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280.371 Process Engineering Operations

Membrane Separation Processes
Lecture 4

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Ultrafiltration (UF)

- For separation and concentration
- Separation based on size
- Size range of separation characterised by MWCo (molecular weight cut-off)
- Separation of large MW compounds and colloids
- Available membranes 500 – 300,000 MWCo, but common 10,000 – 50,000 MWCo
- Operating pressure 0.2 – 1 MPa (2 – 10 bar)

Ultrafiltration membranes

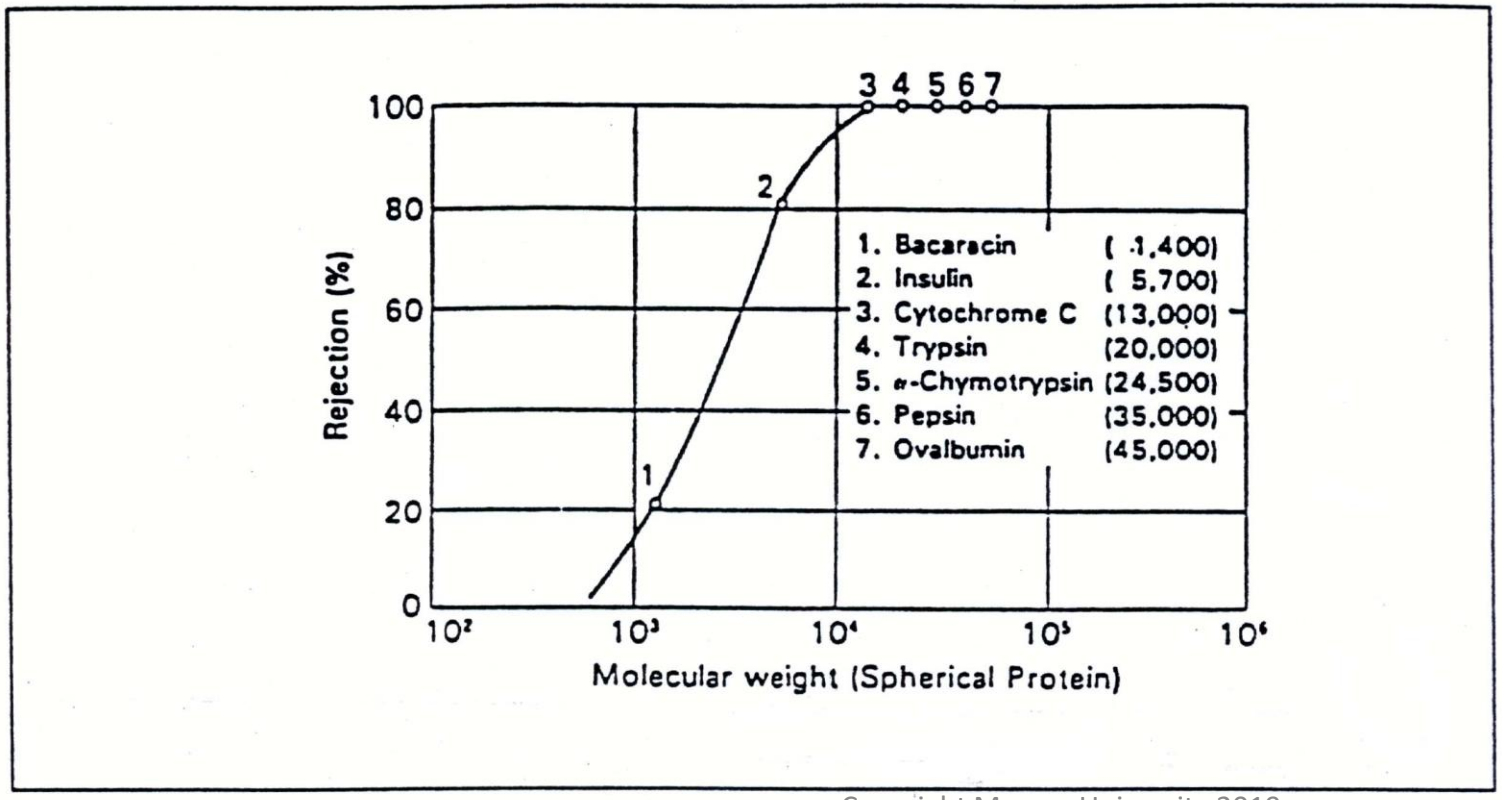
- Asymmetric membranes

- Polysulphone (PS) and Polyethersulphone (PES)
  - Wide temperature range, ph tolerant, chlorine resistance, ease of fabrication
- Polyvinylideneflouride (PVDF)
- Ceramic zirconium oxide

- Membrane characterisation by MWCo or **N**MWCo (nominal molecular weight cut-off)

Rejection and Molecular Weight Cut-off (MWCo)

MWCo for a globular protein	Approximate pore size (nm)
1,000	2
10,000	5
100,000	12
1,000,000	28



(Gutman, 1987; Toyomoto & Higuchi, 1992)

Ultrafiltration membranes

Separation achieved depends on:

- Size, shape and flexibility of molecule
- Membrane hydrophobicity and charge
- Membrane configuration and operating conditions
- Presence of other solutes in the feed
- Physico-chemical environment (pH, ionic strength, temperature)

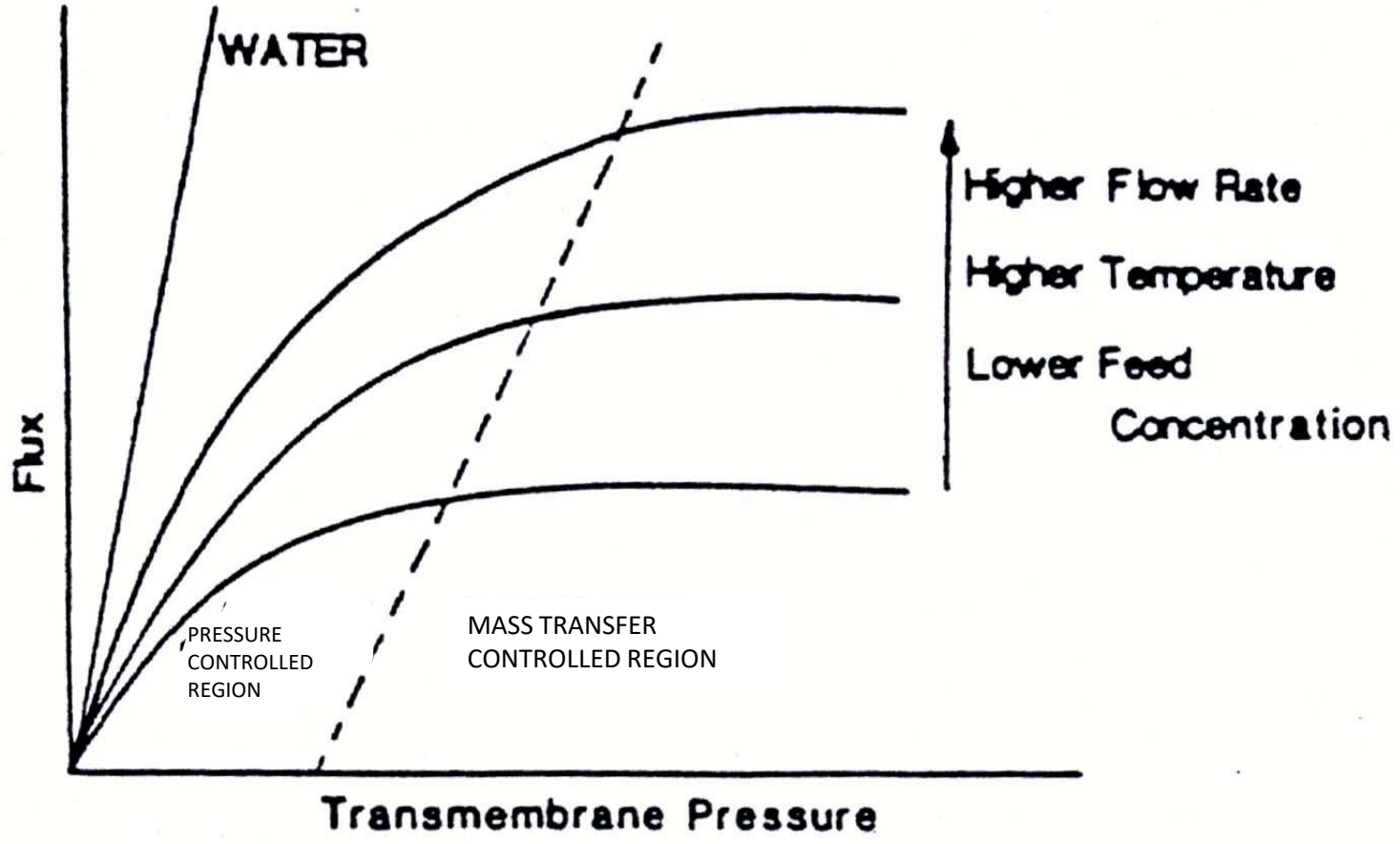
∴ This makes selection of the optimum system and operating conditions difficult

Ultrafiltration – Factors influencing flux

- **Pressure and flow rate**
  - Pure water flux
    - independent of cross-flow velocity
    - directly proportional to applied pressure
  - Limiting flux
    - Pressure controlled region
    - Mass-transfer controlled region

Ultrafiltration – Limiting flux

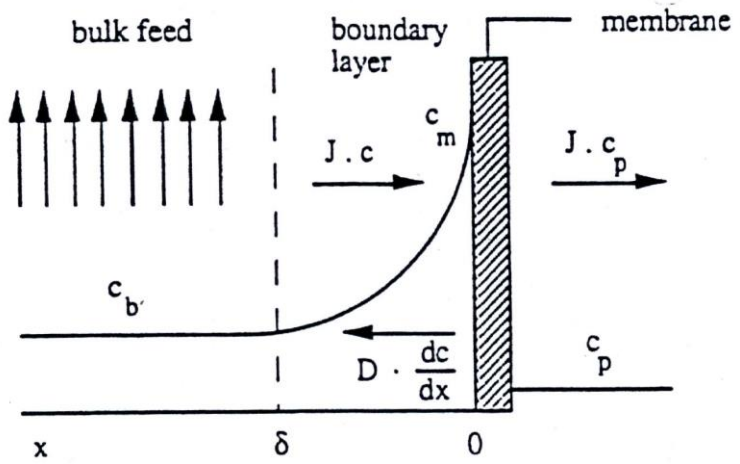
- Typically a process fluid in UF or MF will exhibit limiting flux



Remember

- modelling concentration polarisation

- If a steady state (dynamic equilibrium) is established the following relationship will hold



Solute transport to membrane + back diffusion of solute = removal rate of solute in permeate

(3) $$Jc + D\frac{dc}{dx} = Jc_p$$

limits $x \rightarrow 0$, $c = c_m$
$x \rightarrow \delta$, $c = c_b$

$$\frac{c_m}{c_b} = \exp\left(\frac{J}{k}\right)$$

Ultrafiltration – Limiting flux

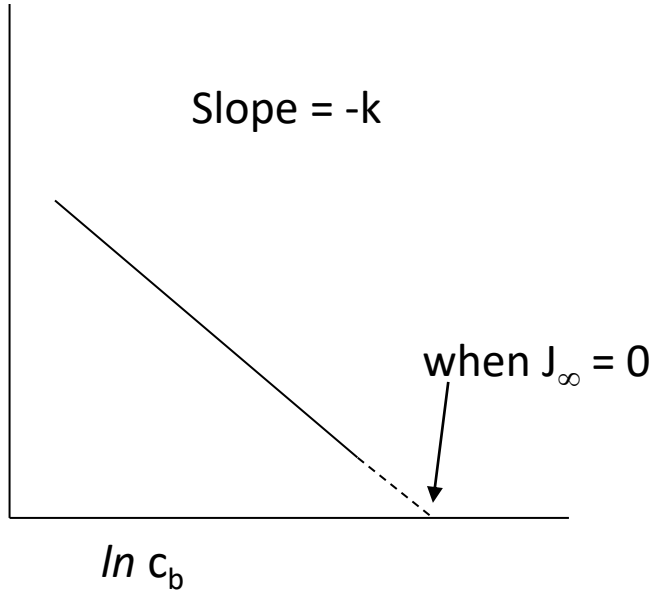
- At limiting flux, flux becomes independent of driving force

$$\frac{c_m}{c_b} = \exp\left(\frac{J}{k}\right)$$

$$Limiting flux \quad J = k \ln\left(\frac{c_m}{c_b}\right)$$

$$J = k \ln c_m - k \ln c_b$$

$$y = c + mx$$



Ultrafiltration

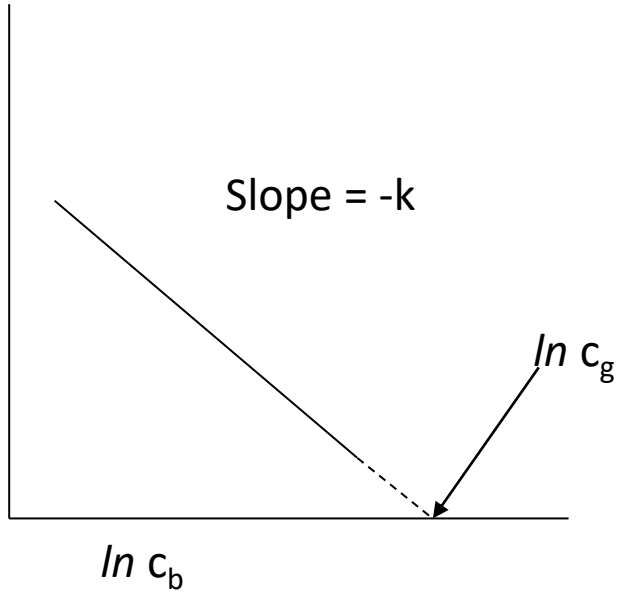
– Models proposed for limiting flux

- Gel Layer Model
  - Formation of protein gel on membrane surface
- Osmotic Pressure Model
  - Increased osmotic pressure adjacent to membrane surface, reducing the effective driving force.

Ultrafiltration

– Limiting flux: Gel layer controlled Mass Transfer

$$J = k \ln\left(\frac{c_g}{c_b}\right)$$



Or from Darcy equation

$$J = \frac{\Delta P}{\mu\left(R_m + R_{gel}\right)}$$

Ultrafiltration

– Limiting flux: Gel layer controlled Mass Transfer

- Especially in UF processes with high fluxes
- Permeate flux constant irrespective of ΔP_{TM}
- Solutes in feed precipitate i.e. gel layer forms
- With time, gel layer increases in thickness, until permeate flux reduces to an equilibrium steady state value
- Increasing ΔP_{TM} will not lead to an increase in flux

Ultrafiltration

– Limiting flux: Osmotic Pressure Effect

- As the concentration of the solution increases, the π on feed side and $\Delta\pi$ will increase
- If ΔP remains constant, the net pressure difference will diminish.

$$J = \frac{\Delta P - \Delta \pi}{\mu R_m}$$

Ultrafiltration
– Factors influencing flux

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Bulk Feed Concentration

Limiting flux equations

If bulk feed concentration increases, limiting flux develops, which results in

- Gel layer formation
- Increase in π on feed side

Temperature

Influences

- Diffusivity
- Viscosity
- Bacterial growth
- Protein denaturation
- Salt precipitation

Ultrafiltration
– Factors influencing flux

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pH

- Flux lowest at iso-electric point of protein
- Salt precipitation increases with increasing pH

Membrane properties

- charge
- hydrophobicity
- pore size distribution

Module design

- Influences hydraulic regime
- Laminar or turbulent flow
- Affects flux and clean-ability
- Mass transfer coefficient

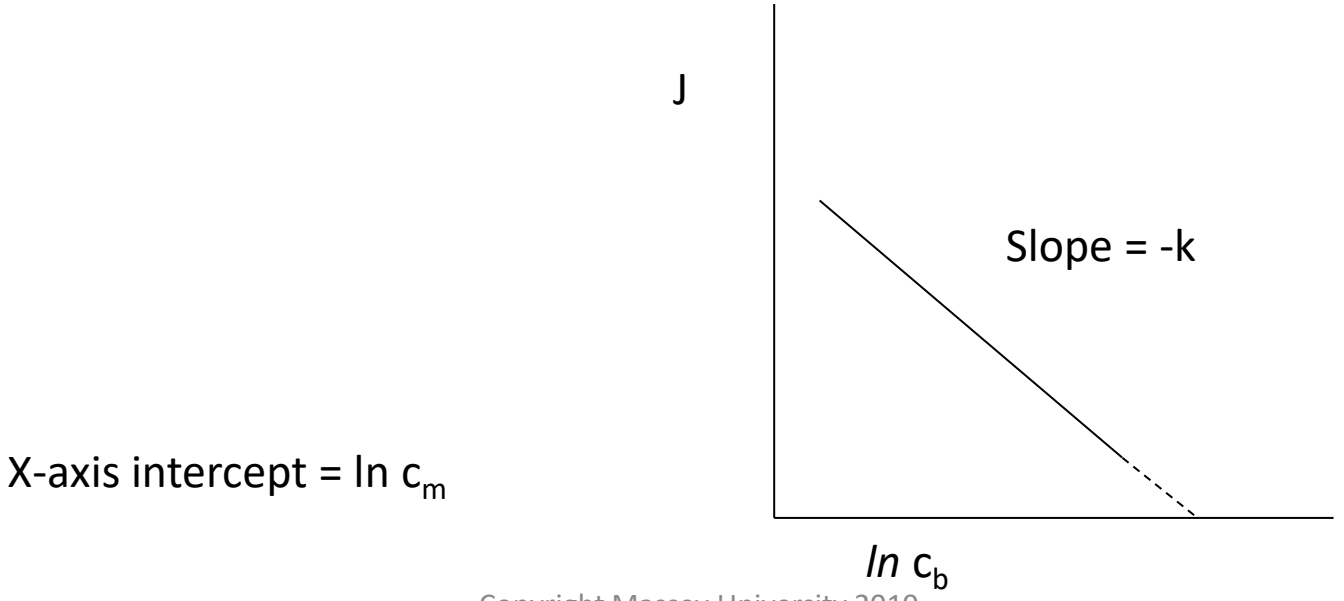
Ultrafiltration – Factors influencing selectivity

- Solute and solvent flux
- Membrane fouling
- Concentration polarisation
- Feed solution pH
- Pre-treatment of feed
- Interactions of individual components

Design and Sizing of UF plants

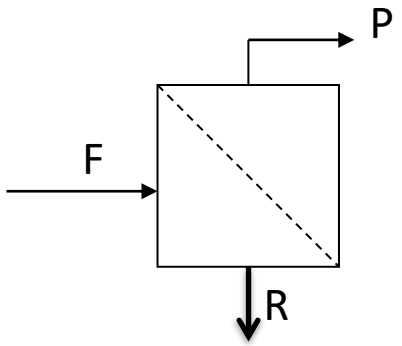
- Establish membrane area and process time
- k and c_m can be determined from a plot of J vs $ln c_b$

$$J = k\, ln\left(\frac{c_m}{c_b}\right)$$



Design and Sizing of UF plants

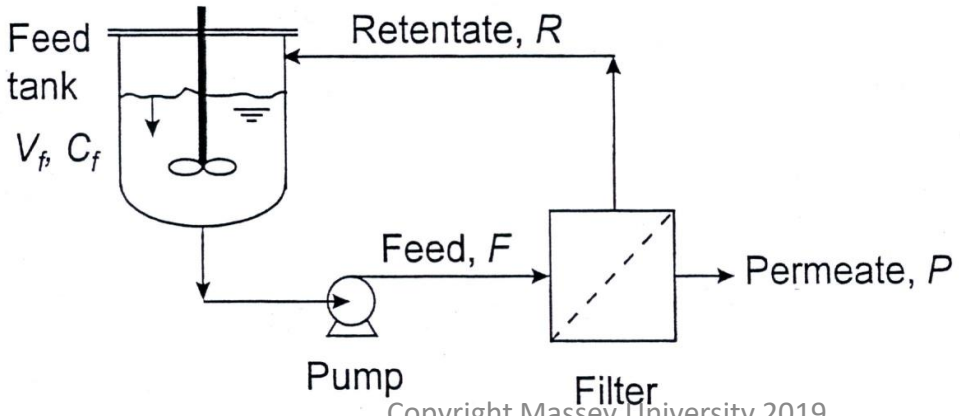
Overall mass balance $F = P + R$



(F, R and P are volumetric flow rates, $\rho_F \approx \rho_R \approx \rho_P$)

Solute Mass Balance - if $c_p = 0$

$$c_F V_F = c_R V_R$$



Volume concentration factor (VCF)

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- Level of concentration achieved or desired

$$\text{VCF} = \frac{\text{initial feed volume}}{\text{retentate volume}} = \frac{\text{initial feed flow rate}}{\text{retentate flow rate}}$$

$$VCF = \frac{F_{initial}}{R} \quad \left(= \frac{V_F}{V_R} \right)$$

$$as \quad c_F V_F = c_R V_R$$

$$VCF = \frac{c_R}{c_F}$$

In simple design procedures assume:

SRC = 1 for macromolecules

SRC = 0 for all else

Average flux, J_{avg}

$$J_{avg} = \frac{permeate\,removed}{(area)(time)}$$

J_{avg} can also be calculated using this empirically derived equation

Breslau Equation:

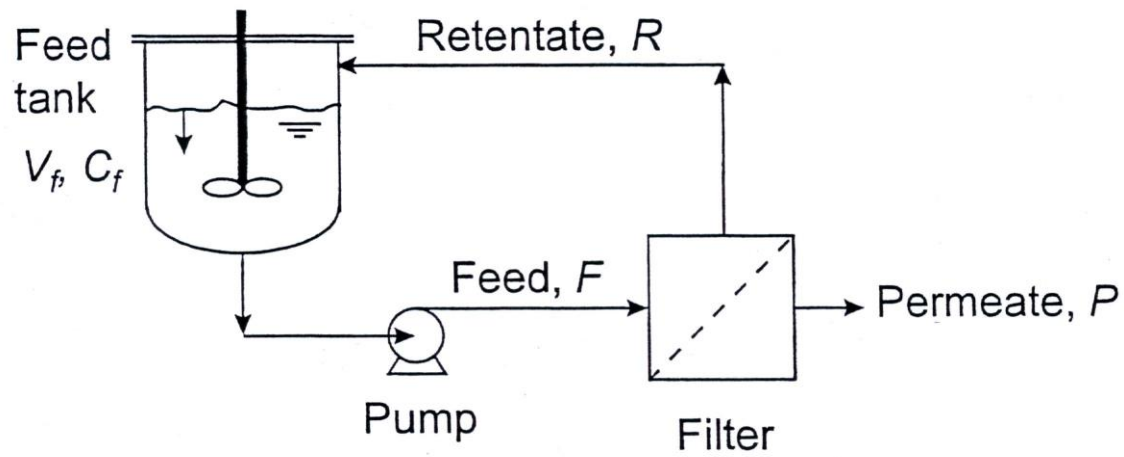
$$J_{avg} = J_{final} + \frac{2}{3}\left(J_{initial} - J_{final}\right)$$

Ultrafiltration – Batch systems

- Usually only run for short periods
- More suited to processing small volumes.

The advantages of batch operation:

- minimum area required
- very flexible system
- lower requirements for control and monitoring

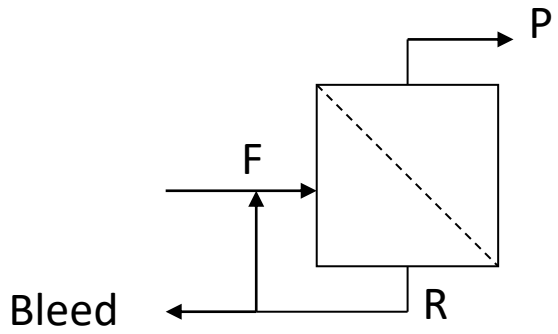


Ultrafiltration – Continuous multi-stage plants

- Suited to large throughputs
- Product quality requirements are high
- Additional costs of monitoring and control can be met.

The advantages of a continuous system:

- very large throughputs can be handled
- residence time is less, therefore, mechanical effects on product quality are minimised
- low residence time improves microbiological quality of product



Ultrafiltration – Considerations for plant design

- Process to be used; UF, MF, etc batch or continuous
- Type of module and its geometry
- Material of membrane
- Pores size of membrane
- Number of stages
- Washing or diafiltration required?
- How is water added; continuously or batchwise
- Operating pressure
- Flow rate through module
- Operating temperature
- Control strategy

Ultrafiltration – Design calculations

- <u>For batch operation:</u>
  1. Determine the required time to concentrate a given volume to the required extent (VCF)
  2. Determined the area required for operation

- <u>For continuous feed and bleed operation</u>
  1. Determine the number of stages used

  (a) Single-stage system - operated at a desired VCF

  (b) Multi-stage systems

  - more than one stage
  - earlier stages operate at lower VCF
  - VCF for each stage chosen to give equal membrane area for each stage
  - VCF for all but last stage selected on a trial and error basis

  2. Determine the total membrane area required

  See Worked Example

Microfiltration membranes

- Symmetric and Asymmetric membranes
- Tubular membranes
- Pore sizes range from 0.1 – 10 μm
- Inorganic membranes; zirconium, titanium, aluminium oxide, stainless steel and borasilicate glass

Determining Flux - theoretical vs empirical

$$J = \frac{driving\ \ force}{resistances} \qquad J = k(driving\ force)$$

$$J = \frac{volumetric\ \ or\ mass\ permeation\ \ rate}{membrane\ area}$$

$$J = \frac{Permeate\ flow\ rate}{membrane\ area} \qquad = \frac{P}{A \times t}$$

For a membrane with cake build-up

$$J = \frac{\Delta P}{\mu(R_m + R_C)}$$

$$Cake\ thickness = \frac{R_C}{\alpha}$$

α = specific cake resistance (m^{-2})

Membrane Processes -Summary

Advantages		Disadvantages
No phase change (except pervaporation and membrane distillation)		Extent of separation is limited
Operating temperature near ambient		Flux decline
Lower energy requirements		Limited membrane life
No thermal deterioration of important compounds		Long cleaning times
Modular		
Batch or continuous operation		
No additives		
Scale-up straight forward		
Sanitary or sterile operation possible		

$$F = P + R$$

$$VCF = \frac{F_{initial}}{R} \quad \left(= \frac{V_F}{V_R} \right)$$

$$as \quad c_F V_F = c_R V_R$$

$$VCF = \frac{c_R}{c_F}$$

$$J = k\, ln\left(\frac{c_m}{c_b}\right)$$

$$J_{avg} = \frac{Permeate\ flow\ rate}{membrane\ area} \qquad = \frac{P}{A \times t}$$

$$J_{avg} = J_{final} + \frac{2}{3}\left(J_{initial} - J_{final}\right)$$

10. Ultrafiltration Worked Example

DESIGN OF UF PLANTS FOR WHEY CONCENTRATION

The flux obtained during UF concentration of acid casein whey is described in Table 1:

Calculate the area required to process 7,500 l/hr whey to VCF = 20 for:

- A batch plant, i.e. to process 7,500 litres in 1 hour (Note: in a preliminary batch experiment 100 litres whey was concentrated to VCF = 20 in 1.36 h with 2 m^2 plant)
-A single-stage continuous plant
-A two-stage plant if the membrane areas in each stage are to be approximately equal

Table 1: Flux data for UF whey

VCF	Flux (LMH)
1.0	45.0
1.19	43.0
1.45	41.0
1.83	38.5
2.42	35.5
3.41	32.5
5.29	28.2
9.42	22.5
20.0	15.0

11. Ultrafiltration - VCF

A continuous flow ultrafiltration plant is required to concentrate 7.5 $m^{-3}\,h^{-1}$ of whey to a volume concentration factor (*VCF*) of 20.
Calculate the membrane area needed.
(Note: A batch process development run showed that 0.1 m3 of whey could be concentrated to a *VCF* of 20 in 1.36 h with a 2 m2 membrane module.)

12. Ultrafiltration – gel layer model

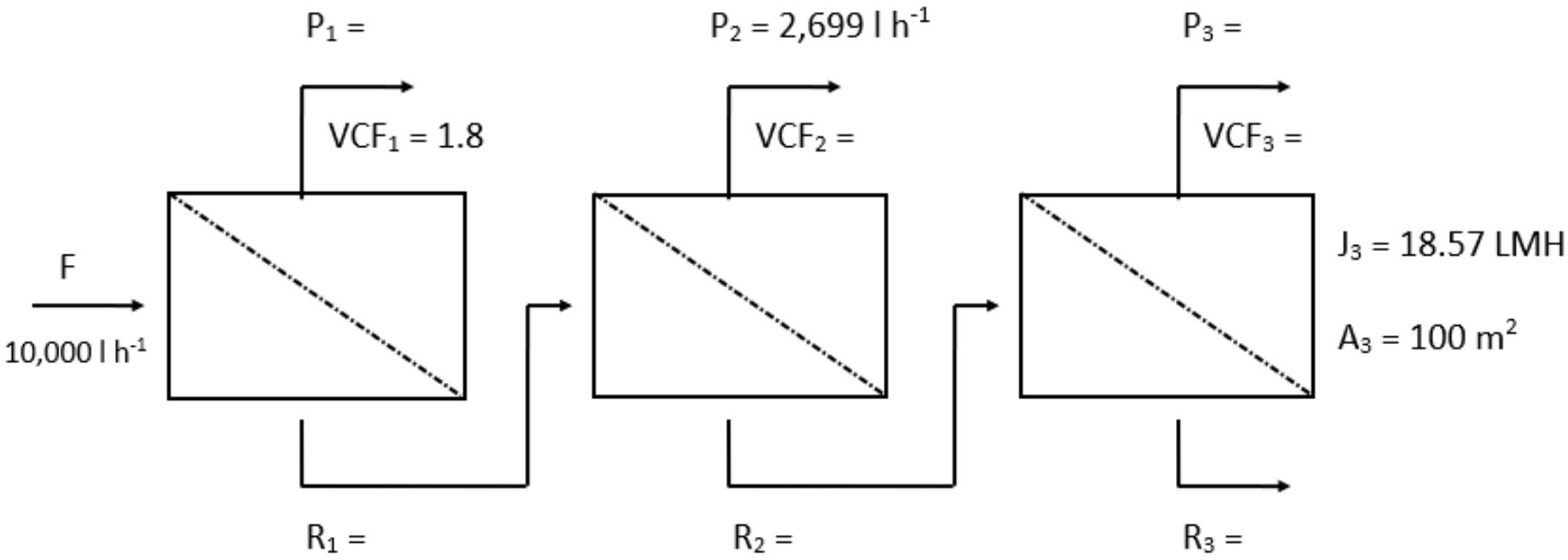
The gel-layer model of concentration polarisation gives

$$J = k \ln\left(\frac{c_g}{c_b}\right)$$

Estimate the values of **k** (in m s^{-1}) and $\mathbf{c_g}$ for the whey data given in the Worked Example (10) using the flux value at VCF = 20.
Assume the initial protein concentration is 0.6 wt % and that SRC = 1.0.
Confirm your answer by calculating the flux at VCF = 10.

13. Ultrafiltration – multistage process

- Calculate the missing values for a three-stage plant as shown:



16. Ultrafiltration – Batch process

A protein solution is concentrated by batch ultrafiltration (UF) in a laboratory trial. The membrane area was 0.1 m^2 and 12 litres of permeate was collected in 4 hours with the plant operating at 20^{o}C. The initial feed volume was 15 litres and the initial protein concentration was 1.5% (w/v). The flux at 4 hours was measured as 18 LMH.

(i) Calculate the average flux, and estimate the gel layer concentration (c_g) and mass transfer coefficient (k).

(ii) If a large batch plant is to process 4,000 litres of feed material in an eight hour period with the same concentration factor, what area would be required? This plant will fun at 10^{o}C, with the consequence that k will reduce by one third from the value at 20^{o}C.