The Combined Effect of Air Layers and Membrane Superhydrophobicity on Biofouling in Membrane Distillation

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Previous studies of membrane distillation (MD) have shown that superhydrophobic membranes experience dramatically less inorganic and particulate fouling. However, little explanation for this improved performance has been given in the literature. Furthermore, studies comparing membrane superhydrophobicity and biofouling are lacking, though superhydrophobic surfaces are known to be more vulnerable to biofouling than other types. In non-membrane surfaces, visible air layers on superhydrophobic surfaces have been correlated with significant decreases in biofouling. Therefore, it was proposed here to use superhydrophobic MD membranes with periodic introduction of air to maintain an air layer on the membrane surface. Superhydrophobic membranes were created with initiated chemical vapor deposition (iCVD) of a fluorinated compound, perfluorodecyl acrylate (PFDA). The substrate membrane was PVDF. To test MD fouling, an MD membrane was placed on top of a fouling solution, with a heater and stirrer to cause evaporation of water through the membrane. Results were analyzed with foulant mass measurements. Alginate gel fouling was examined, as this compound is a common proxy for biological fouling in ocean water. The introduction of air layers was found to dramatically decrease foulant adhesion to the membrane, by 95-97%. Membrane superhydrophobicity made a much smaller impact in reducing fouling.

Keywords

membrane distillation, superhydrophobic surfaces, alginate, air layers, anti-fouling

Nomenclature

α foulant sticking efficiency [-]

δ_c fouling layer average thickness [m]

θ contact angle [°]

ω stirrer rotation rate [rpm]

A experimental pre-exponential factor

A_m membrane area [cm^2]

C_X salt concentration [g/mL]

$\dot{m}_p$ condensate flux [kg/hr]

N number of particles per unit volume [mol/L]

$t_{induction}$ induction time [s]

T temperature [K]

v_p permeate velocity [m/s]

1. Introduction

1.1 Fouling in Membrane Distillation

Membrane distillation desalination uses a porous hydrophobic membrane that passes water vapor while rejecting liquid water [1]. Studies have found MD to be more resistant to fouling than other membrane-based desalination processes, such as reverse osmosis (RO) [2, 3]. The mechanism for this resistance, however, is poorly understood [4]. Fouling on the membrane blocks the surface, which reduces permeate flux and therefore hinders MD performance [5].

In past studies, superhydrophobic MD membranes have been shown to be resistant to inorganic scaling [6, 7] and particulate fouling [8]. Past studies on MD have also found that nucleation in the bulk feed fluid contributes significantly to MD fouling [9].

Superhydrophobic surfaces submerged in seawater with air layers have exhibited minimal biofouling compared to other surfaces [10]. In seawater applications, the remains of algae often cause biological fouling. The anionic polysaccharide alginate is a common model for studying algal fouling [11]. Alginate forms a viscous gummy gel on membrane surfaces, significantly impairing mass transport [12, 13]. In the present study, alginate foulants were tested in a beaker-based MD setup with the introduction of air bubbles saturated with water vapor via syringe. This method was applied to either regular hydrophobic or coated superhydrophobic MD membranes. The mass of foulant deposited was measured to determine the effectiveness of air recharging for fouling reduction on hydrophobic and superhydrophobic MD membranes.

1.2 Fouling Deposition Theory

The deposition of particles on a membrane measured as the change in the fouling layer thickness can be modeled as a function of the particles convected towards the surface. This model has been previously used for RO membranes [14]:

$$\frac{\mathrm{d}\delta_c}{\mathrm{d}t} = \alpha \delta_c v_p C_x \qquad (1.1)$$

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where t is time elapsed, δ_c is the fouling layer average thickness, α is the "foulant sticking efficiency," C_x is the salt mass concentration, and v_p is the permeate velocity passing through the membrane.

An air layer on the feed side of the membrane can block parts of the membrane surface from foulants and increase effective hydrophobicity, thus decreasing α, the foulant sticking efficiency

1.3 Alginate Fouling

Alginate is an anionic polysaccharide, and a major component of the cell walls of algae found in seawater. When exposed to sufficient concentrations of calcium, the calcium replaces the sodium in the alginate. This causes it to form crosslinks, since the +2 charge on calcium ions can form 2 bonds. The cross-linked long molecule chains turn the solution into a gel [15].
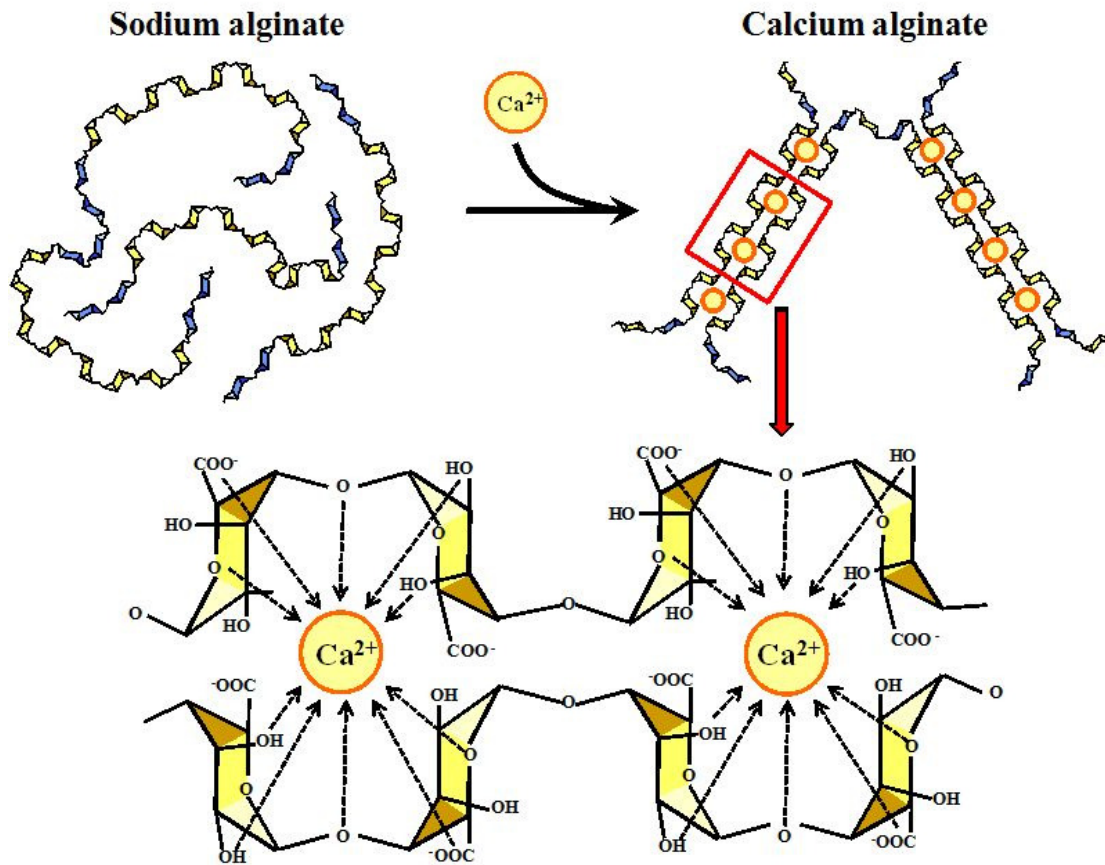
**Figure 1.** Alginate gel formation in the presence of calcium ions, from [16]

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Superhydrophobic surfaces such as those in membrane distillation are known to be more fouling resistant to salts, but more vulnerable to biological fouling [17]. Therefore, improving resistance to biological fouling on these surfaces is a major research goal.

2. Methodology

2.1   Static Membrane Distillation Setup

A "static" MD membrane apparatus was used to examine the periodic introduction of air layers to reduce fouling. The membrane divides a hot alginate solution from ambient air. This feed side is designed to have typical MD conditions, while allowing for quick tests and precise weight measurement.

In a static MD setup as seen in Figure **2**, a membrane floats on the surface of foulant-containing water. The membrane is flush with the edges of the plastic beaker to avoid water getting on top of the membrane and direct evaporation. Insulation minimized heat loss and excess heating of the air. In this study, fouling was measured by weighing the membrane before and after the study. The entire apparatus was placed within a fume hood to maintain consistent operating conditions (Table 2). The system was monitored with a thermocouple temperature probe and humidity meter.

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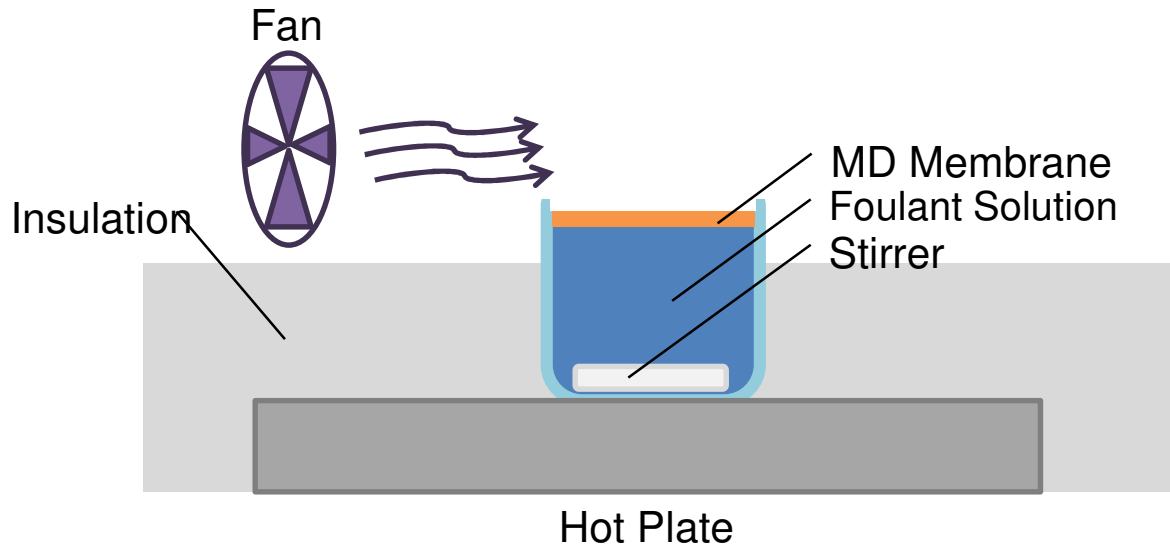
Figure 2. "Static MD" experimental setup of evaporation through an MD membrane for biofouling
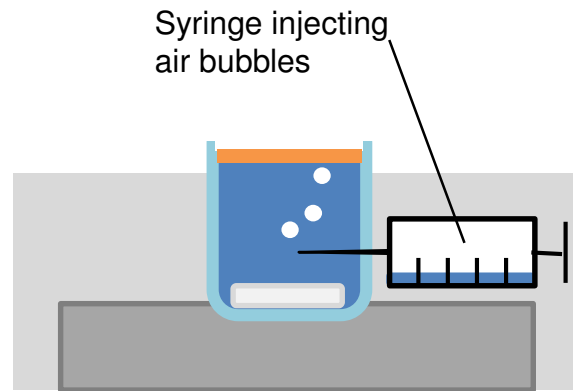
Figure 3. Air was introduced to the system via syringe containing hot saturated air.

 For air recharging with a syringe as seen in Figure 3, saturated air at room temperature was injected into the system every 5 minutes. Each time 5 mL of air was added over ~10 seconds (Table 1), for 4 different trials. The addition of air caused the membrane to lift off the surface.

Table 1. Experimental conditions for air recharging of MD membranes

Foulant weight [%wt]	Air Injection Frequency [min]	Test A	Test B	Test C	Test D
0.04% Alginate 0.029% CaCl$_2$	10	hydrophobic, control	hydrophobic, air introduction	super-hydrophobic, control	super-hydrophobic, air introduction

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In seawater desalination including reverse osmosis, alginate gel layers significantly contribute to creating a biofilm on membrane surfaces. The system was tested with of alginate sufficient to produce a fouling gel layer. The alginate was procured from Sigma-Aldrich. All cases used the same PVDF membrane: the superhydrophobic trials coated this membrane with PPFDA.

Table 2. Experimental Variable Values.

Variables	Symbol	Values	Uncertainty
temperature	$T_{f,in}$	60°C	±2°C
humidity	RH	31%	±4%
condensate flux	$\dot{m}_p$	5 LMH	±0.4 LMH
stirrer rotation	ω	60 rpm	±1 rpm

2.2 Superhydrophobic Membrane Preparation and Testing

The MD membranes used are polyvinylidene fluoride (PVDF) membranes produced by Millipore. They have a 0.2 μm pore size, and a part number of ISEQ 000 10. These membranes were made superhydrophobic with a coating by initiated chemical vapor deposition (iCVD) of poly-(1H,1H,2H,2H-perfluorodecyl acrylate) (PPFDA) [18, 19, 20].

The superhydrophobic membranes were prepared in a reactor using a process described previously [21]. For the coating, a PFDA monomer (97% Sigma-Aldrich) and t-butyl peroxide initiator (TBPO) (98% Sigma-Aldrich) were used. The monomer and initiator were added into the chamber at rates of 0.03 and 1.0 cm^3/min (sccm), respectively. The PPFDA film was 200 nm thick.

The contact angles were measured with a goniometer (model 590, Ramé-Hart) and images were acquired with the software DropImage. An automatic dispenser increased or decreased the drop volume to measure advancing and receding contact angles.

Scanning electron microscope (SEM) images with a JEOL 6010a machine verified the conformity of the superhydrophobic coating.

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3. Results and Discussion

3.1 Fabricated Superhydrophobic Membrane Properties

The PPFDA significantly improved the contact angles of the membranes, as seen in Table 3. Notably, receding contact angles increased the most, by 78°. This result aligns with the literature, where receding contact angles are small for mildly superhydrophobic surfaces, due to pinning of water to the surface. PPFDA provided superior contact angles because it contains more fluorine than PVDF. Additionally, Sidechains also form structures that prevent the fluorine atoms from oriented away from water molecules. The surface roughness overall plays a significant role in increasing surface superhydrophobicity. SEM confirmed that the coating had only a minimal effect on the surface roughness, allowing for an accurate comparison between the membranes.

Table 3. Summary of MD Membrane Contact Angles Used In This Study.

Membrane	Static contact angle (°)
Superhydrophobic	157
Hydrophobic	125
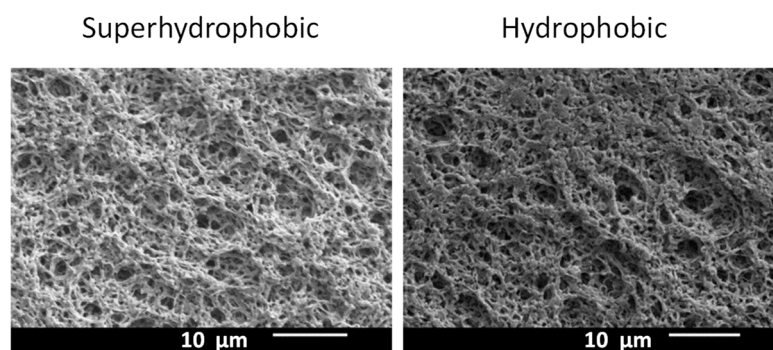
Figure 4. Membrane SEM. The PPFDA coating from iCVD has a minimal effect on the membrane surface structure and does not clog pores
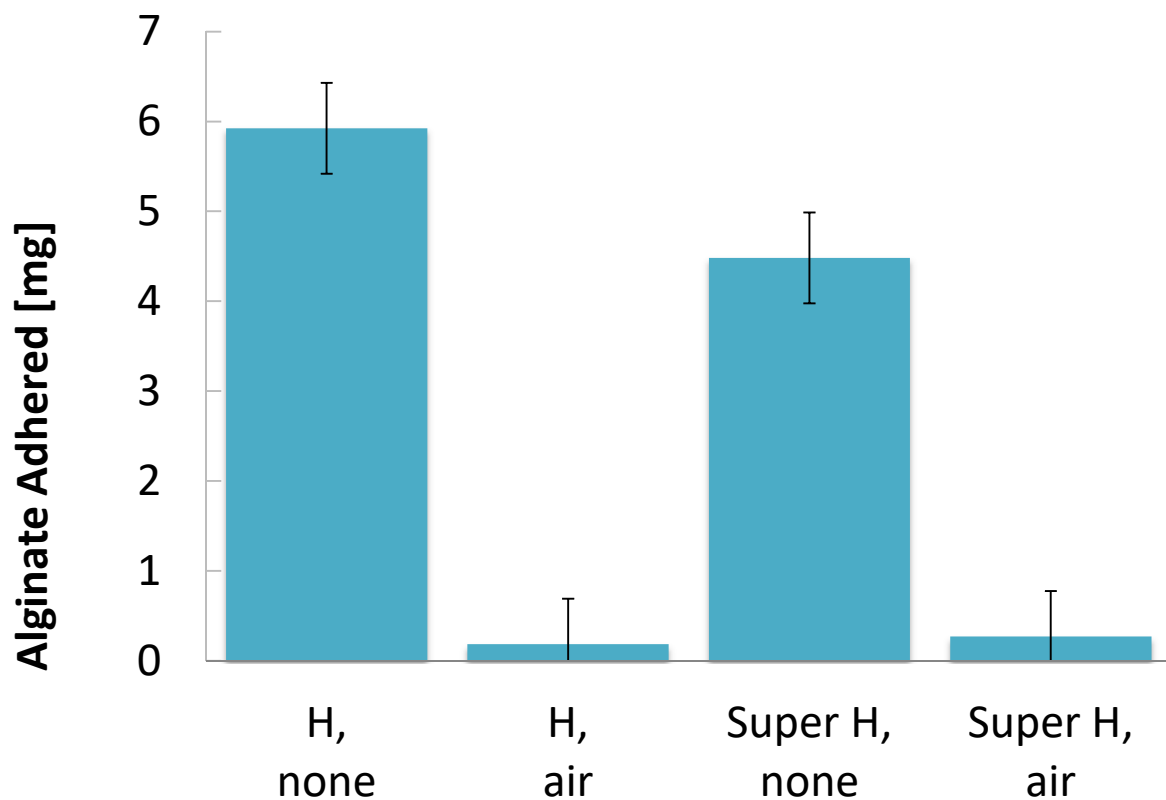
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Figure 5. Photograph of submerged superhydrophobic MD membrane. The membrane appears reflective due to the air layer on the membrane surface.

3.2 Fouling Results

The mass of alginate adhered to the membrane was used to quantify the extent of fouling, as seen in Figure 6.

Figure 6. Weight of Salt Adhered to MD Membrane, 0.04% Alginate, $CaCl_2$. Alginate fouling was found to have been reduced with the introduction of air on both hydrophobic ("H") and superhydrophobic ("Super H") membrane surfaces.

Maintaining air layers dramatically and consistently reduced fouling of alginate on the membrane surface. The gel layers form rapidly when the concentration of calcium is sufficient. Therefore it is not expected that the air affects the formation of gel itself. Instead, the air acts to significantly reduce the adhesion of the gel to the membrane.

It is worth mentioning that no other fouling occurred here, since the salt added, $CaCl_2$, is extremely soluble. Notably, biological fouling can reduce membrane hydrophobicity and increase surface energy,

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so avoiding biological scale may also help reduce break through and reduce fouling of salts on the membrane.

4. Conclusion

The sustained presence of air layers was proven to be extremely effective in reducing biofouling. The air layers reduced the mass of alginate adhered by 95-97%. The introduction of air layers impairs the adhesion of the alginate gel to the membrane surface, as gel is still present in the bulk solution. The deposition of the PPFDA coating via iCVD effectively created a very hydrophobic membrane, with a static contact angle of 157°. The superhydrophobic membrane without air recharging had only slightly less alginate fouling than the uncoated membrane without air recharging. This differs from results for salt precipitation scaling, which have shown superhydrophobic membranes to significantly reduce scaling. Notably, membrane distillation membranes are known to be resistant to inorganic fouling but vulnerable to biofouling, so superhydrophobicity and air layers may be extremely valuable in reducing fouling on MD membranes.

5. ACKNOWLEDGEMENT

6. References

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