Yıldız Technical University
Department of Environmental Engineering

MEMBRANE BIOREACTORs

Week 3th: Membranes, Modules, and Cassettes

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

CEV4362 MEMBRANE BIOREACTORS

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12:00 - 12:50 FZ-82

Instructor: Prof.Dr.Özer ÇINAR, C Bloc 1-010 Environmental

Engineering Department

Phone: 5366   **e-mail:** ocinar@yildiz.edu.tr

Week 3th: Membranes, Modules, and Cassettes

3.3. Membrane Fabrication

➢ **Membrane Fabrication Methods**

➢ **Solubility Parameter for NIPS and TIPS Processes**

➢ **Phase Separation and Triangular Phase Diagram**

3.4. Membrane Characterization

    ➢ **Dimensions**

    ➢ **Pore Size Distribution**

    ➢ **Hydrophilicity (Contact Angle)**

    ➢ **Charge Characters (Zeta Potential)**

    ➢ **Roughness (Atomic Force Microscopy)**

3.3.1. Membrane Fabrication Methods

There are three major membrane fabrication methods;

✓ NIPS (Non-solvent-induced phase separation)

✓ MSCS (Melt spinning cold stretching)

✓ TIPS (Thermal-induced phase separation)

3.3.1.1. NIPS (Non-solvent-induced phase separation)

There are two solvents used:

❖ **Good solvent,** in which the polymer dissolves well in the solvent

❖ **Poor solvent (or non-solvent)**, in which the polymer is incompatible with the solvent. However, the two solvents are compatible with each other.

When the polymer and "good solvent" solution are injected into the "poor solvent," the "good solvent" is extracted inside of the polymer and "good solvent" solution and forms a solution with the "poor solvent," resulting in the gelation (or hardening) of the polymer.

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During the gelation of the polymer, the space where the "good solvent" occupied is converted into membrane pores. After rinsing to remove the residual "good solvent" and "poor solvent" solution and additives, the polymer is dried and acts as a membrane.

The shape and dimension of the injection nozzle and the composition of the polymer and "good solvent" in the solution decide the membrane's outer and inner diameter. Figure 3.4a shows pores on a membrane surface fabricated by the NIPS process.

Polymers have either a crystalline lamella structure (rigid) or an amorphous interlamella structure (flexible). The general structure of polymers is shown at Figure 3.3.

Polymers have two transition temperatures:
- ✓ The glass transition temperature (Tg). The amorphous structure becomes very active at Temperature > Tg.
- ✓ The melting point (Tm). The crystalline structure becomes very active at temperature >Tm.

Amorphous region

Crystalline region
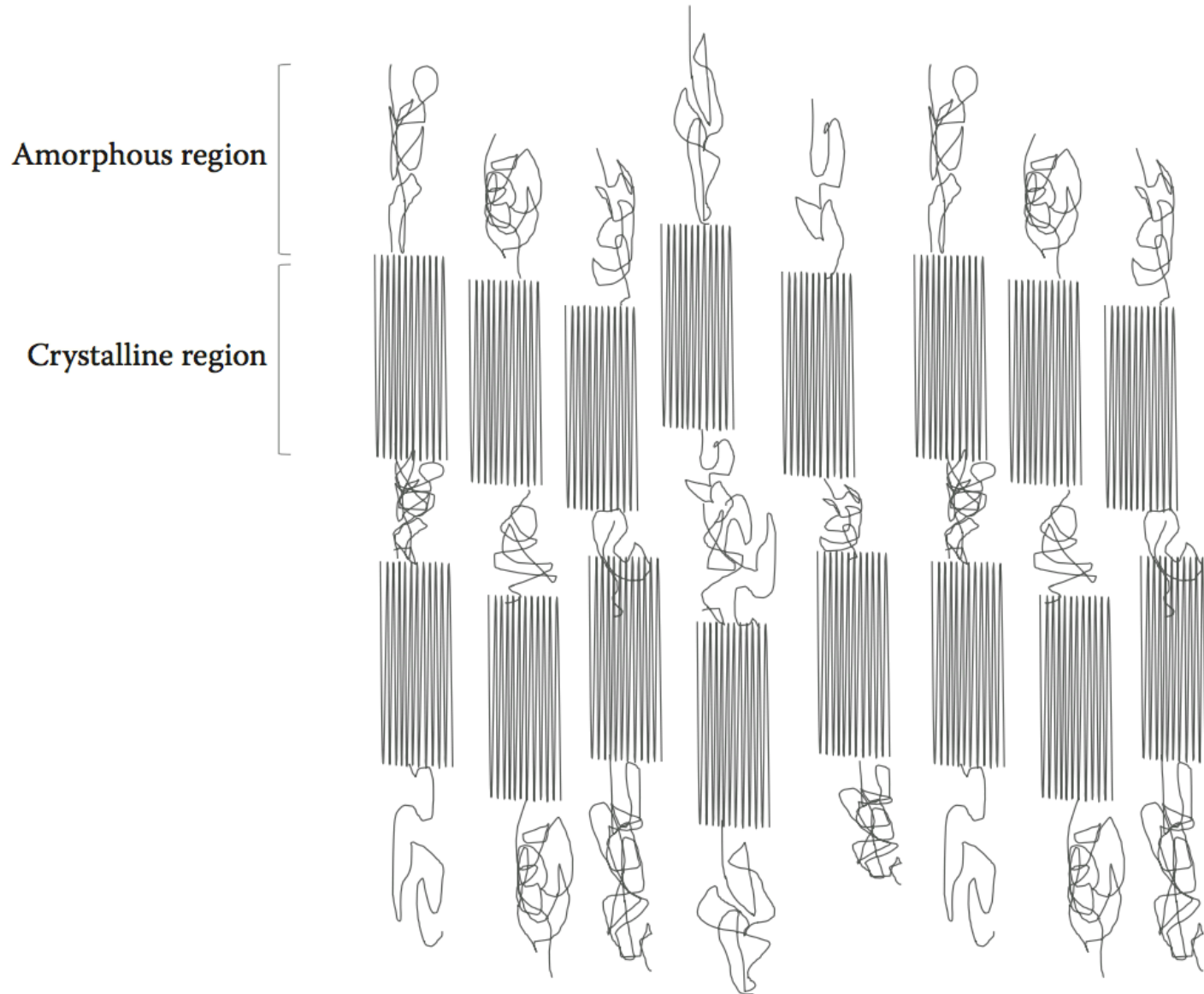
Figure 3.3. Amorphous and crystalline regions in a polymer.

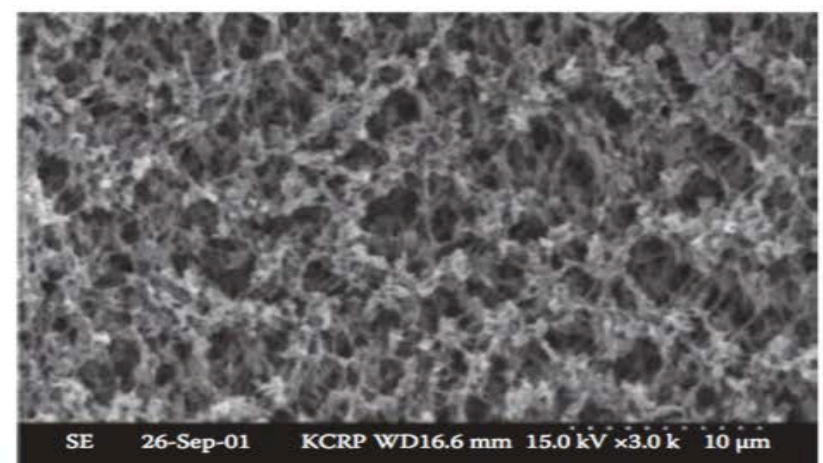**Yıldız Technical University**
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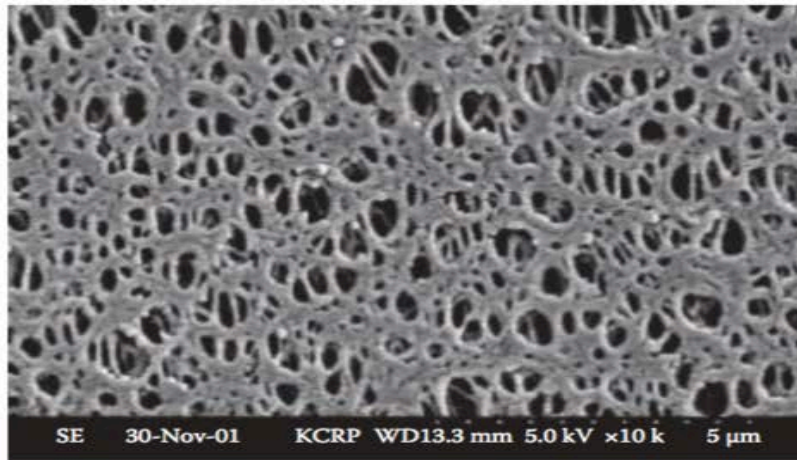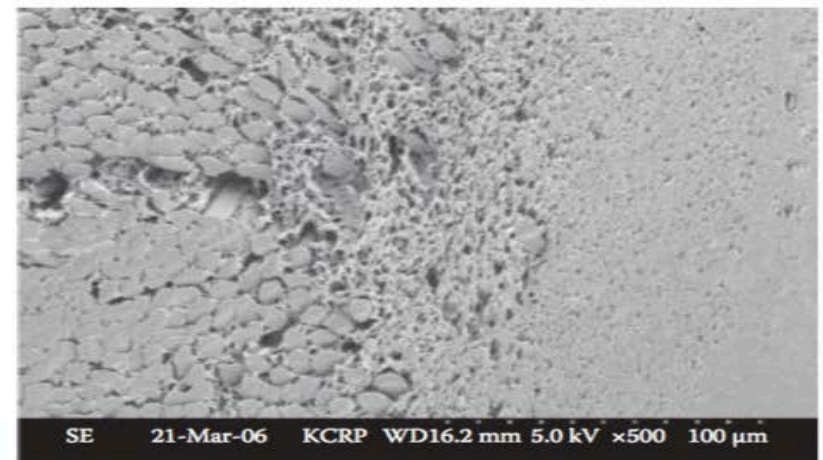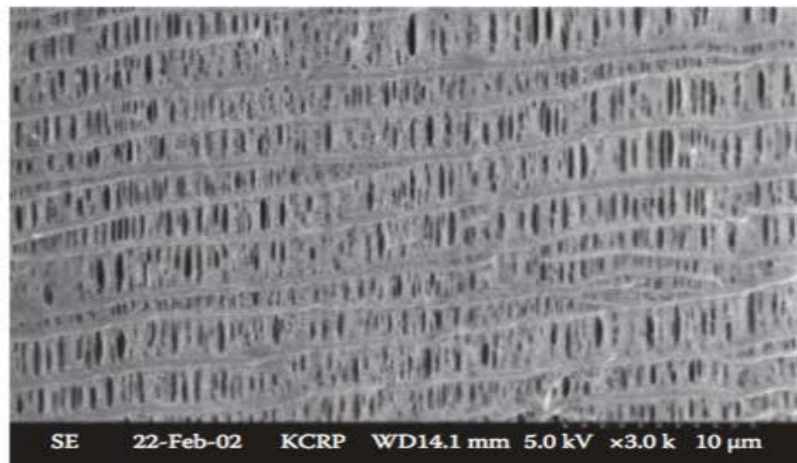
Figure 3.4. Pictures of membranes fabricated by (a) the membrane surface by NIPS, (b) cross section of the reinforced membrane, (c) membrane surface by MSCS, and (d) membrane surface by TIPS.

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3.3.1.2. MSCS (Melt spinning cold stretching)

MSCS uses the Tm of polymers (without "good solvents") at room temperature. Melted polymers are cooled to just under the Tm and one or two directional stretching are applied. The crystalline lamella structure in the polymer retains its morphology, but the amorphous interlamella structure in the polymer is lengthened and has larger spaces that can act as membrane pores.

Figure 3.4b shows that these membranes have very anisotropic pore shapes, resulting at a wider pore size (approximately 0.4 µm) distribution than any other method unfavorable for membrane integrity. It is impossible to make UF membranes with this method. For this reason, MSCS membranes are mainly applied to MBR processes (not drinking water treatment).

MSCS can produce the cheapest membranes because the price of the main polymers for MSCS, such as PE or PP, is cheap.

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3.3.1.3. TIPS (Thermal-induced phase separation)

TIPS has the intermediate position between NIPS and MSCS in terms of fabrication mechanisms.

TIPS uses the difference between solubility and thermal melting point. The TIPS polymer is dissolved by solvents (or diluted) by diluents at a high temperature, and then it is quenched in cold liquid that extracts the solvents (or diluents) and induces membrane pores. Sometimes a stretching process is followed to give mechanical strength (which is one of the major problems in TIPS) to the membrane. All polymers that can be used in NIPS or MSCS methods are applicable.

New membranes that both have strong points of TIPS and NIPS have been developed and are braid (support layer) reinforced membranes. Their tensile strength is 20–30 kgf/cm^2 and is 30 times higher than that of any membrane, and they do not easily break during operation.

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3.3.2.Solubility Parameter for NIPS and TIPS Processes

The compatibility of a solvent to a polymer, that is to say, the intensity of the dissolution tendency of a polymer into a solvent, is also known as the "solubility parameter." A polymer becomes more soluble in a solvent when their relative solubility parameters are close to each other and vice versa.

The quantity $(\Delta E/V)^{1/2}$ is defined as the "solubility parameter" (δ_{sp}) and can be obtained both for the polymer repeating unit and for the solvent. The solubility parameter can be divided into three components;

$$\delta^2_{sp} = \delta^2_d + \delta^2_p + \delta^2_h$$

where
δ^2_d is the van der Waals force
δ^2_p is the dipole moment
δ^2_h is the hydrogen bonding force component

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Example 3.4

See solubility parameters in Tables 3.3 and 3.4 and suggest the compatibility of solvents (hexane, N,N-dimethyl formamide (DMF) and water) with each given polymer:

(a) PE, (b) PAN, and (c) CA (56% acetate groups)

Solution

In Table 3.3 we can see the solubility parameters of hexane, DMF, and water, which are 7.3, 12.1, 23.4 cal/cm^3, respectively. In Table 3.4 the solubility parameters of PE, PAN, and CA are 8.0, 12.5, and 27.8 cal/cm^3. The best matchups will be PE–hexane, PAN–DMF, and CA–water. We can expect the worst compatibility between water and PE because their solubility parameter difference is the biggest.

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3.3.4. Fabrication of Hollow Fiber and Flat Sheet Membrane

The NIPS process has five major steps:

1)   preparation of the polymer solution

2)   injection and molding

3)   quenching

4)   rinsing

5)   drying

In the fabrication process of hollow fiber or flat sheet membranes, the main differences are the injection nozzles and the molding parts.

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3.3.4. Fabrication of Hollow Fiber and Flat Sheet Membrane

Hollow fiber membranes have dual spinning nozzles are used for injection and molding parts. The nozzles have one hole in the center and one donut in the cross section. The polymer–good solvent solution goes through the donut-shaped hole and the poor solvent goes through the center hole. The inner side of the polymer solution meets the poor solvent with the help of the center hole.

Flat sheet membranes have independent injection and molding parts. The polymer–good solvent solution is added to a porous support nonwoven fabric and then is submerged into the quenching tank. The gap between the knife (or blade) and the support is used to control the thickness of the membranes with the control of the concentration of the polymer solution

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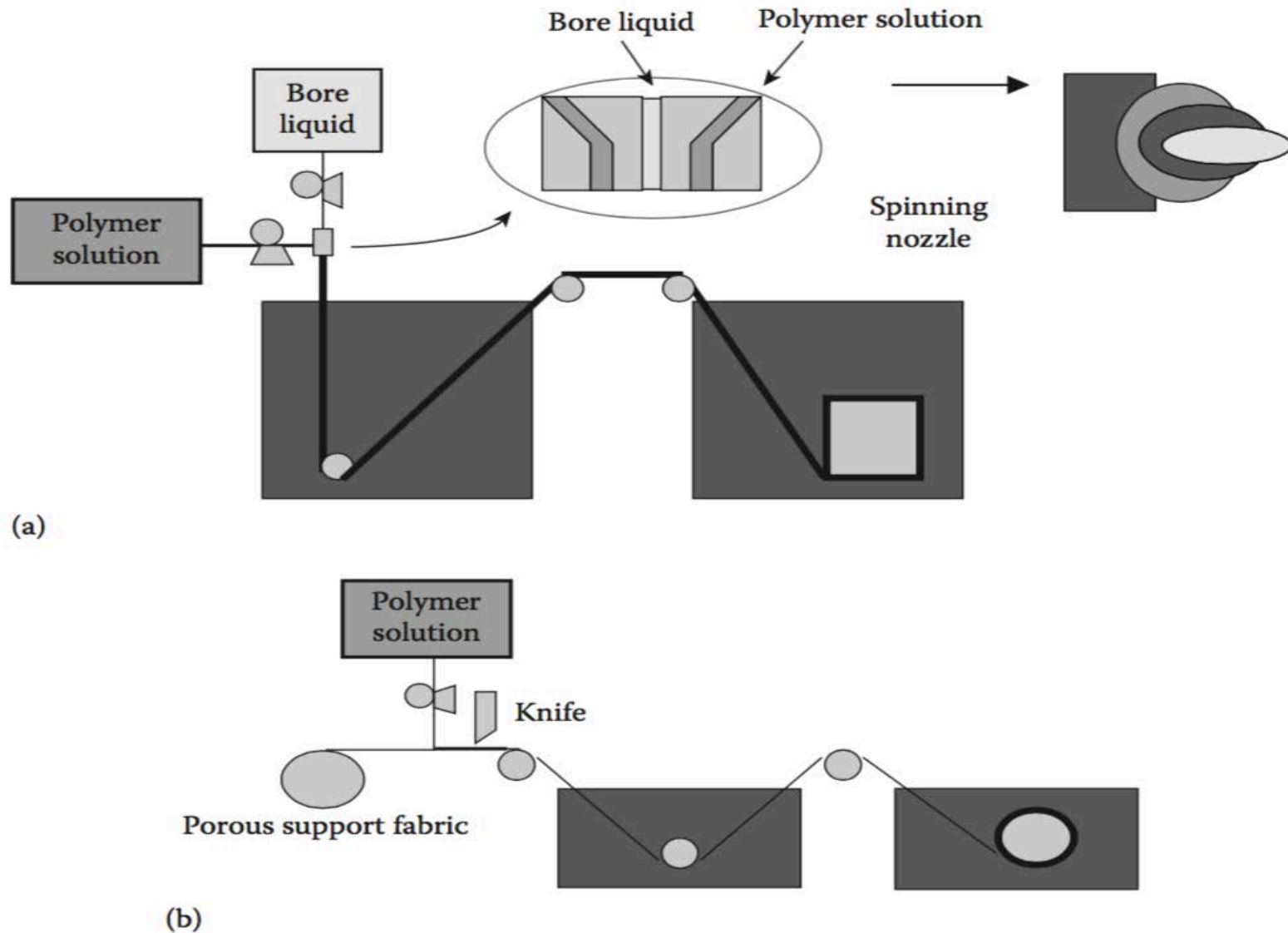
Figure 3.7. Schematic of (a) hollow fiber and (b) flat sheet membrane fabrication process.

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3.4.1. Dimensions

There are two major shapes of membranes;

➢ hollow fiber type

➢ flat sheet type

The main dimensions of hollow fiber membranes are the outer diameter, inner diameter, and membrane length. Hollow fiber membranes are frequently divided into two groups; tubular membranes (membranes diameter > 3 mm) and hollow fiber membrane (membrane diameter < 3 mm). In view of membrane morphology, hollow fiber membranes are divided into two groups: (1) out-to-in permeation type and (2) in-to-out permeation type.

The main dimensions of flat sheet membranes are the thickness, length, and width. Flat sheet membranes are used as flat sheets and sometimes are wound tightly to form spiral wound membranes in modules.

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Example 3.7

Calculate the effective area of the two types of membranes:

(a) *Hollow fiber membrane (out-to-in permeation)*: The inner diameter is 0.80 mm, outer diameter is 1.2 mm, and membrane length is 50 cm.
(b) *Flat sheet membrane*: The width is 0.50 m, length is 1.0 m, and thickness is 0.70 mm. Both sides can act as a membrane.

Solution

(a) The effective *membrane* area of the hollow fiber type is calculated by

$$A = (2\pi r) \times L$$

where the radius of the cross-sectional circle of the membrane (r) is 0.60 mm and the membrane length (L) is 50 cm. Then the effective membrane area A is

$$A = (2\pi)(0.60 \times 10^{-3} \text{ m})(50 \times 10^{-2} \text{ m}) = 1.9 \times 10^{-3} \text{ m}^2$$

(b) The effective membrane area of the flat sheet type is calculated by

$$A = W \times L \times 2$$

where the width of the membrane (W) is 0.50 m and the membrane length (L) is 1.0 m. Then the effective membrane area A is

$$A = (0.50 \text{ m})(1.0 \text{ m})(2) = 1.0 \text{ m}^2$$

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3.4.2. Pore Size Distribution

The direct way to evaluate the pore size distribution of membranes is to measure all pores with a ruler in a picture of a membrane surfaces by an electric microscope (FE-SEM). But, it is difficult to represent the total pore size distribution by measuring FE-SEM images of the membrane surface. We need bulk information of the pore size distribution and there are three methods that can satisfy these needs.

➢ Bubble Point

➢ Particle Rejection

➢ Polymer Rejection

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Bubble Point:

This method is based on the bubble point theory. A dry membrane (all pores are occupied by air) membrane pores are fully wetted by a liquid that has enough surface tension to fill all of the pores occupied by air, there needs to be more pressure so that air goes through the membrane pores again. The larger the pore size, the lower the inlet air pressure that needs to force the air back through the membrane pores. The lowest pressure required is called the "bubble point," and this pressure is directly related to the largest membrane pore diameter, the surface tension of the retained liquid, and the contact angle between the pore and the liquid.

$$P = \frac{4k\sigma\cos\theta}{d}$$

where

P is the lowest applied air pressure, psi

k is the pore shape correction factor, unitless

σ is the surface tension at the liquid/air interphase, dyn/cm

θ is the wetting angle, °

d is the diameter of the largest pore, μm

It is not easy to measure flat sheet–type membranes wetting angles in contrast with hollow fiber type. So, the morphology of most membranes for water and wastewater treatment is mainly of the hollow fiber type.

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Example 3.10

We conducted bubble point tests with several pore sizes of membranes. Calculate the bubble point pressures of the diverse range of membrane pore sizes. The surface tension of water is 72.0 dyn/cm. All of the membrane samples have the same contact angle of 75°:

(a) Pore diameter is 0.00500 μm (UF).
(b) Pore diameter is 0.0100 μm (MF or UF).
(c) Pore diameter is 0.100 μm (MF).

Solution

In Equation 3.13,

$$P = \frac{4k\sigma\cos\theta}{d}$$

(a) where k = 1, σ = 72.0 dyn/cm, cos 75° = 0.259, and d = 0.00500 μm

$$P = \frac{4k\sigma\cos\theta}{d} = \frac{(4)(1)(72.0\ dyn/cm)(0.259)}{(5.00\times10^{-7}\ cm)}$$

$$= 1.49\times10^8\ dyn/cm^2 = 149\ bar$$

(b) where k = 1, σ = 72.0 dyn/cm, cos 75° = 0.259, and d = 0.0100 μm

$$P = \frac{4k\sigma\cos\theta}{d} = \frac{(4)(1)(72.0\ dyn/cm)(0.259)}{(1.00\times10^{-6}\ cm)}$$

$$= 7.46\times10^7\ dyn/cm^2 = 74.6\ bar$$

(c) where k = 1, σ = 72.0 dyn/cm, cos 75° = 0.259, and d = 0.100 μm

$$P = \frac{4k\sigma\cos\theta}{d} = \frac{(4)(1)(72.0\ dyn/cm)(0.259)}{(1.00\times10^{-5}\ cm)}$$

$$= 7.46\times10^6\ dyn/cm^2 = 7.46\ bar$$

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Particle Rejection:
There is an assumption that the size of the smallest rejected particles is the same as the membrane pore size. Several sizes of particle emulsion or suspension standards whose concentrations are known are required. Each standard emulsion or suspension is filtered by a sample membrane, and then the concentration of the permeated water is measured by a ultraviolet-visible spectroscopy (UV-VIS) absorption photometer, reflective index detector, evaporative light scattering detector, etc. The rejection ratio R is calculated from the before and after filtering concentrations as follows:

$$R = \frac{(C_{in} - C_{out})}{C_{in}} \times 100\%$$

where
C_{in} is the reference concentration, %
C_{out} is the concentration of permeated water, %

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Polymer Rejection:

The basic mechanism of polymer rejection is the same as that of particle rejection, but there are two major differences between the two.

One difference is the state of sample solution. Particle standards are in an emulsion or suspension, so when their concentrations are measured by an optical detector, there is a deviation caused by unwanted interactions between the optical equipment and the suspended particles that alter the results. Unwanted interactions are anything that causes light intensity loss that is not absorption like diffraction or reflection.

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Polymer Rejection (Cont.):

The other difference between polymer and particle rejection is the detection method. Sample solutions include continuous size spectrum depending on the molecular weight of the polymer. The molecular weight distribution of each sample and permeate solution is measured by gel permeation chromatography (GPC). Unlike particle rejection, this method shows the linear relation between rejection and molecular weight. If all the molecular weight data need to be converted to particle size information, there are additional analysis methods available such as static laser light scattering spectroscopy.

3.4.3. Hydrophilicity

Most polymer-based membranes are hydrophobic. Hydrophobic membranes are not easily wetted by water, or the air in the membrane pores is not easily substituted by water. Unless the membrane is wetted, there cannot be water permeation through the pores. Without the help of a wetting agent such as glycerin or alcohol, hydraulic pressure will be required to expel the air out of pores.

The most serious disadvantage of hydrophobic membranes is the high fouling potential. The major foulants in MBR are biomass in the forms of activated sludge floc and some organic matters produced by microbes. They are usually hydrophobic, so there is a very strong adhesive potential between foulants and hydrophobic membranes. In order to lessen this problem, some hydrophilic additives are supplied to the membrane in fabrication to reduce hydrophobicity.
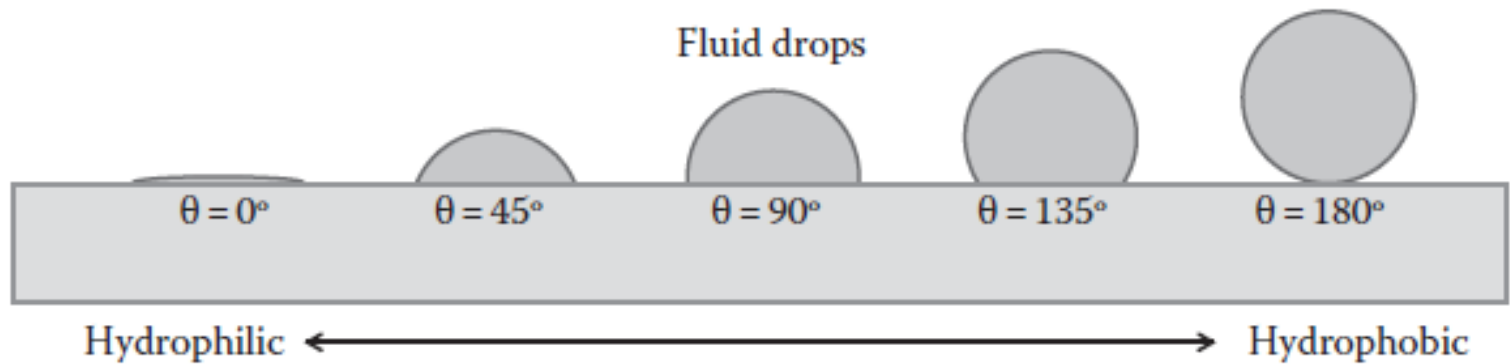
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Figure 3.19   Sessile drops on surfaces of samples.

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3.4.4. Charge Characters (Zeta Potential)

In solution all materials have their own surface electric charge including membranes and foulants. Along with hydrophilicity and roughness, the surface electric charge is closely related to fouling. Foulants are typically divided into four groups:

➢ particles

➢ organic matters

➢ scaling ionic salts

➢ microbes

The major foulants of MF or UF membrane are organic matters. Organic matters generally have negative surface charges in water, so the higher the negative charge a membrane surface has, the less fouling potential the membrane experiences. The zeta potential is the quantitative value representing the electric charge on a membrane surface.

Zeta potential is measured by several methods including electrophoresis, electroosmosis, streaming potential, and sedimentation potential characteristics.
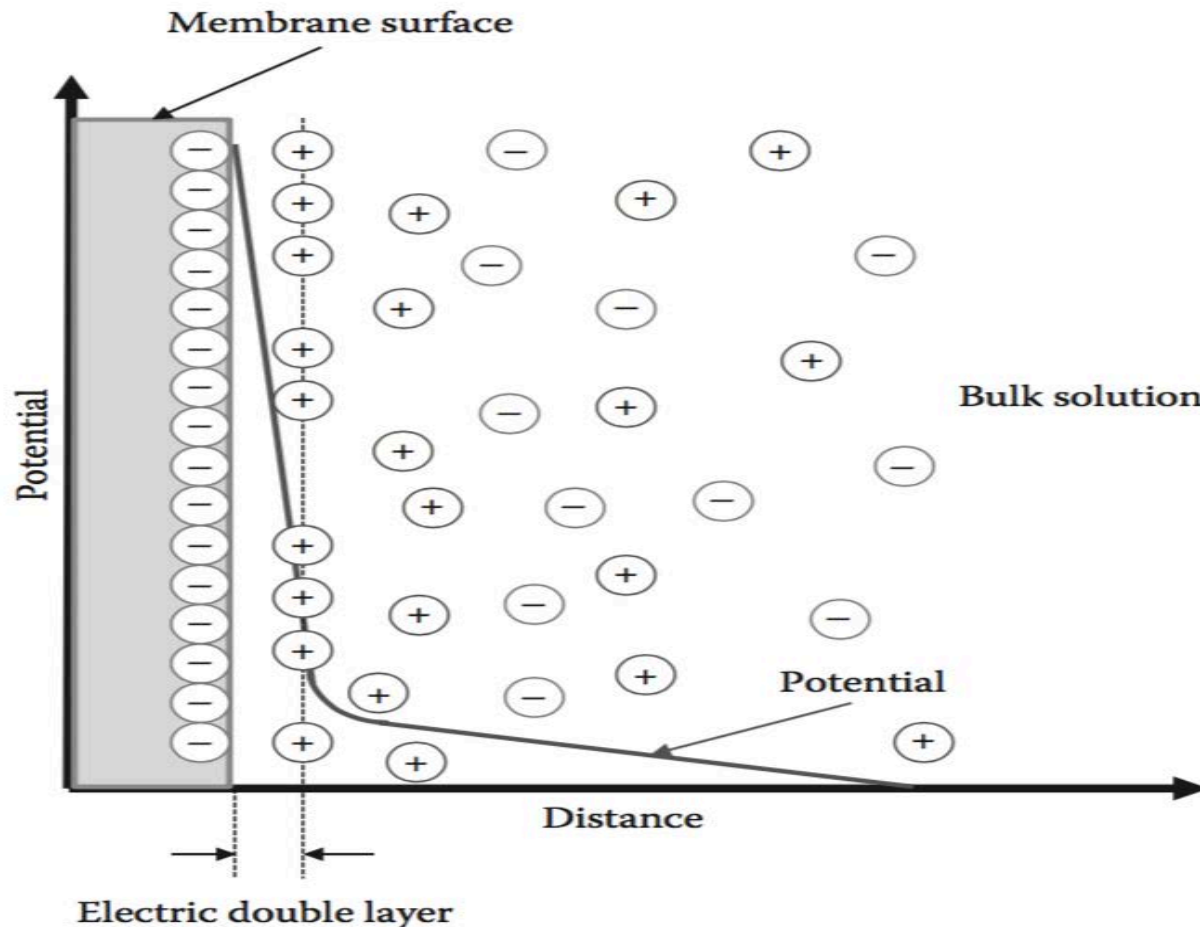

Figure 3.9. The structure of an electric double layer a membrane surface and zeta potential.

3.4.5. Roughness (Atomic Force Microscopy)

The roughness of a membrane surface is an important parameter for fouling. Generally, the rougher a membrane surface is, the more serious membrane fouling will be owing to wider contact areas and more intense interactions between foulants and the membrane surface.

The roughness of MF or UF membranes is measured by an atomic force microscope (AFM). AFMs are a type of scanning probe microscopes (SPMs). It uses a very sharp probe to scan the sample surface. There are many types of probes available and they each have different chemical and physical properties that interact with diverse sample surfaces.

Generally, different kinds of SPMs are classified by the types of probes and are made to measure the roughness;

➢ AFM

➢ magnetic force (magnetic force microscope [MFM])

➢ atomic arrangement (scanning tunneling microscope [STM])

➢ lateral force (lateral force microscope [LFM])

➢ force modulation (force modulation microscope [FMM])

➢ electrostatic force (electrostatic force microscope [EFM])

➢ capacitance (scanning capacitance microscope [SCM]), etc.

AFM uses a cantilever with a 30 nm end tip as the probe and can scan roughness larger than the tip size of the cantilever (30 nm). The interaction between the end tip and the membrane surface is dominated by van der Waals forces. The tip uses the repulsive interaction of van der Waals forces in the contact mode or attractive interaction in the noncontact mode.

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Thank you…