# TOWARD OPTIMIZED MEMBRANE UNIT PROCESSES VIA MULTI-SCALE MODELING

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## Introduction

In 2011 the United States embarked on the Materials Genome Initiative to discover, manufacture, and deploy advanced materials twice as fast as then-current rates, at a fraction of the cost. In the spirit of that initiative we are working to speed the rate at which lower-energy, lower-fouling, and higher-productivity membrane processes are developed. The key to realizing this goal is the development of models that encompass the wide range of scales involved in membrane separations: this includes the molecular-level interactions captured in molecular dynamics simulations up to the bulk water flows through membrane modules captured with computational fluid dynamics (CFD) modeling.

We report here on our progress with CFD models to understand and optimize solute and foulant transport in reverse osmosis (RO) and nanofiltration (NF) processes for desalination and water reuse. We begin with our work on membranes with engineered surface features (patterns) that mitigate fouling at the nano- and micro-scale. We show the ways in which different patterns affect fouling, either to mitigate or exacerbate it. Appropriate patterns are those that cause enhanced shear without creating an abundance of dead zones where foulants can accumulate. The modeling effort greatly increases the number of pattern types that can be evaluated, allowing experiments to focus on those that are most promising.

The overall approach of our program is summarized in the "helical" structure of Figure 1. The approach provides a framework for accelerating the discovery of new surface patterns with appropriate chemistries to improve membrane fouling resistance. The work progresses through subsequent generations of membrane and model development. Each generation builds on the results from multiscale modeling to guide the choice of systems for experimental studies. Experiments provide necessary feedback to train the multiscale models.

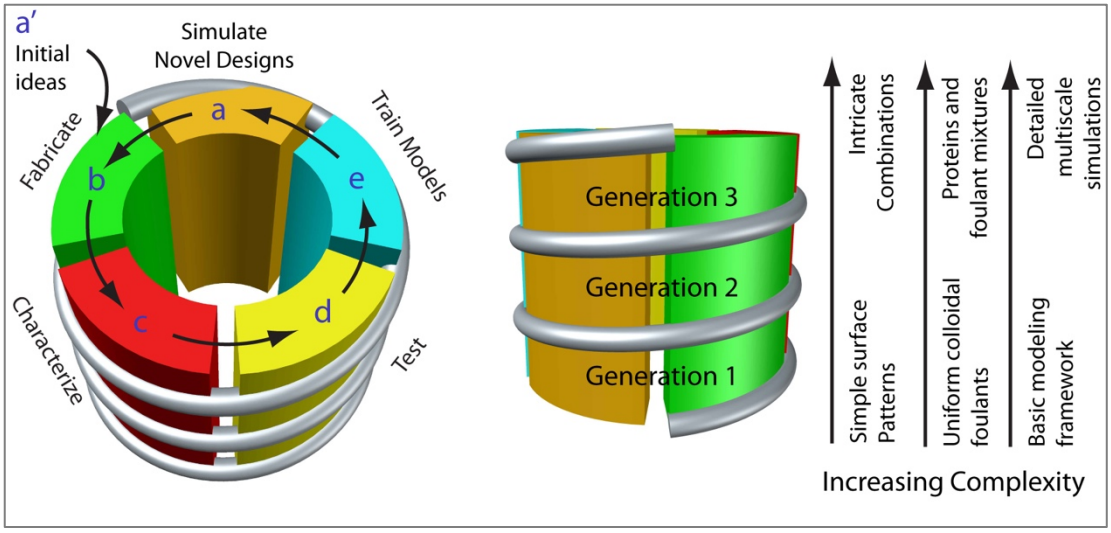


**Figure 1.** Conceptualized helical framework of the research program. A cyclical workflow (left) builds upon itself over multiple generations of membrane development (right). The workflow progresses with (a') initial pattern ideas based on literature and preliminary data, (b) fabrication of 1st-generation patterned membranes, (c) characterization of membrane morphology and chemistry, (d) foulant challenge tests to evaluate performance, and (e) model development and training with data from membrane analyses and fouling tests. The next generation then begins with (a) simulations performed using the calibrated models to evaluate several novel membrane patterns. The most promising subset of patterns is fabricated; these are the Generation 2 membranes and the testing/modeling cycle is repeated. The membrane patterns, chemical coatings, and foulant composition become more complex with each generation, requiring increasingly robust multiscale simulations as the project moves up the helix.

## Research Program Details

### *Initial ideas*

Much of this work is inspired by biological systems that display unique characteristics because of their surface morphology (Golovin et al. 2016). Lotus leaves, for example, have nodules that impart superhydrophobic character. Shark skin has a diamond riblet shape that reduces drag. Our initial ideas for patterns stemmed from similar kinds of designs. To understand the effects of various morphologies, we also performed a series of tests with simple shapes like line-and-groove patterns (Weinman and Husson 2016), triangles, squares, and circles. These basic geometries, help us understand basic effects that lead us to understanding the more complex bioinspired patterns.

### *Fabrication and Characterization*

To create patterns on NF and RO membranes, the patterns are first formed on silicone stamps using lithography techniques. The stamps are then pressed into the membranes at elevated temperature for prescribed time periods. We tested the effectiveness of the patterning method for various membranes from different manufacturers to arrive at a protocol where patterns could be reproduced reliably. Atomic force microscopy (AFM) was used to measure the morphology of the patterned membranes. With the right membranes and stamping procedures the patterns are

permanent; we have not seen relaxation during the time period of the project, even when membranes are wetted and used in filtration experiments.

***Experimental Fouling Tests***

Fouling experiments are conducted with small (~2 cm by 5 cm) membrane coupons in custom-made flow cells. Various flow rates and pressures are employed to first evaluate the integrity of the membrane after patterning and then the effectiveness of the patterns for fouling reduction. These experiments and the testing details have been reported previously (Weinman and Husson 2016).

***Training Models and Testing Novel Designs***

Modeling the fouling behavior in the experimental systems is the main thrust of the research effort. Two modeling methods are coupled in this project: (1) molecular dynamics to understand foulant-membrane interactions at the angstrom and nanometer scale and (2) CFD modeling to understand solvent and solute transport over and around patterns. Information from molecular dynamics simulations is carried forward to the CFD models so that multi-scale coupling is achieved.

As an example of a molecular dynamics simulation, Figure 2 shows an idealized planar membrane surface toward which a foulant molecule is approaching. The radius of gyration of the foulant molecule is evaluated to see if its conformation changes as it adsorbs to the membrane. The change in energy from the non-adsorbed compared with the adsorbed state is used to calculate the binding affinity for the foulant.

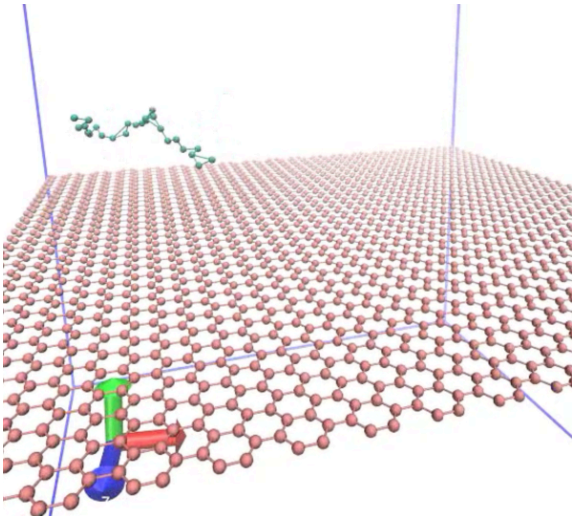

**Figure 2.** Snapshot of a molecular dynamics simulation for an idealized foulant molecule on an idealized membrane surface.

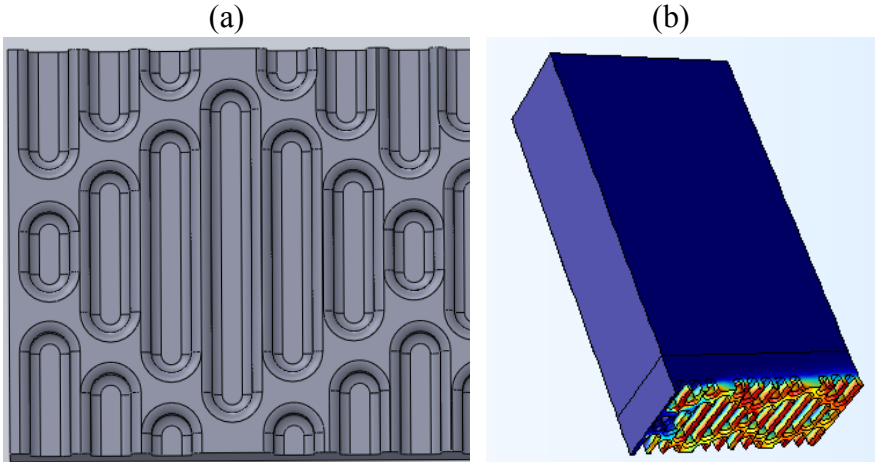


**Figure 3.** (a) Plan view of a shark-skin-inspired pattern. This was reproduced at several sizes for testing (thus no scale bar is shown). (b) Simulation space with concentration profile for solute around a shark-skin-inspired membrane. Crossflow is from left to right. The simulation box is tall enough that the wall opposite the membrane does not affect the fluid flow or solute concentration distribution at the membrane surface.

As an example of a CFD simulation, Figure 3 shows a shark-skin-inspired pattern. The first key in RO and NF modeling is to understand concentration polarization caused by flux and mitigated by crossflow. Most patterns have valleys where salts can accumulate, as shown by the red areas in Figure 3b. The ultimate goal is to discover patterns that cause local mixing and thus ameliorate concentration polarization and fouling, even at normal crossflow velocities. Keeping low crossflow velocity is important because we want to reduce energy costs and increase clean-water recovery.

## Conclusions and Future Outlook

The main outcome of this research is the development of a modeling framework where membrane fouling can be predicted for membranes with various surface topologies. The multi-scale methodology of molecular dynamics simulations coupled with fluid mechanics simulations holds promise because it can capture the wide variety of physical phenomena at play in membrane separations. We anticipate that once this in-silico methodology is fine-tuned, it will allow the discovery of novel membrane designs at a much faster pace than traditional trial-and-error laboratory experiments.

## Acknowledgements

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## References

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