CHEMISTRY: A CRITICAL FOUNDATION IN QUALITY WATER PROVISION

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Learn without limits.

UNISA college of science, engineering and technology

OUTLINE

- Background
  - Global situation
  - South African situation
  - Local challenges as drivers for our RD&I
- Research Journey thus far
  - Main areas of activity
  - Tailor-made Polymer composites - resins
  - Tailor-made Polymer composites - membranes
- Technology Innovation and Demonstration
  - Towards Technology Demonstration and Piloting
- Creating Partnerships
  - Academia, Industry and communities
- Summary
- Acknowledgements

Background: Global Situation

- Globally, 2.1 billion people do not have access to clean, safe drinking water.

- 3.4 million people die each year from contaminated water sources.

- At any given time, half of the world's hospital beds are occupied by patients suffering from diseases associated with lack of access to clean water.

- Millions of women and children spend 3-6 h each day collecting water from distant and polluted sources.

- The average distance to collect clean water from source is 5.92 km.

https://wholives.org/our-mission/mission/

Background: South African Situation

AGGRAVATING FACTORS

- Frequent droughts
  - Since 2015, South Africa experienced *widespread water shortages*.
  - *Climate change effects*, causing rainfall delays and eventually decreased dam levels – day zero…Cape Town, now Gqeberha!
  - Inadequate managerial skills in the water sector.

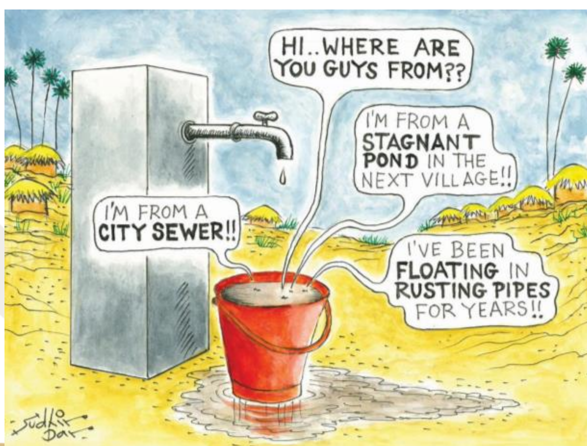
- Lack of awareness on limited water resources
  - Do we care about water enough?
  - South Africans use 234 liters of water usage per person compared to global average of 173 liters.

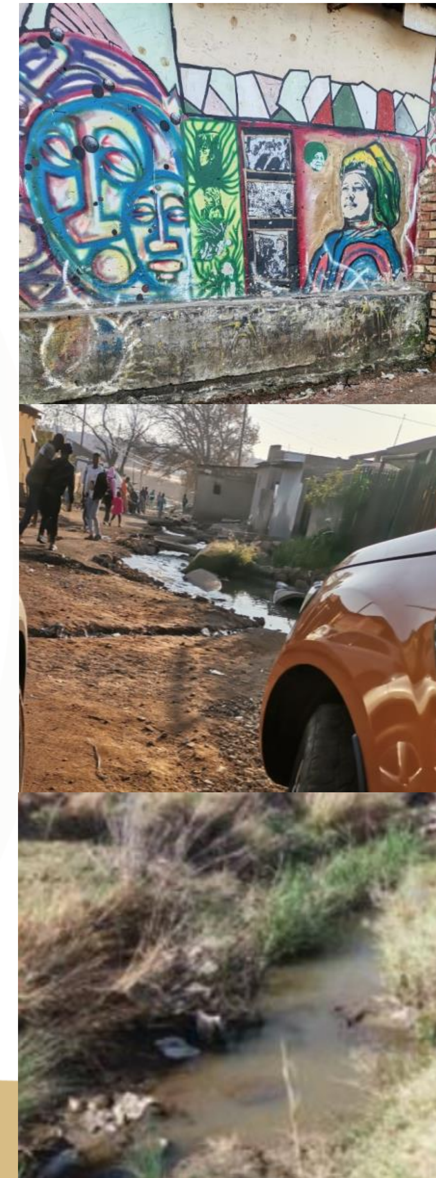
https://www.dbsa.org/article/how-can-south-africa-overcome-its-water-challenges-and-avoid-african-water-crisis

Background: South African Situation

- Wastewater treatment is insufficient
  - Disposal of untreated or poorly treated sewage, industrial and pharmaceutical wastewater into rivers and oceans.
  - A total of >56% of the country's treatment plants are in poor or critical condition.
  - A need to improve wastewater treatment to minimise unsafe drinking water down stream.

- Groundwater is underused,
  - Especially in the agriculture sector
  - To augment limited supply – poor borehole maintenance is a challenge
  - Sometimes of poor quality
    - Ensure appropriate treatment of groundwater in rural areas.
  - Minimise pollution through ingress of wastewater, mine water and domestic sources





Open sewar flow Soweto

Background: South African Situation

SUGGESTED REMEDIES?

- *Tiered water pricing*, where users are charged when they consume a higher rate than what is considered necessary for daily activities.

- *Incentives* for consumers to consider purchasing water-efficient appliances and for using less water.

- *Raising awareness – e.g. water wise*

- Increase use of underground water
  - Ensure adequate treatment for fit-for-purpose
  - Routine maintenance of the boreholes

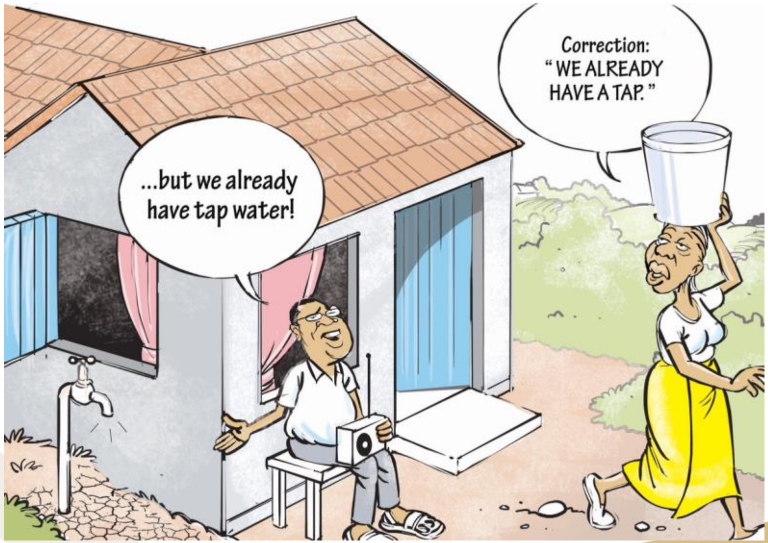
- Reuse wastewater whenever possible
  - Mine impacted water for irrigation of energy and edible crops
  - Treatment to potable standards with concomitant recovery of other resources
  - Greywater reuse is possible

Background: South African Situation

Knowing when you are water poor

- Quality – natural water contains dissolved salts, suspended solids, etc.,
  - with exact or variable concentrations dependent on local conditions.
  - Sometimes, there is presence of pathogens, e.g., E. coli, V. cholerae, etc.

- Quantity - water availability when needed

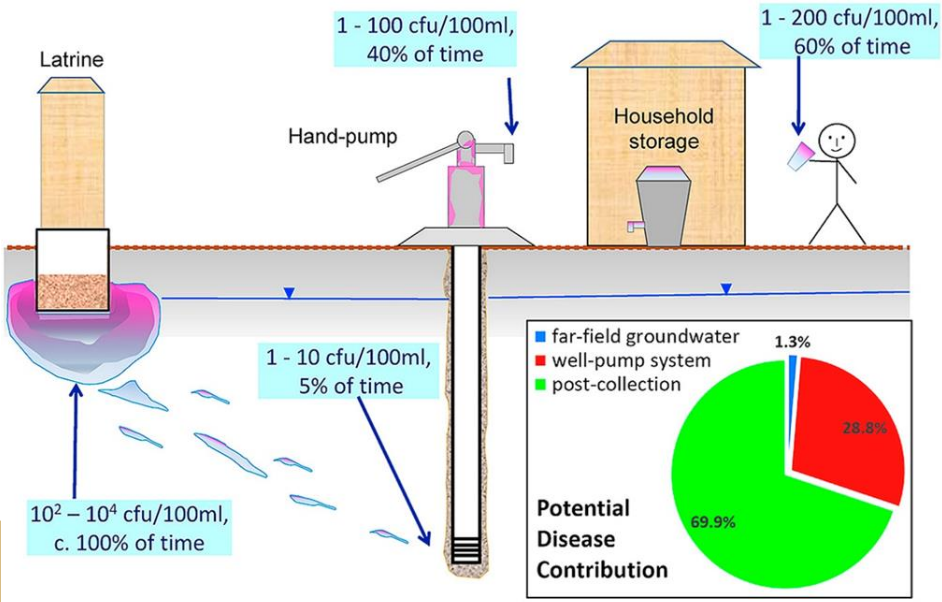


Local challenges as drivers for our RD&I

- Emerging contaminants into catchment areas - monitoring
- Physical availability – *safe reuse*

- Contaminated surface and borehole water due to:
  - Upstream contamination due to dumping and dysfunctional treatment solutions
  - Sharing open sources with livestock
  - Contamination due to proximity to pit-latrines

- Geologically impacted borehole water
  - Hardness
  - Fluorine content



*Water Research, 2017, **124**, 192: Coliform distribution along the pts and points of consumption*

Local challenges as drivers for our RD&I

Finding the right treatment for your water

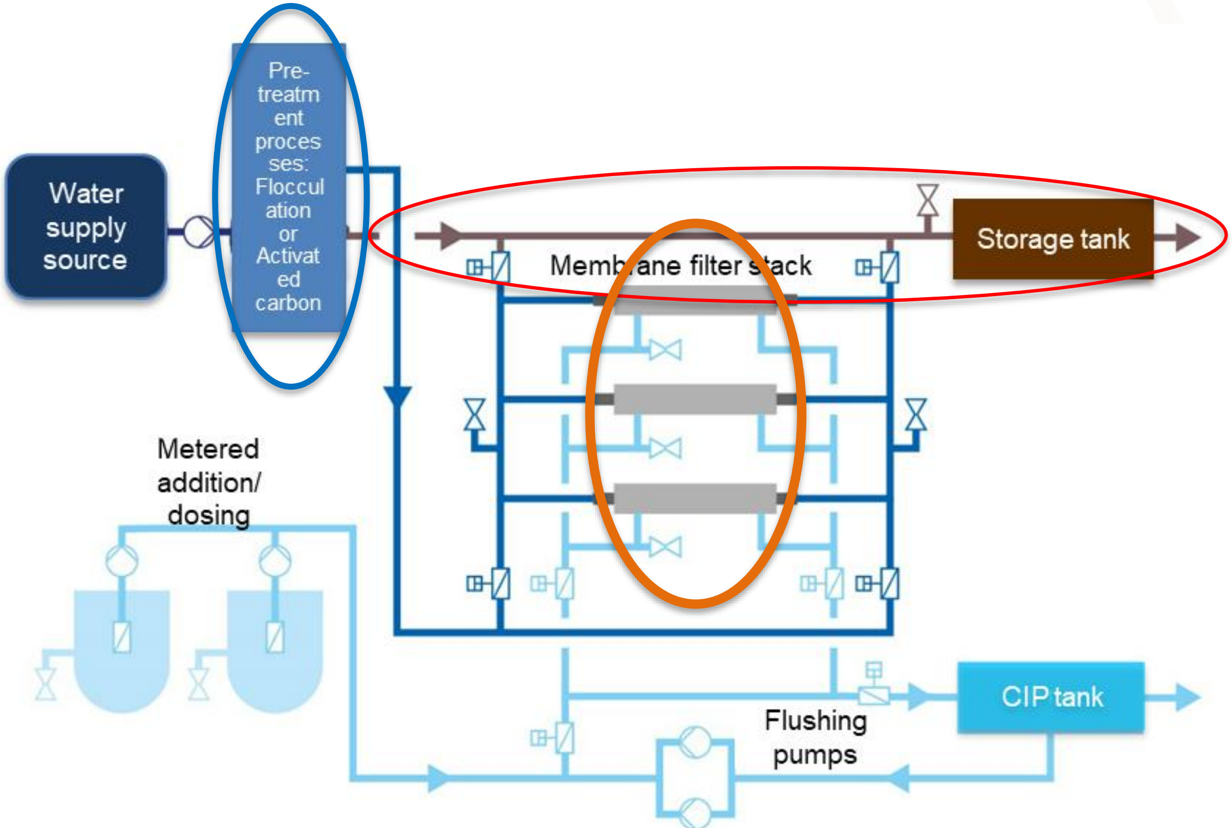
- Critical role of chemistry in water treatment
  - Understand the chemical water composition
    - Leads to appropriate treatment solution choices
    - Minimise interference of treatment process by the matrix
    - One can predict probable outcomes

- Insights into solute-substrate interaction
  - Leads to efficiency gains
  - Tailored applications

- Simplicity of approach is KING
  - No specialised know-how needed
  - Generally cheap to operate and maintain
  - *Usually, not effective for emerging contaminants*

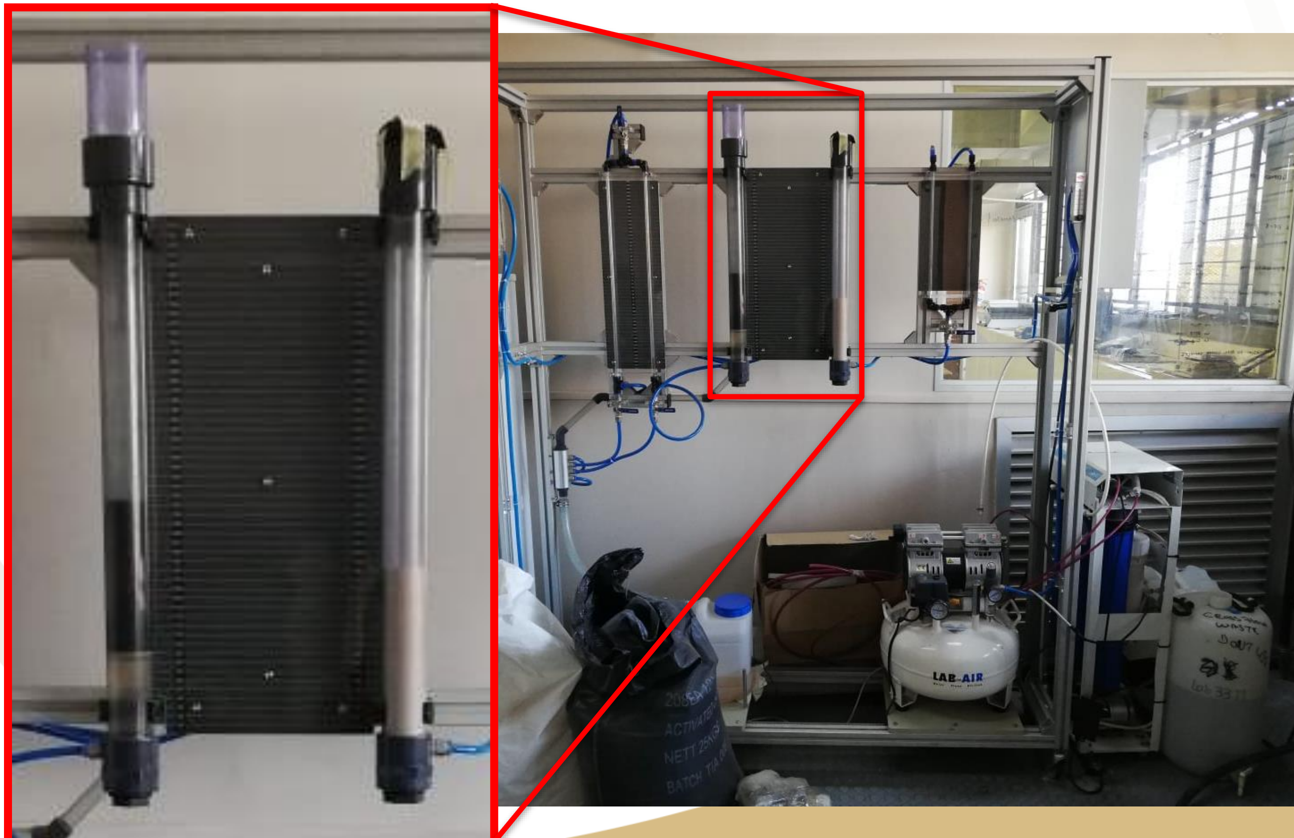
Three main Areas of RD&I

- Pre-treatment protocol development
- Polymer composite material RD&I
- Bacterial and biofilm mitigation



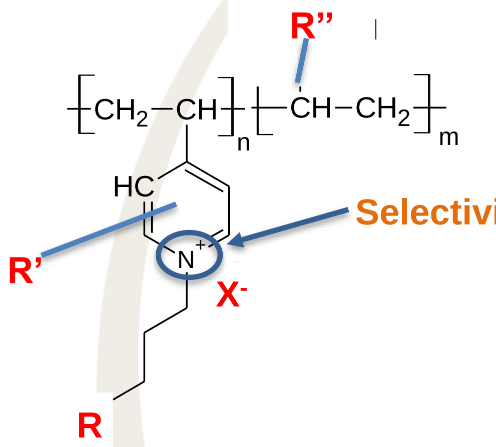
- T. A. Makhetha, R. M. Moutloali, Journal of Membrane Science, 2021, 618, 118733
- T. A. Makhetha, S. C. Ray, and R. M. Moutloali, ACS Omega, 2020, 5, 9626
- S. T. Dube, R. M. Moutloali, S. P. Malinga, Journal of Environmental Chemical Engineering, 2020, 8 (4), 103962
- T. A. Makhetha, R. M. Moutloali, Journal of Membrane Science, 2018, Journal of Membrane Science, 554 (2018) 195

Tailor-Made Polymer composites - Resins



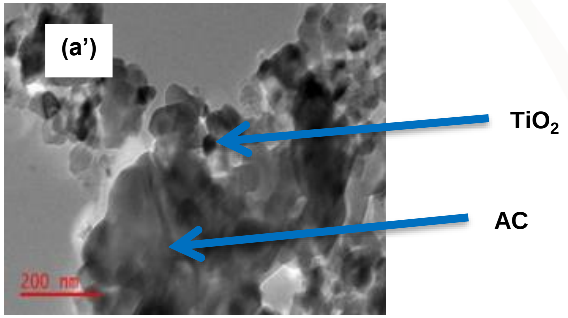
Modified AC for complex water treatment

- Ion-selective beads for cyanide recovery – high CN^- regime
- Photocatalytic beads for cyanide mineralisation – low CN^- regime

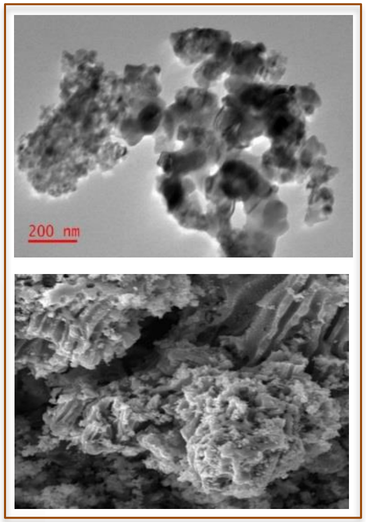


R'' = CO_2H
R' = H
R = CH_3
X = Br

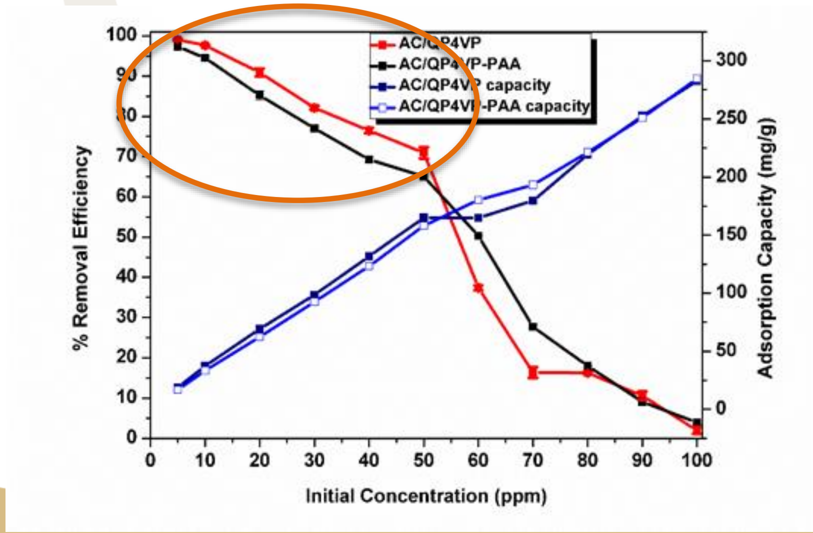
Quaternized poly(4-vinylpyridine)poly(acrylic acid)



(a') TEM micrographs for TiO_2/AC



TEM and SEM for TiO_2/AC/QP4VP



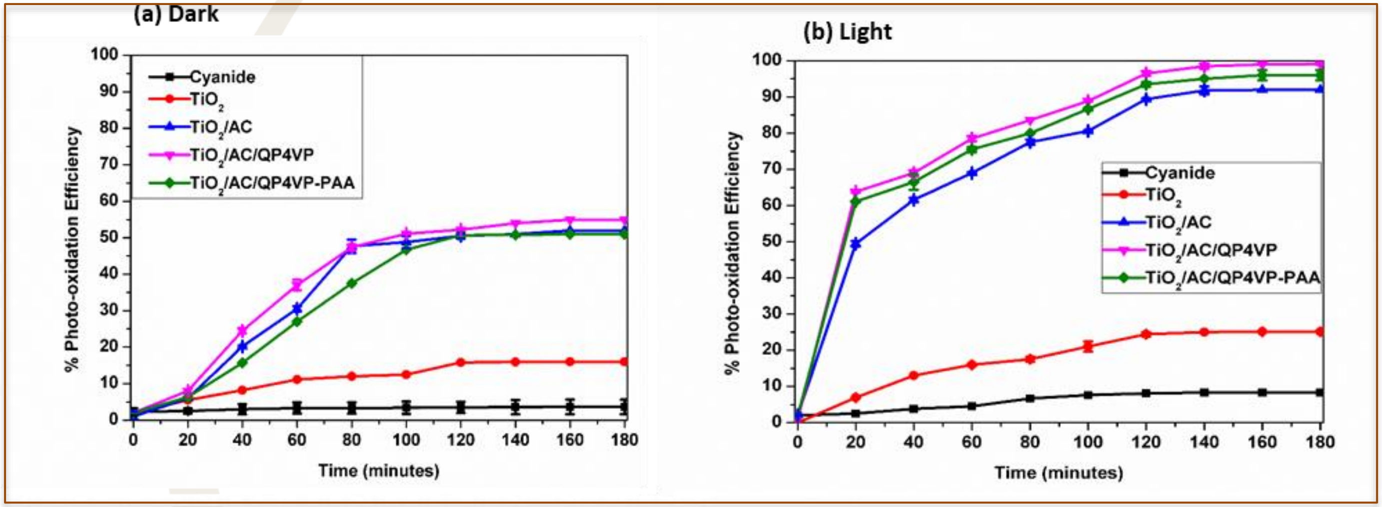
Effect of initial concentration at pH 8, All AC composites (0,05 g) at 50 ml of CN solution

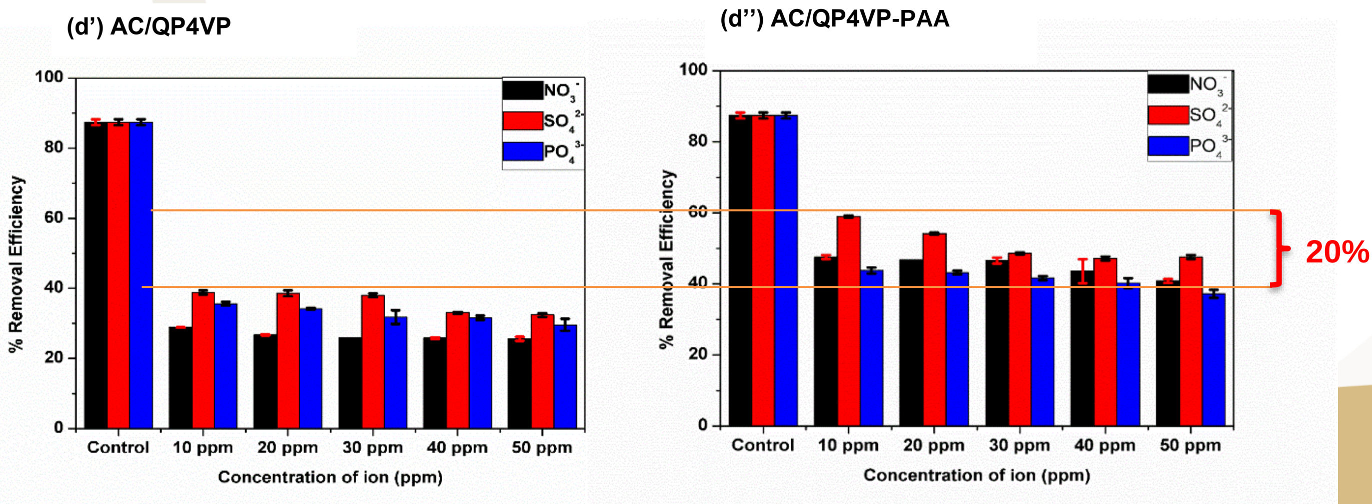
Adsorption Isotherms Results					
	Langmuir		Freundlich		
Sample	b (mg/g)	R^2	K_f	n	R^2
AC/QP4P	285,7	0,8595	41,295	1,881	0, 9682
AC/QP4VP-PAA	467,3	0,8603	21,710	1,325	0, 9863

Modified AC for complex water treatment

Low cyanide concentration photo-oxidation studies

Effect of contact time at pH 8, 10 ppm for (a) dark and (b) irradiated with UV-Light.





Products

(1) $2CN^- + 2OH^-$

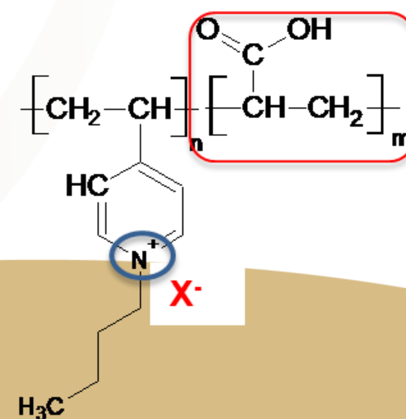
↓

$CN^- + CNO^- + H_2O$

(2) $CNO^- + 8OH^- + 8H^+$

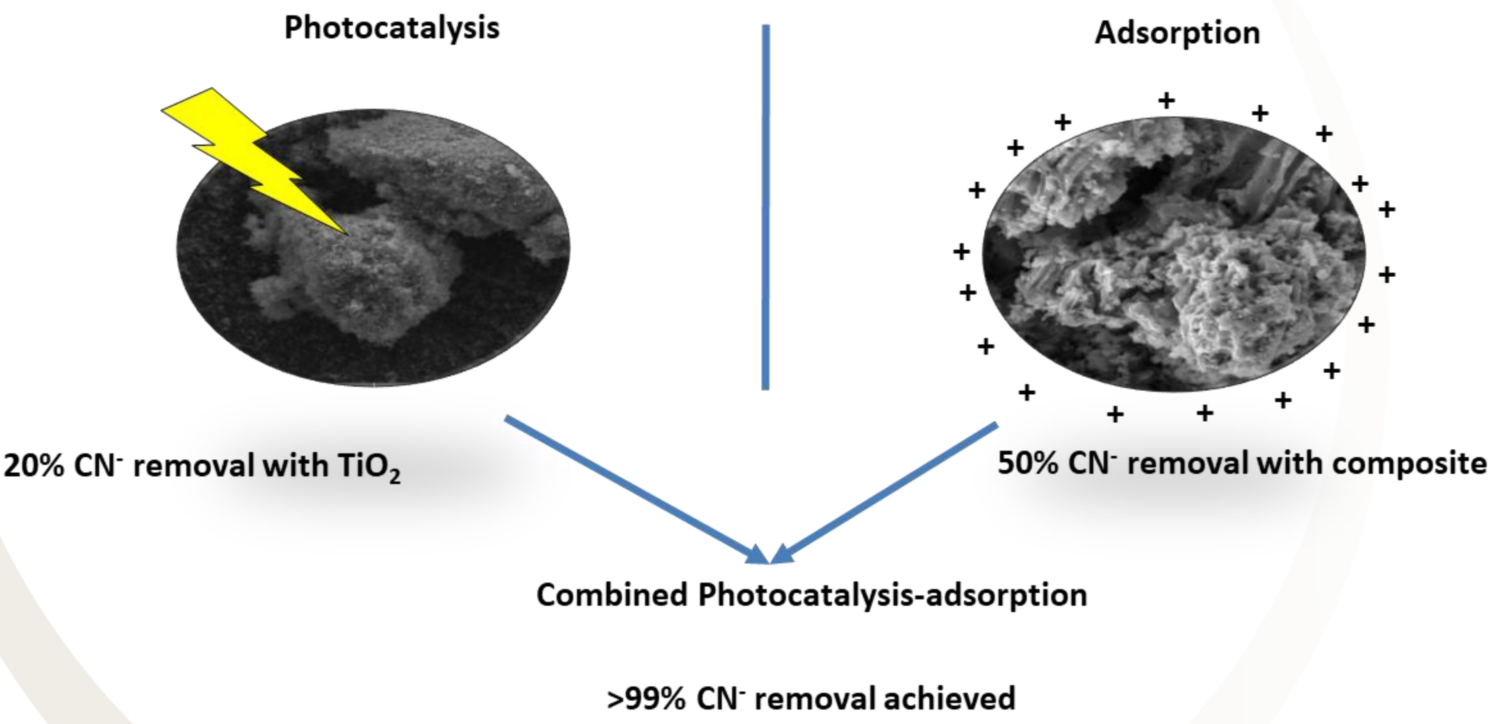
↓

$NO_3^- + CO_2 + 4H_2O$

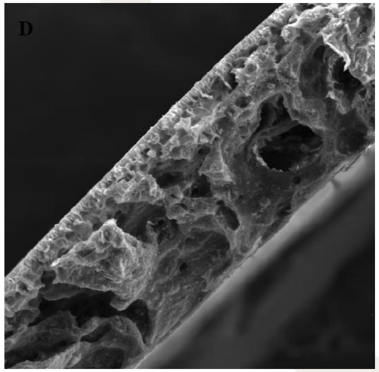


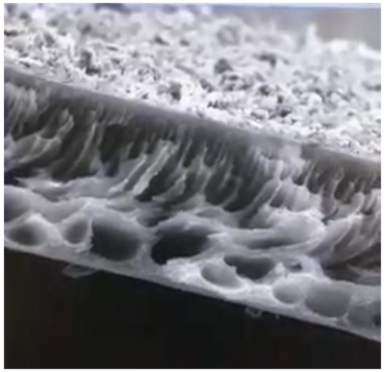
Modified AC for complex water treatment

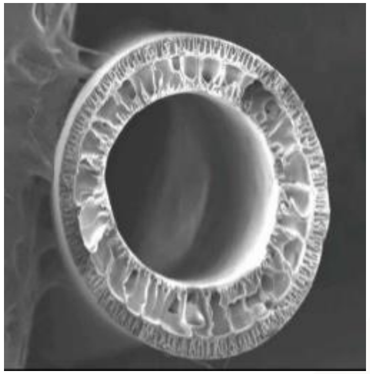
Low cyanide concentration photo-oxidation studies



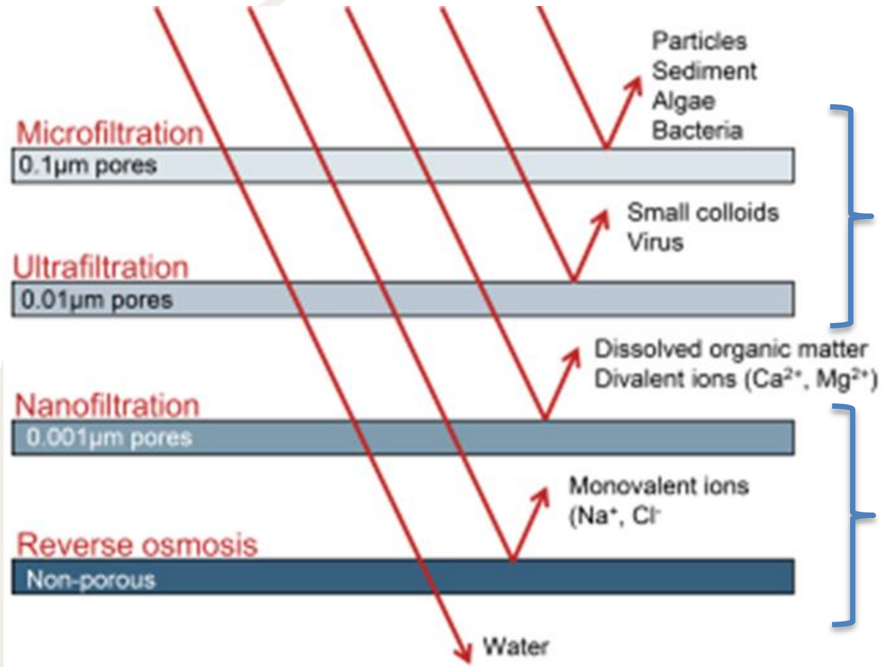
Tailor-Made Polymer composites - Membranes







Membrane Processes Types: Advantages and Challenges



Low pressure systems →
- Surface water
- Borehole water prone to bacterial infiltration

High pressure systems →
- Brackish borehole water
- Seawater desalination

Advantage of membrane filtration:

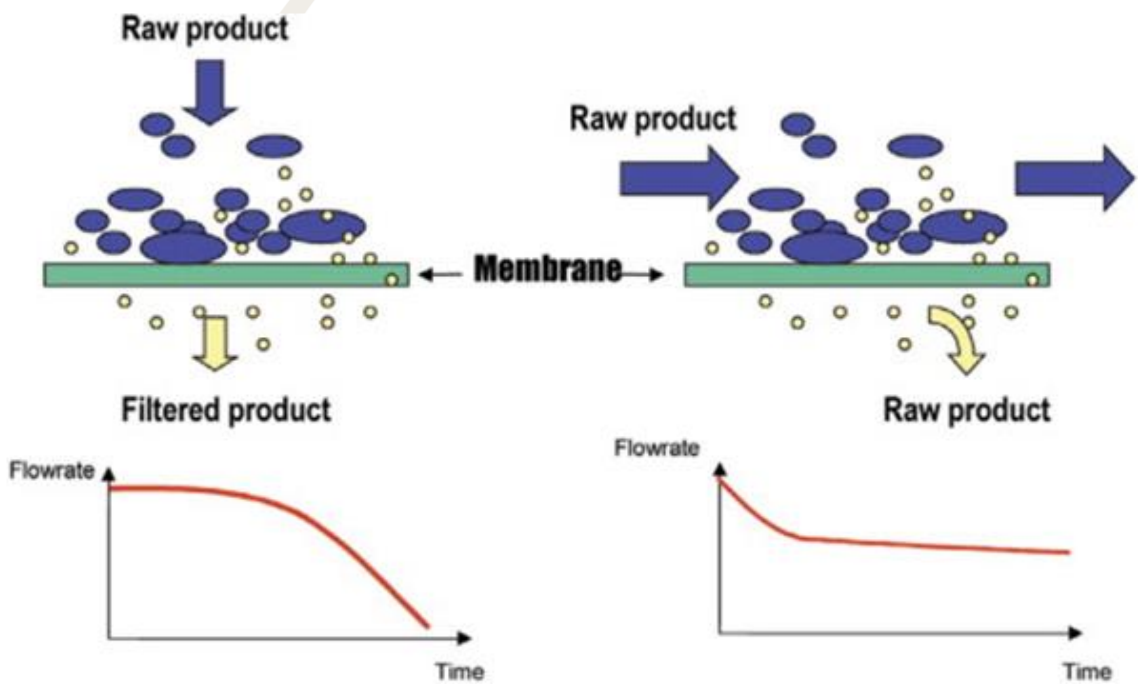
- Flexibility – can be used both as a pre- and main-treatment for suspensions
- Small physical foot-print
- Low energy requirements compared to other technologies
- Non-chemical process, chemical may be needed for clean in place (CIP) processor pre-treatment of difficult wastewater
- Integration with other processes – best outcomes

Membrane Processes Types: Advantages and Challenges

Main Challenge is Fouling

Dead-end

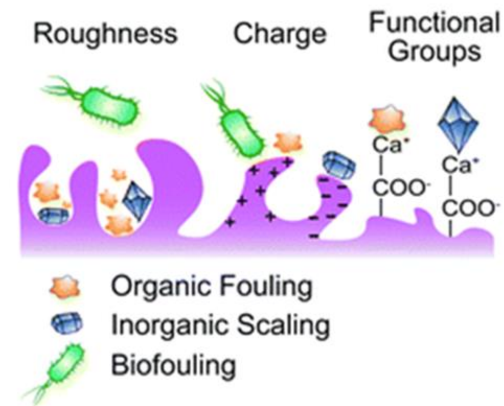
Cross-flow



- Cake formation leading to fouling
- Reduced pure water production
- *Shorter application time*
- *Higher relative cost of application*

- Reduces rate of cake formation leading to low fouling
- Increased production
- *Longer application time*
- *Lower cost of operations*

Difficult fouling processes

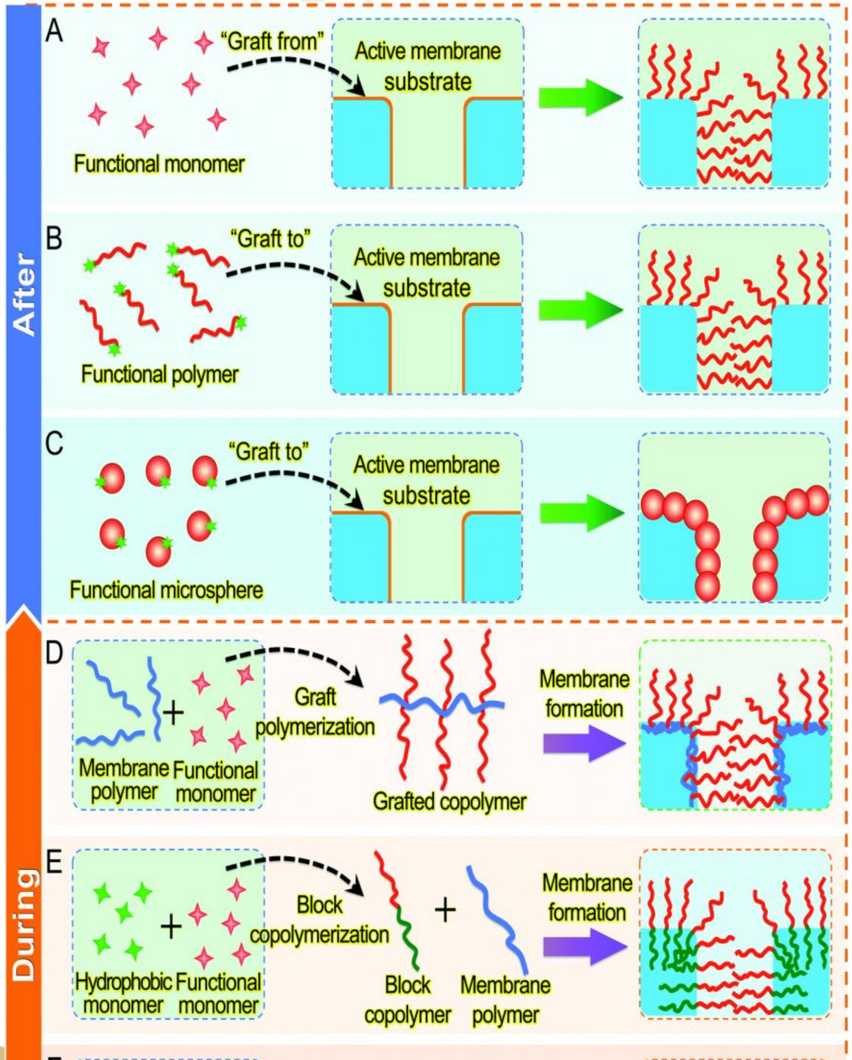


- Smoother – low surface roughness
- Hydrophilic property
- Specific desired interaction with solutes

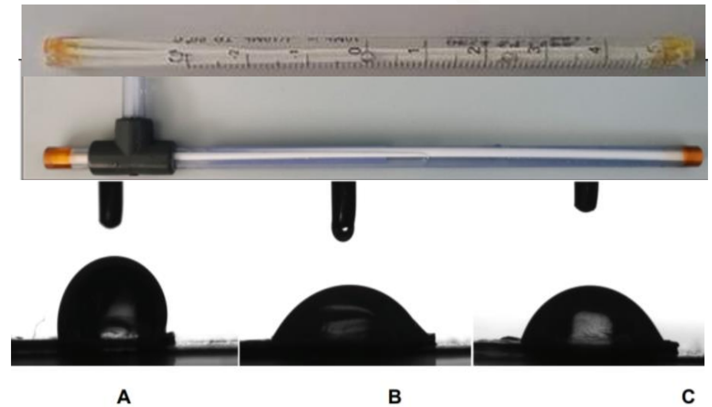
- Grafting –
  - hydrophilicity, desired interactions
- Nanofiller selection –
  - specific interactions, fouling and flux modulation

Tailor-Made Polymer composite Membranes

➢ Polymer Modifications and membrane grafting for improved membrane performance



In-module membrane modification



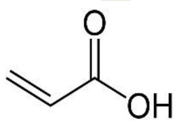
Bulk polymer grafting approach

Z. Liu et al., *Chem. Soc. Rev.* 2016, **45**, 460-475
Matabola, Moutloali, *Procedia Engineering*, 2012, **44**, 1452
Matabola et al., *Materials Today: Proceedings*, 2015, **2**(7), 3957
Ndlwana et al., *Physics and Chemistry of the Earth, Parts A/B/C*, 2018, **106**, 107
Ndlwana et al., *Journal of Membrane Science and Research* 2020, **6**(2), 178

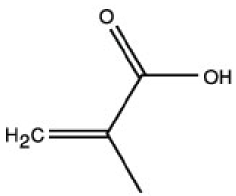
BULK POLYMER GRAFTING TO INCORPORATE OF POLYMER BRUSHES

- Grafting of acrylic brushes onto PES polymer backbone – chemical and microwave initiated
- Typically grafting yields of less than 8%

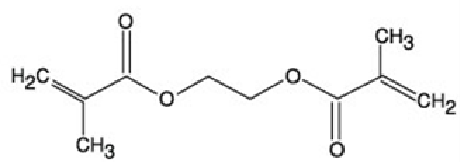
Monomers used



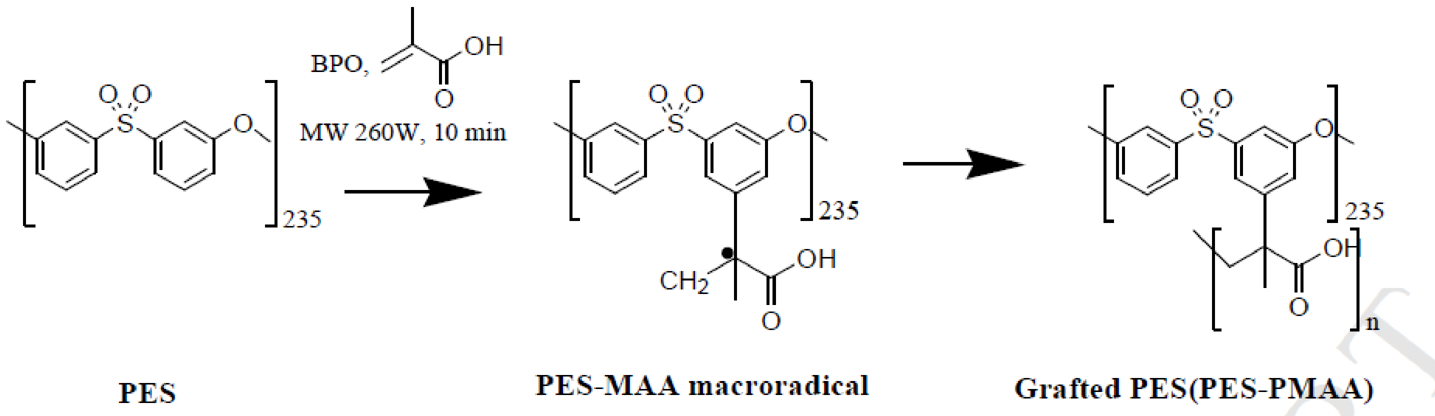
Acrylic Acid

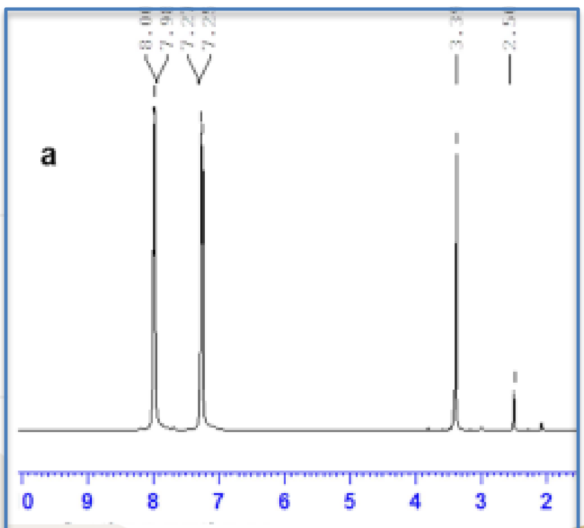


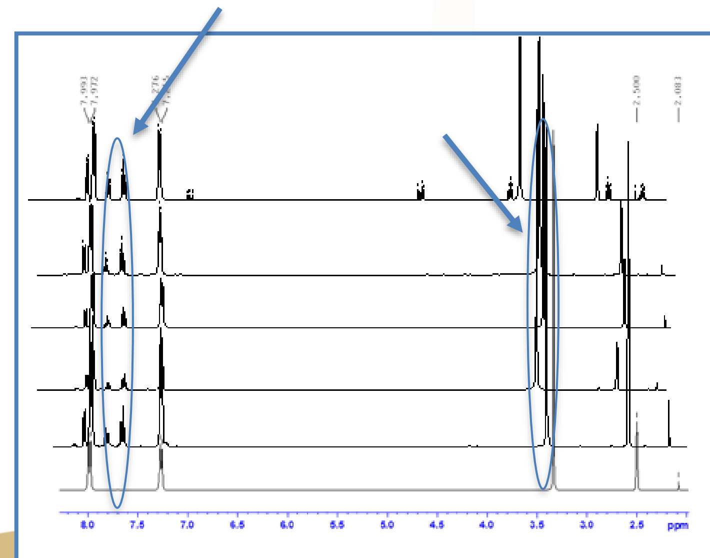
Methacrylic Acid



Ethylene Glycol Dimethacrylate

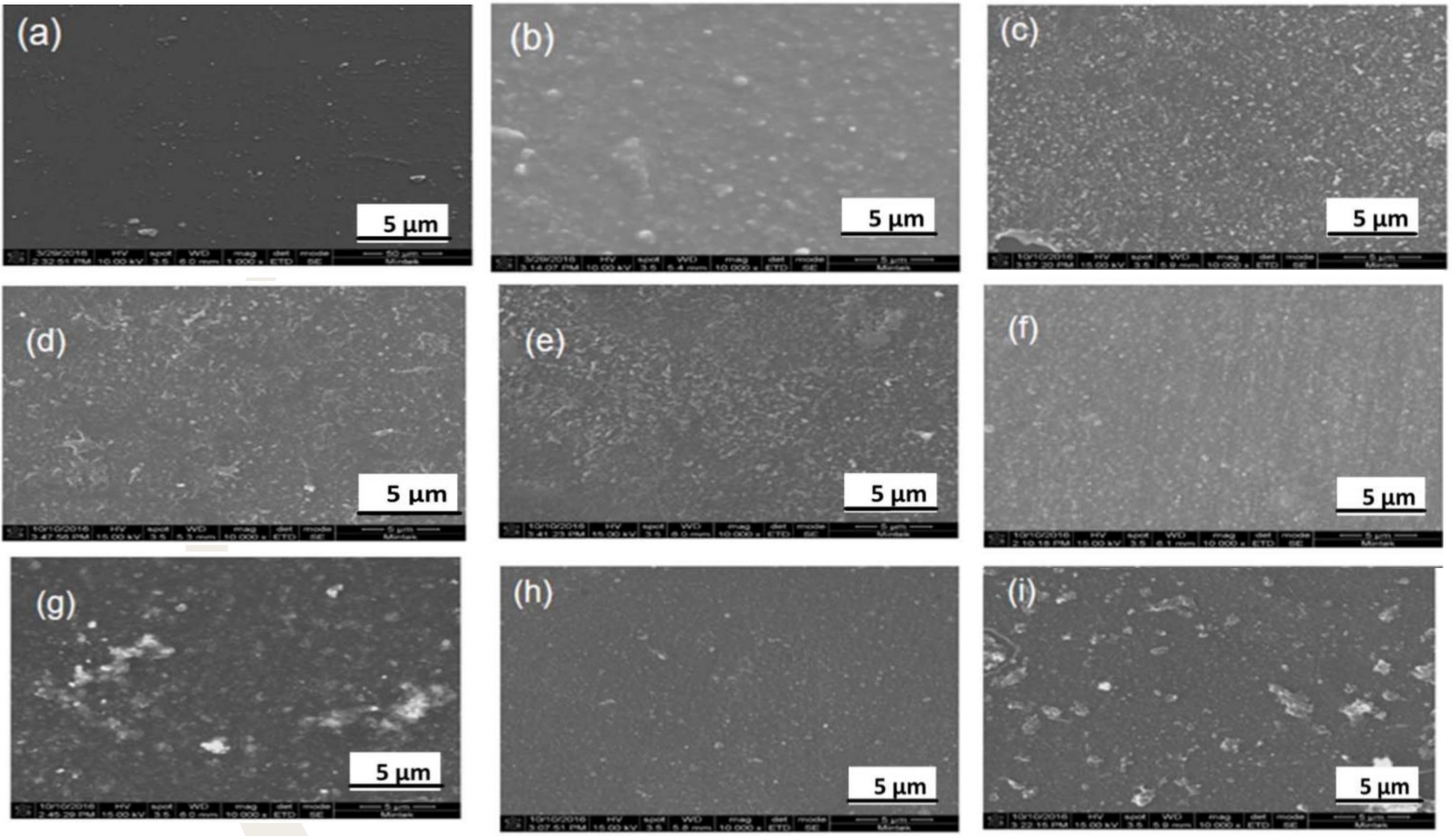




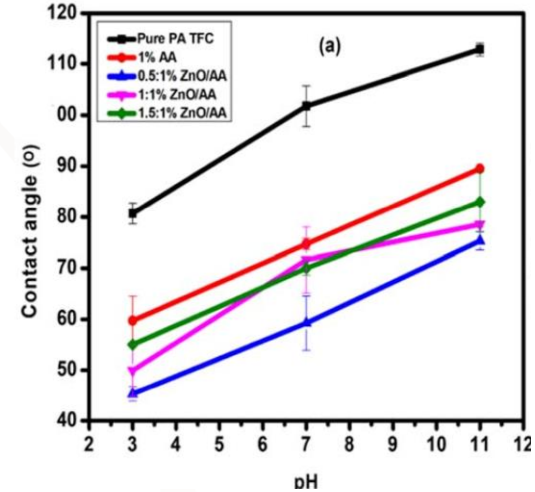


M. L. Kgatle, MSc dissertation, University of Johannesburg, 2016
Ndlwana et al., Physics and Chemistry of the Earth, Parts A/B/C, 2018, ***106****, 107*

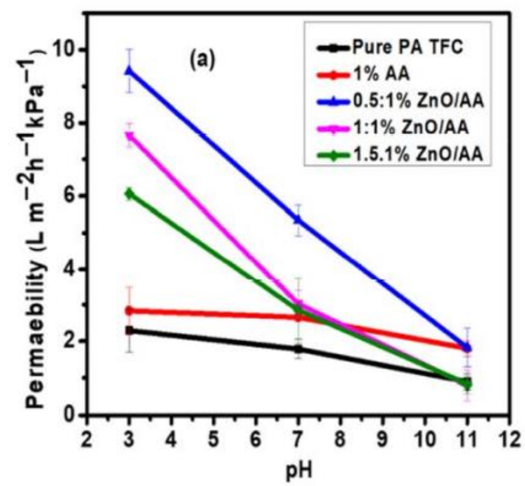
SURFACE GRAFTING TO INCORPORATE OF POLYMER BRUSHES



Surface variation with increase modification



WCA changes as a function of pH



Water flux as a function of pH

- Lack of control at high grafting, leading to surface heterogenicity
- Water permeation was sensitive to pH changes (here shown for ZnO/PAA composite)

Malatjie et al, Membranes 2021, ***12***, 910

Tailor-Made Polymer composite Membranes

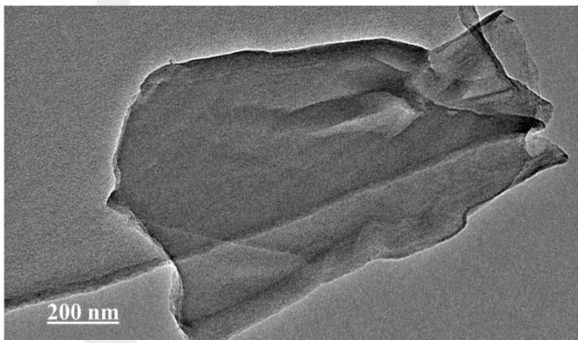
GO modified with zwitterions (GO@ZI) to improve performance and minimize phase incompatibility

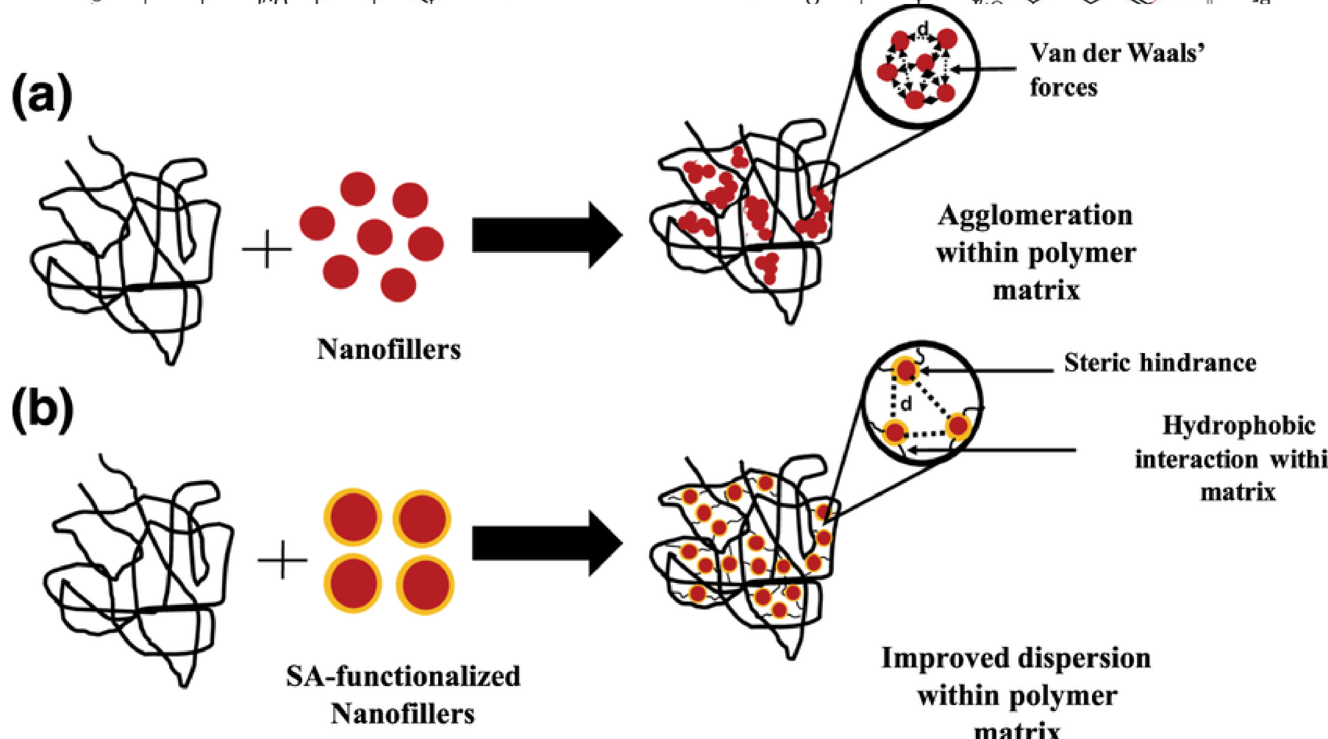
Superhydrophilicity

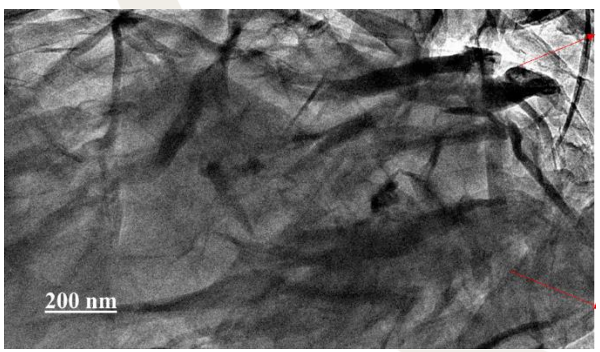
- Decrease water resistance
- Reduce fouling propensity
- Easy to functionalise
- Antimicrobial effects

Phase compatibility

- Decrease interface defects
- Better dispersion within matrix
- Antimicrobial
- Easy to modulate







J. Liu et al., Membranes 2016, 6, 35

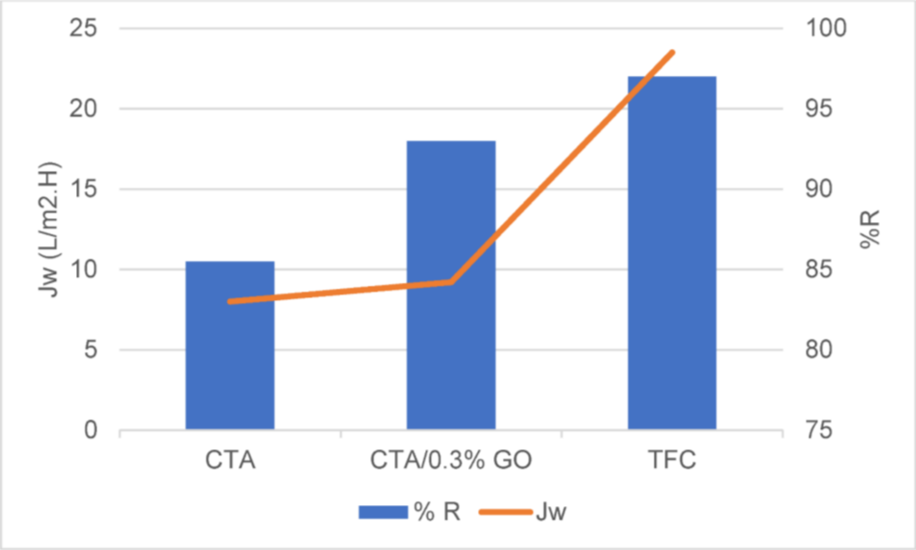
S. Xabela, Mtech Project sponsored by NRF and DST/Mintek Nanotechnology Innovation Center

H. Y. Ang et al., Scientific Reports, 2018, 8, 7409

Membrane Assessment and Testing

- Water treatment and wastewater remediation

- Brackish and Seawater desalination
  - ✓ Desalination of sea water sample from Hurgada–Red Sea coast (Egypt)
  - ✓ NaCl as draw solution at 25°C and flowrate 1.55 $L.min^{-1}$



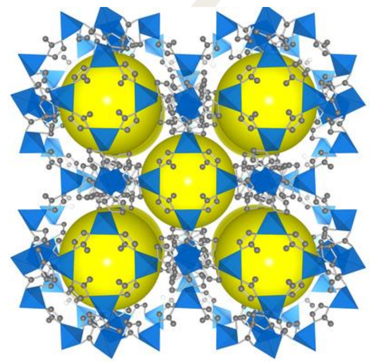
Forward Osmosis membrane assessment

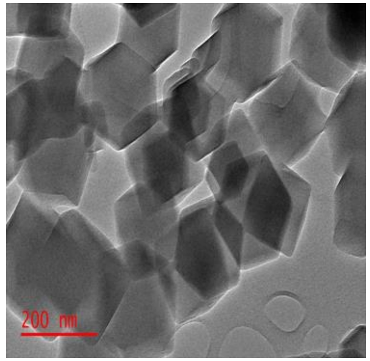
Parameter	Unit	Feed	Permeate	%R
Total dissolved solids (TDS)	$mg.L^{-1}$	42643	640	96.2
Total hardness	$mg.L^{-1}$	7200	110	98.5
Chlorides	$mg.L^{-1}$	25000	25	99.9
Sodium	$mg.L^{-1}$	19200	186	99.0
Magnesium	$mg.L^{-1}$	1498	18	98.8

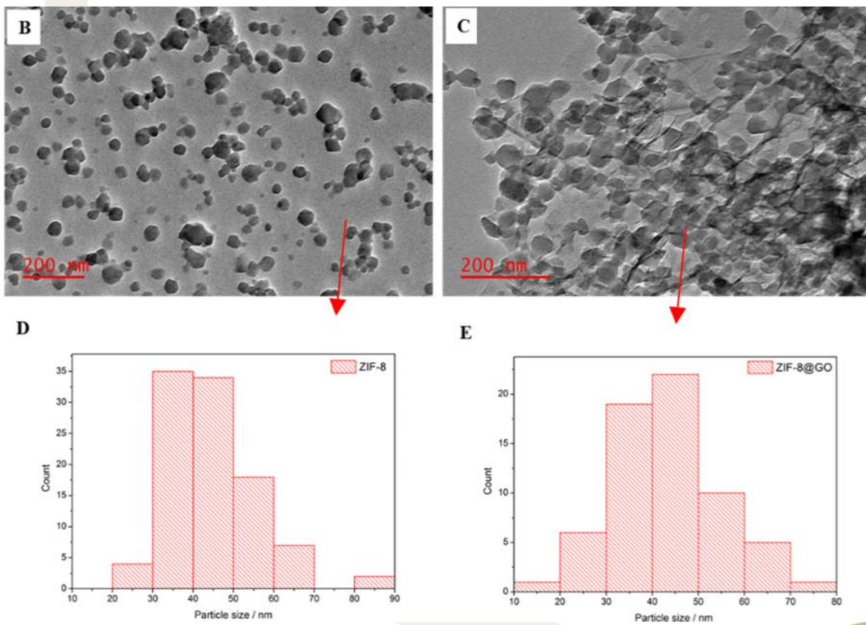
Xabela and Moutloali, J Appl Polym Sci., 2022;139:e52336
Jamil et al, Membranes **2022**, *12*(1), 6;

Tailor-Made Polymer composite Membranes

- GO modified with metal organic membranes (GO@MOF)

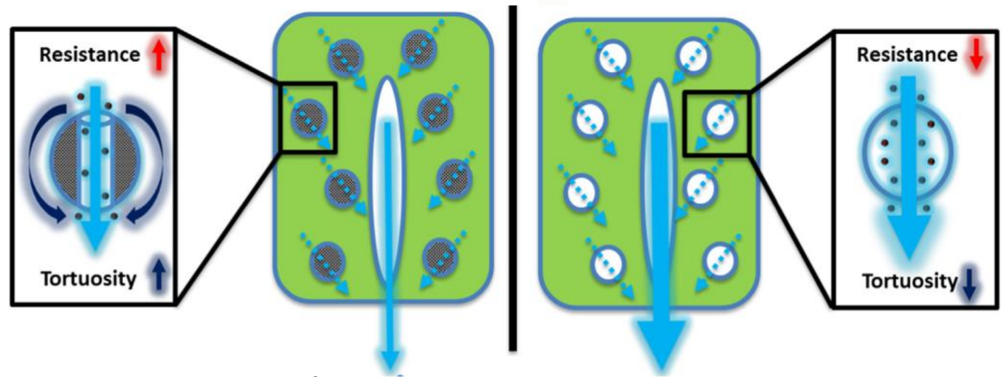


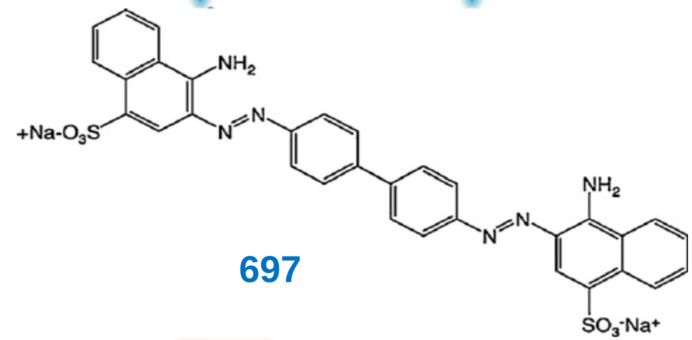




Functional porous structure

- Decrease tortuosity
- Increase solute-filler interactions
- More selectivity and higher flux





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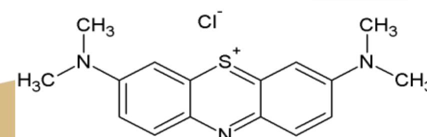

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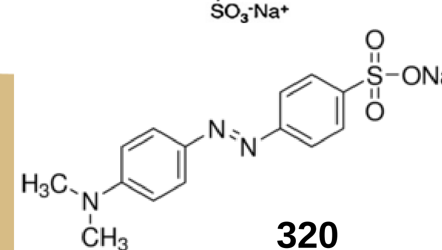

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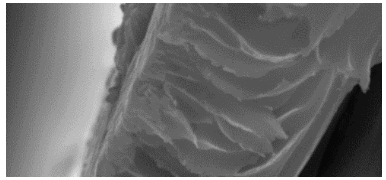
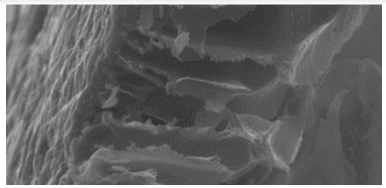
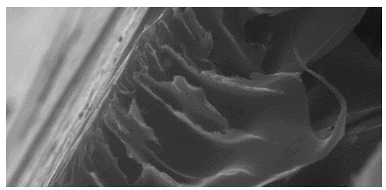
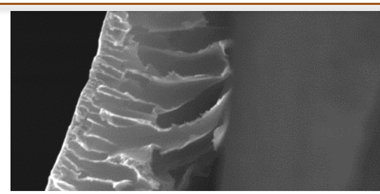
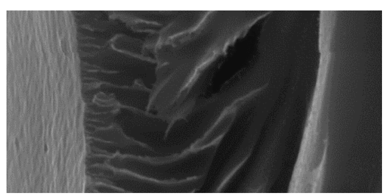
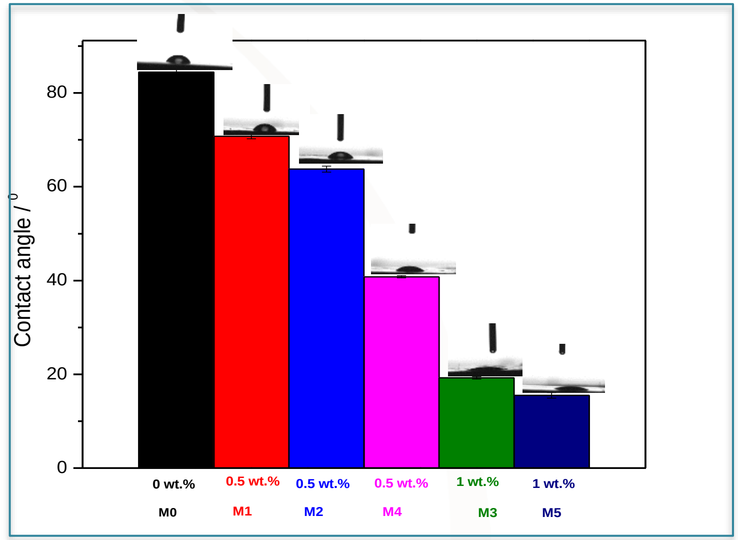
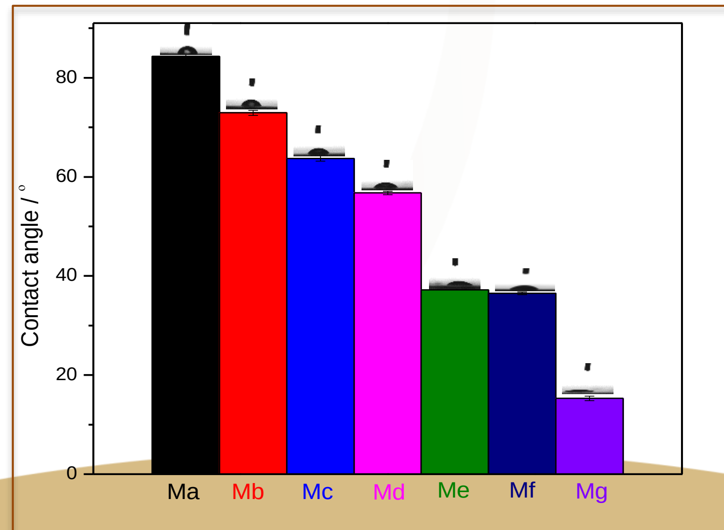
Makhetha, et al., ACS Omega 2020, 5, 17, 9626-9640
Journal of Membrane Science 492 (2015) 392–399

Tailor-Made Polymer composite Membranes

Membrane type	Cross-section
PES	
$[(Cu(tpa))_{0.1}@GO]_1$	
$[(Cu(tpa))_{0.9}@GO]_1$	
$[(ZIF\text{-}8)_{0.1}@GO]_1$	
$[(ZIF\text{-}8)_{0.9}@GO]_1$	

Water contact angles





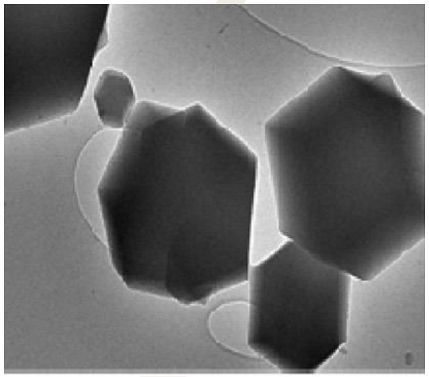
Nothing spectacularly different in their physical properties or surface behaviour…

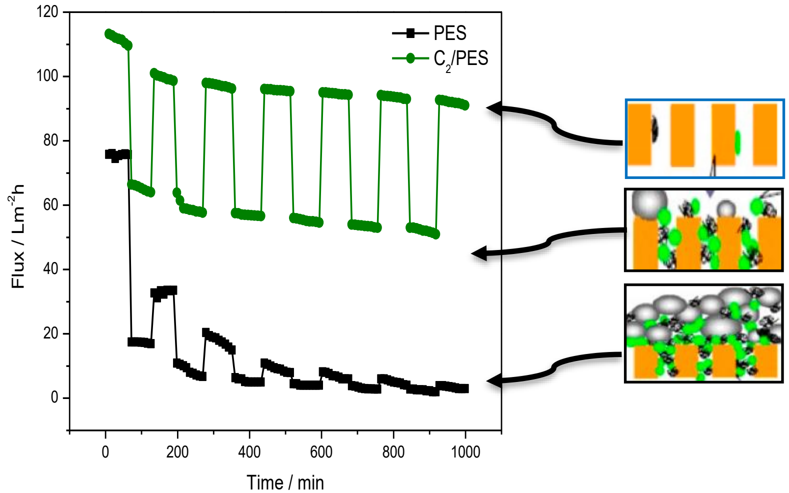
Tailor-Made Polymer composites - Membranes

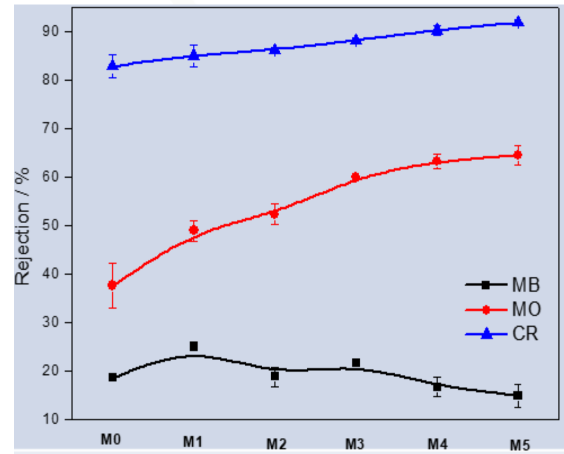
m = 0.5 and 0.9
n = 0.1, 0.5 and 0.9

Fouling mitigation and selectivity modulation

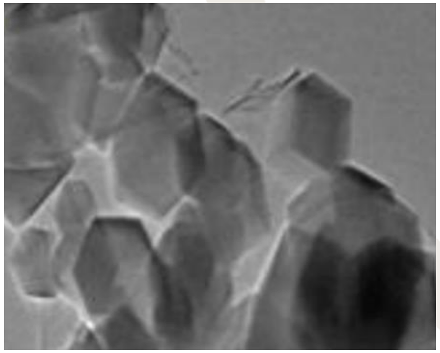
$[(Cu(tpa))_m@GO]_n$

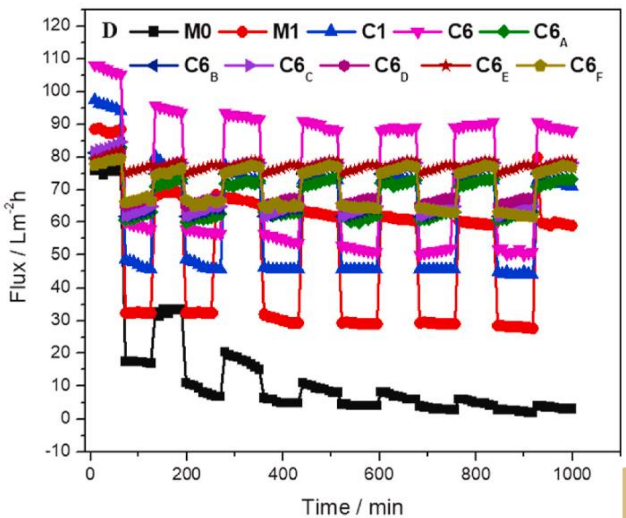


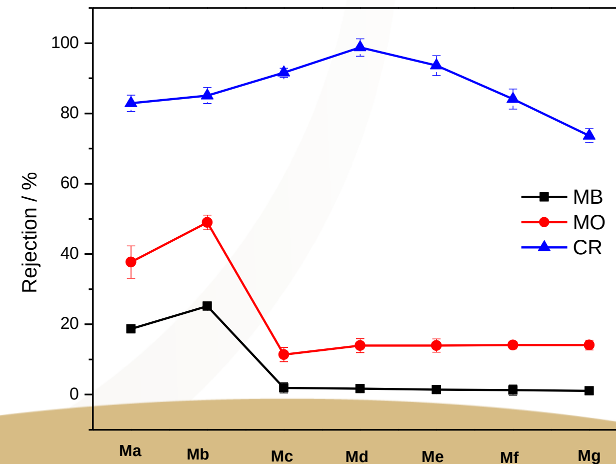




$[(ZIF\text{-}8)_m@GO]_n$



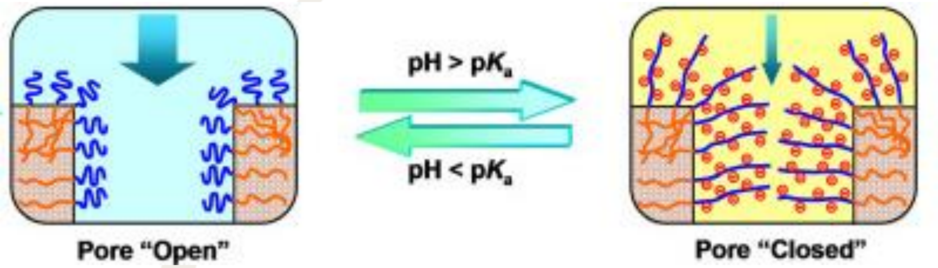


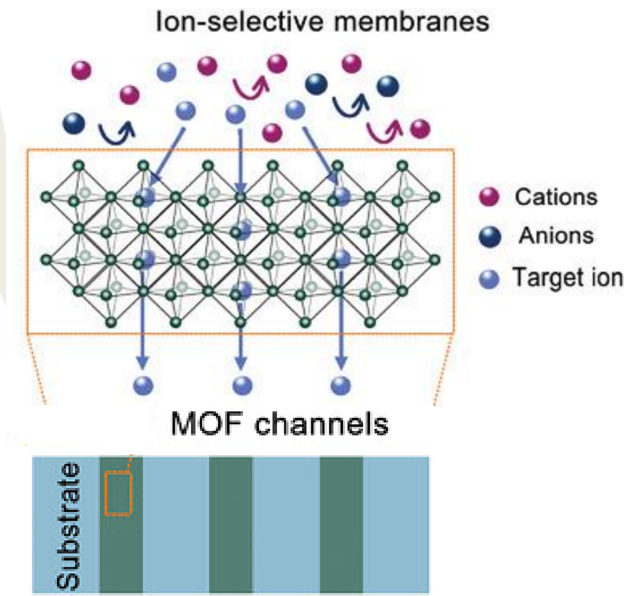


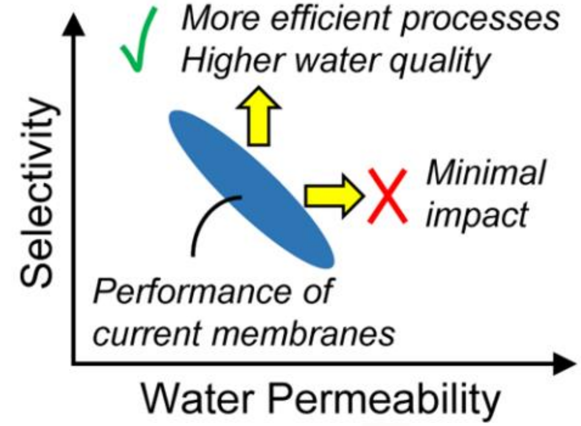
Makhetha and Moutloali. Journal of Membrane Science, 2018
Makhetha and Moutloali, Journal of Membrane Science, 2021, 618, 118733

Tailor-Made Polymer composite Membranes

Progress towards more efficient membrane systems





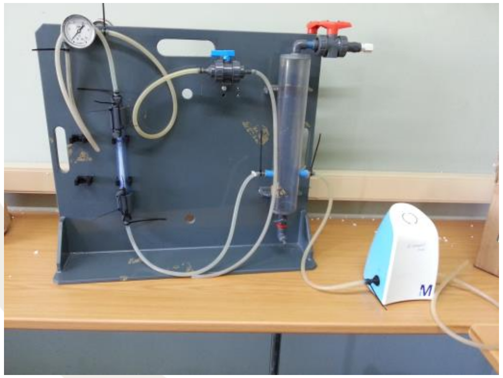


Membranes used for:

- Desalination NF
- Hard water softening NF
- Dye separations – UF and NF
- Greywater upgrade for reuse - UF
- Integration for wastewater to potable reuse

- ➢ Hydrophilic brushes for permeability and rejection
- ➢ MOF properties good for selectivity and permeability

Technology Innovation and Demonstration

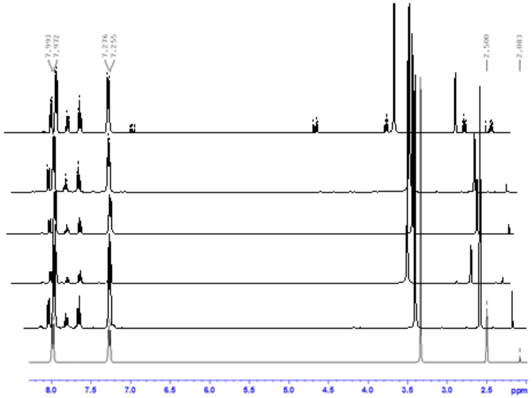


Towards Technology Demonstration and Piloting

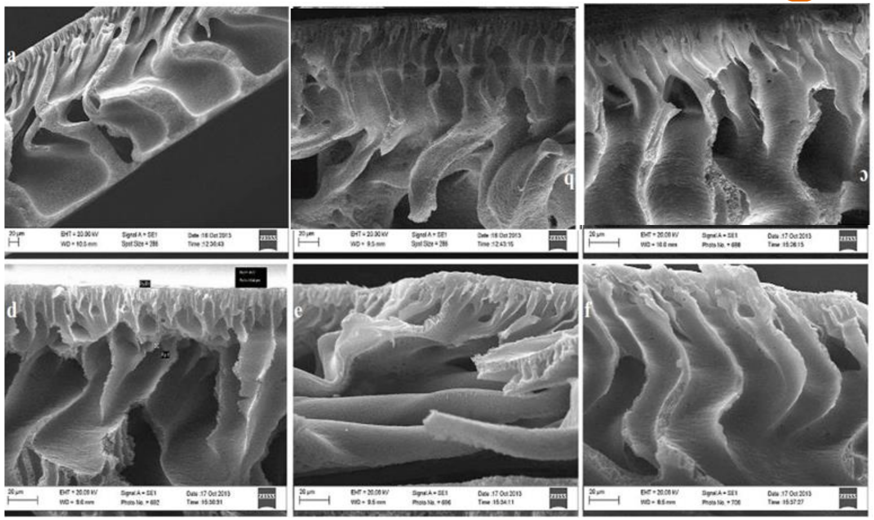
➢ Scale-up: Bulk polymer grafting optimisation

2 L (UJ)

20 L (Mintek) and 50 L (UJ, UNISA)

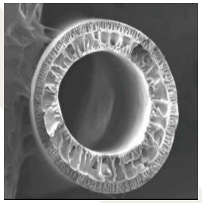


Grafting optimisation



PES-g-PSS (Mintek)
PES-g-VP (UJ) and PES-g-ZI (UJ, UNISA)

➢ Pilot scale membrane production and module potting



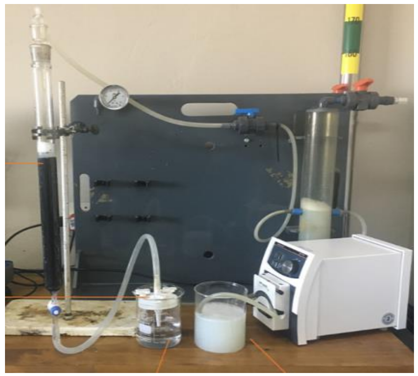
Benchtop system:
Parameter optimisation

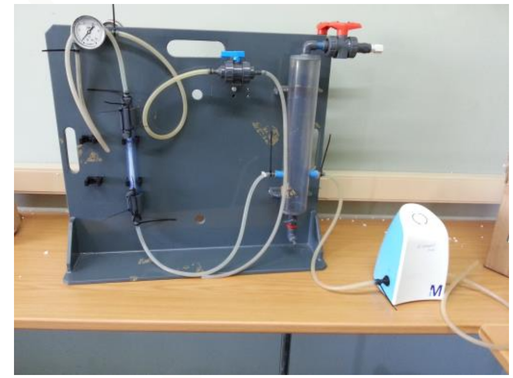
Hollow-fibre membrane pilot production

Membrane module potting and scaling

Towards Technology Demonstration and Piloting

Technology demonstration - *Long term assessment and benchmarking*





Flat-sheet membranes module testing

Hollow-fibre membranes module testing

In-house and Commercial systems for benchmarking

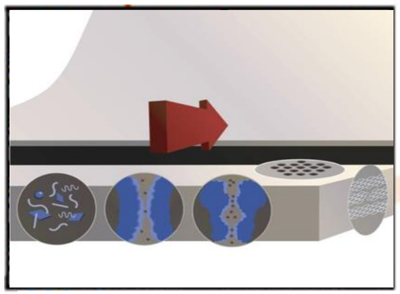
- *K. P. Matabola, B. Vatsha, R. M. Moutloali, Spin Casting of the Modified PES into Capillary Ultrafiltration Membranes, External Report 6642, 18 September 2013; External Report: Ikusasa Water*
- *R. M. Moutloali, P. Matabola, Surface Modification of capillary Ultrafiltration Membranes from Ikusasa Water, External Report 6116, 24 November 2011; External report: Ikusasa Water*
- *P. Matabola, R. M. Moutloali, Surface Modification of capillary Ultrafiltration Membranes from Ikusasa Water- Further Characterisation, External Report 6117, 24 November 2011; External report: Ikusasa Water.*

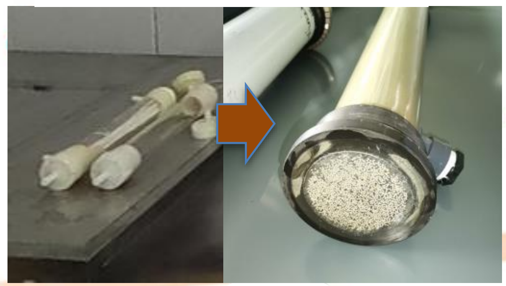
Creating Meaningful Partnerships

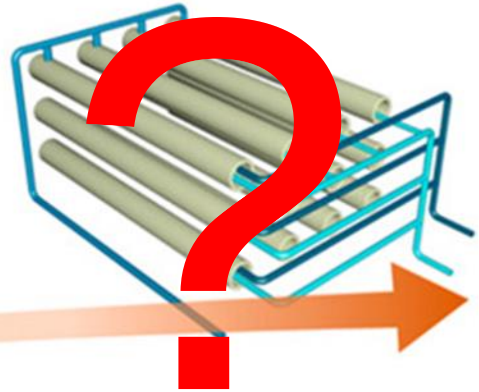
System-scale

Modular scale

Laboratory scale







Water Quality
Process stability

High performance → **High selectivity**

*Z. Yang, L. Long, C. Wu, C. Y. Tang, ACS EST Engg. 2022, **2**,(3), 377*

Creating Meaningful Partnerships

Creating Academic and Industrial Collaboration on the RD&I outputs and quality of students' projects

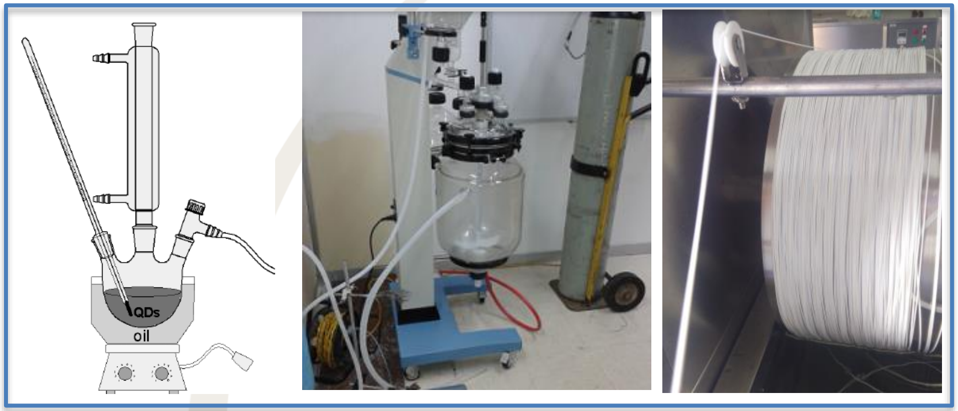
- Collaboration with industry is *critical for academia to create scientific knowledge and obtain industrial data*.
- In turn for industry, collaboration with universities is crucial for organizations in joint, scientific-based research projects in order to *develop solutions for production-sourced problems*.
- Conduct research that is both *practically relevant and scientifically rigorous*, while also making a *great societal impact*.
- Bridge the technology innovation gap

Robinson Lake impacted by AMD and Sibanye Stillwater neutralising plant

Effects of untreated domestic borehole water and construction of RO plant for ground water in Blouberg Municipality

Creating Meaningful Partnerships

Business case must be made early on…



Scale-up: 100 mL to 50 L and 200 g to 5 kg

Demonstration

Piloting?

- Kinetic limitations and Mass transfer considerations – might lead to totally unexpected outcomes
- Might favour side-chain elongation and limit grafting density
- Reproducibility and quality guarantees

Technical…

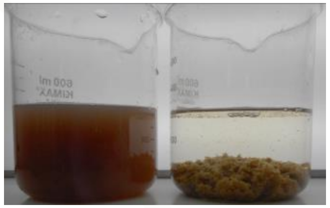
- Bulk polymer and solvent sourcing becomes increasingly critical
- Space, equipment and overheads costs escalation
- Addition of extra non-academic labour costs
- Benchmarking and commercialisation
- Partnerships: Leverage external costs becomes part of planning

Economics…

Creating Meaningful Partnerships

GJP Chemicals

- Assess polyelectrolytes as pre-treatment step
- Access to wastewater from industry
- Explore new opportunities for application



HIMOLOC POLYELECTROLYTES

MINTEK

- Materials research/development for different applications
- Membrane Technology demonstration opportunities

NDA development in progress

MOU at the Legal Services Office

Several technical meetings held

WATERICON

- Validate against industry data
- Technical assistance in technology demonstration and piloting
- Technology benchmarking

NDA development in progress

2 meetings held

BITRI

Collaboration on nanofibre research and upscaling for water filtration. Staff development through project co-supervision and enrolling for higher degrees at UNISA.

MOU at the Legal Services Office

Supplied letter of support of international funding

1 meeting held

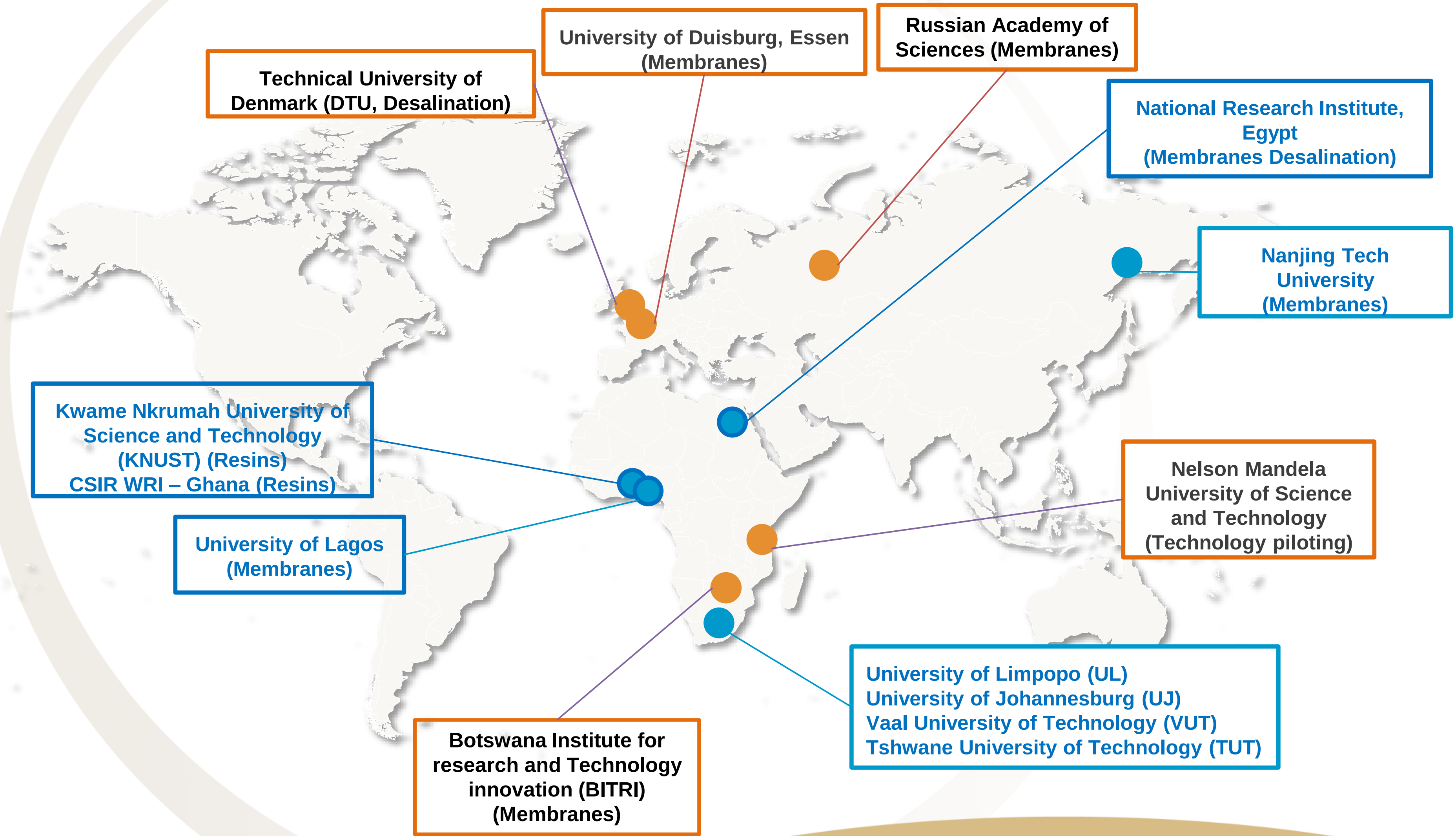
Sibanye Stillwater

- Access to mine wastewater and AMD treatment centres
- Technology demonstration/benchmarking opportunities

Exploratory discussions,

1 meeting held

Current Local and International Academic Networks



Summary

- Quality and safe water provision is still a pipe-dream for some
- Design and assess polymer composite resins and filtration membranes for water treatment
- Creation of technology partnerships
- Societal challenges be driver for academic RD&I
- WATER IS A SCARE RESOURCE, SPARE IT, REUSE IT, SHARE IT…

Acknowledgements

UNISA
institute for nanotechnology and water sustainability

UNISA
university of south africa

science & technology
Department: Science and Technology
REPUBLIC OF SOUTH AFRICA

NIC
DST/ MINTEK
NANOTECHNOLOGY INNOVATION CENTRE

NRF
National Research Foundation

MINTEK

UNIVERSITY OF JOHANNESBURG

PAX REUNION CLUB 86 EDUCATION TRUST
Trust Reg. No: IT502/2008
PAX REUNION CLUB 86

ACKNOWLEDGEMENTS

UJ Research Group: PhD, MSc and in-service candidates

Prof. Moutloali; Dr. Makhetha, Dr. Nqombolo, Prof. B. L. Feringa, Dr. Chauke, Mr. Xabela

The Mintekkers – NIC Team

Pax Reunion Club 86 – Present and the Future

THANK YOU