COE Workshop on MBR, Hokkaido University (Feb. 4, 2004)

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

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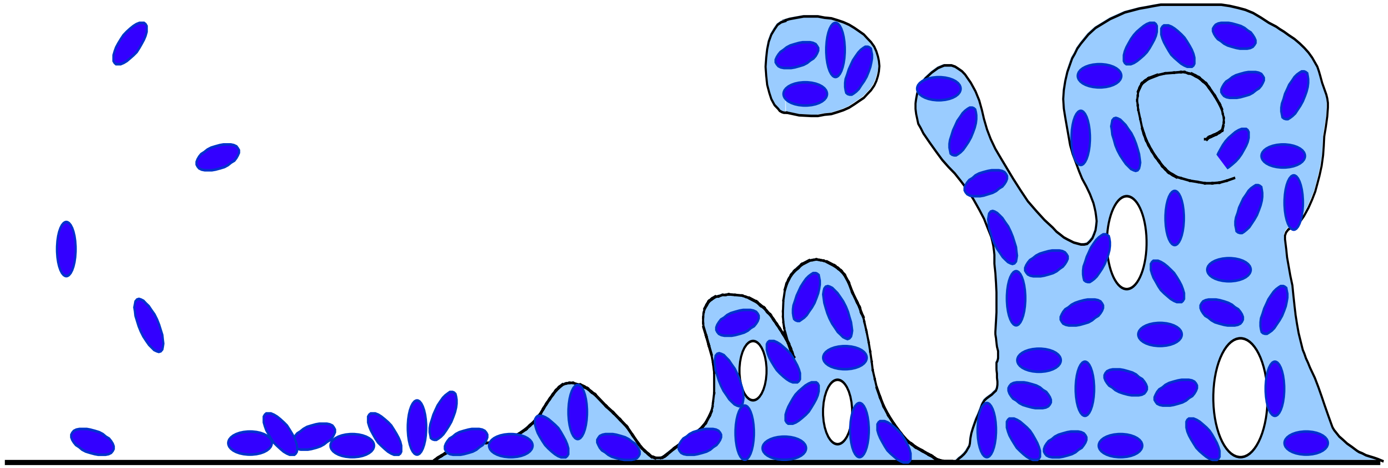
Ultimate Goals of Membrane Bioreactor :

- **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



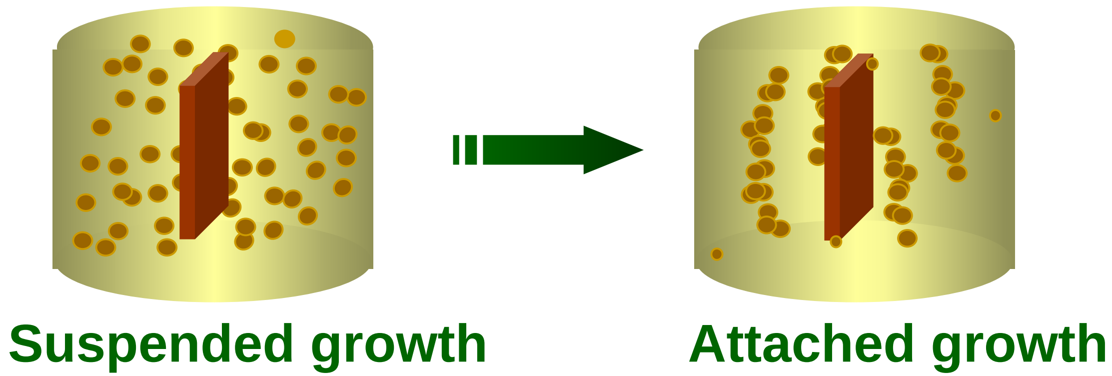
: Membranes in contact with the broth of activated sludge reactor will be colonized within short time by microorganisms, leading to the formation of a composite layer known as biofilm.

: 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

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:

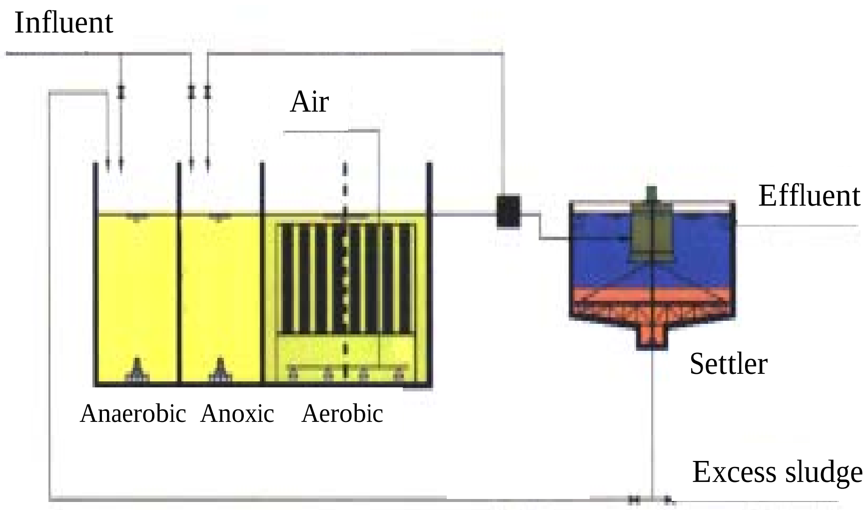
2) To compare two attached growth systems; Fixed bed and Moving bed Biofilms

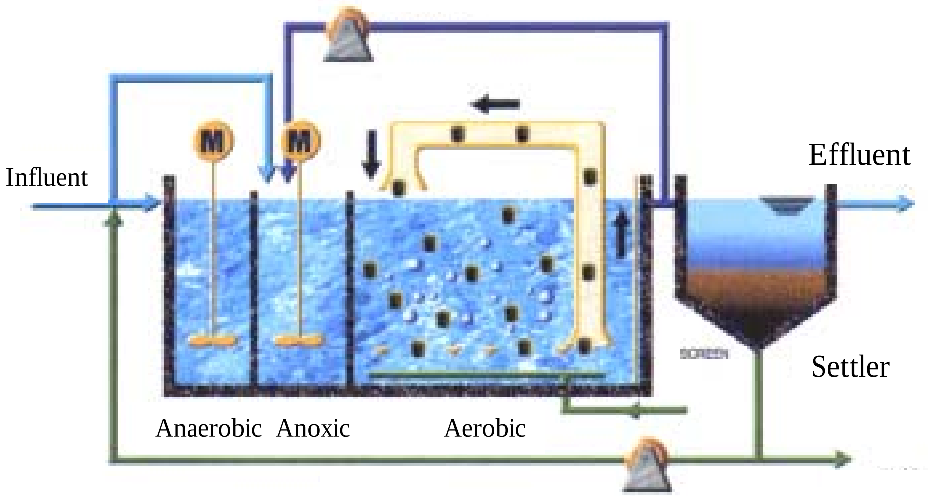
Biofilm process

Biofilm Reactors

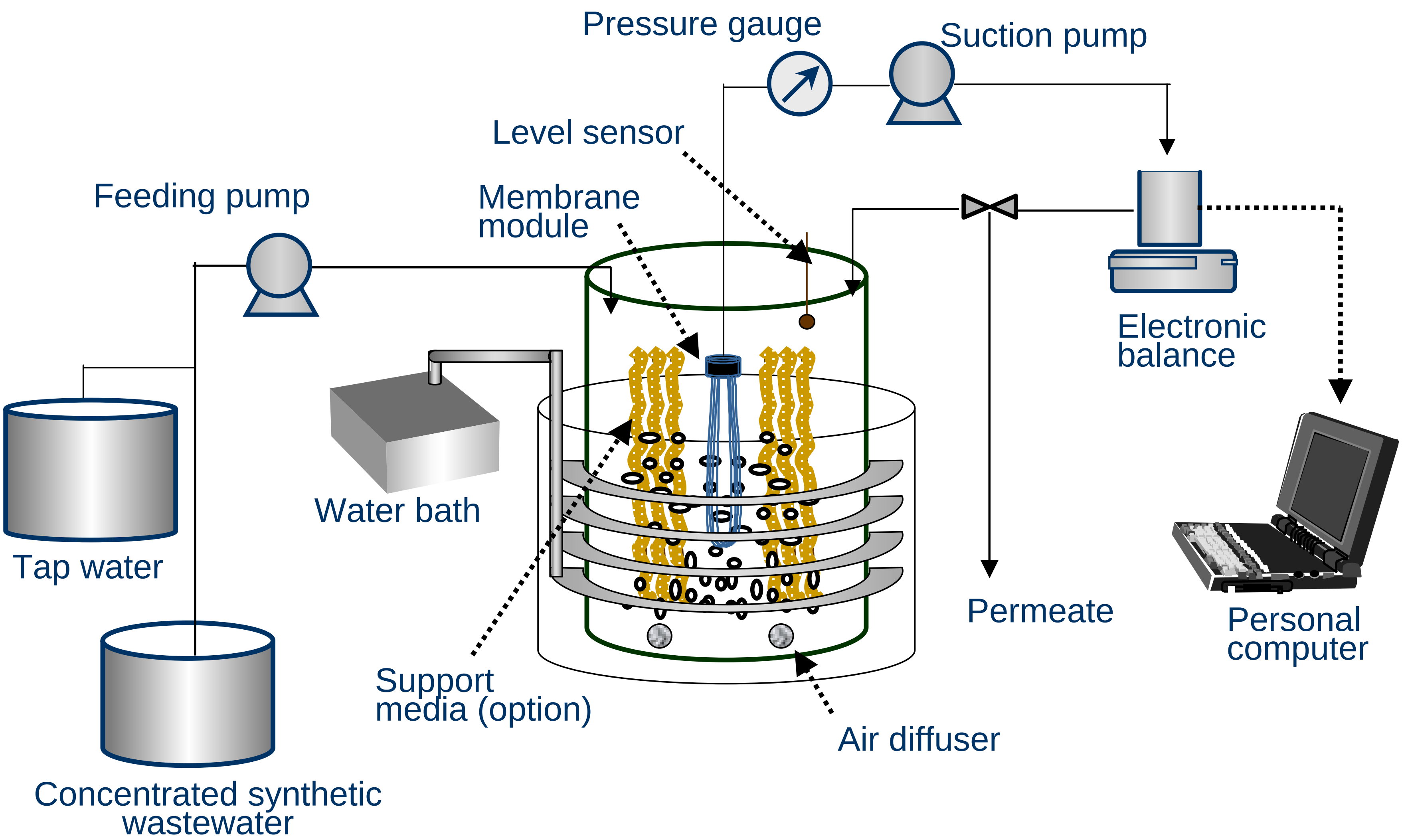
Fixed Bed Biofilm Reactor
- trickling filters
- rotating biological reactors
- submerged granular biofilters

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





Fixed bed Biofilm



Operating Conditions

Constant flux ($L/(m^2 \cdot hr)$)	25
Maximum transmembrane pressure (kPa)	26
Temperature (^oC)	25
Air flow rate (L/min)	2.5
Working volume (L)	5
Hydraulic residence time (hr)	8
Feed concentration (mgCOD/L)	250
Volumetric organic loading ($kg/(m^3 \cdot day)$)	0.75
pH	7.0±0.2
Dissolved oxygen (mgO_2/L)	6.1 ± 0.1

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

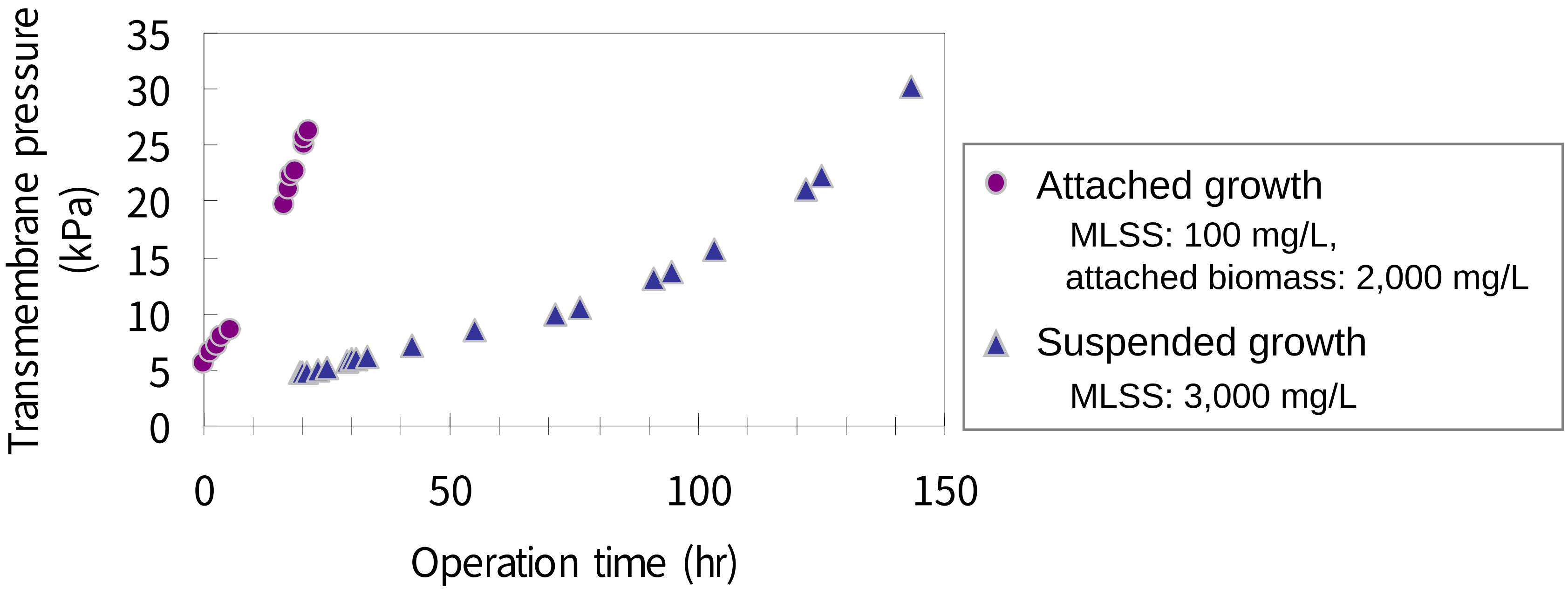
	COD (mg/L)		NH_4^+-N (mg/L)	
Influent	250		20.2 (TN 23.9)	
	Attached growth[a]	Suspended growth[b]	Attached growth[a]	Suspended growth[b]
Permeate	3	5	0.99	0.17
% removal	99	98	95	99

[a]MLSS: 100 mg/L, attached biomass: 2,000 mg/L

[b]MLSS: 3,000 mg/L

Filtration Characteristics

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.

Poor Filtration Characteristics in Attached Growth… WHY?

Membrane fouling : The result of interaction between mixed liquor and membrane

↓

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

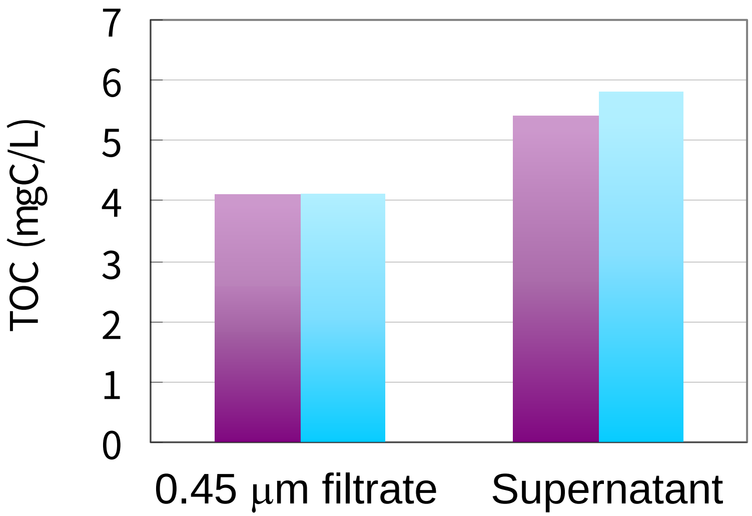
↓

Soluble fraction

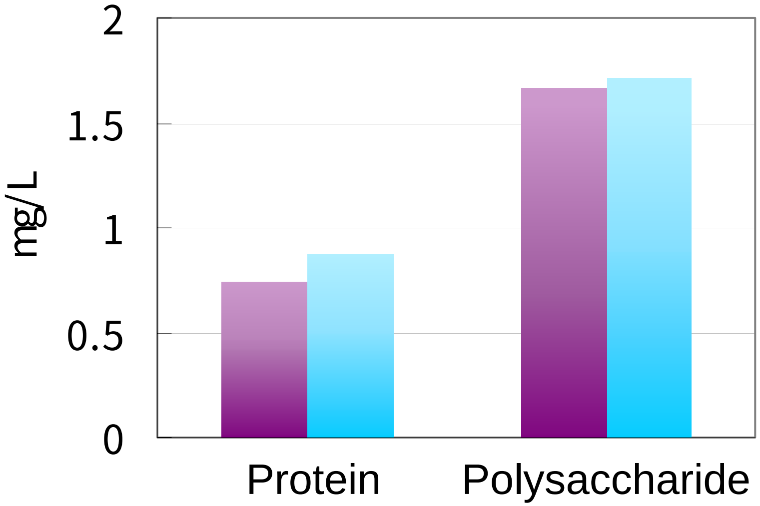
- Quantitative properties
  - Total organic carbon (TOC)
  - Extracellular polymeric substances (EPS)
- Qualitative properties
  - Molecular weight distribution
  - Mean oxidation state of organic carbons

Quantitative Analysis of Soluble Organics

Total organic carbon (TOC)



Extracellular polymeric substances (EPS)



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

Origin of organics	Attached growth reactor MLSS: 100 mg/L, attached biomass: 2,000 mg/L		Suspended growth reactor MLSS: 3,000 mg/L	
	Mean oxidation state of carbon	Estimation of main constituents	Mean oxidation state of carbon	Estimation of main constituents
Mixed liquor	3.08	Organic acid	2.16	Organic acid
Membrane surface after filtration run	-0.84	Protein or polysaccharide	-1.24	Protein or polysaccharide

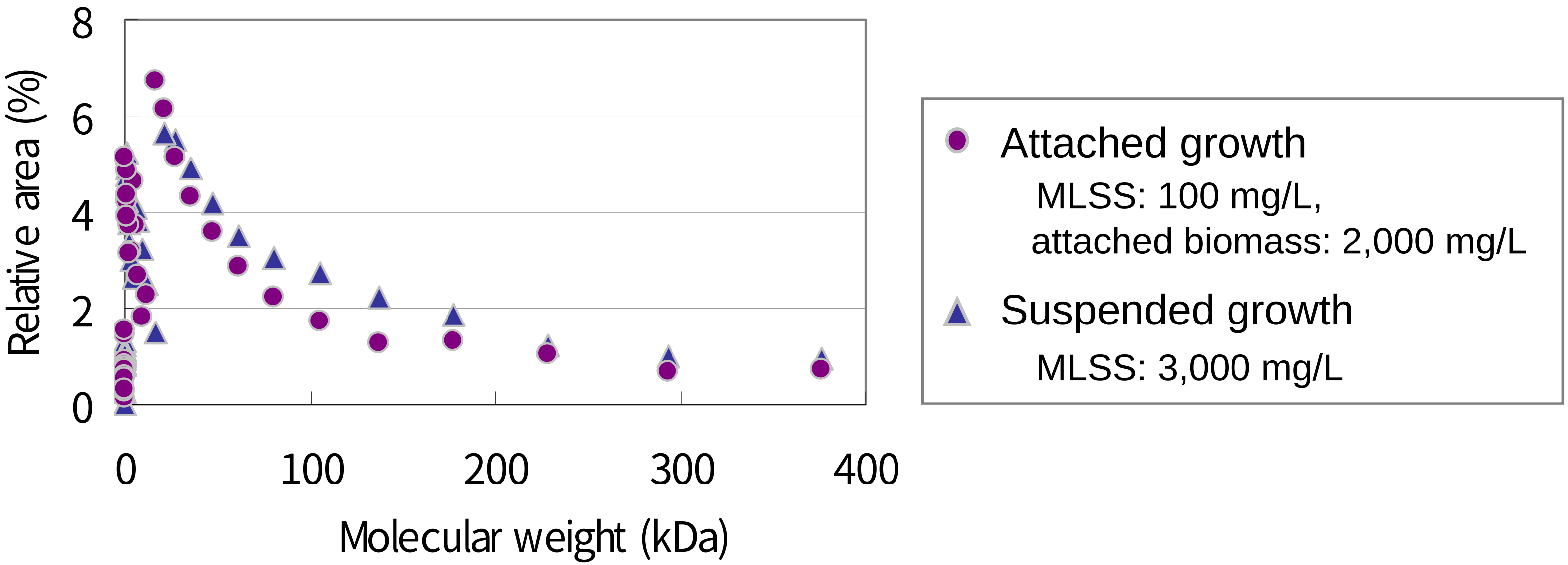
$$\text{Mean oxidation state of organic carbon} = \frac{4\,(\text{TOC} - \text{COD})}{\text{TOC}}$$

(TOC: mol C/L, COD: mol O_2/L)

Stumm W. and Morgan J. J. (1981) *Aquatic Chemistry Aquatic Chemistry,* 2^{nd} ed. pp. 510-511

Qualitative Analysis of Soluble Organics

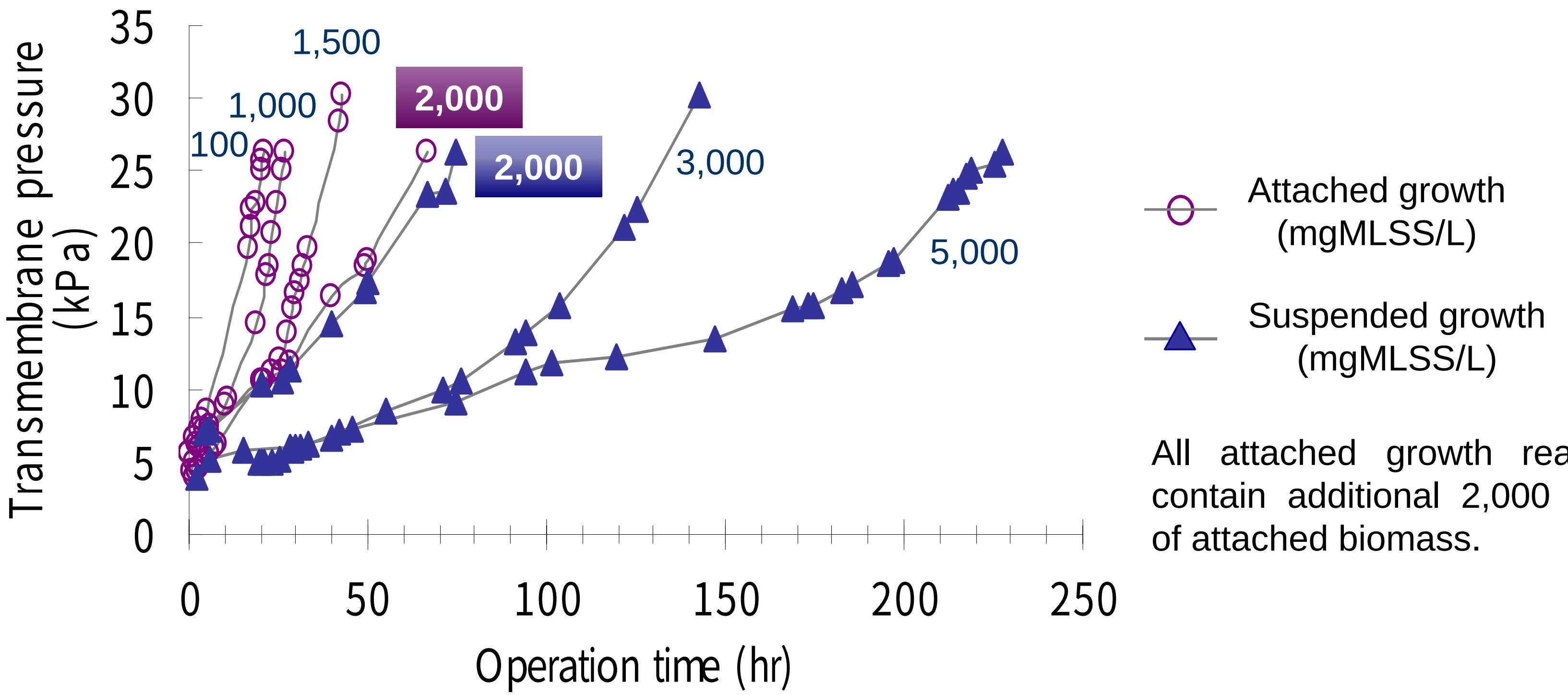
Molecular weight distribution



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

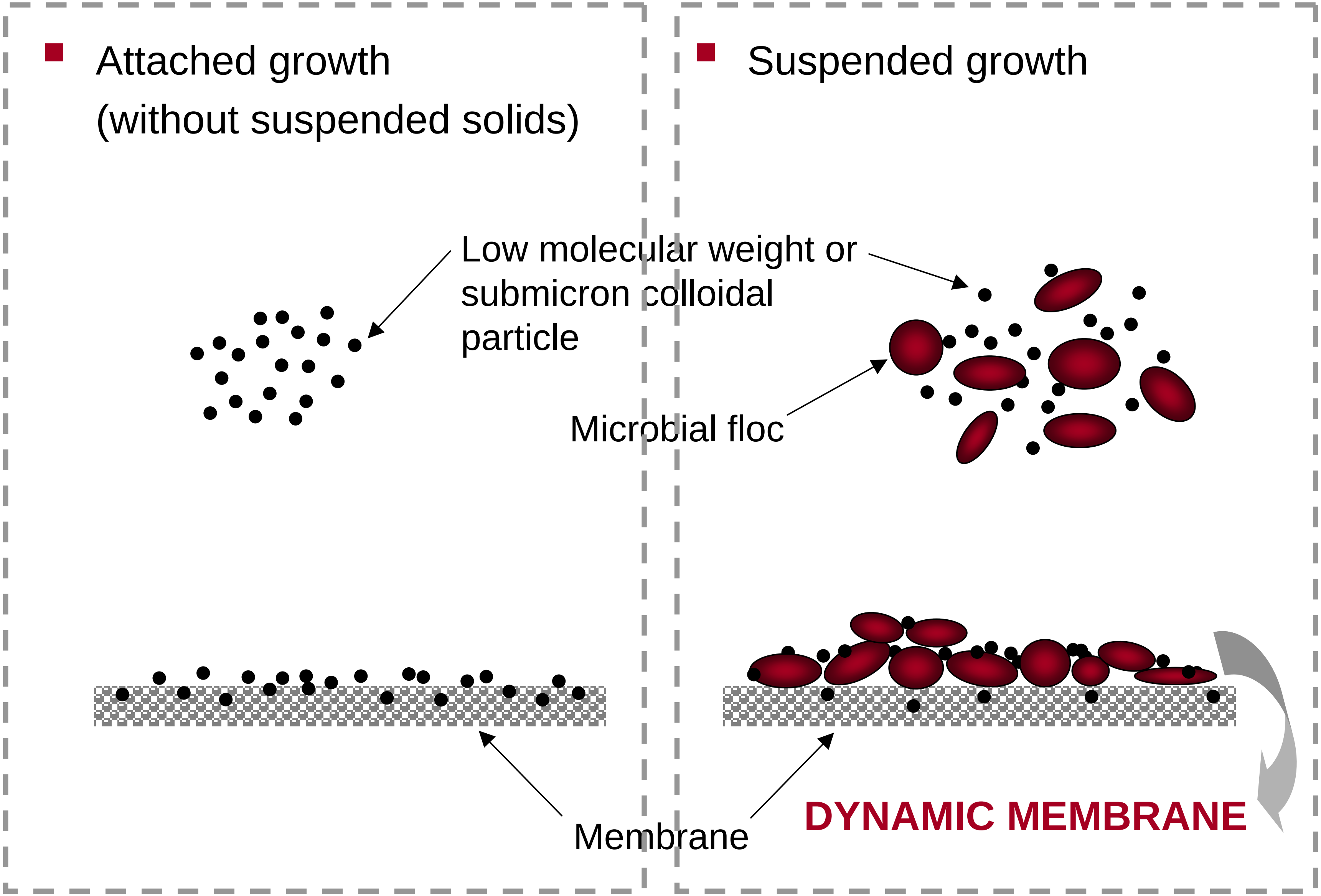
Filtration behaviors with varying MLSS concentration in attached and suspended growth bioreactor



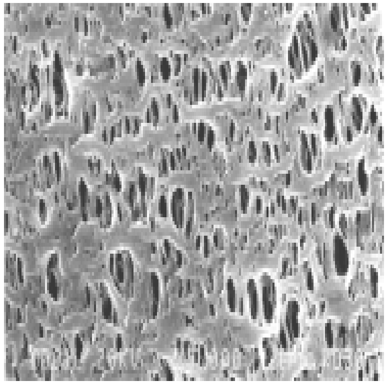
All attached growth reactors contain additional 2,000 mg/L of attached biomass.

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.

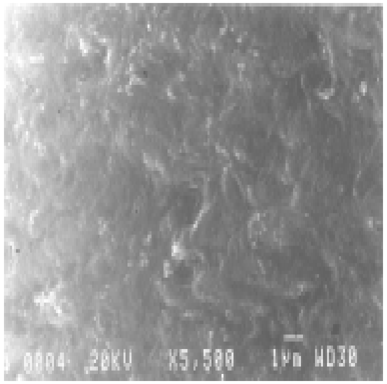
Formation of a Dynamic Membrane by Mixed Liquor Suspended Solids



SEM Images of Cake Layer on Membrane Surfaces after Filtration Run



new membrane
(X 5,000)



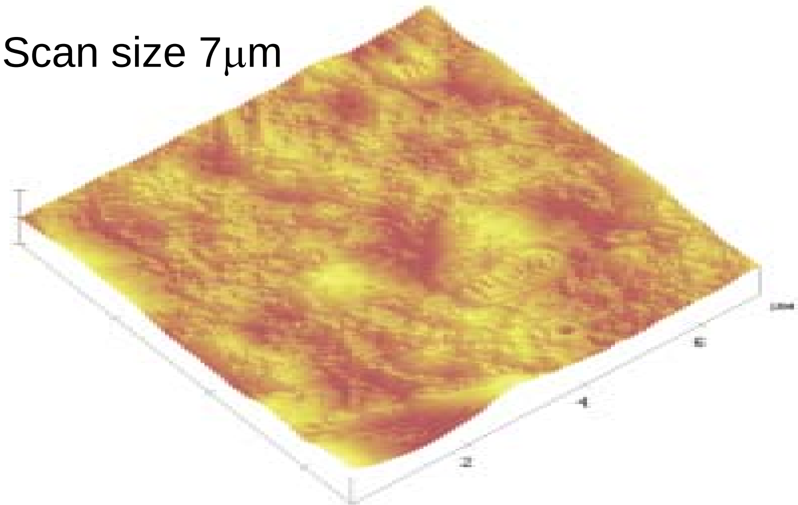
used membrane for
attached growth
(MLSS: 100 mg/L, attached biomass: 2,000 mg/L)
(X 5,500)

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)

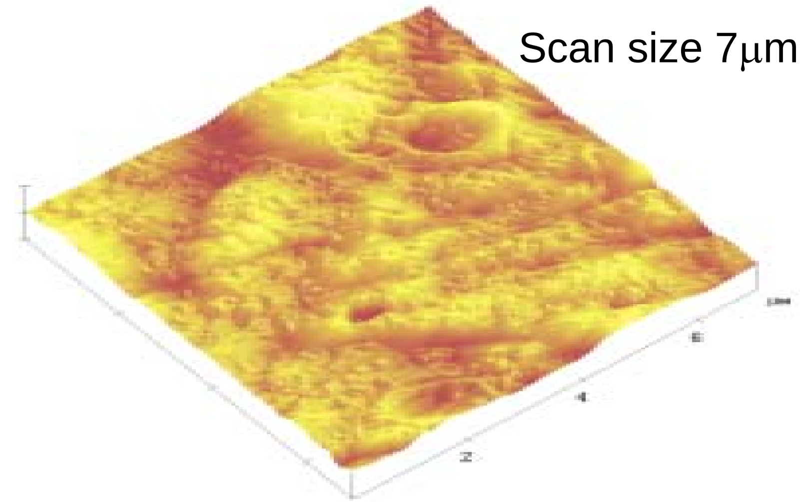
Scan size 7μm



Roughness (rms[a]) : 34 nm

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

Scan size 7μm



Roughness (rms[a]) : 87 nm

AFM: atomic force microscopy , a: root mean square

Effect of Growth Pattern on Each Resistance in the Submerged MBR

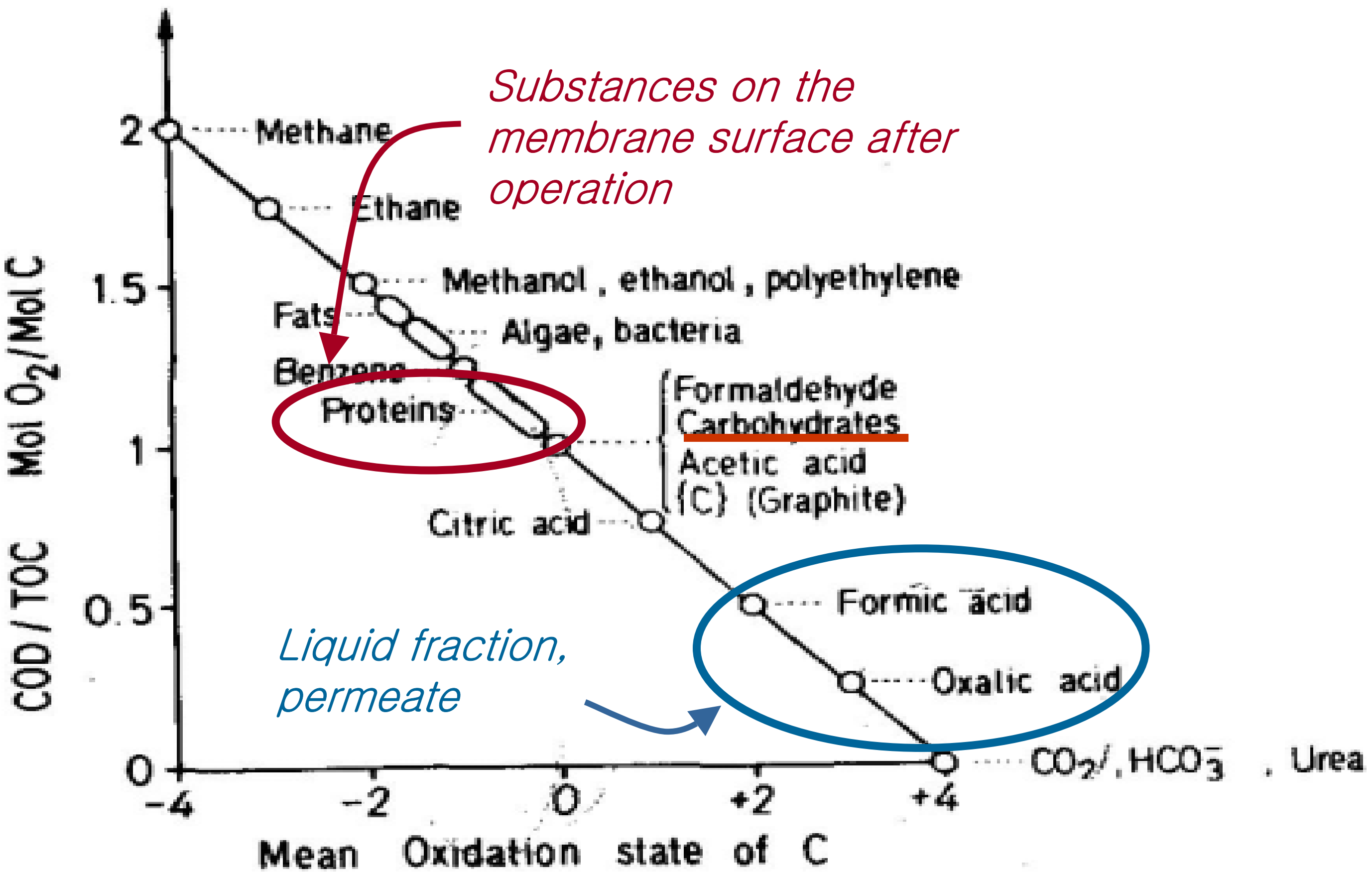
	Attached growth (MLSS: 100 mg/L, attached biomass: 2,000 mg/L)		Suspended growth (MLSS: 3000 mg/L)	
	$10^{12}m^{-1}$	%	$10^{12}m^{-1}$	%
R_m	0.49	12	0.50	12
R_c	2.94	69	3.39	80
R_f	0.81	19	0.35	8
R_t	4.24	100	4.24	100

*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 4.24×10^{12} m^{-1}.

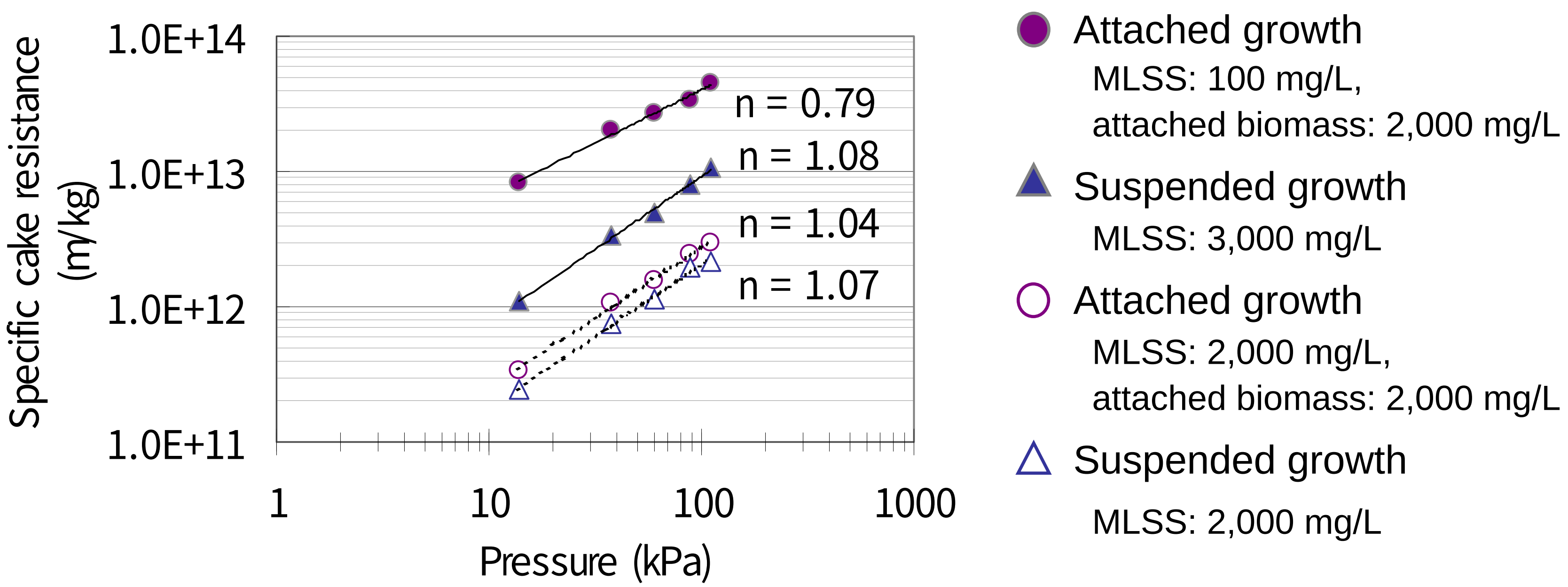
Soluble or colloidal particles as well as microorganisms in the mixed liquor could accumulate and form a cake layer on the surface of membrane, but without microorganisms the internal fouling would be severer.

Substances Causing Membrane Fouling



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. → similar filtration behavior at the same MLSS concentration

Conclusion

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

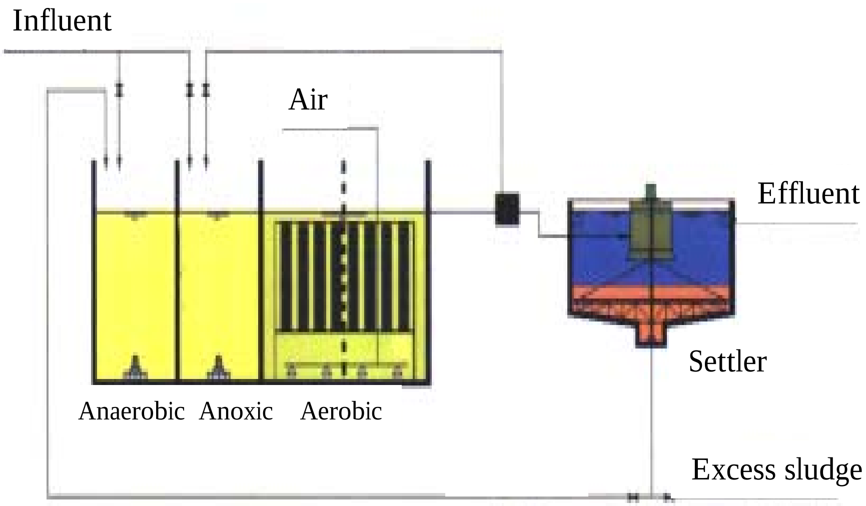
Conclusion

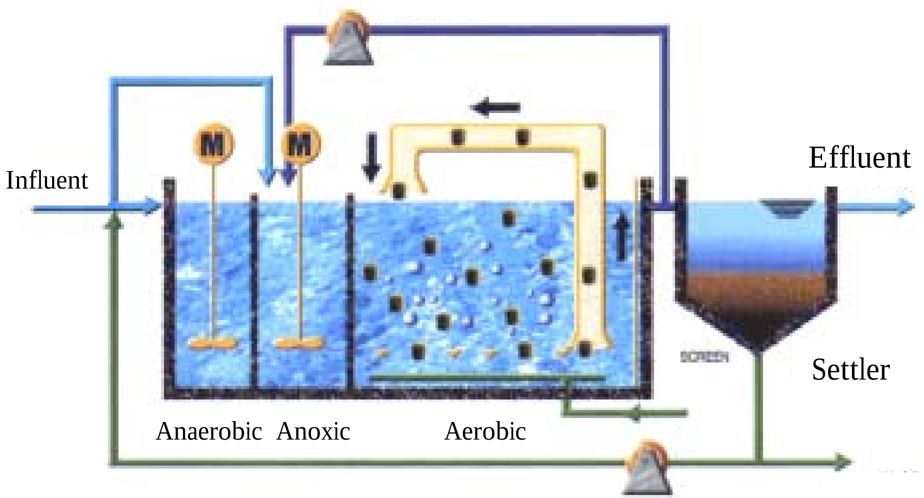
- Better filtrability with the suspended growth could also be due to the rougher cake layer having smaller specific cake resistance than that with the attached growth.

Biofilm process

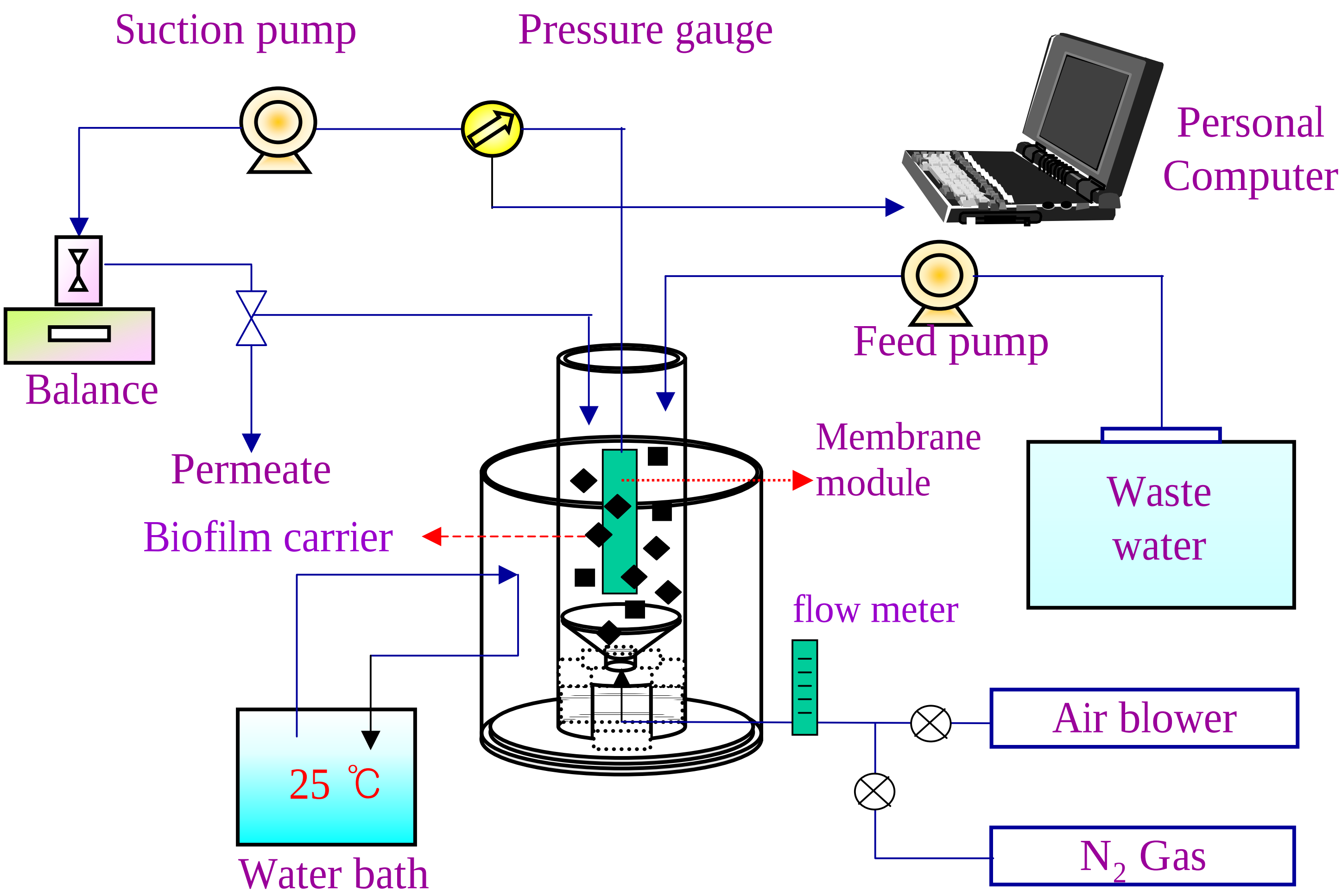
Biofilm Reactors

Fixed Bed Biofilm Reactor	Moving Bed Biofilm Reactor
• Looped cord media	•Rectangular Sponge ; Polyurethane coated with Activated Carbon





Moving bed Biofilm



Materials

- Specifications of the membrane

Module type	Hollow fiber
Pore size	0.1 ㎛
Material	Polyethylene, hydrophilic
Inner diameter	270 ㎛
Outer diameter	410 ㎛
Surface area	0.1 m^2

- Specifications of the biofilm carrier

Material	Shape(cm^3)	Density (g/cm^3)	Surface area (m^2/g)
Polyurethane coated with activated carbon	Porous cubic 1.3×1.3×1.3	0.21	8.50 (35,000 m^2/m^3)

Experimental conditions

Flux [LMH (L/m^2·hr)]	30
Transmembrane pressure [kPa]	< 30
Temperature [℃]	25 (±1)
DO [mgO_2/L]	5 (±0.1)
Working volume [L]	6
HRT [hr]	10
Feed concentration [mg COD/L]	1,000
Organic loading [kg COD/m^3·day]	2.4
Suspended biomass [mg/L]	5,000 (±500)
Attached biomass [mg/L]	17,000 (±1,500)

Composition of synthetic wastewater

Composition	Concentration (mg/L)
Glucose	327.88
Bacto Peptone	245.90
Yeast Extract	32.78
$(NH_4)_2SO_4$	262.30
KH_2PO_4	52.45
$MgSO_4 \cdot 7H_2O$	65.58
$MnSO_4 \cdot 4H_2O$	5.90
$FeCl_3 \cdot 6H_2O$	0.33
$CaCl_2 \cdot 2H_2O$	6.55
$NaHCO_3$	40.98
COD	1,000mg/L

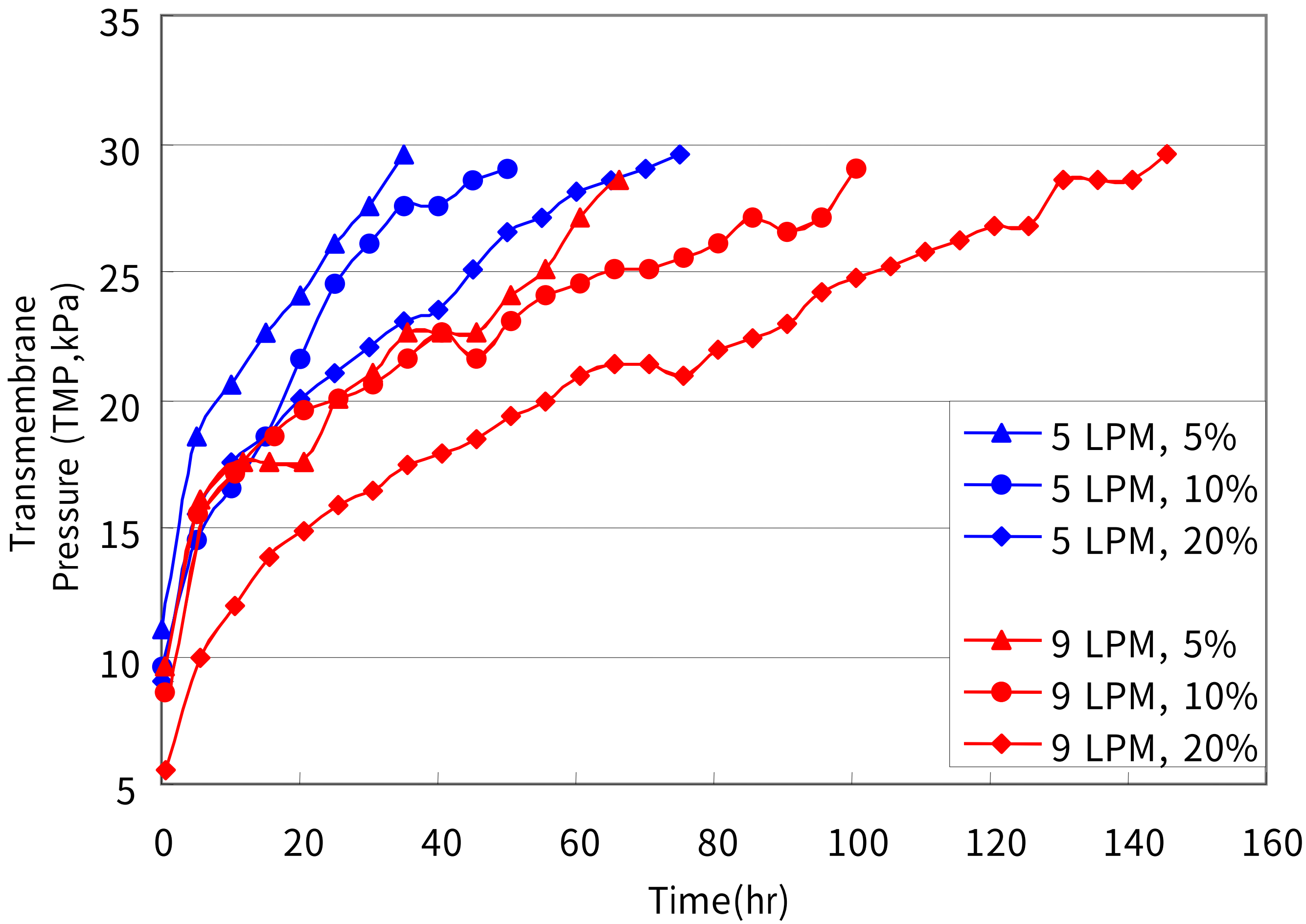
Operating parameters

*** Carrier volume fraction : 5~20 %**

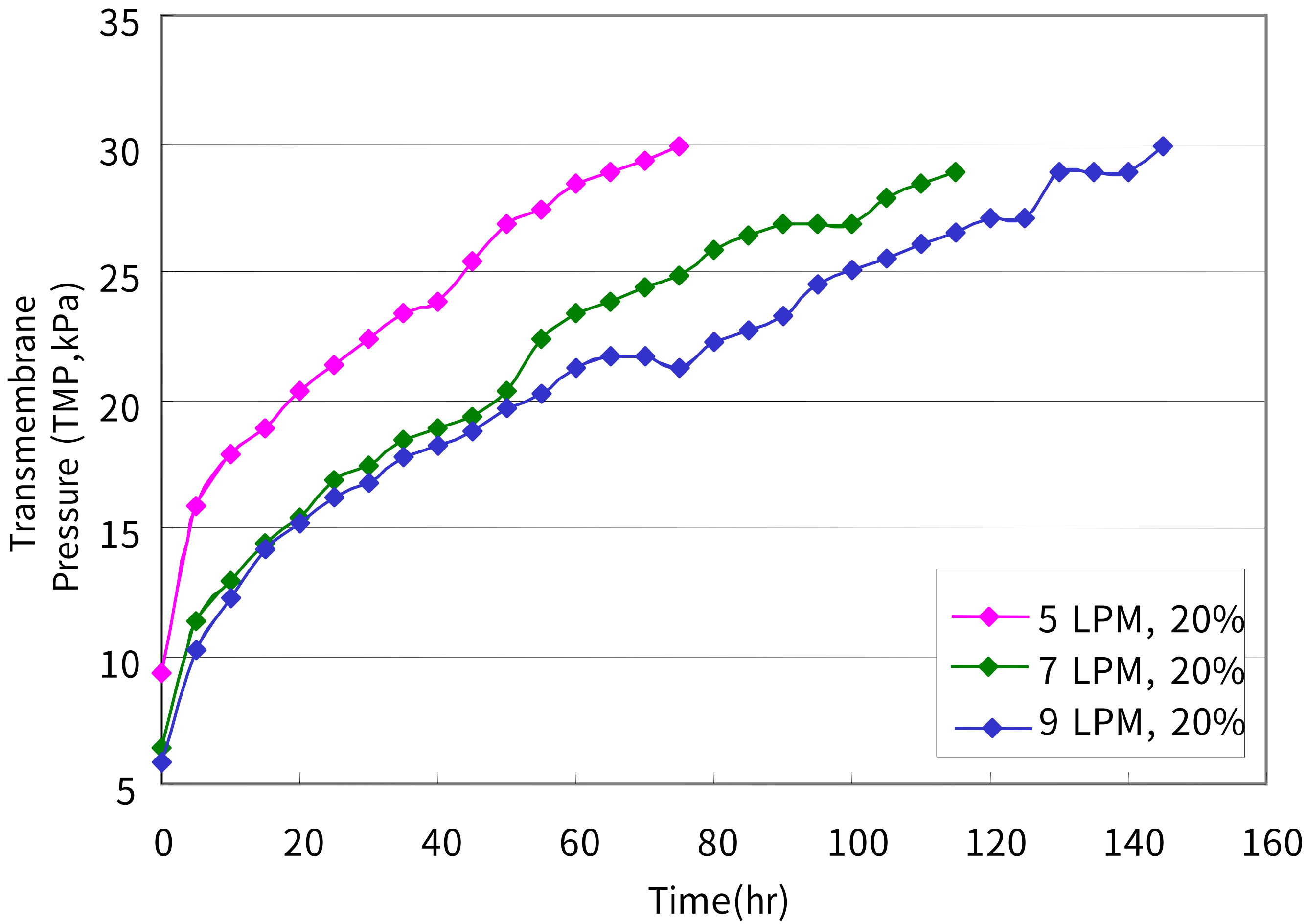
*** Air flow rate : 5~9 LPM(ℓ / min)**

Filtration characteristics

Filtration characteristics



Filtration characteristics



Factors affecting membrane biofouling in conventional MBR

* Soluble COD (SCOD)

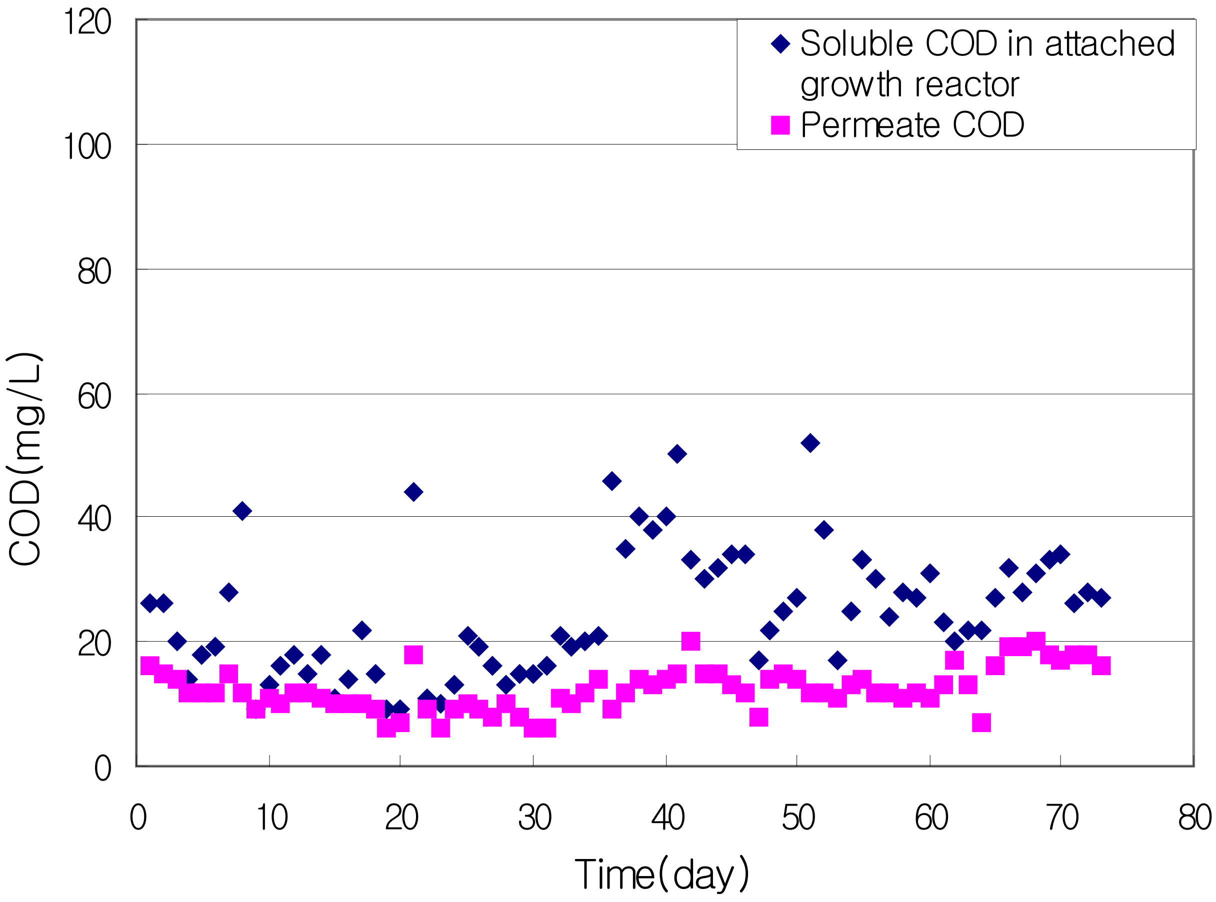
* Microbial floc size

* Extracellular Polymeric Substance (EPS)

  : bound EPS, soluble EPS

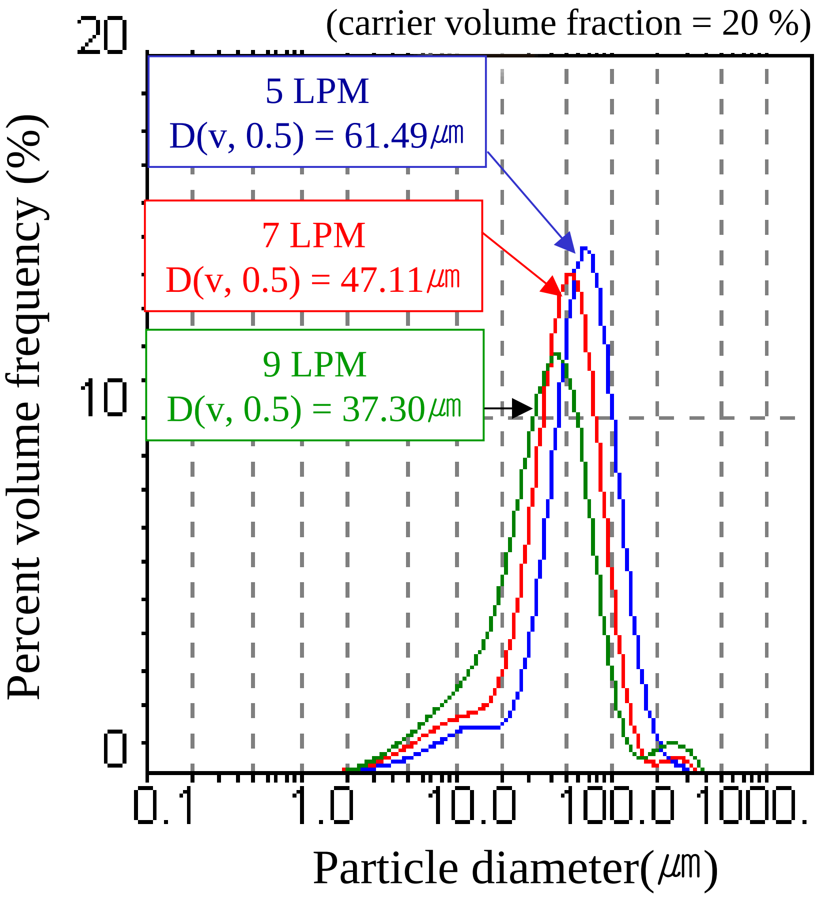
* Compressbility of microbial cake layer

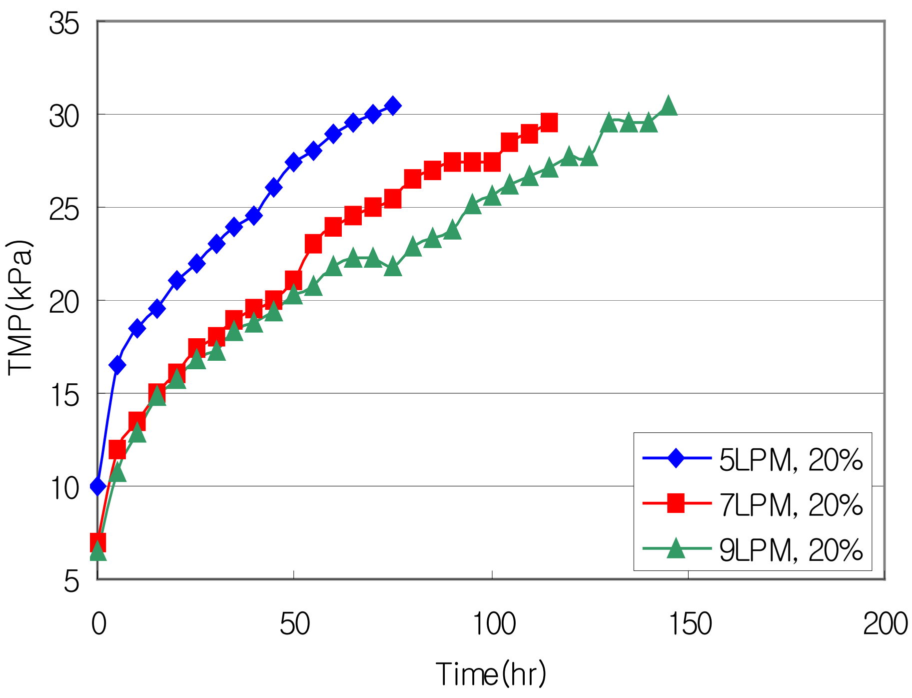
Biochemical effects : SCOD



Biochemical effects : Floc size

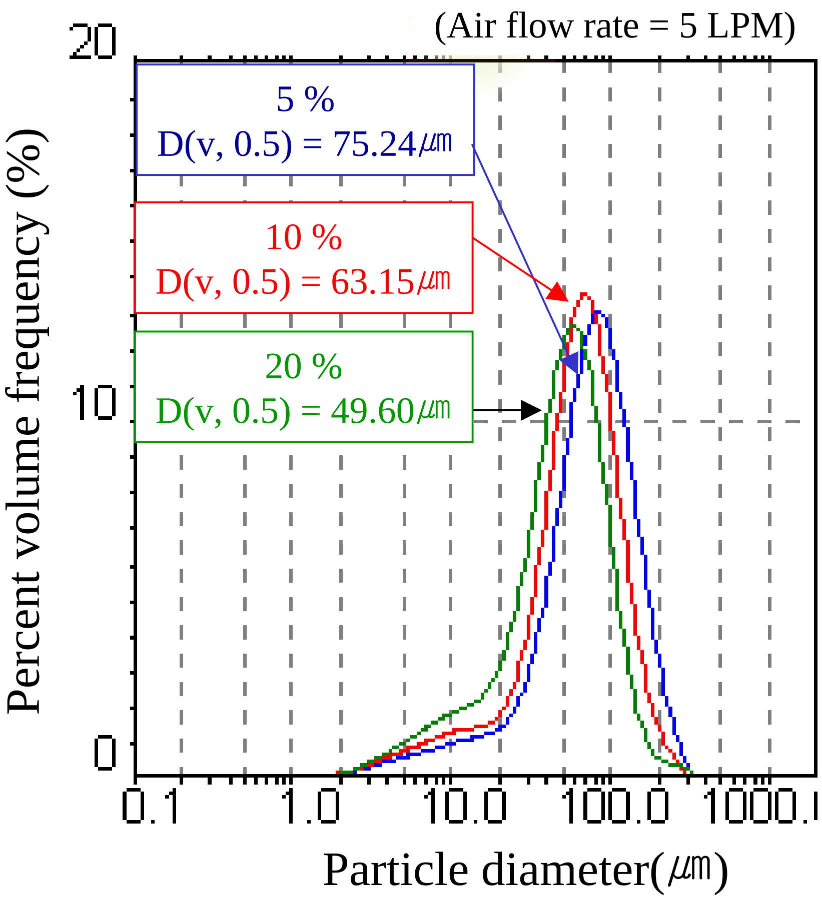
as a function of air flow rate

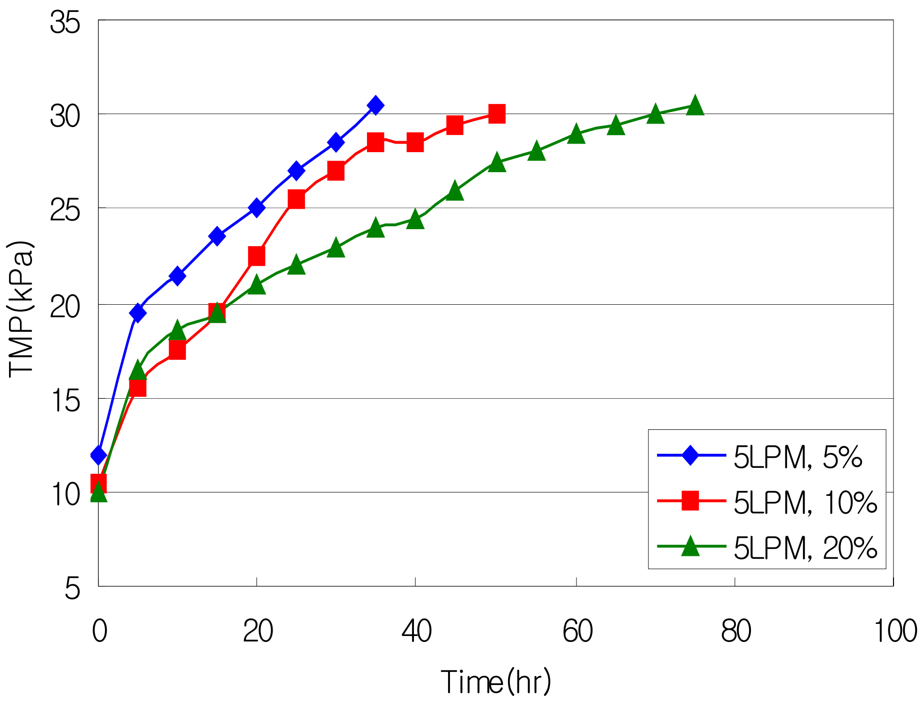




Biochemical effects : Floc size

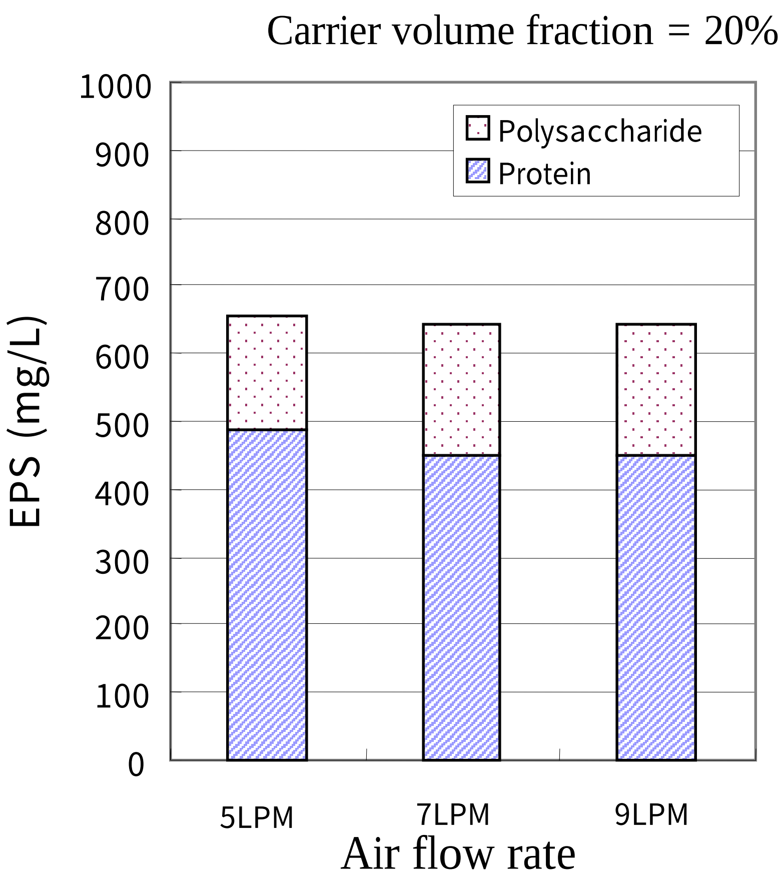
as a function of carrier volume fraction

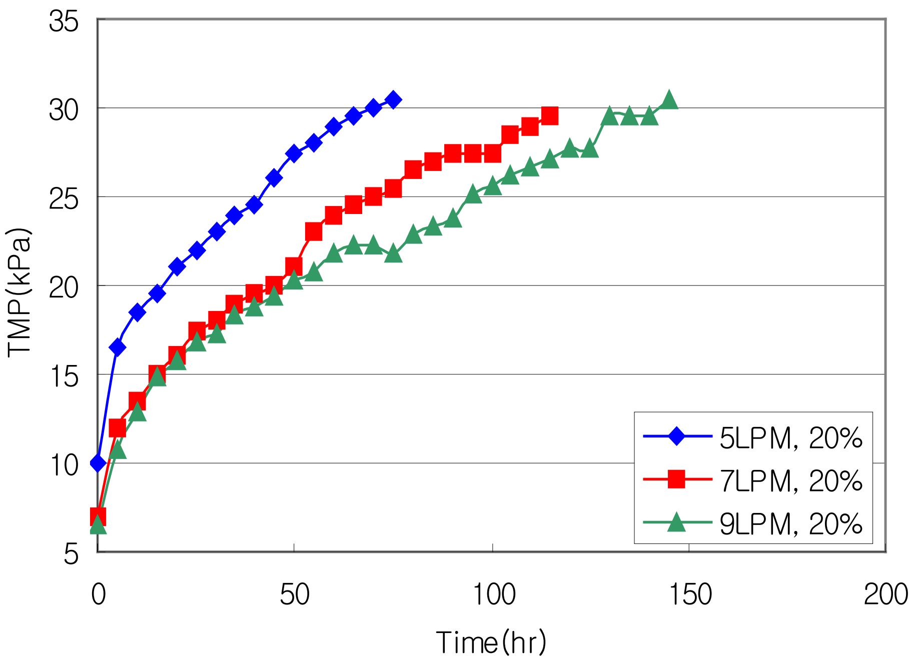




Biochemical effects : Bound EPS

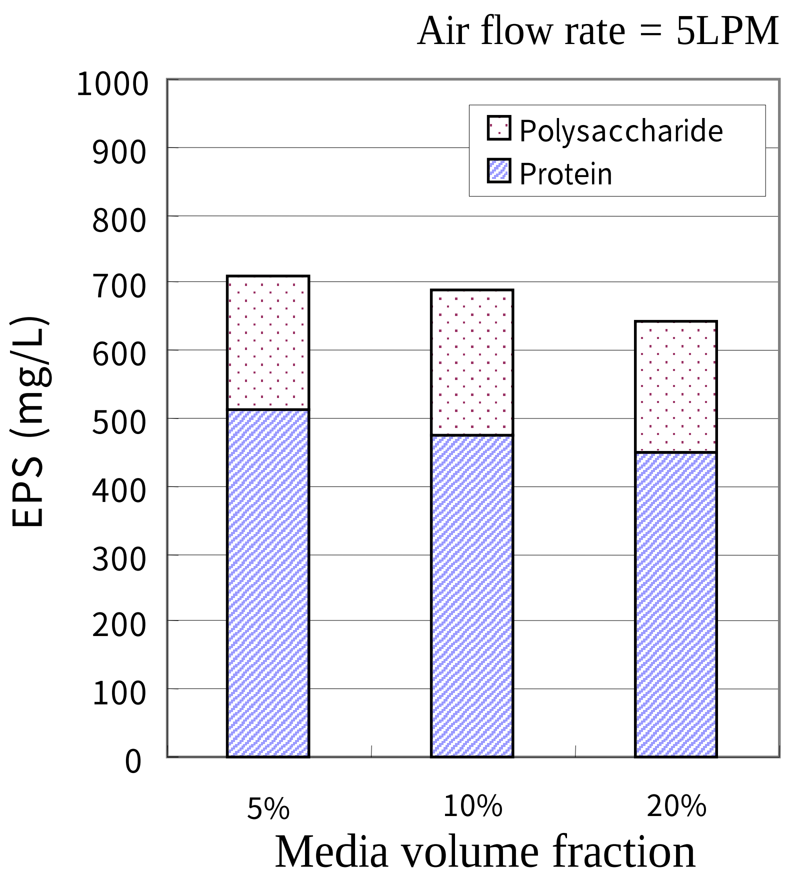
as a function of air flow rate

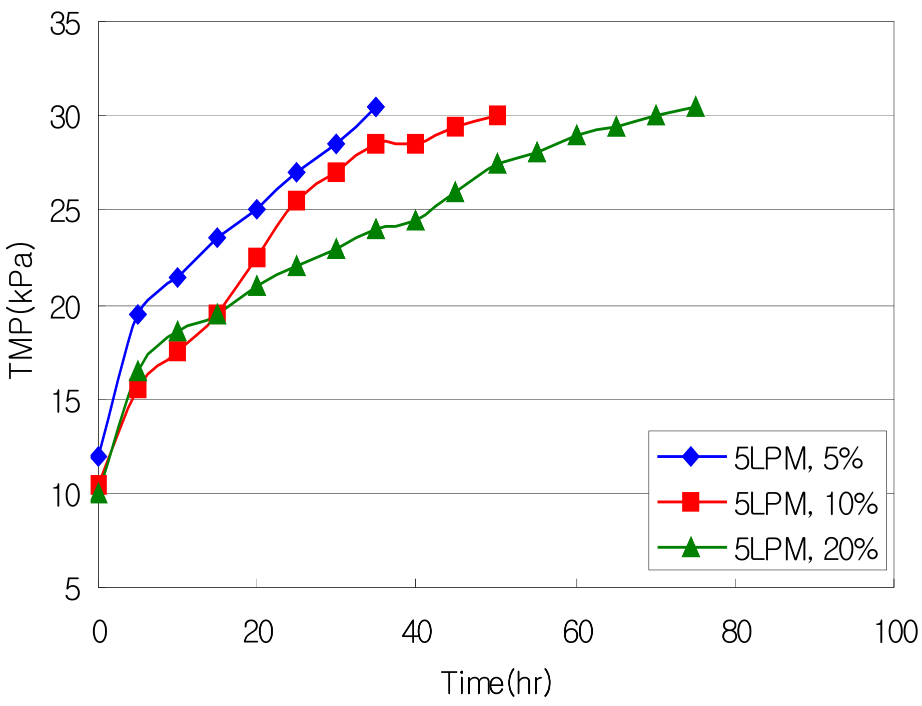




Biochemical effects : Bound EPS

as a function of carrier volume fraction

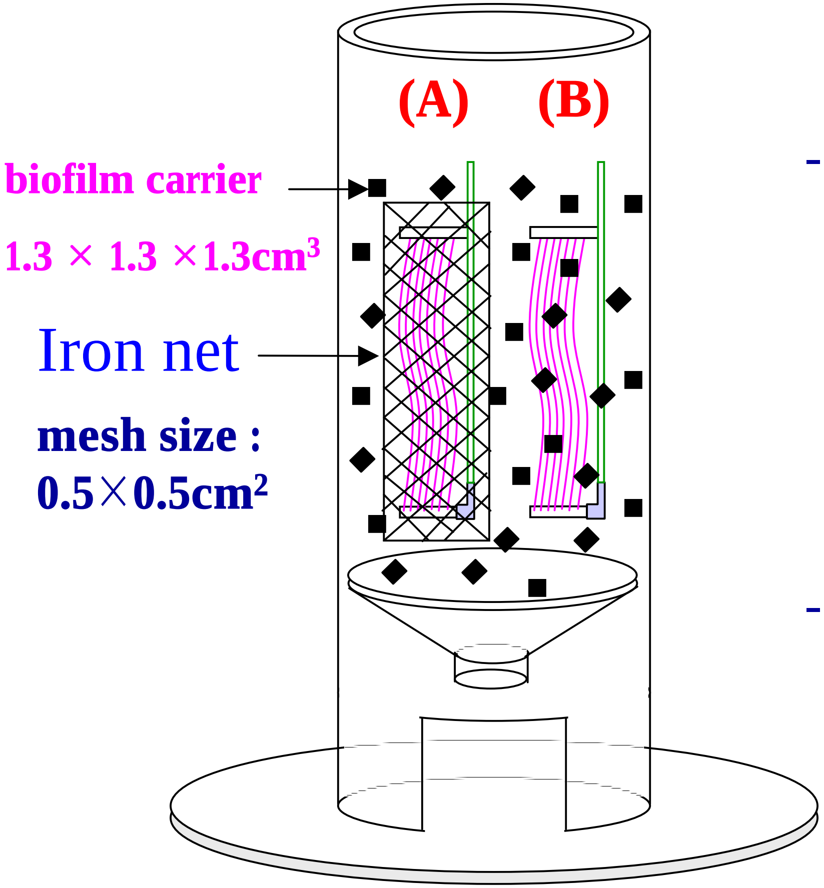




Summary (I)

Membrane filtration characteristics are less dependent on biochemical effects of mixed liquor in M-CMBBR system.

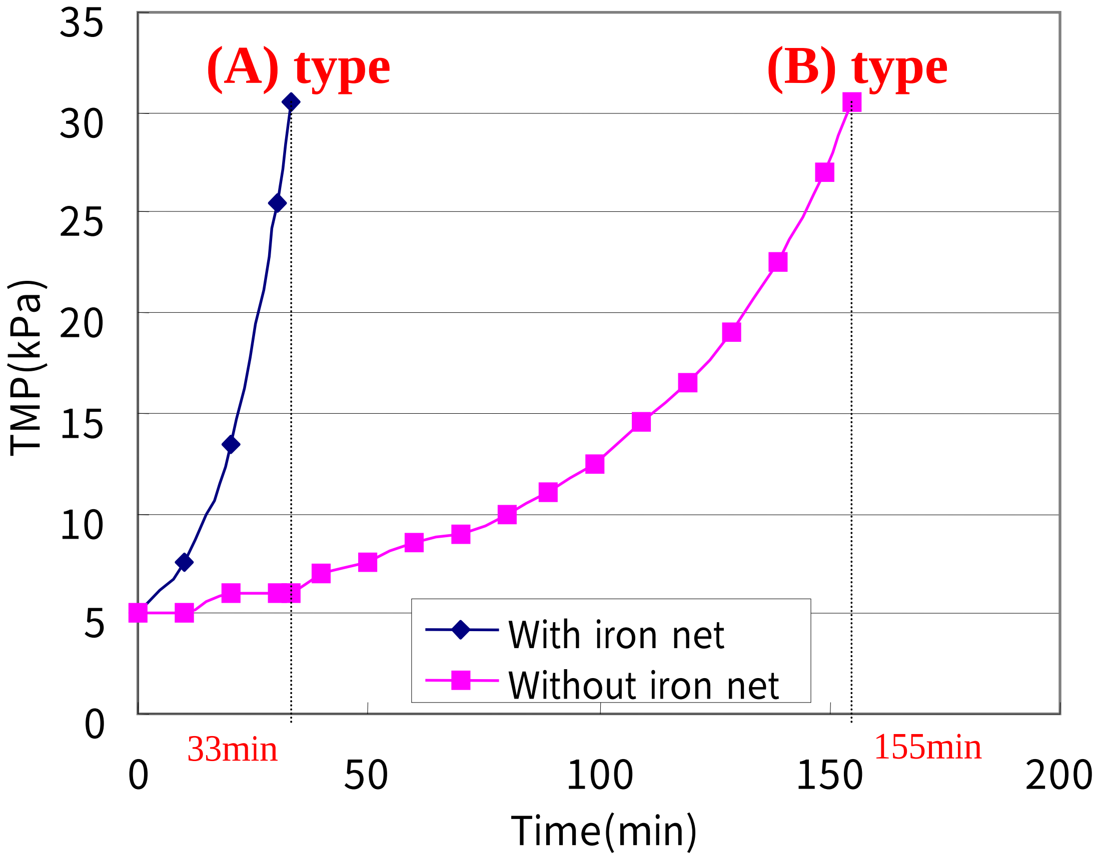
Physical effects : experimental set-up (II)



- (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.

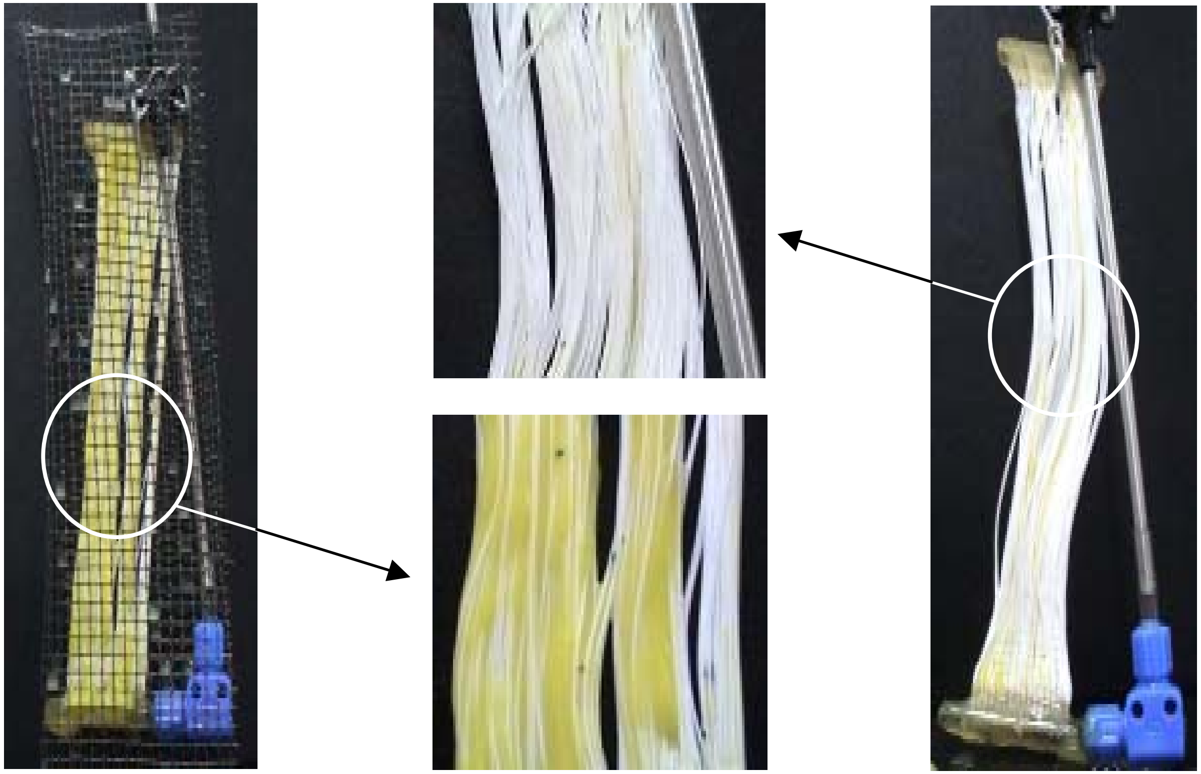
Filtration behaviors with and without iron net



- Operating conditions

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

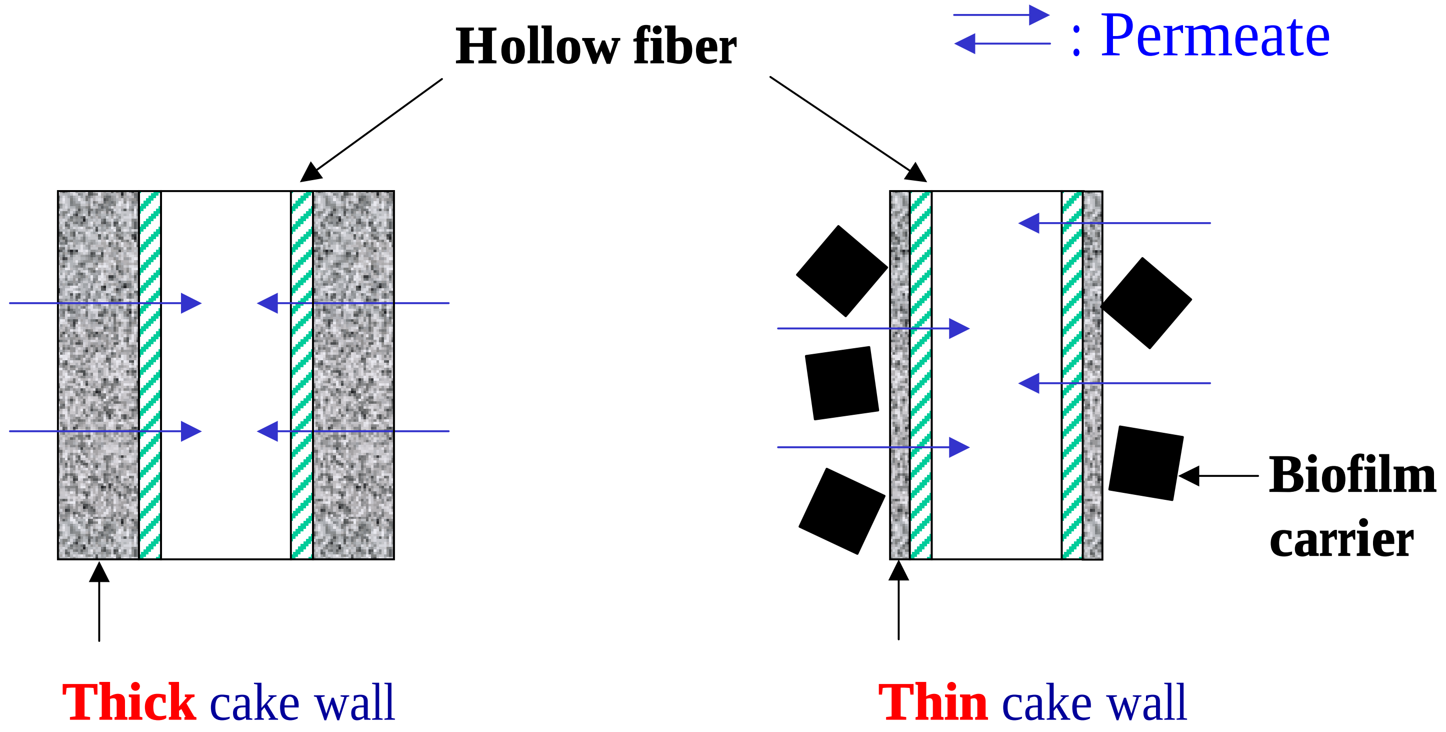
Formation of cake layer on membrane surface



(A) type

(B) type

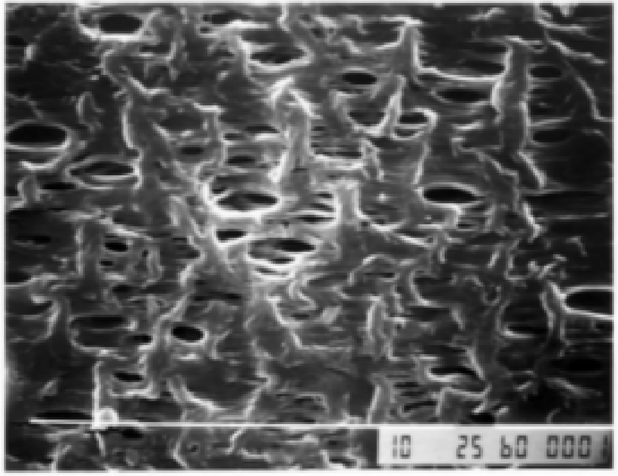
Formation of cake layer on membrane surface



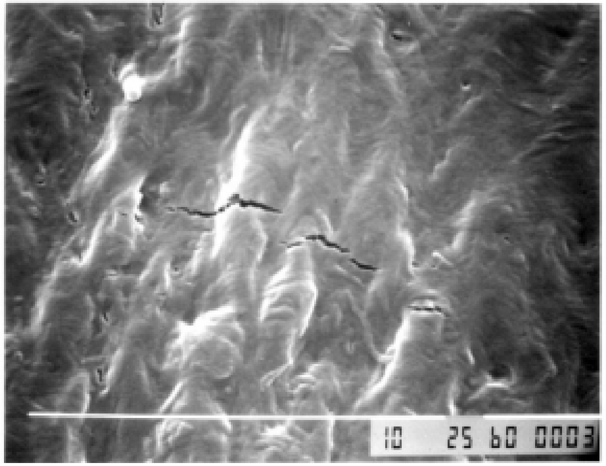
(A) type (with iron net) **(B) type (without iron net)**

SEM images of cake layer on membrane surface

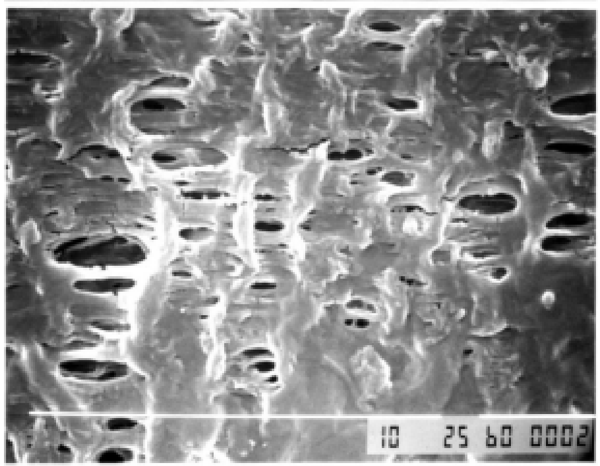
(×7,000)



Virgin membrane surface



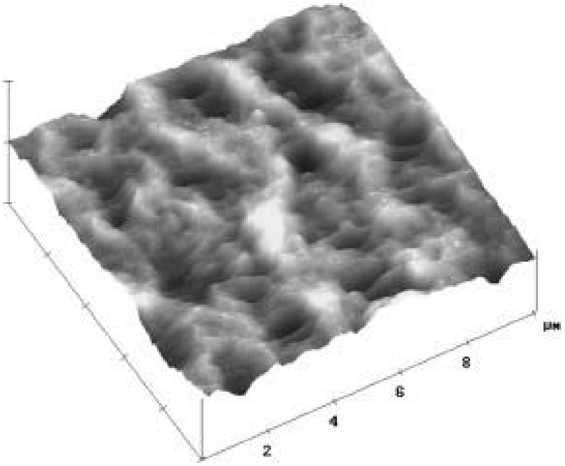
(A) type (with iron net)



(B) type (without iron net)

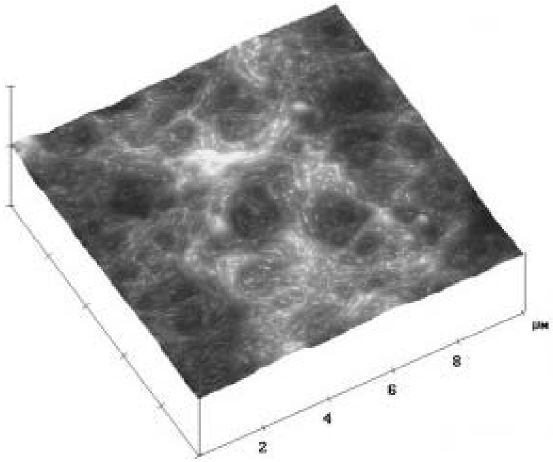
AFM images of cake layer on membrane surface

(scan size : 10㎛)



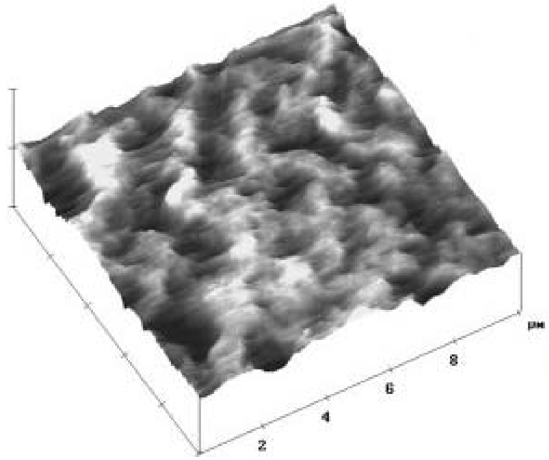
Virgin membrane surface

(roughness(rms) : 153nm)



(A) type (with iron net)

(roughness(rms) : 51nm)



(B) type (without iron net)

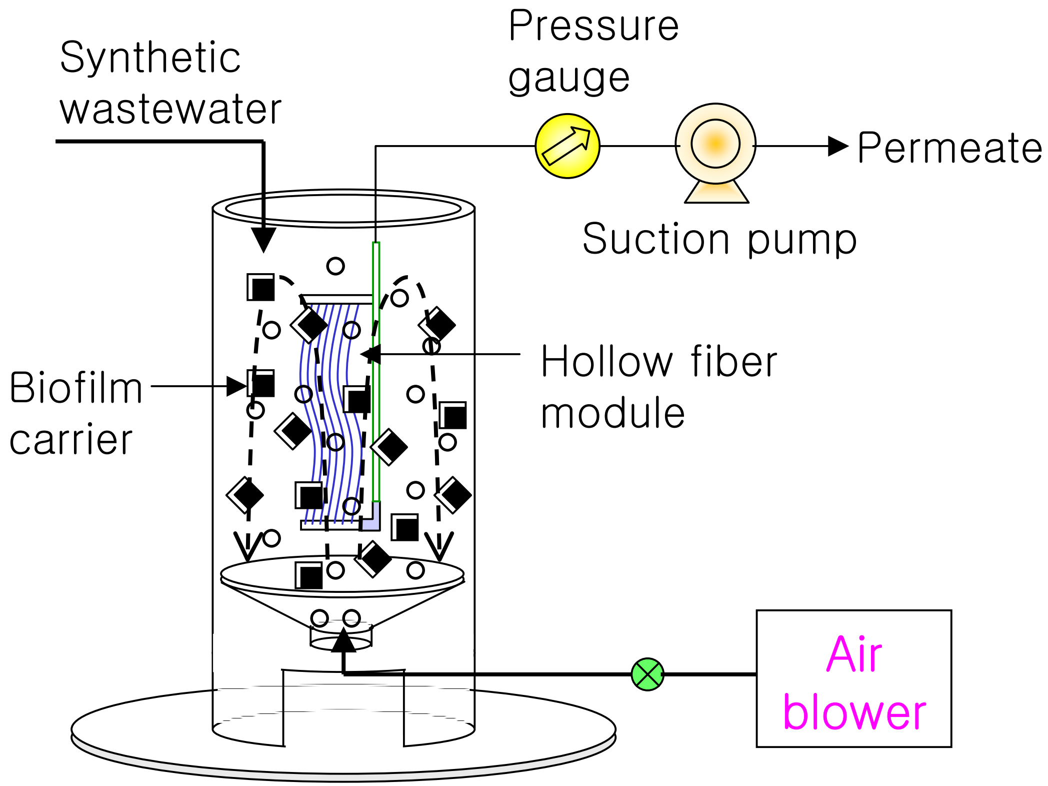
(roughness(rms) : 114nm)

Summary (II)

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)?

M-CMBBR system



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

$$E_{k,R} = \frac{E_{k,T}}{E_{k,T0}}$$

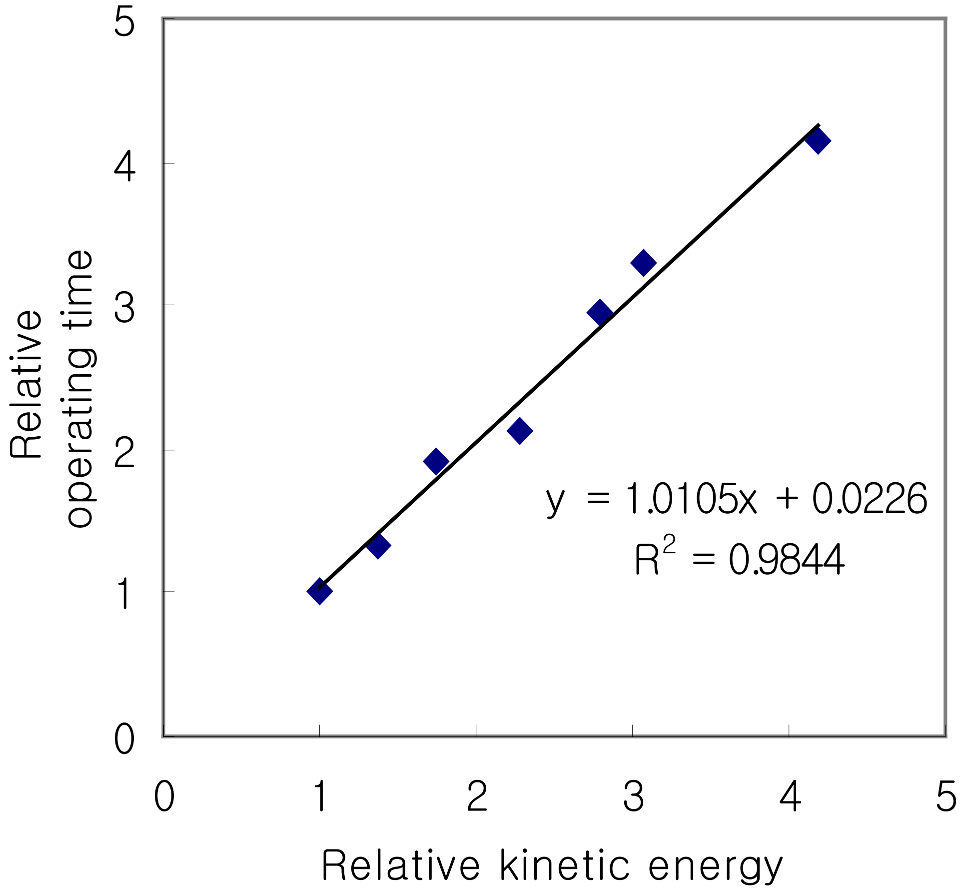
$E_{k,R}$: Relative kinetic energy of biofilm carrier
$E_{k,T0}$: Total kinetic energy at the conditions of 5LPM air flow rate and 5% carrier volume fraction

Calculation of the relative kinetic energy of biofilm carrier and the relative membrane operating time

	Total Kinetic Energy (×10^{-2} J/min)			Membrane Operating Time (hr)		
	5%	10%	20%	5%	10%	20%
5LPM	2.41	3.29	5.51	35	47	75
7LPM	3.07	5.59	7.37	-	-	115
9LPM	4.20	6.70	10.09	67	103	145

	Relative Kinetic Energy			Relative Operating Time		
	5%	10%	20%	5%	10%	20%
5LPM	**1.00**	**1.37**	**2.29**	**1.00**	**1.34**	**2.14**
7LPM	1.27	2.32	**3.06**	-	-	**3.29**
9LPM	**1.74**	**2.78**	**4.19**	**1.91**	**2.94**	**4.14**

Correlation between the relative kinetic energy and the relative operating time



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.

Resistance-in-Series Model

- The concept : "Flux decline arises from a series of resistances."

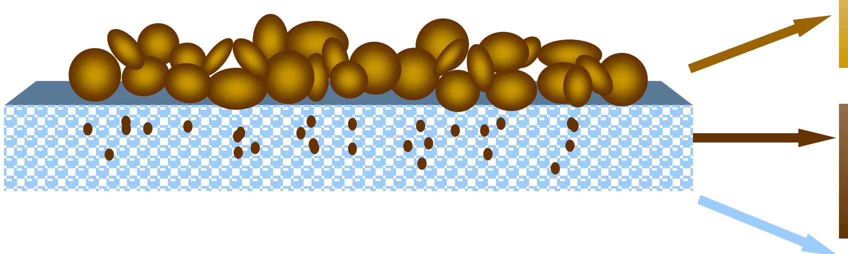
$$J = \frac{\Delta P}{\eta R_t}$$

J : permeate flux ($Lm^{-2}hr^{-1}$)

ΔP : transmembrane pressure (Pa)

η : 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)

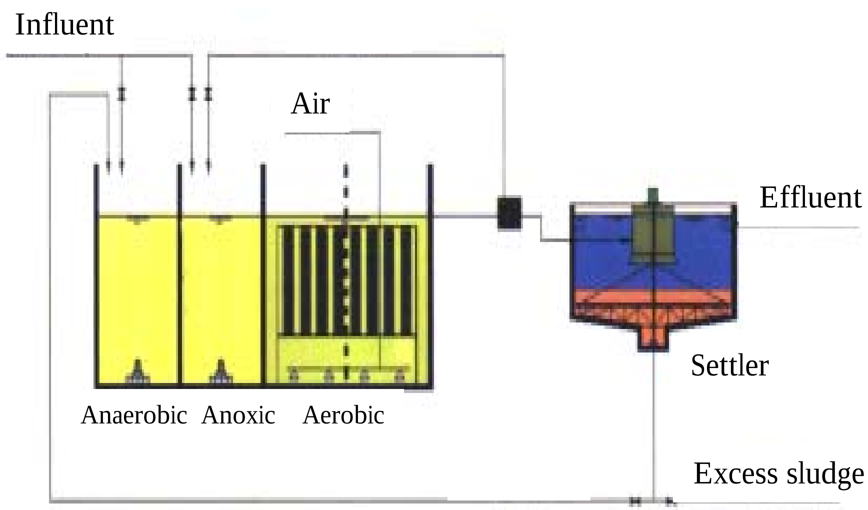
Module type	Hollow fiber
Pore size	0.1 mm
Material	Polyethylene (hydrophilic)
Surface area	0.0673 m^2
Outer diameter	410 mm
Inner diameter	270 mm

Biofilm process

Biofilm Reactors

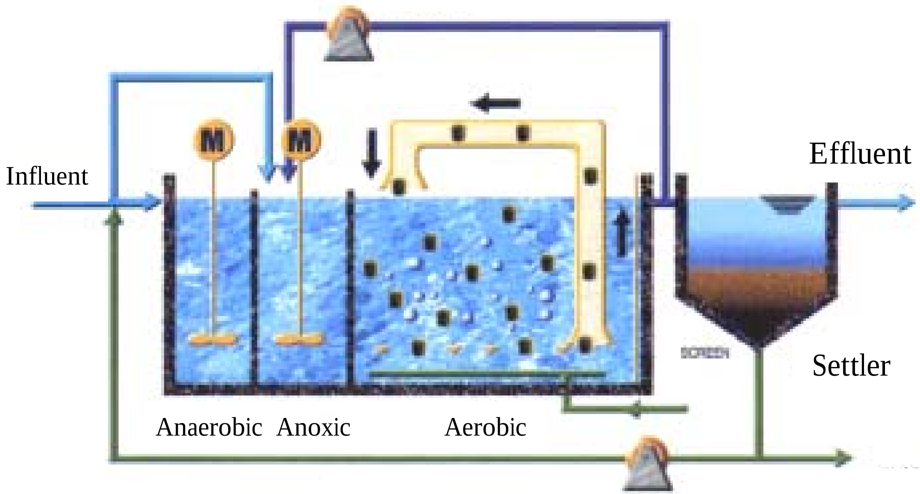
Fixed Bed Biofilm Reactor

- Looped cord media



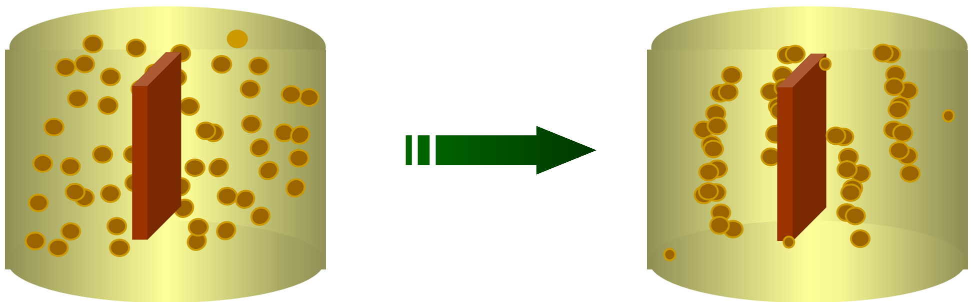
Moving Bed Biofilm Reactor

•Rectangular Sponge ; Polyurethane coated with Activated Carbon



Objectives

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



Suspended growth **Attached growth**

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