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## Functionalized nanoparticles as removable membrane coatings

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### Abstract

Membrane fouling plagues all types of membrane filtration, from large-pore microfiltration to nonporous reverse osmosis (RO). Here we investigate the feasibility of using a coating of one or two layers that serves as a barrier between the membrane and foulant. This coating is electrostatically bound to the membrane at operational pH and removed with a simple pH adjustment once fouling has reduced operational efficiency. The water treatment polymer polydiallyldimethylammonium chloride (polyDADMAC) was used to create a positive charge on the fully aromatic polyamide membrane surface. Carboxy-functionalized polyacrylate nanoparticles (NPs) composite with either silver [Ag-PA(-)] or titanium dioxide [TiO<sub>2</sub>-PA(-)], both approximately 10 nm in size, were then adsorbed onto the polyDADMAC coating to reinstate an overall negative charge to the membrane surface. Acid washing removed the polyDADMAC coating by protonating the carboxyl groups on the membrane, promoting repulsion from the membrane surface. Coating and removal phases were characterized primarily by measurement of the surface zeta potential with an electrokinetic analyzer. Additional characterization was performed using scanning electron microscopy (SEM) and attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy. The overall results serve as a proof of concept that these materials could serve as removable coatings for RO membranes.

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## Introduction

### Background

Despite their promising abilities, membrane filtration processes are limited by fouling. Fouling is a broad term for inorganics, colloids, organic compounds and biological organisms that interact physically or chemically with the membrane surface, resulting in reduced flux. A fouled membrane from a laboratory test is shown in Figure 1. Fouling is largely considered an inevitable phenomenon, though fouling-resistant materials and membrane coatings have been developed to mitigate the problem. The diversity of fouling mechanisms is particularly challenging. Scaling occurs when mineral crystals form on the membrane surface and is often encountered in the treatment of surface water, groundwater and agricultural water (1). Colloidal fouling creates a cake layer, which blocks back diffusion of salt ions from the membrane surface, causing elevation of salt concentration and osmotic pressure at the membrane surface (2). Biofouling occurs when organisms in a groundwater or seawater supply grow on the membrane surface or in no-flow zones among the membrane spacer mesh (3). This fouling results in a characteristic pattern shown in Figure 1. Adsorption commonly occurs in the presence of organic compounds in the feed water, which contain functional groups that interact electrostatically with the membrane surface. These interactions can be strong enough to irreversibly foul the membrane despite vigorous or caustic washing (4).



**Figure 1.** Images of clean and fouled membranes. The fouled membrane image clearly shows the impact of the feed spacer.

Much of the fouling prevention work done previously has been geared toward permanent surface modification (5-7). Permanent modification is useful, but even the most resistant membranes can eventually be fouled. This is especially true for feed waters like wastewater and surface water, which contain a wide variety of organic and inorganic material. For this work, a removable surface

modification is sought. A removable coating would reverse fouling no matter the foulant characteristics because whatever is deposited on top of the coating could be released with the coating. If the coating could be released easily, it would reduce the costs for membrane cleaning and could increase the membrane lifetime.

There is potential to create a removable coating by electrostatically binding a material that can be released by pH manipulation. Polyvinyl alcohol has been investigated as a removable coating paired with a positively charged NF membrane (4). This resulted in a flux recovery of nearly 100% after low pH cleaning, however, the initial flux after coating was reduced compared to the uncoated membrane. A coating is sought that will be more permeable, yet still achieve the same fouling release capabilities.

Here the use of functionalized nanoparticles (NPs) as removable adsorptive coatings was investigated. Functionalized NPs have the potential to create a coating that is more porous than polymeric coatings because of the particle nature of the materials. Several inorganic-polymer composite NPs were examined in this study, including titanium dioxide coupled with polydiallyldimethylammonium chloride (polyDADMAC) to impart a positive charge, titanium dioxide incorporated with polyacrylate to impart a negative charge and silver incorporated with polyacrylate, again to incorporate a negative charge. PolyDADMAC was used as a positively charged binding layer atop the negatively charged membrane surface to adsorb negatively charged nanoparticles.

### **Membrane characterization methods**

Chemical and physical effects and properties of fouling, coatings and modifications are determined by membrane characterization using an array of techniques from materials science, chemical engineering and traditional chemical analysis. Chemical (zeta potential, elemental composition and functional groups present) and physical (hydrophilicity, flux and roughness) properties are observed and compared to the virgin membrane to determine beneficial or detrimental effects. For chemical analysis, zeta potential indicates the overall surface charge and isoelectric point and attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy determines functional groups associated with the membrane surface and foulants. For physical analysis, contact angle measurement indicates hydrophilicity of the membrane material and scanning electron microscopy (SEM) visualizes the membrane surface and any coating or foulant aggregation.

### *Zeta potential measurements*

Electrokinetic characteristics of reverse osmosis membranes have a significant influence on fouling performance and contaminant retention. Polyamide membranes, which have a slightly negative surface charge at neutral pH, can electrostatically repel negatively charged functional groups common to natural organic matter. In the presence of positively charged functional groups, however, the membrane charge is a hindrance and encourages electrostatic binding that can be difficult to remove (4). Significant progress has been made toward understanding the complex chemistries involved in membrane surface interactions, but fouling continues to plague desalination plants and other membrane filtration processes. Studies over the past several decades have investigated the fundamental chemical properties of the membrane surface layer (8, 9). Zeta potential characterization of membrane cleaning studies has also been undertaken, though these studies use complex cleaning agents as used in large-scale operations and recommended by manufacturers (10).

This study uses an electrokinetic analyzer to determine the electrokinetic properties of the membrane surface by forcing an electrolyte solution through a sample cell containing the material of interest; electrodes at each end of the sample cell measure the resulting streaming current and zeta potential is calculated (11). The Fairbrother-Mastin (F-M) approach to calculating zeta potential ( $\zeta$ ), given in Equation 1, improves upon the earlier Helmholtz-Smoluchowski (H-S) approach, accounting for phenomena in the instrument that affect the reported measurements (11).

$$\zeta = \frac{dl}{dp} \times \frac{\eta}{\varepsilon \times \varepsilon_0} \times \frac{L}{A} \quad (1)$$

Here  $dl/dp$  is the measured slope of streaming current versus pressure,  $\eta$  is the electrolyte viscosity,  $\varepsilon$  is the dielectric constant of the electrolyte,  $\varepsilon_0$  is the vacuum permittivity,  $L$  is the length of the streaming channel, and  $A$  is the cross-sectional area of the streaming channel.

### *Contact angle measurements*

Contact angle measurement is used to assess the hydrophilic character of a membrane material and the change resulting from membrane modification or coating. The sessile drop method is most commonly used for membrane analysis. This method involves placement of a liquid droplet onto the membrane surface and photographic visualization with a contact angle goniometer (12). Software is used to determine the contact angle of the drop on the membrane. Titrations can be performed by varying the pH of droplets, allowing

characterization of membrane surface chemistry throughout a range of pH values. The type of liquid used in the droplet can also be varied, and a “wettability” parameter can be identified based on the membrane's affinity for particular liquids (13). A second technique that can be applied to membrane surface characterization is the captive bubble method, in which the surface is immersed face-down in a liquid and a gas bubble is released onto the membrane surface from below (14).

In all contact angle measurements the shape of the drop/bubble is metastable and can be affected by outside pressures, evaporation and other factors. There is also a hysteresis described by Gao & McCarthy (15). An increasing droplet will cover a defined area with changing contact angle until reaching a certain volume, at which point it will increase in area with a constant contact angle; a decreasing droplet will decrease in volume with a changing contact angle until reaching a critical volume, at which point the area will decrease with a constant contact angle. In order to account for both aspects of this phenomenon, contact angle measurements often include additions and subtractions of drops/bubbles to find the constant contact angle (14).

#### *Attenuated total reflectance Fourier-transform infrared spectroscopy*

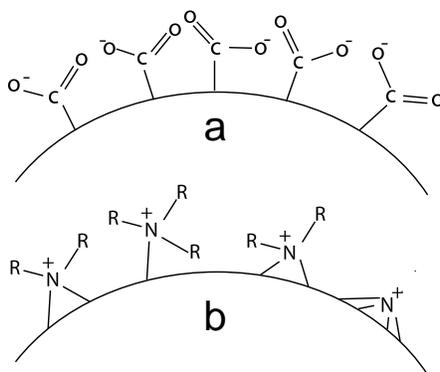
ATR-FTIR spectroscopy is used to confirm functional groups present in the membrane, such as the carboxyl and amine groups expected for a polyamide membrane, or to determine functional groups associated with natural organic matter (NOM) or other foulant materials (16). In RO research, ATR-FTIR is often used to confirm that the membrane, coating or foulant is giving expected results (17). This technique is not often the primary analysis of membranes or membrane coatings, though some studies such as Belfer et al. (18) have demonstrated the benefits of utilizing peak emergence and absorbance changes for assessing membrane coatings. Without extremely sensitive instrumentation, it is difficult to discern the small quantities of coating layers over the dominant vibrational bands of the polysulfone support membrane and ATR-FTIR is of limited benefit (19).

## **Materials and Methods**

### **Coatings**

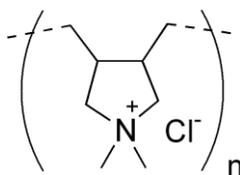
Three nanoparticles (NPs) of similar size but different composition and functionality were obtained from ViveNano Inc. (Toronto, Ontario, Canada):

negatively charged silver-polyacrylate [Ag-PA(-)], negatively charged titanium dioxide-polyacrylate [TiO<sub>2</sub>-PA(-)] and positively charged titanium dioxide-polyDADMAC [TiO<sub>2</sub>-PD(+)]. Figure 2 gives a simplified visualization of nanoparticle surface charge. The NPs were manufactured such that the polymer was incorporated into the NP and functional groups imparted charge at neutral pH. TiO<sub>2</sub>-PD(+) NPs were received in 20% w/w powder form. Ag-PA(-) NPs were received in an aqueous suspension of 1 g/L. TiO<sub>2</sub>-PA(-) NPs were received in 18% w/w powder form. All nanoparticles had an average size of about 10 nm in diameter. Particle size was determined by the manufacturer via dynamic light scattering.



**Figure 2.** Simplification of functionalized nanoparticle charge groups. Acrylate (a) gives net negative charge to silver and titanium dioxide nanoparticles. PolyDADMAC (b) gives net positive charge to titanium dioxide nanoparticles.

The quaternary ammonium polymer polydiallyldimethyl-ammonium chloride (polyDADMAC) Clarifloc C 308-P 20% solution was donated by Polydyne, Inc., a subsidiary of SNF Floerger (Riceboro, Georgia). The monomer structure of polyDADMAC is shown in Figure 3.



**Figure 3.** Monomer structure of polyDADMAC. The formulation used in this study, Clarifloc C 308-P, has an average length of 308 monomers.

## Membranes

Two commercially available RO membranes were selected for this work: SW30HR from Filmtec, a subsidiary of Dow Chemical Company (Midland, Michigan), and SWC4 from Hydranautics, a Nitto-Denko company (Oceanside, California). Both membranes are thin-film fully aromatic polyamide formed from 1,3-benzenediamine and trimesoyl chloride; SWC4 is uncoated while SW30HR is coated with a polyvinyl alcohol layer (20). Both membranes were obtained as dry sheets and stored away from light in sealed plastic bags. Membrane coupons were cut from the same section of membrane to minimize the effects of membrane heterogeneity. One section of SWC4 was used for preliminary experiments. Several sections of SW30HR were used – one designated for Ag-PA(-) experiments, one designated for TiO<sub>2</sub>-PA(-) and one designated for TiO<sub>2</sub>-PD(+).

## Membrane coating process

All coating, soaking and storage occurred in the refrigerator at 4°C. Membrane coupons of approximately 1.5 cm x 2.5 cm were used for all experiments. Coating was performed in 10 mL of coating solution in polypropylene petri dishes. Side-by-side coupons were used for contact angle and SEM measurements.

### *PolyDADMAC coating layer*

PolyDADMAC was used as a positive binding layer to adhere negatively charged nanoparticles to the negatively charged membrane surface. Coating solution was prepared by a hundredfold dilution of the stock solution using doubly deionized (DDI) water, which is purified in house with a MilliQ water system (Millipore, Bedford, Massachusetts). Two dry membrane coupons were soaked in 10 mL of a 0.2% polyDADMAC solution for 24 hours. After 24 hours the membranes were rinsed in DDI water for at least 30 seconds and soaked in 10 mL of DDI water for 12 hours before further coating or analysis.

### *TiO<sub>2</sub>-PD(+) NPs on membrane surface*

TiO<sub>2</sub>-PD(+) NPs were adsorbed directly to the membrane surface. A 1 g/L stock solution of TiO<sub>2</sub>-PD(+) NPs was prepared by dispersing 100 mg powdered TiO<sub>2</sub>-PD(+) NPs into 100 mL DDI water. No buffer was added due to concerns that a buffering species may interfere with NP adsorption to the membrane. A

10% coating solution was prepared by diluting 1 mL stock solution into 9 mL DDI water. Membranes were soaked in coating solution for 24 hours, rinsed in DDI for 30 seconds and soaked in DDI for at least 12 hours before analysis.

#### *Negatively charged NPs on polyDADMAC-coated membranes*

Negatively charged TiO<sub>2</sub>-PA(-) and Ag-PA(-) were adsorbed onto the polyDADMAC coated membrane samples. A 1 g/L stock solution of TiO<sub>2</sub>-PA(-) was prepared by dispersing 100 mg dry TiO<sub>2</sub>-PA(-) into 100 mL DDI water. A 10% coating solution was prepared by diluting 1 mL stock solution into 9 mL DDI water. Ag-PA(-) was received as a 1 g/L solution and a simple tenfold dilution was performed for coating. Membranes were coated for 24 hours, rinsed in DDI for 30 seconds and soaked in DDI for at least 12 hours before analysis.

#### *Control samples*

Control samples were prepared to confirm the electrostatic binding of the coating layers. Controls included TiO<sub>2</sub>-PD(+) exposed to a polyDADMAC-coated membrane, TiO<sub>2</sub>-PA(-) exposed to a virgin membrane and Ag-PA(-) exposed to a virgin membrane. In these controls the NPs were not expected to bind, since electrostatic repulsion should prevent it.

#### **Coating removal process**

Removal of single- and double-layer coatings was tested using simple strong acid and base. Hydrochloric acid (HCl) was used for acid washing at concentrations of 0.1 M (pH 1), 0.01 M (pH 2) and 0.001 M (pH 3). Sodium Hydroxide (NaOH) was used for base washing at a concentration of 0.1 M (pH 13). Control samples of virgin membrane were washed at each pH to determine whether the acid and base solutions altered the properties of the membrane.

To promote coating removal a pair of membranes was vigorously shaken in acid or base for 5 minutes, rinsed thoroughly in DDI water and soaked in the acid or base solution for 6 hours. Kinetics experiments were performed by varying the soaking time to 2, 4, 6 and 8 hours to determine whether time had an effect on removal efficiency. Samples were rinsed for 30 seconds in DDI water after soaking, then soaked in 10 mL DDI water for at least 2 hours before analysis. As with coating, the removal, soaking and storage occurred in the refrigerator at 4°C.

## Membrane characterization

### *Zeta potential measurements*

Membrane zeta potential was determined with a SurPASS electrokinetic analyzer (Anton Paar GMBH, Graz, Austria). Zeta potential,  $\zeta$ , was calculated by VisioLab software (21) from streaming potential measurements using the Fairbrother-Mastin equation (Equation 1). Streaming potential measurements were collected using an adjustable gap cell (AGC) in which an electrolyte solution passed over the membrane surface in a channel 2 cm in length, 1 cm in width and  $105 \pm 5$   $\mu\text{m}$  in height. Membrane coupons covered the 2 cm x 1 cm faces of the channel. Flow was directed through the AGC by linearly ramping pressure from 0 to 300 mbar in both directions. Electrodes measured the streaming current at each end of the sample cell. Two cycles of pressure ramping in each direction were performed and the average zeta potential was used in the titration curve. The electrolyte used was 0.001 M KCl. HCl (0.1 M) and NaOH (0.1 M) were used to adjust the pH. The instrument was fitted with a titration unit for customizable automated titration. Two titrations were performed for each full set of data: an acid titration from ambient pH (~5.5) to pH 3 and a base titration from ambient pH to pH 9. The system was rinsed with nanopure water between titrations to eliminate the buildup of ionic strength within the system. Single measurements were also taken at ambient pH for coated membranes and removal experiments.

### *Attenuated total reflectance Fourier-transform infrared spectroscopy*

ATR-FTIR was used to determine whether the coatings were present in sufficient quantity on the membrane surface to be detected. A Nicolet 6700 FTIR (Thermo Scientific, Waltham, Massachusetts) fitted with a diamond Smart-iTR plate was used with a scanning resolution of 2nm. A total of 32 scans were averaged for each reported spectrum.

### *Contact angle measurements*

Contact angle measurements were taken with a drop shape analysis system (Easy Drop, Krüss, Hamburg, Germany) primarily through the sessile drop method. A volume of 6  $\mu\text{L}$  of DDI water was used for each droplet. Video recording was employed to capture the drop's initial contact with the membrane. Video frames were subsequently analyzed to calculate the contact angle of the drop, fitting a general conic section equation to the drop's profile. Contact angle

measurements were taken between 100 and 300 milliseconds after the drop's initial contact with the membrane surface.

The captive bubble method, in which the membrane was submerged in DDI water and an air bubble was deposited on its surface, was also employed to confirm the hydrophilic properties of the membrane and the coatings.

#### *Scanning electron microscopy*

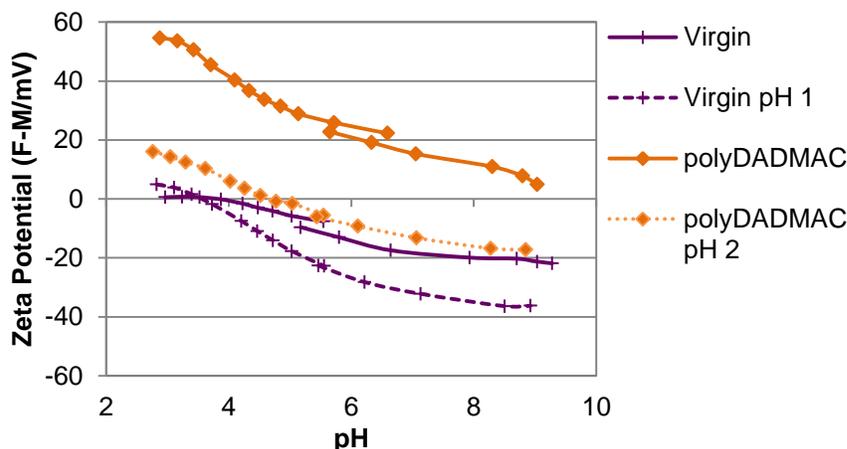
SEM was employed to visualize the effects of the coating and removal processes on the membrane. Membrane samples were sputter coated in gold with a Hummer 6.2 sputtering machine (Anatech Ltd., Battle Creek, Michigan) prior to analysis. Images were taken at magnification of 2.5 k and 10.0 k with a tabletop TM3000 unit (Hitachi High Technologies America, Inc., Dallas, Texas).

## **Results & Discussion**

### **Membrane coatings**

#### *PolyDADMAC coating and removal*

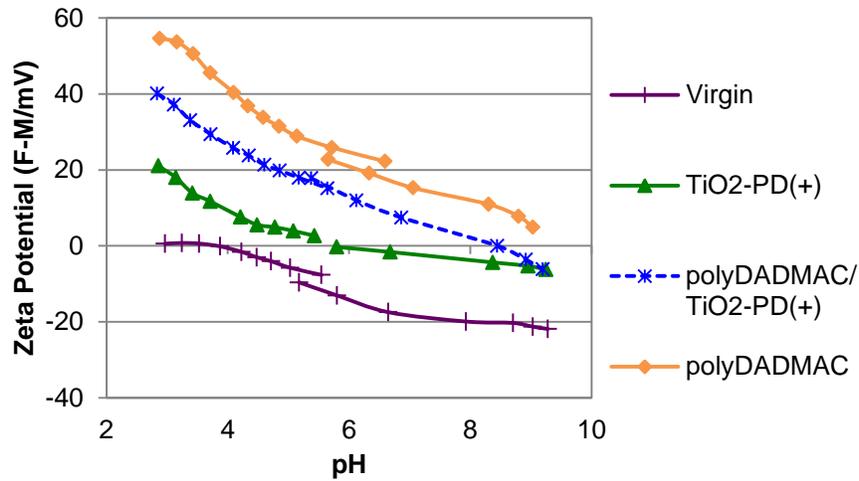
PolyDADMAC was extremely effective in creating a positive layer due to its strong interaction with dangling carboxyl groups in the membrane's polyamide layer. This interaction effectively neutralized the membrane surface charge and imparted the positive character of the polyDADMAC polymer. Because of the polymer's size and linear character, loops or chains of considerable length likely project from the membrane surface as well, exposing a considerable amount of positive charge to the feed solution. Cleaning with strong acid was effective in removing the polymer and nearly restoring the membrane to its virgin state (Figure 4). Acid washing to pH 1 for up to 30 minutes was approved by the manufacturer's technical specification sheet, but a titration performed after this control wash indicated significant changes in the membrane surface chemistry. It was determined that future acid washing should take place over short durations using the weakest effective acid solution. Use of surfactants and other complex cleaning solutions may be driven by similar results of damage to the virgin membrane with highly caustic solutions.



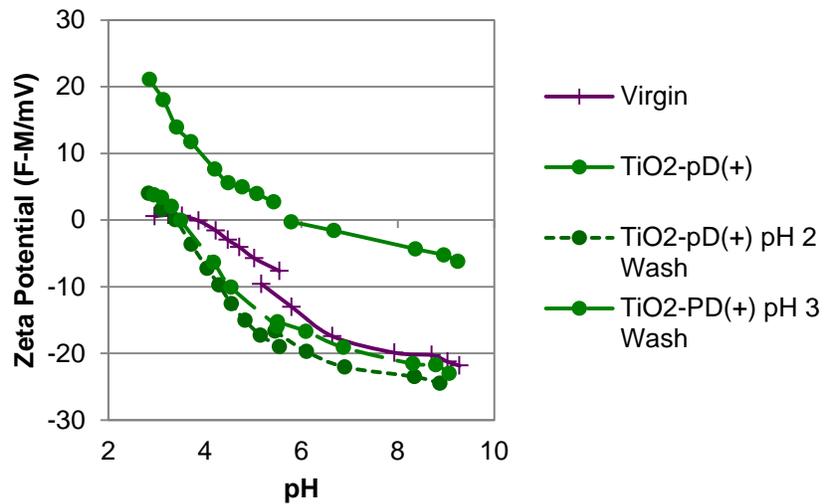
**Figure 4.** SurPASS titrations of virgin, polyDADMAC coated, and acid-washed membranes. PolyDADMAC imparted a strong positive charge and was nearly completely removed with a 30 minute pH 2 wash. Strong acid washing of the virgin membrane with a pH 1 wash altered the surface chemistry of the membrane.

#### *TiO<sub>2</sub>-PD(+) coating and removal*

The TiO<sub>2</sub>-PD(+) nanoparticle, despite containing polyDADMAC, had a very different physical character from the polymer. Coating of the virgin membrane with this positive NP was expected to impart a charge comparable to polyDADMAC but resulted in a significantly lesser positive charge, indicating a lower charge density (Figure 5). Acid washing was extremely effective in removing this coating, suggesting that the lower charge density may have been a beneficial property; whereas polyDADMAC was nearly removed with a strong acid wash, the TiO<sub>2</sub>-PD(+) coating was removed as efficiently with a pH 3 wash as with pH 2 (Figure 6). In the control sample, layering the TiO<sub>2</sub>-PD(+) over polyDADMAC decreased the positive character of the polyDADMAC polymer, confirming the lesser positive charge of the NP.



**Figure 5.** Comparison of TiO<sub>2</sub>-PD(+) and polyDADMAC surface charge. TiO<sub>2</sub>-PD(+) NPs decreased the positive character of the polymer layer, and was much less positively charged when coated onto the bare membrane.

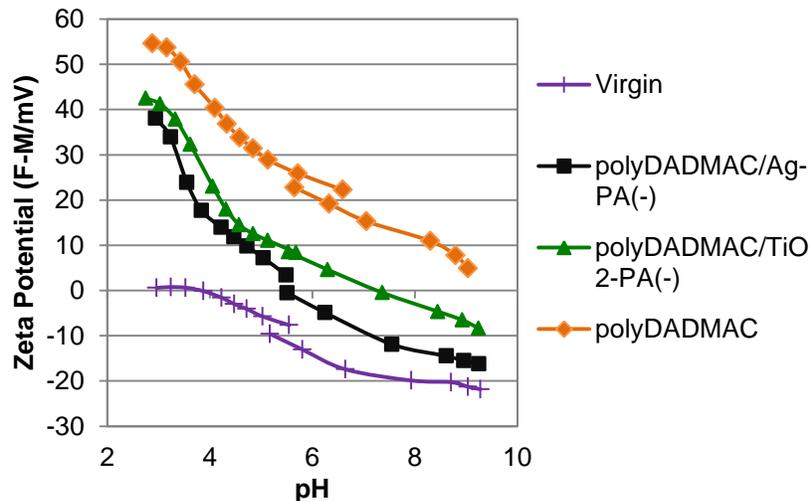


**Figure 6.** Acid cleaning results of TiO<sub>2</sub>-PD(+) coating. NP coating was very effectively removed from the membrane at pH 2 as well as pH 3, which was equally effective.

*Negatively charged NPs self-assemble onto polyDADMAC-coated membranes*

Negatively charged NPs were self-assembled onto the membrane using polyDADMAC as a binding layer. Both NPs decreased the positive charge imparted by polyDADMAC, indicating the charged character of each NP. Ag-PA(-) decreased the positive charge much more than did the TiO<sub>2</sub>-PA(-). It was discovered after these experiments that the Ag-PA(-) coating solution was a much higher concentration than the TiO<sub>2</sub>-PA(-) coating solution, which may explain the greater effectiveness of the Ag-PA(-) coating. The Ag-PA(-) appears to have a more negative character in Figure 7, but this could be caused merely by the concentration difference.

Controls of both Ag-PA(-) and TiO<sub>2</sub>-PA(-) increased both the overall charge of the membrane and the isoelectric point. Ag-PA(-) increased the isoelectric point from ~3.75 to ~4.5 and TiO<sub>2</sub>-PA(-) increased the isoelectric point to ~5.0. These increases indicate that the NPs can bind to the membrane despite charge repulsion and need to be carefully monitored to ensure complete removal during cleaning.



**Figure 7.** Zeta potential measurement of negative NPs after self-assembly onto a polyDADMAC layer. Both negative NPs reduced the net charge of the membrane surface.

## **ATR-FTIR**

ATR-FTIR measurements were taken for several membrane samples, including virgin membrane, polyDADMAC coated, and each negative NP coated onto polyDADMAC. No discernible differences among the spectra were observed. This is likely due to the mass of nanoparticles and polymer on the surface of the membrane being quite small. The full thickness of the active layer was penetrated by this analysis and the backing layer dominated the spectrum. Any contribution from polyDADMAC C-C or C-N bonds would be difficult to discern from those of membrane polyamide. Thus it was reasoned that the coatings were quite thin, even though they were able to significantly alter the surface charge. This bodes well for membrane flux (to be measured in future work), as the thin coatings would not be expected to greatly increase the inherent water transport resistance of the RO membrane.

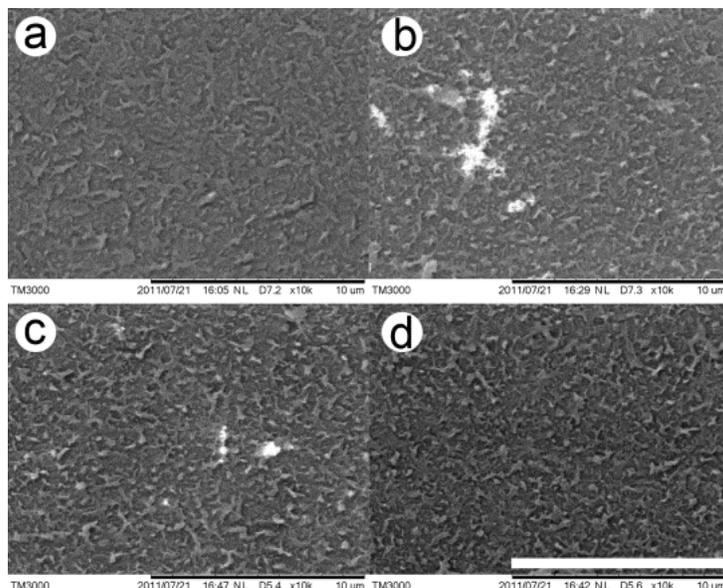
## **Contact angle measurements**

Contact angle measurements were made for most of the samples prepared for this study, but large standard deviation and results that were inconsistent with several literature studies made these results suspect. When sessile-drop method results were inconsistent with reported values the captive-bubble method was attempted, but the results were inconsistent with literature as well as with sessile-drop results. The results that were obtained showed very little deviation between the virgin membrane and double layer coatings, with a contact angle of approximately 80 degrees. Results for polyDADMAC showed an increase in contact angle to approximately 105 degrees. These results, if reliable, demonstrate that association with the membrane surface decreased the highly hydrophilic nature of polyDADMAC polymer. This decrease indicates that the charged ammonium group of the polymer interacts with negatively charged functional groups on the membrane surface, rather than van der Waals interactions of the hydrocarbon portions.

## **SEM imaging**

SEM imaging (Figure 8) was performed for virgin, coated and cleaned membranes. Images did not show significant presence of polyDADMAC or polyDADMAC/TiO<sub>2</sub>-PA(-). Aggregates of Ag-PA(-) were observable, which led to the discovery that the coating solution was ten times more concentrated than originally calculated. The silver aggregates became a useful indicator of cleaning effectiveness in SEM imaging, however, as the lack of aggregates after high pH cleaning indicated that the nanoparticles had been successfully

dissolved or removed. The lack of observable coating layers encourages the conclusion that polyDADMAC and functionalized NP coatings will not significantly alter the flux through the membrane.



**Figure 8.** SEM images of (a) virgin RO membrane, (b) polyDADMAC/Ag-PA(-) coating, (c) Ag-PA(-) coating after pH 1 acid wash, and (d) Ag-PA(-) coating after pH 13 base wash. White scale bar is 10  $\mu\text{m}$ .

## Conclusions

The surface charge of RO membranes was made more positive by the addition of polyDADMAC and/or positively charged nanoparticles. The charge was further modified by adding a second layer of negatively charge functionalized NPs on top of the polyDADMAC. These layers were stable in deionized water overnight and in some cases for several days, but were readily removed by rinsing with an acidic solution. This indicates that these materials could potentially serve as easily washable coatings for RO membranes. However, it was unclear the extent to which the membrane was coated; patchy surface coverage was observed with silver NPs, and similar patchiness may occur with other materials. It is also unclear whether these coatings would be sufficient to prevent other foulants like natural organic matter from attaching irreversibly to the membrane. These questions will be explored in future work.

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