Influence of membrane properties on physically reversible and irreversible fouling in membrane bioreactors

T. Tsuyuhara, Y. Hanamoto, T. Miyoshi, K. Kimura and Y. Watanabe

ABSTRACT

This study aimed to examine the impact of membrane properties on membrane fouling in membrane bioreactor (MBR). Membrane fouling was divided into two categories: physically reversible and irreversible fouling. Membrane properties related to each type of membrane fouling were investigated separately. Five microfiltration (MF) and one ultrafiltration (UF) membranes with different properties (pore size, contact angle, roughness, zeta potential, and pure water permeability) were examined with a laboratory-scale MBR, fed with synthetic wastewater. Two separate experiments were conducted: the first to examine physically reversible fouling, and the second to examine physically irreversible fouling. The correlation between the degree of each type of fouling and membrane properties was studied. High correlation was observed between the degree of physically reversible fouling and roughness ($R^2 = 0.96$). In contrast, with regard to physically irreversible fouling, strong correlation between roughness and degree of membrane fouling can only be found in the case of MF membranes. Except for the membrane with the highest roughness, the degree of physically irreversible fouling can be well correlated with pure water permeability (lower pure water permeability results in higher degree of physically irreversible fouling) including UF membrane. On the basis of the results obtained in this study, it can be concluded that roughness is an important factor in determination of physically reversible fouling regardless of the types of membrane (i.e. MF or UF membranes) and evolutions of physically irreversible fouling can be mitigated when an MBR is operated with membranes with smooth surface and high pure water permeability.

Key words | membrane bioreactor, membrane fouling, membrane properties

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INDRODUCTION

Membrane bioreactors (MBRs) have several advantages such as high-quality effluent, small footprint and less sludge production over conventional activated sludge systems, and are therefore considered to be a promising technology for future wastewater treatment. For wider use of MBRs, however, high-energy consumption in the operation of MBRs, mainly attributed to membrane fouling, needs to be addressed. To overcome the fouling problem in MBRs, it is crucial to select a suitable membrane (Zhang *et al.* 2008). Yamato *et al.* (2006) found that fouling propensity differed depending on membrane polymer materials in a pilot-scale MBR. Zhang *et al.* (2008) examined the affinity between extracellular polymeric substance (EPS) and three ultrafiltration (UF) membranes: polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF) and polyethersulfone (PES), and concluded that the PAN membrane is more resistant to fouling than the others. Choi *et al.* (2009) focused on the effect of pore structure on fouling, and revealed that membrane pore structure was the dominating factor over roughness, surface charge, and hydrophobicity. Although

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there is a consensus that membrane properties should influence the degree of membrane fouling, the understanding of the relationship between membrane properties and membrane fouling is still limited.

Membrane fouling can be divided into two categories: physically reversible fouling, which can be cancelled by physical cleaning (i.e., back wash, surface cleaning) and physically irreversible fouling, which cannot be cancelled by physical cleaning, and therefore chemical cleaning is required. Physically reversible fouling is considered to develop by accumulation of sludge particles whose particle sizes are larger than the membrane pore size. Physically irreversible fouling is considered to occur by the attachment of colloids and solutes inside the membrane pores (Chang *et al.* 2002). Due to their different mechanisms, membrane properties leading to the development of each type of fouling are thought to be different. However, most of previous studies have not investigated the correlation between membrane properties and physically reversible and irreversible fouling separately. In this study, membranes with different properties were examined in a laboratory-scale MBR fed with synthetic wastewater to investigate the relationship between membrane properties and the evolution of physically reversible and irreversible fouling.

MATERIALS AND METHODS

Laboratory-scale MBR

Figure 1 shows a schematic diagram of the MBR. A laboratory-scale MBR with an effective volume of 6.2 L was used in this study. Six flat-sheet membrane elements with a membrane surface area of 0.02 m^2 were submerged in the reactor

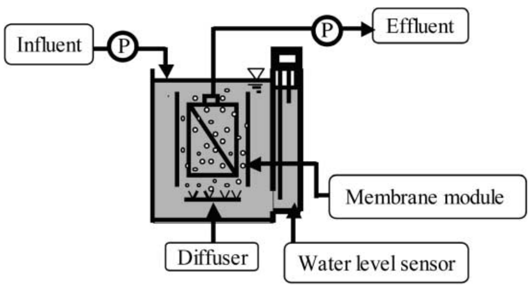

Figure 1 | Shematic diagram of laboratory-scale MBR.

resulting in a total membrane surface of 0.12 m^2. A variety of flat-sheet microfiltration (MF) and UF membranes were examined in this study. Properties of the membranes examined in this study are summarized in Table 1. Constant flow-rate mode of filtration was carried out with the use of peristaltic pumps. Membrane flux was fixed at 0.4 $m^3/m^2/d$ (16.7 LMH) for the first experiment and 0.5 $m^3/m^2/d$ (20.8 LMH) for the second experiment. In the second experiment, when trans-membrane pressure (TMPs) reached approximately 35 kPa, physical cleaning (wiping with a sponge) was performed as the operation was continued. Intermittent operation (1 min pause for every 12 min operation) was also carried out. Hydraulic retention time (HRT) and sludge retention time (SRT) were 3.1 h and 36 days, respectively.

The MBR was inoculated with the sludge collected from a pilot scale MBR installed at a municipal wastewater treatment plant in Sapporo, Japan and fed with synthetic wastewater that mainly consisted of sodium acetate (Table 2).

Biomass was acclimatized to the synthetic wastewater with the condition mentioned above for 3 months. Following this, continuous monitoring of TMP was initiated with new membranes. Concentration of mixed liquor suspended solids (MLSS) in the reactors stabilized to 5,000 mg/L following acclimatization.

Dead end filtration test

A series of dead-end membrane filtration experiments were conducted to determine the filtration resistance of fouled membranes. At the termination of the continuous operation, fouled membranes were cut to 13.9 cm^2 from the module and were placed into the cylindrical filtration unit. Pure water was filtrated under constant pressure (10 kPa) and the flow rate was monitored. Total filtration resistance R_t (m^{-1}) was calculated using the following equation:

$$R_t = \frac{\Delta P}{\mu \cdot J} \qquad (1)$$

where J is the permeation flux ($m^3/m^2/s$), ΔP is TMP difference (Pa), μ is the viscosity of permeate (Pa s).

Table 1 | Membrane properties

Membrane	A	B	C	D	E	F
Material	MF PVDF*	PVDF*	PVDF*	PP*	PTFE*	UF PES*
Nominal pore size (μm)	0.1	0.1	0.22	0.4	0.08	20 kDa† (95%)
Contact angle (°)	106.4	83.4	70.6	98.2	84.9	69.0
Roughness (nm)	30	155	209	98	66	22
Zeta pontential (mV)	−37.4	−35.7	−40.0	−42.3	−34.5	−34.1
Pure water permeability ($L\,m^{-2}\,h^{-1}\,kPa^{-1}$)	52.2	24.7	47.0	53.6	36.9	11.1

*PVDF = polyvinylidene fluoride, PP = polypropylene, PTFE = polytetrafluoroethylene, PES = polyethersulphone.
†MWCO (x% rejection with 2,000 ppm concentration marker).

The total permeation resistance (R_t) can be expressed as the sum of three components:

$$R_t = R_m + R_{ir} + R_r \quad (2)$$

Degree of physically reversible fouling (R_r) can be evaluated by the difference between the resistance between the fouled membrane and the membrane after sponge wiping. Degree of physically irreversible fouling (R_{ir}) can be evaluated by the difference between the filtration resistance between the membrane wiped with sponge and fresh membranes (R_m).

Analytical methods

The measurement of proteins concentration was carried out by Lowry's method (Lowry *et al.* 1951), with BSA used as a standard. The phenol-sulfuric acid method of Dubois *et al.* (1956) was used for carbohydrate concentration determination, with glucose used as a standard. The contact angle measurement for membrane hydrophobicity was carried out according to the sessile drop technique using a goniometer (DropMaster 300, Kyowa Interface Science Co. Ltd., Saitama, Japan). The value of surface roughness of a membrane was measured based on a 5.0 × 5.0 μm scan area using scanning probe microscopy (SPM-9600, Shimadzu, Kyoto, Japan). Surface zeta potentials of tested membranes were measured by an electrophoretic light scattering spectrophotometer (ELS-8000, Otsuka electronics, Tokyo, Japan). The pure water permeability ($L\,m^{-2}\,h^{-1}\,kPa^{-1}$) was determined by filtering deionized water under constant pressure (100 kPa) using cross-flow filtration equipment.

RESULTS AND DISCUSSION

Evolution of TMPs in the first experiment

Figure 2 shows the changes in TMP during the first experiment. From the figure it can be seen that the rate at which TMP increased differed depending on the type of membrane used. It should be noted that filtration conditions during the operation period could be assumed to be identical due to the use of synthetic wastewater under steady state. Concentrations of soluble microbial products (SMP) expressed by concentrations of carbohydrates and proteins were almost constant throughout the experiment (data not shown). Also, reproducibility of the data for the TMPs was verified in the repeated tests (data not shown).

Table 2 | Synthetic wastewater composition

Constituents	Concentration (mg/L)
CH_3COONa	260
$(NH_4)_2SO_4$	71
Peptone	40
KH_2PO_4	18
$NaHCO_3$	56
$FeCl_3{\cdot}6H_2O$	2.4
$CaCl_2{\cdot}2H_2O$	0.37
$MgSO_4{\cdot}7H_2O$	5.1
$MnCl_2{\cdot}4H_2O$	0.28
$ZnSO_4{\cdot}7H_2O$	0.44
$CuSO_4{\cdot}5H_2O$	0.39
$CoCl_2{\cdot}6H_2O$	0.42
$Na_2MoO{\cdot}2H_2O$	1.3

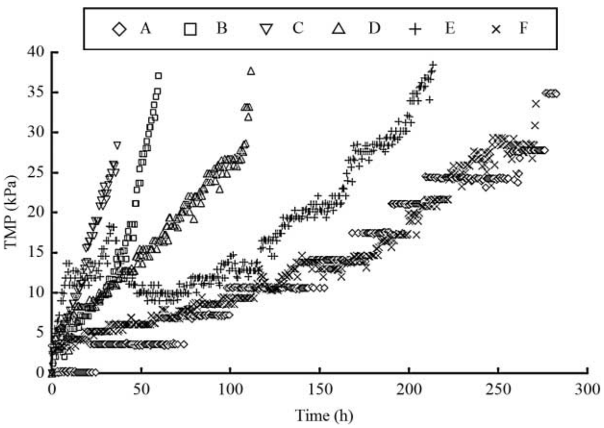

Figure 2 | Evolution of TMPs in the first experiment.

Among the tested membranes, Membranes A, E and F exhibited good performances whereas very rapid increases in TMPs were observed with Membranes B and C. At the end of the continuous operation, degrees of physically reversible and irreversible fouling were assessed by measuring filtration resistance. In all of experiments, wiping with a sponge reduced filtration resistance by >90%, indicating that membrane fouling shown in Figure 2 could be mainly attributed to physically reversible fouling.

Evolution of TMPs in the second experiment

The second experiment was carried out to investigate physically irreversible fouling. Four membranes that showed relatively good performance in the first experiment (membrane A, D, E and F) were selected in order to conduct long-period operation. Figure 3 shows the changes in TMP during the second experiment. Evolution of physically irreversible fouling in each membrane can be estimated by connecting the points recorded just after the implementation of physical cleaning (dashed lines in Figure 3). Membrane A exhibited the least evolution in physically irreversible fouling whereas the most significant evolution of physically irreversible fouling was observed in membrane D. Evolutions in physically irreversible fouling in membranes E and F were moderate.

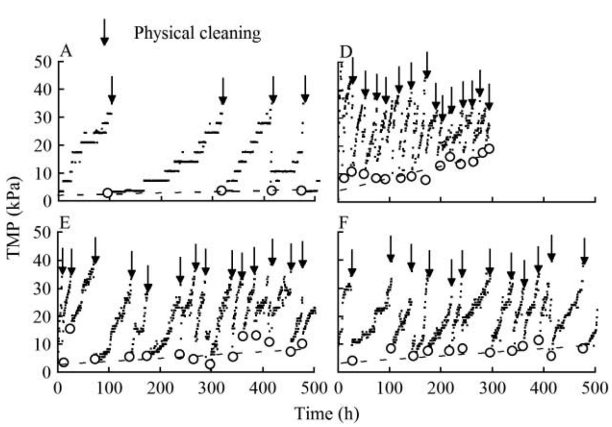

Figure 3 | Evolution of TMPs in the second experiment.

At the termination of the operation, fouled membranes were taken out and dead-end pure water filtration testing was carried out in order to quantify the degree of physically irreversible fouling. Figure 4 shows the filtration resistance caused by physically irreversible fouling (R_{ir}). From this experiment, a clear difference in R_{ir} was observed among the tested membranes. The R_{ir} of membranes A, E, F and D were 11.7, 19.9, 28.9, and 38.1 ($10^{11}\,m^{-1}$), respectively. The order of filtration resistance corresponds to the trend of TMP increment shown in Figure 3. The differences in R_{ir} values can be attributed to membrane properties since the membranes were operated under the identical condition.

The impact of membrane properties on fouling behavior

Figures 5 and 6 show the correlation of membrane properties with physically reversible and irreversible fouling, respectively. In Figure 5, high correlation between roughness and the rate of evolution in TMPs was observed ($R^2 = 0.96$). Membrane properties other than roughness examined in this study did not correlated to the rate of evolution in TMPs. This indicates that roughness is the most important factor determining the propensity of physically reversible fouling. In regard to physically irreversible fouling, it was difficult to establish a clear relationship

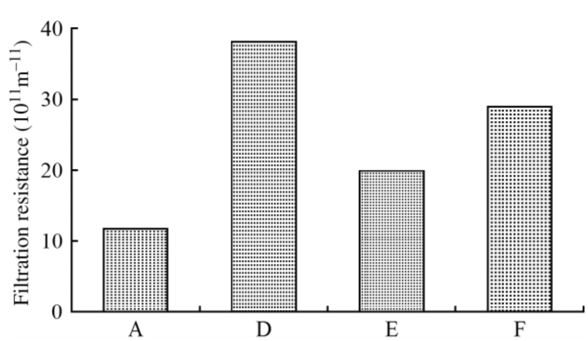

Figure 4 | Filtration resistance caused by physically irreversible fouling (R_{ir}).

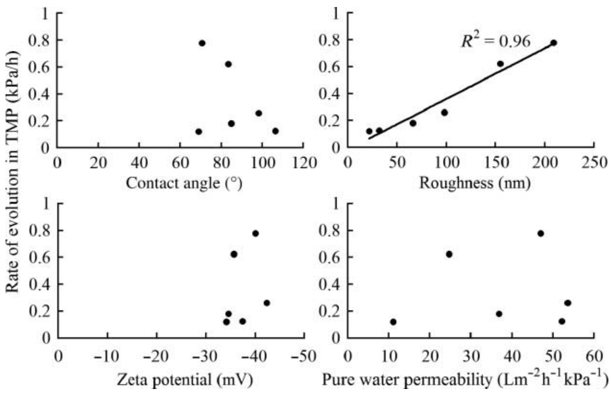

Figure 5 | Correlation between the rate of evolution in TMPs and membrane properties.

between membrane properties examined in this study and the degree of physically irreversible fouling. In Figure 6, roughness correlated to the degree of physically irreversible fouling in the case of MF membranes (A, D and E), implying that roughness is also an important factor in the evolution of physically irreversible fouling. Contact angle and pure water permeability can also be correlated to the degree of physically irreversible fouling in all membranes except for membrane D, which has the highest roughness among the four membranes tested. Choi *et al.* (2009) reported that a membrane with low pure water permeability is expected to cause more fouling due to quick compaction of the fouling layer and pore clogging, which could provide an explanation of the results obtained in this study. Le-Clech *et al.* (2006) mentioned that hydrophobic membranes (higher contact angle) are expected to foul more severely than hydrophilic membranes (lower contact angle) because of the hydrophobic interactions between the foulants and the

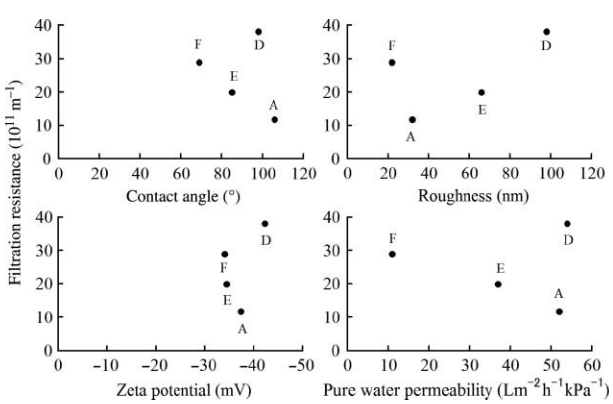

Figure 6 | Correlation between the degree of physically irreversible fouling and membrane properties.

membrane material. However, this did not correspond to the results obtained in this study. In this study, both the values of contact angle and pure water permeability in the membranes (except for membrane D) were ordered as follows: Membrane A > Membrane E > Membrane F. If the effect of pure water permeability on the evolution of physically irreversible fouling is much stronger than that of hydrophobicity of the membranes, the degree of physically irreversible fouling is likely to depend solely on pure water permeability of the membrane. This can partly explain the contradicting results obtained in this study. On the basis of the argument mentioned above, roughness and pure water permeability were suggested to be important factors in determining the degree of physically irreversible fouling. It can also be suggested that membranes with a smooth surface and high pure water permeability are desirable for mitigating the evolution of physically irreversible fouling.

CONCLUSIONS

In this study, the impact of membrane properties on membrane fouling was investigated by comparing six different types of membranes filtered with the same mixed liquor suspension using a laboratory-scale MBR. Two separate experiments were conducted to investigate the correlation between membrane properties with physically reversible and irreversible fouling. In these experiments, the degree of both physically reversible and irreversible fouling differed depending on the type of membrane. On the basis of the results obtained in this study, the relationship between the membrane properties and both physically reversible and irreversible fouling can be summarized as follows:

(1) The rate of evolution in physically reversible fouling correlated with roughness very well. In contrast, correlation with other properties could not be observed. Surface roughness was the dominant factor in the evolution of physically reversible fouling.

(2) In regard to physically irreversible fouling, a clear relationship between the membrane properties and the degree of physically irreversible fouling could not be observed. However, roughness correlated to physically irreversible fouling in the case of MF membranes. Contact angle and pure water permeability correlated

to the degree of physically irreversible fouling except for the roughest membrane. In regard to contact angle, the results obtained in this study could not be explained by hydrophobic interaction (hydrophilic membrane is more susceptible to fouling than hydrophobic membrane). It is likely that pure water permeability was a more influential factor than hydrophobicity. On the basis of the results obtained in this study, a membrane with smooth surface and high pure water permeability is desirable for prevention of physically irreversible fouling.

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