MEMBRANE BIOREACTORs

Week 10th: MBR Operation

Part II

Prof.Dr. Özer ÇINAR
Yıldız Technical University
Department of Environmental Engineering
İstanbul, Turkey

CEV4362 MEMBRANE BIOREACTORS

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Instructor: Prof.Dr.Özer ÇINAR, C Bloc 1-010 Environmental Engineering Department
Phone: 5366 **e-mail:** ocinar@yildiz.edu.tr

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Week 10th: MBR Operation

5.3. Fouling Control

- **Chemical Control**
- **Physical (Hydrodynamic or Mechanical)**
- **Biological Control**
- **Electrical Control**
- **Membranes and Module Modification**

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5.3. Fouling Control

The most important operation and maintenance (O&M) routine in MBR plants is membrane cleaning. As cleaning is closely related to membrane fouling precise understanding of membrane fouling phenomena is crucial for setting up a cleaning operation. Many physicochemical, biological, and operational factors are involved in membrane fouling. So, universal cleaning methods cannot solve all of the fouling problems encountered in all MBR plants.

A more familiar way of categorizing fouling control is through chemical, physical, biological, electrical, and membrane and module developments. This classification focuses on the characteristic nature of cleaning materials or methods. Table 5.2 summarizes the categories of fouling control, some of which are going to be described in more detail in the following sections.

5.3. Fouling Control (2/40)

Fouling Control Strategy	*Details Methods of Fouling Control*	*Classification of Cleaning Methods*
Direct membrane cleaning	Chemicals	
	• Acid/base, ozone, H_2O_2, NaOCl, PAC	Chemical
	• Fouling reducer (polyelectrolytes)	Chemical
	Coarse aeration, intermittent aeration	Physical
	Two-phase flow	Physical
	Backwashing	Physical
	Chemically enhanced backwashing	Physical + chemical
	HVI	Electrical
Fouling prevention	Pretreatment of debris, hair, and grit	Physical
	Critical flux operation	Physical
	HRT, SRT, f/m, DO, and MLSS control	Biological
	Development of antifouling membrane	Membrane/module
	Development of antifouling module	Membrane/module
	Shear (rotating disc, helical membrane, etc.)	Membrane/module
	In situ EC	Electrical
	Quorum quenching	Chemical/ biological
	Nitric oxide	Chemical/ biological
	DC induction	Electrical

Figure 5.2. Classification of the Fouling Control in MBR

5.3. Fouling Control (3/40)

5.3.1. Chemical Control

Membrane cleaning using many different kinds of chemicals has been widely practiced for a long time due to the immediate and excellent capabilities restoring deteriorated filtration performance. In spite of the merits, chemical cleanings have inherent disadvantages.

- ❖ Chemical cleanings always accompany secondary contamination.
- ❖ The added chemicals itself or conjugated with foulants definitely increase the amount of waste.
- ❖ Waste treatment and disposal costs have increased.
- ❖ The chemicals transportation, storage and preparation caused extra costs and labor.

The reversible fouling can be partly prevented by subcritical flux operation and removed by air scouring. However, the irrecoverable fouling cannot be managed by simple subcritical flux operation or other physical cleanings. This is the basic reason why periodical chemical cleanings are still practiced in MBR plants

5.3. Fouling Control (4/40)

5.3.1.1. Cleaning Protocol

Chemical cleanings are carried out by two different cleaning protocols:

1. off-line cleaning
2. cleaning-in-place (CIP)

In the off-line cleaning, membranes or membrane modules are taken out of the bioreactor by hoister and then transferred nearby to a separate tank full of cleaning reagents. The immersed membrane modules in the tank are cleaned. Or the membrane module stays in the aeration tank after draining o all the activated sludge suspension, and the module is immersed in chemical agents for cleaning.

In the CIP cleaning mode, chemical agents are directly injected into the membrane modules in the reverse direction to the normal filtration while the membrane modules are still submerged in the bioreactor. Compared with the off-line cleanings, CIP is much simpler and cheaper. The periodic CIP are often called maintenance cleanings, which is the basic cleaning option most MBR plants employ since it as a primary tool for fouling control.

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Example 5.3: Determination of Resistances after Periodic Chemical Cleanings

A pilot-scale submerged MBR is running under constant flux mode. Whenever the TMP reaches 70 kg m/s^2 cm^2, a chemical cleaning is carried out for 144 min (100 min sodium hypochlorite cleaning and then 44 min water rinsing) to restore the elevated TMP. Determine resistance values after 5, 10, and 15 days of operation using the following data. If data are necessary for the membrane filterability, use the data of Example 4.7 in the previous chapter.

- The membrane surface area, 0.05 m^2
- Initial water flux (J_{iw}) measured before MBR operation with pure water: 30 L/m^2 h
- Operating flux (J): 20 L/m^2 h (LMH)
- Temperature: 20°C
- Permeate viscosity: 1.009×10^{-3} kg/m s
- Assume that the permeate density is 1 g/mL and the 1 bar is 9.996 kg m/s^2 cm^2 (Table 5.3)

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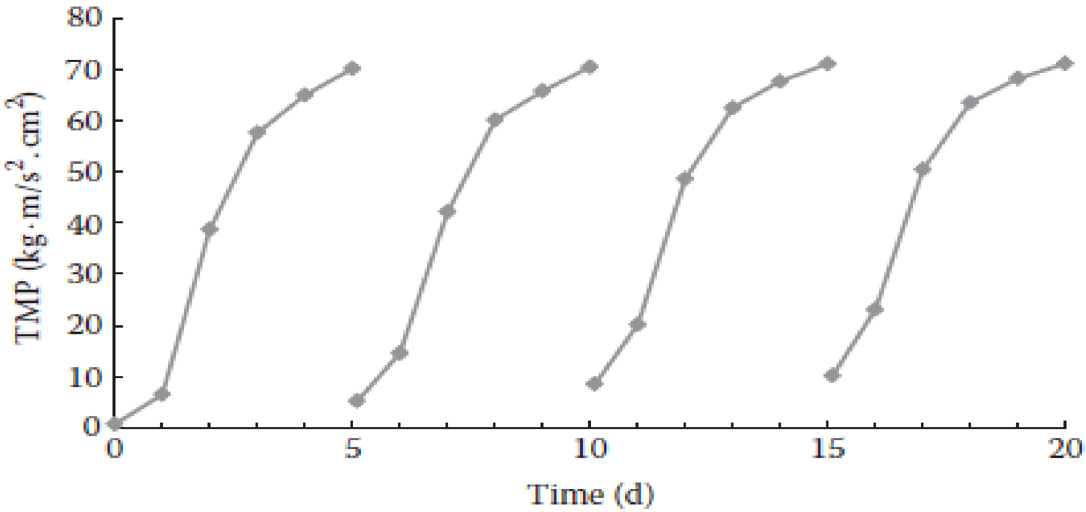
Solution

To calculate the resistances, the pressure unit should be changed from bars to the SI unit as shown in Table 5.4. And operating time versus TMP profile is plotted using the table.



As stated in Chapter 4 and Example 4.7, each resistance value is determined by the following model equations:

$$R_m = \frac{TMP_1}{(\eta \times J_{iw})} \quad \text{(E3.1)}$$

$$R_f = \frac{TMP_2}{(\eta \times J_{fw})} - R_m \quad \text{(E3.2)}$$

$$R_c = \frac{TMP_3}{(\eta \times J)} - (R_m + R_f) \quad \text{(E3.3)}$$

5.3. Fouling Control (5/40)

Table 5.4 TMP Expressed in SI Units as a Function of Operating Time

Time (Day)	*Recorded TMP (Bar)*	*Pressure (kg·m/s² cm²)*	*Cleaning*
0	0.078	0.77969	
1	0.656	6.55738	
2	3.875	38.73450	
3	5.759	57.56696	
4	6.496	64.93402	
5	7.012	70.09195	Chemical cleaning
5.1	0.524	5.23790	
6	1.463	14.62415	
7	4.214	42.12314	
8	6.012	60.09595	
9	6.573	65.70371	
10	7.041	70.38184	Chemical cleaning
10.5	0.857	8.56657	
11	2.015	20.14194	
12	4.861	48.59056	
13	6.247	62.44501	
14	6.762	67.59295	
15	7.104	71.01158	Chemical cleaning
15.1	1.024	10.23590	
16	2.312	23.11075	
17	5.041	50.38984	
18	6.351	63.48460	
19	6.817	68.14273	
20	7.111	71.08156	

5.3. Fouling Control (5/40)

First, information on the TMP_1 and the J_{iw} is necessary for the calculation of R_m: TMP_1 was indicated in Example 4.7, 0.7797 kg m/s² cm², and J_{iw} is given by 30 L/m² h in this example:

- Membrane resistance (R_m) is equal to Example 4.7.
- To calculate R_m, put each value, $J_{iw} = 30$ L/h m², $TMP_i = 0.7797$ kg m/s² cm² and $\eta = 1.009 \times 10^{-3}$ kg/m s into Equation E3.1.

$$R_m = \frac{0.7797\ \text{kg} \cdot \text{m}}{\text{s}^2 \cdot \text{cm}^2} \times \frac{\text{m} \cdot \text{s}}{1.009 \times 10^{-3}\ \text{kg}} \times \frac{\text{m}^2 \cdot \text{h}}{30\ \text{L}} \times \frac{3600\ \text{s}}{\text{h}} \times \frac{100^2\ \text{cm}^2}{\text{m}^2} \times \frac{10^3\ \text{L}}{\text{m}^3}$$

$$R_m = 0.09 \times 10^{13}\ \text{m}^{-1}$$

First, the $R_c + R_f$, called "total fouling resistance (R_{Tf})," means the overall resistances developed until the onset of the chemical cleanings can be calculated as follows:

- Total fouling resistance, R_c+R_f, at day 5.
- TMP_5 is the pressure measured just prior to the chemical cleaning on day 5, which is 70.09195 kg m/s² cm².
- J_5 is the operating flux at day 5. However, the flux is always 20 L/h m² under the constant flux mode.
- Rearrange Equation E3.4 to the resistance form and insert the corresponding values into it.
- $R_c + R_f = TMP_5/(\eta \cdot J_5) - R_m$

$$=\frac{70.09195\times kg\times m}{s^2\times cm^2}\times\frac{m\times s}{1.009\times10^{-3}\,kg}\times\frac{m^2\ h}{20L}\times\frac{3600s}{h}\times\frac{100^2\,cm^2}{m^2}\times\frac{10^3\,L}{m^3}$$

$$-0.09\times10^{13}$$

$$=12.5\times10^{13}\,m^{-1}-0.09\times10^{13}\,m^{-1}$$

- $R_c+R_f=12.41\times10^{13}\ m^{-1}$

Second, the $R_{f,re}$ and the $R_{f,ir}$ are calculated using the filtration data collected after chemical cleaning. After chemical cleaning, the cake layers and the reversible internal foulants are removed. Therefore, the following equation can be applied to calculate the flux just after chemical cleaning at day of 5.1.

$$J_{5.1}=\frac{TMP_{5.1}}{\eta(R_m+R_{f,ir})} \tag{E3.6}$$

- The irreversible internal fouling resistance ($R_{f,ir}$).
- $TMP_{5.1}$ is the pressure measured just after the chemical cleaning of day 5.1, which is 5.23790 kg · m/s² cm².
- $J_{5.1}$ is the operating flux at day 5.1, which is always 20 L/h m² under the constant flux mode.
- Shuffle Equation E3.6 until the resistance form appears and insert the corresponding values into it.
- $R_{f,ir}=TMP_{5.1}/(\eta\cdot J_{5.2})-R_m$

$$=\frac{5.23790\,kg\cdot m}{s^2\cdot cm^2}\times\frac{m\cdot s}{1.009\times10^{-3}\,kg}\times\frac{m^2\cdot h}{20\,L}\times\frac{3600\,s}{h}\times\frac{100^2\,cm^2}{m^2}\times\frac{10^3\,L}{m^3}$$

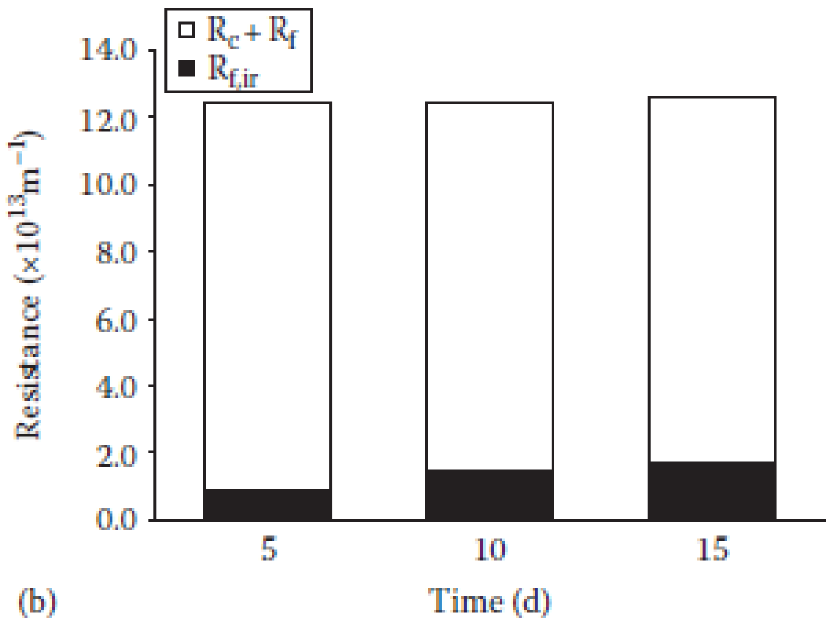
$$-0.09\times10^{13}$$

$$=0.93\times10^{13}\,m^{-1}-0.09\times10^{13}\,m^{-1}$$

- $R_{f,ir}=0.84\times10^{13}m^{-1}$

5.3. Fouling Control (5/40)

	Resistance Values ($x10^{13}\ m^{-1}$)			
	R_m	$R_{f,Ir}$	R_c+R_f	R_T
Day 5	0.09	0.84	12.41	12.50
Day 10	0.09	1.44	12.46	12.55
Day 15	0.09	1.73	12.58	12.67



(b)

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5.3.1.2. Classification of Cleaning Chemicals

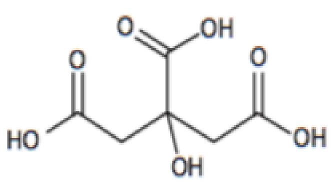
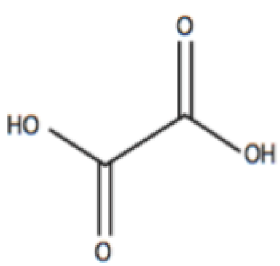
Chemical cleaning reagents used for fouling control in MBR are categorized into the following groups:

- Oxidizing agents
- Acids and bases
- Enzymes
- Chelating agents
- Detergents (or surfactants)
- Coagulants

The chemicals used in MBR are summarized in Table 5.5.

5.3. Fouling Control (6/40)

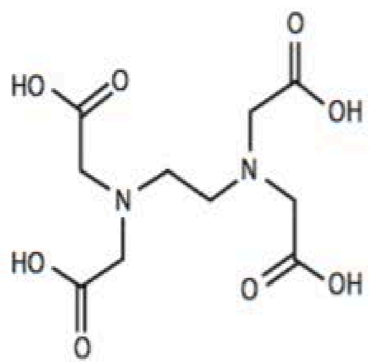
Table 5.5. Chemical Reagents Commonly Used in Membrane Cleanings in MBR

Category	*Chemicals Name*	*Molecular Formula*	*Molecular Weight*	*Chemical Structure*
Oxidizing agents	Sodium hypochlorite	$NaOCl$	74.5	
	Calcium hypochlorite	$Ca(OCl)_2$	143.0	
	Ozone	O_3	48.0	
	Hydrogen peroxide	H_2O_2	34.0	
Inorganic acids	Sulfuric acid	H_2SO_4	98.0	
	Hydrogen chloride	HCl	36.5	
Organic acids	Citric acid	$C_6H_8O_7$	192.1	
	(2-hydroxypropane-1,2,3-tricarboxylic acid)			
	Oxalic acid (ethanedioic acid)	$H_2C_2O_4$	90.0	

(*Continued*)

5.3. Fouling Control (7/40)

Table 5.5. Chemical Reagents Commonly Used in Membrane Cleanings in MBR (Cont.)

Category	*Chemicals Name*	*Molecular Formula*	*Molecular Weight*	*Chemical Structure*
Chelating agent	EDTA	$(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2$	292.4	
Surfactants	Sodium dodecyl sulfate (SDS)	$CH_3(CH_2)_{11}OSO_3Na$	288.4	
Enzyme	Protease, hydrolase, glycolytic enzyme	–		–
PAC	Powdered activated carbon	C	–	–

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5.3.1.3. Hypochlorite Chemistry

The most popular oxidizing agents used for chemical cleanings in MBR, sodium hypochlorite (NaOCl) or calcium hypochlorite ($Ca(OCl)_2$), dissociate into their anion, hypochlorite (OCl^-), and the corresponding cations.

$$NaOCl \leftrightarrow Na^+ + OCl^-$$

$$Ca(OCl)_2 \leftrightarrow Ca^{2+} + OCl^-$$

The hypochlorite forming hypochlorous acid (HOCl). The following equation expresses the ionization of HOCl:

$$HOCl \leftrightarrow OCl^- + H^+$$

The “free available chlorines” refer to the total quantity of HOCl and OCl– existing in aqueous solution. On the other hand, “combined available chlorines” are formed by the reaction of free chlorines with ammonia, which are often called chloramines.

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5.3.1.3. Hypochlorite Chemistry (Cont.)

The free chlorines and the combined chlorines have a disinfection potential, which means they serve as disinfectants killing live microorganisms. The order of disinfection efficiency of these chlorine compounds is as follows:

$$HOCl > OCl^- > \text{Chloramines}(NH_2Cl, NHCl_2, NCl_3) > Cl^-$$

The chloride ion does not have disinfection potential because its oxidation state (−1) is too low to accept electrons from other compounds. Since the oxidation state of the free chlorines (HOCl and OCl^-) and chloramines are all +1, they have a disinfection potential. However, their disinfection efficiency is quite different from each other (the disinfection efficiency of HOCl is about 40–80 times that of OCl^-).

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5.3.1.5. Other Chemical Agents

- Inorganic and organic acids (such as sulfuric and citric acid) dissolve inorganic precipitated foulants and scales.
- Bases can be used for organic foulants removal.
- Surfactants (detergents) are also used for cleaning organic foulants by emulsification.
- Enzymes aiming at specific organic foulants such as proteins and polysaccharides can also be used for cleaning. They are not used alone but formulated with other reagents.
- Chelating reagents (such as ethylenediaminetetraacetic acids (EDTA)) can be used as ligand material for complexing inorganic foulants. Because of pH adjustment requirement, possible interferences and cost, Chelating reagents are not used for fouling control in wastewater treatment.

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5.3.1.6. Activated Carbon

Direct addition of powdered activated carbon (PAC) to a membrane tank;

- leads to a decrease in the compressibility of sludge flocs
- adsorb extracellular polymeric substances (EPSs) inside the microbial flocs
- enhances the biodegradation of recalcitrants or slowly biodegradable compounds

So, the membrane permeability of the PAC-added MBR is obviously enhanced compared with the non-PAC-added MBR.

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5.3.1.7. Chemical Pretreatment and Additives

Chemical pretreatment is considered mandatory to improve the membrane permeability for drinking water treatment. Potential foulants are removed by chemical precipitation prior to the main membrane filtration processes. However, it has not been often tried in MBR applications for wastewater treatment. In special cases, for example, piggery wastewater including high concentration of suspended solids coagulation prior to MBR is reported.

Electrolytic polymers have been reported to be effective in fouling mitigation. The addition of these chemicals makes the cake layer porous and induces a decrease in soluble EPS. Moreover, soluble constituents in the bulk solution, which are potential foulants, are entrapped in sludge flocs during the flocculation process. However, the MBR market does not use these chemicals frequently due to the lack of a long-term evaluation as well as cost.

5.3. Fouling Control (16/40)

5.3.2. Physical (Hydrodynamic or Mechanical) Control

5.3.2.1. Preliminary Treatment

One of the notorious troubles in submerged MBRs is the entanglements of hairs with the membrane fibers, which results in entire system shutdown. Therefore, debris such as grit, particulates, hair, and plastic materials should be removed prior to the main membrane reactor in MBR. Proper selection of the preliminary treatments should be considered more importantly at the design stage of MBR than for conventional wastewater treatment systems. Operation of the preliminary treatment such as screens, bar racks, and grit chamber is described well in other wastewater treatment textbooks.

5.3. Fouling Control (17/40)

5.3.2.2. Backwashing (or Backflushing)

The same principles of the backwashing (or back flushing) for conventional media filtration (sand and/or anthracite filtration for water treatment processes), a reverse direction of water flow expels the foulants from the filter media, can also be applied to membrane separation. Membrane backwashing is the most frequently used tool to maintain a steady flux in membrane filtration processes due to simplicity and controllability.

Basically, backwashing is carried out with permeate or pure water. Occasionally, chemicals are added to the backwashing solution to enhance the cleaning efficiency, which is called chemically enhanced backwashing. The membrane manufacturers give an indication of the maximum pressure allowed for the backwashing.

If backwashing is periodically repeated in conventional filtration, the filter media is lost out of the filtration beds. Periodic repeating of backwashing in MBR could result in severe damages to the membrane structure.

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5.3.2.3. Air Scouring (Coarse Aeration)

The basic idea is that coarse aeration in a membrane tank accomplishes dual goals:

- air transfer to cells for microbial growth and metabolism
- aeration for fouling control

Excessive and extensive coarse aeration onto the membrane surfaces has been practiced commonly to vibrate the submerged membranes mechanically and remove sludge cakes on the membrane surfaces. However, coarse aeration consumes large amounts of energy for air blowing. Depending on MBR sites, aeration consumes about 49%–64% of the total energy required for MBR plant operation. Coarse aeration for fouling control inevitably introduces strong shear forces to the microbial flocs, so that the sludge flocs are apt to experience floc disintegration.

One of the effective use of air is the introduction of a two-phase (air+ liquid) flow to MBR as shown in Figure 5.7. Different flow regimes are formed according to the ratio of flow rates of air and liquid: bubble, slug, churn, annular, and mist flow.

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5.3.2.4. Intermittent Suction

Since membrane separation is as pressure-driven processes, abrupt pressure relaxation (or retardation) can cause a temporary back transport of permeates, which then helps to dislodge cake layers away from the membrane surfaces. Instant cessation of suction pressure in submerged MBR or stopping pressurization in side-stream MBR has been used widely for fouling prevention in MBR.

An intermittent suction (i.e., temporary cessation of suction) can provide an alternative tool for suppression of membrane fouling in MBR. is technique is called a cyclic filtration because on and o suctions repeat periodically.

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5.3.2.5. Abrasion

In abrasion mechanism, free moving materials in membrane tanks can rub the membrane surface, helping to dislodge cake layers o the membrane. They move freely to cake layers and then take them off by mechanical scouring, leading to increased membrane permeability. Soft sponge balls (or cubes) or hard plastic media have been used for the free moving media causing abrasion.

For the purpose of making biological activated carbon (BAC), granular activated carbon (GAC) is added to MBR. The BAC has dual duties:

- ✓ original duty of providing spaces for biomass attachment and growth
- ✓ moving carriers for abrasion

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5.3.2.6. Critical Flux Operation

The critical flux in an MBR system denotes the operating flux where no fouling occurs under the proper fouling control conditions. If the strict meaning of critical flux (the flux where no fouling occurs) is applied to MBR, a significantly lower flux would be identified as the critical flux.

Typical values of critical flux in MBR plants range from 10 to 40 LMH depending on the various factors (module configuration, flow regime, microbial community etc.) affecting membrane fouling.

5.3.3. Biological Control

Biological fouling control has been developed recently thanks to the innovative developments in the fields of molecular biology over the last couple of decades. They show a potential for MBRs to become more able to cope with membrane fouling than ever before. A representative biological fouling control development is quorum quenching technology.

5.3. Fouling Control (24/40)

5.3.3.1. Quorum Quenching

The quorum sensing (QS) is a means of bacterial communication by signal molecules called autoinducers (AIs) emitted by bacteria. QS is triggered when AI molecules exceed a critical threshold, after which point the AIs bind to receptors on the bacteria and make the whole bacteria population express certain kinds of genes together. Biofilm formation is a typical example of QS.

The principle idea of application of QS to fouling control in MBR is "quorum quenching." The microorganisms in the bio-cakes on membrane surfaces communicate with each other using AIs. Membrane fouling caused by biofilm formation and deposition to membrane surfaces by microorganisms could be inhibited by the addition of AIs inhibitors. (Kim et al., 2013) found that the time to reach TMP of 70 kPa was extended 10 times compared with the control, indicating the fouling rate was significantly reduced due to the use of beads.

5.3. Fouling Control (25/40)

5.3.3.2. Other Biological Control

Other types of biological control techniques besides quorum quenching are (1) nitric oxide to induce biofilm dispersal, (2) enzymatic disruption of EPSs, and (3) disruption of biofilm by bacteriophages.

1. Addition of low levels of nitric oxide (NO) causes dispersal of biofilms, indicating that it can be used as a potential alternative for fouling control. However, it has not been investigated for fouling control in MBR. Further studies are needed.

2. Since EPSs are mainly composed of proteins and polysaccharides, EPSs could be hydrolyzed to their building blocks by some specific enzymes such as protease and polysaccharases. If the EPSs are readily degraded by enzymes addition, less membrane fouling would be anticipated. Several studies have indicated that this kind of enzyme cleaning showed better cleaning efficiency than alkaline cleaning. However, many limitations are still present to applying enzyme cleaning techniques to MBR.

5.3.3.2. Other Biological Control (Cont.)

3. The addition of bacteriophages reduces microbial attachment to membrane surfaces in MBR by disrupting biofillm formation, which is caused by infection of host bacteria. However, further and wider studies on characteristics of specific parasites between the bacteria and phages are needed to apply MBR.

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5.3.4. Electrical Control

Electricity has been used for conventional pressure-driven membrane filtration processes. Particularly, attention to fouling control using an electrical application in MBR has been paid extensively. The application of electricity to enhance membrane filtration performance is categorized into three groups:

1. Induction of electric field
2. In situ ElectroCoagulation
3. High-voltage impulse

5.3. Fouling Control (36/40)

5.3.5 Membranes and Module Modification

5.3.5.1. Membranes Modification

Physicochemical modifications of membrane materials have been tried to improve performances of membrane processes for a long time. Although surface morphology, structure, charge, and roughness of membranes are subject to be changed, an improvement of surface hydrophilicity is a key factor to get a better flux and antifouling performance. Patterned morphology on membrane surfaces such as pyramid, prism, and embossing patterns, using a lithographic method, was developed recently. Deposition of microbial cells on the patterned membrane was significantly reduced compared to that on the at membrane in MBR.

Researchers are focusing on the application of nanomaterials to modify the membrane properties. **Silver nanoparticles (nAg), titanium oxide (TiO_2) nanoparticles, carbon nanotube (CNT), and fullerene (C_{60})** could be potential candidates expected to show an improved performance when used to modify the membrane properties.

Thank you…