

FINAL REPORT
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LOW-ENERGY PROCESS FOR CONCENTRATION OF STICK WATER

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Lay Summary: The goal of the proposed work was to evaluate forward osmosis, an emerging low-energy membrane process, for the concentration of stick water to high solids levels. Our hypothesis was that an integrated forward osmosis/reverse osmosis (FO/RO) membrane process would be able to concentrate stick water to >50 wt% solids with a much lower operating cost than an evaporative process. Achieving this solids content is important because it would enable subsequent processing by spray drying, which is not practical at low solids concentrations.

Stick water contains high concentrations of proteins, fats and other components that have nutritional value. Dewatering of stick water to recover edible protein conventionally is done by evaporation and drying, which is energy intensive and can degrade some of the components that are important to the nutritional value. While spray drying could be an alternative, initial dewatering is needed to concentrate the stick water to above 50% prior to this unit operation. Stick water is a highly viscous material, containing solids content of 5-15 wt%. Concentrating this material is very challenging, and conventional pressure-driven membrane technologies such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis fail due to the high resistance caused by solids deposited on the membrane surface.

Forward osmosis uses a membrane that is permeable to water but not other dissolved solutes. A draw solution of high ionic strength is used on the permeate side of the membrane to “draw” water from the feed solution through the membrane, thus concentrating the feed. In this project, we evaluated FO for concentration of stick water. We determined the roles of important operating variables on the rate of water removal and the maximum achievable concentration. We demonstrated that FO could concentrate the stick water up to 45 wt% and remove 85% of the water. Unfortunately, we also observed that the stick water becomes a paste above about 30 wt%. Thus, pumping the fluid through a membrane flow cell is problematic. Dewatering using a rotary drum FO membrane system may be an option.

An operating cost analysis showed that the cost of FO could be as low as 3% of the cost of evaporative drying assuming a 2-year membrane lifetime. Given the low operating cost of the membrane operation and its limitation with regard to its achievable concentration, one option might be to use FO as a primary step to concentrate stick water to <30 wt% (~75% water removal), followed by further concentration using other non-membrane technologies.

Objective (s): The project proposal listed three objectives.

1. Carry out a set of batch forward osmosis runs in concentration mode to determine the maximum achievable stick water concentration. Evaluate the roles of feed and draw solution stir rates, temperature, and draw solution ionic strength (from 0.5 to 3.0 M NaCl).

Use at least two commercial forward osmosis membranes from Hydration Technology Innovations. [Completed]

2. Measure permeate flux as a function of stick water feed side solids concentration, draw solution ionic strength, and feed and draw solution cross-flow velocities using the same commercial forward osmosis membranes from Hydration Technology Innovations. [Completed with change of measurement method. Exploring alternate process to cross flow filtration.]

3. Perform a preliminary cost analysis for operating the forward osmosis/reverse osmosis membrane separation process. This preliminary analysis will consider relative costs of energy and consumables versus energy costs for an evaporative concentration process. [Completed]

Project Overview: (See full report following the acknowledgments paragraph. This report will serve as the starting point for drafting a journal manuscript.)

Impacts and Significance: This work provided data needed to evaluate a new, low-energy process for concentration of stick water to high solids levels. The heart of the process is an emerging membrane technology called forward osmosis, which uses an osmotic driving force to dewater the feed. We determined the maximum achievable stick water concentration and water removal rate using commercial forward osmosis membranes and a range of operating conditions.

A preliminary cost analysis was done for operating a forward osmosis/reverse osmosis membrane separation process. This preliminary analysis compared relative costs of energy and consumables for the membrane process to the energy costs for an evaporative concentration process. A rough estimation finds that the FO/RO process would use 1.3% of the energy that would be required to thermally evaporate the same volume of water, assuming no heat integration. Overall operating costs depend on the membrane lifetime, but could be as low as 3% of the cost of evaporation assuming a 2-year membrane lifetime. Replacing the energy-intensive evaporative process with the proposed low-energy membrane process would be expected to improve process economics.

The FO operation would dewater the feed at low temperature (below 75°C) to a concentration that may allow efficient spray drying (directly or after additional concentration). Thus, in addition to being a low energy process, the FO process with spray drying would avoid long-term contact of the recovered protein material with high temperatures that may degrade it. While the focus of this project was concentration of stick water, we appreciate that there may be other applications where low-energy, low-temperature dewatering of solutions may benefit the industry.

Publications: This project was featured in an ACREC Solutions article in Render Magazine (Oct. 2015).

Outside funding: n/a

Future Work: Nothing is planned. One of the difficulties that we faced is that concentration of the stick water makes it difficult to process. Implementation of the FO process would need to use a process configuration that is amenable to high solids content materials (e.g., rotary drum or another configuration that allows continuous removal of the solids from the membrane unit).

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Project Overview

LOW-ENERGY PROCESS FOR CONCENTRATION OF STICK WATER

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Abstract

This contribution describes the application of forward osmosis to concentrate stick water. The objectives of the study were to carry out a set of batch forward osmosis runs in concentration mode to determine the maximum achievable stick water concentration and to perform a preliminary cost analysis for operating a forward osmosis/reverse osmosis membrane separation process for comparison to an evaporative concentration process. The study examined the roles of feed and draw solution stir rates, temperature, feed concentration, and draw solution ionic strength on flux using commercial cellulose triacetate membranes. Results show that forward osmosis could concentrate the stick water up to 45 wt%; however, concentrations above about 30 wt% would be difficult to process through conventional membrane configurations. Operating cost estimations show that the energy cost of the FO process is about 1.3% of the energy costs for a thermal evaporation process, and, assuming a 2-year membrane lifetime, the total operating cost using FO membranes was estimated to be about 3% of the operating cost using a thermal evaporation process.

Key words: Dewatering, Engineered Osmosis, Fouling, Rendering, Wastewater

1. Introduction

Dewatering of stick water to recover edible protein conventionally is done by evaporation and drying (e.g., in a drum dryer or disc dryer). In these high temperature operations, some degradation of substances important to the nutritional value of the recovered protein will occur. Spray drying or spray granulation [1] may be an option, as the short residence times minimize degradation reactions. Still, initial dewatering is needed prior to the drying step. Anecdotal information suggests that stick water feed solids concentration to the spray dryer should be >50 wt% for practical operation. Beyond operational considerations, higher feed solids may also decrease off-flavor intensity for some protein products [2].

This study explored a low-temperature membrane alternative to evaporation for the initial dewatering of chicken feather stick water. An initial set of measurements found that *pressure-driven* membrane processes (microfiltration, ultrafiltration, RO) were unsuccessful due to the high resistance caused by solids deposited on the membrane surface. Prior work has shown that this resistance increases with applied pressure because the solids layer is compressible [3]. Unlike pressure-driven membrane processes, forward osmosis uses a high ionic strength draw

solution on the permeate side of the membrane to “draw” water from the feed to the permeate. As a result, FO is capable of concentrating chicken feather stick water. Comprehensive work was conducted to explore the impact of operating factors on the rate of water removal and the maximum achievable stick water concentration during batch operation. These factors include draw solution ionic strength, the starting feed concentration, temperature, and the feed and draw solution stirring velocities. Operation cost estimations were made to compare FO and thermal evaporation processes.

2. Experimental

2.1. Materials

Commercial cellulose triacetate (CTA) FO membranes were provided by Hydration Technology Innovations, LLC (HTI; Albany, OR). Stick water samples were provided by a local rendering facility and were stored in plastic containers at ~ 2 °C until filtration. Sodium chloride (99.5%) was used as received from Fisher Scientific. Deionized water was produced from distilled water that was passed through a Milli-Q water purification system (EMD-Millipore).

2.2. Forward Osmosis Apparatus

A forward osmosis apparatus was designed and constructed for batch stick water concentration experiments. Figure 1 shows a picture of the apparatus. A $\Phi 47$ mm membrane disk was placed in a modified Amicon Stir Cell (EMD-Millipore) that allows the membrane to have direct contact with the feed and draw solutions. The effective filtration area is 15.5 cm^2 . The upper chamber of the cell was filled with a known mass of stick water, and the cell was partially immersed into a draw solution bath with a large enough volume to keep the draw solution concentration nearly constant. An overhead stirrer and a magnetic stir plate were used to stir the feed and draw solution, respectively. A thermal jacket was placed outside of the cell. Hot water was pumped through the thermal jacket to heat the cell and maintain a constant temperature.



Figure 1. Forward osmosis apparatus for concentration of stick water: 1 – Concentration cell, 2 – Draw solution bath, 3 – Hot water reservoir, 4 – Peristaltic pump, 5 – Overhead stirrer, 6 – Magnetic stirrer plate.

2.3. Concentration Data Collection

During concentration, the cell mass was measured and recorded at different times. The mass of residual wastewater (m_{res} , g) was determined using Equation 1:

$$m_{res} = m_t - m_0 \quad (1)$$

m_t is the mass (g) of the cell and residual stick water, and m_0 is the mass (g) of the clean cell. Water removal was calculated using Equation 2:

$$m_{removal} = m'_0 - m_{res} \quad (2)$$

m'_0 is the initial mass (g) of stick water in the cell. Stick water concentration (C_t) was calculated using Equation 3:

$$C_t = \frac{m_{res}}{m'_0} C_0 \quad (3)$$

C_0 is the initial concentration of stick water. The initial and final stick water concentrations also were measured directly using a Thermogravimetric Analysis system (TGA). The TGA results matched closely with the concentration calculated by Equation 3.

2.4. Membrane Flux Determination

Equation 4 was used to calculate average flux over short time intervals during batch concentration.

$$J = 600 \times \frac{m_{res,t2} - m_{res,t1}}{(t_2 - t_1)A} \quad (4)$$

J is the flux ($Lm^{-2}h^{-1}$), t_i (min) is time point the measurement was taken, and A is the membrane area (cm^2).

2.5. Water Removal Determination

Percentage water removal from the original stick water (R%) is an important indicator of the process efficiency. Equation 5 was used to measure R%:

$$R\% = \frac{m_{res} \times (1 - C_t)}{m'_0 \times (1 - C_0)} \quad (5)$$

3. Results and discussion

Like other wastewater streams generated by the rendering industry, stick water concentration varies temporally. In this study, two batches of stick water were received, each with different solids content: Sample I (14.1 wt%) and Sample II (6.7 wt%). Figure 2 presents the required percentage water removal to reach different concentration levels (weight fraction solids) of stick water from Sample II. Concentration from 6.7 to 20 wt% solids would require 71% of the water to be removed. Over 90% of the water would have to be removed to reach 50 wt% solids.

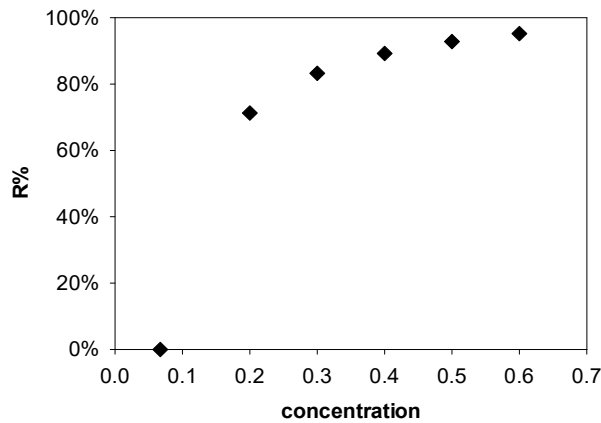


Figure 2: Required percentage water removal to concentrate stick water to a target concentration (shown in weight fraction solids).

3.1. Role of draw solution concentration

Figure 3a shows the stick water concentration (solids fraction) over time using different draw solutions. Data were collected using Sample I for these experiments. Both draw solution and feed solution stirring speeds were set to be 360 rpm. As is expected, higher concentration draw solutions were more effective at concentrating the stick water since FO is driven by the osmotic pressure difference across the membrane. In the case of 1.5 M NaCl draw solution, the stick water was concentrated to 41 wt%. In the case of 0.1 M NaCl draw solution, the stick water was diluted, indicating that the osmotic pressure of the stick water itself is higher than that of 0.1 M NaCl. The concentration increased only slightly using a 0.25 M NaCl draw solution.

Figure 3b presents water removal flux using draw solutions with different concentrations. In general, the flux decreased as the stick water concentration increased. The flux reduction could be attributed to two factors: 1) the concentration increase of the wastewater reduced the osmosis pressure difference across the membrane; and 2) a foulant layer developed on the membrane surface, which increased in thickness over time. The 1.5 M NaCl draw solution had the highest initial flux, but it also experienced the fastest flux reduction rate. Again, the flux was low using the 0.25 M NaCl draw solution suggesting that the osmotic pressure of the untreated stick water was equivalent to that for the 0.25 NaCl draw solution.

Assuming that feed side osmotic pressure increased linearly with concentration, Figure 3c replots the flux versus the corresponding osmotic pressure difference using the two draw solutions with the highest salt concentration. Using the initial flux and osmotic pressure difference as the reference, Figure 3d plotted the relative flux change versus the relative osmotic pressure difference. In Figure 3d, relative flux using 1.50 M NaCl draw solution decreased faster than that using 0.50 M NaCl. This result suggests that membrane fouling was more significant using higher concentration draw solution, as might be expected since higher initial flux brings more foulant material to the surface. This behavior has been described many times in the fouling literature.

3.2. Role of feed and draw solution stirring speeds

Figures 4a and 4b show the impact of feed solution and draw solution stirring on the concentration process with Sample I. In both cases, a 0.5 M NaCl draw solution was used. Increasing the stirring speed on the feed and draw solution sides of the membrane from 0 to 360 rpm improved the initial flux; however, no significant difference in the final concentration was observed by increasing the stirring speed from 180 to 360 rpm. The role of stirring is to disrupt concentration polarization layers on the feed side and dilutive concentration polarization on the draw solution side of the membrane.

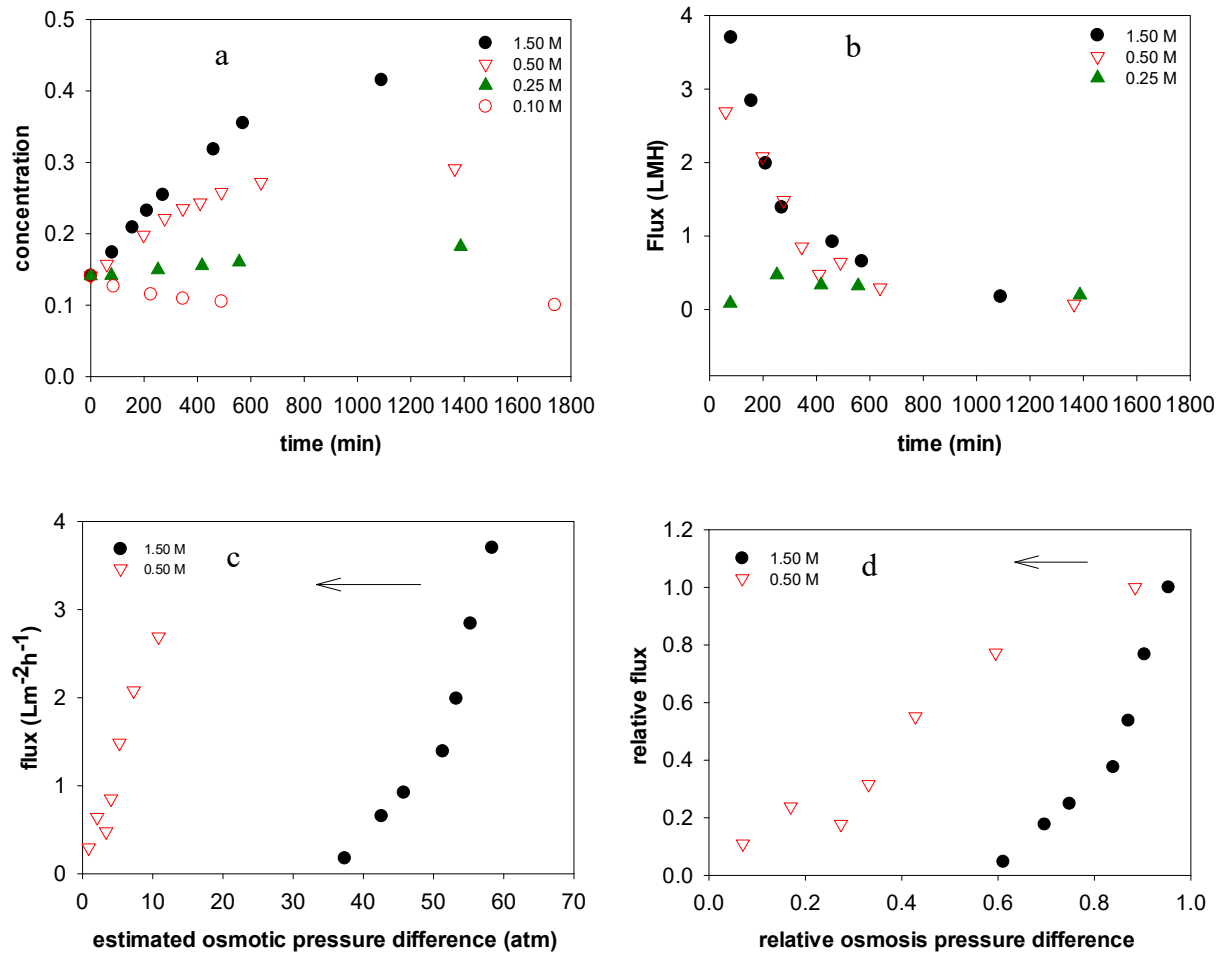


Figure 3: Impacts of draw solution concentration on stick water concentration and dewatering flux – a). Stick water concentration change with time using different draw solution concentrations; b). Water removal flux change over time using different draw solution concentrations; c). Water removal flux change versus estimated osmotic pressure difference across the membrane (the arrow indicates the direction of change during dewatering); d). Relative water removal flux versus relative osmotic pressure difference (the arrow indicates the direction of change during dewatering).

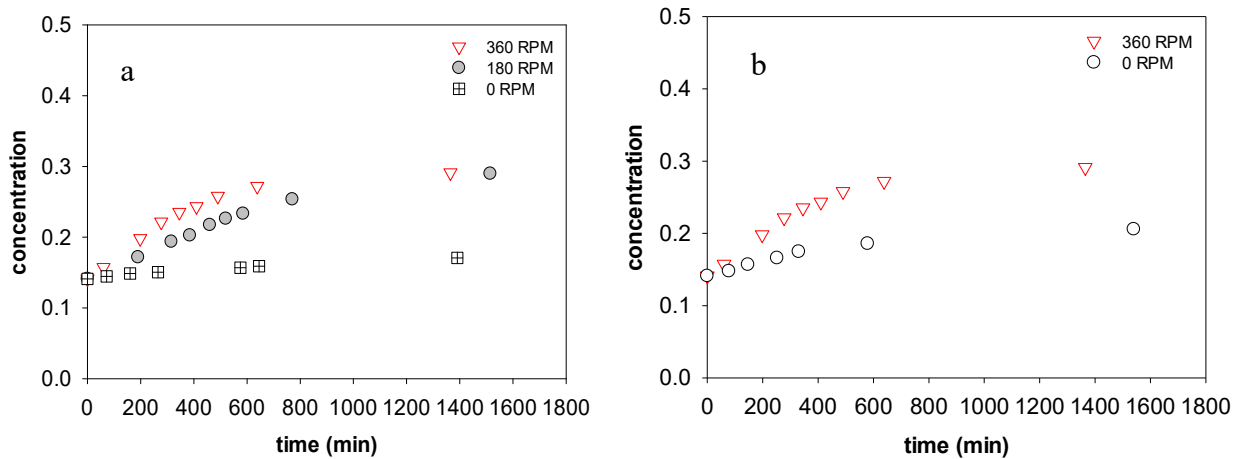


Figure 4: a) Stick water concentration change with time using different feed side stir speeds and constant draw solution stir speed of 360 rpm; b) Stick water concentration change with time using different draw solution stir speeds and constant feed stir speed of 360 rpm.

3.3. Role of stick water concentration

Figure 5 compares the concentration process for Sample I and Sample II stick waters. Since the solids content of the samples differed, the volume of stick water charged to the cell was adjusted to keep the total solids content constant. Sample II, with a lower starting concentration, had a faster rate of concentration than Sample I, which is consistent with the fact that there is a higher osmotic driving force at the lower initial feed concentration; however, the rates of concentration eventually became the same at longer times when the concentration curves merged. One conclusion from this study is that the FO method is able to handle fluctuations in feed concentration, which is an advantage for treating rendering facility wastewaters that change regularly depending on the input to the rendering facility.

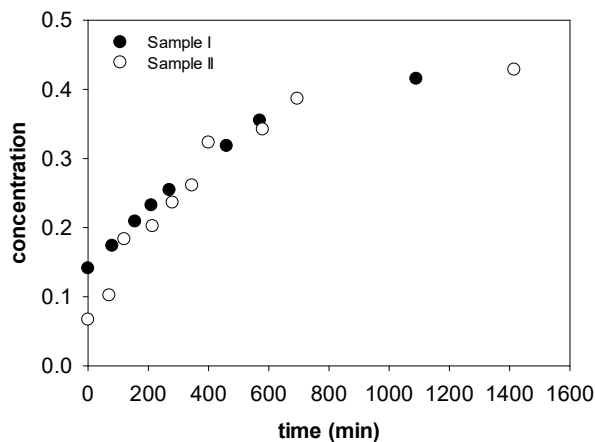


Figure 5: Impact of stick water concentration on the rate of concentration.

3.4. Role of temperature

Figure 6 shows the impacts of operating temperature on the stick water concentration process. This set of studies used 1.0 M NaCl solution as the draw solution. Stirring speeds of 360 rpm were applied on both feed and draw solution sides. Figure 6a shows the change of stick water concentration over time at elevated temperatures. For concentration studies at 65 and 75 °C, the maximum concentration attained was around 45 wt%, which was slightly higher than the maximum concentration attained at room temperature. The concentrated stick water started to become a thick paste at around 30 wt%. Above this concentration, the stick water was difficult to remove from the membrane cell. Figure 6b shows the percentage of water removed from the original stick water using different temperatures. Whereas it took about 800 minutes to remove 80% of water at room temperature, it took only about 230 minutes to remove 80% of water at 65 °C and about 150 minutes at 75 °C. After 70% water removal, the stick water was concentrated to 30 wt%. Figure 6c shows the flux change versus percentage water removed at different temperatures. For all the three temperatures, flux decreased with increasing stick water concentration. Similarly, the flux reduction can be attributed in part to increasing feed side ionic strength, which increases feed solution osmotic pressure and decreases the dewatering driving force. In addition, as water was removed from the feed side, a cake layer was observed on the FO membrane surface. The cake layer increases the transport resistance significantly. The dewatering flux was higher at higher temperature, which is expected due to the lower viscosity of the solution. Interestingly, after 80% water removal, the flux decreased by 69% at room temperature, by 55% at 65 °C and by 35% at 75 °C. The lower flux reductions at higher temperatures may be explained by enhanced Brownian motion, which could reduce the foulant deposition.

3.5. Target stick water concentration

The highest stick water concentration that can be achieved by FO appears to be about 45 wt%. However, as is shown in Figure 6, the water flux is low at concentrations > 30 wt% (i.e. >80% water removal for Sample II). We also observed that the stick water becomes a paste above about 30 wt%. Thus, pumping the fluid through a flow cell or membrane module is problematic.

Of note, 80% of the water was removed to achieve a stick water concentration of 30 wt%. Thus, a low percentage of water removal would be needed to reach the target concentration of 50 wt% for spray drying. Given these considerations, one approach might be to concentrate stick water to 30 wt% or lower using membrane FO, followed by thermal evaporation or other technologies to concentrate it to the target value. Based on the flux data collected, we estimated the membrane area that would be needed for a plant treating 66,000 lb/day stick water. Assumptions were that the original stick water has a concentration of 6.8 wt% and that the goal is to remove 80 wt% of the water. Table 1 reports the estimated minimum membrane area depending on the filtration temperature. This estimation did not consider membrane cleaning and replacement. At 75 °C, the required membrane area is only 30% of the area that is required at room temperature.

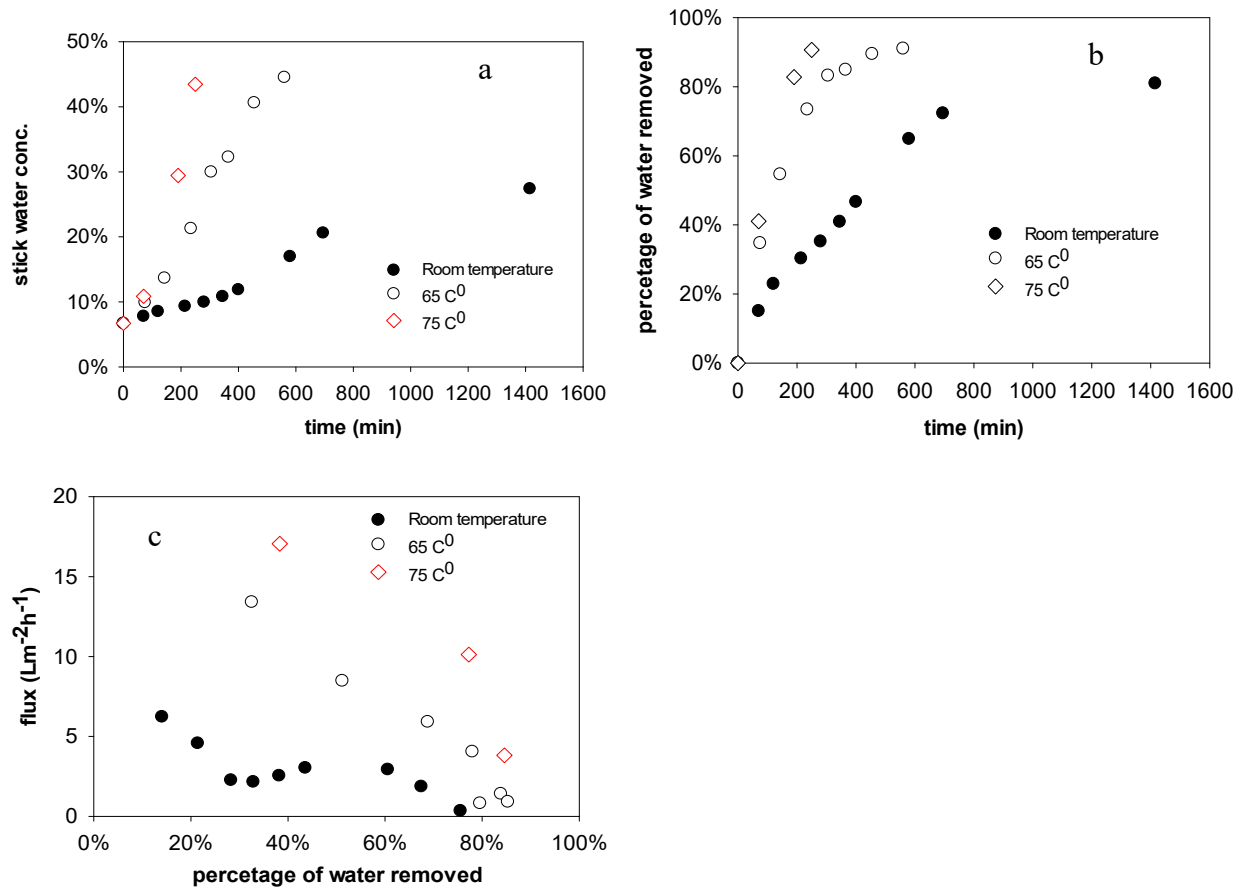


Figure 6: a) Solid concentration of stick water over time at different temperatures. b) Percentage of water removed over time at different temperatures. c) Dewatering flux versus percentage of water removed at different temperatures. Starting concentration was 6.7 wt%.

Table 1: Estimated minimum membrane area.

stick water flux (Lh ⁻¹)	average membrane flux (Lm ⁻² h ⁻¹)	membrane area (m ²)	Temp. (°C)
1022	13.5	76	75
1022	9.5	108	65
1022	4	256	room

3.6. Operating cost estimation

An operating cost estimation was conducted based on the data collected in this study. Five key assumptions were used in this estimation:

- 1) Plant output is 66,000 lb stick water per day;

- 2) Stick water has a concentration of 6.8 wt% and the goal is to remove 80 wt% of the water;
- 3) Membrane cost is \$50/m²;
- 4) Operating cost comprises only material cost and energy cost. For FO, the material cost is assumed to be membrane cost only.
- 5) Thermal evaporation is used as a comparison. At 1 atm, it takes 8,092 BTUs to evaporate one gallon of water (assuming pure water). Natural gas has a heating value of 1,000 BTUs per cubic foot (1 Therm = 100,000 BTUs). The approximate cost of natural gas is \$0.50 per Therm. Based on this very basic formula, it should cost about \$0.04 of fuel to evaporate one gallon of water.

Table 2 summarizes the estimated cost break down using FO membranes and boiling water evaporation methods. The manufacturer suggests FO membrane lifetime to be 2 years. Table 2 presents the operating cost assuming different membrane lifetimes. In an extreme case where membranes last only 3 months, the results indicate the total cost using FO could still be 80% less than that using evaporation. If the membrane lifetime is 2 years, the FO operating cost could be as low as 3% of the cost for evaporation. Moreover, the energy cost using FO is only 0.6% of the boiling water evaporation method.

Table 2: Estimated material and energy cost using FO and boiling water evaporation methods.

Frequency of membrane replacement	Membrane cost (\$)	Dry material weight (kg)	FO Material Cost \$/1000 Lb dry material	FO Energy Cost \$/1000 Lb dry material	Total FO Cost \$/1000 Lb
3 months	3900	185,760	9.6	0.3	9.9
6 months	3900	371,520	4.8	0.3	5.1
12 months	3900	743,040	2.4	0.3	2.7
24 months	3900	1,486,080	1.2	0.3	1.5
boiling water evaporation cost	0	0	0	47.9	47.9

4. Conclusions

This project provided data needed to evaluate a new, low-energy process for concentration of stick water to high solids levels. The forward osmosis operation would dewater the feed at low temperature ($\leq 75^{\circ}\text{C}$) to concentrations that would allow efficient spray drying. Thus, in addition to being a low energy process, the combination of forward osmosis and reverse osmosis with spray drying would avoid long-term contact of the recovered protein material with high temperatures that may degrade it.

Although FO could not concentrate the stick water above the 50 wt% target, the new process is effected at concentrating the wastewater to 30 wt%, which corresponds to 80% water removal. FO membranes could be used as the first dewatering step to remove the majority of water, followed by a second unit operation to remove residual moisture. Based on operating cost estimations, this hybrid approach would have substantially lower cost than thermal evaporation

alone..

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References

- [1] Baeling, P.; Ehnstroem, L. A process for the production of animal feed stuff from liquid raw materials. Patent application WO1983000006 A1, 1983.
- [2] Park, C.W.; Bastian, E.; Farkas, B.; Drake, M. The effect of feed solids concentration and inlet temperature on the flavor of spray dried whey protein concentrate. *J. Food. Sci.* 79, 19-24 (2014).
- [3] Zhou, J.; Wandera, D.; Husson, S.M. Mechanisms and control of fouling during ultrafiltration of high strength wastewater without pretreatment. *J. Membr. Sci.*, accepted.