Opportunities in Membrane Technology in Water Resources

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Presentation Outline

1. Introduction
2. Membrane Applications
3. Nanomaterials in Membrane Technology
4. Advanced Membrane Technology
   i. Forward Osmosis
   ii. Photocatalytic membrane
5. Concluding Remarks

Global Water Crisis:

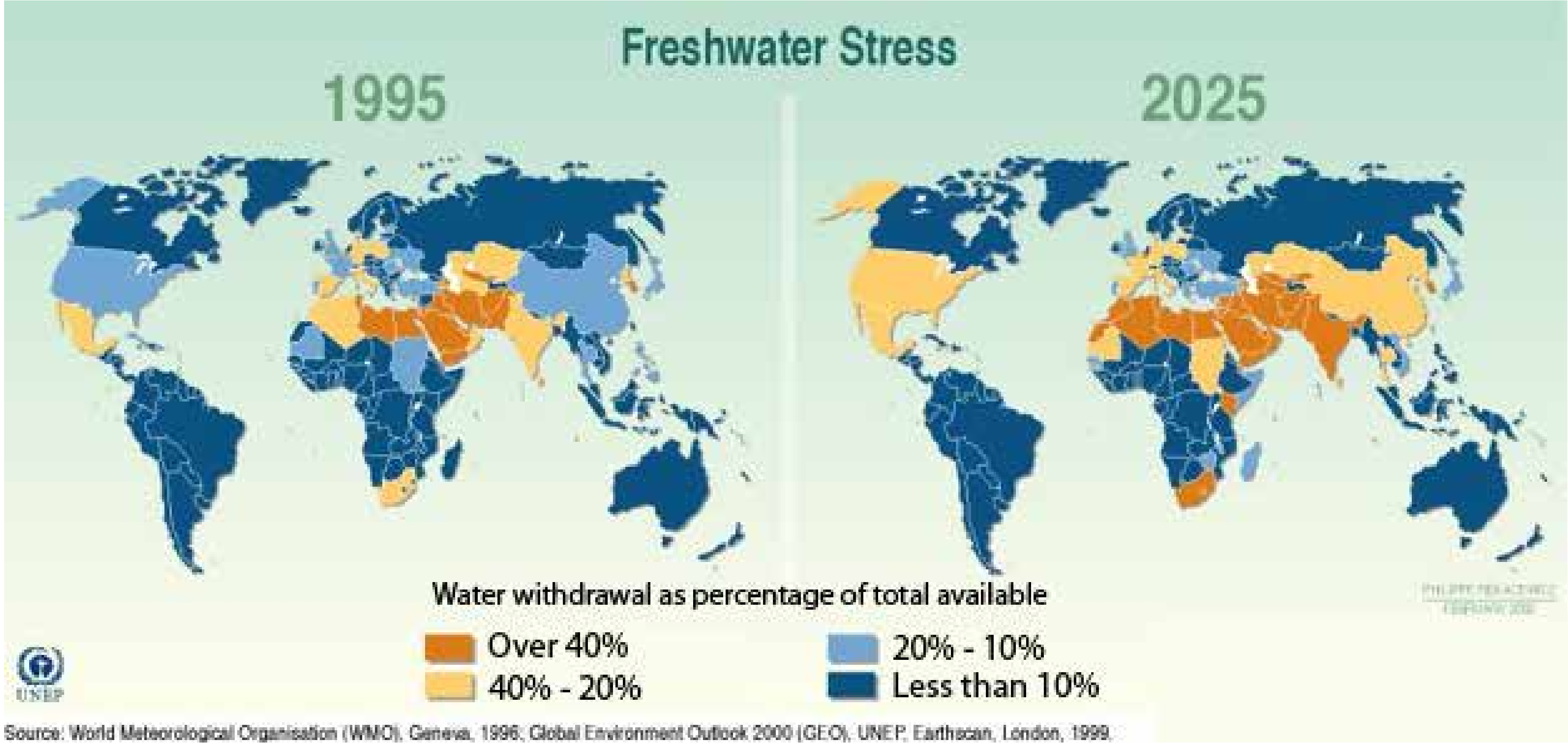
H_2O QUICK FACTS

Do you know that…

- Over the past 40 years the world's population has doubled and use of water has quadrupled.
- 783 million people (1 in 10 people) do not have access to clean and safe water.
- In developing countries, as much as 80% of illnesses are linked to poor water and sanitation conditions.
- Compared to today, five times as much land is likely to be under "extreme drought" by 2050.
- By 2050, 1 in 5 developing countries will face water shortages.

Sources: United Nation's Food and Agriculture Organization; World Health Organization; UNICEF, 2015

Water-stress Regions-A Worsening Scenario



Sources: World Meteorology Organization

Factors Leading to Water Crisis

Climate and Geography

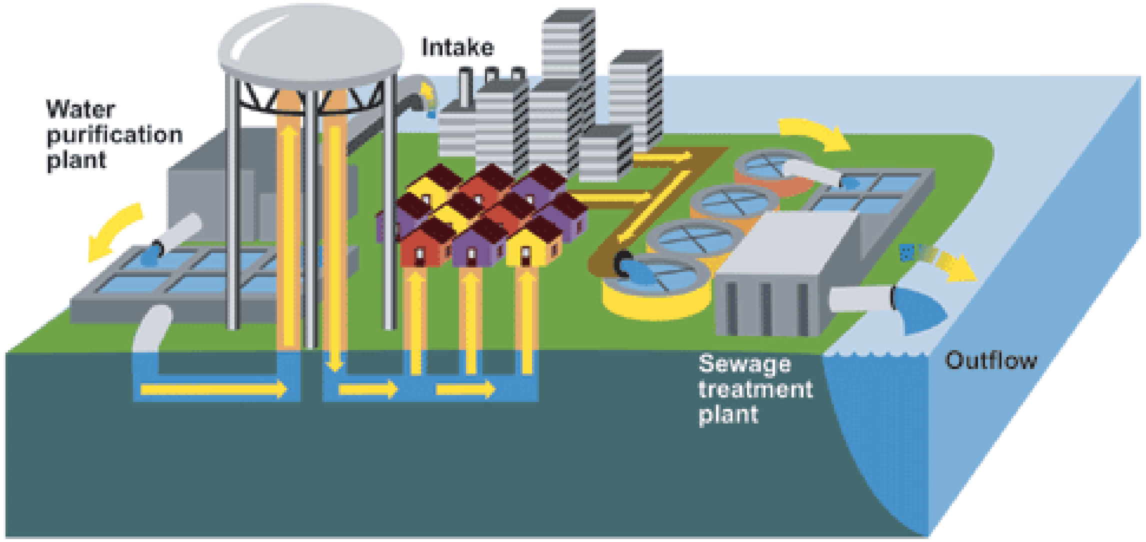
Poor Water Infrastructure and Sanitary

Water Pollutions

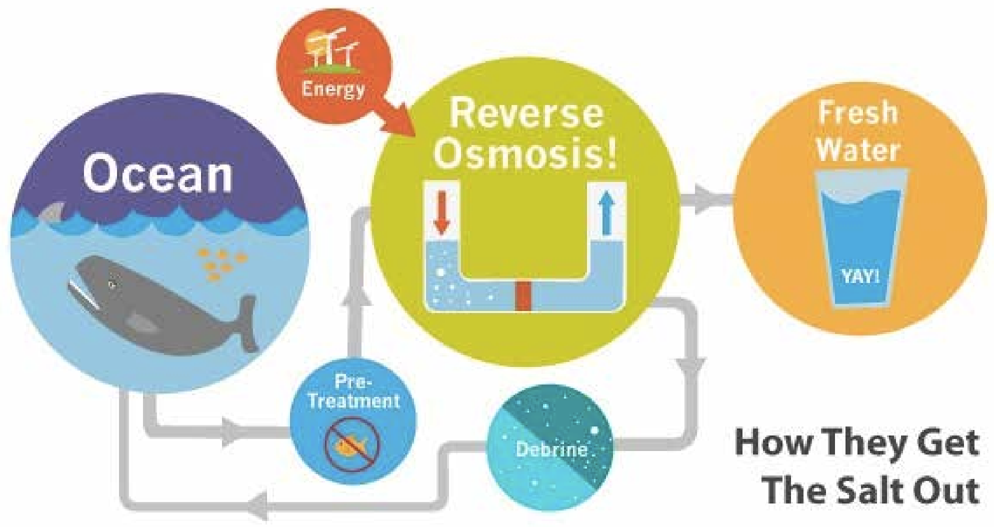
Can Membrane Cope?

Engineering Solutions: Membrane Technology

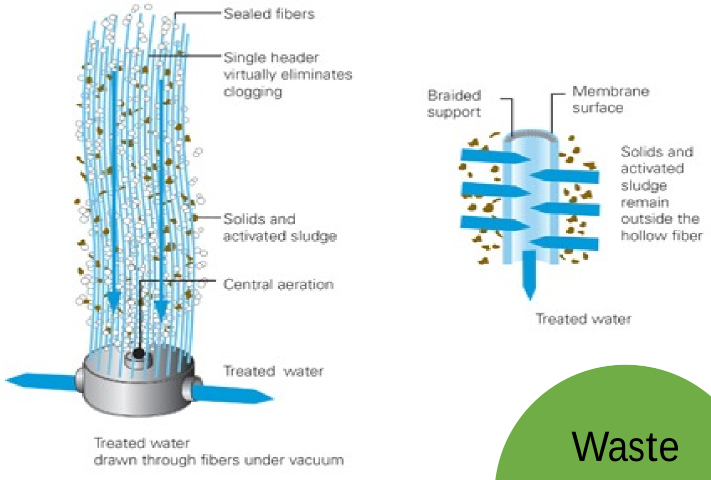
Wastewater Treatment

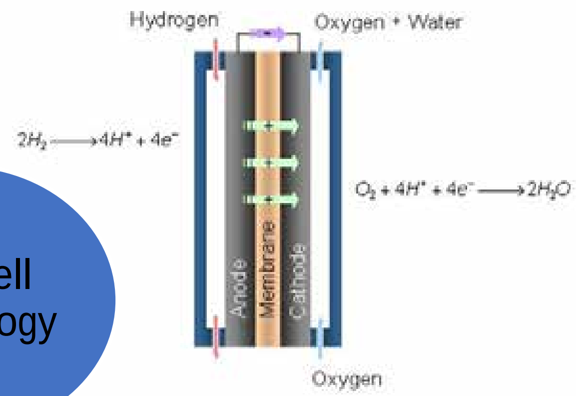


Desalination



MEMBRANE APPLICATION





MEMBRANE APPLICATIONS

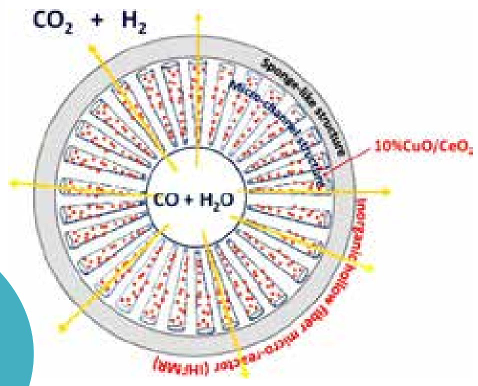
Fuel Cell Technology

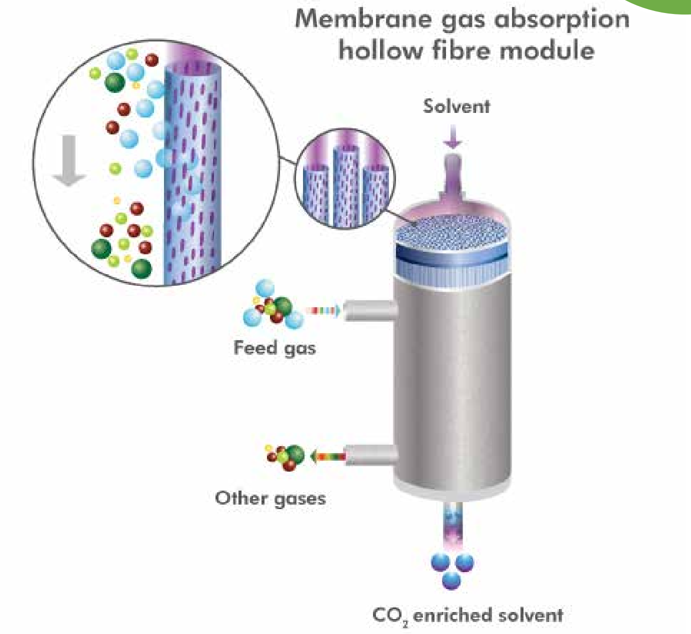
Waste water Treatment

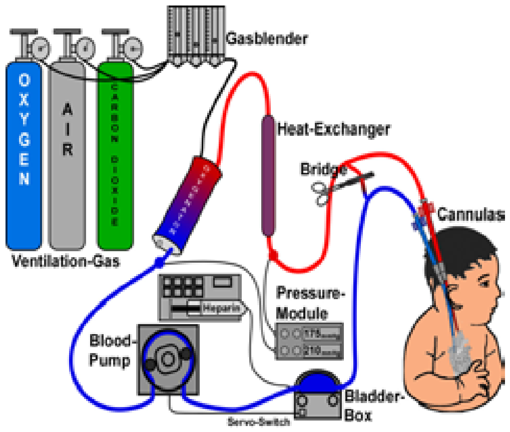
Microreactor (Chemical Industry)

Gas separation

Medicine & Pharmacy

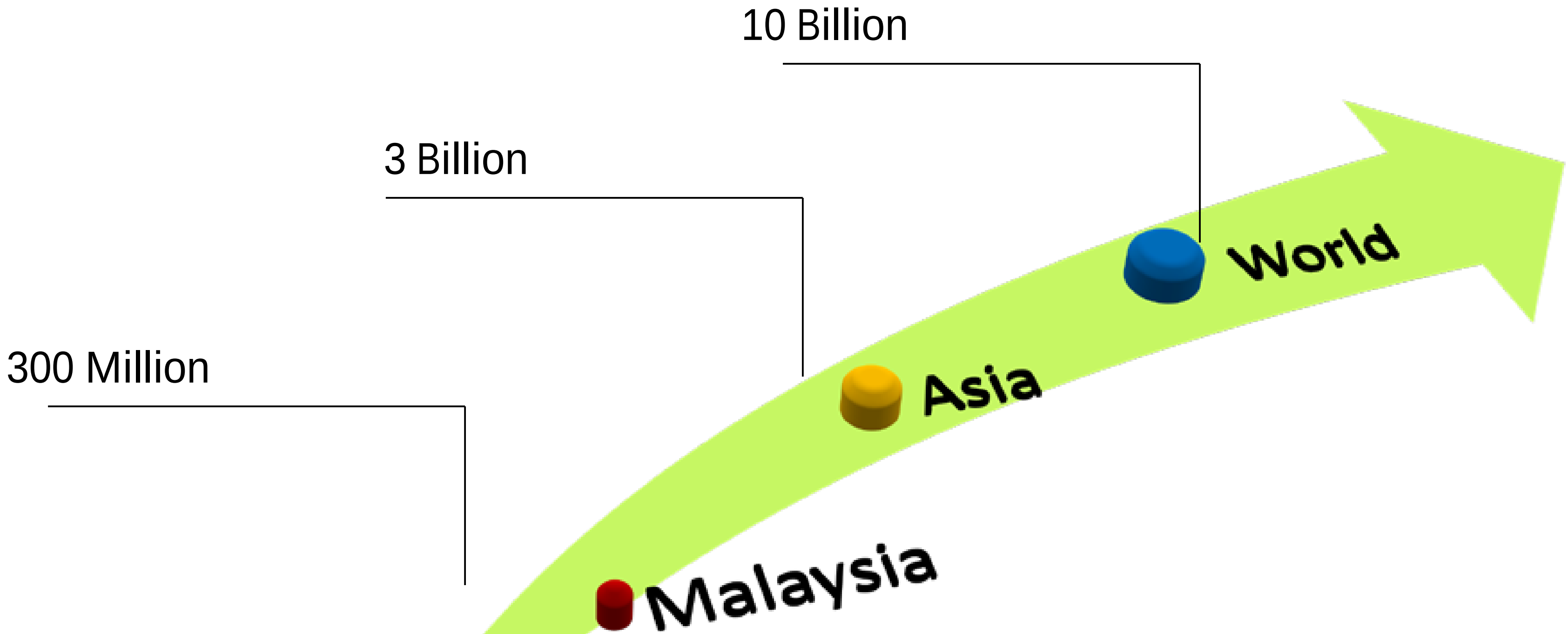






Extracorporial Membrane Oxygenation (ECMO)

Projected Demand of Membrane Technology in 2015 (USD)



The East Asia growth is spurred by expansion of :

- **The chemical related industry**,
- The need to desalinate seawater,
- Growing power plant ultrapure water requirements,
- The incorporation of cross flow filtration in the upscale commercial
- Purify municipal and industrial wastewater for reuse.

McIlvaine-Co, 2011

Membrane Chronological Development

- Thin Film Composite Membrane for Desalination

- Nanofiltration for BPA removal
- Ultrafiltration for Wastewater Treatment

- Carbon Nanotube for Desalination
- Membrane Distillation

- **Forward Osmosis**
- **Photocatalytic Membrane**
- **Adsorptive Membrane**

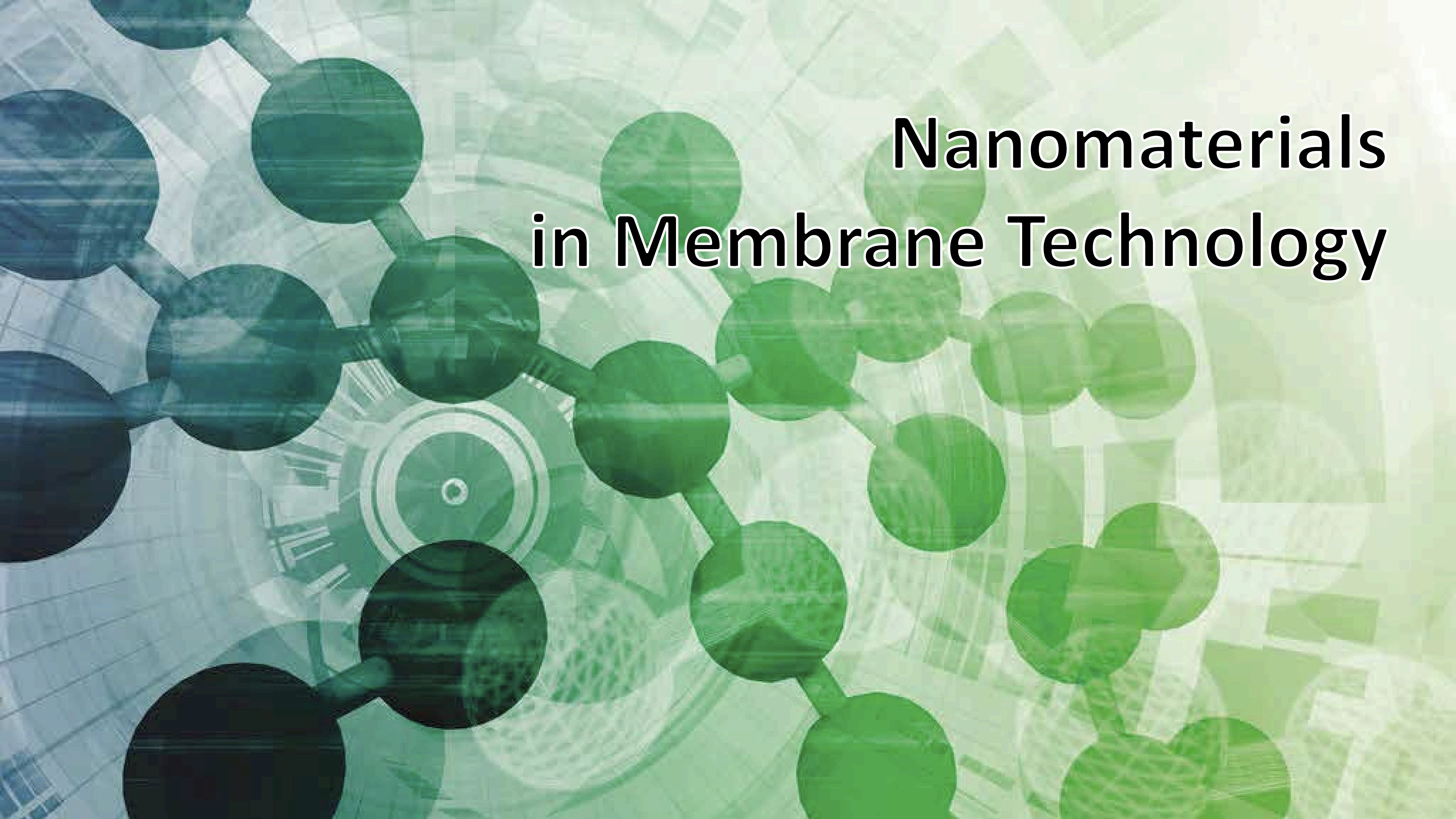
→ **Advanced Membranes**

2010 **2013** **2015** **2016** **Future**

- Thin Film nanocomposite for Desalination
- Boron Nitrate Membrane for Sea Water Desalination
- Ceramic Membrane for Ammonia Removal

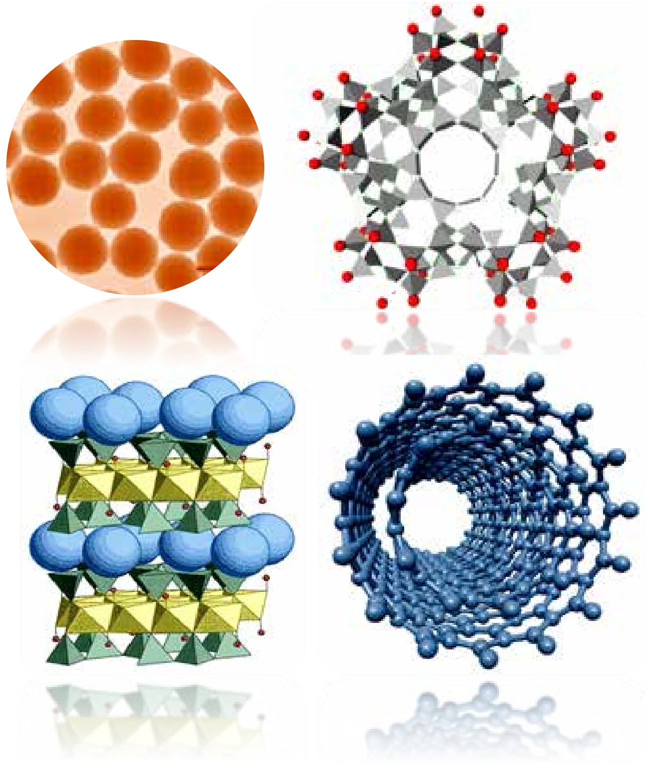
New membrane & process development

Nanomaterials in Membrane Technology



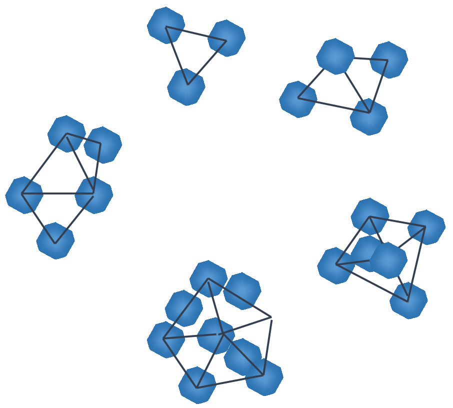
The Next Big Thing: Engineered Nanomaterials

- Nanomaterials are typically defined as materials smaller than 100 nm in at least one dimension.
- At this scale, materials often possess novel size-dependent properties different from their large counterparts.
- Water and wastewater treatment utilize the scalable size-dependent properties of nanomaterials which relate to:
  - High specific surface area and sorption capacity
  - High selectivity and reactivity
  - Fast transport
  - Antimicrobial



Classes of Nanomaterials

a) Clusters (0D)

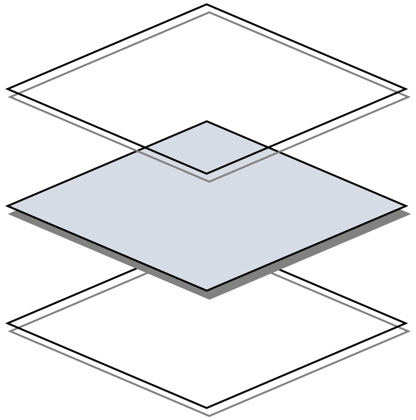


Examples: TiO_2, Al_2O_3, ZrO_2, SiO_2, ZnO, Ag

b) Nanotubes/rods (1D)

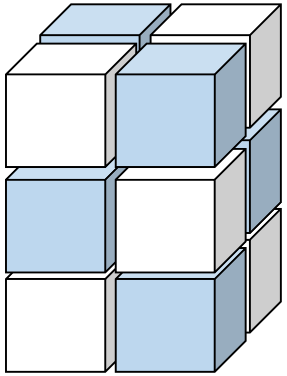
Examples: SWCNTs, MWCNTs, titania nanotube

c) Films/ exfoliated (2D)



Examples: grahene, graphene oxide, clay silicate

d) Polycrystal (3D)

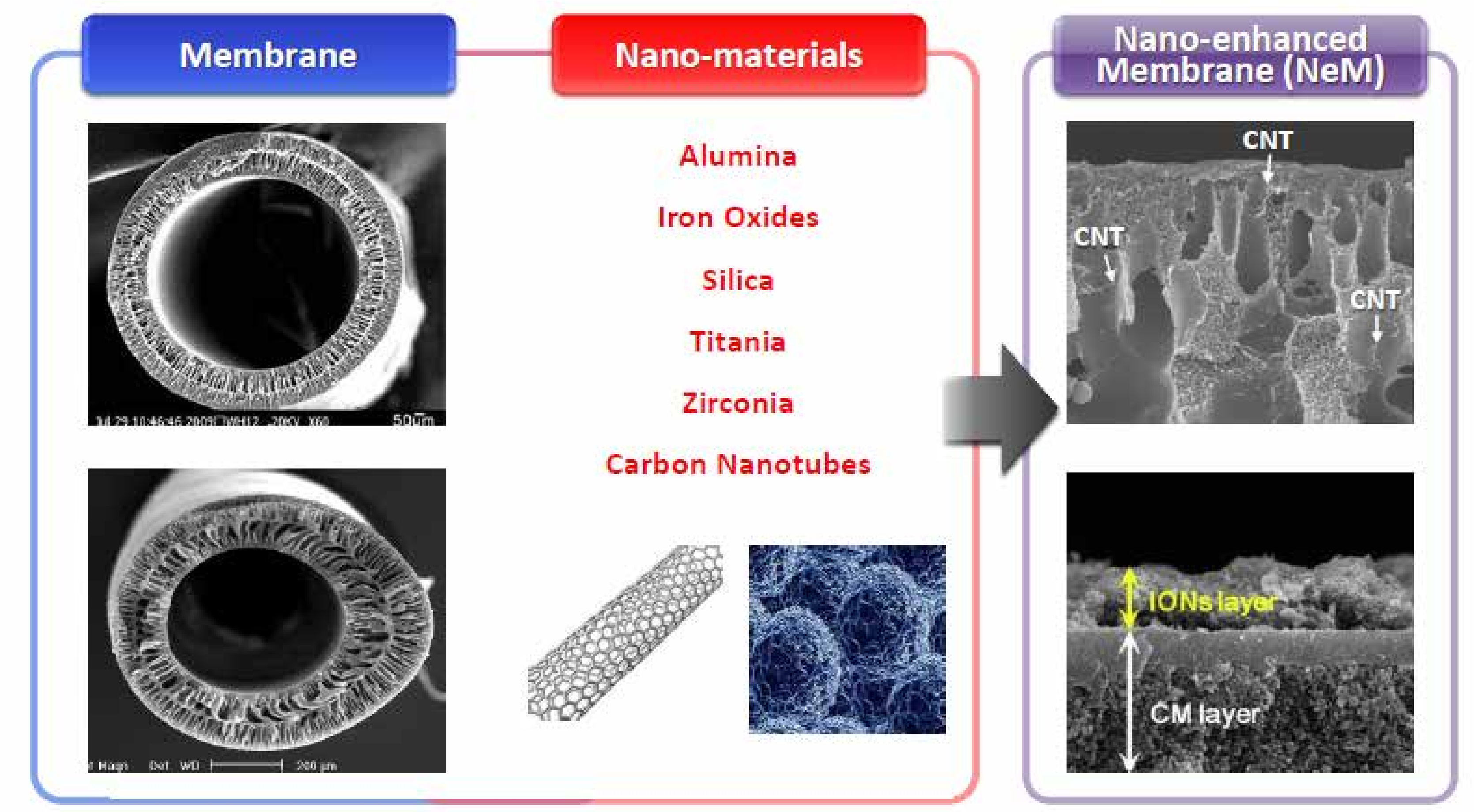


Examples: zeolite, metal organic framework

How Does Nanotechnology Help?

- Recent advances in nanotechnology offer leapfrogging opportunities to develop next-generation water supply systems
- The highly efficient, modular, and multifunctional processes enabled by nanotechnology-provide high performance, affordable and sustainable solutions.
- Less reliance on large infrastructures
- New treatment capabilities that allow economic utilization of unconventional water sources to expand the water supply

Membrane Enhanced with Emerging Nanomaterials



Advanced Membrane Technology

i. Forward osmosis
ii. Photocatalytic membrane

(i) FORWARD OSMOSIS-The Principles

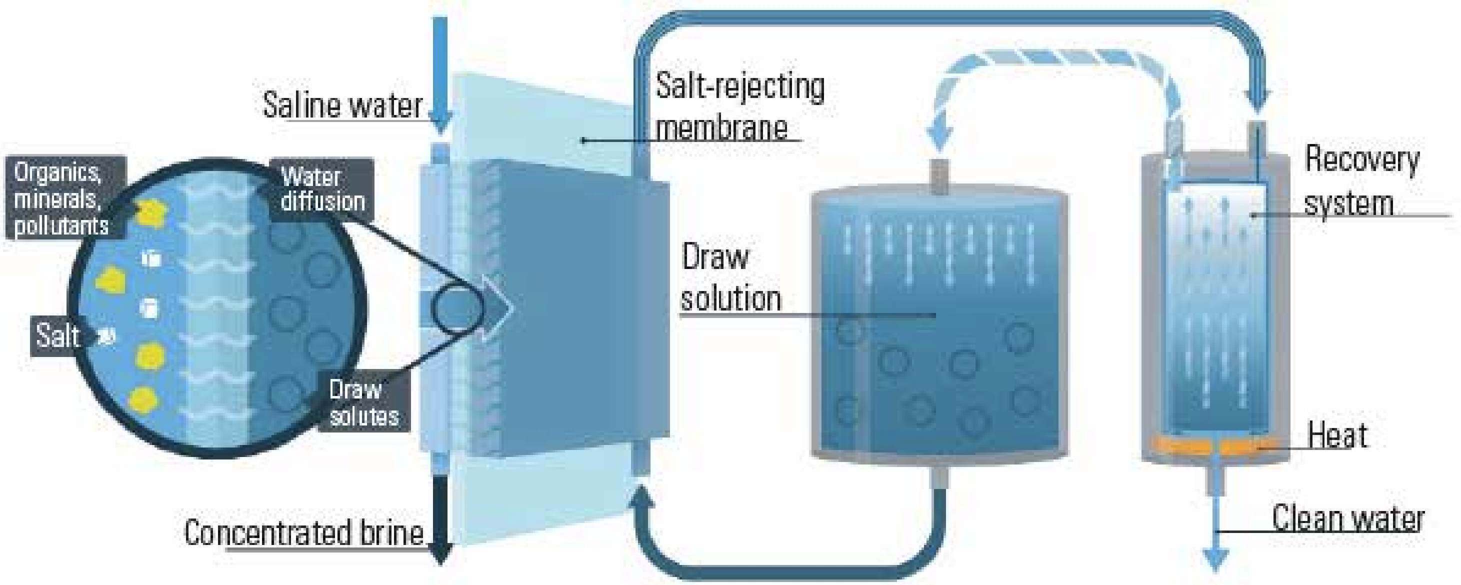


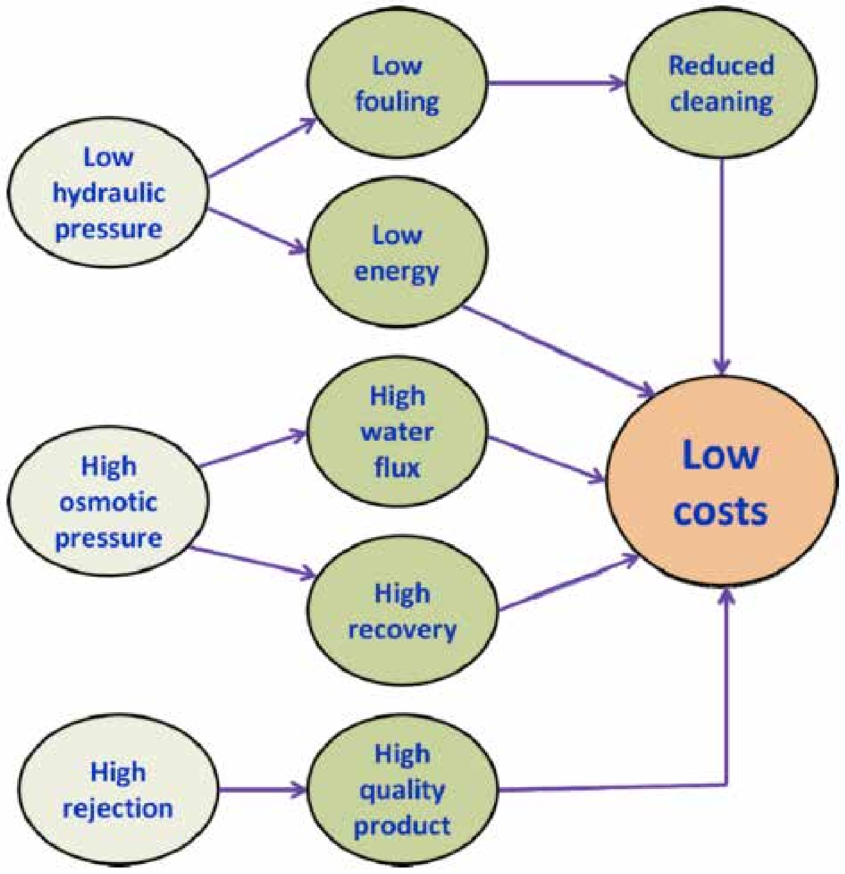
Image: Oasys Water

- FO is an **osmotically driven membrane process** that takes advantage of the osmotic pressure gradient to drive water across the semipermeable membrane from the **feed solution** (low osmotic pressure) side to the draw solution (high osmotic pressure) side.

Advantages of FO over Conventional Pressure Driven Membrane Processes

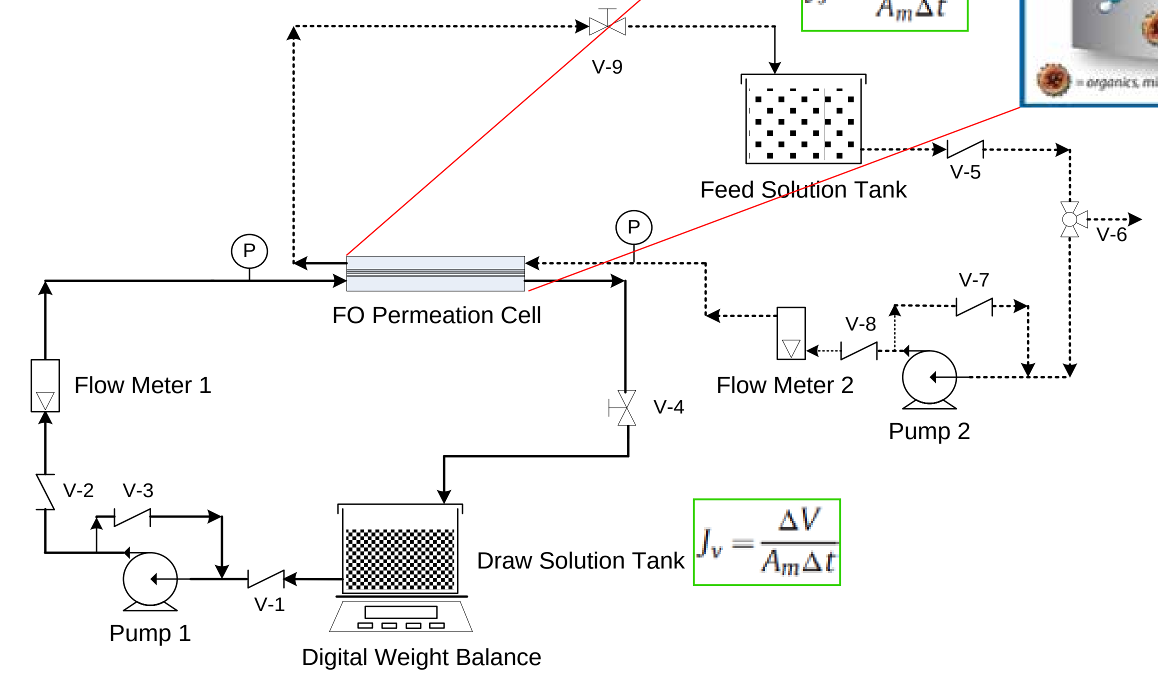
- Due to the very low hydraulic pressure required, FO delivers many potential advantages such as:
  - less energy input
  - lower fouling tendency
  - easier fouling removal
  - higher water recovery

The potential benefits of FO used in water treatment



Zhao et al. Journal of Membrane Science 396 (2012) 1– 21

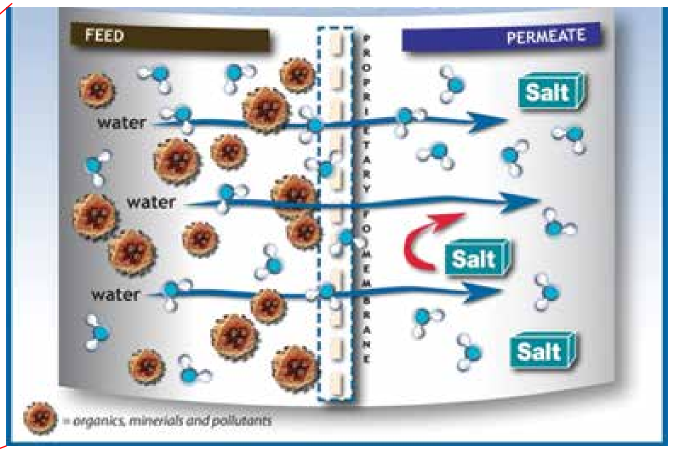
FO Membrane Experimental Set-Up

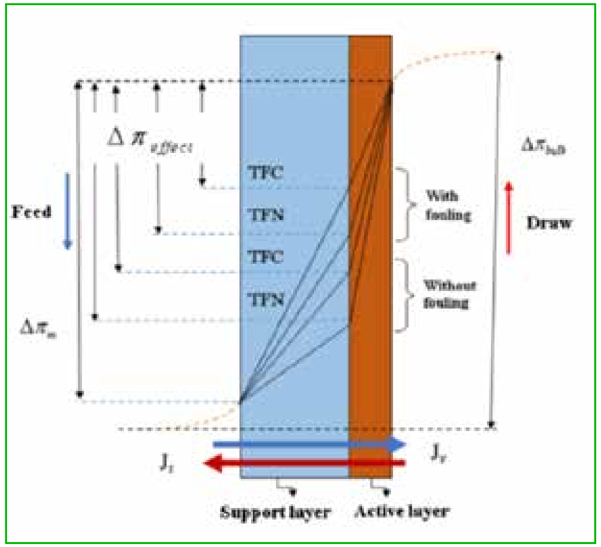


$$J_s = \frac{\Delta(C_t V_t)}{A_m \Delta t}$$

$$J_v = \frac{\Delta V}{A_m \Delta t}$$

Low osmotic Pressure High osmotic Pressure



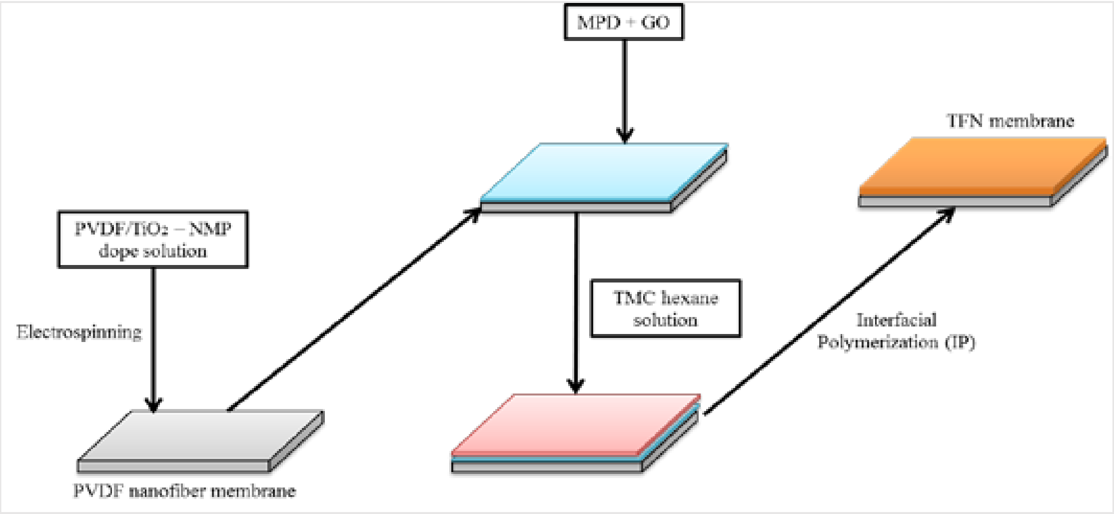


Jv=water permeation flux (based on the volume change in the draw or feed solution)

Js=Salt reverse diffusion flux from the draw solution (based on the conductivity different)

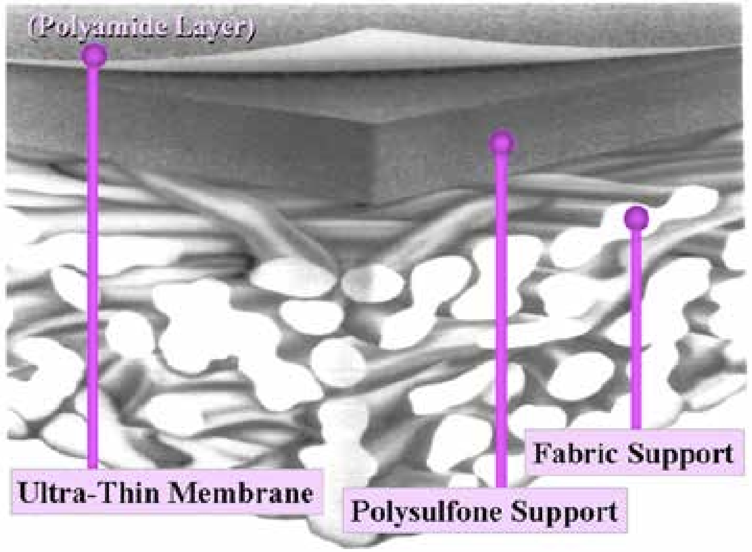
FO Membrane Characteristics

- The polyamide (PA) thin filmcomposite (TFC) (synthesized via interfacial polymerization of MPD (m-phenylenediamine) and TMC(trimesoylchloride), Mitchelle et al., 2010) FO membranes are excellent to the existing asymmetric membranes as they exhibit higher water flux and salt rejection.

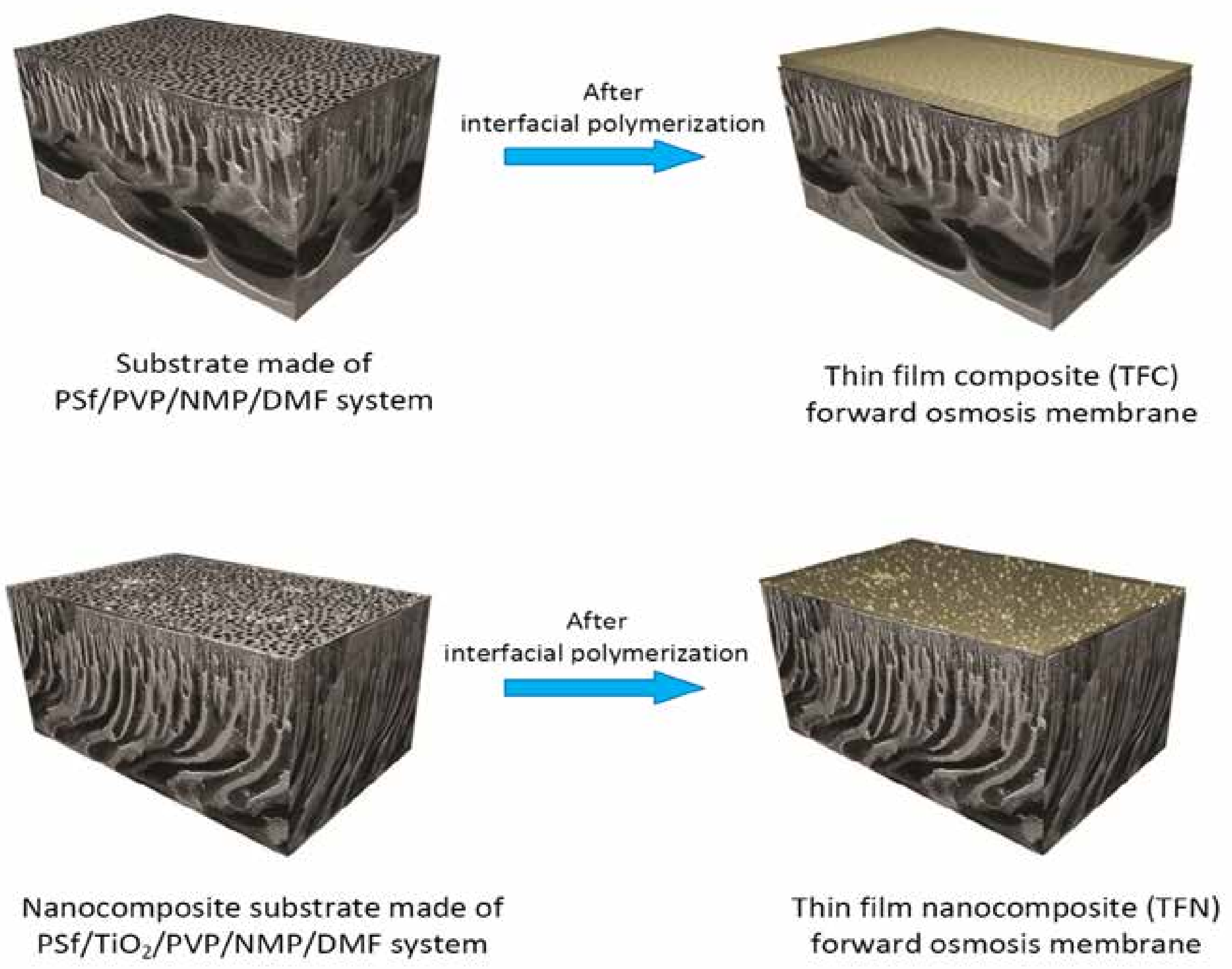


The desired characteristics of TFC FO membranes:

•A Thin semi-permeable PA layer free of defects with high water flux and high solute rejection
•A microporous substrate with low ICP
•Highly hydrophilic to improve water flux and antifouling behavior
•High mechanical strength against cleaning and vibration throughout operation

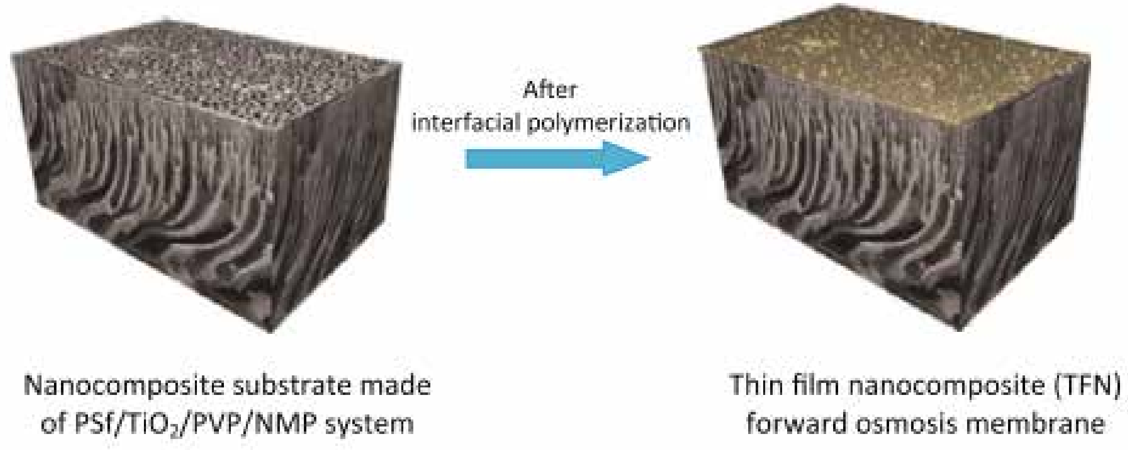


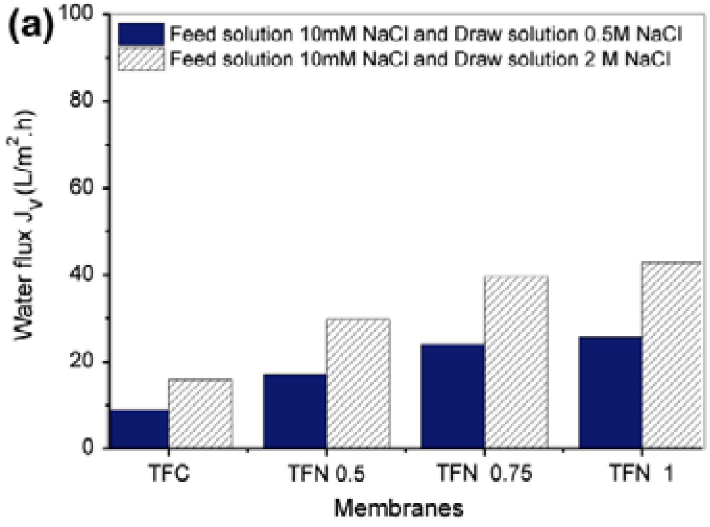
TFN membrane in FO – the structure



Thin Film Nanocomposite FO membrane for Desalination

Polyamide TFN with PSf–TiO2 nanocomposite substrate



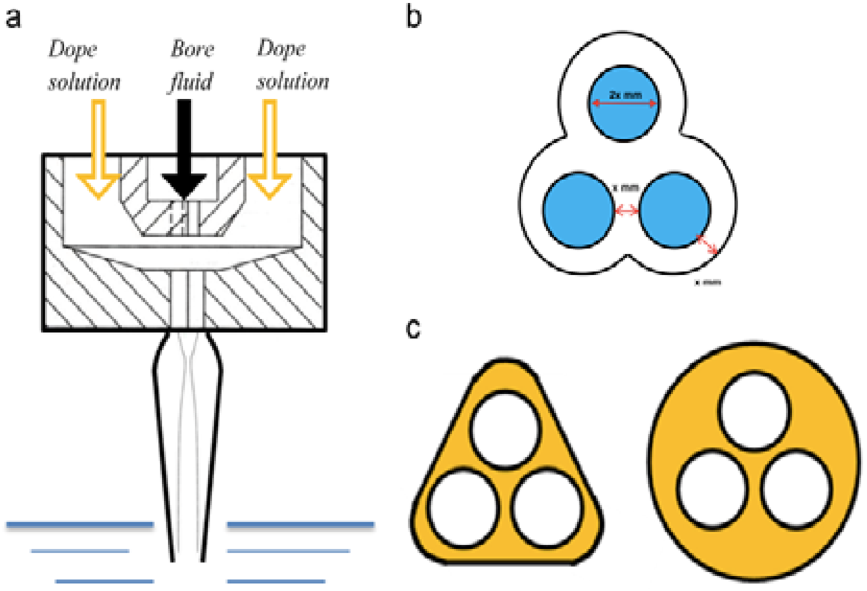


- The hydrophilicity and porosity of the PSf– TiO2 nanocomposite substrate was improved upon addition of TiO2.
- The increase in water permeability can be attributed to decrease in structural parameter which resulted in decreased internal concentration polarization (ICP).

A.F. Ismail et al. / Chemical Engineering Journal 237 (2014) 70–80

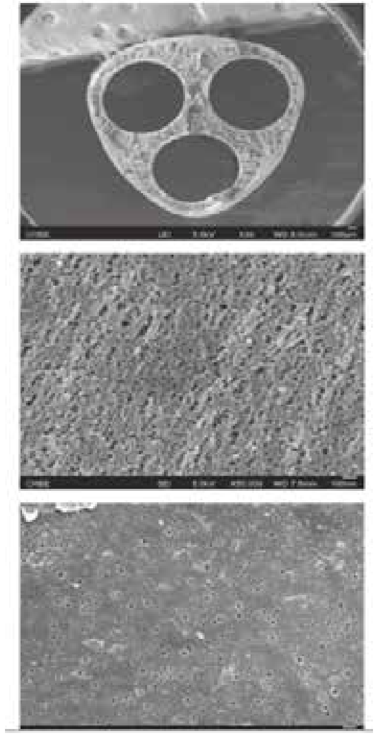
Hollow Fiber FO membrane for Desalination

Tri-bore hollow fiber membrane



(A) Single layer tri-needle spinneret; (B) bottom view of the tri-needle spinneret; (C) cross sections of as-spun tri-bore HFs.

- The triangle TFC-FO membrane exhibits improved water permeability than the round one. The TFC-triangle FO membrane has the highest water fluxes of 11.8 LMH with low salt reverse fluxes of 2.5 gMH FO modes.
- In addition, much more fibers can be packed in a FO module if TFC tri-bore HF membranes have a triangle shape instead of a round one.



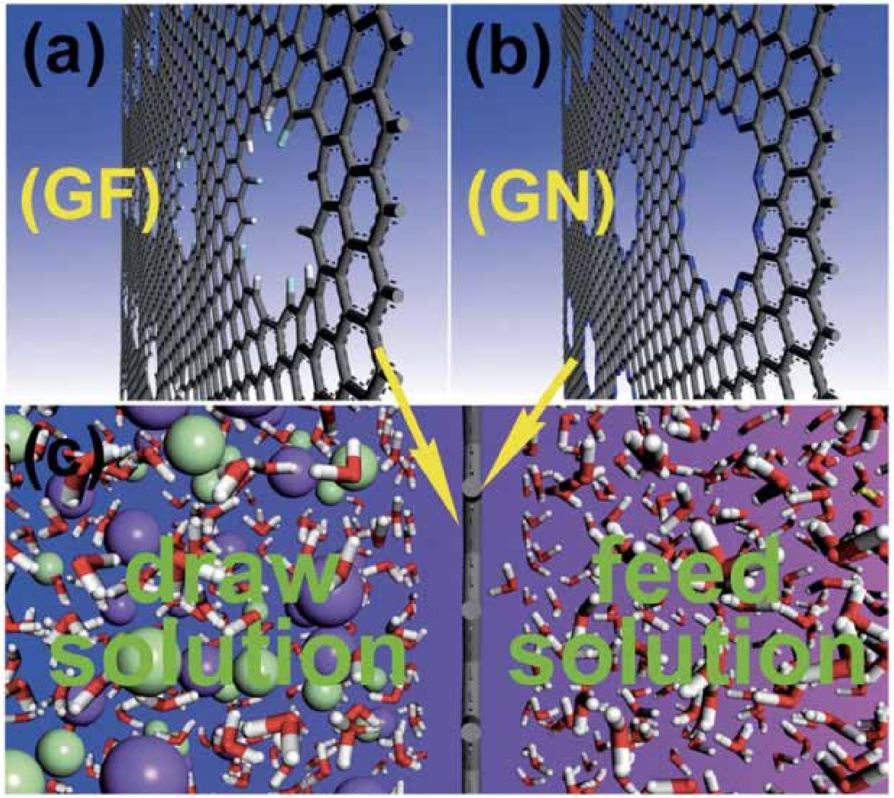
Luo et al. Journal of Membrane Science 461 (2014) 28–38

Graphene FO Membrane For Desalination-Molecular Dynamic Simulation

- Porous graphene can be used as an FO membrane without the requirement of a support layer. Hence exhibits zero Internal Concentration Polarization (ICP) if external hydraulic pressure is not necessary.
- The dangling bonds in the graphene pores can be saturated with N or F atoms to form functional graphene monolayers:
  - Fluorinated porous graphene (GF)
  - Nitriding porous graphene (GN)

TUNABLE PORE PROPERTIES-The flux and rejection can be tuned by the presence of F and N:
With N atom-**water flux decreases** and **salt rejection increases** (due to stronger attractions between membrane pores and solutions)

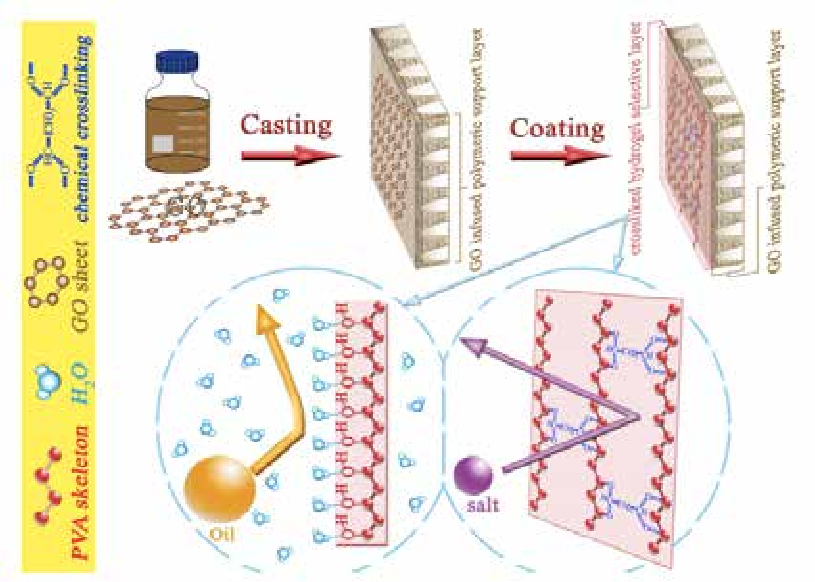
With F atom-**ultrafast water flux** due to less adsorption energy compared to N atoms.

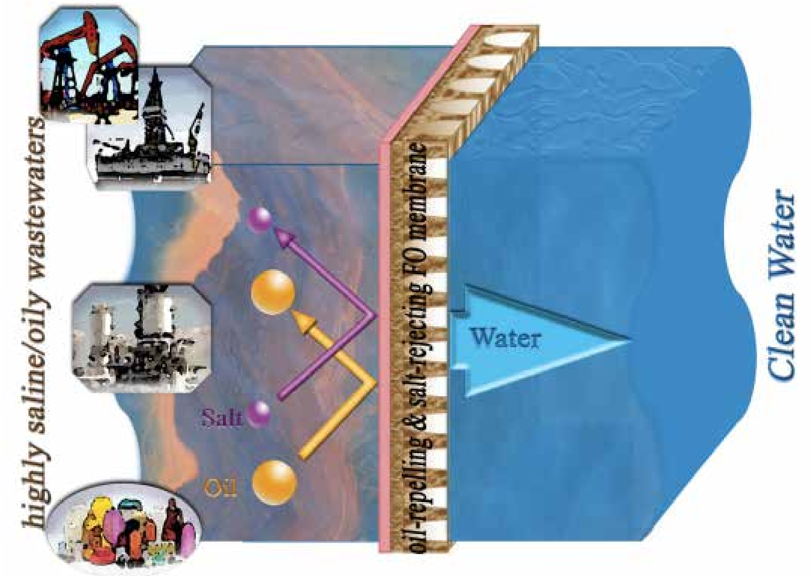


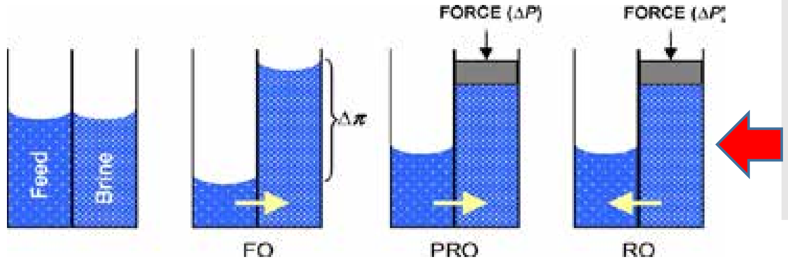
Gai et al. J. Mater. Chem. A,2014, 2, 4023

Nanocomposite FO membrane for Shale Gas (Highly Saline oil) Wastewater Treatment

Nanocomposite FO membrane composed of an oil-repelling and salt rejecting hydrogel selective layer on top of a graphene oxide (GO) nanosheets infused polymeric support layer for **simultaneous oil-repellency and salt-rejection**







Parameters and intrinsic properties accountable for S value determination:

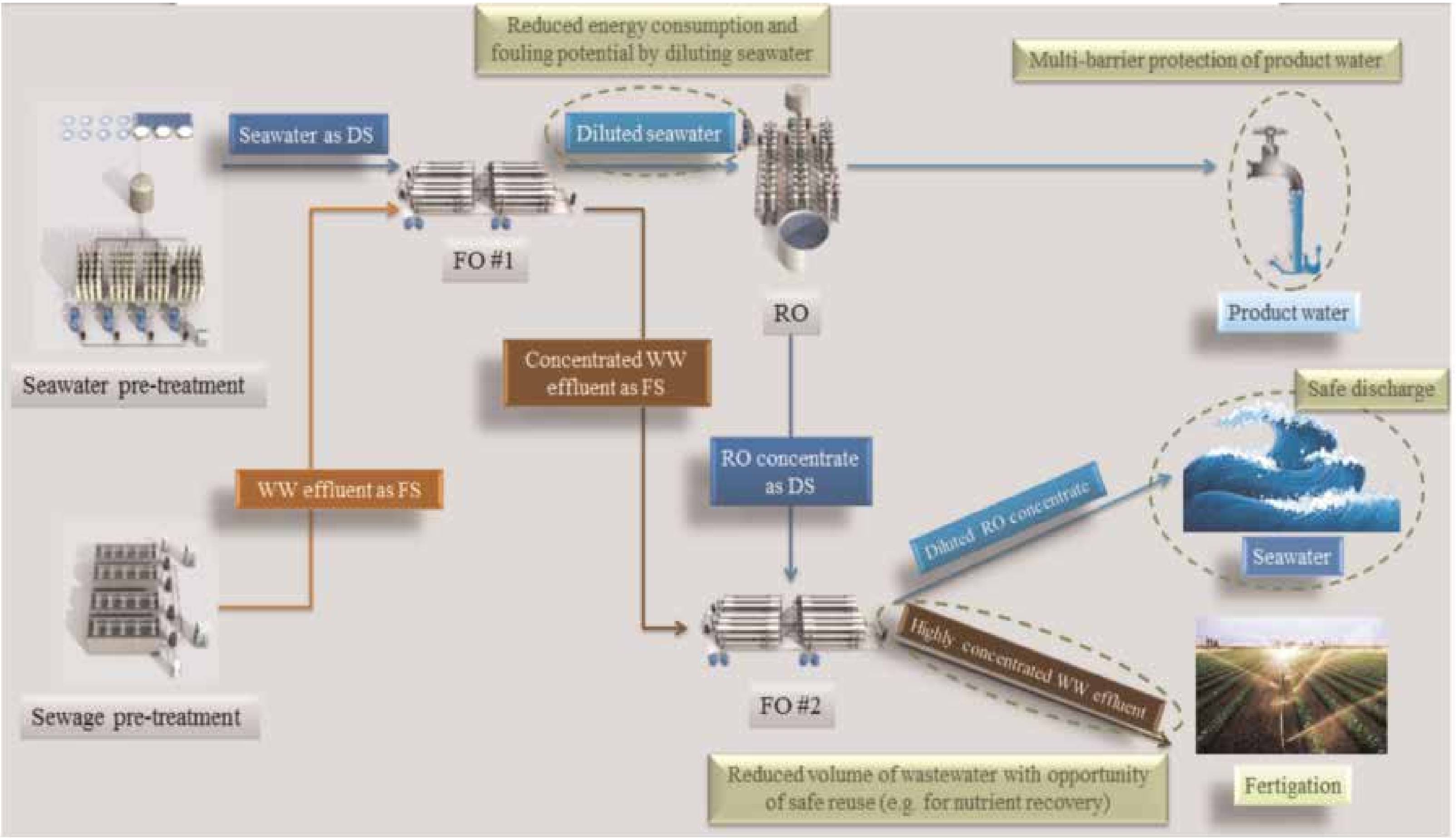
- The pure water membrane permeability coefficient (A)
- The salt permeability coefficient (B)
- The water flux J_w – IN FO MODE – at a given osmotic driving force

The synthesized FO membranes possess ultrahigh rejections of multivalent inorganic ions as well as emulsified oils.

The infused GO nanosheet plays a crucial role to improve FO membrane structure (reducing structural parameter, S value=resistance of membrane's support layer towards solute diffusion) by reducing the tortuosity as well as increasing the porosity of the support layer, and consequently lead to constantly high water flux

Qin at al. Nature Scientific Reports **5**, Article number: 14530 (2015)

FO-RO hybrid system



Schematic of an FO–RO hybrid process plant for simultaneous treatment of wastewater and seawater desalination (DS: draw solution; FS: feed solution; RO: reverse osmosis; WW: wastewater)

Chekli et al. Journal of Membrane Science 497 (2016) 430–449

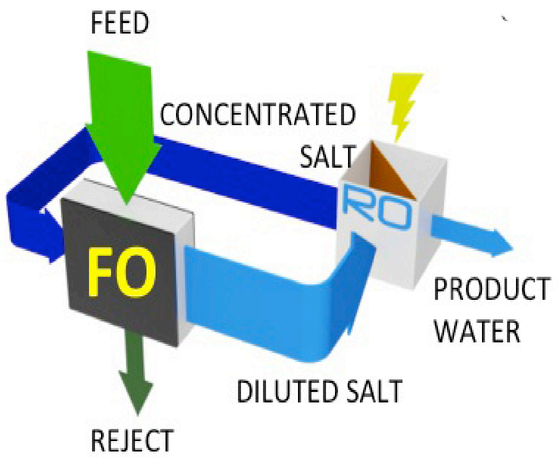
Hybrid FO System for Desalination

FO acts as pretreatment in conventional desalination

FO + RO

- Produces high quality water
- Uses simple salt as a draw
- FO is low fouling and provides nano-level pre-treatment for RO

1. FO as pre-treatment for RO

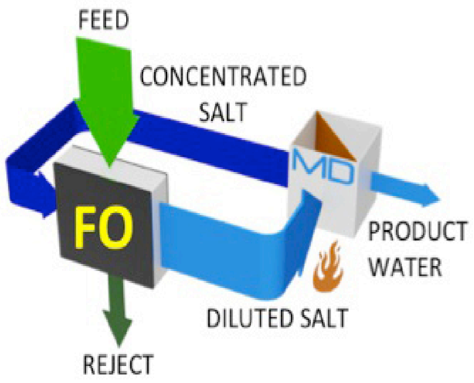


FO + Thermal Draw Recovery

- Efficient if waste heat is available

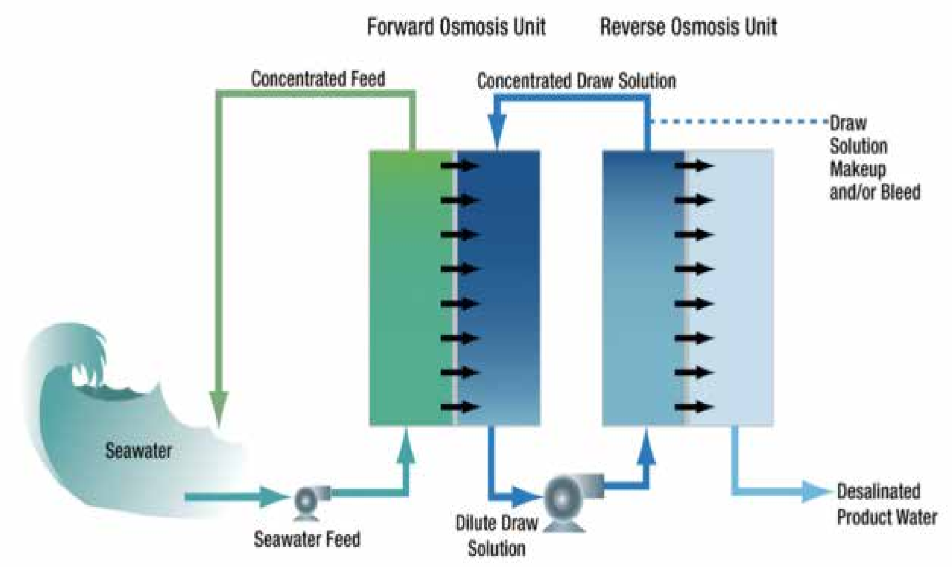
2. FO + Membrane Distillation (MD)

- Uses simple salt as a draw
- FO reduces fouling of MD



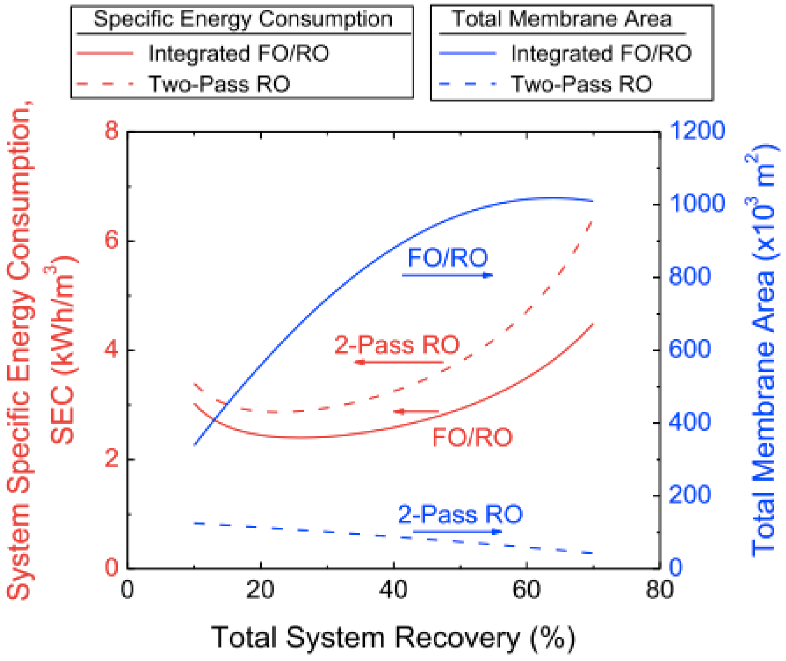
Images: International Forward Osmosis Association

FO-RO Desalination



The key benefits include

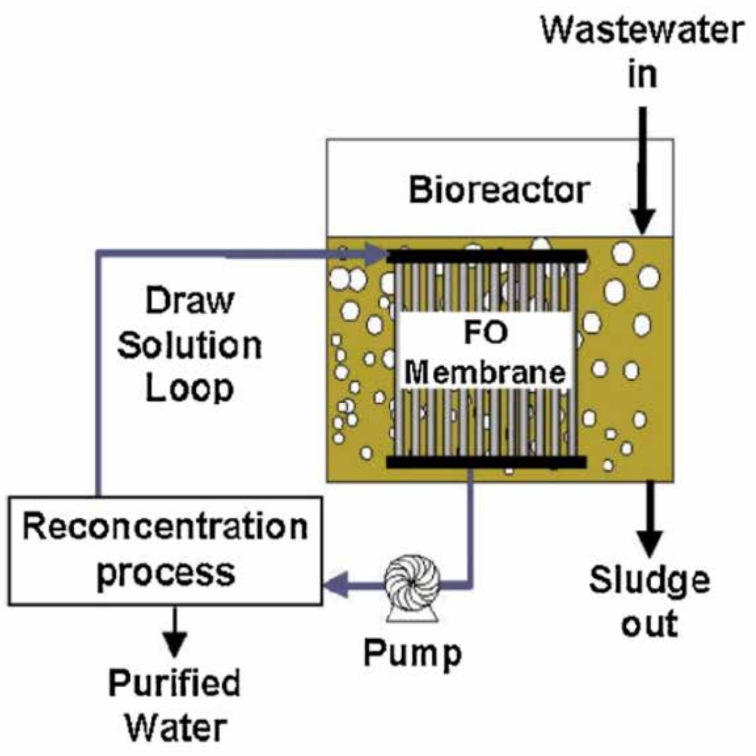
(i) Energy saving
(ii) chemical storage and feed systems may be reduced for capital and operations and maintenance cost savings,
(iii) water quality is improved for increased consumer confidence and reduced process piping costs
(iv) the overall sustainability of the desalination process is improved.



Specific energy consumption (SEC) and total membrane area of an integrated FO-RO seawater desalination process compared to a two-pass RO process.

Shaffer et al. / Journal of Membrane Science 415–416 (2012) 1–8

FO for Osmotic Membrane Bioreactor (OMBR)



Compared to seawater, general wastewater has lower osmotic pressure but much higher fouling propensity. Low fouling tendency is one of the most pronounced advantages of FO.

The ratio of the membrane salt permeability (B) to the water permeability (A) (i.e. B/A) and the ratio of hydraulic retention time (HRT) to sludge retention time (SRT) (i.e. HRT/SRT) are two important parameters for the optimization of OMBR operation.

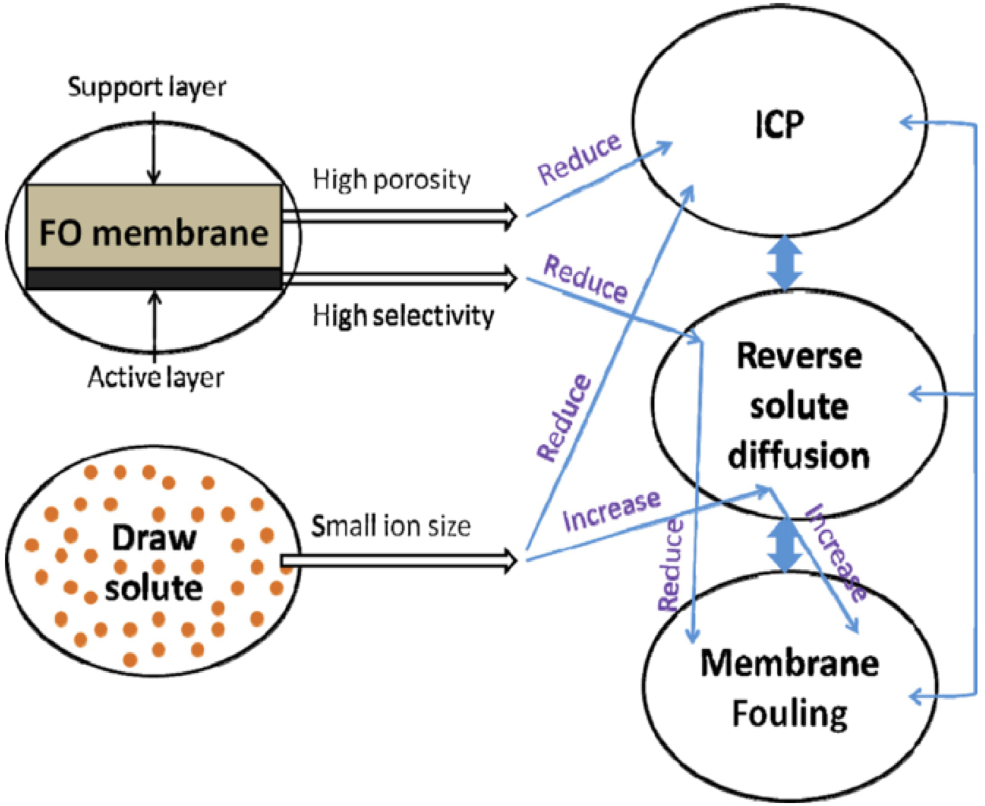
To minimize the flux decline caused by salt accumulation, these two ratios should be low

Achilli et al. Desalination 239 (2009) 10–21

Challenges of FO for Water Reclamation

1. Concentration polarization
2. Membrane fouling
3. Reverse solute diffusion
4. The need for membrane development
5. The design of the draw solute

Relationships between ICP, membrane fouling, reverse solution diffusion, membrane characteristics and draw solute properties in FO



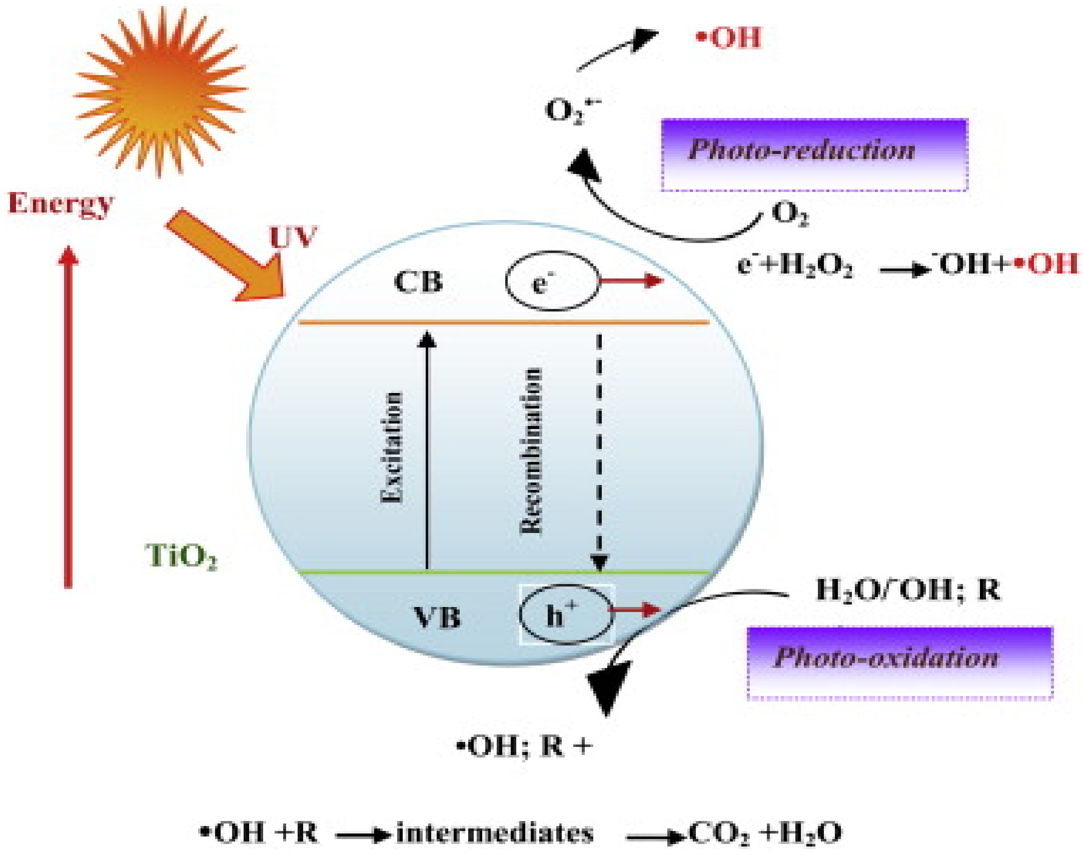
Zhao et al. Journal of Membrane Science 396 (2012) 1– 21

(ii) Photocatalysis

Photocatalysis is the acceleration of chemical reaction based on the OH- generation, induced by the absorption of light by a catalyst (TiO2; remarkable charge transfer property and oxidation ability). One of its application is to treat the organic pollutant in water.

Two types of photocatalytic reactors:
1. Separated photocatalysis and separation chamber
2. Hybrid chamber

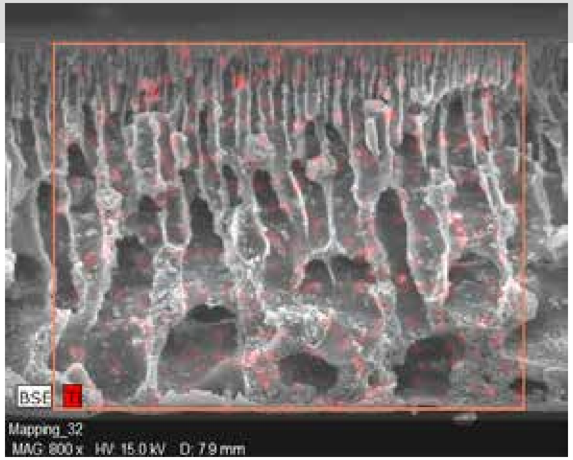
Advantages:
1. Reaction and separation occurred simultaneously
2. Eliminate separation step for catalyst

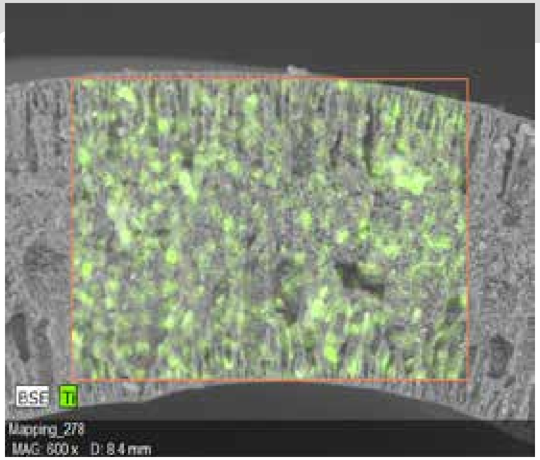


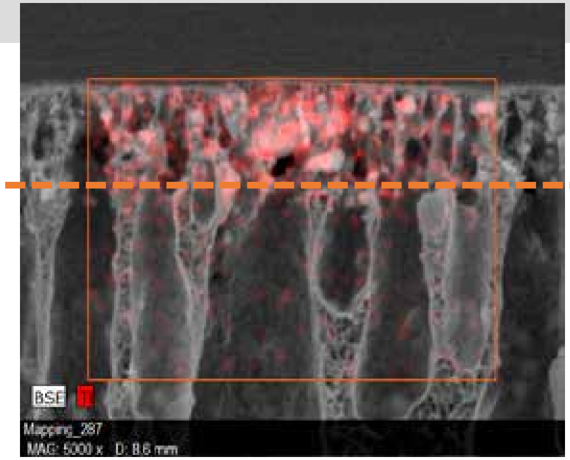
CB- Conductance band
VB- Valence band

Type of Photocatalytic Membranes

Cross-section





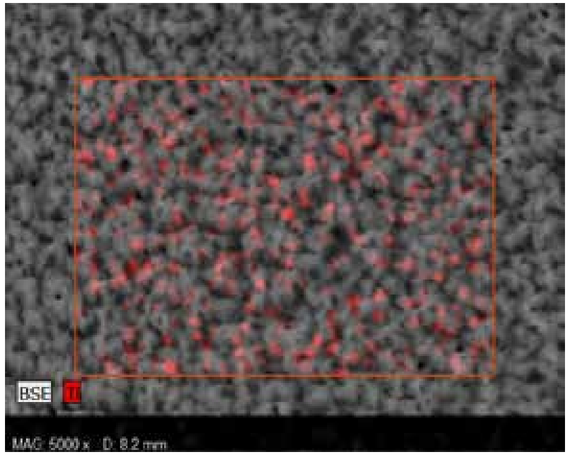


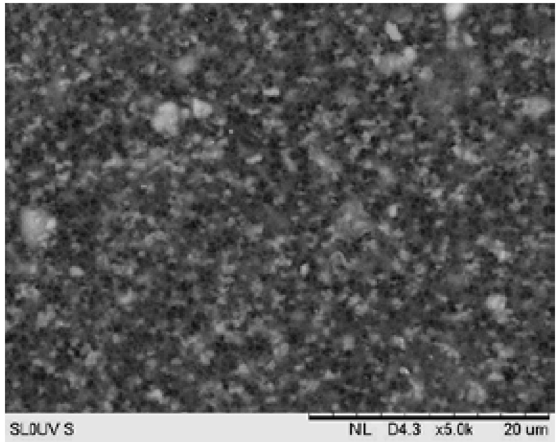
Flat sheet membrane

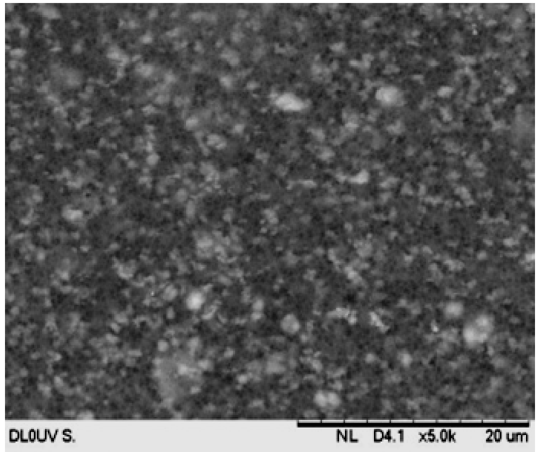
Single layer hollow fibre

Dual layer hollow fibre

Membrane surface

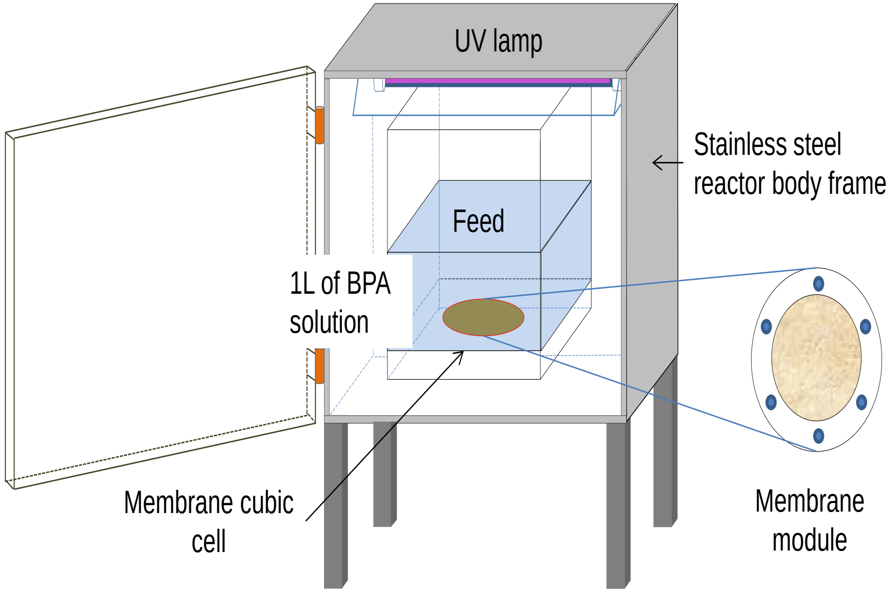




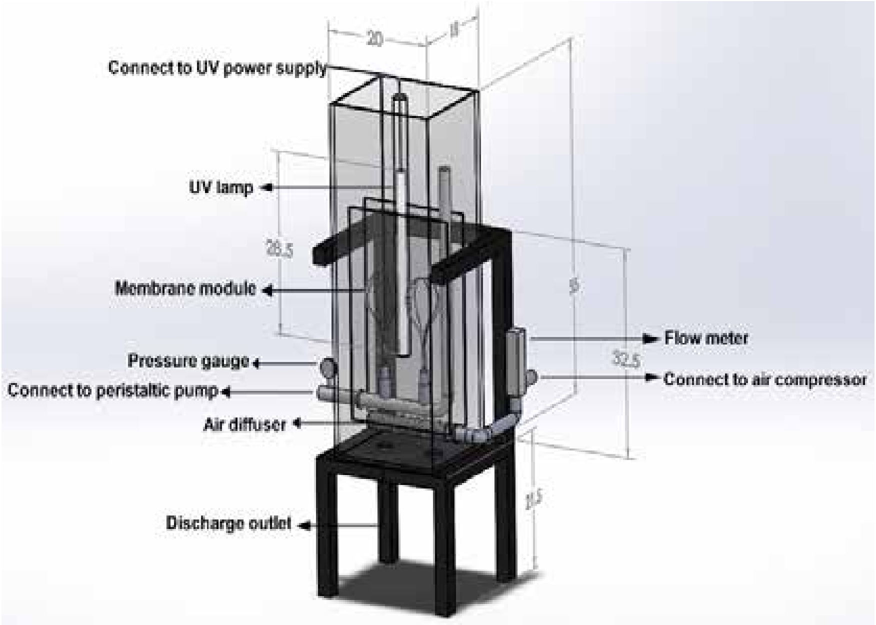


Photocatalytic Membrane Reactor

Membrane: Flat sheet membrane
Pollutant: Biphenol A (BPA)

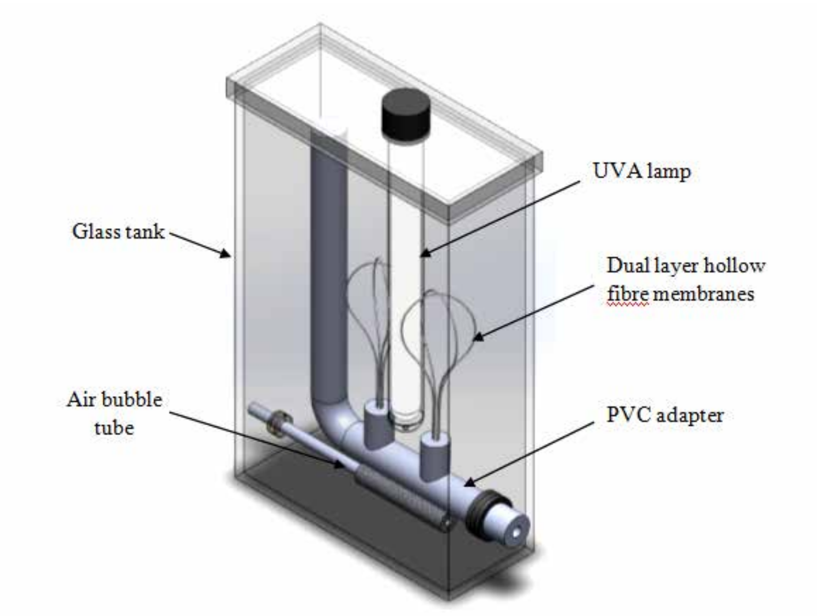


Membrane: Single layer hollow fiber membrane
Pollutant: Oily wastewater

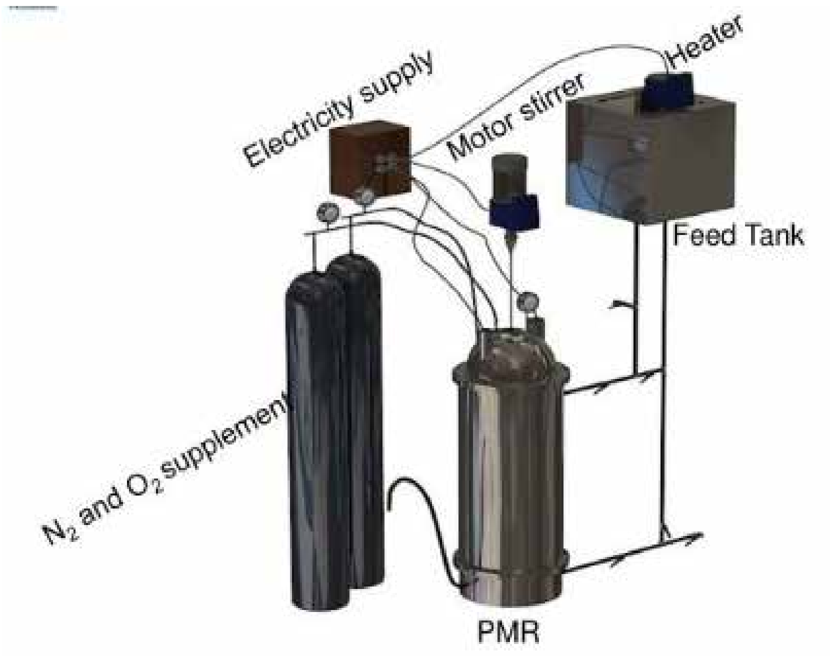


Photocatalytic Membrane Reactor

Membrane: Dual layer hollow fiber membrane
Pollutant: Nonylphenol (NP)



Membrane: Flat sheet / Hollow fiber membrane
Pollutant: Oily wastewater



PHOTOCATALYTIC DUAL LAYER HOLLOW FIBRE MEMBRANES FOR NONYLPHENOL DEGRADATION

ü Distribution of TiO_2 nanoparticles within membrane is a crucial part of this process because much of the reaction relies on the performance of the catalyst.

ü Via co-spinning process (involves 2 different phase inversion pathways simultaneously), dual-layer hollow fibre membrane with TiO_2 distributed onto selected outer layer can be produced.

Comparison of single and dual layer hollow fibres' properties (ratio TiO_2/PVDF: 0.5)

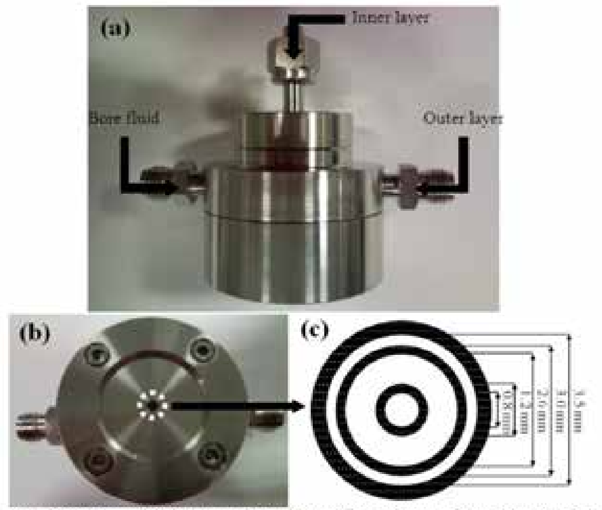
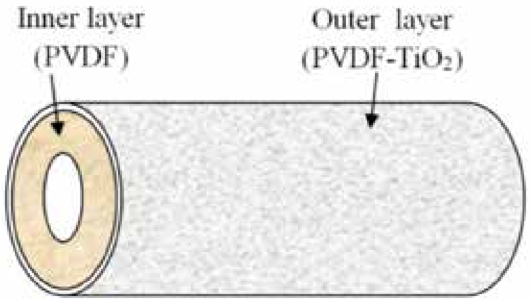
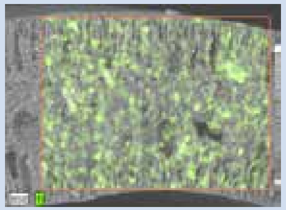
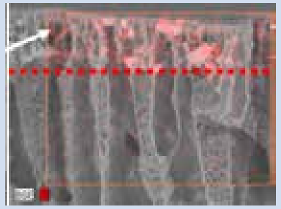


Fig. 2. Photographic images of (a) triple orifice spinneret from side, (b) triple orifice spinneret from bottom, and (c) dimension of the triple orifice spinneret [17].

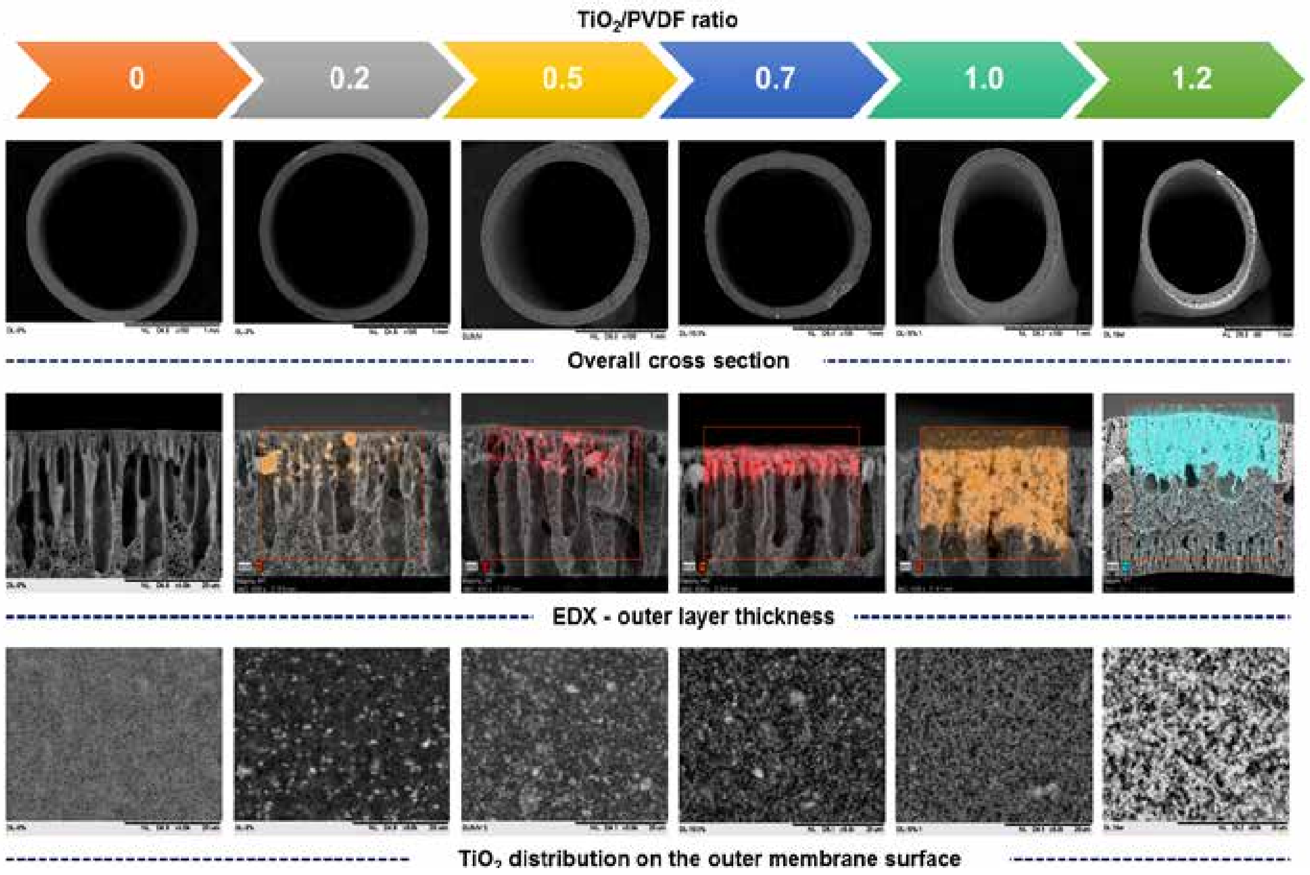


Properties	Single layer	Dual layer
TiO_2 distribution		
Contact angle	84.0 °	77.6 °
Nonylphenol degradation	70%	85%

A.F. Ismail et al., Chemical Engineering Journal 269 (2015) 255-261

PHOTOCATALYTIC DUAL LAYER HOLLOW FIBRE:
Effect of Different Loadings of TiO_2 on Membrane Structures

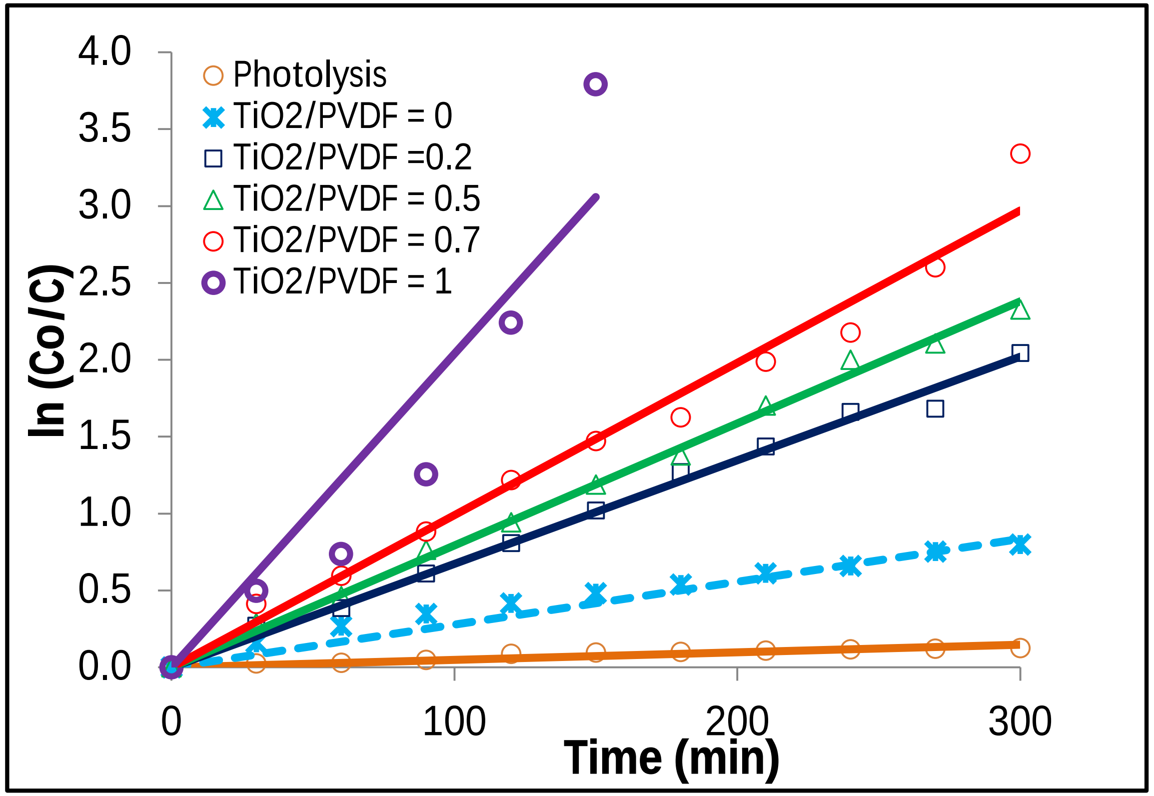
- Hollow fibres with TiO_2/PVDF ratio of 0 to 1.2 were developed via co-spinning process
- Inner layer consisted of 100% PVDF, while outer layer was a mixture of TiO2/PVDF
- Thickness of outer layer varied with the loading, the higher the loading, the thicker the thickness
- Good adhesion between inner and outer layers can be achieved even for very high loading of TiO_2



A.F. Ismail et al., Journal of Membrane Science 479 (2015) 123-131

PHOTOCATALYTIC DUAL LAYER HOLLOW FIBRE:
Effect of Different Loadings of TiO_2 on Nonylphenol Degradation

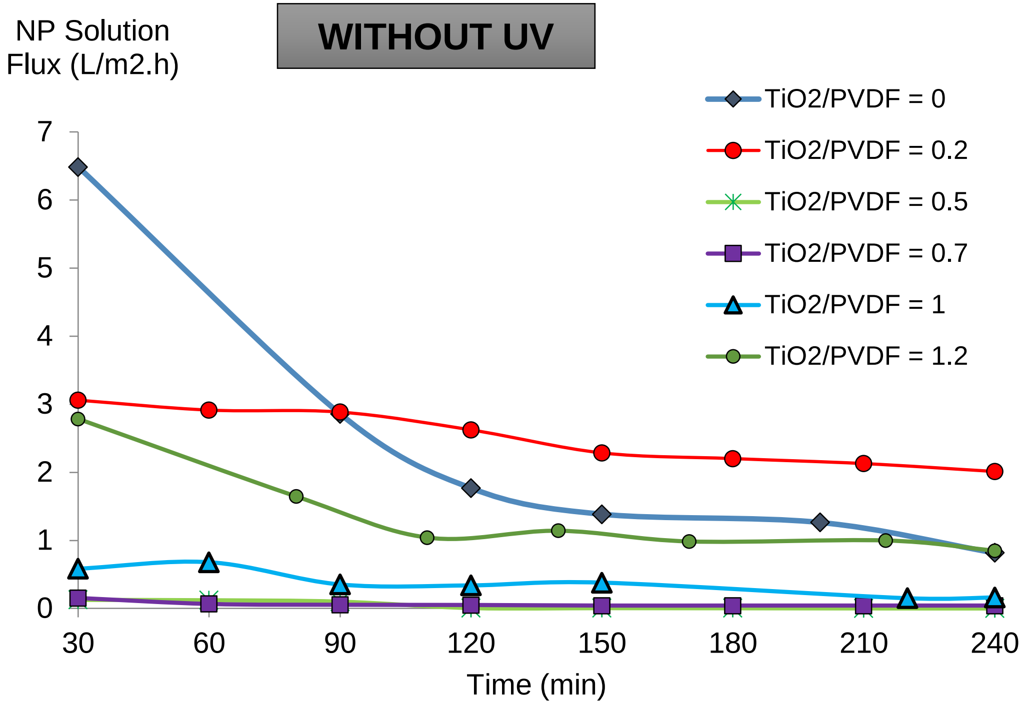
- No degradation occurs under photolysis conditions
- The photocatalytic degradation of NP did not occur since no catalyst was immobilized on the membrane.
- The degradation activity which represented by kinetic showed a significant increase when TiO2 loading was increased.
- Achieved the fastest degradation for the membrane with the highest TiO_2 loading.

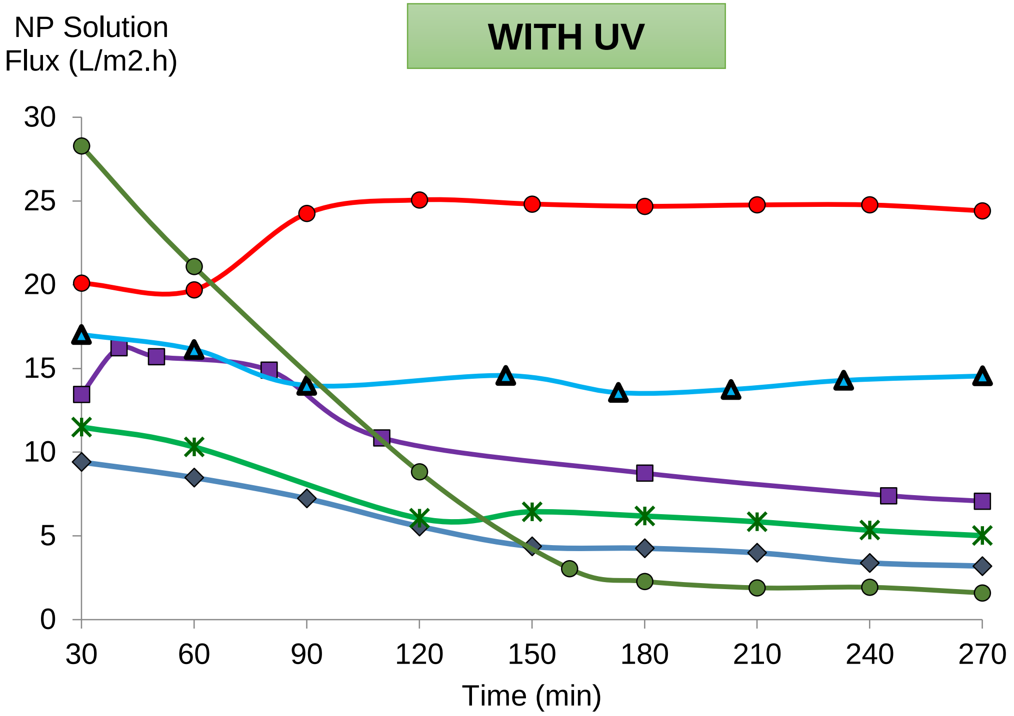


Degradation kinetics of NP using different ratio of TiO_2/PVDF membrane

A.F. Ismail et al., Reactive and Functional Polymers 479 (2015) 123-131

PHOTOCATALYTIC DUAL LAYER HOLLOW FIBRE:
Effect of Different Loadings of TiO_2 on Filtration Performance

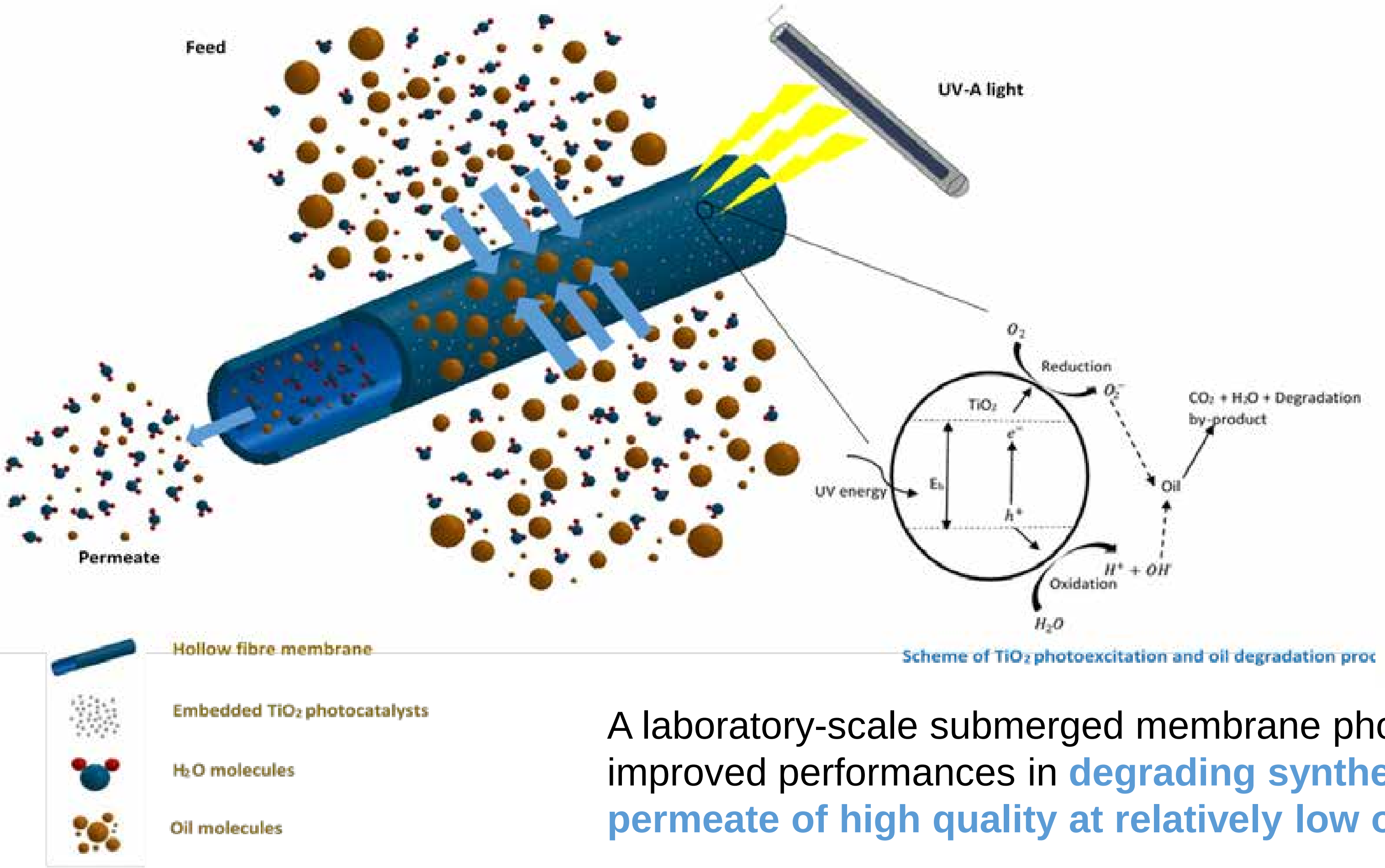




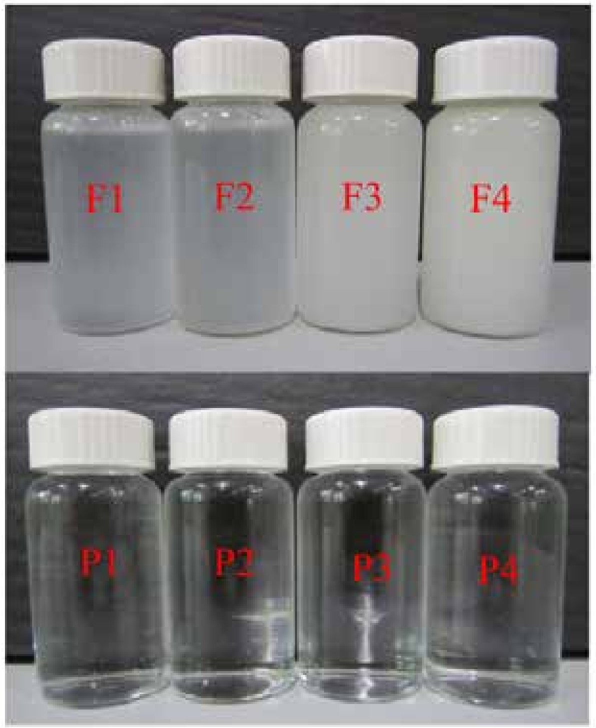
ü **TiO_2 may partially prevent the decline of permeate flux** and allow to reach a higher stabilized flux more rapidly than without UV irradiation.

ü **0.2 TiO_2/PVDF** ratio shows an **optimum value** for NP flux compared to other, it may due to the **distribution of TiO_2 nanoparticles** at the outer layer in DLHF membranes.

PHOTOCATALYTIC MEMBRANE FOR OILY WASTEWATER TREATMENT



Scheme of TiO₂ photoexcitation and oil degradation proc



FEED with different concentration of cutting oil

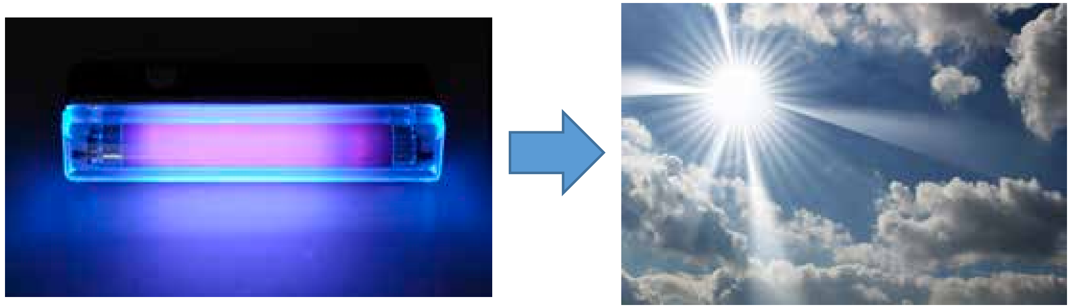
PERMEATE with clear solution that comply discharge standard

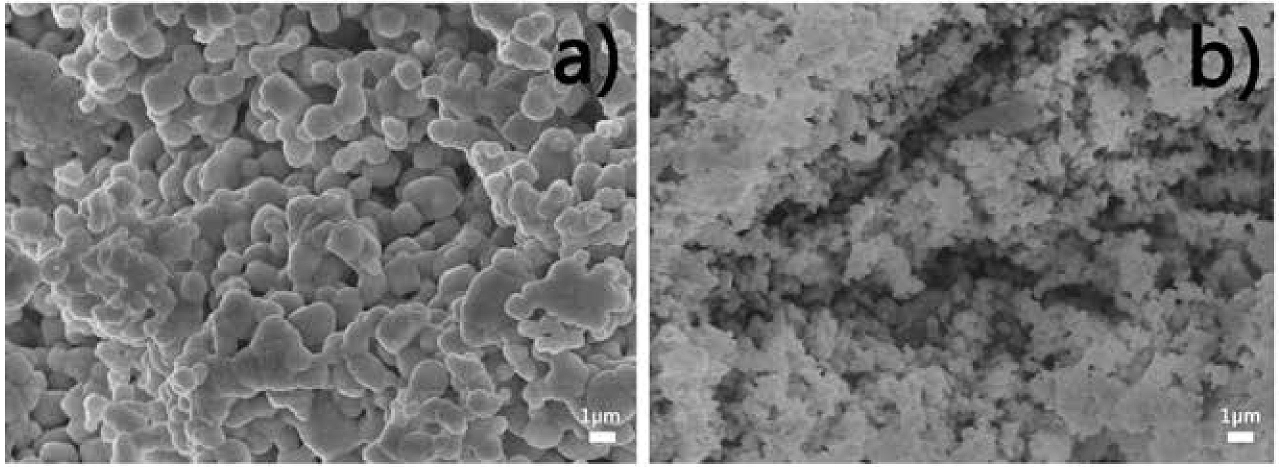
A laboratory-scale submerged membrane photocatalytic reactor (sMPR) exhibited remarkably improved performances in **degrading synthetic cutting oil wastewater** and producing **permeate of high quality at relatively low operating cost.**

C.S. Ong, W.J. Lau, P.S. Goh, A.F. Ismail et al Desalination 353 (2014) 48–56

Current Challenges of Photocatalytic Membrane

- Tendency for nanoparticle photocatalyst agglomeration at high loading → reduce photocatalytic activity performance, mechanical strength
- High operation cost due to high UV light's power consumption
- Instable PVDF as base membrane when exposure to UV at long term





<u>Way forward of Photocatalytic Membranes</u>

- Co-spinning is able to reduce the effect of nanoparticle agglomeration
- Shifting from UV-driven to visible light driven photocatalyst
- The use of robust ceramic membrane to replace polymeric membrane

5. Concluding Remarks

- Membrane technology provides engineering solution for water shortage through water reclamation (wastewater treatment and desalination)
- The application of nanomaterials have further heightened the performances of membrane technology
- Emerging advanced membrane processes offered Lower energy consumption, higher removal efficiency/water recovery and simple process
- More breakthroughs are expected to in this field to provide sustainable engineering solutions to address water scarcity

Acknowledgement

- Members and students of AMTEC, UTM
- Universiti Teknologi Malaysia
- Ministry of Education Malaysia
- Ministry of Science, Technology and Innovation Malaysia

Community Services

Community Service to Supply Drinkable Water at Kiulu, Sabah (2017)

- The portable drinking water filtration system has been developed by AMTEC, UTM to provides clean and safe drinking water to community in Kampung Rumindako Kiulu, Tamparuli, Sabah
- Water resource that is used for the treatment of process water is obtained from ground water
- The system capable to supply 2000 Liter per day of which can cater around 1000 peoples.

Community Services

Community Service for Flood Relief at Kelantan (2016)

- The integrated mobile reverse osmosis (RO) water purification system (UTM Membrane) is developed by AMTEC, UTM.
- Water resources that are used for the treatment of process water is obtained from river water, tube well and seawater.
- To provide quality water support to small units where the distribution of water is not feasible during the occurrence of natural disaster.
- The system provides clean water support without committing large water production assets from the logistics support structure.
- The system tailors water production capacity to fulfil the demands of independent Special Operations Forces, detachments and units typically engaged in remote site missions.

Community Services

Earth Quake Relief at Ranau, Sabah (August 2015)

Community Services

Flood Relief at Pekan, Pahang (Jan 2015)

Community Services

Pantai Senok Desalination Plant (2017)

Site: **Kampung Pantai Senok, Kelantan** (Private Land)

Current Scenario

- No natural supply of potable water- over dependent on tube well supply
- Yellowish and poor water quality supply

The Necessity & Societal Benefits

- SWRO DESAL with max. capacity of 0.5 MLD can benefit 3,300 residents (150 Litre/person) for sustainable daily freshwater supply.
- The clean and sustainable water supply is the catalyst to revive the tourisms industry

AMTEC'S Products

1 TYPE A – UTM Membrane

Output: 40,000 litre/day (2 unit for 80,000Litre/day)

Water source: Surface water/ River water

- Treated water production for drinking water with the capacity of 80,000 litre/day.
- To cater for 5,000 users.
- 2 units installed at Kg. Sinarot for CSR earthquake relief.

ADVANTAGES:

- Portable system
- Beneficial to 5,000 users
- High water quality <0.1 NTU
- 99.9 % bacteria and viruses removal
- 100% colloidal removal
- Low cost and maintenance
- No chemicals are required
- Includes back flushing system for cleaning purpose

SPECIFICATION:

- Max Capacity : 80,000 L/day (2 unit)
- Operating pressure : 1-10 bar
- Operating temperature : Max 50 ° C
- pH range : 3.0-12.0
- Conductivity : Raw (>500µS/cm)
  : Filtrate (<100µS/cm)

PRICING: USD185,000.00 /unit

2 TYPE B – UTM Membrane

Output: 20,000 litre/day.

Water source: Surface water/ River water

- Treated water production for drinking water with the capacity of 20,000 litre/day.
- To cater for 2,000 users.
- 1 units installed at Kg. Rumidako, Kiulu for CSR on water shortage.

ADVANTAGES:

- Portable system
- Beneficial to 2,000 users
- High water quality <0.1 NTU
- 99.9 % bacteria and viruses removal
- 100% colloidal removal
- Low cost and maintenance
- No chemicals are required
- Includes back flushing system for cleaning purpose

SPECIFICATION:

- Max Capacity : 20,000 L/day
- Operating pressure : 1-10 bar)
- Operating temperature : Max 50 ° C
- pH range : 3.0-12.0
- Conductivity : Raw (>500µS/cm)
  : Filtrate (<100µS/cm)

PRICING: USD120,000.00

3 TYPE C – UTM Membrane

Output: 1,000 litre/day.

Water source: Surface water/ River water

- **Treated water production for drinking water with the capacity of 2,000 litre/day.**
- **To cater for 500 users.**
- **4 units delivered to Jabatan Air Kelantan as CSR water purification system in disaster.**

BENEFITS:

i. Integrated mobile RO water purification unit is specialized design using Ultrafiltration and Reverse Osmosis membrane to produced a drinking water.

ii. The unit can treats any water source including river water, surface water, turbid and contaminated water sources.

SPECIFICATION:

- Max Capacity : 1000 L/day
- Operating pressure : 1-7 bar
- Operating temperature : Max 50 ° C
- pH range : 3.0-12.0
- Conductivity : <100µS/cm

PRICING: USD35,000.00

4 TYPE D – UTM Membrane

Output: 6,000 litre/day (Utilities Water),
1,000 litre/day (Drinking Water)

Water source: Brackish water/ Seawater

- 1 units installed at Endao as CSR unit.

ADVANTAGES:

- Portable system
- Beneficial to 300-500 users
- High water quality < 0.1 NTU
- 99.9 % bacteria and viruses removal
- 100% colloidal removal
- Low cost and maintenance
- No chemicals are required
- Includes back flushing system for cleaning purpose

SPECIFICATION:

- Max Capacity : 6000 L/day
- Operating pressure : Low (1-5 bar)
- : High (50-70 bar)
- Operating temperature : Max 50 °C
- pH range : 3.0-12.0
- Conductivity : Raw (>30 mS/cm)
  : 2nd pass RO (<400µS/cm)

PRICING: USD75,000.00

Conclusions

- AMTEC is now in the right direction to become a hub of membrane-based technology for nation human capital development and wealth creation for the future, especially in the niche area of water reclamation
- Apart from FO, photocatalytic and adsorptive membranes, AMTEC also gives attention to the development of membrane contactor, graphene based membrane and pressure retarded osmosis membrane
- Current AMTEC's way forward is to produce affordable water purification system for local communities use

AMTEC'S Video

THANK YOU

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HAKONE, 2009