Membrane filtration characteristics in membrane-coupled activated sludge system — the effect of physiological states of activated sludge on membrane fouling

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Abstract

The effect of sludge physiology on membrane fouling was investigated in a membrane-coupled activated sludge (MCAS) system. A series of ultrafiltrations were performed to assess the flux behaviors according to foaming potential, solids retention time (SRT), growth phase and nutrient condition of the activated sludge. The foaming sludge showed greater flux decline than the non-foaming sludge. The extraordinary increase, that is, more than 100 times in membrane fouling for the foaming sludge, was attributed to the hydrophobic and waxy nature of the foaming sludge surface, which was confirmed by a comparison with relative hydrophobicity. Membrane fouling tendency was increased as SRT decreased. A greater flux decline was observed at the endogenous phase than at the log growth phase. The activated sludge acclimated to the nitrogen deficient substrates produced less extracellular polymeric substances (EPS) and exhibited higher flux than the control activated sludge. The quantitative measurements of EPS content in order to estimate the extent of membrane fouling in various activated sludges showed that, in any physiological states of activated sludge, the higher the content of EPS the activated sludge had, the greater the membrane fouling proceeded. The EPS content of activated sludge is suggested as a probable index for the membrane fouling in a MCAS system.

Keywords: Activated sludge; Foaming; SRT; Nitrogen limitation; Membrane; EPS

1. Introduction

The advantages of the membrane-coupled activated sludge (MCAS) process have been well documented elsewhere [1–3]. While this process has many advantages over the conventional activated sludge system, its practical application has been restricted due to the inherent membrane fouling problem, which leads to frequent membrane replacements and cleaning procedures.
In the MCAS system, membrane fouling is a result of the interaction between the membrane material and the components in activated sludge broth. The broth includes feed components, cells, microbial metabolites, such as extracellular polymeric substances (EPS), etc. But the broth has no fixed composition and its properties may be a function of time [4]. For instance, the broth at an endogenous phase may consist of more lysed cells, cell debris than at a log growth phase. This unknown and varying composition of broth has made it more difficult to study membrane fouling in MCAS systems.

However, it is well known that exocellular materials excreted from cells are one of the most important membrane foulants. Stec and Field showed that the extracellular properties of a microbial cell was important when the mechanisms of flux reduction was considered [5]. Their results emphasized the importance of the knowledge of sludge surface characteristics for the membrane filtration of microorganism. It was reported that the key role of bacterial extracellular matrix as a major factor affecting membrane flux during filtration of marine organism SW8 [6].

Mukai et al. have recently reported that the flux was influenced by the growth phase of the activated sludge during ultrafiltration of supernatants containing extracellular materials released from the activated sludge bacterial mixture or Sphaerotilus natans strains [7].

It is important to establish a sort of general rule about the effect of sludge physiology on the membrane fouling because the EPS is known to be a major foulant, and furthermore its excretion seems to depend largely on the physiological states of the activated sludge. However, there is little information available on the quantitative evaluation of EPS according to the sludge physiology and its correlation to the extent of membrane fouling in MCAS systems.

The purpose of this study was to investigate the effect of physiological states of activated sludge on the membrane fouling. Especially, the effects of foaming, SRT, growth phase and nutrient condition of activated sludge were emphasized, respectively, in this research. This study may lead to a better understanding and/or prediction of membrane fouling tendency in MCAS systems.

2. Materials and methods

2.1. Cultivation of activated sludge

A synthetic wastewater was used throughout this study in order to ensure the consistent quality of the influent to the reactor. 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. Using a fill and draw technique, sludge was allowed to settle 30 min, and the supernatant was withdrawn and discarded. Then, the reactor was refilled with the fresh feed solution and aeration restated. 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. An activated sludge had been acclimated to this synthetic wastewater for 3 months to achieve a steady state prior to the membrane filtration experiments.

Table 1
Composition of synthetic wastewater

<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>1,600</td>
</tr>
<tr>
<td>(NH₄)₂SO₄</td>
<td>12,800</td>
</tr>
<tr>
<td>KH₂PO₄</td>
<td>2,560</td>
</tr>
<tr>
<td>MgSO₄ • 7H₂O</td>
<td>3,200</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>2,000</td>
</tr>
</tbody>
</table>
Three sets of activated sludge were cultivated using laboratory scale reactors. The first set of cultivation was carried out to make the activated sludge with a foaming potential. To prepare such a foaming activated sludge, two reactors were operated at higher SRT and lower F/M ratio. A control reactor, i.e., non-foaming activated sludge, was also operated in parallel with the two foaming reactors. But any oil or grease was not added to the influent synthetic wastewater to induce only biological foaming. The temperature ranged between 30 and 35 °C during cultivation.

The second set of activated sludge was cultivated to get different SRT. The SRT of activated sludge was controlled by wasting an appropriate volume of mixed liquor every day.

The third set of activated sludge was cultivated in a different nutrient condition. Nitrogen limitation was imposed by altering carbon to nitrogen ratio of the synthetic wastewater from its normal value 16:1 to 207:1 (based on COD:TKN). This change in the C/N ratio was achieved by decreasing ammonium sulfate content in synthetic wastewater. The control reactor was operated in parallel with the nitrogen limited reactor. Except for the C/N ratio, operating conditions of the control reactor were the same as those of the nitrogen-deficient reactor.

2.2. Analytical methods

Analysis of MLSS, COD, TKN and SVI for the influent, effluent and mixed liquor samples was conducted, respectively, using the procedures described in Standard methods [8]. Particle size analysis of the activated sludge was conducted with a particle size analyzer (MasterSizer/E, Malvern Co., U.K.).

2.3. Measurement of relative hydrophobicity of activated sludge

The procedure was the same as given by Rosenberg et al. [9] except some modifications as follows: To a 50 ml separatory funnel containing 30 ml of washed sludge suspended in Tris buffer (pH=7.1) were added 15 ml of hexadecane. A series of experiments with a change of hexadecane volume showed that this quantity was enough for activated sludge to adhere to hexadecane droplets. The mixtures were agitated uniformly for 5 min. After allowing 30 min for the hydrocarbon phase to rise completely, the aqueous phase was carefully transferred into other glassware. A series of experiments with change of standing time showed that 30 min were sufficient to obtain reproducible results. Relative hydrophobicity is expressed as a ratio of MLSS concentration in the aqueous phase after emulsification (MLSSf) to MLSS concentration in the aqueous phase before emulsification (MLSSi).

Relative hydrophobicity (%) = 100 ×
(1 - MLSSf/MLSSi) (1)

2.4. Measurement of EPS content

EPS solution was obtained using the thermal treatment method [10]. It was known to be the most effective extraction method among the various methods because it released a significant quantity of exocellular polymer from the flocs and caused less cellular disruption than the other methods [11].

The mixed liquor of activated sludge was centrifuged in order to remove the bulk solution (3200 rpm, 30 min). After discarding the supernatant, the remaining pellet was washed and resuspended with saline water (0.9% NaCl solution). The extracted solution was obtained from heat treatment (100°C, 1 h) of this resuspended solution. The extracted solution was centrifuged again under the same operating condition. The supernatant obtained in this way was named as the “EPS solution”. The EPS content was measured by analyzing volatile solids (VS) of this EPS solution without further precipitation procedure.
Table 2
Characteristics of membranes used in stirred cell experiments

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>YM30</td>
</tr>
<tr>
<td>Molecular weight cut-off (Dalton)</td>
<td>30,000</td>
</tr>
<tr>
<td>Material of skin layer</td>
<td>Regenerated cellulose</td>
</tr>
<tr>
<td>Contact angle with water (θ)</td>
<td>Totally wettable</td>
</tr>
</tbody>
</table>

2.5 Fractionation of activated sludge suspension

In order to find out which components in the mixed liquor of the activated sludge were mainly responsible for the flux reduction, the activated sludge suspension was divided into three fractions: bulk solution, cell and EPS.

The original activated sludge suspension was filtrated with 0.45 μm membrane filter. The filtrate refers to the bulk solution. The sludge pellet was then washed with the saline water, followed by the addition of the saline water to make the “floc solution”.

EPS was extracted from the floc solution using the heat treatment method described previously. EPS was determined from the supernatant (EPS solution) after the centrifugation of the heat-treated floc solution. And then, the remaining cell pellet was resuspended with saline water. This resuspended solution refers to “cell solution”.

2.6. Membranes and filtration apparatus

A stirred batch cell (8200, Amicon, USA) connected to an electronic top-loading balance was used to filtrate the activated sludge suspensions with three kinds of ultrafiltration membranes of different hydrophobicity (YM30, XM50 and PM30, Amicon, USA). Some characteristics of each membrane are provided in Table 2. Relative hydrophobicity of each membrane was characterized by measuring the contact angle between water droplets and membrane surface with a goniometer (NRL, Rame Hart, USA). Based on the contact angle measurements, the order of the relative hydrophobicity was found to be PM30 > XM50 > YM30 membrane in decreasing order (Table 2).

The fresh membrane was first rinsed by letting it float skin-side down in ultrapure water for 90 min. The rinsing water was changed three times during this cleaning period. The cleaned membrane was placed in a stirred batch cell (8200, Amicon, USA). The permeate flux was determined by weighing permeates on an electronic top-loading balance connected to a personal computer equipped with an autoreading program. Transmembrane pressure was regulated at 1.4 bars using nitrogen gas and the stirring speed was about 180 rpm for all tests in this work. The MLSS concentration of each activated sludge suspension was adjusted to 3500±100 mg/l prior to the membrane filtration in order to exclude the concentration effect on the permeate flux.

2.7. Measurements of various flux

In this article, the terms of initial water flux ($J_w$), permeate flux ($J$) and final water flux ($J_{fw}$) were used to characterize the performance of membrane filtration. $J_w$ is simply a water flux through the cleaned membrane. Before the filtration of activated sludge suspension, $J_{fw}$ of each membrane was determined by filtration of ultrapure water when a steady flux was reached. The stirred cell was then emptied and filled with
the activated sludge suspension. Ultrafiltration has been performed until the volume concentration factor equal to 5. The permeate flux at this moment is denoted as $J_s$. Then the stirred cell was emptied again and refilled with the ultrapure water. The surface rinsing of the tested membrane with the ultrapure water continued for 10 min without applying pressure, and then the rinsing water was discarded. $J_{fw}$ was determined by the ultrapure water right after the surface rinsing.

3. Results and discussion

3.1. Effect of biological foaming on membrane fouling

Most activated sludge plants suffer from foaming problems, an operation disorder that leads to effluent quality deterioration, hazardous working conditions and odor in the surrounding area [12]. The foaming is caused by high SRT, warm temperature, oil and grease in the influent wastewater, low F/M ratio and high MLSS levels [13–16]. Since the typical operating conditions of the MCAS system, such as high SRT and MLSS levels and low F/M ratio, is more likely to induce biological foaming, a comparison was made between activated sludge, with and without foaming potential with respect to membrane fouling.

Fig. 1a and b show the flux declines during ultrafiltration of the foaming and non-foaming activated sludge with YM30 and PM30 membranes, respectively. The purpose of the experiment with “foaming 2” activated sludge was merely to confirm the reproducibility of this test. Irrespective of the membrane materials, e.g., whether hydrophilic or hydrophobic, the foaming sludge showed a much greater flux decline than the non-foaming sludge. And the flux decline was even worse with the hydrophobic PM30 membrane.

To characterize the above results quantitatively, a resistance-in-series model was applied to evaluate the characteristics of membrane fouling. According to this model, the permeate flux ($J$) took the following form:

$$ J = \frac{\Delta P}{\eta \cdot R_t} $$

$$ R_t = R_m + R_c + R_f $$

Fig. 1a. Flux vs. concentration factor during ultrafiltration of foaming and non-foaming activated sludge with the YM30 membrane.

Fig. 1b. Flux vs. concentration factor during ultrafiltration of foaming and non-foaming activated sludge with the PM30 membrane.
where $\Delta P_T$ 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 cake layer deposited over membrane surface, and the fouling resistance, $R_f$ is the resistance caused by pore plugging and/or solute adsorption onto the membrane pore and surface. Each resistance value ($R_m$, $R_c$, and $R_f$) can be obtained through Eqs. (4) to (6) and the experimentally determined $J_{nw}$, $J_{fw}$, and $J_f$.

$$R_m = \Delta P_T (\eta \cdot J_{nw}) \tag{4}$$

$$R_f = \Delta P_T / (\eta \cdot J_{fw}) - R_m \tag{5}$$

$$R_c = \Delta P_T (\eta \cdot J_f) - (R_m + R_f) \tag{6}$$

Various resistances for both membranes were determined using the above relationship and are summarized in Table 3. The contribution of $R_f$ to the total resistance, $R_T$, was negligible. The two membranes with any type of sludge behaved the same way. This result seems to be originated from the experimental procedure, i.e., dead-end filtration. However, $R_c$ for the foaming sludge increased by more than 100 times compared with the non-foaming sludge and made up 99% of $R_T$. The jump of $R_c$ was more pronounced with the hydrophobic PM30 membrane.

The significant increase in membrane fouling level was attributed to the hydrophobic and waxy nature of the foaming sludge surface. Goddard and Foster [17] have shown that the foaming sludge, *Nostothrix limicola*, contained a greater lipid concentration (>4 times) in mixed liquor than that of the non-foaming sludge. Richard [18] also indicated that noocardial foams contained substantial lipid contents, responsible for their cell surface hydrophobicity, up to 40% of dry weight vs. 5~10% for *Nocardia* free activated sludge.

In this study, the hydrophobic and waxy nature of the foaming sludge was confirmed by measuring the relative hydrophobicity, as shown in Table 4. There is a distinct difference in the hydrophobicity between the two types of activated sludge. The relative hydrophobicity for the foaming sludge was greater than that for the non-foaming sludge. A similar tendency was reported by others [19]. From the above results, a possible explanation for a large flux difference between foaming and non-foaming sludge is the “hydrophobic interaction” [20] between the membrane material and foaming sludge. The higher hydrophobicity of foaming sludge could render a stronger adherence of floc particles with one another as well as onto the membrane surface, thereby augmenting the $R_c$ and/or $R_f$.

Table 3
Resistance in ultrafiltration of the foaming and non-foaming activated sludges with the YM30 and PM30 membranes

<table>
<thead>
<tr>
<th></th>
<th>$R_m \times 10^{11} \times m^{-1}$</th>
<th>$R_c \times 10^{11} \times m^{-1}$</th>
<th>$R_f \times 10^{11} \times m^{-1}$</th>
<th>$R_t \times 10^{11} \times m^{-1}$</th>
<th>$R_c/R_t %$</th>
</tr>
</thead>
<tbody>
<tr>
<td>YM30:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-foaming</td>
<td>16</td>
<td>23</td>
<td>3</td>
<td>42</td>
<td>54.8</td>
</tr>
<tr>
<td>Foaming 1</td>
<td>17</td>
<td>2860</td>
<td>1</td>
<td>2878</td>
<td>99.4</td>
</tr>
<tr>
<td>Foaming 2</td>
<td>17</td>
<td>4190</td>
<td>3</td>
<td>4210</td>
<td>99.5</td>
</tr>
<tr>
<td>PM30:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-foaming</td>
<td>5</td>
<td>37</td>
<td>8</td>
<td>50</td>
<td>74.0</td>
</tr>
<tr>
<td>Foaming 1</td>
<td>3</td>
<td>3490</td>
<td>12</td>
<td>3505</td>
<td>99.6</td>
</tr>
<tr>
<td>Foaming 2</td>
<td>3</td>
<td>5690</td>
<td>9</td>
<td>5702</td>
<td>99.8</td>
</tr>
</tbody>
</table>
Biological foaming takes the form of a floating layer of activated sludge of mouse-like consistency, containing entrapped air bubbles in a mainly filamentous floc structure [21]. When the foaming sludges accumulate on the membrane surface, the entrapped air bubbles might play a role in reducing the actual porosity of sludge cakes and thus increase the $R_c$. This may be another possible reason for the extraordinarily high value of $R_c$ for the foaming sludge.

In conclusion, it is very important to prevent biological foaming during the operation of MCAS systems.

### 3.2. Effect of SRT on membrane fouling

For the YM30, XM50 and PM30 membranes, the flux declines for each membrane during ultrafiltration of the activated sludge with different SRT were plotted as a function of the concentration factor (Fig. 2a–c). As the SRT increased, the flux also increased regardless of membrane materials. However, the extent of flux decline was significantly different from one another i.e., the degree of flux decline was intimately related with the membrane hydrophobicity. This phenomenon could be attributed to the hydrophobic interaction discussed in the previous section.

A series of resistances measured according to SRT revealed that the cake resistance ($R_c$) appears to determine the overall resistance ($R_t$) as indicated by the $R_c/R_t$ column in Table 5. As SRT increased, the decrease of $R_c$ was so pronounced, unlike the $R_f$.
Fig. 2a. Flux vs. concentration factor during ultrafiltration of activated sludge with different SRT with the YM30 membrane.

The mixed liquor of an activated sludge is comprised of floc particles and bulk solution. On the interior and/or in the envelopes of the floc particles, there are lots of cells and EPS. Therefore, the following relationship can easily be set up:

\[
\text{Activated sludge broth} = \text{bulk solution} + \text{floc}\]

(7)

\[
= \text{bulk solution} + \text{cell} + \text{EPS}\]

(8)

To investigate the flux limiting component of the mixed liquor of activated sludge, ultrafiltration of the floc solution and the bulk solution was performed with the YM30 membrane, respectively. Table 6 shows the resistance values for each filtration. As \( R_c \) in floc fraction appeared to be a controlling resistance, the floc solution was further fractionated into the cells and EPS. Another ultrafiltration of the cell and EPS solution was performed with the YM30 membrane to investigate which component of the floc particles would reduce the flux more severely. From
Table 6
Resistance in ultrafiltration of the floc fraction and bulk solution with the YM30 membrane

<table>
<thead>
<tr>
<th></th>
<th>$R_m$ ($10^{11} \times m^{-1}$)</th>
<th>$R_e$ ($10^{11} \times m^{-1}$)</th>
<th>$R_f$ ($10^{11} \times m^{-1}$)</th>
<th>$R_t$ ($10^{11} \times m^{-1}$)</th>
<th>$R_c/R_t$ (％)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Floc fraction</td>
<td>18</td>
<td>29</td>
<td>0.1</td>
<td>47</td>
<td>62</td>
</tr>
<tr>
<td>Bulk fraction</td>
<td>19</td>
<td>7</td>
<td>0.2</td>
<td>26</td>
<td>27</td>
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</table>

Table 7
Resistance in ultrafiltration of the cell fraction and EPS fraction with the YM30 membrane

<table>
<thead>
<tr>
<th></th>
<th>$R_m$ ($10^{11} \times m^{-1}$)</th>
<th>$R_e$ ($10^{11} \times m^{-1}$)</th>
<th>$R_f$ ($10^{11} \times m^{-1}$)</th>
<th>$R_t$ ($10^{11} \times m^{-1}$)</th>
<th>$R_c/R_t$ (％)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPS</td>
<td>22</td>
<td>131</td>
<td>1</td>
<td>154</td>
<td>85</td>
</tr>
<tr>
<td>Cell</td>
<td>22</td>
<td>69</td>
<td>0.1</td>
<td>91</td>
<td>76</td>
</tr>
</tbody>
</table>

It was reported that the extracellular matrix affected the cake resistance by filling the void spaces between the cell particles in the cake resulting in a drastic reduction of permeate flux [6]. Chiemchaisri and Yamamotto [22] also indicated that the extracellular materials of activated sludge could act as cake resistance. However, they did not measure the amounts of extracellular materials that existed in the interior and envelopes of the activated sludge floc. Hence, the correlation of quantified EPS with the cake resistance could strongly support the above suggestions.

The above hypothesis was confirmed by the analysis of the EPS contents in the activated sludges with different SRT (Table 8) and by comparing them with the corresponding resistance values in Table 5.

Fig. 3 distinctly shows the relationship between the EPS contents and cake resistance ($R_c$). The regression coefficients ($r^2$) were 0.92 (YM30), 0.93 (XM50) and 0.94 (PM30), respectively.

Table 8
EPS content of activated sludge at different SRT

<table>
<thead>
<tr>
<th>SRT (days)</th>
<th>EPS content</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Range (VS mg/g·MLSS)</td>
</tr>
<tr>
<td>3</td>
<td>234–276</td>
</tr>
<tr>
<td>8</td>
<td>228–273</td>
</tr>
<tr>
<td>33</td>
<td>187–242</td>
</tr>
</tbody>
</table>

Therefore, the EPS contents of activated sludge may be a suitable factor for estimating membrane fouling. This hypothesis is described in the following section of this paper.

3.3. Effect of growth phase on membrane fouling

In practice, the activated sludge reactors operate at different growth regimes, e.g. log, declining, stationary, endogenous, etc. According to the growth regime, microorganisms may grow at different physiological states and it may also affect the extent of membrane fouling. A series of ultrafiltrations with YM30 and PM30 membranes
were performed with the activated sludge at the log growth and endogenous phase, respectively. Prior to ultrafiltration, MLSS concentrations of both phases were adjusted to 2900 mg/l in order to exclude the concentration effect on membrane fouling.

Fig. 4a and b show the flux decline profiles during the ultrafiltration of the activated sludge at different growth phases with YM30 and PM30 membranes. There is a remarkable difference in flux reduction between both phases. Flux reduction occurred more severely at the endogenous phase than at the log growth phase. The resistance terms show that the $R_t$ was also controlled by the $R_c$ (Table 9). The $R_c$ at the endogenous phase was about two times greater than at the log growth phase for both membranes.

To correlate the EPS content to flux pattern, the EPS contents within the floc particles at both phases were measured and compared with each other (Table 9). The EPS contents at the log growth and endogenous phase were 202 and 271 mg.VS/g.MLSS, respectively. A remarkable increase of EPS content was observed during the endogenous phase. This result is in good agreement with the report of Pavoni et al. [23] who found that EPS was synthesized intensively at the endogenous phase.

As a result, the EPS content could also be the index for the membrane fouling tendency of activated sludge at different growth phases in MCAS systems.

3.4. Effect of nitrogen limitation on membrane fouling

The nitrogen content in the raw wastewater is regarded as a necessary feed constituent for the synthesis of new cell substances such as protein...
Table 9
Resistance in ultrafiltration of activated sludge broth and EPS contents at different growth phases

<table>
<thead>
<tr>
<th>Phases</th>
<th>( R_e ) (10^{11} \times m^{-1})</th>
<th>( R_c ) (10^{11} \times m^{-1})</th>
<th>( R_f ) (10^{11} \times m^{-1})</th>
<th>( R_t ) (10^{11} \times m^{-1})</th>
<th>( R_c / R_t ) (%)</th>
<th>EPS (VS mg/g·MLSS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YM30:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low growth</td>
<td>18</td>
<td>33</td>
<td>0.1</td>
<td>51</td>
<td>65</td>
<td>202</td>
</tr>
<tr>
<td>Endogenous</td>
<td>20</td>
<td>63</td>
<td>0.1</td>
<td>83</td>
<td>76</td>
<td>271</td>
</tr>
<tr>
<td>PM30:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Log growth</td>
<td>4</td>
<td>42</td>
<td>13</td>
<td>59</td>
<td>71</td>
<td>292</td>
</tr>
<tr>
<td>Endogenous</td>
<td>3</td>
<td>82</td>
<td>11</td>
<td>96</td>
<td>85</td>
<td>271</td>
</tr>
</tbody>
</table>

and nucleic acid. If the microorganisms were in nitrogen deficient environment, their physiological state would be altered and it might affect the membrane fouling in the MCAS system.

The control and nitrogen limited activated sludge reactors were run in the same operating condition, and the performance of each reactor is shown in Table 10. The effluent quality from N-deficient reactor was inferior to that from the control reactor in terms of COD and SS.

Fig. 5 shows the flux reduction profile during the ultrafiltration of the activated sludge in different nutrient conditions with the YM30 membrane. The steady-state flux of the activated sludge acclimated to nitrogen limitation was about 30–40% more than that of the control-activated sludge, and \( R_c \) made up 70–80% of \( R_t \) (Table 11). It also shows the EPS contents extracted from the two activated sludge suspensions. The average values of EPS contents of the nitrogen limited and control-activated sludge were 151 and 245 mg.VS/g·MLSS, respectively. Similar work with activated sludge showed that the polysaccharide production of the exocellular polymer decreased as the substrate nitrogen composition was reduced [24]. This clearly shows that the incomplete metabolism for the activated sludge cultivated at the nitrogen limitation results in less EPS production than the normal activated sludge. If the EPS content were compared with \( R_t \) in Table 10, we can again confirm that the flux reduction matches well with the EPS content.

It could be considered that the floc structure and particle size as well as the EPS content were important factors determining the magnitude of cake resistance. However, the floc structures of the above two activated sludge suspensions seemed to be similar because they showed very similar SVI values. In addition, the shape of particle size distribution was very similar to each other (Fig. 6). Based on all of the above results, the discrepancy in flux decline between the control and N-deficient activated sludge certainly comes from the difference in EPS content.
Table 11
Resistance in ultrafiltration of activated sludge and EPS contents under different nutrient conditions with the YM30 membrane

<table>
<thead>
<tr>
<th>Sludge type</th>
<th>( R_m ) ((10^{11} \times \text{m}^{-1}))</th>
<th>( R_c ) ((10^{11} \times \text{m}^{-1}))</th>
<th>( R_f ) ((10^{11} \times \text{m}^{-1}))</th>
<th>( R_t ) ((10^{11} \times \text{m}^{-1}))</th>
<th>( R_c / R_t ) (%)</th>
<th>EPS ((\text{VS mg/g-MLSS}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>19</td>
<td>97</td>
<td>1</td>
<td>117</td>
<td>83</td>
<td>245</td>
</tr>
<tr>
<td>N-limitation</td>
<td>18</td>
<td>57</td>
<td>2</td>
<td>77</td>
<td>74</td>
<td>151</td>
</tr>
</tbody>
</table>

Fig. 5. Flux decline during ultrafiltration of activated sludge broths under different nutrient conditions with the YM30 membrane.

Fig. 6. Comparison of the floc size distribution between control and nitrogen-limited activated sludge.

4. Conclusions

In this study, the membrane fouling tendency in a MCAS system was examined under various physiological states of activated sludge and the following conclusions were drawn:

- The relative hydrophobicity of foaming sludge was higher by 40% than that of non-foaming sludge. The extraordinary high value of \( R_c \) \((2-6 \times 10^{14} \text{m}^{-1})\) for the foaming sludge was attributed not only to the hydrophobic interaction but also to the entrapped air bubbles which might reduce the actual porosity of sludge cake.
- Through the separation of the activated sludge broth into three portions, i.e., bulk, cell and EPS fraction, it was found that EPS was the major contributing component to the total membrane resistance, \( R_t \).
- The activated sludge cultivated under N-deficient condition produced less EPS and had higher steady-state flux by 30–40% than the control sludge.
- In the ultrafiltration of activated sludge under different SRT, growth phase and nutrient
condition, the EPS content of each sludge matched well with the overall flux reduction. The greater amount of EPS the activated sludge had, the greater flux reduction was observed regardless of physiological state and membrane material. Therefore, the EPS content is suggested to be a probable index for membrane fouling in MCAS systems.

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