# MEMSIS WORKSHOP

## 13 JULY 2018

# ABSTRACTS

# Membrane Fouling: Observation and Control

**A.G.(Tony) Fane**

UNESCO Centre for Membrane Science & Technology, UNSW,
Singapore Membrane Technology Centre, NTU

Abstract

The successful application of membrane technology requires, inter alia, an understanding of membrane fouling and strategies to limit its impact. A strong theme at the Singapore Membrane Technology Centre has addressed the fouling problem for a range of membrane processes. In order to understand fouling we have used and developed several observation and monitoring techniques that will be briefly reviewed, including direct observation through the membrane (DOTM), optical coherence tomography (OCT), electrical impedance spectrometry (EIS), ultrasonic time domain reflectometry (UTDR), the feed fouling monitor and the salt pulse tracer technique. These methods can detect foulant deposition characteristics and help to identify critical or threshold flux conditions for various membrane processes. This information then guides methods for fouling control.

Examples of fouling characterisation and control to be discussed include, (i) fouling in membrane bioreactors controlled by fluidized media, vibrations and scrapers, (ii) fouling in reverse osmosis controlled by flux/crossflow and biofouling controlled by bioenabled strategies including biopretreatment, and (iii) fouling in osmotic membrane processes that is influenced by internal concentration polarisation (ICP) that is unique to these processes. The fouling in FO and RO have been compared for the same initial conditions and it is shown that FO is more prone to fouling, in terms of foulant load, but is more resilient, in terms of flux, due to self-compensation of driving force because of ICP. There is no evidence of the frequently claimed ‘low pressure’ benefit for FO in terms of fouling resistance. Finally some potential applications of in-situ fouling monitors to pre-empt fouling will be presented.

# Nanocomposite and Multifunctional Membranes for Water Remediation

Professor D. Bhattacharyya (DB)

University Alumni Chair Professor and Director of the Center of Membrane Sciences
Dept. of Chemical and Materials Engineering
University of Kentucky, Lexington, KY, USA
Email: db@uky.edu; Phone: 859-312-7790

**Abstract:** Membranes are finding extensive applications ranging from water treatment and reuse to catalysis to advanced affinity-based purification. The contamination of aquifers by toxic metals and organic compounds is a widespread problem that prevents these potentially potable sources from being used for drinking water. The development of tunable, multifunctional materials and membranes for environmental and energy-related applications requires a high level of control of both the characteristics of the base polymeric or inorganic support layer, as well as, its corresponding surface properties. The special features for membrane processes that make them attractive for industrial applications are their compactness, ease of fabrication, operation, and modular design. Although membrane processes such as, Reverse Osmosis, Nanofiltration, Ultrafiltration, and Microfiltration have provided many successful applications ranging from high quality water production to material recovery, but incorporation of nanostructured aspects with tunable properties (learning from life sciences) in microfiltration type membranes has added immense value in the area of separations, reactions, water applications, and green synthesis. The use of macromolecules, such as, poly-acrylic acid, poly-glutamic acid provide pH responsive behavior through helix-coil transitions, whereas poly-N-isopropylacrylamide provides temperature responsive behavior. The scalability (lab-scale to full-scale) of functionalized membranes for efficient separations, and selective catalysis (with nanoparticles) is needed for economic and sustainable exploitation of a wide range of applications. The presentation will include: (1) synthesis and pore functionalization approaches, and trace toxic metal capture applications, (2) pH and temperature responsive behavior, and catalytic nanoparticle synthesis in pores for environmentally important reductive and oxidative reactions, (3) nanostructured membranes for water detoxification. The authors acknowledge the support of NSF KY EPSCoR program, NSF-EAGER, NIH-NIEHS-SRC program, Southern services Co, and Chevron Corporation. The authors also acknowledge the highly significant research contributions of Drs. Li, Lewis, Hernandez, Meeks, and Gui, and current PhD students, A. Saad, H. Wan, A. Colburn, S. Islam, J. Craven, and A. Aher.

**Brief Bio:** Prof. Dibakar Bhattacharyya (DB) is the University of Kentucky Alumni Chair Professor of Chemical and Materials Engineering, Director of the UK Center of Membrane Sciences, and a Fellow of the American Institute of Chemical Engineers. For 2015-June 2016 he was the President of North American Membrane Society, and he is the Co-Chair of NAMS 2018 Annual Conference. He received his Ph.D. from the Illinois Institute of Technology, M.S. from Northwestern University, and B.S. from Jadavpur University. He has published over 200 refereed journal articles, books, and book chapters. He and his students have nine US patents in the area of membranes and water related area. Dr. Bhattacharyya has received a number of awards for his research and educational accomplishments, including the 2018 Sturgill award for Graduate Research and Education, 2015 Water Resources Research Institute award. 2013 Dean's Inaugural Outstanding Research Achievement Award, 2010 Epstein Service award from AICHE, 2009 Gerhold award on Separations technology from AICHE, 2004 Kirwan Prize for Outstanding Research, 1989 Larry K. Cecil AIChE Environmental Division Award, the Kentucky Academy of Sciences Distinguished Scientist Award, Henry M. Lutes Award for Outstanding Undergraduate Engineering Educator, AIChE Outstanding Student Chapter Counselor Awards, and the University of Kentucky Great Teacher (1984,1996, and 2008) Awards. His recent book includes, Responsive Membranes and Materials (John Wiley, 2013).

# Evapoporometry for Determining the Pore-Size Distribution – Conception to Commercial Prototype

William B. Krantz[a,b] and Jia Wei Chew[b,c]

[a] Department of Chemical & Biological Engineering, University of Colorado, Boulder, CO 80309-0424, USA

[b] Singapore Membrane Technology Center, Nanyang Environment and Water Research Institute, Nanyang Technological University, Singapore 637141

[c] School of Chemical and Biomedical Engineering, Nanyang Technological University, Singapore 637459

## Abstract

Evapoporometry (EP) for characterizing the pore-size distribution (PSD) of membranes and other porous media such as catalyst particles, adsorbents and fuel-cell electrodes has been developed and patented by the Singapore Membrane Technology Center (SMTC) of the Nanyang Environment and Water Research Institute (NEWRI) at Nanyang Technological University. The operating principle of EP is based on the vapor-pressure depression of a volatile wetting liquid in the pores of a membrane or other porous medium. The relationship between the pore diameter and the vapor-pressure depression is described by the Kelvin equation. By the design of a special test cell that permits maintaining thermodynamic saturation conditions at the surface of the porous sample whose PSD is being characterized, the pores will drain sequentially from the largest to the smallest. Hence, by determining the instantaneous mass of the test cell and porous sample, the instantaneous pore diameter can be extracted from the evaporation rate. This presentation will review the progress that has been made in extending the capability of EP to detect pore diameters ranging from 4 nm to nearly 400 nm and in characterizing the PSD of both flat sheet, and both the outer surface and lumen side of hollow fiber membranes. Recent advances in determining the PSD for all the pores as well as just the continuous pores that determine the permselective properties of ultra- and microfiltration membranes will be reviewed. The unique capability of EP to assess the effect of internal pore fouling on the PSD and the effectiveness of backwashing on restoring the PSD of fouled membranes will be underscored. A highlight of this presentation is an overview of the hardware and software design of a prototype commercial evapoporometer that has been developed recently by NEWRI.

**Osmotic Processes for Purification, Concentration and Dilution**

Emile Cornelissen
KWR Watercycle Research Institute,The Netherlands

**Abstract:**
Osmotically driven membrane processes (ODMP) advanced rapidly over the last decade as a result of newly developed osmotic membranes. Several advantages include a low energy demand, low fouling propensity and a high rejection of undesired compounds, such as emerging substances. ODMPs can be used to concentrate waste streams, dilute brine streams or seawater, produce high quality water or produce osmotic energy. Depending on the application of ODMPs research questions include: optimizing membrane performance of osmotic membranes, optimization of mass transport in osmotic membrane elements, minimizing reverse solute leakage, minimizing membrane fouling and minimizing the energy requirement in closed-loop systems.

ODMP research is nowadays focused on small-scale laboratory work usually on synthetic feed solutions. There is a strong need for pilot scale ODMP research using real feed waters, to identify the practical restrictions during application of ODMPs. In a presentation an overview is provided of research on ODMP over the last 10 years, focusing on the osmotic membrane bioreactor (OMBR) project and the Sewer Mining project. In our Sewer Mining project a technological concept is proposed by extracting water from raw sewage by means of forward osmosis (FO). FO, in combination with a re-concentration system, e.g. reverse osmosis is used to recover high-quality water. Furthermore, the subsequent concentrated sewage (containing an inherent energy content) can be converted into a renewable energy source (i.e. biogas).

Finally during the presentation an overview is given on different potential directions and market potential of FO applications for concentration, purification and briefly energy production.

**Microgranular Adsorptive Filtration (μGAF) for Membrane Pretreatment – Mechanisms and Effectiveness**

**Mark M. Benjamin and Siamak Modarresi**
**MicroHAOPs, Inc.**
**Seattle WA**

Natural organic matter (NOM) is a major foulant of microfiltration (MF) and ultrafiltration (UF) membranes and the cause of several other problems in drinking water treatment systems. Although coagulation with aluminum or iron salts can remove a portion of the NOM and mitigate membrane fouling, improving these outcomes remains a high priority. One approach for doing so is to combine coagulation with adsorption onto activated carbon.

Over the past decade, our group has published several papers on NOM adsorption onto heated aluminum oxide particles (HAOPs). HAOPs collect NOM more efficiently than conventional coagulants do, and pretreating lake water with HAOPs in well-mixed reactors reduces membrane fouling. More significantly, the fouling reduction can be greatly enhanced by passing the feed through a thin, tightly packed layer of HAOPs before the water contacts the membrane; we refer to this process as "microgranular adsorptive filtration" (μGAF).

Our prior work with μGAF used HAOPs as the sole adsorbent. We have recently expanded this effort to explore adsorption of NOM onto mixtures of HAOPs and powdered activated carbon (PAC). For a fixed total adsorbent dose, pure PAC removed more NOM than pure HAOPs did in both batch and μGAF reactors. However, rather than steadily declining as the more effective adsorbent (PAC) was replaced by the less effective one (HAOPs), NOM adsorption first increased, then peaked and declined, with most mixtures removing more NOM than either adsorbent did in isolation. Furthermore, membrane performance steadily improved (i.e., fouling declined) as PAC was replaced by HAOPs, despite the fact that PAC alone removed more NOM than HAOPs did. A conceptual and mathematical model has been developed that can explain these observations, yielding valuable insights into both the fundamentals of competitive adsorption and practical aspects of membrane fouling control.

# Development of an in-situ and on-line membrane monitoring system for Spiral wound modules


by

Professor Hans G. L. Coster

CMS Innovations Pty, Ltd and School of Chemical and Biomolecular Engineering, University of Sydney, Australia

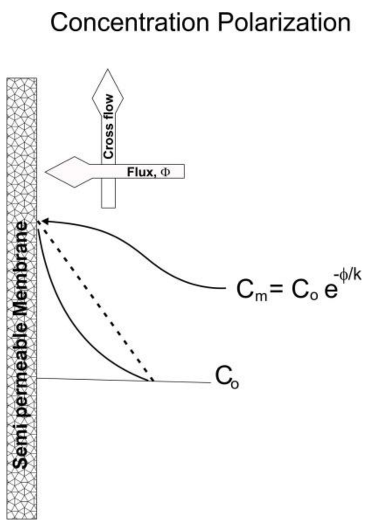

*Background*

Electrical impedance spectroscopy (EIS) can be used to determine the dielectric substructure of membranes and dynamic layers such as the concentration polarization (CP) layer at the surface of a membrane. This technique has been used in laboratory studies to monitor changes in regions within the CP layer in time and to detect the very earliest stages of membrane fouling [eg. See ref1-7]

When a flux is driven through a membrane that selectively blocks the passage of solutes, concentration polarization is an inevitable result of maintaining such a flux through the membrane.

Concentration polarization will, of course, also occur of suspended, colloidal, particles in the feed solution.

The layer adjacent to the membrane surface where concentration polarization takes place is not sharply defined; rather the degree of CP rises exponentially towards the surface of the membrane. It should be remembered that the higher the flux, the greater the CP.




A mitigating factor to CP is the back diffusion of material out of the CP layer back into the bulk solution and the stirring provided by the cross flow, which is encapsulated into the *mass transfer coefficient,* k.

*Imaging the Concentration Polarization layer*

Whilst the concentration of solutes and suspended particles in the CP layer are enhanced, it is not possible to image this layer in the traditional sense.

By injecting small AC currents through the membrane from the feed channel to the permeate channel, it is possible to perturb the local ionic concentration profiles to “interrogate” the electrical properties of the solution on the feed side of the membrane and detect the CP layer without actually making direct contact with it. By varying the frequency of the AC perturbations we are then able to “image” the CP layer. In this way we can monitor the dielectric properties in-situ during operations and track changes that occur in the CP layer that eventually lead to fouling of the membrane.

One EIS-derived parameter is the normalized conductance of the diffusion polarization ($G_{DP}$) layer which is located within the concentration polarization layer.

This parameter reflects two stages of accumulation of material in the CP layer. The first stage is related to the accumulation of solutes such as silica which form a colloidal but mobile phase. The second stage relates to the formation of a more immobile "cake" layer that begins to re\duce the mass transfer coefficient in the CP layer.

For biofouling, the initial stages is the deposition of bacteria, followed by a subsequent second stage in which deposition of the extracellular polymeric substances (EPS) takes place. Again, $G_{DP}$, the EIS derived parameter, reflects these two stages of the, in this case, biofouling process.

*Development of an EIS monitoring devise for Spiral wound RO Membrane modules*

EIS monitoring requires the injection of small alternating currents (AC) through the membrane and the measurement of the AC voltage (response) developed across the membrane. These measurement are performed at a plurality of frequencies to obtain an impedance spectrum. One important requirement is the measurement of not only the variation of the magnitude of the impedance with frequency but also the phase shift between the current injected (the stimulus) and voltage developed across the membrane (the response).

To implement this inside a spiral wound membrane module requires special elctrodes and electrode configurations.
Further to allow such EIS enable membrane modules to readily deployed in industry requires the associated electronics and software to be readily implemented without disruption of the normal operations of the plant.
To this end, we developed an EIS electronic device that was small enough to be placed inside a spiral wound module. Further, to eliminate the need for cable connections, the electronics communicates data via a WiFi though the wall of the pressure vessel and the power required for the EIS electronics is supplied by induction from a unit attached to the outside of the pressure vessel.

This arrangement allows for flexibility of where this "eModule" is located in a pressure vessel and does not require any changes to the vessel or the normal operation of the plant.

A brief overview will be given of the EIS method and the development of the CMS eModules which incorporate this technology.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**Advanced Chemical Application in the Desalination and Reclamation Process**

Mr. Hideyuki KOMORI Kurita R&D Asia Singapore

I would like to introduce 3 topics for advanced chemical application in water treatment.

1. RO related chemical
2. wastewater treatment solution(CORR system)
3.organic dispersant

These chemicals and equipment are promising to keep stable operation at actual water treatment site.

In particular, complicated organic compounds needs optimal treatment before UF and RO using new concept.

# A Novel Polypropylene-Based Superhydrophobic Membrane

**I Gede Wenten[1,2]* and Nurul Faiqotul Himma[3]**

[1] Department of Chemical Engineering, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia
[2] Research Center for Nanosciences and Nanotechnology, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia
[3] Department of Chemical Engineering, Universitas Brawijaya, Jl. Mayjen Haryono 167, Malang 65145, Indonesia

*Corresponding author (Email: igw@che.itb.ac.id)

**Abstract**. Having intrinsic hydrophobicity, polypropylene (PP) is one of the most promising materials for membrane fabrication to be used for various applications such as membrane distillation and membrane contactor. However, the performance of PP membrane for such applications is still far from expectations due to the fact that the membrane can be gradually wetted by the liquid phase, resulting in deteriorated performance over a long operating period. To address this problem, numerous studies have been devoted to increasing the hydrophobicity of PP membrane, that is, by endowing superhydrophobicity. In this article, PP-based superhydrophobic membranes are reviewed. A brief description about hydrophobicity of PP membrane as well as the targeted characteristics of superhydrophobicity is first presented. Superhydrophobic PP membrane preparation, characteristic, and performance are then discussed. Development of a novel PP-based superhydrophobic membrane is emphasized. Concluding remarks and future perspective are finally pointed out.

**Keywords:** polypropylene membrane, superhydrophobicity, novel superhydrophobic membrane, wetting

*Abstract*

**Membrane-Based Seawater Desalination: Present Practice and Future Trends**

Gary Amy
Visiting Professor, National University of Singapore
Dean's Distinguished Professor, Clemson University

The presentation will discuss the present status of the *conventional* seawater reverse osmosis (SWRO) technology, including global and regional trends in installed capacity, SWRO versus thermal process trends, specific energy consumption trends, and SWRO pretreatment trends, Given its environmental impacts, the *greening* of SWRO will also be discussed. The presentation will address recent developments towards reduction in specific energy consumption with ultra-high permeability (ULP) RO membranes and closed circuit SWRO. Also discussed will be emerging desalination processes including forward osmosis, membrane distillation, and various hybrids as well as salinity gradient energy processes including pressure retarded osmosis and reverse electrodialysis.