Acknowledgements

Membrane Materials and Transport Studies for Sustainable Water, Energy & Life Sciences

Ngoc Bui

University of Connecticut, CT (with Dr. **Jeffrey R. McCutcheon**)
Lawrence Livermore National Laboratory, CA (with **Dr. Kuang-Jen Wu** and **Dr. Francesco Fornasiero**)
Lawrence Berkeley National Laboratory, CA (with **Dr. Jeffrey J. Urban**)

NSRDEC

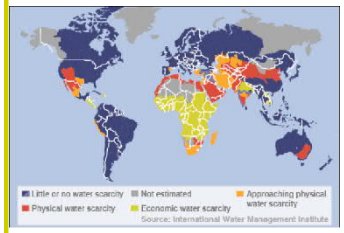
Acknowledgements

Water and Energy are inextricably linked and must be addressed together.

CHALLENGES

Global Water Scarcity

By 2025,



1.8 billion people will be living in regions with absolute water scarcity.

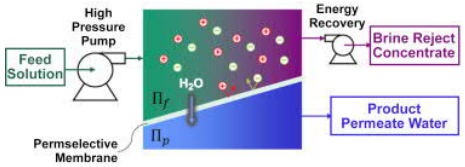
2/3 of the world's population could be living under water stressed conditions.

Desalination and water reuse are keys for supplying fresh water.

"Water in Crisis: A Guide to the World's Fresh Water Resources" – I.A. Shiklomanov, Oxford Univ. Press, NY, 1993;
http://www.ccsenet.org/journal/index.php/eer/article/view/14320

Current State-of-the-Art Technologies

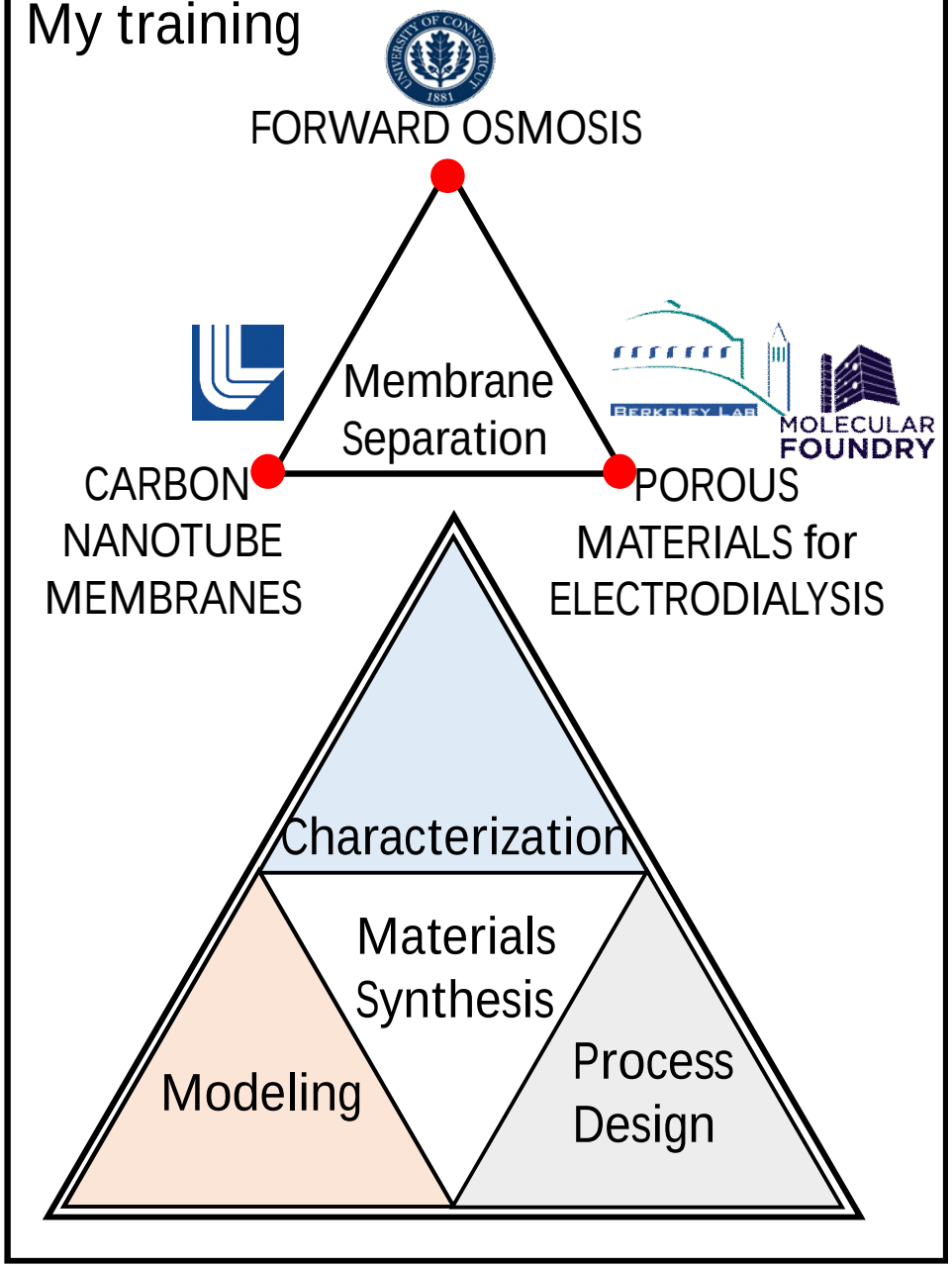
Reverse Osmosis



- Energy-intensive
- Centralized
- Lack of selectivity
- Ineffective in high-concentration ranges

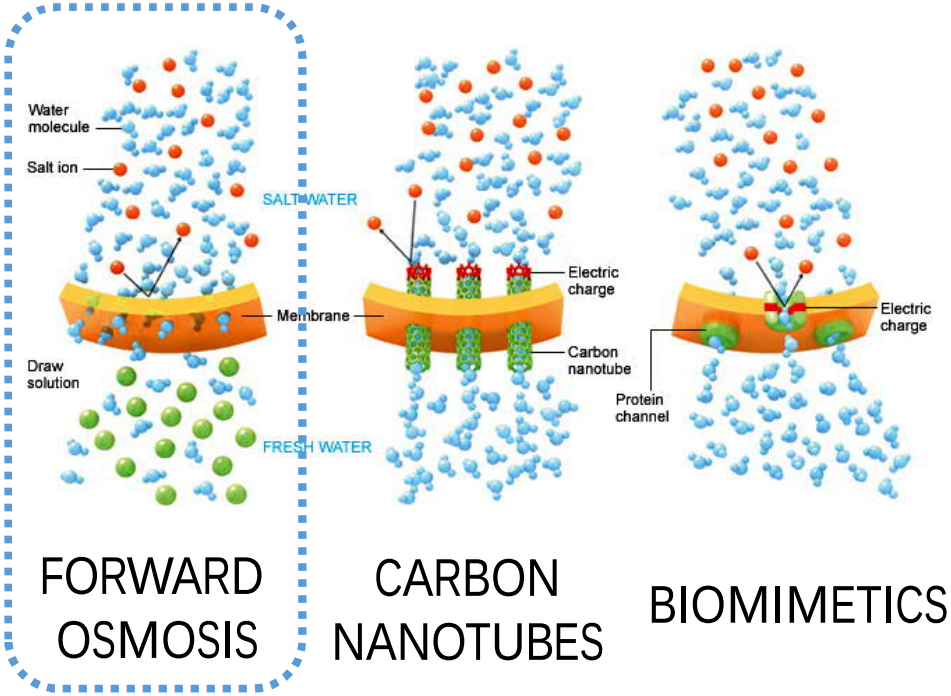
NEEDS - Advanced materials & robust methods for low-energy water remediation

My training



Forward Osmosis

3 technologies promise to reduce energy requirements of desalination by up to 30%



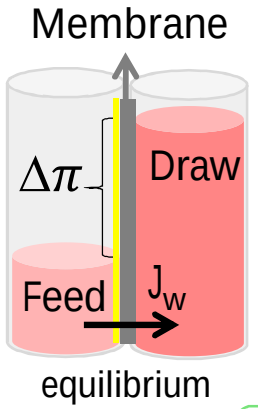
FORWARD OSMOSIS

CARBON NANOTUBES

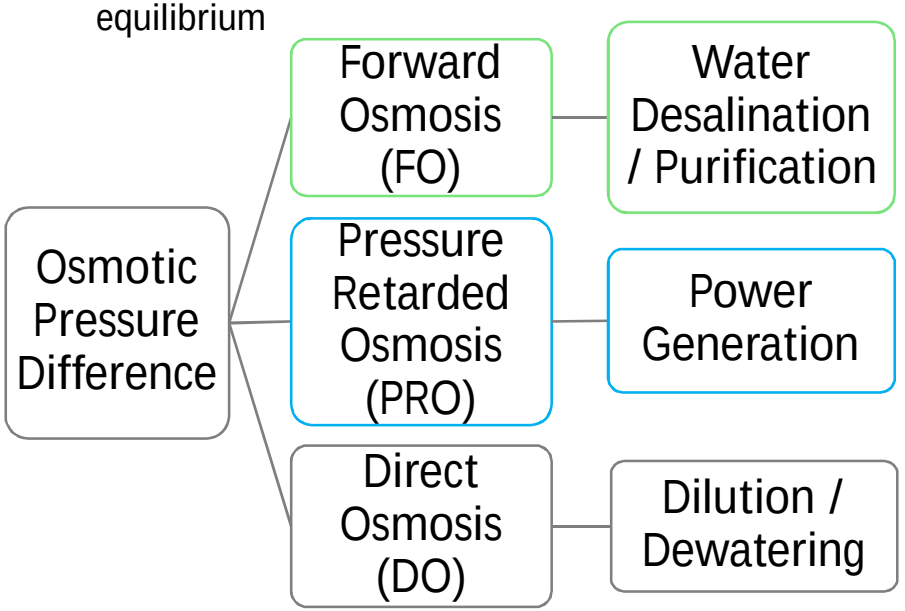
BIOMIMETICS

http://ngm.nationalgeographic.com/big-idea/09/desalination-pg2

Driven by osmotic pressure generated by a salinity gradient created across a semipermeable membrane

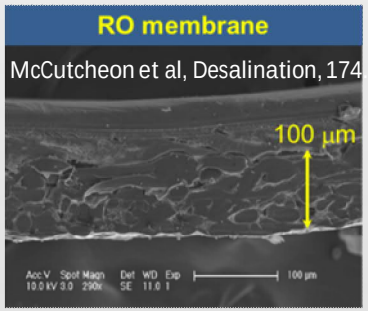


$$J_W = A(\pi_{draw} - \pi_{feed})$$

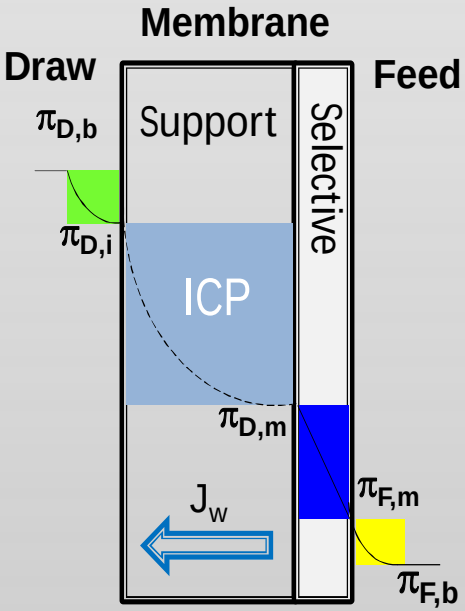


Internal Concentration Polarization (ICP) as a Detrimental Effect in FO

Thick, tortuous support layers of conventional membrane cause ICP, <u>diminishing the effective driving force.</u>



Structural parameter



$$S = \frac{t\tau}{\varepsilon}$$

Thickness, t
Tortuosity, τ
Porosity, ε

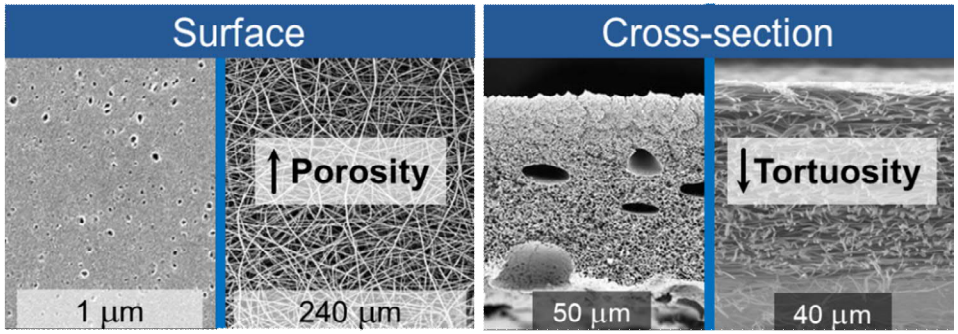
Conventional membranes designed for reverse osmosis no longer suited for FO

Membrane Design Catalyzes FO Advancement beyond Conceptualization

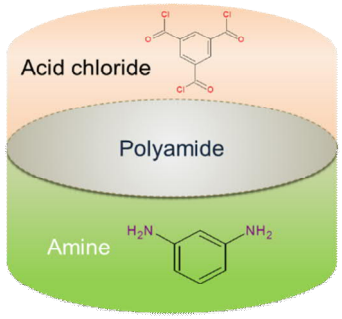
NEED to redesign thin-film composite (TFC) membranes for FO

Redesign FO membranes by Bridging Membrane Science with Nanotechnology

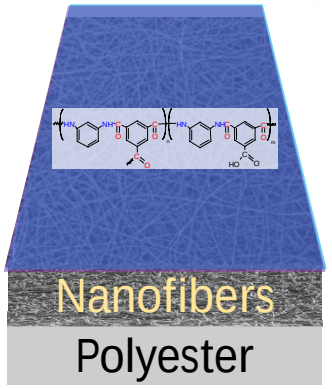
- Electrospun Nanofibrous Supports -



Membrane Synthesis



Polyamide



Membrane Generations

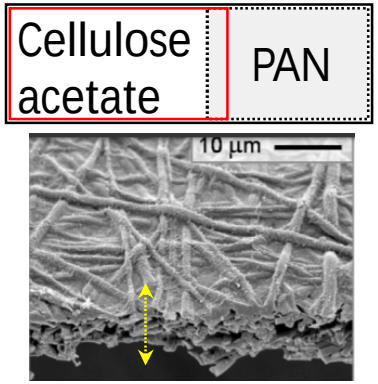
Gen-1

Polysulfone

Bui N., Lind M., Hoek E., McCutcheon J., J. Memb. Sci., V385-386, 2011 and WO 2011/060202 A1

Gen-2

Polymeric blends

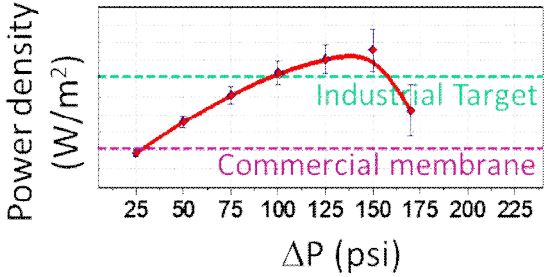


Bui N., McCutcheon J., Envi. Sci. & Tech., V47, 2013.

Gen-3

PRO membrane

$W_{max} = A(\Delta\pi^2/4)$

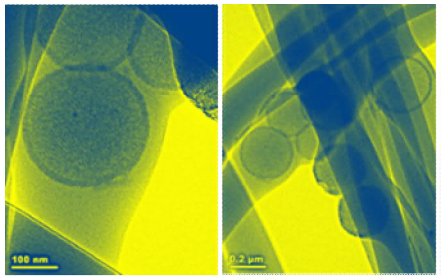


- Fiber diameter
- Crosslinking degree of selective layer

Bui N.N., McCutcheon J.R., Envi. Sci. & Tech., V48, 2014.

Gen-4

Nanocomposite

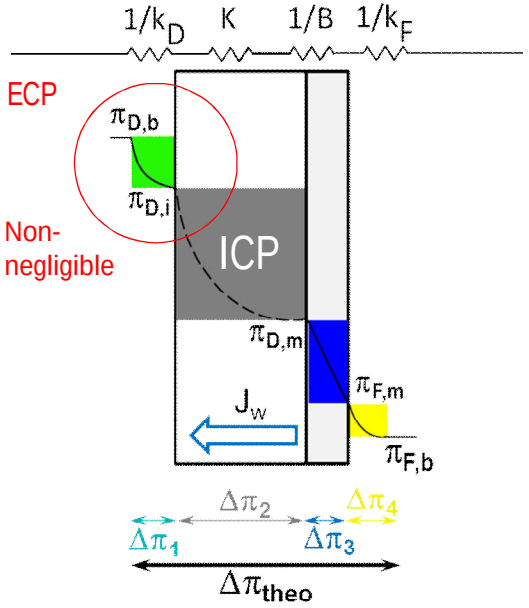


Bui N.*, McCutcheon J., J. Membr. Sci., V518, 2016.

Compared to the HTI commercial FO membranes

- 10x decrease in structural parameter,
- 7x increase in osmotic water permeability, and
- 3.5x increase in water/salt selectivity.

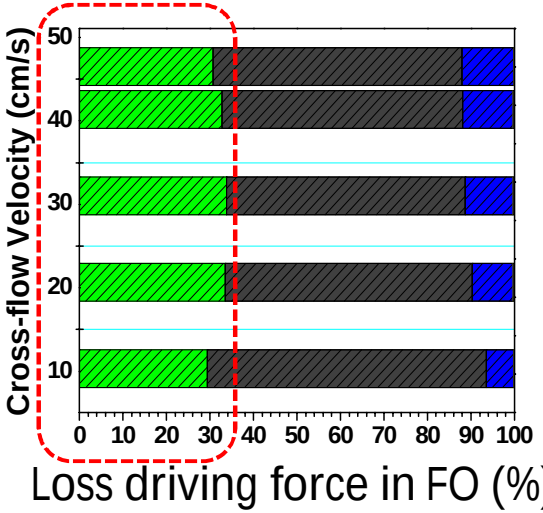
Introduced a Math Flux Model that allows for a deconvolution of all mass transfer resistances present for solute transport during osmosis



Osmotic Water Flux $J_W = A(\pi_{D,m} - \pi_{F,m})$

$$J_w^{FO} = A\left\{\frac{\pi_{D,b}\exp\left[-Jw\left(\frac{1}{k_D}+\frac{S}{D_D}\right)\right]-\pi_{F,b}\exp\left(\frac{J_w}{k_F}\right)}{1+\frac{B}{J_w}\left\{\exp\left(\frac{J_w}{k_F}\right)-\exp\left[-Jw\left(\frac{1}{k_D}+\frac{S}{D_D}\right)\right]\right\}}\right\}$$

Neglecting ECP will result in an inaccurate accounting of the severity of ICP

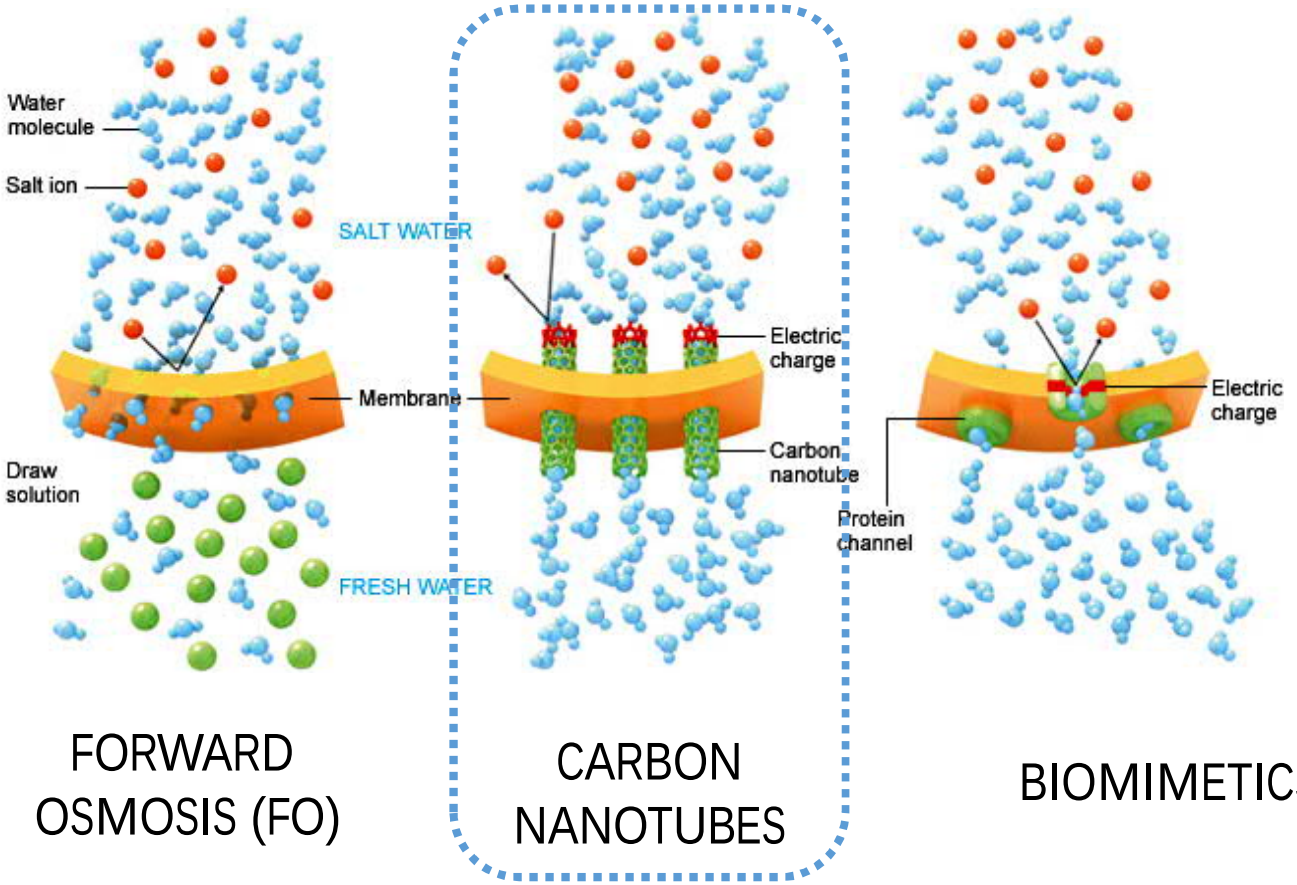


Bui N.N., Arena J., McCutcheon J.R., Journal of Membrane Science, V492, 2015.

This work allows for a more accurate calculation of typical membrane design metrics, such as structural parameter.

Efficient Separation Approaches

http://ngm.nationalgeographic.com/big-idea/09/desalination-pg2



3 technologies promise to reduce energy requirements of desalination by up to 30%

Smart Dynamics Membrane Materials for Breathable and Protective Fabrics

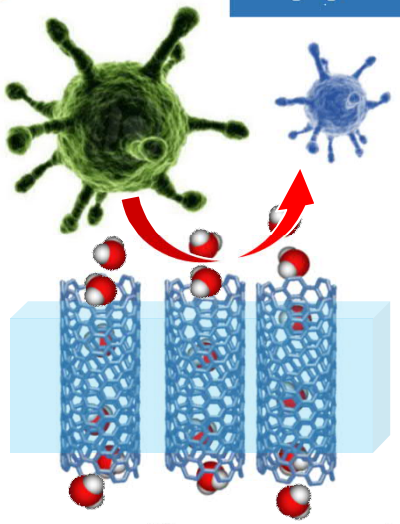
Need

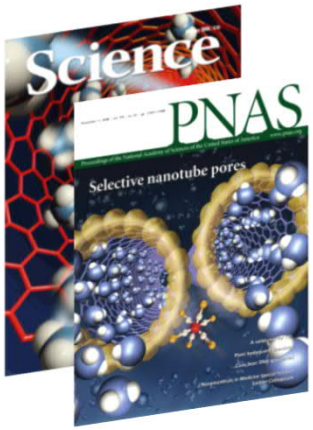
Problem: Conventional protective fabrics block perspiration.

Blueprint for Protective Fabrics

- High breathability (moisture vapor transport rate)
- High protection from toxic chemicals and bio-threats
- Dynamic response to the threats

Approach

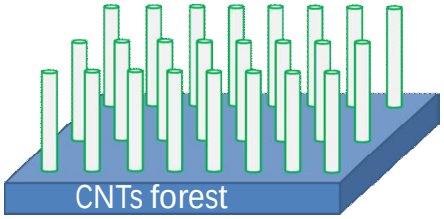




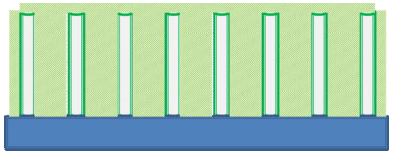
Fast flow = High breathability
Narrow channels = Protection

Sense → Transduce → Response → Function → Refresh

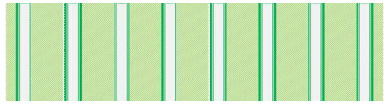
Vertically-aligned Carbon Nanotubes Membranes with Outstanding Breathability and Protection



Polymer infiltration



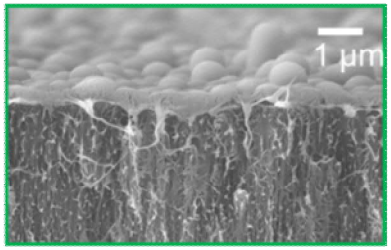
Pore opening



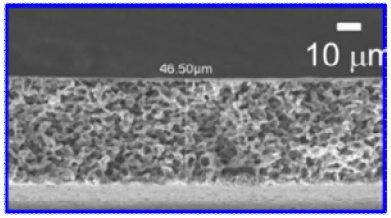
CNT properties:

- Narrow CNTs (2-5 nm wide)
- Good graphitization, high G/D ratio

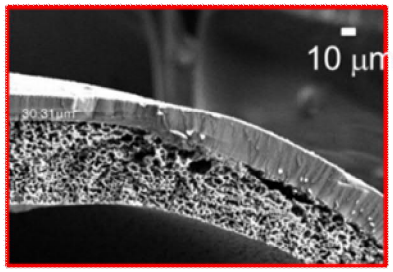
SWNT/PAN

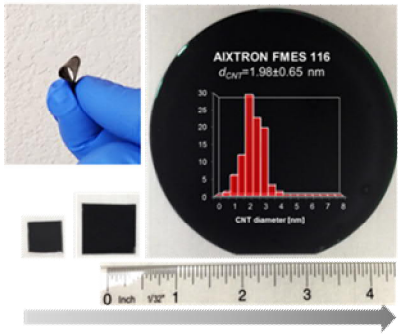


Nylon 6,6

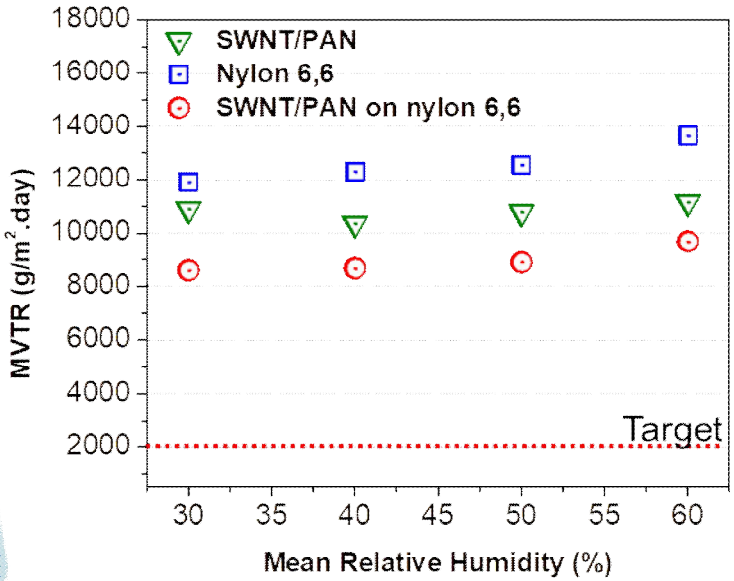


SWNT/PAN on Nylon 6,6

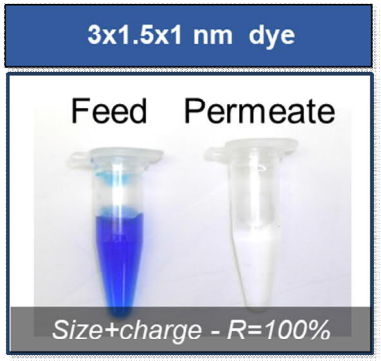




Flexible membrane

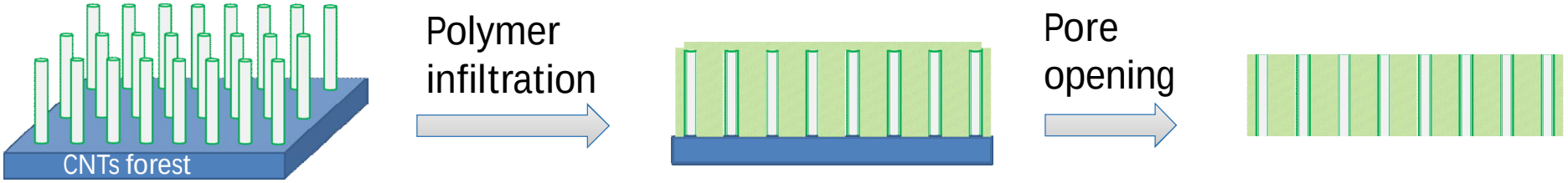


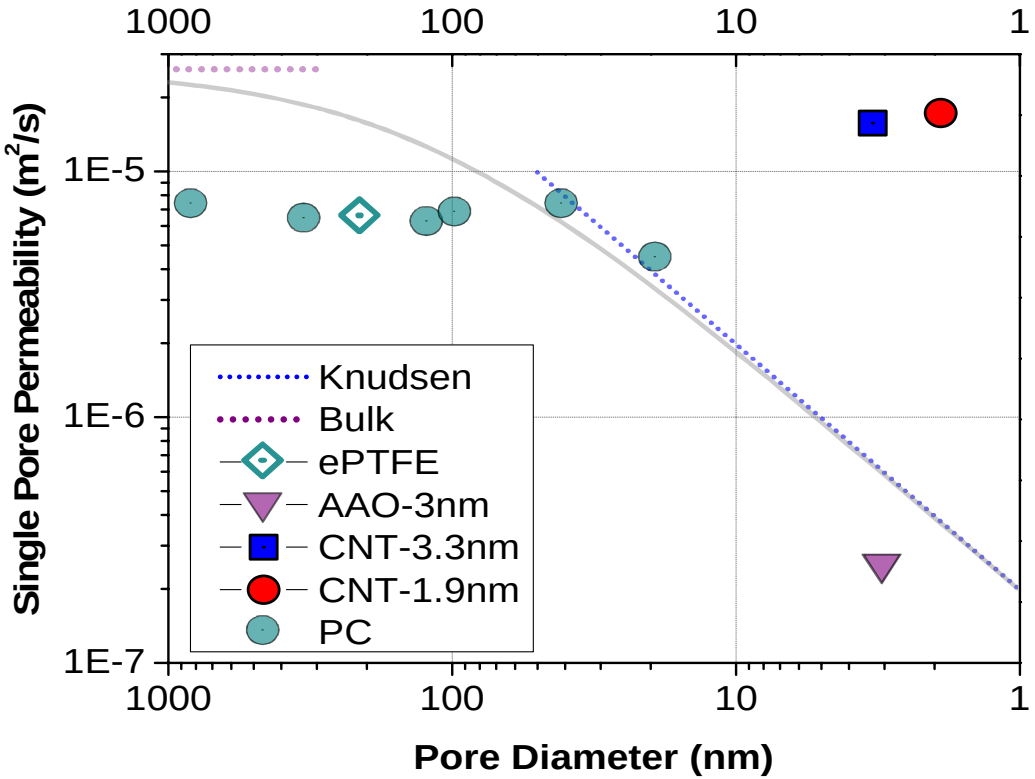
Efficient exclusion of contaminants



Bui, N., Meshot, E., Kim, S., J. Penã, Gibson, P., Wu, K.J., Fornasiero, F., Advanced Materials, V28, 2016.

Vertically-aligned Carbon Nanotubes Membranes with Outstanding Breathability and Protection





First experimental evidence of enhanced gas transport in CNTs driven by concentration gradient.

Bui, N., Meshot, E., Kim, S., J. Penã, Gibson, P., Wu, K.J., Fornasiero, F., Advanced Materials, V28, 2016.

Selective Ion Capture

Energy Sciences Area

MOLECULAR FOUNDRY

ENERGY TECHNOLOGIES AREA

MOTIVATION:

Develop low-energy means to separate crucial ions of interest from water using new classes of ion-selective polymers. Ion-selective electrodialysis enables concentration of ions for energy applications or catalysis while also purifying water for re-use.

Undifferentiated solid waste product

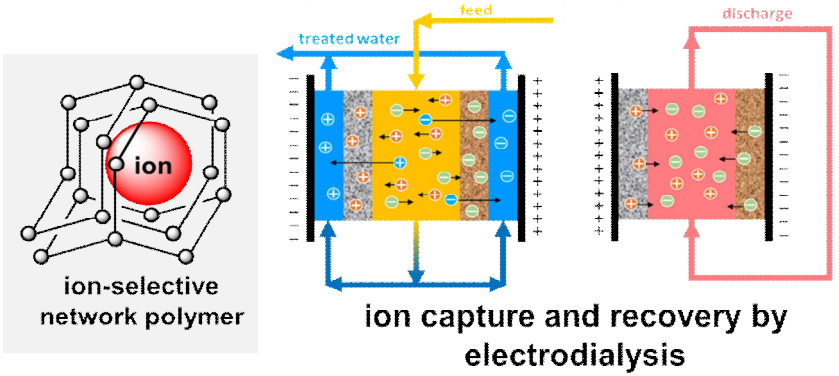
Lack of selective ions adsorbent

https://www.hydrofinity.com

NEED

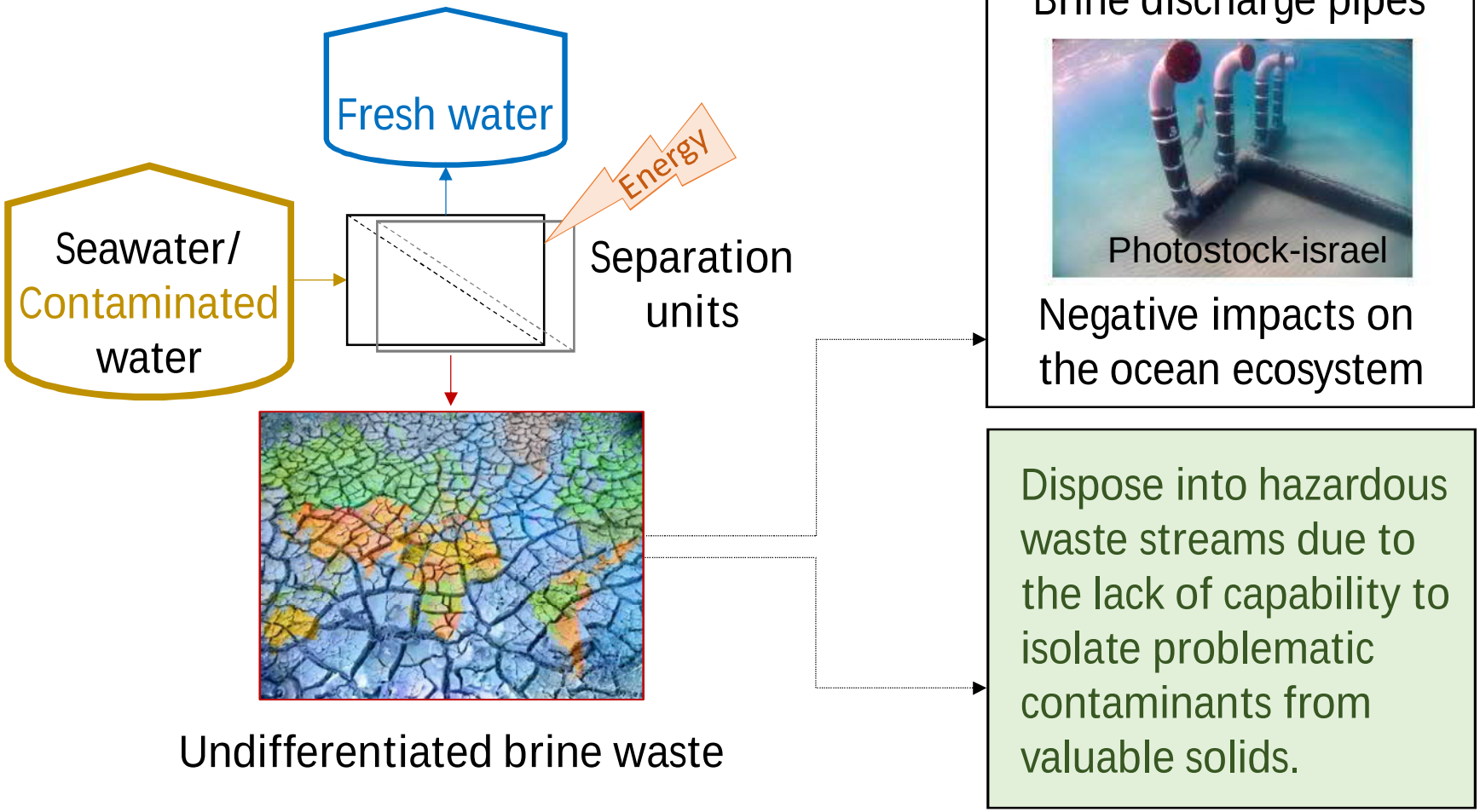
A resilient platform that is tunable to specific elements (e.g. radionuclides) and toxic species

APPROACH Ion-Selective Membranes



Porous materials

Energy-efficient Chemoselective Separations are Critical to Avoid Costly Brine Disposal



https://www.hydrofinity.com

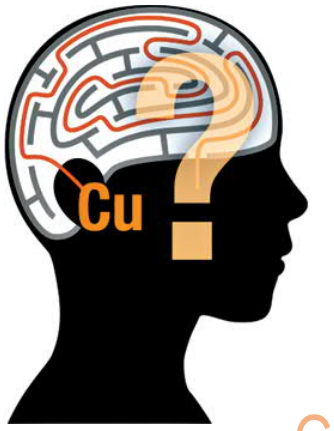
Some Key Target Cations and Anions

	Water Purification	Ion Recovery	
Radioactive Elements	Environmental Cs^+ I^- Nuclear Waste Actinides, radionuclides	Li^+, Rb^+	Alkali metals for energy applications
Toxic Species	Cd^{2+}, Hg^+, Pb^{2+} Borates, Arsenates, Chromates	Rh^{3+}, Pd^{2+}, Pt^{2+}, Au^+	Precious metals for catalysis
Desalination	Na^+ Cl^-		

Key
= cations
= anions

Copper, an Unwelcome Guest in Waste Brine

OTCs Today
https://www.pharmacist.com



Copper promotes neurological function by playing a role in antioxidant defense and neurotransmitter synthesis.

Copper deficiency

Impact

- Growth
- Neurodevelopment
- Immune system
- Connective tissue structures

Copper excess

Damage

- Nervous system
- Organs (liver, kidney) function

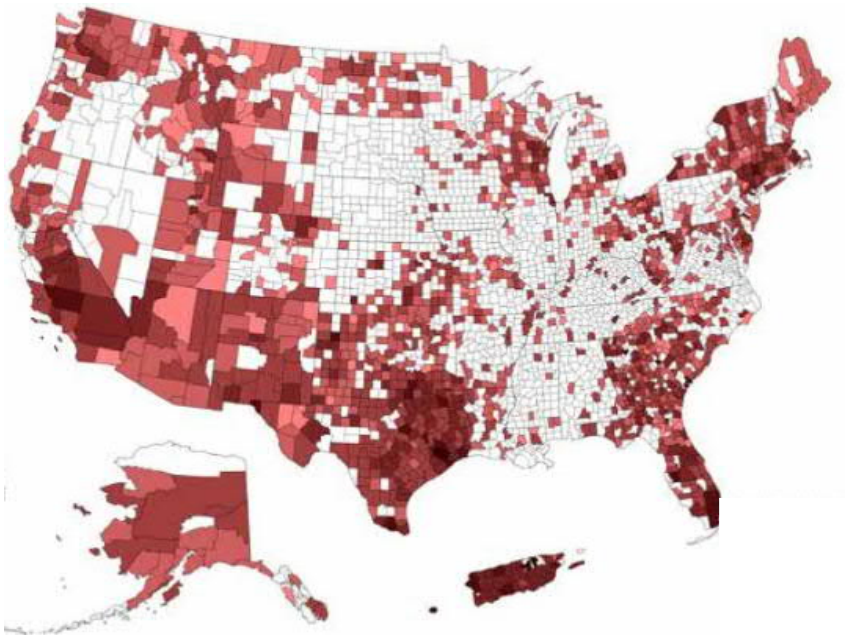
May lead to death

Wilson Disease: Pathogenesis, Molecular Mechanisms, Diagnosis, Treatment and Monitoring, Chapter 2: “Normal Human Copper Metabolism”, Zeid and Kaler 2019

Copper, an Unwelcome Guest in Waste Brine

OTCs Today
https://www.pharmacist.com

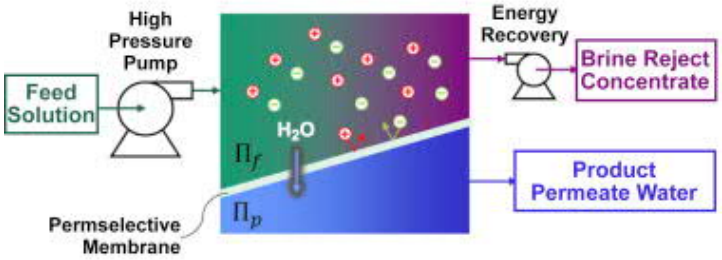
Number of people served where lead and copper levels exceed EPA guidelines



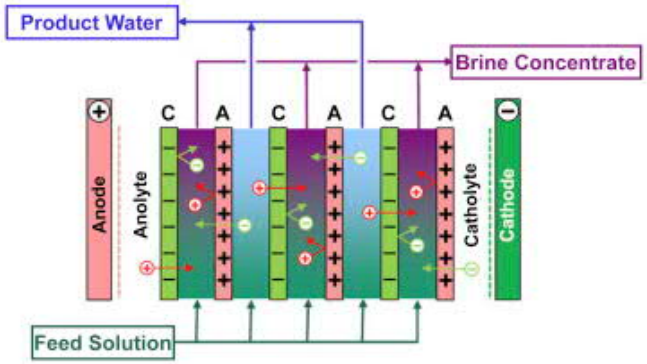
100 OR LESS	101 - 1,000	1,001 - 10,000	10,001 - 100,000	100,001 OR MORE

Current Separation Technologies are Lack of Specificity

Reverse osmosis (RO)



Electrodialysis (ED)



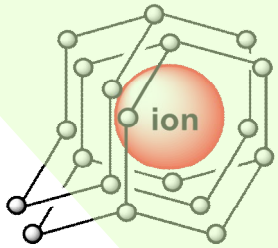
- Broad-spectrum separation
- Resin-based
- Optimized only for trivial ions, e.g. Na^+, Cl^-, etc.
- Requires several cycles to remove contaminants such as Boron, Arsenic, etc.
- Energy-intensive

NEED
Resilient materials that are tunable to specific toxic species

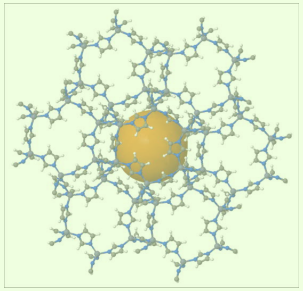
No "champion" material to remove Cu^{2+} fast, selective, & at large scale

Urban, J.J., Joule, 2017, 665-688

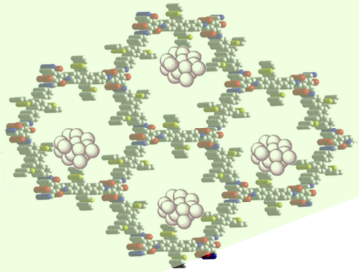
Advanced Porous Materials



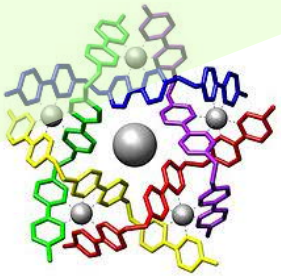
ion-selective
network polymer



MOF



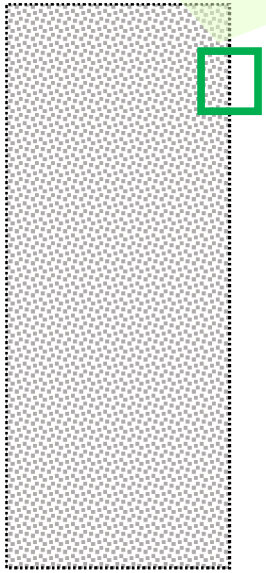
COF



SCC

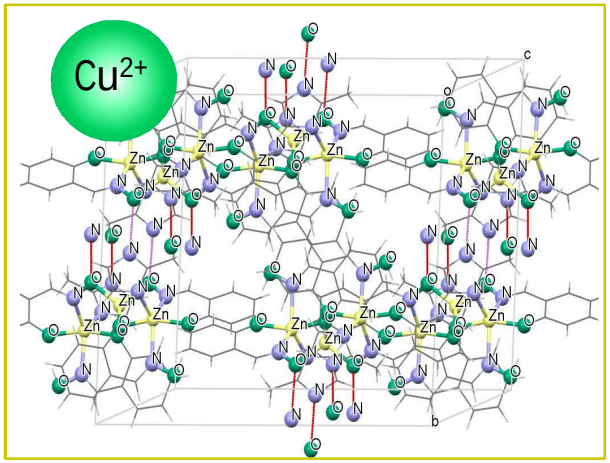
@ Jeff Long group /UCB

@ Molecular Foundry/Jeff Urban



Mixed-matrix membrane

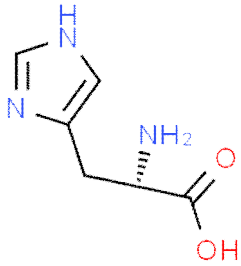
- Stable in water
- Reproducible
- Selective
- Scalable
- Low cost



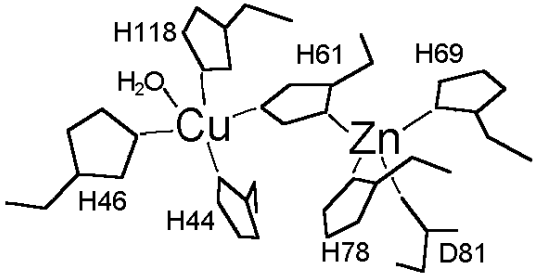
Supramolecular Coordinating Complex (SCC)

J. Am. Chem. Soc. 2017, 139, 17082–17088

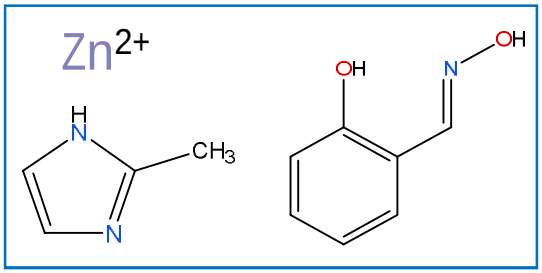
A New H-bonded Supramolecular Coordination Complex was Synthesized for Copper (II) Ions Removal



Histidine (H)



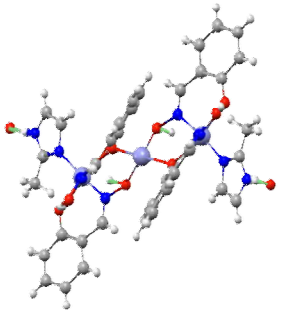
Zn-Cu Superoxide dismutase



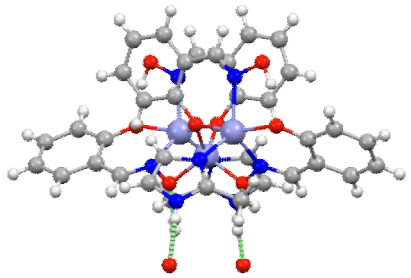
Building blocks for the new material

Zinc-based Imidazole Oxime Supramolecule (ZIOS)

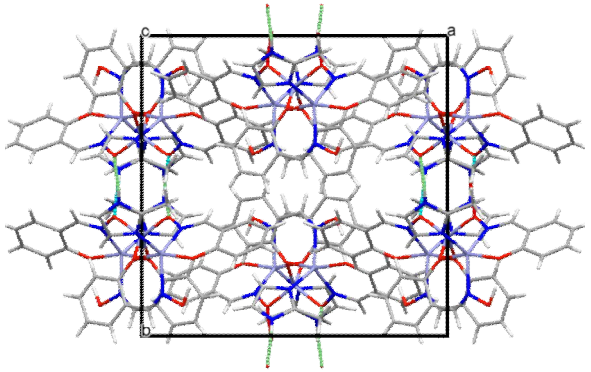
View along b-axis

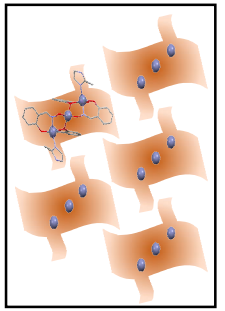


View along c-axis



Stacked 2D material

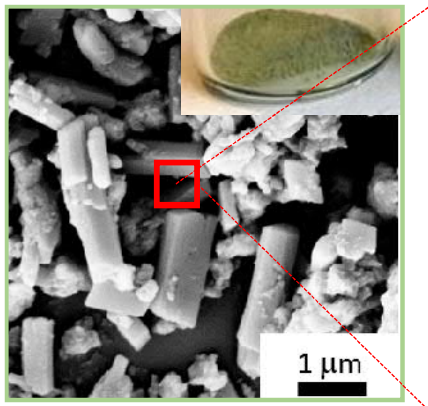




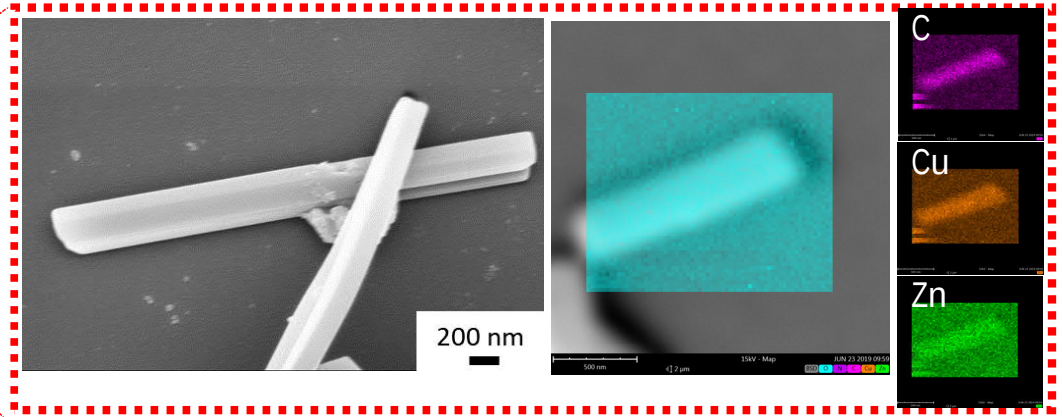
Lattice Expansion and Contraction are Observed when Water Molecules were Introduced into ZIOS Frameworks

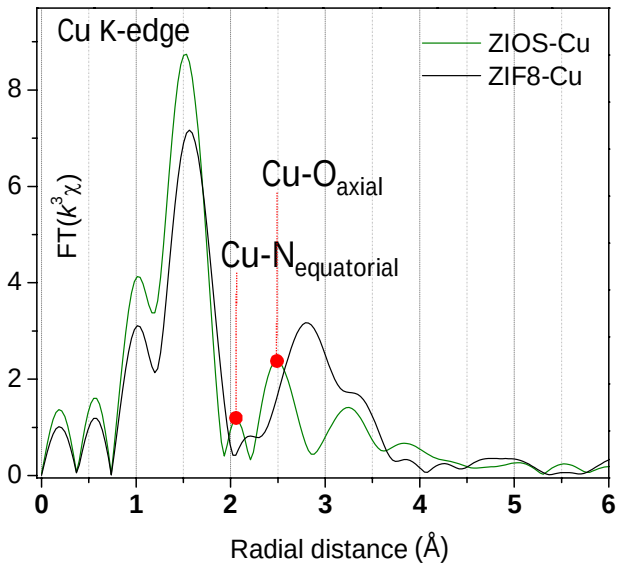
Bui, N., Urban J. et al, under review.

ZIOS Offers Unprecedented Fast Cu^{2+} Adsorption Kinetics



ZIOS → Cu^{2+}-adsorbed ZIOS

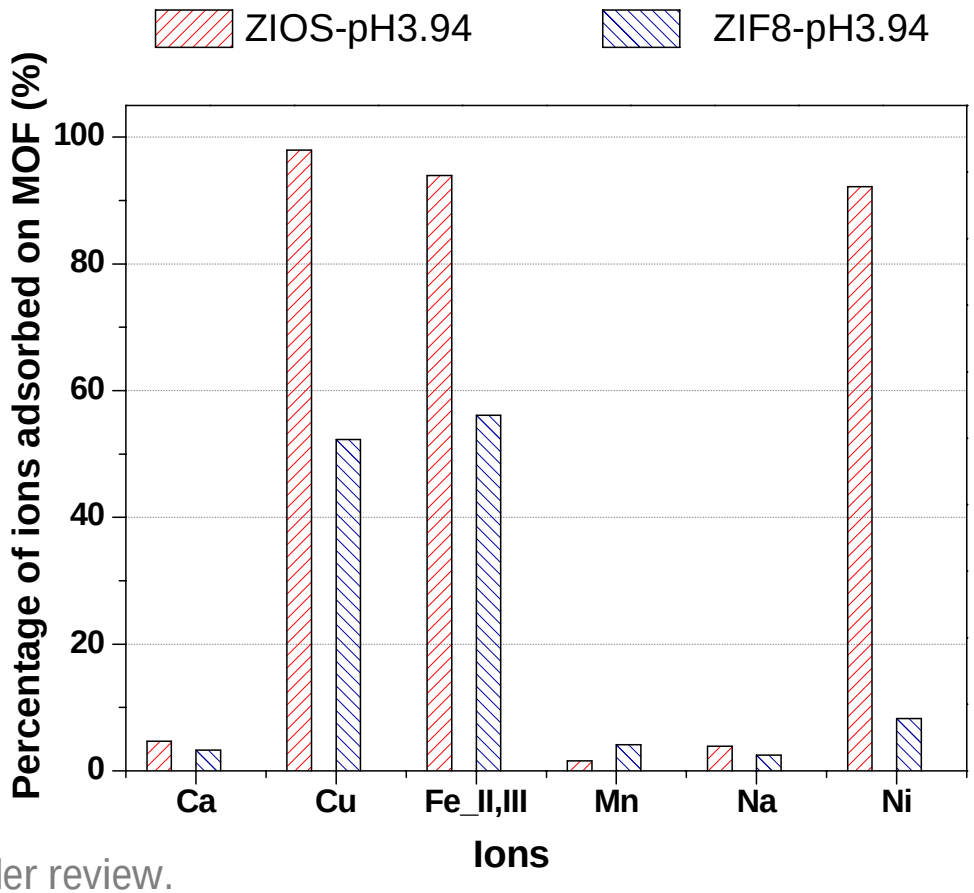




Bui, N., Urban J. et al, under review.

Materials	k_2 (mg/mg.min)
ZIF8 *(this study)	3.4 ± 1.6 (x)
Zeolite, biomass-derived adsorbents	≤ x
Silica-based polymers	≤ x
PAF-1-SMe*	5.2 (~ x)
Metal sulfide ion exchangers	5.8 – 23.9 (x – 7x)
Ca-MOF*	32 ± 5 (9x)
ZIOS (this study)	155.3 ± 26.5 (46x)

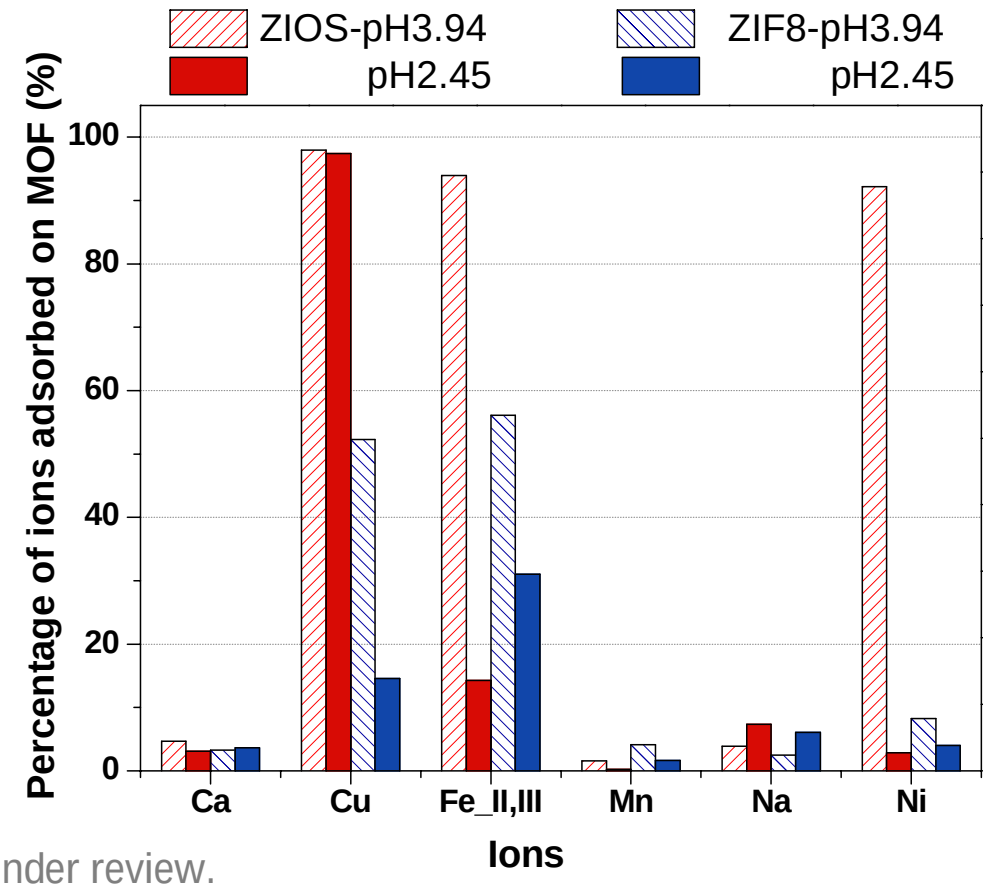
ZIOS Selectively Removed Cu^{2+} at pH < 3



Bui, N., Urban J. et al, under review.

- ZIOS successfully scavenged Cu^{2+} in the presence of competing ions.
- ZIOS performed a high K_d (distribution coefficient), showing the effectiveness of ZIOS at scavenging Cu^{2+} from the aqueous solution and the selectivity of the ZIOS adsorbents for Cu^{2+}.

ZIOS Selectively Removed Cu^{2+} at pH < 3



Bui, N., Urban J. et al, under review.

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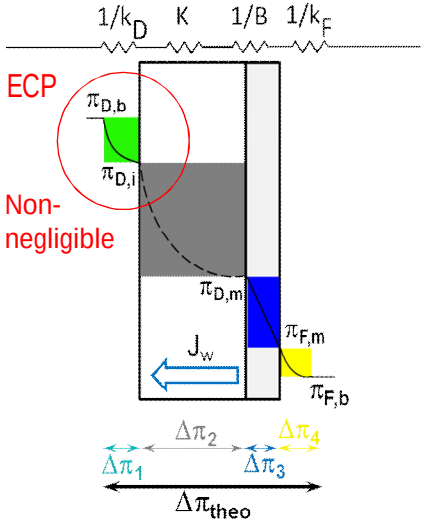
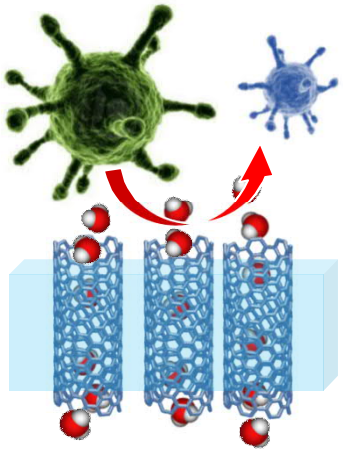
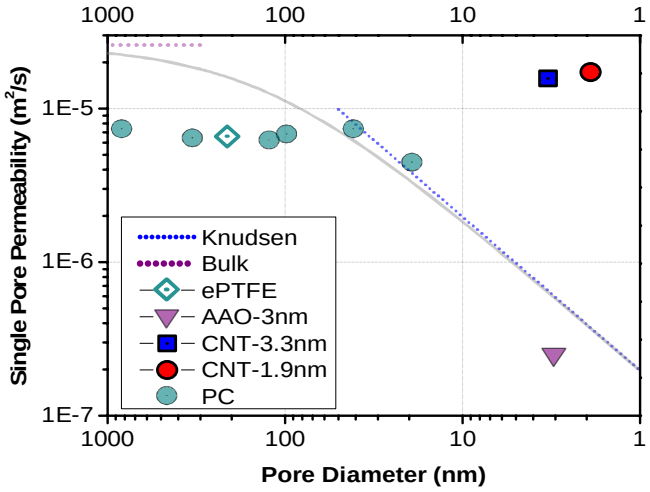
Concluding Remarks

FORWARD OSMOSIS MEMBRANES

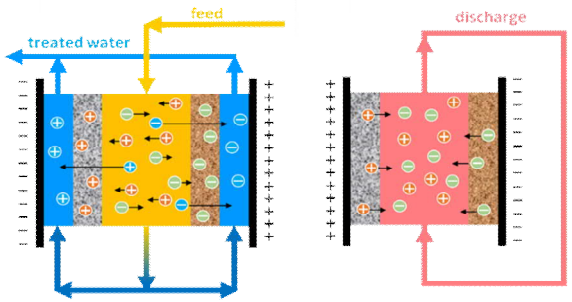


CARBON NANOTUBE MEMBRANES

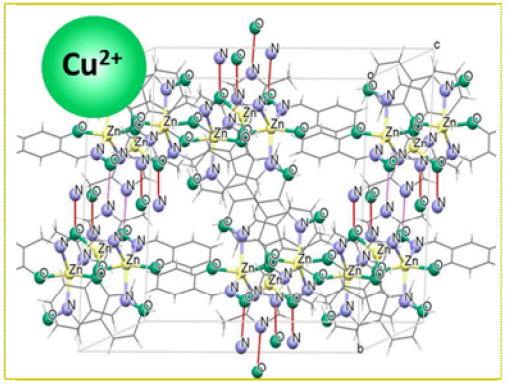




ADVANCED ELECTRODIALYSIS MEMBRANES



ion capture and recovery by electrodialysis



Supramolecular Coordinating Complex (SCC)