

BIOMIMETIC MEMBRANE COATINGS FOR >2x HIGHER FLUX WASTERWATER TREATMENT USING FORWARD OSMOSIS, MICROFILTRATION AND ULTRAFILTRATION

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Abstract

Active layers enhance or enable the function of membranes. For example, thin film polyamide active layers enable ultrafiltration membranes to function as reverse osmosis membranes do to the poor solubility of salt in the polyamide active layer. In biology, the cell uses molecular bilayers comprised of lipids to separate water from the solutes inside and outside of the cell. Lipid only mimics of the cellular membrane have demonstrated three orders of magnitude higher permeability and six orders of magnitude higher salt rejection than current forward osmosis membranes.

Here we present the properties of active layers for ultrafiltration and microfiltration membranes containing lipid inspired active layers. In addition, these membranes can be used in forward osmosis applications. These active layers are comprised of a z-dimensional structure of alternating lamella of silica and surfactants. The natively hydrophilic silica and polar surfactant surface demonstrate >50% increase in wetting in comparison to poly sulfone and poly ethersulfone membranes. The charge of the surfactants can be non-ionic, cationic, anionic, or zwitterionic. Additionally, the in plane surface charge density of the surfactant lamella is as high as +1e or -1e per 45 amu versus -1e per 426 amu for amorphous polysulfone. Surfactant based membranes can be cationic, anionic, zwitterionic or non-ionic, a desirable feature for the development of process specific membranes. When the active layer is applied to an ultrafiltration membrane, the layer is pore spanning. It is observed as a measurable decrease in molecular weight cutoff. When the active layer is applied to a microfiltration membrane, the layer is conformal. There is no observed change in the molecular weight cutoff.

As an example, application, we demonstrate how the lipid inspired active layer improves membrane performance when filtering waste laundry water. The active layer increase flux of an ultrafiltration membrane flux by 1.54x, COD removal by 2.50x, and calcium removal by 11.6% compared to the control ultrafiltration membrane. Similarly, the active layer improves microfiltration flux by 1.44x, has comparable COD removal, and calcium removal by 15.3% compared to the control ultrafiltration membrane. Data detailing the performance of membranes containing the active layer for when filtering emulsions will also be presented.

Forward osmosis (FO) is used as a pretreatment to minimize reverse osmosis (RO) membrane fouling in short and long term spacecraft wastewater treatment processes. Presented here is data characterizing the

performance of an unsupported forward osmosis zNANO ML-1 membrane in terms of water flux rates and contaminant rejection. Testing results indicated that the unsupported forward osmosis zNANO ML-1 membrane has a 12 times greater flux rate than that of commercially available forward osmosis membrane when deionized water was used as the feed and with 2 mol/l sodium chloride brine was used as the brine. When secondary wastewater was used as the feed water, the unsupported forward osmosis zNANO ML-1 membrane has 4.4 times the flux rate vs. the commercially available forward osmosis membrane. In addition, the unsupported forward osmosis zNANO ML-1 membrane rejects $82\pm 14\%$, $90\pm 7\%$, $92\pm 4\%$, $92\pm 3\%$, $88\pm 3\%$, and $86\pm 17\%$ of ammonium, potassium, magnesium, calcium, nitrate, sulfate, and total organic carbon respectively. The ion specific rejection suggests an electrostatic mechanism, not a solubility diffusion mechanism.

Biomimetic Active Layers: Making Better Membranes

In biology, lipids create the barrier into and out of the cell. Lipidic membranes outperform current commercial membranes: simultaneously improving upon both water flux and solute rejectionⁱ. Lipids are a subset of surfactants. zNano is pioneering biomimetic active layers comprised of lipid like surfactants for filtration applications. Figure 1 LEFT contains a cartoon of the biomimetic membrane structure. Unlike biology where there is only one 5.0 nm lipid bilayer, the zNano biomimetic active layers are comprised of z-dimensional structures alternating between surfactant lamella and silica. These active layers contain several features which improve the function of membranes: improved wettability and improved charged density. The result is higher flux, lower fouling, and improved retention/removal. Figure 1 RIGHT contains an image comparing water droplet spreading on four different membranes: three commercial membranes and one membrane with a biomimetic coating. Figure 1c contains a representative image of 10 ul of RO water on a polysulfone ultrafiltration membrane, two different microfiltration polyethersulfone membranes, and the zNano CA1 membrane coating on a 0.1 um polyethersulfone membrane. The increased spreading diameter of water droplet on the CA1 coated polyethersulfone 0.03 micron microfiltration membrane qualitatively demonstrates its improved wetting by water relative to uncoated polyethersulfone microfiltration and polysulfone ultrafiltration membranes. Table 1 lists the size of the water drops on each membrane. The diameter of the water drop on the CA1 coated polyethersulfone 0.03 micron microfiltration membrane is 1.726 cm, 0.893 cm for 0.03 um PES microfiltration membrane, 0.923 for 0.10 um PES microfiltration membrane, and 0.298 for the 100k PS UF membrane. Table 1 compares the diameter of the water droplet on each material. With the biomimetic active layer, the diameter of the water droplet increases by 1.87x for the microfiltration membrane and 3.46x for the ultrafiltration membrane.

Biomimetic Active Layer

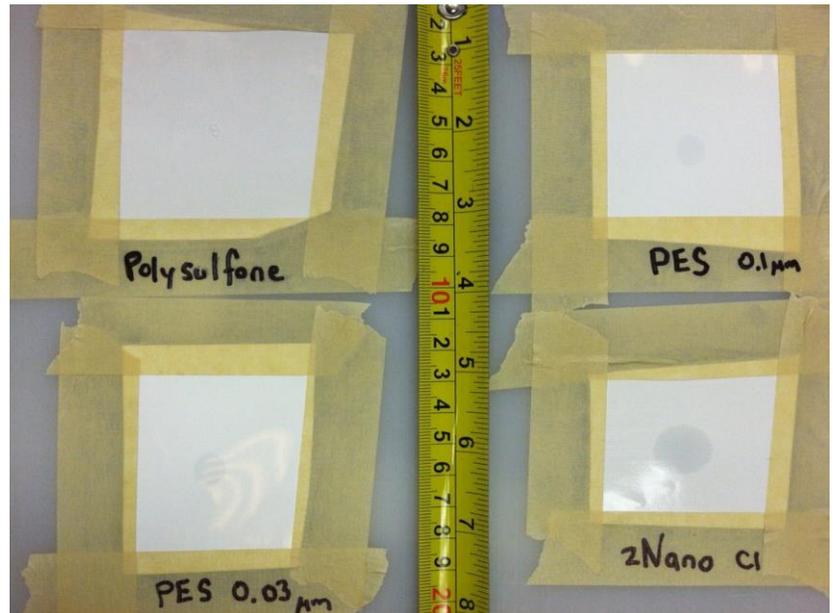
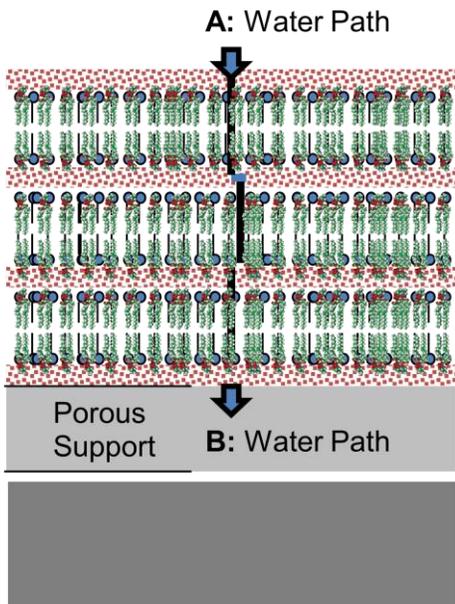


Figure 1 LEFT contains a diagram of the biomimetic active layer. The active layer is comprised of alternating layers of lipid like lamella of surfactants (blue and green ball and sticks) and silica. The orientation of the surfactants orthogonal to the plane of the porous ultrafiltration membrane support creates a non-tortuous path for water enabling high permeability. **Figure 1 RIGHT** is an image of four membrane coupons where three are as is from the manufacturer and one contains an AP2 biomimetic active layer. With the active layer, the diameter of the water droplet increased by a factor of 1.87x. Water droplet spreading is an approximation of contact angle, a direct measure of surface wetting.

Table 1 contains the diameter of 10 ul reverse osmosis water droplets on 3 different support membranes and 3 different coatings (none, AP1, and AP2). Measurements were made using digital images in combination with ImageJ software.

Biomimetic Active Layer	Membrane	Diameter (cm)
NONE	100k MWCO UF PS	0.298
AP1	100k MWCO UF PS	0.76
AP2	100k MWCO UF PS	1.03
NONE	0.03 micron PES	0.893
NONE	0.10 micron PES	0.923
AP1	0.1 micron PES	1.726

Biomimetic coatings improved the performance of UF and MF membranes

Table 2 compares the relative performance of ultrafiltration (UF) membranes from three different manufacturers with and without a biomimetic active layer, UP2. With the biomimetic active layer the flux of reverse osmosis water through each of the membranes increased by a factor of 1.4x – 2.4x. Water flux was measured by

collecting the total permeate of each membrane in parallel over a period of one hour. Membranes were housed in 47 mm membrane holders. Each experiment contained one control membrane (without a biomimetic active layer) and one experimental membrane (with a biomimetic active layer). The materials maintained their improved flux when filtering highly fouling model wastewater. Briefly, 3,000 ppm of sodium dodecyl benzyl sulfonic acid sodium salt, 30,000 ppm of vegetable oil and 35,000 ppm of instant ocean were mixed by stirring for one hour. After mixing, the highly concentrated solution was diluted 9:1 by 35,000 ppm instant ocean in tap water. The dilute emulsion was mixed for one hour using a pump. The resulting solution was filtered by two or three membranes, in parallel where at least one membrane did not have a biomimetic active layer and at least one membrane did have a biomimetic active layer. The surface area of each membrane was 19 cm². The tests were performed in a home built crossflow cell. Tests were performed at 8.0 psi. Emulsion flux was measured by collecting the total permeate of each membrane in parallel over a period of one hour. All permeates demonstrated at least 99% rejection of turbidity. Influent turbidity was greater than 100 NTU and was measured using a handheld turbidity meter from Oakton. All of the membranes containing biomimetic active layers had improved flux >3.1x vs. membranes without biomimetic active layers. In addition, the sample from manufacturer B without the biomimetic active layer demonstrated < 0.1 GFD over a period of one hour. The sample from manufacturer B with the biomimetic active layer demonstrated a flux of 10.96 GFD over a period of one hour. The membranes tested from UF manufacturers A and C were cut from production runs of greater than 100 linear feet of material. Samples were cut from several locations within the production run. Each test was performed in triplicate.

To ensure membrane integrity was maintained after coating, poly(ethylene glycol) (PEG) removal of coated and control materials were compared. Briefly, PEG rejection was measured by collecting the permeate of both a control (w/o biomimetic) and a biomimetic coated membrane (w/biomimetic) plumbed in parallel after a period of one hour. Both membranes were housed in 47 mm membrane holders (Sterlitech Kent, WA). PEG concentration was measured using a Atago pocket optical refractometer that had been calibrated to PEG concentrations. Table 3 compares the molecular weight cutoff of ultrafiltration (UF) membranes from two different manufacturers with and without a biomimetic active layer. With the biomimetic active layer the rejection of PEG increases by 5% to 60% depending on the pore size of the support and the biomimetic active layer. The membranes tested from UF manufacturer A were cut from production runs of greater than 100 linear feet of material. Samples were cut from several locations within the production run. Each test was performed in triplicate. Along with Table 2, these results demonstrate an improvement in **BOTH** flux and rejection for ultrafiltration membranes.

Table 2 is a comparison of the improvement in both water flux and emulsion flux of three different ultrafiltration membranes from three different manufacturers with and without a biomimetic active layer. With all three membranes, the biomimetic active layer UP2 increased the flux for both reverse osmosis (RO) water and an emulsion. The error is the average difference between the measured flux and the mean flux.

Biomimetic Active Layer	UF Manufacturer	UF Chemistry	MWCO	Water Flux Improvement	Emulsion Flux Improvement
UP2	A	PES	100k	2.4 +/- 0.30	3.1 +/- 0.35
UP2	B	PES	30k	1.4 +/- 0.32	>10x
UP2	C	PES	20k	1.4 +/- 0.43	10.1 +/- 1.63

Table 3 is a comparison of poly(ethylene glycol) rejection for two different ultrafiltration membranes and two different biomimetic active layers. For all three classes of materials, the biomimetic active layer containing material had greater rejection than the control material. Each value was the average of three measurements.

Biomimetic Active Layer	UF Manufacturer	UF Chemistry	PEG MW	Rejection w/o Biomimetics	Rejection w/Biomimetics
UP2	A	PES	100k	60% +/- 10%	65% +/- 10%
UP2	D	PES	35k	0%	60% +/- 10%
AP2	D	PES	35k	0%	40% +/- 10%

Table 4 compares the relative performance of microfiltration (MF) membranes from three different manufacturers with and without a biomimetic active layer. With the biomimetic active layer the flux of reverse osmosis water increases through one of the membranes by 1.14x. Briefly, 3,000 ppm of sodium dodecyl benzyl sulfonic acid sodium salt, 30,000 ppm of oil and 35,000 ppm of instant ocean were mixed by stirring for one hour. For manufacturers A and C, the oil was vegetable oil (Safeway Pleasanton, CA). For manufacturer B, the oil was Valvoline. After mixing, the highly concentrated solution was diluted 9:1 by 35,000 ppm instant ocean in tap water. The dilute emulsion was mixed for one hour using a pump. The resulting solution was filtered by two or three membranes, in parallel where at least one membrane did not have a biomimetic active layer and at least one membrane did have a biomimetic active layer. The surface area of each membrane was 19 cm². The tests were performed in a home built crossflow cell. Emulsion flux was measured by collecting the total permeate of each membrane in parallel over a period of one hour. All permeates demonstrated at least 98% rejection of turbidity. There is no data for the other two manufacturers. In addition, the improved wettability with the biomimetic active layer maintains a high flux when filtering model wastewater with 3 wt% oil in water for all three manufacturers by 1.48x - 1.55x.

Table 4 compares the flux of three different microfiltration membranes with the biomimetic coating. The microfiltration membranes are either poly(ether sulfone) (PES) or poly(vinylidene fluoride) (PVDF). The pore size of the membranes is either 0.1 micron or 0.2 micron. The water permeability was only compared for one membrane, BP2 C PVDF 0.1 micron. The reported flux is the average flux of three measurements where the flux during each experiment was averaged over one hour.

Biomimetic Active Layer	MF Manufacturer	MF Chemistry	Pore Size	Water Flux Improvement	Emulsion Flux Improvement
AP2	A	PVDF	0.2	N/D	1.51 +/- 0.32
AP2	B	PES	0.1	N/D	1.55 +/- 0.10
BP2	C	PVDF	0.1	1.14 +/- 0.37	1.48 +/- 0.39

Table 5 compares the relative performance of microfiltration (MF) membranes from a single manufacturer with biomimetic active layers of various charge: cationic, anionic, zwitterionic, and non-ionic. Briefly, 3,000 ppm of sodium dodecyl benzyl sulfonic acid sodium salt, 30,000 ppm of Valvoline and 35,000 ppm of instant ocean were mixed by stirring for one hour. After mixing, the highly concentrated solution was diluted 9:1 by 35,000 ppm instant ocean in tap water. The dilute emulsion was mixed for one hour using a pump. The resulting solution was filtered by two or three membranes, in parallel where at least one membrane did not have a biomimetic active layer and at least one membrane did have a biomimetic active layer. The surface area of each membrane was 19 cm². The tests were performed in a home built crossflow cell. Emulsion flux was measured by collecting the total permeate of each membrane in parallel over a period of one hour. All permeates demonstrated at least 99% rejection of turbidity. The improved wettability with the biomimetic active layer maintains a high flux when filtering model wastewater with 3 wt% oil for all three manufacturers by 1.17x -

1.55x depending on charge. For the zwitterionic material, the flux is decreased to 0.48x. In all cases, the materials show improved rejection of 3% wt oil in water in comparison to the control.

Table 5 is a comparison of the performance of materials with biomimetic coating of various surface charge. The support membrane for all of the material is the same. It is a PES 0.1 micron membrane. In testing without a coating, the membrane failed to maintain rejection of turbidity after 30 to 90 minutes.

Biomimetic Active Layer	Charge	MF Manufacturer	Emulsion Flux Improvement	Rejection
<i>None</i>	<i>N/A</i>	<i>B</i>	<i>1.00x</i>	<i>51.31%</i>
AP2	Cationic	B	1.55x	98.56%
AN2	Anionic	B	1.17x	86.24%
AZ2	Zwitterionic	B	0.48x	99.28%
ANI2	Non -ionic	B	1.44x	97.42%

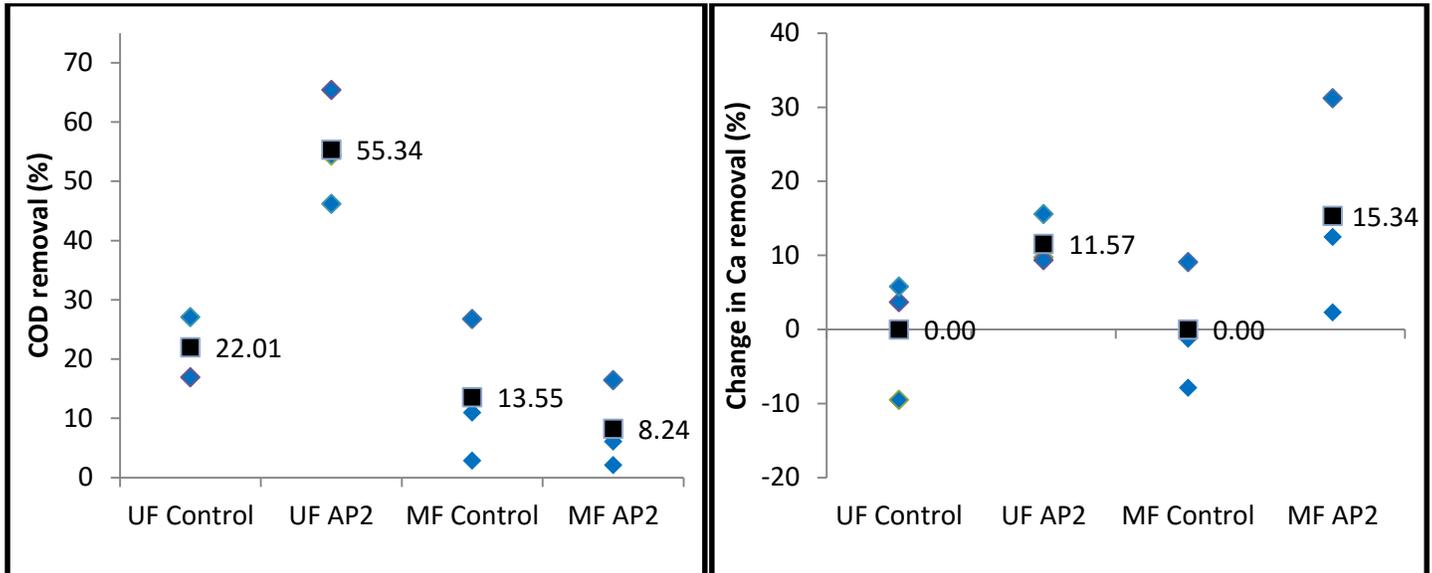
Application of biomimetic coating on UF and MF Membranes: Wastewater Filtration from Laundry Applications

Table 6 compares the relative performance of on both an ultrafiltration membrane and a microfiltration (MF) membrane for a specific application: greywater filtration. Six wastewater samples from top loading washing machines were filtered within 24 hours of collection. For both the UF (100,000 MWCO) and the MF (0.1 um) materials, the addition of a positively charged active layer improved flux by 1.54x and 1.44x respectively. In addition, Figure 2 shows higher removal of chemical oxygen demand and calcium when the active layer is applied to an ultrafiltration membrane. Figure 2 also shows slightly lower removal of chemical oxygen demand and a higher removal of calcium by the microfiltration membrane.

Table 6 is a comparison of the performance of both UF and MF membranes with and without active biomimetic active layers. All experiments were performed in parallel. In separate testing, it was found that the molecular weight cutoff (MWCO) of the UF membranes decreased with the biomimetic coating to 35,000 daltons from 100,000 daltons.

Biomimetic Active Layer	Membrane Chemistry	MWCO or Pore Size	Average GFD per PSI	Turbidity Rejection
AP2	PS	100,000	5.47 +/- 2.49	99.11%
NONE	PS	100,000	3.55 +/- 0.64	99.22%
AP2	PES	0.1 um	5.78 +/- 2.87	97.15%
NONE	PES	0.1 um	4.02 +/- 2.07	98.73%

Figure 2 LEFT is a plot of chemical oxygen demand (COD) removal by the ultrafiltration and microfiltration membranes in the laundry water experiment. The ultrafiltration membrane with the biomimetic AP2 coating removed 2.514 more COD than the control UF membrane. The MF membrane with the biomimetic AP2 coating removed 60.81% of the COD of the control MF membrane. **Figure 2 RIGHT** is a plot of the change in calcium removal by both the UF and MF membrane with the biomimetic AP2 coating. In both samples, the biomimetic active layer increased the calcium removal of the membrane by more than 10%.



Biomimetic active layers for forward osmosis membranes

In biology, plants use osmosis to get water through their roots. In chemical engineering, this process is called forward osmosis. In the data below, we demonstrate how our prototype ML1 membrane improves upon the flux of commercial forward osmosis membranes by 12x using DI water and 4.4x using wastewater. Figure 3 TOP compares the DI water flux of a commercial membrane and the zNano membrane using 2 M NaCl as a draw solution over a period of 5 hours. The zNano membrane has 12x the flux of the commercial membrane. Figure 3 BOTTOM compares the wastewater flux of a commercial membrane and the zNano membrane using 2 M NaCl as a draw solution over a period of 5 hours. The zNano membrane has 4.4x the flux of the commercial membrane. Both experiments were performed with zero pressure gradient across the test cell. The tests with the commercial membrane were performed test setup A. The tests with the biomimetic forward osmosis membrane were performed in test setup B. The exact dimensions of these setups are described in Table 7.

Figure 3 compares the DI water flux and the wastewater flux of a commercial forward osmosis membrane and a biomimetic forward osmosis membrane. **TOP** figures compare the DI water flux for a commercial membrane and the biomimetic membrane using a osmotic agent of 10 wt% NaCl. **BOTTOM** figures compare the wastewater flux of the commercial forward osmosis membrane and the biomimetic membrane using a osmotic agent of 10 wt% NaCl.

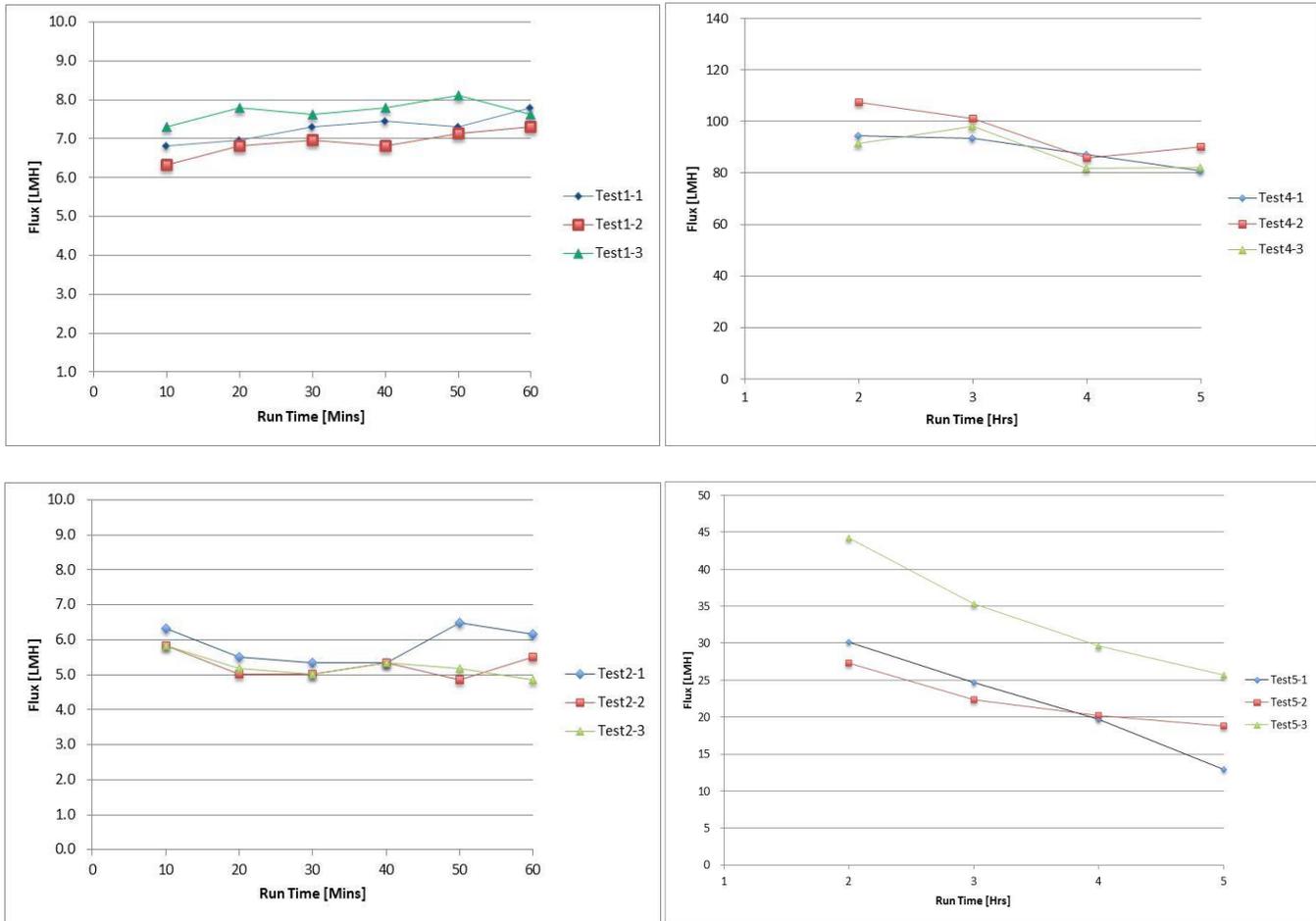


Table 7 compares the ion rejection of the commercial and the biomimetic forward osmosis membrane. The biomimetic forward osmosis membrane achieves comparable, but lower, removal of contaminants in comparison to the commercial membrane. With high flux and lower rejection, it is desirable for applications with higher discharge limits and/or additional downstream treatment such as FO/RO systems.

Table 7 compares the removal of ions by a commercial forward osmosis membrane and a biomimetic forward osmosis membrane. The rate at which the biomimetic membrane demonstrates removal of ions is not dependent upon the size of the ion.

Contaminant	Rejection	Commercial Membrane	Biomimetic Membrane
NH ₄ ⁺	%	97 +/- 2	82 +/- 14
K ⁺	%	98 +/- 2	90 +/- 7
Mg ²⁺	%	98 +/- 1	92 +/- 4
Ca ²⁺	%	98 +/- 1	92 +/- 3

NO ³⁻	%	100 +/- 1	75 +/- 11
SO ₄ ²⁻	%	96 +/- 3	88 +/- 3
TOC	%		86 +/- 17

Experimental Materials and Methods

Wettability Comparison

To compare the wettability of the coated and uncoated membranes, surface wettability was measured. Solid silica has a water-air-surface contact angle of zero degrees whereas solid polysulfone (PS) and polyethersulfone (PES) have contact angles between 40 degrees and 50 degrees. Because all of the materials studied wet with water, a qualitative comparison of surface wettability was performed by measuring the spreading of a fixed volume of water. To perform the measurement, all of the samples for comparison were taped onto a solid piece of polyethylene. Then, a ten microliter drop of water was placed on each freshly prepared surface. Afterwards, digital image was taken which contained each surface used for comparison. Within the image was a ruler to set the scale for the image. The diameters of each drop were measured using the image processing software ImageJ (NIH.GOV).

Water Permeability

The water permeability for all membranes were measured and compared using a home built test cell where three could be tested in parallel. Each membrane has an active area of 3 sq inches. The test cells have a water input port (Feed) and a water output port (Retentate) such that water can pass through the test cell without crossing the membrane. For water permeability tests, the flow rate through the retentate was 0.0 gallons per hour. The test cells also have an output port (Permeate). Water collected at the Permeate must permeate through the membrane to be collected. For all membranes, filtration was performance in dead end (DE) mode. Specifically, the flow of retentate was blocked using a valve so that all water had to be filtered. Typically, the pressure gradient across the membranes was 5.5 psi +/- 0.5 psi although we did not control the pressure gradient. All experiments were performed using a March 201 pump (Ryan Herco San Jose, CA). Permeate and retentate (if any) samples were collected in 20 minute intervals over a period of one hour. Turbidity was measured using a 2100P Hach Portable Turbidimeter.

PEG removal

Poly(ethylene glycol) (Sigma Aldrich St Louis, MO) (PEG) removal was measured using a feed solution of 0.5 wt% PEG. PEG concentrations of the retentate and permeate were compared after one hour. Rejection was calculated by taking the ratio of the difference between the concentration of retentate and the permeate to the concentration of the retentate. Rejection of 1.00 (100%) indicates no PEG in the permeate while rejection of 0 (0%) indicates equal concentration of PEG in the retentate and the permeate. The performance of the membranes (either UF or MF) each membrane (CA2, CA1, and Control) were compared using a home built test cell where three could be tested in parallel. Each membrane has an active area of 3 sq inches. The test cells

have a water input port (Feed) and a water output port (Retentate) such that water can pass through the test cell without crossing the membrane. The test cells also have an output port (Permeate). Water collected at the Permeate must permeate through the membrane to be collected. For the UF membrane set, filtration was performed in tangential flow filtration (TFF) mode. Specifically, the test cells were configured such that the flow rate through the cell was 10 ml per second +/- 1 ml and pressure gradient across the membrane was set at 4.0 psi +/- 0.2 psi. For the MF membrane set, filtration was performance in dead end (DE) mode. Specifically, the flow of retentate was blocked using a valve so that all water had to be filtered. Typically, the pressure gradient across the membranes was 5.5 psi +/- 0.5 psi although we did not control the pressure gradient. All experiments were performed using a March 201 pump (Ryan Herco San Jose, CA). Permeate and retentate (if any) samples were collected in 20 minute intervals over a period of one hour. Turbidity was measured using a 2100P Hach Portable Turbidimeter.

Emulsion Preparation: Cationic and Anionic Oil Water Emulsions with and without NaCl

To compare the purification efficiencies of various membrane technologies, we created an oil water emulsion using a modified versions of Resolution MEPC.107(49) Revised ¹. Briefly, 0.9 g of either negatively charged Sodium Dodecylbenzene Sulfonic Acid (SDDBSA) or positively charged cetyl trimethyl ammonium bromide (CTAB) was mixed with 178 ml of Tap Water for two minutes on a hot plate at room temperature. The emulsion was created via the addition of 9 g of SAE 20W-50 Valvoline and was subsequently stirred for one hour on a hot plate at room temperature. Finally, the emulsion was added to Tap Water such that the emulsion was 6 wt% of the final solution. For emulsions containing 30,000 ppm of NaCl, 100g Instant Ocean (www.instantocean.com) were also added to the final solution. The final solution was mixed using a centripetal pump for one hour. The concentration of Valvoline was roughly 3,000 ppm in the final solution. A picture of the emulsion and the Valvoline are contained in Figure 1. It is important to note that there are zero suspended solids other than those in the emulsion.



Figure 4 LEFT. The oil used for the emulsion. RIGHT. An image of the emulsion before it is diluted to 6 wt% of using Tap Water.

The final solution was mixed using a centripetal pump for one hour. The concentration of Valvoline was roughly 3,000 ppm in the final solution. A picture of the emulsion and the Valvoline are contained in Figure 1. It is important to note that there are zero suspended solids other than those in the emulsion.

Table 1: Emulsion Turbidity	Surfactant Charge	Turbidity [NTU]
Oil Water Emulsion 01	Anionic	264 - 514
Oil Water Emulsion 02	Cationic	>1000
Oil Water Emulsion 03 + 33 g per L NaCl	Anionic	98.7 - 162

Table 8 Measurements of the turbidity of two different oil water emulsions. There were zero suspended solids (TSS) in the emulsion except for those created by the oil water surfactant mixture.

Creating an Emulsion:

¹ Revised guidelines and specifications for pollution prevention equipment for machinery space bilges of ships. MEPC 49/22/Add 2. ANNEX 13 Adopted July 18th, 2003

Briefly, 3,000 ppm of sodium dodecyl benzyl sulfonic acid sodium salt, 30,000 ppm of oil and 35,000 ppm of instant ocean were mixed by stirring for one hour. The oil was either vegetable oil (Safeway Pleasanton, CA) or Valvoline. After mixing, the highly concentrated solution was diluted 9:1 by 35,000 ppm instant ocean in tap water. The dilute emulsion was mixed for one hour using a pump. The resulting solution was filtered by two or three membranes, in parallel where at least one membrane did not have a biomimetic active layer and at least one membrane did have a biomimetic active layer. The surface area of each membrane was 19 cm². The tests were performed in a home built crossflow cell. Emulsion flux was measured by collecting the total permeate of each membrane in parallel over a period of one hour. All permeates demonstrated at least 99% rejection of turbidity.

Feed Water: Filtering Washing Machine Water

To compare the purification efficiencies of various membrane technologies, we sampled 1.5 gallons of water from a washing machine during the first cycle. The washing machine was a Whirlpool top loading washing machine (FIG 1A). The amount of detergent, *ALL* (FIG 1B), was used at the recommended level by the manufacturer. The load was a cold water, color wash of clothes mostly worn for office work. Laundry water (1.5 gallons) was collected 8 minutes into the first cycle. The turbidity and conductivity of the laundry water were measured daily due to the continuous settling of particles within the water (TABLE 1). Finally, a picture comparing tap water (for reference), zNano CA1 filtered laundry water, and the unfiltered laundry water (FIG 1D) reveals that the zNano CA 1 membrane removes most of the turbidity (cloudiness) of the laundry water. In the next section, we compare the performance of the three zNano membranes and two commercial membranes.

The performance of the membranes (either UF or MF) each membrane (CA2, CA1, and Control) were compared using a home built test cell where three could be tested in parallel. Each membrane has an active area of 3 sq inches. The test cells have a water input port (Feed) and a water output port (Retentate) such that water can pass through the test cell without crossing the membrane. The test cells also have an output port (Permeate). Water collected at the Permeate must permeate through the membrane to be collected. For the UF membrane set, filtration was performed in tangential flow filtration (TFF) mode. Specifically, the test cells were configured such that the flow rate through the cell was 10 ml per second +/- 1 ml and pressure gradient across the membrane was set at 4.0 psi +/- 0.2 psi. For the MF membrane set, filtration was performed in dead end (DE) mode. Specifically, the flow of retentate was blocked using a valve so that all water had to be filtered. Typically, the pressure gradient across the membranes was 5.5 psi +/- 0.5 psi although we did not control the pressure gradient. All experiments were performed using a March 201 pump (Ryan Herco San Jose, CA). Permeate and retentate (if any) samples were collected in 20 minute intervals over a period of one hour. Turbidity was measured using a 2100P Hach Portable Turbidimeter.



Figure 5 A. The top loading Whirlpool washing machine from which 1.5 gallons of water were sourced. Water was removed from the first cycle 8 minutes after beginning the washer. The load was full and was colors. B. The detergent used to specification for a full load. C. 180 mls of the sourced wash water in a beaker. The turbidity (i.e. water clarity) was 71 NTU. D. A picture comparing ~15 mls of tap water (for reference), zNano CA1 membrane filtered laundry water, and unfiltered laundry water.

Forward Osmosis Testing Materials and Test Setup

Experimental setup and flow diagrams of the test setup A are shown in Figures 1 left and 2, and setup B in Figures 1 right and 3. . Commercially available membranes and the zNANO membranes are used. The membranes used are single flat sheets with membrane areas of 0.037m² for setup A and 4.25×10m² for setup B. DI water produced by a system with an electrical conductivity of less than 10 μS/cm is used as a feed and 2 mol/l of brine is used as a draw solution. Stir plates are used to keep the solution well mixed. For setup A, the membrane is installed in a stainless steel housing where it is sandwiched between plastic net spacers. O-rings and stainless steel plates are bolted together with fasteners. The solution flows into the module at the bottom and exits at the top outlet. This configuration allows air to exit from the top of the module. For the feed and brine side, flow rates and pressures are measured with analog gauges. A centrifugal magnetic drive pump (Cole Parmer 07003-04) is used to recirculate the brine solution at 7GPH. Electrical conductivity and temperature of the feed are measured using a bench top conductivity meter (YSI 3200). A calibration curve is generated to correlate the conductivity measurement and sodium chloride concentration. A stir plate is used to stir the feed and brine solution. The volume of the feed solution is measure using a scale. Setup B has an active membrane area of 4.25×10⁻⁴ m². The zNANO membrane is provided by the zNANO LLC. and cut to the same size as the commercially available membrane. For setup B, there is no pressure gauge and flow rate gauge for both the feed and brine lines. Masterflex double head peristaltic pump (Cole-Palmer 77120-62) are used to recirculate solution through both sides of the membrane at 14mL/hr. Conductivity, temperature, and mass of the feed solution are automatically recorded via hyper terminal for 24 hours.

Table 9 is a summary of the test parameters for the forward osmosis (FO) tests.

<i>Test No.</i>	<i>Membrane</i>	<i>Setup</i>	<i>Feed Solution</i>	<i>Draw Solution</i>	<i>Area</i>	<i>Flow Rate</i>
No.1 1-1: 1-3	<u>Commercial</u>	A	<u>DI Water</u> 8 Liters	2 M NaCl 0.5 Liters	0.037 m ²	Feed: 60 GPH Brine: 7 GPH
No.2 2-1:2-3	<u>Commercial</u>	A	<u>Wastewater</u> 8 Liters	2 M NaCl 0.5 Liters	0.037 m ²	Feed: 60 GPH Brine: 7 GPH
No.3	<u>Commercial</u>	B	<u>DI Water</u>	2 M NaCl	4.3x10 ⁻⁴ m ²	Feed: 0.236 GPH

No.4 4-1:4-3	<u>zNano ML1</u>	B	1 Liter <u>DI Water</u>	0.5 Liters 2 M NaCl	4.3x10 ⁻⁴ m ²	Brine: 0.236 GPH Feed: 0.236 GPH
			2 Liters	2 Liters		Brine: 0.236 GPH
No.5 5-1:5-3	<u>zNano ML1</u>	B	<u>Wastewater</u>	2 M NaCl	4.3x10 ⁻⁴ m ²	Feed: 0.236 GPH Brine: 0.236 GPH
			1 Liter	0.5 Liters		Brine: 0.236 GPH

ⁱ S. Paula, A. G. Volkov, A. N. Van Hoek, T. H. Haines, and D. W. Deamer (1996) "Permeation of Protons, Potassium Ions, and Small Polar Molecules Through Phospholipid Bilayers as a Function of Membrane Thickness", *Biophysical Journal*, Volume 70, January, 339-348