MEMBRANE BIOREACTORs

Week 5th: Membrane Fouling

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

Yıldız Technical University
Department of Environmental Engineering

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Time and Room: Wednesday 11:00 - 11:50 FZ-82
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Instructor: Prof.Dr.Özer ÇINAR, C Bloc 1-010 Environmental Engineering Department
Phone: 5366 **e-mail:** ocinar@yildiz.edu.tr

Week 5th: Membrane Fouling

4.1. Fouling Phenomena

- **Fouling Rate**

4.2. Classification of Fouling

- **Reversible versus Irreversible and Recoverable versus Irrecoverable Fouling**
- **Classification of Fouling by Location of Fouling**
- **Solids Deposit Pattern**
- **Solute Fouling**

4.3. Types of Foulants

- **Particulates**
- **Soluble Matter**

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4. Membrane Fouling

Membrane fouling is a major problem encountered during the application of membrane separation processes in water and wastewater treatment. A main limiting step in membrane bio-reactors (MBRs) is membrane fouling.

The success of MBR operation is largely dependent upon how to cope with membrane fouling, which is affected by many factors such as the wastewater influent water quality, membrane characteristics, bioreactor operational conditions, and membrane cleaning methods.

To understand membrane fouling in MBR, it must be known that classification of foulants, dominant foulants, and factors affecting membrane fouling.

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4.1. Fouling Phenomena

Membrane fouling can be perceived by a decrease in permeation flux or an increase in transmembrane pressure (TMP) according to the operation mode. Constant pressure filtration behavior is typified by a rapid flux decline at the start of filtration followed by a more gradual decrease until a steady-state or a pseudo-steady-state flux is reached.

Figure 4.1 shows the typical pattern of the fouling phenomena according to the operation mode in MBR. It is very natural that the lines in Figure 4.1a and b are exactly opposite because TMP and flux reciprocate

Whether proper cleaning has been provided during the operation of MBRs or not, an abrupt increase in the TMP will be observed following the gradual rise in the TMP. Figure 4.2a shows the typical pattern of the slow TMP rise and then the abrupt jump (two-stage TMP riseup).

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4.1. Fouling Phenomena (2/7)

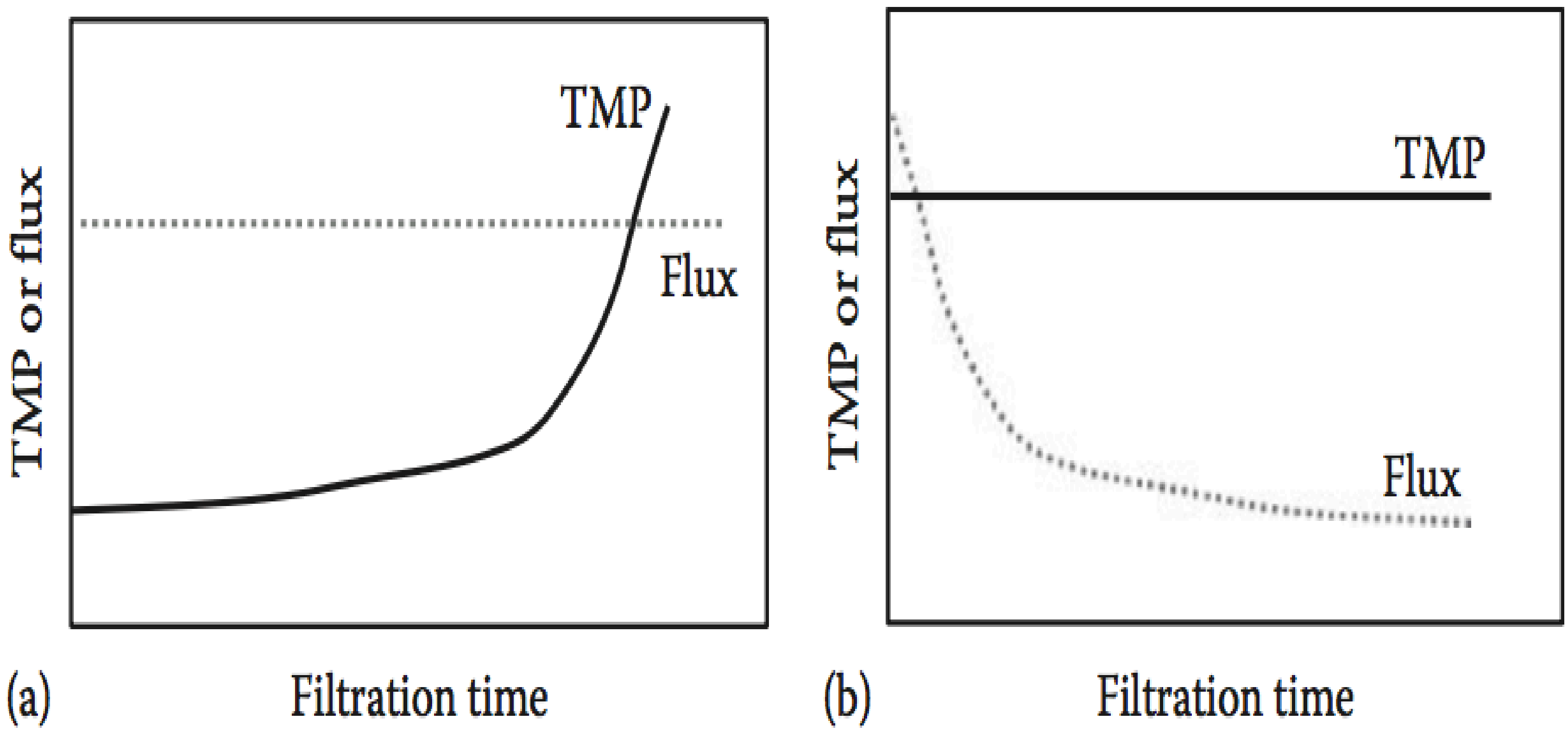

Figure 4.1. Two methods for tracking membrane fouling encountered in MBRs according to operation modes: (a) constant flux mode and (b) constant pressure mode.

4.1. Fouling Phenomena (3/7)

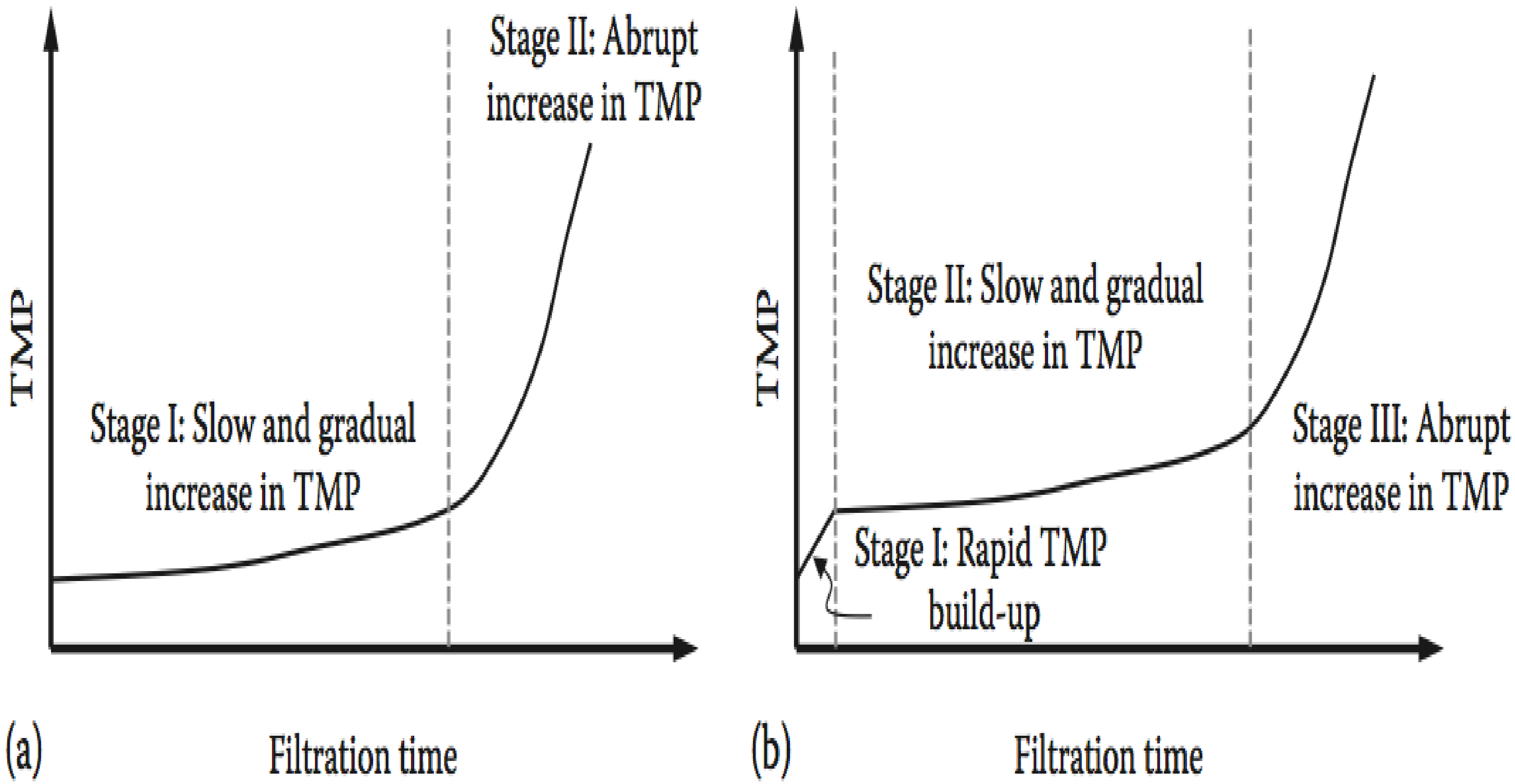

Figure 4.2. Typical TMP jump patterns found in MBR: (a) two-stage TMP jump and (b) three-stage TMP jump.

4.1.1. Fouling Rate

Four consecutive steps can be defined during fouling:

1. blockage of the smallest pores
2. coverage of the larger pores' inner surface
3. superimposition of particles and direct blockage of larger pores
4. creation of the cake layer

The easiest way to have an insight into the fouling propensity is to express the fouling rate. As shown in Figure 4.3a, the derivative form of TMP buildup at a particular time (i.e., dTMP/dt) is the commonly used term to represent the fouling rate. Thus, the unit should be kPa/h or psi/h.

The fouling rate is dependent on the operating flux as shown in Figure 4.3b, i.e., the higher is the operating flux maintained, the faster is the fouling rate. As the operating flux increases (J4 → J3 → J2 → J1), the fouling rate increases until the breakthrough point flux, $J_{critical}$ (critical flux).

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4.1.1. Fouling Rate (Cont.)

Typical critical flux values in MBR plants for domestic wastewater treatment, are usually between 10 and 40 LMH. If the MBR plant treats industrial wastewater or highly variable influent feed stream, the critical flux may differ.

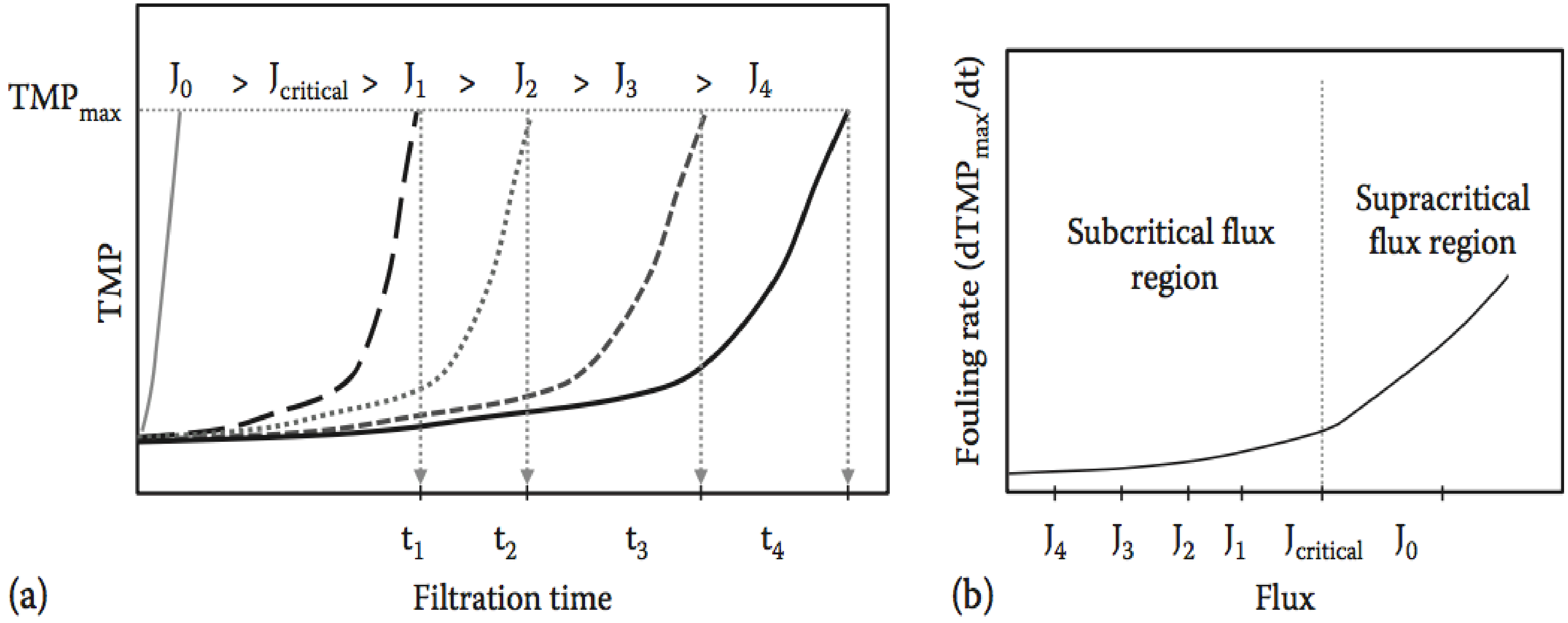

Figure 4.3. (a) Typical TMP rise pattern and (b) fouling rate as a function of flux.

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4.2. Classification of Fouling

There have been many classifications of membrane fouling in MBR by many researchers, but still unified terms describing fouling phenomena have not been set yet. Therefore, membrane fouling in MBR can be classified into different categories according to what the classifying criterion is applied to. classifications of membrane fouling in MBR provides at Table 4.1.

According to this criterion fouling is divided into reversible, irreversible, and irrecoverable fouling. Based on the second criterion, fouling can be classified into clogging, cake layer deposition, and internal pore fouling.

The pattern of solid buildup is the last criterion. Cake layer formation, pore narrowing, and pore blocking fall into this fouling class. Although membrane compaction is not classified as a kind of fouling, it deteriorates the membrane filtration performance like clogging.

4.2. Classification of Fouling(2/16)

Table 4.1. Classification of Membrane Fouling in MBRs

Criteria Classifying Fouling	*Fouling Phenomena*	*Description*
Flux recovery after cleaning	Reversible fouling	Flux is recovered after simple or chemical cleaning.
	Irreversible fouling	Flux is not recovered by any kind of cleaning.
	Recoverable fouling	Flux is recovered after simple cleaning such as backwashing or relaxation.
	Irrecoverable fouling	Flux is recovered only by chemical cleaning.
Places of fouling occurrence	Clogging	Sludge accumulation between hollow fibers and flat sheet membrane channels inside the module.
	Cake layer deposition	Sludge deposition on the membrane surface.
	Internal pore fouling	Adsorption of solutes smaller than the pores to the membrane pore walls.

4.2. Classification of Fouling(3/16)

Table 4.1. Classification of Membrane Fouling in MBRs (Cont.)

Solids deposition pattern	Cake layer formation	Vertical buildup of layer on the membrane surface.
	Pore narrowing	Narrowed pore size due to the accumulation of solutes inside pore walls.
	Pore blocking (or plugging)	Particle blockage of the entrance of pores or pore walls.
Solute fouling	Concentration polarization	Concentration gradient of solutes near the membrane surface.
	Gel layer formation	Consolidation of the initially adhered solutes (as well as solids) on the membrane surface.
Nonfouling	Compaction	Compression of membrane structure by the applied pressure.

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4.2.1. Reversible versus Irreversible and Recoverable versus Irrecoverable Fouling

Reversible fouling literally means that the flux is recovered after simple cleaning such as backwashing, pressure relaxation, and air scouring, but the flux is recovered only after chemical cleaning when irrecoverable fouling has occurred. On the other hand, irreversible fouling means that the flux cannot be recovered by any means of cleaning (Figure 4.4).

Summarizing this relationship, the following equation on fouling can be expressed:

Total fouling = reversible fouling + irreversible fouling
= recoverable fouling + irrecoverable fouling + irreversible fouling

Recoverable fouling can be restored easily by simple cleaning (e.g., backwashing or air scouring) during the stage I.

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4.2.1. Reversible versus Irreversible and Recoverable versus Irrecoverable Fouling

Irrecoverable fouling might originate from the gel layer, which has been consolidated at the interface between the membrane surface and the cake layer as well as from the strong adsorption of solutes to the pores and/or pore walls. The gel layer and the adsorbed layer in the pores are not easily removed by conventional cleaning protocols but need to be removed by chemical cleaning. Irreversible fouling is relatively smaller than reversible fouling at the initial stage, but it will gradually develop thereafter.

TMP abruptly jumps at the onset of stage II and rapidly reaches the maximum allowable TMP. The fouling developed during this short period is mostly reversible fouling (=recoverable fouling + irrecoverable fouling). Chemical cleaning using oxidizing agents such as sodium hypochlorite will decrease the TMP again.

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4.2. Classification of Fouling(6/16)

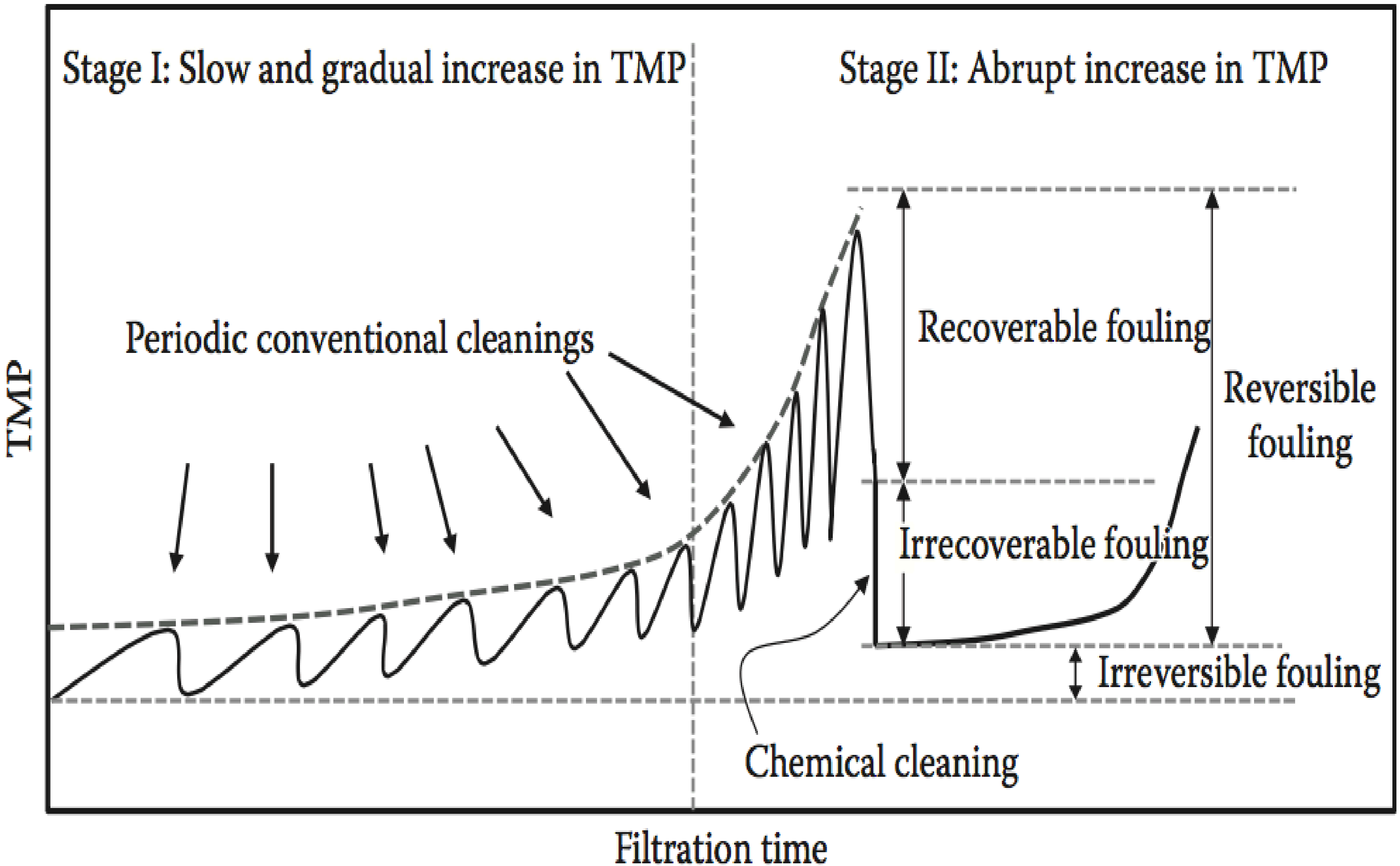

Figure 4.4. TMP profile according to the fouling classification.

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4.2.2. Classification of Fouling by Location of Fouling

The location where fouling occurs is another criteria to classify membrane fouling:

- clogging,
- cake layer deposition,
- internal pores fouling.

Clogging occurs at the outer space of the membrane bundle, typically between the membrane channels. The cake layer is formed on the membrane surface, which contributes to the most important fouling, whereas internal pore fouling develops inside the membrane.

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4.2.2.1. Clogging

Sludge flocs, small particles, and debris in bulk solution are easily migrated and then accumulated to the spaces within the hollow fibers or flat sheet membranes inside a membrane module. Thus, the stream to the membrane surface is choked up completely. This is called clogging (Figure 4.7), and it blocks the convection flow to the membrane surfaces (permeate flux reduce). Clogging mainly due to mal-pretreatment of Suspended Solids (SSs) and debris.

Clogging should not be classified into fouling, but it obviously leads to the same result (i.e., the flux reduction or the TMP buildup like other fouling phenomena).

Proper preliminary treatments for the influent wastewater such as screens, bar racks, and grit chambers could reduce clogging problems.

4.2. Classification of Fouling(9/16)

Figure 4.7. Photo of typical clogging in the hollow fiber membrane channels.

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4.2.2.2. Cake Layer

Cake layer formation has been known to be a predominant fouling mechanism in MBR. Mixed liquors and SSs deposit onto the membrane surface from the beginning of filtration due to the convective flows from bulk solution to the membrane.

The thickness of the cake layer increases at the initial stage of cake deposition, but it reaches a plateau. Hydrodynamic conditions near the membrane surface resulting from extensive coarse aeration do not allow the cake layer to develop further. Cake layer thicknesses mainly depending on the membrane applied pressure and aeration intensity. Thicker cake layer could induce higher cake resistance. Cake Resistance (R_C) formula is;

$$R_c = \frac{\alpha \cdot m}{A_m}$$

where

α is the specific cake resistance of the biofilm, m/kg

m is the mass of the biofilm, kg

A_m is the membrane area, m^2

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4.2.2.2. Cake Layer (Cont.)

According to the Carman–Kozeny equation, both the size of particles (e.g., microbial flocs) and porosity are key parameters determining the specific cake resistance of a cake layer:

$$\alpha = \frac{180(1-\varepsilon)}{\rho_p . d_p^2 \cdot \varepsilon^3}$$

where

ε is the porosity of the cake layer
ρ_p is the density of particles, kg/m^3
d_p is the particle diameter, m

The most predominant factor affecting the specific cake resistance is the particle size (d) and the porosity (ε). Therefore, the filterability of a thick cake would be greater than that of a thin cake if the latter is made of finer and smaller particles than the former.

4.2. Classification of Fouling(12/16)

4.2.2.3. Internal Pore Fouling

Dissolved solute and fine particulate adsorption to internal pore walls govern internal fouling. From the early stage of filtration, adhesion occurs when dissolved matter and colloidal particles in mixed liquor begin to attach to the pore entrance and pore walls of the membranes, narrowing the pore diameter. After sufficient cake buildup on the membrane surface, the dissolved matter and fine particulates are prone to attach preferentially to the sticky cake layer prior to being transported to the membrane pore walls, also called cohesion.

Generally speaking, the predominant fouling resistance is the cake layer resistance (Rc) rather than the internal fouling (Rf). Several to tens of times larger cake resistances compared to internal fouling have been reported in most cases of MBRs.

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4.2.3. Solid Deposit Pattern

According to the pattern on how the solids and solutes are deposited onto the membrane, fouling can be classified into (Figure 4.10);

- cake layer formation
- pore narrowing
- pore plugging

Cake layer formation has been already explained in the previous section. Pore plugging occurs when particles become stuck in the pores of a membrane. Particles and/or microbial cells slightly bigger than the pore size, or particles of the same size as the pore size are caught in pores, resulting in jammed particles in pores. Pore narrowing also happens when solute and particulates smaller than the pore diameter deposit onto the surface of a membrane as well as in the interior pore walls.

These individual fouling patterns always occur simultaneously, and cannot be observed in activated sludge filtration.

4.2. Classification of Fouling(14/16)

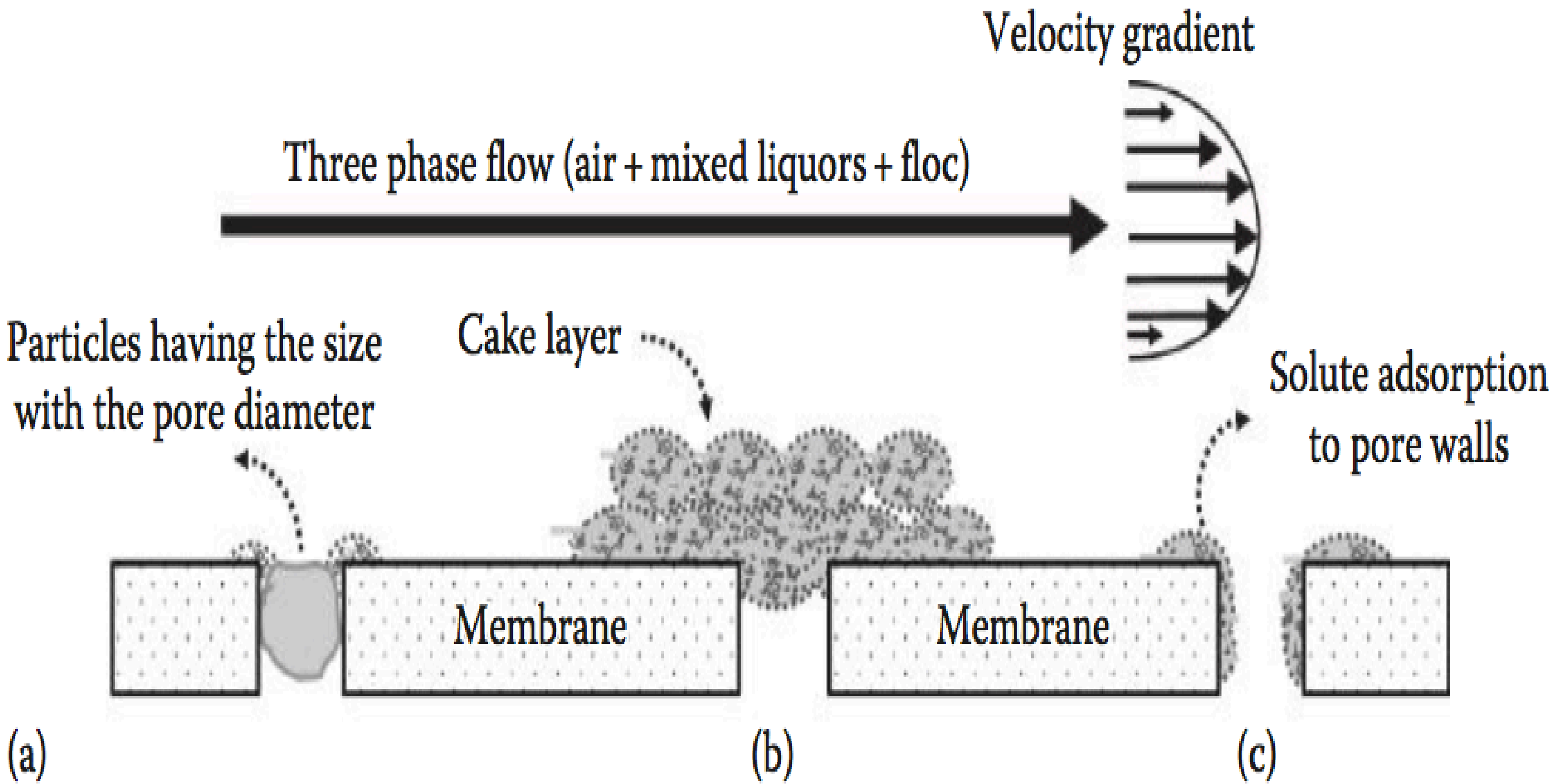

Figure 4.10. Membrane fouling pattern in MBR (a) pore clogging (or plugging) caused by particles with sizes similar to the pore, (b) cake layer deposition, and (c) pore narrowing mainly caused by dissolved solutes.

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4.2.4. Solute Fouling

4.2.4.1. Concentration Polarization

Concentration polarization due to concentration gradients formed near the membrane surface also happens in MBR as like all other membrane filtration processes.

Concentration polarization cannot be distinguished well from the cake layer, and as a result, concentration polarization is not considered important in MBR operation.

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4.2.4.2. Gel Layer Formation

Gel layers are often confused with the cake layers. A gel layer consists of highly concentrated solutes and macromolecules rather than particulates. As the concentration polarization progresses near the membrane surface, the gel layer forms and expands. However, gel layers are easily incorporated into cake layers so it is difficult to distinguish the two. Gel layers are simple and consolidated cake layers.

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4.3. Types of Foulants

Unlike the simple and well-defined chemical nature of membrane properties, mixed liquor in an aeration basin has complex characteristics because it consists of many constituents that are not easily defined.

Figure 4.11 summarizes each constituent present in mixed liquor as potential candidates for foulants.

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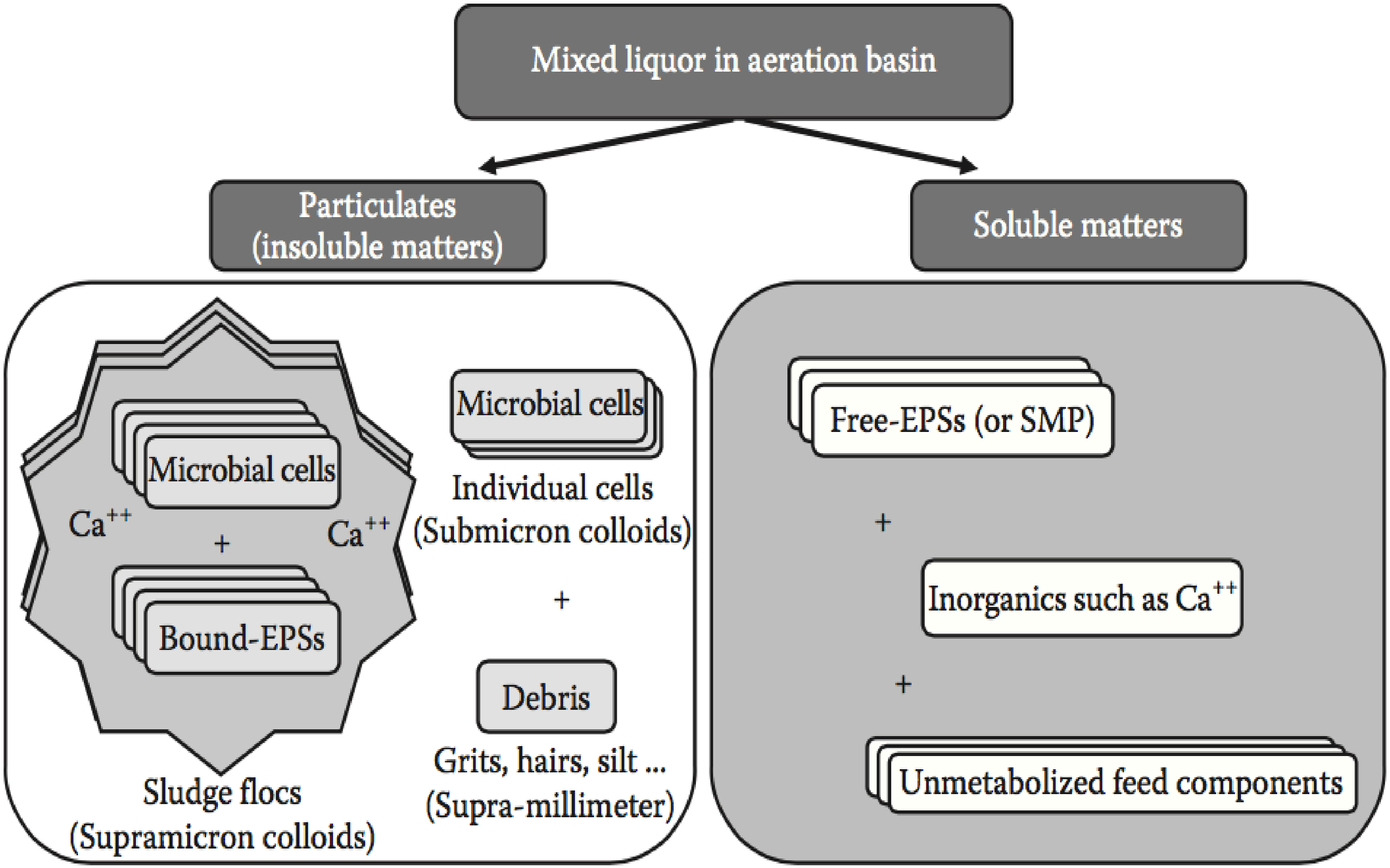

Figure 4.11. Conceptual illustration showing each component of activated sludge mixed liquor.

4.3. Types of Foulants(3/17)

4.3.1. Particulates

Membrane filtration is basically a sort of solid–liquid separation, the particulates in an aeration basin should be primarily considered as important foulants in the MBR. The majority of particles in the mixed liquor based on mass are the activated sludge flocs.

4.3.1.1. Flocs

An activated sludge floc can be defined as a microbial entity that is formed by different species. Individual microbial cells are interconnected by EPSs and cations such as Ca^{2+} ions.

MLSS is a basic in activated sludge. So, the effect of MLSS concentration on membrane fouling is very important. MLSS concentration is believed strongly to have a correlation with fouling. Because the viscosity of mixed liquor and filtration resistance increases as the MLSS concentration increases.

Debris such as grit, hair, and plastic materials are categorized into particulates. Proper preliminary treatments such as screens and/or grit chambers can solve these kinds of problems.

4.3.1.2. Floc Size

Figure 4.12 is one example diagram showing floc size distribution of activated sludge suspensions with different MLSS concentrations.

Particles that are between 1 and 100 μm in size are often classified as supracolloidal solids, and particles >100 μm are called settleable solids. Colloidal particles are between 0.001 and 1 μm in size

The majority of the mixed liquor of activated sludge seems to belong to the settleable solids based on sludge volume frequency. However, the number of small (>10 μm) and colloidal (>1 μm) particles is greater than that of the settleable solids.

The particles in the cake layer deposited on membrane surfaces are compressed by the convection flow toward membrane surfaces. However, the particles move backward from the cake layer to the bulk solution simultaneously due to diffusion caused by concentration gradients (back transport).

4.3. Types of Foulants(5/17)

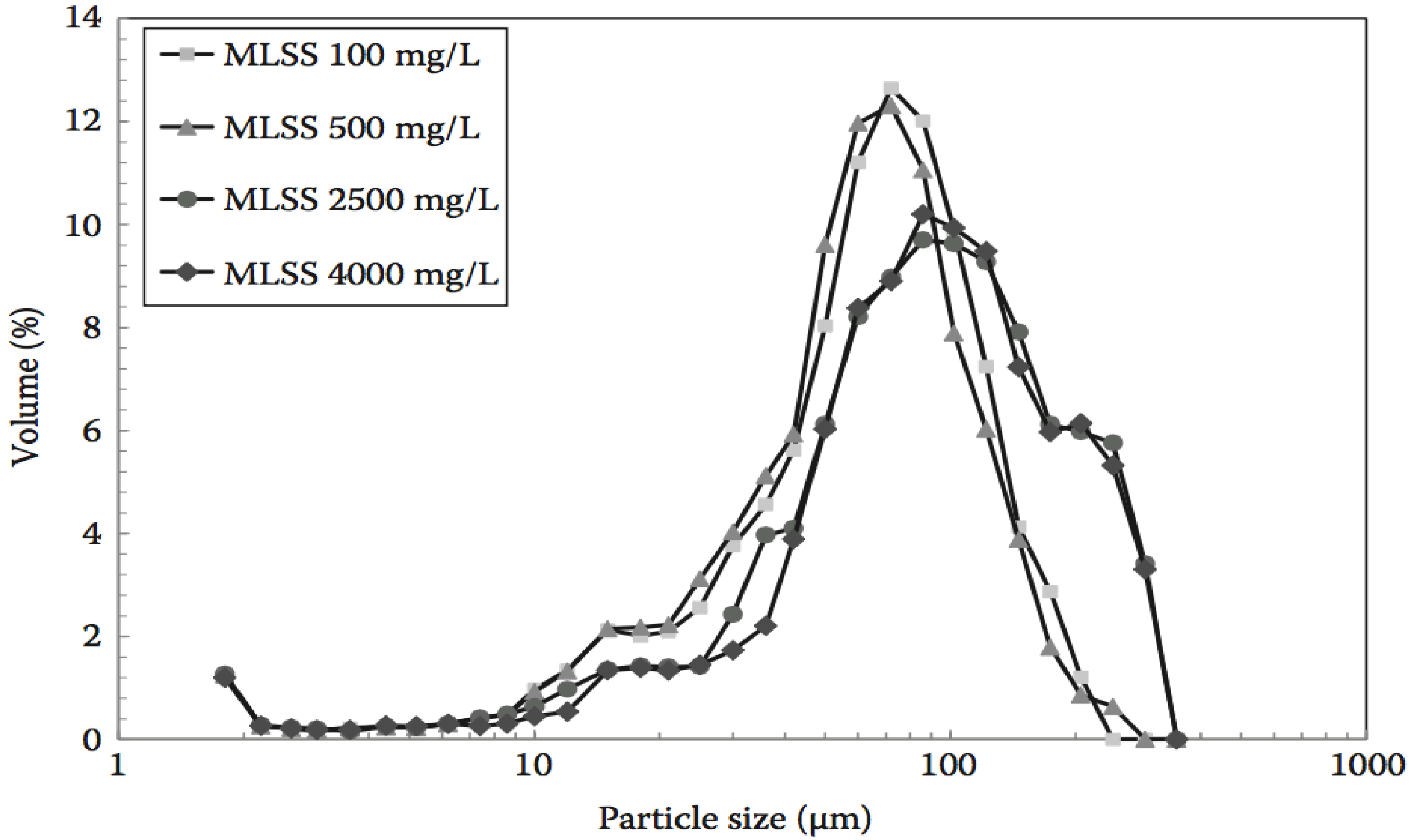

Figure 4.12. Typical particle size distribution of activated sludge with different MLSS concentrations.

The smaller the particle size is, the slower back transport is. This results in a diminished scouting impact on the cake layer, leading to insufficient cleaning.

4.3. Types of Foulants(6/17)

4.3.1.2. Floc Size (Cont.)

Therefore, particle size is one of the most important parameters related to membrane fouling in MBRs. The average floc size found in conventional submerged- type MBR is around 80–160 μm.

Floc size depending on;

- ✓ microbial physiology
- ✓ influent characteristics
- ✓ WWTP site

Average floc size in sidestream MBR is much smaller than that of submerged-type MBR. Because, transfer provides the flocs a shear force, and the flocs experience disintegration (or deflocculation).

A small number of bigger particles occupy most of the total volume. the number of fine particles is obviously greater than that of the bigger particles. Because the contribution of smaller particles to membrane fouling is more important than that of bigger particles.

4.3. Types of Foulants(8/17)

4.3.1.3. Extracellular Polymeric Substances

Microbial EPSs are high-molecular-weight mucous secretions from microbial cells. EPSs play an important role in floc formation of individual cells and include heterogeneous polymeric materials including polysaccharides, proteins, lipids, and humic-like substances as major components and phospholipids and nucleic acids such as DNA and RNA as minor constituents. Among these components, polysaccharides and proteins play a significant role in membrane fouling.

EPSs provide a highly hydrated gel matrix, so they provide a significant barrier to permeate flow in MBRs. The EPSs inside flocs are called bound EPSs, and the EPSs that are present in the bulk solution in a soluble state are called free EPSs.

Generally speaking, high concentrations of EPSs inside flocs as well as in bulk solution are responsible for rapid fouling buildup.

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4.3.1.4. EPS Extraction and Quantitative Analysis of RPS Components

Quantitative determination of foulant concentrations is important for setting up a strategy for fouling control. Figure 4.14 shows a general protocol for EPS extraction from fouled membranes in MBR.

The main components of EPSs that affect membrane fouling are proteins and polysaccharides. Carbon 13 isotope nuclear magnetic resonance (^{13}C-NMR) analysis confirmed that foulants are rich in proteins and polysaccharides. Fourier transform infrared (FTIR) analysis also confirmed the presence of amide I and II peaks (1638 and 1421 cm^{-1}) and a carbohydrate-like substance peak.

The molecular weight distribution of bound EPSs could be identified by chromatographic analyses, such as size-exclusion chromatograph (or gel permeation chromatograph). Gorner et al. (2003) revealed that the proteins' molecular weight ranged from 45 to 670 kDa. However, the polysaccharides had very small sizes of <1 kDa and were present in smaller amounts than the proteins.

4.3. Types of Foulants(10/17)

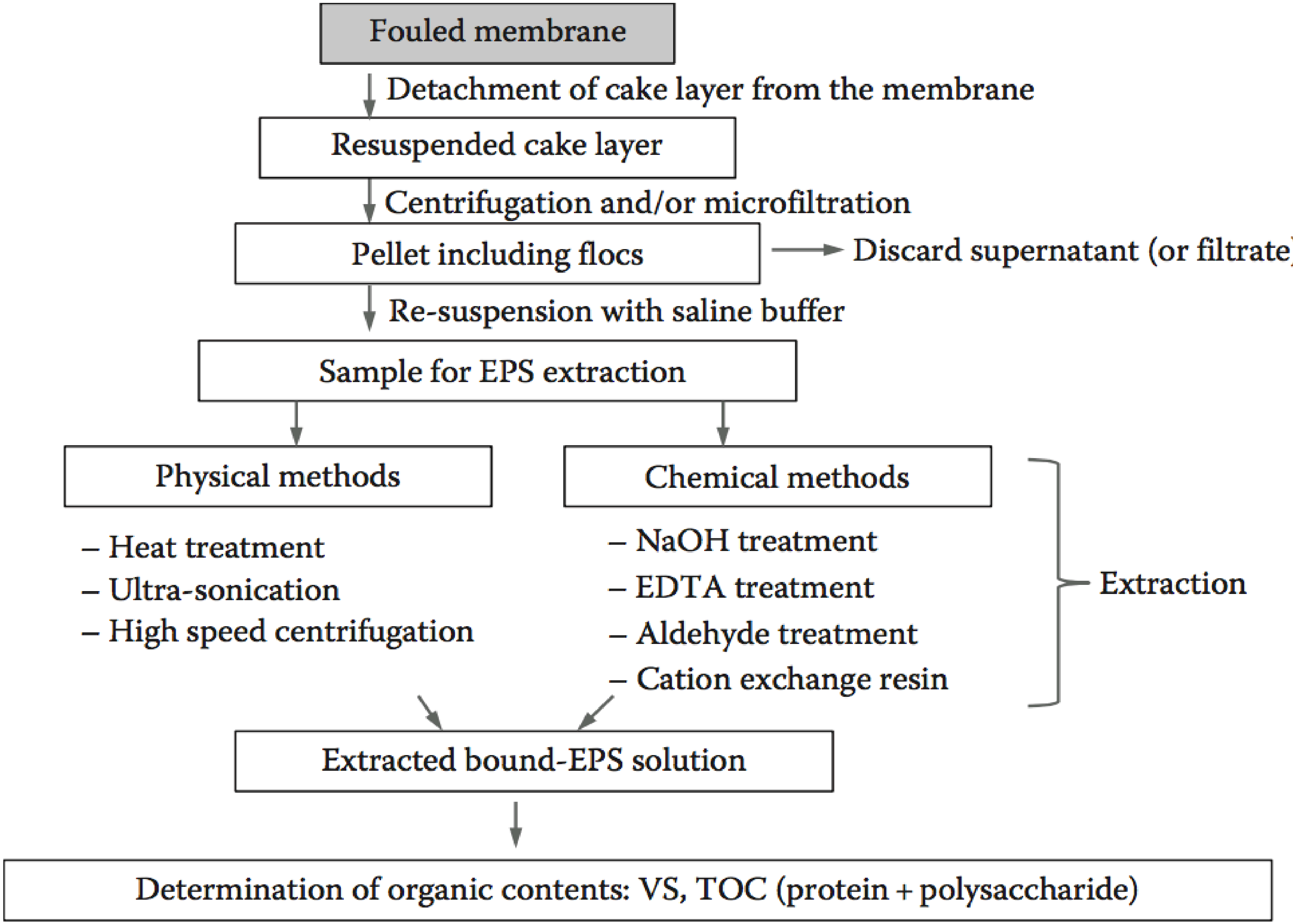

Figure 4.14. EPS extraction procedure for a fouled membrane in MBRs.

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4.3.2. Soluble Matter

Soluble matter is divided into two categories:

1. Unmetabolized feed components from influent wastewater
2. SMPs secreted by microorganisms.

SMP is a more comprehensive term than soluble EPSs because soluble EPSs indicate only the macromolecules. However, it is very difficult to distinguish both of them by chemical analysis because their basic chemical composition is similar, the proteins and polysaccharides.

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4.3.2.1. SMPs or Free EPSs (Soluble EPSs)

The terms SMPs and soluble EPSs are used with confusion when they are used to describe key membrane foulants in MBRs. Basically:

- **SMPs** represent all kinds of soluble organics excreted from microbial metabolism including monomers, oligomers, or polymers.
- **EPSs** obviously have a polymeric nature, but the borderline dividing polymers and oligomers is obscured to some extent. Moreover, unmetabolized feed components are not related to microbial excretion products, but they are categorized into SMPs or soluble EPSs when they are chemically analyzed.

Practically, it is difficult to analyze or differentiate SMPs and EPSs no matter where they originate (either cells or feed solution). Therefore, some research groups categorize all EPSs and SMPs into a single group called biopolymeric cluster (BPC). Le-Clech et al. (2006) distinguished between EPSs and SMP as shown in Figure 4.15, and they proposed a method for EPS and SMP extractions and measurements.

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4.3. Types of Foulants(13/17)

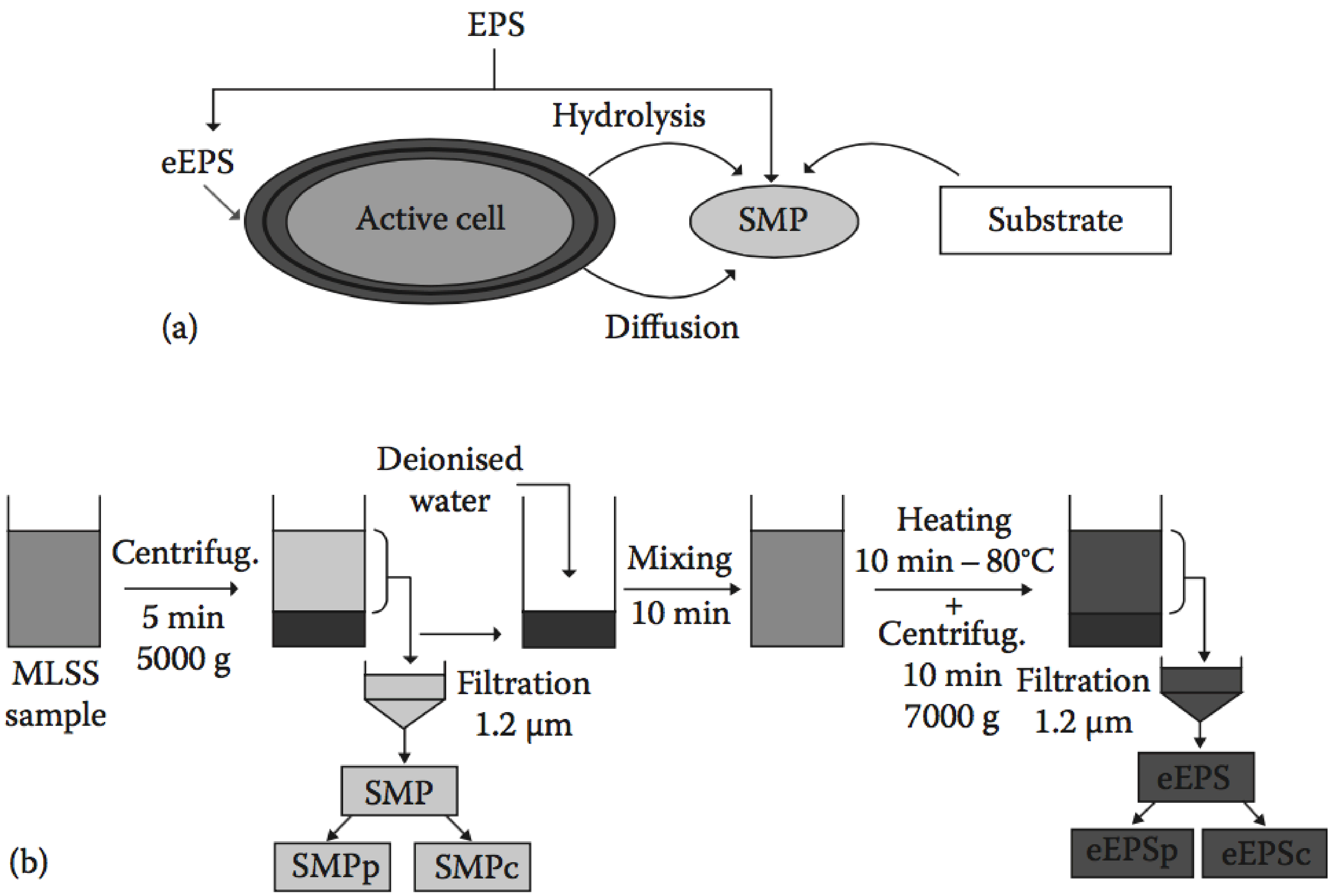

Figure 4.15. (a) Simplified illustration of Eps, eEPS, and SMP and (b) a proposed method for EPS and SMP extractions and measurements.

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4.3.2.1. SMPs or Free EPSs (Soluble EPSs) (Cont.)

The protein and carbohydrate components of the SMPs are analyzed further and designated as either SMPp or SMPc. The pellet remaining after centrifugation is resuspended by de-ionized water and the eEPSs (i.e., bound EPSs) are extracted by one of the procedures described previously. Finally, they are separated into eEPSp (proteins) and eEPSc (carbohydrates).

The fouling caused by the free EPSs is believed to be less severe than that of the fouling caused by bound EPSs because the predominant fouling in MBRs is usually dependent on the extent of cake layer fouling.

Wang and Wu (2009) reported that the MW of EPS in MBR was 2.2–2,912 kDa, and conventional activated sludge (CAS) systems contained MWs that ranged from 2.4 to 18,968 kDa.

Thank you…