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액상유기성슬러지로부터 용존유기물의 회수를 위한 막결합형 발효 시스템의 여과 특성

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Filtration Characteristics of Membrane-coupled Fermentor System for Dissolved Organics Recovery From Liquid Organic Sludge

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요 약: 본 연구는 액상유기성 슬러지로부터 용존 유기물을 회수하기 위한 막결합형 발효 시스템의 여과특성의 검토에 초점을 두었다. 0.1 μm~5 μm 범위에서 6종류의 막공경을 대상으로 한 슬러지 발효액의 정밀여과 특성으로 막공경이 작을수록 전체저항이 큰 값을 나타내었고 케익층의 형성에 의한 저항이 전체저항의 68~88%를 차지하여 막투과유속의 저하는 주로 입자간의 물리화학적 상호작용에 의한 막표면에의 강한 입자침전에 기인함을 알 수 있었다. 발효액의 고형물 농도가 증가함에 따라 막투과유속은 감소하였으나 일정이상의 고형물 농도에서는 비례관계를 보이지 않았다. 막면유속이 증가할수록 그리고 5.0~6.0의 pH범위에서 높은 막투과유속이 얻어졌고 에너지 효율측면에서는 가능한 낮은 압력에서 여과하는 것이 유리한 것으로 나타났다. 0.1 μm과 0.2 μm의 막공경에서는 100%의 미생물 제거율을 보였다. 액상 유기성 슬러지로부터 용존 유기물을 효율적으로 회수하기 위한 최적 막공경은 제안된 기준의 관점에서 볼 때 1 μm 정도라 판단되어진다.

Abstract: This study was focused on the investigation of filtration characteristics of membrane-coupled fermentor system for dissolved organics recovery from liquid organic sludge. On the filterability of MF over the range of 0.1~5 μm, the magnitude of total membrane resistance (R_t) is ranged as follows in the order; 0.1 μm>0.2 μm>0.5 μm>1 μm>2 μm> 5 μm. The cake layer resistance (R_c) occupied about 68~88% of total resistance with fermented sludge. Permeation flux decline was mainly attributed to the R_c, which was formed by a strong deposition from physico-chemical interactions of solids on membrane surface. Higher suspended solids (SS) concentration of suspension caused lower permeation flux. However, there was not a proportion relation beyond a certain SS concentration. The cross-flow velocity on the membrane surface was faster, which resulted in the higher permeation flux and also more efficient with low trans membrane pressure (TMP) in viewpoint of energy efficiency. The appropriate pH of suspension was over the range of 5.0~6.0 for dissolved organics recovery as well as the permeation flux. It is possible for bacteria to be separated perfectly with 0.1 μm and 0.2 μm membrane pore size. Based on experimental results, most appropriate membrane pore size for the recovery is believed to around 1 μm.

Keywords: *membrane-coupled fermentor system, liquid organic sludge, microfiltration, ceramic membrane*

1. Introduction

The recent development of less expensive and more efficient microfiltration (MF) or ultrafiltration (UF) membranes has generated a new concept in anaerobic biological treatment. In anaerobic treatment, membrane-coupled anaerobic process is used as a modification of the conventional anaerobic treatment process. The extended contact time between the microbe and organic solutes enhances the biodegradation and/or mineraliza-

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Table 1. Characteristics and Specification of Ceramic Membrane

Filtration type of membrane	MF
Pore size	Monolith : 0.1, 0.2, 0.5 (μm), Tubular : 1.0, 2.0, 5.0 (μm)
Material	Fine ceramic
Effective surface area	Tubular: 0.035 (m^2), Monolith: 0.12 (m^2)
Dimension	Tubular : ϕ 30* ϕ 22* 500 L (mm), Monolith: ϕ 30* ϕ 4-19 hole* 500 L (mm)
Filtration type	Cross-flow
Pressure method	Suction from outside
Internal rupture strength	Tubular : $\geqq$30 (kgf/cm^2), Monolith : $\geqq$100 (kgf/cm^2)
pH resistance range	0 - 14

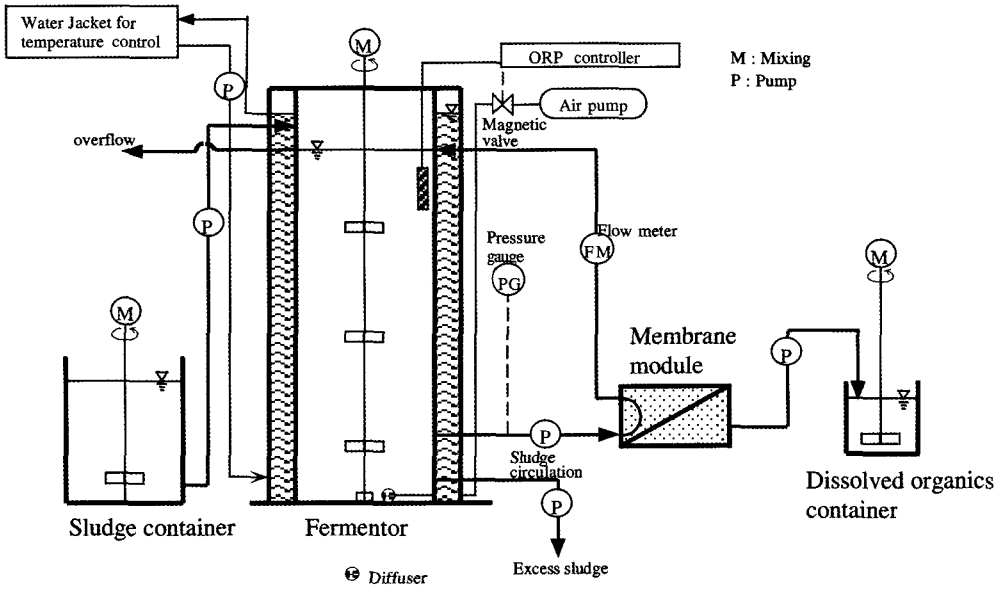

Fig. 1. Schematic diagram of membrane-coupled fermentor system.

tion of these solutes by microbial enzyme [1,2]. Thus, a membrane-coupled anaerobic bioreactor incorporating UF or MF as the separation step after the anaerobic bioreactor has been developed to completely retain biomass in the reactor.

Although the anaerobic fermentation process has long been popular in the wastewater treatment field, it has been mainly employed to stabilize the suspended organic material and to provide a source of energy. Therefore, relatively few studies have focused on the acid-phase step of the process, especially, using membrane as solid-liquid separation tool as well as condensing of biomass in the reactor [3].

The dissolved organic compounds containing volatile fatty acids (VFAs) can be used effectively as hydrogen donor for biological nitrogen and phosphorous removal or basic material for the synthesis of polymer [4].

Based on the above discussions, this study was focused on the ceramic membrane filterability corresponding to operational parameters and the relationship between water quality of permeate, flux and membrane pore size. Ultimately, the most appropriate membrane pore size was determined for the effective recovery of dissolved organics from fermented liquid sludge.

2. Experimental

2.1. System Description

Membrane filter medium for solid-liquid separation is made from ceramic with many fixed pores. The total set-up used in this study is shown in Fig. 1. The outward of ceramic membrane is illustrated in Fig. 2. A

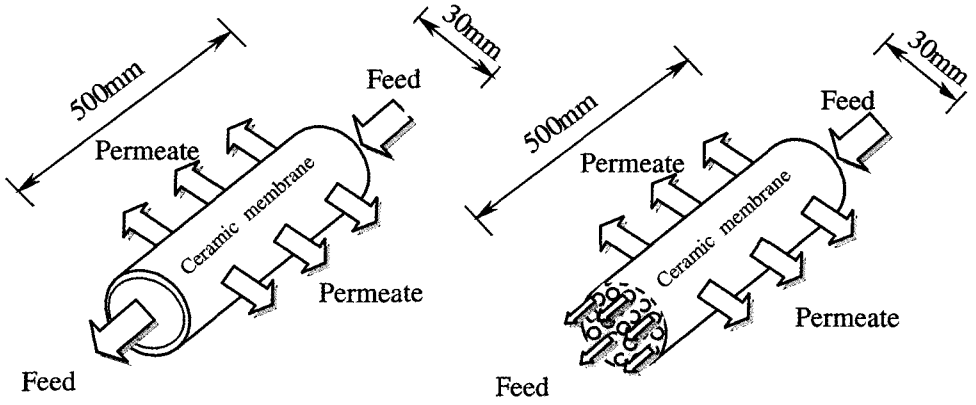

Fig. 2. Ceramic membrane filter element tube.

cross-flow MF unit (supplied by Nihon Gaishi Co., Ltd.) was used. The properties and specification of ceramic membrane are summarized in Table 1. Membrane pore size tested in this study was informed value from company and means a nominal pore size. The system, with a total working volume of 76 L consisted of an anaerobic acid fermentor, a ceramic MF module, sludge container and VFAs container.

Suspension was continuously fermented at 35°C in advance as pre-cultivation. Coagulated fresh sludge with the dosage of poly aluminum chloride (PAC) (10 mg/L) was used as the fermentation substrate. Coagulated raw sludge was screened with a sieve of 3 mm for smooth circulation before it was supplied. The ceramic membrane module was equipped with a pump for feed circulation. The cross-flow velocity through the membrane module was adjusted by the regulation of the pump, while the pressure was regulated with a pump attached to the membrane module. Targeted range of trans membrane pressure (TMP), cross-flow velocity and suspended solids (SS) concentration were 30 to 200 (kPa), 0.1 to 0.4 (m/s) and 2 to 18 (g/L), respectively. For the investigation of pH effect on permeation flux, monolith type membrane of 1 μm pore size was used. After pH was adjusted with HCl and NaOH, then the flux after 20 min filtration was measured.

In analysis, permeation resistances and flux of each pore size membrane were analyzed to determine appropriate pore size for VFAs recovery. General bacteria, SS, aluminum, phosphorous, VFAs and total organic carbon (TOC) concentrations in permeate are considered as targeted items. TOC was measured with a TOC analyzer (TOC-5000, Shimadzu, Kyoto) and the concentrations of Al ion were measured by ICPU (ICPS 4960, Shimadzu, Kyoto). Concentration of VFAs was measured by Gas chromatograph (GC-14A, Shimadzu, Kyoto). Measurements of other items were conducted by standard methods [5].

2.2. Calculation of Permeation Flux

The resistance-in-series model was applied to evaluate the characteristics of membrane fouling. The model is illustrated in Fig. 3. In this model, the permeation flux (J) is expressed as the following equations:

$$J=\Delta P/(\mu \cdot R_t) \quad (1)$$

$$R_t=R_m+R_p+R_c \quad (2)$$

$$1/J_i=(\mu/\Delta P) \cdot R_m \quad (3)$$

$$1/J_w=(\mu/\Delta P) \cdot (R_m+R_p) \quad (4)$$

J_i is initial pure water flux of membrane, while J_w are the flux by pure water flux after cleaning of membrane; ΔP is the TMP (Pa) ; μ is the dynamic visco-

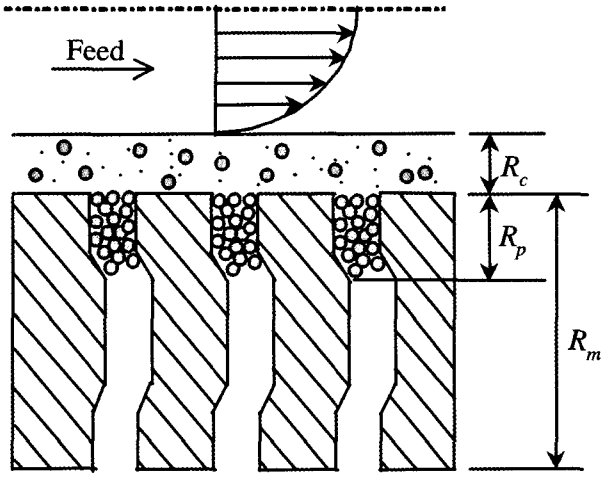

Fig. 3. Conceptual description of membrane-resistance model.

Table 2. The Standard of Optimal Membrane Pore Size for Dissolved Organics Recovery

Associated parameter	Value
Rejection of Bacteria	more than 6 log
SS concentration in permeate	less than 1 (mg/L)
VFAs recovery ratio of (permeate/fermented suspension)	more than 80%
Permeation flux at steady state	more than 0.5 (m^3/m^2/day)

sity of the permeate (Pa·s); R_t is the total resistance (m^{-1}); R_m is the membrane resistance (m^{-1}); R_p is the plugging layer resistance due to some colloidal adsorption (m^{-1}) and R_c is the external fouling resistance formed by a strongly deposited cake layer on the membrane surface (m^{-1}). These equations were used to calculate the values of each resistance term of membrane.

2.3. Optimal Membrane Pore Size for Dissolved Organics Recovery

One of the most important objectives of this study is to determine the optimal membrane pore size for dissolved organics recovery from liquid sludge among test ceramic membranes. The standard of optimal membrane pore size was shown in Table 2. Considering the use of electron donor of obtained dissolved organics for biological denitrification, as associated parameters, rejection ratio of bacteria and suspended solids, VFAs concentration of (permeate/fermented suspension) and permeation flux were compared with suggested membrane pore sizes.

3. Results and Discussion

3.1. Effect of Membrane Pore Size on Flux

The fouling tendency varied according to membrane pore size. Permeation resistances and flux of each membrane pore size are shown in Table 3 and Fig. 4. Both are the results after 7 h filtration.

Steady state means the moment when the flux does not change any more during continuous filtration. Generally, though the flux increases with the pressure, when the flux reached fixed value it was not affected the pressure. Like this, limiting flux is defined the flux independence of pressure increase at steady state. In this experiment, the permeation flux was not changed after 7 h, thus this value is determined as limiting flux and this time is considered to steady state.

The resistance of membrane itself (R_m) was de-

Table 3. Permeation Resistances of Each Pore size

Unit (*10^{11}, m^{-1})

Type	Pore size (μm)	R_m (%)	R_p (%)	R_c (%)	R_t (%)
Monolith	0.1	51.3 (25.3)	0.4 (0.2)	151.1 (74.5)	202.6 (100)
	0.2	50.8 (27.5)	0.3 (0.2)	133.5 (72.3)	184.6 (100)
	0.5	50.3 (30.9)	0.6 (0.4)	112.0 (68.7)	162.9 (100)
Tubular	1.0	15.8 (10.8)	0.8 (0.6)	129.1 (88.6)	145.7 (100)
	2.0	15.3 (11.6)	1.3 (1.0)	115.4 (87.4)	131.9 (100)
	5.0	14.0 (10.8)	1.6 (1.2)	114.2 (88.0)	129.8 (100)

(ΔP:75 kPa, SS: 18 g/L, Cross-flow velocity : 0.4 m/s, Temperature : pure water 25°C, fermented suspension 35°C, Viscosity: pure water 0.73 cP, fermented suspension 0.78cP)

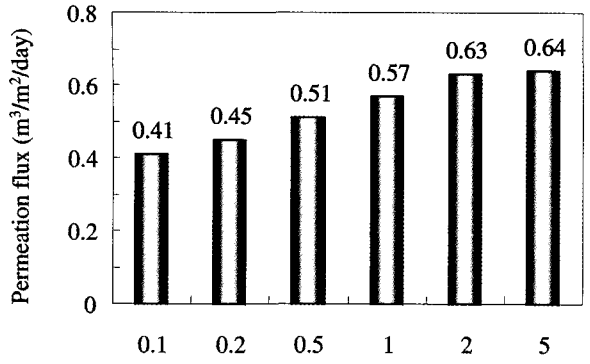

Fig. 4. Permeation flux versus membrane pore size at steady state.

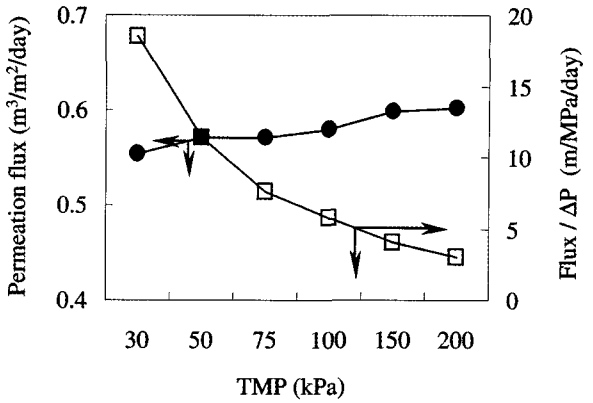

Fig. 5. Relationship between TMP and permeation flux.

creased with pore size increase. The value of (R_m/R_t) in monolith type indicates higher than that of tubular type. Plugging layer resistance (R_p) due to some colloidal adsorption was at a maximum in 5 μm pore size under the same pressure condition. From this result, we can understand that biomass and colloidal particles easily deposit in membrane cavity with pore size increase. The value of R_c with 0.1 μm pore size indicated 1.3 times greater than that of 5 μm pore size. The discrepancy of R_c between 0.5 μm and 1 μm may be attributed to the difference of monolith type and tubular type. The magnitude of total membrane resistance (R_t) of various filters is ranged as follows; 0.1 μm>0.2 μm >0.5 μm>1 μm>2 μm>5 μm. The cake layer resistance (R_c) was about 68 to 88% of R_t. Therefore, membrane fouling was mainly attributed to permeate resistance of cake layer (R_c), which was formed by a strongly deposited from physico-chemical interactions of solids on the membrane surface. Relationship between permeation resistance and membrane pore size was illustrated in Fig. 4. From this figure, it was also found that permeation flux of each pore size was in proportion to total membrane resistance (R_t).

3.2. Effect of TMP and Cross-flow Velocity on Permeation Flux

Fig. 5. shows the variation of permeation flux and limiting flux per unit pressure ($J_L/\Delta P$) with pressure increase. Monolith type of membrane with 1 μm pore size was used in this experiment. Though the permeation flux increased with pressure increase, the value of $J_L/\Delta P$ was decreased on the contrary. Therefore, it is favorable for pressure to operate with minimum pressure that can be obtained the limiting flux in viewpoint of energy efficiency.

This can be explained as follows: the permeation flux becomes low in the case of low pressure at steady state. Then, cake layer on membrane surface becomes thin and allows giving a low permeation resistance. On the other hand, the permeation flux becomes high in case of high pressure. Then, cake layer on membrane surface becomes thick and resulted in high permeation resistance. Increased pressure and resistance are offset and effective pressure decreases on the whole. Eventually, the result is the same as the low-pressure operation.

Cross-flow filtration is a process in which the formation of a filter cake is limited by flow of the suspension parallel to the membrane filtration surface. In contrast, in case of dead-end filtration, the particles are retained by the filter medium while the liquid flows through the filter cake and through the medium. It is clear that, in case of dead-end filtration, clogging occurs in a short time due to the build-up of filtered cake, while in cross-flow filtration, particles deposited on the filter medium are swept away by the cross-flow velocity action.

Fig. 6 shows the relationship between the cross-flow velocity and the permeation flux. In this figure, the permeation flux was increased with cross-flow velocity increase. It is hardly to form the cake layer on mem-

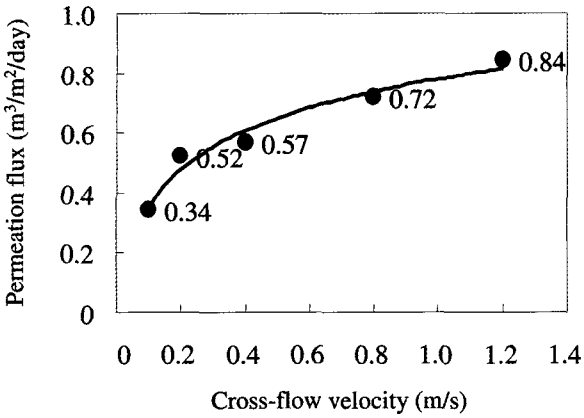

Fig. 6. Relationship between cross-flow velocity and permeation flux.

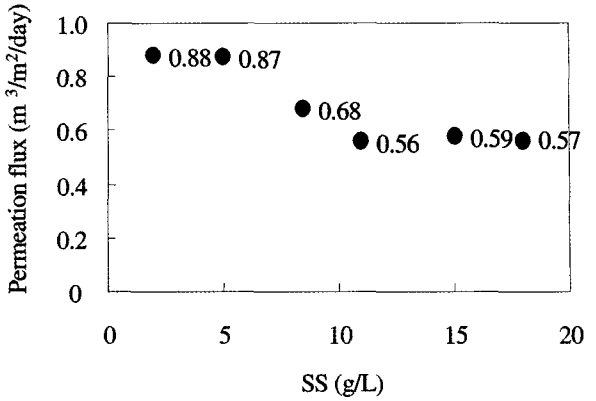

Fig. 7. Relationship between SS concentration and permeation flux.

brane surface because materials movement was improved in high cross-flow velocity. Thus, high permeation flux can be obtained. It is necessary to increase the cross-flow velocity for high permeation flux keeping. As shown in Table 4, it was also found that the smaller the cross-flow velocity was, the greater the cake layer resistance indicated. However, the plugging layer resistance was increased with the cross-flow velocity increase.

3.3. Effect of SS and pH on Permeation Flux

The SS concentration had a great influence in the permeation flux as well. The relationship between SS concentration in the reactor and the permeation flux was shown in Fig. 7. Up to 10 (g/L) of SS concentration, the higher SS concentration was, the smaller the permeation flux was. Beyond 10 (g/L) to 18 (g/L) of SS concentration, the permeation flux was not greatly affected by the increase of SS concentration. Researches for biomass condensing in the reactor are being investigated to enhance the treatment efficiency. However, it is necessary to investigate on the proper concentration and flux in consideration of these opposite relations.

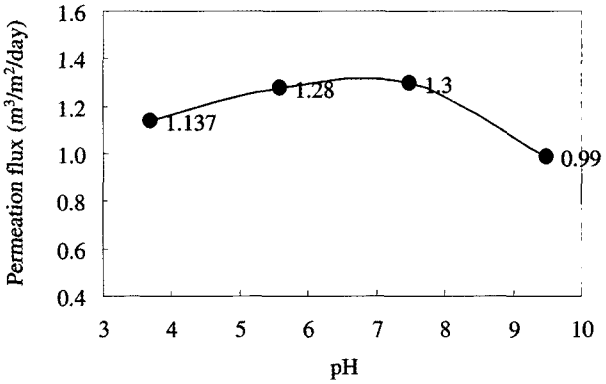

Fig. 8. Permeation flux variation with respect to pH.

Fig. 8. shows the effect of pH on permeation flux. As a result, the permeation flux was high in the range of pH 5.5 to 7.5. This may be attributed to the fact that the particles precipitate rapidly on membrane surface in the strong acid and base region. That is, in

Table 4. Cross-flow Velocities Versus the Permeation Resistance

Pore size (μm)	Cross-flow velocity (m/s)	Flux ($m^3/m^2/day$)	Permeation resistance ($*10^{11}$, m^{-1})			
			R_m	R_p	R_c	R_t
1	0.1	0.3	15.8	0.6	227.6	244.0
	0.2	0.5	15.8	0.6	146.2	162.6
	0.4	0.6	15.8	0.8	129.1	145.7
	0.8	0.7	15.8	1.0	100.2	117.0
	1.2	0.8	15.8	1.3	82.0	99.1

(ΔP:75 kPa)

Table 5. Biomass Rejection Ratios at Each Membrane Pore Size

Permeate	Bacteria (cells/mL)	Rejection (%)
Feed suspension	$7*10^7$	
0.1 μm	0	100
0.2 μm	0	100
0.5 μm	1*101	99.9999 (6 log)
1 μm	4*101	99.9999 (6 log)
2 μm	7*102	99.999 (5 log)
5 μm	3*104	99.9 (3 log)
5 $\mu m^{(a)}$	3*106	95 (1.3 log)

5 $\mu m^{(a)}$: filtration during 5 min after initiation
Filtration conditions; [P: 75(kPa), Feed velocity: 0.4(m/s), Suspension temperature: 35(°C), SS:18(g/L)]

case the iso-electric point of protein or particles is changed to high or low by the variation of suspension pH, the precipitation rate of particles on membrane surface is higher than that in neural range of pH. When 50 (mg/L) of $KMnO_4$ were used at the unadjusted pH value around 7.5, the flux was 8000 ($L/m^2/h$) after 20 min of the membrane filtration. But when the same concentration was used at a pH of around 10, the flux was only 330 ($L/m^2/h$) after 13 min of filtration [6].

3.4. Water Qualities of Permeate and Bacteria Rejection on Each Pore Size

Leakage of biomass is easy to cause as much as the pore size of membrane is large. Therefore, it is expected that the SS concentration will increase in permeate with large membrane pore size. The results regarding leakage of bacteria, SS concentration and turbidity at each membrane pore size were shown in Table 5 and Fig. 9, respectively.

In the case of membrane pore size 0.1 and 0.2 μm, biomass can be separated completely. Although the rejection ratio was 95% during 5 min of filtration initiation, it was increased to 99.9% of rejection ratio at steady state with pore size 5 μm. This can be explained by the blocking action of biomass that was formed on membrane surface or internal part.

SS rejection was also 100% in case of pore size 0.1 and 0.2 μm and it was somewhat high value of 11.6 (mg/L) with 5 μm. Turbidity of permeates showed the proportion relationship with SS concentration. Turbidity was increased with the pore size increase. This tendency can be an important factor to determine the appropriate membrane pore size for organics recovery from fermented liquid sludge.

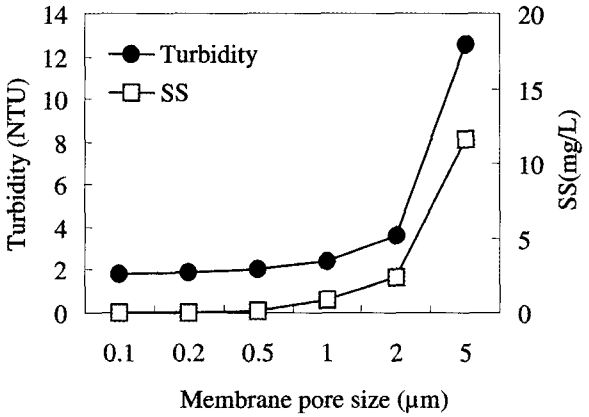

Fig. 9. SS concentration and turbidity in permeate corresponding to membrane pore size.

On the other hand, the VFAs concentration ratio of suspension and permeate was shown in Fig. 10. and the aluminum and phosphorous concentration of permeate was illustrated in Fig. 11, respectively. The greater membrane pore size was, the higher concentration ratio was obtained. The concentration ratio exceeded more than 80% in the cases of 1, 2 and 5 μm and showed the about 1.1 to 1.5 times greater than that of 0.1, 0.2 and 0.5 μm.

There was not significant differences of concentration at each membrane pore size on phosphorus and aluminum concentration in permeates. Based on experimental results, it is considered that most appropriate membrane pore size is around 1 μm for the recovery

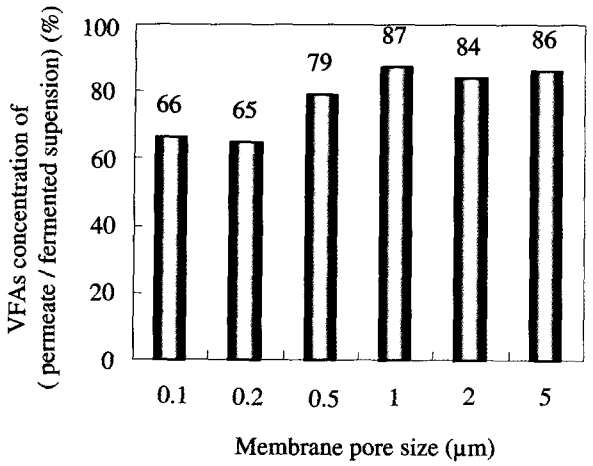

Fig. 10. Relationship between VFAs concentration of (permeate/fermented suspension) and membrane pore size.

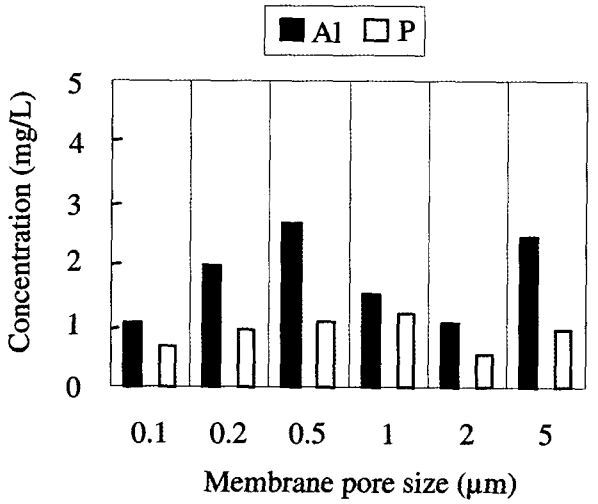

Fig. 11. Aluminum and phosphorous concentrations in permeates corresponding to membrane pore size.

of dissolved organic material.

4. Conclusions

Based on the results obtained in the present study, the main conclusions can be summarized as follows:

The magnitude of total membrane resistance (R_t) of various filters is ranged as follows in the order; 0.1 μm>0.2 μm>0.5 μm>1 μm>2 μm>5 μm. The cake layer resistance (R_c) was about 68~88% of R_t. High SS concentration of suspension caused low permeation flux. The cross-flow velocity on the membrane surface was faster, which resulted in the higher permeation flux and also more efficient with low pressure operation. The appropriate pH range of suspension was over the range of 5.0~6.0 for organic material recovery as well as the permeation flux. TOC recovery ratio was almost the same among the filters of 1, 2 and 5 μm pore size. Therefore, most appropriate membrane pore size for the recovery of dissolved organics from fermented liquid is believed to around 1 μm.

Acknowledgements

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