huang and O. J. Hao (1999), "Ultrafiltration Processes for Removing Humic Substances: Effect of Molecular Weight Fraction and PAC Treatment," *Wat. Res.*, **33**, pp. 1252-1264.
15. Snoeyink, V. L., C. Campos and B. J. Marinas (2001), "Design and Performance of Powdered Activated Carbon/Ultrafiltration Systems," *Water Sci. Technol.*, **42**(12), pp. 1-10.
16. Li, F., K. Ebie, Y. Azuma, A. Yuasa, T. Hagishita and Y. Matsui (2000), "Influence of Water pH on Activated Carbon Adsorption of Humic Matter Remaining after Coagulation," *J. Japan Water Works Assoc*., **69**(11), pp. 9-19.
17. Lee, M. C., V. L. Snoeyink and C. Crittenden (1981), "Activated Carbon Adsorption of Humic Substances," *J.Am. Water Works Assoc.*, **73**, pp. 440-446.
18. Iritani, E., T. Hayashi and T. Murase (1991), "Analysis of Filtration Mechanism of Crossflow Upward and Downward Ultrafiltration," *J. Chem. Eng. Japan*, **24**, pp. 39-44.