Effects of membrane fouling on solute rejection during membrane filtration of activated sludge

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Abstract

To assess the relationship between solute rejection and membrane fouling in a MBR system, membrane filtrations of activated sludge in different physiological states were carried out with ultrafiltration membranes. Regardless of the physiological states of the activated sludge (foaming, bulking, pin-point floc, exponential growth, endogenous phase, normal state sludge), the hydrophobic membrane (PM30) always showed greater solute rejection than the hydrophilic membrane (YM30). To investigate the key factors affecting solute rejection, the cake layer resistances ($R_c$) and the fouling resistances ($R_f$) were measured. The $R_c$ and $R_f$ values for the PM30 were always higher than for the YM30 and the $R_c$ prevailed over the $R_f$ in all cases. The solutes rejection by the adsorption onto/into the membrane was relatively small. This suggests that the cake layer deposited on the membrane surfaces played an important role in the solute rejection, i.e. dominant solute removals were attributed to the adsorption and/or sieving onto the cakes. Consequently, the difference in solute rejection efficiency between hydrophilic and hydrophobic membranes was mainly due to the degree of sieving and/or adsorption onto the cakes deposited on the membrane, and partly due to adsorption into membrane pores and the surfaces. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Activated sludge; Fouling; Membrane bioreactor (MBR); Membrane; Ultrafiltration

1. Introduction

The advantages of the membrane bioreactor (MBR) process have been substantially reviewed [1–10]. The absolute retention of all microorganisms by a membrane makes it possible to treat the wastewater effectively. There are 500 commercial MRBs in operation worldwide, with many more proposed or currently under construction [4].

Negative aspects, however, include high capital, maintenance and operating costs, which are to some extent exacerbated by membrane fouling. Fouling leads to permeate flux decline, making frequent membrane replacement and cleaning necessary which then increases maintenance and operating costs [5]. Therefore, most MBR studies performed recently aim to identify, investigate, control, and model membrane fouling [6–10]. A need for comprehensive study of membrane fouling still remains because there are many unknowns regarding the fouling mechanisms in such a complex biomass system.

Membrane fouling is a result of the interaction between membrane and activated sludge broth. For example, the floc-structure of activated sludge, the particle size distribution and the EPS (Extracellular Polymeric Substances) contents of activated sludge are well known factors controlling membrane fouling [1,7,10,11]. Additionally, the fouling is in close association with solute rejection because the membrane fouling could be originated from adsorption of organic species and adhesion of microbial cells at the membrane surfaces [12]. However, there is little information available on the relationship between membrane fouling and solute rejection. In the MBR process, the activated sludge can be in many physiological states because the activated sludge is a living microorganism. So the purpose of this study is to investigate the effects of membrane fouling on solute
rejection according to the microbial physiology of activated sludge.

2. Materials and methods

2.1. Membrane and filtration apparatus

Ultrafiltration membranes, YM30 and PM30 (Amicon, USA) were used for filtration. The MWCO (Molecular Weight Cut Off) of both membranes was 30 000 Da. Relative hydrophobicity of each membrane was characterized by measuring the contact angles between water droplets and membrane surface with goniometer (NRL, Rame Hart, USA). PM30 membrane was found to be relatively hydrophobic (contact angle was 66°) and YM30 was hydrophilic (totally wettable with water droplets).

Membrane filtration is carried out using a stirred batch cell (8200, Amicon) as shown in Fig. 1. Transmembrane pressure and stirring speed were regulated at 1.4 bars and 180 rpm respectively. The permeation flux was determined by weighing permeates on an electronic top loading balance connected to a personal computer equipped with an auto-reading program.

Before each experiment the pure water flux ($J_{iw}$) was measured with deionized water. The stirred cell was then emptied and filled with the activated sludge suspension. Ultrafiltration was performed until the volume concentration factor reached to 5. The stirred cell was emptied again and refilled with deionized water. Surface rinsing of the tested membrane with the pure water continued for 10 min without applying pressure and the rinsing water was discarded. Pure water flux was determined with the ultrapure water immediately after surface rinsing ($J_{fw}$). The resistance-in-series model is applied to evaluate the filtration characteristics.

$$J = \Delta P_T / (\eta \cdot R_t)$$

$$R_t = R_m + R_c + R_f$$

where $J$ is the permeation flux, $\Delta P_T$ is the transmembrane pressure, $\eta$ is the viscosity of the permeate; $R_t$ is the total resistance; $R_m$ is the intrinsic membrane resistance; $R_c$ is the cake resistance formed by the cake layer deposited over the membrane surface; and the fouling resistance, $R_f$, is the resistance caused by solute adsorption into the membrane pores and walls. Each resistance value can be obtained through Equations 3–5.

$$R_m = \Delta P_T / (\eta \cdot J_{iw})$$

$$R_t = \Delta P_T / (\eta \cdot J_{iw} - R_m)$$

$$R_c = \Delta P_T / (\eta \cdot J - (R_m + R_f))$$

$J_{iw}$, $J_{fw}$ and $J$ are flux values determined experimentally. $J_{iw}$ is the initial water flux before ultrafiltration, $J_{fw}$ is final water flux after removing cake layer, and $J$ is stabilized flux with activated sludge suspension.

2.2. Cultivation of activated sludge

Activated sludge suspensions in different physiological conditions were used in this study. Using a laboratory scale reactor, activated sludge acclimated to synthetic wastewater were cultivated in a different operating condition. The synthetic wastewater was prepared from a sterile concentrated solution with the composition shown in Table 1. Concentrated feed solution was stocked in the refrigerator and diluted with tap water to the desired concentration prior to feeding it to the activated sludge reactor. Each bioreactor was constructed of Perspex having a working volume of 2 l. Using a fill and draw technique, sludge was allowed to settle 30 min and the supernatant was withdrawn and discarded. The reactor was then refilled with the fresh feed solution and aeration restarted. These fill and draw processes were repeated every 12 or 24 h. Aeration and mixing were provided through a porous stone diffuser delivering compressed air.

Different physiological states, i.e. foaming sludge, bulking sludge, pin-point floc, exponential phase sludge, endogenous phase sludge, and normal sludge, were obtained. Table 2 shows the physiological states of each activate sludge suspension.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>16 000</td>
</tr>
<tr>
<td>Peptone</td>
<td>12 000</td>
</tr>
<tr>
<td>Yeast extract</td>
<td>1600</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>12 800</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>2560</td>
</tr>
<tr>
<td>MgSO₄ 7H₂O</td>
<td>3200</td>
</tr>
<tr>
<td>MnSO₄ 4·5H₂O</td>
<td>288</td>
</tr>
<tr>
<td>FeCl₃ 6H₂O</td>
<td>16</td>
</tr>
<tr>
<td>CaCl₂ 2H₂O</td>
<td>320</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>2000</td>
</tr>
</tbody>
</table>

To measure the degree of foaming, relative hydrophobicity of activated sludge was used [11]. The relative
hydrophobicity of foaming 1, 2 and normal sludge were 80, 82 and 57%, respectively (Table 2). Sludge volume index (SVI) was used as one of the measures to monitor the floc structure of sludge. The SVI values of normal sludge, pin-point floc and bulking sludge were 70, 30, 249 ml/g, respectively. The suspended solid (SS) and turbidity of the supernatant after settling the mixed liquor for 30 min could be indirectly related to the floc structures, because it was known that the pin-point floc sludge has a very turbid supernatant, while bulking sludge has a relatively clean supernatant. In this experiment, the supernatant of pin-point floc sludge was very turbid (SS = 130 mg/l, Turbidity = 47 NTU), whereas those of normal and bulking sludge were much less turbid (Normal sludge: SS = 44 mg/l, Turbidity = 14NTU, Bulking sludge: SS = 21 mg/l, Turbidity = 11NTU). According to the growth regime, microorganisms may grow at different physioogical states. Sludge in different growth regime, exponential growth phase and endogenous phase, were prepared using a batch reactor ($S_o/X_o = 0.36$). The other activated sludge suspension was taken from the aeration basin in the Chonan City Wastewater Treatment Plant in Korea. The physiological state of this suspension is bulking. Analyses of COD, MLSS, pH and SVI for the activated sludge suspension were conducted, respectively, using the procedures described in Standard Methods in [13].

3. Results and discussion

3.1. Soluble COD rejection

Fig. 2 shows the variation of soluble-COD concentration before and after ultrafiltration of activated sludge suspensions in different physiological states. It should be noted that the solute rejections of the hydrophobic membranes (PM30) were always greater than those of hydrophilic membrane (YM30). Regardless of the feed COD concentration and the physiological states of biomass, the permeate COD concentration of the hydrophobic membrane was always lower than that of the hydrophilic membrane. It is well known that the hydrophilic membrane maintains a higher flux than the hydrophobic one [1,14]. However, there is little information about the relationship between membrane hydrophilicity (or hydrophobicity) and solute rejection.

To understand the results above further, a solute rejection mechanism during ultrafiltration of activated sludge is proposed and illustrated schematically in Fig. 3. The solutes can be removed by the membrane pore itself, i.e. a sieving mechanism (Fig. 3a). Adsorption into the membrane pores and surfaces is also considered as a second mechanism for solute rejection (Fig. 3b). Finally, the solutes can be removed by sieving/adsorption onto the cake layer that has been formed over the membrane surface (Fig. 3c).

Considering that the MWCOs for both membranes were 30 000 Da, the contribution of the sieving by mechanism 1 to the overall solute rejection is equal to each membrane. Consequently, the difference in COD rejection between YM and PM membranes could be explained by the 2nd and 3rd mechanisms, i.e. the...
solute removal depends on how much the solutes are sieved and/or adsorbed onto the cakes as well as into membrane pores and surfaces. This hypothesis will be confirmed by the assessment of cake resistance \((R_c)\) and fouling resistance \((R_f)\) in the following section.

### 3.2. Contribution of membrane fouling to solute rejection

A set of resistances during ultrafiltration of activated sludge in different physiological states is shown in Fig. 4, where the fouling tendencies may be characterised in detail. In any cases of ultrafiltration, the cake resistance \((R_c)\) appeared to be a controlling resistance, whereas the fouling resistance \((R_f)\) was relatively small. It is worth noting that the \(R_c\) of the PM30 were always higher than that of the YM30. Considering the higher COD rejection for the PM30 membrane, the fouling tendencies are in close association with the solute rejection. This suggests that the cake layer deposited over the membrane plays an important role in the solute rejection.

The cake resistance \((R_c)\) is often expressed by the following equation [15]:

\[
R_c = \alpha V C_b
\]

where \(\alpha\) is a specific cake resistance, \(V\) is the permeate volume, \(C_b\) is the bulk concentration of mixed liquor. The biomass concentration \((C_b)\) was adjusted to 3500 mg/l before all ultrafiltrations performed in this study. The permeation volume \((V)\) was the same in all ultrafiltrations. Therefore, \(\alpha\) can be used as an alternative to express the cake layer resistance. According to the Carmen-Kozeny equation for the conventional filtration, the specific cake resistance \((\alpha)\) is a function of particle diameter \((d_p)\), porosity of cake layer \((\epsilon)\), and particle density \((\rho)\) as follows [16]:

![Fig. 3. Proposed mechanism for solutes rejection during ultrafiltration of activated sludge.](image)

![Fig. 4. Comparison of cake and fouling resistances during ultrafiltrations of activated sludge suspension in different physiological states.](image)
Therefore, the amounts of solutes sieved and the membrane would be formed tighter than that of the YM30. The cake layers deposited over the PM30 membranes are in the sub-micron range, the floc size of the activated sludge ranged from 2 to 300 μm. These experiments were performed in the cases of Run 7 and Run 8. These results strongly support the fact that the COD removal is dominated by the sieving/adsorption onto the cake layer. In the case of Run 8, similar results were observed. The total amounts of COD removed during the ultrafiltration with the YM30 and PM30 were 102 mg/l (=128−26) and 106 mg/l (=128−22), respectively. The amounts of COD removed by membrane pores/surfaces were 8 mg/l (=28−20) and 18 mg/l (=28−10). In summary, COD removal during the ultrafiltration of activated sludge is mainly attributed to the sieving/adsorption onto the cakes deposited on the membrane surface and partly to the adsorption into the membrane pores/surfaces.

### 4. Conclusions

The relationship between membrane fouling and solute rejection was investigated experimentally using a stirred batch cell system. With hydrophilic and hydrophobic membranes, a series of ultrafiltration of the activated sludge in different physiological states was performed and the following conclusions were drawn: (1) Regardless of the physiological states of activated sludge, the hydrophobic membrane (PM30) always showed greater solute rejection than the hydrophilic membrane (YM30). (2) The cake layer resistances \( R_c \) and the fouling resistances \( R_f \) for the PM30 were always higher than for the YM30, and the \( R_f \) values prevailed over the \( R_c \) in every physiological state of activated sludge. (3) The cake layer deposited over the membrane surfaces played an important role in the solute rejection, i.e. the predominant solute removals were attributed to the sieving and/or adsorption onto the cakes. And some parts of solutes were adsorbed into the membrane pores and surfaces. Consequently, the difference in the solute rejection efficiency between hydrophilic and hydrophobic membranes was mainly

\[
x = 180(1 - \varepsilon)/(\rho \cdot d_p^2 \cdot \varepsilon^3).
\]

Considering that the \( R_f \) of the PM30 was always higher than that of the YM30, the porosity \( (\varepsilon) \) of the cake layer on the PM30 membrane would be smaller than that of the YM30 membrane because the other factors \( (\rho \) and \( dp \) affecting \( x \) behaved equally with both membranes. The cake layers deposited over the PM30 membrane would be formed tighter than that of the YM30. Therefore, the amounts of solutes sieved and/or adsorbed onto the cakes on the PM30 were greater than those of the YM30. Consequently, the difference in the solute rejection between the PM30 and the YM30 membranes could be explained by the 3rd mechanism described above.

Although the pore sizes of PM30 and YM30 membranes are in the sub-micron range, the floc size of the activated sludge ranged from 2 to 300 μm in general. The cause of fouling resistance \( (R_f) \) is therefore not attributed to the floc itself but to the solutes and fine colloids in bulk solution. In every case of ultrafiltration, the \( R_f \) of the PM30 membrane also exhibited higher values than that of the YM30 (Fig. 4). The membrane structure was modified due to adsorption of solute material of molecular size, which reduced the flux performance of the membrane. It clearly indicated that the solutes were more easily adsorbed to the pores/surfaces of the PM30 than YM30. So the difference in the COD reduction between the PM and the YM was attributed partly to adsorption tendency to the membrane pores and surfaces (the 2nd mechanism).

To investigate the adsorption tendency of the solutes into the pores/surfaces in both membranes, the floc fraction in the activated sludge suspension was removed using a microfilter with a 0.45 μm pore size. The filtrates of activated sludge suspension were filtered again with the YM30 and PM30 membranes. Experimental conditions were the same as those of ultrafiltration of activated sludge. These experiments were performed in the cases of Run 7 and Run 8.

Table 3 shows the variation of COD of the activated sludge and the filtrates before and after ultrafiltration. For Run 7, total amounts of COD removed during the ultrafiltration with the YM30 and PM30 were 17 mg/l (=55−38) and 28 mg/l (=55−27), respectively; the amounts of COD removed by membrane pores/surfaces were only 3 mg/l (=46−43) and 7 mg/l (=46−39), respectively. The amounts of COD removed by membrane pores/surfaces were 8 mg/l (=28−20) and 18 mg/l (=28−10). In summary, COD removal during the ultrafiltration of activated sludge is mainly attributed to the sieving/adsorption onto the cakes deposited over the membrane surface and partly to the adsorption into the membrane pores/surfaces.

### Table 3
COD removals during ultrafiltration of the activated sludge and the 0.45 μm filtrates

<table>
<thead>
<tr>
<th>Characteristics of feed solution</th>
<th>COD (mg/l)</th>
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<tbody>
<tr>
<td></td>
<td>Feed solution</td>
</tr>
<tr>
<td>Run 7 (Normal sludge)</td>
<td></td>
</tr>
<tr>
<td>Activated sludge suspension</td>
<td>55</td>
</tr>
<tr>
<td>Filtrates of activated sludge with 0.45 μm microfilter</td>
<td>46</td>
</tr>
<tr>
<td>Run 8 (Chonan WWTP)</td>
<td></td>
</tr>
<tr>
<td>Activated sludge suspension</td>
<td>128</td>
</tr>
<tr>
<td>Filtrates of activated sludge with 0.45 μm microfilter</td>
<td>28</td>
</tr>
</tbody>
</table>
due to the degree of sieving and/or adsorption onto the cakes deposited over the membrane, and partly due to adsorption into membrane pores and surfaces.

References


