

Spring 2017

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Pribonic, Michael, "Electrospinning and Polarization of PVDF Fiber Mats for Adsorption of NaCl" (2017). *Honors Research Projects*. 540.

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Electrospinning and Polarization of PVDF Fiber Mats for Adsorption of NaCl

4200 497-002

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4/28/17

Executive Summary

Potable water has become less of a commodity. The current processes for water purification from sea water are rigorous, expensive, and relatively inefficient. Reverse osmosis has been the headline process for water purification for the past fifty years. Advances in treatment technology have been scarce and would be very beneficial to the availability of potable water. An important aspect to any filtration process is the material of the membrane used. The ability of the material used in a filtration process can be measured using capture efficiency and pressure drop of the treated fluid. A material with high capture efficiency and low pressure drop could reduce operating costs significantly in a process, thus making the supply of potable water much greater. The ability for Polyvinylidene Fluoride electrospun fiber mats has been proposed as a material for this purpose.

In the analysis of this material's ability to adsorb NaCl from water, the material showed percent increases in weight ranging from 0-165% with an average of 47%. The effect of residence time on the batch adsorption process was noticeable. The salt adsorbed did not converge to a saturation value, but actually fluctuated. The salt adsorbed also fell back into a solution with DI water. This result along with the effect of residence time implied the adsorption was more of a physical process rather than a chemical attraction. The effect of the polarization of this material on its adsorption ability was also questioned. The polarization process was not a success and did not result in a polarized mat. The treated material, though, was still compared to the untreated material with regards to adsorption of NaCl. The treated mat showed a surface charge near 0 kV across the material. The untreated mat showed a surface charge near -2 kV. Neither of the mats were polarized; however, the untreated mat displayed a better ability to

adsorb salt. The treated mat showed an increase in weight of 13.6 % while the untreated showed 107%. This result implies the surface charge had a positive effect on its capture ability. The polarization results were a small sample size and further experimentation would be beneficial.

From the work done in this project, a great experience and mild knowledge on the electrospinning process was obtained. The concept of piezoelectricity was also brought to my attention along with the concepts of Curie temperature and the polarization process of a material. Along with technical skills obtained, the experience of working in a lab for an individual research project was also obtained. This lab work was drastically different from class lab work as a great deal of individual research and learning was needed as there was no manual telling me what to do. Overall the individuality of the project created strides in my ability to work independently.

In the future for this project, the polarization technique should be reviewed and many iterations be done to create a large sample size to give confidence in the results. A steady state treatment in a filtration apparatus should also be done to determine the materials filtration index. This equipment was not available to me and experimental data from this equipment would be very beneficial to the analysis of PVDF's ability for the adsorption of NaCl. For students working on research projects, I would emphasize the effect of individual research prior to starting on the quality of experiments. This would enable time to be used efficiently and ensure higher quality results.

Introduction

Water purification has proven to be a difficult process. Insufficient technology for water desalination/purification has led to an extreme global water shortage. It is estimated that 748

million people worldwide currently have no access to an improved source of water (Goldberg, 2014). Currently reverse osmosis is the most common method used for large scale water purification. Reverse osmosis offers many pros and cons to being a water purification technique. Many steps are required due to the different sized contaminants in the water. One membrane that works to separate salt from water may not filter dangerous pesticides that have a much smaller molecular structure. For this reason carbon filters must be used in conjunction with other membranes (Donner, 2017). Reverse osmosis also notably separates the naturally occurring minerals that are important to the human body's functions. The removal of these alkaline minerals make the water more acidic and potentially harmful to the body. Reverse osmosis is also a very expensive process. Reverse osmosis requires high pressures leading to high utility costs and it is a very inefficient process as, on the average, two to three gallons of water are wasted for every gallon produced. Water desalination processes account for 0.04% of the global electricity consumption at 75.2 Twh/yr (Herndon, 2013). This inefficiency adds to the slow pace of the process. Reverse osmosis has been the flagship process for clean water production for the last fifty plus years but, capital spent researching new methods to save money has been scarce. With strong competition in the industry it has been difficult to generate profits and conduct research for more efficient methods for water filtration. Aside from an entire different process, efforts to save on energy and new membrane technology are alternative ways to save money. The focus of the proceeding work was to explore the ability of a nanofiber mat made of Polyvinylidene fluoride (PVDF) to adsorb NaCl dissolved in water. Nanofiber technology is becoming more prevalent in filter media due to the improved capture efficiency as a result of high surface area to volume ratios and well defined pore structures, but the lowered pore diameter increases the subsequent pressure drop. PVDF is also piezoelectric. The fluorine atoms

in the molecular structure induce the polarity that could potentially be suitable to attract the ionic character of NaCl. The PVDF nanofiber mats were made via electrospinning and exposed to multiple salt water solutions. PVDF mats were also set in a custom polarization device to induce polarity. The treated mats were also exposed to the salt water solutions to observe the difference in adsorption ability.

Background

The most abundant source of water is sea water. Sea water contains a high amount of salt dissolved in it and must be desalinated to be potable. Current technology such as reverse osmosis utilizes semi-permeable membranes to act as a filter for water by enabling water to permeate through the membrane, but not minerals such as NaCl. Reverse osmosis is a relatively inefficient technology and alternative methods would be very beneficial. The proposed method of water desalination is the adsorption of salt in PVDF nanofiber mats.

PVDF has been proposed to be a suitable material given its polymer character that allows it to be made into long fibers and its piezoelectricity is of interest to attract particles of high ionic character. Polyvinylidene fluoride is semi-crystalline and is composed of units of vinylene difluoride. The repeat unit is $\text{CH}_2\text{-CF}_2$. The hydrogen atoms are prone to sharing their electrons while the fluorine atoms are extremely electronegative. To give PVDF its piezoelectric properties, it must be stretch while an electromagnetic field induces polarity. Stretching the polymer molecules orients the molecules to align fluoride atoms away from the hydrogen atoms of other molecules. The material is heated at a high temperature at a specific rate to help induce the dipole with the help of the electromagnetic field and the material is then cooled quickly to hold structure and polarity of the polymer.

The PVDF nanofiber mats were made by electrospinning. Electrospinning is one of the most common methods to produce nanoscale fibers and is notable for its simplicity and ease of maintenance (Huang et al., 2003). Electrospinning consists of applying a high voltage to a droplet of solution. The high voltage charges the body of the solution. This charge creates electrostatic repulsive forces between the molecules in the droplet. These forces counteract the cohesive forces from surface tension that bring the molecules together and as a result stretch the molecules. Eventually the molecules reach a breaking point from the surface of the droplet and a stream is emitted. This phenomenon leads to the formation of a Taylor cone. The solution is then dried in the air on its way to the collector as the solvent evaporates. The charge from the solution also transitions to the fiber and is responsible for the whipping or coiling motion of the fiber on its way to the collector. The collector is grounded to attract the charged fibers (Huang et al., 2003). The collector in this experiment was a drum of tin foil continuously rotating to ensure a well distributed thickness for the mat. The quality of the material can be a result of many different parameters in the electrospinning process. The solvent used can be critical. If the solvent evaporates too quickly, the fibers will not be formed and, instead, will be collected as specks of PVDF on the collector. The voltage applied to the needle is important. If not enough voltage is applied, the Taylor cone will not form and the solution will remain in droplets. The flow rate of the pump is also important. The flow rate must be controlled to ensure a consistent stream and the process be done at a reasonable rate. The distance from the needle to the collector is important to ensure a well distributed mat. If the needle is too close to the collector, the fiber tends to accumulate on a single spot and climb toward the needle. Ambient conditions are also important. These affect the ability of the solvent to evaporate and the amount of static charge on

materials. A typical electrospinning apparatus, Taylor cone, and fiber mat can be seen below in

Figure 1.

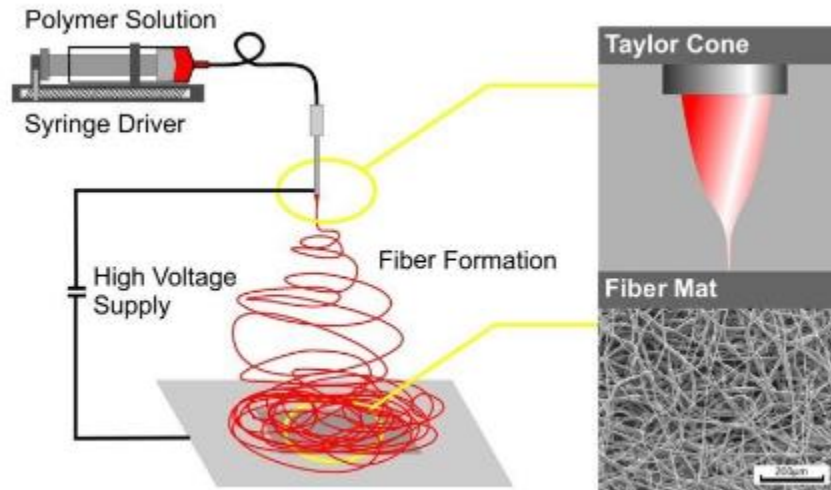


Figure 1 Shows a lab-scale electrospinning process in which the polymer solution is pumped through a syringe and needle and subjected to a high voltage. The Taylor cone is formed at the end of the needle and the fiber mat is collected on the grounded collector (Electrospinning, 2017)

In this work the electrospun mats were made to test their ability to adsorb dissolved salt from water. Mats of different thicknesses were subject to salt water solutions of varying salt content. Mats of 20 gsm and 30 gsm were spun and tested in salt water solutions of 5,10, and 20 wt% NaCl. The time allowed for adsorption was also varied. Residence times of 2 hours, 4 hours, and 24 hours were used. Ideally the mats would be tested in a steady state process in which the concentration of the water being purified does not change with time. A steady state apparatus for testing was not available and thus a batch process was to be done. Mats were also

treated to induce piezoelectric properties of PVDF and then tested to determine their ability for salt adsorption.

Experimental Methods

A solution of PVDF was made using Kynar 741, acetone, and dimethylformamide (DMF) was made. PVDF (10 g) was added to a 100 mL beaker. Acetone (32 g) was then added to the beaker. This solution was heated at a magnetic plate surface temperature setting of 90 °C. A stir bar was added to the solution to promote mixing. The initially white solution was heated and stirred until clear. Once finished, DMF (8 g) was added to the 100 mL beaker. These amounts gave a 10 wt% PVDF solution with acetone and DMF added at a 4:1 ratio. This solution was heated and stirred at the same settings for 30 minutes. A 40 cm x 31 cm sheet of foil was cut and weighed. The initial weight of the foil was roughly 7.8 g. The foil was then wrapped and taped around the collecting drum. At these dimensions, 2.53 g and 3.80 g of PVDF fibers needed to be collected on the foil to permit thicknesses of 20 and 30 gsm respectively. A 5 mL syringe and needle was then obtained and extended using tubing and adapters for the syringe and needle to the tubing. The tip of the needle was ground to a flat tip to allow for an ideal droplet. The PVDF solution was then pulled into the syringe. The syringe was then placed in a syringe pump. The pump was set to a volume of 5 mL and a rate of 15 mL/hr. The needle was placed in its mount which had multiple needle holes for the needle to be slotted. This enabled the fibers to be spun evenly across the collector. The distance from the end of the needle to the collecting drum was

maintained at 15 cm. The positive end of the voltage source was then attached to the needle while the ground was attached to the bearing of the collecting drum. The syringe pump was then started. Once a droplet was emitted from the needle the voltage source was turned on at a setting of 20 kV. A stream of PVDF was emitted and collected on the collector. Often during the process, the syringe would empty and need to be refilled. Upon stopping, the needle would clog and a new needle would need to be used. Periodically the foil with PVDF fibers would need to be weighed to monitor the mat thickness. This process continued until a net weight of 2.53 or 3.80 g for PVDF fibers was observed. Once spinning was complete, the mats were left in a heater overnight and dried at 70 °C. The dried mats were then cut into uniform sections to be used for salt water adsorption testing. Salt water solutions of 5, 10, and 20 wt% were made. The solutions totaled 20 g each and were made in 20 mL vials. Stir bars were added to the vials. The dry mats were weighed before being added to the solutions. The mats were then placed in the solutions and stirred for varying times of 2 hours, 4 hours, and 24 hours. Each thickness was tested in each wt % solution for each amount of time. Once testing was done, the mats were removed from solution and dried in the heater overnight at 70 °C. Once dry, the mats were weighed again to determine how much salt was adsorbed. After being weighed the mats were then placed in deionized water to determine if the salt would fall back into solution to imply if the salt was physically and not chemically bound to the PVDF fibers. The weight of the mats was then measured after. To observe the difference in ability between polarized and unpolarized mats, mats were stretched, heated, and quenched. Mats (10 cm x 6 cm) were cut and placed in a Teflon frame to be stretched. The frame was equipped with two 8 cm x 8 cm aluminum electrodes on each side of the stretcher. The mat was then stretched to a length of 11 cm. The frame and mat were then placed in a furnace. The contents were heated at a rate of 20 °C/min from room

temperature to the Curie temperature of 150 °C for PVDF. The Curie temperature was then held for 20 minutes. The contents were then cooled to room temperature at 20 °C/min. While the contents were heated and cooled in the furnace, the two electrodes were connected to a potential difference of 25 kV. With the orientation of the electrodes relative to the fiber mat, the electric field would be applied perpendicular to the mat's surface. Once the treatment was complete, the surface charge of the mats was measured using a handheld electrostatic field meter (Simco-Model FMX-003). The device was tared to an initial reading of 0 kV using ambient air before the mat surfaces were tested. Once surface charge readings were complete, the mats were then placed in salt solution to observe the adsorption capabilities.

Data and Results

The electrospun PVDF mats were characterized using Scanning Electron Microscopy (SEM). Images of mats are shown below in **Figures 1** and **2**. The diameters of the fibers ranged between 1 and 10 μm .

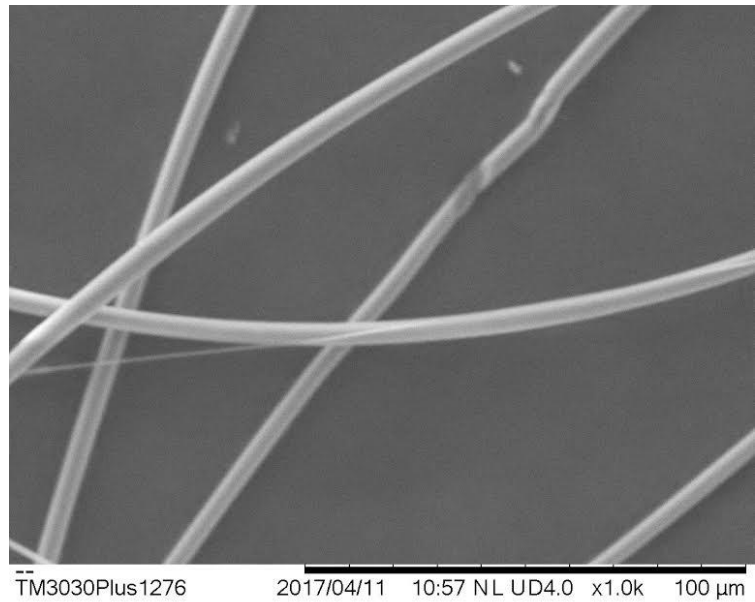


Figure 1 Shows an SEM image of electrospun PVDF fibers.

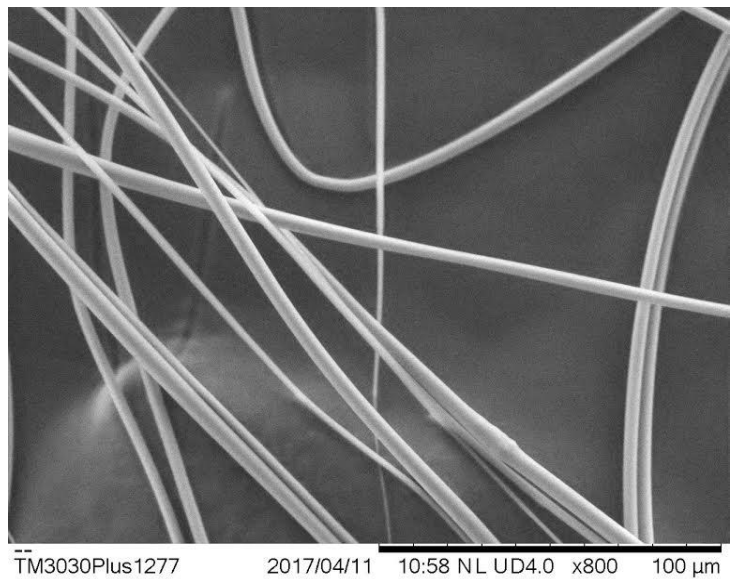


Figure 2 Shows an SEM image of electrospun PVDF fibers

The ability of the PVDF fiber mats to adsorb NaCl from water solution was measured in percent weight gained of the mat. A filter index could not be determined since the testing process was a batch process. The pressure drop could not be tested and the process could not reach steady state concentrations unless the mats became saturated. The same mat for a given time period could not also be used for another time period since the mats had to be dried to measure the weight of NaCl adsorbed. This action would have removed the actual amount of water from the system and disturbed the mass balance. The weights of PVDF mats before and after adsorption of NaCl at 20 and 30 gsm, in solutions of 5, 10, and 20 wt% NaCl, and at residence times of 2, 4, and 24 hours are shown below in **Table 1** and **Table 2** respectively. The percent change in weight of the mat per residence time can be seen in **Table 3**.

Table 1 Shows weights (g) of 20 gsm PVDF fiber mats before (top of cell) and after (bottom of cell).

Time	5 wt%	10 wt%	20 wt%
2 hrs	0.244	0.23	0.21
	0.38	0.321	0.453
4 hrs	0.194	0.187	0.21
	0.2044	0.253	0.223
24 hrs	0.195	0.184	0.182
	0.24	0.426	0.483

Table 2 Shows weights (g) of 20 gsm PVDF fiber mats before (top of cell) and after (bottom of cell).

Time	5 wt%	10 wt%	20 wt%
2 hrs	0.297	0.287	0.304
	0.316	0.329	0.331
4 hrs	0.278	0.279	0.277
	0.279	0.359	0.706
24 hrs	0.341	0.36	0.302
	0.377	0.443	0.388

Table 3 Shows the % increase in weight for 20 gsm PVDF fiber mats for the adsorption of NaCl over residence times of 2, 4, and 24 hours.

Time (h)	5 wt%	10 wt%	20 wt%
2	56%	40%	116%
4	5%	35%	6%
24	23%	132%	165%

Table 4 Shows the % increase in weight for 30 gsm PVDF fiber mats for the adsorption of NaCl over residence times of 2, 4, and 24 hours.

Time	5 wt%	10 wt%	20 wt%
2	6%	15%	9%
4	0%	29%	155%
24	11%	23%	28%

After adsorption, the mats were placed back in DI water to observe if the salt would fall back into solution. The weight measurements for 20 gsm and 30 gsm before and after DI water treatment are shown in **Tables 5** and **6** respectively.

Table 5 Shows 20 gsm PVDF fiber mats with adsorbed NaCl before (top) and after (bottom) DI water treatment.

Time	5%	10%	20%
2 hrs	0.38	0.321	0.453
	0.255	0.231	0.225
4 hrs	0.2044	0.253	0.223
	0.197	0.241	0.2
overnight	0.24	0.426	0.483
	0.197	0.208	0.213

Table 6 Shows 30 gsm PVDF fiber mats with adsorbed NaCl before (top) and after (bottom) DI water treatment.

Time	5%	10%	20%
2 hrs	0.316	0.329	0.331
	0.298	0.291	0.276
4 hrs	279	0.359	0.706
	0.25	0.1988	0.338
overnight	0.377	0.443	0.388
	0.354	0.365	0.312

Due to time constraints, only 30 gsm to be put in 20 wt% NaCl solution was chosen for polarization treatment. After polarization the surface charge of the treated mat was near 0 kV, which was measured after the device was zeroed. Upon this result, the surface charge of an untreated mat was measured and determined to be nearly 2 kV. The two mats were placed in 20 wt% solution. The percent increase in mass for the treated mat at 0 kV was 13.6%. The percent increase in mass for the untreated mat at nearly 2 kV was 107%.

Discussion

With regards to the results of the project, there were good outcomes and shortcomings to the research done. The fiber mats produced by electrospinning did not meet the nanofiber criteria. The fibers were characterized at 1-10 μm . Perhaps a needle of small diameter be used to produce smaller diameters. The adsorption of NaCl in the PVDF mats showed positive results for their physical adsorption of salt as the percent increase in mass was noticeable with some mats almost doubling in mass. There were a few outliers in which the mats either adsorbed nearly no salt or adsorbed a lot more salt relative to the average. These results may be due to experimental error. It was also noted that over the different residence times, the adsorption results varied and did not necessarily converge to a saturation point. This implies the adsorption was more of a physical process rather than being chemically bound by polarity. This observation also aligns with the result of the NaCl falling back into solution with DI water. The unpolarized PVDF mats showed a good ability to adsorb NaCl. The durability of the mats, capture efficiency, and attributed pressure drop for a PVDF filter would be of curiosity and be a good experiment in a steady state filtration process for future work.

The polarization process for the PVDF mats was not a success. The results from previous work done by Dinesh Lolla in his Fabrication, Polarization of Electrospun Polyvinylidene Fluoride Electret Fibers and Effect on Capturing Nanoscale Solid Aerosols could not be repeated. The treated mats showed negligible surface charge and could not be polarized. In fact, the untreated mats showed better capture results. This may have been due to the static charge developed on the mats after the electrospinning process as the untreated mats, though not polarized, showed higher surface charges than treated mats. A repeated polarization experiment or adjusted experimental design for the polarization process may be beneficial to this project.

Literature Cited

1. 15 Interesting Facts About Desalination <http://www.seametrics.com/blog/desalination/> (accessed Apr 28, 2017).
2. Dooner, S. Reverse Osmosis & RO Membranes <http://reverseosmosischemicals.com/reverse-osmosis-ro-membranes> (accessed Apr 28, 2017).
3. Key Benefits <http://www.porex.com/technologies/materials/porous-plastics/polyvinylidene-fluoride/> (accessed Apr 28, 2017).
4. Lolla, D.; Lolla, M.; Abutaleb, A.; Shin, H. U.; Reneker, D. H.; Chase, G. G. Fabrication, Polarization of Electrospun Polyvinylidene Fluoride Electret Fibers and Effect on Capturing Nanoscale Solid Aerosols. *Materials*2016, 1–19.
5. Herndon, A. Energy Makes Up Half of Desalination Plant Costs: Study <https://www.bloomberg.com/news/articles/2013-05-01/energy-makes-up-half-of-desalination-plant-costs-study> (accessed May 3, 2017).
6. Goldberg, E. Despite Progress, 748 Million Still Lack Access To Clean Water: New Report (HOW TO HELP) http://www.huffingtonpost.com/2014/05/19/who-water-report_n_5353233.html (accessed May 3, 2017).
7. Huang, Z.-M.; Zhang, Y.-Z.; Kotaki, M.; Ramakrishna, S. A review on polymer nanofibers by electrospinning and their applications in nanocomposites. *Composites Science and Technology*2003, 63 (15), 2223–2253 DOI: 10.1016/s0266-3538(03)00178-7.

8. Electrospinning <http://www.oxolutia.com/technology/electrospinning/> (accessed May 3, 2017).