Fouling monitoring during microfiltration of humic acid by streaming potential measurement

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ABSTRACT

Fouling by natural organic matter like humic substances is one of the major factors limiting the application of microporous membranes for water production. The charge of the pore surface of membrane, which can be characterized by the streaming potential(SP) measurement as the apparent zeta potential ζ_{obs}, has a large effect on its fouling performance. However the relationship between the fouling condition and the apparent zeta potential is not always clear. The objective of this study was to develop a fouling monitoring technique during the microfiltration of humic acid by streaming potential measurement. The apparent zeta potential was measured continuously during the filtration. The apparent zeta potential increased with the increase in filtration resistance during filtration. The apparent zeta potential of fouled membrane was depended on the degree of the fouling however the absolute value of the apparent zeta potential was not same with the zeta potential of Humic acid, which was obtained by electrophoresis method. And it was demonstrated that the apparent zeta potential is useful for the confirmation of the effect of the cleaning of the fouled membrane by the cleaning experiments using pure water and alkali detergent.

KEYWORDS

Microfiltration membrane, Streaming potential, Fouling

INTRODUCTION

The membrane fouling is one of the major factors limiting the application of microporous membrane. As membrane filtration of natural organic matter(NOM), such as humic substance, for drinking water supply is becoming increasingly widespread[1)], the fouling mechanism of humic acid has been of interest. Humic acid fouling mechanisms was reported by Wei, et al. from the view point of flux decline in UF[2)] and in MF[3)]. C.Combe et al., studied adsorptive fouling by humic acid using various surface modified CA membranes[4)]. Seong-Hoon et al. showed the effect of calcium ion on the humic acid fouling in NF membrane[5)].

The charge of the pore surface of membrane, which can be characterized by the streaming potential(SP) measurement as the apparent zeta potential, has a large effect on its fouling performance. We have developed the continuous streaming potential measurement method[6)] and studied about the effect of the pore structure of membrane on the apparent zeta potential[7)]. However the relationship between the fouling and the apparent zeta potential is not clear.

The objective of this work is to investigate the relationship between the fouling and the apparent zeta potential in the filtration of humic acid and show the ability of the streaming potential measurement for the fouling monitoring technique. The apparent zeta potential was measured continuously during filtration by pulse pressurizing method. The effect of cleaning condition using pure water and alkali detergent for the fouled membrane on the apparent zeta potential was studied.

EXPERIMENTAL

Cellulose acetate membranes(Fuji Film, FM series) with pore sizes of 0.22μm were used. These membranes have asymmetric pore structure and was normally used in the direction from the top(shiny) surface to the bottom(dull) surface.

1mM KCl solution filtered with a 0.5μm membrane filter was used as the electrolyte for streaming potential measurement. Fouling studies were performed with humic acid(Aldrich Chemical). 0.1g/L Humic acids solutions were prepared by dissolving 0.1g of the powdered Humic acid in 100mL of 0.01N NaOH with stirring for 3hrs and stirring for 24hrs after neutralization with 1N HCl and diluting with pure water to 1L and filtering with a 0.5μm membrane filter before use. Feed humic acid solutions were prepared by diluting the 0.1g/L Humic acids with the 1mM KCl solution. The zeta potential of the humic acid in the solution was –33.6mV measured by a electrophoretic light scattering spectrophotometer (Otsuka Electronics, ELS-8000). The concentration of humic acid was measured on a UV spectrophotometer (Shimadzu, UV1200) at 260nm.

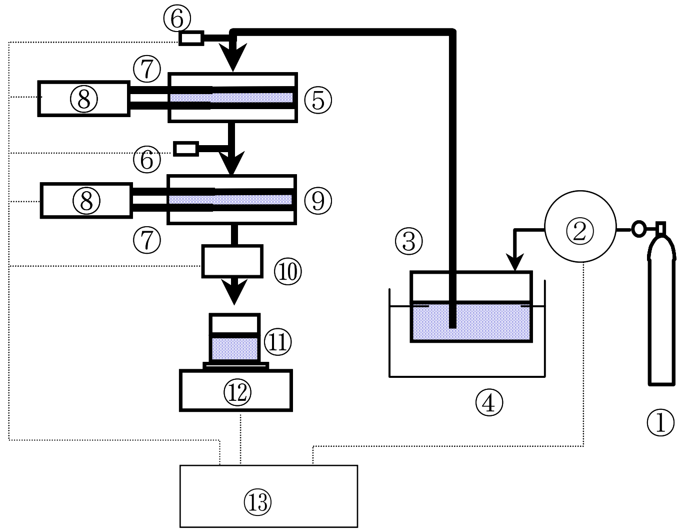

Fig.1 Experimental apparatus for streaming potential measurement: 1:N_2 gas cylinder, 2:Pressure controller, 3:Pressure holding tank, 4:Temperature control bath, 5:Membrane filter for particle removal, 6:Pressure transducer, 7: Electrodes, 8:Digital multi meter, 9:Measuring membrane holder, 10:Conductivity flow cell, 11:Filtrate reservoir, 12:Electric balance, 13:Personal computer.

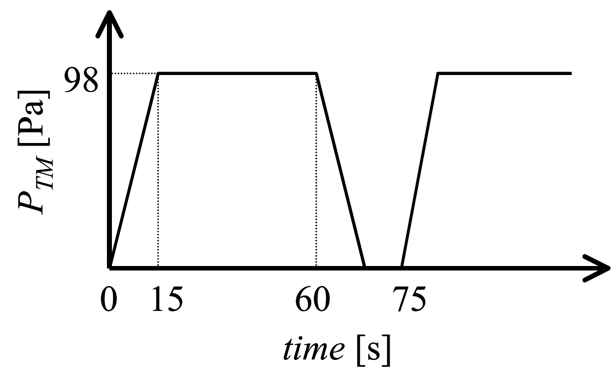

Fig.2 Pulse pattern of applied pressure.

Fig.1 shows experiment apparatus. Two membrane housings(25mm diameter) were connected in series. These membrane housings had platinum electrodes to measure the electrical potential difference generated across the membrane. The permeate flux, trans-membrane pressure, electrical potential difference across membrane and conductivity of permeate solution were measured with a electric balance(Shimadzu, EB3300SW), pressure transducer(Kyowa, PVL-5KB), digital multi meter(Advantest, R6441) and conductivity meter(TOA, CM-40G), respectively. The measuring data were recorded by a personal computer. Temperature in feed tank was kept at 298K. Applied pressure was controlled at the constant value of 98kPa or the pulse pattern (0-98kPa) as shown in Fig.2.

A new membrane was set into the each membrane holders. After the measurements of the pure water flux at 98kPa, the streaming potential and permeate flux with 1mM KCl solution, humic acid solution was filtered. During the filtration the permeate flux, absorbances at 260nm of the permeate solution and the streaming potential were measured. After the filtration the streaming potential with 1mM KCl solution was measured again.

Membrane cleaning effects were examined by measuring the streaming potential and the permeate flux with 1mM KCl solution. The fouled membrane was rinsed twice with 50ml pure water and then cleaned with 50ml alkali detergent (0.1% Ultrasil 11) for 30minuts. The humic acid filtration was repeated 3times with the cleaned membrane.

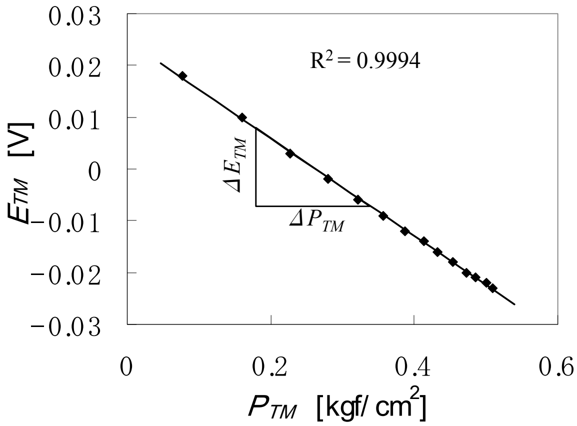

Fig.3 The relationship between P_{TM} and E_{TM} for the membrane of pore size 0.22µm.

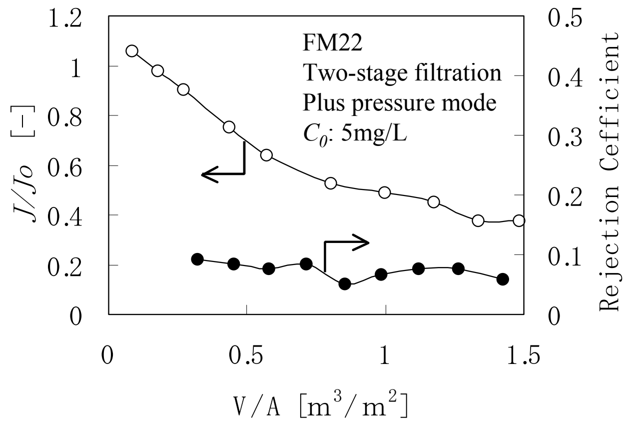

Fig.4 Filtrate flux and humic acid rejection coefficients for the two-stage serial filtration with 0.22µm membranes(FM22) of 5mg/L humic acid solution of the pulse pressure mode.

RESULT AND DISCUSSION

Streaming Potential Measurement

Fig.3 shows a typical result for streaming potential measurement. The relationships between the electrical potential difference, E_{TM}, and the pressure difference, P_{TM}, showed good linearity, which shows the validity of the measurement. The streaming potential(*SP*) was defined as the slope of the line,

$$Streaming\ Potential\ (SP) = \frac{\Delta E_{TM}}{\Delta P_{TM}}. \qquad (1)$$

SP was determined by linear regression for the plots of which the coefficient of determination R^2 is above 0.998.

The observed zeta potential, ζ_{obs}, was estimated using Helmholtz- smoluchouski equation,

$$\zeta_{obs} = \frac{\mu\ \lambda}{\varepsilon_0\ \varepsilon_r}\frac{\Delta E_{TM}}{\Delta P_{TM}} = \frac{\mu\ \lambda}{\varepsilon_0\ \varepsilon_r} SP \qquad (2)$$

where μ is the solution viscosity, λ is the solution conductivity, ε_0 is the permittivity of vacuum, ε_r is the dielectric constant of the medium.

Humic Acid Fouling

Fig.4 shows typical results for the flux and the humic acid rejection coefficient based on E_{260},

$$Rejection\ coefficient = 1 - \frac{E_{260\,filtrate}}{E_{260\,feed}}, \qquad (3)$$

as functions of filtrate volume per unit membrane area, *V/A*, during the two-stage serial filtration with 0.22µm membranes(FM22) of 5mg/L humic acid solution in the pulse pressure mode. The flux was normalized by J_0, the pure water flux evaluated before the filtration. Flux declined with increase in filtrate volume and became about 0.5 at *V/A* of 1m. Rejection coefficient was lower than 0.1 throughout the filtration. Almost same rejection coefficient was also obtained in the case of one-stage filtration with the same membrane.

The place where the fouling take place was confirmed by the comparing the filtration resistances, that reflects pressure drop, of the 1st and 2nd stage membranes,

$$J = \frac{P_{TM,Total}}{\mu R_{Total}} = \frac{P_{TM,1} + P_{TM,2}}{\mu (R_1 + R_2)} = \frac{P_{TM,1}}{\mu R_1} = \frac{P_{TM,2}}{\mu R_2} \quad (4)$$

where *R* is filtration resistance and subscripts 1 and 2 mean 1st and 2nd stage membrane, respectively. Fig.5 shows the comparison of the filtration resistance between the 1st stage membrane and 2nd stage one. The filtration resistance was normalized by the filtration resistance measured with pure water before the filtration. The filtration resistance of 1st stage membrane increased with increase in filtration volume while that of 2nd stage membrane showed almost 1 throughout the filtration. This shows that the fouling took place at the filtration surface of 1st stage membrane and did not take place inside of the pore. And it is expected that the fouling would be caused by the humic acid aggregates and would not be caused by the dissolved humic acid.

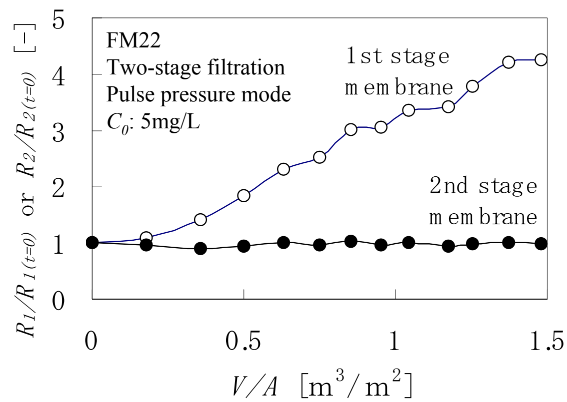

Fig.5 Comparison of filtration resistance between 1st stage membrane and 2nd stage membrane during the two-stage filtration with 0.22µm membranes(FM22) of 5mg/L humic acid solution of the pulse pressure mode.

Fig.6 shows the ζ_{obs} estimated from *SP* measured for both 1st and 2nd membranes during the filtration. The ζ_{obs} of the FM22 membrane in clean condition showed negative value of –20±2mV. ζ_{obs} of the 1st stage membrane increased with increase in filtration volume from the initial value of –18.4mV to –7mV while that of 2nd stage membrane showed almost constant value of –20mV throughout the filtration. The tendencies of the change in ζ_{obs} during filtration of the each membrane were almost the same as those in the filtration resistance as was shown in Fig.5. It is seemed that the change in ζ_{obs} during the filtration would reflect the change in the fouling condition. It was expected that ζ_{obs} of fouled membrane would approach to the zeta potential of the humic acid of –33.4mV, but ζ_{obs} changed to the opposite direction from the initial ζ_{obs} value of –18.4mV. The reason is not clear. From these observations it was shown that the change in ζ_{obs} during the filtration could indicate the degree of the fouling but the meaning of the absolute value of ζ_{obs} is not clear.

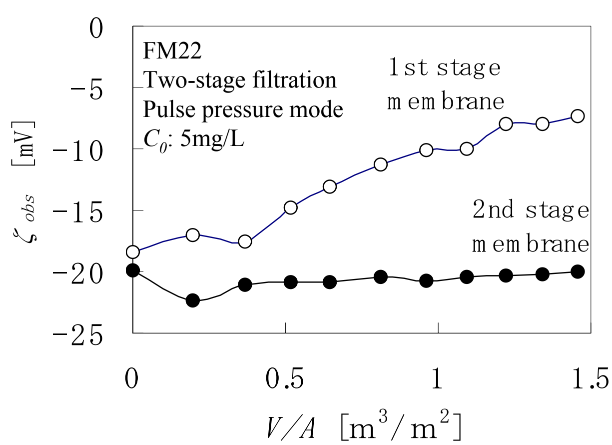

Fig.6 Change in ζ_{obs} during the two-stage filtration with 0.22µm membranes(FM22) of 5mg/L humic acid solution in the pulse pressure mode.

Membrane Cleaning

In order to clarify if the ζ_{obs} is applicable for the effect of membrane cleaning the ζ_{obs} and permeate flux were measured with 1mM KCl solution before and after the fouling and cleaning experiments. Table 1 shows the change in ζ_{obs} estimated at the fouling and the cleaning steps.

Table 1 The change in ζ_{obs} and flux measured with 1mM KCl solution before and after fouling and cleaning.

	Membrane	Clean condition (before filtration)	Fouled condition (after filtration)	After the rinsing with pure water	After the cleaning with the alkali detergent
ζ_{obs} [mV]	1st stage	-21.1	-10.1	-15.8	-19.1
	2nd stage	-20.3	-21.0	-21.5	-20.7
Flux×10^3 [m/s]		1.89	0.88	1.40	1.94

The ζ_{obs} of the 1st stage membrane changed from –10.1mV of the fouled condition to –15.8mV by the rinsing with pure water and then recovered to –19.1mV, which was almost the same value of the clean membrane, after the cleaning with the alkali detergent. The other hand, the flux improved depending on the each cleaning step and recovered to the almost same value of the clean membrane after the cleaning with the alkali detergent. The ζ_{obs} of the 2nd stage membrane, which didn't show the increase in the filtration resistance during the humic acid filtration, was almost constant value of 21±1mV independently of the fouling and the cleaning steps. It was demonstrated that the ζ_{obs} is a useful for the effect of membrane cleaning.

CONCLUSION

(1) The fouling during the microfiltration of humic acid solution with 0.22μm membranes(FM22) was caused by humic acid aggregates at the filtration surface of the membrane and the dissolved humic acid did not cause the fouling.
(2) The change in ζ_{obs} during the filtration had a relation to the change in the filtration resistance and could indicate the degree of the fouling. However the meaning of the absolute value of ζ_{obs} was not clear.
(3) It was demonstrated that the effect of cleaning condition for the fouled membrane could be confirmed by the change in the apparent zeta potential.

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