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Impact of Spray Coating on the Performance of Hydrophobic Membranes

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Abstract

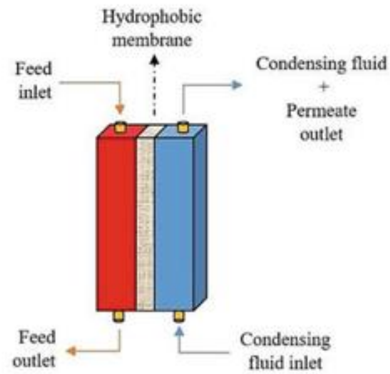
Membrane distillation (MD) is a rapidly emerging water treatment technology used to combat the global water crisis. Membrane pore wetting is a primary barrier to widespread industrial use of MD. The primary causes of membrane wetting are membrane fouling and an exceedance of liquid entry pressure. The development of different types of polymer membranes and the use of pretreatment have led to significant movement towards the prevention of wetting in MD. We sought to take a new approach to combat membrane wetting that involves coating these membranes with hydrophilic chemical compounds, which consequently would decrease their air permeability. Pulling data from our HVAC group's latest papers, we used two different compounds for our coats: Graphene Oxide (GO) and Pebax 1657. After heating and mixing, these compounds were spray coated onto polypropylene membranes at 10 mL, 20mL, and 30 mL worth of solution. 7 membranes with area 38mm x 44 mm were created, including one uncoated for control, and placed into a porometer to measure the gas permeability. We discovered that 30 mL of Pebax and GO made an equal, strong difference in combating wettability. In the future, these membranes can be used in membrane distillation to measure the performance of their coats' ability to combat wetting. These experiments serve as a big step in the move toward the industrialization of membrane distillation with the goal of overcoming the freshwater shortages of the world.

Introduction

As the world's population steadily rises, so too does the consumption of the little freshwater we have on our planet. Water scarcity has actualized because of poor infrastructure, water contamination, and poor management of water resources. All these factors are aggravated by the growing threat of climate change. 1.1 billion people lack access to clean drinking water and 2.7 billion experience water scarcity at least one month a year. Scarcity can realize in ways such as poor sanitation, a lack of drinking water, and damage to irrigation systems [11]. When these systems fail the threat of diseases like cholera surge. Most developing arid countries possess neither the resources nor the experience to solve the problem.

Water covers 71% of the Earth's surface – 97% oceans, 3 % freshwater (69 % of the freshwater on the planet is unavailable because it is frozen or beneath the Earth). The world will eventually run out of natural freshwater and need to rely on new ways to get safe, potable water. The ocean is the only place left for us to extract water, but it cannot be consumed due to its high salinity and need to be filtered for usage [13].

Desalination has arisen as a process to remove salts and other contaminants from oceans and rivers to supply potable water. The separation of potable water from saline sources can be achieved by applying pressure, electricity, or a phase change to the water. Reverse Osmosis involves pressurizing salty water through a semipermeable membrane, leaving behind the salty brine, and filtering out clean drinkable water [2]. Membrane Distillation (MD) is a thermally driven process that involves evaporating the water fed to the system to pass through a hydrophobic membrane and then cooled to return to liquid potable water [2].



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Polymeric membranes used in desalination processes can either be dense or porous. Dense membranes allow only the passage of materials the polymer is soluble with. Porous membranes have holes, or micropores, that allow only the passage of materials that the polymer is selective to [4]. Selectivity of porous membranes can be classified as hydrophilic or hydrophobic. Hydrophilic membranes wet, meaning liquid can pass through the pores. Hydrophobic membranes do not wet and do not allow liquid to pass through its pores [3,4]. MD uses hydrophobic porous membranes to allow mass transfer to happen in the vapor phase, while the salty brine is left behind in the feed or recycled to another system to be purified [4].

Penetration of the feed solution into the pores of the membrane is called wetting. This occurs when the transmembrane hydrostatic pressure exceeds the liquid entry pressure (LEP, or the minimum pressure that must be applied to a solution before it can go through an unwetted pore). This can occur when a membrane is damaged by fouling [1]. Different types of fouling in MD can be classified by the deposited materials, some examples include organic fouling, biological fouling, or scaling (the precipitation of salts on the membrane surface). These hydrophilic deposits can reduce LEP, damage the membrane, and lower the permeate flux [1]. The feed solution, if not treated, can contain surfactants that decrease the surface tension of the feed. All these occurrences lead to a less hydrophobic membrane and therefore a membrane more susceptible to wetting [1]. When a membrane is fully wetted, it cannot separate the salinity from the pure final product, making MD ineffective.

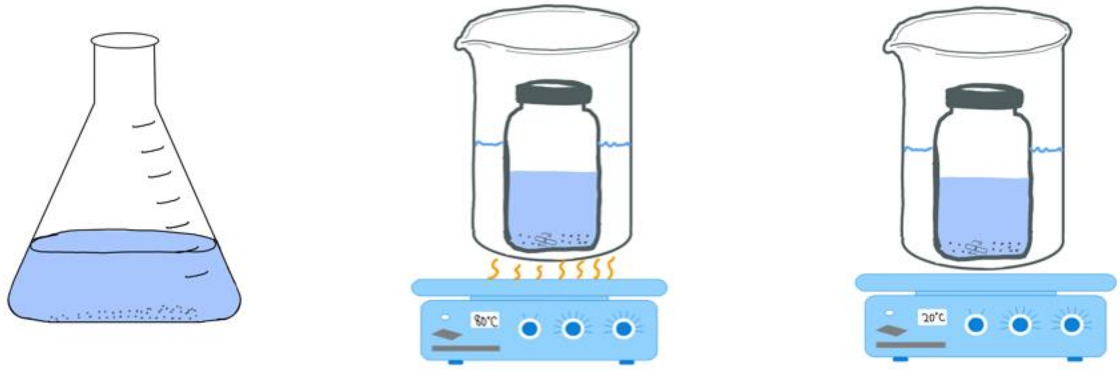
The selection of membranes in MD depends on the system it is operating in as well as the goal of the system itself. Vacuum membrane distillation (VMD) is used because of its high permeate flux, low heat loss, and high salt rejection [9]. Compared to other MD configurations, VMD has a much higher partial vapor pressure gradient that allows higher flux to be achieved at lower operating temperatures. VMD is therefore a large energy saver in the desalination world, especially when coupled with Reverse Osmosis (RO). RO cannot handle the salinity that VMD can, so if joined together in stages then a higher final yield can be achieved. VMD can be operate at lower temperatures and compared to other MD configurations has a much more efficient energy consumption/permeate flow ratio. VMD systems can also utilize renewable energy sources like solar or waste heat [9].

In VMD, Polypropylene is commonly used as the polymeric membrane because of its thermal conductivity and smaller pore size that is more resistant to scaling. Unfortunately, VMD's partial vapor pressure gradient is so strong that wetting will happen much faster than in other MD modules [9]. Using membranes with superhydrophobic properties has been a method to prevent this [1-5]. Wetting has also been prevented by pretreatment, which is a method of removing harmful substances from the feed water, such as surfactants that diminish the hydrophobicity of the membrane's pores [9]. This method resists wetting and fouling without the consequence of decreased flux.

Coating membranes has arisen as a new way to keep out foulants and surfactants from the permeate side of the module. There are many methods to coat the membrane, but they each share a goal to decrease their permeability of unwanted materials [3,4]. Spray coating was used in this experiment because it is the only form of coating that has a coated and uncoated side. This is needed for the method of testing the coat's air permeability, which determines the coat's uniformity [3,4]. Coating membranes will be essential for MD's future of industrialization because it resists scaling, which collapses the efficiency of the process.

Methods

Pebax 1657 is a hydrophilic microphase-separated block copolymer. In the form of pellets, a 3 wt. % Pebax solution was added to a 30/70 water-ethanol mixture. The final solution was obtained by dissolving the pellets at 80 degrees C for 3 hours in a sealed jar placed in a water bath. After these 3 hours, the solution sat for 24 hours to cool to room temperature before using it for spray coating. There was a magnetic stir bar present in the jar stirring the solution while it heated and cooled to ensure the polymer was properly solved and no solid remained. This method is pictured in the figure below. This solution alone was used for 3 of the membranes in the spray coating test at 10 mL, 20mL, and 30mL.



Add 30/70 Water/Ethanol solution and 3% by weight solution of Pebax 1657 pellets to flask

Add to container inside of water bath
Heat at 80° C for 3 hours and mix with stir bar

Cool to room temp for 24 hours

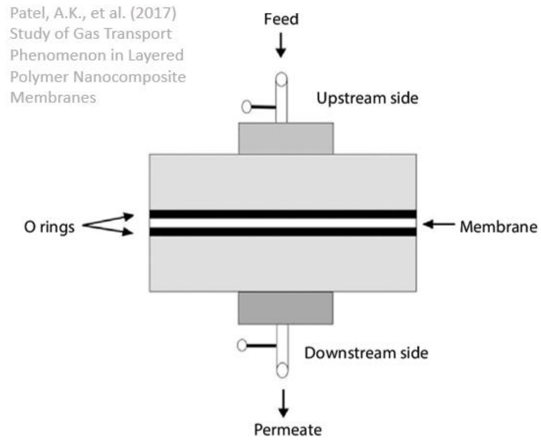
The next 3 membranes were coated using a small amount of Graphene Oxide to the mixture. Using the equation found below, we hoped to achieve a GO loading of 1.5 wt. %. 100mL of this solution were created [3]. This loading amount was achieved using 63.66 mL distilled water (1mL/mg), 26.26 g of the Pebax 1657 solution created in the last step, and 3 mL of our pre-prepared wet GO paste (4mL/mg). Finally, stir this solution in a room temperature water bath for 24 hours and immediately begin spray coating to avoid the solution settling.

$$GO\ loading\ (wt\%) = \frac{Weight\ of\ GO\ (g)}{Weight\ of\ GO\ (g) + Weight\ of\ Pebax\ (g)} \times 100$$

7 total membranes were fabricated. After the Pebax 1657 solution cooled for 24 hours in room temperature, it was sprayed onto 3 different membranes using 10 mL, 20 mL, and 30mL. Next the paint cup was filled with the GO + Pebax solution and spray coated the same quantities onto the next 3 membranes. Each 10 mL paint cup took 200 seconds to empty at a pressure of 32 psi. The final membrane was completely uncoated and used as a control variable.

Spray coating is done by hand as the airbrush needed to be rotated in circles so that it could uniformly coat the entire membrane. There is little ability to control waste and precision due to the lack of automation. It is best to spray from at least 1 foot away from the membrane as to not clog its pores and instead coat the outside of it. It was necessary for the membranes to dry for at least a day after being coated because they would have lost their uniformity if still damp. 7 membranes were initially oven dried, but due to its inconclusive effect on the results, it was determined that air drying them is ample enough to avoid this.

To test whether these coats clogged the pores of the membrane or allowed flow as well as a proof of decrease porosity/pore size, they went through a gas permeability test. Gas permeance through the polymeric membranes was measured by placing them in a capillary flow porometer. The goal of this test was to measure the flux of air per pressure over time of air that was able to pass through the membrane. The machine can be summarized in the figure below.

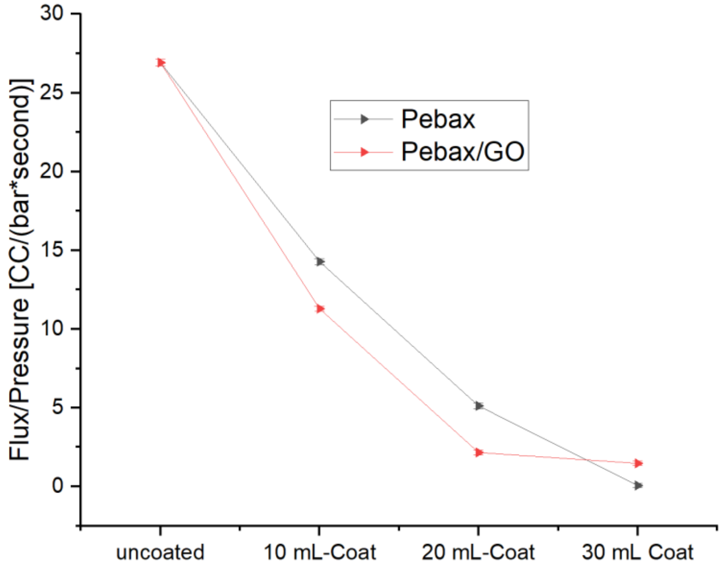


Each of the 7 membranes were 38 x 44 mm in area. The gas permeance test required a cut of the membrane in the form of a circle with a radius of 5 mm. Next place the cut of the membrane into the machine with the coat facing in the direction of the exit stream of the air permeating it. N_2 gas was then pushed through the membrane at pressures ranging from 0 to 2 bar (0 to 32 PSI). This test ultimately measured the pore size of the membranes after coating. The lower the flux of N_2 gas, the smaller the pores [3,4,10].

Spray coating is one of the many ways to coat membranes. Dip coating involves lying the membranes in the solution, drying, and repeating multiple times to coat both sides of it. This experiment required a coated and an uncoated side of the membrane. Our method of spray coating involves the use of an air brush, the same tool used for artwork. The airbrush has a conical paint cup that holds 10 mL.

Results

As seen in the figure below, the more coated the membrane, the more resistant it is to air flow. It is important to keep in mind that the air flow, the less water vapor will flow as well, meaning the process will be slower and less efficient for industrialization. There does not need to be more than one coat. The number of coats should be determined by the desired flux of the entire process, as well as the composition of the feed solution. The less treated the water, the more coats necessary. Pretreatment of the feed solution should therefore be a method used in conjunction with coating membranes, as well as using the most efficient polymer possible. If flux is desired, polypropylene should not be used due to its already small pores. If keeping heat in the system is the most important factor of the module, the polypropylene would be the choice of polymer. These results are important not because they solve an issue, but because they are just another step in the right direction.



The figure illustrates an uncoated hydrophobic porous membrane's ability to resist air, and it is not very strong. A high air permeability is consistent with a lower liquid entry pressure, meaning wetting happens faster. So, the coat is necessary to maximize the liquid entry pressure keeping in mind that each coat makes the MD process slower.

Conclusion

Wetting is one of the largest drawbacks for MD's industrial use. As the process of MD goes on, so to does the decay of each of its components. The pores get fouled with harsh, damaging materials that decrease the flux of the entire process, and work toward making it fruitless as it leads to wetting. Wetting is a phenomenon, when it occurs in full, that eliminates the separation aspect of desalination. Pretreatment of the water that is inputted into the system is necessary for removing large foulants and surfactants. Membrane coating has proven to be an up and coming way to eliminate the smaller foulants that enter in through the feed.

VMD is a process that would benefit heavily from these results because of its already high flux that can counteract the flux loss because of coating. VMD struggles because of its high susceptibility to wetting, and if it can prevent through coating then the next steps of preventing water scarcity can be realized. VMD can most importantly be used to clean up the exit brine streams from other filtration processes like RO, and that is an important start for MD's move into industry.

Future work

In the future, the coating process can be improved. Dip coating is a machine coating mechanism that involves dipping the membrane into the substance instead of spraying it on. They both require similar drying methods by simply letting them hang at in room temperature for at least a day. Air permeability tests do not work if both sides of the membrane are coated, however. To compare spray coating to dip coating different tests need to measure the performance of these membranes. Water vapor permeability tests are a great way to achieve this, except they need much larger membranes than the ones tested in this experiment. Nonetheless, dip coating must be explored in MD as it is used extensively in other areas within the field of purification.

This method of spray coating can also be promoted to HVAC systems that coat their substrates with materials like TiO_2 to purify air. Dip coating is primarily used in these systems, but spray coating may provide something to the HVAC world that has not yet been explored.

Finally, once determined the perfect method of coating that involves little waste, uniformity, and proven results, these coated membranes can be applied to real MD systems and put to the real test. If wetting can be proven to reduced, while also maintaining the system's flux at the rates of current MD systems, then coating may just be the next step in allowing MD to accomplish its goal in providing a new source of water for the arid regions of the world.

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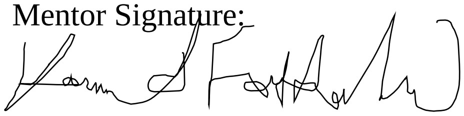

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