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Characteristics of Membrane Filtration as a Post Treatment to Anaerobic Digestion

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혐기성 소화의 후처리로서 분리막의 여과특성 연구

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Abstract: Filtration characteristics according to membrane materials were studied in the ultrafiltration of anaerobic digestion broth as a post treatment method. A series of resistances for different membranes were quantitatively assessed on the basis of the resistance-in-series model. Flux behavior observed with the digestion broth was irrelevant to initial water permeabilities of each membrane. The fluoro polymer membrane showed the most significant improvement of flux with increase of cross-flow velocity, which suggests that the cake layer formed on this membrane is more weakly attached to the membrane surface than those on the other membranes. Flux reduction during longtime running was attributed to the polarization layer resistance(R_p) as well as the fouling layer resistance(R_f). Continuous increase of R_p may reflect the variation in the characteristics of cake layers, which could result from size, shape, and structure changes due to lysis and growth of biomass. Hydrophilic cellulosic membrane had a much lower fouling tendency than hydrophobic polysulfone membrane. The depressurization method induced a small increase in flux of 5–10 $L/m^2/h$. During washing and cleaning, filtrability of each membrane was rapidly recovered within 15 minutes until a stationary value was reached.

요 약: 혐기성 소화액의 한외여과에 의한 후처리에서 분리막의 재질에 따른 여과특성을 연구하였다. 상이한 분리막의 여과특성을 정량적으로 평가하기 위해 저항 모델을 이용하였다. 소화액에 대한 플럭스의 양태는 초기의 물에 대한 분리막의 투과도에 무관하게 나타났다. 플루오로 폴리머 막의 경우에 유속의 증가에 따라 큰 플럭스의 향상을 보였는데 이것은 다른 분리막에 비해 막표면에 형성된 케이크층의 부착성이 약해 쉽게 제거될 수 있음을 시사해준다. 장시간 운전에서 플럭스의 감소는 오염층 저항의 증가에서 뿐만아니라 분극층 저항의 증가에서도 기인되었는데, 이와같은 계속적인 분극층 저항의 증가는 미생물의 분해 및 성장에 따른 케이크층 내의 성상변화를 반영할 수 있다. 막표면이 친수성인 셀룰로오즈 막은 소수성인 폴리술폰 막에 비해 낮은 막오염도를 보여주었다. 감압을 통해 플럭스를 5–10 $L/m^2/h$ 회복시킬 수 있었다. 세척단계에서 여과저항을 평가함으로써 15분의 단시간내에 세척이 완료됨을 알 수 있었다.

1. Introduction

Anaerobic digestion has been recognized as an energy-saving process for the stabilization of high strength organic wastes like alcohol-distillery wastes[1]. However, the major drawbacks of the anaerobic process are its low reaction rate and poor settling ability, which reduce the treatment efficiency and require a relatively long hydraulic retention time(HRT). In order to surmount these obstacles and upgrade the efficiency of anaerobic treatment, the use of immobilized growth process or more efficient solid separation technique is taken into account[2–5]. Currently, advanced membrane separation technology is being applied as a post treatment to anaerobic digestion of organic wastes[6, 7]. Incorporation of the membrane process as a post treatment to the biological wastewater treatment process not only significantly prompts the enhancement of performance such as COD removal, biomass retention, and solid retention time(SRT), but also reduces reactor volume and capital cost. In fact, Dorr-Oliver has developed an activated sludge process followed by a membrane filtration step in the sewage treatment system. Membrane-enhanced anaerobic digestion has also been attempted to give rise to complete treatment[8–10].

In spite of its favorable prospects and significance, the essential limitation in the extensive use of membranes is attributed to fouling, which results in the reduction of membrane permeability and is thus gaining wide interest[11–13]. Several remedies have been tried to prevent this phenomenon, such as increasing shear stress, backflushing, and chemical cleaning[14, 15]. The effects of membrane module, pore size, multiphasic flow, and electrical potential on flux improvement were also examined[16–18]. However, a great deal still remains to be done in the development and optimization of the membrane process. The selection of membranes and optimum operating conditions becomes the key factor in promoting economic gains in practical aspects. Hence, for the purpose of determining appropriate membranes and optimum operating conditions, it is necessary that more attention be paid to the filtration characteristics such as flux, membrane fouling, and cleaning tendency.

In this study, cross-flow ultrafiltration with polymeric membranes was carried out as a post treatment to anaerobic digestion and filtration characteristics such as flux behavior, membrane fouling, and cleaning tendency were quantitatively assessed according to membrane materials.

2. Model description

The resistance-in-series model was applied to evaluate the fouling tendency of each membrane and the effectiveness of the cleaning procedure. According to this model, the filtration flux can be expressed by the following resistance equations:

$$J_{wi}=P/\mu R_m \quad (1)$$

$$J_v=P/\mu(R_m+R_f+R_p) \quad (2)$$

$$J_{wf}=P/\mu(R_m+R_f) \quad (3)$$

$$J_{wc}=P/\mu R_{mc} \quad (4)$$

where J_{wi} is the initial water flux, J_v is the filtration flux in real operation, J_{wf} is the final water flux after washing the membrane surface with tap water, and J_{wc} is the final water flux after washing and cleaning the membrane with chemical; R_m is the intrinsic membrane resistance, R_f is the fouling layer resistance due to adsorption and plugging, R_p is the polarization layer resistance caused by the formation of boundary layer and the build-up of solutes on the membrane surface, and R_{mc} is the hydraulic membrane resistance obtained after the cleaning procedure with chemicals. The value of each resistance can be determined by the combination of the above four equations.

3. Experimental materials and methods

A schematic diagram of the experimental setup is shown in Figure 1. The system consisted of an anaerobic digester and an ultrafilration(UF) module. Maintained at a thermophilic temperature of 53–55℃,

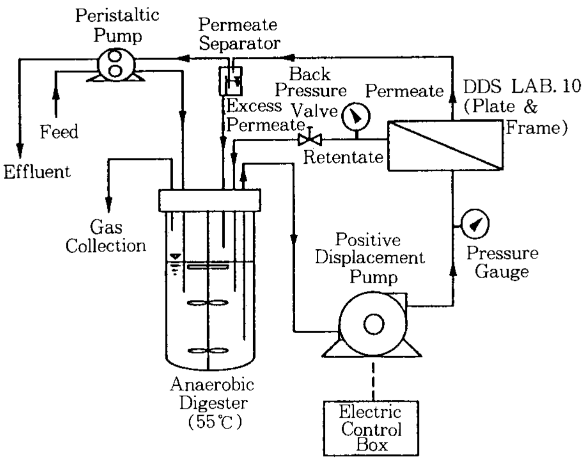

Fig. 1. Schematic diagram of an anaerobic digester coupled with an ultrafiltration system.

the anaerobic reactor was thoroughly mixed by mechanical stirring of 120 rpm. The UF module was a plate and frame type(DDS Lab. 10) with four plates in series, equipped with a positive displacement pump for the feed supply. While the fluid velocity through the channel was adjusted by the regulation of gear speed revolved in the pump and ranged from 0.808 m/s to 1.55 m/s, the transmembrane pressure was regulated using the back pressure valve. The retentate from the UF loop and excess permeate were returned back to the reactor.

With a working volume of 4 L, the digester was continuously operated at a hydraulic retention time (HRT) of 15 days. The biomass concentration of the anaerobic digestion broth was about 17,000 mg-MLSS/L. The pretreated alcohol-distillery wastes were used as anaerobic digestion feed whose compositon is as follows: COD, 22,600 mg/L; pH, 3.7; suspended solids, 417 mg/L; and volatile fatty acid, 2,180 mg/L as acetic acid.

The total surface area of the membrane was 0.0336 m^2. Four kinds of polymeric membranes were used during experimental runs and all the membranes had asymmetric structure and hydrophilic surface characteristics except the GR 61PP membrane which was hydrophobic[19]. The properties of membranes are detailed in Table 1.

Table 1. The Important Properties of Ultrafiltration Membranes

Membranes (MWCO)	Material	pH Tolerance	Temperature Limit(℃)	Pressure Limit(bar)
FS61PP (20,000)	Fluoro Polymer	1–12	0–65	0–15
GR61PP (20,000)	Polysulfone	1–13	0–75	0–10
ETNA20A (20,000)	Coated Cellulose	1–12	0–60	0–15
RC70PP (10,000)	Regenerated Cellulose	1–10	0–60	0–10

Pure water flux was initially measured using ultrapure water for each membrane to evaluate the intrinsic membrane resistance(R_m). The cross-flow filtration of anaerobic digestion broth was conducted with four flat sheets of membranes. For each membrane, the effects of transmembrane pressure, fluid velocity, and operating time on flux were assessed.

After each filtration experiment, the membrane was washed with tap water and chemically cleaned to remove the cake layer and fouling residuals. The cleaning reagent was a commercial alkali detergent, RO-DAN PLUS(NOVADAN KEMI A/S). The operating conditions for washing and cleaning are given in Table 2. After washing the membrane surface with tap water, pure water flux was measured again to evaluate the fouling layer resistance(R_f). During the fixed cleaning procedure, the cleaning flux was recorded in order to chart the variation in filtration resistance. When the cleaning procedure was finished, pure water flux was also measured to evaluate the cleaned membrane resistance(R_{mc}). The dynamic viscosity of each product was measured using a RV 20 Rotovisco(HAKKE, Germany). The values obtained were 0.475 centipoise for the permeate of digestion broth at 53℃, and 0.893 centipoise for ultrapure water at 25℃.

Table 2. Operating Conditions for Washing and Cleaning of Membranes

	Fluid	Velocity (m/s)	Trans-membrane Pressure (bar)	Time (min)	Temperature (℃)
Water Washing	Tap Water	1.55	0.45	10 (single-pass)	20
Chemical Cleaning	Alkali Detergent (1%)	1.55	0.50	30 (recycle)	40-60

4. Results and discussion

To identify the inherent water permeability of UF membranes, pure water flux was measured as a function of transmembrane pressure. The results are shown in Figure 2. Although the four membranes have similar molecular weight cut-offs(10, 000-20,000), FS61PP and GR61PP membranes had higher fluxes of more than 300 L/m^2/h at 2 bar, whereas modified cellulosic membranes obtained lower fluxes of less than 100 L/m^2/h. This may reflect the differences in surface porosity, thickness, tortuosity, and pore size distribution of the membranes. From the slope of flux versus transmembrane pressure, intrinsic membrane resistance(R_m) can be calculated for each UF membrane on the basis of the resistance model and used as the criterion for evaluating the degree of fouling or cleaness of each membrane.

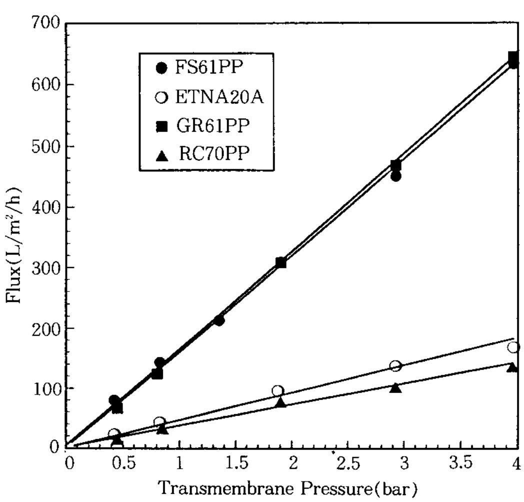

Fig. 2. Pure water flux as a function of transmembrane pressure: Operating temperature 25℃.

The effect of transmembrane pressure on flux where anaerobic digestion broth was used as the feed for the UF step is depicted in Figure 3. Although limiting flux was reached around the transmembrane pressure of 2–3 bar, the limiting flux of FS61PP was almost double that of GR61PP. (Discrepancy between the FS61PP membrane and the GR61PP membrane should be pointed out in particular, since these membranes had analogous initial water permeabilities as shown in Figure 2.) This result suggests that the GR61PP membrane (polysulfone) has greater fouling tendency toward the digestion broth than the FS61PP membrane (fluoro polymer).

A series of resistances, fouling and cleaning tendencies for various membranes, are summerized in Table 3. Fouling level, relative fouling increment (RFI), and cleaning efficiency are defined as R_f/R_m+R_f, R_f/R_m, and R_m/R_{mc}, respectively. The GR61PP membrane gave the highest fouling level

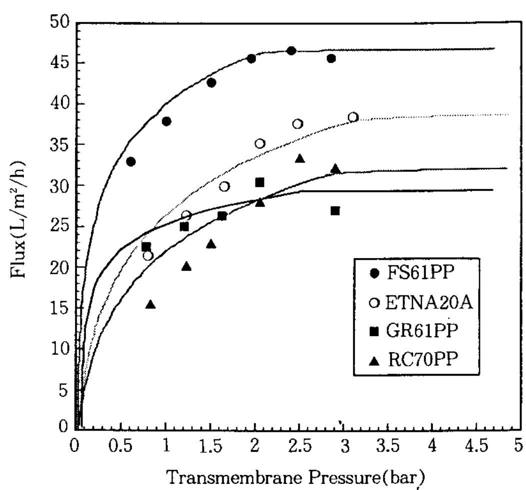

Fig. 3. Effect of transmembrane pressure on filtration flux for UF membranes: Fluid velocity 1.38 m/s.

Table 3. A Series of Resistances for UF Membranes($10^{12}m^{-1}$)

Membranes	R_m	R_f	R_p	R_t	R_{mc}	$\frac{R_f}{R_m+R_f}$	$\frac{R_f}{R_m}$	$\frac{R_m}{R_{mc}}$
FS61PP	1.89 (6.0)	1.83 (5.8)	27.8 (88.2)	31.5	1.88	0.49	0.97	~1.0
GR61PP	2.17 (5.9)	3.21 (8.8)	31.1 (85.3)	36.5	2.18	0.60	1.48	~1.0
ETNA20A	4.30 (13.0)	1.66 (5.0)	27.2 (82.0)	33.2	4.05	0.28	0.39	~1.0
RC70PP	8.02 (19.4)	1.43 (3.5)	31.8 (77.1)	41.3	8.01	0.15	0.18	~1.0

R_t: total resistance
$R_t = R_m + R_f + R_p$
( ): the percent of total resistance

while cellulosic membranes such as ETNA20A and RC70PP exhibited relatively low fouling level. These results must be associated with the chemical composition of feed and properties of membrane materials. Polysulfone membrane(GR61PP) which is hydrophobic seems to have the stronger affinity toward organic matters in the digestion broth such as feed residuals, extracellular enzymes, lysates, and intermediate metabolites. The cellulosic membranes are, however, marginally hydrophilic and thus have lower RFI values, which suggests that for these membranes, the declining of flux is slower than that of hydrophobic membranes. The cellulosic membranes could be an attractive material for long-term running in the UF step of the digestion broth. The RC70PP membrane shows lower fouling tendency than the ETNA20A membrane. This may be explained by the fact that the RC70PP membrane is less exposed to foulants in the feed stream due to higher intrinsic membrane resistance, R_m. The cleaning efficiencies of alkali detergent were almost 100 percent for the four membranes used.

To verify the reduction of membrane permeability due to the presence of the polarization layer, the effect of fluid velocity on flux was investigated(Figure 4). When cross-flow velocity through the channel increased from 0.808 m/s to 1.38 m/s under constant transmembrane pressure, the fluoro polymer membrane(FS61PP) gave more pronounced flux improvement than the other membranes. This could be refered to the relatively weaker attachment of the gel layer to the membrane surface and the low intrinsic membrane resistance(R_m) in the case of the FS61PP membrane. Table 3 also illuminates the removable large R_p percent of total resistance for the FS61PP membrane.

For the ETNA20A and RC70PP membranes, the effect of the elevated velocity on flux was not so

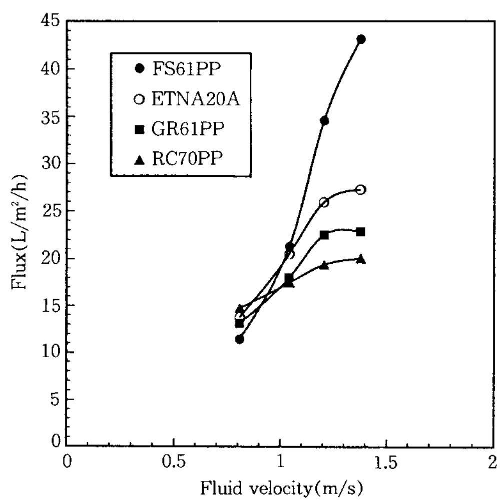

Fig. 4. Effect of fluid velocity on filtration flux for UF membranes: Transmembrane pressure 1.5 bar.

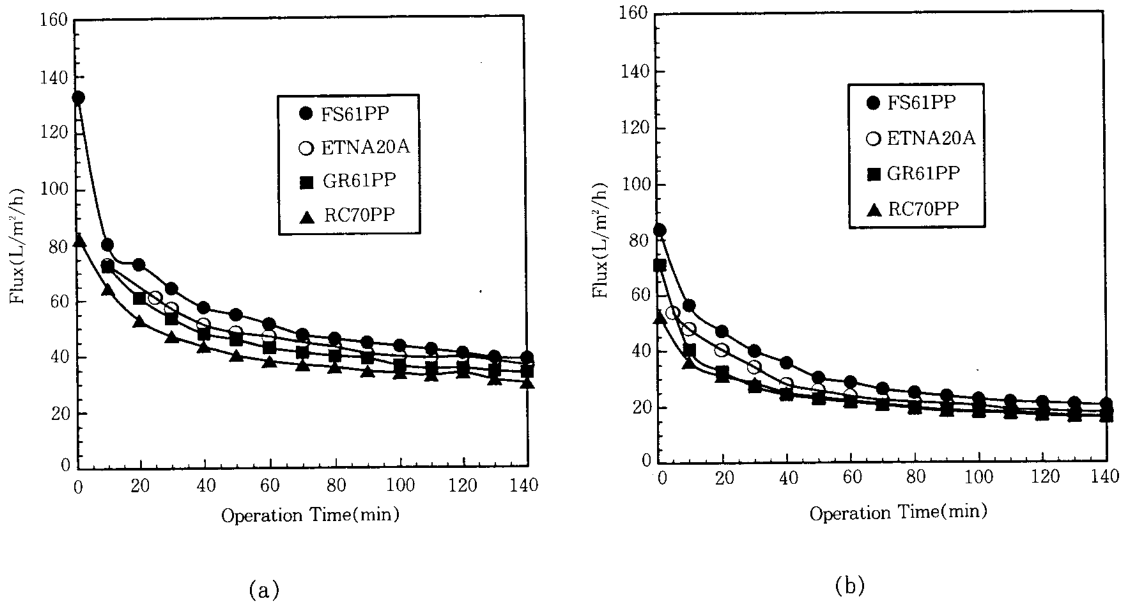

Fig. 5. Flux decline with operating time during ultrafilration of anaerobic digestion broth: Transmembrane pressure 1.5 bar. (a) Fluid velocity 1.38 m/s; (b) Fluid velocity 1.04 m/s.

drastic as compared with the FS61PP membrane because for these membranes, intrinsic membrane resistances are greater than 13 percent of the total resistance and are irrespective of the fluid velocity. The fouling layer resistance for the GR61PP membrane is about 9 percent of the total resistance. The fouling component caused from some irreversible adsorption can not be readily eliminated, which explains that the GR61PP membrane also shows little improvement of flux with increased velocity.

Figure 5 shows how the flux declined with operating time for different membranes tested at fluid velocity of 1.04 m/s and 1.38 m/s, respectively. All membranes showed exponential decline of flux in the early stage of ultrafiltration but then gradually reduced to reach the constant level. It could be hypothesized that the permeate flux in the early stage depends mainly on the intrinsic membrane resistance, but with continuous operation, both the fouling layer and the polarization layer resistances become more important in equalizing the fluxes for different membranes. Table 3 indicates that this hypothesis is reasonable because the values of R_p plus R_f for all membranes are similar and much greater than the R_m. This phenomenon was observed markedly at lower fluid velocity of 1.04 m/s, since the applied pressure accelerated the accumulation of gel layer on the membrane surface at the decreased velocity.

In order to elucidate the cause of flux decline with operating time, four filtation resistances of the FS61PP membrane were determined at the operating time of 3 hours and 20 hours, respectively (Table 4). In general, R_p increases rapidly at the outset of ultrafilration of macromolecular solution and is stabilized to the constant level within an hour. In the ultrafiltration of anaerobic digestion broth, however, R_p as well as R_f appear to increase continuously. The longtime increase of R_p reflects the variation in size, shape, and structure of microorganisms at the polarization layer due to lysis and growth of biomass.

As an attempt to improve the permeate flux, a depressurization method was carried out. Depress-

Table 4. Comparison of Filtration Resistances for 3 - and 20-hour Operations of the FS61PP Membrane(Transmembrane Pressure 1.5 bar; Fluid Velocity 1.38 m/s)

Resistances ($10^{12}m^{-1}$)	Operating Time(hr)	
	3	20
R_m	1.9	1.9
R_f	1.8	2.9
R_p	27.8	43.1
R_t	31.5	47.9

urization is applied as the back pressure valve of the UF module is fully opened and the transmembrane pressure is almost zero. The result of depressurization of the GR61PP membrane is shown in Figure 6. As the polarization layer resistance, R_p is a function of applied pressure. Depressurization reduced R_p and brought a transient elevation in flux of 10–15 L/m^2/h. When fluid velocity just after the depressurization was elevated, the flux decreased more sluggishly, scouring the polarization layer from the membrane surface.

The chemical cleaning of the membrane was carried out to remove foulants and restore the initial

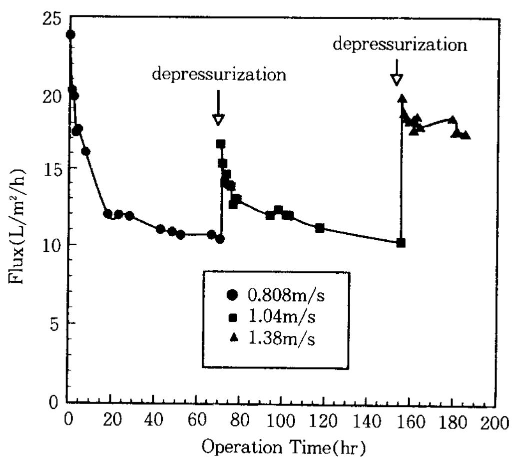

Fig. 6. Effect of depressurization and fluid velocity on filtration flux for the GR61PP membrane: Depressurization from 0.7 bar to about zero.

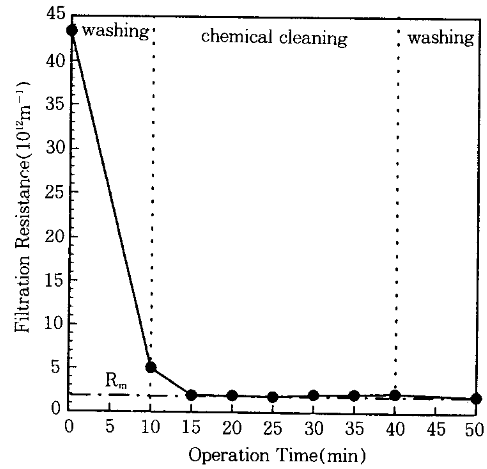

Fig. 7. Change of filtration resistance during washing and cleaning operations: FS61PP membrane.

hydraulic permeability. Figure 7 shows the variation in filtration resistance of the FS61PP membrane with washing and cleaning operations. During these procedures, filtration resistance decreased rapidly within 15 minutes until a stationary value was acquired near R_m. This proves that foulants can be easily removed from the membrane used in the UF step of anaerobic digestion broth.

5. Conclusions

Filtration characteristics of anaerobic digestion broth were studied using four types of membrane materials and evaluated on the basis of the resistance-in-series model. The following conclusions were made:

1. The superior performance of fluoro polymer membrane at high cross-flow velocities reflects the easier detachment of the cake layer from the membrane surface with low inherent membrane resistance.

2. Longtime increase of polarization layer resistance results from size, shape, and structure changes in the constituents of the cake layer due to lysis and growth of microbial cells.

3. Cellulosic membranes have lower fouling tendency, which is attributed to the hydrophilic property of the membrane surface and less exposure to foulants due to high membrane resistance.

4. Physical cleaning method as a depressurization was somewhat effective, instantaneously eliminating the boundary layer and the cake layer. Chemical cleaning of each UF membrane was quantified through hydraulic analyses and the flux recovery using chemicals was independent of membrane materials.

Acknowledgement

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Nomenclature

μ	Dynamic viscosity(centipoise)
J_v	Filtration flux in real operation($L/m^2/h$)
J_{wc}	Final water flux after washing and cleaning the membrane with chemicals($L/m^2/h$)
J_{wf}	Final water flux($L/m^2/h$)
J_{wi}	Initial water flux($L/m^2/h$)
P	Transmembrane pressure(bar)
R_f	Fouling layer resistance(m^{-1})
R_m	Intrinsic membrane resistance(m^{-1})
R_{mc}	Hydraulic membrane resistance after the cleaning procedure with chemicals(m^{-1})
R_p	Polarization layer resistance(m^{-1})

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