UTS
UNIVERSITY OF TECHNOLOGY, SYDNEY

Forward osmosis research activities at UTS

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Outline

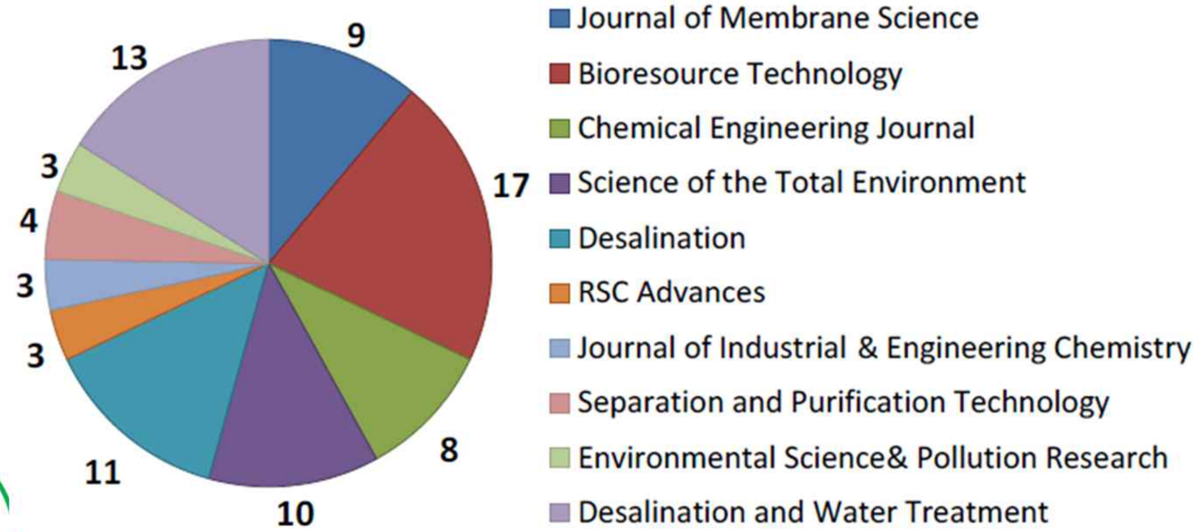
- UTS
- FO: current progress
- FO activities at UTS
- Fertiliser-drawn forward osmosis
- Graphene oxide incorporated forward osmosis membrane
- Pilot-scale forward osmosis demonstration
- How to reduce reverse salt flux
- Acknowledgements

UTS

Course type	Now
Higher degree research	1623
Postgraduate coursework	10,979
Undergraduate	28,037
Total	40,639

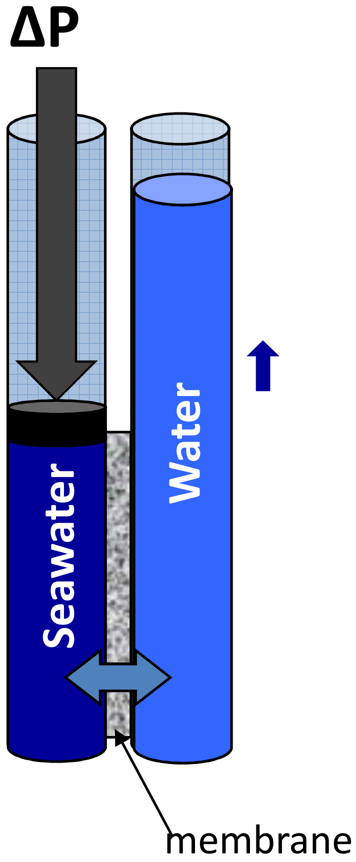
Centre for Technology in Water and Wastewater (CTWW)

- 66 Members, 10 Academic Staff, 6 Research Fellows, 50 Postgraduates



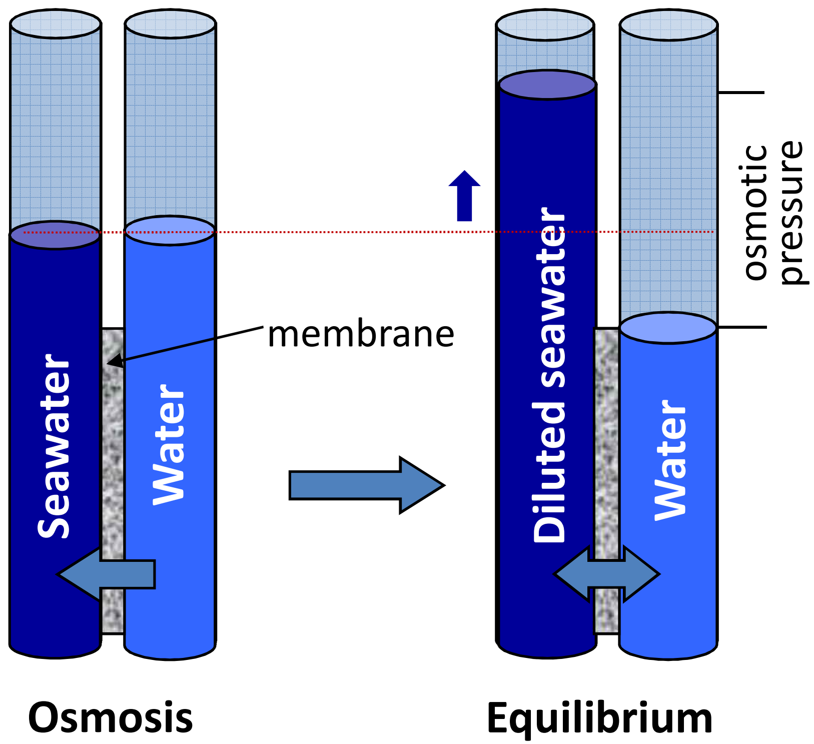
FO

Reverse Osmosis



Driving force = External energy

Forward Osmosis

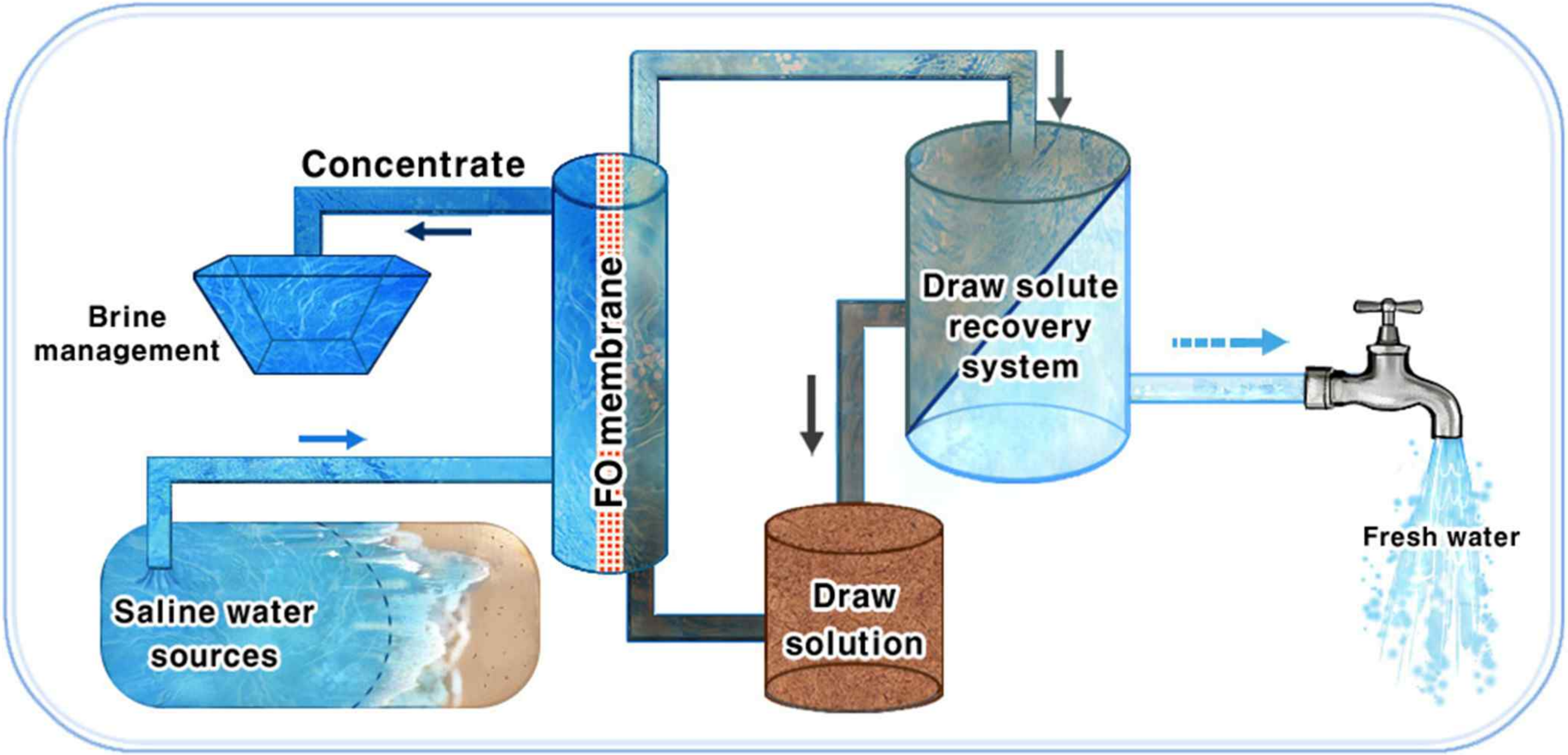


Seawater as Draw Solution (DS)

Driving force = concentration/osmotic gradient

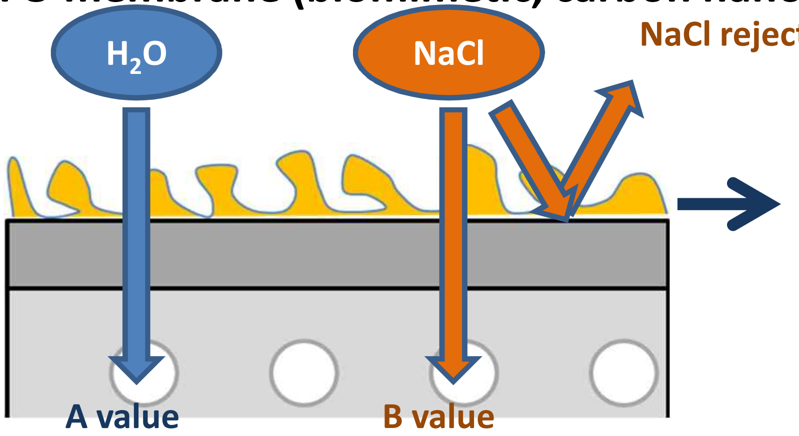
Forward Osmosis

FO membrane, Draw solute, Membrane fouling, Operating parameter, Application



FO Membrane and Module Configuration

- ➢ Existing commercial CTA FO membranes
- ➢ New generation of FO membranes (PA based TFC)
- ➢ Hollow fibre FO membrane
- ➢ Doubled skinned FO membrane
- ➢ Futuristic FO membrane (biomimetic, carbon nanotube, graphene, etc)



* Integrity of polyamide layer
: Dominated by top surface of support layer

- Water permeability

$$A = \frac{J_w}{\Delta P}$$

- Salt rejection and Reverse salt permeability

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \qquad B = J_w \frac{1-R}{R} \exp\left(-\frac{J_w}{k}\right) \qquad k = \frac{Sh \cdot D}{d_h}$$

(k: mass transfer coefficient)

- Permeate Water flux

$$J_v = \frac{\Delta V_{draw}}{A_m \Delta t}$$

- Reverse Salt Flux (RSF)

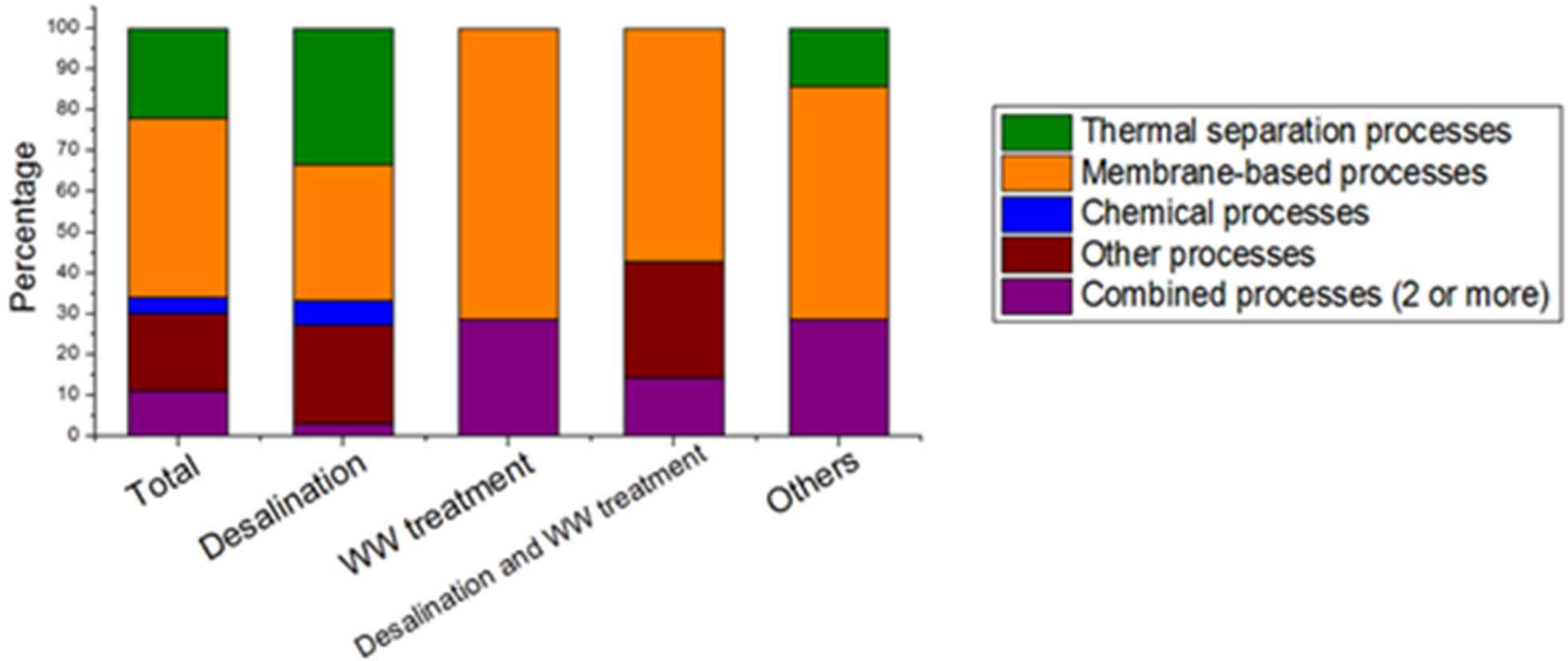
$$J_s = \frac{\Delta C_{t,feed} V_{t,feed}}{A_m \Delta t}$$

- Specific Reverse Salt Flux (SRSF)

$$SRSF = \frac{J_s}{J_v}$$

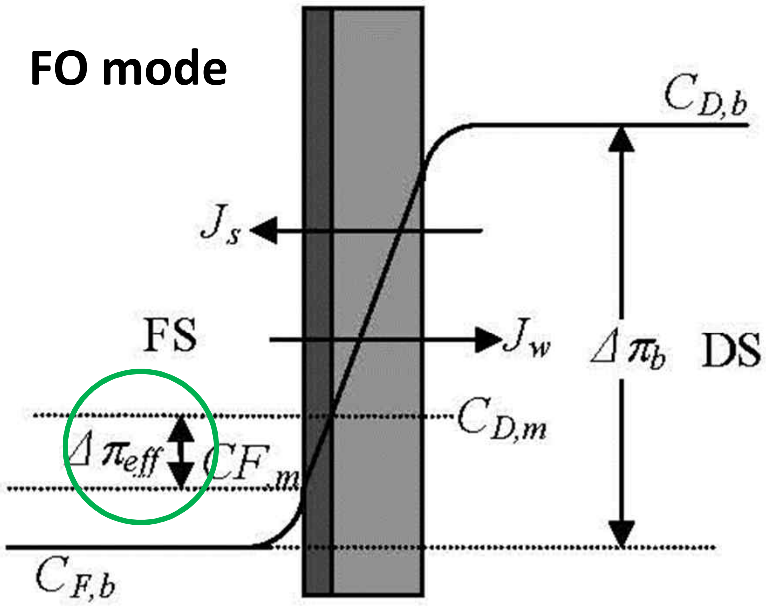
Draw solutes

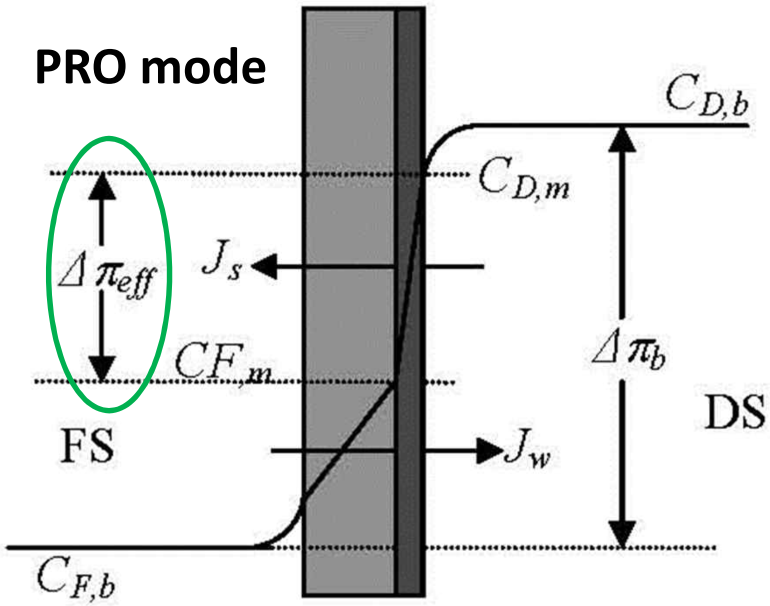
- Commercial DS: RO concentrate, sugar, chemical additives for cooling tower, NH_4HCO_3, seawater
- Separation methods of DS



Membrane Fouling

- Membrane fouling: organic, inorganic, biofouling, ICP/ECP
- Standard method of flux and RSF
- Modular design
- Difficult feed water





Applications

FOOD & BEVERAGE

Product Concentration

Waste Concentration & Reuse

Water Recycling

Why consider FO?
New products, low cost, sustainability, & higher purity

OIL & GAS

Unique drilling fluid chemistry and reuse

ZLD concentration of oilfield brines

Small footprint offshore treatment

Why consider FO?
High temperatures, high TDS

MANUFACTURING & MINING

Product concentration

High purity processing

Waste concentration and reuse

Why consider FO?
High temperatures, new products, low cost, small footprint

WATER & AGRICULTURE

Ultimate technology for potable reuse

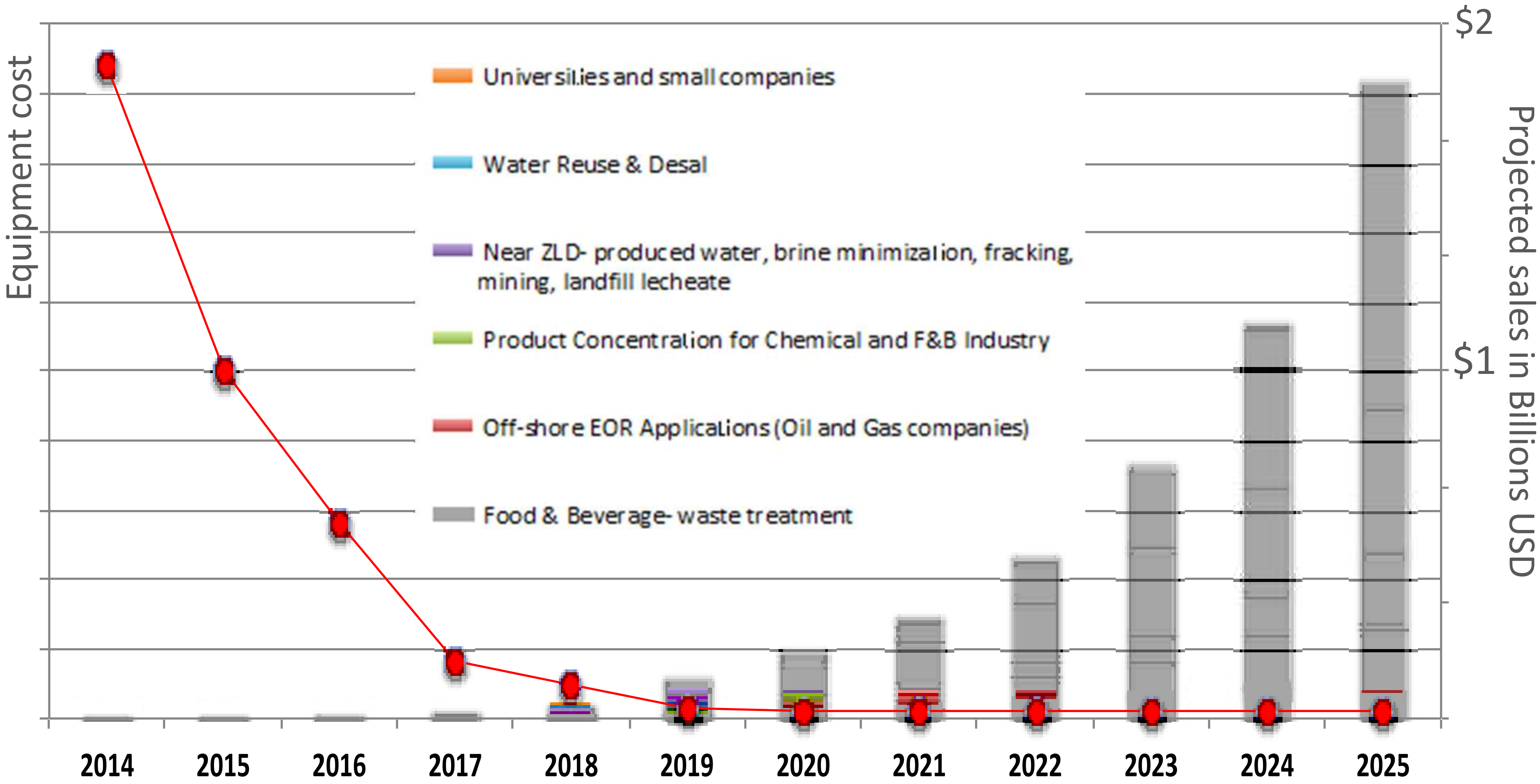
Why consider FO?
High contaminant removal, unprecedented membrane integrity monitoring

FTSH2O Fluid Technology Solutions · MODERNWATER · OASYS WATER · TOYOBO Ideas & Chemistry · LOTTE CHEMICAL

TREVI SYSTEMS · Porifera · AQUAPORIN · TORAY Innovation by Chemistry

Porifera, 2015

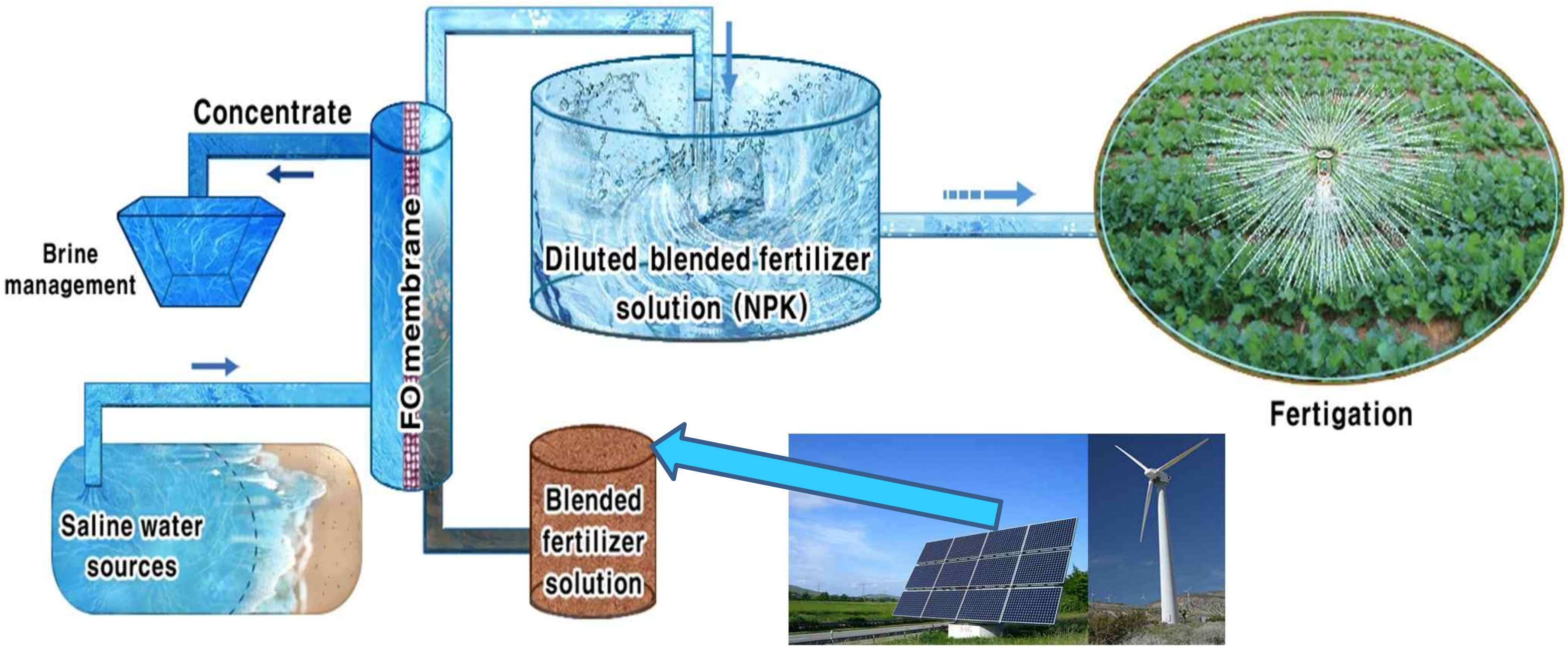
Equipment cost reduction will drive market expansion



Porifera, 2015

UTS FO Research Activities

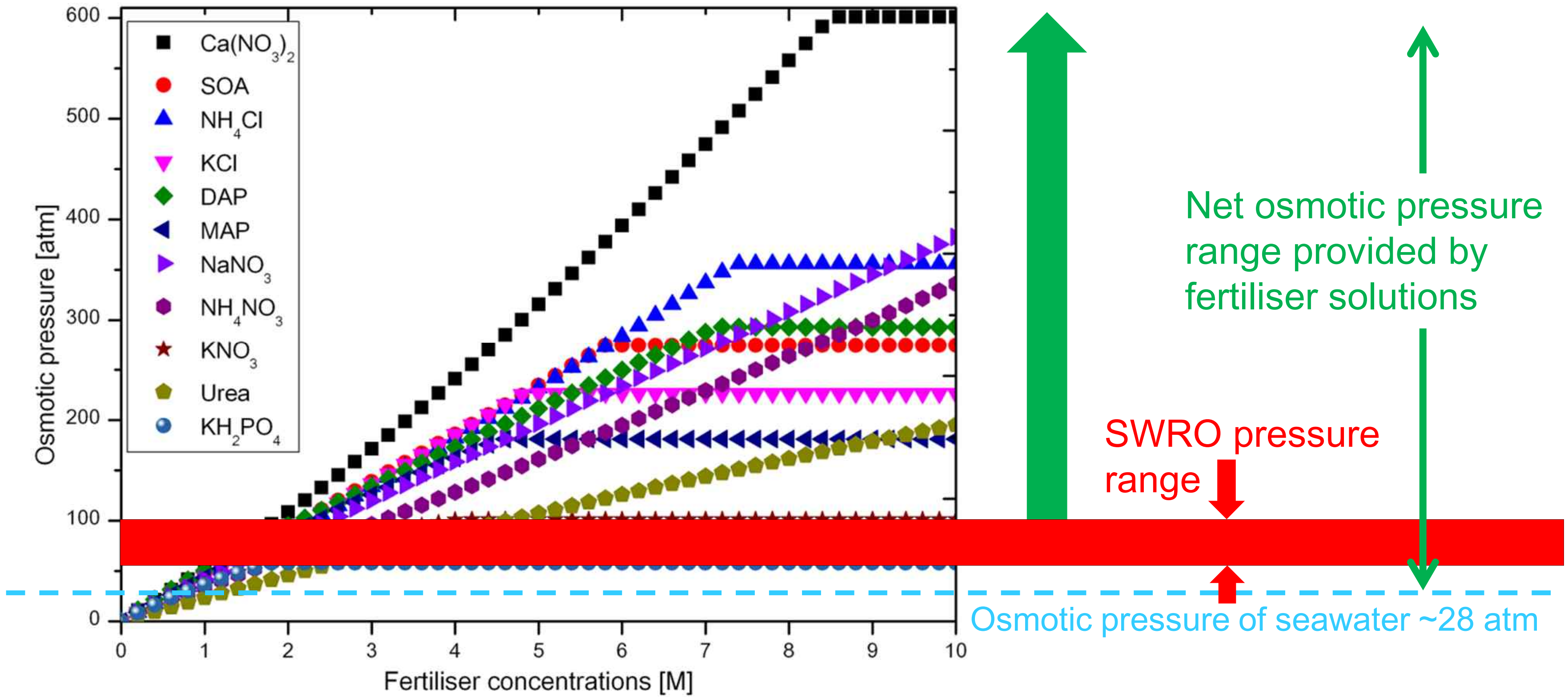
Fertilizer drawn forward osmosis process



- ❑ FO desalination for non-potable purpose such as irrigation is ideal
- ❑ Concentrated fertilizer solution is used as DS
- ❑ Diluted fertilizer solution can be used directly for fertigation
- ❑ The FDFO process does not require separation process

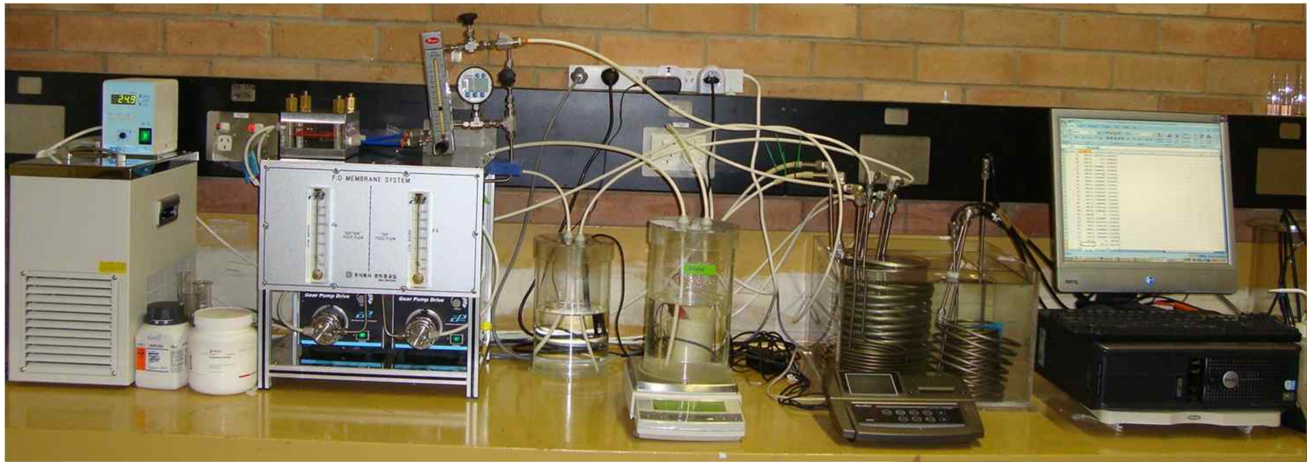
Fertilisers as draw solutes for FDFO desalination

- ❑ **Most soluble fertilisers can be used** as draw solutes for FDFO desalination
- ❑ Investigated 11 different fertilisers as draw solutions
- ❑ Osmotic pressure: important factor for FO process
- ❑ All fertilisers generates **osmotic pressure higher than seawater (28 atm)**

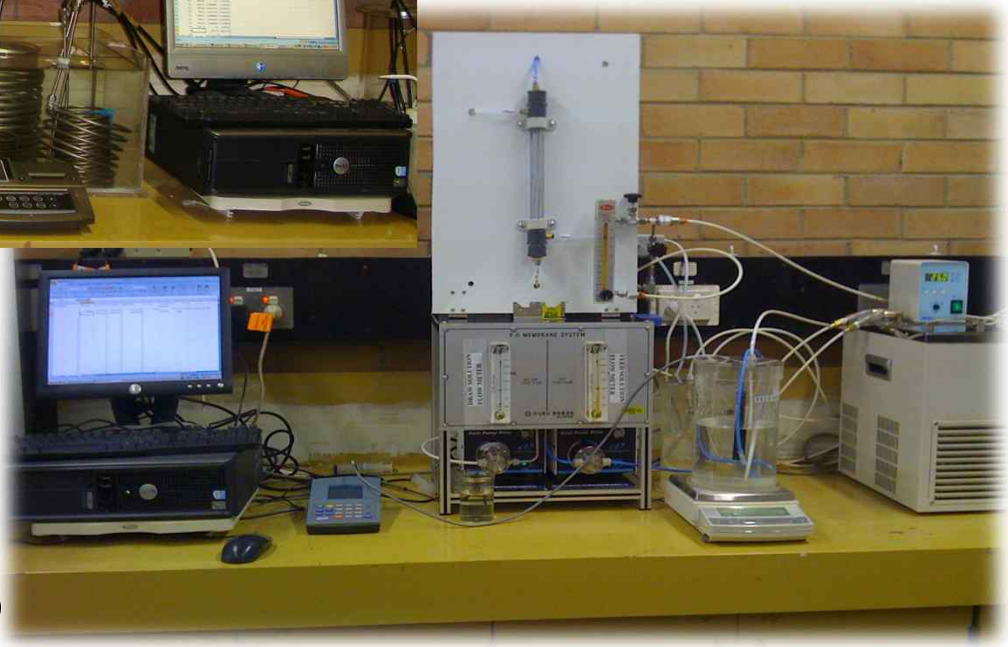


Lab-scale experimental setup

- ❑ Used cellulose triacetate FO Membrane from HTI
  - ❑ FO cell dimensions of 2.6 x 7.7 x 0.3 cm (0.002 m^2 membrane area)
- ❑ Fertiliser reagent grade from Sigma-Aldrich
- ❑ Temperature – 25˚C
- ❑ Cross flow rates: 8.5 m/s in counter current mode of operation

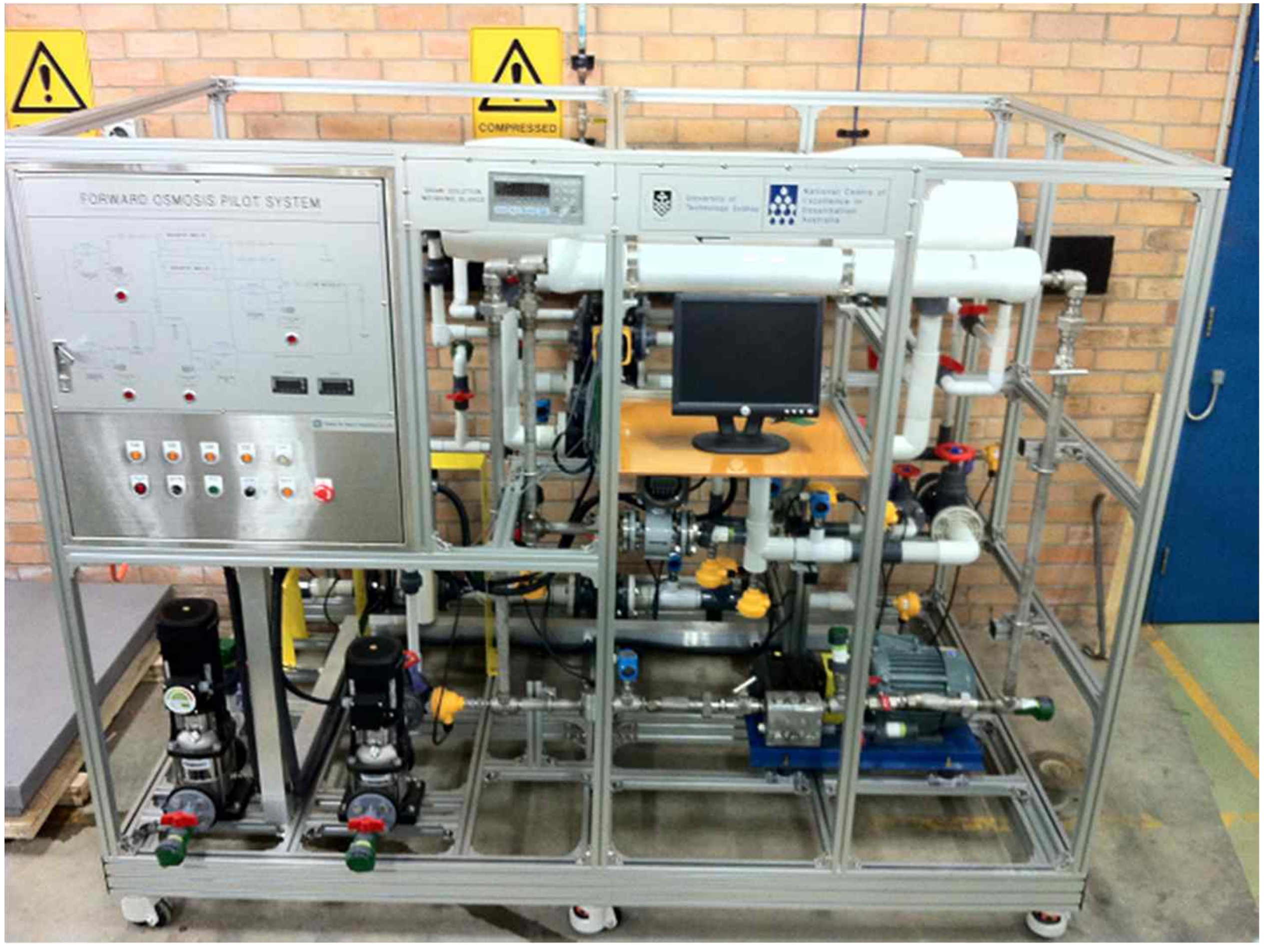


❑ Flat sheet FO cell setup



❑ Hollow fiber FO cell setup

Pilot-scale experimental setup

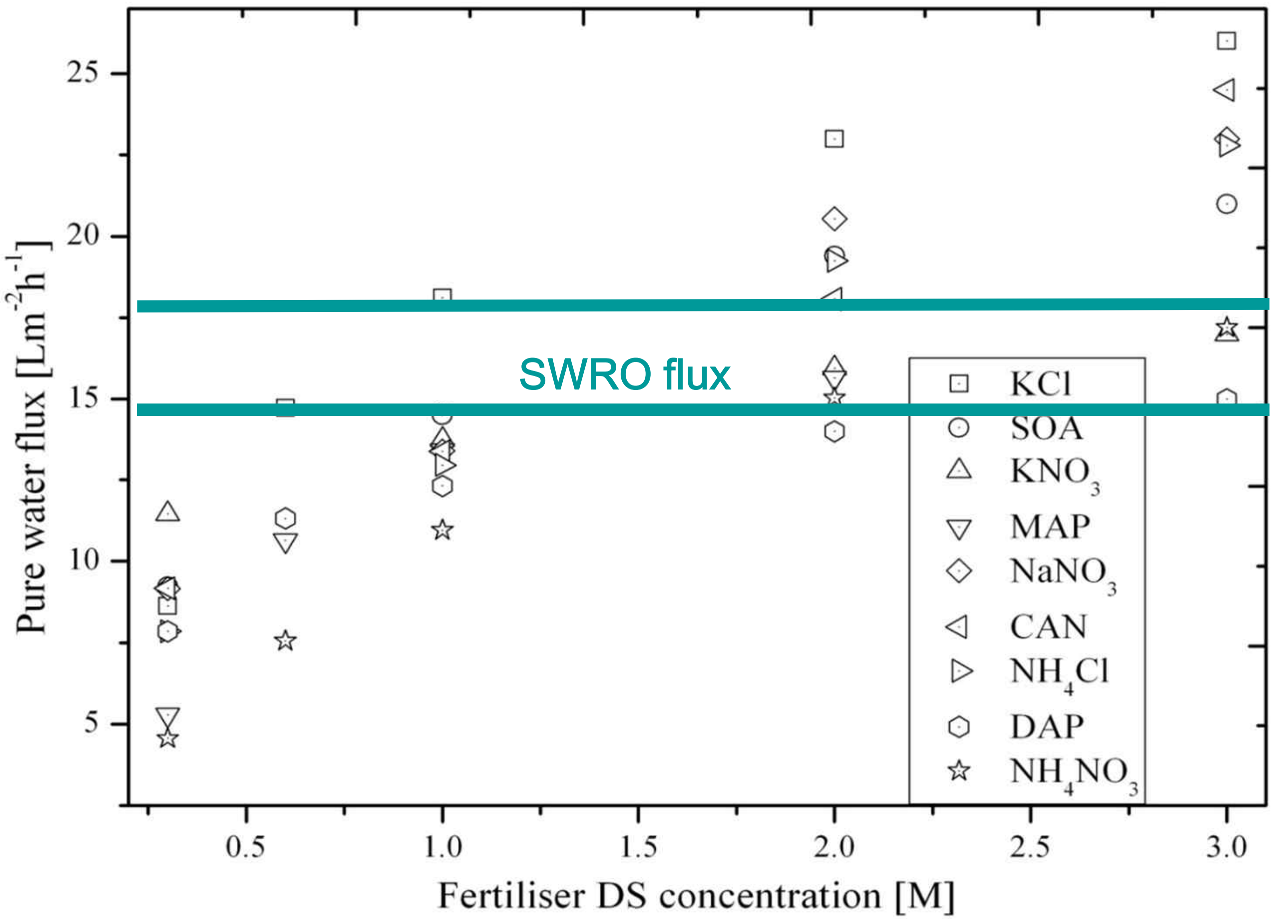


Flat sheet FO setup

Hollow fiber FO setup

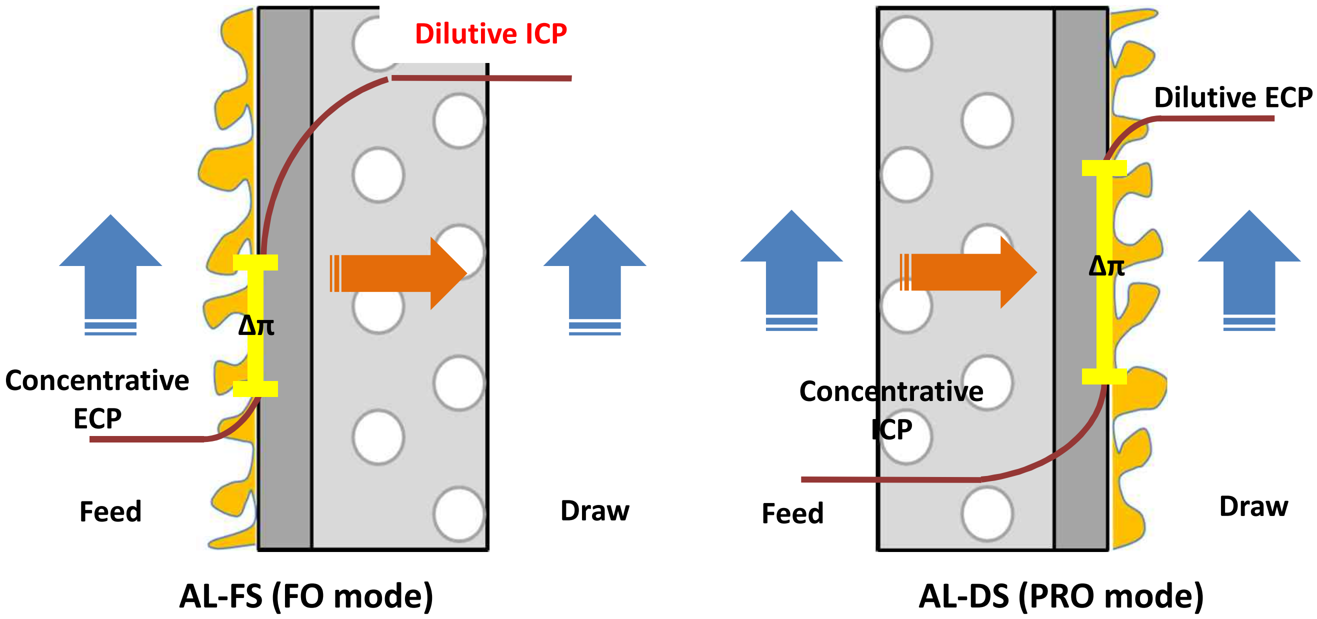
Performance: Water flux in the FDFO process

- The types of fertilisers used, osmotic pressure and concentration of DS
- Water flux is comparable to RO desalination process



One of major challenges in FO process

Concentration polarization



* How to mitigate the concentration polarization

- ECP: Optimizing **operating conditions** such as cross flow velocity and Temperature.

- ICP: Optimizing ***support layers** to be well diffusion of the solute ions in Draw solution.

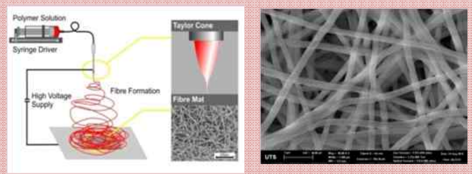
- ❑ Higher porosity
- ❑ Lower tortuosity
- ❑ Smaller membrane thickness
- ❑ Hydrophilic property
- ❑ Smaller structural parameter (S value)

FO membrane fabrication

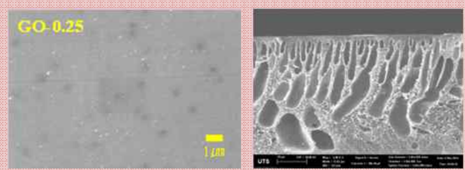
Development of high performance membranes for desalination

Membrane support/active layer

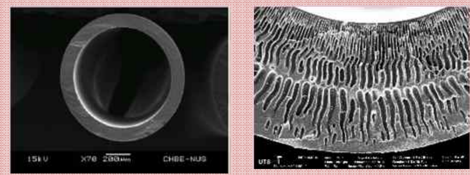
Electrospinning



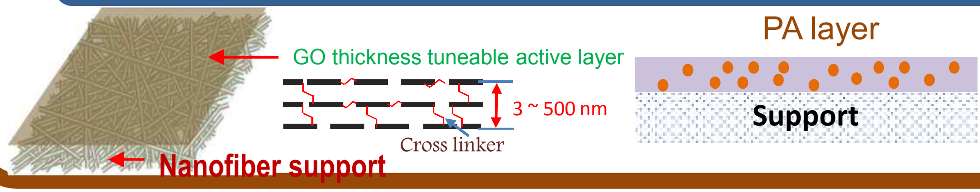
Flat sheet casting

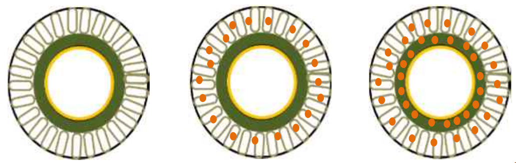


Hollow fiber spinneret



- ❑ Mixed matrix membrane with nanomaterials
- ❑ Modification of membrane support or selective layer using nanomaterials



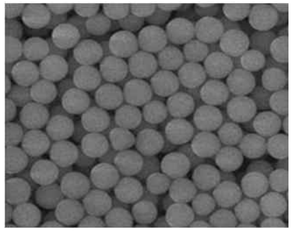


Thin-film nanocomposite membranes

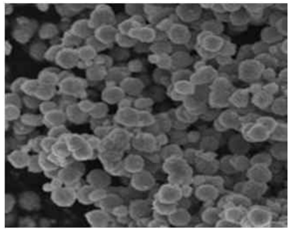
TFC FO membrane development with nanomaterials

*** Preparation of nanocomposite membranes is one of the promising membrane support modification techniques**

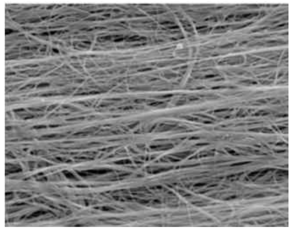
Various nano-materials for membrane modification



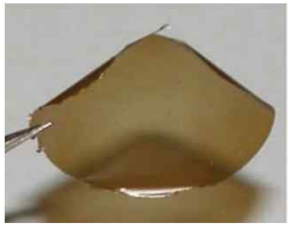
Colloidal silica



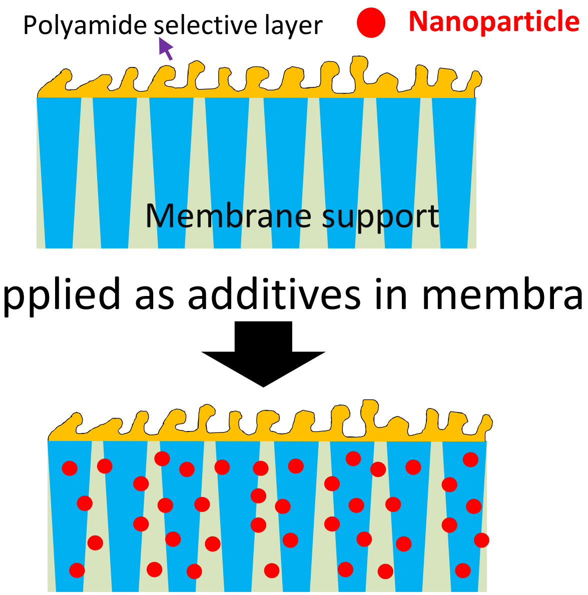
Titanium oxide



Modified CNT



Graphene oxide

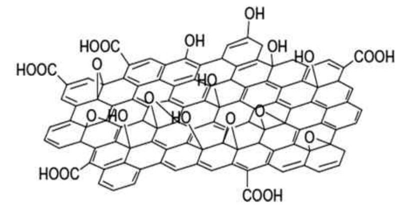


TFC with nanocomposite support

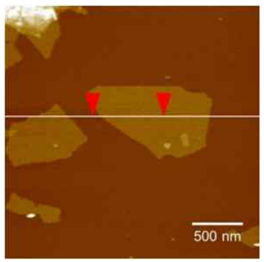
- Higher Porosity
- Higher Water flux
- Hydrophilic property
- Mechanical strength
- Lower structural parameter

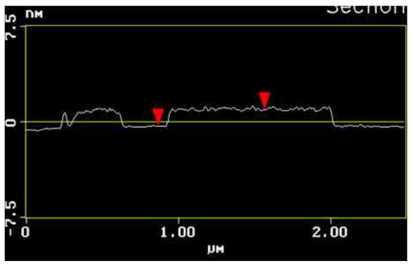
→ **Mitigate the ICP**

Graphene oxide(GO): Excellent candidate as a filler

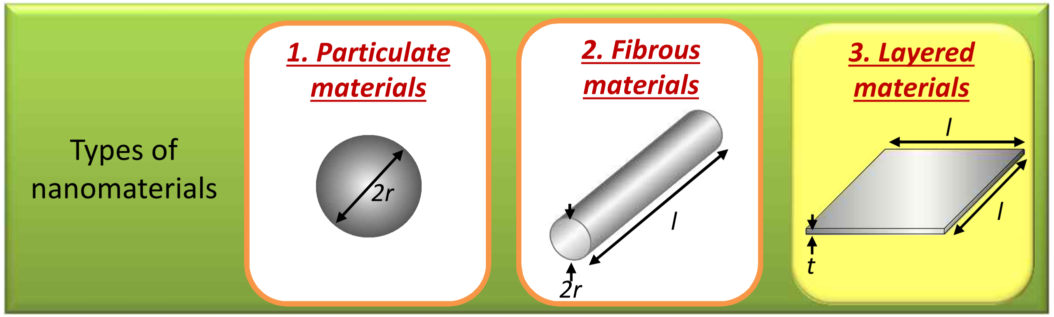


- **Typical 2-dimensional (2D) atomic thick material (T=1~2 nm, single layer)**
- **Hydroxyl, epoxy and carboxyl functional groups (hydrophilic character)**
- **High chemical stability**
- **High surface area-to-volume ratio**





GO thickness = 1.2~1.3 nm

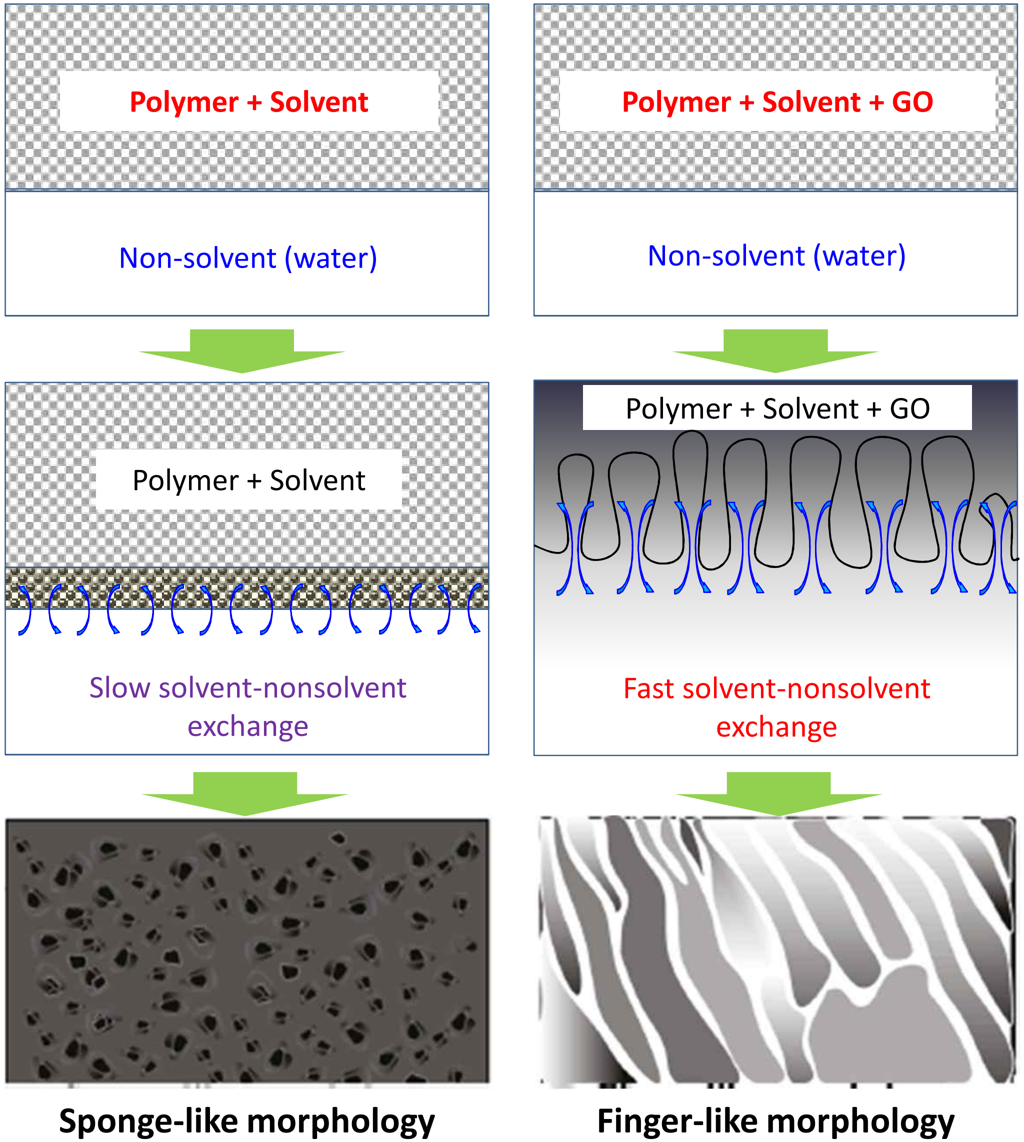


Filler type	Example	L (nm)	r or t (nm)	Aspect ratio(unitless)	Surface area to volume ratio (nm^{-1})
1	Spherical nanoparticle (i.e. fumed silica)	-	5	1	0.60
2	Nanotubes (i.e. carbon nanotube, CNT)	3000	5	1500	0.41
3	Platelets (i.e. graphene oxide, GO)	3000	1	3000 ✓	2.00 ✓

A. Alubaidy et. al, Nanofibers reinforced polymer composite microstructures, Intech Open Science, 2013, Chapter 7

Effect of GO incorporation in membrane support

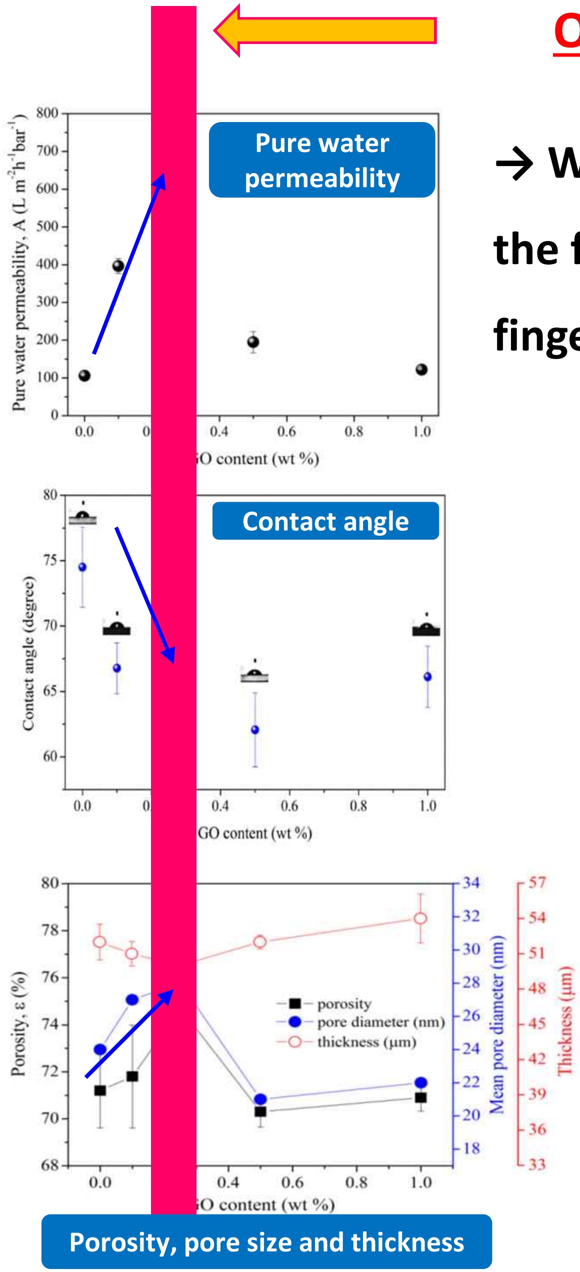
Membrane formation



Different membrane characteristics caused by addition of hydrophilic GO

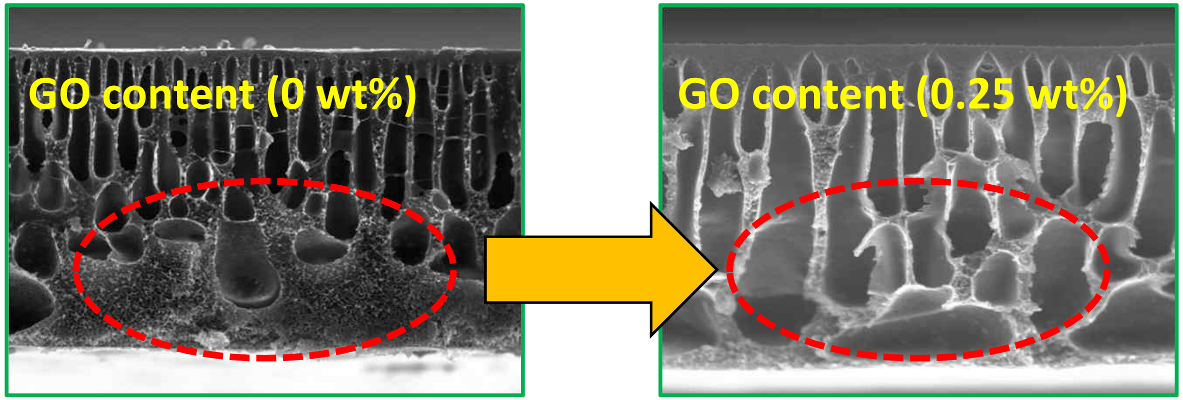
1. Hydrophilic GO accelerates the solvent-nonsolvent exchange and resulted to creates **highly porous structure.**
2. Bigger macro-void and porosity **enhance water permeability.**
3. Presence of GO in membrane also improves in surface **hydrophilicity.**

Effect of GO incorporation in membrane support



Optimum GO loading (0.25wt%) in polysulfone support

→ Well dispersion of hydrophilic GO in polymer solution induced the formation of sponge-like structure, instead revealed larger finger-like structure

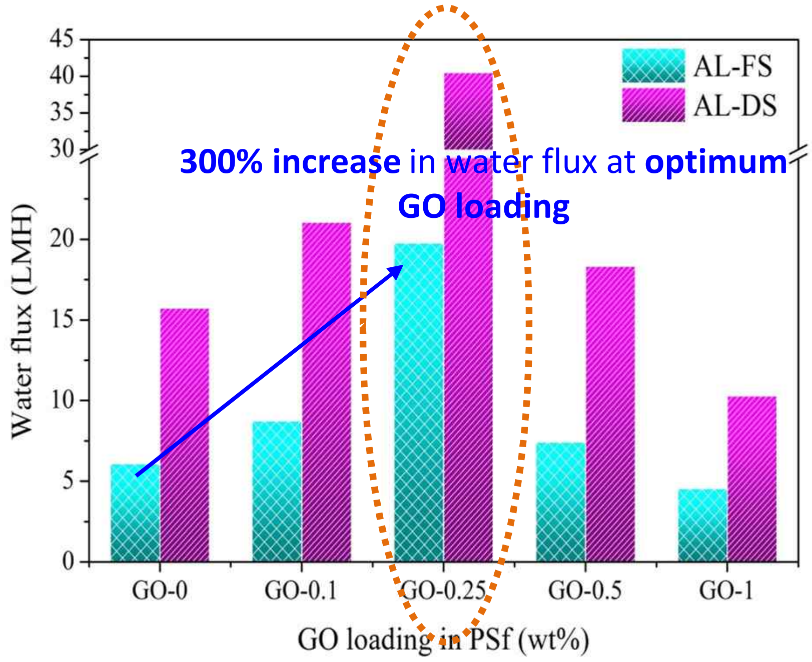


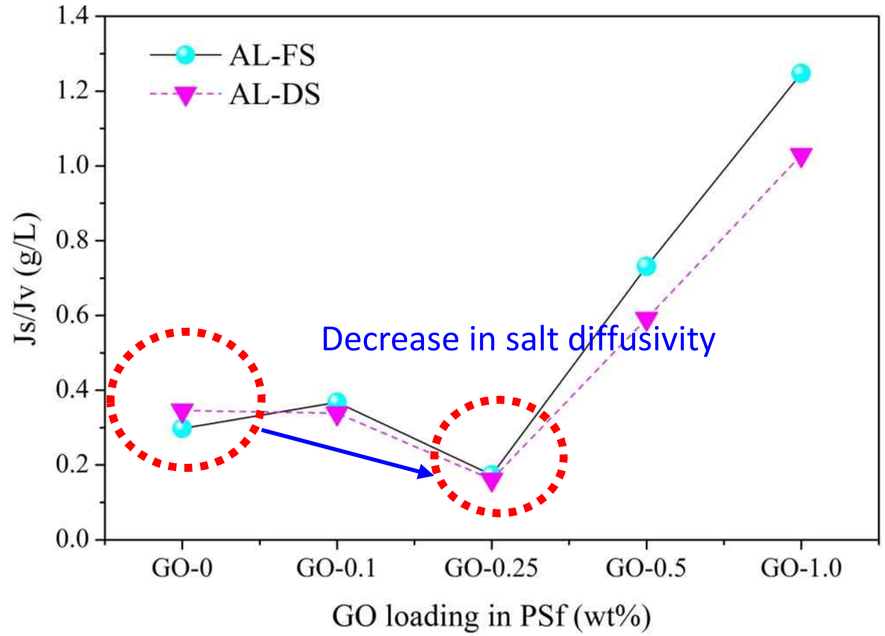
Larger finger-like structure

- **Hydrophilicity**
- **Water permeability**
- **Porosity**
- **Pore size**

FO/RO performances

Feed solution: DI water, Draw solution: 0.5 M NaCl





RO performance

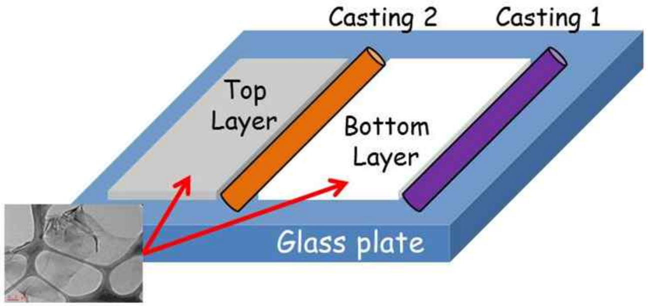
A and R values ↑ **B and S values** ↓

GO loading in PSf	A (L/m².h.bar)	B (L/m².h)	B/A (bar)	R (%)	S value()
GO-0	0.91	0.24	0.26	97.04	1060
GO-0.1	1.23	0.39	0.32	96.56	697
GO-0.25	1.76	0.19	0.11	98.71	191
GO-0.5	0.99	0.62	0.63	93.09	765
GO-1.0	0.91	0.91	0.99	90.09	1630

Structural parameter (s) = 1060 (GO-0) → 191 (GO-0.25)

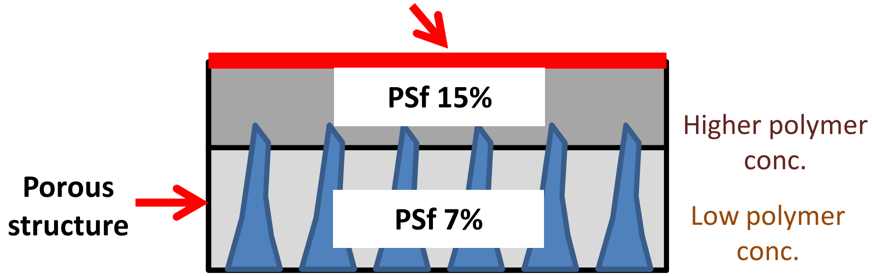
Dual-layered support incorporated with GO

Double-blade casting

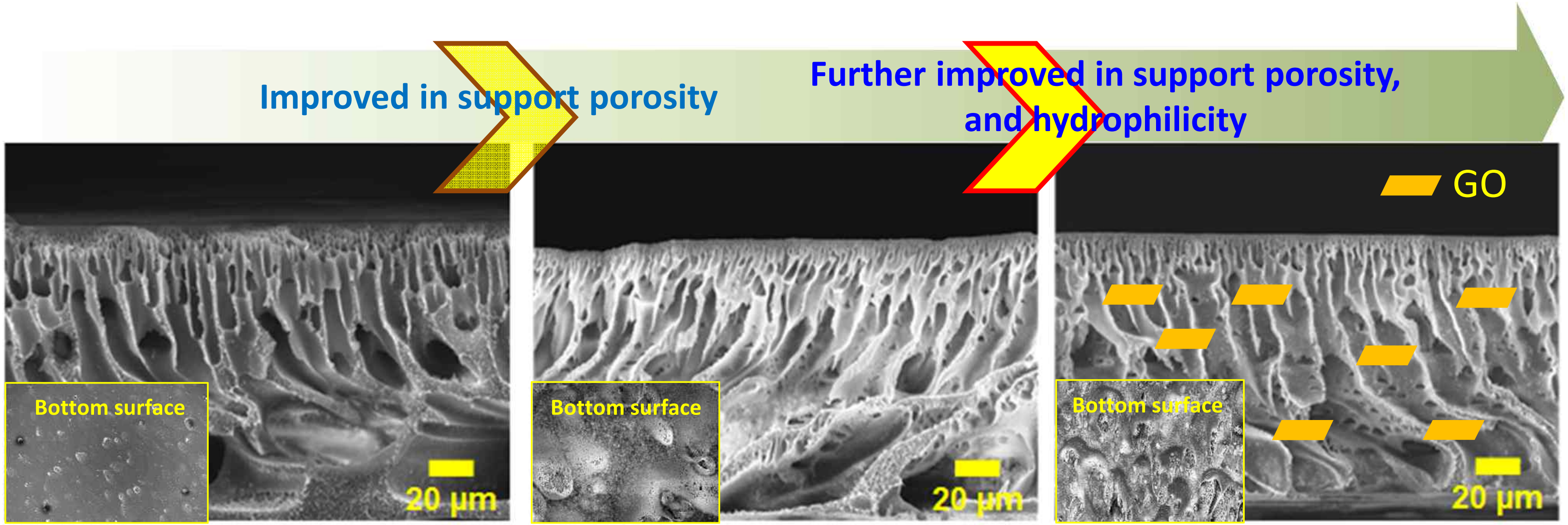


GO nanosheets (Optimum condition at 0.25 wt %) [1)]

Desirable surface morphology for PA formation



More porous and opened structure at bottom layer



Single layered support

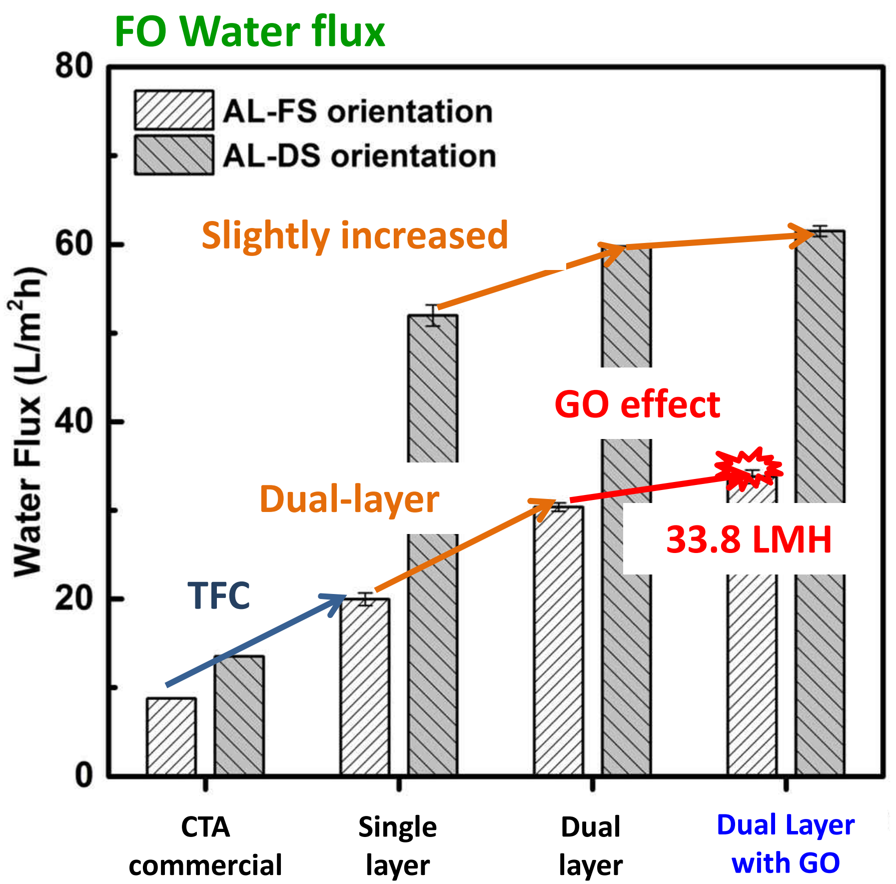
Double layered support

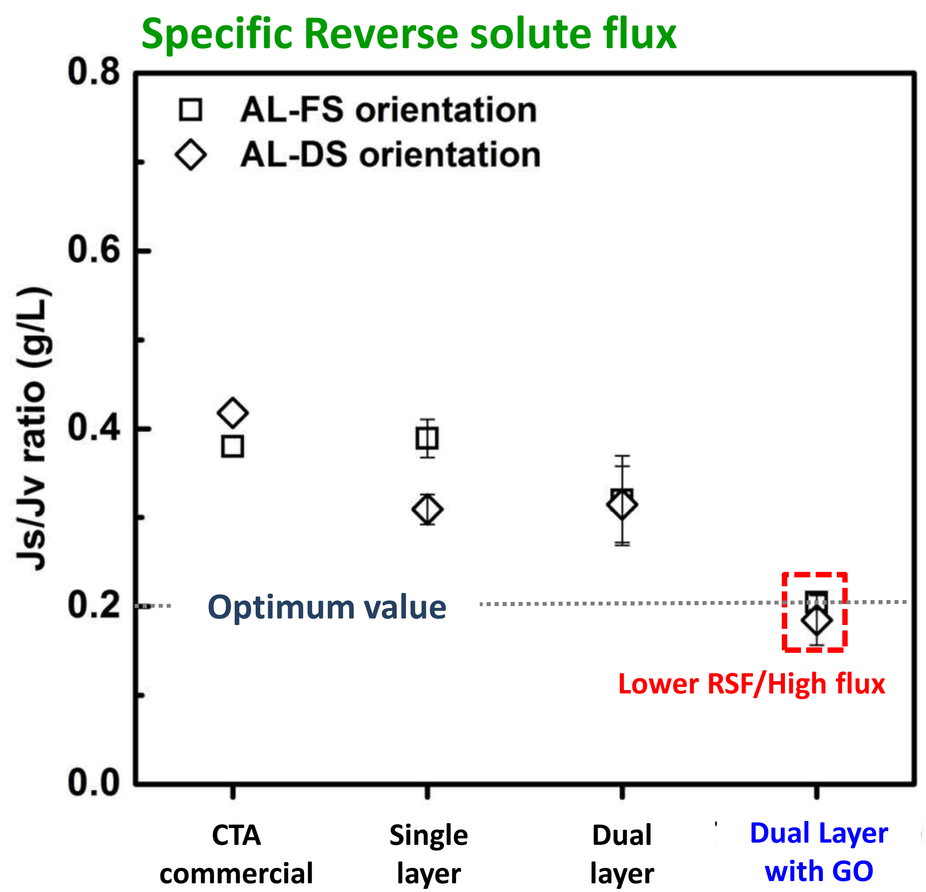
GO incorporated double layered support

FO performance

*Dual-layered substrate improved FO flux

➡ **FO performance was further enhanced by GO incorporation**

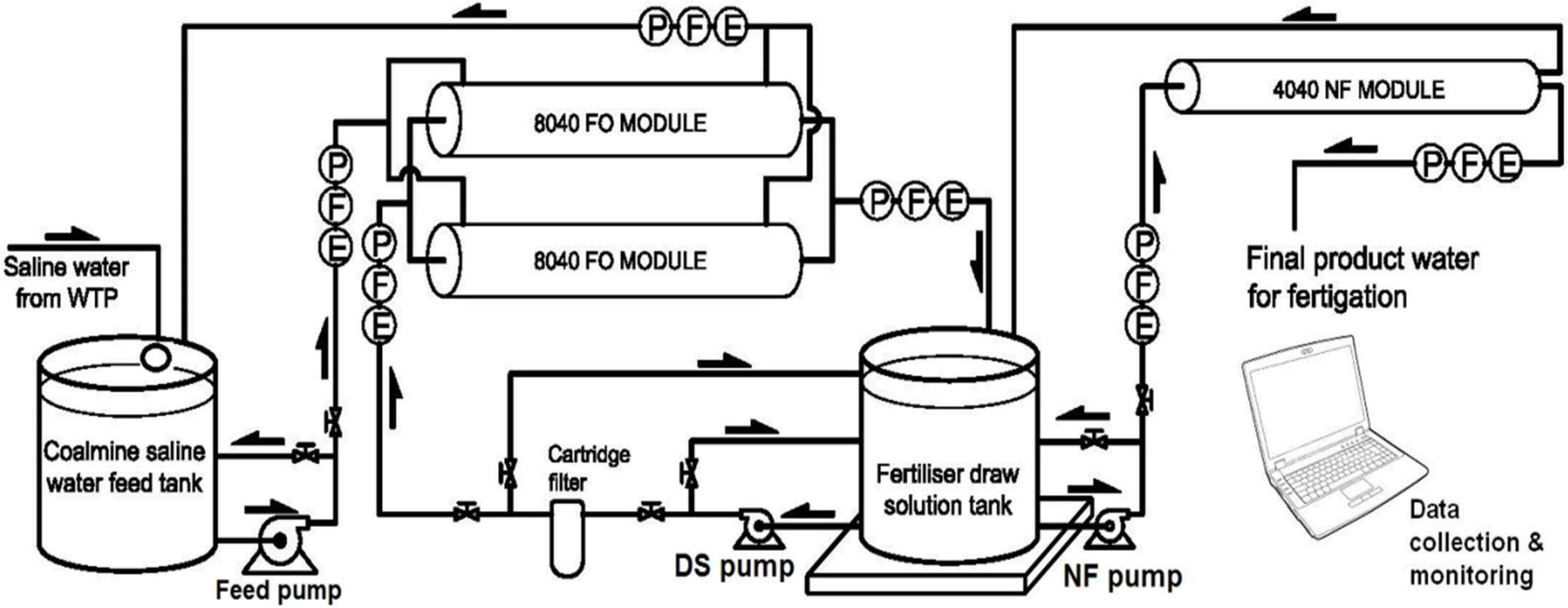




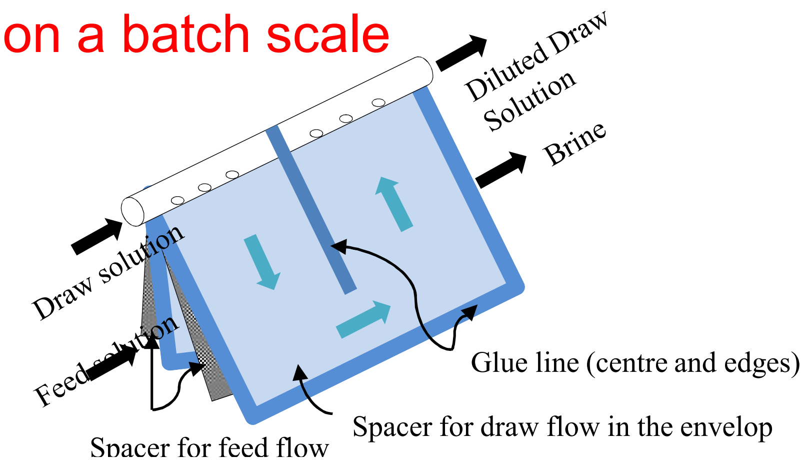
* **S value:** Single layer (426 μm) ➡ Dual-layer (222 μm) ➡ Dual-layer-GO (179 μm)

Pilot-scale testing at Centennial Coal Mine

Pilot-scale FDFO-NF unit

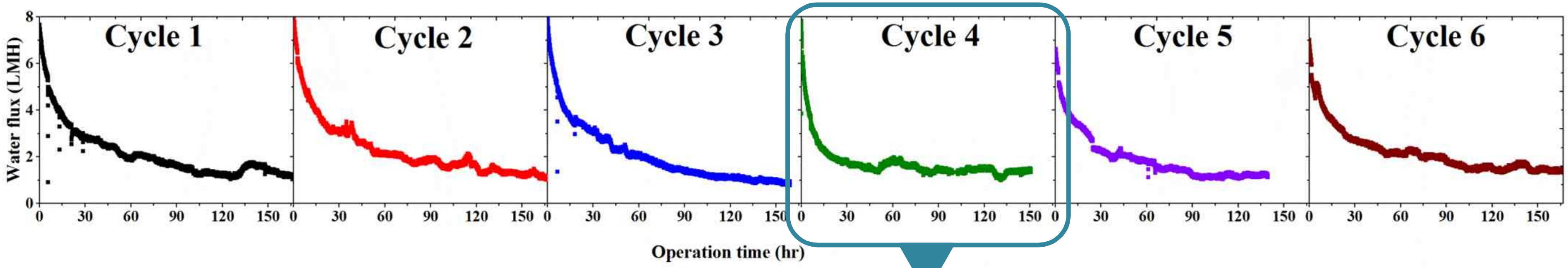


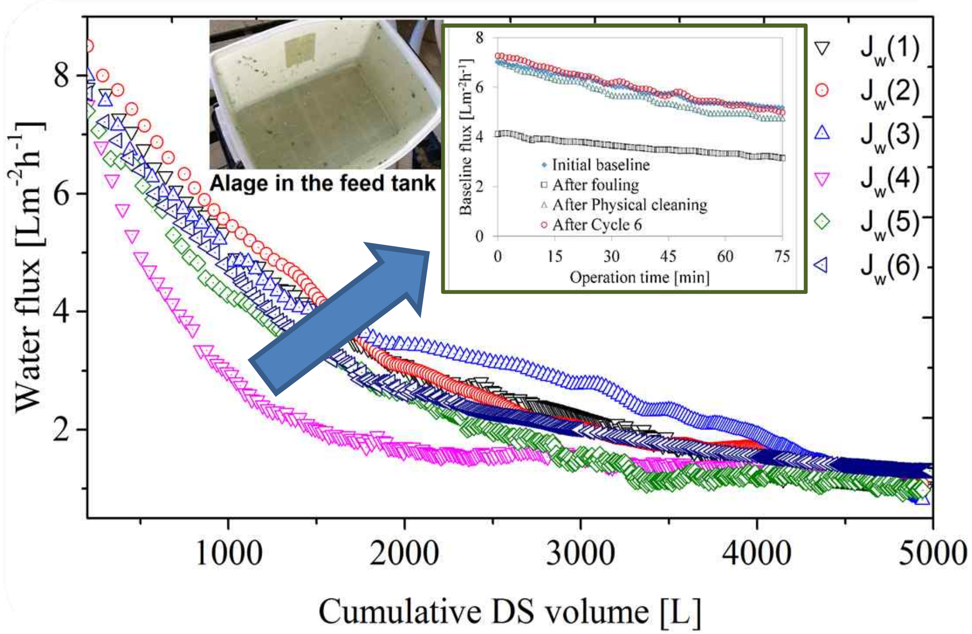
With only 2#- 8040 FO elements (HTI) and 1#-4040 NF (Toray), the pilot-scale system was operated on a batch scale



Long-term operation of the FDFO process

❑ Variation of water flux with operation time

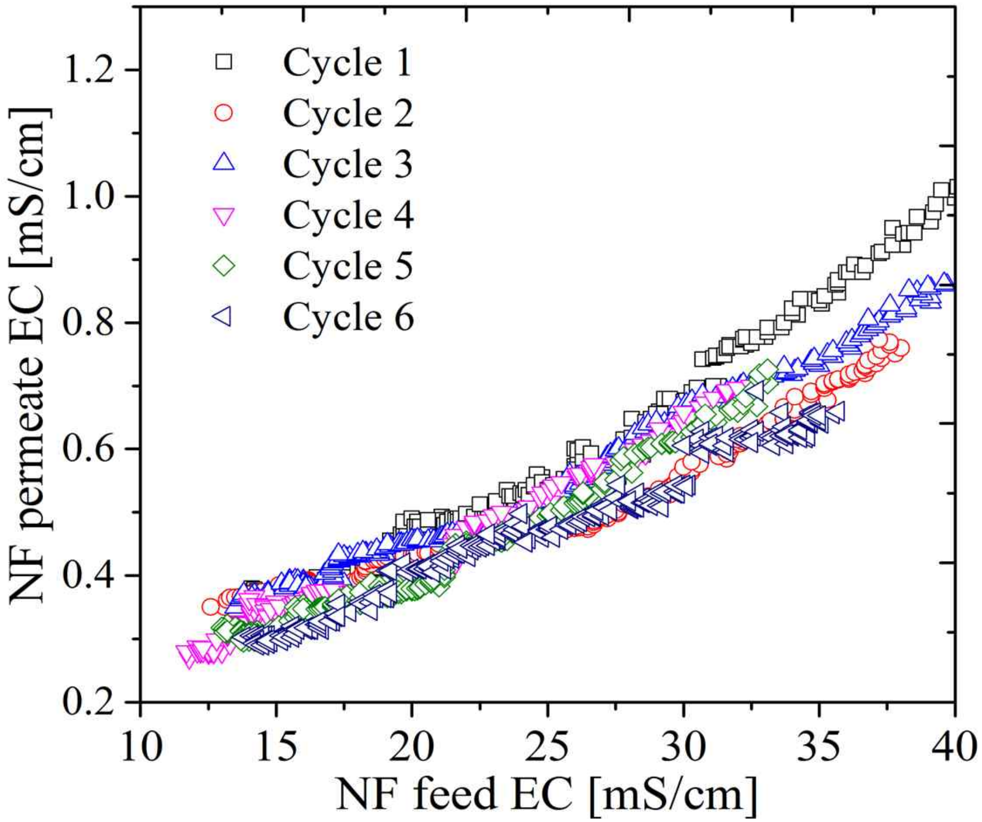




- **Consistent performance** of the FDFO process
- However, the water flux in **the fourth cycle** is **significantly lower** than others.
- **Flux decline was due to algal growth**
- Baseline test (0.5 M SOA and tap water as FS) showed that after **hydraulic cleaning**, the flux was almost **fully** recovered.

NF process: Post-treatment

NF permeate EC



- The permeate EC = the quality of the product water for direct fertigation
- NF permeate EC consistently ranged 0.3 – 1.0 mS/cm
- **Average EC about 0.5-0.6 mS/cm**
- Consistent performance of the NF process under each batch process.

Feasibility assessment of FDFO-NF

❑ Sustainability of FDFO-NF process



17 March | 09 May | 07 July



➢ **Test fertigation using final product water indicates that FDFO-NF is suitable for fertigation of turf grass**

Feasibility assessment of FDFO-NF

❑ Sustainability of FDFO-NF process

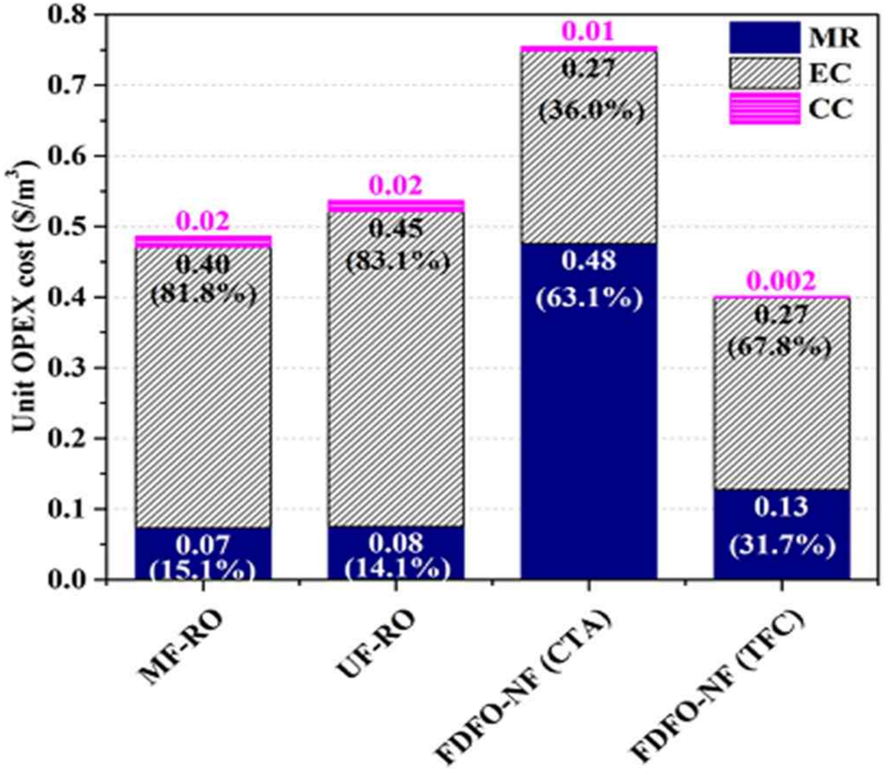
Type 1: Tap water, Type 2: FDFO-NF desalinated water

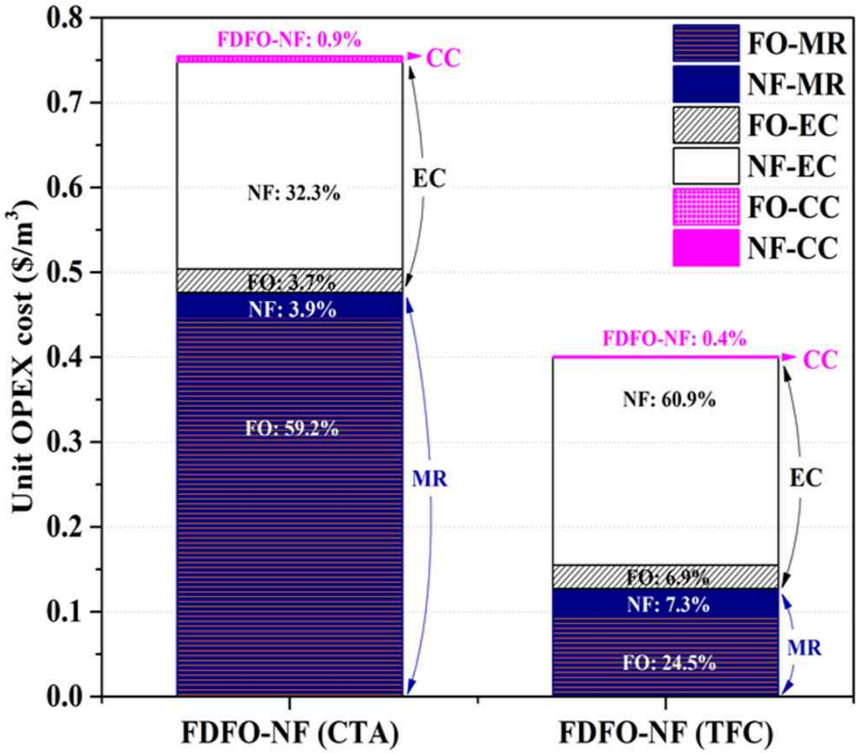
Type 3: FDFO-NF desalinated water diluted with tap water [1:1]

Type 4: FDFO-NF desalinated water mixed with raw saline water [4:1]

➢ **Test fertigation using final product water indicates that FDFO-NF is suitable for fertigation of turf grass**

Unit cost of FDFO-NF product water





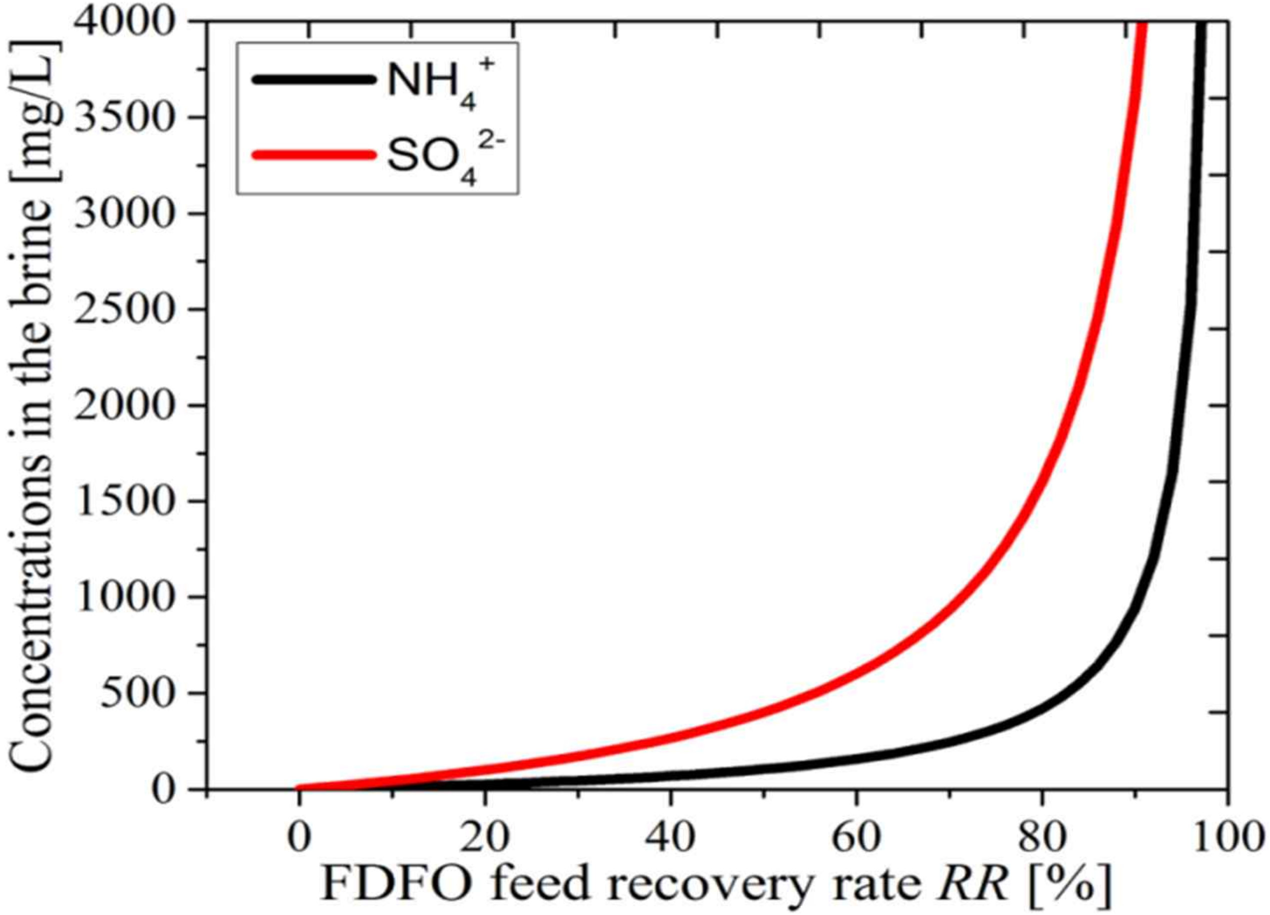
DS: 1 M SOA

FS EC: 5.3 mS/cm

Electricity cost (EC), membrane replacement (MR) cost, and cost of chemicals for membrane cleaning (CC)

- ❑ FDFO-NF using TFC FO membrane hybrid system
  - ❑ 48% lower energy consumption than MF-RO hybrid system
  - ❑ 67% lower energy consumption than UF-RO hybrid system
  - ❑ Unit cost of product water for fertigation $ 0.41/kL for 5.3 mS/cm brackish water

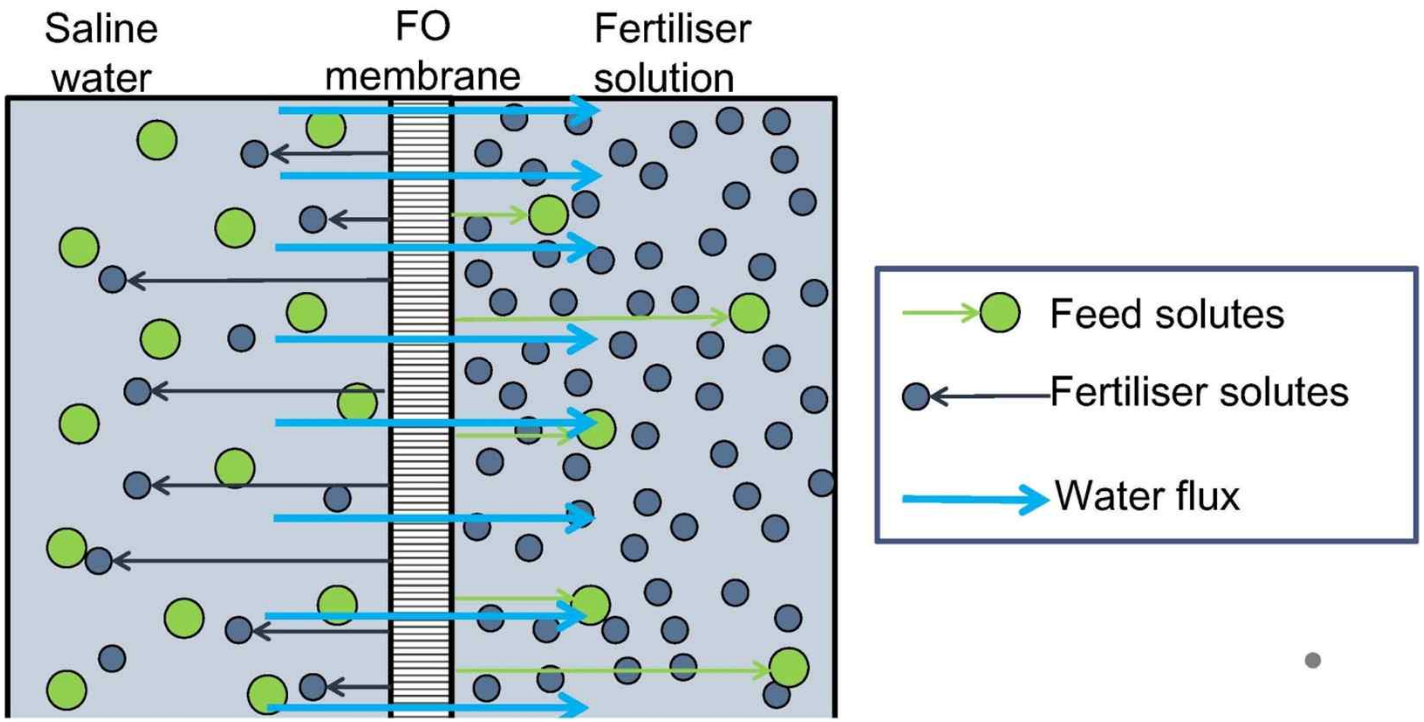
Issues of FDFO-NF applications



- ❑ NH_4 concentration from RSF increases in the feed with feed recovery rate
- ❑ Without adequate bleeding from FO and NF membranes, lower FO rejection of feed salt would result in accumulation in a closed loop system

Challenges of FDFO process: reverse diffusion of DS

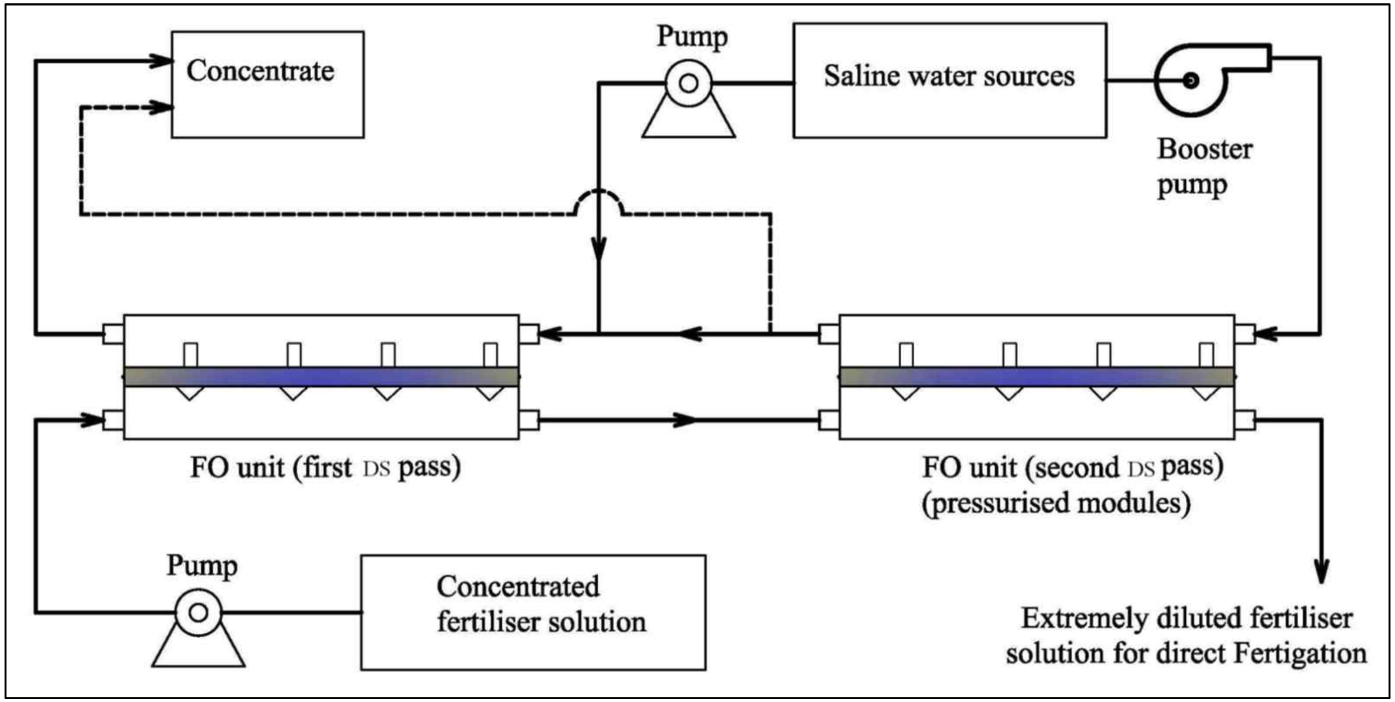
- Reverse diffusion of fertiliser salts to feed water
  - Economic loss of fertiliser
  - Complicates concentrate management due to presence of fertiliser in the feed concentrate
- Reverse diffusion of solutes can be minimised by
  - Using of high rejection membranes
  - Use fertiliser containing multivalent ions



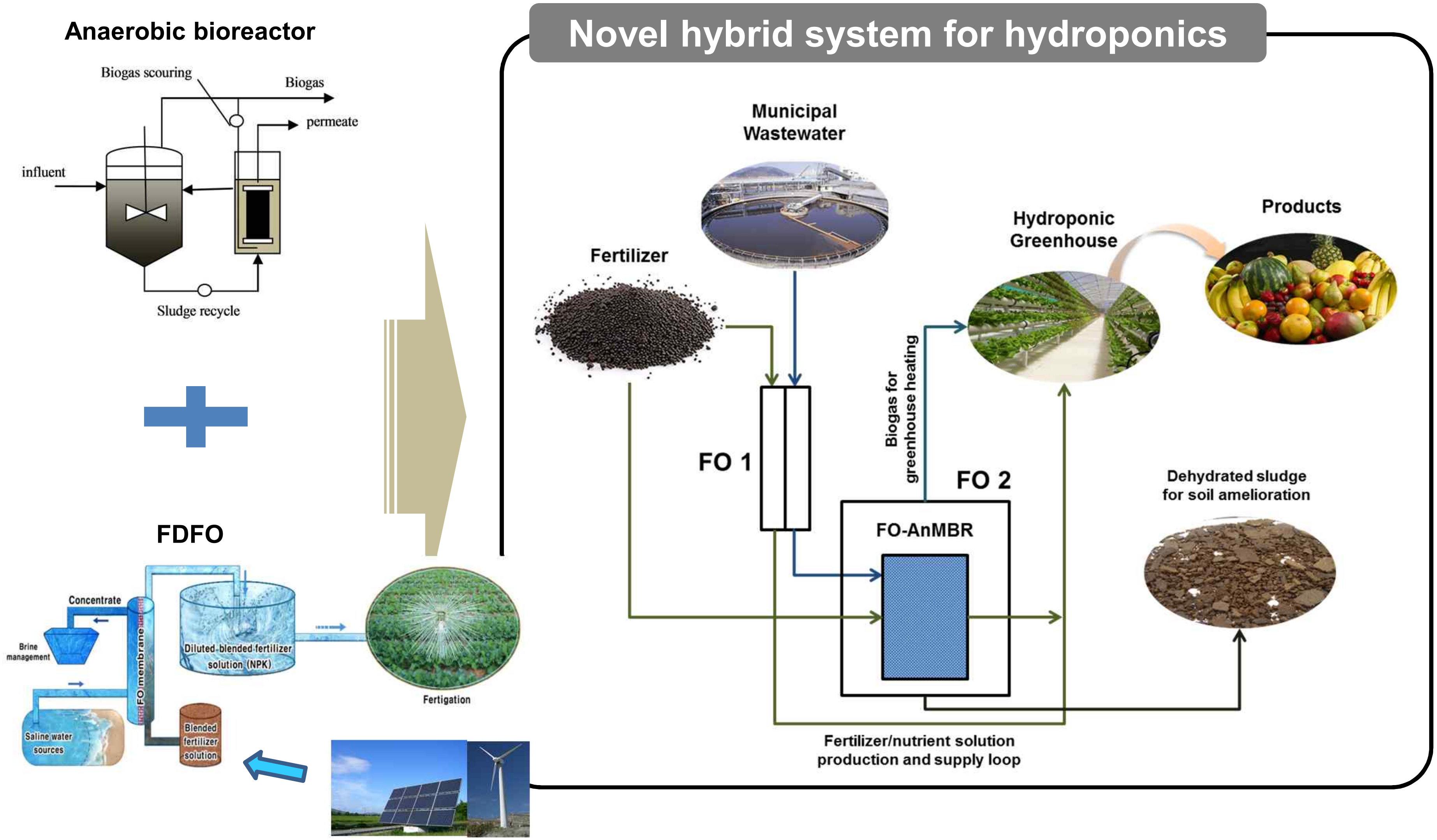
Option 1: Pressure assisted forward osmosis (PAO)

- At osmotic equilibrium (OE), ($\Delta\pi = \pi_F - \pi_D = 0$)
- Applied pressure need not overcome feed π_F
- Applied pressure to dilute DS beyond OE
- Final DS concentrations will be significantly reduced

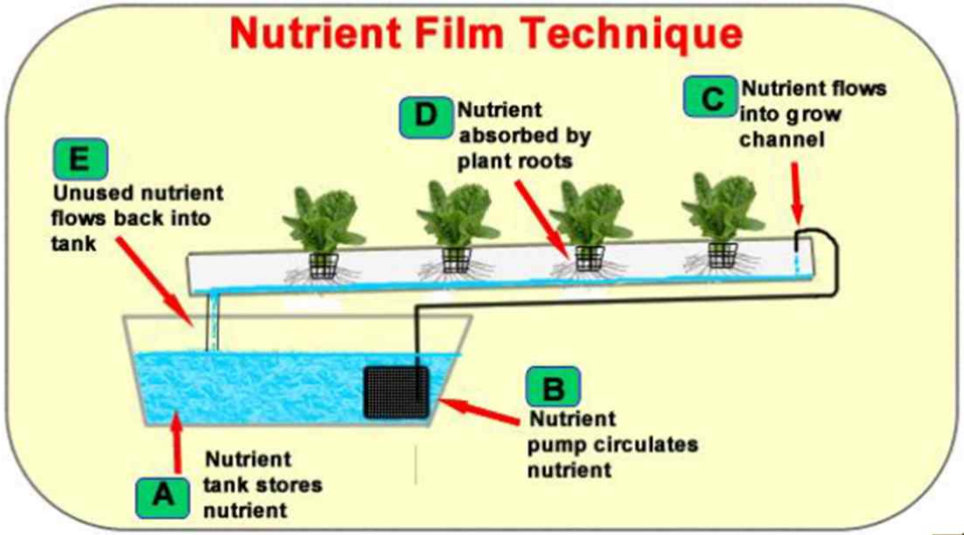
$$J_w = A\left[\pi_{D,b}\exp\left(J_w K\right) - \pi_{F,b}\exp\left(J_w / k)\right) + \Delta P\right]$$



Options 2: FDFO – AnMBR hybrid system for hydroponics



Hydrophonic application



NFT unit requirement for lettuce:
120 L/week for up to 6 weeks
→ 720 L of nutrient solution

Lettuce seedlings

18 replicates for each NFT unit

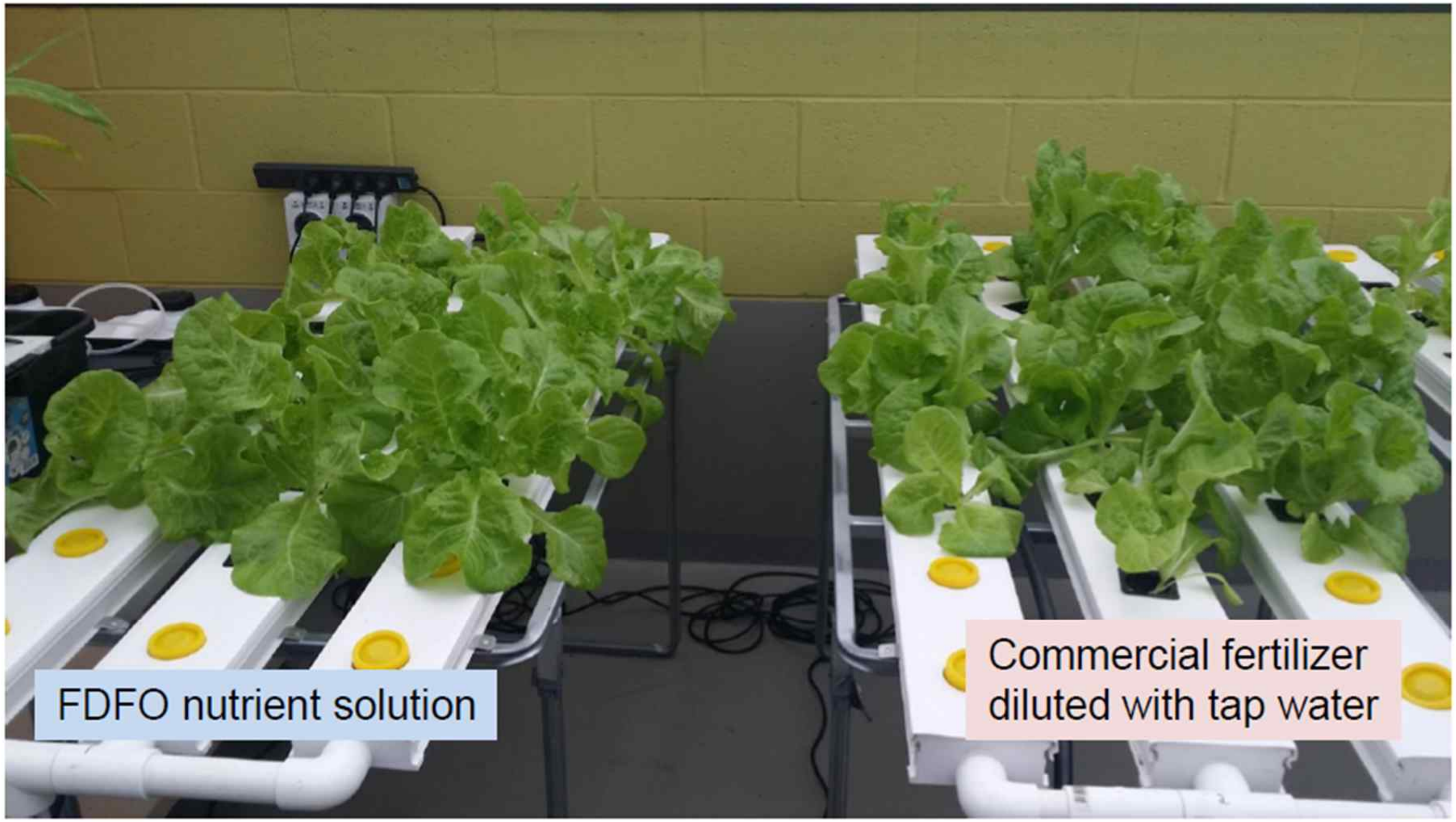
FDFO nutrient solution

Commercial fertilizer diluted with tap water

Standard "Huett" lettuce formulation

Hydrophonic application

<u>After five weeks:</u> Promising results



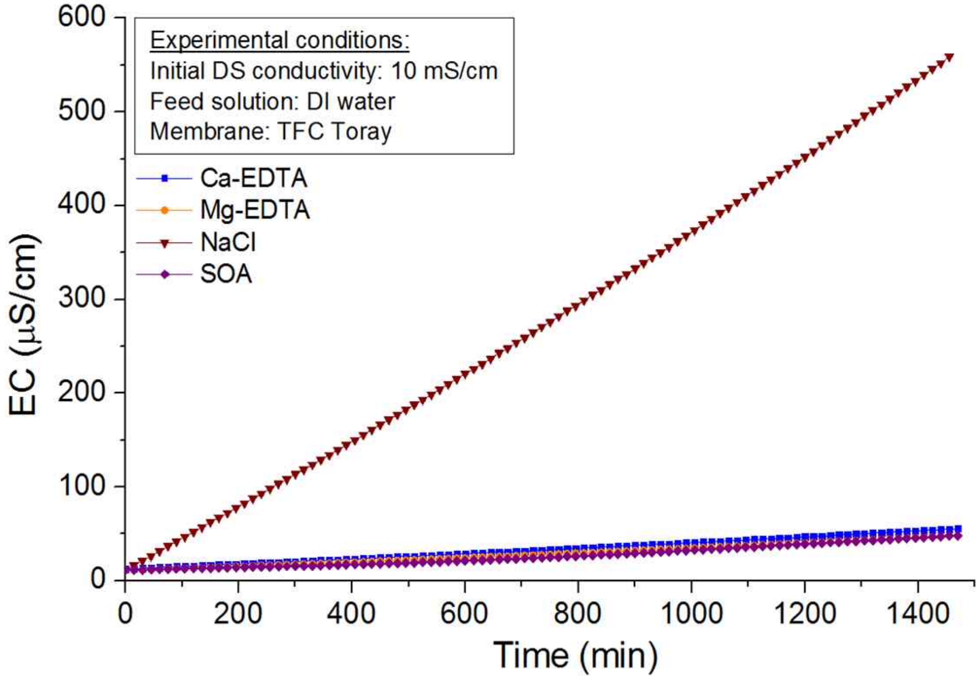
Good response of the hydroponic lettuce to the FDFO nutrient solution
No apparent nutritional problems (i.e. deficiency symptoms)

Novel potential draw solutions for FDFO?

Target: Finding new DS with low RSF and reasonable flux

Chelated-macronutrients (Ca and Mg EDTA)

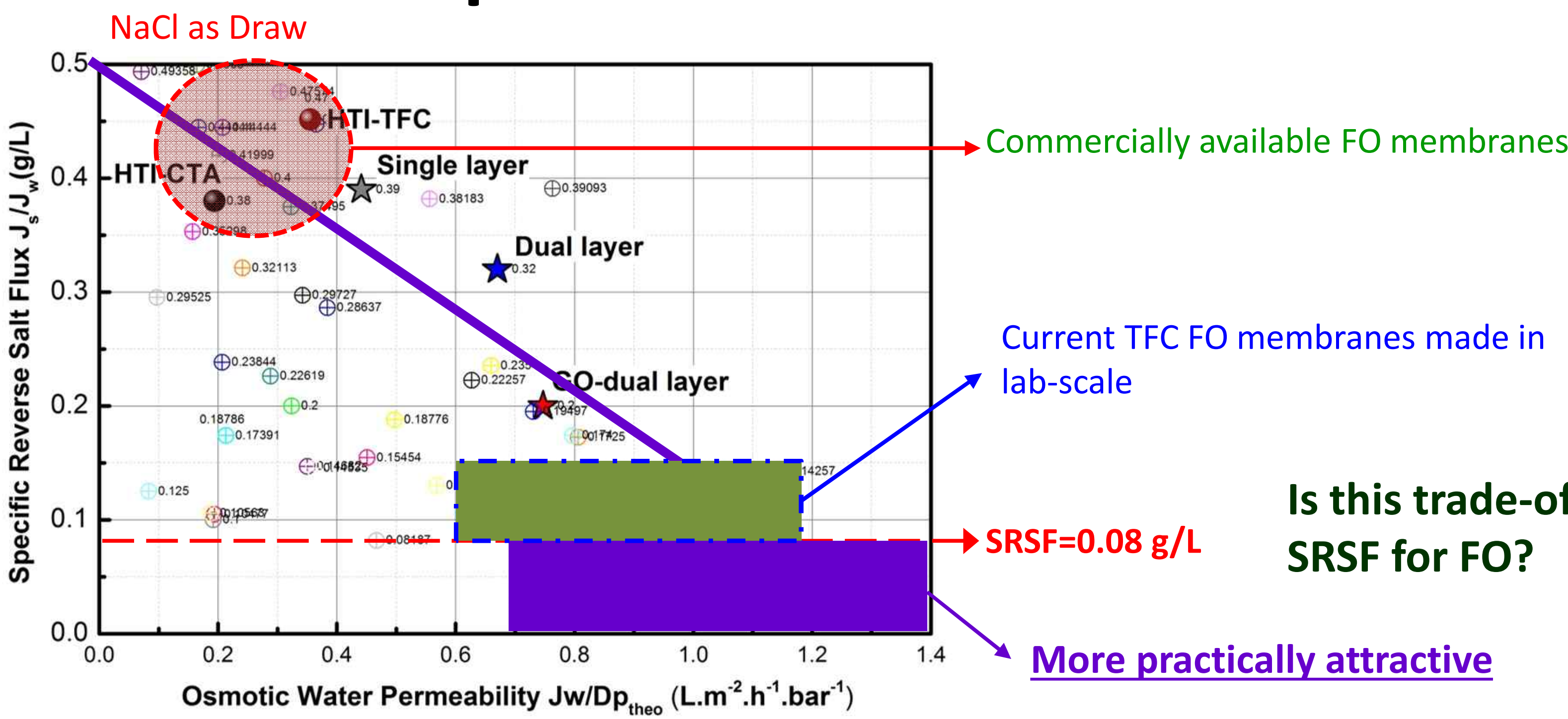
- Chelation keeps a macronutrient from undesirable reactions (e.g. precipitation)
- Highly recommended with soils having a pH greater than 6.5
- Most widely used chelating agent: EDTA
- EDTA has a very high molecular weight (compared to inorganic salts): 292.2 g/mol
- Previous studies showed that Na_2-EDTA used as DS showed comparatively low RSF



Preliminary results

	Water flux (LMH)	RSF (gMH)	SRSF (g/L)
[redacted]			
SOA	5.0	0.80	0.16
[redacted]			**0.13**
Ca-EDTA	6.5	0.91	**0.14**

Salt selectivity of polyamide (PA) layer required to be improved as like RO membrane



Is this trade-off value of SRSF for FO?

Future studies on FO membrane development need to be more focused on the improvement in salt selectivity of PA layer, not only increased in water permeability

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Thank Prof. Hiroaki Furumai and RECWET members