Expert Talk Series No: 1, 13 August 2020, Kuala Lumpur, Malaysia

STATE OF THE ART AND RECENT PROGRESSES IN MEMBRANE TECHNOLOGIES FOR WATER/WASTEWATER TREATMENT

Professor Mohammed Saedi Jami

Dept. of Biotechnology Eng.
INTRNATIONAL ISLAMIC
UNIVERSITY
MALAYSIA

CONTENTS

- Background
- Current Trend in Water Treatment
- Our Research Activities
- Ceramic Membrane Microfiltration
- Modified Graphene Oxide Membrane

بِسْمِ ٱللَّهِ ٱلرَّحْمَٰنِ ٱلرَّحِيمِ

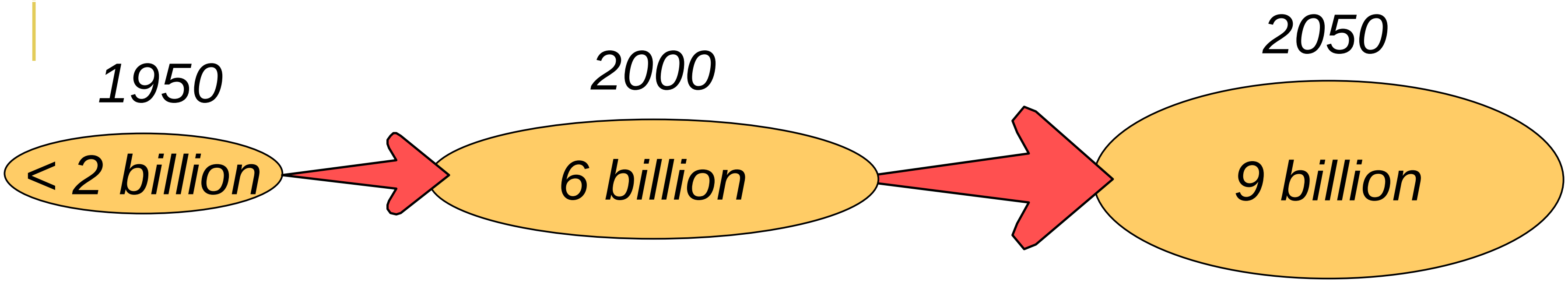
أَوَلَمْ يَرَ ٱلَّذِينَ كَفَرُوٓا۟ أَنَّ ٱلسَّمَٰوَٰتِ وَٱلْأَرْضَ كَانَتَا رَتْقًا فَفَتَقْنَٰهُمَا ۖ وَجَعَلْنَا
مِنَ ٱلْمَآءِ كُلَّ شَىْءٍ حَىٍّ ۖ أَفَلَا يُؤْمِنُونَ ﴿٣٠﴾

And have not the ones who disbelieved seen that the heavens and the earth were an integrated (mass),
then We unseamed them, and of water We have made every living thing? Would they then not believe?
Surah Al-Anbya [21:30] - Quran

“ WHEN THE WELL IS DRY, WE KNOW THE WORTH OF WATER” (FRANKLIN, B. 1746)

BACKGROUND

World Population



1950

< 2 billion

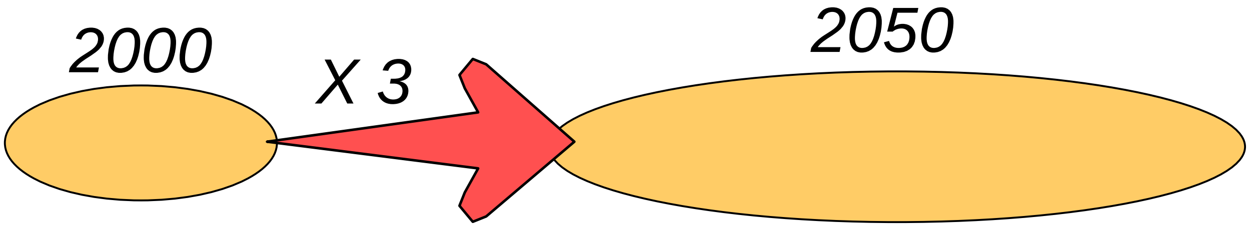
2000

6 billion

2050

9 billion

Water Demand



2000

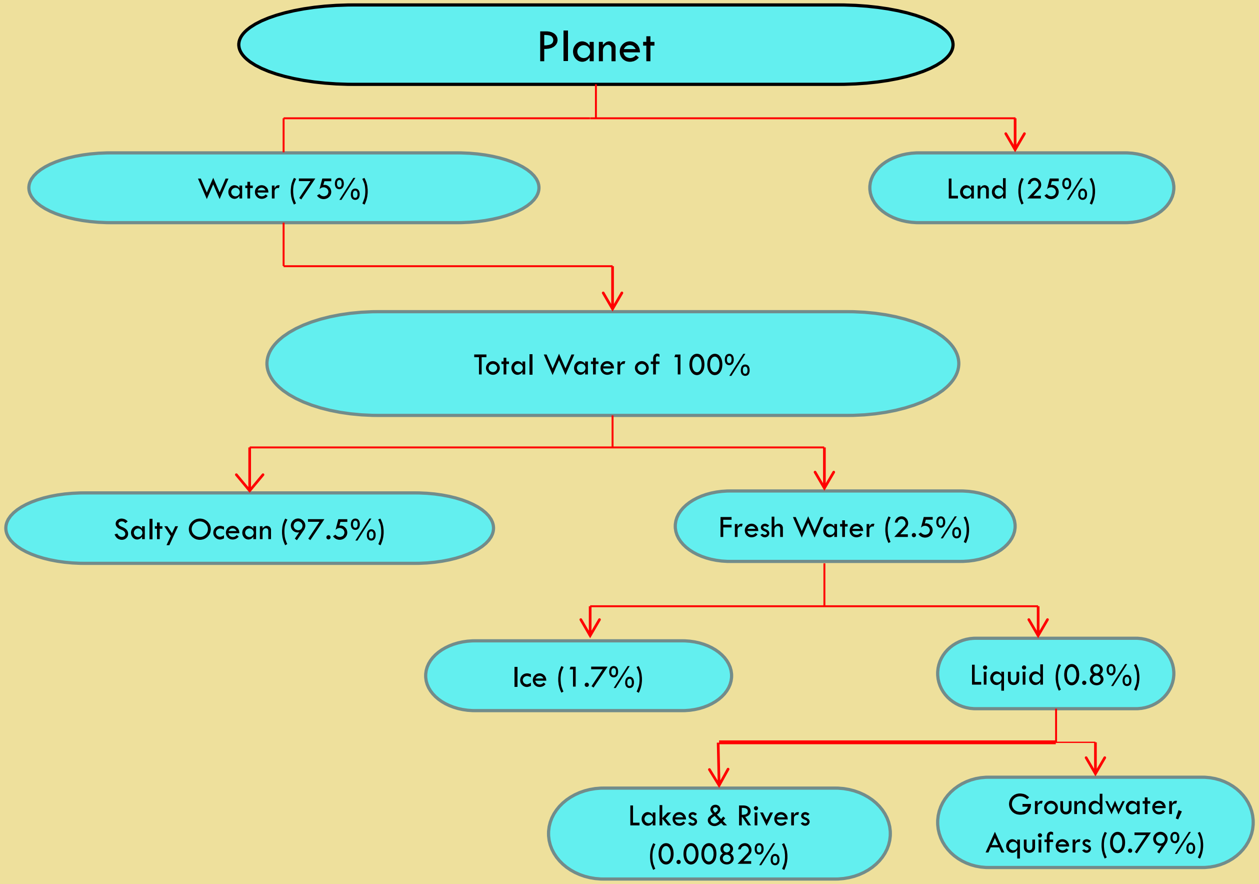
X 3

2050

- *Lack of drinking water*
  (1.1 billion people)
- *Lack of adequate sanitary water*
  (2.4 billion people)

Water Management

Local → *Global*



Planet

Water (75%)

Land (25%)

Total Water of 100%

Salty Ocean (97.5%)

Fresh Water (2.5%)

Ice (1.7%)

Liquid (0.8%)

Lakes & Rivers (0.0082%)

Groundwater, Aquifers (0.79%)

WORLD WATER APPROPRIATION


% of the population with access to improved drinking water (2000)

About a billion people do not have access to safe drinking water. That's one out of nine people in the world.

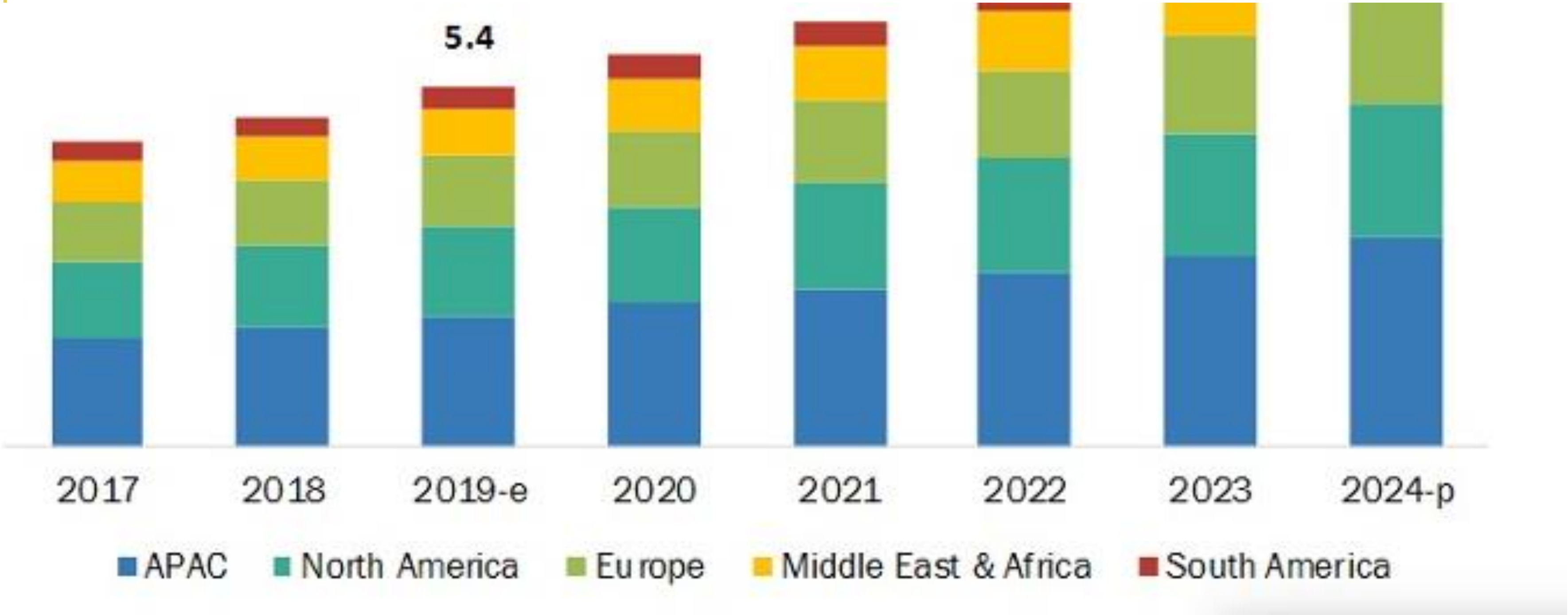
The average distance that women in Africa and Asia walk to collect water is 3.7 miles.

By 2025 at the rate we are going, it is estimated that two thirds of the world will be living with water scarcity or total water deprivation.

Globally, 1.1 billion people still do not have access to safe drinking water and 2.6 billion people – half of the developing world – lack even basic sanitation facilities(source: UNICEF and World Health Organization Report (2015). 25 Years of Progress on Sanitation and Drinking Water. Available from: www.wssinfo.org)

The increasing urbanization and population, shifting climates and industrial pollution has made fresh water to become the humanity's most precious resource, hence, water is being called *the "Blue Gold" of the 21st century.*

MEMBRANE MARKET



Membranes Market by Material (Polymeric, Ceramic), Technology (RO, UF, MF, NF), Application (Water & Wastewater Treatment, Industrial Processing), Region (North America, APAC, Europe, MEA, South America) - Global Forecast to 2024

Source: https://www.marketsandmarkets.com/Market-Reports/

MEMBRANE PROCESSES
ADVANTAGES

Low energy consumption

  - one fourth of distillation process

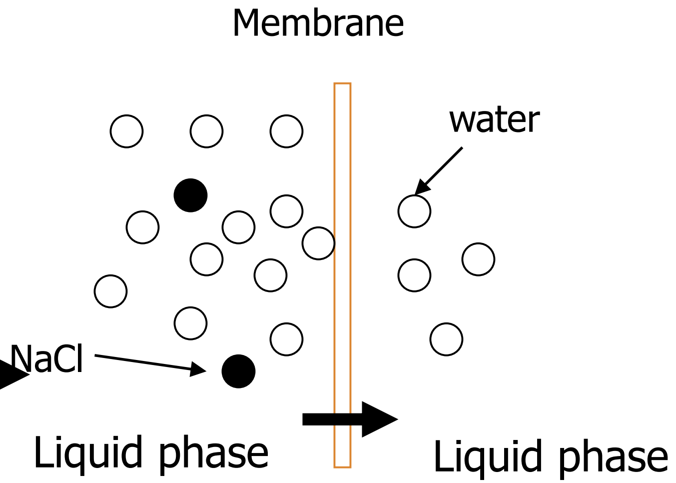
Operable at low temperature

  - non-destructive treatment of heat sensitive matters

Easily expanded

  - by adding a series of modules

MEMBRANE TECHNOLOGY
ADVANTAGES



Low energy consumption

Operable at low temperature

Easily expanded

MEMBRANE TECHNOLOGY
DISADVANTAGES

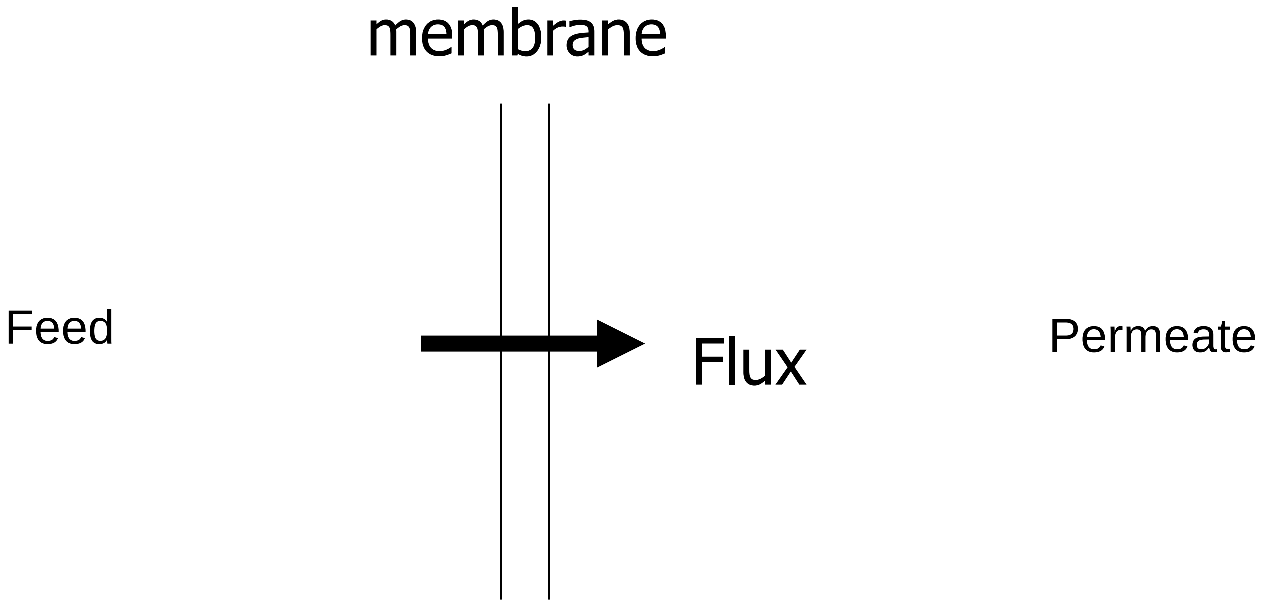
Membrane cost

- prices are going down year by year

Membrane instability

- chemical(Selectivity change)
- thermal
- compaction
- fouling(Flux change)

CLASSIFICATION OF MEMBRANE PROCESSES BY DRIVING FORCE



membrane

Feed

Flux

Permeate

Driving Force; pressure, concentration, electric

PRESSURE DRIVEN PROCESS

Reverse Osmosis (RO)

seawater desalination, ultrapure water production, waste water treatment, food processing, pharmaceutical applications

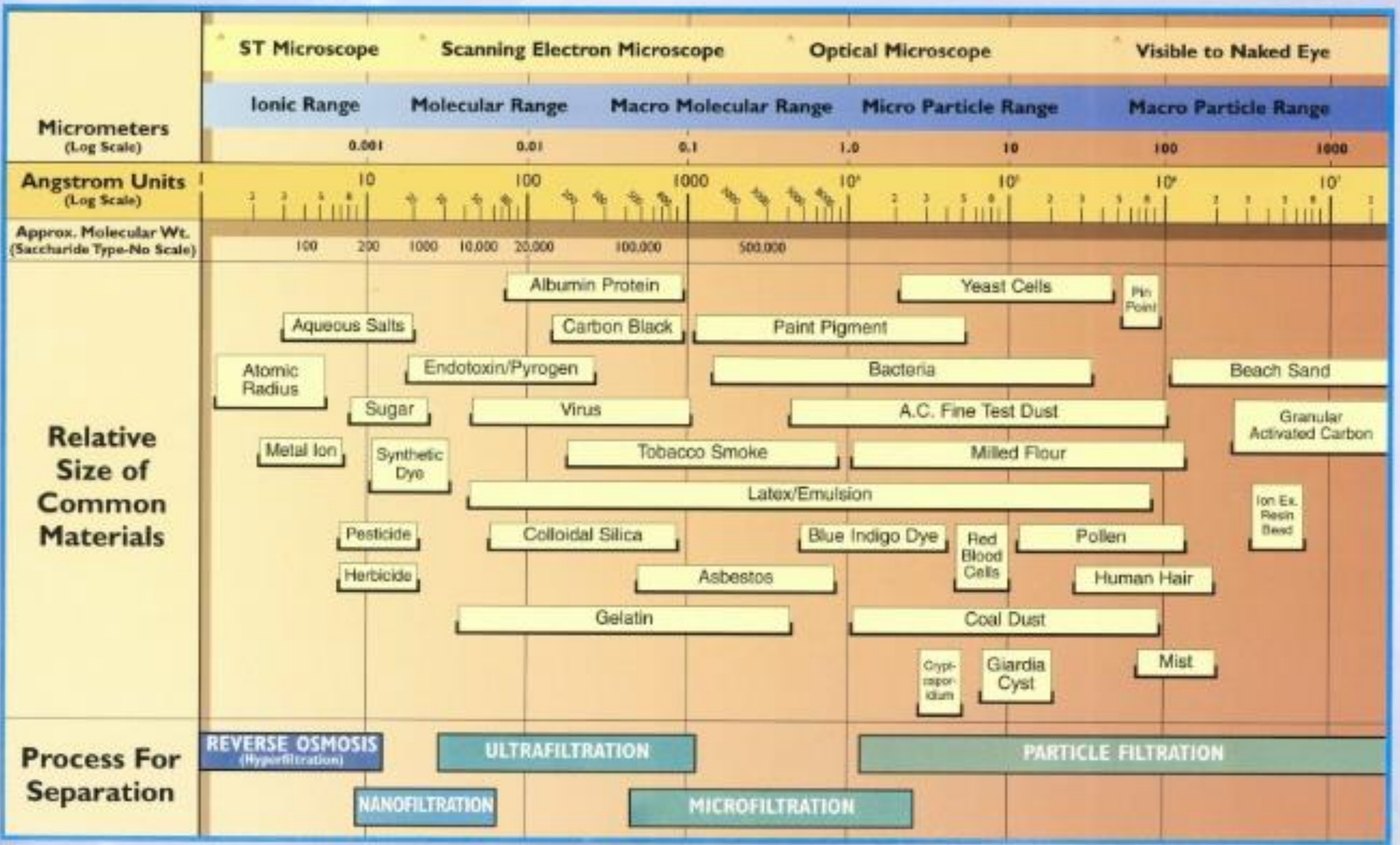
Ultrafiltration (UF)

milk whey production, waste water pretreatment

Microfiltration (MF)

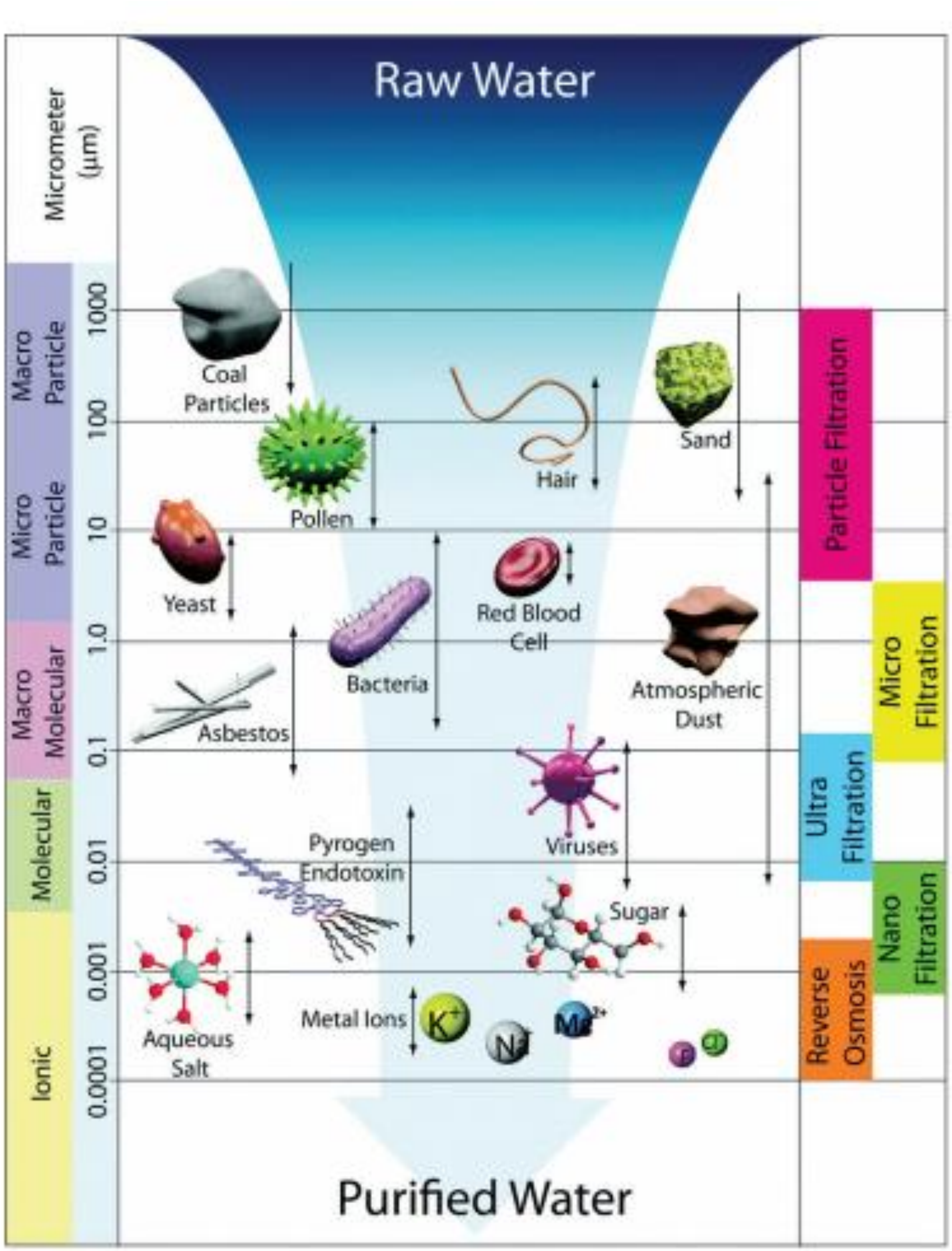
bacteria removal, waste water treatment prior to RO

The Filtration Spectrum



Note: 1 Micron (1×10^{-6} Meters) = 4×10^{-5} Inches (0.00004 Inches)
1 Angstrom Unit = 10^{-10} Mters = 10-4 Micrometers (Microns)

PORE SIZES OF RO, UF AND MF MEMBRANES



PRESSURE DRIVEN PROCESS-CONTINUED

Membrane Gas Separation

CO2 removal from natural gas & flue gas, air separation

Membrane Vapor Separation

VOC removal from air, dehumidification of air

Pervaporation and Membrane Distillation

Alcohol/water separation, solvent dehydration, VOC removal from water

ELECTRICALLY DRIVEN PROCESSES

Electrodialysis

salt production, seawater desalination

Electrolysis

sodium hydroxide production

Bipolar Membrane

waste water treatment

Membrane Separator

fuel cells, batteries

CONCENTRATION DRIVEN PROCESSES

Dialysis

artificial kidney, artificial lung, etc.

Hemodialysis

blood treatment

Controlled drug release

pharmaceutical applications

Membrane extraction

HISTORY OF MEMBRANE PROCESS DEVELOPMENT

Microfiltration	1920	Zsigmondy
Ultrafiltration	1930	
Hemodialysis	1950	Kolff
Electrodialysis	1955	
Reverse Osmosis	1960	Loeb and Sourirajan
Ultrafiltration	1960	

MEMBRANE MATERIAL

PROPERTIES OF POLYMERS

Chain Flexibility/rigidity

Crystallinity

Hydrophilicity/hydrophobicity

Molecular Weight

Chemical Property

Thermal Property

Mechanical Property

Electrochemical Property

CHAIN FLEXIBILITY/RIGIDITY

Presence of bulky pendant groups hinders the rotational motion around the main chain

Increase in interchain void space > small molecules diffuse easily

Inrease in chain rigidity > large meolecules' diffusion hindered

HYDROPHILICITY/HYDROPHOBICITY

Contact angle measurement

Solubility parameter

MOLECULAR WEIGHT

Increase in molecular weight > Increase in selectivity

ELECTROCHEMICAL PROPERTY

Ion exchange capacity: membranes for fuel cells, membranes for electrodialysis, most of nanofiltration membrane

MECHANICAL PROPERTY

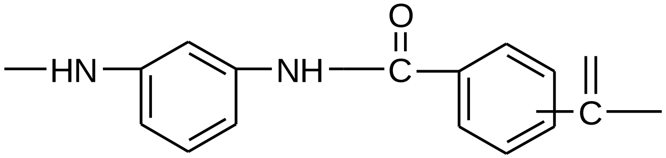
A sufficiently high Young’s modulus

POLYMERIC MEMBRANES FOR MEMBRANE SEPARATION PROCESSES

REVERSE OSMOSIS (RO) MEMBRANES

Cellulose acetate

Aromatic polyamide



(Aromatic polyamide polymer)

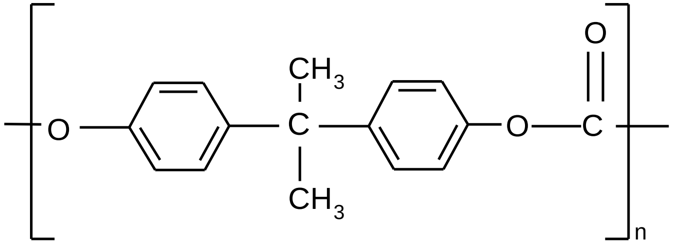
ULTRAFILTRATION MEMBRANES

Typical UF membrane materials are polysulfone (PS), polyethersulfone (PES), polyetheretherketone (PEEK), cellulose acetate (CA), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polyimide (PI), and polyetherimide (PEI).

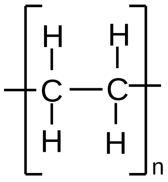
Tgs >145 degree C

MICROFILTRATION MEMBANES

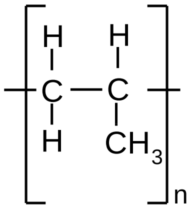
polysulfone (PS), polyethersulfone (PES), cellulose (CE) and cellulose acetate (CA), polyamide (PA), polyimide (PI), polyetherimide (PEI) and polycarbonate (PC). Typical hydrophobic materials are polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE, Teflon) and polyvinylidene fluoride (PVDF).



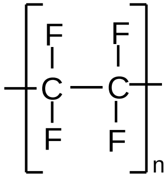
(PC)



(PE)



(PP)



(PTFE)

MEMBRANE PREPARATION METHOD

Membranes without asymmetric structure

Membranes with asymmetric structure:

(integrally skinned asymmetric membrane), (composite membrane)

MEMBRANES WITHOUT ASYMMETRIC STRUCTURE

Track etching

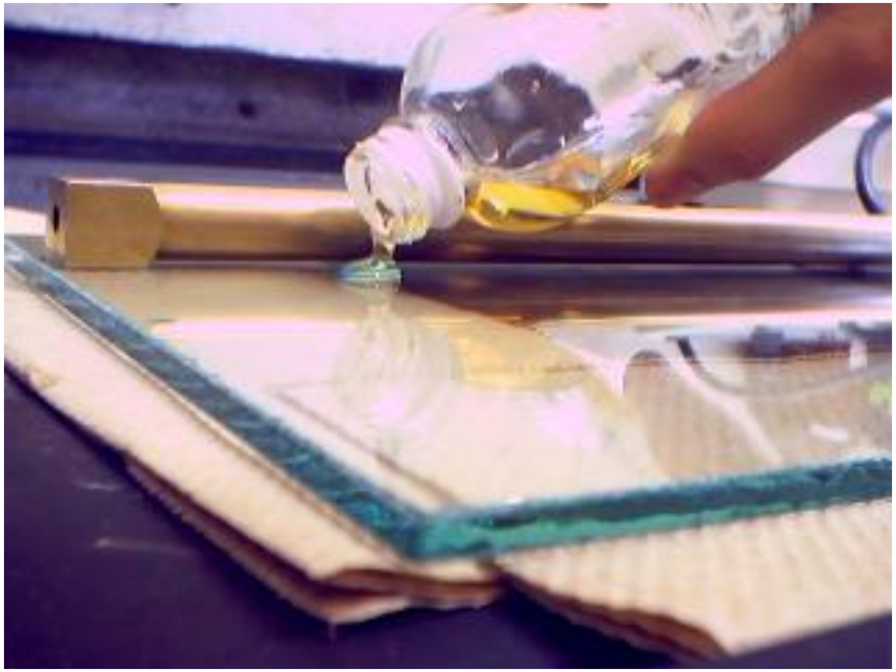
Precipitation from the vapour phase

MEMBRANE MANUFACTURING

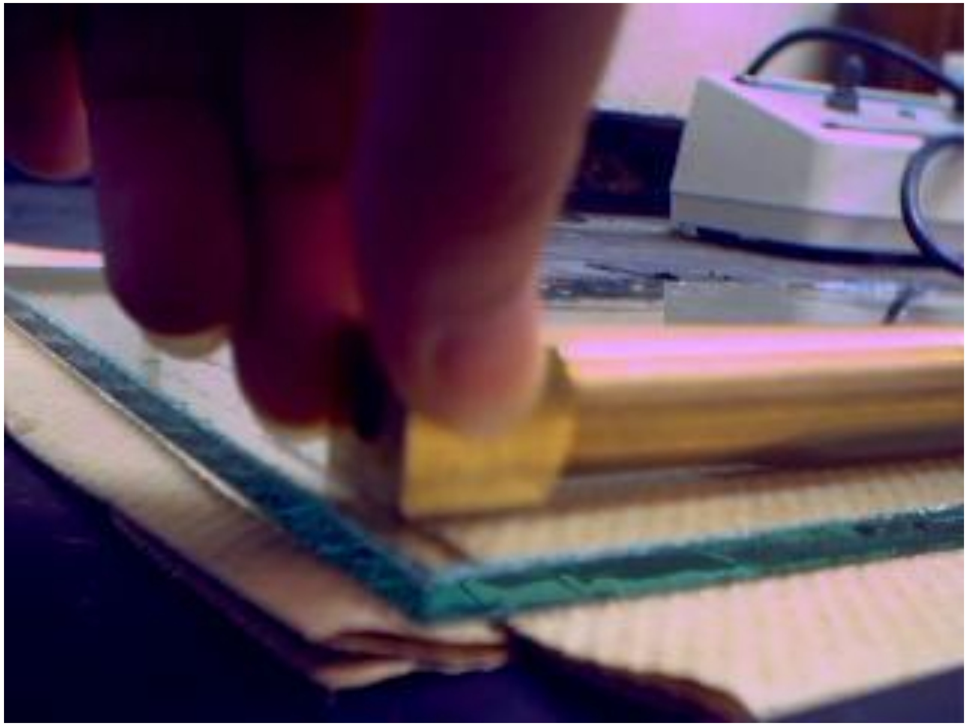
Steps within the phase inversion technique

- Mixing of the casting solution
  - composition (%Solvent, %POLYMER(PES) and %SMM)
- Casting in glass plate
  - membrane thickness
- Evaporation step
  - time
- Gelation step

  in cold water
- Drying (optional)



CASTING STEP



COMPOSITE MEMBRANE PREPARATION: MEMBRANE SURFACE COATING

Dip coating (Spin coating)

Interfacial in-situ polymerization

Chemical modification

Plasma polymerization

Graft polymerization

Surface modification by surface modifying macromolecules (SMMs)

MEMBRANE CHARACTERIZATION

PORE SIZE MEASUREMENT

Bubble point method

Mercury intrusion

Adsorption

Permporometry

Thermoporometry

Gas permeability

Molecular probe permeation

MEMBRANE MORPHOLOGY

Scanning electron microscope (SEM)

Transmission electron microscope (TEM)

Atomic force microscope (AFM)

SPECTROSCOPIC METHOD

Fourier Transform Infrared (FTIR)

Raman spectroscopy (RS)

Electron spin resonance (ESR)

Nuclear magnetic resonance (NMR)

Wide angle X-ray spectroscopy (WAX)

X-ray photoelectron spectroscopy (XPS)

Small angle neutron scattering (SANS)

Positoronium annihilation (PA)

Ultrasonic spectra

OTHER METHODS

Contact angle

Zeta potential

Differential scanning calorimetry (DSC)

Thermogravimetry analysis (TGA)

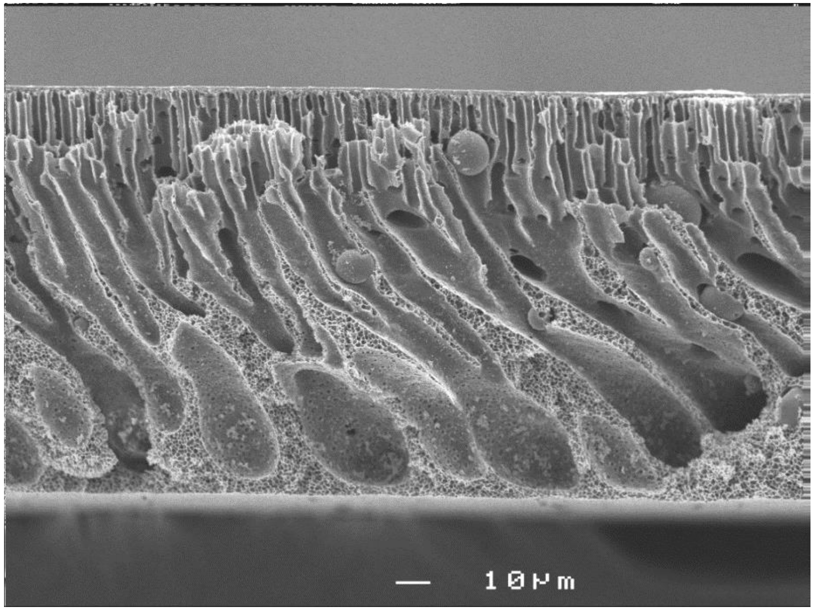
Tensile strength

Morphology Study Using SEM

V1

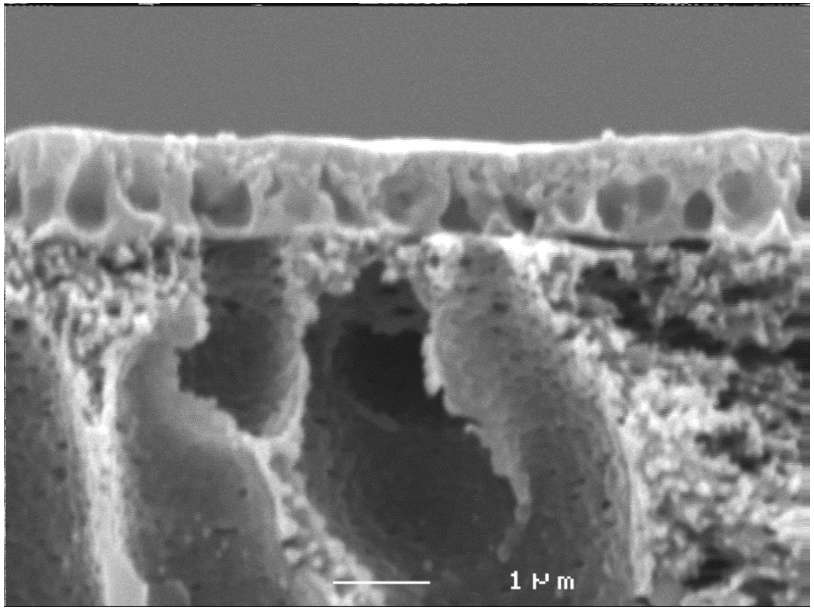
Membrane profile
(× 500)

119 μm

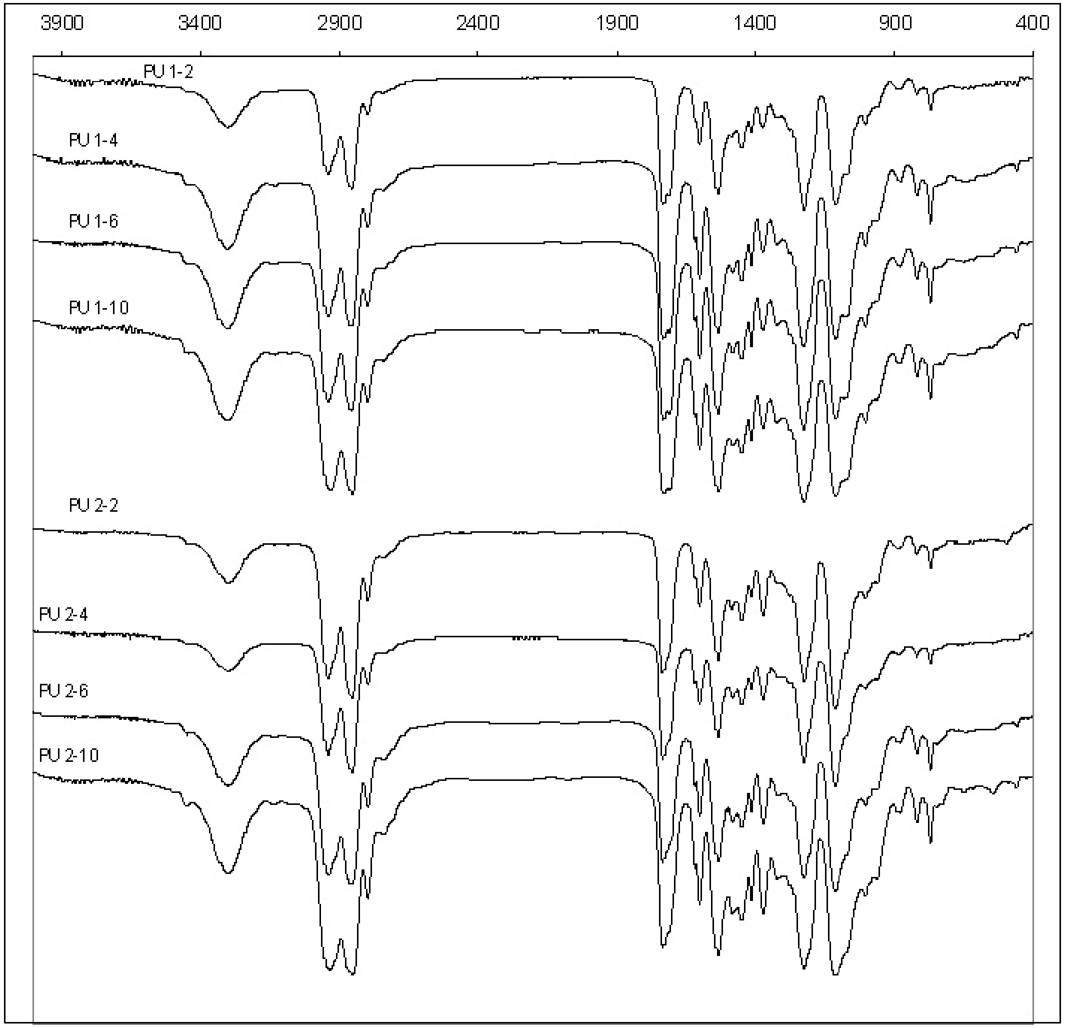


Top surface part
(× 1500)

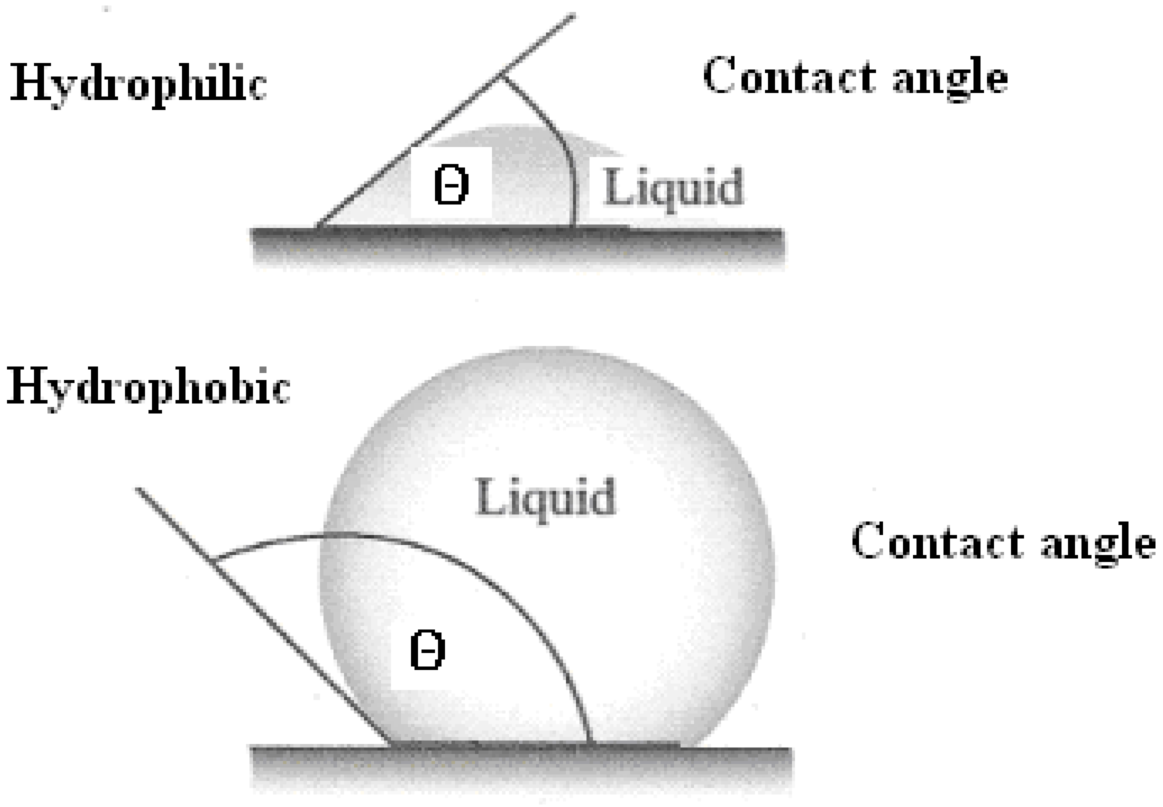
0.84 μm



FTIR (PREPARATION OF POLYURETHANE MEMBRANE-DISAPPEARANCE OF NC=O PEAK AT 2270CM-1)



CONTACT ANGLE



FUNDAMENTALS IN MEMBRANE TRANSPORT

FUNDAMENTAL EQUATIONS ENABLE PREDICTION OF FLUX AND SEPARATION

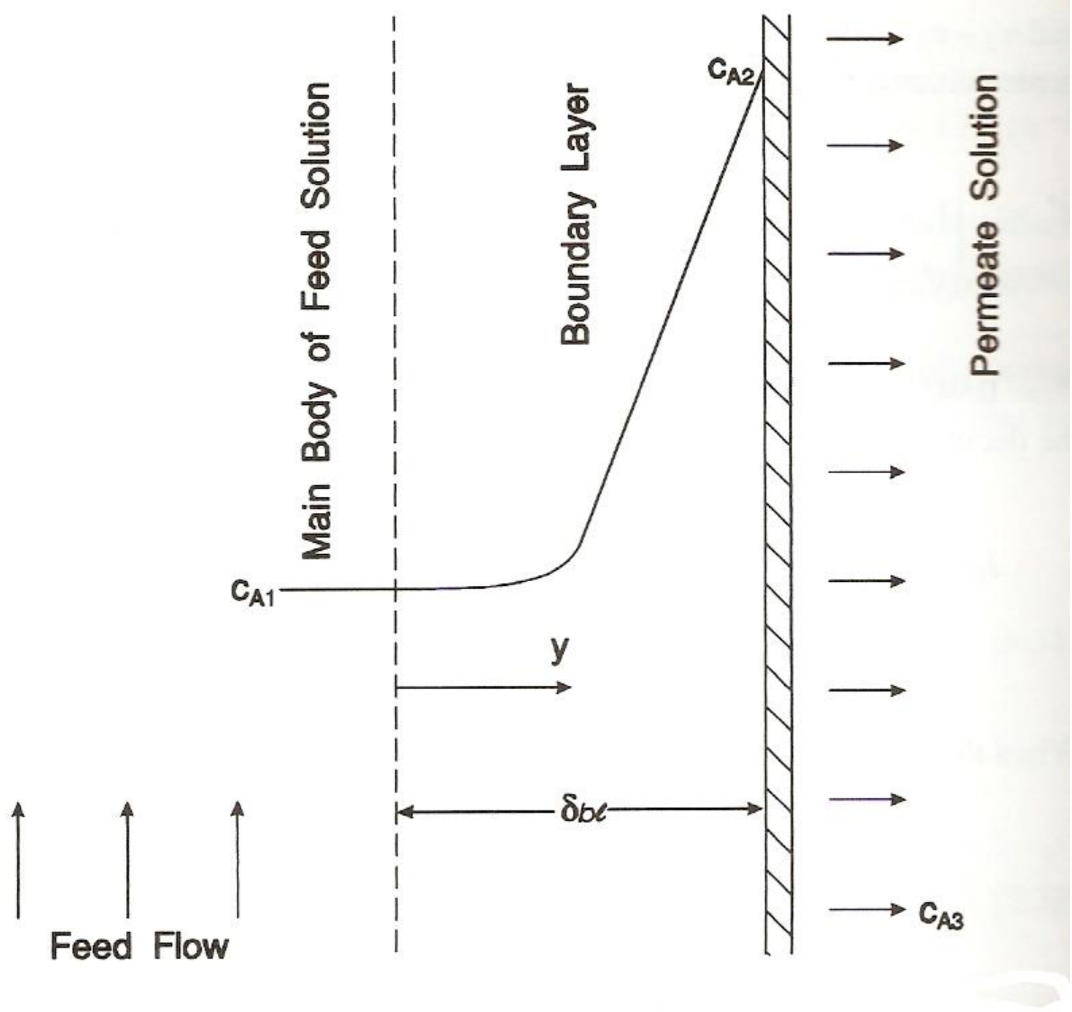
$$J_{water} = A(\Delta P - \Delta \Pi)$$

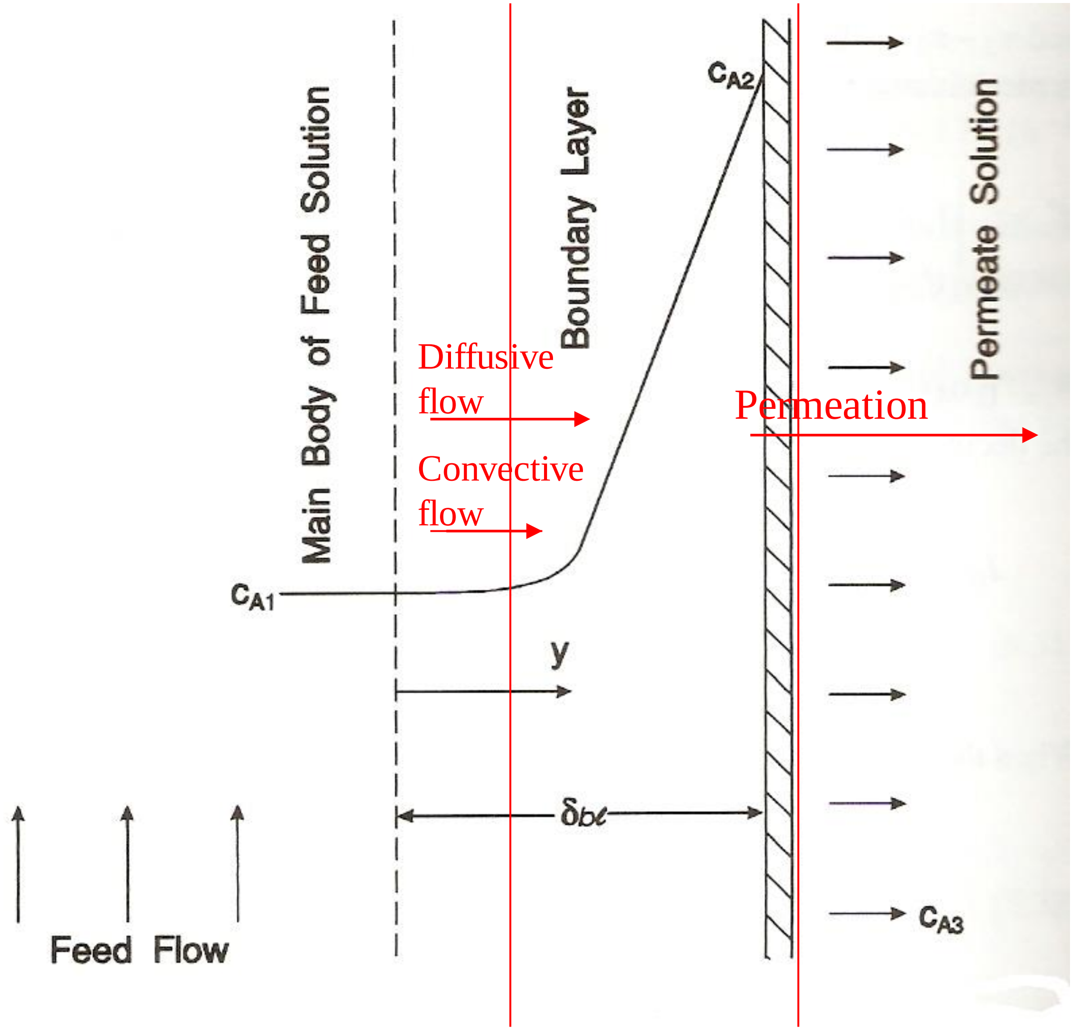
$$J_{solute} = \left(\frac{D_{AM}}{K\delta}\right)(c_{A2} - c_{A3})$$

$$J_{water} = ck(1 - X_{A3}) \ln \frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}}$$

- A (water permeability); $D_{AM}/K\delta$ (solute transport parameter); k (mass transport parameter) should be provided.

CONCENTRATION POLARIZATION




Main Body of Feed Solution
Boundary Layer
Permeate Solution
c_{A2}
c_{A1}
c_{A3}
y
$\delta_{b\ell}$
Feed Flow
Diffusive flow
Convective flow
Permeation

EQUATIONS

$$-D_{AB}\frac{dc_A}{dy}+vc_A=vc_{A3}$$

Solving

$$\ln(c_A-c_{A3})=\frac{v}{D_{AB}}y+C$$

With boundary conditions

$$\ln\frac{(c_{A2}-c_{A3})}{(c_{A1}-c_{A3})}=\frac{v}{D_{AB}}\delta_{bl}$$

$$k=\frac{D_{AB}}{\delta_{bl}}$$

$$\frac{c_{A2}-c_{A3}}{c_{A1}-c_{A3}}=\exp(\frac{v}{k})$$

GEL FORMATION AT THE BOUNDARY LAYER

$$\frac{c_{A2} - c_{A3}}{c_{A1} - c_{A3}} = \exp(\frac{v}{k})$$

When cA3 = 0

$$\ln \frac{c_{A2}}{c_{A1}} = \frac{v}{k}$$

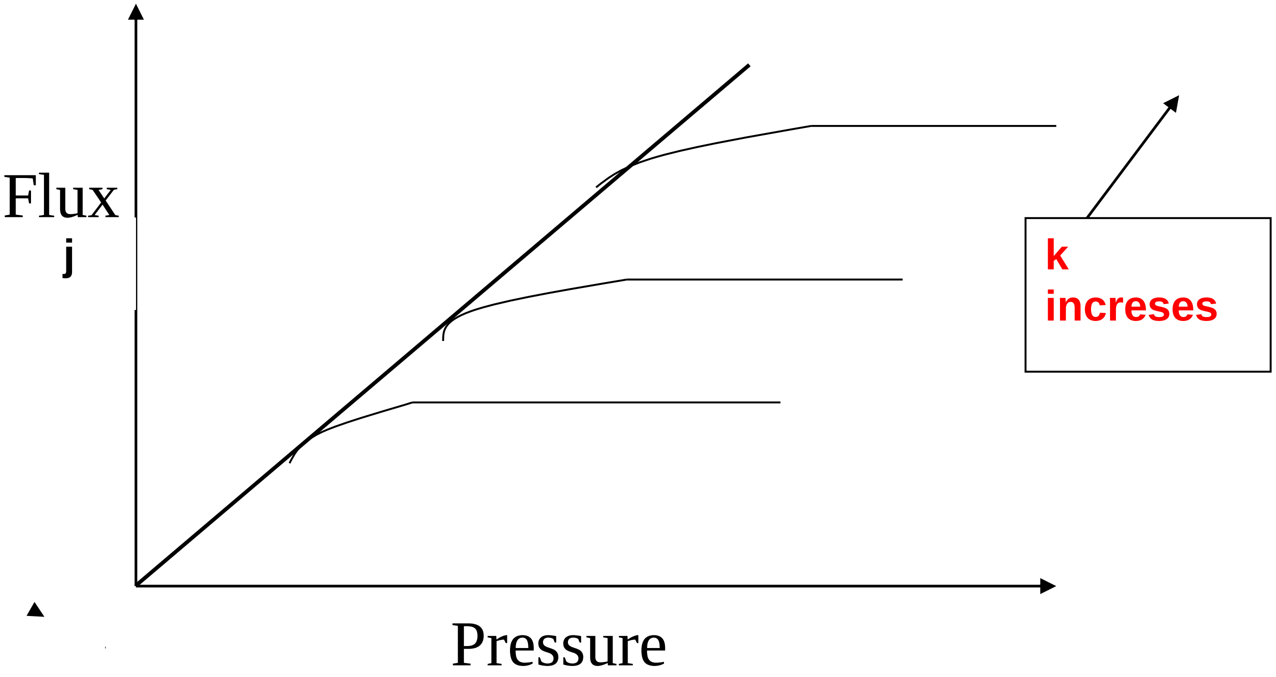
For a given C_{A1} .

,

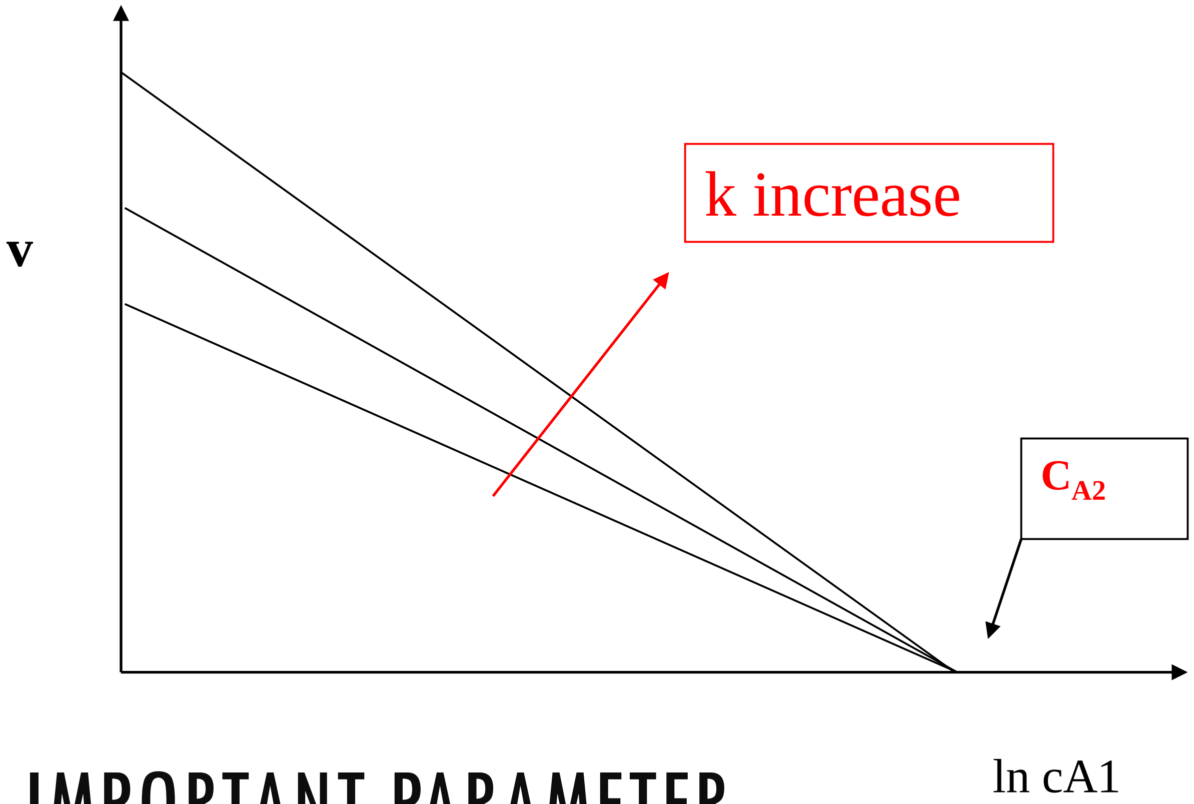
as pressure increases, *v* increases and so does c_{A2}

When c_{A2} **reaches a limiting value, called gel concentration, *v* becomes constant**

PRESSURE VS PERMEATION RATE



FEED CONCENTRATION VS PERMEATION RATE



K IS AN IMPORTANT PARAMETER

To increase k, turbulence is promoted.

MEMBRANE MODULE

MEMBRANE MODULES

Plate and Frame

Tubular

Spiral wound

Hollow Fiber

SURFACE AREA/MODULE SPACE (M**2/M**3)

Plate and frame	100-400
Tubular	300
Spiral wound	300-1000
Hollow fiber	up to 30,000

The module becomes smaller as the ratio increases, but membrane cleaning becomes more difficult.

PLATE AND FRAME MODULE

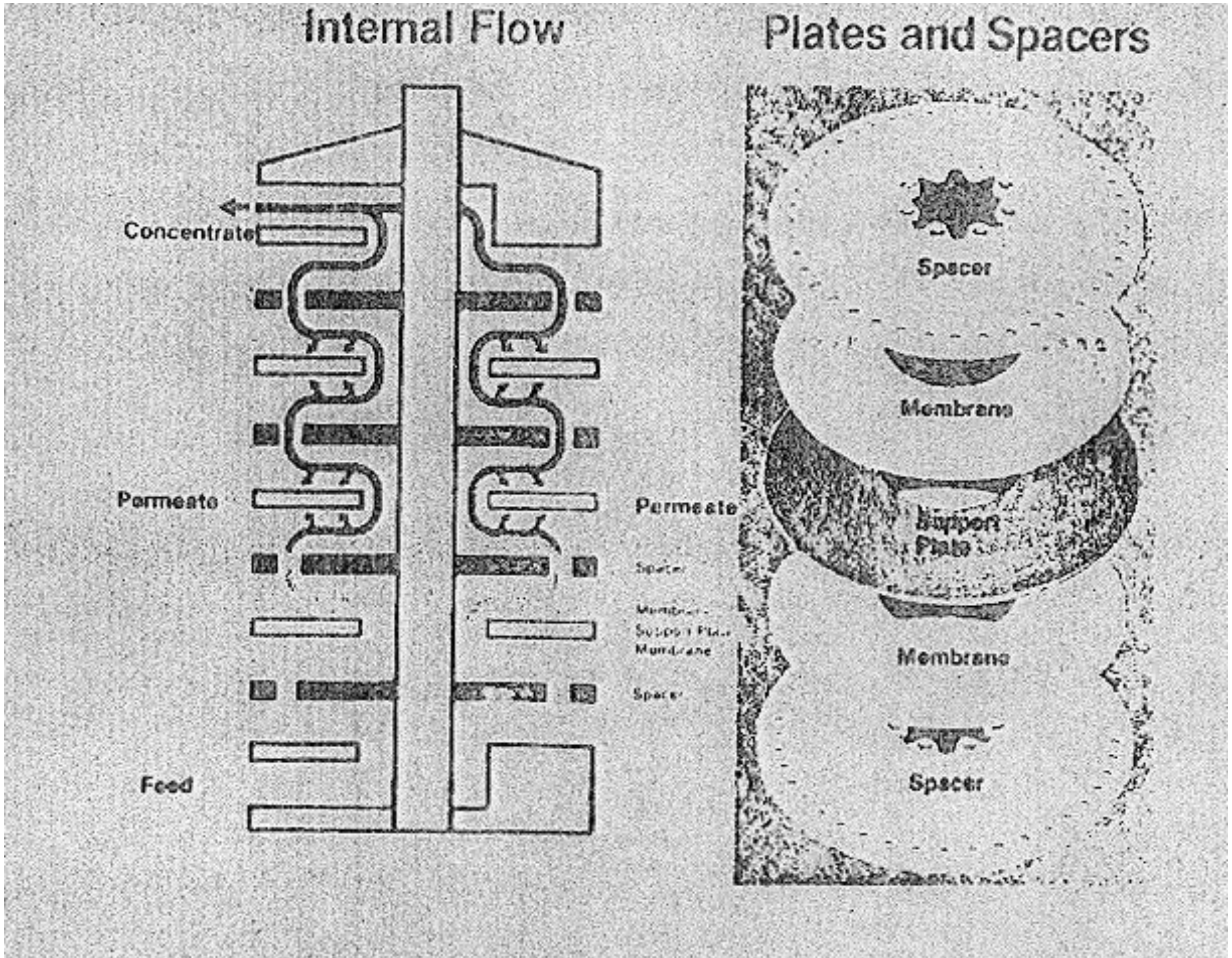
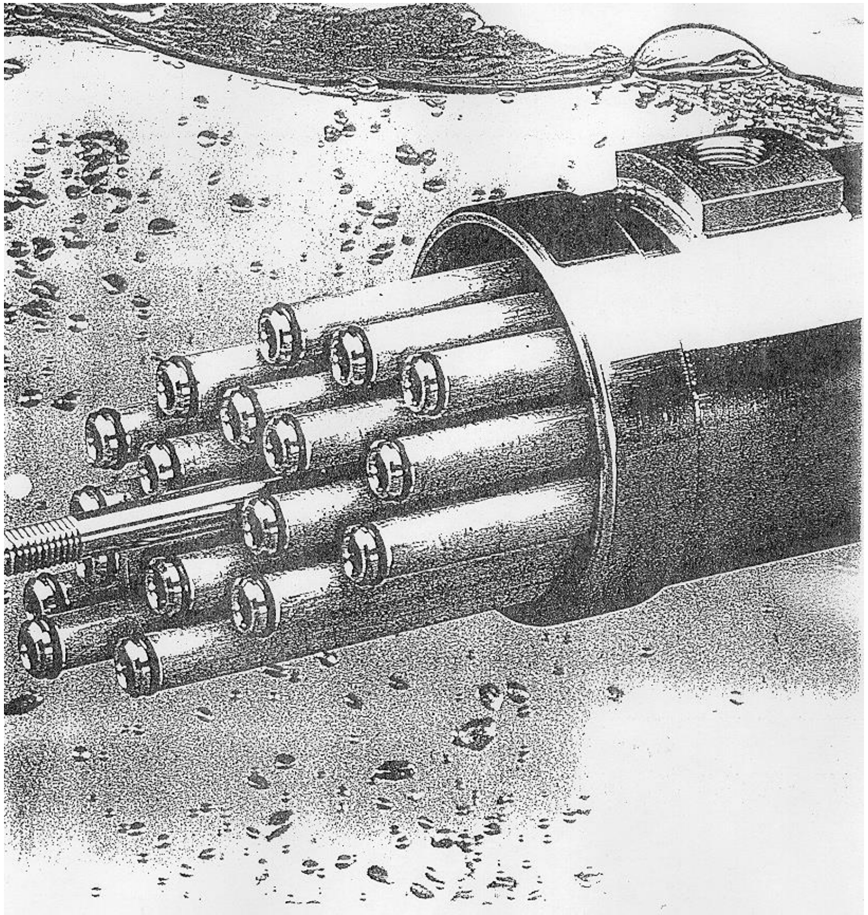
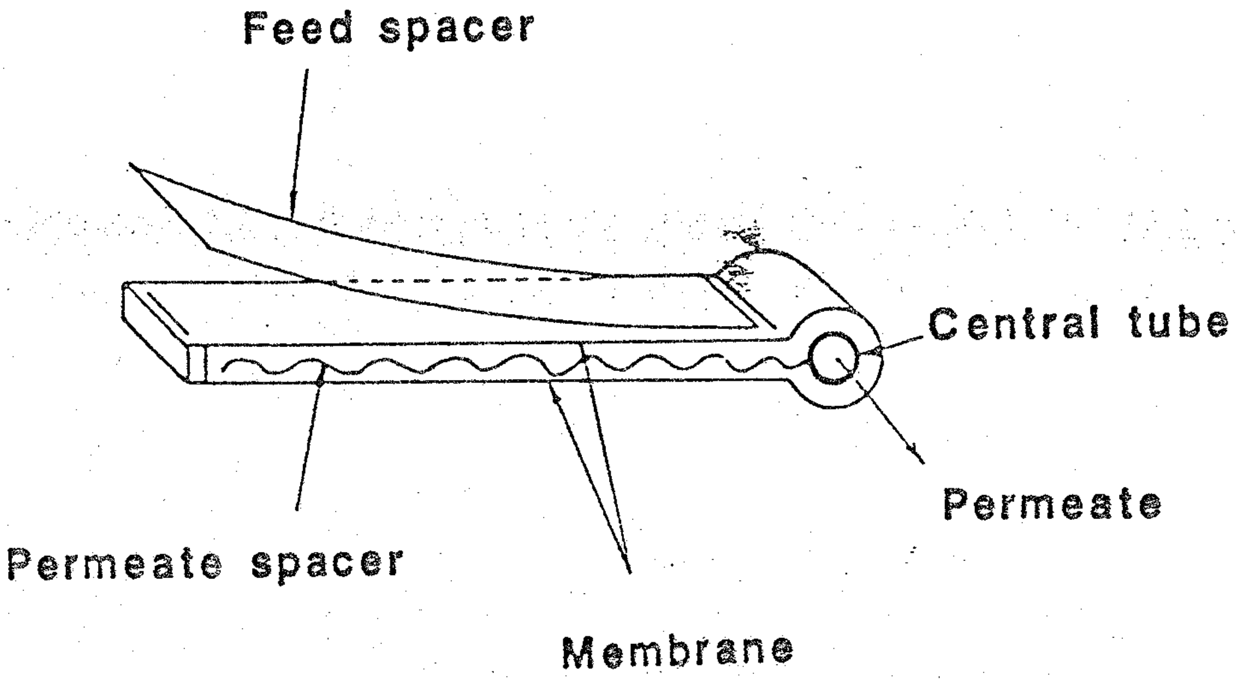


Figure 8-2. Schematic representation of one type of internal fluid flow pattern in a DDS plate-and-frame module design.
(Reproduced with permission from DDS, Nakskov, Denmark).

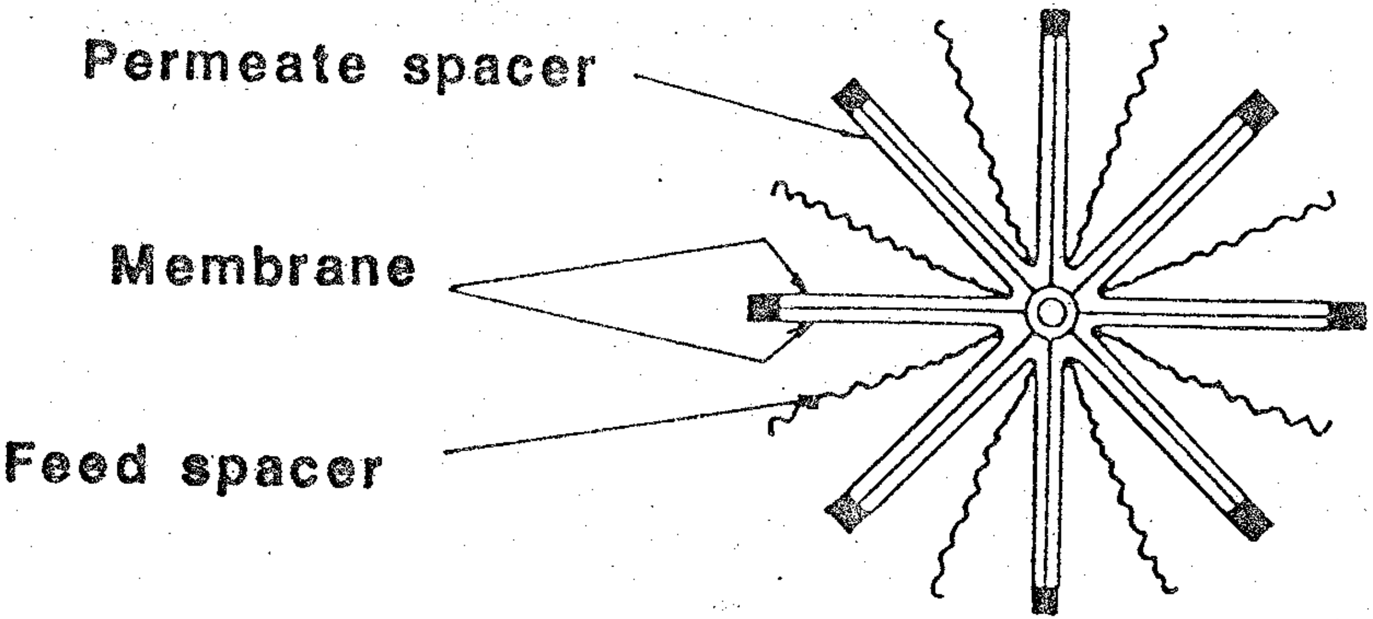
APPEARANCE OF TUBULAR MODULE



ONE LEAF SPIRAL WOUND MODULE



MULTI-LEAVES SPIRAL WOUND MODULE



SPIRAL WOUND MODULE OVERVIEW

Spiral wound module

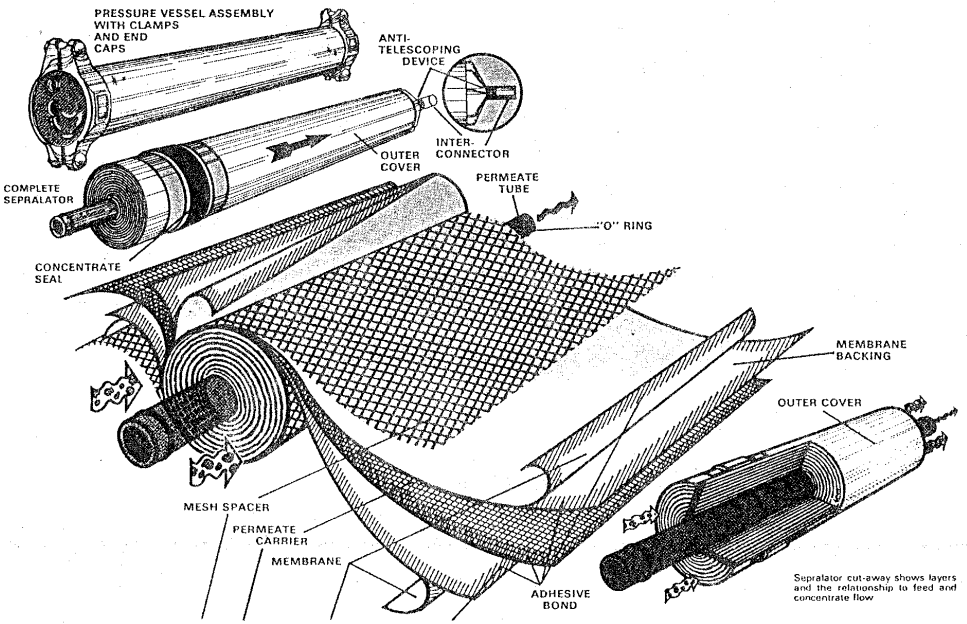
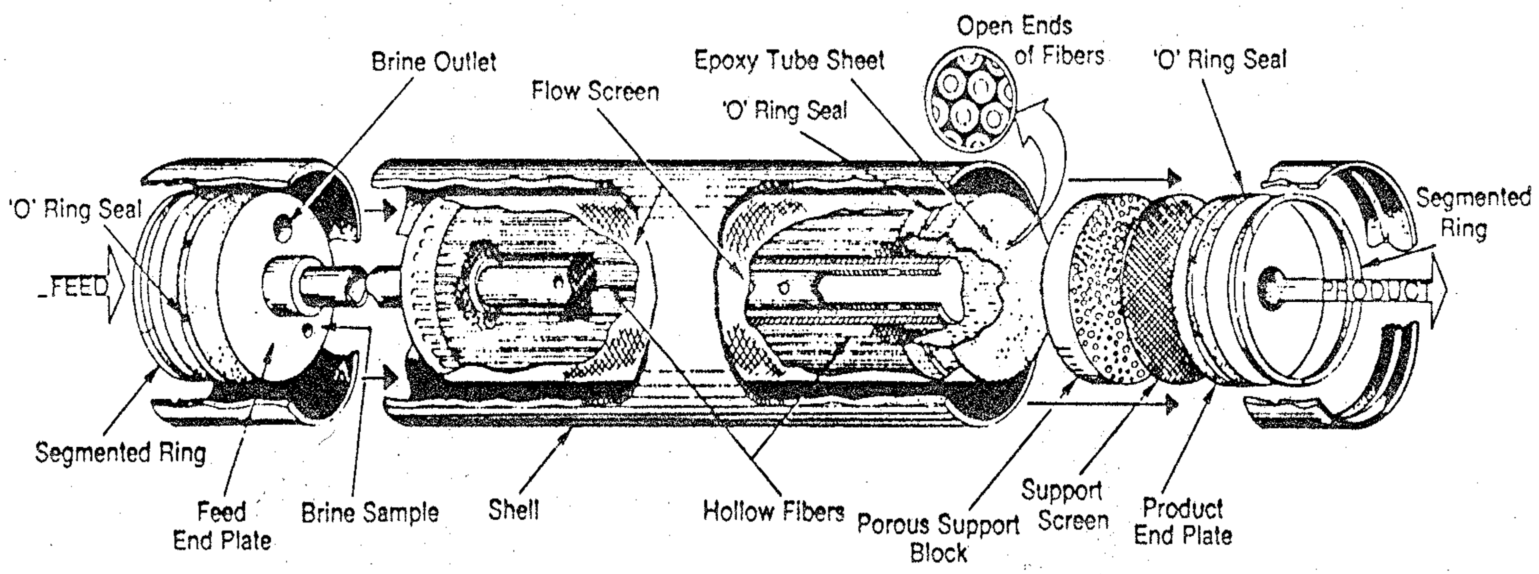


Figure 7.6. Structure of osmonics-type spiral-wound module. (From Technical Bulletin of Osmonics, Inc., with permission.)

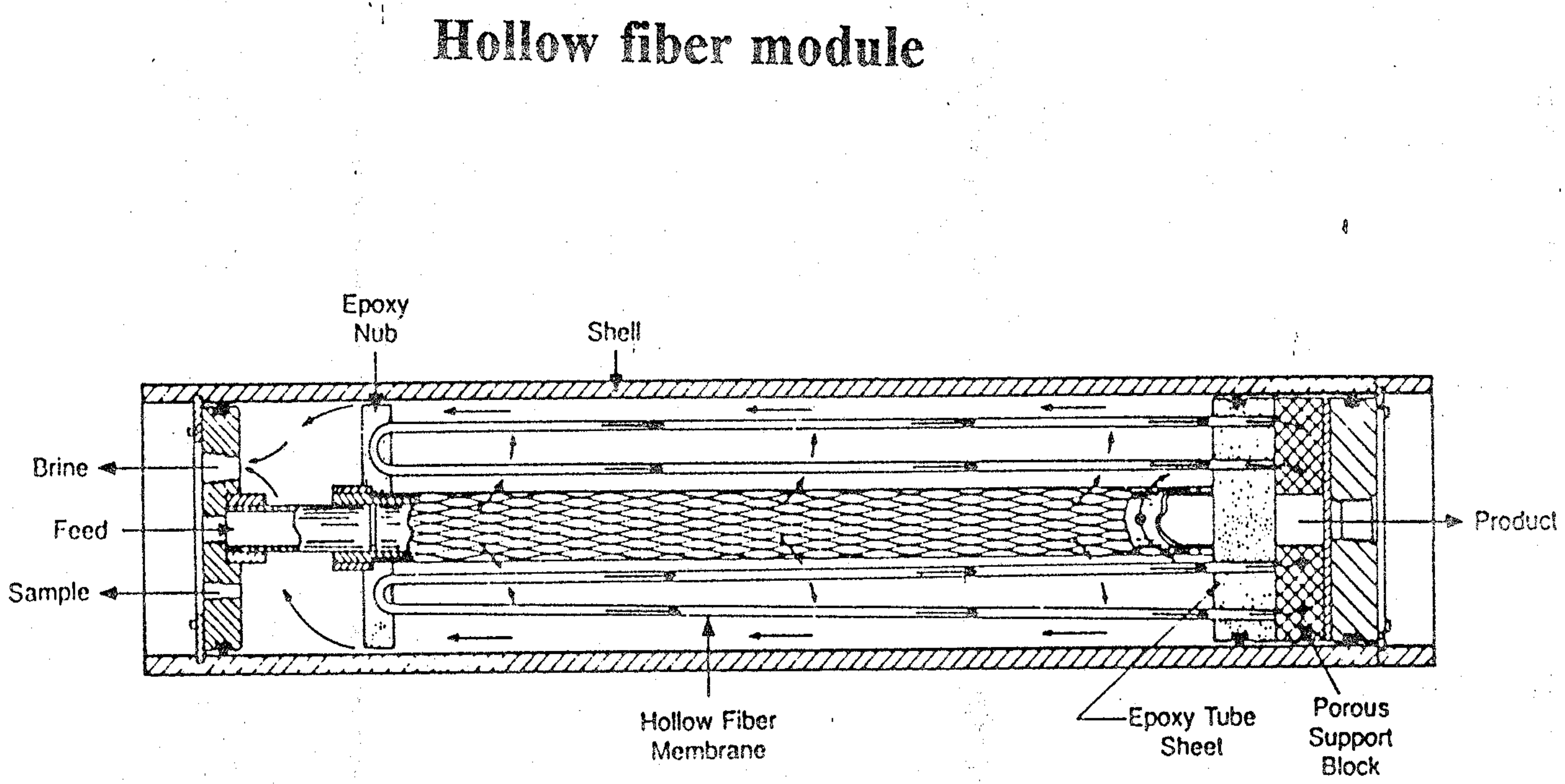
APPEARANCE OF A HOLLOW FIBER

https://www.forwardosmosistech.com/

APPEARANCE OF A HOLLOW FIBER MODULE



CROSS-SECTIONAL VIEW OF HOLLOW FIBER MODULE



ANTI-FOULING MEMBRANES

STRATEGY FOR THE DEVELOPMENT OF ANTI-FOULING MEMBRANES

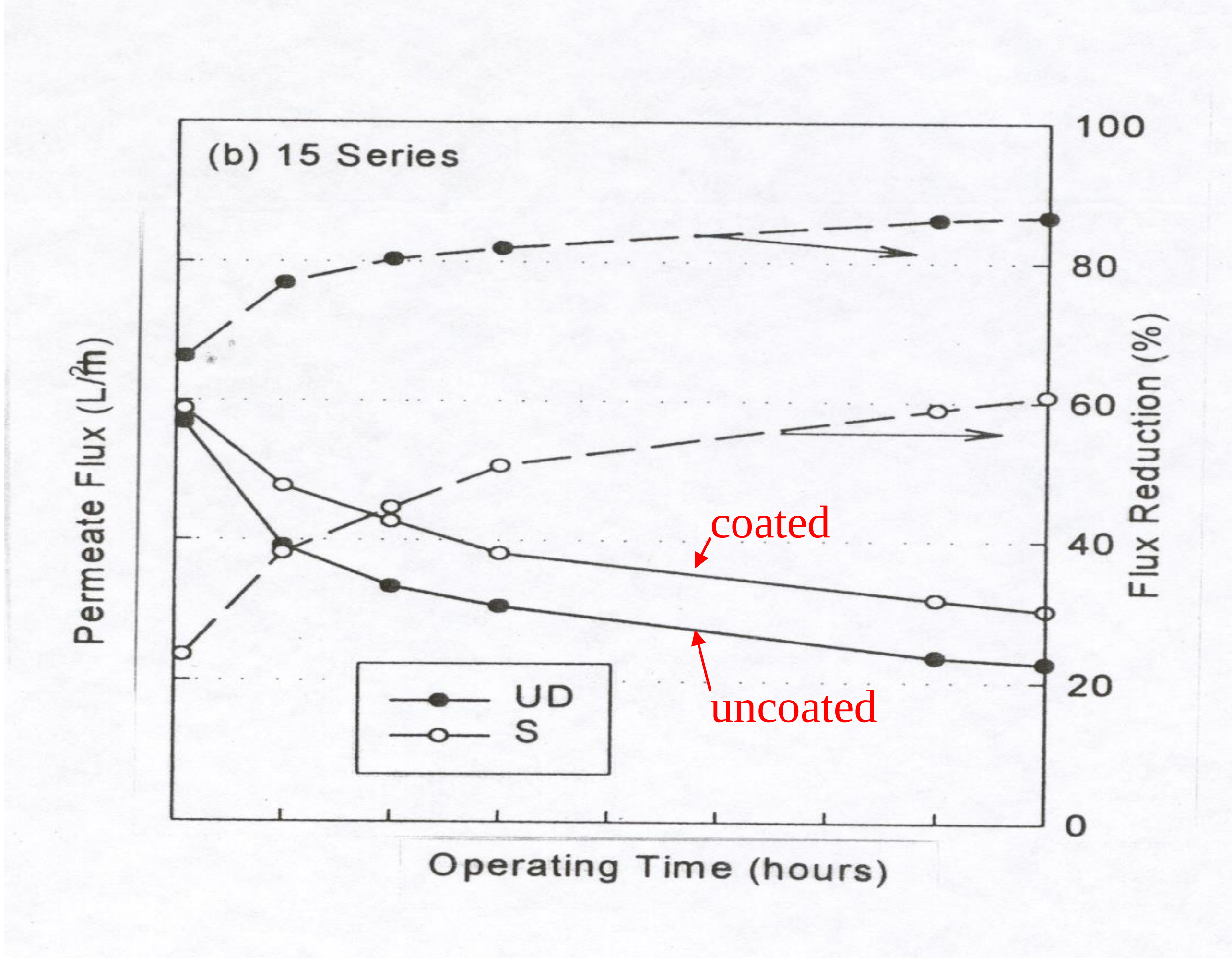
Surface with negative charge: most of nano-filtration membranes

Hydrophilic surface: Saehan, Filtration Solutions

Smooth surface: GE Water Technologies, Osmonics

Surface coating to prevent the pore blocking of porous membranes, NC State University-MTR

FOULING REDUCTION BY COATING SPPO LAYER (LATEX + CLAY MIXTURE)



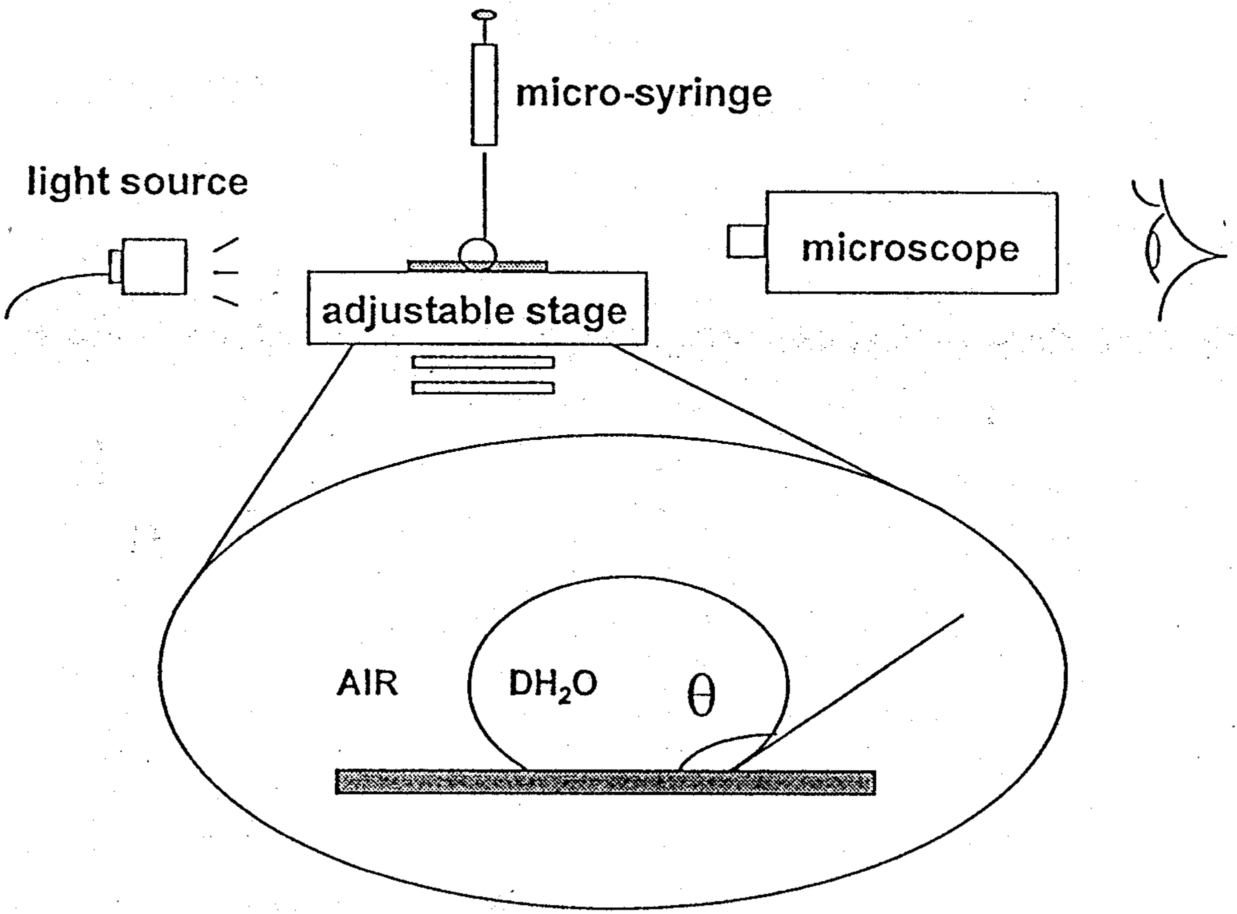
MEMBRANE SURFACE CHEMISTRY

Surface Hydrophilicity/phobicity

Solubility parameter

Contact angle measurement

Apparatus for Contact Angle Studies



SUPERPHILIC MEMBRANES BY FILTRATION SOLUTIONS, INC.

Modified Polyacryl Polymer

Contact Angle 4 Degree

Chemical Resistance

Treatment of Oily Wastewater

PERFECTLY HYDROPHOBIC SURFACE (ONDA ET AL. 1996)

SURFACE MODIFICATION

Surface Coating

Photochemical Grafting

Blending Surface Modifying Macromolecules (SMM)

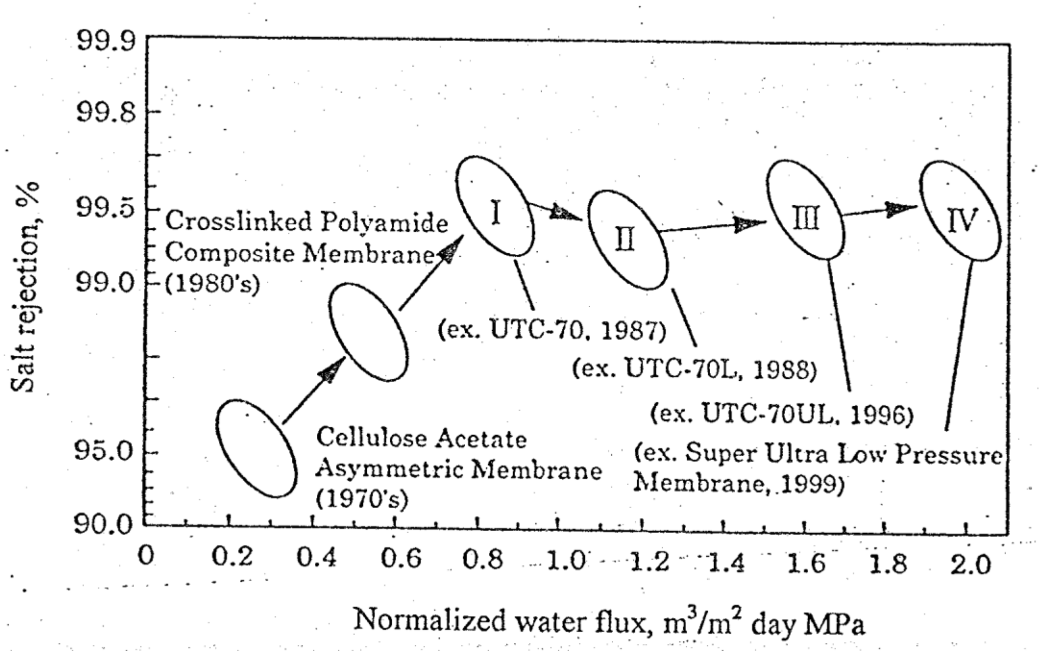
Hydrophilic SMM

Hydrophobic SMM

Charged SMM

RECENT ADVANCES IN MEMBRANE WATER TREATMENT

ADVANCES IN FLUX AND SEPARATION OF TORAY RO MEMBRANE



ADVANCES IN DOW RO MEMBRANE

Year	Production capacity (gpd)	Salt rejection (%)
Brackish water		
1990	8,000	98
1998	10,000	99.2
2007	11,000	99.8
Seawater		
1990	4,000	99.4
1998	5,500	99.5
2007	7,500-8,000	99.8

DEMAND FOR HIGH REMOVAL OF SOLUTES

Boric acid

Arsenic salts

Endocrine disruptor

Trace organics

Trihaloethane, Trihalomethane

Nitrate

REQUIREMENT FOR LOW BORIC ACID CONCENTRATION

EU recomends 1 ppm boric acid

WHO established a limit of 0.3 ppm.

Requirement in certain agricultural areas is below 0.1 ppm.

Average boric acid concentration in seawater is 5 ppm.

Current RO systems produce permeate with 0.8-1.3 ppm.

SOME EXPERIMENTAL DATA FOR BORON REJECTION-EFFECT OF PH

pH	Boron concentration (ppm)	Rejection (%)
7	10.7	43
10	10.7	90

TrisSep cooperation: A-4040-X201-TSF RO element tested at 10% recovery, 1500 ppm NaCl at 150 psig, NaCl rejection 99.5%

EFFECTS OF ARSENIC

- Cancer : bladder, lung, skin, kidney, and liver
- Harms the central, periphera nervous, heart, and blood vessels systems
- Serious skin problems
- Birth defects and reproductiv problems

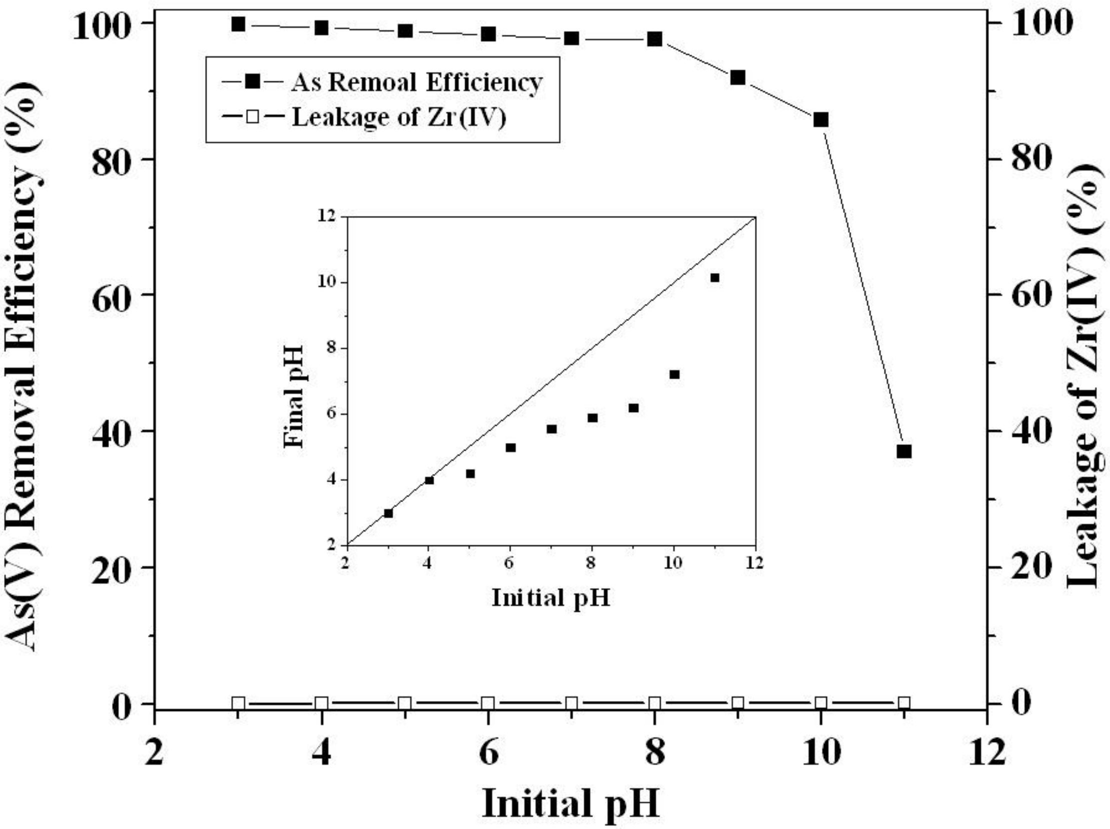
ARSENIC LEVEL IN TAP WATER AND CANCER RISK

Arsenic Level in Tap Water (ppb)	Approximate Total Cancer Risk (assuming 2 liters consumed/day)
0.5	1 in 10,000
1	1 in 5,000
3	1 in 1,667
4	1 in 1,250
5	1 in 1,000
10	1 in 500 (year 2006)
20	1 in 250
25	1 in 200
50	1 in 100 (year 1942)

NEW STANDARD FOR DRINKING WATER
23RD JANUARY 2006

© 2006 - Padu

AS(V) REMOVAL


As(V) Removal Efficiency (%)
Leakage of Zr(IV) (%)
Initial pH
As Remoal Efficiency
Leakage of Zr(IV)
0
20
40
60
80
100
2
4
6
8
10
12
Final pH
Initial pH

ENDOCRINE DISRUPTION COMPOUNDS (EDCS)

EDCs disturb the endocrine system by mimicking, blocking or also disrupting function of hormone

The major exposure route both for humans and animals is by ingestion of EDCs via food/drink intake which leads to bioaccumulation and biomagnification

TYPICAL EDCS

Bisphenol A (BPA)

Nonylphenol

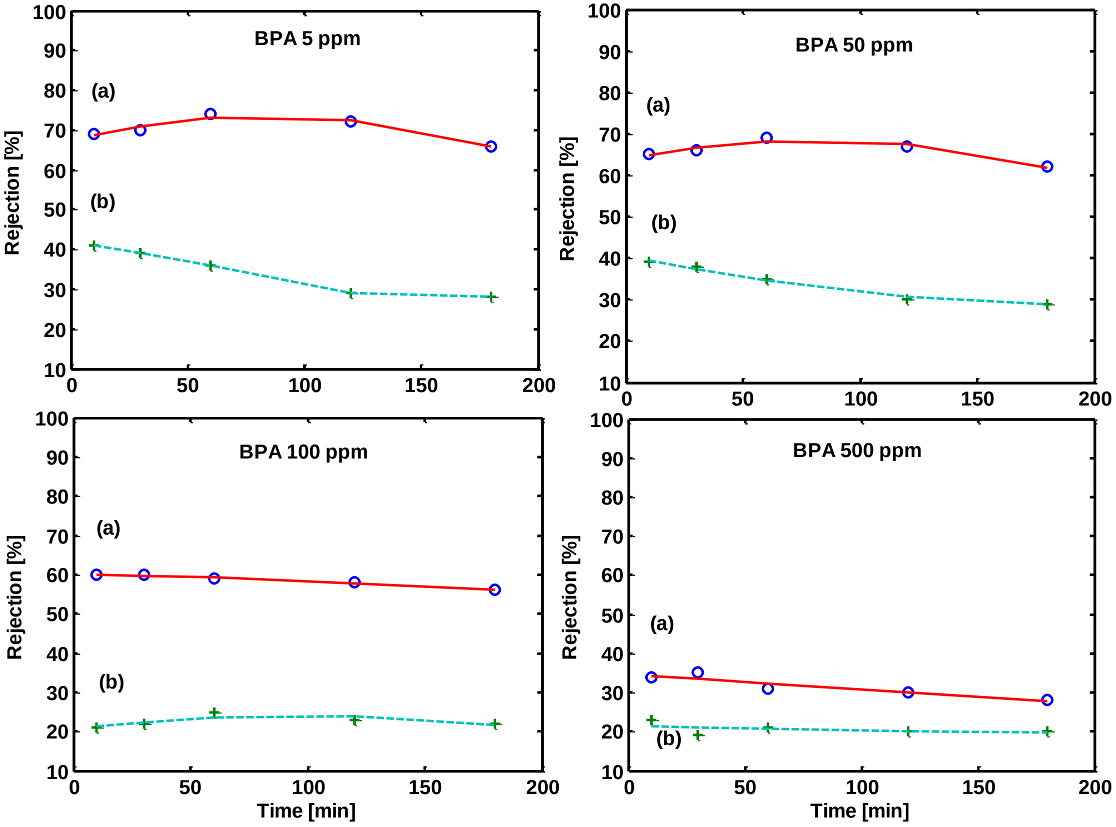
Octylphenol

Perfluorooctanoic acid

Perfluorooctyl sulfonate

Phthalates

BPA REMOVAL BY MODIFIED (--)AND UNMODIFIED (--)PES HOLLOW FIBERS



HYBRID SYSTEM-MEMBRANE BIO REACTOR (MBR)

PROCESS CONFIGURATION

Process Configuration

Parameter	**Conventional Activated sludge Process**	**Immersed Membrane as a secondary Clarifier (MLSS=600 mg/L)**	**Membrane bioreactor (MLSS=10,000 mg/L)**
Retention Time	**> 10 hours**	**> 10 hours**	**< 2 hours**
BOD	**20 mg/L**	**< 4 mg/L**	**< 8 mg/L**
Suspended solid	**> 10 mg/L**	**< 1.0 mg/L**	**< 1.0 mg/L**
Turbidity	**< 10 NTU**	**< 0.4 NTU**	**< 0.5 NTU**
Total Coliforms	**> 20,000 cfu/100ml**	**< 20 cfu/100ml**	**< 20 cfu/100ml**
Bacteriophages	**> 1.4 × 10(4)**	**< 1.9**	**< 1.9**
SDI	**> 5**	**< 2**	**< 3**

NANOTECHNOLOGY APPLICATIONS

Incorporation of Nanoparticles in the membrane

- Biofouling reduction by Ag nanoparticle

Electrospun nanofiber membrane (ENM)

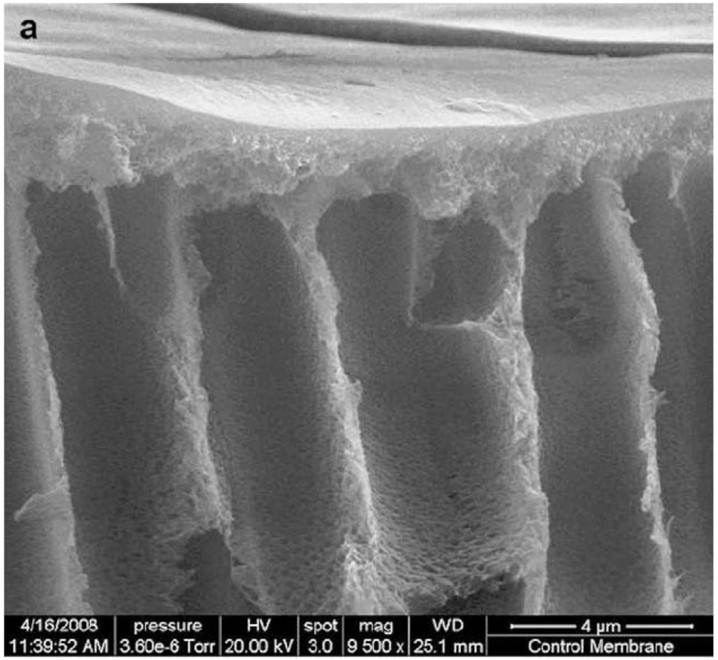
- Membrane Adsorption by Carbonized ENM

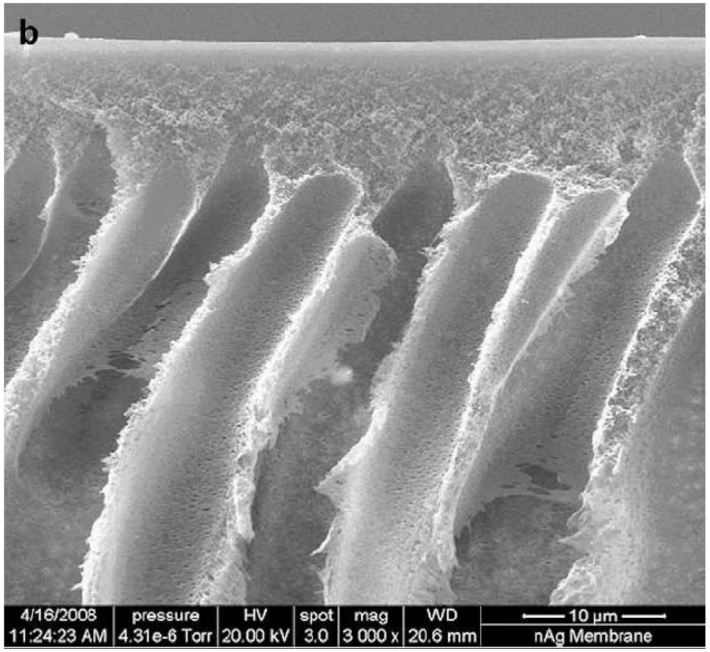
SILVER NANOPARTICLES INCORPORATED IN POLYSULFONE ULTRAFILTRATION MEMBRANE (BIOFOULING REDUCTION)

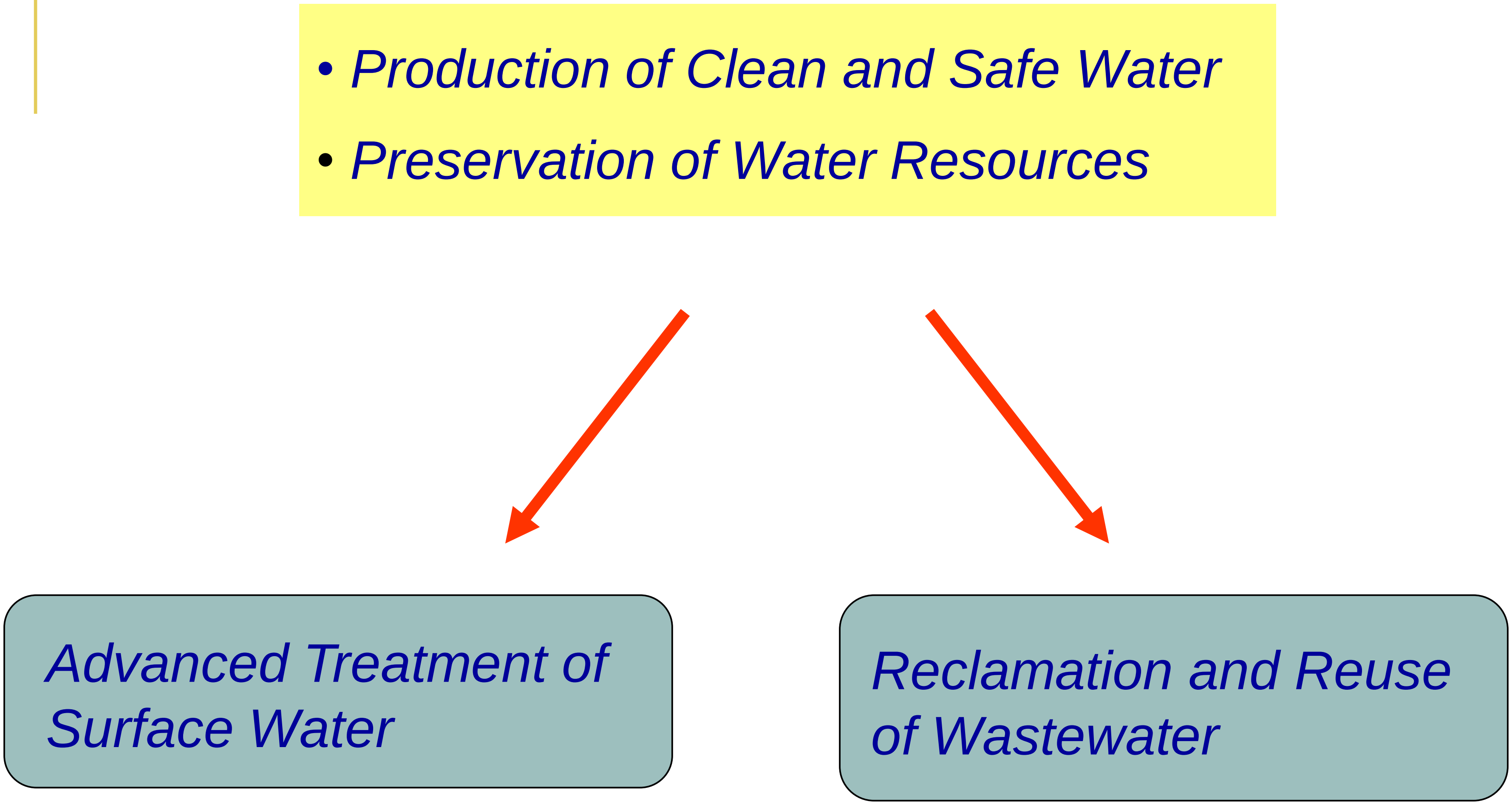
Membrane preparation

- Membranes prepared by phase inversion technique from polymer solution (15% polysulfone, 10% polyvinylpyrrolidone, 75% n-methyl pyrrolidone and 0.22% Ag-nanoparticle).
- Asymmetric membrane is formed

PICTURES OF ASYMMETRIC MEMBRANE (FROM ZODROW ET AL. WATER RESEARCH 43(2009) 715)







- *Production of Clean and Safe Water*
- *Preservation of Water Resources*

Advanced Treatment of Surface Water

Reclamation and Reuse of Wastewater

Environmental Protection

Pollution of Water Resources due to Economic Activities

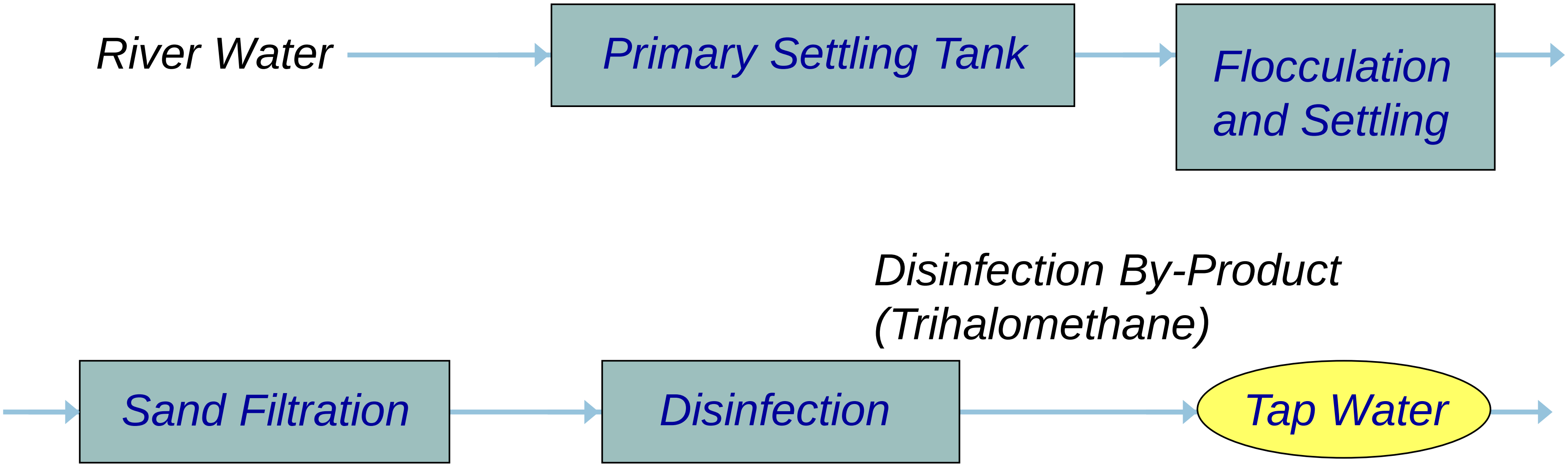
Highly Polluted Raw Water

- *Nutrients*
- *Microbial Contaminants*
- *Inorganic Ions*
- *Refractory Organics*

→ *Beyond Naturally Decomposable Limits*

CURRENT TREND IN WATER TREATMENT

Surface Water Treatment in Japan



River Water

Primary Settling Tank

Flocculation and Settling

Sand Filtration

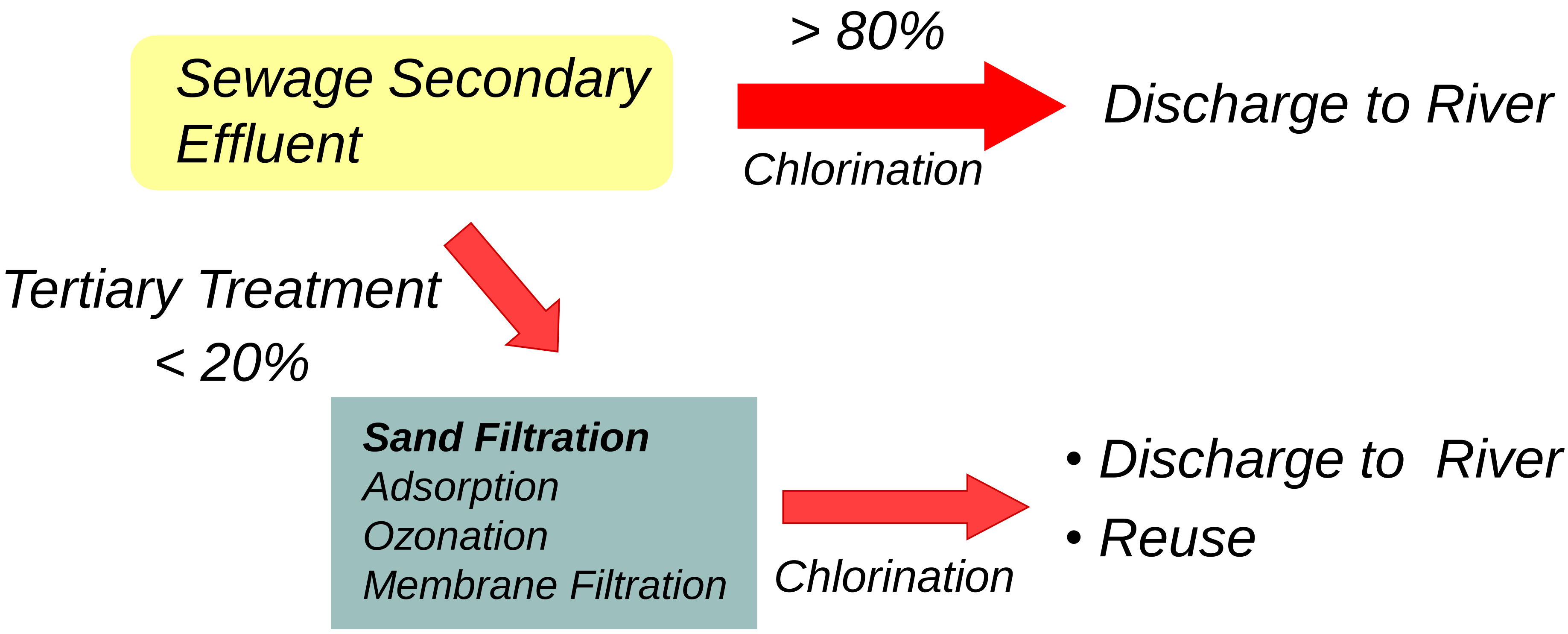
Disinfection

Disinfection By-Product
(Trihalomethane)

Tap Water

CURRENT TREND IN WATER TREATMENT

Wastewater Reclamation and Reuse in Japan



Sewage Secondary Effluent

> 80%

Chlorination

Discharge to River

Tertiary Treatment

< 20%

Sand Filtration
Adsorption
Ozonation
Membrane Filtration

Chlorination

- *Discharge to River*
- *Reuse*

- *Increase in Importance of Water Reclamation and Reuse*
- *Especially the Necessity for Urban Reuse*

OUR RESEARCH ACTIVITIES UNDER NATIONAL PROJECT

- *Hybrid Membrane Separation System for Advanced Treatment of Surface Water*

Supported by Future Program of Japan Society for the Promotion of Science

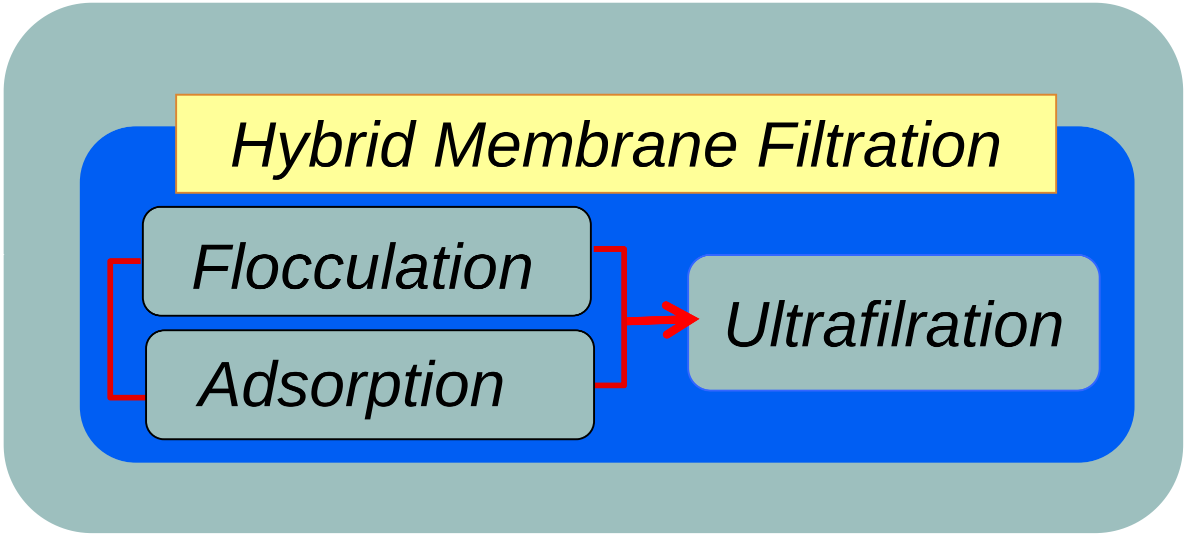
- *Water Reclamation and Reuse through Advanced Treatment of Wastewater*

Promoted by Japan Science and Technology Corporation

Hybrid Membrane Separation System for Advanced Treatment of Surface Water

River Water

Primary Settling



Hybrid Membrane Filtration

Flocculation

Adsorption

Ultrafilration

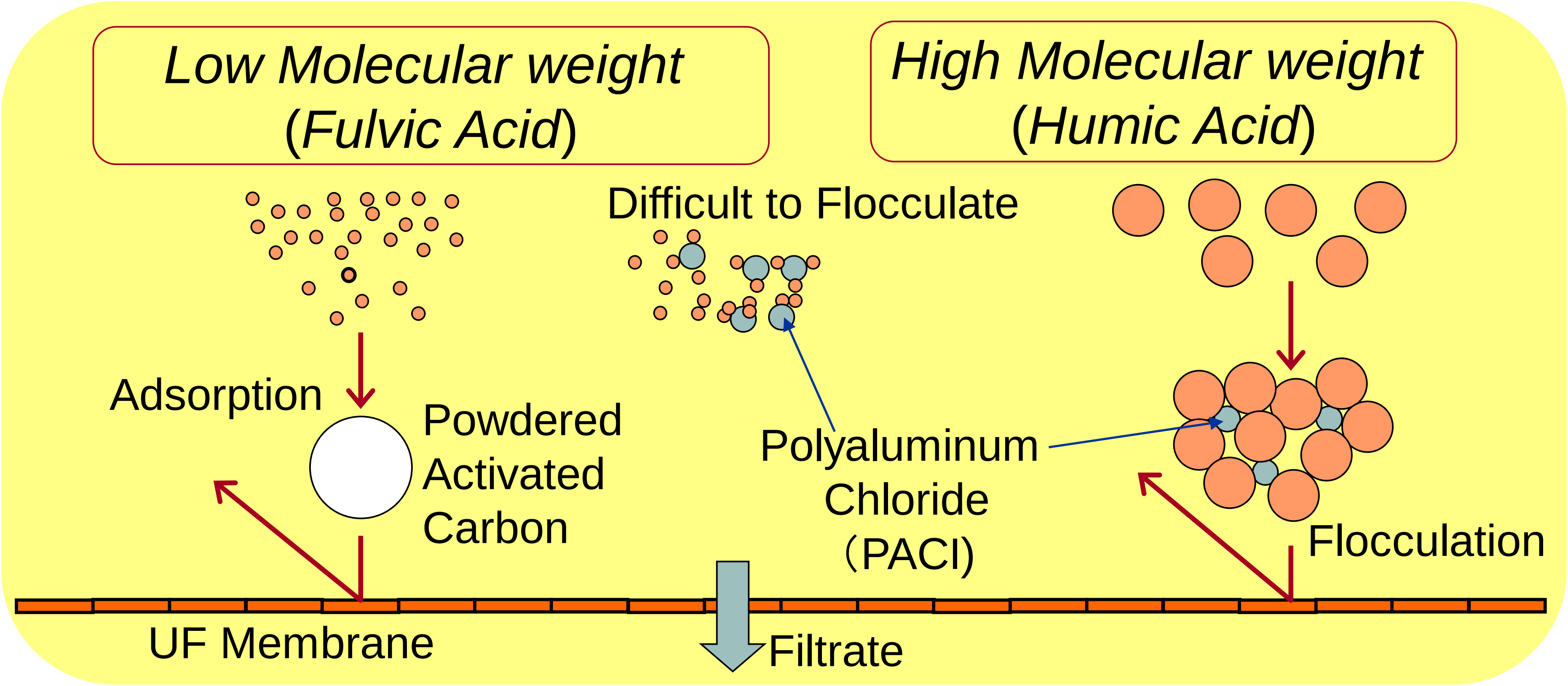
Tap Water

Target Contaminants to be Eliminated from Surface Water → *Humic Substances*

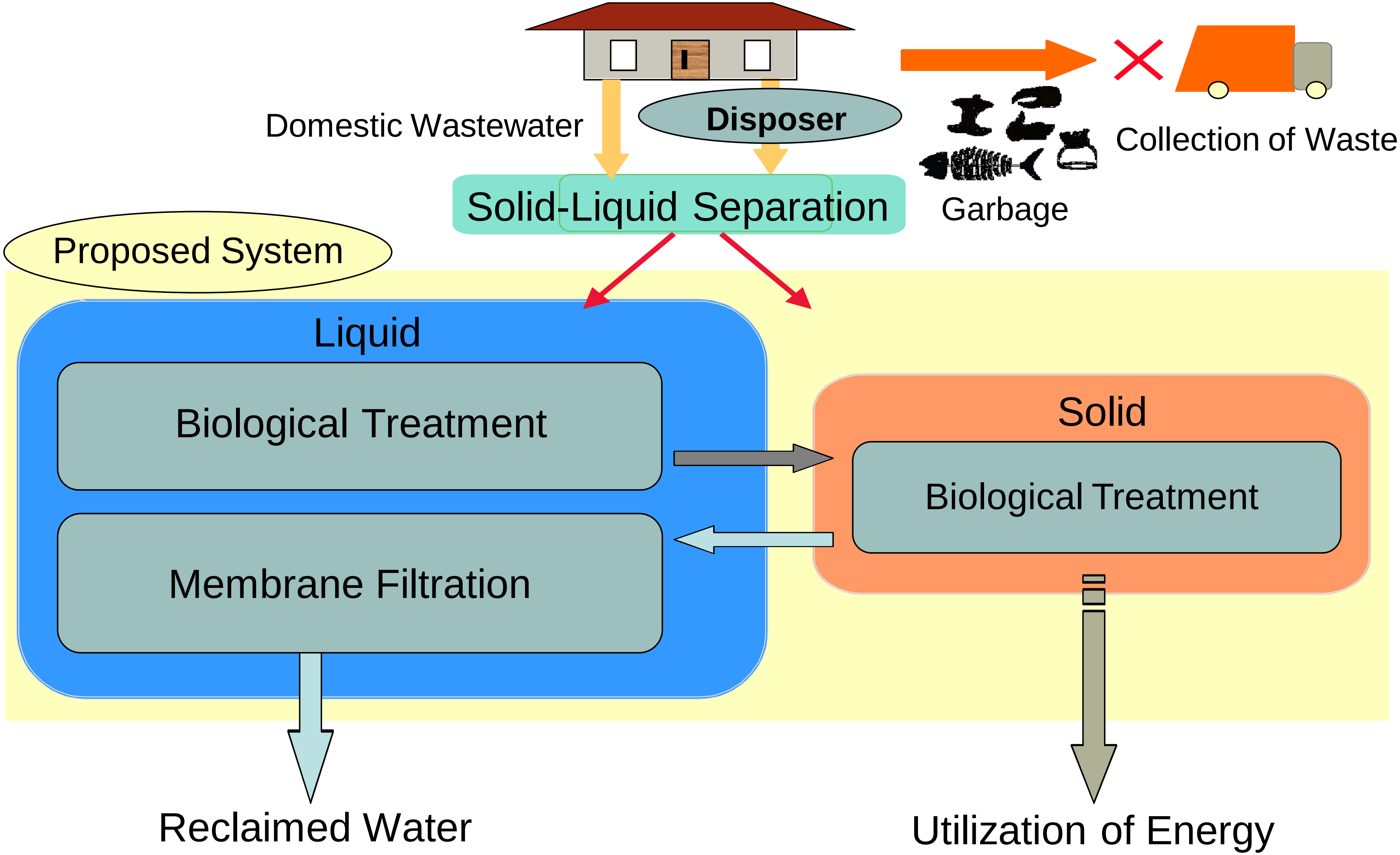
- *Formation of Trihalomethane (Carcinogen)*
- *Color*

Wide Range of Molecular Weight → *Difficult to Remove by Conventional Method*

Separation Mechanism



Water Reclamation and Reuse through Advanced Treatment of Wastewater



Domestic Wastewater

Disposer

Garbage

Collection of Waste

Solid-Liquid Separation

Proposed System

Liquid

Biological Treatment

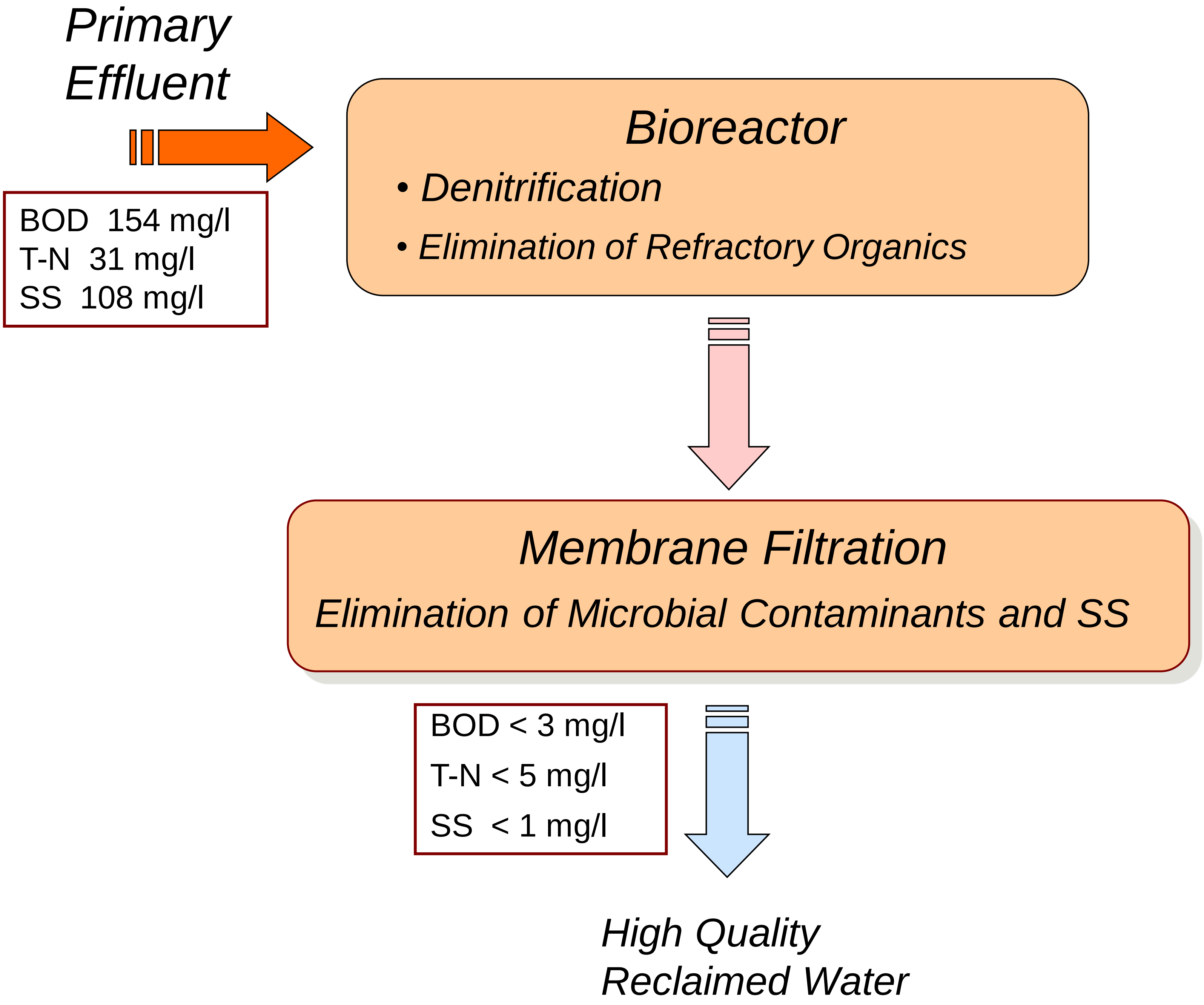
Membrane Filtration

Solid

Biological Treatment

Reclaimed Water

Utilization of Energy



Primary Effluent

BOD 154 mg/l
T-N 31 mg/l
SS 108 mg/l

Bioreactor

- *Denitrification*
- *Elimination of Refractory Organics*

Membrane Filtration

Elimination of Microbial Contaminants and SS

BOD < 3 mg/l
T-N < 5 mg/l
SS < 1 mg/l

High Quality
Reclaimed Water

COMBINED SYSTEM OF MEMBRANE FILTRATION AND COAGULATION WITH CYCLIC BACKWASHING

Merits of Membrane Filtration

- *Stable Water Quality*
- *Compact Plant Design*
- *Easiness of Automatic Control*

Sewage Secondary Effluent

Microfiltration

Poor Quality

Lower Rejection than Ultrafiltration

Combination with Coagulation Pretreatment

Improvement of Water Quality and Permeate Flux by Coagulation

Sewage Secondary Effluent

Coagulation

Microfiltration

High Rejection

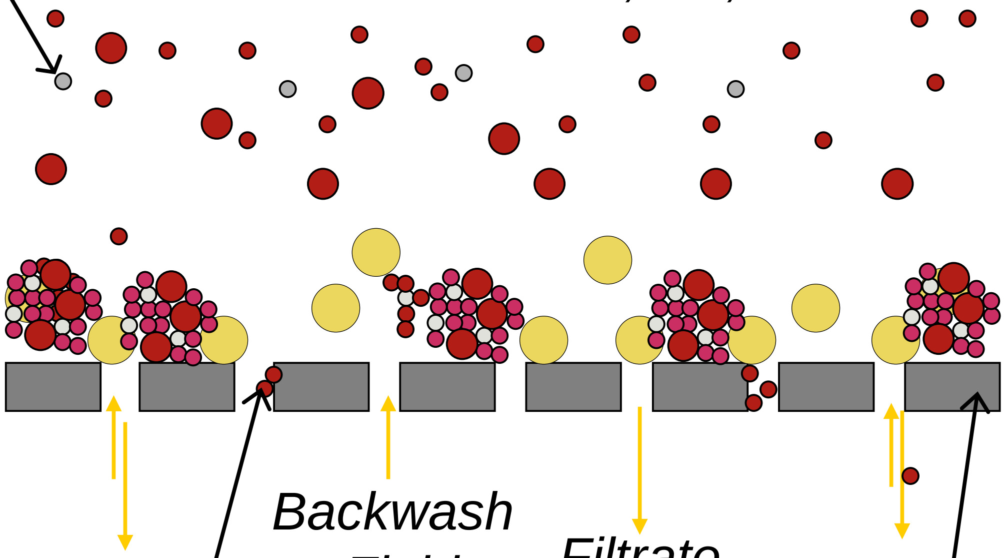
High Quality

Coagulant (PACl)

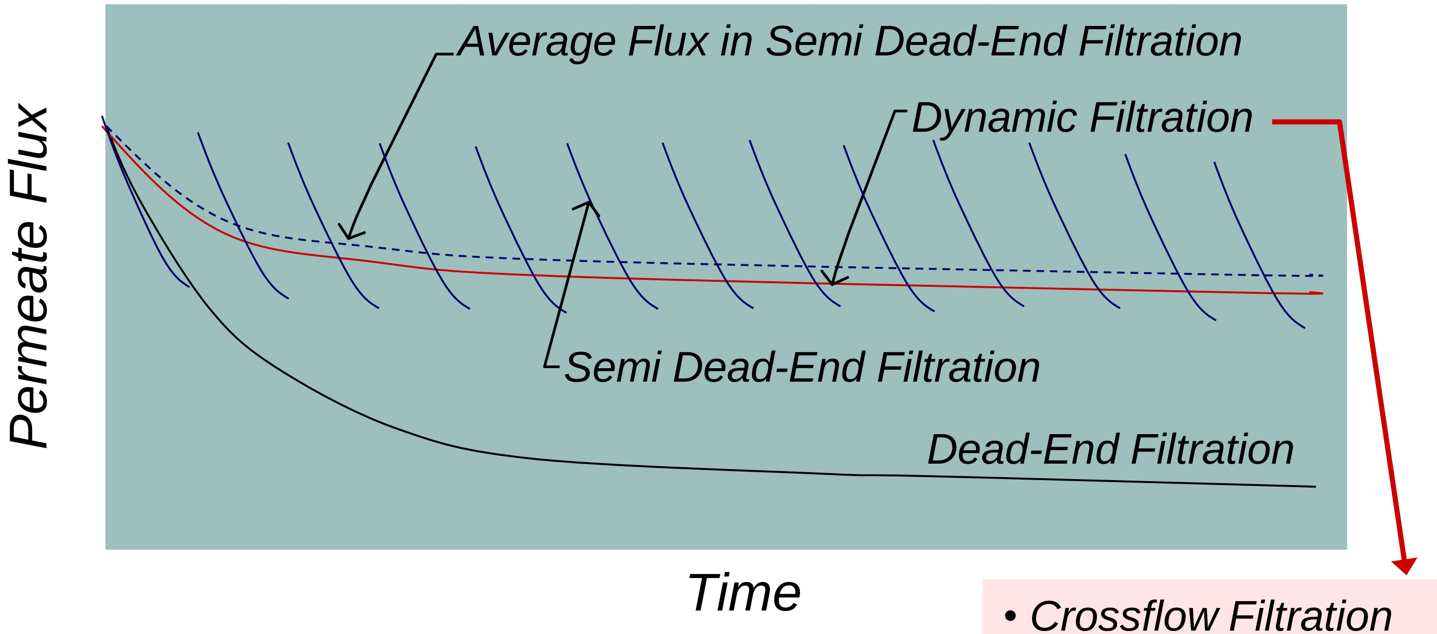
Coagulated Sewage Secondary Effluent

Microbial Contaminants, SS, etc.

- *Enhancing Removal of Microbial Contaminants, SS, etc.*
- *Reducing Foulant Penetration into pore*
- *Formation of More Porous Cake*
- *Enhancing Particle Backtransport*



Microfiltration with Cyclic Backwashing



- *Crossflow Filtration*
- *Rotating Type Filtration, etc.*

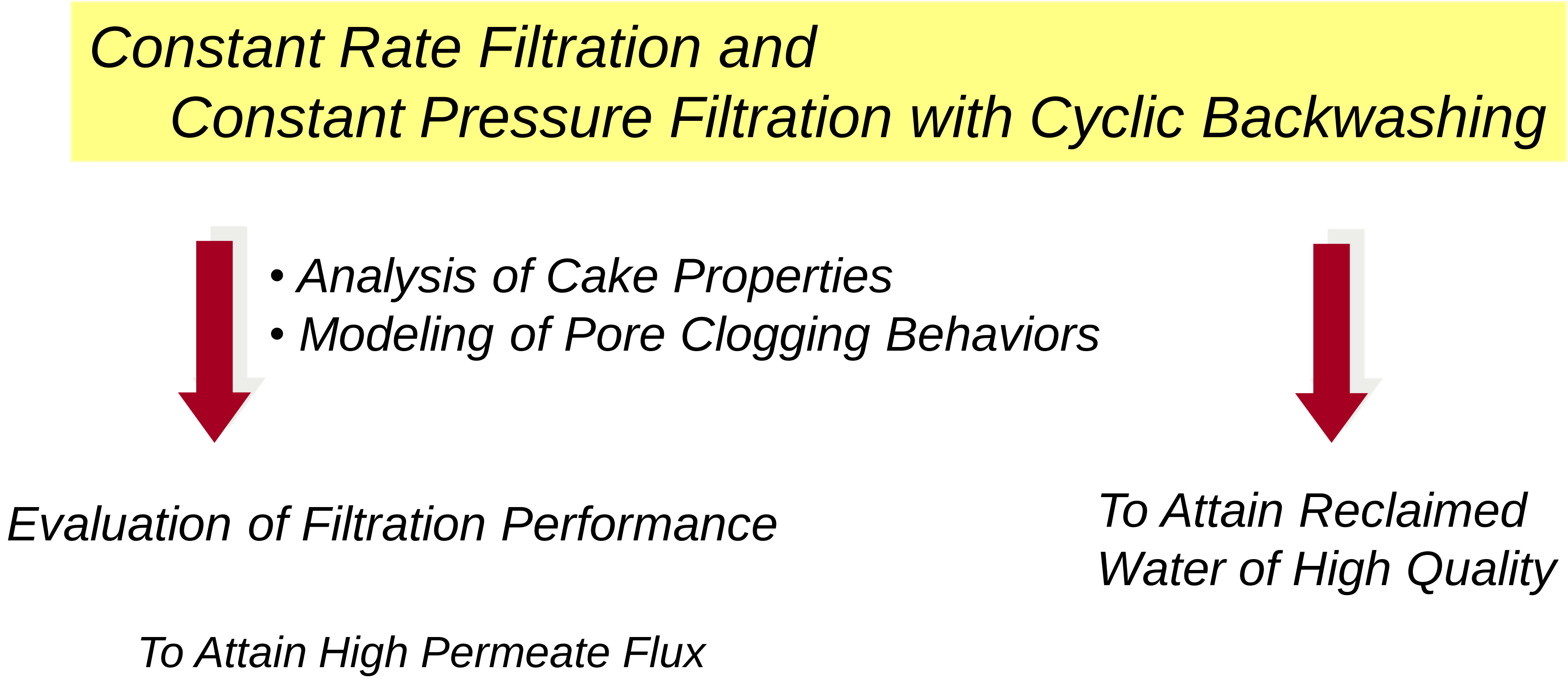
Ceramic Membrane

Resistant to

- *High Pressure Backwashing*
- *Chemically Enhanced Backwashing*

Lack of Information on

- *Cake Formation*
- *Pore Blocking*



Constant Rate Filtration and
Constant Pressure Filtration with Cyclic Backwashing

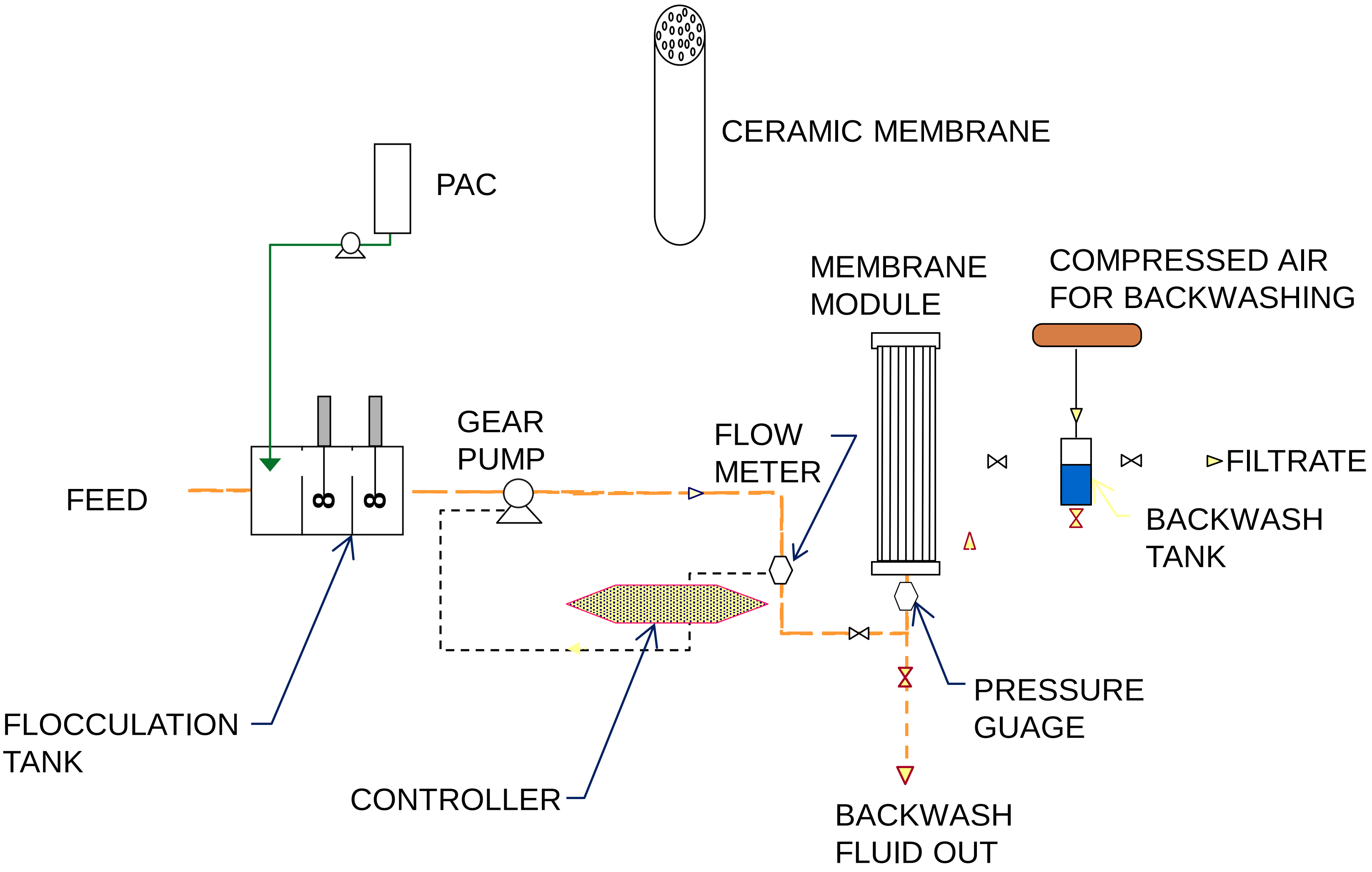
- *Analysis of Cake Properties*
- *Modeling of Pore Clogging Behaviors*

Evaluation of Filtration Performance

To Attain High Permeate Flux

To Attain Reclaimed Water of High Quality

LAB SCALE EXPERIMENTAL APPARATUS



CERAMIC MEMBRANE

PAC

MEMBRANE
MODULE

COMPRESSED AIR
FOR BACKWASHING

GEAR
PUMP

FLOW
METER

FILTRATE

FEED

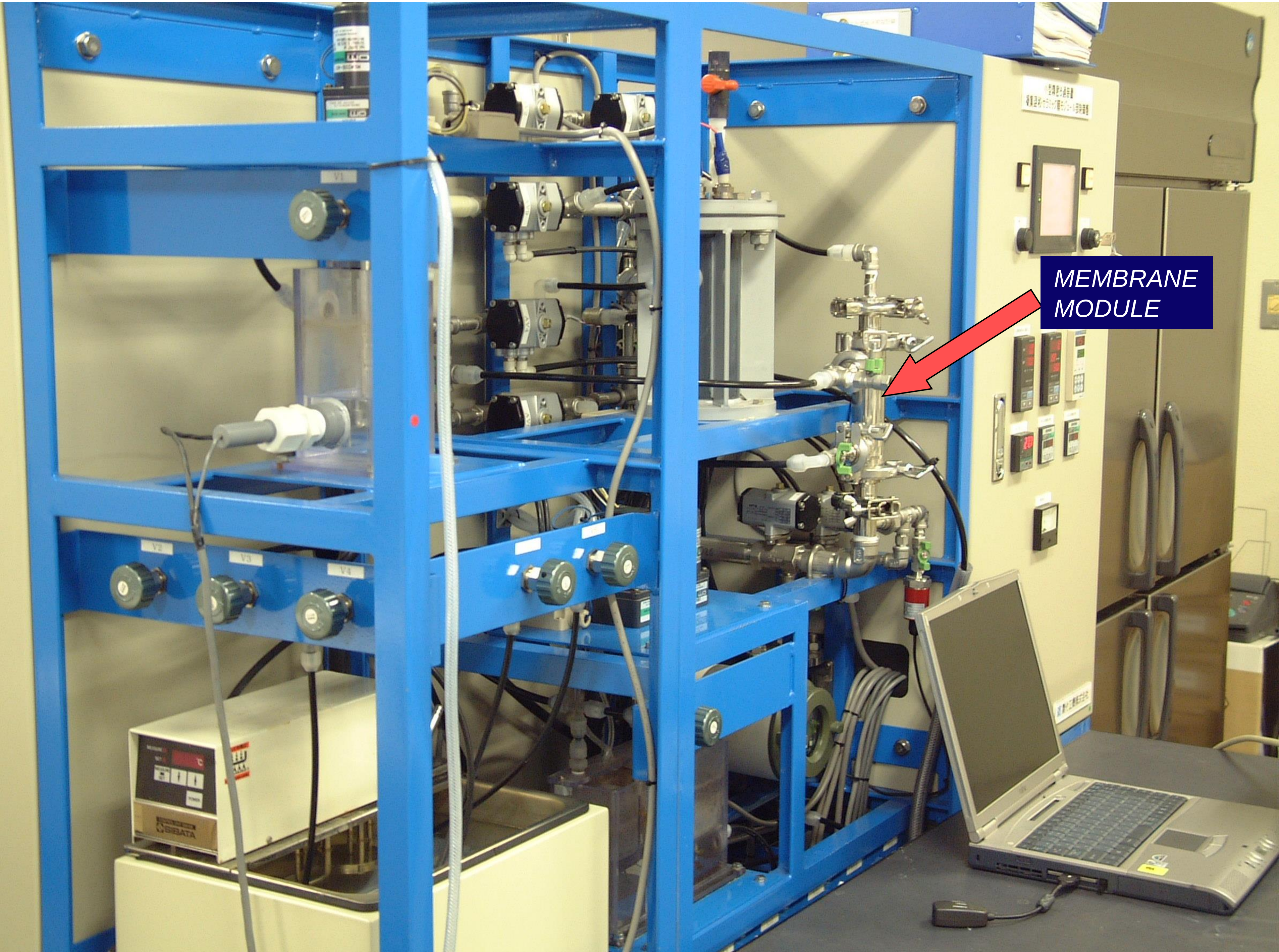
BACKWASH
TANK

PRESSURE
GUAGE

FLOCCULATION
TANK

CONTROLLER

BACKWASH
FLUID OUT


MEMBRANE MODULE

Sewage Secondary Effluent

Coagulation *2 ppm-Al of PACl*

Constant Rate Operation

$J_v = 2.8$ m/d

$\Delta p_{cf} = 30, 60, 90$ kPa

Constant Pressure Operation

$p = 60$ kPa

$J_{vf} = 2$ m/d

Backwash Pressure : 500 kPa

- *Measurements of Pressure and Permeate Flux*
- *Analysis of Water Quality* (E.coli, SS, Turbidity, BOD, etc.)

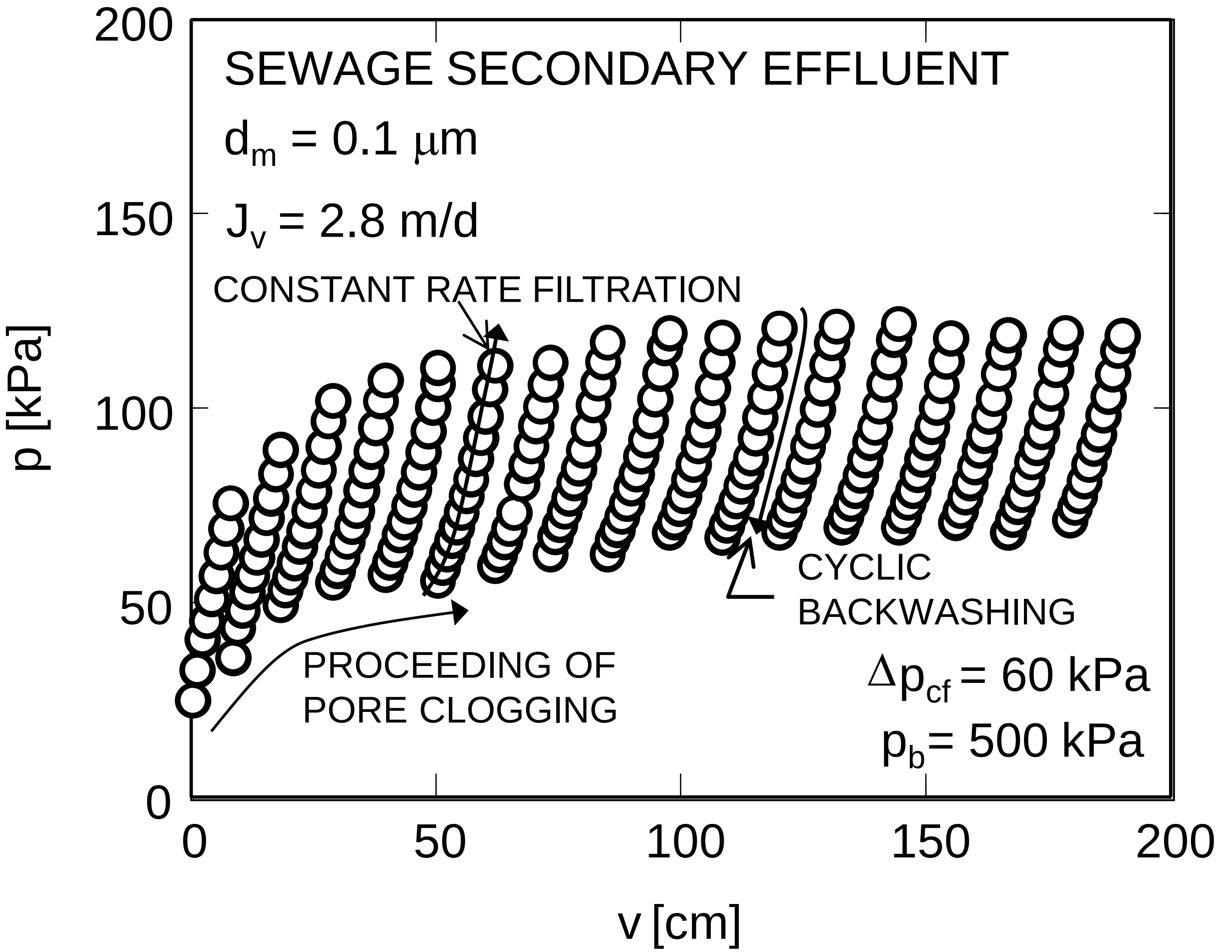
Water Quality

	E.Coli [100 ml^{-1}]	SS [mg/l]	Turbidity [mg/l-kaolin]	BOD [mg/l]
Feed*	1.7×10^4	3	6	15
Filtrate	Nil	<1	< 1	1.3
Target**	50	-	< 5	< 3

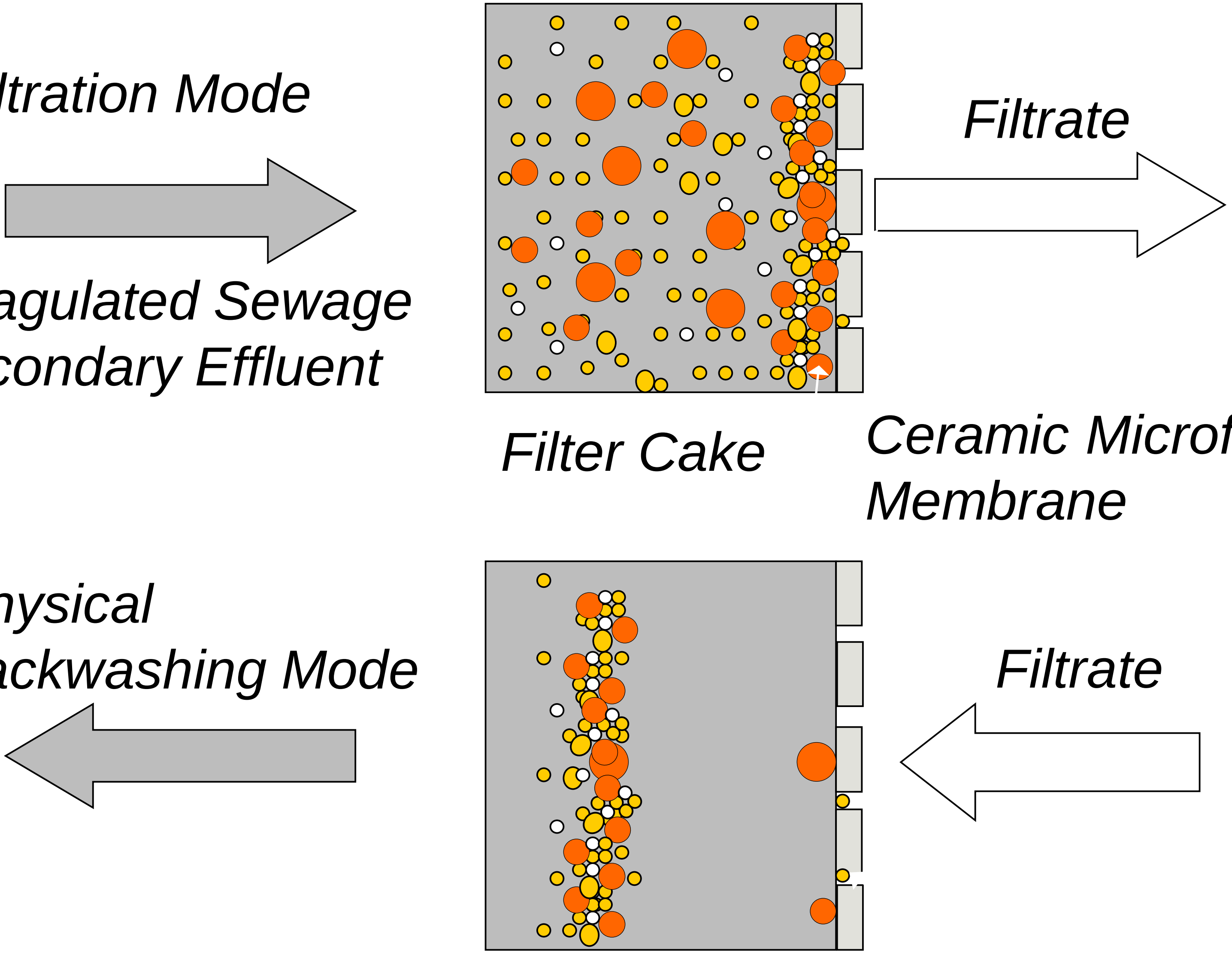
*) *Feed: Sewage Secondary Effluent*

**) *Target: Adequate Sanitary Water*

Constant Rate Filtration with Cyclic Backwashing



Role of Physical Backwashing



(a) Filtration Mode

Coagulated Sewage
Secondary Effluent

Filtrate

Filter Cake

Ceramic Microfiltration
Membrane

(b) Physical
Backwashing Mode

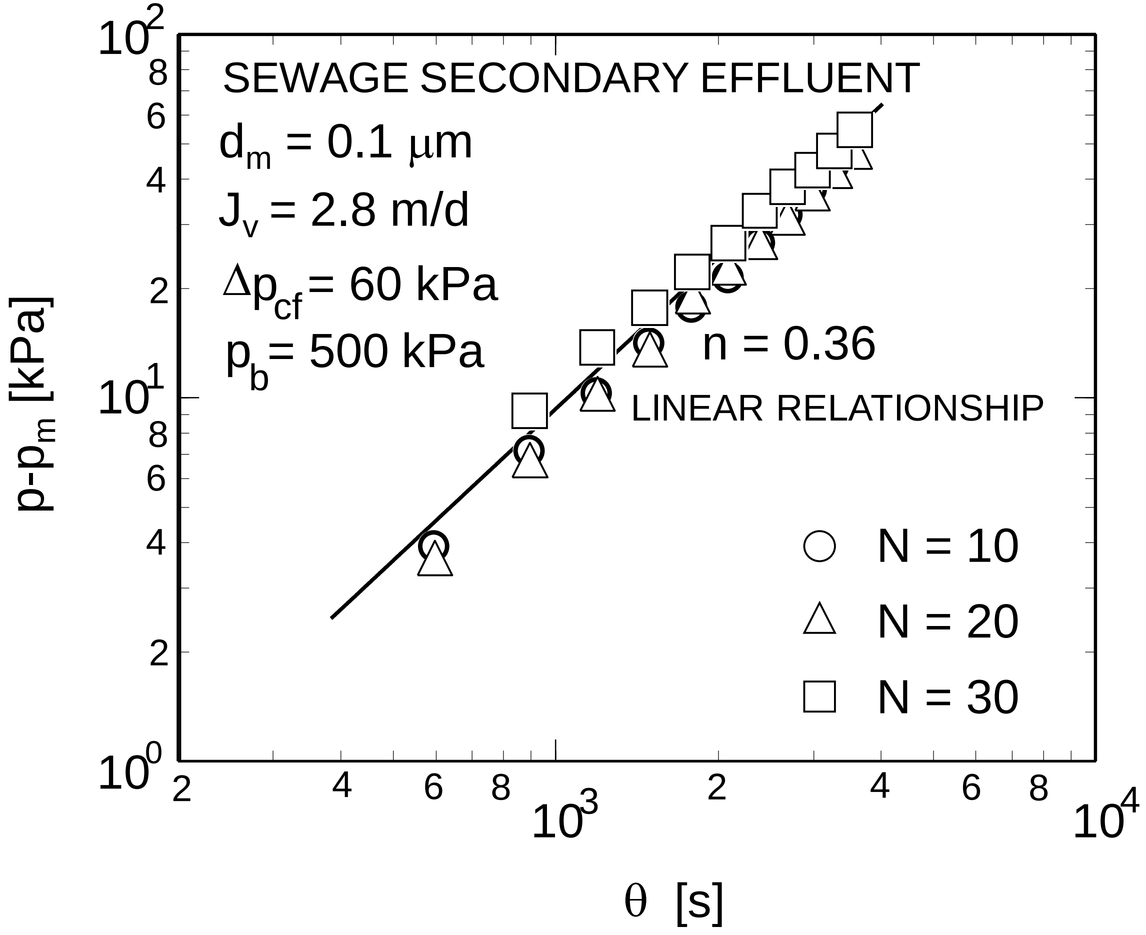
Filtrate

Irreversible Pore Clogginging

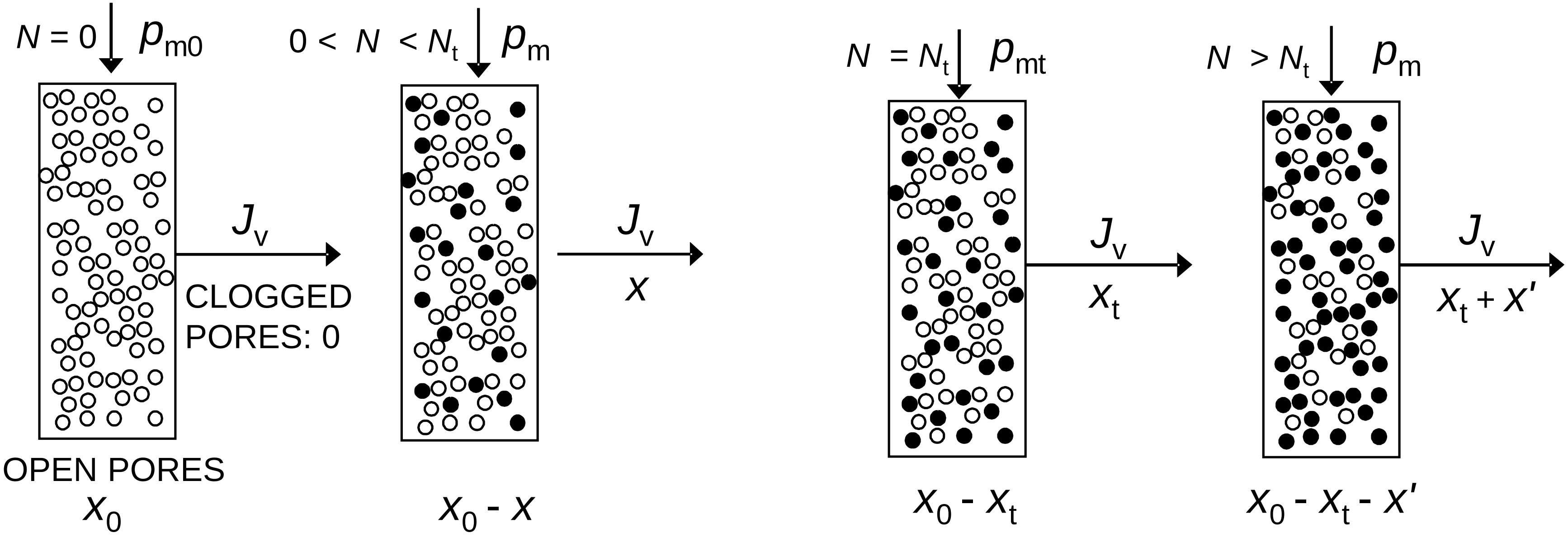
Cake Filtration Equation under Constant Rate Condition

(For Each Filtration Cycle)

$$p - p_m = \left(\frac{\mu\alpha_0\rho s J_v^2}{1-ms}\right)^{\frac{1}{1-n}} \theta^{\frac{1}{1-n}} \qquad (1)$$



Pore Clogging in Constant Rate Filtration



(a) First Stage (Rapid Clogging Period)

(b) Second Stage (Gradual Clogging Period)

$N = 0$ ⇨ $$J_v = k x_0 p_{m0} \quad (2a)$$

$N \le N_t$ ⇨ $$J_v = k(x_0 - x)p_m \quad (3a)$$

Intermediate blocking law ⇨ $$x = x_0\{1 - \exp(-\eta N)\} \quad (4a)$$

$$p_m = p_{m0}\exp(\eta N) \quad (5a)$$

$N = N_t$ ⇨ $$J_v = k(x_0 - x_t)p_{mt} \quad (2b)$$

$N \ge N_t$ ⇨ $$J_v = k(x_0 - x_t - x')p_m \quad (3b)$$

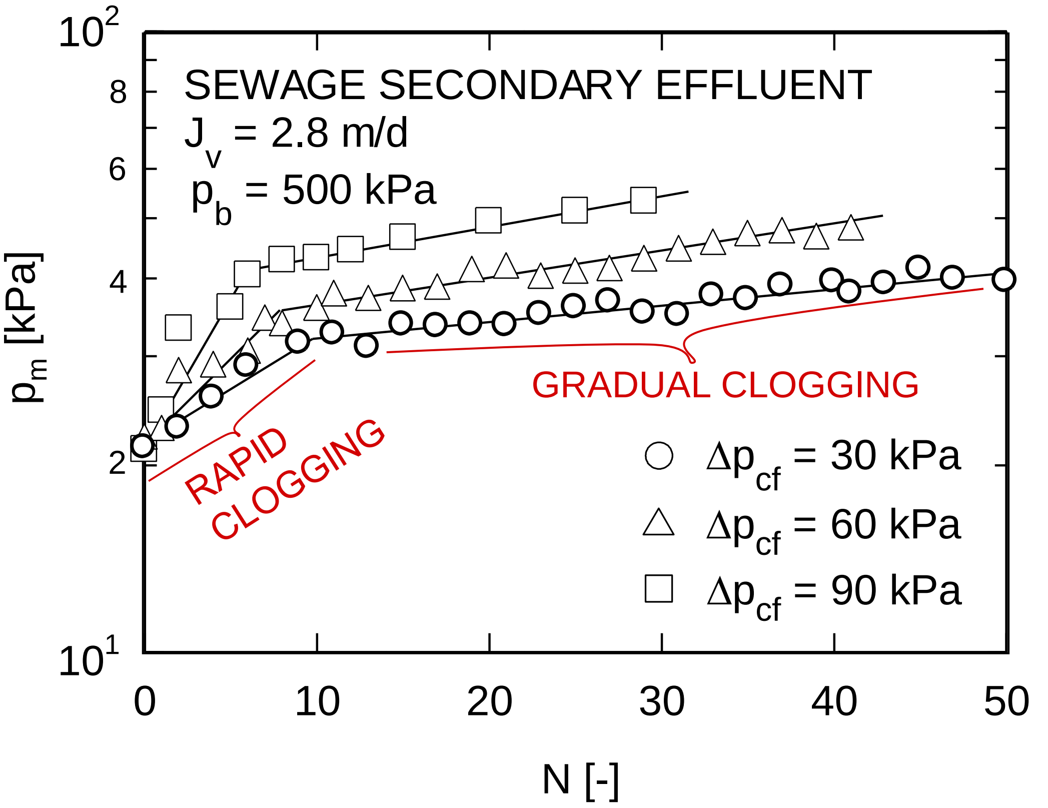
$$x = (x_0 - x_t)[1 - exp\{-\eta(N - N_t)\}] \quad (4b)$$

$$p_m = p_{mt}\exp\{\eta'(N - N_t)\} \quad (5b)$$

Increase in Pore Clogging Resistance

$$p_m = p_{m0} \exp(\eta N) \qquad \text{where } N \le N_t \qquad (5a)$$

$$p_m = p_{mt} \exp\{\eta'(N - N_t)\} \qquad \text{where } N \ge N_t \qquad (5b)$$

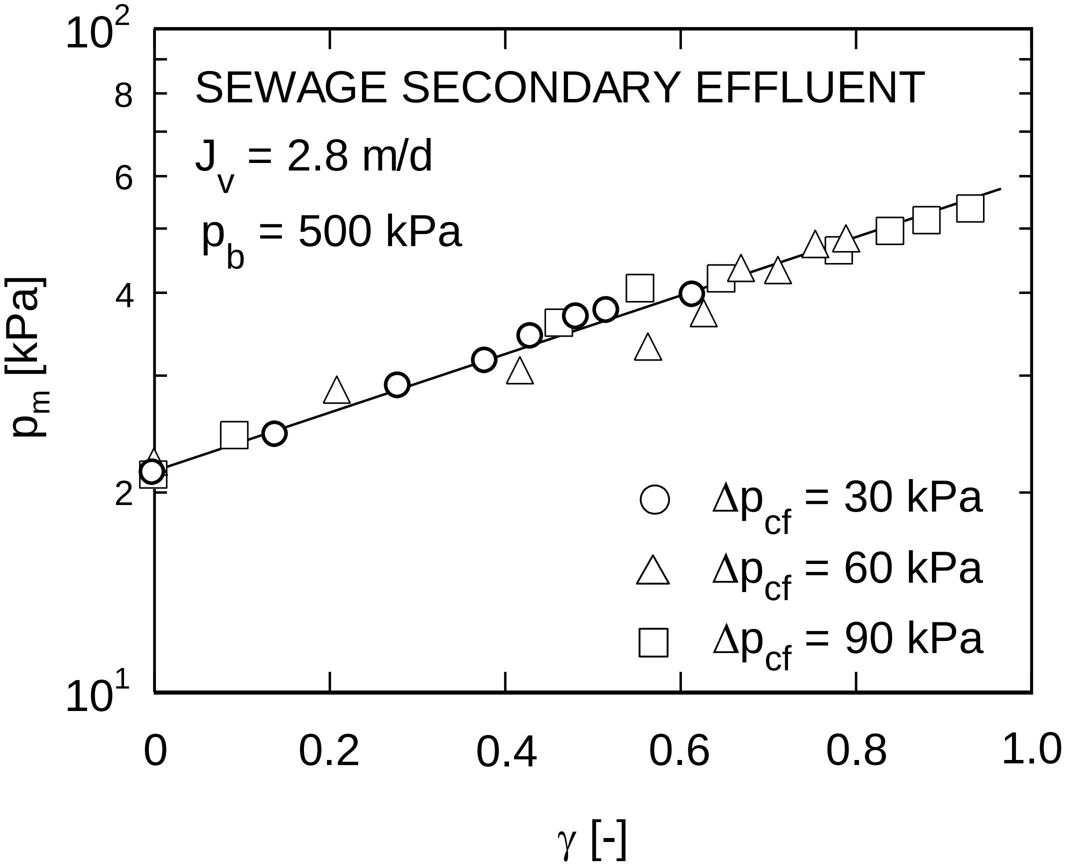


Integral Description of Rapid and Gradual Clogging

$$p_m = p_{mi} \exp(\gamma) \qquad (6)$$

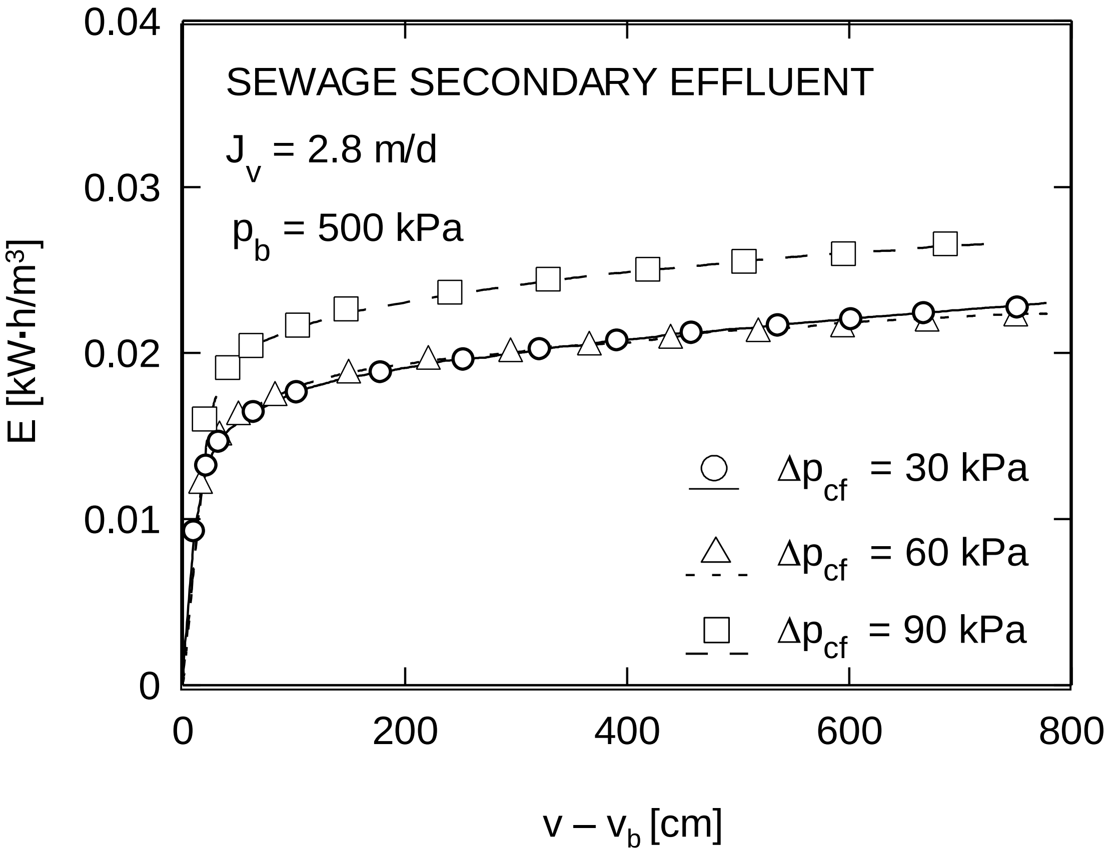
$\gamma = \eta N$, $p_{mi} = p_{mo}$ where $N \leq N_t$

$\gamma = \eta'(N - N_t)$, $p_{mi} = p_{mt}$ where $N \geq Nt$



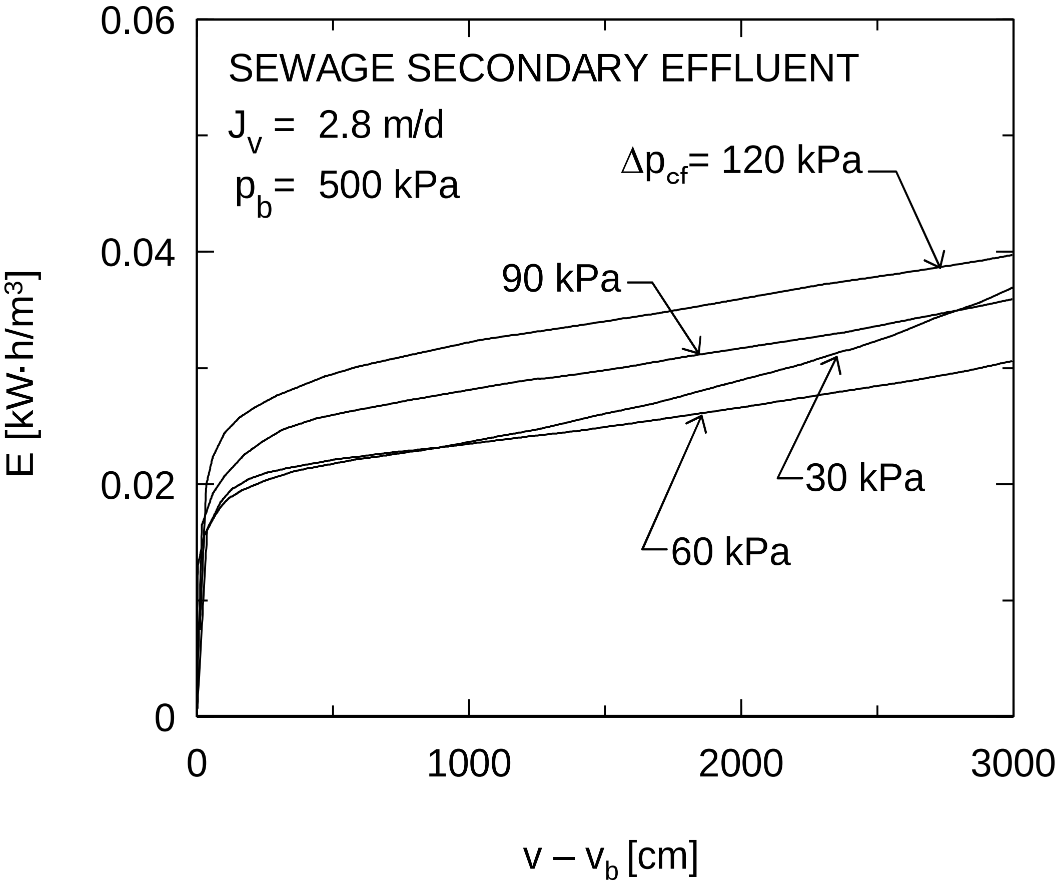
Energy Consumption per Net Unit Volume of Filtrate (Comparison between Experiments and Calculations)

$$E = \frac{\int_0^v p\,dv + p_b v_b}{v - v_b} \qquad (7)$$

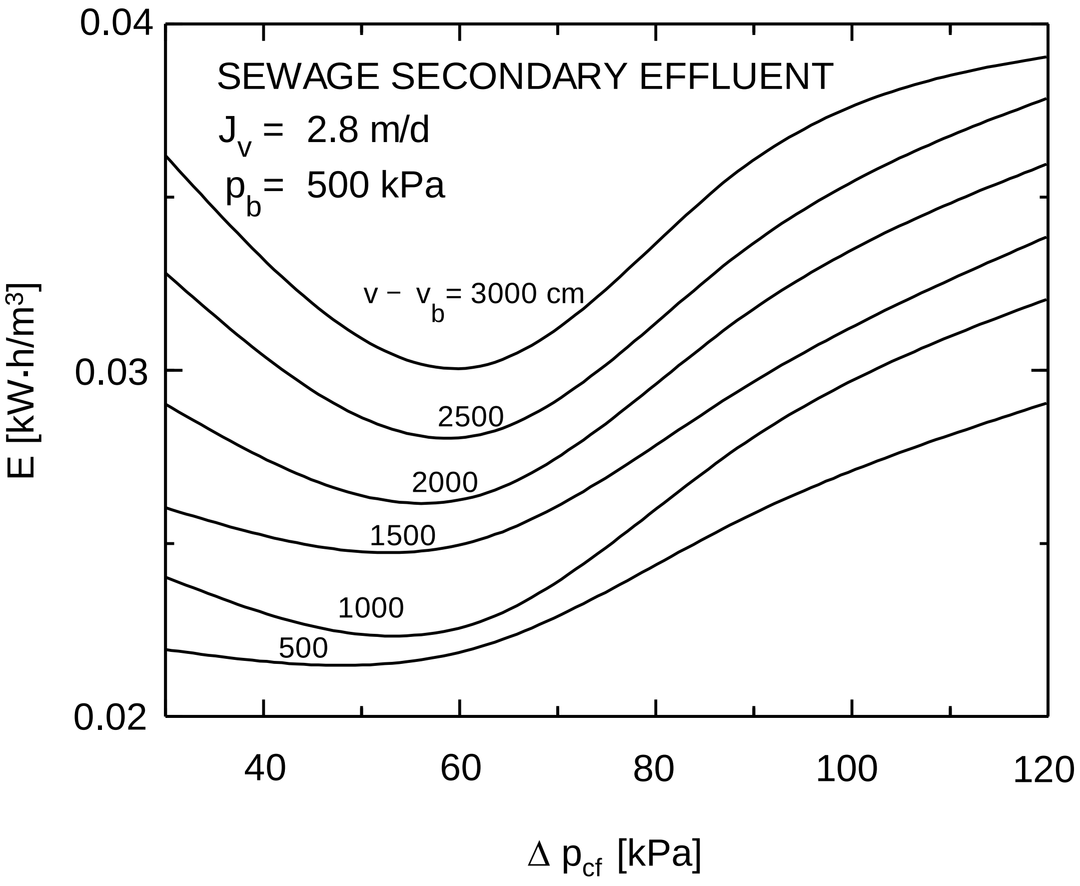


Energy Consumption per Net Unit Volume of Filtrate (Evaluation for Longer Operation)

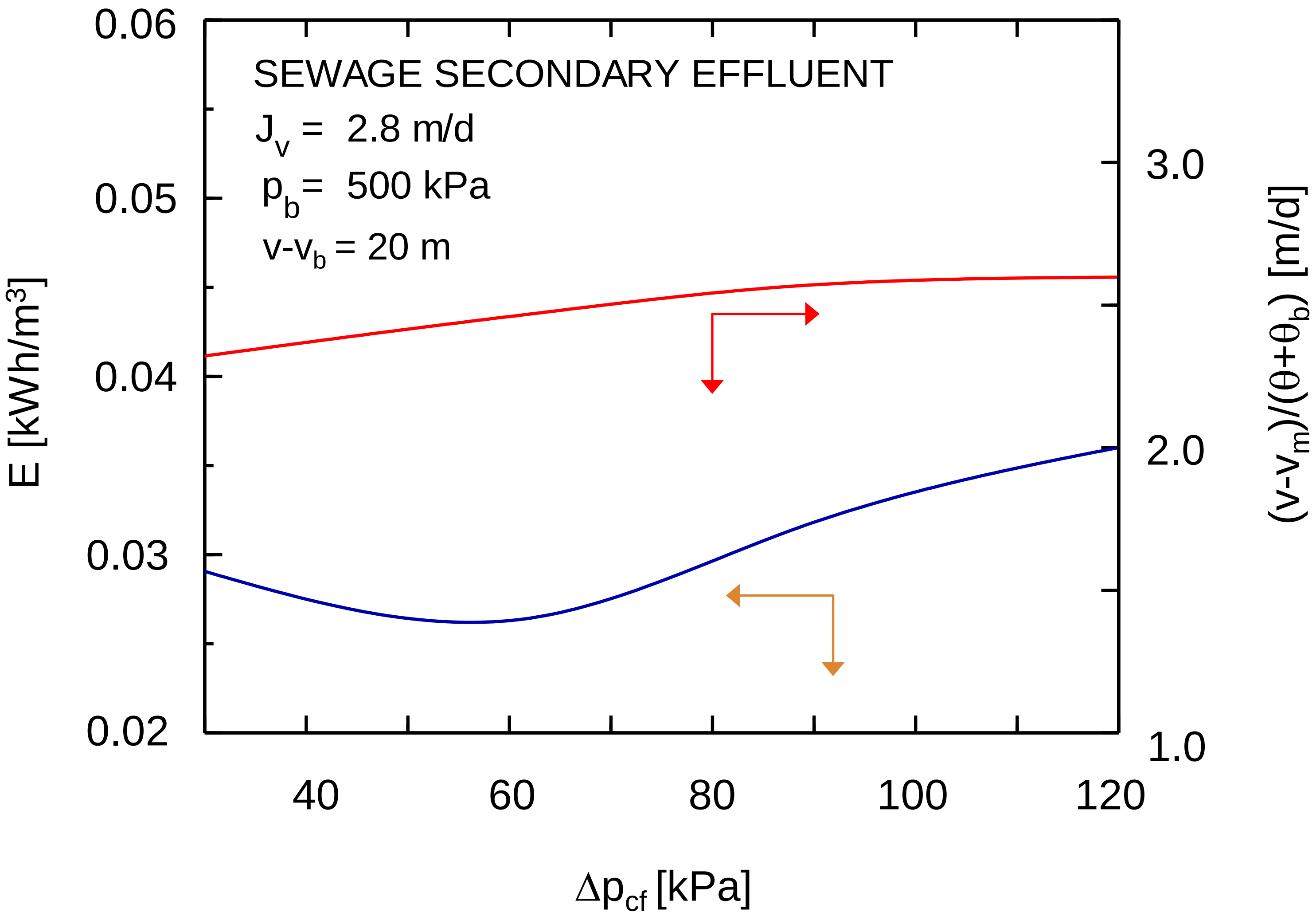
$$E = \frac{\int_0^v p\,dv + p_b v_b}{v - v_b} \qquad (7)$$



Energy Consumption per Net Unit Volume of Filtrate
(Determination of Δp_{cf} Corresponding to Minimum E-value)

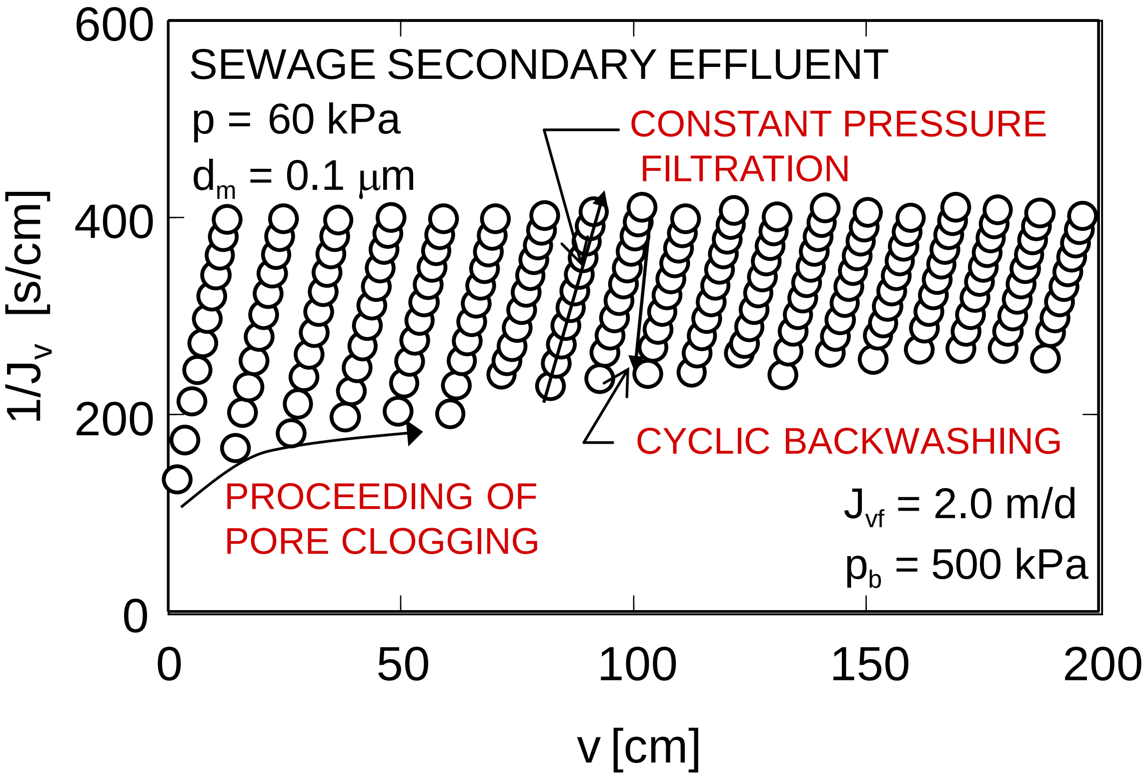


Energy Consumption and Effective Flux



Constant Pressure Filtration with Cyclic Backwashing

$$\frac{1}{J_v} = \frac{1}{J_{vm}} + \frac{2}{K_v} v_N \qquad (8)$$



Cake Filtration Equation under Constant Pressure Condition

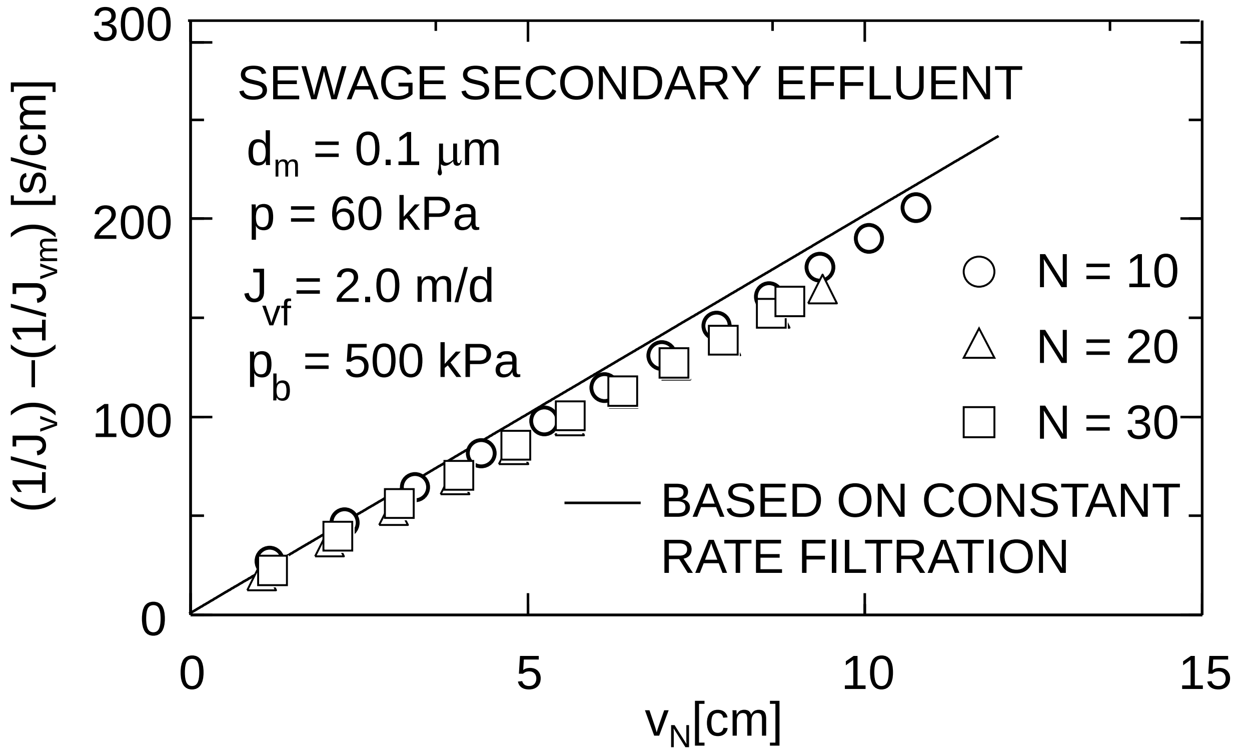
(For Each Filtration Cycle)

Constant Rate Filtration ⇨ $p - p_m = \left(C J_v^2\right)^{\frac{1}{1-n}} \theta^{\frac{1}{1-n}}$ where $C = \dfrac{\mu \alpha_0 \rho s}{(1 - ms)}$ (1)

Constant Pressure Filtration ⇨ $\dfrac{1}{J_v} = \dfrac{2}{K_v} v_N + \dfrac{1}{J_{vm}}$ (8)

Sperry's Eq. ⇨ $\alpha_{av} = \alpha_0 p^n$ (9)

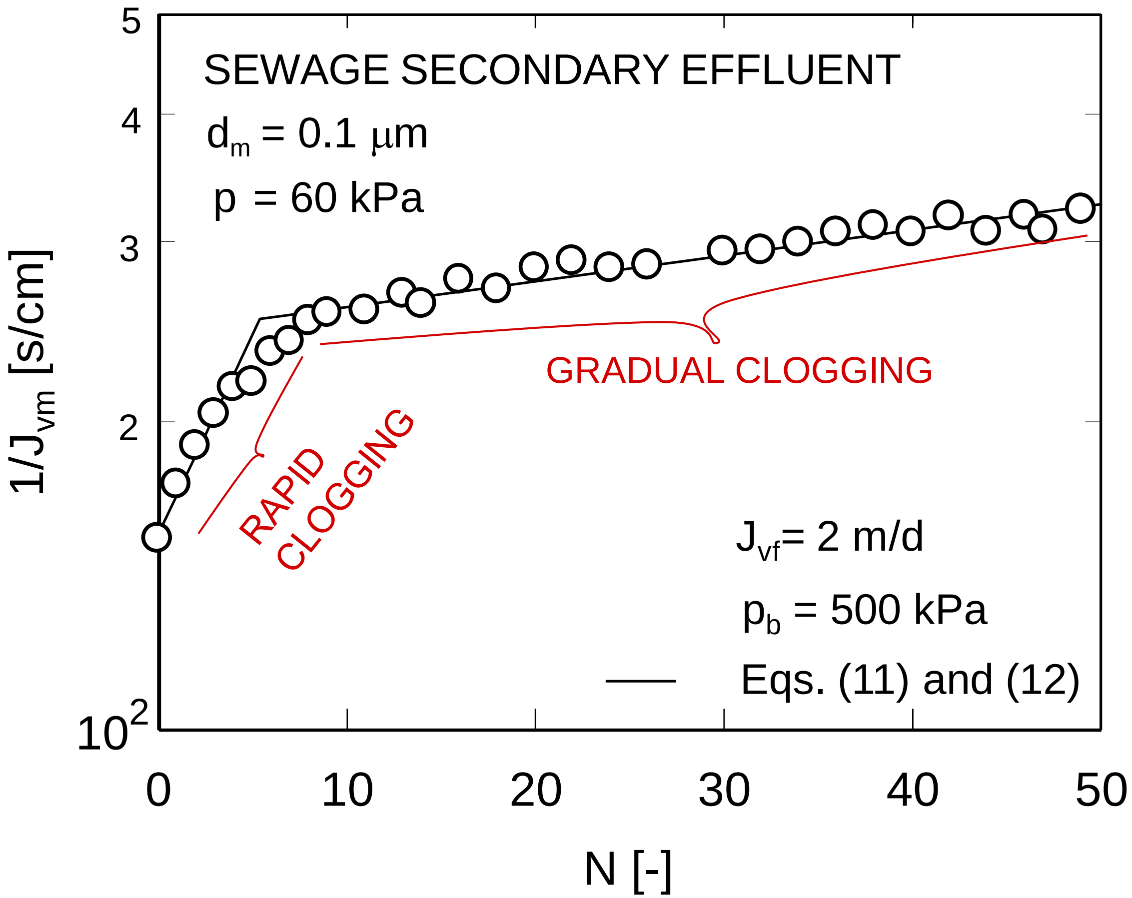
Filtration Coefficient ⇨ $K_v = \dfrac{2(1 - ms) p^{1-n}}{\mu \alpha_0 \rho s}$ ⇨ $K_v = \dfrac{2 p^{1-n}}{C}$ (10)



Increase in Pore Clogging Resistance

$$J_{vm} = J_{vo} \exp(-\eta N) \quad \text{where } N < N_t \tag{11}$$

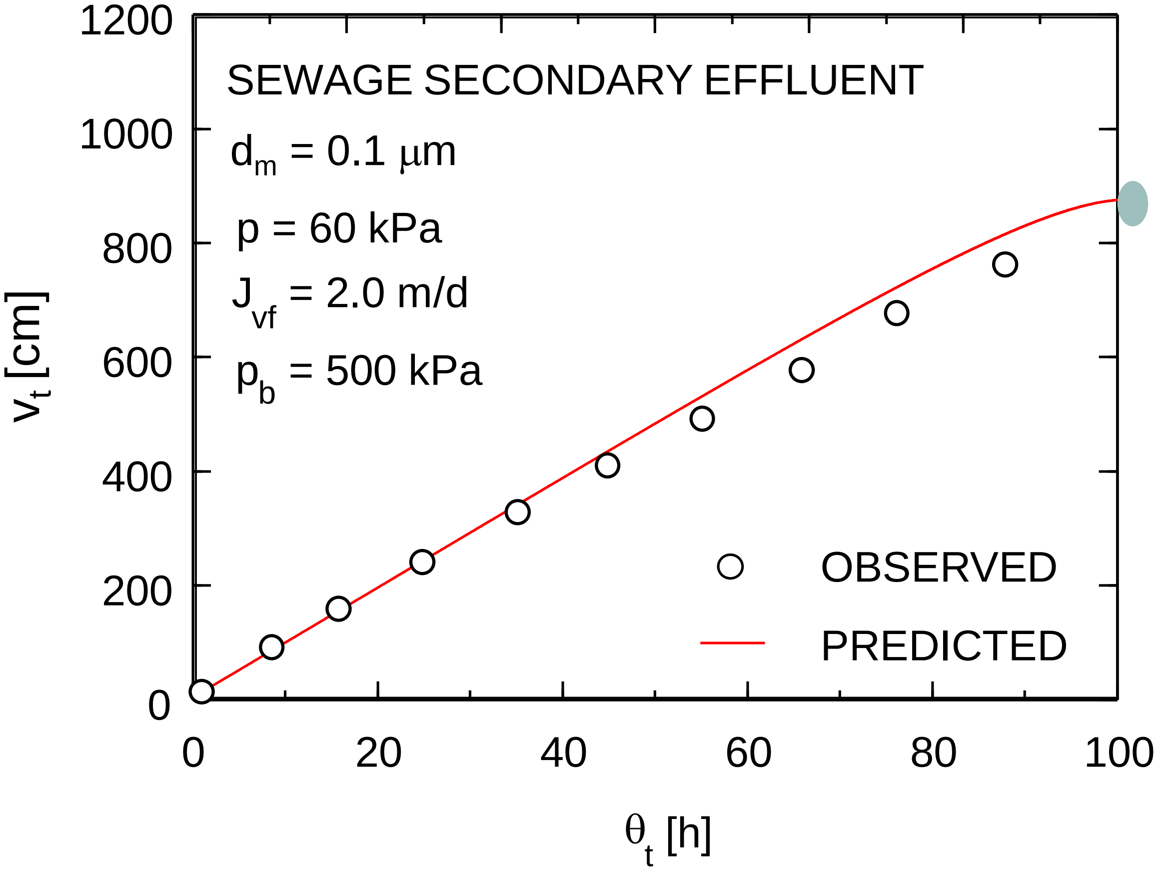
$$J_{vm} = J_{vmt} \exp\{-\eta'(N - N_t)\} \quad \text{where } N \geq N_t \tag{12}$$



Effective Filtrate Volume per Unit Membrane Area (Comparison between Experiments and Calculations)

$$v_t = \sum_{N=0}^{N}\left(v_N - v_b\right) \qquad \text{where} \qquad v_N = \frac{K_v}{2}\left\{\frac{-1}{J_{vm}} + \left(\frac{1}{J_{vm}^2} + \frac{4\theta}{K_v}\right)^{\frac{1}{2}}\right\} \tag{13}$$

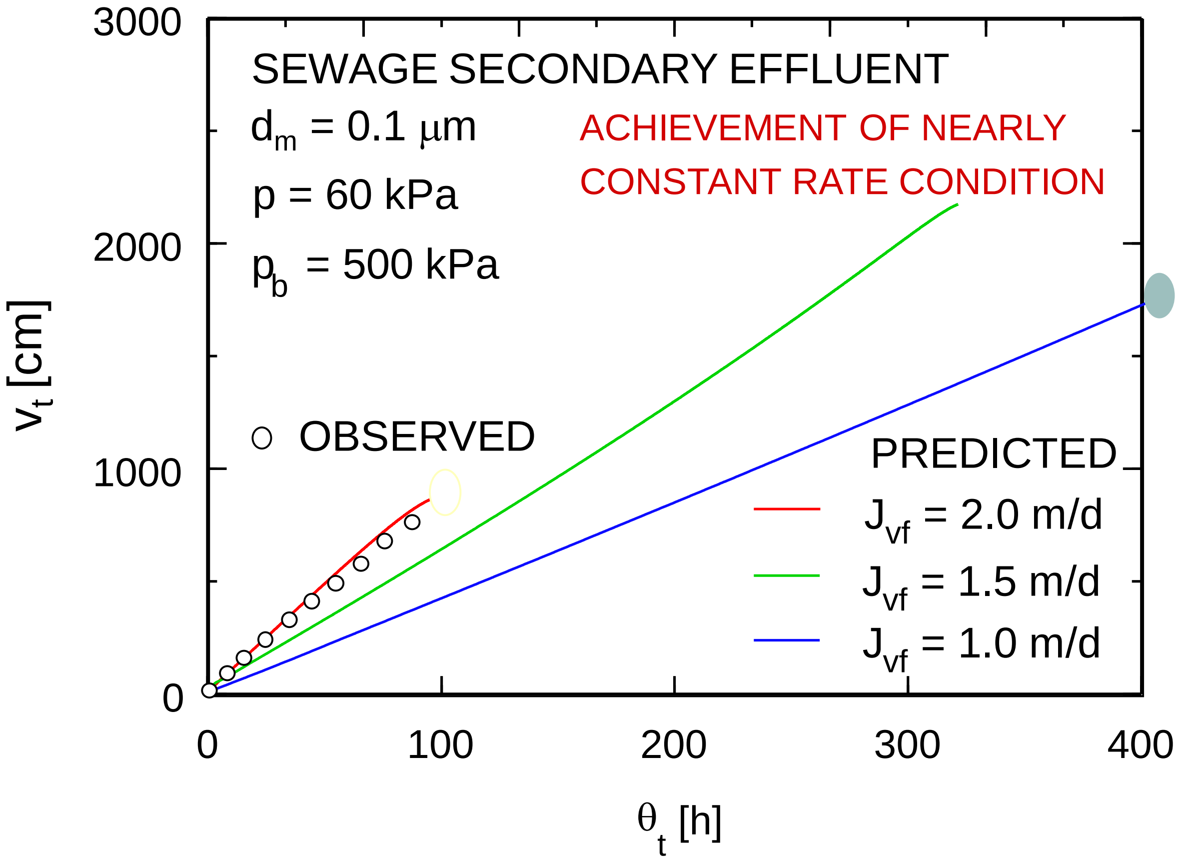
$$\theta_t = \sum_{N=0}^{N}(\theta_N + \theta_b) \tag{14}$$



Effective Filtrate Volume per Unit Membrane Area (Evaluation for Longer Operation)

$$v_t = \sum_{N=0}^{N}(v_N - v_b) \quad \text{where} \quad v_N = \frac{K_v}{2}\left\{\frac{-1}{J_{vm}} + \left(\frac{1}{J_{vm}^2} + \frac{4\theta}{K_v}\right)^{\frac{1}{2}}\right\} \qquad (13)$$

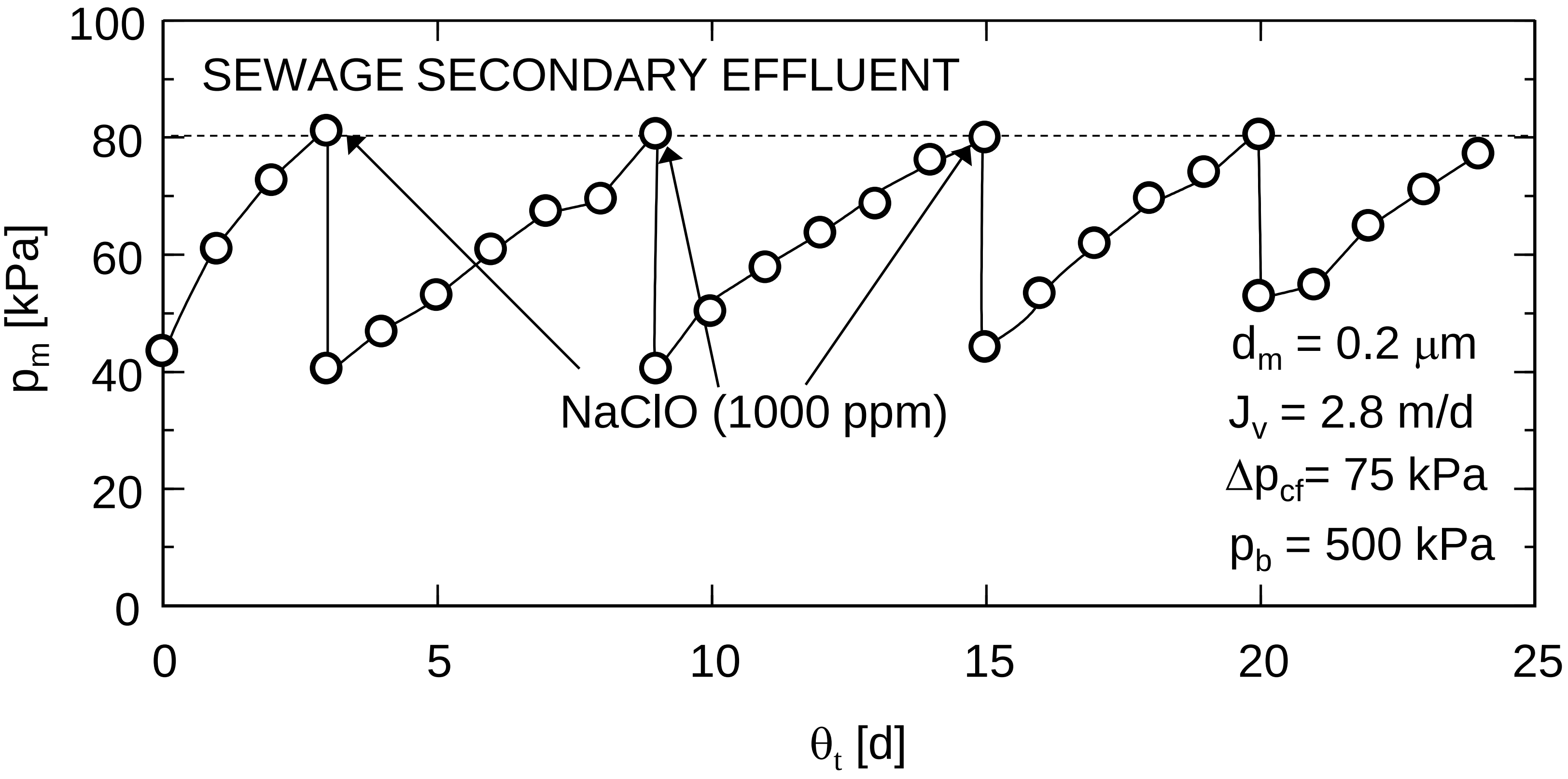
$$\theta_t = \sum_{N=0}^{N}(\theta_N + \theta_b) \qquad (14)$$



Onsite Experimental Apparatus in Sewage Treatment Plant

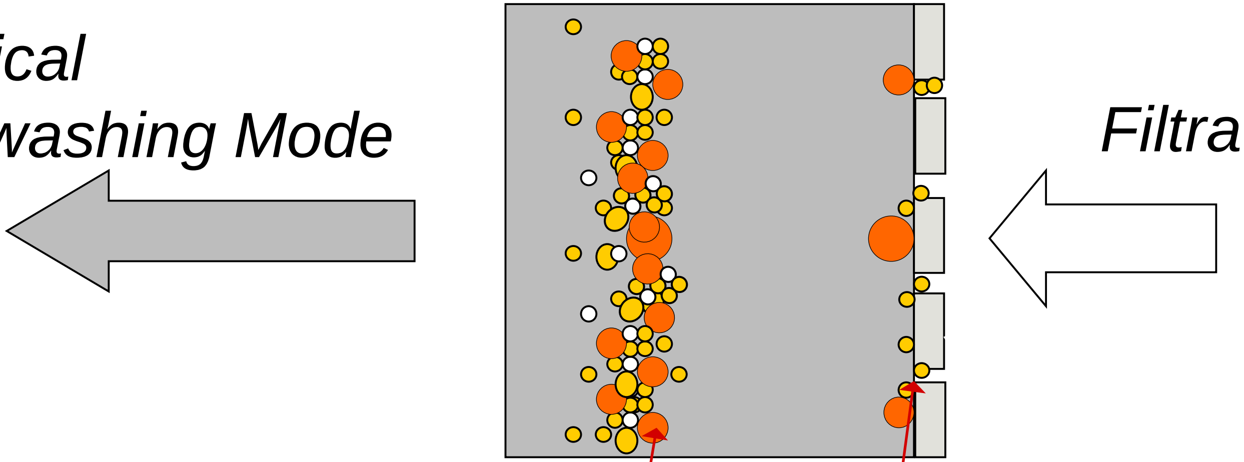
Membrane Module

Constant Rate Filtration with Chemically Enhanced Backwashing



Role of Chemically Enhanced Backwashing

(a)Physical Backwashing Mode



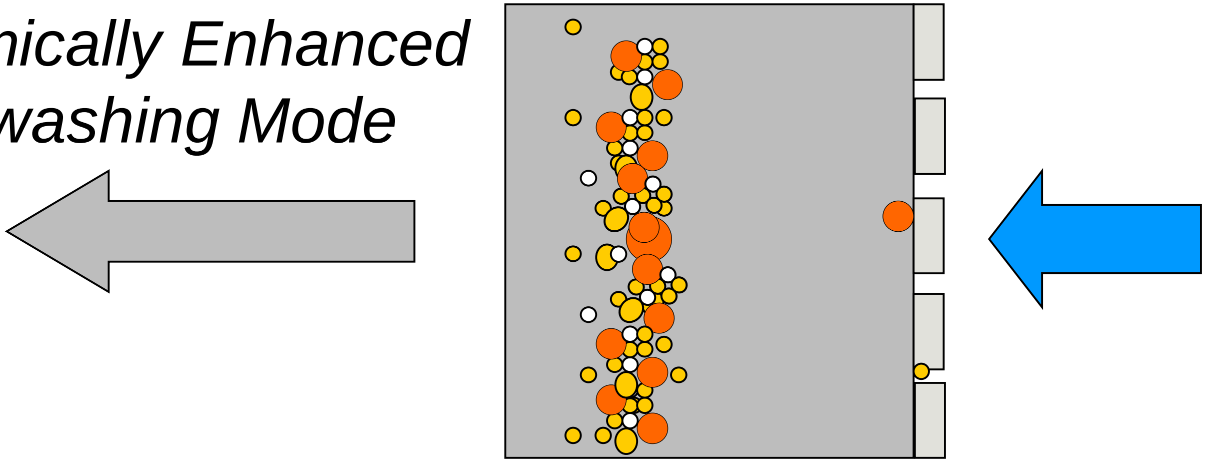
Filtrate

Filter Cake

Irreversible Pore Clogging

Ceramic Microfiltration Membrane

(b) Chemically Enhanced Backwashing Mode



Filtrate Containing NaClO

CONCLUSIONS

Purification of Secondary Municipal Wastewater

Cyclic Operation of Semi Dead-End Microfiltration System

Upgrading of Water Quality

- *Removal of E.coli, SS, etc.*

Reclaimed Water with
High Quality for Urban Reuse

Analysis of Cake Formation and Pore Clogging

- *Evaluation of Energy Consumption (Constant Rate Filtration)*
- *Evaluation of Effective Filtrate Volume (Constant Pressure Filtration)*

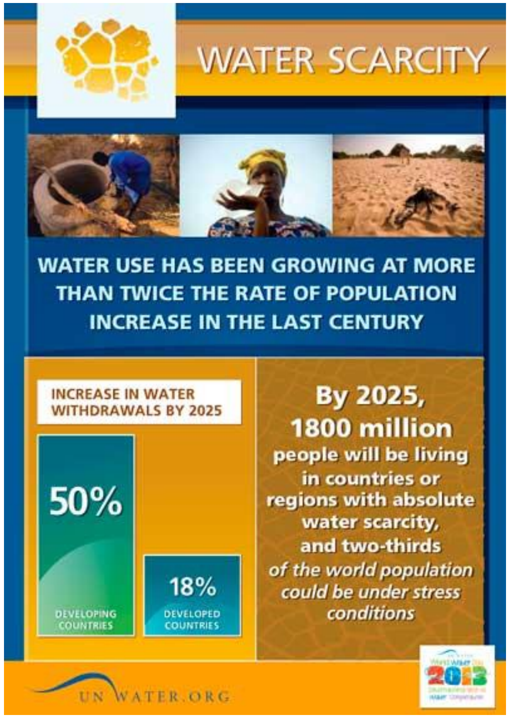
Investigation of Optimum Operating Conditions

MODIFIED GRAPHENE OXIDE MEMBRANE FOR LEAD REMOVAL FROM WASTEWATER

- Growing world population
- Climate change (drought/floods)- high demand of clean water

United Nation expects that the world’s population will encounter water scarcity by 2025

Heavy metals contamination in wastewater is one of the major problems



WATER SCARCITY

WATER USE HAS BEEN GROWING AT MORE THAN TWICE THE RATE OF POPULATION INCREASE IN THE LAST CENTURY

INCREASE IN WATER WITHDRAWALS BY 2025

50% DEVELOPING COUNTRIES

18% DEVELOPED COUNTRIES

By 2025, 1800 million people will be living in countries or regions with absolute water scarcity, and two-thirds *of the world population could be under stress conditions*

UN WATER.ORG

- lead contamination- mining industries; lead-acid battery manufacturing, electronic and semiconductor industries

Malaysia Environmental Quality Report stated lead is one of the highest contaminants' concentration found in tested water (Class II risk)

ENVIRONMENTAL AND HEALTH CONCERN

- Water/wastewater pollution with high toxicity
- lead exposure: high blood pressure, kidney damage, brain damage, and behavioural disruption of children

LIMITATION OF CONVENTIONAL MEMBRANES

- permeability/selectivity trade off
- high fouling propensity
- high cost for large scale application
- Excess energy, incomplete removal

- Free-GO membrane difficult to use without any support
- Few studies on adsorption/filtration mechanism of GPN membrane
- Most of research were done on lab scale, using synthetic waste water

1)SYNTHESIS OF GO

STAGE 1 (ROOM TEMPERATURE)

-Graphite exfoliation

$NaNO_3 + H_2SO_4 \rightarrow HNO_3 + NaHSO_4$

STAGE 2 (COLD)

-Shows the ability of Mn_2O_7 to selectively oxidize the unsaturated aliphatic double bonds over aromatic double bonds

$2\ KMnO_4 + H_2SO_4 \rightarrow K2SO4 + Mn_2O_7 + H_2O$

STAGE 3 (HOT)

...CONTINUE

WASHING STEPS

Then put a lot of deionized water and proceed with the washing steps

Add HCl to the GO solution and centrifuge to remove all metal impurities

discard the supernatant and continue wash with DI water several times until pH near neutral

Sent to freeze dry to get the powder form

BEFORE WASH

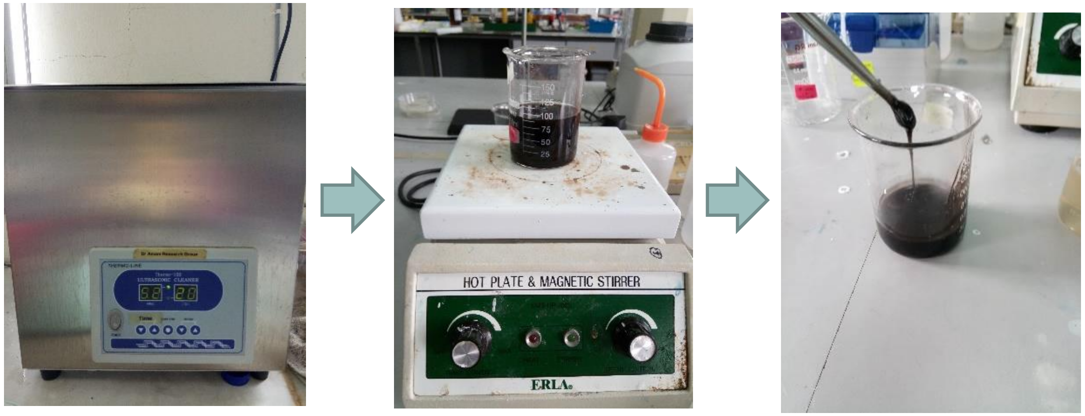
AFTER WASH, pH neutral

after freeze drying, to get powder form

2)PREPARATION OF POLYMER SOLUTION

A homogenous electrospinning precursor solution of PES and GO will be prepared

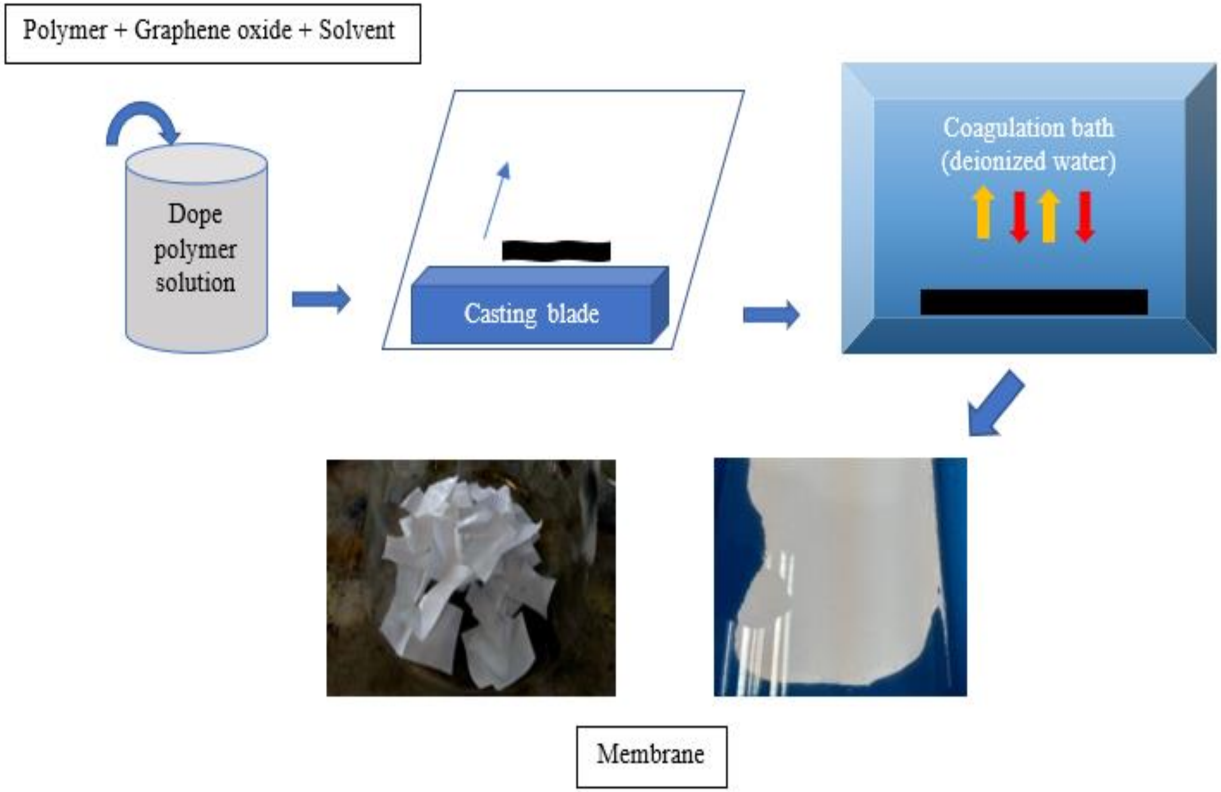
GPN Membrane	PES (wt.%)	DMF (wt.%)	GO (wt.%)	PVP (wt.%)
Bare PES (GPN0)	17.0	83.0	-	-
PES-0.1GO (GPN1)	17.0	82.9	0.1	-
PES-0.5GO (GPN2)	17.0	82.5	0.5	-
PES-1.0GO (GPN3)	17.0	82.0	1.0	-
PES-0.5GO0.5PVP (GPN4)	17.0	82.0	0.5	0.5



Bare PES was dissolved in DMF by mixing it for 24 h at 50 ° C

- GO solution was dispersed in DMF by sonication for 1hour
- Then, PES and PVP was added to the above solutions
- the mixture was fully dissolved by stirring it for 24 h at 50 ° C.

3)FABRICATION OF GPN MEMBRANE BY NON-SOLVENT INDUCED PHASE SEPARATION (NIPS) METHOD



Polymer + Graphene oxide + Solvent

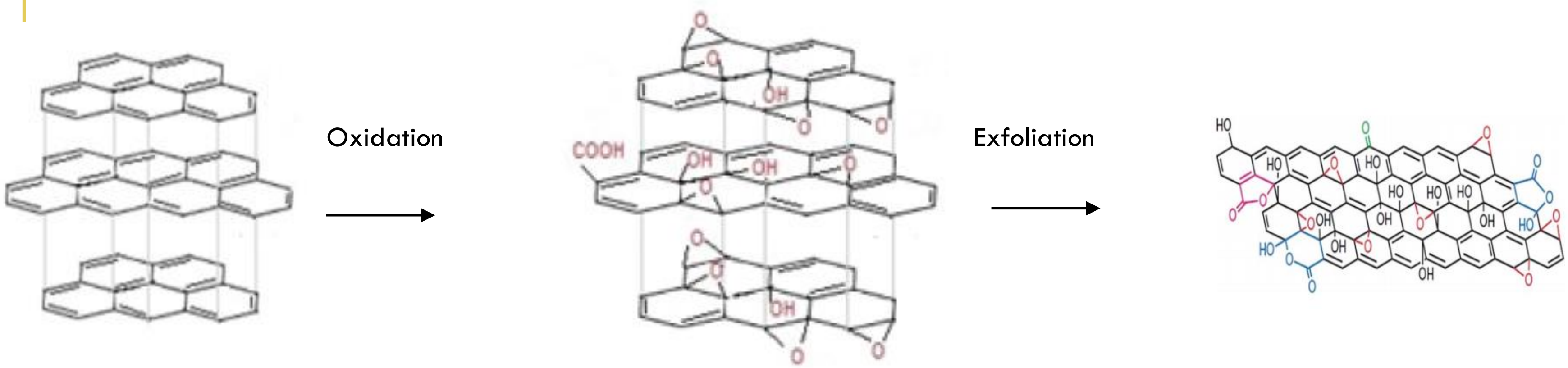
Dope polymer solution

Casting blade

Coagulation bath (deionized water)

Membrane

SYNTHESIS OF GO



Oxidation

Exfoliation

Graphite

Graphite oxide

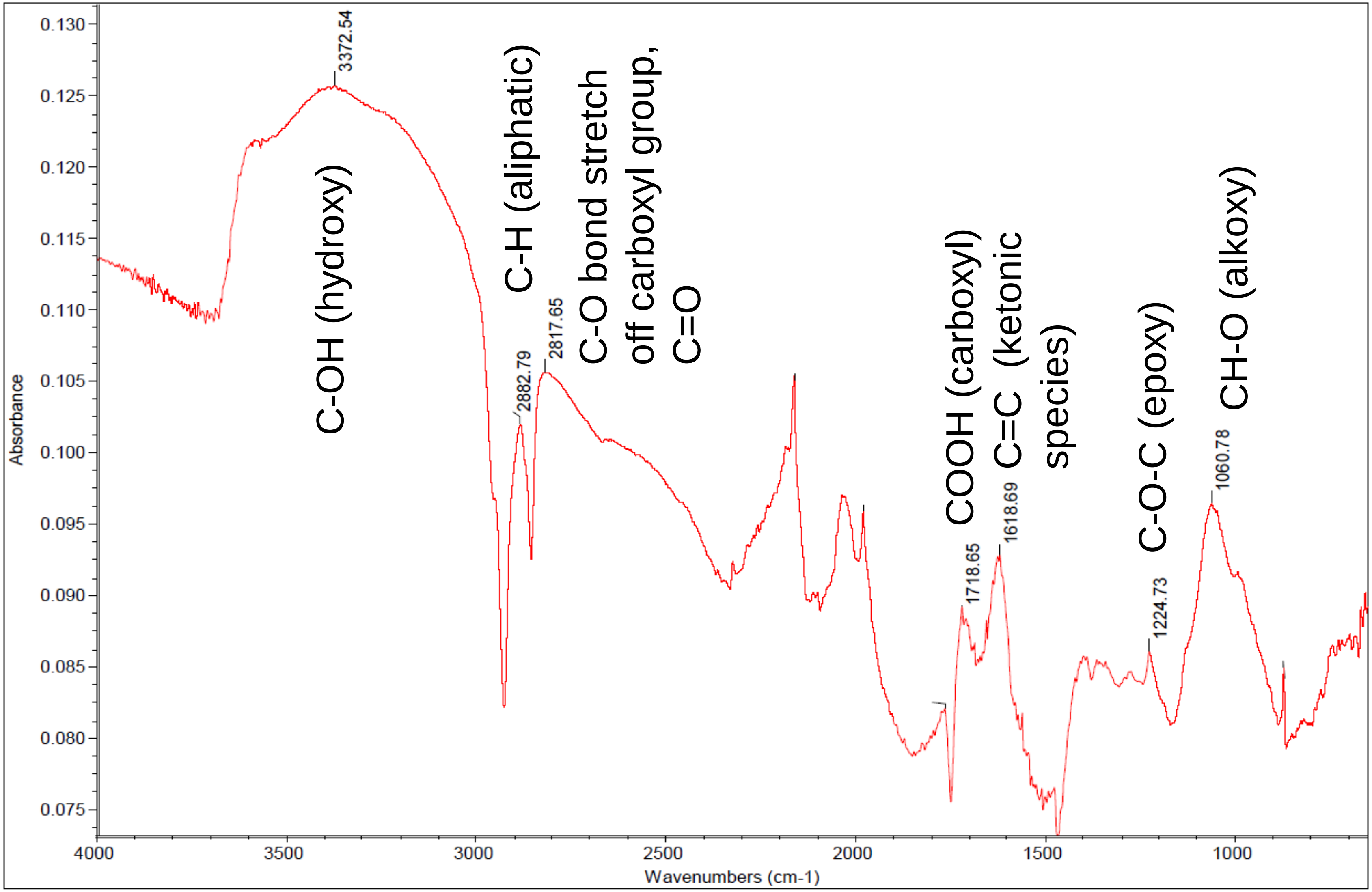
Graphene oxide

Modified Hummer’s method

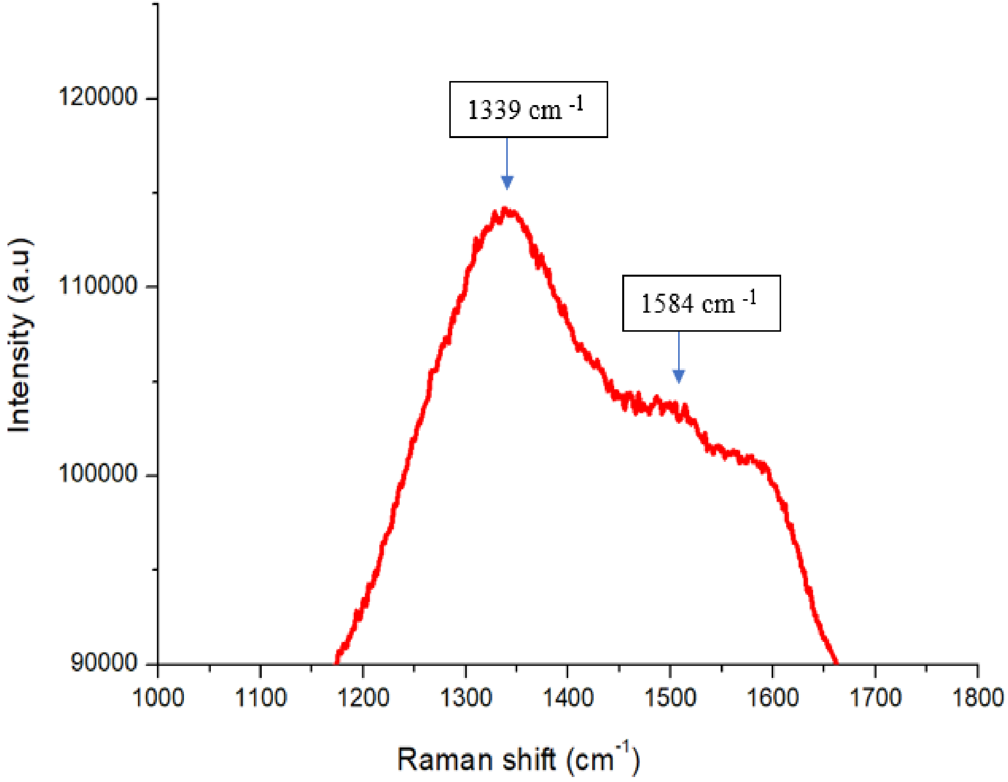
$NaNO_3$ / H_2SO_4/ $KMnO_4$/H_2O_2

1) CHARACTERIZATION OF GO

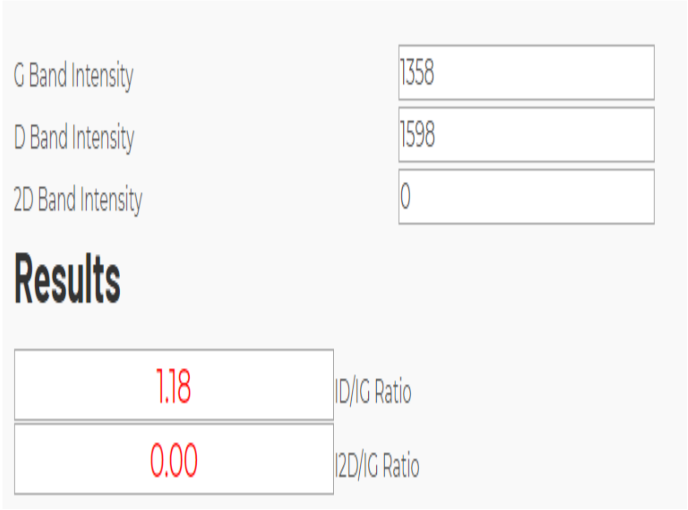
FTIR ANALYSIS



RAMAN SPECTROSCOPY



- The D-band of the GO is located at 1358 and G-band peak is at 1598
- High intensity ratio **I_D/I_G =1.18** confirms the oxidation of graphite



G Band Intensity 1358

D Band Intensity 1598

2D Band Intensity 0

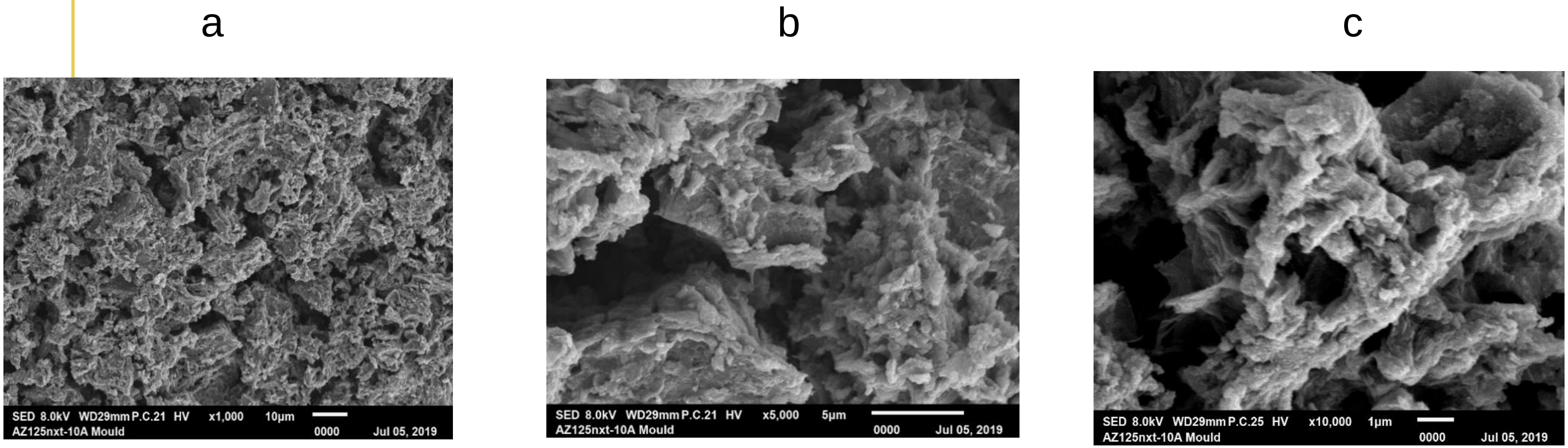
Results

1.18 ID/IG Ratio

0.00 I2D/IG Ratio

https://www.instanano.com/2017/03/Raman-Characterization-Graphene.html

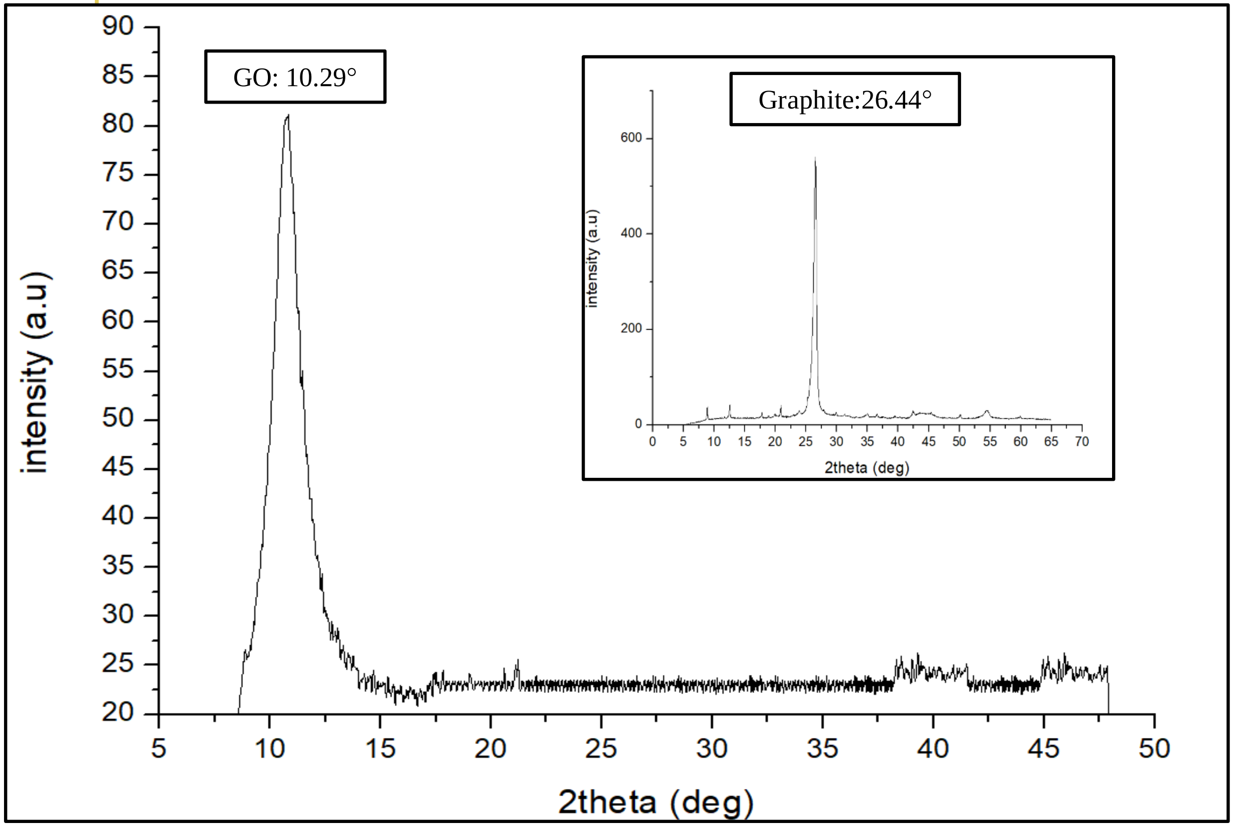
SEM OF GO



SEM images a) 1k X b) 5k X and c)10k X of produced GO.

It was found that GO consists of randomly aggregated and crumpled, showed some wrinkle and fold area on the surface of GO. This result confirmed that the graphite was well exfoliated during the oxidation process to produce GO (Rattana et al. 2011; Yusoff, Samad, Loh & Lee 2018). The SEM morphology also indicate that the GO were thicker at the edges due to oxygen-containing functional groups (carboxyl and hydroxyl) at the edges of GO (Alam, Sharma & Kumar, 2017).

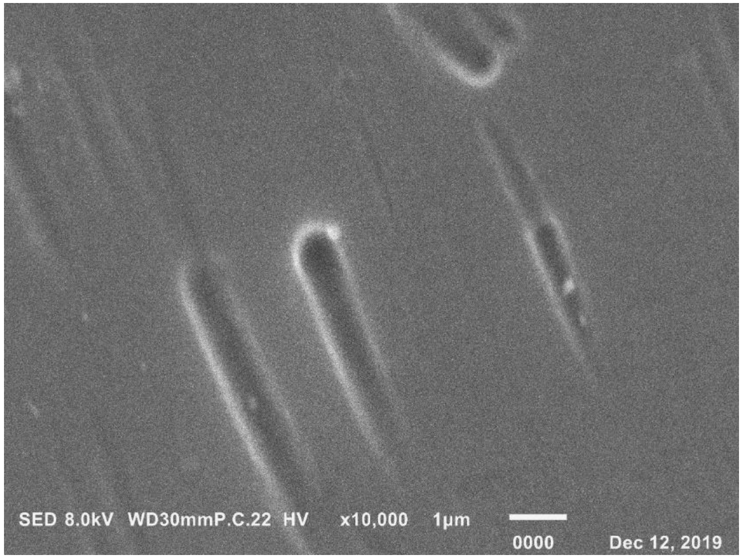
XRD ANALYSIS

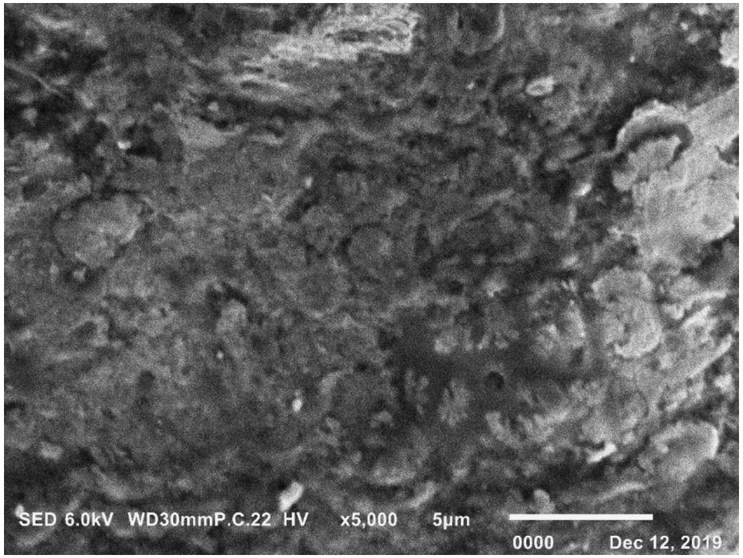


B

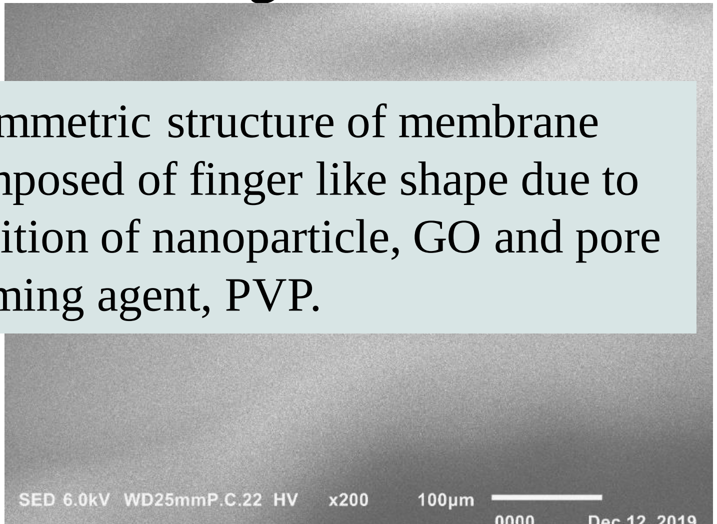
- graphite sample at 26.44° corresponding to d = 3.35 nm (A)
- GO sample at 10.29, d-spacing= 8.59 nm (B)
- diffraction peak of graphene oxide is shifted from **26.44°** to **10.29°**
- functional groups on GO **increases the distance between the layers** thus **d-spacing value increased**.

SEM IMAGES FOR BARE PES MEMBRANE

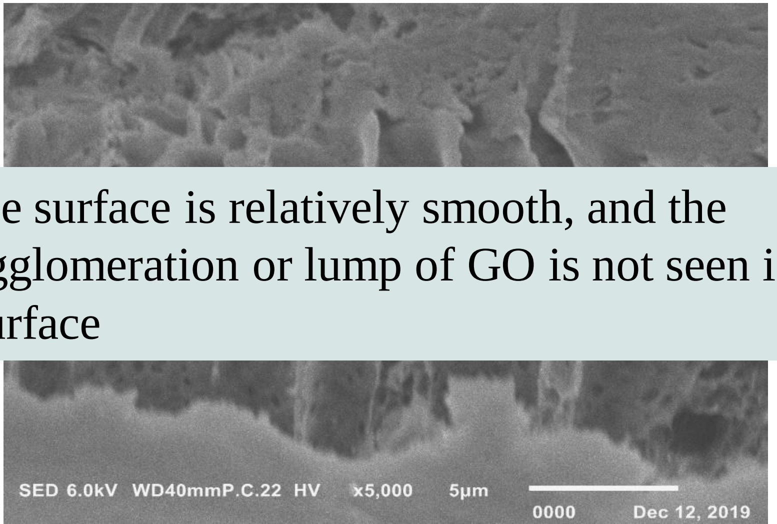




SEM images for GPN4 membrane

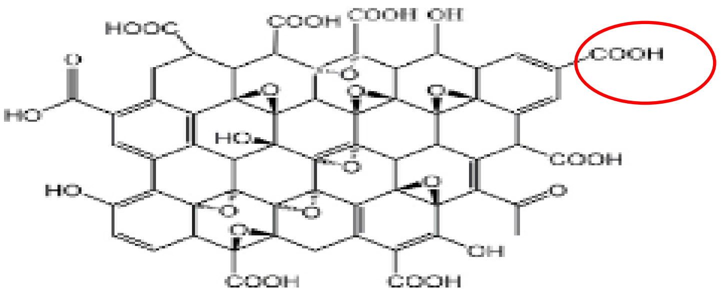


asymmetric structure of membrane composed of finger like shape due to addition of nanoparticle, GO and pore forming agent, PVP.



the surface is relatively smooth, and the agglomeration or lump of GO is not seen in the surface

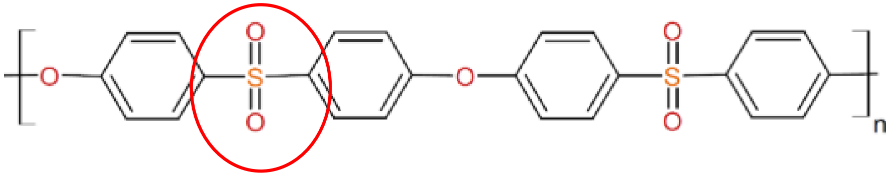
INTERACTION BETWEEN GO, PES AND PVP



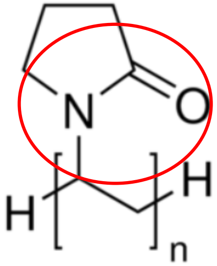
Graphene oxide (GO)

+

Polyethersulfone (PES):



+

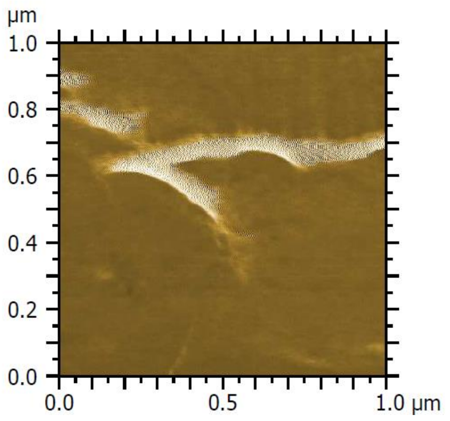


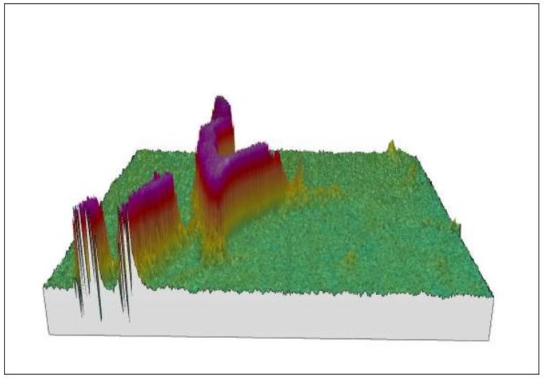
Polyvinylpyrrolidone (PVP)

The strong hydrogen bonding interaction between the carboxylic groups in GO and the sulfone group in PES makes the GO nanoparticles highly dispersible and not easily detached from the PES matrix

The interaction between amide group which is present in the PVP and the sulfone group in PES elucidated the formation of large pores in the structure of membrane

AFM ANALYSIS (SURFACE TOPOGRAPHY &3D IMAGE OF GPN4





- the green region indicates valleys or membrane pores
- the purple region represents peaks of the highest point of the membrane surface
- few peaks existed on the surface profile possibly due to some errors such as improper dispersing of GO, noise vibration

References

Takeshi Matsuura
Fundamentals of Membrane Processes for Water Treatment, University of Ottawa, Workshop on Membrane Technology for Energy, Water and Environmental Applications
April 29, 2010, UTM, Kuala Lumpur

Membrane Technology for Water
and Wastewater Treatment,
Energy and Environment,
Ahmad Fauzi Ismail
Advanced Membrane Technology Research Centre (AMTEC),
Universiti Teknologi Malaysia (UTM), Skudai, Johor, Malaysia


thank you!