

# **CAREER: Disinfection Using Membranes: Optimizing Virus and Disinfection By-Product Control**

SHANKAR CHELLAM

*University of Houston, Department of Civil and Environmental Engineering and Department of Chemical and Biomolecular Engineering, Houston, TX 77204-4003, USA. E-mail: [chellam@uh.edu](mailto:chellam@uh.edu)*

*ABSTRACT: Membrane technologies such as nanofiltration and microfiltration have the ability to purify drinking water and wastewater to a high degree. Even though membranes are capable of achieving a very high quality of filtered water, to date the mechanisms by which they function are not well understood. For this reason, we (Prof. Chellam's research group at the University of Houston) have been performing laboratory experiments and computer simulations to quantitatively delineate their separation mechanisms including hindered convection, diffusion, electromigration, and adsorption. An approximate two-month long visit by the Principal Investigator to the Centre Européen de Recherche et d'Enseignement des Géosciences de l'Environnement (CEREGE) in Aix-en-Provence, France was undertaken in order to develop a collaboration between the two institutions. During this time several potential topics for future collaboration were identified following discussions of our mutual research interests and capabilities and one in particular in the broad area of implementing innovative electrocoagulation methods for purifying suspended and dissolved contaminants from industrial effluents is currently being pursued. This trip also served to broaden the interactions of Prof. Chellam with European scientists, to better understand the research methodology of a leading French institution, and to initiate the writing of manuscripts for peer-review prior to publication.*

## **INTRODUCTION**

Professor Chellam and his research group at the University of Houston including undergraduate, masters, and doctoral students have been studying environmental aspects of membrane filtration including their fouling and selectivity. Our NSF-funded research focuses on the purification of drinking water and wastewater using porous membranes. In particular, we are using nanofiltration membranes for removing salt, macromolecules, and micropollutants and investigating fouling of microfiltration membranes and enhancing their ability to control microorganisms.

Through funding from the CAREER program, we are rigorously and quantitatively establishing the relative roles of convection, diffusion, and electromigration on the transport of salts and neutral organic molecules across nanofiltration membranes [1, 3-6], the influence of adsorption, steric interactions, and electrostatic interactions on amino acids transport across polymeric nanofilters [7, 8], the interactions between and removal of colloids, natural organic matter, bacteria, and viruses using microfiltration membranes [2, 9-11, 12, 13, 14], and stimulating reactive oxygen species generation by photocatalyzed nanoparticles to inactivate viruses [15].

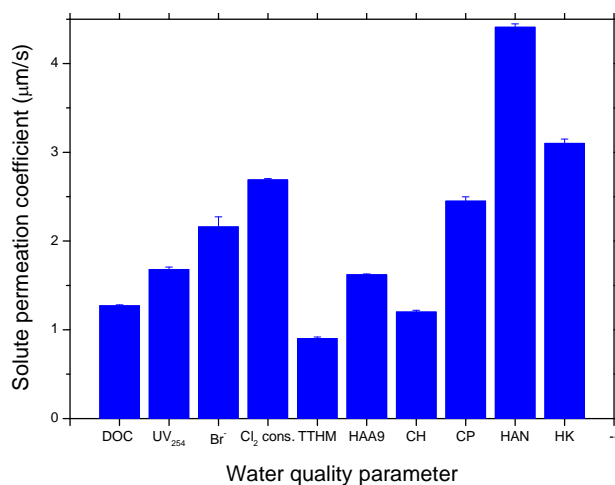
We have specifically been interested in the control of disinfection by-products (both trihalomethanes and haloacetic acids) using nanofiltration membranes as well as inhibiting the secretion of extracellular polymeric substances in order to reduce bacterial attachment to polymeric membranes. We are investigating the chemistry of halogenated trihalomethanes and haloacetic acids formation in membrane permeate and feed waters.

Professor Jean-Yves Bottero leads a large interdisciplinary research group at the Centre Européen de Recherche et d'Enseignement des Géosciences de l'Environnement (CEREGE) in Aix-en-Provence, France. CEREGE is one of the leading research organizations studying the environmental impacts of nanoparticles and the use of membrane filtration technologies for water and wastewater purification. CEREGE researchers are serving or have served on the Editorial Boards of numerous well-respected scientific journals including *Clay Minerals*, *Journal of Crystal Growth*, *Geochimica et Cosmochimica Acta*, *Journal of Colloid and Interface Science*, *Water Research*, *Water Technology Science*, *Langmuir*, *International Journal of Mineral Processing*, *Colloids and Surfaces*, etc. demonstrating their leadership in environmental geochemistry. In particular, senior scientist Dr. Jérôme Rose has pioneered the development of catalytic ceramic membranes for water treatment by using ferroxane nanoparticles. Additionally, Dr. Armand Masion is an expert on aluminium coagulation chemistry. Given the complementary nature of their research and on-going work at the University of Houston, it was a natural choice for the PI at the University of Houston (Chellam) to reach out to them in order to establish collaborations with CEREGE.

The PI, Dr. Chellam worked at CEREGE from May 24, 2008 to May 31, 2008 and again between June 6, 2008 and August 3, 2008. Funding was not requested for any students to accomplish the PI to France.

### RESEARCH ACTIVITIES AND ACCOMPLISHMENTS OF THE INTERNATIONAL COOPERATION

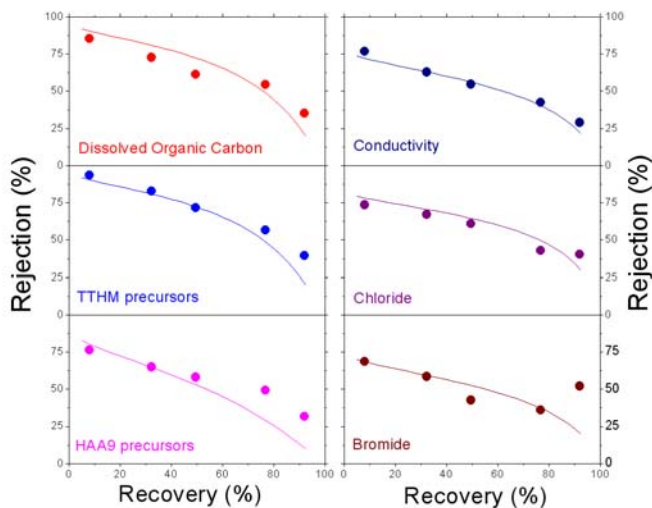
The PI primarily interacted with the scientists, professors, graduate students, and laboratory technicians at CEREGE to generate ideas and proposals for future submission. In addition, Prof. Chellam wrote and submitted three manuscripts during this trip, all of which have since been published [1, 9, 14].



**Figure 1.** Summary of solute permeation coefficients ( $k_s$ ) measured for contaminant transport across nanofiltration membranes [14].

In our nanofiltration research, we analyzed the removal of various water treatment contaminants including natural organic matter and disinfection by products and salts while operating at high recovery. A summary of all permeation coefficients of relevance to drinking water treatment determined in this study is given in Figure 1. Note that a higher value of the permeation coefficient  $K_s$  means lower rejection. Therefore, Figure 1 suggests that trihalomethane precursors are either (a) higher molecular weight components of natural organic matter compared with haloacetic acid precursors or (b) nanofiltration changed the reactivity of natural organic matter preferentially towards haloacetic acid formation (compared to trihalomethanes). Similarly, the lowest natural organic matter molecular weight fractions are probably haloacetonitriles precursors or nanofiltration dramatically increased natural organic matter-chlorine reactivity to form haloacetonitriles. This is consistent with amino acids and peptides serving as precursors to nitrogenous disinfection by products and being of low molecular weight can permeate preferentially across nanofilters compared to precursors to carbonaceous disinfection by products such as trihalomethanes and haloacetic acids. Also as can be expected, the bromide ion permeates more easily than natural organic matter. To our

knowledge these are the first systematic reports of chloral hydrate, chloropicrin, haloacetone, and haloacetonitrile permeation across nanofiltration membranes.



**Figure 2.** High recovery nanofilter performance while operating on surface water at a flux of  $2.2 \mu\text{m/s}$  [1].

chloride, and bromide were also obtained from the literature.

Very high reflection coefficients for natural organic matter and disinfection by product precursors demonstrate that their rejection is controlled by diffusion and that convective contributions are negligible for these macromolecules. These results are similar to an earlier empirical study of trihalomethanes and haloacetic acids precursor control using nanofilters [16]. Under our experimental conditions, increasing feed water recovery also reduced the average crossflow velocity and consequently decreased overall brine-side mass transfer. The resulting higher membrane surface concentration increased the transmembrane concentration gradient driving diffusive transport of these macromolecules across the membrane at higher recoveries. This suggests that increasing the crossflow velocity by recycling the concentrate (especially in the second or third stage of a staged-plant) can counteract the propensity for reduced removals of natural organic matter and disinfection by products precursors at high recoveries in full-scale nanofiltration installations.

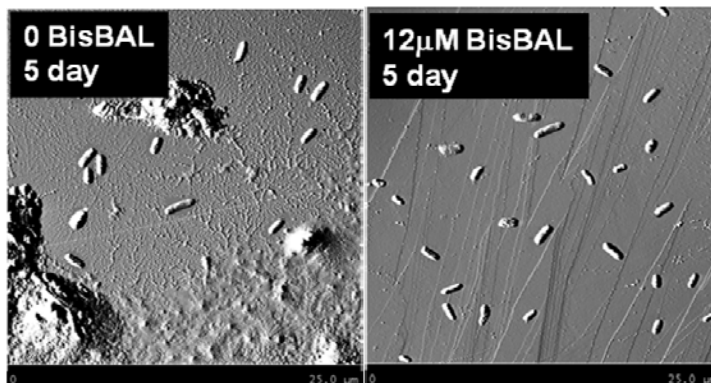
It should again be emphasized that calculations of solute removal from Lake Houston water at high recoveries shown in Figure 2 did not involve any fitting to data and are pure predictions. Hence, close agreement ( $R^2 > 0.9$ ) between experimental measurements and theoretical calculations of removal of various macromolecules and ions of interest to drinking water quality shown in Figure 2 demonstrate that the phenomenological model coupled to the differential element approach can be employed to accurately predict permeate water quality during nanofiltration of natural water. In other words, factors affecting steric and polar interactions between natural organic matter and the polymeric nanofilters, electrostatic interactions between ions and the membrane surface, and ion coupling and complexation all were accurately simulated for selectivity at high recovery using parameters derived solely from low recovery experiments. To date, software programs provided by membrane manufacturers are only capable of predicting salt rejection. Excellent agreement between theoretical calculations and experimental measurements shown in Figure 2 indicates that commercially available software packages can be updated to include the phenomenological model to make projections of trihalomethanes and haloacetic acid precursor concentrations in the permeate water with changing operating conditions.

## BROADER IMPACTS OF THE INTERNATIONAL COOPERATION

The international travel allowed the PI to broaden the scope of our work to include “nano” and “bio” flavors to our current and future research. For example, CEREGE scientists are interested in our on-going research on the production and characterization of extracellular polymeric substances by bacteria. Recent

In a separate publication [1], we developed a first principles approach towards transport of a variety of solutes across nanofiltration membranes. Experimental measurements of reflection coefficients were highest for natural organic matter including trihalomethane and haloacetic acid precursors, which were higher than monovalent co-ions reflecting the general rejection trend for thin film composite nanofiltration membranes. The brine side mass transfer coefficients for natural organic matter, trihalomethane, and haloacetic acid precursors were calculated using an “average” literature reported value of  $5 \times 10^{-6} \text{ cm}^2/\text{s}$  for natural organic matter diffusivity. The NaCl binary diffusion coefficient was employed for conductivity and diffusion coefficients of sodium,

results from our lab has shown that addition of small (less than minimum inhibitory concentration) levels of bismuth thiols substantially reduce the production of EPS [2, 9]. Atomic force micrographs of *Brevundimonas diminuta* with and without bismuth thiol-treatment are depicted in Figure 3. As observed, treatment at the minimum inhibitory concentration significantly reduced EPS secretion compared with the control (no BisBAL). In the absence of BisBAL, a substantial EPS layer was visible after 5 days. Exposure of bacteria to BisBAL visibly reduced EPS expression as seen in Figure 3b. CEREGE scientists and I are planning to expand this work to include nanoparticles' effects on EPS production either through transport across the cell membrane or through



**Figure 3.** AFM images of reductions in EPS secretion by *B. diminuta* upon exposure to 12  $\mu$ M BisBAL [2].

reactive oxygen species formation. Another area of future research we identified is the use of innovative electrocoagulation and chemical coagulation methods for nanoparticle removal from industrial waste streams. Laboratory experiments are being designed currently to be performed at the University of Houston. A third direct benefit for me was to start familiarizing with the European approach towards water quality regulations, especially related to disinfection by-products. The French are leaders in membrane implementation towards municipal drinking water treatment. Their knowledge on micropollutant removals by nanofilters was extremely important to my own broad understanding of this filtration technique. These lines of inquiry were made possible through the international travel experience.

## DISCUSSION AND SUMMARY

Topics being addressed in my research group including those related to drinking water quality, purification of natural (surface) waters, transport of microcontaminants across membrane filters, bacterial clogging or fouling of filters, etc. are all complex in nature and require an interdisciplinary approach. The international collaboration made possible through the IREE program has set up an exciting crossfertilization of ideas between my research group and scientists at CEREGE, especially the group lead by Jean-Yves Bottero that has improved the scope, nature, and depth of our approaches to make progress towards topics of mutual interest. We are beginning to extend the scope of my original research grant by including engineered nanoparticles in addition to viruses and organics as water treatment contaminants. In fact, CEREGE scientists and I have been in regular contact by email to further develop these research ideas. Dr. Jérôme Rose and I will be further discussing our collaboration in person during the International Water Association Particle Separation Conference that will be held in Durham in June 2009.

## ACKNOWLEDGEMENTS

The Principal Investigator (Prof. Shankar Chellam) appreciates the support of the National Science Foundation through grant CBET 0134301 as well as the assistance of his program officers Dr. Cindy Ekstein and Dr. Clark Liu. He appreciates the opportunity to collaborate with scientists at CEREGE in Aix-en-Provence, France and the hospitality of Prof. Jean-Yves Bottero, Dr. Jérôme Rose, Dr. Armand Masion as well as numerous technicians and graduate students.

## REFERENCES

1. Sharma, R. and S. Chellam (2008). Solute Rejection by Porous Thin Film Composite Nanofiltration Membranes at High Feed Water Recoveries. *Journal of Colloid and Interface Science* **328**: 353-366.

2. Badireddy, A.R., S. Chellam, S. Yanina, P.L. Gassman, and K.M. Rosso (2008). Bismuth Dimercaptopropanol (BisBAL) Inhibits the Expression of Extracellular Polysaccharides and Proteins by *Brevundimonas diminuta*: Implications for Membrane Microfiltration. *Biotechnology and Bioengineering* **99**(3): 634–643.
3. Sharma, R.R., R. Agrawal, and S. Chellam (2003). Temperature Effects on Sieving Characteristics of Thin-Film Composite Nanofiltration Membranes: Pore Size Distributions and Transport Parameters. *Journal of Membrane Science* **223**: 69-87.
4. Sharma, R.R. and S. Chellam (2005). Temperature Effects on the Morphology of Porous Thin Film Composite Nanofiltration Membranes. *Environmental Science and Technology* **39**(13): 5022-5030.
5. Sharma, R.R. and S. Chellam (2006). Temperature and Concentration Effects on Electrolyte Transport across Porous Thin Film Composite Nanofiltration Membranes: Pore Transport Mechanisms and Energetics of Permeation. *Journal of Colloid and Interface Science* **298**: 327-340.
6. Sharma, R.R. and S. Chellam (2006). Frictional Interpretation of Thermodynamic Transport Parameters for Porous Nanofiltration Membranes *Journal of Water Supply: Research and Technology (Aqua)* **55** (invited paper for the special theme issue “New Developments in Particle Separation”)(6–7): 571–587.
7. Shim, Y. and S. Chellam (2007). Steric and Electrostatic Interactions Govern Nanofiltration of Amino Acids. *Biotechnology and Bioengineering* **98**(2): 451–461.
8. Shim, Y., W.G. Rixey, and S. Chellam (2008). Influence of Sorption on Removal of Tryptophan and Phenylalanine during Nanofiltration. *Journal of Membrane Science* **323**(1): 99-104.
9. Badireddy, A.R., B.R. Korpil, S. Chellam, P.L. Gassman, M.H. Engelhard, A.S. Lea, and K.M. Rosso (2008). Spectroscopic Characterization of Extracellular Polymeric Substances from *Escherichia coli* and *Serratia marcescens*: Suppression using Sub-Inhibitory Concentrations of Bismuth Thiols. *Biomacromolecules* **9**(11): 3079-3089.
10. Baltus, R.E., A.R. Badireddy, W. Xu, and S. Chellam (2008). Analysis of Configurational Effects on Hindered Convection of Non-spherical Bacteria and Viruses across Microfiltration Membranes. *Industrial and Engineering Chemistry Research* **In press** (doi:10.1021/ie800579e).
11. Zhu, B., D.A. Clifford, and S. Chellam (2005). Comparison of Electrocoagulation and Chemical Coagulation Pretreatment for Enhanced Virus Removal using Microfiltration Membranes. *Water Research* **39**(13): 3098-3108.
12. Zhu, B., D.A. Clifford, and S. Chellam (2005). Virus Removal by Iron Coagulation-Microfiltration. *Water Research* **39**(20): 5153–5161.
13. Bagga, A., S. Chellam, and D.A. Clifford (2008). Iron Chemical Coagulation and Electrocoagulation Pretreatment for Microfiltration of Surface Water. *Journal of Membrane Science* **309**(1-2): 82–93.
14. Chellam, S., R.R. Sharma, G.R. Shetty, and Y. Wei (2008). Nanofiltration of Pretreated Lake Houston Water: Disinfection by-Product Speciation, Relationships, and Control. *Separation and Purification Technology* **64** 160-169.
15. Badireddy, A.R., E.M. Hotze, S. Chellam, P.J.J. Alvarez, and M.R. Wiesner (2007). Inactivation of Bacteriophages via Photosensitization of Fullerol Nanoparticles. *Environmental Science and Technology* **41**(18): 6627 – 6632.
16. Chellam, S. (2000). Effects of Nanofiltration on Trihalomethane and Haloacetic Acid Precursor Removal and Speciation in Waters Containing Low Concentrations of Bromide Ion. *Environmental Science and Technology* **34**(9): 1813-1820.

## BRIEF BIOGRAPHIES OF RESEARCHERS

**Shankar Chellam** received the B.E. (Hons.) degree in Mechanical Engineering and the M.Sc. (Hons.) degree in Chemistry from the Birla Institute of Technology and Science, Pilani, India in 1986. He then worked as an engineer with J.K. Synthetics Ltd. (India) responsible for the operation and maintenance of the facilities for treatment of drinking water, wastewater, and industrial grade ultra-pure water. He joined Rice University in Houston, TX in 1989 to later receive his M.S. and Ph.D. degrees in Environmental Engineering in 1991 and 1996, respectively. Following this, he worked for four years as an environmental consulting engineer with Montgomery Watson Inc., Herndon, VA joining the University of Houston in the Department of Civil and Environmental Engineering as an Assistant Professor in 1999. Since then he has been promoted to the rank of Professor in 2008 and also has a courtesy appointment in the Department of Chemical and Biomolecular Engineering. His research interests include various aspects of membrane transport phenomena related to fouling and water quality. Another aspect of his research (not related to this particular NSF grant) includes the trace level measurements of metals in airborne particulate matter and their apportionment to various sources including the petroleum refining industry and automobiles.