New York State Pollution Prevention Institute  
R&D Program  
2015-2016 Student Competition  

Great Minds » New Solutions

Project Report – Cover Page

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<th>University/College Name</th>
<th>University at Buffalo</th>
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<td>Team Name</td>
<td>Anti-fouling Membrane (AFM)</td>
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<tr>
<td>Team Member Names</td>
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<td></td>
<td>Jennifer Y. Park</td>
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<td></td>
<td>Yi-Chen Tu</td>
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<td>External Affiliation/Business Partner</td>
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<td>Project Name</td>
<td>One-Step Facile Strategy to Enhance Membrane Antifouling Properties for Wastewater Reuse</td>
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<td>Environmental area/opportunity addressed</td>
<td>Community Environmental Challenge</td>
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Please provide a brief one paragraph summary of your project:

Polymeric membranes have emerged as an attractive technology for wastewater reuse due to their inherently high energy efficiency, small footprint and low cost. However, the membranes are often subjected to fouling by contaminants in the water. Our objective is to develop a facile one-step approach to modify membrane surface using dopamine and sulfobetaine methacrylate for commercial water purification membranes. We have demonstrated that nanometer-thick coating with great hydrophilicity has formed on the membrane surface, which increases the resistance to fouling and thus water permeance.

[Student Team Member Signatures]
One-Step Facile Strategy to Enhance Membrane Antifouling Properties

for Wastewater Reuse

Problem Statement

The State of New York is faced with challenges in maintaining and upgrading the wastewater infrastructure [1]. Reducing the wastewater produced and adopting low-cost technologies for treatment and reuse would help to reduce the burden and dependence on wastewater treatment systems. Manufacturers in New York have the opportunity to clean and reuse process water through the use of various filtration methods, depending on the application. In most cases, relatively clean water is desired and is best achieved using membrane separation technologies. While membranes (such as ultrafiltration) have been extensively used in a wide range of applications, a common problem that either limits or inhibits application of membrane technology is fouling, a phenomenon where contaminants in the wastewater either coats the membrane surface or clogs up internal pores. The water permeate flux decreases due to fouling and can render the process cost prohibitive. For example, Perry’s Ice Cream in Akron, NY is planning to clean and reuse approximately 50% of the 60,000 gal/day they purchase and discharge at an annual cost of $250,000. Membrane filtration testing performed thus far indicated that certain foulants are reducing flux to lower than economically acceptable levels [2].

We propose a novel facile approach that focuses on one step surface modification to enhance the membrane antifouling properties which will allow for a cost-effective wastewater recovery. The proposed technology can be applied to treat the wastewater from the Perry’s Ice Cream plant to reuse the water, which directly addresses the topic of Community Environmental Challenge under this solicitation. The proposed work has positive effects related to sustainability (environmental, economic and social impacts). Water recycling will result in less water
consumed and less wastewater created. Companies can also save money. This combination of reducing environmental impacts and improving economic competitiveness is also a sign of social responsibility to make New York a safe and financially stable state for citizens to live in.

**Project Summary/Background**

The research focuses on improving membrane performance of wastewater containing bovine serum albumin (BSA) as a model biofoulant. As the next step the real industrial wastewater that is generated at Perry’s Ice Cream in Akron, NY, can be tested with the treated membranes. Perry’s is located approximately 16 miles from UB, so retrieving and analyzing samples can be accomplished quite easily. The company is seeking to reuse up to 30,000 gal/day of water which can save them $250,000/year.

Several strategies have been adopted to mitigate membrane fouling, such as pretreatment flocculation, aggressive and frequent chemical cleaning of membranes, frequent backflushing of UF membranes, and ultimately membrane replacement [3-6]. However, these approaches increase the capital and operating cost of wastewater treatment. Recently, membrane surface modifications to increase hydrophilicity aiming to reduce favorable interactions between membrane surface and foulants have been extensively explored, such as thin film coating, self-assembled monolayers, and polymeric grafting by chemical treatment (such as UV or plasma treatment) [5, 7-11]. The thin film coating of a hydrophilic polymer is particularly interesting because the coating can be easily implemented into the current membrane production process [5, 8, 11-19]. The hydrophilic coating, such as poly(ethylene glycol) (PEG), can strongly bind water molecules forming a hydration layer, which prevents the adsorption of the foulants on the surface, mitigating the external fouling and eliminating the internal fouling [8, 10]. The key to
the success of this approach is that the hydrophilic coating layer must be thin enough so that its resistance to water transport is much lower than that in the virgin membrane and therefore, the surface coating does not significantly decrease water flux. However, thin film coating may not be stable in the long term, leading to reduced antifouling property over time.

Professor Benny Freeman’s laboratory at University of Texas at Austin has developed a two-step process to accomplish this contradicting requirement, i.e., coating with Polydopamine (PD) followed by the PEG layer [5, 20]. Lin et al. at UB is currently exploring this approach with funding support from NYSP2I. In contrast to the activities undergoing in Lin’s lab, the AFM group explored a facile one-step approach to modify the surface. Specifically, the team applied only one coating on Polyacrylonitrile (PAN) membranes from a solution containing both dopamine and sulfobetaine methacrylate (SBMA) as the zwitterionic material and examined the antifouling properties for treating the wastewaters containing BSA.

**Relationship to Sustainability**

From a sustainability perspective, this study will have positive effects related to environmental, economic and social impacts. If Perry’s Ice Cream can see improved membrane flux performance, they are more apt to purchase and install a 30,000 gal/day membrane system to recycle 50% of their water. 50% recycle will reduce water consumption and wastewater discharge by 50%. Estimated annual savings would be around $250,000 year. If fouling is minimized, a reasonable payback can be realized since capital and operating costs would be lower. Long-term savings for Perry’s will help to keep the company profitable and make a positive contribution to the local community. Successful development of an effective anti-fouling membrane process has significant potential impacts to NY State, the country and even the entire
Better management of industrial wastewater through water recycling will reduce strain on the current wastewater treatment infrastructure since less wastewater will be ultimately discharged; the risk of pollutant releases to the environment would be mitigated. Water recycling will also save companies money since less water would need to be purchased and sewer fees would be lower. There are many industry sectors in NY that use significant amounts of water which could potentially benefit from a cost-effective membrane recycling system. Companies that can become more profitable while reducing their environmental footprint will retain and create more jobs; these initiatives help to sustain the economy and make New York a safe and stable state to live in. If successful, application of low fouling membranes would have little environmental tradeoffs. Capital equipment would be needed along with tanks, pumps and piping. Energy would also be consumed to drive the pumps for the membrane system and transfer operation.

Materials and Methods

Three students participated in this project. The graduate student, Nima Shahkaramipour, leaded in the planning of the experiments. The other graduate student, Yi-Chen Tu, and the undergraduate student, Jennifer Park, contributed equally on the experimental work.

Task 1: Select Commercial Membranes

To study the effect of modifying membranes on antifouling properties, we have selected one of the most common commercial ultrafiltration membranes for wastewater reuse. Polyacrylonitrile (PAN) with molecule weight cut off of 50 kDa from Sepro was chosen in this study.
Task 2: Modify Membrane Surface

Coating with PD or SBMA/PD solution. Before coating the membranes, the glycerin inside the pores (to preserve pore structure) was removed by soaking in ethanol and then in water. The coating was performed by exposure the membrane surface to the solution containing PD or PD and SBMA in a rocking platform shaker. Fig. 1 shows the schematic of our modification approach. Applied modification conditions to PAN-50 samples are presented in Table 1.

![Schematic of surface modification approach](image)

**Fig. 1.** Schematic of the surface modification approach.

**Surface hydrophilicity characterization.** The hydrophilicity of dried uncoated and coated samples was examined by using a Ramé Hart contact angle goniometer. Water drops with the volume of 10 µL were injected onto the membrane surface. The values were taken as an average of at least five points.

Table 1. Modification conditions applied to PAN-50 samples (DT: deposition time).

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>PAN-50</th>
</tr>
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<tbody>
<tr>
<td>PD Coated</td>
<td>PDA=2g/l, DT=1.5h</td>
</tr>
<tr>
<td>SBMA/PD Co-Deposition</td>
<td>PDA=1g/l, SBMA=4g/l, DT=1.5h</td>
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Task 3: Determine Water Flux with Simulated Foulants

**Pure water flux determination.** The pure water flux was determined using dead-end filtration cells. The water permeance, \( A_W \) (liter per \((m^2 \text{ hr bar})\), LMH/bar), can be calculated using the following expression:

\[
A_W = \frac{1}{\Delta p \cdot A_m} \frac{dV_w}{dt}
\]  

(1)

where \( \Delta p \), \( A_m \) and \( dV_w/dt \) are the pressure difference across the membrane, membrane effective area and water flux, respectively. Six membrane samples were tested and an average water permeance is reported here.

**Fouling tests using a crossflow system.** Fouling tests were conducted using different concentrations of bovine serum albumin (BSA) as a model biofoulant. BSA with concentrations of 1 and 3 g/l were prepared and filtered in a cross flow filtration system. The membrane test apparatus was designed and built in our laboratory for antifouling experiments, as shown in Fig. 2. Three filtration cells with a surface area of 19.4 cm\(^2\) each were used in series. The membrane feed side Reynolds number was estimated to be 1000-1100.

![Fig. 2. Schematic of a crossflow membrane test apparatus.](image-url)
Results, Evaluation and Demonstration

Effect of coating the PAN-50 samples using PD and SBMA/PD solutions on surface hydrophilicity can be seen in Table 2. Because of hydrophilic nature of PD, the water contact angle decreased from 63 to 55 when a PAN-50 membrane was treated using a 2 mg/ml PD solution for 1.5 h. To further increase the membrane surface hydrophilicity, the combination of PD and SBMA (a superhydrophilic zwitterionic monomer) was prepared and PAN-50 was coated using it. When exposed to oxygen, dopamine forms a layer of PD, which has excellent adhesion to any type of surface. More importantly, the amine groups in the PD are expected to react with acrylate groups through Michael addition, which anchors the superhydrophilic SBMA on the membrane surface, leading to excellent antifouling properties \[21, 22\]. Thus, the SBMA/PD modified sample for fouling experiments exhibited even lower contact angle relative to that of PD modified analog. This decrease was from 55° to 46°.

Table 2. Water contact angle for unmodified, PD coated, and SBMA/PD coated PAN-50 membranes used in the fouling tests.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Virgin</th>
<th>PD</th>
<th>SBMA +PD</th>
</tr>
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<tbody>
<tr>
<td>Contact Angle</td>
<td>63±4</td>
<td>55±3</td>
<td>46±3</td>
</tr>
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</table>

Table 3 presents the effect of PD and SBMA/PD depositions on relative water permeance of PAN-50 membranes. The relative water permeance is defined as the ratio of the permeance of coated samples to that of uncoated membrane. Error values are the standard deviations of measurements from six membrane samples.

PD coating of a PAN-50 membrane decreased the relative water permeance, presumably because the coating of an additional layer increased mass transfer resistance on the membrane surface. Zwitterionic materials such as SBMA contain both positively and negatively charged
moieties, in a manner that the overall charge is neutral [23]. As the SBMA was added to the coating solution, more interactions between water and surface were made through electrostatic forces and the relative water permeance increased. This behavior was presumably due to the enhanced wettability of the membrane surface and/or membrane pores [24]. The SBMA enhanced the surface hydrophilicity which resulted in an increase in water flux.

Table 3. Relative water permeance for unmodified, PD coated, and SBMA/PD coated PAN-50 membranes used in the fouling tests.

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Virgin</th>
<th>PD</th>
<th>SBMA +PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Water</td>
<td>1</td>
<td>0.71±0.09</td>
<td>0.88±0.11</td>
</tr>
<tr>
<td>Permeance</td>
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</table>

The coating with SBMA/PD increased the long term water permeance compared to the unmodified membranes (Fig. 3). For example, the SBMA/PD coated PAN-50 showed 67% improvement in the permeance than the virgin membrane when testing with a solution containing 1 g/L BSA. As the BSA content increased to 3 g/l, the permeance enhancement by SBMA/PD coating increased to 81%. On the other hand, in both cases, the coating of PD did not seem to improve the water permeance compared to virgin membranes. This may be due to the compromised effect of favorable hydrophilicity improvement and unfavorable transport resistance derived from the PD coating.

The difference in final fluxes can be noted as the key metric and used to quantify the reduction in membrane area needed to achieve a desired overall flowrate. For example, results using an unmodified PAN-50 tested with a 3 g/l BSA, indicated a final flux of 26.3 GFD (gallons/ft²/day) after 3 h of filtration. Applying the SBMA/PD modification enhanced the final flux to 47.6 GFD.
The total area of membrane required to process 30,000 gal/day can be calculated for unmodified and SBMA/PD modified membranes:

30,000 gal per day / 26.3 gallons/ ft²/day = 1140.7 ft² of membrane needed (unmodified)

30,000 gal per day / 47.6 gallons/ ft²/day = 630.2 ft² of membrane needed (SBMA/PD modified)

**Fig. 3.** Permeate permeance as a function of filtration time for unmodified, PD modified, and SBMA/PD coated PAN-50 membranes when tested with water containing (a) 1 g/L BSA, (b) 3 g/L BSA.

So by enhancing the final flux from 26.3 to 46.7 GFD, the number of membrane modules can be decreased by 45%, resulting in capital and operating cost savings and making the recycling process more cost-effective. Capital and operating costs will be estimated based on energy rates and commercially available membrane systems, from which payback can be calculated.
For the Earth Day Student Competition, a poster and PowerPoint presentation that describes the novel anti-fouling approach, flux results and economic analysis will be created. Water samples in jars will also be on display to demonstrate how membranes can produce clean, recyclable water. Two membrane cells with a pristine membrane and modified membrane will be operated for wastewater treatment to compare the two membranes side by side.

**Conclusion**

PAN-50 was selected and modified using a PD and also a SBMA/PD coating solution in order to increase the antifouling properties when tested with a wastewater containing BSA. Water contact angle measurements were performed to confirm the coating of PD and/or SBMA/PD and the enhancement of surface hydrophilicity. A PD modified sample exhibited a lower water contact angle relative to an unmodified analog and the surface hydrophilicity further increased when the membrane was treated with a SBMA/PD coating solution. To study the effect of surface modification on membrane’s productivity water flux measurements were done. The results revealed that PD coating decreased the relative water permeance. Employing the SBMA/PD modification enhanced the membrane’s productivity when compared with the PD coated samples, presumably because of increasing the surface wettability. Overall, the fouling results were highly promising because it clearly demonstrated that by modifying the surface of PAN-50 membrane using super-hydrophilic layers the rate of fouling by BSA deposition during de-watering can be significantly decreased. Furthermore the impact was greater at higher BSA concentrations (81% improvement in the final flux after 3 h of filtration for a 3 g/l BSA). We believe that there is significant potential for further improvement by optimizing the coatings and developing a module enabling higher Reynolds number (Re) operation.
References


2. Extended RO Test to Verify Water Purity, to Perry's Ice Cream Co, Inc. New York State Pollution Prevention Institute, Rochester Institute of Technology, 2013.


