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Direct Contact Membrane Distillation of Hydroponic Solutions for Recycling of Phosphate and Potassium

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Abstract: A critical issue facing extraterrestrial expansion has always been long-term life support capabilities. The large energy requirements to move even small amounts of material from Earth necessitate the ability to reuse and recycle as much as possible, particularly waste. The weight of food supplies eventually starts to limit the length of the expedition. Hydroponic growth systems offer the ability to grow plants, and with them, a miniature ecosystem. This offers the ability to repurpose both carbon dioxide and waste salts such as ammonia and other compounds, such as those found in urine. A major issue facing hydroponic systems is the need to provide a stable water-based nutrient stream. Direct contact membrane distillation (DCMD) was tested for viability as a method of re-concentrating and stabilizing the nutrient-rich water stream. Polytetrafluoroethylene (PTFE)- and polyvinylidene (PVDF)-based polymer hydrophobic membranes were used to separate solutes from water. The DCMD method was tested with the feed stream operating at temperatures of 50 °C, 65 °C, and 80 °C. The results were analyzed using UV-Visible spectroscopy to determine concentrations. The benefits and limitations of the PTFE and PVDF membranes in DCMD were compared. The larger-pore PTFE membranes concentrated solutions effectively at 80 °C, while the PVDF membranes removed more water at lower temperatures, but permitted detectable phosphate ion leakage. Adjusting temperature and flow rates can help maintain stable ion and water transfer, benefiting hydroponic systems in achieving reliable nutrient levels.

Keywords: concentrating; PTFE; PVDF; waste; water purification; nutrients; deep space; Moon

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1. Introduction

NASA plans to build a Base Camp near the Moon's south pole as a part of the Artemis mission, which will require a fresh food source for the human crew [1]. Non-soil-based farming methods, such as hydroponics, have shown promise in providing higher yields in equivalent space when compared to traditional farming practices [2]. For example, traditional rice farming practices produce an average of 340–408 kg per acre, whereas hydroponic farming produces 5400 kg per equivalent acre [3].

Hydroponics proposed for lunar missions have the advantage of producing food crops while simultaneously regulating the oxygen and carbon dioxide concentrations of the air [4]. Issues facing hydroponic systems are the regulation of the nutrient stream feeding the plants. The nutrient solution consists primarily of various salts that are usually present in the living soil. These include elements commonly used to support plant growth: carbon, hydrogen, nitrogen, phosphorus, potassium, and oxygen. In hydroponics, these elements are supplied in an aqueous stream using various forms of water-soluble salts. The balance of the microbiome within the root system of plants must be maintained properly as well. If the nutrient concentration is too low, the plants will have decreased yields and may not grow properly at all [5]. As plants use up nutrients in the solution, the concentration needs to be refreshed. For terrestrial operations, this can be accomplished by routinely dumping water and flushing the system with fresh water, and then restarting the system's nutrient system. In a lunar environment, this would not be preferable. Instead, a new form of regulating the concentration of the nutrient system would be needed. Membrane-based distillation offers the potential to remove water from the solution, thus concentrating it to remain in the process and lessening the need to purge the system.

Direct contact membrane distillation (DCMD) is a new membrane-based process for separating water from aqueous solutions. The process operates by taking advantage of the vapor pressure gradient created by differences in the temperature across a hydrophobic membrane. A stream that is being concentrated is heated and runs underneath a cooled water stream [6–8] with a membrane in-between in contact with both liquids. The water vapor molecules in the heated solution will then move through the membrane, condensing and joining the colder water stream on the other side of the membrane. As there is no need to fully vaporize the water to recover it from an aqueous stream, the energy requirements are greatly reduced. As the hydrophobic membranes theoretically only allow for vapor to be transferred between the two sides of the membrane, this reduces the need for the pre-process separations of contaminants. Since there is no need for the stream to be fully vaporized, nor is a vacuum needed, it also allows for a simpler system. In sharp contrast to DCMD, traditional distillation requires either large amounts of energy to be added to the system in the form of heat or decreasing the pressure to a low enough level that the liquid begins to vaporize, as in the case of vacuum distillation [6]. For traditional high-temperature-based distillation, the heat of vaporization represents a significant energy barrier that must be overcome. In vacuum distillation, the apparatus needed tends to be complex. For these reasons, DCMD has been explored as a mechanism for processing sea water for desalination [9].

In this study, the primary advantage of DCMD is the recovery of water in a more energy-efficient method than traditional evaporation methods and not using pressurized water systems such as reverse osmosis (RO). RO has major drawbacks in phosphate-rich environments. This is due to the fact that many metals are required as macro nutrients in complex biological systems such as hydroponics. RO systems typically concentrate at extreme ratios (75–90%) on industrial scales depending on the operating pressure. This runs the risk of membrane fouling as metal phosphates form and become insoluble on the membranes acting as a solid foulant. For example, copper phosphate is extremely insoluble in water, but copper is required for many cellular operations, such as enzyme production and signaling. RO fouling with metal phosphates is a major problem in an environment such as space where replacement membranes are essentially nonexistent. Metal phosphates also do not dissolve in standard acid-washing steps used for membrane-cleaning processes. Thus, any membranes fouled with metal phosphates represent an extreme loss. While anti-scalants exist to handle this issue in traditional industrial applications, these often contain toxic polymers to stabilize and chelate the metals. This can represent a hazard to sensitive biological systems and limit the flexibility and usability of downstream processes. Table 1 compares some of these processes.

Table 1. Advantages and disadvantages of concentration and water separation methods.

Separation Method	Advantage	Disadvantage
Reverse Osmosis	High membrane flux, well understood	Rejection rate is dependent upon membrane type, high energy costs due to the pressure gradient required, and prone to fouling
Evaporation	Well understood, highly pure distillate product, large number of commercial products available	High energy costs
DCMD	Low energy usage, secondary application as a heat exchanger	Low water flux

The present work investigated the viability of DCMD (with varying hot stream temperatures) to concentrate nutrient solutions. The nutrient solution incorporated two of the most critical nutrients: phosphate in the form of sodium dihydrogen phosphate monohydrate ($NaH_2PO_4 \cdot H_2O$) and potassium in the form of potassium carbonate (K_2CO_3). We investigated the effects of flux change (dependent on temperature difference), membrane change, and concentration effects.

2. Materials and Methods

2.1. Materials

For the nutrient solution to be tested, NH_4NO_3 was purchased from Flinn Scientific Inc., (Chicago, IL, USA, Ammonium Nitrate, Catalog# A0056), while laboratory-grade $NaH_2PO_4 \cdot H_2O$ and anhydrous laboratory-grade K_2CO_3 were purchased from hBARSCI (Rochester, NY, USA, The Curated Chemical Collection).

Polytetrafluoroethylene (PTFE) and polyvinylidene (PVDF) based polymer membranes were purchased from Sterlitech (Kent, WA, USA). The PTFE membrane used was a 0.45 μm flat sheet membrane with a laminated polypropylene netting backer, Lot#: J000014897; the PVDF used was a 0.1 micron Novamem Microfiltration (MF) flat sheet membrane, Lot#: 624096PVDF100.

A checker disc kit to test for phosphate content and a colorimetric kit to test for nitrate were purchased from Hanna instruments (Woonsocket, RI, USA, HI38061 for phosphate and HI3874 for nitrate). A Viso ECO potassium-1 kit was purchased from Thomas Scientific (Pittsburgh, PA, USA, CHM03Q286). The system was designed to mimic the nutrient feeds of an upstream hydroponic system that utilizes waste organics as a feed source. As a result of this, nitrogen compounds were added to the solution. Initially attempts to separate nitrates using a standard NH_4NO_3 concentration testing kit failed to provide meaningful results, so that is not discussed in this work.

2.2. Methods

2.2.1. Solution Preparation

The salts NH_4NO_3, $NaH_2PO_4 \cdot H_2O$, and K_2CO_3 were used to produce an aqueous solution. A large stock solution (a mother solution) was prepared by stirring at ambient temperature and subsequently diluted with deionized water (DI) to create a nutrient solution simulant with approximately 10 ppm of each salt. Samples (450 mL) of this diluted nutrient solution were taken and prepared for testing. The general ppm for nitrates is highly variable in both irrigation and hydroponic systems; however, it is commonly between 5 and 50 ppm. The concentration was chosen to represent a depleted nutrient stream; this would traditionally be concentrated using RO [10].

2.2.2. Direct Contact Membrane Distillation (DCMD)

An acrylic DCMD cell from Sterlitech Corporation (Kent, WA, USA, 1160042) was used to perform DCMD on the solutions with ~10 ppm of each salt. The setup had a heated aqueous nutrient solution peristaltically pumped using a Masterflex L/S Easy-Load II Cole-Parmer Instrument Company (Vernon Hills, IL, USA) to the bottom of a PTFE or PVDF membrane while cooled DI water was pumped above the polymer membrane in a crossflow manner. A membrane made up of laminated flat sheet polytetrafluoroethylene (PTFE) with spacers (Sepa CF Medium Foulant Spacer, PP 145 mm × 97 mm) having a surface coverage area of 0.014 m^2, thickness of 64–127 μm, and a pore size of 0.45 μm was used. Similarly, a polyvinylidene fluoride (PVDF) flat sheet membrane of pore size of 0.1 μm and a surface coverage area of 0.014 m^2 was used for PVDF application.

DCMD operates in a similar fashion to membrane-based pervaporation. By leveraging a vapor gradient created in the pores of a hydrophobic membrane, the membrane acts as an ambient pervaporation mechanism. This vapor gradient is created by using a temperature differential between the two streams. Due to the hydrophobic nature of the membrane, the bleed over effect due to osmotic pressure is significantly decreased. This allows for permeated water to be used as an upstream feed to more sensitive water consumption processes or more traditional water separation processes such as RO and NF. As the primary methodology for water removal is vapor-based, this enables the membrane to concentrate feed water while acting as a heat exchanger. Feed is recirculated on both the permeate and feed sides of the membrane to mimic a closed-loop process. Further details on the system are available in our previous work [11]. DCMD runs were conducted at three feed temperatures: 50 °C, 65 °C, and 80 °C. Two runs were performed at each feed temperature. The cool side water was 200 mL initially and it was weighed before and after the experiment. During the trials, an initial sample was taken, and follow-up samples were taken every half hour until the end of the 2 h testing phase, with each sample having a target volume of 50 mL. The cold temperature liquid ran through tubes in a 5 °C chilled water bath. This resulted in the cold water at the top of the membrane being kept at room temperature (approximately 25 °C). Water was removed from the process and the concentrated solution samples were weighed and stored. Flux was calculated by the following equation:

$$Flux = \frac{water_{recovered}}{membrane\ area \cdot time}$$

where *Flux* is in units of liters/(m^2·h) or LMH, $water_{recovered}$ is in liters, *membrane area* is in m^2, and *time* is in hours.

2.2.3. UV-Vis Spectroscopy

UV-Visible spectroscopy was used to measure the salt concentrations of the aqueous solutions. While the ions of interest do not normally absorb light, a secondary testing solution was used to create a color phase shift that could be seen with and measured by the UV-Vis. A five-point calibration curve was created to test for the absorbance of the created colored complexes. This resulted in a 5–25 ppm standard with intervals every 5 ppm. The standard testing protocols for the industrial testing kits needed to be modified for repeatability and standardization. Testing was carried out using a standard 1 cm path length cuvette with a 1 nm slit length using a UV-2401PC UV-Vis spectrometer from Shimadzu Corporation (Kyoto, Japan). Modifying the testing methodology required processing all the solid reagent materials into an aqueous solution that could be standardized and incorporated into the needed dilution rate for UV-Vis testing. This was performed to standardize all the dilution rates across the different nutrient salt streams. A five-point calibration curve was created for all three tested components: nitrate, potassium, and phosphate. These indicated that at the respective localized peaks, the relationship between concentration and absorbency was linear. The calibrations are shown in the Supplemental Materials in Figures S1–S3. This initial calibration resulted in the determination that the nitrate testing would not be viable for quantitative measurements as it could not produce an absorbance of less than 2 without such an extreme dilution that it would make the accuracy of the test questionable.

3. Results and Discussion

3.1. Flux Through PVDF and PTFE Membranes

The final weight of the samples and the feed and permeate solutions were used to determine the total flux of the system. The average water recovered for each membrane at each temperature tested is shown in Figure 1 and Table S1 in the Supplemental Materials. The mass of recovered water was then compared to the feed temperature to find the point of inflection where the membranes would have similar results in water recovery.

The data in Figure 1 indicates that the PVDF membrane is significantly more effective at lower feed temperatures for recovering water. Water recovery for the PVDF membrane of 105.4 g occurs at 65 °C and 107.8 g was recovered at 80 °C. Thus, there is no significant difference between the amount recovered at 65 °C and 80 °C. A lower temperature is preferable since the process would require less energy at 65 °C compared to 80 °C. This phenomenon may be due to the smaller pores in the PVDF membrane inhibiting the mass transfer of the water vapor so that it is the same at both temperatures. Alternatively, fouling could be occurring. Fouling tends to occur in hydrophobic membranes when organic contaminants adhere to the membrane, which could increase with higher temperatures [12].

However, the nutrient solutions contain ionic species rather than organic ones, suggesting that a mass transfer limitation is more likely. The difference between the PTFE and PVDF membranes disappeared at the highest feed temperature. For the PTFE membrane, water recovery increased linearly from 38.5 g at 50 °C to 110.8 g at 80 °C. The larger pore size of the PTFE membrane may mean that no mass transport limitations for the water vapor may occur. The linearity of the PTFE membrane recovery rate curve implies that even higher DCMD temperature could further increase flux. The vapor pressure difference between the hot side and cold side of the membrane is the driving force for water vapor movement [12]. Since water vapor pressure increases with temperature, a higher ΔT increases the driving force for flux through the hydrophobic gas-filled membrane.

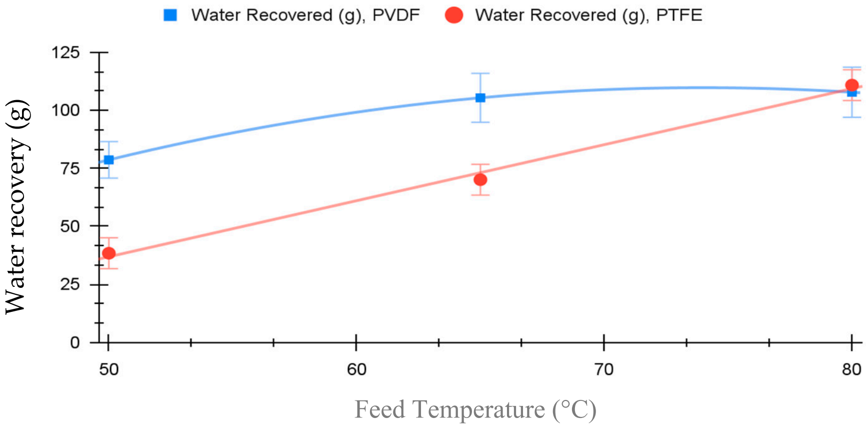


Figure 1. Water recovered from the DCMD process at the tested feed temperature from the PVDF membrane (top curve) and PTFE (bottom curve).

Figure 2 shows the average flux though the the PTFE and PVDF membranes. The method for flux calculation is described in Section 2.2.2.

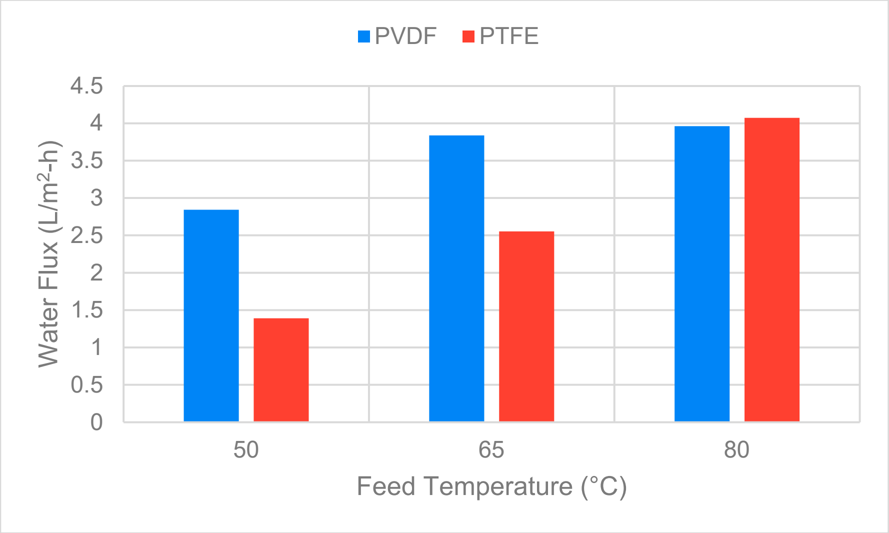
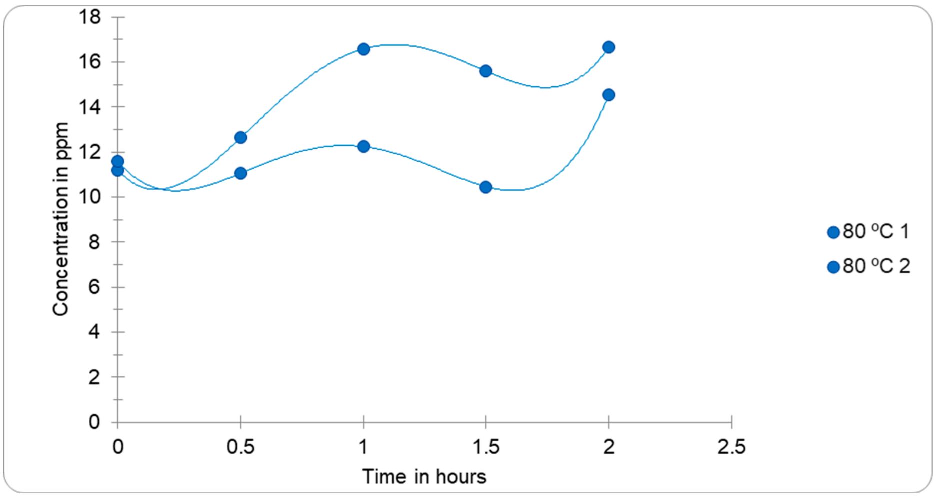


Figure 2. Average water flux through membrane.

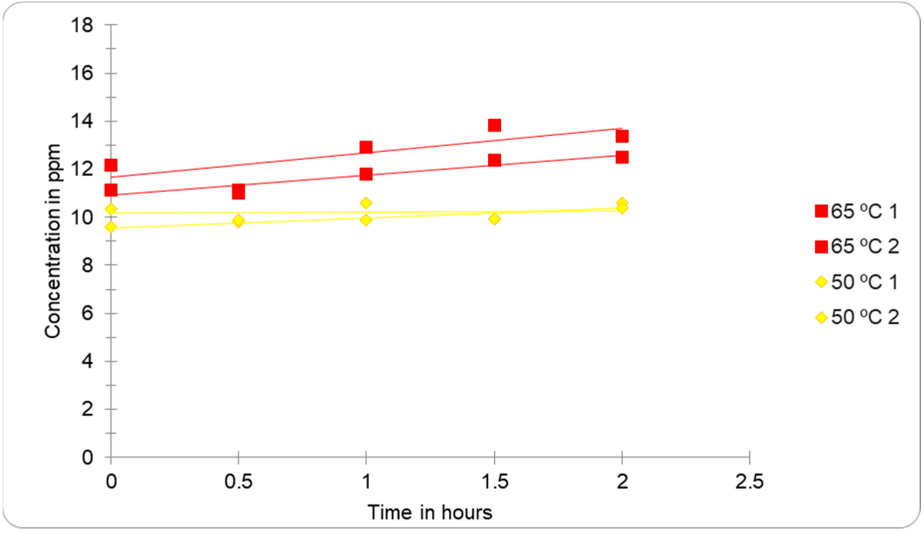
3.2. Concentration with Time

A wavelength of 719 nm with UV-Vis was used with the calibration curve to find the concentration of phosphate with DCMD time; the results for the PTFE membrane are shown in Figure 3a,b. Little increase in concentration was observed for the 50 °C and 65 °C runs. These findings are consistent with the water removal seen in Figure 1 for the PTFE membrane. For 80 °C, the PTFE membrane gave an increase in the phosphate concentration of 37% after 2 h. Something of a sinusoidal curve can be seen for the concentration with time for the 80 °C data. This finding suggests that the phosphate ions may progress backward through the membrane if the solution becomes more concentrated in phosphate, creating a gradient. Figure 3c,d show the concentration of potassium with time. Again, little change is seen with the 50 °C and 65 °C runs. At 1 h, the DCMD at 80 °C gave the highest concentration of potassium in the solution, with an increase of 50%. Running the DCMD process longer caused a decrease in the potassium concentration. Table S2 in Supplementary Materials shows the concentrations after 2 h of DCMD processing.

The reduction in the potassium concentration after one hour requires an explanation. The potassium ion is much smaller than a 5-atom phosphate ion. Normally, potassium ions in a water-based solution are surrounded by a hydration shell [13], making them unlikely to pass through a hydrophobic membrane. Higher temperatures tend to disrupt the hydration shell, which may allow easier passage through the membrane [14]. However, as the solution becomes more concentrated, a potassium concentration gradient is created. This gradient may induce potassium ions to pass backward through the membrane as contaminants. To test this hypothesis, tests were carried out to see if there were detectible levels of ions in the final permeate water, and indeed, ions were measurable in the removed permeate. This finding suggests that a shorter 1 h DCMD process at 80 °C may be preferable for concentrating the nutrient solution with a PTFE membrane.

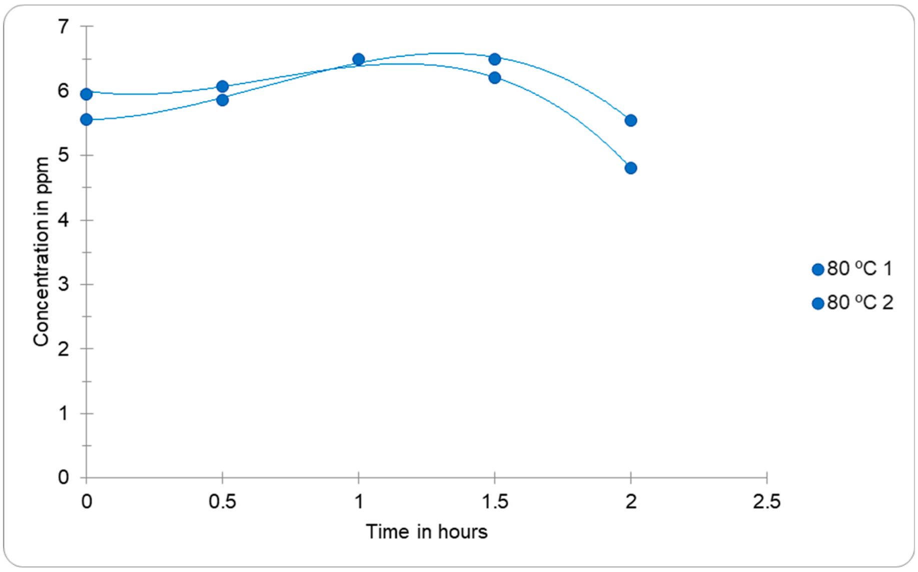


(**a**)

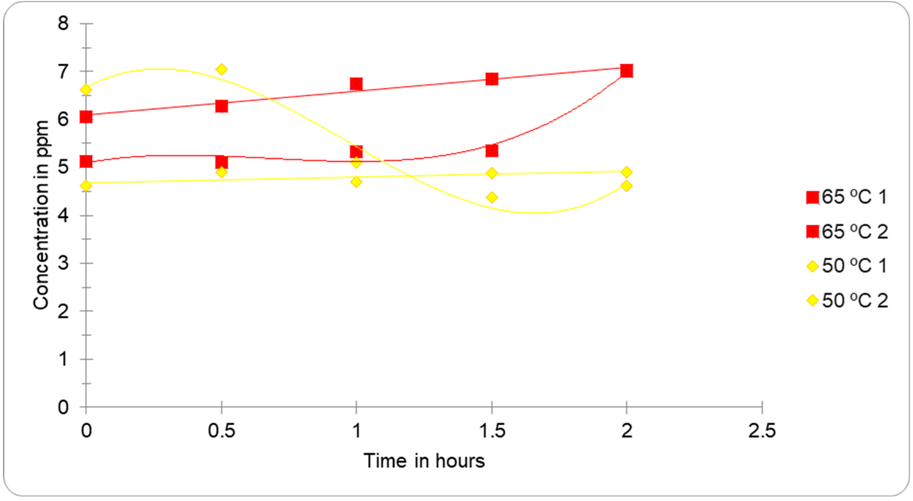


(**b**)

Figure 3. *Cont.*



(**c**)

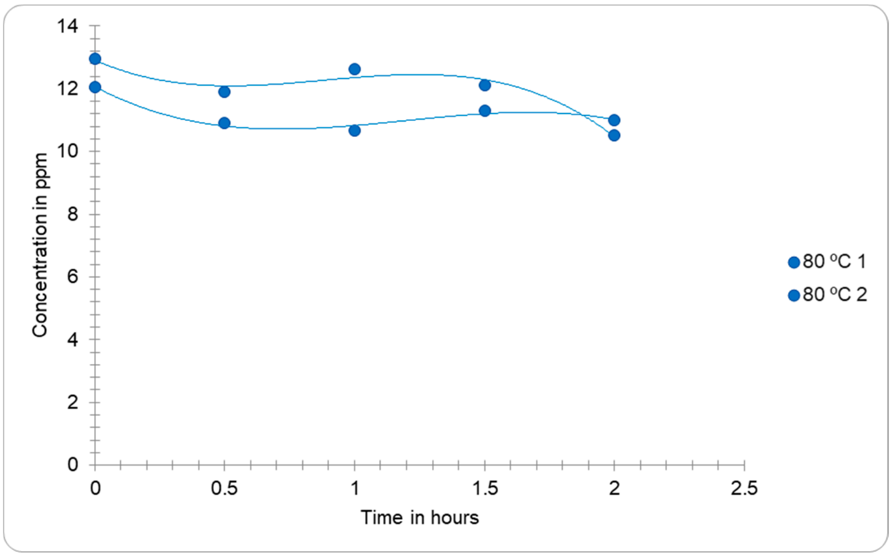


(**d**)

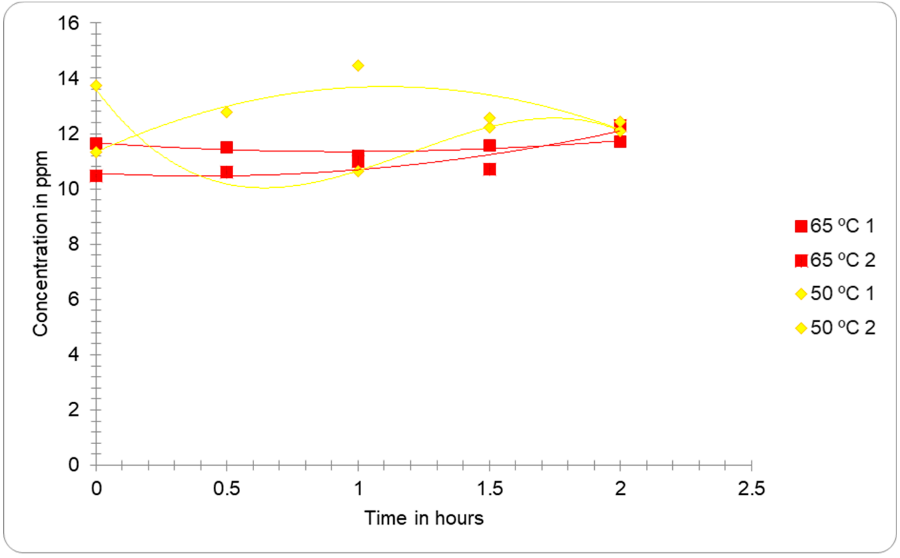
Figure 3. Concentration vs. time in the DCMD process with the PTFE membrane from the two different runs of (**a**) phosphate at 80 °C, (**b**) phosphate at 65 °C and 50 °C, (**c**) potassium at 80 °C, and (**d**) potassium at 65 °C and 50 °C.

Figure 4a,b show the concentration of phosphate with DCMD time for the PVDF membrane. Little change in the phosphate concentration can be seen. The fact that little change in concentration is seen for the PVDF membrane may be due to the smaller pore size of this membrane and the large ionic radius of the 5-atom phosphate ion.

Similar findings for potassium are seen with the PVDF membrane (Figure 4c,d) as were found for the PTFE membrane. At 80 °C, a 1 h DCMD run appears to give the greatest concentration, most likely for the same reasons as suggested for the PTFE membrane. Table S2 in Supplementary Materials shows the concentrations after 2 h DCMD.



(**a**)



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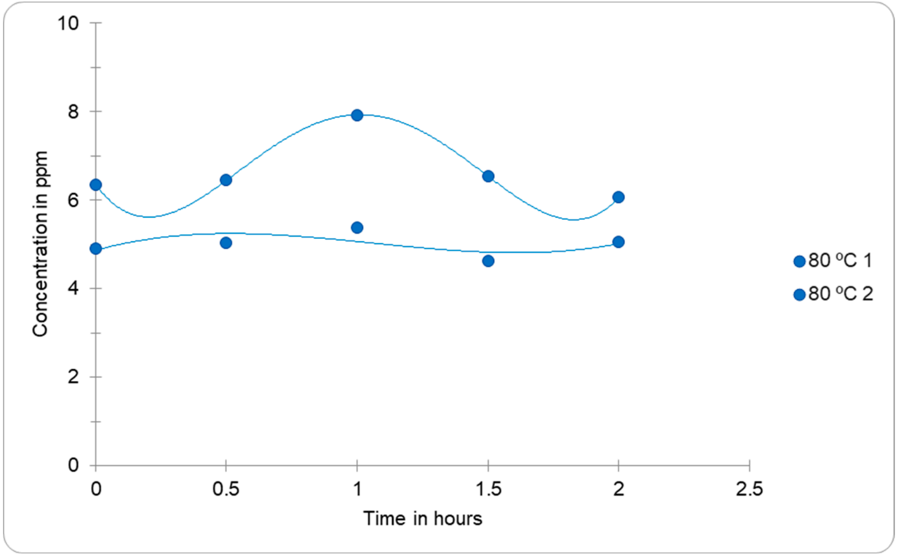
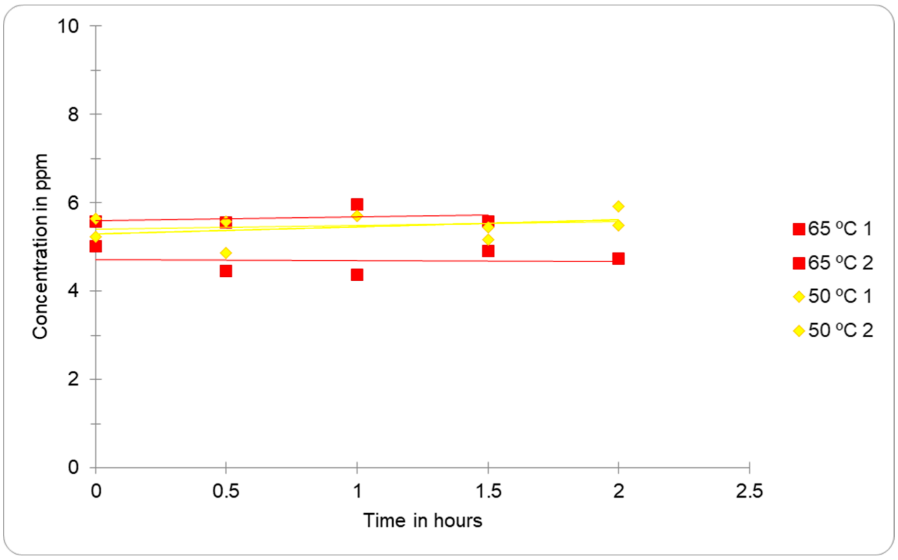


(**c**)

Figure 4. *Cont.*



(**d**)

Figure 4. Concentration vs. time in the DCMD process with the PVDF membrane from the two different runs of (**a**) phosphate at 80 °C, (**b**) phosphate at 65 °C and 50 °C, (**c**) potassium at 80 °C, and (**d**) potassium at 65 °C and 50 °C.

4. Conclusions

DCMD showed potential in concentrating hydroponic water-based nutrient streams. The larger-pore PTFE membranes showed a benefit in concentrating the solution at 80 °C after 1 h. PVDF removed more water operating below 80 °C but did not concentrate the solution well for phosphate. Ion transfer across the membrane varied with time. This could prove useful in hydroponic systems, as the nutrient stream needs to stay at a reliable concentration. By modifying the temperature and flow rate, it could be possible to create a system that would transfer ions and water at a rate that would keep the nutrient concentration at a stable level. Such a system would diffuse water at a constant rate and transfer ions if the stream became too concentrated to bring about dilution. Further work with varied DCMD operating conditions is needed to find if this method could stabilize nutrient concentrations for future space exploration missions.

Supplementary Materials: The following supporting information can be downloaded at https://www.mdpi.com/article/10.3390/waste2040027/s1, Table S1: Water flux over two-hour run time in grams of water retained from feed solution; Figure S1: Nitrate absorbency charted at various wavelengths, five-point calibration curve; Figure S2: Potassium absorbency at various wavelengths in a five-point calibration curve; Figure S3: Phosphate absorbency at various wavelengths in a five-point calibration curve; Table S2: Effect of the type of membrane on the concentration of aqueous ions at three different operating temperatures after 2 h.

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