Influence of suspension viscosity and colloidal particles on permeability of membrane used in membrane bioreactor (MBR)

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Abstract In this study, pilot scale experiments were carried out to examine membrane fouling occurring in membrane bioreactors (MBR) with or without pre-treatment (coagulation/sedimentation). Especially, the influence of suspension viscosity and dissolved organic matter (DOM) on membrane fouling was investigated. The pre-coagulation/sedimentation process improved the performance of a MBR in terms of membrane permeability by controlling irreversible fouling and formation of thick cake layer. The upper limit of MLSS concentration for an efficient operation in MBR without pre-treatment was suggested to be around 10 g/L based on the measurement of suspension viscosity. In this study, it was difficult to directly relate membrane fouling to DOM detected in the membrane chamber. A series of laboratory scale dead-end filtration experiments was carried out to investigate which fractions in biomass suspension would be the most influential in the deterioration of membrane permeability. Based on the dead-end tests, it was shown that the deterioration of membrane permeability was mainly caused by the colloidal particle fraction in the biomass suspension.

Keywords Colloidal matter; membrane bioreactor; membrane fouling; pre-coagulation/sedimentation; suspension viscosity

Introduction
Application of submerged membrane bioreactors (MBRs) for the treatment of wastewater in which biological treatment and solid–liquid separation are simultaneously carried out in a single reaction chamber has received much attention recently (Yamamoto et al., 1989; Stephenson et al., 2000; Roset et al., 2002). This is partly because high quality of treated water and smaller footprint can be expected by using a MBR, compared with other existing biological wastewater treatment processes such as the activated sludge process. The main obstacle for wider application of MBRs is, however, deterioration of membrane permeability (membrane fouling) with operation time.

Membrane fouling in MBR is caused by various types of physicochemical interactions between suspension containing biomass and the membrane itself. Various definitions of membrane fouling have been proposed by many researchers; for example reversible fouling and irreversible fouling (Chang et al., 2002). Reversible fouling is defined as the fouling that can be tackled by a physical washing protocol (e.g. backwashing). On the other hand, irreversible fouling is defined as the fouling that needs chemical membrane cleaning to be removed. In our previous study, it was suggested that the degree of reversible fouling in a submerged MBR used for municipal wastewater treatment was related to the MLSS kept in the reactor, while irreversible fouling might be caused by adsorption of dissolved organic matter (DOM) on the membrane (Itonaga and Watanabe, 2004). Soluble microbial products (SMP) produced by biomass and organic matter contained in the raw wastewater with poor biodegradability were thought to cause such irreversible fouling. Many researchers have reported the influence of SMP on deterioration of membrane permeability in the operation of MBRs (Mukai et al., 2000; Huang et al., 2000). However, these studies
were based on laboratory-scale and short-term experiments and used synthetic wastewater. Therefore, it is not clear whether experimental results obtained in the previous literatures can be applied to the operation of full-scale MBRs.

Analysis of the particle size distribution of organic substances in raw municipal wastewater has shown that a large part of the organic matter in raw municipal wastewater (63–70%, measured by TOC tests) is associated with particles that are larger than 0.1 µm (Leven et al., 1985), which can be easily removed by coagulation and sedimentation. Therefore, installation of coagulation and sedimentation processes at the first stage of the wastewater treatment process train seems to be reasonable (Ødegaard, 1988). Coagulation and sedimentation as pre-treatment for MBRs dealing with municipal wastewater were examined by the authors and were found to considerably suppress membrane fouling. Also, by installing coagulation and sedimentation, the quality of the treated water from the MBRs was obviously improved (Itonaga and Watanabe, 2004).

In this study, pilot scale experiments were carried out to compare membrane fouling occurring in a MBR without pre-treatment (hereafter called conventional MBR (CMBR)) with fouling occurring in a MBR with pre-coagulation/sedimentation (hereafter called hybrid MBR (HMBR)). Especially, the influence of suspension viscosity and DOM on membrane fouling was investigated. A series of laboratory scale dead-end filtration experiments was also carried out to investigate which fraction (i.e. suspended solids (SS), colloidal matter and soluble matter) contained in biomass suspension would be the most influential in deterioration of membrane permeability.

**Materials and methods**

**Pilot scale MBR**

Figure 1 shows a schematic diagram of the pilot plant installed at an existing municipal wastewater treatment plant (Soseigawa treatment plant, Sapporo, Japan). This treatment plant receives wastewater collected by a combined sewer system. Effluent from the primary clarifier was used as the raw water in this study. Two long-term experiments (Runs 1 and 2) were conducted in this study. In Run 1, the effect of installation of coagulation/sedimentation as pre-treatment of MBR was examined. In Run 2, the influence of DOM on membrane permeability was investigated. A jet mixed separator (JMS) with inclined tube settlers was used for pre-coagulation/sedimentation (Watanabe et al., 1990; Watanabe et al., 1998). Flow rate and HRT in the JMS were set at 50 m³/day and 1.5 hours, respectively. Iron based coagulant, poly-silicato iron (PSI) (Hasegawa et al., 1991), was used as coagulant. Dosage of PSI was fixed at 10 mg-Fe/L. Table 1 summarizes the operating conditions for each run. In both runs, two identical MBRs were operated with different feed water in parallel. Primary clarifier effluent was directly fed to CMBR while HMBR was fed with pre-treated wastewater (coagulation/sedimentation). Table 2 shows the characteristics of the raw water fed to the MBRs.

Hollow fiber MF membrane modules (Mitsubishi Rayon, Japan) were submerged in the membrane chambers and used for the experiments. The material of the membrane and the effective membrane area of each module were polyethylene and 3 m², respectively. The aeration devices were installed right below the membrane modules for oxygen supply and cake layer removal. The effective volume of each MBR was 0.18 m³. When deterioration in membrane permeability became significant, the membrane module was taken out from the membrane chamber and physically washed by spraying with pressurized water.

When significant restoration in membrane permeability was not recognized after physical cleaning, the membrane module was soaked in hydrochloric acid (pH = 2) and subsequently in a solution of sodium hypochlorite (500 ppm) for 24 hours, respectively (chemical membrane cleaning).
Laboratory scale dead-end membrane filtration experiment

A series of dead-end membrane filtration experiments was conducted to investigate which fraction in biomass suspension would be the most influential in deterioration of membrane permeability. Biomass suspensions collected from the MBRs during Run 2 were used in these experiments. Flat plate membranes were used for the dead-end tests. Nominal pore size and effective area of the used membrane were 0.1 µm and 26.9 cm², respectively. Operating pressure was maintained at 40 kPa. During the dead-end tests, the permeate flux was periodically monitored. By using the data obtained in the dead-end tests, membrane fouling caused by the suspensions was evaluated.

The resistance-in-series model was applied to determine membrane filtration resistances (Stephenson et al., 2000). Based on this model, the permeate flux on the applied transmembrane pressure (TMP) can be described by Darcy’s law as follows:

\[ J(t) = \frac{1}{A} \frac{dV}{dt} = \frac{\Delta P}{\mu(R_f)} = \frac{\Delta P}{\mu(R_m + R_f)} \]  

where \( J \) is the permeate flux (m³/m²/s), \( V \) is the total volume of permeate (m³), \( A \) is the

Table 1 Operating conditions of the MBRs

<table>
<thead>
<tr>
<th></th>
<th>Run 1</th>
<th>Run 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRT in MBR (hr)</td>
<td>3.6–6.0</td>
<td>4.5</td>
</tr>
<tr>
<td>MLSS conc. (g/L)</td>
<td>3–25</td>
<td>10</td>
</tr>
<tr>
<td>Permeate flux (m³/m²/day)</td>
<td>0.3–0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Pore size of membrane (µm)</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Operation cycle</td>
<td>Suction for 12 min.</td>
<td>Stop for 3 min.</td>
</tr>
</tbody>
</table>

Table 2 Characteristics of the raw water fed to MBRs

<table>
<thead>
<tr>
<th>Feed water</th>
<th>Run 1</th>
<th>Run 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary clarifier effluent</td>
<td>JMS effluent</td>
<td>Primary clarifier effluent</td>
</tr>
<tr>
<td>Temp (°C)</td>
<td>17.8 (10.8–24.2)</td>
<td>17.8 (10.8–24.2)</td>
</tr>
<tr>
<td>pH</td>
<td>7.7 (7.1–8.5)</td>
<td>6.8 (6.5–7.2)</td>
</tr>
<tr>
<td>DO (mg/L)</td>
<td>1.7 (0.9–3.5)</td>
<td>1.9 (0.8–3.9)</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>53.2 (33.3–89.1)</td>
<td>9.0 (1.7–26.0)</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>35.3 (13.5–71.2)</td>
<td>16.7 (4.6–34.5)</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>20.6 (10.1–40.3)</td>
<td>12.9 (4.6–29.7)</td>
</tr>
<tr>
<td>T-N (mg/L)</td>
<td>29.7 (13.3–56.0)</td>
<td>20.7 (5.2–51.3)</td>
</tr>
<tr>
<td>T-P (mg/L)</td>
<td>2.6 (0.5–6.5)</td>
<td>0.5 (0.1–1.1)</td>
</tr>
</tbody>
</table>

* minimum and maximum values in the parentheses
membrane area (m²), $\Delta P$ is the TMP (Pa), $\mu$ is the permeate viscosity (Pa·s), $R_t$ is the total membrane filtration resistance (m⁻¹), $R_m$ is the intrinsic membrane filtration resistance (m⁻¹), and $R_f$ is the filtration resistance due to membrane fouling (m⁻¹). $R_f$ is calculated for each filtration test based on the steady state flux.

**Classification of particles contained in biomass suspension**

In this study, particles contained in a biomass suspension were divided into three categories: suspended solids (SS), colloidal matter, and soluble matter. Using the dead-end filtration apparatus described above, the degree of filtration resistance caused by each fraction was separately evaluated. Three different suspensions were prepared from the biomass suspension transferred from the experimental site and then used for the dead-end filtration test. Depending on the treatment done prior to the dead-end test, the characteristics of particles contained in suspension were different and therefore the observed filtration resistance would be different as well. Some amount of the transferred suspension was directly applied to the dead-end filtration test. Filtration resistance determined in this test was attributed to all particles (i.e. SS, colloidal matter and soluble matter). A portion of the biomass suspension was centrifuged at 3,000 rpm for 5 min, and the resulting supernatant was applied to the dead-end test. In this case, determined resistance could be attributed to colloidal matter and soluble matter. Another portion of the biomass suspension was filtered with a membrane with nominal pore size of 0.5 µm, and the filtrate was used for the subsequent test. Filtration resistance due to soluble matter could be determined from this test. By comparing these three resistances, the contribution of each fraction to the total filtration resistance (determined for the original suspension) was evaluated.

**Analytical methods**

MLSS and VSS were determined by *Standard Methods* (1995). Suspension viscosity was measured by using a rotating torque cylinder (Model B, Viscometers, Toki Sangyo, Japan). DOC was analyzed by using a TOC analyzer (TOC-V, Shimazu, Japan) after filtering samples with a membrane with nominal pore size of 0.5 µm. The Lowry method was used to determine protein concentration (Lowry et al., 1951). Albumin was used as standard. The phenolsulfuric acid method was used to determine carbohydrate concentration (Dubois et al., 1956). Glucose was used as standard. Particle size distribution of the suspensions was determined by using a granulometric analyzer (SALD-3000, Shimazu, Japan).

**Results and discussion**

**Effect of installation of coagulation/sedimentation as pre-treatment for MBRs**

Run 1 was carried out to examine the effect of coagulation/sedimentation as the pre-treatment for MBRs. As described before, CMBR and HMBR were operated in parallel in order to clearly demonstrate the differences between them. Figure 2 shows the changes in total membrane filtration resistance ($R_t$) observed in Run 1. $R_t$ was determined by equation (1). The permeate flux was varied during Run 1 and the variation of it is also shown in Figure 2. Figure 3 shows the changes in MLSS concentrations. Until 148 days of the operation, the MLSS concentration in both MBRs was not controlled and consequently increased with operation time. After day 148, the MLSS concentration in both MBRs was attempted to be kept around 15 g/L. As seen from Figure 3, MLSS concentrations were similar in CMBR and HMBR throughout Run 1.

In CMBR, rapid increase in $R_t$ was observed from the beginning of the operation. After 19 days of operation, the membrane module was taken out from CMBR and physical membrane washing (i.e. spraying pressurized water) was carried out. However, no significant restoration in membrane permeability was recognized and consequently chemical processes...
membrane cleaning was needed. After chemical cleaning, rapid increase in $R_t$ of CMBR was observed again and the second membrane cleaning had to be carried out. After 36 days of operation, permeate flux of CMBR reduced to 0.3 m/day. By reducing the permeate flux, the increase rate of $R_t$ in CMBR was considerably retarded although $R_t$ started to increase rapidly after 100 days of operation. After day 130, the permeate flux of CMBR is increased to the same flux as that of HMBR. As a result, rapid increase in $R_t$ was frequently observed in CMBR. When the membrane module was taken out from CMBR for physical cleaning, the formation of a thick and sticky cake layer (i.e. deposition of biomass suspension) on the membrane surface was recognized. In contrast with the results with CMBR, a relatively high membrane permeability was maintained with HMBR. A much lower frequency of membrane cleaning is required in the operation of HMBR. Recorded values of $R_t$ just after physical cleaning should represent the magnitude of irreversible fouling since physical cleaning was supposed to remove reversible fouling. Based on this assumption, changes in irreversible fouling in Run 1 are also plotted in Figure 2 (dotted lines) by connecting $R_t$'s observed just after physical cleaning. As clearly shown in Figure 2, accumulation of irreversible membrane filtration resistance increased with operation time. Accumulation of irreversible resistance observed in HMBR was 40% less rapid than that in CMBR. From these results, it can be concluded that pre-coagulation/sedimentation would improve the performance of MBR in terms of membrane permeability by controlling both formation of a sticky cake layer on the membrane surface and irreversible fouling.

**Influence of suspension viscosity on membrane fouling in CMBR**

In spite of the fact that MLSS concentrations were almost the same in CMBR and HMBR, evolution of $R_t$ was much more significant in CMBR, as previously described. This result clearly demonstrates that membrane fouling in a MBR cannot be explained solely by MLSS concentration. The increase in MLSS concentration and the corresponding rise in suspension viscosity were reported to have a negative impact on membrane permeability according to Ueda *et al.* (1996). A similar trend was shown in our previous study (Itonaga and Watanabe, 2002). The relationship between MLSS concentration and suspension viscosity observed in Run 1 is shown in Figure 4. As clearly shown in Figure 4, the suspension viscosity of CMBR was greater than that of HMBR especially in high MLSS concentration ranges. By referring to Figure 2 (a) and Figure 3, it can be seen that membrane permeability of CMBR was significantly deteriorated after 100 days of operation when the MLSS concentration was maintained above 15 g/L. Such a high MLSS concentration caused high
suspension viscosity in CMBR. On the other hand, the suspension viscosity observed in HMBR was maintained at a low level even when the MLSS concentration was high (i.e. above 15 g/L). This difference in suspension viscosity in both MBRs probably explains the difference in the evolution of $R_t$ (Figure 2). Namely, more rapid increase of $R_t$ in CMBR than HMBR was due to the high suspension viscosity in CMBR. Thus, in order to efficiently operate a MBR, suspension viscosity in the membrane chamber should be maintained at a low level. This can be achieved easily in the case of HMBR, implying the advantage of this process. However, lower suspension viscosity (i.e. low MLSS concentration) in the membrane chamber is necessary for efficient membrane separation. Moderately high viscosity seems to be good for the maintenance of membrane permeability since such a viscosity would enhance the efficiency of physical cleaning associated with aeration inside the chamber. In addition, of course, high MLSS concentration (i.e. high biomass concentration) leads to a high quality treated water. Careful inspection of Figure 4 reveals that an inflection point where the gradient of the suspension viscosity of CMBR obviously changes exists around 10 g-MLSS/L. When CMBR operation was conducted with MLSS concentrations well below the inflection point, formation of a thick and sticky cake layer on the membrane surface was not observed. On the other hand, when the MLSS concentration in CMBR was far beyond the inflection point (e.g. 15 g-MLSS/L), the increase in suspension viscosity was considerable and an immediate formation of the cake layer occurred. Based on these arguments, the upper limit of MLSS concentration for an efficient operation in CMBR was suggested to be around 10 g/L in this study. When a MBR is used as the HMBR, higher MLSS concentration would be applicable.
Influence of DOM on membrane permeability of MBRs

Run 2 was carried out to investigate the influence of DOM on membrane permeability. Both CMBR and HMBR were examined in Run 2 as well. In Run 2, MLSS concentration in both MBRs was fixed at 10 g/L based on the results described in the previous section. Figure 5 shows the changes in $R_t$ and DOM concentrations in the membrane chambers observed in Run 2. In Run 2, evolution of $R_t$ in both MBRs were suppressed compared with Run 1 probably because MLSS concentrations were kept at the appropriate value. Consequently, there was no need to carry out membrane cleaning throughout Run 2. Until 60 days of operation, an almost linear increase in $R_t$ was observed in both MBRs. The effect of pre-treatment for HMBR was confirmed again in Run 2. Namely, the increase rate of $R_t$ observed in HMBR was 30% less rapid than that in CMBR until day 60.

Until 60 days of operation, the DOC concentration in the membrane chamber fluctuated from 5 to 10 mg/L in CMBR while that in HMBR was stable around 5 mg/L. Concentrations of dissolved carbohydrate in both membrane chambers were similar while dissolved protein was hardly detected in either membrane chamber. Higher DOC concentration in CMBR probably corresponded to more rapid evolution of $R_t$ in CMBR. Ishiguro et al. (1994) have reported the relationship between membrane fouling in MBRs and DOM such as protein and carbohydrate. However, significant differences are not seen between CMBR and HMBR in terms of carbohydrate and protein, as shown in Figure 5. This implies that DOM cannot be accounted for by carbohydrate and protein causing membrane fouling in MBRs.

Role of suspended solids, colloidal matter and soluble matter in membrane fouling of MBRs

A series of laboratory scale dead-end filtration experiments was carried out to examine the contribution of different fractions (i.e. SS, colloidal matter and soluble matter) contained in suspension to total membrane fouling. In order to separately assess the degree of filtration resistance due to each fraction, three different suspensions were prepared by the treatment described in the experimental section. Suspensions tested in dead-end filtration were obtained from the membrane chambers of CMBR and HMBR at 68 days of operation in Run 2 when rapid membrane fouling occurred in HMBR. It occurred because of a sudden decrease of the F/M ratio in the inflow. This implied that the suspension collected from HMBR was likely to cause greater membrane fouling compared with that from CMBR.

Figure 6 shows the changes in permeate flux during the dead-end tests. In all of the dead-end tests, a rapid decrease in permeate flux was observed at the initial stage and the permeate flux reached a stable value within a filtration time of 30 min. For all of the tests, filtration...
resistance was determined by equation (1). The calculation was based on steady state (30 min of filtration) and the results are summarized in Table 3. As previously mentioned, the HMBR suspension tested in the dead-end test, which was collected during the occurrence of rapid membrane fouling (Figure 5b), was likely to have a greater fouling potential compared with the CMBR suspension. This was confirmed in the dead-end tests. From Table 3, it can be seen that the resistance caused by the suspension from HMBR was about two times higher than the one determined for CMBR, except for the case after filtration. Comparing the resistance determined after filtration, it is found that soluble matter in the HMBR suspension was less likely to cause fouling than that in CMBR. Comparing the three resistances shown in Table 3, the degrees of resistance due to SS, colloidal matter and soluble matter are separately evaluated. The difference between the first row in Table 3 (biomass suspension) and the second row (after centrifugation) represents the resistance due to SS. In a similar manner, the resistance due to colloidal matter can be represented. Values in the third row (after filtration) directly represent the resistance due to soluble matter. By carrying out this analysis, it was found that colloidal matter had the greatest fouling potential in the suspension collected from HMBR. The rapid increase in $R_t$ seen in Figure 5b would be explained by this colloidal matter in the suspension. On the other hand, soluble matter accounted for most of the fouling potential in CMBR where the operation was stable.

**Conclusions**

In this study, pilot scale experiments were carried out to examine membrane fouling occurring in MBRs with and without pre-coagulation/sedimentation. Based on these experiments, the influence of DOM on membrane fouling was investigated. A series of laboratory scale dead-end filtration experiments was also carried out to examine the contribution of particles with different sizes to the total membrane filtration resistance. The experimental results obtained in this study can be summarized as follows.

1. Pre-coagulation/sedimentation process improved the performance of a MBR in terms of membrane permeability by the control of both irreversible fouling and suspension viscosity in the membrane chamber.
2. The upper limit of MLSS concentration for efficient operation in CMBR was suggested to be around 10 g/L beyond which substantial increase in suspension viscosity would be expected.

3. DOM that could not be accounted for by carbohydrate and protein seemed to be important in interpreting membrane fouling in MBRs.

4. The colloidal fraction in the biomass suspension played an important role in membrane fouling.

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References


