"Comparison of membrane filtration characteristics between two MBRs with fixed and moving bed biofilms."

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Ultimate Goals of Membrane Bioreactor:

- Higher Flux (L/m²/h)
- Longer Membrane Life Time
- Easy of Membrane Cleaning
- Lower Energy Consumption

→ directly related to Economical Feasibility and thus determine Competitiveness of MBR business
→ in close association with biofilm (biofouling)
Biofouling

Membranes in contact with the broth of activated sludge reactor will be colonized within short time by microorganisms, leading to the formation of a composite layer known as biofilm.

Biofouling has restricted the widespread application of MBR, because i) it limits the maximum flux obtainable, ii) it leads to substantial cleaning requirements, iii) it shortens membrane life time
An alternative to alleviate membrane fouling due to cake layer: ATTACHED GROWTH SYSTEM!

1) To compare the attached growth with the suspended growth system:
2) To compare two attached growth systems; Fixed bed and Moving bed Biofilms
Biofilm process

Biofilm Reactors

Fixed Bed Biofilm Reactor
- trickling filters
- rotating biological reactors
- submerged granular biofilters

Moving Bed Biofilm Reactor
- 2-phase fluidized beds
- 3-phase fluidized beds
- air-lifts circulating beds
### Operating Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant flux (L/(m²·hr))</td>
<td>25</td>
</tr>
<tr>
<td>Maximum transmembrane pressure (kPa)</td>
<td>26</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25</td>
</tr>
<tr>
<td>Air flow rate (L/min)</td>
<td>2.5</td>
</tr>
<tr>
<td>Working volume (L)</td>
<td>5</td>
</tr>
<tr>
<td>Hydraulic residence time (hr)</td>
<td>8</td>
</tr>
<tr>
<td>Feed concentration (mgCOD/L)</td>
<td>250</td>
</tr>
<tr>
<td>Volumetric organic loading (kg/(m³·day))</td>
<td>0.75</td>
</tr>
<tr>
<td>pH</td>
<td>7.0±0.2</td>
</tr>
<tr>
<td>Dissolved oxygen (mgO₂/L)</td>
<td>6.1 ± 0.1</td>
</tr>
</tbody>
</table>
Submerged Membrane Bioreactor (MBR)

Attached Growth Reactor
(MLSS: 100~2,000 mg/L, attached biomass: 2,000 mg/L)

Suspended Growth Reactor
(MLSS: 2,000~5,000 mg/L)
Quality of Treated Water

<table>
<thead>
<tr>
<th>Influent</th>
<th>COD (mg/L)</th>
<th>NH$_4^+$-N (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>250</td>
<td>20.2 (TN 23.9)</td>
</tr>
<tr>
<td>Permeate</td>
<td>Attached growth$^a$</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Suspended growth$^b$</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Attached growth$^a$</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>Suspended growth$^b$</td>
<td>0.17</td>
</tr>
<tr>
<td>% removal</td>
<td>99</td>
<td>98</td>
</tr>
</tbody>
</table>

$^a$MLSS: 100 mg/L, attached biomass: 2,000 mg/L
$^b$MLSS: 3,000 mg/L
Variations of suction pressure during the submerged MBR operation of attached growth and suspended growth

Contrary to expectations, membrane fouling proceeded much faster with the attached growth system than with the suspended growth.
Membrane fouling: The result of interaction between mixed liquor and membrane

Mixed liquor:
1) soluble fraction
2) suspended solids including biomass and other colloids

Soluble fraction
- Quantitative properties
  - Total organic carbon (TOC)
  - Extracellular polymeric substances (EPS)
- Qualitative properties
  - Molecular weight distribution
  - Mean oxidation state of organic carbons
Quantitative Analysis of Soluble Organics

Total organic carbon (TOC) vs. Extracellular polymeric substances (EPS)

- **TOC (mgC/L)**
- **0.45 µm filtrate**
- **Supernatant**

- **EPS (mg/L)**
- **Protein**
- **Polysaccharide**

*Attached growth; MLSS: 100 mg/L, attached biomass: 2,000 mg/L*

*Suspended growth; MLSS: 3,000 mg/L*

No significant difference in the amount of soluble organics of mixed liquor from both attached and suspended growth!
Qualitative Analysis of Soluble Organics

Rough estimation of organic molecules

<table>
<thead>
<tr>
<th>Origin of organics</th>
<th>Attached growth reactor</th>
<th>Suspended growth reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MLSS: 100 mg/L, attached biomass: 2,000 mg/L</td>
<td>MLSS: 3,000 mg/L</td>
</tr>
<tr>
<td>Mean oxidation state of carbon</td>
<td>Estimation of main constituents</td>
<td>Mean oxidation state of carbon</td>
</tr>
<tr>
<td>Mixed liquor</td>
<td>3.08</td>
<td>Organic acid</td>
</tr>
<tr>
<td>Membrane surface after filtration run</td>
<td>-0.84</td>
<td>Protein or polysaccharide</td>
</tr>
</tbody>
</table>

Mean oxidation state of organic carbon \(= \frac{4(\text{TOC} - \text{COD})}{\text{TOC}} \) (TOC: mol C/L, COD: mol O\(_2\)/L)

Qualitative Analysis of Soluble Organics

Molecular weight distribution

Qualitative characteristics of the soluble organic fractions in the mixed liquors did not vary according to the growth conditions!
Effect of MLSS on Filtration Behavior

Filtration behaviors with varying MLSS concentration in attached and suspended growth bioreactor

The rate of membrane permeability loss (e.g., the rising rate of TMP) was retarded along with the increase in MLSS concentrations regardless of growth conditions.
Formation of a Dynamic Membrane by Mixed Liquor Suspended Solids

- Attached growth (without suspended solids)
- Suspended growth

Low molecular weight or submicron colloidal particle

Microbial floc

Membrane

DYNAMIC MEMBRANE
SEM Images of Cake Layer on Membrane Surfaces after Filtration Run

new membrane (X 5,000)

used membrane for attached growth (MLSS: 100 mg/L, attached biomass: 2,000 mg/L) (X 5,500)

used membrane for suspended growth (MLSS: 3,000 mg/L) (X 5,000)
AFM Images of Cake Layer on Membrane Surfaces after Filtration Run

Used membrane for **attached growth** (MLSS: 100 mg/L, attached biomass: 2,000 mg/L)

Scan size 7µm

Roughness ($\text{rms}^a$) : 34 nm

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Used membrane for **suspended growth** (MLSS: 3,000 mg/L)

Scan size 7µm

Roughness ($\text{rms}^a$) : 87 nm

AFM: atomic force microscopy, $a$: root mean square
### Effect of Growth Pattern on Each Resistance in the Submerged MBR

<table>
<thead>
<tr>
<th></th>
<th>Attached growth</th>
<th>Suspended growth</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(MLSS: 100 mg/L, attached biomass: 2,000 mg/L)</td>
<td>(MLSS: 3000 mg/L)</td>
</tr>
<tr>
<td></td>
<td>$R_m$</td>
<td>$10^{12}$ m$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>0.49</td>
<td>4.24</td>
</tr>
<tr>
<td></td>
<td>$R_c$</td>
<td>2.94</td>
</tr>
<tr>
<td></td>
<td>0.81</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>$R_f$</td>
<td>4.24</td>
</tr>
<tr>
<td></td>
<td>$R_t$</td>
<td>4.24</td>
</tr>
</tbody>
</table>

*R_m*, $R_c$, and $R_f$ were measured right after the TMP reached 26 kPa.

*It took 20 hrs for attached and 140 hrs for suspended growth to obtain the same total resistance of $4.24 \times 10^{12}$ m$^{-1}$.

*Soluble or colloidal particles as well as microorganisms in the mixed liquor could accumulate and form a **cake layer** on the surface of membrane, but without microorganisms the **internal fouling** would be severer.*
Substances Causing Membrane Fouling

Substances on the membrane surface after operation

Liquid fraction, permeate

Aquatic Chemistry,
Werner Stumm & James J. Morgan, 2nd Ed.,
Wiley-Interscience
Specific Cake Resistances of Mixed Liquors

The mixed liquor of attached growth would have a higher fouling potential compared with that of suspended growth.

At the same MLSS of 2,000 mg/L, mixed liquor from both attached and suspended growth revealed similar cake properties at the same MLSS concentration.
In this study, two types of submerged MBR (attached and suspended growth systems) were compared with respect to various aspects in order to elucidate different filtration behavior from each other.

- The loss of membrane permeability proceeded more rapidly with the attached growth system than with the suspended one.

- Better filtration performance with suspended growth was attributed to the role of dynamic membrane formed on the membrane surface.
  - quantitatively and qualitatively similar properties of soluble organic compounds in mixed liquors for both systems
  - improvement of membrane permeability with increasing in MLSS concentrations regardless of growth conditions
  - confirmed by SEM and AFM images
Better filtrability with the suspended growth could also be due to the rougher cake layer having smaller specific cake resistance than that with the attached growth.
Biofilm process

Biofilm Reactors

Fixed Bed Biofilm Reactor
- Looped cord media

Moving Bed Biofilm Reactor
- Rectangular Sponge; Polyurethane coated with Activated Carbon

Influent

Air

Effluent

Settler

Excess sludge

Anaerobic Anoxic Aerobic
### Materials

#### Specifications of the membrane

<table>
<thead>
<tr>
<th>Module type</th>
<th>Hollow fiber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore size</td>
<td>0.1 µm</td>
</tr>
<tr>
<td>Material</td>
<td>Polyethylene, hydrophilic</td>
</tr>
<tr>
<td>Inner diameter</td>
<td>270 µm</td>
</tr>
<tr>
<td>Outer diameter</td>
<td>410 µm</td>
</tr>
<tr>
<td>Surface area</td>
<td>0.1 m²</td>
</tr>
</tbody>
</table>

#### Specifications of the biofilm carrier

<table>
<thead>
<tr>
<th>Material</th>
<th>Shape(cm³)</th>
<th>Density (g/ cm³)</th>
<th>Surface area (m²/ g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyurethane coated with activated carbon</td>
<td>Porous cubic 1.3×1.3×1.3</td>
<td>0.21</td>
<td>8.50 (35,000 m²/ m³)</td>
</tr>
</tbody>
</table>
### Experimental conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux $[\text{LMH} (L/ m^2 \cdot \text{hr})]$</td>
<td>30</td>
</tr>
<tr>
<td>Transmembrane pressure $[\text{kPa}]$</td>
<td>$&lt; 30$</td>
</tr>
<tr>
<td>Temperature $[^\circ \text{C}]$</td>
<td>25 ($\pm 1$)</td>
</tr>
<tr>
<td>DO $[\text{mgO}_2/ L]$</td>
<td>5 ($\pm 0.1$)</td>
</tr>
<tr>
<td>Working volume $[L]$</td>
<td>6</td>
</tr>
<tr>
<td>HRT $[\text{hr}]$</td>
<td>10</td>
</tr>
<tr>
<td>Feed concentration $[\text{mg COD/ L}]$</td>
<td>1,000</td>
</tr>
<tr>
<td>Organic loading $[\text{kg COD/ m}^3 \cdot \text{day}]$</td>
<td>2.4</td>
</tr>
<tr>
<td>Suspended biomass $[\text{mg/ L}]$</td>
<td>5,000 ($\pm 500$)</td>
</tr>
<tr>
<td>Attached biomass $[\text{mg/ L}]$</td>
<td>17,000 ($\pm 1,500$)</td>
</tr>
</tbody>
</table>
# Composition of synthetic wastewater

<table>
<thead>
<tr>
<th>Composition</th>
<th>Concentration (mg/ L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>327.88</td>
</tr>
<tr>
<td>Bacto Peptone</td>
<td>245.90</td>
</tr>
<tr>
<td>Yeast Extract</td>
<td>32.78</td>
</tr>
<tr>
<td>((\text{NH}_4\text{)}_2\text{SO}_4)</td>
<td>262.30</td>
</tr>
<tr>
<td>(\text{KH}_2\text{PO}_4)</td>
<td>52.45</td>
</tr>
<tr>
<td>(\text{MgSO}_4\cdot 7\text{H}_2\text{O})</td>
<td>65.58</td>
</tr>
<tr>
<td>(\text{MnSO}_4\cdot 4\text{H}_2\text{O})</td>
<td>5.90</td>
</tr>
<tr>
<td>(\text{FeCl}_3\cdot 6\text{H}_2\text{O})</td>
<td>0.33</td>
</tr>
<tr>
<td>(\text{CaCl}_2\cdot 2\text{H}_2\text{O})</td>
<td>6.55</td>
</tr>
<tr>
<td>(\text{NaHCO}_3)</td>
<td>40.98</td>
</tr>
<tr>
<td><strong>COD</strong></td>
<td>1,000mg/ L</td>
</tr>
</tbody>
</table>
Operating parameters

* Carrier volume fraction: 5~20%
* Air flow rate: 5~9 LPM (l/min)

Filtration characteristics
Filtration characteristics

Graph showing transmembrane pressure (TMP) in kPa over time (hr) for different flow rates and filtration rates:
- 5 LPM, 5%
- 5 LPM, 10%
- 5 LPM, 20%
- 9 LPM, 5%
- 9 LPM, 10%
- 9 LPM, 20%
Factors affecting membrane biofouling in conventional MBR

* Soluble COD (SCOD)
* Microbial floc size
* Extracellular Polymeric Substance (EPS)
  : bound EPS, soluble EPS
* Compressibility of microbial cake layer
Biochemical effects: SCOD

Soluble COD in attached growth reactor
Permeate COD

Graph showing the variation of COD (mg/L) over time (day) with two different trends.

- Soluble COD in attached growth reactor
- Permeate COD
Biochemical effects: Floc size as a function of air flow rate

(carrier volume fraction = 20%)

5 LPM
D(v, 0.5) = 61.49 μm

7 LPM
D(v, 0.5) = 47.11 μm

9 LPM
D(v, 0.5) = 37.30 μm

TMP (kPa)

Time (hr)
Biochemical effects: Floc size as a function of carrier volume fraction

(Air flow rate = 5 LPM)

- 5%: $D(v, 0.5) = 75.24 \mu m$
- 10%: $D(v, 0.5) = 63.15 \mu m$
- 20%: $D(v, 0.5) = 49.60 \mu m$
Biochemical effects: Bound EPS as a function of air flow rate

Carrier volume fraction = 20%

- Polysaccharide
- Protein

Air flow rate: 5LPM, 7LPM, 9LPM

EPS (mg/L) and TMP (kPa) over time for different air flow rates.
Biochemical effects: Bound EPS as a function of carrier volume fraction

Air flow rate = 5LPM

EPS (mg/L) vs Media volume fraction

EPS vs Time (hr) with TMP (kPa)

- 5LPM, 5%
- 5LPM, 10%
- 5LPM, 20%
Membrane filtration characteristics are less dependent on biochemical effects of mixed liquor in M-CMBBR system.
- (A) type membrane module is covered with iron net to prevent collision between biofilm carrier and membrane module. But, mixed liquor and air bubble is freely pass through the iron net.

- (B) type membrane module (without iron net) is exposed to circulating biofilm carrier.
Filtration behaviors with and without iron net

- Operating conditions
  - Membrane surface area: 0.05 m²
  - Constant Flux: 30 LMH
  - Air flow rate: 5 LPM
  - Carrier volume fraction: 20%

![Graph showing TMP (kPa) over time (min) with and without iron net.](image)
Formation of cake layer on membrane surface

(A) type

(B) type
Formation of cake layer on membrane surface

(A) type (with iron net)  (B) type (without iron net)

Hollow fiber

Thick cake wall

Thin cake wall

Biofilm carrier

Permeate
SEM images of cake layer on membrane surface

Virgin membrane surface  (A) type (with iron net)  (B) type (without iron net)
AFM images of cake layer on membrane surface

Virgin membrane surface
(roughness(rms) : 153nm)

(A) type (with iron net)
(roughness(rms) : 51nm)

(B) type (without iron net)
(roughness(rms) : 114nm)

(scan size : 10μm)
It is obvious that friction between biofilm carriers and membrane surfaces mitigate the formation of cake layer on the membrane surface.

Then, what is the quantitative relationship between permeability and operating condition (the air flow rates & carrier volume fractions)?
Membrane - Coupled Moving Bed Biofilm Reactor (M-CMBBR)
**Definitions**

- **Kinetic energy**

  \[ E_k = \frac{1}{2} \times m \times v^2 \]
  
  - \( E_k \): kinetic energy of a biofilm carrier
  - \( m \): mass of a biofilm carrier
  - \( v \): velocity of a biofilm carrier

- **Total kinetic energy**

  \[ E_{k,T} = E_k \times n \]
  
  - \( E_{k,T} \): Total kinetic energy of biofilm carrier
  - \( n \): number of biofilm carrier

- **Relative kinetic energy**

  \[ E_{k,R} = \frac{E_{k,T}}{E_{k,T0}} \]
  
  - \( E_{k,R} \): Relative kinetic energy of biofilm carrier
  - \( E_{k,T0} \): Total kinetic energy at the conditions of 5LPM air flow rate and 5% carrier volume fraction
**Calculation of the relative kinetic energy of biofilm carrier and the relative membrane operating time**

<table>
<thead>
<tr>
<th></th>
<th>Total Kinetic Energy ((x 10^2 \text{ J/min}))</th>
<th>Membrane Operating Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5%</td>
<td>10%</td>
</tr>
<tr>
<td>5LPM</td>
<td>2.41</td>
<td>3.29</td>
</tr>
<tr>
<td>7LPM</td>
<td>3.07</td>
<td>5.59</td>
</tr>
<tr>
<td>9LPM</td>
<td>4.20</td>
<td>6.70</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Relative Kinetic Energy</th>
<th>Relative Operating Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5%</td>
<td>10%</td>
</tr>
<tr>
<td>5LPM</td>
<td>1.00</td>
<td>1.37</td>
</tr>
<tr>
<td>7LPM</td>
<td>1.27</td>
<td>2.32</td>
</tr>
<tr>
<td>9LPM</td>
<td>1.74</td>
<td>2.78</td>
</tr>
</tbody>
</table>
Correlation between the relative kinetic energy and the relative operating time

\[ y = 1.0105x + 0.0226 \]

\[ R^2 = 0.9844 \]
Conclusions

• In M-CMBBR system, unlike a conventional MBR system, membrane performance is much more dependent on **physical effects of moving biofilm carrier** (kinetic energy, collision frequency etc.) than **biochemical effects of mixed liquor** (SCOD, EPS etc.).

• **Frictional force** exerted by moving biofilm carrier to submerged membrane mitigates the formation of **cake layer** on the membrane surface and thus enhances the membrane permeability.

• The higher the circulating **velocity** and **volume fraction** of biofilm carrier, the better the membrane performance.
The concept: “Flux decline arises from a series of resistances.”

\[ J = \frac{\Delta P}{\eta R_t} \]

- \( J \): permeate flux (Lm\(^{-2}\)hr\(^{-1}\))
- \( \Delta P \): transmembrane pressure (Pa)
- \( \eta \): viscosity of the permeate (cP)
- \( R_t \): total membrane resistance (m\(^{-1}\))

\[ R_t = R_m + R_c + R_f \]

- \( R_c \): Cake resistance
  - microbial flocs + EPS (EPS: extracellular polymeric substances)
- \( R_f \): Fouling resistance
  - low molecular weight particles
- \( R_m \): Virgin membrane resistance

\( R_c \) has been reported as a main contributor to \( R_t \)! (Chiemchaisri and Yamamoto, 1994; Choo and Lee, 1996a; Choo and Lee, 1996b; Chang and Lee, 1998; Kim et al., 1998; Chang et al., 1999; Lee, 1999; Park et al., 1999)
## Specifications of the Membrane

(Mitsubishi Rayon Co. Ltd., Japan)

<table>
<thead>
<tr>
<th>Feature</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Module type</td>
<td>Hollow fiber</td>
</tr>
<tr>
<td>Pore size</td>
<td>0.1 mm</td>
</tr>
<tr>
<td>Material</td>
<td>Polyethylene (hydrophilic)</td>
</tr>
<tr>
<td>Surface area</td>
<td>0.0673 m²</td>
</tr>
<tr>
<td>Outer diameter</td>
<td>410 mm</td>
</tr>
<tr>
<td>Inner diameter</td>
<td>270 mm</td>
</tr>
</tbody>
</table>
Biofilm process

Biofilm Reactors

Fixed Bed Biofilm Reactor

- Looped cord media

Moving Bed Biofilm Reactor

- Rectangular Sponge; Polyurethane coated with Activated Carbon
Objectives

An alternative to alleviate membrane fouling due to cake layer: ATTACHED GROWTH SYSTEM!

1) To compare the attached growth with the suspended growth system in terms of filtration characteristics & quality of treated water.