Nanoporous Membranes With In Situ Synthesized Polymeric Particles: Preparation, Characterization and Applications to Sustainable Chemistry, Engineering and Materials (SusChEM)

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11th Korea US Forum on Nanotechnology
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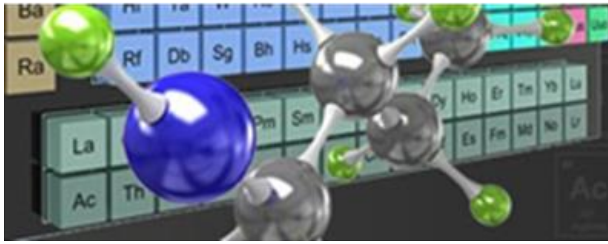
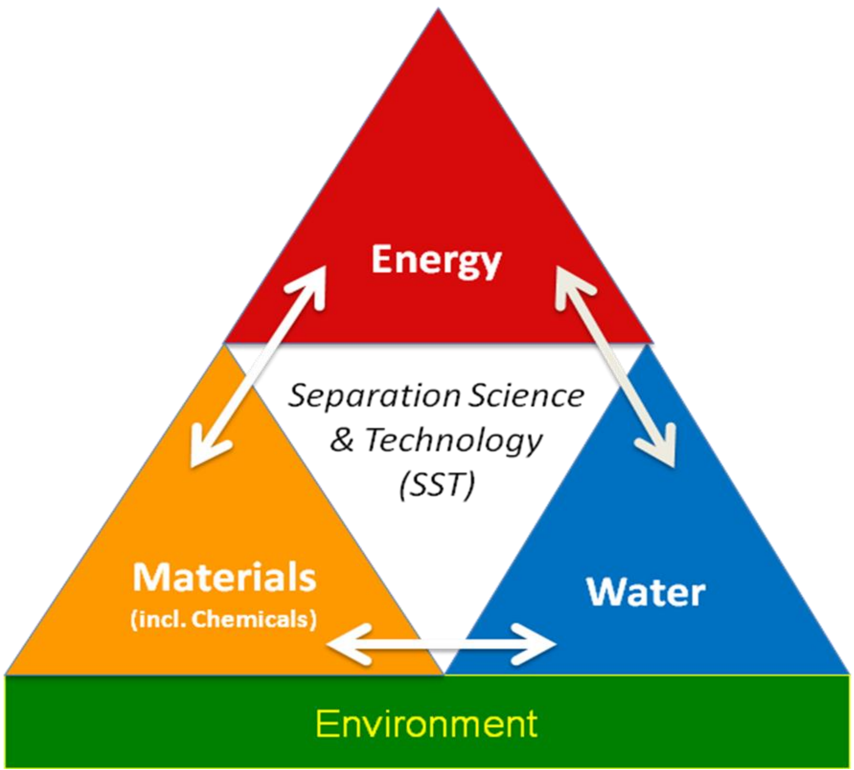


Separation Science and Technology (SST) as a Convergence Platform for *SusChEM, Sustainable Chemistry, Engineering and Materials*

Mamadou Diallo as Co-Chair of an ACS Presidential Symposium (August 12-13, San Francisco, 2014: NSF CBET Funding)

Separation Science and Technology (SST) for Sustainable Chemistry, Engineering and Materials (SusChEM)



Separation S&T Platform

Separation Processes

Separation Materials

Separation Systems

Integral Element

Reclaiming and Maintaining

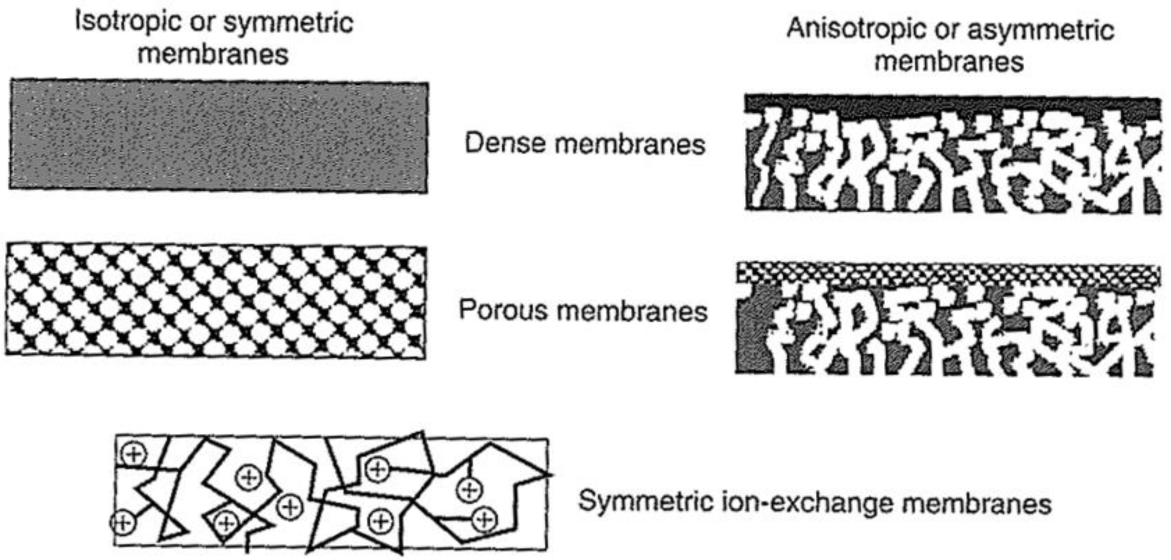
The Environment

Membrane Technology for SusChEM

- **Polymeric membranes are critical for a broad range of sustainability related applications including**
  - **Energy conversion and storage**
  - **Water treatment, reuse and desalination**
  - **Gas separations**
  - **Biofuel processing**
  - **Metal and resource recovery**
  - **Biochemical separations and purifications**

Current Polymeric Membranes

- **Current commercial polymeric membranes perform a single function such as**
  - **Salt rejection in desalination using a dense and composite membrane**
  - **Particle rejection in algae separations and harvesting using a porous and low-pressure membrane**
  - **Proton transfer in fuel cells by a cation-exchange membrane**



Multifunctional Polymeric Membranes

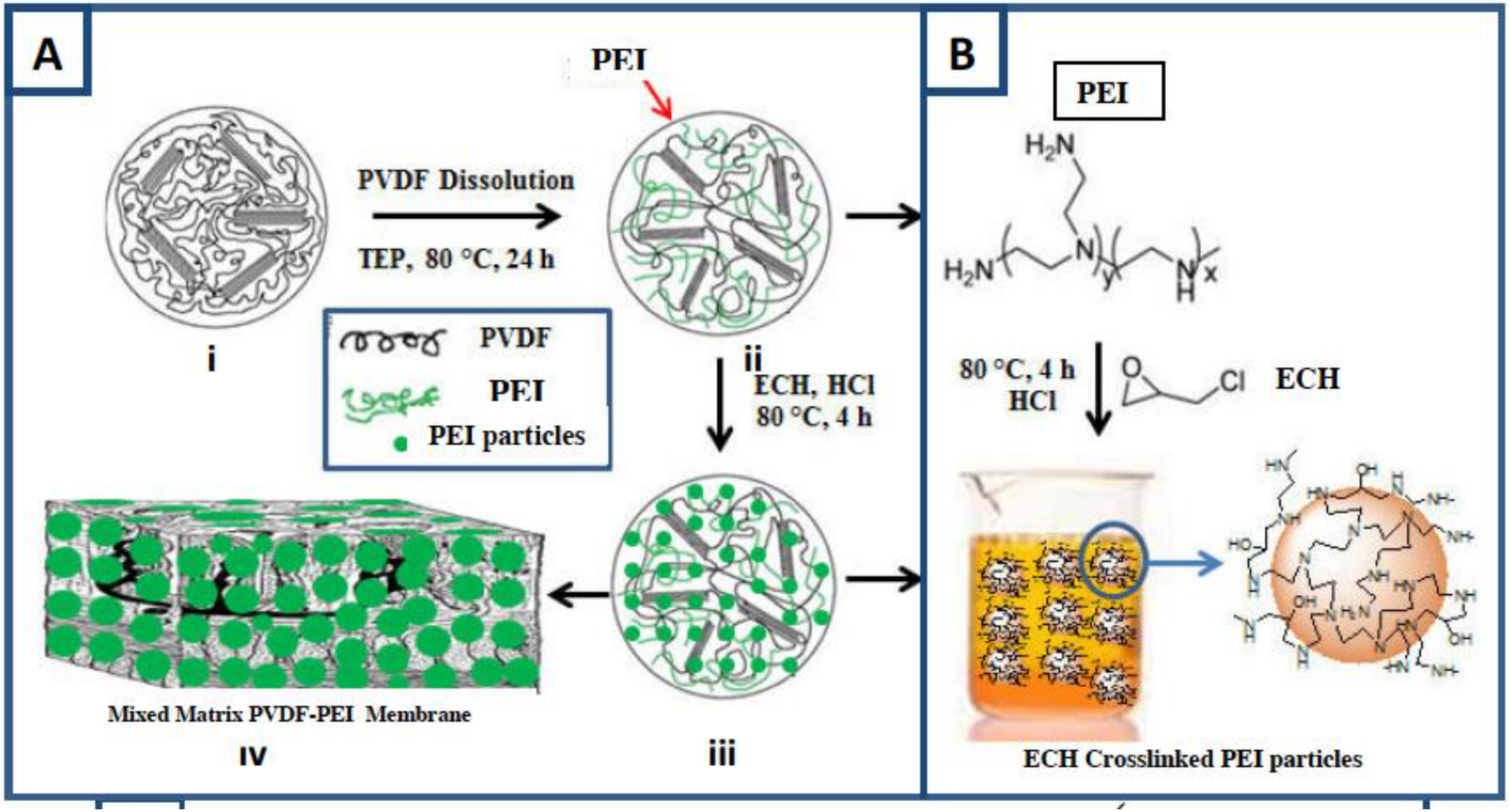
- **Membrane technology is moving towards advanced membranes that perform multiple functions with improved flux and fouling resistance including:**
  - **Solute rejection**
  - **Sorption**
  - **Catalysis**
  - **Charge transport**

Next Generation Polymeric Membranes: Mixed Matrix Membranes With Embedded Nanomaterials

- **Convergence of membrane technology and nanotechnology to prepare mixed matrix membranes (MMMs) with embedded nanomaterials**

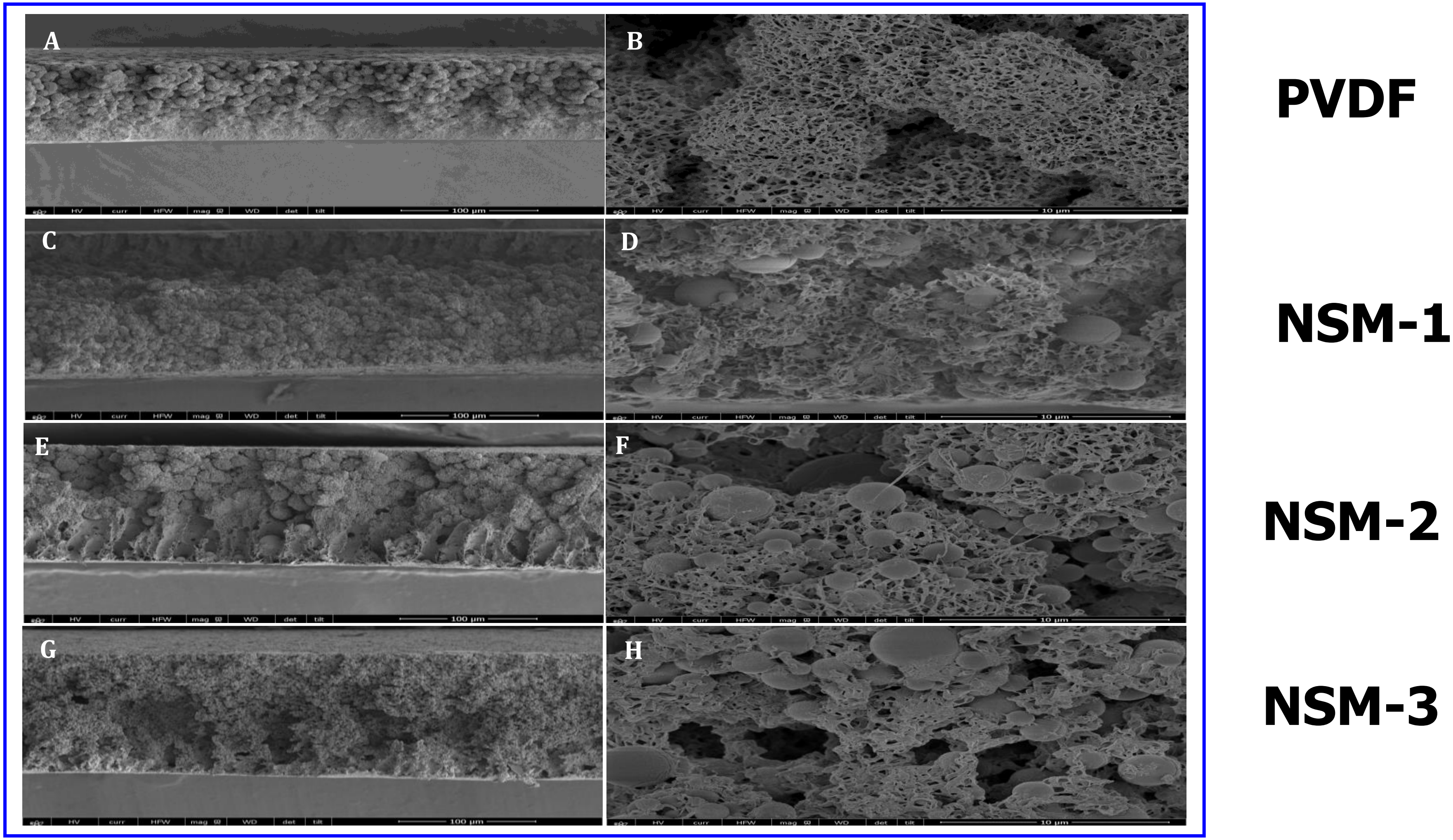
  - Carbon nanotubes
  - Graphene
  - Zeolites
  - Metal oxide nanoparticles
  - Metal organic frameworks
  - **Dendritic macromolecules (Our Group)**
  - **Polymeric nanoparticles (Our Group)**

Example 1: MMMs With In-Situ Generated Polyethyleneimine (PEI) Particles as Weak-Base Membrane Absorbers



Kotte, M. R., Cho, M. and Diallo, M. S. A Facile Route to the Preparation of Mixed Matrix Polyvinylidene Fluoride Membranes with *In-Situ* Generated Polyethyleneimine Particles. *J. Mem. Sci* **.2014**, 450, 93-102.

SEM Images of MMMs With In-Situ Generated PEI Particles



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Composition of MMMs With In-Situ Generated Polyethyleneimine (PEI) Particles

Membrane Composition	NSM-1		NSM-2		NSM-3		PVDF (Neat)	
	Wt , g	Wt, %	Wt, g	Wt, %	Wt, g	Wt, %	Wt, g	Wt, %
PVDF	5.25	**73.32**	5.25	**62.16**	5.25	**52.27**	5.25	**100**
[a] PEI Particles	1.91	**26.68**	3.196	**37.84**	4.794	**47.73**	--	--

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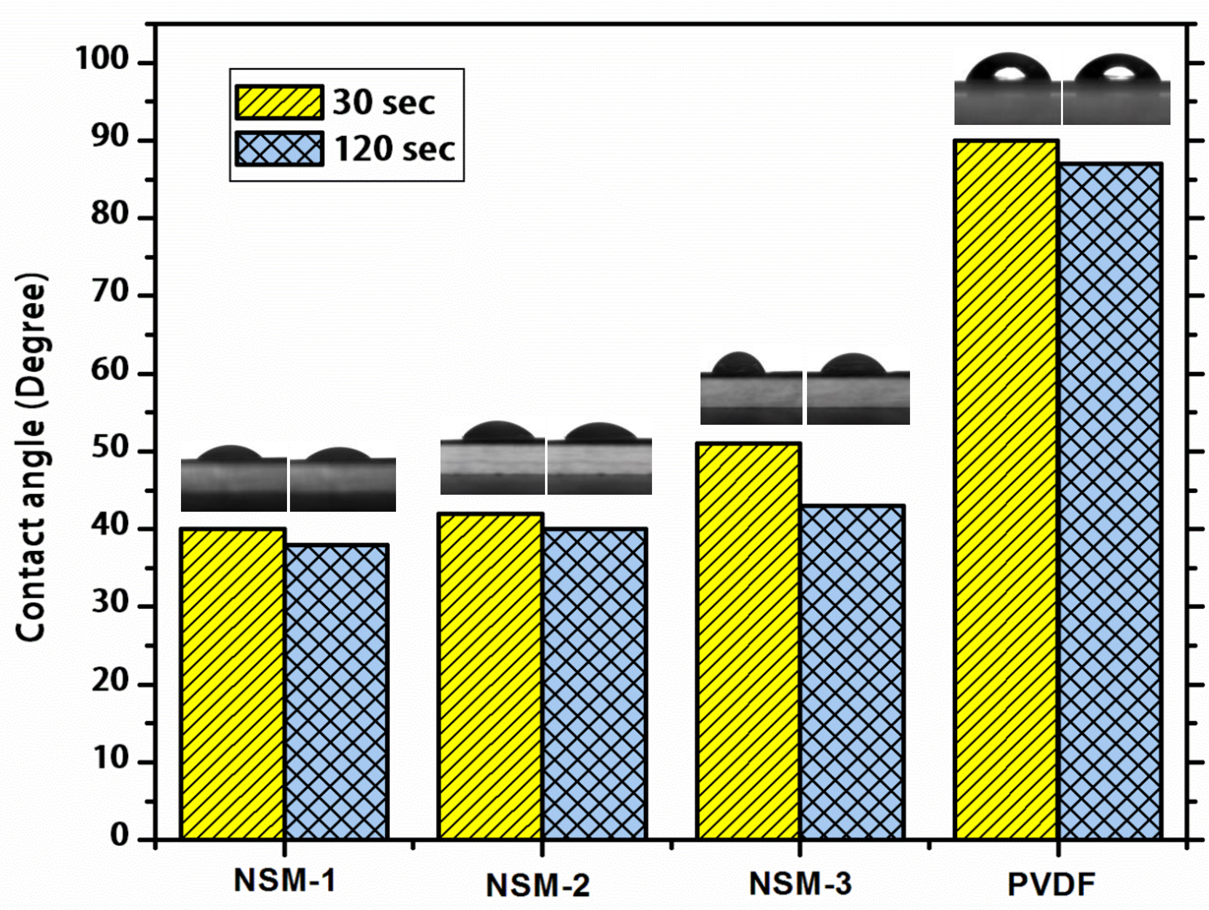
Surface Compositions of MMMs With *In-Situ* Generated PEI Particles As Determined by XPS

Membrane Sample	Concentration (wt%)			
	C	**F**	**O**	**N**
PVDF	51.71	48.29	---	---
NSM-1	53.93	38.2	6.85	1.02
NSM-2	54.46	36.01	8.25	1.28
NSM-3	57.37	28.41	12.38	1.84

Kotte, M. R., Cho, M. and Diallo, M. S. A Facile Route to the Preparation of Mixed Matrix Polyvinylidene Fluoride Membranes with *In-Situ* Generated Polyethyleneimine Particles. *J. Mem. Sci* **.2014**, 450, 93-102.

Contact Angles of MMMs With In-Situ Generated PEI Particles



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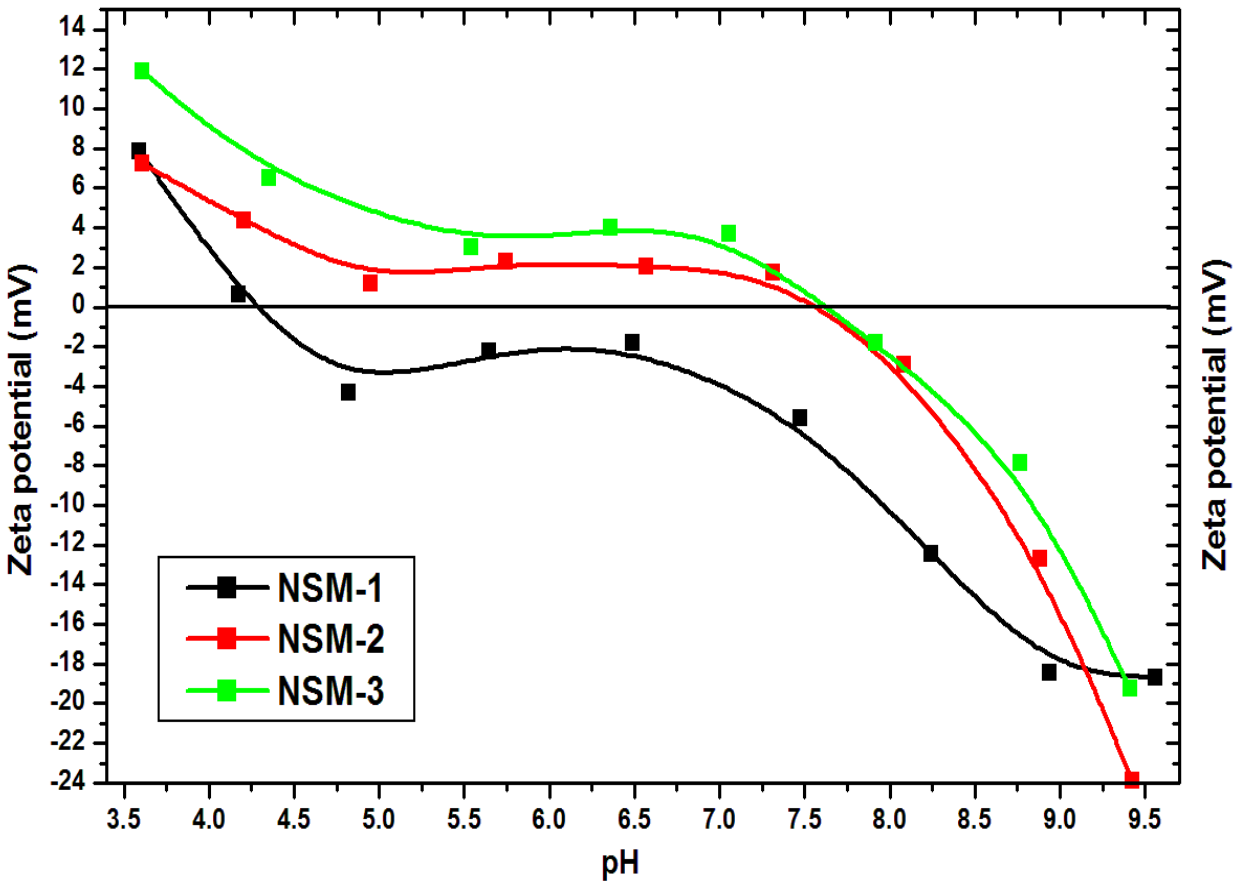
Zeta Potentials of MMMs With In-Situ Generated PEI Particles



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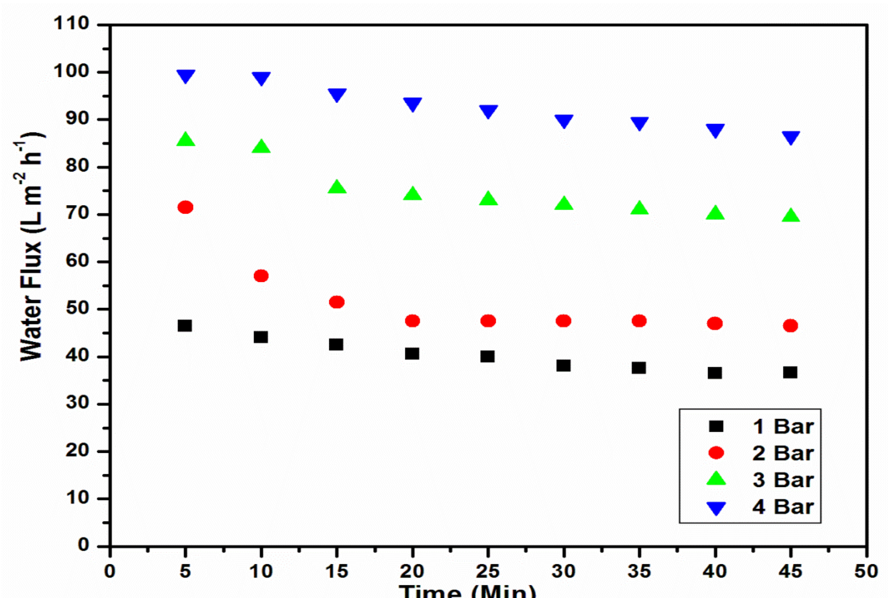
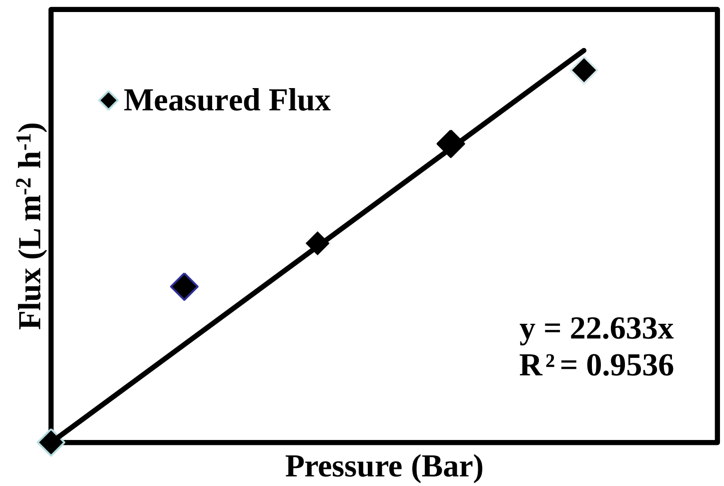
Water Permeability of the NSM-2 Membrane With In-Situ Generated PEI Particles





Water permeability of the NSM-2 membrane is equal to ~23 Liters/m^2/hr/bar.

Water permeability of an ultrafiltration (UF) membrane typically varies from 50 to 800 Liters/m^2/hr/bar.

NSM-2 membrane behaves as a "tight" UF membrane

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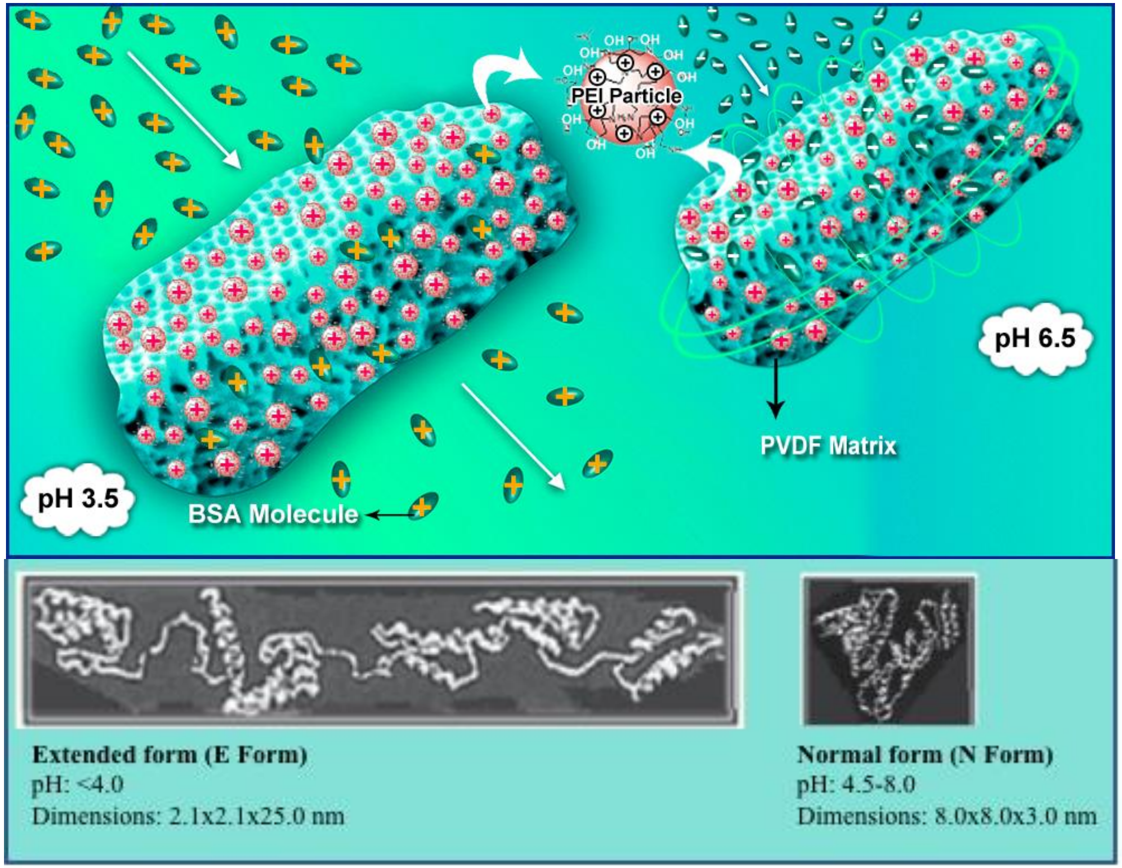
MMMs With In-Situ Generated PEI Particles as Weak-Base Membrane Absorbers

BSA: Bovine Serum Albumin Protein (1000 mg/L)



NSM-2 UF Membrane

Pressure = 1 bar

Particle loading: 38 wt%

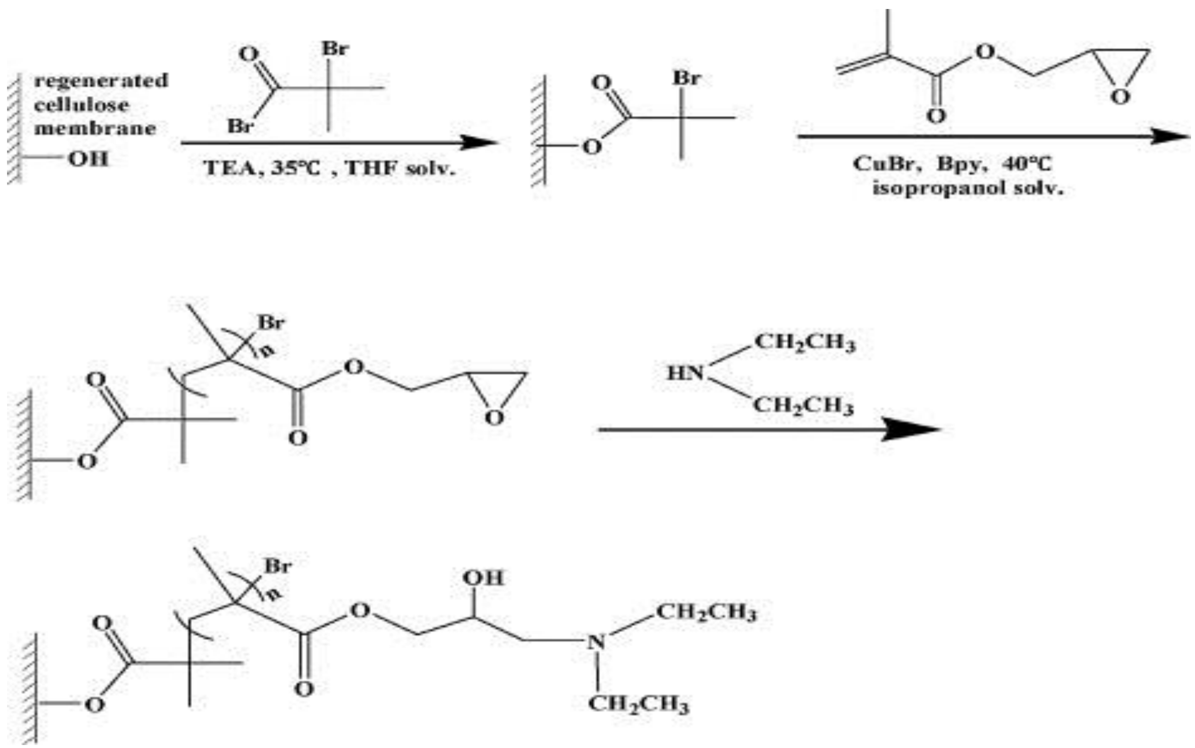
BSA rejection: 90%

BSA binding capacity; 105 mg of protein per mL of membrane at pH 6.5

Kotte, M. R., Cho, M. and Diallo, M. S. A Facile Route to the Preparation of Mixed Matrix Polyvinylidene Fluoride Membranes with In-Situ Generated Polyethyleneimine Particles. J. Mem. Sci ***.2014****, 450, 93-102.*

Other Reported Preparation Routes for Weak-Base Membrane Absorbers

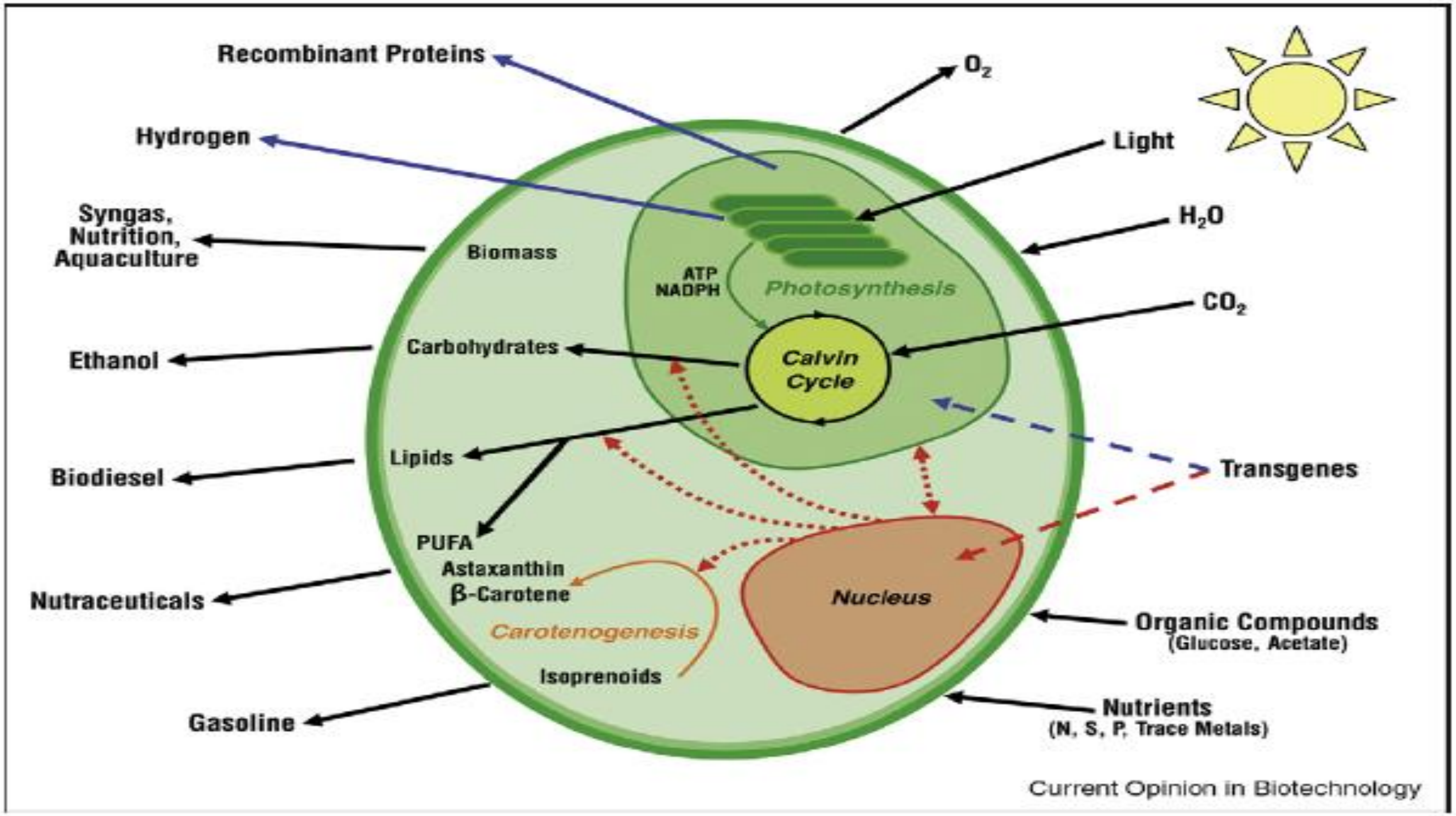
Surface-initiated atom transfer radical polymerization



BSA binding capacity: 96 mg of protein per mL of membrane in PBS buffer (pH ~7)

Qian et al. *Appl. Surf. Sci*. 271, **2013**, 176–183

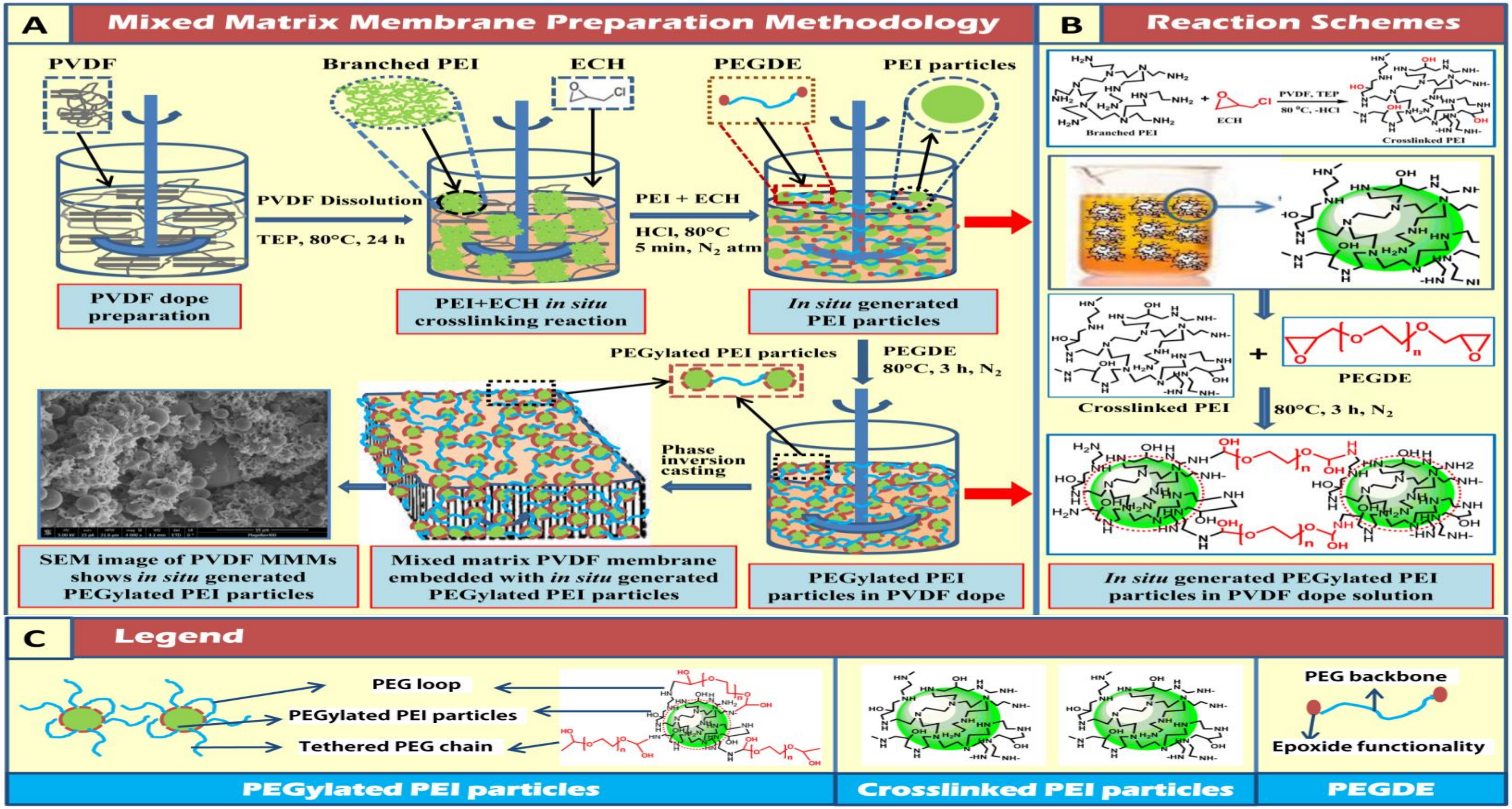
Example 2: Microalgae Biotechnology as Platform for a Sustainable Energy, Water, Materials and Food Nexus



Rosenberg, J.N., Oyler, G.A., Wilkinson, L., Betenbaugh, M.J., 2008. Curr. Opin. Biotechnol. 19, 430-436.

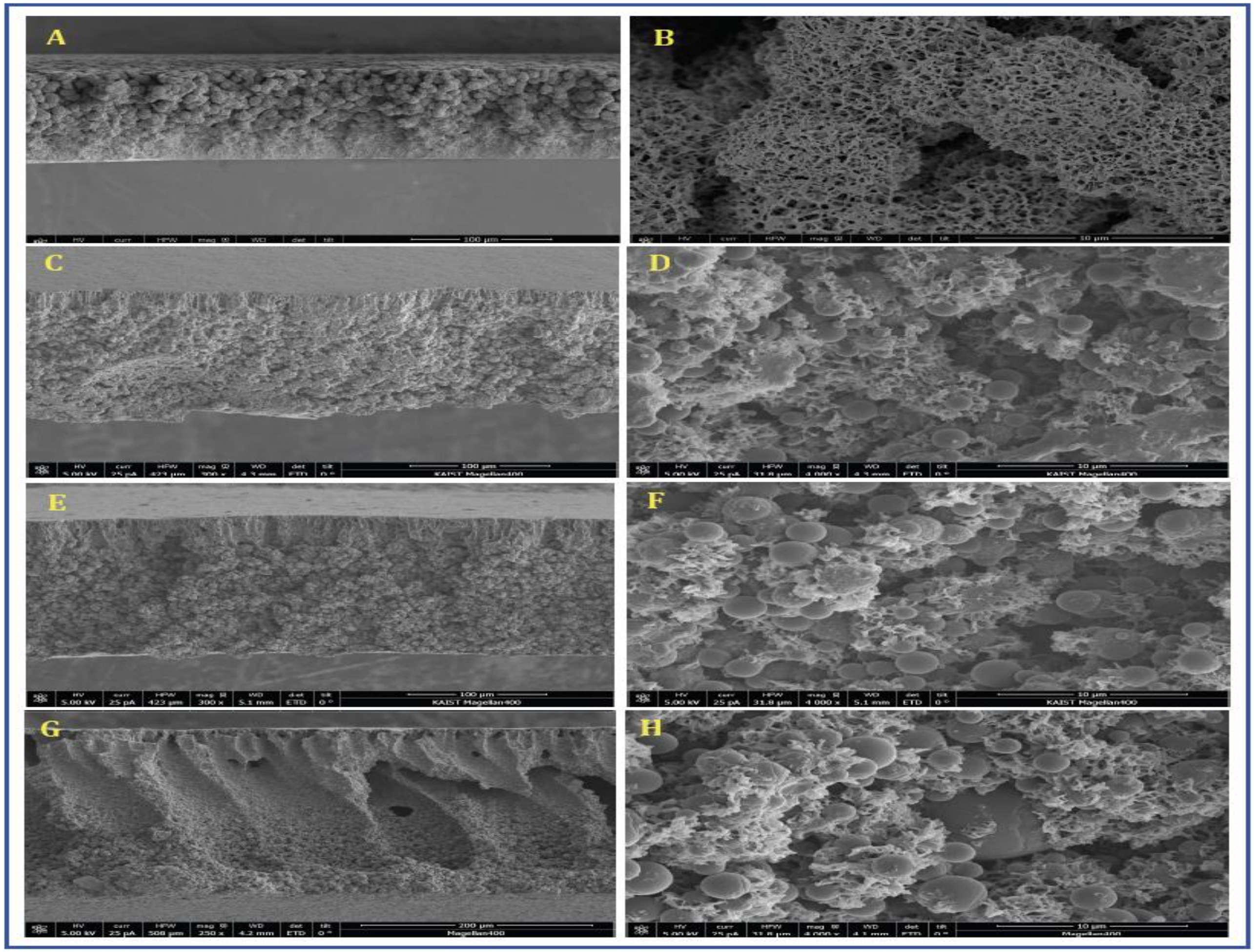
Microalgae extraction and concentration for dilute culture media remains a major and unresolved challenge

Example 2: MMMs with In Situ Synthesized and PEGylated PEI Particles as Fouling Resistant Membranes for Microalgae Recovery and Harvesting



Kotte, M. R., Hwang, T., M.; Han, J-I. and Diallo, M. S. A One-Pot Method for the Preparation of Mixed Matrix Polyvinylidene Fluoride Mem branes with In Situ Synthesized and PEGylated Polyethyleneimine Particles. J. Mem. Sci. **2014. In Press.** DOI: 10.1016/j.memsci.2014.09.044.

SEM Images (Cross Sections) of MMMs with In Situ Synthesized and PEGylated PEI Particles



Neat PVDF

PPNM-1 (35 wt%)

PPNM-2 (47 wt%)

PPNM-2 (57 wt%)

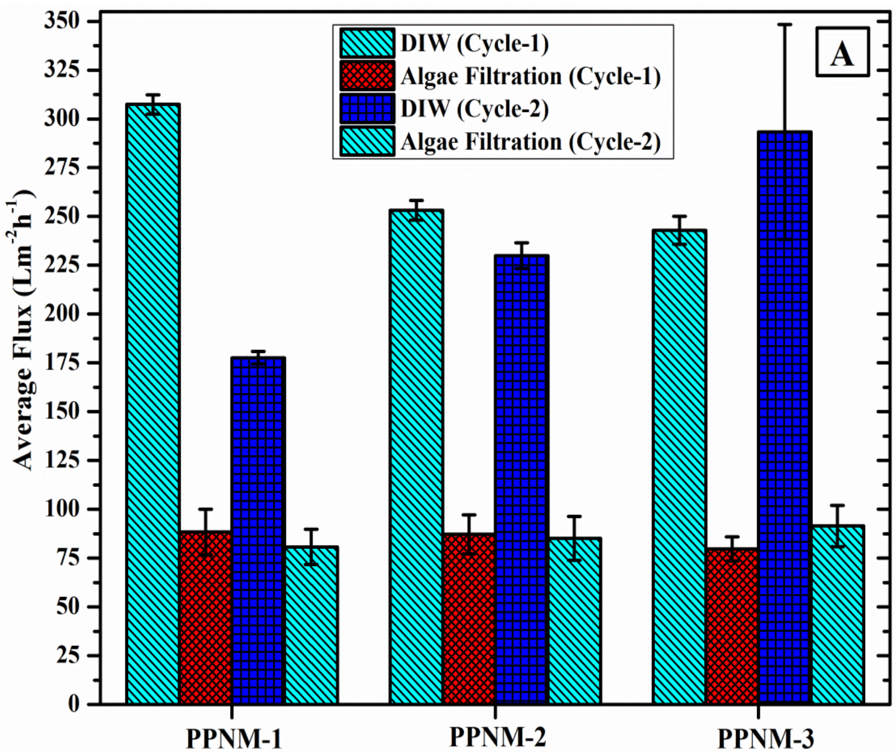
Kotte, M. R., Hwang, T., M.; Han, J-I. and Diallo, M. S. A One-Pot Method for the Preparation of Mixed Matrix Polyvinylidene Fluoride Mem branes with In Situ Synthesized and PEGylated Polyethyleneimine Particles. J. Mem. Sci. ***2014.*** **In Press.** DOI: 10.1016/j.memsci.2014.09.044.

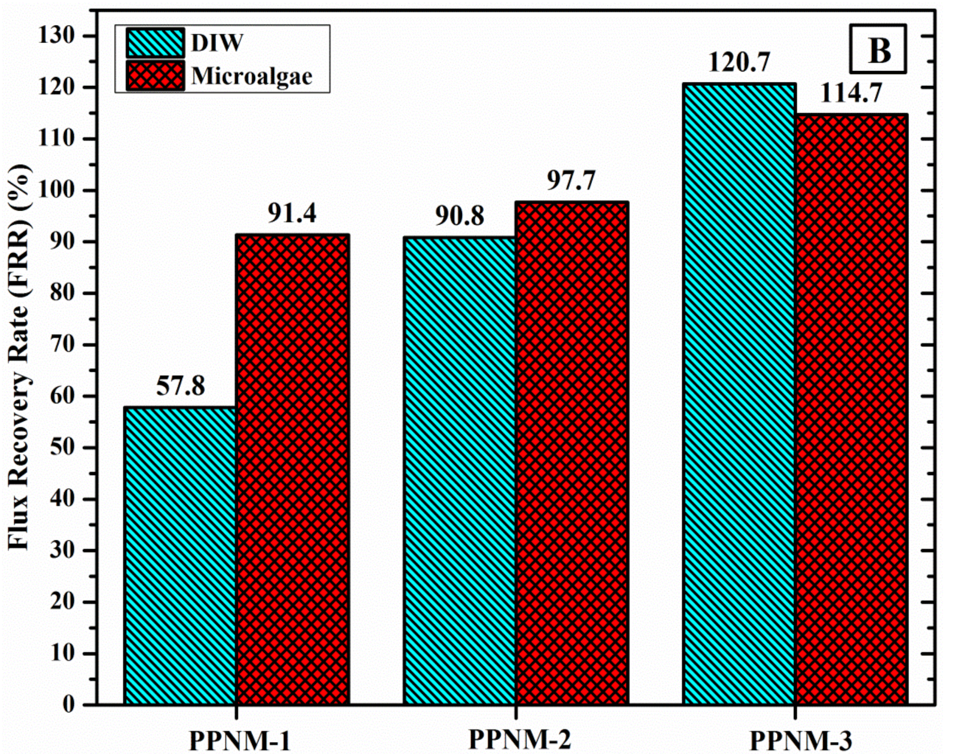
Selected Physicochemical Properties of MMMs with In Situ Synthesized and PEGylated PEI Particles

Membrane	Contact angle (Degree)	Zeta potential (mV) pH 7	Average pore diameter (nm)		PEGylated PEI particle diameter (nm)	
			Adsorption	Desorption	Minimum	Maximum
PPNM-1	53	8.59	20.22	15.98	599	2092
PPNM-2	51	2.27	24.04	19.50	751	2215
PPNM-3	43	4.23	23.55	19.01	925	3642
PVDF (Neat)	87	-5.9	16.87	12.79	---	---

Kotte, M. R., Hwang, T., M.; Han, J-I. and Diallo, M. S. A One-Pot Method for the Preparation of Mixed Matrix Polyvinylidene Fluoride Membranes with In Situ Synthesized and PEGylated Polyethyleneimine Particles. J. Mem. Sci. ***2014*****, In Press.** DOI: 10.1016/j.memsci.2014.09.044.

MMMs with In Situ Synthesized and PEGylated PEI Particles as Fouling Resistant UF Membranes for Microalgae Recovery





Suspensions of Chlorella *sp. KR-1* microalgae (1.2-1.4 g/L dry biomass)

Kotte, M. R., Hwang, T., M.; Han, J-I. and Diallo, M. S. A One-Pot Method for the Preparation of Mixed Matrix Polyvinylidene Fluoride Membranes with In Situ Synthesized and PEGylated Polyethyleneimine Particles. J. Mem. Sci. ***2014.*** **In Press.** DOI: 10.1016/j.memsci.2014.09.044.

Journal Articles (Published and Submitted)

1. Kotte, M. R., Cho, M. and Diallo, M. S. A Facile Route to the Preparation of Mixed Matrix Polyvinylidene Fluoride Membranes with *In-Situ* Generated Polyethyleneimine Particles. *J. Mem. Sci* .**2014**, 450, 93-102.
2. Kotte, M. R.; Hwang, T.; Han, J-I. and Diallo, M. S. A One-Pot Method for the Preparation of Mixed Matrix Polyvinylidene Fluoride Membranes with In Situ Synthesized and PEGylated Polyethyleneimine Particles. *J. Mem. Sci*. **2014. In Press.** DOI: 10.1016/j.memsci.2014.09.044.
3. Hwang, T.; Kotte, M. R.; Han, J-I.; Oh, Y-K and Diallo, M. S. Microalgae Recovery by Ultrafiltration Using Novel Fouling-Resistant PVDF Membranes With In Situ PEGylated Polyethyleneimine Particles. **Submitted. Under Review.**

Caltech/KAIST Joint Patents (Published and Filed)

1. Diallo, M.S., Goddard, W. A. III., Park, S-G and Cho, M-K. Filtration Membranes, and Related Nano and/or Micro fibers, Composites, Methods and Systems. *US Patent Application.* Pub No: US20130112618 A1. **Publication Date: May 9, 2013.**
2. Diallo, M. S. and Kotte, M. R. Filtration Membranes and Related Compositions, Methods and Systems. *US Patent Application*. Pub No US20130213881 A1. **Publication Date: August 22, 2013.**
3. Diallo, M. S. and Kotte, M. R. Mixed Matrix Membranes With Embedded Polymeric Particles and Networks and related Compositions, Methods, and Systems. US and PCT Applications (Pending). **Expected Publication Date: January 30, 2015.**

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- **Senior Collaborators: Prof. William A. Goddard III (Caltech), Prof. Jean Frechet (Then at UC-Berkeley), Prof. James H. Johnson (Howard U) Prof. Donald Tomalia (Central Michigan University) and Dr. Glenn Waychunas (Lawrence Berkeley Lab)**
- **Staff Scientists/ Post Doctoral Research Associates : Dr. Hang Ting Chang (AquaNano), Dr. Vyacheslav Bryantsev (Caltech), Dr. Tapan Shah (Caltech), Dr. Joytsnendu Giri (Caltech), Dr. Yi Liu (Caltech), Dr. CJ Yu (AquaNano), Dr. Emine Boz (UC-Berkeley), Dr. Samuel Webb (Stanford Synchrotron Radiation Laboratory) and Dr. Pirabalina Swaminathan (Howard U)**
- **Graduate/Undergraduate Students: Himanshu Mishra(Caltech), Simone Christie (Howard U), Sa'Nia Carasquero (Howard U), Kwesi Falconer (Howard U), (Howard U) (Caltech) and John Howard (Caltech)**
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