

HARVESTING ENERGY AND WATER FROM FERTILIZER OSMOSIS

by

POUYAN POURMOVAHED

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Oakland University
Rochester, Michigan

Doctoral Advisory Committee:

Jonathan Maisonneuve, Ph.D., Chair
Laila Guessous, Ph.D.
Fay Hansen, Ph.D.
Mark Lefsrud, Ph.D.
Xia Wang, Ph.D.

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To my family

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Pouyan Pourmovahed

ABSTRACT

HARVESTING ENERGY AND WATER FROM FERTILIZER OSMOSIS

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Adviser: Jonathan Maisonneuve, Ph.D.

The potential for concentrated fertilizer to drive water treatment, nutrient recovery, and power generation has received increased attention. Large amounts of energy are wasted in agricultural systems each time concentrated fertilizers are diluted in water for fertigation, such as is common in hydroponic cultivation. This energy can be harnessed and converted to mechanical work or electricity to take a considerable load off specific farm subsystems, such as pumping and ventilation, or can directly drive desalination and filtration of non-potable waters such as seawater and wastewater. This thesis analyzes membrane processes for converting fertilizer energy to useful work. First, the novel concept of using fertilizer to generate power via pressure retarded osmosis (PRO) is introduced. Second, the concept of fertilizer PRO is experimentally validated, and power generation and energy recovery are shown for a range of common fertilizers. Third, the thermodynamic and practical limitations of recovering energy from fertilizer are established using a number of new analytical, numerical, and experimental methods. Finally, an alternative to energy recovery is examined, namely the possibility of using fertilizer to drive forward osmosis (FO) to recover clean irrigation water from wastewater feed sources. The limitations of fertilizer

FO are also established, again using a number of new analytical, numerical, and experimental methods. Results indicate that up to 1200 l of water and 125 Wh of energy may theoretically be recovered per kg of fertilizer, when low-concentration municipal wastewater is available. Given typical nutrient requirements for hydroponic plant cultivation, such values approach nearly 500 % of necessary irrigation water and 5 % of the electricity consumed by a typical greenhouse. However, practical limitations and non-ideal transport dynamics reduce these values and must be overcome in future research, so that fertilizer energy can be economically deployed to farm systems. To conclude, other applications of fertilizer energy are introduced and pathways for future research and development are discussed. This research may contribute to the future of sustainable agriculture by opening up new possibilities for energy efficiency, water security, and food productivity.

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CHAPTER ONE

INTRODUCTION

Global population is expected to reach 10 billion by the year 2050, requiring increased food production [1]. However, approximately 40 % of ice-free land and 70 % of withdrawn freshwater are already used for farming [2]. In addition, farms consume tremendous amounts of valuable fertilizer, including limited stores of phosphorous and energy-intensive nitrogen [3,4]. To ensure a sustainable future, these systems must increase capacity, accessibility, and efficiency while also protecting the environment and climate. Increasing food production to sustainably feed a growing population will require innovation to improve the efficiency of energy, water, and fertilizer use in agriculture [3–10].

Controlled plant environments are increasingly considered as attractive means of efficiently intensifying production, while improving food security and quality [11–17]. This includes trends towards indoor farming, urban agriculture, and hydroponic plant cultivation. Hydroponics is a technique of growing plants in nutrient solutions instead of soil. This offers many benefits such as faster growth, less water consumption, higher yields, and more control.[18] Furthermore, urban agriculture offers several advantages over conventional farming by producing food directly inside or near the city, including reduced transportation costs, improved food freshness, and improved food quality. In addition, the prospect of repurposing industrial buildings for indoor vertical plant production offers advantages of environmental control for optimized production, year-round production, reduced land footprint, elimination of agricultural runoff and soil

degradation, water savings, and socio-economic opportunities [15,19]. These systems will however require significant energy supply for HVAC and other loads, water for irrigation, and fertilizer for plant nutrition.

At the food-energy-water nexus of many agricultural systems, there is currently an important resource that is largely wasted, namely the energy that is released whenever concentrated fertilizers are diluted in water – a common practice in hydroponic agriculture and fertigation (when soluble fertilizers are integrated into the irrigation system). Harvesting energy from fertilizer dilution was first proposed in 2011 [20]. It was suggested that fertilizer solution can be used to drive water filtration. Super concentrated fertilizer solutions can produce a large driving force to draw clean water from wastewater feed source through a semi-permeable membrane. The product is fertigation water that can be delivered to the plants, and no further treatment of draw solution is required.[21–24]. More recently, we proposed the possibility of harnessing fertilizer energy to generate mechanical or electrical power. In 2018, the novel concept of using fertilizer PRO to generate power was introduced by our group [25,26] and then experimentally validated [27]. Fundamentally important questions remain about the potential for this energy source to provide significant amounts of energy to farms and about amounts of water that can be recovered from batch operations, and how significant recovery volumes are relative to the overall water balance of crops. This dissertation investigates the concept of harnessing fertilizer energy to generate power, treat wastewater and dehumidify air. A chapter is dedicated to each of these applications.

Chapter Two introduces the novel concept of harnessing energy from fertilizer via pressure retarded osmosis (PRO). This is the first-ever suggestion of using fertilizer PRO to produce energy and irrigation water. An overview of fundamental theory, performance, and potential of fertilizer driven osmosis for water treatment and energy recovery are presented .

The tradeoff between energy recovery and power that exists in a fertilizer PRO batch process is experimentally demonstrated in Chapter Three. This is only the second time in the literature that the novel concept of power generation from fertilizer osmosis is demonstrated and experimentally validated. Power generation is evaluated using a commercially available cellulose triacetate membrane, and power density throughout the batch process is used to analyze practical limits of fertilizer energy recovery. The dilution of several common single solute and fertilizer blends is considered, including cases that have not yet been documented in the literature.

In Chapter Four, we establish fundamental and practical limitations to how much energy can be recovered from fertilizer. This is the first time that the potential and significance of this energy source compared to farms requirements is demonstrated. We establish (1) the fundamental thermodynamic energy limits of fertilizer, (2) the energy recovery limits of a fertilizer PRO batch process when operated at constant pressure, and (3) the practical limitations imposed by the need to maintain competitive power levels. These theoretical limitations are compared against a series of experimentally-calibrated simulations showing the maximum energy recovery when non-ideal transport dynamics are considered, including reverse solute flux and concentration polarization. Based on

these, we illustrate the potential of common nitrogen, phosphorus and potassium fertilizers and conclude by evaluating the energy that can be recovered during cultivation of common hydroponic plant crops including tomato, cucumber, lettuce, and basil.

In Chapter Five, we investigate the concept of water recovery from wastewater sources via fertilizer-driven osmosis, a process that has the potential to both improve the efficiency of fertilizer use, and to reduce the freshwater footprint of crops. We establish (1) the fundamental thermodynamic limits to water recovery from fertilizer osmosis that are imposed by osmotic equilibrium, (2) the practical limitations that are imposed by the need to maintain competitive flux levels, and (3) the effect that non-ideal transport dynamics such as reverse solute flux and concentration polarization have on flux and therefore water recovery limits. To do this, we describe a series of analytical, numerical, and experimental tools that can be applied to this fertilizer osmosis but may also find use in analysis of other membrane-based batch process. Previous to this work, the limits of fertilizer osmosis batch operation for water recovery and the significance of recovered volumes relative to overall water balance of crops were not established in the literature, so this chapter provides an important baseline of the potential of this application.

Chapter Six outlines future work including (1) the possible application of fertilizer for greenhouse dehumidification applications and (2) the need to better understand multi-ion transport dynamics including concentration polarization. Preliminary analysis of both of these future research tracks is provided.

CHAPTER TWO

A NEW CONCEPT: USING FERTILIZER DRAWN OSMOSIS TO PRODUCE IRRIGATION WATER AND ENERGY FOR HYDROPONIC FARMING

2.1 Original Publication

Chapter Two is based primarily on a conference paper that was originally published in the Proceedings of the ASABE. This publication served as a rapid communication to introduce our novel concept to the literature. A complete reference for the published work is as follows:

P. Pourmovahed and J. Maisonneuve, “Using fertilizer drawn osmosis to produce irrigation water and energy for hydroponic farming,” Proceedings of the ASABE Annual International Meeting, Detroit, MI, July 2018. <https://doi.org/10.13031/aim.201801174>

2.2 Introduction

Membrane based technologies have received increased attention as alternatives to conventional water treatment methods due to their cost, energy efficiency, and low operation and maintenance costs [28]. These technologies can be used to desalinate or filter non-potable waters such as seawater or wastewater and also have the potential to produce energy [29]. Membrane based systems have minimal carbon footprint, making them a suitable clean energy and water recovery process for the future.

One application of membrane technology is for energy recovery via the principle of natural osmosis from large concentration gradients [20,30]. During osmosis, or as it is

often called forward osmosis (FO), concentrated fertilizer solution is separated from a diluted water stream by a membrane that is only permeable to water. To balance the potential of each solution, water passes through the membrane by osmosis, thereby diluting the fertilizer solution.

Many agricultural systems consume tremendous amounts of concentrated fertilizer. When fertilizer is mixed with water prior to distribution to plants, energy is released that can be used to drive osmosis and do useful work. This chapter introduces the new concept of using fertilizer to drive pressure retarded osmosis (PRO) for power generation. Preliminary analysis including theory, methods and results are presented. A case study is provided to illustrate application to an urban hydroponic lettuce and tomato farm. This chapter also provides preliminary analysis of the viability and efficiency of such systems and gives insight into whether fertilizer osmosis is a suitable choice for water treatment and energy production in any given hydroponic system.

2.3 Theory

2.3.1 Fertilizer-Driven Forward Osmosis

Fertilizer osmosis works on the principle of natural osmosis. Two solutions with different osmotic concentrations are separated by a semi-permeable membrane. The membrane allows only water to pass and blocks solutes. Therefore, water permeates from the less concentrated solution (feed solution) towards the more concentrated solution (draw solution) to balance the osmotic pressures. The process is illustrated in Figure 2.1(a). Figure 2.1 (b) shows how fertilizer driven FO filters wastewater to produce a

clean diluted fertigation solution. Clean water permeates through the membrane and dilutes the super concentrated fertilizer solution which can then be delivered to the plants.

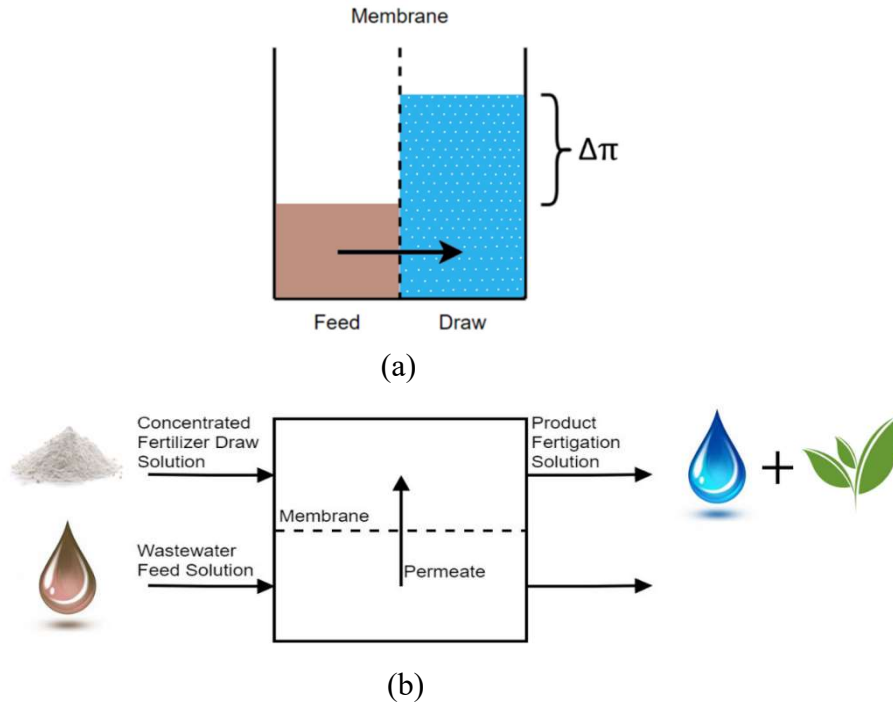


Figure 2.1. (a) Forward osmosis (FO) with wastewater as feed solution, and (b) fertilizer driven forward osmosis to produce irrigation water from wastewater feed source

Energy consumption of FO is very low because the process is self-driven and does not require any applied hydraulic pressure. Many wastewater sources can be used as feed for fertilizer driven FO, for example municipal wastewater, raw sewage, and brackish water. For the draw solution, fertilizers with heavier molecular weights and higher osmotic pressures are preferred. There are therefore many possibilities for fertilizer driven FO to serve as a reliable, energy efficient means of producing fertigation water especially for indoor water-based farming systems.

The osmotic pressure difference $\Delta\pi$ is the driving force for this process and is defined by van't Hoff equation as a function of concentration difference Δc , as shown by the expression (see section 5.7 for detailed analysis on osmotic pressure),

$$\Delta\pi \approx i R T \Delta c \quad (2.1)$$

Where i is the number of ions of solutes, R is the gas constant, and T is absolute temperature. As the draw solution is gradually diluted, $\Delta\pi$ decreases until finally the process stops when $\Delta\pi = 0$. Permeate flux J_w is defined as the rate of water permeation by osmotic diffusion across the material with water permeability A .

$$J_w = A \Delta\pi \quad (2.2)$$

2.3.2 Fertilizer-Driven Pressure Retarded Osmosis

Mixing fertilizer with water releases energy that can be recovered for useful purposes. PRO is a membrane-based process that converts this energy to useful mechanical work in the form of an expanding volume of pressurized solution. This is done by applying an opposing hydraulic pressure Δp to the draw side that is smaller than the driving osmotic pressure difference $\Delta\pi$ [30]. The process is shown in Figure 2.2 (a), with a concentrated fertilizer as the draw solution and freshwater as the feed solution. Fertilizer driven PRO can recover some of the mixing energy to power farm loads such as pumps and fans as shown in Figure 2.2 (b).

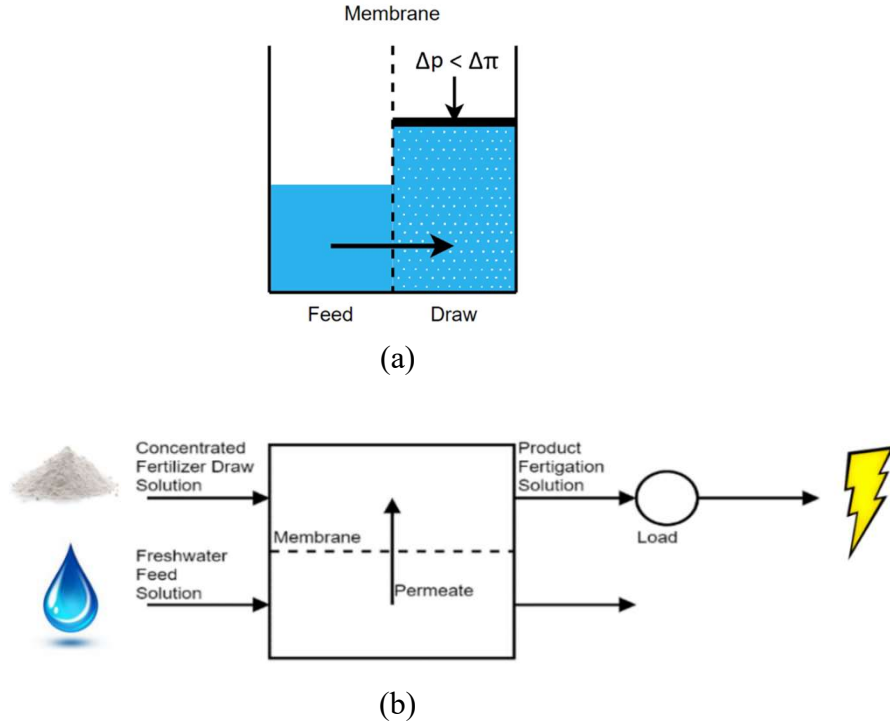


Figure 2.2. (a) Pressure retarded osmosis (PRO) with clean water as feed, and (b) recovering energy from mixing of fertilizer with irrigation water via fertilizer driven pressure retarded osmosis

The rate at which this energy is recovered can be normalized over membrane area a , to obtain power density as a function of permeate flux J_w . Permeate flux in PRO is smaller than FO and is defined by the difference in osmotic pressure and applied pressure and the water permeability of the membrane A .

$$J_w = A (\Delta\pi - \Delta p) \quad (2.3)$$

$$\frac{\dot{W}}{a} = J_w \Delta p \quad (2.4)$$

Where $\Delta\pi$ is the osmotic driving force, and A is the membrane permeability to water. Osmotic pressure π is commonly expressed as a function of concentration c using the van't Hoff equation shown in equation (2.1).

Figure 2.3 shows how changing applied pressure Δp influence flux and power density. FO flux is obtained when $\Delta p = 0$ and then water flux decreases as the applied pressure increases, until it reaches zero and eventually reverse the flux direction. When $\Delta p > \Delta\pi$ the flux direction reverses. As seen in equations (2.3) and (2.4), maximum power density is obtained when applied pressure is half of the osmotic pressure.

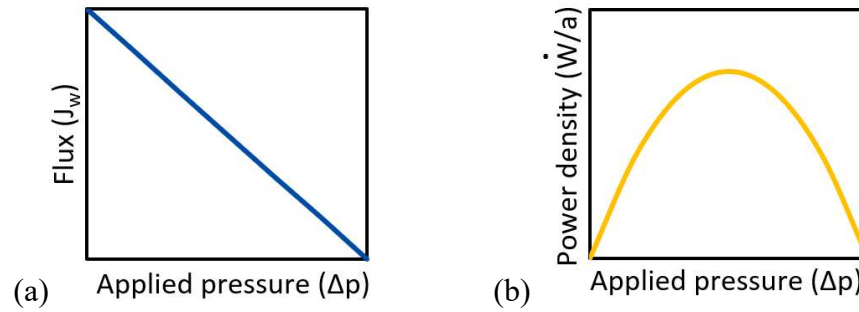


Figure 2.3. (a) Flux is the rate of water permeate and is obtained by osmotic diffusion across material. Increasing the applied pressure will reduce flux. (b) Power density is the rate of work obtained from flux and applied pressure normalized over membrane area.

2.4 Methodology

2.4.1 Preliminary Analysis of Water Recovery Volumes from Fertilizer Forward

Osmosis

The maximum volume of water that can be extracted from the feed source is equal to the amount of water permeate that balances the osmotic pressure of the two solutions

across the membrane. This volume $\Delta V_{\max}$ is determined using equation (2.5), which shows the concentration differences as the main driving force of the process.

$$\frac{\Delta V_{\max}}{m_{\text{fertilizer}}} = \left(\frac{1}{c_F} - \frac{1}{i c_D} \right) \quad (2.5)$$

c_F and c_D are the concentration of the solutes in feed and draw solutions, and $m_{\text{fertilizer}}$ is the mass of the fertilizer, which is a function of the plant's nutrient requirements. When nutrient requirements are expressed in terms of single elements, they can be converted to fertilizer mass using the molar ratio of the specific element to the fertilizer, as shown in equation (2.6).

$$\frac{m_{\text{fertilizer}}}{m_{\text{element}}} = \frac{M_{\text{fertilizer}}}{M_{\text{element}}} \quad (2.6)$$

For example, consider the required nutrient concentrations of hydroponic tomato and lettuce as listed in Table 2.1 [28,31]. These concentrations can be converted to nutrient mass by assuming that a typical tomato plant consumes about 0.5 l of irrigation water daily and that a typical lettuce plant consumes about 0.2 l of water [32]. Daily fertilizer requirements can then be calculated with equation (2.6) and are listed in Table 2.1. Assuming that calcium nitrate $\text{Ca}(\text{NO}_3)_2$, potassium chloride KCl , ammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$, and magnesium sulfate MgSO_4 are the primary nutrient sources, the fertilizer requirements are listed in Table 2.2.

There are however several operational challenges that make it impractical to obtain the theoretical maximum volume of water. First, to be economically viable, water must be extracted at an efficient rate per unit membrane area.

Table 2.1. Required nutrient concentrations for hydroponic plants.

	Concentration (mg/l)						
	N	P	K	Ca	Mg	S	Cl
Tomato	280	40	390	480	73	96	280
Lettuce	195	31	215	90	12	12	10

Table 2.2. Daily fertilizer requirements for a single hydroponic plant

	Mass (mg/day)			
	Ca(NO ₃) ₂	NH ₄ H ₂ PO ₄	KCl	MgSO ₄
Tomato	984	74	372	183
Lettuce	74	23	82	9

This means that while draw solutions are diluted during the process, the decreasing concentration gradient may not be sufficient to produce flux that balances the cost of operation. Nasr et al. [33] suggest that after a certain point (usually 6 M) increasing draw solution concentration will not result in higher flux. Also, for certain crops, the product water from fertilizer driven FO does not meet the concentration standards for plants and post processes such as nanofiltration or further dilution with a clean water source are necessary, which increases cost of operation [34,35]. These limitations will result in a much lower volume than the theoretical maximum, which we estimate at 30 %.

2.4.2 Preliminary Analysis of Energy Recovery from Fertilizer Pressure Retarded Osmosis

The maximum theoretical energy released when mixing two solutions is equal to the Gibbs free energy ΔG as shown in equation (2.7) [29]. This energy is related to the thermodynamic state and chemical composition of each solution.

$$\Delta G = R T \sum_i x_i \ln x_i \quad (2.7)$$

Where x_i is the mole fraction of the solute i over the total number of moles in the mixture. Due to thermodynamic irreversibility, it is impossible to harness all of this energy.

PRO captures a fraction of this mixing energy at some applied pressure. PRO energy E is defined by the product of applied hydraulic pressure Δp and volume of water permeate ΔV ,

$$E = \Delta p \Delta V \quad (2.8)$$

Among the challenges for fertilizer PRO is the fact that large concentration gradients between feed and draw solutions result in very high osmotic pressure differences. Harnessing this energy with PRO therefore requires the application of very large hydraulic pressure of up to 100 bar. Current membranes in the market cannot withstand such pressures. This is therefore one the limits for practical PRO energy recovery with fertilizer draw.

The rate at which this energy is captured (i.e. power) is also important. Like with FO, to be commercially viable, PRO systems must recover energy at rates that are economically viable. The high concentration gradients between the feed and draw sources

in this case, means that PRO systems can produce very large amount of power, however this large gradient also causes mixing to proceed very quick and reduces the amount of energy captured. All of these factors place limits on energy extraction from PRO, which we estimate at 20 % of the total theoretical limit.

2.5 Results

2.5.1 Preliminary Estimate of Water Recovery from Fertilizer Osmosis

The estimated volume of water that a unit mass of fertilizer can theoretically extract from wastewater is shown in Table 2.3. For hydroponic tomato this is approximately 3.2 l/plant/day, and for lettuce it is almost 0.4 l/plant/day. These both compare favorably with the daily requirements of 0.5 l/plant/day for tomato, and 0.2 l/plant/day for lettuce. The practical estimates of extractable water are also provided in Table 2.3, and still compare favorably with required volumes. Practical volumes account for over 200 % of required irrigation water in the case of tomato, and almost 70 % in the case of lettuce.

Table 2.3. Extractable water volumes compared to irrigation requirements

	Volume (l/plant/day)						
	Ca(NO ₃) ₂	NH ₄ H ₂ PO ₄	KCl	MgSO ₄	Theoretical Total	Practical Total	Required Total
Tomato	1.97	0.15	0.74	0.37	3.23	1.04	0.5
Lettuce	0.15	0.05	0.16	0.02	0.38	0.13	0.2

Water extraction is highly dependent on the type of wastewater source that is used as the feed solution. Figure 2.3 shows the effect of feed source concentration on practical water extraction by fertilizer osmosis. Weaker sources of wastewater feed lead to higher concentration differences and more water extraction. For example, about 5 times more water can be extracted from a diluted source such as weak wastewater with 0.1 g/l concentration, compared to when a feed source with 0.5 g/l is used, such as brackish water. These FO systems are therefore more effective for less concentrated feed sources.

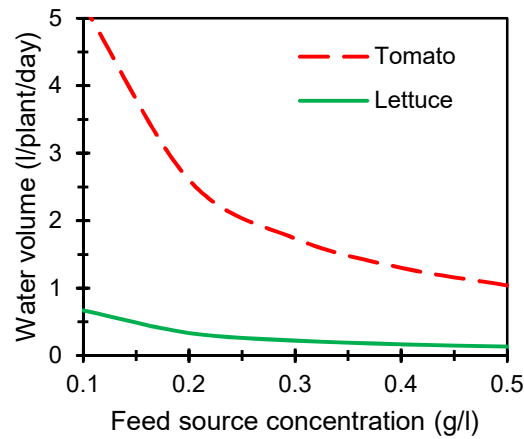


Figure 2.4. Water recovery by fertilizer driven forward osmosis (FO) as a function of initial feed source concentration

2.5.2 Preliminary Estimate of Energy Recovery from Fertilizer Pressure Retarded Osmosis

The theoretical and practical energy recovery values based on daily fertilizer requirements of plants are estimated and listed in Table 2.4. Calcium nitrate as the main source of nitrogen has the largest mass and therefore has the largest potential for energy

production, as well as for water extraction as shown previously. The significance of these energy values is illustrated below with a case study.

Table 2.4. Theoretical and practical energy production with pressure retarded osmosis (PRO)

	Energy (J/day/plant)				Theoretical Total	Practical Total
	Ca(NO ₃) ₂	NH ₄ H ₂ PO ₄	KCl	MgSO ₄		
Tomato	330	29	136	45	540	97
Lettuce	25	9	10	2	46	8

2.6 Conclusion

Fertilizer osmosis has received increasing attention as a reliable method of filtering water for irrigation, especially for agriculture in arid regions. In this chapter, the concept of fertilizer PRO for energy recovery and power generation is introduced and illustrated for the case of hydroponic tomato and lettuce production. Preliminary results suggest that fertilizers consumed by plants have the potential to produce all of the required irrigation water from wastewater sources. Energy recovery from mixing of fertilizer and irrigation water is also analyzed. Although this energy is rather small relative to the total electricity consumed by a greenhouse or farm system, it could however take a considerable load off specific farm subsystems, such as hydroponic pumping. Although additional analysis is required, using utilizing fertilizer energy for efficient hydroponic plant cultivation would represent a great step towards improving global food and water security. Realizing this possibility will require advances in membrane technology, which can increase the performance of FO and PRO processes by

raising the limits of economical extraction rates. Performance is also strongly dependent on the agricultural system and scale, plant requirements, fertilizer selection, and wastewater quality. Additional analysis is needed to consider application to other farming systems.

2.7 List of Symbols in Chapter 2

c	concentration (g l^{-1})
G	Gibbs energy (J)
i	number of ions
m	mass (kg)
M	molar mass (g mol^{-1})
p	pressure (Pa)
R	gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
T	absolute temperature (K)
V	volume (m^3)
x	mole fraction

Greek symbols:

π	osmotic pressure (Pa)
-------	-----------------------

Subscripts/Superscripts:

D	draw
F	feed
i	initial

CHAPTER THREE

EXPERIMENTAL VALIDATION: DEMONSTRATION OF POWER GENERATION FROM FERTILIZER SOLUTIONS VIA PRESSURE RETARDED OSMOSIS

3.1 Original Publication

Chapter Three is based primarily on a journal paper that is published in the Transactions of the ASABE. This publication was only the second in literature to ever experimentally validate the concept of power generation from fertilizer PRO. A complete reference for the published work is as follows:

P. Pourmovahed and J. Maisonneuve, “Demonstration of power generation from fertilizer via pressure retarded osmosis,” Transactions of the ASABE 64, 495-505 (2021).

<http://doi.org/10.13031/trans.14220>

3.2 Introduction

Currently, large amounts of energy are wasted from agro-systems each time concentrated fertilizers are diluted in water – a common practice in fertigation and hydroponics. This source of free energy (or Gibbs energy) has been widely considered for saltwater power (known as Blue Energy) [36–42], but has been mostly overlooked for agricultural applications. As of 2020, worldwide consumption of ammonia (NH_3), phosphoric acid (H_3PO_4), and potash (K_2O) is estimated at 273 million tons per year. This fertilizer has an energy potential of up to 27.16 TWh/year. At electricity rates of 6.83 cents per kWh, this energy has a value of \$1.86 B that is wasted every year.

Converting this energy to useful work can be done via several processes, but to date, most literature has focused on using fertilizer potential to drive osmosis for water filtration. This was first demonstrated by Phuntsho et al. in 2011 [20] who showed seawater desalination via fertilizer osmosis. Since then, several other studies have followed considering a range of fertilizers and wastewater sources [34,35,43–47]. While water recovery has shown promise, the possibility of using this potential to drive power generation has received much less attention.

The novel concept of using fertilizer to drive pressure retarded osmosis (PRO) for conversion to mechanical work was proposed in our previous work [25] as well as by Volpin [27]. Figure. 3.1 illustrates the process of fertilizer driven PRO (or Green PRO). In this process, concentrated fertilizer is used to draw permeate across a semi-permeable membrane from a low-concentration feed source. When this occurs against some applied pressure or load, the expanding volume of fertilizer solution represents mechanical energy that can be used to do work. Energy conversion via PRO has been widely studied for seawater gradients [48–55], but its development has been limited by several key challenges. These include: (1) The significant energy requirements of pre-treatment that is necessary to mitigate membrane fouling from natural river and seawater sources; and (2) the modest energy potential of seawater relative to freshwater [56]. Fertilizer PRO offers advantages in both of these regards. First, hydroponic solutions are typically prepared from a clean irrigation source with minimal dissolved ions. Therefore, fouling concerns should be minor, and the need for costly pre-treatment can be avoided. Second, fertilizer solutions are typically prepared from solutes stored on the farm.

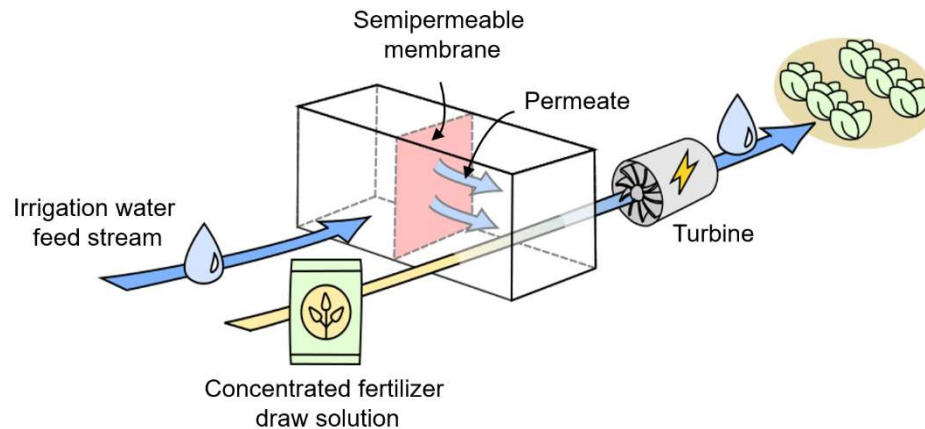


Figure 3.1. Pressure retarded osmosis (PRO) can be used to generate mechanical energy from concentrated fertilizer gradients in the form of an expanding volume of pressurized fertilizer solution

Initial draw concentrations will approach the solubility limit, offering very high initial potentials. As shown in Figure 3.2, the potential of common fertilizer solutes compares very favorably to other super-concentrated resources, and far surpasses the potential of seawater, which has mostly been considered for PRO power [57–60]. We estimate that up to 150 Wh of energy is released when a kg of pure common fertilizer such as potassium chloride is diluted in an infinite volume of irrigation water [29,61]. While promising, the literature related to fertilizer PRO remains limited [25,27], Fundamental questions remain about the practical limits of energy recovery. As illustrated in Figure. 3.3, it is most appropriate to consider fertilizer PRO as a batch process, which would produce a diluted fertilizer solution compatible with current hydroponic systems, and suitable for plant nutrition. Therefore, throughout the batch process, it is expected that the high potential of initially super concentrated fertilizer, will rapidly drop.

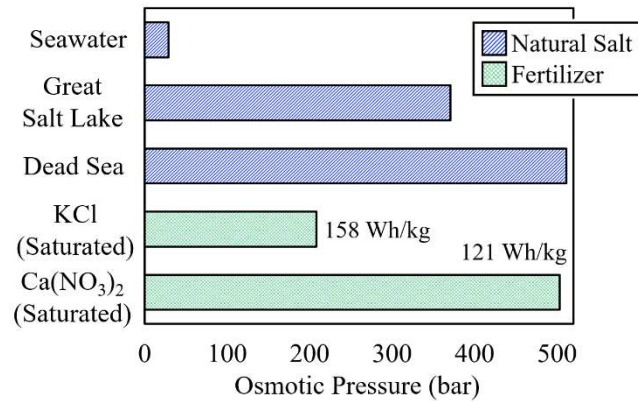


Figure 3.2. The potential of concentrated fertilizer solutions relative to freshwater is compared here against that of natural saltwater gradients

This drop in potential will likely impose a practical limit to energy recovery, because rates of recovery (i.e. power) will eventually drop below viable or practical levels, requiring unreasonable membrane areas or unreasonable time for further recovery.

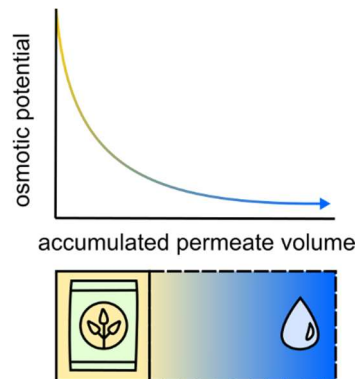


Figure 3.3. For integration with hydroponic and fertigation systems, fertilizer PRO is likely to be operated as a batch process, wherein a sharp drop in potential will be observed throughout the dilution process. The resulting drop in power (related to osmotic potential) may impose a practical limit to energy recovery (related to accumulated permeate volume).

Therefore, the main objective of the present chapter is to experimentally demonstrate the tradeoff between energy recovery and power that exists in a fertilizer PRO batch process. Power generation was evaluated using a commercially available cellulose triacetate membrane, and power density throughout the batch process was used

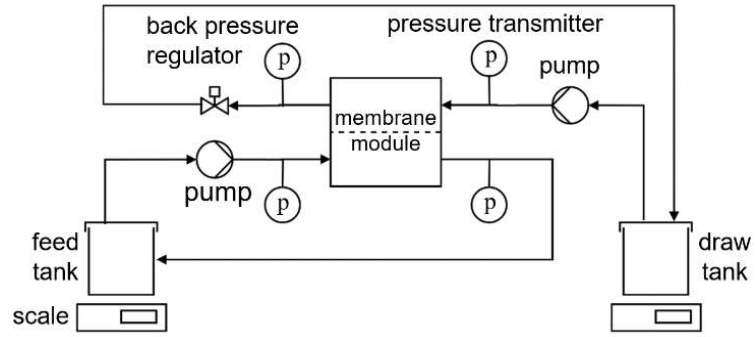
to analyze practical limits of fertilizer energy recovery. The dilution of several common single solute and fertilizer blends was considered, including cases that have not yet been documented in the literature.

3.3 Materials and Methods

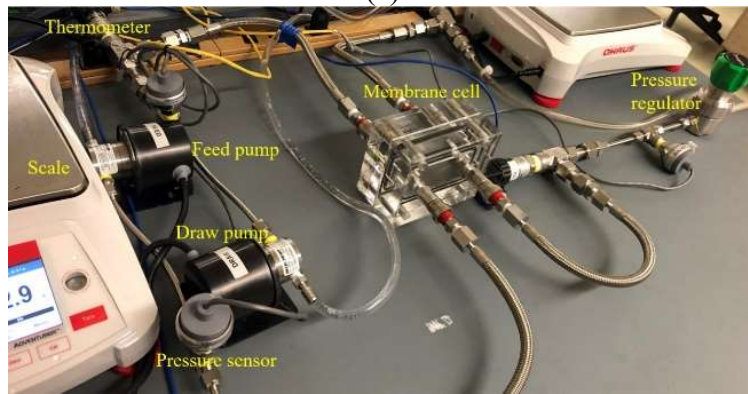
A series of fertilizer PRO tests were conducted to determine flux and power as a function of diluting fertilizer concentration throughout the energy recovery batch process. Experiments were conducted using the custom osmosis test bench shown in Figure. 3.4. The bench consisted of a membrane module supplied by feed and draw solutions at flow rates controlled by variable speed pumps (Micropump, Vancouver, WA). The applied pressure was controlled via a spring-loaded back-pressure regulator (Swagelok, Solon, OH). Pressure transmitters (± 0.625 psi, Cole-Parmer, Vernon Hills, IL) were mounted at each of the four membrane ports. Masses and pressures were recorded every second by an auto-logging system (Precision Digital, Hopkinton, MA) connected to a PC.

Water volume transport across the membrane was evaluated using a mass balance approach, where change in feed and draw mass (Δm) was measured over a given time interval Δt . Recirculated feed and draw solutions were weighed using digital scales (± 0.2 g, OHAUS, Parsippany, NJ), and permeate flux was evaluated using the expression,

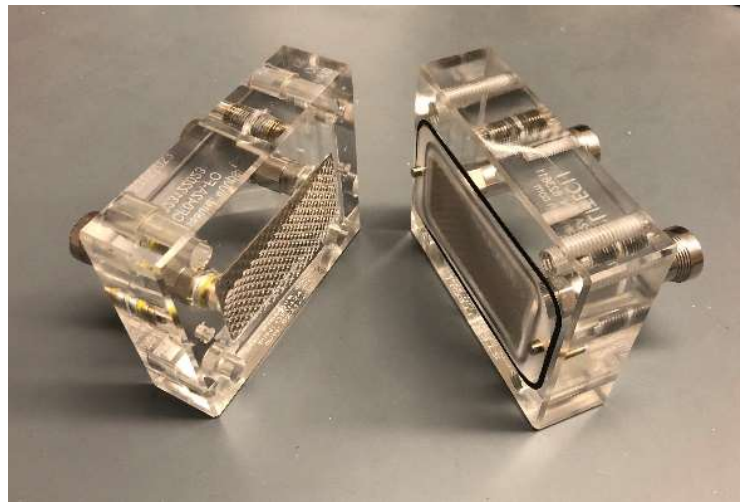
$$J_w = \frac{\Delta m}{a \rho \Delta t} \quad (3.1)$$



(a)



(b)



(c)

Figure 3.4. (a) Schematic of the laboratory PRO test bench. (b) Laboratory test bench at Oakland University. (c) Clear acrylic membrane housing module with membrane and spacer in place.

Where a is the membrane surface area, and ρ is the solution density. For verification, changes in mass Δm of both the feed and draw solutions was recorded and analyzed.

Reverse leakage of solute from the draw stream was evaluated by measuring the concentration of the feed stream c_F using a conductivity probe ($\pm 10 \mu\text{S}$, Omega, Norwalk, CT). Reverse solute flux, was then determined using the following expression, obtained by considering the mass balance of water and solute transport.

$$J_s = \frac{c_{F,\text{out}} V_{F,\text{out}} - c_{F,\text{in}} V_{F,\text{in}}}{a \Delta t} \quad (3.2)$$

Where V_F is the volume of the feed solution at the inlet and outlet respectively.

PRO flux and power generation was evaluated over a range of applied pressures and for several common fertilizers including Hoagland solution A (consisting of potassium nitrate KNO_3 , magnesium sulfate MgSO_4 , and ammonium dihydrogen phosphate $(\text{NH}_4)\text{H}_2\text{PO}_4$), Hoagland solution B (consisting simply of calcium nitrate $\text{Ca}(\text{NO}_3)_2$), and potassium chloride KCl . Results were compared against a sodium chloride NaCl draw solution for reference. Feed solution was maintained at 0.1 g/l NaCl , approximating municipal tap water which is commonly used in hydroponics. All fertilizer solutes were commercial grade of at least 99 % purity (Fisher Scientific, Hampton, NH).

A commercial forward osmosis (FO) cellulose triacetate (CTA) membrane from FTS H2O (Albany, OR) was selected for this study. This membrane has been considered in several prior FO and PRO studies [62–67]. Flat-sheet membranes were mounted in a clear acrylic module (108 mm length, 39 mm width, and 2.3 mm channel depth) accommodating samples with an effective area of 42 cm^2 (Sterlitech, Kent, WA). To facilitate operation at the desired flow velocities, and to

Table 3.1. PRO test conditions.

Membrane Module Parameters	
Module configuration	Flat sheet
Dimensions (L × W × D)	108 mm × 39 mm × 2.3 mm
Effective channel depth	0.9 mm
Effective membrane area	42 cm ²
Spacer	31 mil diamond-cut
Operating Conditions	
Trial length	60 ± 10 minutes
Temperature	20 ± 0.3 °C
Flow configuration	counter
Applied pressure	0, 2, 5, 7 ± 0.05 bar
Velocity	15 ± 0.01 cm/s
Feed concentration	0.1 ± 0.125 g/l
Fertilizer Draw Concentration	
<i>Hoagland A</i>	
Potassium nitrate	25 to 100 × strength
KNO ₃	Where 1 × strength
Magnesium sulfate	0.607 g/l KNO ₃
MgSO ₄	0.493 g/l MgSO ₄
Ammonium phosphate	0.115 g/l (NH ₄)H ₂ PO ₄
(NH ₄)H ₂ PO ₄	
<i>Hoagland B</i>	
Calcium nitrate	10 to 600 g/l
Ca(NO ₃) ₂	
Potassium chloride KCl	10 to 300 g/l
Sodium chloride NaCl	10 to 300 g/l

provide support to the membranes, shims were inserted into both feed and draw chambers reducing the effective channel depth to 0.9 mm. The feed channel was equipped with 31 mil diamond shaped-cut spacer to provide support during PRO. Velocities of 15 ± 0.125 cm/s were maintained throughout all test trials. A summary of all test parameters and conditions is provided in Table 3.1. A detailed presentation of raw data and analysis is also included in Supplementary Note 6.2.

3.4 Results and Discussion

Experimental results from PRO testing are summarized in Figure 3.5. Flux and power generation were observed throughout the PRO process, as nearly saturated fertilizer solution was diluted by water permeate. Dilution of the fertilizer is represented in the x-axis by a drop in concentration, an accumulation of permeate volume (normalized per unit of fertilizer mass), and the recovery of energy (again normalized per unit of fertilizer mass). In some cases, flux of up to 40 lmh (liter per square meter per hour) is observed at initially high concentrations, followed by a sharp drop in flux as the concentration decreases rapidly through the early stages of permeate volume accumulation.

The result of this drop in flux is a proportional drop in power, which approaches zero as energy is recovered from the process. A maximum of nearly 5 Wh/kg was recovered in the laboratory, but much of this was obtained at low recovery rates. Operating at such low power density becomes impractical and economically unattractive. Maintaining some minimum power therefore necessarily requires sacrificing some energy in a single stage PRO process [68]. For example, if power of at least 5 W/m^2 is targeted,

then only about 1 Wh/kg can be recovered from NaCl, much less than that for KCl and Hoagland B, and none for Hoagland A. This tradeoff between recovering energy and maintaining high power is one of the primary challenges and considerations of fertilizer PRO and demonstrates a sort of practical limit to the process. That said, membranes with improved permeability make it possible to recover more energy while maintaining a certain power target (see Supplementary Note 3.6.2. for more information about the tests and uncertainty analysis).

The power and energy generation tradeoff also showed an interesting relationship to pressure. Results at four different applied pressures are presented, ranging from $\Delta p = 0$ (i.e., forward osmosis operation) which yields zero power and energy, up to $\Delta p = 7$ bar, which yields maximum power and energy under certain conditions. Under other conditions, we observed that $\Delta p = 5$ bar yields maximum power or energy. A cross-over point between these two pressure curves is also observed. For example, the power curves for KCl cross-over somewhere around 0.8 Wh/kg. This suggests that depending on the power target, it is preferable to operate at different applied pressures. For example, if the target is to maintain power $> 2.2 \text{ W/m}^2$ then applied pressure of 7 bar will recover more energy. On the other hand, if operation $< 2.2 \text{ W/m}^2$ is acceptable, then applied pressure of 5 bar will allow for maximum energy recovery.

This phenomenon can be explained by the relationship between flux and pressure in the fertilizer PRO process. At any given concentration, there will be some pressure that yields maximum power. In this process however, concentration is variable, and drops

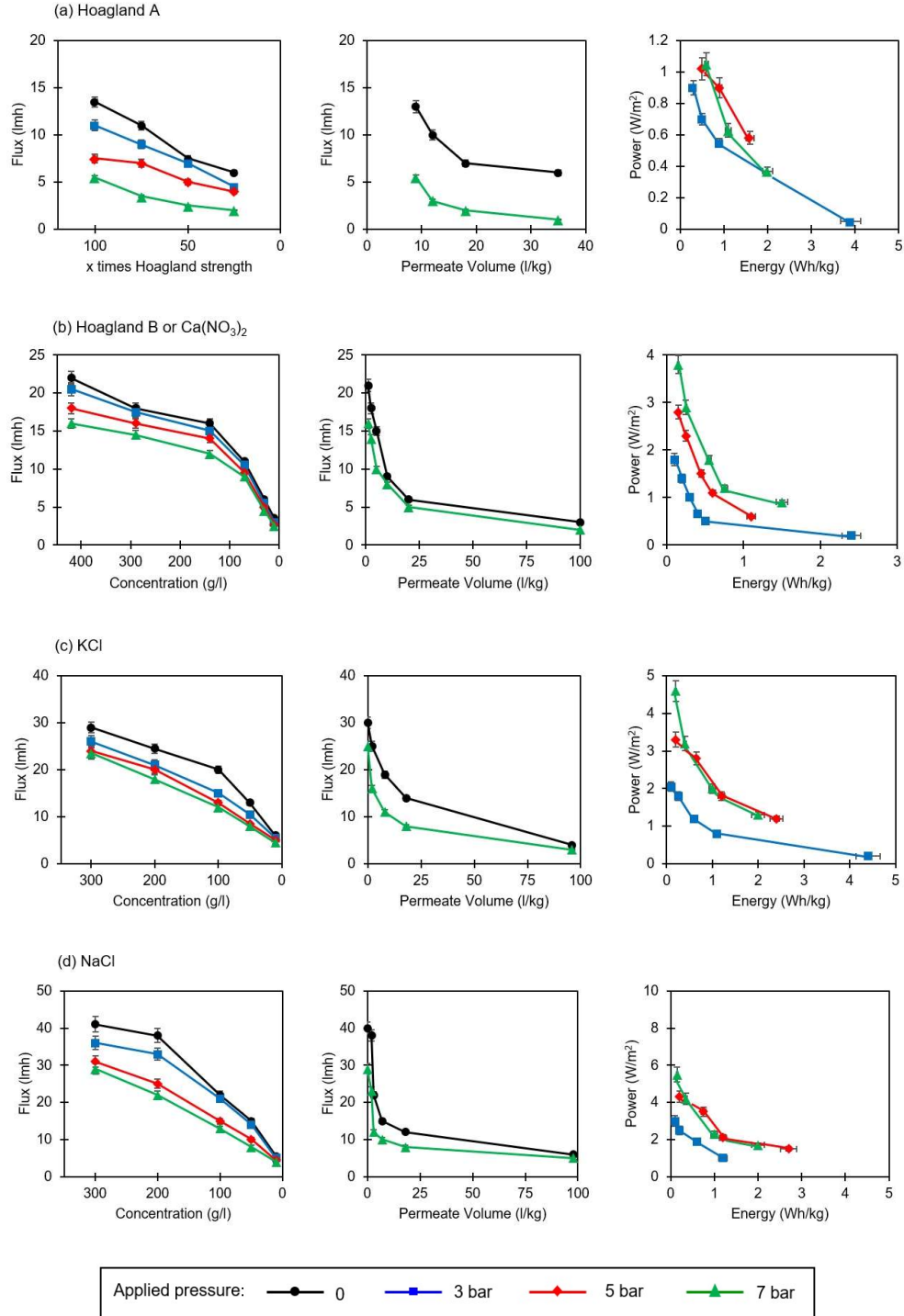


Figure 3.5. Flux and power observed during fertilizer PRO (using FTS H₂O membrane under test conditions summarized in Table 3.1). Dilution of the fertilizer draw solution is represented in the x-axis by a drop in concentration, an accumulation of permeate volume (normalized per unit of fertilizer mass), and the recovery of energy (again normalized per unit of fertilizer mass). Several fertilizers draw solutions are shown including (a) Hoagland A, (b) Hoagland B (which is calcium nitrate), (c) potassium chloride KCl, and (d) sodium chloride NaCl.

throughout the process. As such, maximum power at one stage of dilution may be different then at another stage. Ideally, the applied pressure would vary accordingly, and the applied pressure that yields maximum power would be maintained at each instantaneous concentration.

Figure. 3.5 provides a comparison of fertilizer performance. Results are shown for three common fertilizers (a) Hoagland A, (b) Hoagland B (i.e. calcium nitrate $\text{Ca}(\text{NO}_3)_2$), and (c) potassium chloride (KCl), as well as (d) sodium chloride (NaCl) for reference. The greatest water flux was observed for NaCl, followed by KCl, $\text{Ca}(\text{NO}_3)_2$, and finally Hoagland A. The flux is the result of several variables including membrane selectivity, solute diffusivity and solubility, and molar concentration of each ion, however the dominant dynamic is the osmotic potential of each solute at saturation. For example, NaCl has initial potential of 280 bar, as compared to 210 bar for KCl. Although the potential is short lived because fertilizers are rapidly diluted, this demonstrates the importance of the initial osmotic potential to the fertilizer PRO process.

3.5 Conclusions

In this chapter we have experimentally demonstrated power production and energy recovery from a range of common fertilizers via a PRO batch process. Up to 6 W/m^2 power density was observed in the laboratory with KCl fertilizer and commercial CTA membranes. These power levels were shown to rapidly decrease throughout the fertilizer PRO batch process, and the tradeoff between maintaining reasonable power levels and recovering energy was demonstrated. Up to 5 Wh energy recovery per kg of fertilizer was demonstrated in the laboratory with commercial CTA membranes, but

much of this was obtained at power levels less than 5 W/m². Further progress in high performance membrane development will allow for additional energy recovery at elevated power.

Harnessing fertilizer energy can open up new and interesting possibilities at the food-energy-water nexus of fertilizer systems. As demonstrated here, fertilizer energy can be effectively converted to mechanical work, which can then be used for a number of useful applications. For example, electricity can be generated from the pressurized product although this will require additional energy conversion, with associated losses. We suggest that the pressurized fertilizer can be most effectively used as direct mechanical work, and thereby replace pumping energy typically used for circulating fertigation solution to plants. Future work should consider integration of fertilizer PRO with existing fertigation and hydroponic systems.

3.6 Supplementary Information

3.6.1 Supplementary Note 6.1: Sample A, B, S characteristic tests

SAMPLE A TEST

Test description: RO test for A characterization, 20 °C, FTS CTA

Test date: 03/05/21 @ 14:30

Table 3.2. Test preparation.

Parameter	Value	Measurement or Analysis
<i>Solution Preparation</i>		
Feed water mass m_{F,H_2O}	3000 ± 0.2 g	AX8201, Ohaus (Parsippany, NJ), 8000 ± 0.2 g
Feed salt mass $m_{F,NaCl}$	0	AX8201, Ohaus (Parsippany, NJ), 8000 ± 0.2 g
Feed concentration c_F	0	$c_F = \frac{m_{salt}}{m_{H_2O}/\rho_{H_2O}}, \frac{\delta c_F}{c_F} = \frac{\delta m_{salt}}{m_{salt}} + \frac{\delta m_{H_2O}}{m_{H_2O}}$
<i>Flow Rate Calibration</i>		
Change in feed water mass Δm_{H_2O}	324 ± 0.2 g	AX8201, Ohaus (Parsippany, NJ), 8000 ± 0.2 g
Change in time Δt	60 ± 1 s	Stopwatch
Feed flow rate $\dot{V}_F$	0.32 ± 0.00575 lpm	$\dot{V} = \frac{\Delta m_{H_2O}}{\Delta t/\rho_{H_2O}}, \frac{\delta \dot{V}}{\dot{V}} = \frac{\delta \Delta m_{H_2O}}{\Delta m_{H_2O}} + \frac{\delta \Delta t}{\Delta t}$

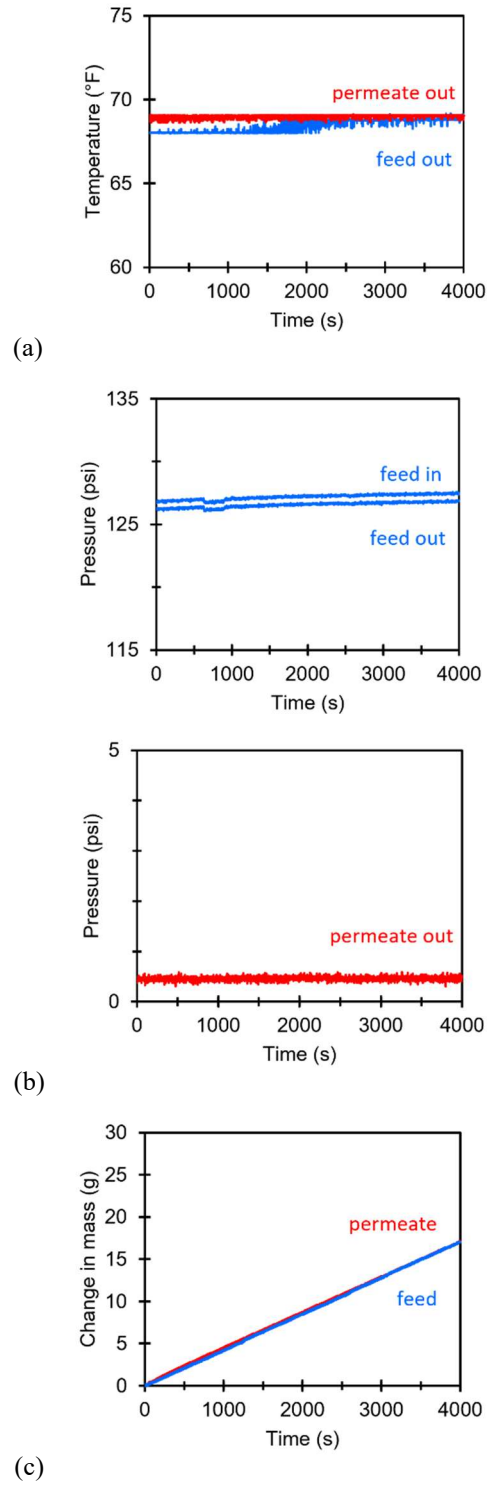


Figure 3.6. Raw test data. Feed and permeate (a) temperature measurement by transmitters (800 series, Noshok (Berea, OH), 200 ± 0.837 °F), (b) pressure measurement by transmitters (EW-68075-50, Cole-Parmer (Vernon Hills, IL), 250 ± 0.625 psi), and (c) change in mass measurement by scales (AX8201, Ohaus (Parsippany, NJ), 8000 ± 0.2 g).

Table 3.3. Analysis of test results (average over the length of trial).

Parameter	Value	Measurement or Analysis
Feed temperature T_F	20.237 ± 0.465 °C	$T_F = T_{F,out}$, $\delta T_F = \delta T_{F,out}$
Permeate temperature T_P	20.552 ± 0.465 °C	$T_P = T_{P,out}$, $\delta T_P = \delta T_{P,out}$
Feed pressure p_F	8.748 ± 0.004 bar	$p_F = \frac{p_{F,in} + p_{F,out}}{2}$, $\delta p_F = \sqrt{\delta p_{F,in}^2 + \delta p_{F,out}^2}$
Permeate pressure p_P	0.015 ± 0.003 bar	$p_P = p_{P,out}$, $\delta p_P = \delta p_{P,out}$
Pressure difference Δp	8.732 ± 0.005 bar	$\Delta p = p_F - p_P$, $\delta \Delta p = \sqrt{\delta p_F^2 + \delta p_P^2}$
Change in mass Δm	17.1 ± 0.283 g	$\Delta m = \frac{\Delta m_F + \Delta m_P}{2}$, $\delta \Delta m = \sqrt{\delta \Delta m_F^2 + \delta \Delta m_P^2}$
Change in time Δt	4000 ± 1 s	
Water flux J_w	3.65 ± 0.01 lmh	$J_w = \frac{\Delta m}{a \rho \Delta t}$, $\frac{\delta J_w}{J_w} = \frac{\delta \Delta m}{\Delta m} + \frac{\delta \Delta t}{\Delta t}$
Water permeability A	0.418 ± 0.001 lmh/bar	$A = \frac{J_w}{\Delta p}$, $\frac{\delta A}{A} = \frac{\delta J_w}{J_w} + \frac{\delta \Delta p}{\Delta p}$

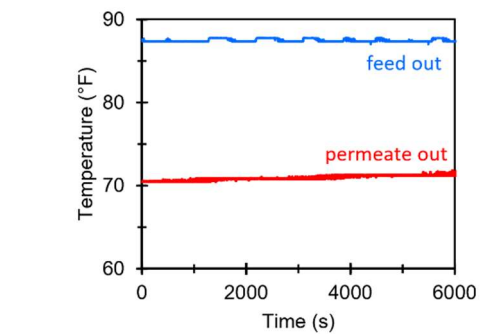
SAMPLE B TEST

Test description: RO test for B characterization, 30 °C, FTS CTA (2-50)

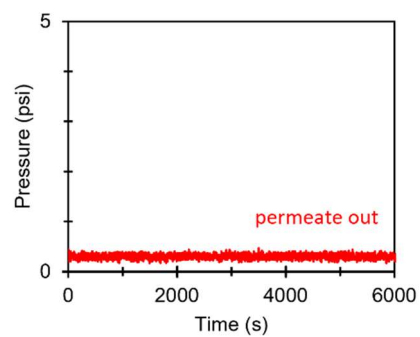
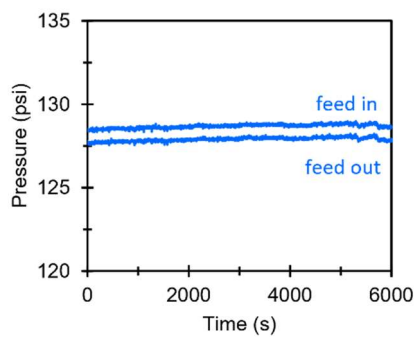
Test date: 12/09/20 @ 16:03

Table 3.4. Test preparation.

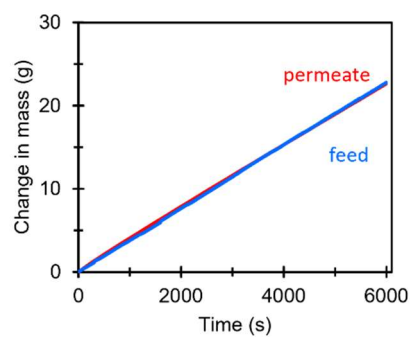
Parameter	Value	Measurement or Analysis
<i>Solution Preparation</i>		
Feed water mass m_{F,H_2O}	$3000 \pm 0.2 \text{ g}$	AX8201, Ohaus (Parsippany, NJ), $8000 \pm 0.2 \text{ g}$
Feed salt mass $m_{F,NaCl}$	$6 \pm 0.2 \text{ g}$	AX8201, Ohaus (Parsippany, NJ), $8000 \pm 0.2 \text{ g}$
Feed concentration c_F	$2 \pm 0.07 \text{ g/l}$	$c_F = \frac{m_{salt}}{m_{H_2O}/\rho_{H_2O}}, \frac{\delta c_F}{c_F} = \frac{\delta m_{salt}}{m_{salt}} + \frac{\delta m_{H_2O}}{m_{H_2O}}$
<i>Flow Rate Calibration</i>		
Change in feed water mass Δm_{H_2O}	$332 \pm 0.2 \text{ g}$	AX8201, Ohaus (Parsippany, NJ), $8000 \pm 0.2 \text{ g}$
Change in time Δt	$60 \pm 1 \text{ s}$	Stopwatch
Feed flow rate $\dot{V}_F$	$0.332 \pm 0.095 \text{ lpm}$	$\dot{V} = \frac{\Delta m_{H_2O}}{\Delta t/\rho_{H_2O}}, \frac{\delta \dot{V}}{\dot{V}} = \frac{\delta \Delta m_{H_2O}}{\Delta m_{H_2O}} + \frac{\delta \Delta t}{\Delta t}$



(a)



(b)



(c)

Figure 3.7. Raw test data. Feed and permeate (a) temperature measurement by transmitters (800 series, Noshok (Berea, OH), 200 ± 0.837 °F), (b) pressure measurement by transmitters (EW-68075-50, Cole-Parmer (Vernon Hills, IL), 250 ± 0.625 psi), and (c) change in mass measurement by scales (AX8201, Ohaus (Parsippany, NJ), 8000 ± 0.2 g).

Table 3.5. Analysis of test results (average over the length of trial).

Parameter	Value	Measurement or Analysis
Feed temperature T_F	30.819 ± 0.465 °C	$T_F = T_{F,out}$, $\delta T_F = \delta T_{F,out}$
Draw temperature T_P	21.582 ± 0.465 °C	$T_P = T_{P,out}$, $\delta T_P = \delta T_{P,out}$
Feed pressure p_F	8.844 ± 0.004 bar	$p_F = \frac{p_{F,in} + p_{F,out}}{2}$, $\delta p_F = \sqrt{\delta p_{F,in}^2 + \delta p_{F,out}^2}$
Permeate pressure p_P	0.010 ± 0.003 bar	$p_P = p_{P,out}$, $\delta p_P = \delta p_{P,out}$
Pressure difference Δp	8.834 ± 0.005 bar	$\Delta p = p_F - p_P$, $\delta \Delta p = \sqrt{\delta p_F^2 + \delta p_P^2}$
Change in mass Δm	24.7 ± 0.283 g	$\Delta m = \frac{\Delta m_F + \Delta m_P}{2}$, $\delta \Delta m = \sqrt{\delta \Delta m_F^2 + \delta \Delta m_P^2}$
Change in time Δt	6535 ± 1 s	
Water flux J_w	3.240 ± 0.22 lmh	$J_w = \frac{\Delta m}{a \rho \Delta t}$, $\frac{\delta J_w}{J_w} = \frac{\delta \Delta m}{\Delta m} + \frac{\delta \Delta t}{\Delta t}$
Permeate conductivity σ_P	279.6 ± 5 μ S/cm	CDCE-90-1 Omega, (Norwalk, CT) 10000 ± 5 μ S,
Conversion factor f	0.00044 ± 0.000091 g/l / μ S/cm	
Permeate concentration c_P	0.124 ± 0.02 g/l	$c_P = f \sigma_P$, $\frac{\delta c_P}{c_P} = \frac{\delta f}{f} + \frac{\delta \sigma_P}{\sigma_P}$
Salt rejection R	0.938 ± 0.013	$R = 1 - \frac{c_P}{c_F}$, $\frac{\delta R}{R} = \frac{\delta c_P}{c_P} + \frac{\delta c_F}{c_F}$
Salt permeability B	0.211 ± 0.006 lmh	$B = J_w \left(\frac{1-R}{R} \right) \exp\left(-\frac{J_w}{k}\right)$, $\delta B = \frac{\delta R}{R} J_w \exp\left(-\frac{J_w}{k}\right)$ $+ \frac{1-R}{R} \exp\left(-\frac{J_w}{k}\right) \left(\frac{k-J_w}{k}\right) \delta J_w$

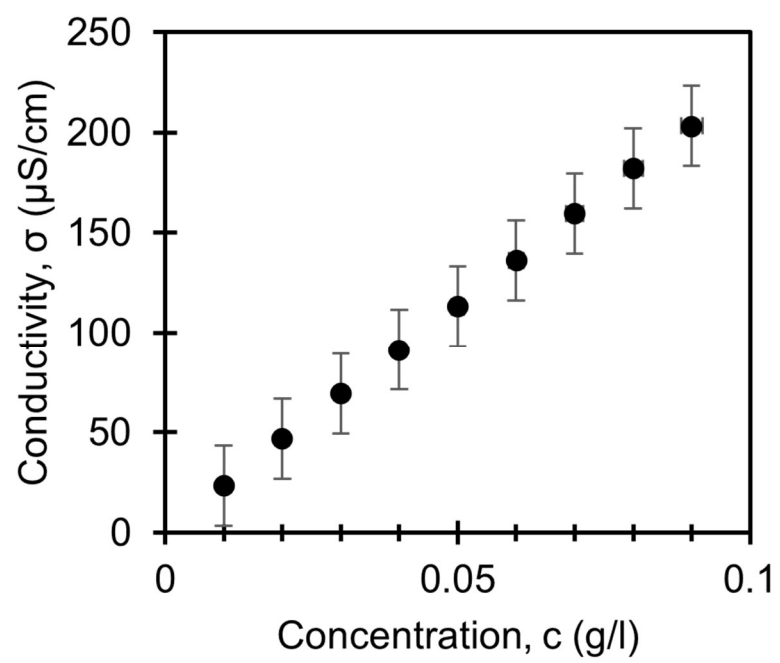


Figure 3.8. Conductivity calibration curve.

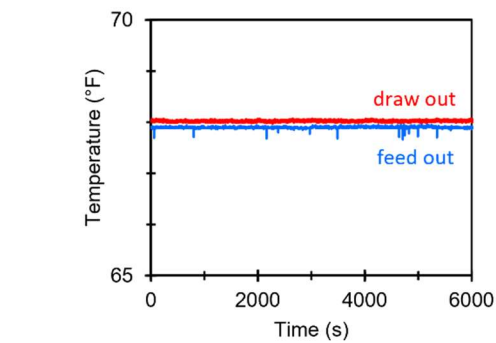
SAMPLE S TEST

Test description: FO test for S characterization, 20 °C, FTS CTA

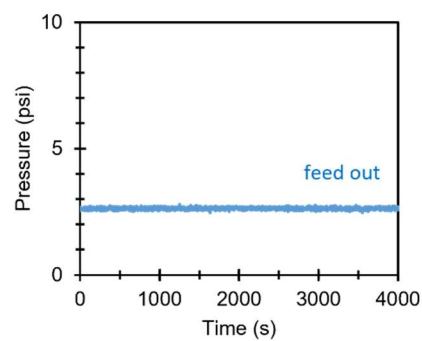
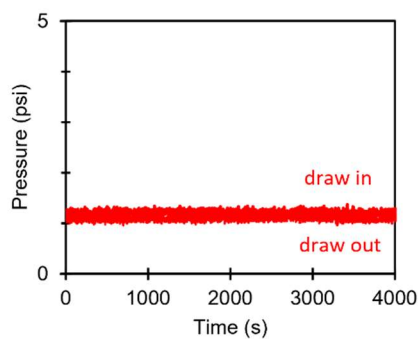
Test date: 12/11/20 @ 11:52

Table 3.6. Test preparation.

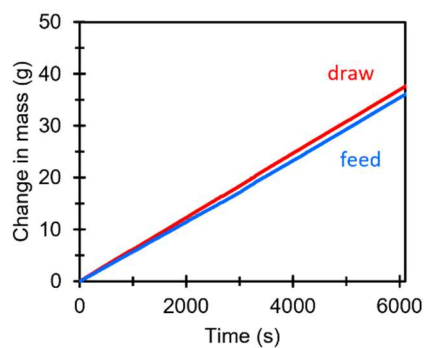
Parameter	Value	Measurement or Analysis
<i>Solution Preparation</i>		
Feed water mass m_{F,H_2O}	3000 ± 0.2 g	AX8201, Ohaus (Parsippany, NJ), 8000 ± 0.2 g
Feed salt mass $m_{F,NaCl}$	0	AX8201, Ohaus (Parsippany, NJ), 8000 ± 0.2 g
Feed concentration c_F	0	$c_F = \frac{m_{NaCl}}{m_{H_2O}/\rho_{H_2O}}, \frac{\delta c_F}{c_F} = \frac{\delta m_{NaCl}}{m_{NaCl}} + \frac{\delta m_{H_2O}}{m_{H_2O}}$
Draw water mass m_{D,H_2O}	3000 ± 0.2 g	AX8201, Ohaus (Parsippany, NJ), 8000 ± 0.2 g
Draw salt mass $m_{D,NaCl}$	175.32 ± 0.2 g	AX8201, Ohaus (Parsippany, NJ), 8000 ± 0.2 g
Draw concentration c_D	58.44 ± 0.07 g/l	$c_D = \frac{m_{NaCl}}{m_{H_2O}/\rho_{H_2O}}, \frac{\delta c_D}{c_D} = \frac{\delta m_{NaCl}}{m_{NaCl}} + \frac{\delta m_{H_2O}}{m_{H_2O}}$
<i>Flow Rate Calibration</i>		
Change in feed water mass Δm_{H_2O}	139.1 ± 0.2 g	AX8201, Ohaus (Parsippany, NJ), 8000 ± 0.2 g
Change in time Δt	26 ± 1 s	Stopwatch
Feed flow rate $\dot{V}_F$	0.330 ± 0.095 lpm	$\dot{V} = \frac{\Delta m_{H_2O}}{\Delta t/\rho_{H_2O}}, \frac{\delta \dot{V}}{\dot{V}} = \frac{\delta \Delta m_{H_2O}}{\Delta m_{H_2O}} + \frac{\delta \Delta t}{\Delta t}$



(a)



(b)



(c)

Figure 3.9. Raw test data. Feed and permeate (a) temperature measurement by transmitters (800 series, Noshok (Berea, OH), 200 ± 0.837 °F), (b) pressure measurement by transmitters (EW-68075-50, Cole-Parmer (Vernon Hills, IL), 250 ± 0.625 psi), and (c) change in mass measurement by scales (AX8201, Ohaus (Parsippany, NJ), 8000 ± 0.2 g).

Table 3.7. Analysis of test results (average over the length of trial).

Parameter	Value	Measurement or Analysis
Feed temperature T_F	20.012 ± 0.465 °C	$T_F = T_{F,out}$, $\delta T_F = \delta T_{F,out}$
Draw temperature T_D	19.943 ± 0.465 °C	$T_D = T_{D,out}$, $\delta T_D = \delta T_{D,out}$
Feed pressure p_F	0.128 ± 0.004 bar	$p_F = \frac{p_{F,out} + (p_{F,in}=0)}{2}$, $\delta p_F = \delta p_{F,out}$
Draw pressure p_D	0.042 ± 0.003 bar	$p_D = \frac{p_{D,in} + p_{D,out}}{2}$, $\delta p_D = \sqrt{\delta p_{D,in}^2 + \delta p_{D,out}^2}$
Pressure difference Δp	0.087 ± 0.005 bar	$\Delta p = p_F - p_D$, $\delta \Delta p = \sqrt{\delta p_F^2 + \delta p_D^2}$
Change in mass Δm	37.5 ± 0.283 g	$\Delta m = \frac{\Delta m_F + \Delta m_D}{2}$, $\delta \Delta m = \sqrt{\delta \Delta m_F^2 + \delta \Delta m_D^2}$
Change in time Δt	6208 ± 1 s	
Water flux J_w	5.85 ± 0.10 lmh	$J_w = \frac{\Delta m}{a \rho \Delta t}$, $\frac{\delta J_w}{J_w} = \frac{\delta \Delta m}{\Delta m} + \frac{\delta \Delta t}{\Delta t}$
Structure parameter S	1039 ± 49.5 μm	$S = \frac{D}{J_w} \ln \left(\frac{B + A \pi_D}{B + J_w + A \pi_F} \right) ,$ $\delta S = \frac{\delta J_w}{J_w} \frac{D}{B + J_w + A \pi_F} + \delta B \frac{D}{J_w} \frac{J_w + A (\pi_F - \pi_D)}{(B + J_w + A \pi_F)^2} +$ $\delta A \frac{D}{J_w} \frac{J_w \pi_D + B (\pi_D - \pi_F)}{(B + J_w + A \pi_F)^2} + \delta \pi_D \frac{D}{J_w} \frac{A}{B + J_w + A \pi_F} +$ $\delta \pi_F \frac{D}{J_w} \frac{J_w + A (A \pi_D + B)}{(B + J_w + A \pi_F)^2} .$

3.6.2 Supplementary Note 6.2: Sample PRO test

Test description: PRO test, Feed temperature: 20 °C, Draw temperature: 20°C, FTS CTA

Test date: 09/09/20 @ 14:30

Table 3.8. Test preparation.

Parameter	Value	Measurement or Analysis
<i>Solution Preparation</i>		
Feed water mass m_{F,H_2O}	3000 ± 0.2 g	AX8201, Ohaus (Parsippany, NJ), 8000 ± 0.2 g
Feed salt mass $m_{F,NaCl}$	0.3 ± 0.2 g	AX8201, Ohaus (Parsippany, NJ), 8000 ± 0.2 g
Feed concentration c_F	0.1 ± 0.07 g/l	$c_F = \frac{m_{NaCl}}{m_{H_2O}/\rho_{H_2O}}, \frac{\delta c_F}{c_F} = \frac{\delta m_{NaCl}}{m_{NaCl}} + \frac{\delta m_{H_2O}}{m_{H_2O}}$
Draw water mass m_{D,H_2O}	3000 ± 0.2 g	AX8201, Ohaus (Parsippany, NJ), 8000 ± 0.2 g
Draw salt mass $m_{D,NaCl}$	105 ± 0.2 g	AX8201, Ohaus (Parsippany, NJ), 8000 ± 0.2 g
Draw concentration c_D	35 ± 0.07 g/l	$c_D = \frac{m_{NaCl}}{m_{H_2O}/\rho_{H_2O}}, \frac{\delta c_D}{c_D} = \frac{\delta m_{NaCl}}{m_{NaCl}} + \frac{\delta m_{H_2O}}{m_{H_2O}}$
<i>Flow Rate Calibration</i>		
Change in feed water mass Δm_{H_2O}	260 ± 0.2 g	AX8201, Ohaus (Parsippany, NJ), 8000 ± 0.2 g
Change in time Δt	60 ± 1 s	Stopwatch
Feed flow rate $\dot{V}_F$	0.26 ± 0.095 lpm	$\dot{V} = \frac{\Delta m_{H_2O}}{\Delta t/\rho_{H_2O}}, \frac{\delta \dot{V}}{\dot{V}} = \frac{\delta \Delta m_{H_2O}}{\Delta m_{H_2O}} + \frac{\delta \Delta t}{\Delta t}$

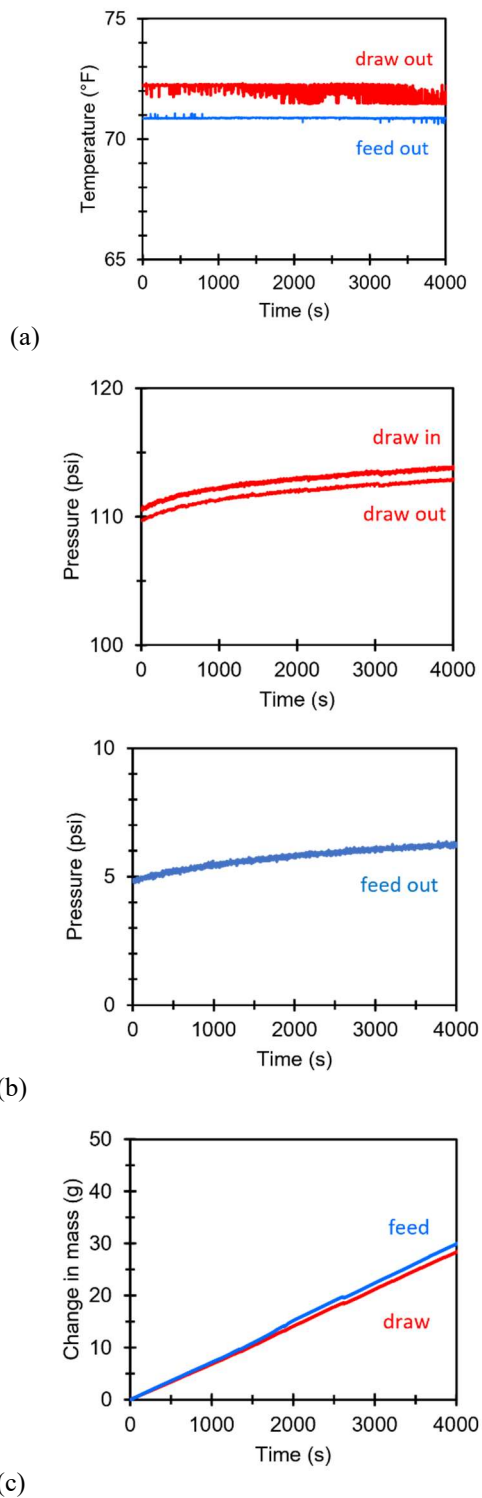


Figure 3.10. Raw test data. Feed and permeate (a) temperature measurement by transmitters (800 series, Noshok (Berea, OH), 200 ± 0.837 °F), (b) pressure measurement by transmitters (EW-68075-50, Cole-Parmer (Vernon Hills, IL), 250 ± 0.625 psi), and (c) change in mass measurement by scales (AX8201, Ohaus (Parsippany, NJ), 8000 ± 0.2 g).

Table 3.9. Analysis of test results (average over the length of trial).

Parameter	Value	Measurement or Analysis
Feed temperature T_F	21.597 ± 0.465 °C	$T_F = T_{F,out}$, $\delta T_F = \delta T_{F,out}$
Draw temperature T_D	22.224 ± 0.465 °C	$T_D = T_{D,out}$, $\delta T_D = \delta T_{D,out}$
Feed pressure p_F	0.398 ± 0.003 bar	$p_F = \frac{p_{F,out} + (p_{F,in}=0)}{2}$, $\delta p_F = \delta p_{F,out}$
Draw pressure p_D	7.747 ± 0.003 bar	$p_D = \frac{p_{D,in} + p_{D,out}}{2}$, $\delta p_D = \sqrt{\delta p_{D,in}^2 + \delta p_{D,out}^2}$
Pressure difference Δp	7.349 ± 0.005 bar	$\Delta p = p_D - p_F$, $\delta \Delta p = \sqrt{\delta p_F^2 + \delta p_D^2}$
Change in mass Δm	32.2 ± 0.283 g	$\Delta m = \frac{\Delta m_F + \Delta m_D}{2}$, $\delta \Delta m = \sqrt{\delta \Delta m_F^2 + \delta \Delta m_D^2}$
Change in time Δt	4000 ± 1 s	
Water flux J_w	6.223 ± 0.155 lmh	$J_w = \frac{\Delta m}{a \rho \Delta t}$, $\frac{\delta J_w}{J_w} = \frac{\delta \Delta m}{\Delta m} + \frac{\delta \Delta t}{\Delta t}$
Power density $\dot{W}$	1.30 ± 0.0621 W/m ²	$\dot{W} = J_w \Delta p$, $\frac{\delta \dot{W}}{\dot{W}} = \frac{\delta J_w}{J_w} + \frac{\delta \Delta p}{\Delta p}$

3.7 List of Symbols in Chapter 3

A	membrane water permeability ($\text{m s}^{-1} \text{Pa}^{-1}$)
a	membrane surface area (m^2)
B	membrane salt permeability (m s^{-1})
c	concentration (g l^{-1})
D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
d_h	hydraulic diameter (m)
i	number of ions
J_w	permeate flux ($\text{l m}^{-2} \text{s}^{-1}$)
J_s	solute flux ($\text{g m}^{-2} \text{s}^{-1}$)
k	diffusion transfer coefficient (m s^{-1})
m	mass (kg)
M	molar mass (kg mol^{-1})
p	pressure (Pa)
R	gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
Re	Reynolds number
S	structure parameter (m)
Sc	Schmidt number
t	time (s)
T	absolute temperature (K)
V	volume (m^3)
W	work (J)
$\dot{W}$	power (W)

Greek symbols:

π	osmotic pressure (Pa)
δ	boundary layer thickness (m)
γ	mass transfer constant
ρ	density (kg m^{-3})

Subscripts:

D draw

F feed

3.8 Acknowledgments

We acknowledge support from the Michigan Space Grant Consortium grant number NNX15AJ20H.

CHAPTER FOUR

THERMODYNAMIC LIMITS OF USING FERTILIZER OSMOSIS TO PRODUCE MECHANICAL WORK VIA PRESSURE RETARDED OSMOSIS

4.1 Original Publication

Chapter Four is based primarily on a journal paper that is published in the Journal of Membrane Science. This publication contributed to the so far limited literature on fertilizer PRO by clearly establishing the limits to energy and work. A complete reference for the published work is as follows:

P. Pourmovahed and J. Maisonneuve, “Thermodynamic limits of using fertilizer osmosis to produce mechanical work via pressure retarded osmosis,” Journal of Membrane Science 629 (2021) 119268. <https://doi.org/10.1016/j.memsci.2021.119268>.

4.2 Introduction

In this chapter we investigate the concept of harnessing fertilizer energy to generate power via pressure retarded osmosis (PRO). This can open up new possibilities for energy efficiency, water security, and food productivity in agriculture. Harvesting fertilizer energy to do useful work was first proposed in 2011, when it was suggested that fertilizer could be used to drive water filtration via forward osmosis (FO) [20]. The fertilizer osmosis concept takes advantage of the high osmotic potential of super concentrated fertilizers and uses this driving force to spontaneously draw clean water permeate across a semipermeable membrane from a wastewater feed source. Unlike

typical FO, fertilizer osmosis requires no draw regeneration, but rather produces a diluted fertilizer solution that can be delivered to plants [21–24]. Since being first proposed, fertilizer FO has received significant attention, and its potential has been evaluated for various feed water sources (seawater [20], brackish water [34,35,69,70], raw sewage [43], municipal wastewater [31,46,71], aquaculture wastewater [72], mine impaired water [45,47], and urine [73,74]), for various fertilizers (single fertilizers [20], all-purpose fertilizer blends [34], and commercial liquid products [43]), and for application to various plant systems (hydroponic lettuce [31], and ornamental indoor green walls [43]). More recently, the possibility of harnessing fertilizer energy to generate mechanical or electrical power was proposed. In 2018, the novel concept of using fertilizer PRO to generate power was introduced [25,26] and then experimentally validated [27].

The fertilizer PRO process (or “Green PRO”) is illustrated in Figure. 4.1. In this process, a pressurized fertilizer solution is used to osmotically draw clean water permeate across a membrane, thereby generating an expanding volume of pressurized nutrient solution that can be used to do mechanical work and then delivered to plants.

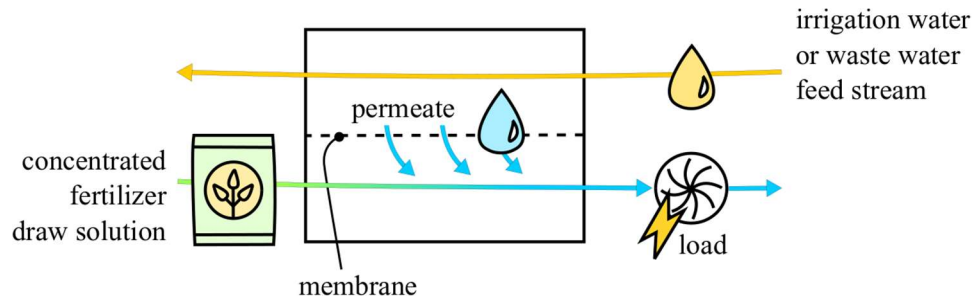


Figure 4.1. In fertilizer PRO, a concentrated fertilizer solution is used to draw water permeate across a membrane and against a load. The result is an expanding volume of pressurized fertilizer that can be used to do mechanical work before being delivered to plants.

The PRO process itself is not new, and has been widely studied for power production, especially from seawater and river water (or “Blue PRO”) [36–38,59]. So far, attempts to commercialize such power systems have met limited success [56,75]. This has been due primarily to issues of membrane fouling caused by impurities in the water sources, and also due to low power generated from the modest concentration gradients available between seawater and river water. Fertilizer PRO has advantages in both of these regards. Namely, concentrated fertilizers have tremendous initial osmotic potentials, and hence power densities that can be one or two orders of magnitude greater than for seawater [25–27]. Also, membrane fouling may be significantly mitigated in many agricultural applications, for example in hydroponic cultivation where water is typically already pre-treated to ensure feed water quality [76,77].

Due to the novelty of the concept, the literature related to fertilizer PRO remains limited [25–27]. While the concept has been validated [27], important questions remain about the potential for this energy source to provide significant amounts of energy to farms. In this chapter we address this important gap in the literature by establishing fundamental and practical limitations to how much energy can be recovered from fertilizer. We establish (1) the fundamental thermodynamic energy limits of fertilizer, (2) the energy recovery limits of a fertilizer PRO batch process when operated at constant pressure, and (3) the practical limitations imposed by the need to maintain competitive power levels. These theoretical limitations are compared against a series of experimentally-calibrated simulations showing the maximum energy recovery when non-ideal transport dynamics are considered, including reverse solute flux and concentration polarization. Based on these, we illustrate the potential of common N, P, K

fertilizers and conclude by evaluating the energy that can be recovered during cultivation of common hydroponic plant crops including tomato, cucumber, lettuce, and basil.

4.3 Thermodynamic Analysis

4.3.1 Gibbs Energy of Mixing Fertilizer and Water

The energy released when concentrated fertilizer solution and irrigation feed water are mixed osmotically across a membrane, is defined by the Gibbs free energy of mixing [29,61,78,79]. This energy is illustrated by the area beneath the osmotic pressure curve $\Delta\pi$ shown in Figure. 4.2 and expressed in eq. (4.1).

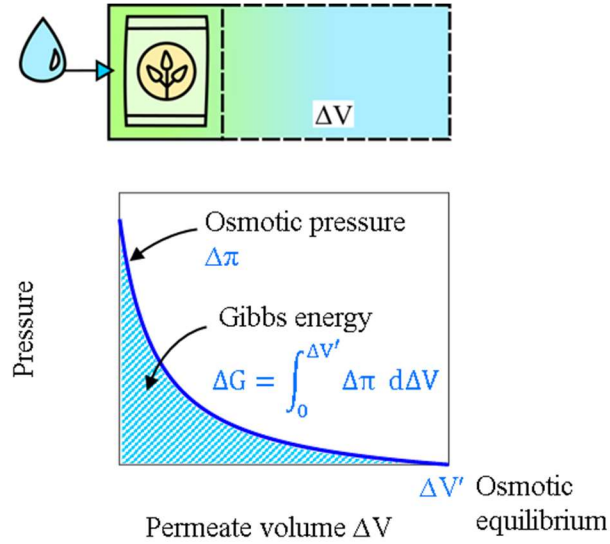


Figure 4.2. The theoretical limit to energy recovery from fertilizer osmosis is defined by the Gibbs energy of mixing ΔG , which is represented by the area beneath the curve for osmotic pressure difference $\Delta\pi$.

$$\Delta G = \int_0^{\Delta V'} \Delta\pi d\Delta V \quad (4.1)$$

Where ΔV is the permeate volume of irrigation water drawn into the concentrated fertilizer solution, $\Delta V'$ is the volume that establishes osmotic equilibrium between the two solutions, and $\Delta\pi$ is the osmotic pressure difference between the concentrated fertilizer draw π_D and the diluted irrigation feed π_F , i.e. $\Delta\pi = \pi_D - \pi_F$.

When ideal behavior of the solutions is assumed, an exact solution for eq. (4.1) can be analytically obtained for Gibbs energy per unit mass of fertilizer solute m_D (see Supplementary Note 4.1 for detailed derivation).

$$\frac{\Delta G}{m_D} = \frac{\pi_D^o}{c_D^o} \ln \left(1 + c_D^o \frac{\Delta V'}{m_D} \right) - \frac{\pi_F^o}{\theta} \frac{\Delta V'}{m_D} \ln \left(\frac{1}{1 - \theta} \right) \quad (4.2)$$

$$\frac{\Delta V'}{m_D} = \frac{1}{c_D^o} \left(\frac{\pi_D^o}{\pi_F^o} (1 - \theta) - 1 \right) \quad (4.3)$$

π_D^o and π_F^o are the initial draw and feed osmotic pressures, as obtained from $\pi = \gamma i R T c$, where i is the number of ions, R is the gas constant, T is absolute temperature, c is concentration, and γ is the activity coefficient, which is unity for ideal solutions [27,29,61,78,79]. c_D^o is the initial concentration of the fertilizer draw, and θ is the recovery ratio, which is the ratio between permeate volume ΔV and initial feed volume V_F^o , i.e. $\theta = \Delta V / V_F^o$.

To illustrate, consider common N, P, K fertilizers such as calcium nitrate $\text{Ca}(\text{NO}_3)_2$, monoammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$, and potassium chloride KCl as they are mixed with diluted feed of varying sodium chloride NaCl concentrations. Solution properties are summarized in Table 4.1.

Figure. 4.3 (a) shows the Gibbs energy ΔG and equilibrium permeate volume $\Delta V'$ for each of these fertilizers as a function of feed concentration and recovery ratio.

Table 4.1. Fertilizer and feed solution chemistry.

Feed Water with Diluted Sodium Chloride NaCl			
Concentration c_F^o (g/l)	0.1 – 5		
Activity coefficient γ	1		
Number of ions i	2		
Concentrated Fertilizer Draw Solution			
	Calcium nitrate Ca(NO ₃) ₂	Monoammonium phosphate NH ₄ H ₂ PO ₄	Potassium chloride KCl
Solubility c_D^o (g/l)	1212	374	342
Molar mass (g/mol)	164	115	75
Activity coefficient γ	1	1	1
Number of ions i	3	2	2

As shown, between 77 and 125 Wh of energy is theoretically available per kg of fertilizer when mixed with an abundant source of dilute feed water (i.e. both c_F^o and $\theta \rightarrow 0$, which we will refer to as case 1). These energy limits are more than one order of magnitude greater than those previously reported in [27]. This is because the energy density in [27] appears to be underestimated as it is defined based on the Gibbs energy per volume of total mixed solution [29] $\Delta G / (V_D^o + V_F^o)$, which is then divided by draw concentration c_D^o . This does not give energy per unit fertilizer as reported, because $\Delta G / m_D \neq \Delta G / (V_D^o + V_F^o) \times V_D^o / m_D$. The energy limits derived in eq. (4.2) therefore provide the correct evaluation of fertilizer potential, and results from Figure. 4.3 suggest significantly greater potential than has been otherwise reported in the literature.

The effect of feed concentration and recovery ratio are also shown in Figure. 4.3 (b), where an increase in either of these variables significantly reduces the available energy. To illustrate, consider two likely scenarios. First, when clean irrigation water c_F^o

$= 0.1 \text{ g/l}$ is used as a feed source, it is likely that high recovery ratios $\theta \rightarrow 1$ will be required (which we will refer to as case 2). Under these conditions Gibbs energy is reduced to 40-80 Wh/kg. Second, when concentrated wastewater sources are used such as $c_F^o = 5 \text{ g/l}$, it is likely that lower recovery ratios may be acceptable, for example $\theta = 0.5$ (which we will refer to as case 3). Under these conditions 25-50 Wh/kg is measured.

Figure. 4.3 (c) also describes the osmotic equilibrium volume for fertilizers. As shown here, equilibrium permeate volume is strongly dependent on feed concentration. This response is driven by the reciprocal relationship between permeate volume and feed concentration that is described in eq. (4.3). For feed concentrations of $c_F^o = 5 \text{ g/l}$, and given reasonable recovery ratios of $\theta = 0.5$, permeate volumes from 50-75 l/kg will establish osmotic equilibrium.

This provides useful context for recent efforts to use fertilizer energy to drive water recovery by fertilizer osmosis. As overviewed in this chapter's Introduction, the related body of literature is significant, however fundamental limits have not yet been established for how much water can be recovered from wastewater by fertilizer osmosis

[34,35,43,45,69–74]. While the focus of this study is on the limits to energy recovery, this analysis, and in particular the expression in eq. (4.3), can provide a useful basis for evaluating the limits to water recovery, which can be undertaken in future work.

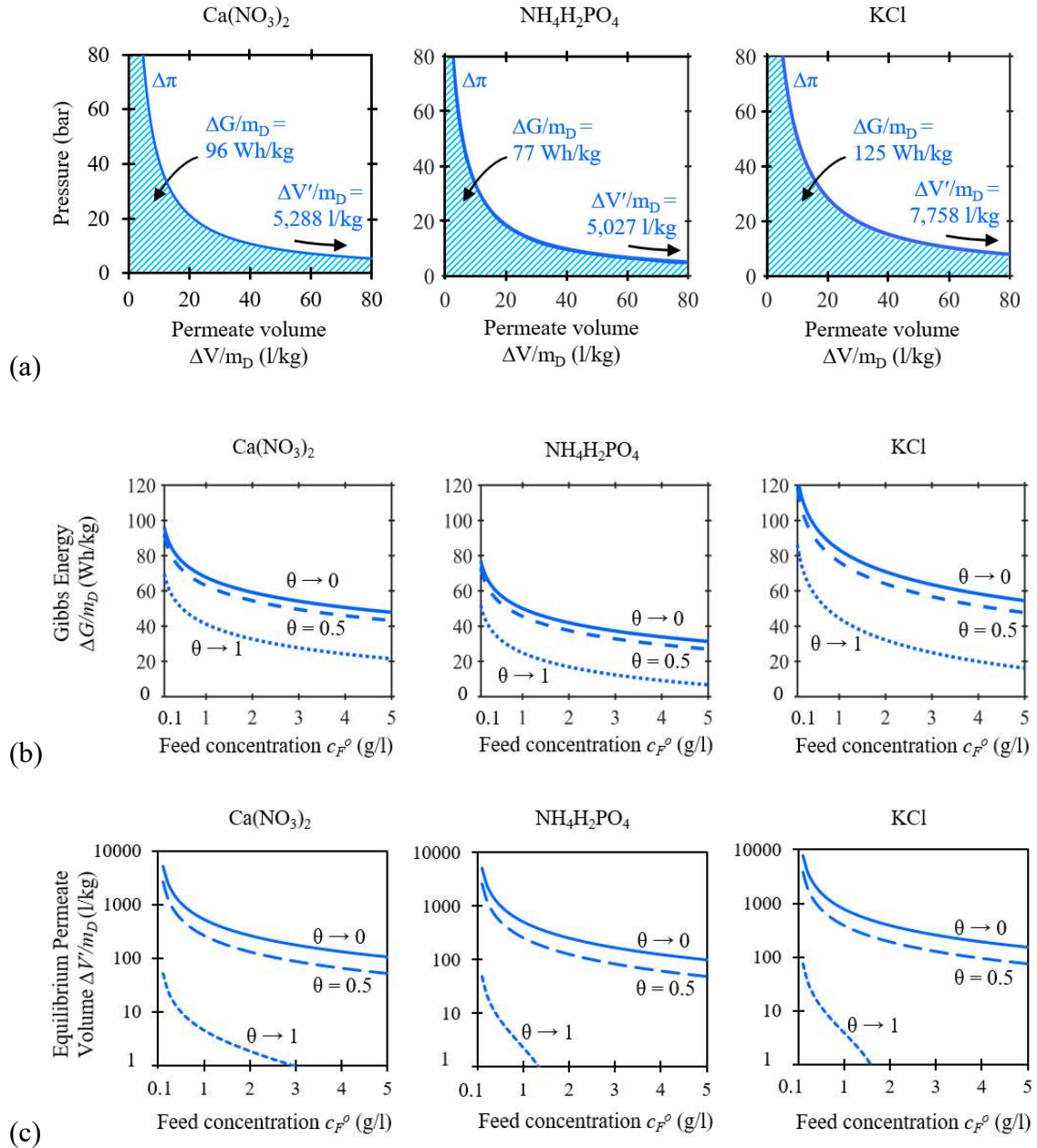


Figure 4.3. In (a) the Gibbs energy of mixing $\Delta G/m_D$ is shown for common N, P, K fertilizers given the specific case where an abundant source of clean irrigation water is available (i.e. feed concentration $c_F^0 = 0.1$ g/l and recovery ratio $\theta \rightarrow 0$). This energy is represented by the area beneath the osmotic pressure curve $\Delta\pi$. In (b) and (c) the Gibbs energy $\Delta G/m_D$ and equilibrium permeate volume $\Delta V'/m_D$ are shown more generally as functions of feed concentration c_F^0 and recovery ratio θ .

4.3.2 Fertilizer Energy from PRO at Constant Applied Pressure

Converting the Gibbs energy of mixing to useful work would require a thermodynamically reversible process. In PRO such a reversible process would theoretically involve an infinite number of pressure stages wherein applied pressure is varied so as to remain just below osmotic pressure throughout the mixing process. While multi-stage variable-pressure processes have been proposed for several osmosis applications they are limited by cost and inefficiencies, and therefore PRO systems are commonly considered at constant applied pressure [68,80–83]. Work done by osmosis against a constant applied pressure is the product of applied pressure Δp and permeate volume ΔV , as stated in eq. (4.4). This will be considerably less than the Gibbs energy of mixing, as illustrated in Figure. 4.4.

$$W = \Delta p \Delta V \quad (4.4)$$

In PRO, equilibrium is established as osmotic pressure drops throughout the mixing process and approaches the applied pressure difference $\Delta\pi \rightarrow \Delta p$. This limits the work that can be recovered. Figure. 4.4 shows the work that is recovered by PRO as a function of the applied pressure and the equilibrium point that it imposes on the process. As illustrated, there is some applied pressure Δp^* and permeate volume ΔV^* that will yield maximum area beneath the curve, or in other words, maximum PRO energy W^* . This represents an energy limit to fertilizer PRO when operated at constant applied pressure. The limit to fertilizer energy from constant pressure PRO can be determined by assuming ideal behavior of the solutions and then solving for the peak energy, which is obtained from $dW / d\Delta p = 0$.

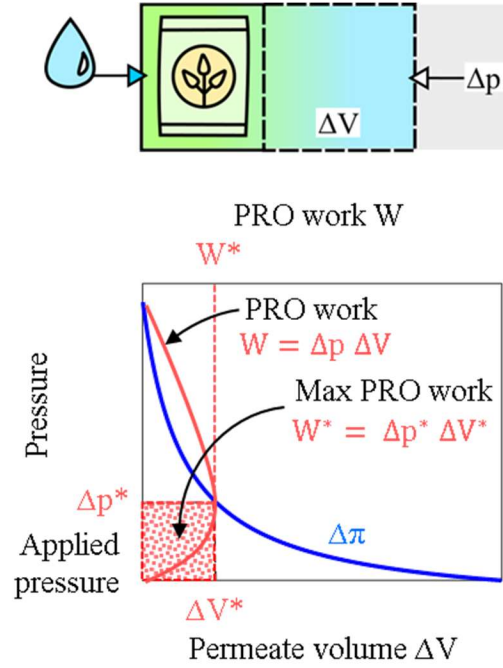


Figure 4.4. Work W from PRO is obtained in the form of a permeate volume ΔV at an applied pressure difference Δp . The maximum work W^* that can be done by PRO is represented by the shaded area which is a product of Δp^* and ΔV^* .

When normalized per unit of fertilizer solute m_D , the maximum PRO energy point is described in eqs. (4.5)-(4.7) (see Supplementary Note 4.2 for detailed derivation).

$$\frac{W^*}{m_D} = \Delta p^* \frac{\Delta V^*}{m_D} \quad (4.5)$$

$$\Delta p^* = \frac{\sqrt{\pi_D^o \pi_F^o} - \pi_F^o}{1 - \theta} \quad (4.6)$$

$$\frac{\Delta V^*}{m_D} = \frac{1}{c_D^o} \left(\sqrt{\frac{\pi_D^o}{\pi_F^o}} (1 - \theta) - 1 \right) \quad (4.7)$$

To illustrate, Figure. 4.5 shows the maximum PRO work W^* that can be obtained from common N, P, K fertilizers. As shown, between 11.2 and 17.4 Wh/kg is obtained at constant applied pressure between 3.6 and 6.7 bar, when fertilizers are mixed with an abundant source of diluted feed water (i.e. both c_F^o and $\theta \rightarrow 0$). This is over one order of magnitude less than the available Gibbs energy reported previously in Section 2.1. When the feed concentration and recovery ratio are increased, a drop in maximum PRO work is observed, and the required applied pressure increases as shown in Figure. 4.5 (b) and (c). For cases where clean irrigation water $c_F^o = 0.1$ g/l is used as a feed source, and high recovery ratios $\theta \rightarrow 1$ are required, maximum PRO work is reduced to 9-15 Wh/kg and the required applied pressure is drastically increased to 70 bar and above. PRO operation at such elevated pressure can be problematic and lead to membrane failure [84]. For cases where wastewater sources are used such as $c_F^o = 5$ g/l, and lower recovery ratios $\theta = 0.5$ are acceptable, similar maximum work from 7-12 Wh/kg is obtained at more moderate applied pressures between 45-85 bar. Comparing these two scenarios suggests that for fertilizer PRO it may be preferable to use low recovery of wastewater feed instead of clean irrigation water, because it can provide comparable work at lower applied pressure. In addition, the use of wastewater feed has the added benefit of recovering water permeate for use in fertigation. As shown in Figure. 4.5 (d), 4-8 l/kg of water permeate is recovered at maximum PRO work for the scenario with $c_F^o = 5$ g/l and $\theta = 0.5$.

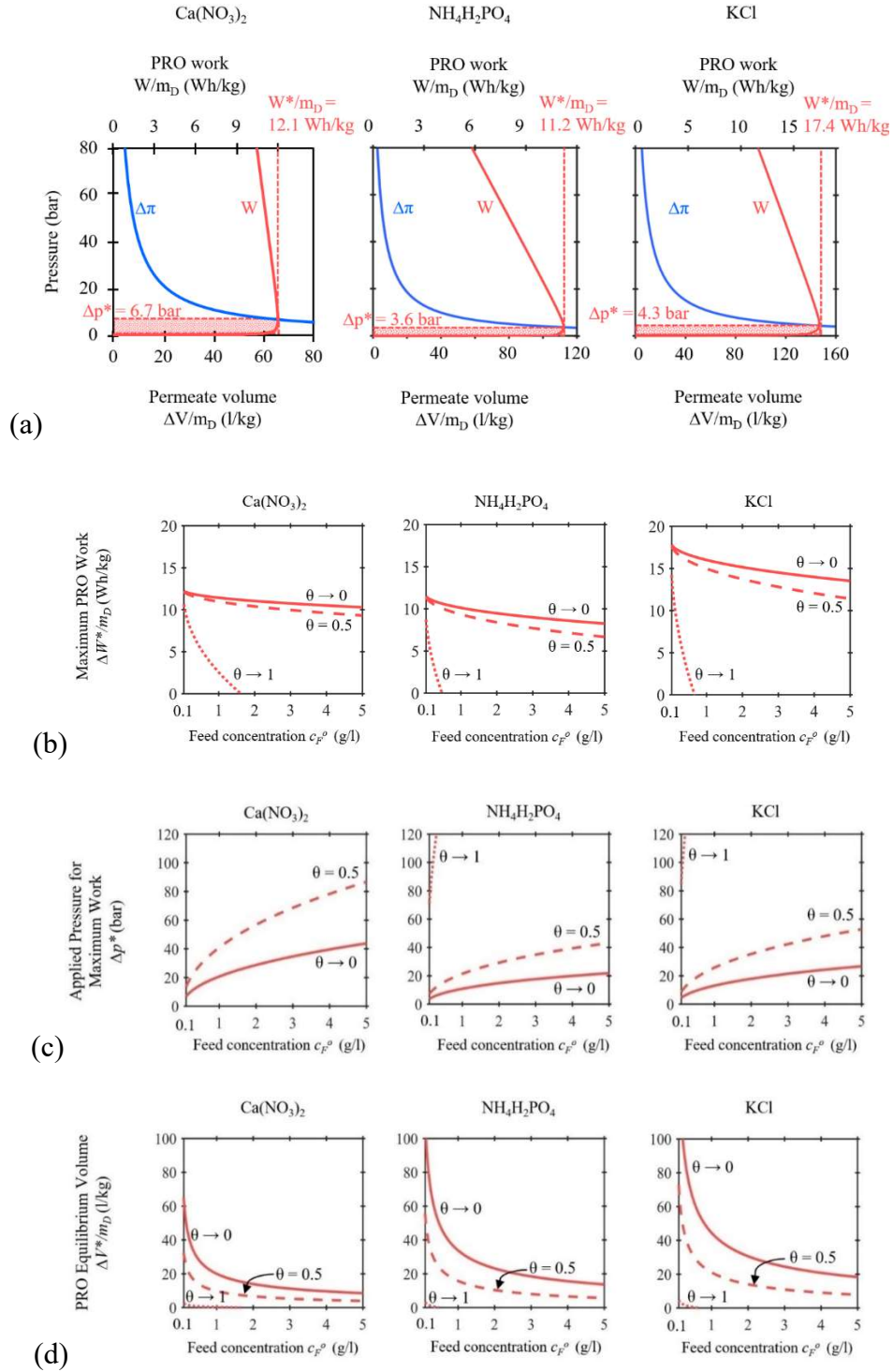


Figure 4.5. In (a) the maximum PRO work W^*/m_D is shown for common N, P, K fertilizers given the specific case where an abundant source of clean irrigation water is available as feed (i.e. feed concentration $c_F^o = 0.1 \text{ g/l}$ and recovery ratio $\theta \rightarrow 0$). This is represented by the largest rectangular area beneath the osmotic pressure curve $\Delta\pi$. In (b) the maximum practical PRO work W^*/m_D is shown more generally as a function of feed concentration c_F^o and recovery ratio θ . The constant applied pressure Δp^* and equilibrium permeate volume $\Delta V^*/m_D$ that yield the maximum PRO work are shown in (c) and (d) respectively.

4.3.3 Fertilizer Energy from Pro with Practical Power Levels

In addition to the energy limits that are imposed by operation at constant pressure, a viable fertilizer PRO system must recover energy at cost-effective rates. Power density $\dot{W}/a$ as defined in eqs. (4.8) and (4.9) is a useful metric in this regard because the rate of energy recovery $\dot{W}$ will be proportional to return on investment, and the membrane area a will be proportional to capital cost.

$$\frac{\dot{W}}{a} = \Delta p \frac{\Delta \dot{V}}{a} \quad (4.8)$$

$$\frac{\Delta \dot{V}}{a} = J_w = A (\Delta \pi - \Delta p) \quad (4.9)$$

Where $\Delta \dot{V}/a$ is the volume rate of permeate per unit membrane area, commonly referred to as permeate flux J_w , and where A is the membrane permeability to water.

Maintaining power density above some economically competitive target is a prerequisite to practical energy recovery by fertilizer PRO. Figure. 4.6 illustrates the challenge of maintaining high power during fertilizer PRO, where a batch of concentrated fertilizer will likely be diluted from 100 to 1,000 times initial concentration in order to produce nutrient solution that is suitable for plants. As permeate volume is accumulated by the pressurized fertilizer solution, the driving force $\Delta \pi - \Delta p$ drops, and as the PRO process nears equilibrium, the permeate flux and power effectively approach zero (i.e. $J_w \rightarrow 0$ and $\dot{W} \rightarrow 0$). Energy recovery at such low rates is impractical and therefore it is unlikely that such a process would be allowed to operate until equilibrium. Therefore, maintaining power density above some economic target will impose a practical limit on the amount of energy that can be recovered by fertilizer PRO.

This practical limit can be established by defining the minimum power target $\dot{W}^{**}$ for the fertilizer PRO process. Solving eqs. (4.8) and (4.9) together gives the following expression which describes the applied pressure that will yield target power at any given osmotic pressure difference throughout the PRO process (see Supplementary Note 4.3 for detailed derivation).

$$\Delta p = \frac{1}{2} \left(\Delta \pi \pm \sqrt{\Delta \pi^2 - \frac{4 \dot{W}^{**}}{A a}} \right) \quad (4.10)$$

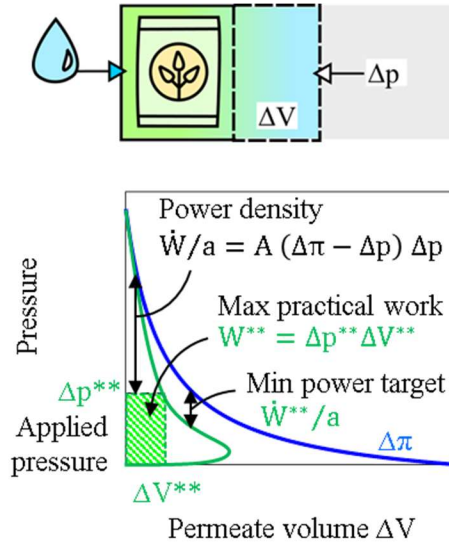


Figure 4.6. Work from PRO is limited by the need to maintain power above a practical target $\dot{W}^{**}$. This target can be met by operating at any point along the target power curve (green), which maintains a sufficient difference between applied pressure Δp and osmotic pressure $\Delta\pi$. The maximum practical PRO work W^{**} is represented by the largest shaded area beneath the target power curve.

To illustrate the significance of eq. (4.10), Figure. 4.7 (a) shows curves for the applied pressure that will satisfy PRO power targets of 5 W/m^2 and 10 W/m^2 for common N, P, K fertilizers, given membrane permeability of $A = 4.3 \text{ lmh/bar}$ [85]. Operation at

any point along these curves will yield power greater than or equal to the power target throughout the duration of the fertilizer PRO batch process. However, operation at only one specific point along each curve will yield maximum work, which we define here as the practical limit to PRO work W^{**} . An exact solution for this limit cannot be obtained analytically, however a numerical approach is used to determine the maximum practical PRO work W^{**} (see Supplementary Note 4.3 for detailed description of numerical methods).

As shown in Figure. 4.7 (a), the maximum PRO work that can be obtained while maintaining practical power is between 8.5 and 14.9 Wh/kg for common N, P, K fertilizers, given the availability of an abundant source of diluted feed (i.e. both c_F^o and $\theta \rightarrow 0$) and assuming membrane permeability of $A = 4.3 \text{ lmh/bar}$ [48]. This practical work is 15-25 % less than the maximum PRO work that was reported in Section 2.2. Figure. 4.7 (a) also illustrates the significance of the selected power target. In general, we observe that higher power targets will shift the target pressure curve to the left, reducing the maximum area under the curve, and requiring higher constant applied pressure. For example, in the case of $\text{Ca}(\text{NO}_3)_2$ practical PRO work drops from 11.1 to 10.8 Wh/kg as the power target is increased from 5 to 10 W/m^2 . A doubling of the power target therefore requires a relatively modest sacrifice in work of only about 3 %. Figure. 4.7 (b) shows the maximum practical PRO work W^{**} that can be obtained across a range of feed concentrations and recovery ratios, for power targets of both 5 and 10 W/m^2 . When the feed concentration and recovery ratio are increased, a drop in the maximum practical PRO work W^{**} is observed, and the required applied pressure Δp^{**} increases as shown in Figure. 4.7 (c).

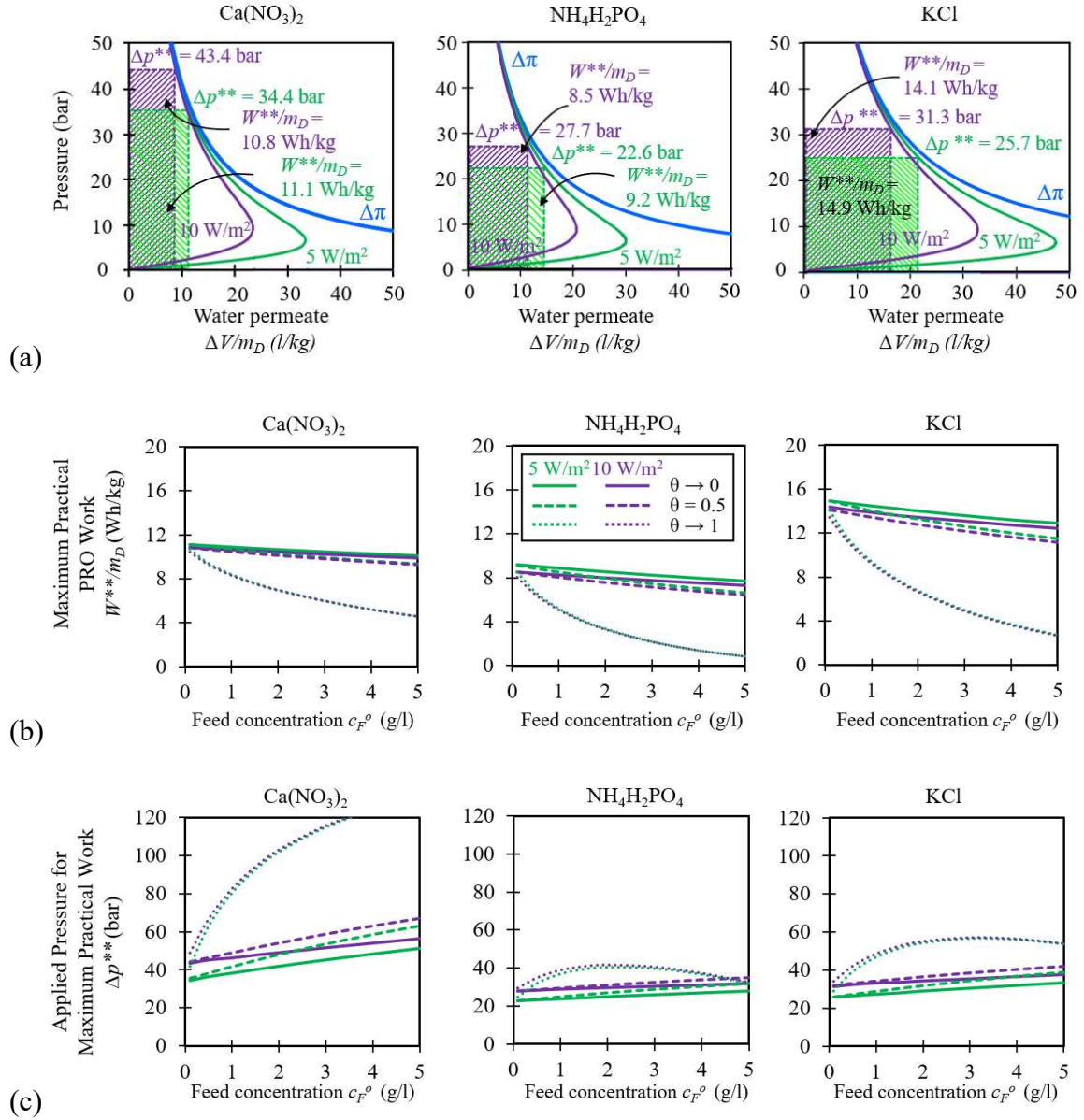


Figure 4.7. In (a) the maximum practical PRO work W^{**}/m_D is shown for common N, P, K fertilizers given the specific case where an abundant source of clean irrigation water is available as feed (i.e. feed concentration $c_{F^0} = 0.1$ g/l and recovery ratio $\theta \rightarrow 0$), and given membrane permeability of $A = 4.3$ l/mh/bar. This is represented by the largest rectangular area beneath the power target curve $\dot{W}^{**}/a$. Curves are shown for power targets of both 5 W/m^2 and 10 W/m^2 . In (b) the maximum practical PRO work W^{**}/m_D is shown more generally as a function of feed concentration c_{F^0} and recovery ratio θ . The constant applied pressure Δp^{**} that yields this maximum practical PRO work is shown in (c).

For cases where clean irrigation water $c_{F^0} = 0.1$ g/l is used as a feed source, and high recovery ratios $\theta \rightarrow 1$ are required, maximum practical work is between 8 and 14

Wh/kg. For cases where wastewater sources are used such as $c_F^o = 5$ g/l, and lower recovery ratios $\theta = 0.5$ are acceptable, maximum practical work from 7-12 Wh/kg is obtained.

4.4. Transport Analysis

4.4.1 Numerical Methods

Maintaining target power levels for practical energy recovery is further challenged by non-ideal transport dynamics that reduce the effective concentration difference across the membrane, and hence reduce the osmotic driving pressure. These dynamics include reverse leakage of fertilizer solute through the membrane, and concentration polarization in the internal membrane support structure and at its external surfaces. The resulting drop in power density further limits the amounts of energy that can be practically recovered from fertilizer PRO. To evaluate this, we introduce here a numerical transport model, and show simulation results predicting energy recovery given non-ideal transport.

The model is based on our previously validated work [52,86,87], and considers batch process dynamics, wherein feed and draw mass balances are updated as a function of time (see Supplementary Note 4.7.6 for details). This includes consideration for water mass permeate as previously described in eq. (4.9), and solute mass permeate which accounts for the leakage of fertilizer solute from the concentrated fertilizer draw solution towards the feed stream.

$$\frac{\Delta \dot{m}}{a} = J_s = B \Delta c \quad (4.11)$$

Where $\Delta m/a$ is the mass rate of solute permeate per unit membrane area, commonly referred to as solute flux J_s , and B is the membrane permeability to fertilizer solute.

The effective concentration difference Δc that remains across the active membrane layer (given internal and external polarization and the resulting concentration gradient) is solved numerically at each instant of the batch process, based on an exact solution to the solution-diffusion equation [52,86,87].

$$\Delta c = \frac{c_D \exp\left(\frac{-J_w \delta_D}{D}\right) - c_F \exp\left(\frac{J_w (\delta_F + S)}{D}\right)}{1 + \frac{B}{J_w} \left(\exp\left(\frac{J_w (\delta_F + S)}{D}\right) - \exp\left(\frac{-J_w \delta_D}{D}\right) \right)} \quad (4.12)$$

Where D is the solute diffusion coefficient, S is the membrane structure parameter, and the thickness of concentration boundary layers at the membrane surfaces are $\delta = D/k$. Where k is the diffusion transfer coefficient which can be calculated as a function of the Sherwood number Sh and the hydraulic diameter d_h , $k = Sh \times D/d_h$. In this case, expressions for Sh are selected for flat sheet spacer filled channels, as listed in Table 4.2.

Simulations were run for several scenarios, including the same common N, P, K fertilizers, and the three cases described previously for feed sources c_F^o and recovery ratios θ . When possible, applied pressures were selected to match the constant applied pressure Δp^* that yields maximum PRO work as described in Section 2.2. This was limited in some cases when this pressure exceeded manufacturer specifications.

Table 4.2. Input parameters for fertilizer PRO transport model simulations.

	Calcium nitrate Ca(NO ₃) ₂	Monoammonium phosphate NH ₄ H ₂ PO ₄	Potassium chloride KCl
<i>Membrane and module parameters</i>			
Membrane area a (length $l \times$ width w)		0.0042 m ² (0.107 m $\times$ 0.039 m)	
Channel depth (m)		0.0008	
Hydraulic diameter d_h , feed draw (m)		0.0010 0.0016	
Water permeability A			
Solute permeability B		experimentally obtained	
Structure parameter S		(see Figure. 4.8)	
<i>Fertilizer draw parameters</i>			
Initial concentration c_D^o (g/l)	1212	374	342
Initial volume V_D^o (l)	0.3	0.3	0.3
Diffusivity D ($\times 10^{-10}$ m ² /s)	5.10	6.70	9.04
Flow rate (lpm) Velocity (m/s)		275 0.147	
Sherwood number Sh		Sh = 1.85 Re ^{1/3} Sc ^{1/3} (d _h / l) ^{1/3} [88]	
Applied pressure Δp (bar)			
CTA FO membrane	35	35	35
TFC RO membrane	8	3.1	3.5
<i>Feed source parameters</i>			
Initial concentration c_F^o (g/l)			
Case 1 (i.e. $c_F^o \rightarrow 0$ and $\theta \rightarrow 0$)	0.1	0.1	0.1
Case 2 (i.e. $c_F^o \rightarrow 0$ and $\theta \rightarrow 1$)	0.1	0.1	0.1
Case 3 (i.e. $c_F^o = 5$ g/l and $\theta = 0.5$)	5	5	5
Initial volume V_F^o (ml)			
CTA FO membrane			
Case 1 (i.e. $c_F^o \rightarrow 0$ and $\theta \rightarrow 0$)	∞	∞	∞
Case 2 (i.e. $c_F^o \rightarrow 0$ and $\theta \rightarrow 1$)	1600	300	290
Case 3 (i.e. $c_F^o = 5$ g/l and $\theta = 0.5$)	6300	1400	1500
TFC RO membrane			
Case 1 (i.e. $c_F^o \rightarrow 0$ and $\theta \rightarrow 0$)	∞	∞	∞
Case 2 (i.e. $c_F^o \rightarrow 0$ and $\theta \rightarrow 1$)	160	140	50
Case 3 (i.e. $c_F^o = 5$ g/l and $\theta = 0.5$)	3000	2000	350
Flow rate (lpm) Velocity (m/s)		275 0.165	
Sherwood number Sh		Sh = 0.46 Re ^{0.36} Sc ^{0.36} [88]	

In other cases, non-ideal transport dynamics clearly shifted results away from the maximum energy recovery point, and therefore some other reasonable pressure was applied, Although it is outside the scope of this study to optimize this applied pressure. A complete list of input values used for simulations is provided in Table 4.2.

To calibrate the model, membrane parameters A, B, and S were measured in our laboratory, following standard test procedures [89]. Figure. 4.8 shows parameters for the two commercial membranes that were selected for this study, which are asymmetric cellulose triacetate (CTA) FO membranes supplied by FTS H2O and polyamide thin film composite (TFC) RO membranes supplied by Dow Filmtec. A comparison of the two membranes is intended to provide some indication of permeability and selectivity tradeoffs in fertilizer osmosis applications.

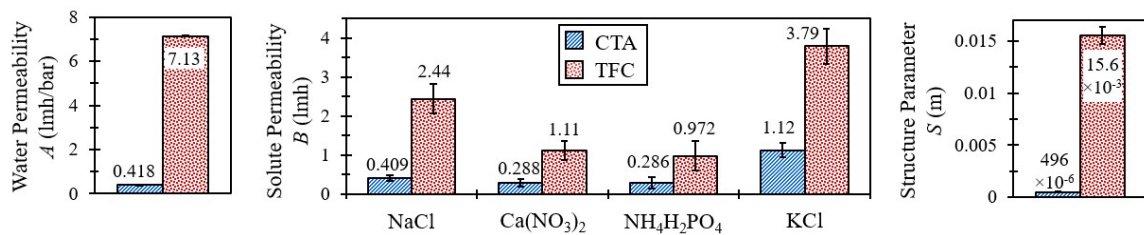


Figure 4.8. Measurements for membrane parameters water permeability A, solute permeability B, and structure parameter S obtained in laboratory experiments at Oakland University following standard test methods [89] for asymmetric cellulose triacetate (CTA) and polyamide thin film composite (TFC) membranes.

4.4.2 Simulation Results

Throughout the fertilizer PRO batch process energy is recovered as permeate volume is accumulated at some applied pressure. The resulting change in feed and draw

potentials yields a diminishing rate to this recovery process over time. Figure. 4.9 illustrates these dynamics, showing a sample of the results for the case where an abundant feed source of clean irrigation water is available (i.e. $c_F^o \rightarrow 0$ and $\theta \rightarrow 0$, case 1). As shown, permeate flux J_w drops as permeate volume $\Delta V/m_D$ is recovered, and likewise, power density $\dot{W}/a$ drops as energy is recovered $\Delta W/m_D$. In this figure, time is plotted on the x-axis and is normalized with respect to membrane area, and although dynamics will not exactly scale linearly with module size, this normalization nonetheless allows the results to be interpreted more generally. In these particular examples between 8-10 Wh/kg of energy can be recovered before equilibrium is reached. However, if power density is to be maintained above a competitive target such as 5 W/m², only between 5-7 Wh/kg can be recovered. This is significantly less than the 9-14 Wh/kg that was suggested for these same examples when ideal transport dynamics were assumed in Section 2.3.

This analysis is extended to additional scenarios, including the case where a limited volume of clean irrigation water is available as feed (i.e. $c_F^o \rightarrow 0$ and $\theta \rightarrow 1$, case 2), and the case where a wastewater source is used as feed (i.e. $c_F^o = 5$ g/l and $\theta = 0.5$, case 3), and including the TFC RO membrane. Figure. 4.10 provides a summary of the results. The plots show the drop in power density that occurs as energy is recovered. Where possible, the target power density is indicated.

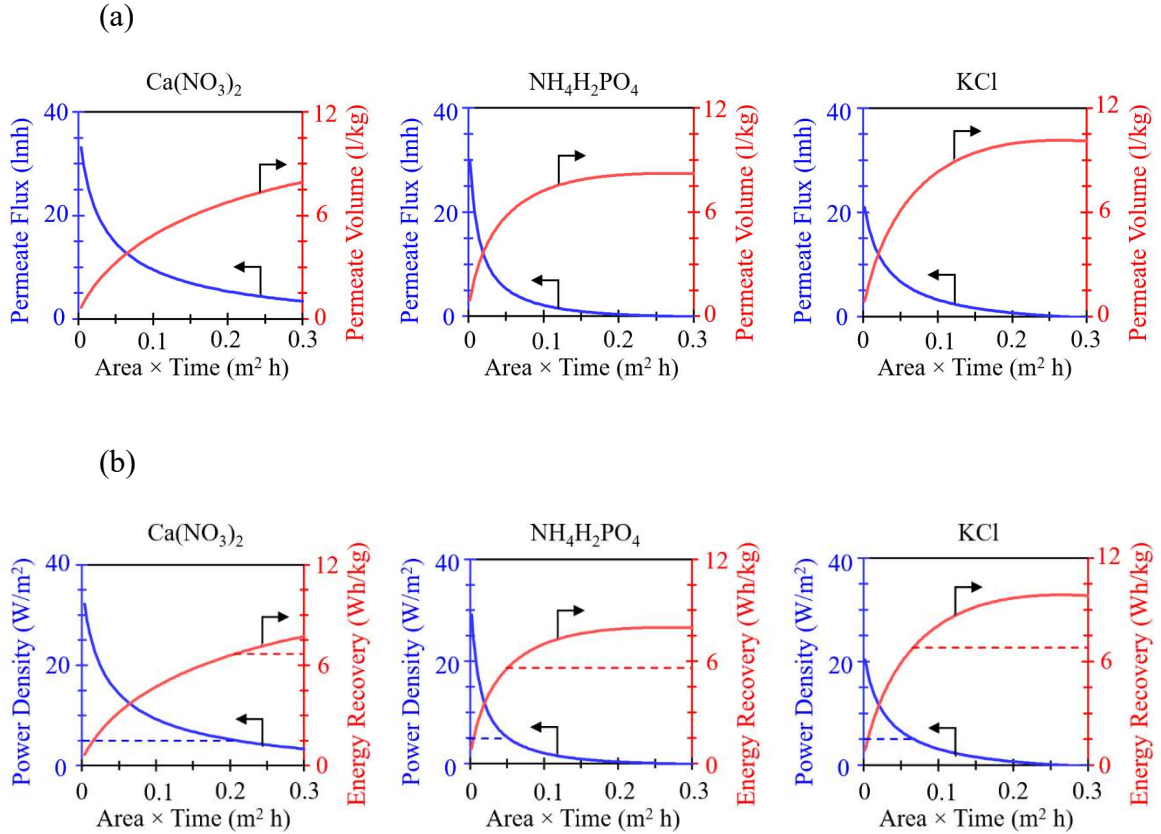


Figure 4.9. Simulated transport results showing the fertilizer PRO batch process as a function of time and membrane area, in which concentrated fertilizer is recirculated causing (a) flux to drop as permeate volume is accumulated, and (b) power density to drop as energy is recovered. Assumes an infinite volume of clean feed water is available (i.e. case 1, $c_{F^0} \rightarrow 0$, and $\theta \rightarrow 0$) and that CTA FO membrane is used. Simulation parameters are summarized in Table 4.2.

A comparison of the two membranes suggests that membrane selection will have an important impact on how much energy can be recovered from fertilizer PRO. As shown, the TFC RO membrane performs poorly in this application with less than 1.5 Wh/kg of energy recovered at equilibrium, and zero energy recovered above the power target of $5 \text{ W}/\text{m}^2$. This is due to the very high structure parameter which leads to extreme polarization, and low osmotic driving pressures. So much so, that low applied pressures must be used with this membrane so as to avoid reversing the direction of water permeate. We note that the wide range of applied pressures used in cases 1-3 for the

different N-P-K fertilizers is not optimized as it is outside the scope of this study. However, the results clearly indicate the importance of careful membrane selection for effective fertilizer PRO, and in this example, we see that high water permeability A is not sufficient to justify high solute permeability B and a very high support structure parameter S.

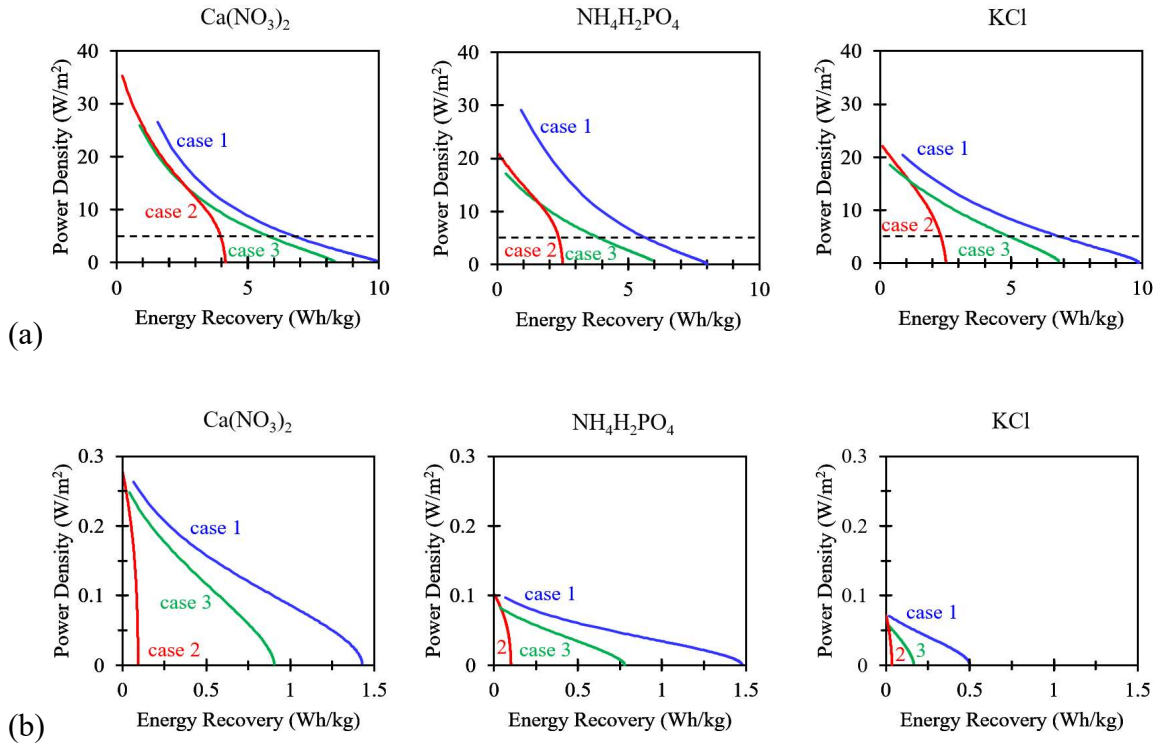


Figure 4.10. Simulated transport results showing energy recovery and power density throughout the fertilizer PRO batch process for (a) asymmetric cellulose triacetate (CTA) FO membranes supplied by FTS H2O and (b) polyamide thin film composite (TFC) RO membranes supplied by Dow Filmtec. Simulation parameters are summarized in Table 4.2. Cases 1-3 are defined as follows. Case 1: An abundant source of clean irrigation water is available as feed (i.e. $c_F^p \rightarrow 0$ and $\theta \rightarrow 0$) Case 2: A limited volume of clean irrigation water is available as feed (i.e. $c_F^p \rightarrow 0$ and $\theta \rightarrow 1$) Case 3: A wastewater source is used as feed, from which half the volume is recovered as permeate (i.e. $c_F^p = 5 \text{ g/l}$ and $\theta = 0.5$).

Results for the CTA FO membrane are more promising. Case 1 results show energy between 8-10 Wh/kg obtained at equilibrium, and between 6-7 Wh/kg when competitive power targets of at least 5 W/m^2 are maintained. Energy recovery drops for more the realistic cases 2 and 3. Case 2 is characterized by a sharp drop in power that

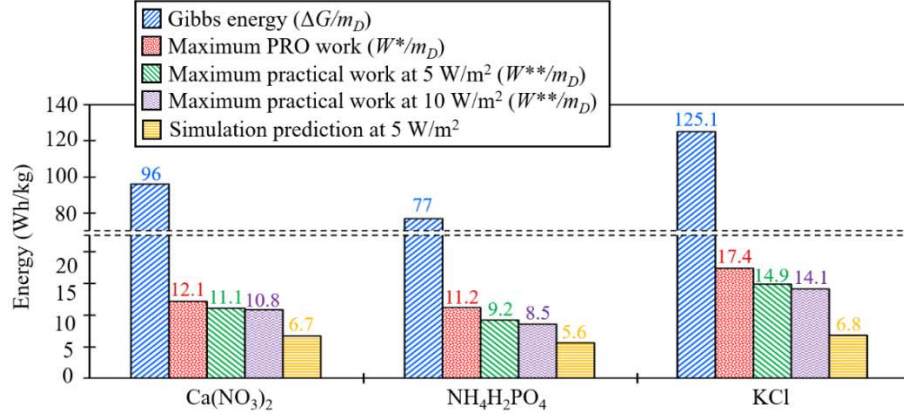
occurs as the recovery ratio approaches 1. By comparison, the drop in energy is relatively modest for case 3, with between 6-8 Wh/kg obtained at equilibrium, and between 4-6 Wh/kg when competitive power targets of at 5 W/m^2 are maintained. This comparison suggests that using wastewater with 50 % volume recovery is a promising feed source for fertilizer PRO.

4.5 Discussion

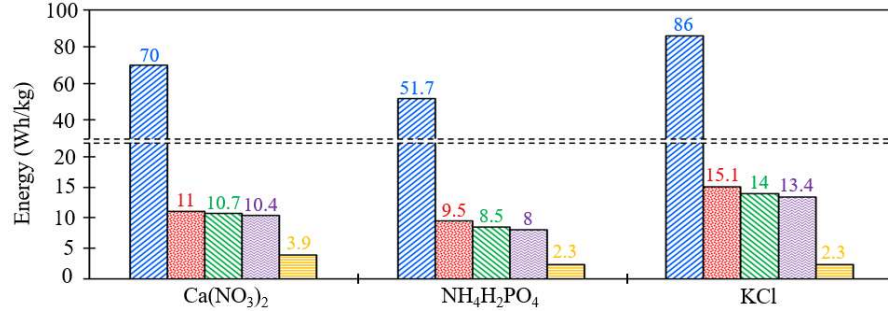
4.5.1 Energy Potential of Common Fertilizers

The energy limits of common N, P, K fertilizers are summarized in Figure. 4.11. As shown, the Gibbs energy potential of fertilizers can reach up to 125 Wh/kg, although it is highly specific to fertilizer type, feed concentration, and recovery ratio, which are illustrated in the several cases. This energy density is more than one order of magnitude greater than the thermodynamic limits reported in [27], which were less than 7 Wh/kg. This corrects an inconsistency in the literature and suggests that fertilizer energy is significantly greater than previously thought. Figure. 4.11, also shows that PRO at constant applied pressure imposes a major limitation on energy recovery and reduces work to 17.4 Wh/kg or less. This suggests that major improvements in fertilizer energy recovery could be achieved by the development of variable-pressure PRO [80,81,81–83]. In contrast, the additional limitation imposed by the need to maintain high power leads only to a minor drop in work.

(a) Case 1: An abundant source of clean irrigation water is available as feed (i.e. $c_F^o \rightarrow 0$ and $\theta \rightarrow 0$)



(b) Case 2: A limited volume of clean irrigation water is available as feed (i.e. $c_F^o \rightarrow 0$ and $\theta \rightarrow 1$)



(c) Case 3: A wastewater source is used as feed, from which half the volume is recovered as permeate

(i.e. $c_F^o = 5$ g/l and $\theta = 0.5$)

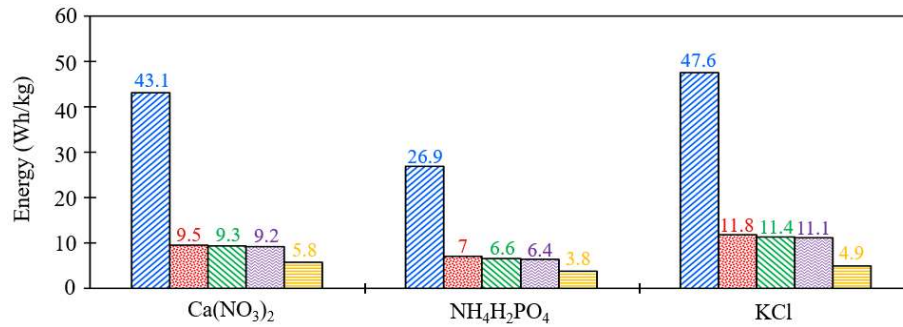


Figure 4.11. The Gibbs energy $\Delta G/m_D$, the maximum PRO work W^*/m_D , the maximum PRO work W^{**}/m_D that satisfies practical power targets of 5 W/m^2 and 10 W/m^2 , and the experimentally-calibrated simulation results for CTA membrane at 5 W/m^2 power target. These limits are shown for calcium nitrate, monoammonium phosphate, and potassium chloride fertilizer, and for several cases of different feed concentrations c_F^o and recovery ratios θ as described in (a), (b), and (c).

For cases where the power target is 5 W/m^2 , this drop reduces work to 14.9 Wh/kg or less, and where the target is 10 W/m^2 , the drop reduces work to 14.1 Wh/kg or less. Finally, when non-ideal transport dynamics are modelled, energy recovery of 6.8 Wh/kg is predicted. The results in Figure. 4.11 are organized into three specific cases. In Case 1, an abundant source of clean irrigation water is available as feed, and therefore $c_F^o = 0.1 \text{ g/l}$ and $\theta \rightarrow 0$. This case shows the highest energy and work; however, the scenario is unlikely to be realized in the field where valuable irrigation water is not unlimited. In more realistic scenarios, where feed concentration and recovery ratio increase, we observe a decrease in energy potential and work. Case 2 shows results for when a limited source of clean irrigation water is available as feed, and therefore $c_F^o = 0.1 \text{ g/l}$ and $\theta \rightarrow 1$. Case 3 shows results for when a wastewater source is used as feed, from which half the volume is recovered as permeate, and therefore $c_F^o = 5 \text{ g/l}$ and $\theta = 0.5$. While the difference in Gibbs energy between these cases is major, the difference in maximum work is much less. For example, consider KCl , where the Gibbs energy drops from 86.0 Wh/kg in case 2, to 47.6 Wh/kg in case 3. In contrast, the maximum work (at 5 W/m^2 power) drops from 14.9 to 11.4 Wh/kg . Or consider $\text{Ca}(\text{NO}_3)_2$, where the Gibbs energy drops from 70.0 Wh/kg in case 2, to 43.1 Wh/kg in case 3, but maximum work (at 5 W/m^2) only drops from 10.4 to 9.2 Wh/kg . This suggests that wastewater may be an appropriate feed source for fertilizer PRO.

We observe also in Figure. 4.11 that for both the thermodynamic and practical limits, the energy potential of KCl appears superior to that of $\text{Ca}(\text{NO}_3)_2$ and $\text{NH}_4\text{H}_2\text{PO}_4$. This is due to the higher molar solubility of the KCl salt. Extending this same analysis to

additional fertilizers would similarly show high potential for salts that have high initial concentrations.

4.5.2 Energy Potential of Common Crops

In this section, we describe the potential for fertilizer PRO during cultivation of common plant crops, including hydroponic tomato, cucumber, lettuce, and basil. Table 4.3 provides a summary of the N-P-K nutrient requirements for each plant. Since nutrient requirements vary significantly throughout plant life cycle, the reported values are the average daily requirements [90]. These nutrients can be supplied to plants via a number of sources, and many commercial and in-house fertilizer recipes are available. We consider here that they are supplied by the three common fertilizers analyzed throughout this study: $\text{Ca}(\text{NO}_3)_2$, $\text{NH}_4\text{H}_2\text{PO}_4$ and KCl . The fertilizer amounts needed to meet nutrient requirements are summarized in Table 4.3. Based on these requirements, and given the thermodynamic and practical energy limits of each fertilizer as described previously, the potential from cultivation of each crop can be determined.

Table 4.3. Average nutrient and fertilizer consumption, and plant spacing for common vegetable crops.

	Average Nutrient Requirement [90] (mg/plant/day)			Average Fertilizer Requirement (mg/plant/day)			Spacing [91–94] (plant/m ²)
	N	P	K	$\text{Ca}(\text{NO}_3)_2$	$\text{NH}_4\text{H}_2\text{PO}_4$	KCl	
Tomato	89	16	43	519	53	81	3.5
Cucumber	171	18	54	997	60	102	1.7
Lettuce	48	3	18	280	10	34	25
Basil	55	3	20	320	10	38	25

Figure. 4.12 shows the energy and work available from fertilizer used during hydroponic cultivation of tomato, cucumber, lettuce, and basil. These energy results are normalized per plant, and also per unit growing area based on plant densities [93,94]. As expected, we observe that heavy feeding plants such as tomato have greater fertilizer energy density per plant, while closely spaced plants such as lettuce and basil have greater energy density per unit area.

To provide context to these results, consider that a typical mid-latitude greenhouse consumes on the order of 7 kWh/m²/year [95–97]. By comparison, nearly 330 Wh/m²/year of energy is released from fertilizer during high-density basil cultivation, or nearly 5 % of the electricity load of a typical greenhouse. However, only a fraction of this can be converted to work with a PRO process at constant applied pressure. For basil cultivation, the maximum PRO work is 40 Wh/m²/year. Furthermore, the need to maintain competitive power levels throughout the batch process imposes additional limits. When power of at least 10 W/m² is maintained throughout the process, maximum energy is reduced to about 37 Wh/m²/year for basil, or only 0.5 % of a typical greenhouse electric load. Also, non-ideal transport dynamics are anticipated to further reduce energy recovered to 23 Wh/m²/year for basil. This suggests that while the energy available from fertilizer represents a significant opportunity, the potential for energy recovery from PRO operated at constant pressure is modest. Nonetheless, even modest amounts of energy may be useful for limited applications such as mechanical pumping and circulation of irrigation water, provided this energy can be economically recovered. Improving process efficiency and approaching the Gibbs potential of the fertilizer will require advances in low-cost membranes for low-power, variable-pressure PRO operation.

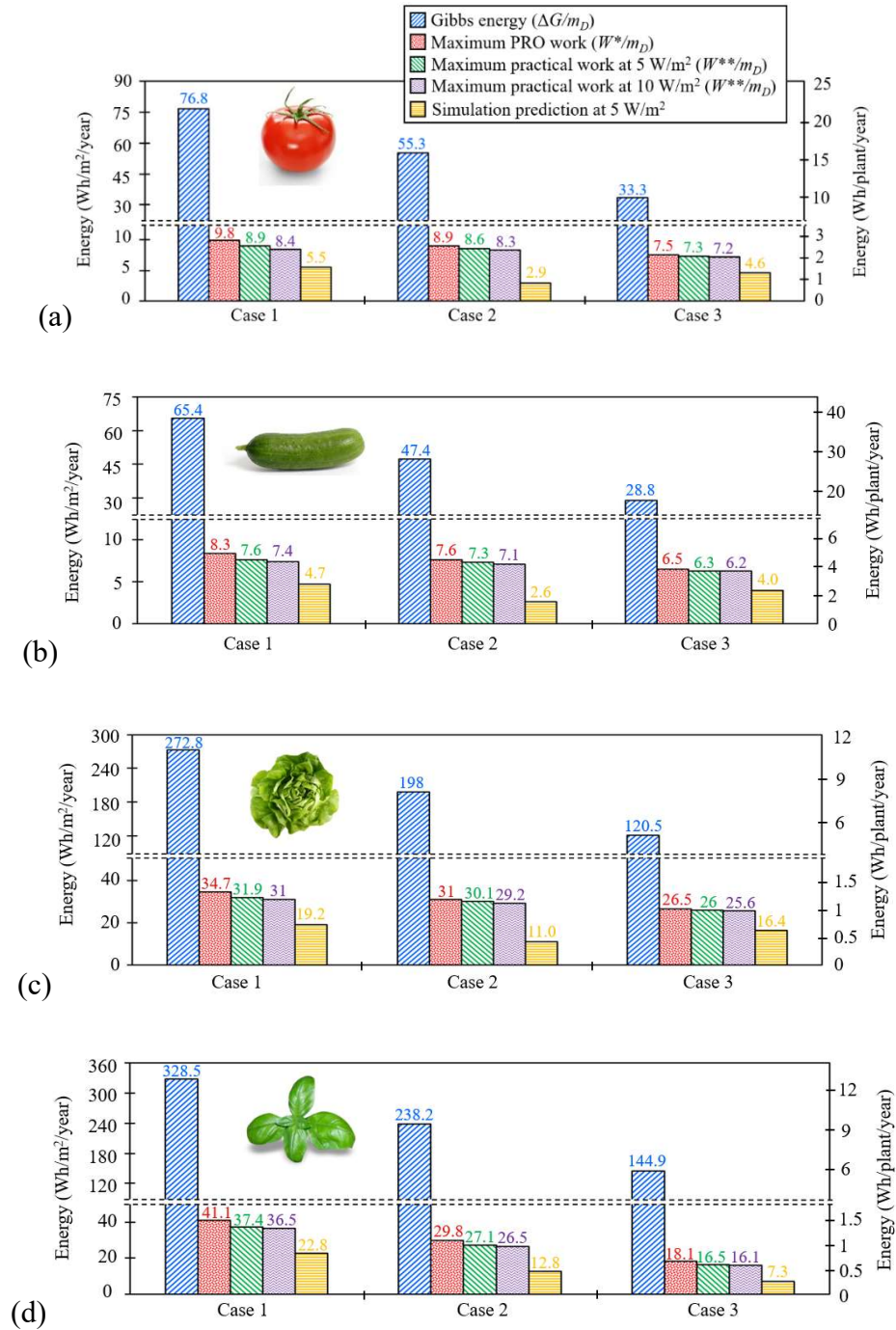


Figure 4.12. The Gibbs energy $\Delta G/m_D$, the maximum PRO work W^*/m_D , the maximum PRO work W^{**}/m_D that satisfies practical power targets of 5 W/m² and 10 W/m², and the experimentally-calibrated simulation results for CTA membrane at 5 W/m² power target. These limits are shown for hydroponically cultivated (a) tomato, (b) cucumber, (c) lettuce, and (d) basil, and for several cases of different feed concentrations c_{Fo} and recovery ratios θ . In case 1 an abundant source of clean irrigation water is available as feed (i.e. $c_{Fo} \rightarrow 0$ and $\theta \rightarrow 0$). In case 2 a limited volume of clean irrigation water is available as feed (i.e. $c_{Fo} \rightarrow 0$ and $\theta \rightarrow 1$). In case 3 a wastewater source is used as feed, from which half the volume is recovered as permeate (i.e. $c_{Fo} = 5$ g/l and $\theta = 0.5$).

4.6 Conclusions

In this chapter we have introduced an analytical and numerical approach to evaluating the thermodynamic and practical limits of recovering mechanical work from a fertilizer osmosis batch process. This contributes to the so far limited literature on fertilizer PRO by clearly establishing the limits to energy and work. Common N, P, K fertilizers are analyzed including calcium nitrate, monoammonium phosphate, and potassium chloride. From among these, highly soluble potassium chloride shows the greatest potential due to large osmotic gradients that can be exploited during the early stages of dilution. Up to 125 Wh per kg KCl is released during mixing with large volumes of low concentration feed. This potential is over one order of magnitude greater than previously reported in [27]. Of this potential, up to 14.1 Wh/kg can be recovered as mechanical work using a PRO batch process that maintains power of at least 5 W/m² throughout. When non-ideal transport dynamics are considered, it is anticipated that up to 6.8 Wh/kg of energy can be recovered, given an appropriately selected membrane. For integration with plant cultivation systems, densely planted crops such as lettuce and other similar greens show the greatest potential on a per foot basis. In the case of basil, up to 330 Wh/m²/year is released from fertilizers used during cultivation. This is equivalent to 5 % of the electricity consumed by a typical greenhouse. However, only about 7 % of this energy can be reasonably converted to mechanical work, based on the current state of PRO technology.

These limits provide useful targets for future research and development, and insight into what innovations offer the greatest potential for advancing fertilizer PRO. It

is clear from this study that advances in membrane technology will be of great importance to the process. Simulation results show a wide discrepancy in results for different commercial membranes, with equilibrium energy approaching 10 Wh/kg for the CTA FO membrane, and only 1.5 Wh/kg with the TFC RO membrane. Development of a “perfect” membrane (with high permeability, high selectivity, and low structure factor) would theoretically allow fertilizer PRO to approach the limit described by W^{**} . Furthermore, making these membranes “low-cost” would reduce power density targets (for example, below the 5 and 10 W/m² that were assumed here) and allow the PRO process to proceed towards equilibrium, and thereby approach the limit described by W^* . Finally, approaching the Gibbs energy limit will require development of a variable-pressure process [68,80–83] to reduce applied pressure as the fertilizer batch is diluted. We expect that the most practical application of fertilizer work will be to generate a reservoir of pressurized fertilizer solution for on-demand delivery to plants, however it is unclear how this might be integrated with a strategy for variable-pressure to be applied to the PRO process. While significant hurdles remain for “Green PRO” to be deployed in agricultural systems, its potential to open up new and interesting possibilities at the food-energy-water nexus warrants further investigation.

4.7 Supplementary Information

4.7.1 Supplementary Note 4.1: Gibbs Energy of Mixing Fertilizer and Water

The energy available from concentrated fertilizer draw solution and irrigation feed water, is defined by the Gibbs free energy of mixing.

$$\Delta G = \int_0^{\Delta V'} \Delta \pi \, d\Delta V \quad (4.1)$$

$$\Delta G = \int_0^{\Delta V'} (\pi_D - \pi_F) \, d\Delta V \quad (4.S1)$$

Where ΔG is defined using a positive sign convention for energy released. ΔV is the volume of irrigation water drawn into the concentrated fertilizer solution, and $\Delta V'$ is the volume that establishes osmotic equilibrium between the two solutions. $\Delta \pi$ is the osmotic pressure difference between the concentrated fertilizer draw π_D and the diluted irrigation feed π_F (i.e. $\Delta \pi = \pi_D - \pi_F$), and osmotic pressure is approximated by the Van't Hoff equation:

$$\pi = \gamma i R T c \quad (4.S2)$$

Where γ is the activity coefficient, i is the number of ions, R is the gas constant, T is absolute temperature, and c is concentration.

To solve the Gibbs energy in eq. (4.1), it is necessary to define osmotic pressure as a function of permeate mixing volume, i.e. $\pi = f(\Delta V)$. Since concentration is a function of volume, osmotic pressure can be written as a function of permeate volume as follows:

$$\pi = \gamma i R T \frac{n}{V^o \pm \Delta V} = \gamma i R T c^o \frac{V^o}{V^o \pm \Delta V} = \gamma \pi^o \frac{V^o}{V^o \pm \Delta V} \quad (4.S3)$$

Where n is the amount of salt in the solution, V^o is the initial volume of water in the solution, and ΔV is the permeate volume which will be positive for the draw solution and negative for the feed. c^o is the initial concentration, and π^o is the initial osmotic pressure.

The activity coefficient γ is also a function of concentration and therefore permeate volume, but because such relationships are largely empirical, an exact analytical solution to eq. (4.1) requires an assumption that γ is equal to a constant, which we assume in this study to be unity. Future work may consider using numerical methods to include this, but we note that others have made the same assumption [29,27,61,78,79] and recognize that such will introduce error to the evaluation of Gibbs energy. Furthermore, we note that for the fertilizer solutions considered in this study, the ideal equation for osmotic pressure shows only minor variation with empirical results reported by OLI commercial software, as shown in Figure. 4.13.

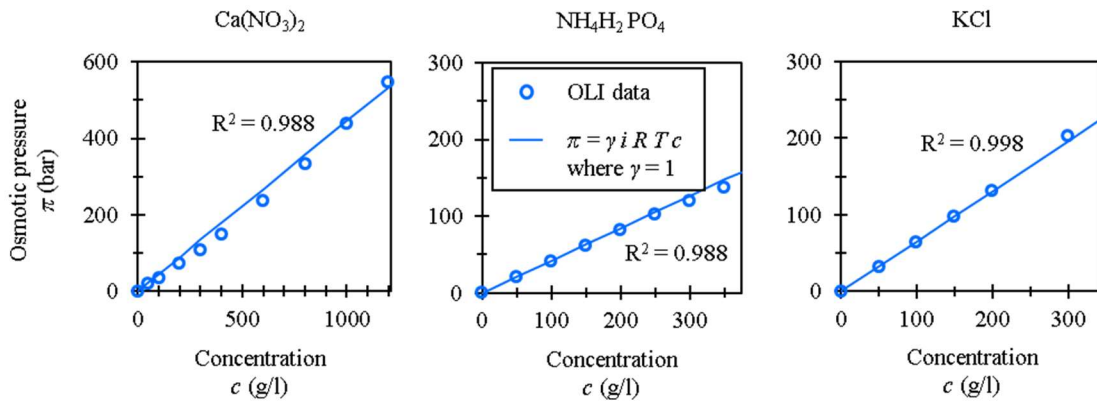


Figure 4.13. Osmotic pressure of highly concentrated fertilizer solutions as predicted by the Van't Hoff equation and by OLI commercial software data.

The Gibbs energy equation can therefore be written as a function of permeate volume.

$$\Delta G = \int_0^{\Delta V'} \left(\pi_D^0 \frac{V_D^0}{V_D^0 + \Delta V} - \pi_F^0 \frac{V_F^0}{V_F^0 - \Delta V} \right) d\Delta V \quad (4.S4)$$

Solving the integral and normalizing energy per unit fertilizer mass, allows us to obtain eq. (4.2) as was shown in Section 2.1.

$$\Delta G = \pi_D^o V_D^o \ln \left(\frac{V_D^o + \Delta V'}{V_D^o} \right) - \pi_F^o V_F^o \ln \left(\frac{V_F^o}{V_F^o - \Delta V'} \right) \quad (4.S5)$$

$$\frac{\Delta G}{m_D} = \frac{\pi_D^o V_D^o}{m_D} \ln \left(1 + \frac{\Delta V'}{V_D^o} \right) - \frac{\pi_F^o V_F^o}{m_D} \ln \left(\frac{1}{1 - \frac{\Delta V'}{V_F^o}} \right) \quad (4.S6)$$

$$\frac{\Delta G}{m_D} = \frac{\pi_D^o}{c_D^o} \ln \left(1 + c_D^o \frac{\Delta V'}{m_D} \right) - \frac{\pi_F^o \Delta V'}{\theta' m_D} \ln \left(\frac{1}{1 - \theta} \right) \quad (4.2)$$

Where θ is the recovery ratio which is the ratio of permeate volume to total feed volume, i.e. $\theta = \Delta V' / V_F^o$, and where $\Delta V'$ is the equilibrium permeate volume. This volume can be determined by considering the condition for equilibrium $\pi_D = \pi_F$. Combining with eq. (S3) and assuming again ideal osmotic behavior with activity coefficient of unity, we obtain the analytical solution for equilibrium volume, as was previously shown in eq. (4.3) Section 2.1.

$$\pi_D = \pi_F \quad (4.S7)$$

$$\pi_D^o \frac{V_D^o}{V_D^o + \Delta V'} = \pi_F^o \frac{V_F^o}{V_F^o - \Delta V'} \quad (4.S8)$$

$$\Delta V' = V_D^o \left(\frac{\pi_D^o}{\pi_F^o} \left(1 - \frac{\Delta V'}{V_F^o} \right) - 1 \right) \quad (4.S9)$$

$$\frac{\Delta V'}{m_D} = \frac{1}{c_D^o} \left(\frac{\pi_D^o}{\pi_F^o} (1 - \theta) - 1 \right) \quad (4.3)$$

To illustrate the equilibrium permeate volume and Gibbs energy limits of fertilizer, consider common N, P, K fertilizers such as calcium nitrate $\text{Ca}(\text{NO}_3)_2$, monoammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$, and potassium chloride KCl when mixed with

diluted feed sources approximated by sodium chloride NaCl concentrations from 0.1 to 5 g/l. The properties of these solutions are summarized in Table 4.1. Figure. 4.14 shows Gibbs energy per unit mass of each of the N, P, K fertilizers as a function of feed concentration c_F and recovery ratio θ . As expected, mixing fertilizer with an infinite volume of low concentration feed maximizes the available energy (i.e. $c_F \rightarrow 0$ and $\theta \rightarrow 0$). Under these conditions, energy on the order of 100 Wh/kg is observed.

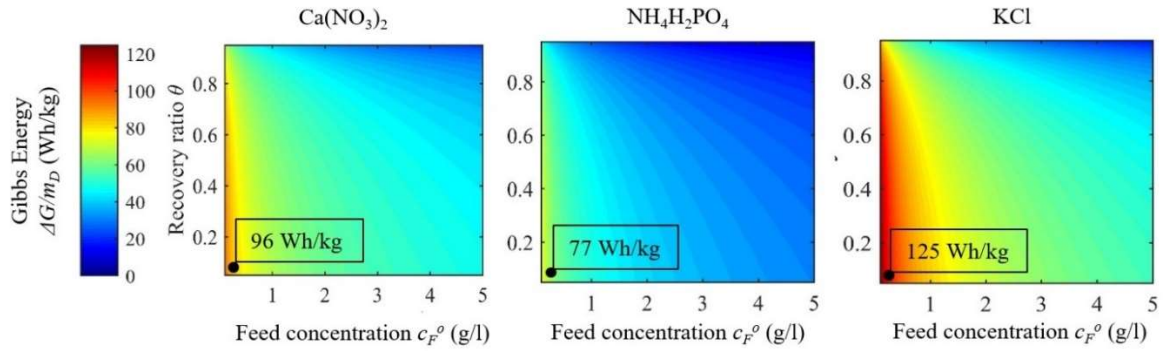


Figure 4.14. Gibbs energy ΔG per unit of fertilizer m_D for calcium nitrate $\text{Ca}(\text{NO}_3)_2$, monoammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$, and potassium chloride KCl as a function of feed concentration c_F^o and recovery ratio θ . The data point highlights the specific case where an abundant source of clean irrigation water is available (i.e. feed concentration $c_F^o = 0.1$ g/l and recovery ratio $\theta \rightarrow 0$).

4.7.2 Supplementary Note 4.2: Fertilizer Energy from PRO at Constant Applied

Pressure

When PRO is operated at constant applied pressure Δp , only a portion of Gibbs energy is recovered as work.

$$W = \Delta p \Delta V \quad (4.4)$$

Where ΔV is the permeate volume that establishes PRO equilibrium between the osmotic driving force and the constant applied pressure, i.e. when $\Delta p = \Delta \pi$. Since osmotic pressure is a function of permeate volume ΔV as previously described in eq. (4.S3) for

ideal solution with activity coefficient of unity, we can express the PRO equilibrium point as:

$$\Delta p = \Delta \pi \quad (4.S10)$$

$$\Delta p = \pi_D^o \frac{V_D^o}{V_D^o + \Delta V} - \pi_F^o \frac{V_F^o}{V_F^o - \Delta V} \quad (4.S11)$$

This shows that, permeate volume is inversely related to applied pressure. Since work is the product of both, there will be some applied pressure that will produce the greatest product and yield maximum work for PRO at constant applied pressure. This pressure can be determined analytically by considering eq. (4.S11) and solving for the peak obtained when $dW / d\Delta V = 0$.

$$\frac{dW}{d\Delta V} = \frac{d\Delta p \Delta V}{d\Delta V} = 0 \quad (4.S12)$$

$$\frac{d}{d\Delta V} \left(\pi_D^o \frac{V_D^o}{V_D^o + \Delta V} - \pi_F^o \frac{V_F^o}{V_F^o - \Delta V} \right) \Delta V = 0 \quad (4.S13)$$

$$\pi_D^o \left(\frac{V_D^o}{V_D^o + \Delta V^*} \right)^2 - \pi_F^o \left(\frac{V_F^o}{V_F^o - \Delta V^*} \right)^2 = 0 \quad (4.S14)$$

$$\Delta V^* = V_D^o \left(\sqrt{\frac{\pi_D^o}{\pi_F^o} \left(1 - \frac{\Delta V^*}{V_F^o} \right)} - 1 \right) \quad (4.S15)$$

The limit to energy recovery from PRO at constant applied pressure is then obtained from $W^* = \Delta p^* \Delta V^*$.

$$W^* = \left(\pi_D^o \frac{V_D^o}{V_D^o + \Delta V^*} - \pi_F^o \frac{V_F^o}{V_F^o - \Delta V^*} \right) \Delta V^* \quad (4.S16)$$

Normalizing over fertilizer amount m_D yields the expressions for PRO equilibrium volume and maximum PRO work at constant applied pressure, as shown previously in Section 2.2.

$$\frac{\Delta V^*}{m_D} = \frac{1}{c_D^o} \left(\sqrt{\frac{\pi_D^o}{\pi_F^o}} (1 - \theta) - 1 \right) \quad (4.7)$$

$$\frac{W^*}{m_D} = \left(\pi_D^o \frac{1}{1 + c_D^o \frac{\Delta V^*}{m_D}} - \pi_F^o \frac{1}{1 - \theta} \right) \frac{\Delta V^*}{m_D} \quad (4.5)$$

$$\frac{W^*}{m_D} = \left(\frac{\sqrt{\pi_D^o \pi_F^o} - \pi_F^o}{1 - \theta} \right) \frac{\Delta V^*}{m_D} \quad (4.5)$$

The pressure that yields this maximum PRO work is obtained by considering eq. (4.S11) together with the result in eq. (4.7).

$$\Delta p^* = \pi_D^o \frac{V_D^o}{V_D^o + \Delta V^*} - \pi_F^o \frac{V_F^o}{V_F^o - \Delta V^*} \quad (4.S17)$$

$$\Delta p^* = \pi_D^o \frac{1}{1 + c_D^o \frac{\Delta V^*}{m_D}} - \pi_F^o \frac{1}{1 - \theta} \quad (4.S18)$$

$$\Delta p^* = \frac{\sqrt{\pi_D^o \pi_F^o} - \pi_F^o}{1 - \theta} \quad (4.6)$$

To illustrate consider again the same N,P, K fertilizers previously described in Table 4.1. Figure. 4.15 shows maximum PRO work per unit mass W^*/m_D as a function of feed concentration c_F and recovery ratio θ . For cases where an abundant source of diluted feed water (i.e. both c_F^o and $\theta \rightarrow 0$) is used, approximately 10-20 Wh/kg of work is possible.

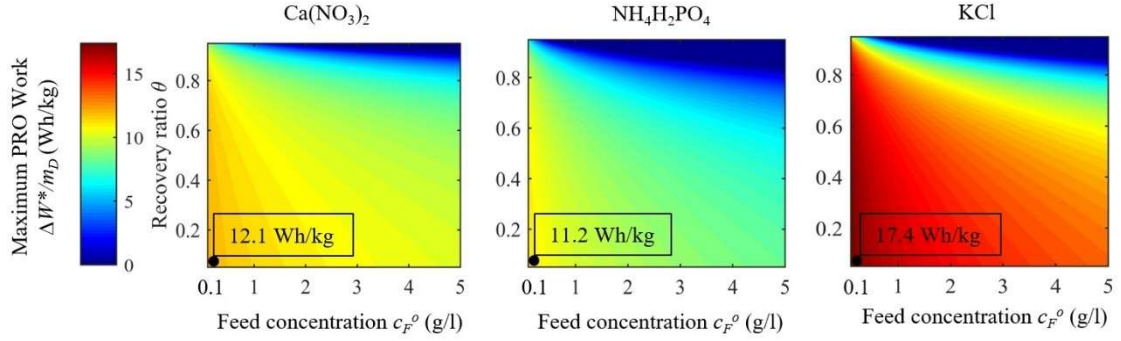


Figure 4.15. Maximum PRO work W^* per unit of fertilizer m_D for calcium nitrate $\text{Ca}(\text{NO}_3)_2$, monoammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$, and potassium chloride KCl as a function of feed concentration c_F^o and recovery ratio θ . The data point highlights the specific case where an abundant source of clean irrigation water is available as feed (i.e. feed concentration $c_F^o = 0.1$ g/l and recovery ratio $\theta \rightarrow 0$).

4.7.3 Supplementary Note 4.3: Fertilizer Energy from PRO at Practical Power Levels

The practical limits to energy recovery via fertilizer PRO can be established by considering the need to maintain cost effective power throughout the PRO process. Taking power density $\dot{W}^{**}/a$ and permeate flux $\Delta\dot{V}^{**}/a$ as defined previously in eqs. (5.8) and (5.9) of Section 2.2, we can determine the applied pressure that satisfies the power target by using the quadratic formula.

$$\frac{\dot{W}^{**}}{a} = \frac{\Delta\dot{V}}{a} \Delta p = A (\Delta\pi \Delta p - \Delta p^2) \quad (4.S19)$$

$$0 = \Delta p^2 - \Delta\pi \Delta p + \frac{1}{A} \frac{\dot{W}^{**}}{a} \quad (4.S20)$$

$$\Delta p = \frac{1}{2} \left(\Delta\pi \pm \sqrt{\Delta\pi^2 - \frac{4}{A} \frac{\dot{W}^{**}}{a}} \right) \quad (4.10)$$

The solution in eq. (5.10) describes the applied pressure that will yield the power target for any given osmotic pressure difference throughout the PRO batch process.

Obtaining two solutions from eq. (5.10) reflects the quadratic nature of the relationship between power and applied pressure, and the fact that a given power may be obtained from either a low or high applied pressure. Obtaining a non-real number from eq. (5.10) reflects the case where an osmotic potential is insufficient to generate the target power, regardless of the applied pressure.

As it is expressed in eq. (5.10), the applied pressure that satisfies target power is shown as a function of osmotic pressure difference, which itself changes throughout the fertilizer batch process as a function of permeate volume. These relationships describe a system of equations that can be solved to establish the maximum work that can be practically recovered from a fertilizer PRO batch process while maintaining minimum target power levels. The system of equations is summarized as follows.

$$\Delta p = \frac{1}{2} \left(\Delta \pi \pm \sqrt{\Delta \pi^2 - \frac{4}{A} \frac{\dot{W}^{**}}{a}} \right) \quad (4.10)$$

$$\Delta \pi = \pi_D^o \frac{1}{1 + c_D^o \frac{\Delta V}{m_D}} - \pi_F^o \frac{1}{1 - \theta} \quad (4.S21)$$

$$W = \Delta p \Delta V \quad (4.4)$$

And when combined and reorganized the following statement is obtained.

$$W = \frac{1}{2} \left(\left(\pi_D^o \frac{1}{1 + c_D^o \frac{\Delta V}{m_D}} - \pi_F^o \frac{1}{1 - \theta} \right) \pm \sqrt{\left(\pi_D^o \frac{1}{1 + c_D^o \frac{\Delta V}{m_D}} - \pi_F^o \frac{1}{1 - \theta} \right)^2 - \frac{4}{A} \frac{\dot{W}^{**}}{a}} \right) \Delta V \quad (4.S22)$$

Finding the permeate volume $\Delta V/m_D$ that yields maximum work in eq. (4.S22) establishes the point we define as the maximum practical work W^{**} . Since an exact analytical solution for eq. (4.S22) is difficult, we employ a numerical iterative approach in which $\Delta V/m_D$ is guessed and then updated as W is compared to the previous results. The approach was implemented in MATLAB and used to identify the maximum practical work for a number of scenarios.

To illustrate consider again the N, P, K fertilizers previously described in Table 4.1. Figure. 4.16 shows the maximum practical PRO work per unit mass W^{**}/m_D as a function of feed concentration c_F and recovery ratio θ . For cases where an abundant source of diluted feed water is used (i.e. both c_F^o and $\theta \rightarrow 0$) 9.2-14.9 Wh/kg of work can be practically recovered if the power target is 5 W/m², or 8.5-14.1 Wh/kg if the target is 10 W/m².

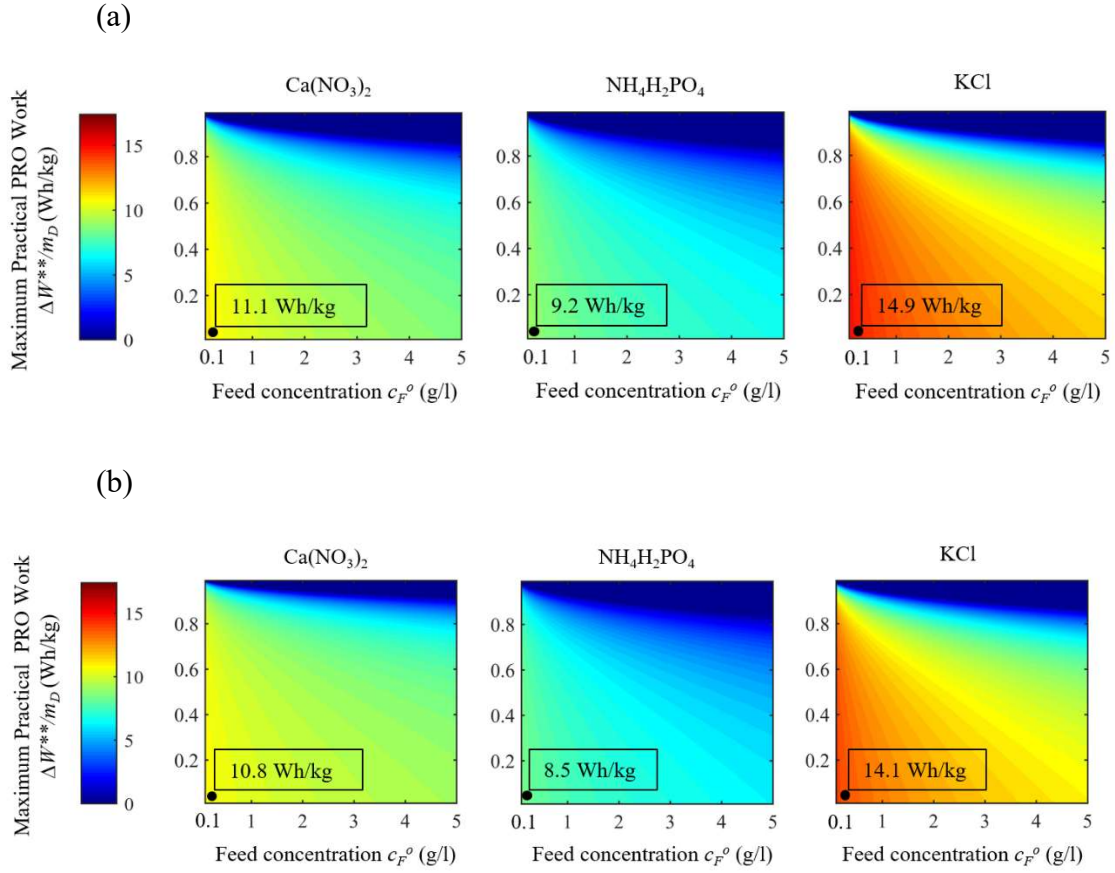


Figure 4.16. Maximum PRO work W^{**} per unit of fertilizer m_D that can be recovered while maintaining power above the practical targets of (a) 5 W/m² and (b) 10 W/m². The data point highlights the specific case where an abundant source of clean irrigation water is available as feed (i.e. feed concentration $c_{F^\circ} = 0.1$ g/l and recovery ratio $\theta \rightarrow 0$).

4.7.4 Supplementary Note 4.4: MATLAB Codes for Generating Heat Maps

This MATLAB code uses fertilizer properties, feed concentration and feed recovery ratio as inputs and generates heatmaps for Gibbs energy and maximum PRO work shown in Figures 4.15 and 4.16.

```
clear;
iD=3; %Draw number of ions [unitless]
MD=164.1; %Draw molar mass [g/mol]
```

```

cD0=1212; %Draw maximum sollubility [g/l]

iF=2; %Feed number of ions [unitless]
MF=58.44; %Feed molar mass [g/mol]

Jwdoubleprime=5; %minumum required flux [lmh]
AA = 4.3; %membrane permeability lmh/bar
Jmin=(Jwdoubleprime/AA)*100; %Jw/A [J/l]

A = linspace(0,15,1000);
cF= repmat(A,1000,1); %feed concentration [g/l]
B=linspace(0,1,1000)';
theta=repmat(B,1,1000); %recovery ratio

R=8.314; %gas constant [J/mol/K]
T=293.15; %Temperature [K]

piD0=iD*R*T*cD0/MD; %initial draw osmotic pressure [J/l]
piF=iF*R*T*cF/MF; %feed osmotic pressure [J/l]

Vprime=(1./cD0).*((piD0.*(1-theta)./piF)-1); %theoretical
volume limit[l/g] *1000 [l/kg]
Vdoubleprime=(1./cD0).*(piD0./(Jmin+piF./(1-theta))-1);
%practical volume limit [l/g]
G=(piD0./cD0).*(log(1+cD0.*Vprime))-
(piF.*Vprime./theta.*log(1./(1-theta))); %Gibbs energy[J/g]
/3.6 [Wh/kg]
Vstar=(1./cD0).*((sqrt(piD0./piF).*(1-theta))-1); % [l/g]
practical volume for max work *1000 [l/kg]
Pstar=piD0.*(1./(1+cD0.*Vstar))-piF.*(1./(1-theta)); %[J/l]
practical pressure for maimum work /100 [bar]
Wstar=Pstar.*Vstar; %[J/g] /3.6 [Wh/kg]

h=imagesc(A,100*B,G/3.6);
colormap('jet');
caxis([0 400]);
set(gca,'YDir','normal')
set(gca,'FontName','Arial')
set(gca,'FontSize',16)
set(gca,'linewidth',1.2)

xlabel('Feed concentration c_F^0 (g/l)')
ylabel('Recovery ratio \theta')

```

4.7.5 Supplementary Note 4.5: MATLAB Codes for Variable Recovery Ratio Figures

This MATLAB code uses fertilizer properties as inputs and shows energy and work as a function of feed concentration and recovery ratio θ . Figures 4.3, 4.5 and 4.7 are created with this code.

```
clear;
iD=2; %Draw number of ions [unitless]
MD=115.03; %Draw molar mass [g/mol]
cD0=374; %Draw maximum solubility [g/l]

iF=2; %Feed number of ions [unitless]
MF=58.44; %Feed molar mass [g/mol]

Jwdoubleprime=10; %minimum required flux
AA = 4.3; %membrane permeability
Jmin=(Jwdoubleprime/AA)*100; %Jw/A [J/l]

cF= linspace(0.01,5,10000);

theta1=0.01;
theta2=0.10;
theta3=0.20;
theta4=0.30;
theta5=0.40;
theta6=0.50;
theta7=0.60;
theta8=0.70;
theta9=0.80;
theta10=0.90;
theta11=0.99;

R=8.314; %gas constant [J/mol/K]
T=293.15; %Temperature [K]
```

```

piD0=iD*R*T*cD0/MD; %initial draw osmotic pressure [J/l]
piF=iF*R*T*cF/MF; %feed osmotic pressure [J/l]

Vprime1=(1./cD0).*( (piD0.*(1-theta1)./piF)-1); % [1/g]
*1000 [1/kg]
Vdoubleprime1=(1./cD0).*(piD0./(Jmin+piF./(1-theta1))-1);
G1=(piD0./cD0).*(log(1+cD0.*Vprime1))-
(piF.*Vprime1./theta1.*log(1./(1-theta1))); %[J/g] /3.6
[Wh/kg]
Vstar1=(1./cD0).*((sqrt(piD0./piF).*(1-theta1))-1); % [1/g]
*1000 [1/kg]
Pstar1=piD0.*(1./(1+cD0.*Vstar1))-piF.*(1./(1-theta1));
%[J/l] /100 [bar]
Wstar1=Pstar1.*Vstar1; %[J/g] /3.6 [Wh/kg]

Vprime2=(1./cD0).*( (piD0.*(1-theta2)./piF)-1); % [1/g]
*1000 [1/kg]
Vdoubleprime2=(1./cD0).*(piD0./(Jmin+piF./(1-theta2))-1);
G2=(piD0./cD0).*(log(1+cD0.*Vprime2))-
(piF.*Vprime2./theta2.*log(1./(1-theta2))); %[J/g] /3.6
[Wh/kg]
Vstar2=(1./cD0).*((sqrt(piD0./piF).*(1-theta2))-1); % [1/g]
*1000 [1/kg]
Pstar2=piD0.*(1./(1+cD0.*Vstar2))-piF.*(1./(1-theta2));
%[J/l] /100 [bar]
Wstar2=Pstar2.*Vstar2; %[J/g] /3.6 [Wh/kg]

Vprime3=(1./cD0).*( (piD0.*(1-theta3)./piF)-1); % [1/g]
*1000 [1/kg]
Vdoubleprime3=(1./cD0).*(piD0./(Jmin+piF./(1-theta3))-1);
G3=(piD0./cD0).*(log(1+cD0.*Vprime3))-
(piF.*Vprime3./theta3.*log(1./(1-theta3))); %[J/g] /3.6
[Wh/kg]
Vstar3=(1./cD0).*((sqrt(piD0./piF).*(1-theta3))-1); % [1/g]
*1000 [1/kg]
Pstar3=piD0.*(1./(1+cD0.*Vstar3))-piF.*(1./(1-theta3));
%[J/l] /100 [bar]
Wstar3=Pstar3.*Vstar3; %[J/g] /3.6 [Wh/kg]

Vprime4=(1./cD0).*( (piD0.*(1-theta4)./piF)-1); % [1/g]
*1000 [1/kg]
Vdoubleprime4=(1./cD0).*(piD0./(Jmin+piF./(1-theta4))-1);
G4=(piD0./cD0).*(log(1+cD0.*Vprime4))-
(piF.*Vprime4./theta4.*log(1./(1-theta4))); %[J/g] /3.6
[Wh/kg]

```

```

Vstar4=(1./cD0).*((sqrt(piD0./piF).*(1-theta4))-1); % [1/g]
*1000 [1/kg]
Pstar4=piD0.*(1./(1+cD0.*Vstar4))-piF.*(1./(1-theta4));
%[J/l] /100 [bar]
Wstar4=Pstar4.*Vstar4; %[J/g] /3.6 [Wh/kg]

Vprime5=(1./cD0).*((piD0.*(1-theta5)./piF)-1); % [1/g]
*1000 [1/kg]
Vdoubleprime5=(1./cD0).*(piD0./(Jmin+piF./(1-theta5))-1);
G5=(piD0./cD0).*(log(1+cD0.*Vprime5))-
(piF.*Vprime5./theta5.*log(1./(1-theta5))); %[J/g] /3.6
[Wh/kg]
Vstar5=(1./cD0).*((sqrt(piD0./piF).*(1-theta5))-1); % [1/g]
*1000 [1/kg]
Pstar5=piD0.*(1./(1+cD0.*Vstar5))-piF.*(1./(1-theta5));
%[J/l] /100 [bar]
Wstar5=Pstar5.*Vstar5; %[J/g] /3.6 [Wh/kg]

Vprime6=(1./cD0).*((piD0.*(1-theta6)./piF)-1); % [1/g]
*1000 [1/kg]
Vdoubleprime6=(1./cD0).*(piD0./(Jmin+piF./(1-theta6))-1);
G6=(piD0./cD0).*(log(1+cD0.*Vprime6))-
(piF.*Vprime6./theta6.*log(1./(1-theta6))); %[J/g] /3.6
[Wh/kg]
Vstar6=(1./cD0).*((sqrt(piD0./piF).*(1-theta6))-1); % [1/g]
*1000 [1/kg]
Pstar6=piD0.*(1./(1+cD0.*Vstar6))-piF.*(1./(1-theta6));
%[J/l] /100 [bar]
Wstar6=Pstar6.*Vstar6; %[J/g] /3.6 [Wh/kg]

Vprime7=(1./cD0).*((piD0.*(1-theta7)./piF)-1); % [1/g]
*1000 [1/kg]
Vdoubleprime7=(1./cD0).*(piD0./(Jmin+piF./(1-theta7))-1);
G7=(piD0./cD0).*(log(1+cD0.*Vprime7))-
(piF.*Vprime7./theta7.*log(1./(1-theta7))); %[J/g] /3.6
[Wh/kg]
Vstar7=(1./cD0).*((sqrt(piD0./piF).*(1-theta7))-1); % [1/g]
*1000 [1/kg]
Pstar7=piD0.*(1./(1+cD0.*Vstar7))-piF.*(1./(1-theta7));
%[J/l] /100 [bar]
Wstar7=Pstar7.*Vstar7; %[J/g] /3.6 [Wh/kg]

Vprime8=(1./cD0).*((piD0.*(1-theta8)./piF)-1); % [1/g]
*1000 [1/kg]
Vdoubleprime8=(1./cD0).*(piD0./(Jmin+piF./(1-theta8))-1);

```

```

G8=(piD0./cD0).*(log(1+cD0.*Vprime8))-
(piF.*Vprime8./theta8.*log(1./(1-theta8))); %[J/g]    /3.6
[Wh/kg]
Vstar8=(1./cD0).*((sqrt(piD0./piF).*(1-theta8))-1); % [1/g]
*1000 [1/kg]
Pstar8=piD0.*(1./(1+cD0.*Vstar8))-piF.*(1./(1-theta8));
%[J/l]    /100 [bar]
Wstar8=Pstar8.*Vstar8; %[J/g]    /3.6 [Wh/kg]

Vprime9=(1./cD0).*((piD0.*(1-theta9)./piF)-1); % [1/g]
*1000 [1/kg]
Vdoubleprime9=(1./cD0).*(piD0./(Jmin+piF./(1-theta9))-1);
G9=(piD0./cD0).*(log(1+cD0.*Vprime9))-
(piF.*Vprime9./theta9.*log(1./(1-theta9))); %[J/g]    /3.6
[Wh/kg]
Vstar9=(1./cD0).*((sqrt(piD0./piF).*(1-theta9))-1); % [1/g]
*1000 [1/kg]
Pstar9=piD0.*(1./(1+cD0.*Vstar9))-piF.*(1./(1-theta9));
%[J/l]    /100 [bar]
Wstar9=Pstar9.*Vstar9; %[J/g]    /3.6 [Wh/kg]

Vprime10=(1./cD0).*((piD0.*(1-theta10)./piF)-1); % [1/g]
*1000 [1/kg]
Vdoubleprime10=(1./cD0).*(piD0./(Jmin+piF./(1-theta10))-1);
G10=(piD0./cD0).*(log(1+cD0.*Vprime10))-
(piF.*Vprime10./theta10.*log(1./(1-theta10))); %[J/g]
/3.6 [Wh/kg]
Vstar10=(1./cD0).*((sqrt(piD0./piF).*(1-theta10))-1); %
[1/g]    *1000 [1/kg]
Pstar10=piD0.*(1./(1+cD0.*Vstar10))-piF.*(1./(1-theta10));
%[J/l]    /100 [bar]
Wstar10=Pstar10.*Vstar10; %[J/g]    /3.6 [Wh/kg]

Vprime11=(1./cD0).*((piD0.*(1-theta11)./piF)-1); % [1/g]
*1000 [1/kg]
Vdoubleprime11=(1./cD0).*(piD0./(Jmin+piF./(1-theta11))-1);
G11=(piD0./cD0).*(log(1+cD0.*Vprime11))-
(piF.*Vprime11./theta11.*log(1./(1-theta11))); %[J/g]
/3.6 [Wh/kg]
Vstar11=(1./cD0).*((sqrt(piD0./piF).*(1-theta11))-1); %
[1/g]    *1000 [1/kg]
Pstar11=piD0.*(1./(1+cD0.*Vstar11))-piF.*(1./(1-theta11));
%[J/l]    /100 [bar]
Wstar11=Pstar11.*Vstar11; %[J/g]    /3.6 [Wh/kg]

```

```

plot(cF,Vdoubleprime1*1000,'color','[0,0.4,1]','LineWidth',
3)
hold on
plot(cF,Vdoubleprime2*1000,'color','[0,0.4,1]','LineStyle',
'--','LineWidth',3)
hold on
plot(cF,Vdoubleprime3*1000,'color','[0,0.4,1]','LineStyle',
'-.','LineWidth',3)
hold on
plot(cF,Vdoubleprime4*1000,'color','[0,0.4,1]','LineStyle',
'-.','LineWidth',3)
hold on
plot(cF,Vdoubleprime5*1000,'color','[0,0.4,1]','LineStyle',
'-.','LineWidth',3)
hold on
plot(cF,Vdoubleprime6*1000,'color','[0,0.4,1]','LineStyle',
'-.','LineWidth',3)
hold on
plot(cF,Vdoubleprime7*1000,'color','[0,0.4,1]','LineStyle',
':','LineWidth',3)
hold on
plot(cF,Vdoubleprime8*1000,'color','[0,0.4,1]','LineStyle',
':','LineWidth',3)
hold on
plot(cF,Vdoubleprime9*1000,'color','[0,0.4,1]','LineStyle',
':','LineWidth',3)
hold on
plot(cF,Vdoubleprime10*1000,'color','[0,0.4,1]','LineStyle',
':','LineWidth',3)
hold on
plot(cF,Vdoubleprime11*1000,'color','[0,0.4,1]','LineStyle',
':','LineWidth',3)

%red [1,0.314,0.314]
%blue [0,0.4,1]

set(gca, 'FontName', 'Times new roman')
set(gca,'FontSize',12)
set(gca,'TickDir','both')
set(gca,'FontSize',18);
set(gca,'linewidth',1.6)

xlabel('Feed concentration c_F^0 (g/l)')

```

4.7.6 Supplementary Note 4.6: MATLAB Codes for Including Non-ideal Effects

This MATLAB code uses fertilizer properties and membrane transport constants A,B and S as inputs to generate power density vs energy recovery and time by including non-ideal effect such as polarization and using effective concentration eq. 4.12. Figures 4.9, 4.5 and 4.10 are created with this code.

```
clear all
clc

% FERTILIZER DRIVEN OSMOSIS

% CONSTANTS
R=8.314; % [J/K/mol] gas constant
T=20+273.15; % [K] temperature
i=2; % [unitless] number of salt ions
M=0.07455; % [kg/mol] molar mass of salt

% INITIAL BATCH PREP
VFo=10; % [m^3] volume of water
cFo=0.1; % [kg/m^3] feed concentration
mFo=cFo*VFo; % [kg] mass of salt

VDo=0.0003; % [m^3] volume of water
cDo=342; % [kg/m^3] draw concentration
mDo=cDo*VDo; % [kg] mass of salt in feed

% OPERATING CONDITIONS
VFlpm=0.275;% [lpm] feed flow
VFdot=VFlpm/1000/60; % [m3/s] feed flow
VDlpm=0.275; % [lpm] draw flow
VDdot=VDlpm/1000/60; % [m3/s] draw flow
dp=35e5; % [Pa] applied pressure difference

% FLUID PROPERTIES
rhoF=1000; % [kg/m^3] feed density
rhoD=1030; % [kg/m^3] draw density
vF=0.001; % [Pa*s] feed viscosity
vD=0.001; % [Pa*s] draw viscosity

% MEMBRANE MODULE
```

```

l=0.107;% [m] membrane length
w=0.039; % [m] membrane width
a=w*l; % [m2] membrane area
t=0.0023; % [m] channel height
tshim=0.0014986; % [m] shim thickness
heff=t-tshim; % [m] effective channel height
pspacer=0.89; % [unitless] spacer porosity ...based on
what? this should be available from Sterlitech...
dD=2*heff; % [m] draw hydraulic diameter
dF=4*pspacer/((2/heff)+((1-pspacer)*(8/heff)));% [m] feed
hydraulic diameter

% MEMBRANE PROPERTIES
Almh=0.418; % [l/m2/h/bar] water permeability
A=Almh/10^5/1000/3600; % [m^3/s/m^2/Pa] water permeability
Blmh=1.125; % [l/m2/h] salt permeability
B=Blmh/1000/3600; % [m^3/s/m^2] salt permeability
S=0.000496147; % [m] structure parameter

% SOLVE BATCH PROCESS AT t=1
deltat=60*30; % [s] time step
tt=3*24*60*60/deltat; % range of variable
for t=1:tt; % variable
ts(1)=deltat; % [s] time
ts(t+1)=t*deltat; % [s] time
th(1)=ts(1)/60/60; % [h] time
th(t+1)=ts(t+1)/60/60; % [h] time

% DEFINE FLOW AT t=1
mFt(1)=mFo; % [kg] feed solute mass
mDt(1)=mDo; % [kg] draw solute mass
VFt(1)=VFo; % [m^3] feed volume
VDt(1)=VDo; % [m^3] draw volume
cFt(1)=cFo; % [kg/m^3] feed concentration
cDt(1)=cDo; % [kg/m^3] draw concentration

% REDEFINE FLOW
mF=mFt(1); % [kg] feed solute mass
mD=mDt(1); % [kg] draw solute mass
VF=VFt(1); % [m^3/s] feed volume
VD=VDt(1); % [m^3/s] draw volume
cF=cFt(1); % [kg/m^3] feed concentration
cD=cDt(1); % [kg/m^3] draw concentration

% BOUNDARY LAYERS
uF=VFdot/heff/w/pspacer; % [m/s] feed velocity

```

```

uD=VDdot/heff/w; % [m/s] draw velocity
ReF=dF*uF*rhoF/vF; % [unitless] feed Reynolds
ReD=dD*uD*rhoD/vD; % [unitless] draw Reynolds
DF=6.725e-6*exp(1.546e-4*cF-2513/T); % [m^2/s] feed
diffusion
DD=9.04e-10;
ScF=vF/rhoF/DF; % [unitless] feed Schmidt
ScD=vD/rhoD/DD; % [unitless] draw Schmidt
ShF=0.46*ReF^0.36*ScF^0.36; % [unitless] feed Sherwood
ShD=1.85*ReD^0.33*ScD^0.33*(dD/l)^0.33; % [unitless] draw
Sherwood
kF=ShF*DF/dF; % [m/s] feed diffusion transfer coefficient
kD=ShD*DD/dD; % [m/s] draw diffusion transfer coefficient
yF=DF/kF; % [m] feed boundary thickness
yD=DD/kD; % [m] draw boundary thickness

% SOLVE CONCENTRATION PROFILE
    dcguess(1)=cDo-cFo; % [kg/m^3] guess concentration
    for n=1:1:1000000; % [unitless] iterations for
numerical solution of system of equations
        dOn(n)=i*R*T*dcguess(n)/M; % [Pa] osmotic pressure
difference
        Jwn(n)=A*(dOn(n)-dp); % [m^3/(m^2*s)] water permeate
flux
        dcn(n)=(cD*exp(-Jwn(n)*yD/DD)-
cF*exp((S+yF)*Jwn(n)/DF))/(1+B/Jwn(n)*(exp((S+yF)*Jwn(n)/DF)
)-exp(-Jwn(n)*yD/DD)); % [kg/m^3] effective concentration
difference
        if (abs(dcguess(n)-dcn(n))>0.1);
            dcguess(n+1)=dcguess(n)-0.01;
        else
            break
        end
    end

% EFFECTIVE RESULTS GIVEN POLARIZATION EFFECT
dO=dOn(n); % [Pa] effective osmotic pressure difference
Jw=Jwn(n); % [m^3/s/m^2] effective water permeate flux
dc=dcguess(n); % [kg/m^3] effective salinity difference
cFS=(cF+B*dc/Jw)*exp(Jw*yF/DF)-B*dc/Jw; % [kg/m^3]
concentration at feed side of support structure
cFm=(cF+B*dc/Jw)*exp(Jw*(S+yF)/DF)-B*dc/Jw; % [kg/m^3]
concentration at feed side of membrane
cDm=(cD+B*dc/Jw)*exp(-Jw*yD/DD)-B*dc/Jw; % [kg/m^3]
concentration at draw side of membrane
dcm=cDm-cFm; % [kg/m^3] check concentration difference

```

```

% BASED ON SOLUTION DEFINE VALUES FOR t=1

% REDEFINE BOUNDARY LAYERS
uFt(1)=uF; % [m/s] feed velocity
uDt(1)=uD; % [m/s] drauFw velocity
ReFt(1)=ReF; % [unitless] feed Reynolds
ReDt(1)=ReD; % [unitless] draw Reynolds
DFt(1)=DF; % [m^2/s] feed diffusion
DDt(1)=DD; % [m^2/s] draw diffusion
ScFt(1)=ScF; % [unitless] feed Schmidt
ScDt(1)=ScD; % [unitless] draw Schmidt
ShFt(1)=ShF; % [unitless] feed Sherwood
ShDt(1)=ShD; % [unitless] draw Sherwood
kFt(1)=kF; % [m/s] feed diffusion transfer coefficient
kDt(1)=kD; % [m/s] draw diffusion transfer coefficient
yFt(1)=yF; % [m] feed boundary thickness
yDt(1)=yD; % [m] draw boundary thickness

% OUTPUT RESULTS
Jwt(1)=Jw; % [m^3/s/m^2] water permeate flux
Jwlmh(1)=Jw*1000*3600; % [l/m^2/h] water permeate flux
deltaV(1)=Jw*a*deltat; % [m^3] water permeate volume
Vt(1)=deltaV(1); % [m^3] cumulative water permeate volume
phit(1)=Vt(1)/VFo; % [unitless] recovery ratio

Wdott(1)=Jw*dp; % [W/m^2] power density
deltaE(1)=Wdott(1)*a*deltat; % [J] energy recovered
Et(1)=deltaE(1); % [J] cumulative energy recovery

Jst(1)=B*dc; % [kg/s] salt permeate flux
deltam(1)=B*dc*a*deltat; % [kg] salt permeate mass

dct(1)=dc; % [kg/m^3] effective concentration difference
dcmt(1)=dcm; % [kg/m^3] check concentration difference
dOt(1)=dO; % [Pa] effective osmotic pressure difference
cFSt(1)=cFS; % [kg/m^3] concentration at feed side of
support structure
cFmt(1)=cFm; % [kg/m^3] concentration at feed side of
membrane
cDmt(1)=cDm; % [kg/m^3] concentration at draw side of
membrane

% SOLVE CONCENTRATION POLARIZATION AT t=2

% FLOW PARAMETERS FOR i=2

```

```

mFt(2)=mFt(1)+deltam(1); % [kg] feed salt mass
mDt(2)=mDt(1)-deltam(1); % [kg] draw salt mass
VFt(2)=VFt(1)-deltaV(1); % [m^3] feed volume
VDt(2)=VDt(1)+deltaV(1); % [m^3] draw volume
cFt(2)=mFt(2)/VFt(2); % [kg/m^3] feed concentration
cDt(2)=mDt(2)/VDt(2); % [kg/m^3] draw concentration

% REDEFINE FLOW PARAMETERS
mF=mFt(t+1); % [kg] feed salt mass
mD=mDt(t+1); % [kg] draw salt mass
VF=VFt(t+1); % [m^3] feed volume
VD=VDt(t+1); % [m^3] draw volume
cF=cFt(t+1); % [kg/m^3] feed concentration
cD=cDt(t+1); % [kg/m^3] draw concentration

% BOUNDARY LAYERS
uF=VFdot/heff/w/pspacer; % [m/s] feed velocity
uD=VDdot/heff/w; % [m/s] draw velocity
ReF=dF*uF*rhoF/vF; % [unitless] feed Reynolds
ReD=dD*uD*rhoD/vD; % [unitless] draw Reynolds
DF=6.725e-6*exp(1.546e-4*cF-2513/T); % [m^2/s] feed
diffusion
DD=9.04e-10;
ScF=vF/rhoF/DF; % [unitless] feed Schmidt
ScD=vD/rhoD/DD; % [unitless] draw Schmidt
ShF=0.46*ReF^0.36*ScF^0.36; % [unitless] feed Sherwood
ShD=1.85*ReD^0.33*ScD^0.33*(dD/1)^0.33; % [unitless] draw
Sherwood
kF=ShF*DF/dF; % [m/s] feed diffusion transfer coefficient
kD=ShD*DD/dD; % [m/s] draw diffusion transfer coefficient
yF=DF/kF; % [m] feed boundary thickness
yD=DD/kD; % [m] draw boundary thickness

% SOLVE CONCENTRATION PROFILE
dcguess(1)=cDo-cFo; % [kg/m^3] guess concentration
for n=1:1:1000000; % [unitless] iterations for
numerical solution of system of equations
dOn(n)=i*R*T*dcguess(n)/M; % [Pa] osmotic pressure
difference
Jwn(n)=A*(dOn(n)-dp); % [m^3/(m^2*s)] water permeate
flux
dcn(n)=(cD*exp(-Jwn(n)*yD/DD)-
cF*exp((S+yF)*Jwn(n)/DF))/(1+B/Jwn(n)*(exp((S+yF)*Jwn(n)/DF)
)-exp(-Jwn(n)*yD/DD)); % [kg/m^3] effective concentration
difference
if (abs(dcguess(n)-dcn(n))>0.1);

```

```

    dcguess(n+1)=dcguess(n)-0.01;
else
break
end
end

% EFFECTIVE RESULTS GIVEN POLARIZATION EFFECT
dO=dOn(n); % [Pa] effective osmotic pressure difference
Jw=Jwn(n); % [m^3/(m^2*s)] effective freshwater permeate
flux
dc=dcguess(n); % [kg/m^3] effective salinity difference
cFS=(cF+B*dc/Jw)*exp(Jw*yF/DF)-B*dc/Jw; % [kg/m^3]
concentration at feed side of support structure
cFm=(cF+B*dc/Jw)*exp(Jw*(S+yF)/DF)-B*dc/Jw; % [kg/m^3]
concentration at feed side of membrane
cDm=(cD+B*dc/Jw)*exp(-Jw*yD/DD)-B*dc/Jw; % [kg/m^3]
concentration at draw side of membrane
dcm=cDm-cFm; % [kg/m^3] check concentration difference

% BASED ON SOLUTION DEFINE VALUES FOR i=t+1

% REDEFINE BOUNDARY LAYERS
uFt(t+1)=uF; % [m/s] feed velocity
uDt(t+1)=uD; % [m/s] draw velocity
ReFt(t+1)=ReF; % [unitless] feed Reynolds
ReDt(t+1)=ReD; % [unitless] draw Reynolds
DFt(t+1)=DF; % [m^2/s] feed diffusion
DDt(t+1)=DD; % [m^2/s] draw diffusion
ScFt(t+1)=ScF; % [unitless] feed Schmidt
ScDt(t+1)=ScD; % [unitless] draw Schmidt
ShFt(t+1)=ShF; % [unitless] feed Sherwood
ShDt(t+1)=ShD; % [unitless] draw Sherwood
kFt(t+1)=kF; % [m/s] feed diffusion transfer coefficient
kDt(t+1)=kD; % [m/s] draw diffusion transfer coefficient
yFt(t+1)=yF; % [m] feed boundary thickness
yDt(t+1)=yD; % [m] draw boundary thickness

% OUTPUT RESULTS
Jwt(t+1)=Jw; % [m^3/m^2/s] water permeate flux
Jwlmh(t+1)=Jw*1000*3600; % [l/m^2/h] water permeate flux
deltaV(t+1)=Jw*a*deltat; % [m^3] water permeate volume
Vt(t+1)=Vt(t)+deltaV(t+1); % [m^3] cumulative water
permeate volume
phit(t+1)=Vt(t+1)/VFo; % [unitless] recovery ratio

Wdott(t+1)=Jw*dp; % [W/m^2] power density

```

```

deltaE(t+1)=Jw*dp*a*deltat; % [J] energy recovered
Et(t+1)=Et(t)+deltaE(t+1); % [J] cumulative energy recovery

Jst(t+1)=B*dc; % [kg/m^2/s] salt permeate flux
deltam(t+1)=B*dc*a*deltat; % [kg] salt permeate mass

dct(t+1)=dc; % [kg/m^3] effective concentration difference
dcmt(t+1)=dcm; % [kg/m^3] check concentration difference
dOt(t+1)=dO; % [Pa] effective osmotic pressure difference
cFSt(t+1)=cFS; % [kg/m^3] concentration at feed side of
support structure
cFmt(t+1)=cFm; % [kg/m^3] concentration at feed side of
membrane
cDmt(t+1)=cDm; % [kg/m^3] concentration at draw side of
membrane

% FLOW PARAMETERS FOR i=t+2
mFt(t+2)=mFt(t+1)+deltam(t+1); % [kg] feed salt mass
mDt(t+2)=mDt(t+1)-deltam(t+1); % [kg] draw salt mass
VFt(t+2)=VFt(t+1)-deltaV(t+1); % [m^3/s] feed volume
VDt(t+2)=VDt(t+1)+deltaV(t+1); % [m^3/s] draw volume
cFt(t+2)=mFt(t+2)/VFt(t+2); % [kg/m^3] feed concentration
cDt(t+2)=mDt(t+2)/VDt(t+2); % [kg/m^3] draw concentration

% REDEFINE FLOW PARAMETERS
mF=mFt(t+2); % [kg] feed salt mass
mD=mDt(t+2); % [kg] draw salt mass
VF=VFt(t+2); % [m^3] feed volume
VD=VDt(t+2); % [m^3] draw volume
cF=cFt(t+2); % [kg/m^3] feed concentration
cD=cDt(t+2); % [kg/m^3] draw concentration

end

xlswrite('K1cta.xls', th, 'Sheet 1', 'b1')
xlswrite('K1cta.xls', Jwlmh, 'Sheet 1', 'b2')
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4.8 List of Symbols in Chapter 4

A	membrane water permeability ($\text{m s}^{-1} \text{Pa}^{-1}$)
a	membrane surface area (m^2)
B	membrane salt permeability (m s^{-1})
c	concentration (g l^{-1})
D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
d_h	hydraulic diameter (m)
G	Gibbs energy (J)
i	number of ions
J_w	permeate flux ($\text{l m}^{-2} \text{s}^{-1}$)
J_s	solute flux ($\text{g m}^{-2} \text{s}^{-1}$)
k	diffusion transfer coefficient (m s^{-1})
m	mass (kg)
$\dot{m}$	mass flow rate (kg s^{-1})
p	pressure (Pa)
R	gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
Re	Reynolds number
S	structure parameter (m)
Sc	Schmidt number
Sh	Sherwood number
R	gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
T	absolute temperature (K)
V	volume (m^3)
W	work (J)
$\dot{W}$	power (W)

Greek symbols:

π	osmotic pressure (Pa)
δ	boundary layer thickness (m)
θ	recovery ratio

Subscripts/Superscripts:

D	draw
F	feed
o	initial
'	osmotic limit
*	constant pressure limit
**	practical limit

4.9 Acknowledgments

This work was funded by the Michigan Space Grant Consortium, NASA grant #NNX15AJ20H.

CHAPTER FIVE

USING FERTILIZER TO PRODUCE CLEAN FERTIGATION SOLUTION FROM WASTEWATER VIA FORWARD OSMOSIS

5.1 Original Publication

Chapter Five is based primarily on a journal paper that has been submitted to the Journal of Membrane Science and is currently under review. This paper addresses an important gap in the literature, which has so far not adequately addressed the question of how significant the water permeate volumes are that can be recovered from fertilizer osmosis. A complete reference for the published work is as follows:

P. Pourmovahed, M. Lefsrud and J. Maisonneuve, “Thermodynamic Limits of Using Fertilizer to Produce Clean Fertigation Solution from Wastewater via Forward Osmosis” Journal of Membrane Science, revisions submitted 11/2021.

5.2 Introduction

In this chapter, we investigate the concept of water recovery via fertilizer-driven osmosis, a process that has the potential to both improve the efficiency of fertilizer use, and to reduce the fresh water footprint of crops. The fertilizer-driven osmosis concept (referred to hereafter as ‘fertilizer osmosis’) is illustrated in Figure 5.1. In this process, a concentrated fertilizer solution is used to draw clean water permeate through a semi-permeable membrane from a lower concentration wastewater feed stream. The result is a

clean and diluted fertilizer product that can be delivered to plants to provide essential nutrients and hydration. The separation of clean water permeate from the wastewater feed is spontaneous, and therefore the fertilizer osmosis process is energy efficient, requiring only minimal work to circulate fluids across the membrane surface. For example, electricity consumption of as little as 0.01 kWh per m³ of water recovery has been reported for a brackish feed source [69].

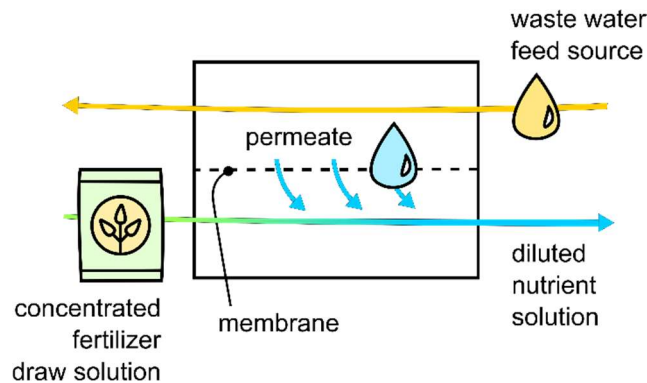


Figure 5.1. In fertilizer driven FO, a concentrated fertilizer solution is used to draw water permeate across a semi-permeable membrane. The product is a diluted fertilizer solution that can be delivered directly to plants without any additional treatment.

Although the concept of fertilizer osmosis was proposed a decade ago [20], and has been studied by several research groups since [8,10,27,28,31,34,35,43,45–47,60,70,72–74,98–104], there remain fundamental questions about how much water can be recovered from batch operations, and how significant recovery volumes are relative to the overall water balance of crops. In their first publication on the fertilizer osmosis concept, Phuntsho et al. [20] suggested that up to 60 l of water permeate per kg of fertilizer solute would be theoretically required to establish equilibrium with a brackish

feed source. Since this initial estimate, very few publications have reported water recovery volumes per unit fertilizer mass. El Zayat et al. [104] mention briefly that their laboratory testing demonstrated nearly 5 l/kg recovered from desalination brine. Other publications report total recovery volumes from a given batch process, but not the normalized water recovery per unit fertilizer input. In some cases we can carefully scrutinize reported test conditions to normalize performance over input parameters and based on this we estimate that a wide range between 4 and 96 l/kg has so far been experimentally obtained and reported in the literature [31,45–47,70,71], but in most publications insufficient detail makes it impossible to normalize and interpret results. The lack of systematic analysis of water recovery per unit fertilizer means that it is as yet unclear how successful current experimental tests have been. It is necessary to establish the fundamental thermodynamic and transport limits of fertilizer osmosis as a baseline for future analysis, as well as for a proper understanding of what fertilizer osmosis potential means to sustainable agriculture.

In this chapter, we establish (1) the fundamental thermodynamic limits to fertilizer osmosis that are imposed by osmotic equilibrium, (2) the practical limitations that are imposed by the need to maintain competitive flux levels, and (3) the effect that non-ideal transport dynamics such as reverse solute flux and concentration polarization have on flux and therefore water recovery limits. To do this, we describe a series of analytical, numerical, and experimental tools that can be applied to fertilizer osmosis, as well as other membrane-based batch process analysis. The water recovery limits of a selection of common fertilizers, and the significance of these limits to water recovery for a number of hydroponic crops is established.

5.3 Thermodynamic Analysis

5.3.1 Equilibrium Limits of Water Recovery from Fertilizer Osmosis

The thermodynamic limit to water recovery from fertilizer osmosis is defined by osmotic equilibrium. Figure 5.2 illustrates the fertilizer osmosis process and shows that as a volume of water permeate is recovered across the membrane, the fertilizer draw solution expands and is diluted. The result is a drop in the osmotic pressure difference between draw and feed and ultimately, the establishment of equilibrium at which point the limit to water recovery is defined.

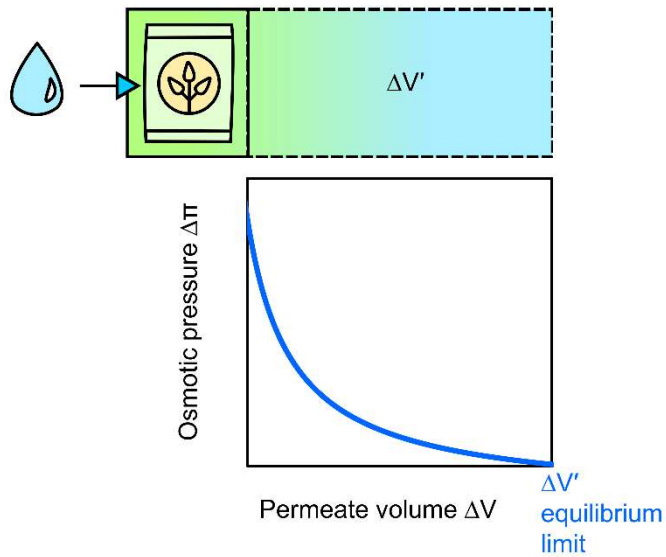


Figure 5.2. The thermodynamic limit to water recovery from fertilizer osmosis is defined by osmotic equilibrium at which point the permeate volume $\Delta V = \Delta V'$ and the osmotic pressure difference between wastewater feed and fertilizer draw $\Delta\pi = \pi_D - \pi_F = 0$.

An exact solution for the equilibrium permeate volume can be obtained analytically by assuming ideal behavior of the feed and draw solutions. With this

assumption, the osmotic pressure π of each solution is described as the inverse function of permeate volume ΔV (Supplementary Note 5.1 for detailed derivation) [103].

$$\pi_F = \pi_F^o \frac{V_F^o}{V_F^o - \Delta V} \quad (5.1)$$

$$\pi_D = \pi_D^o \frac{V_D^o}{V_D^o + \Delta V} \quad (5.2)$$

Where V_F^o and V_D^o are the initial feed and draw volumes, and π_F^o and π_D^o are the initial osmotic pressures.

Given that equilibrium is established when the osmotic pressure difference between feed and draw equals zero, a solution for the equilibrium volume $\Delta V'$ can be obtained from equations (5.1) and (5.2), which is normalized here per unit mass of fertilizer m_D^o (Supplementary Note 5.1 for detailed derivation).

$$\frac{\Delta V'}{m_D^o} = \frac{1}{c_D^o} \left(\frac{\pi_D^o}{\pi_F^o} (1 - \theta') - 1 \right) \quad (5.3)$$

Where c_D^o is the initial concentration of the fertilizer, and θ' is the recovery ratio at equilibrium. In general, the recovery ratio is defined as the permeate volume relative to the initial feed volume $\theta = \Delta V / V_F^o$, and therefore the equilibrium recovery ratio is a measure of the feed volume that is made available for the fertilizer osmosis process.

To illustrate the equilibrium limits of fertilizer osmosis, consider common N, P, K fertilizers calcium nitrate $\text{Ca}(\text{NO}_3)_2$, monoammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$, and potassium chloride KCl . A summary of these fertilizer draw solutions and their properties is provided in Table 5.1. While activity coefficients of fertilizer solutions may deviate from unity, especially for very concentrated solutions, error from the assumption of unity

will be minimal. An inspection of equation (5.3) reveals that the activity coefficients of feed and draw are only expressed as a ratio of one to another. Additional discussion related to activity is provided in Supplementary Note 1.

Table 5.1. Fertilizer draw and wastewater feed solution chemistry.

Concentrated Fertilizer Draw Solution			
	Calcium nitrate $\text{Ca}(\text{NO}_3)_2$	Monoammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$	Potassium chloride KCl
Solubility c_D° (g/l)	1212	374	342
Molar mass (g/mol)	164	115	75
Activity coefficient γ	1	1	1
Number of ions i	3	2	2

Figure 5.3 shows the osmosis process for each of the fertilizer draw solutions as they recover water permeate from a feed source that approximates municipal wastewater with a sodium chloride NaCl concentration $c_F^\circ = 0.16$ g/l, and with sufficient feed volume so that equilibrium recovery ratio $\theta' = 75$ %. As shown, potential for water recovery per unit fertilizer $\Delta V'/m_D^\circ$ ranges from 790 – 1220 l/kg, with the greatest potential among the three sample fertilizers shown for KCl. This is due largely to the fact that equilibrium $\Delta V'$ is normalized here per unit mass m_D° , and KCl happens to have the lowest molar mass M . In general, high molar solubility c_D°/M will favor a greater osmotic equilibrium point.

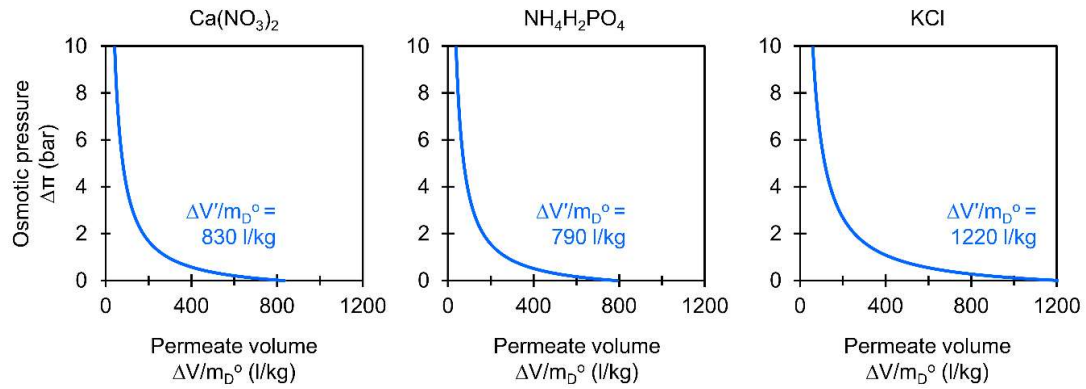


Figure 5.3. Osmotic pressure difference $\Delta\pi$ between concentrated N, P, K fertilizer draw solutions and municipal wastewater feed solution (given $c_F^\circ = 0.16$ g/l and $\theta' = 75$ %) as permeate volume ΔV is recovered by the fertilizer. Equilibrium limits are identified by $\Delta V'$ and normalized per unit mass of fertilizer m_D° .

This equilibrium limit will be largely a function of the available wastewater feed source, with its concentration and target recovery ratio. To illustrate, consider several possible feed sources including municipal wastewater [71], hydroponic wastewater [105], brackish water [28], and urine [74]. These cases are approximated by sodium chloride NaCl solutions of varying concentrations as specified in Table 5.2.

Table 5.2. Wastewater feed solution chemistry

Feed Water with Diluted Sodium Chloride NaCl				
	Municipal Wastewater [71]	Hydroponic Wastewater [105]	Brackish Water [28]	Urine [74]
Concentration c_F° (g/l)	0.16	0.25	5	15.8
Recovery ratio θ (%)	75	65	40	20
Activity coefficient γ	1	1	1	1
Number of ions i	2	2	2	2

Figure 5.4 shows the normalized equilibrium permeate volume $\Delta V'/m_D^0$ for each of the fertilizers as a function of feed concentration and recovery ratio. As shown, an increase in either of these variables significantly reduces the potential for water recovery. To illustrate, each of the four wastewater cases are highlighted. In the case where municipal wastewater is available, and given a high recovery target ($c_F^0 = 0.16$ g/l, $\theta' = 75$ %), water recovery is limited to 791 – 1221 l/kg, as shown previously in Figure 5.3. For the case where hydroponic wastewater is available, again with a high recovery target ($c_F^0 = 0.25$, $\theta' = 65$ %), water recovery is limited to 709 – 1094 l/kg. Comparing these two cases suggests that limits are much more sensitive to feed concentration than recovery ratio, since even a slight increase in concentration is shown here to produce a significant drop in the equilibrium volume, despite a decrease in the target recovery ratio. Other cases shown include water recovery from a brackish water feed source ($c_F^0 = 5$ g/l, $\theta' = 40$ %) and from a urine feed source ($c_F^0 = 15.8$ g/l, $\theta' = 20$ %), in which cases water recovery is limited to 58-91 l/kg and 24-39 L/kg respectively.

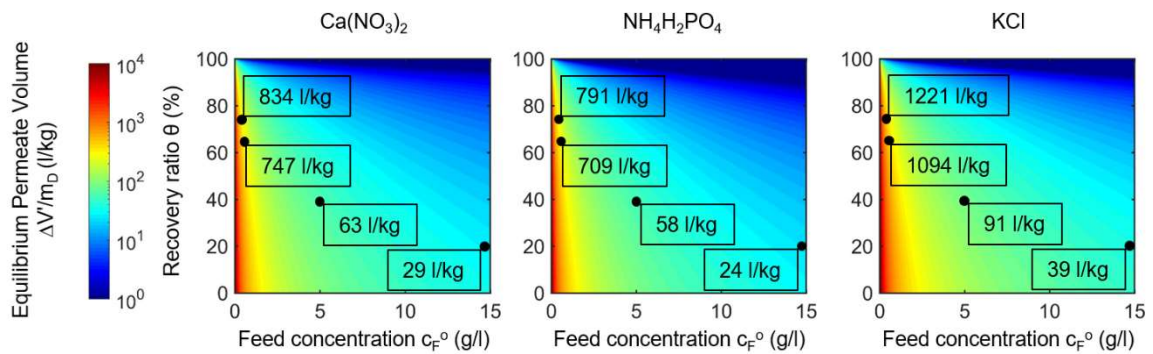


Figure 5.4. Osmotic pressure difference $\Delta\pi$ between concentrated N, P, K fertilizer draw solutions and municipal wastewater feed solution (given $c_F^0 = 0.16$ g/l and $\theta' = 75$ %) as permeate volume ΔV is recovered by the fertilizer. Equilibrium limits are identified by $\Delta V'$ and normalized per unit mass of fertilizer m_D^0

5.3.2 Limits of Water Recovery from Fertilizer Osmosis with Practical Water Flux

In addition to the water recovery limits that are imposed by osmotic equilibrium, a viable fertilizer osmosis system must recover water at practical, cost-effective rates.

Water permeate flux J_w as defined in Eq. (5.4), is a useful metric in this regard because the volume rate of water recovery $\Delta\dot{V}$ is an indicator of return on investment, while the membrane surface area a is an indicator of capital cost.

$$\frac{\Delta\dot{V}}{a} = J_w = A \Delta\pi \quad (5.4)$$

Where A is the membrane's permeability to water.

Maintaining water flux above some target for economic viability is a requirement for practical fertilizer osmosis, and this imposes a limitation on the volume of water permeate that can be practically recovered. As illustrated in Figure 5.5, the osmotic pressure difference that drives water permeate rapidly drops as volume is recovered, fertilizer draw solution is diluted, and wastewater feed is concentrated. Since membrane permeability A can be treated as a constant in response to a range of osmotic pressure differences, the drop in osmotic pressure will therefore be proportional to a drop in water flux, as illustrated in the second vertical axis in Figure 5.5. As the process nears equilibrium, the process slows and water flux approaches zero. Recovering water at such low rates is likely to be impractical. Therefore, the requirement to stop the fertilizer osmosis batch process at some minimum flux target J_w'' will impose a practical limitation on the water recovery volume $\Delta V''$.

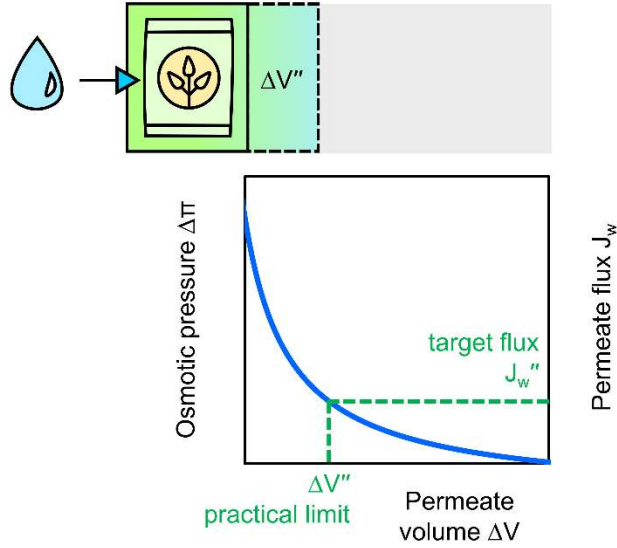


Figure 5.5. The practical limit to water recovery from fertilizer osmosis is defined by the minimum rate of water recovery that can be economically justified, which we call the target flux J_w'' , at which point the permeate volume $\Delta V = \Delta V''$.

To illustrate, Figure 5.6 shows the osmotic pressure difference between common N, P, K fertilizer draw solutions and a feed source that approximates municipal wastewater with a sodium chloride NaCl concentration $c_F^0 = 0.16$, and an equilibrium recovery ratio $\theta'' = 75\%$. The resulting water permeate flux is shown on the second y-axis, for a membrane with water permeability $A = 4.3 \text{ lmh/bar}$ [52]. Flux targets of $J_w'' = 5$ and 10 lmh are selected since these have previously been suggested for FO to be competitive with various reverse osmosis (RO) processes [106,107]. As shown, the maximum permeate volume that can be recovered is between 247 and 382 l/kg when minimum flux of 5 lmh is maintained, and between 145 and 226 l/kg when minimum flux of 10 lmh is maintained. These practical limits to water recovery are approximately one order of magnitude less than the equilibrium limits previously reported in Section 2.1.

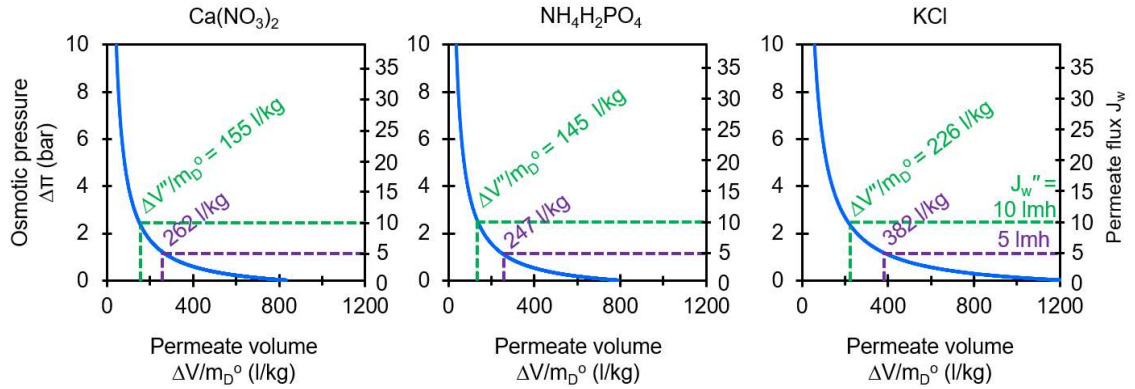


Figure 5.6. Osmotic pressure difference $\Delta\pi$ between concentrated N, P, K fertilizer draw solutions and municipal wastewater feed solution (given $c_F^0 = 0.16$ g/l and $\theta'' = 75$ %), and the resulting permeate flux J_w given a membrane permeability $A = 4.3$ lmh/bar. Practical limits to water recovery $\Delta V''$ are identified for permeate flux targets of $J_w'' = 5$ and 10 lmh.

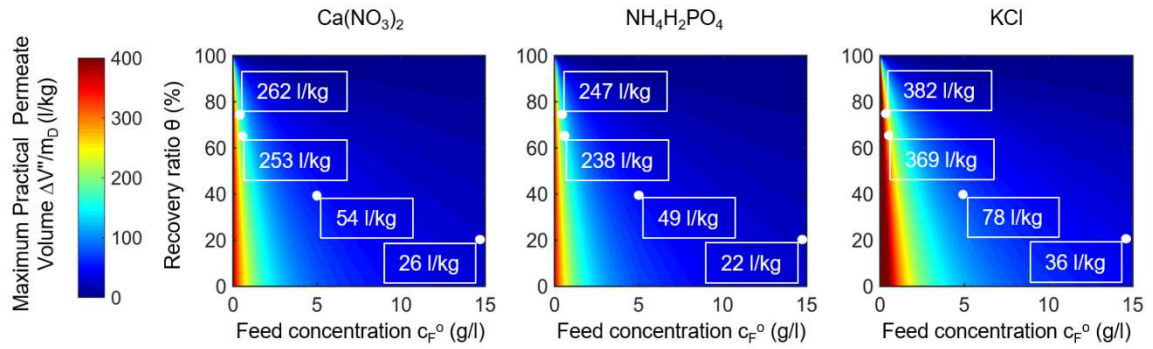
Analysis of these practical limits can be extended more generally, by considering an analytical solution for $\Delta V''$. This can be obtained by defining the minimum target flux for the process J_w'' . Then, combining equations (5.1), (5.2), and (4) we establish an expression for permeate volume $\Delta V''$ (Supplementary Note 5.2 for derivation details).

$$\frac{\Delta V''}{m_D^0} = \frac{1}{c_D^0} \left(\frac{\pi_D^0}{\frac{J_w''}{A} + \frac{\pi_F^0}{1 - \theta''}} - 1 \right) \quad (5.5)$$

Figure 5.7 shows the practical permeate limits $\Delta V''/m_D^0$ for common N, P, K fertilizer draw solutions, and wastewater feed sources with a range of concentrations and recovery ratios. Results are shown in (a) and (b) for water flux targets of $J_w'' = 5$ and 10 lmh respectively. The same wastewater sources defined previously in Table 5.2 are again highlighted here for reference. A significant drop in water recovery is observed as compared to the equilibrium limits described previously in Figure 5.4. Interestingly, this drop is much more pronounced at low feed concentrations. For example, when municipal

wastewater feed is supplied ($c_F^0 = 0.16$ g/l, $\theta'' = 75$ %) the practical recovery volume is only 20 % of the equilibrium limit. And, when brackish feed is used ($c_F^0 = 5$ g/l, $\theta'' = 40$ %) the practical recovery volume is almost 75 % of the thermodynamic limit. The reason for this more severe drop is that with such high recovery ratios, large volumes of water permeate are recovered at low flux. However once minimum flux targets are imposed, these volumes recovered at low flux become unattractive.

(a) Minimum flux target of 5 lmh



(b) Minimum flux target of 10 lmh

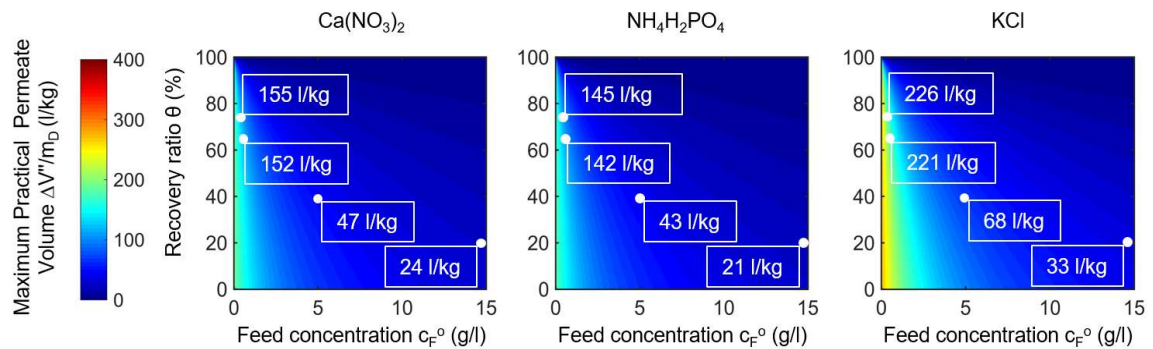


Figure 5.7. Practical limits of water recovery $\Delta V''$ per unit mass of fertilizer m_D^0 when flux is maintained at or above targets of (a) $J_w'' = 5$ lmh and (b) $J_w'' = 10$ lmh. Results are shown for N, P, K fertilizer draw solution during dilution with various feed sources c_F^0 and given various target recovery ratios θ'' as defined in Tables 5.1 and 5.2.

5.4 Transport Analysis

5.4.1 Numerical Methods

Driving fertilizer osmosis at target recovery rates is additionally challenging because of non-ideal transport dynamics that reduce flux. These include leakage of fertilizer across the imperfectly selective membrane, and accumulation of solutes in the membrane support structure and boundary layers. The result is a reduction in the effective concentration difference across the membrane, and hence a lower osmotic driving force. To evaluate the significance of these effects, key transport dynamics are introduced in this section, and a numerical model is used to simulate fertilizer osmosis across a range of conditions.

The proposed model uses a mass balance approach to describe concentration variations in a 2-dimensional space that is normal and tangent to the flat sheet membrane surface. A similar modelling approach has been described in elsewhere [52,86,87]. Governing equations describing water and solute transport across the membrane and its boundary layers are numerically solved at each instant of the batch process, as fertilizer and wastewater are recirculated through the membrane module.

Osmosis across the membrane is defined as previously stated in eq. (5.4). Diffusion of fertilizer solute $\Delta\dot{m}$ across the membrane is normalized per unit membrane area, and defined as solute flux J_s .

$$\frac{\Delta\dot{m}}{a} = J_s = B \Delta c \quad (5.6)$$

Where B is the membrane solute permeability and Δc is the effective concentration difference across the membrane. This concentration difference is much less than the difference between the bulk fertilizer draw solution and the wastewater feed source, and can be analytically evaluated by considering polarization across the membrane.

Concentration polarization across the membrane internal support layer and external boundary layers can be described by considering solute transport across each of these layers, which is defined by the difference between convection (driven by water flux J_w), and diffusion (driven by the concentration gradient in the normal direction n).

$$\frac{\Delta \dot{m}}{a} = J_s = D \frac{dc}{dn} - J_w c \quad (5.7)$$

Taking Eqs. (5.6) and (5.7), an exact solution can be obtained for the effective concentration difference across the membrane (Supplementary Note 5.3 for detailed derivation).

$$\Delta c = \frac{c_D \exp\left(-J_w \frac{\delta_D + S}{D}\right) - c_F \exp\left(J_w \frac{\delta_F}{D}\right)}{1 + \frac{B}{J_w} \left(\exp\left(J_w \frac{\delta_F}{D}\right) - \exp\left(-J_w \frac{\delta_D + S}{D}\right) \right)} \quad (5.8)$$

Where D is the solute diffusion coefficient, S is the membrane structure parameter, and $\delta = D / k$ is the thickness of boundary layers at the membrane surface. Where $k = Sh D / d_h$ is the diffusion transfer coefficient which can be calculated as a function of the Sherwood number Sh and the hydraulic diameter d_h . In this case, expressions for Sh are selected for flat sheet spacer filled channels, as listed in Table 5.3.

Table 5.3. Input parameters for fertilizer osmosis batch process simulations.

<i>Membrane and module parameters</i>				
Membrane area a (length $l \times$ width w)	0.0042 m ² (0.107 m $\times$ 0.039 m)			
Channel depth	0.0008 m			
Hydraulic diameter d_h , feed draw	0.0010 m 0.0016 m			
	CTA FO membrane		TFC FO membrane	
Water permeability A	experimentally obtained (see Figure 5.8)			
Solute permeability B				
Structure parameter S				
<i>Fertilizer draw parameters</i>				
Flow rate Velocity	275 lpm 0.147 m/s			
Sherwood number Sh	$Sh = 1.85 \text{ Re}^{1/3} \text{ Sc}^{1/3} (d_h / l)^{1/3}$ [88]			
	Calcium nitrate $\text{Ca}(\text{NO}_3)_2$	Monoammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$	Potassium chloride KCl	
Initial concentration c_D^o (g/l)	1212	374	342	
Diffusivity D ($\times 10^{-10}$ m ² /s)	5.10	6.70	9.04	
<i>Feed source parameters</i>				
Flow rate Velocity	275 lpm 0.165 m/s			
Sherwood number Sh	$Sh = 0.46 \text{ Re}^{0.36} \text{ Sc}^{0.36}$ [88]			
	Municipal wastewater [71]	Hydroponic wastewater [105]	Brackish water [28]	Urine [74]
Initial concentration c_F^o (g/l)	0.16	0.25	5	15.8
Recovery ratio θ (%)	75	65	40	20

Simulations were run for several scenarios, including a variety of common fertilizers and wastewater feed sources. A summary of simulation parameters is provided in Table 5.3. Feed concentrations were approximated by sodium chloride NaCl solutions as specified.

Two commercial semi-permeable membranes were selected for this study including asymmetric cellulose triacetate (CTA) FO membranes supplied by FTS H₂O (Albany, OR) and polyamide thin film composite (TFC) FO membranes supplied by

Porifera (Hayward, CA). The transport model was calibrated with characteristic membrane parameters that were experimentally measured in our laboratory following standard procedures [89]. Results are shown in Figure 8. A comparison of the two membranes is intended to provide some indication of permeability and selectivity tradeoffs in fertilizer osmosis applications.

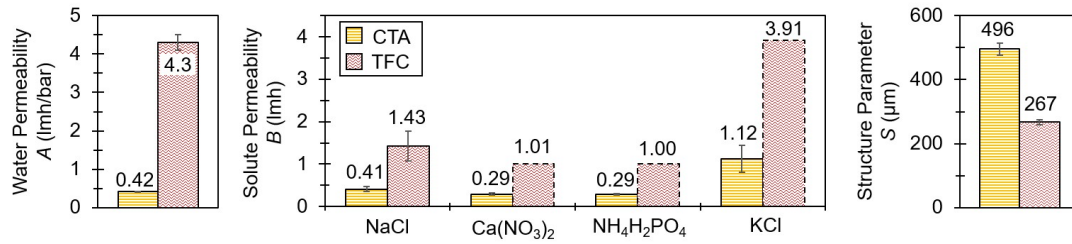


Figure 5.8. Characteristic parameters for asymmetric cellulose triacetate (CTA) and polyamide thin film composite (TFC) were obtained in laboratory experiments at Oakland University following standard test methods [52,89].

5.4.2 Simulation Results

Throughout the fertilizer osmosis batch process, fertilizer draw solution is diluted as water permeate is recovered from the wastewater feed source. The result is a drop in the potential gradient that drives osmosis, and therefore a diminishing rate of water recovery that can be observed with respect to time. Figure 5.9 shows simulation results illustrating these batch process dynamics with respect to time, with three sample fertilizers that are recirculated across a CTA membrane opposite a municipal wastewater feed source (i.e. $c_F^0 = 0.16$ and $\theta'' = 75\%$). In this figure, time is plotted on the x-axis and is normalized with respect to membrane area, and although dynamics will not exactly scale linearly with module size, this normalization nonetheless allows the results to be interpreted more generally. As shown, permeate flux J_w drops as permeate volume

$\Delta V/m_D^0$ is recovered, and between 50-130 l/kg is obtained before equilibrium is finally reached. However, if water flux must be maintained above a practical target such as 5 l/mh, only 8-15 l/kg of water permeate can be recovered. This is significantly less than the range of 247-382 l/kg that was suggested for the same scenarios in Section 2.2., where ideal transport dynamics were assumed. This drop is due to severe internal and external polarization across the membrane support structure and boundary layers, which reduce the effective concentration difference across the active membrane layer to one order of magnitude less than the bulk concentration difference. A detailed analysis of polarization profiles is provided in Supplementary Note 5.3. This confirms the importance of considering non-ideal transport dynamics when evaluating the water recovery limits of fertilizer osmosis, and suggests that mitigation of non-ideal dynamics is critical for water recovery potential to be realized.

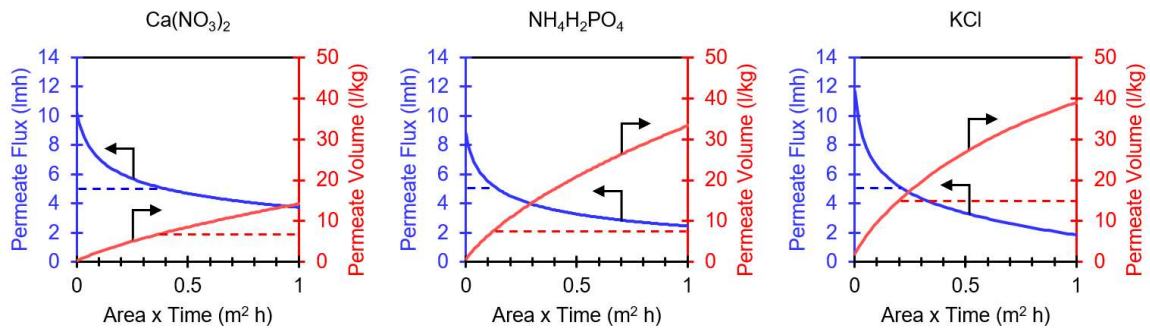


Figure 5.9. Simulated transport results showing the fertilizer osmosis batch process in which concentrated N, P, and K fertilizers are used to recover water permeate from municipal wastewater feed as a function of time and membrane area. Fertilizer properties, wastewater properties, and other simulation parameters are summarized in Table 5.3. CTA membrane specifications are provided in Figure 5.8.

This numerical analysis is extended to additional scenarios, including for both CTA and TFC membranes, and for several wastewater feed sources. Figure 5.10 provides

a summary of the simulation results, showing the drop in water recovery rates as water permeate volume is accumulated. For reference the flux target of $J_w'' = 5 \text{ lmh}$ is labelled. Comparing results in Figures 5.10 (a) and (b) respectively, illustrates the importance of carefully selecting membranes for application to fertilizer osmosis.

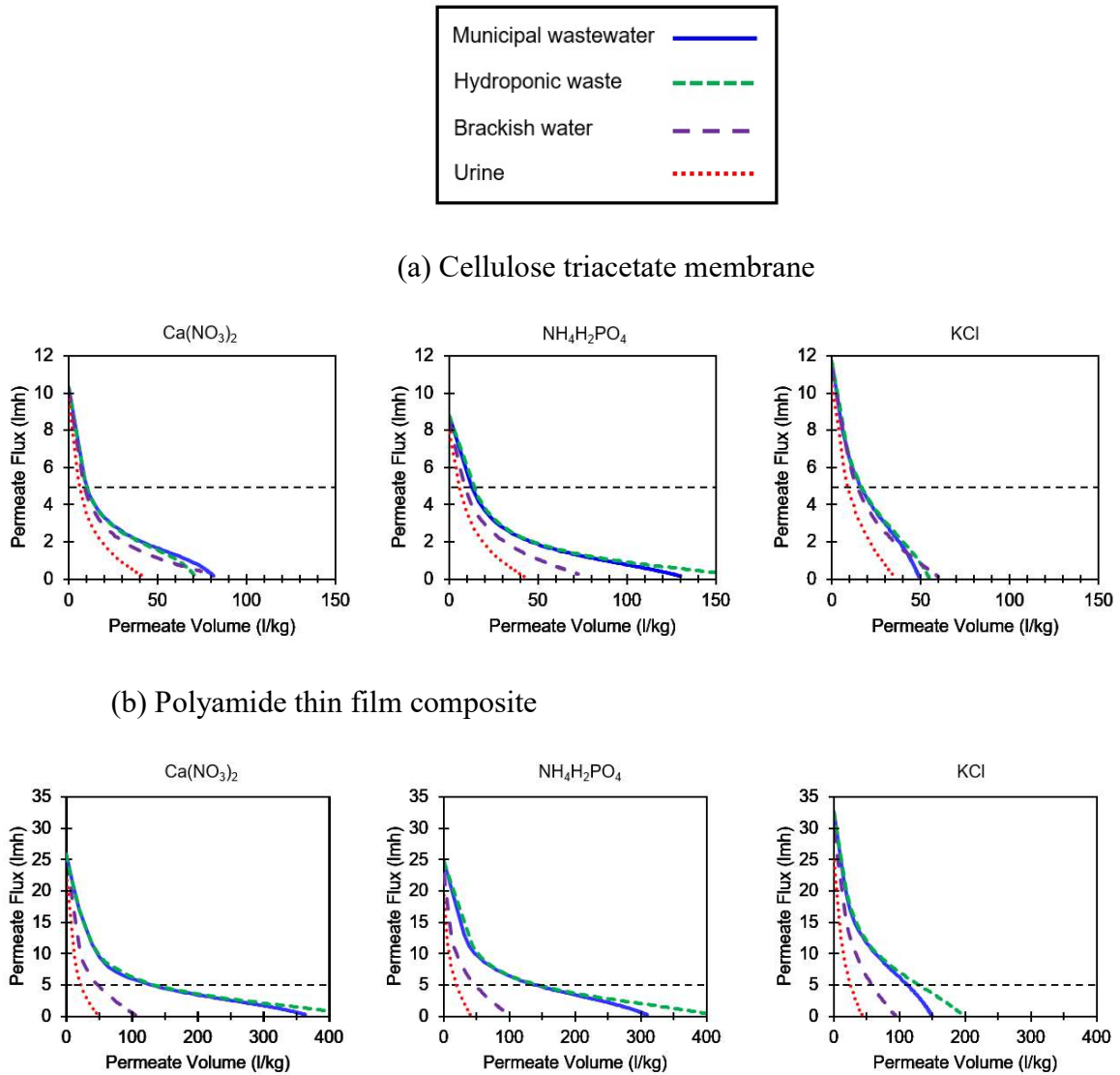


Figure 5.10. Simulated transport results showing permeate flux and volume throughout the fertilizer osmosis batch process for (a) asymmetric cellulose triacetate (CTA) FO membranes supplied by FTS H2O and (b) polyamide thin film composite (TFC) FO membranes supplied by Porifera. Fertilizer properties, wastewater properties, and other simulation parameters are summarized in Table 5.3.

As shown, water permeate rates with the CTA membrane remain low throughout the batch process, and quickly drops below the minimum water flux, limiting water recovery to 7-19 l/kg for the various wastewater sources. Poor performance is attributed primarily to the low water permeability and relatively high structure parameter which exacerbates polarization, as were reported in Figure 5.8. These outweigh any benefits of the membrane's low solute permeability. Results from the highly permeable TFC FO membrane are more promising. Between 112-143 l/kg is recovered from the diluted feed sources such as municipal and hydroponic wastewater before flux drops below practical rates of 5 lmh. The importance of balancing characteristic membrane properties is well documented for other membrane processes [108–110], and should be carefully considered for effective fertilizer osmosis.

5.5. Discussion

5.5.1 Water Recovery Potential of Common Fertilizers

The water recovery limits of common fertilizer draw solutions and a variety of wastewater feed sources are summarized in Figure 5.11. These limits include the thermodynamic limit imposed by osmotic equilibrium, the practical limit imposed by requirements to maintain flux of at least 5 or 10 lmh, and finally the predicted water recovery based on simulation of a fertilizer osmosis batch process with non-ideal transport dynamics.

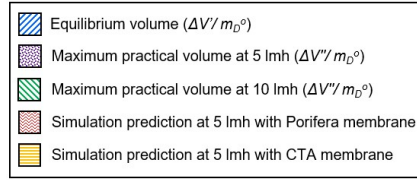
As shown in (a) and (b), on the order of 1000 l of water permeate per kg of fertilizer establishes osmotic equilibrium with modest wastewater feed sources such as municipal and hydroponic waste. This drops off severely though as feed concentration is

increased, such that equilibrium requires less than 100 l/kg with brackish water and urine feed sources, as shown in (c) and (d).

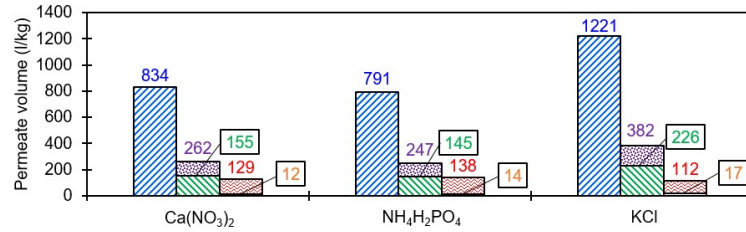
The requirement to maintain practical flux is also shown to severely limit water recovery volumes. This is especially true when high recovery ratios are desired (i.e. feed volume is limited with respect to permeate volume). For example, in cases (c) and (d), where recovery ratios are less than 50 %, we see only a minor drop from the equilibrium limit down to the practical limit, but in cases (a) and (b) where recovery ratios are much higher, the drop in water recovery volumes is almost 2/3. This is further exacerbated by non-ideal transport dynamics including severe polarization (documented in Supplementary Note 5.3). The resulting drop in flux makes additional volumes of water recovery impractical, especially in scenarios where high recovery ratios are desired. Figures 5.11 (a) and (b) illustrate this most obviously as we see a big drop from the practical water recovery volumes, to the predicted volumes from non-ideal simulation.

The importance of selecting high-performance membranes is also clearly shown. For example, up to a 10-fold difference in water recovery volumes is observed by comparing simulation results with CTA and TFC membranes. This difference is associated with the favorable water permeability, solute selectivity, and thin support layer of the TFC membranes. Membrane characteristics, and other hydrodynamic strategies for mitigating polarization should be further studied in future work.

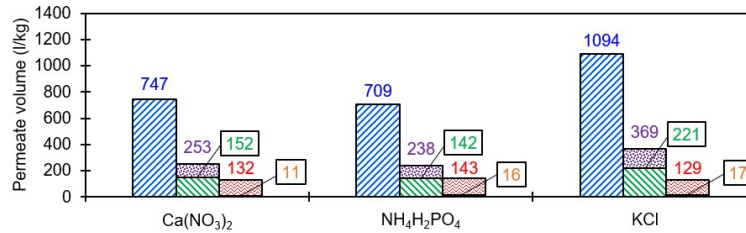
A selection of the simulation results is provided in Figure 5.12, and compared to experimental data reported throughout the literature. Published results are for a range of different scenarios, and as such, they show a wide range of observed permeate volumes.



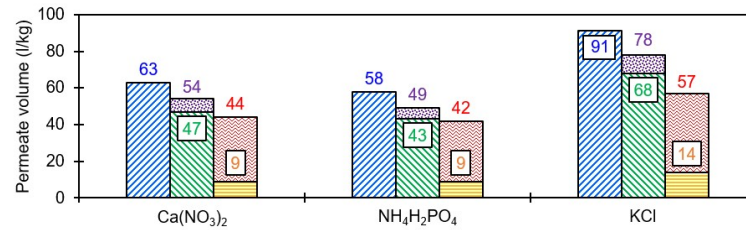
(a) Municipal wastewater feed ($c_F^0 = 0.16$ g/l and $\theta = 75$ %)



(b) Hydroponic wastewater feed ($c_F^0 = 0.25$ g/l and $\theta = 65$ %)



(c) Brackish water feed ($c_F^0 = 5$ g/l and $\theta = 40$ %)



(d) Urine feed ($c_F^0 = 15.8$ g/l and $\theta = 20$ %)

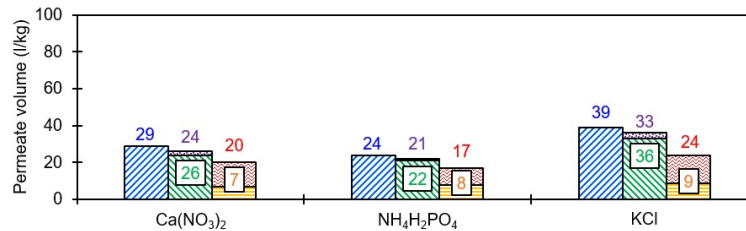


Figure 5.11. Equilibrium permeate volume $\Delta V'/m_D^0$, maximum practical permeate volume $\Delta V''/m_D^0$ that satisfies practical flux targets of 5 lmh and 10 lmh and simulation results. These limits are shown for calcium nitrate, monoammonium phosphate, and potassium chloride fertilizer, and for several different feed sources (a), (b), and (c). Fertilizer properties, wastewater properties, and other simulation parameters are summarized in Table 5.3.

For example, El Zayat et al [104] show the case for fertilizer osmosis with a very concentrated feed brine, and obtain water permeate of only 5 l/kg. On the other hand, Xiang et al [71] show the case for deionized feed water, and obtain water recovery of up to 53 l/kg. Other factors such as draw solute and initial concentration, membrane type, and recovery ratio also affect permeate results.

In all of the literature cases however, we see that observed permeate volumes fall well short of the theoretical volumes predicted by our simulations. This provides some context for what has so far been accomplished in the literature, and also raises questions about current test protocols. The relatively low performance is largely due to the fact that the specific metric of normalized permeate volumes has not been prioritized or systematically studied in any of the referenced studies. For example, only El Zayat et al [104] mention only in passing that up to 5 l/kg of water permeate was obtained. Otherwise, for all of the other studies, obtaining the permeate volume results plotted in Figure 5.12 required careful scrutiny of each publication's test conditions and outcomes to normalize collected permeate volumes by the mass of fertilizer input. In much of the literature, insufficient information is reported and therefore it is impossible to normalize recovered water permeate in this way. It is reasonable to assume that if normalized permeate was studied as a key performance indicator, observed results would improve and approach the simulation predictions. This highlights the need for future work to experimentally analyze the potential for water recovery per unit of fertilizer input.

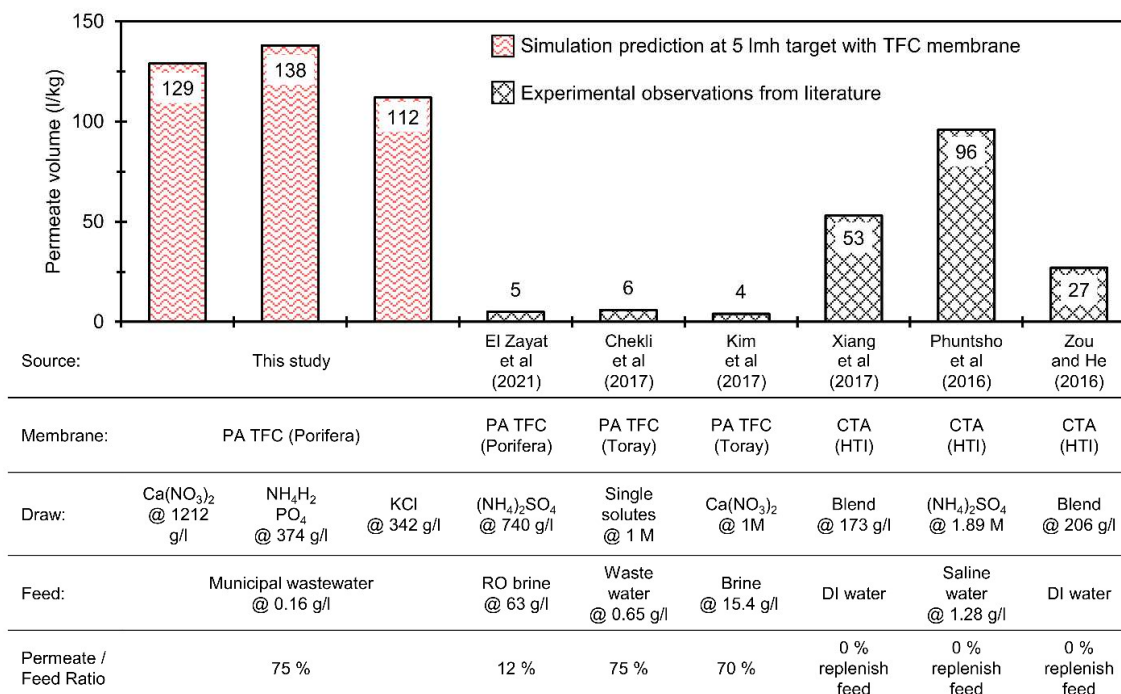


Figure 5.12. Normalized water permeate volumes recovered by fertilizer osmosis as predicted by simulation results from this study and as reported in experiments throughout the literature [45–47,70,71,104].

5.5.2 Water Recovery Potential of Common Crops

In this section, we describe the potential for fertilizer osmosis to spontaneously produce clean fertigation solution from a variety of wastewater feed sources, during hydroponic cultivation of common plant crops including tomato, cucumber, lettuce, and basil. To do this, the thermodynamic and practical water recovery limits previously described for essential N, P, K fertilizers are factored by individual plant nutrient requirements. The nutrient requirements and necessary fertilizer consumption of each crop are listed in Table 5.4. Since nutrient requirements vary significantly throughout plant life cycle, the reported values are the average daily requirements [90]. These nutrients can be supplied to plants via a number of sources, and many commercial and in-

house fertilizer recipes are available, however we assume here that they are supplied by the three common fertilizers analyzed throughout this study: $\text{Ca}(\text{NO}_3)_2$, $\text{NH}_4\text{H}_2\text{PO}_4$ and KCl .

Table 5.4. Average nutrient and fertilizer consumption, and plant spacing for common vegetable crops.

	Average Nutrient Requirement [90] (mg/plant/day)			Average Fertilizer Requirement (mg/plant/day)			Required irrigation water
	N	P	K	$\text{Ca}(\text{NO}_3)_2$	$\text{NH}_4\text{H}_2\text{PO}_4$	KCl	(ml/plant/day)
Tomato	89	16	43	519	53	81	600
Cucumber	171	18	54	997	60	102	600
Lettuce	48	3	18	280	10	34	300
Basil	55	3	20	320	10	38	300

Figure 5.13 shows the water recovery potential of fertilizer osmosis during hydroponic cultivation of tomato, cucumber, lettuce, and basil. Water recovery volume is normalized per plant and also compared to the irrigation requirements of each crop. For all crops, we observe that the equilibrium limit exceeds 100 % of the volume required for plant irrigation, so long as diluted feed is available such as municipal and hydroponic wastewater. This establishes that the thermodynamic potential for water recovery can be very significant relative to crop needs. However, only a portion of this potential can be practically realized, because of the need to maintain high flux above at least 5 lmh, despite non-ideal transport dynamics including severe concentration polarization. A significant drop in water recovery volumes is shown in the results for practical limits and simulated performance. For example, in the case of cucumber, up to 3 l/plant/day of

water permeate is required to establish osmotic equilibrium with diluted feed sources such as municipal and hydroponic wastewater. This high potential is due to the fact that fruit crops tend to be heavy feeders, and water recovery potential is directly proportional to quantities of fertilizer consumed by each plant. However, water recovery volume is reduced to approximately 0.6 l/plant/day for cucumber with dilute feed sources, due to the need to maintain practical flux despite non-ideal dynamics. This translates to approximately 75 % of the irrigation water required for hydroponic cucumber cultivation, which is nonetheless significant. In fact, for all crops, the simulated prediction for water recovery approaches at least 40 % of plant water requirements, so long as diluted feed water is available. This suggests that fertilizer osmosis has the potential to recover very meaningful volumes of water from moderate waste sources such as municipal and hydroponic wastewater, while maintaining competitive flux above 5 lmh. On the other hand, the potential for water recovery is much more limited with more concentrated feed sources. For example, simulation predictions for water recovery from brackish water and urine do not exceed 26 % of required plant irrigation volumes, and in some cases are as low as 3 %.

5.6 Conclusions

In this chapter, we have introduced a series of analytical and numerical methods for evaluating the thermodynamic and practical limits of recovering water from a fertilizer osmosis batch process. This addresses an important gap in the literature, which has so far not adequately addressed the question of how significant the water permeate volumes are that can be recovered from fertilizer osmosis.

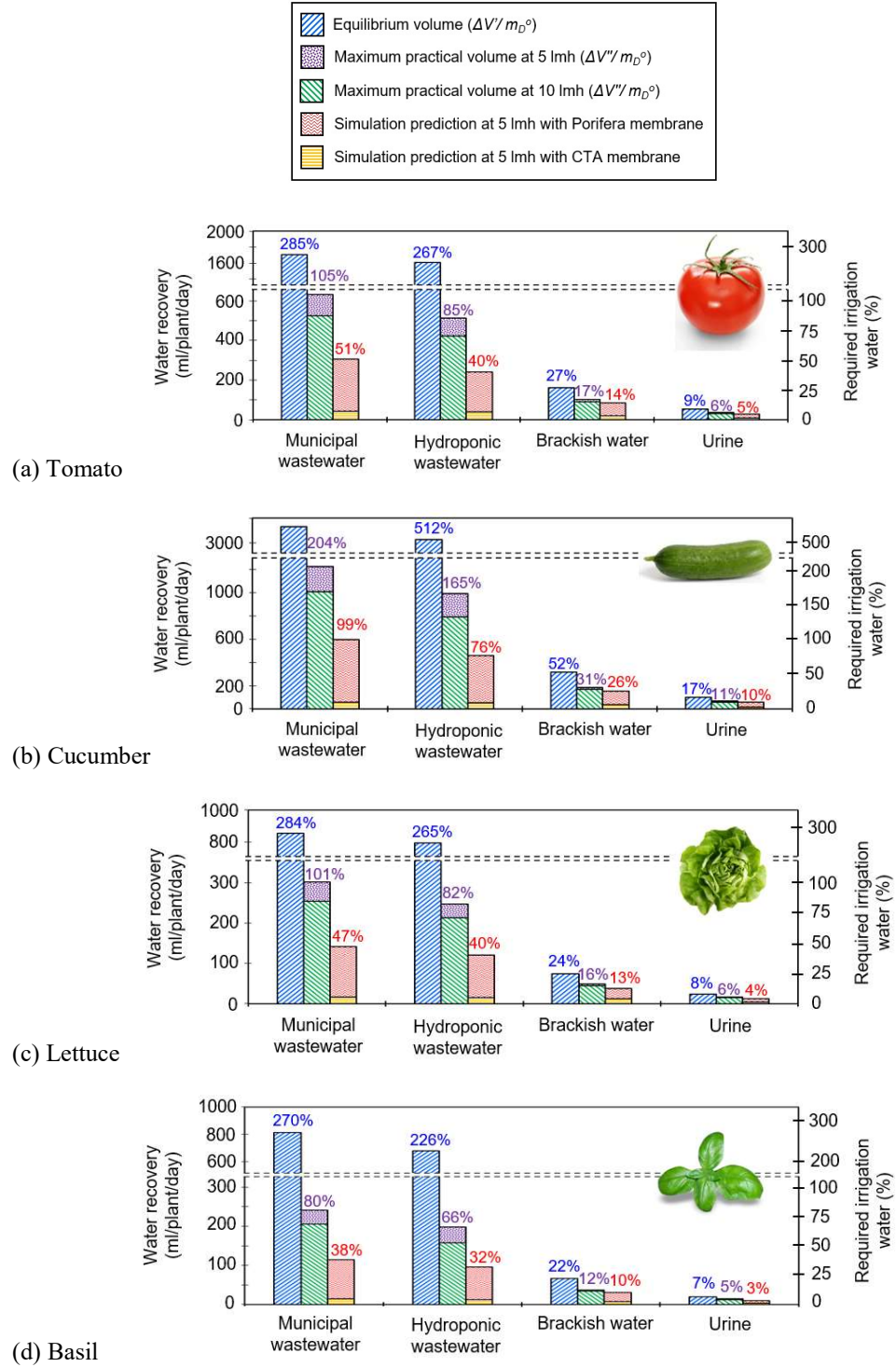


Figure 5.13. Equilibrium permeate volume $\Delta V''/m_D^\circ$, maximum practical permeate volume $\Delta V''/m_D^\circ$ that satisfies practical flux targets of 5 lmh and 10 lmh and simulation results . These limits are shown for hydroponically cultivated (a) tomato, (b) cucumber, (c) lettuce, and (d) basil, and for several cases of different feed concentrations c_F° and recovery ratios θ .

We found that common N, P, K fertilizers including calcium nitrate, monoammonium phosphate, and potassium chloride can recover between 112-138 l/kg via fertilizer osmosis from a municipal wastewater feed source with a target recovery ratio of 75 %, while maintaining practical flux of at least 5 lmh despite severe concentration polarization. So far, batch tests of fertilizer osmosis reported in the literature have only managed to recover between 4-96 l per kg fertilizer solute. This wide range of results, and the discrepancy between these values and our predicted potential, is due largely to the fact that normalized water recovery potential is not systematically treated in these reference papers, nor is it even mentioned in other fertilizer osmosis literature. This is the first attempt to evaluate the water recovery limits of fertilizer osmosis, and to investigate the effect that various batch process conditions have on the apparent tradeoff between water recovery volumes and the need to maintain cost effective flux. The thermodynamic and practical limits established here will provide a useful baseline against which future work can be evaluated. In particular, future experimental analysis is needed to verify the water recovery per unit fertilizer that can be achieved under a range of conditions.

Results were also extended to evaluate the significance of water recovery volumes relative to the irrigation requirements of different hydroponic crops. We found that between 32-99 % of a plant's irrigation water can be supplied by fertilizer osmosis at competitive flux levels, provided that low concentration feed such as municipal or hydroponic wastewater is available. Such recovery volumes represent a significant portion of the plant water balance, and this should justify additional future research in the area of fertilizer osmosis. On the other hand, the use of more concentrated feed sources such as brackish water and urine was found to have only limited water recovery potential.

5.7 Supplementary Information

5.7.1 Supplementary Note 5.1: Equilibrium Limits of Water Recovery from Fertilizer

Osmosis

Water recovery by fertilizer osmosis is driven by the osmotic pressure difference $\Delta\pi$ between the concentrated fertilizer draw solution π_D and the wastewater feed source π_F .

$$\Delta\pi = \pi_D - \pi_F \quad (5.S1)$$

Where osmotic pressure is approximated by the Van't Hoff equation,

$$\pi = \gamma i R T c \quad (5.S2)$$

And where γ is the activity coefficient, i is the number of ions, R is the gas constant, T is absolute temperature, and c is concentration.

To determine the permeate volume that establishes equilibrium it is necessary to define osmotic pressure as a function of permeate volume, i.e. $\pi = f(\Delta V)$. Since concentration is a function of volume, osmotic pressure can be written as a function of permeate volume.

$$\pi = \gamma i R T \frac{n}{V^o \pm \Delta V} = \gamma i R T c^o \frac{V^o}{V^o \pm \Delta V} = \gamma \pi^o \frac{V^o}{V^o \pm \Delta V} \quad (5.S3)$$

Where n is the amount of salt in the solution, V^o is the initial volume of water in the solution, and ΔV is the permeate volume, which will be positive for the draw solution and negative for the feed. c^o is the initial concentration, and π^o is the initial osmotic pressure.

The activity coefficient γ can also be considered as a function of concentration (and therefore permeate volume), but because such relationships are largely empirical, obtaining an exact analytical solution from equation (5.S3) requires an assumption that γ is equal to a constant, which we assume in this study to be unity. We note that other thermodynamic studies have made a similar assumption [27,29,61,78,79]. Furthermore, for the fertilizer solutions considered in this study, the ideal equation for osmotic pressure shows only minor variation with empirical results reported by OLI commercial software (OLI Stream Analyzer 9.5, Parsippany, NJ), as shown in Figure 5.14.

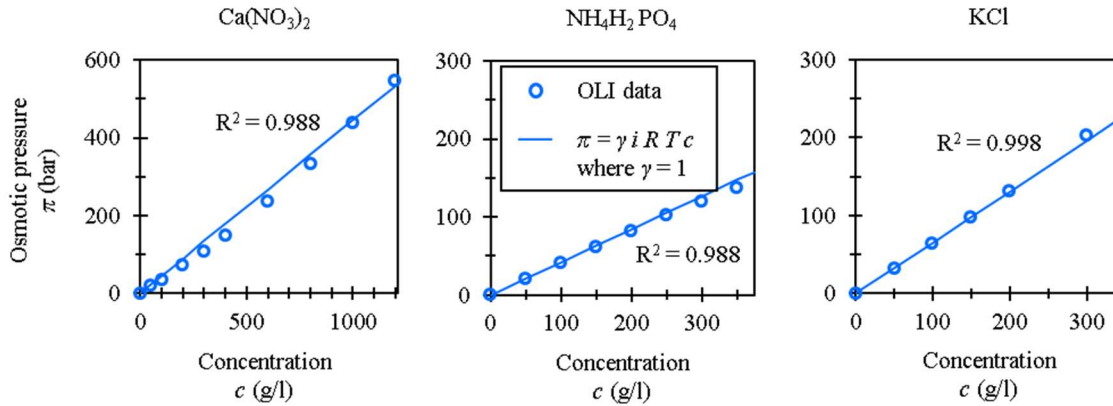


Figure 5.14. Osmotic pressure of highly concentrated fertilizer solutions as predicted by the Van't Hoff equation and by OLI commercial software (OLI Stream Analyzer 9.5, Parsippany, NJ) data.

Therefore, by assuming ideal behavior of the feed and draw solutions, the osmotic pressure of each solution can be described by equations (5.1) and (5.2) that were introduced in Section 2.1.

$$\pi_F = \pi_F^o \frac{V_F^o}{V_F^o - \Delta V} \quad (5.1)$$

$$\pi_D = \pi_D^o \frac{V_D^o}{V_D^o + \Delta V} \quad (5.2)$$

Where V_F^o and V_D^o are the initial feed and draw volumes, and π_F^o and π_D^o are the initial osmotic pressures.

To evaluate the limit to water recovery, we consider the condition for osmotic equilibrium at which point the osmotic pressure difference between draw and feed solutions is reduced to zero. Then, combining equations (5.1) and (5.2) and solving analytically, we establish the equilibrium permeate volume $\Delta V'$, which represents a fundamental thermodynamic limit to water recovery by fertilizer osmosis. When normalized per unit of fertilizer mass m_D^o we obtain equation (5.3) as reported in Section 2.1.

$$\Delta\pi = 0 \quad (5.S4)$$

$$\pi_D = \pi_F \quad (5.S5)$$

$$\pi_D^o \frac{V_D^o}{V_D^o + \Delta V'} = \pi_F^o \frac{V_F^o}{V_F^o - \Delta V'} \quad (5.S6)$$

$$\Delta V' = V_D^o \left(\frac{\pi_D^o}{\pi_F^o} \left(1 - \frac{\Delta V'}{V_F^o} \right) - 1 \right) \quad (5.S7)$$

$$\frac{\Delta V'}{m_D^o} = \frac{1}{c_D^o} \left(\frac{\pi_D^o}{\pi_F^o} (1 - \theta') - 1 \right) \quad (5.3)$$

Where θ' is the equilibrium recovery ratio. In general, the recovery ratio is defined as the permeate volume relative to the initial feed volume $\theta = \Delta V / V_F^o$, and therefore the equilibrium recovery ratio is a measure of the feed volume made available for the fertilizer osmosis process.

To illustrate the equilibrium limits of fertilizer osmosis, consider common N, P, K fertilizer draw solutions such as calcium nitrate $\text{Ca}(\text{NO}_3)_2$, monoammonium phosphate

$\text{NH}_4\text{H}_2\text{PO}_4$, and potassium chloride KCl when supplied with various wastewater feed sources approximated by a range of sodium chloride NaCl concentrations. The properties of the fertilizer draw solutions are summarized in Table 5.1.

Figure 5.15 shows the equilibrium permeate volume per unit mass for each of the fertilizers. The recovery volumes are plotted on a logarithmic scale, extending across a tremendous range of five orders of magnitude, as a function of feed concentrations and equilibrium recovery ratios. As expected, the potential for water recovery is greatest when diluted feed sources are available in abundant quantities (i.e. both c_F^0 and $\theta' \rightarrow 0$). Increasing the equilibrium recovery ratio leads to an exponential drop in the water permeate volume as for example, increasing θ' from 0 to 50 % leads to only a modest drop in water recovery, while increasing θ' beyond 90 % has a more dramatic effect, reducing recovery to nearly 0. The effect of increasing feed concentrations on the other hand is more severe at low concentrations, as for example increasing c_F^0 from 0 to 1 g/l reduces water recovery by over one of magnitude, while further reduction in c_F^0 from 1 to 5 g/l leads to a drop of less than 10-fold.

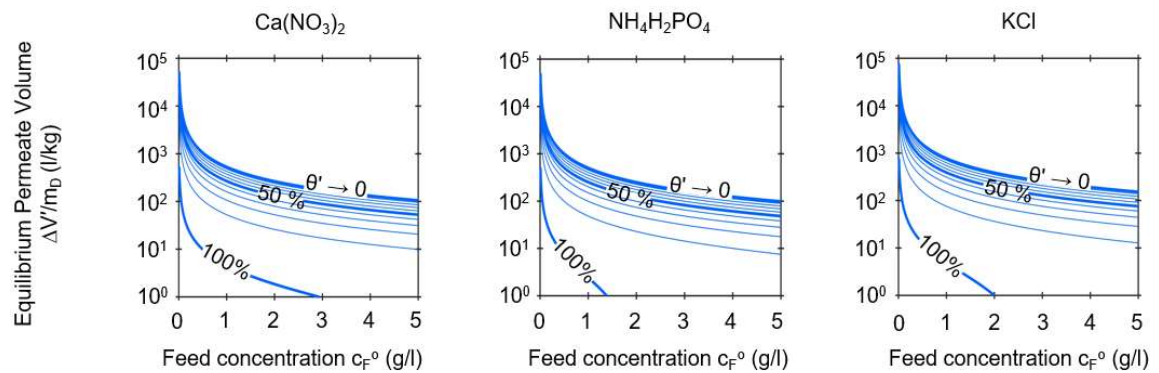


Figure 5.15. Equilibrium permeate volume $\Delta V'$ per unit of fertilizer m_D for calcium nitrate $\text{Ca}(\text{NO}_3)_2$, monoammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$, and potassium chloride KCl as a function of feed concentration c_F^0 and equilibrium recovery ratio θ' .

5.7.2 Supplementary Note 5.2: Practical Limits of Water Recovery from Fertilizer

Osmosis

The practical limits to water recovery via fertilizer osmosis can be established by considering the need to maintain cost effective water flux throughout the batch process. Taking water flux as defined previously in eq. (5.4) of Section 2.2., and substituting eq. (5.S1), we can define flux as a function of water permeate volume.

$$\frac{\Delta \dot{V}}{a} = J_w = A \Delta \pi \quad (5.4)$$

$$J_w = A \left(\pi_D^o \frac{V_D^o}{V_D^o + \Delta V} - \pi_F^o \frac{V_F^o}{V_F^o - \Delta V} \right) \quad (5.S8)$$

Then, defining the minimum water flux target J_w'' , we can rearrange to obtain a solution for the maximum water permeate volume as reported previously in eq. (5.5) of Section 2.2.

$$J_w'' = A \left(\pi_D^o \frac{V_D^o}{V_D^o + \Delta V''} - \pi_F^o \frac{V_F^o}{V_F^o - \Delta V''} \right) \quad (5.S9)$$

$$J_w'' = A \left(\pi_D^o \frac{1}{1 + c_D^o \frac{\Delta V''}{m_D^o}} - \pi_F^o \frac{1}{1 - \theta''} \right) \quad (5.S10)$$

$$\frac{\Delta V''}{m_D^o} = \frac{1}{c_D^o} \left(\frac{\pi_D^o}{\frac{J_w''}{A} + \frac{\pi_F^o}{1 - \theta''}} - 1 \right) \quad (5.5)$$

To illustrate the practical limits of fertilizer osmosis, consider again a selection of common N, P, K fertilizer draw solutions when supplied with various wastewater feed

sources approximated by a range of sodium chloride NaCl concentrations. The properties of the fertilizer draw solutions are summarized in Table 5.1.

Figure 5.16 shows the water recovery limit for each of the fertilizers, when a practical flux target of at least $J_w'' = 10$ lmh is maintained throughout the osmosis batch process. The permeate recovery volumes are plotted here on a linear scale, extending across a much more limited range than seen previously for the equilibrium limits. Maximum practical permeate volumes between 150 and 300 l/kg are determined when diluted feed sources are available in abundant quantities (i.e. both c_F^0 and $\theta' \rightarrow 0$), and then much less when concentration and recovery ratio of the feed increases.

5.7.3 Supplementary Note 5.3: Non-Linear Concentration Gradients in Fertilizer

Osmosis

Maintaining high water recovery rates throughout the fertilizer osmosis process is challenging because of non-ideal transport dynamics that reduce flux.

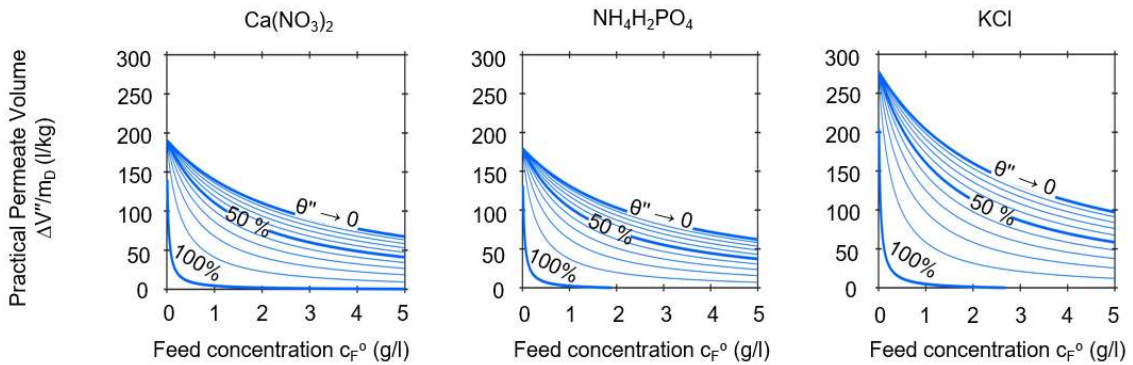


Figure 5.16. Practical permeate volume $\Delta V''$ per unit of fertilizer m_D^0 to satisfy minimum flux of $J_w'' = 10$ lmh for calcium nitrate $\text{Ca}(\text{NO}_3)_2$, monoammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$, and potassium chloride KCl fertilizer solutions. as a function of feed concentration c_F^0 and recovery ratio θ'' .

These include leakage of fertilizer across the imperfectly selective membrane, and accumulation of solutes in the membrane support structure and boundary layers.

Figure 5.17 illustrates the resulting non-linear concentration profile and shows that effective concentration difference across the membrane is effectively reduced. This dynamic is typically referred to as concentration polarization and has been widely studied for a number of osmosis applications [86,111,112], but for convenience a brief derivation is provided here.

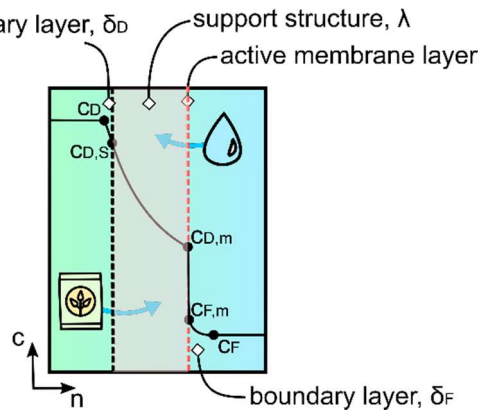


Figure 5.17. A non-linear concentration profile across the membrane $c(n)$ is formed as a function of solute diffusion and water permeate rates. As a result, the effective potential difference across the active membrane layer $\Delta c = c_{D,m} - c_{F,m}$ is much less than the potential difference between the bulk solutions c_D and c_F .

Concentration polarization across the membrane profile can be described by considering solute transport across the membrane. Solute transport through the active membrane layer is driven by diffusion, as defined in eq. (5.6). And solute transport through the membrane support structure and surface boundary layers is driven by both convection from water flux and back diffusion along the concentration gradient, as defined in eq. (5.7).

$$\frac{\Delta \dot{m}}{a} = J_s = B \Delta c \quad (5.6)$$

$$\frac{\Delta \dot{m}}{a} = J_s = D \frac{dc}{dn} - J_w c \quad (5.7)$$

Where B is the membrane solute permeability, Δc is the effective concentration difference across the membrane, D is the solute diffusion coefficient, dc/dn is the concentration gradient normal to the membrane surface.

By conservation of mass, the steady state solute transport through any and all of these layers will be equal, and therefore we combine eqs. (5.6) and (5.7).

$$D \frac{dc}{dn} - J_w c = B \Delta c \quad (5.S11)$$

Then, a general solution for the concentration profile can be obtained by rearranging and integrating.

$$\int \frac{dc}{(B \Delta c + J_w c)} = \int \frac{dn}{D} \quad (5.S12)$$

$$\frac{1}{J_w} \ln(B \Delta c + J_w c) = \frac{n}{D} + N \quad (5.S13)$$

$$c = N \exp\left(J_w \frac{n}{D}\right) - \frac{B \Delta c}{J_w} \quad (5.S14)$$

Where N is a constant.

To determine the specific concentration gradient across the membrane, boundary conditions from Figure 6.1 are used to define constant N . A solution for concentration at each of the membrane surfaces is provided here.

$$c_{F,m} = \left(c_F + \frac{B \Delta c}{J_w}\right) \exp\left(J_w \frac{\delta_F}{D_F}\right) - \frac{B \Delta c}{J_w} \quad (5.S15)$$

$$c_{D,m} = \left(c_D + \frac{B \Delta c}{J_w} \right) \exp \left(-J_w \left(\frac{\delta_D}{D_D} + \frac{\lambda}{D_S} \right) \right) - \frac{B \Delta c}{J_w} \quad (5.S16)$$

$$c_{D,S} = \left(c_D + \frac{B \Delta c}{J_w} \right) \exp \left(-J_w \frac{\delta_D}{D_D} \right) - \frac{B \Delta c}{J_w} \quad (5.S17)$$

Where diffusivity of the solute D through the support structure and the feed and draw boundary layers is distinguished here with respective subscripts. For simplicity, we will assume here that diffusivity through the feed and draw boundary layers are equal, and therefore $D_F = D_D = D$. Furthermore, define a structure parameter $S = D \lambda / D_S$ to describe the effective thickness of the membrane support layer.

Finally, by combining eqs. (5.S.15) and (5.S.16) we obtain an expression that describes the effective concentration difference across the active membrane layer assuming it is oriented to face the feed solution, as is commonly suggested for FO.

$$\Delta c = c_{D,m} - c_{F,m} \quad (5.S18)$$

$$\Delta c = \frac{c_D \exp \left(-J_w \frac{\delta_D + S}{D} \right) - c_F \exp \left(J_w \frac{\delta_F}{D} \right)}{1 + \frac{B}{J_w} \left(\exp \left(J_w \frac{\delta_F}{D} \right) - \exp \left(-J_w \frac{\delta_D + S}{D} \right) \right)} \quad (5.8)$$

When the active membrane is oriented to face the draw solution, as is commonly suggested for pressure retarded osmosis (PRO), the corresponding boundary conditions give the following expression for effective concentration difference.

$$\Delta c = \frac{c_D \exp \left(-J_w \frac{\delta_D}{D} \right) - c_F \exp \left(J_w \frac{\delta_F + S}{D} \right)}{1 + \frac{B}{J_w} \left(\exp \left(J_w \frac{\delta_F + S}{D} \right) - \exp \left(-J_w \frac{\delta_D}{D} \right) \right)} \quad (5.S19)$$

To illustrate the significance of concentration polarization in fertilizer osmosis, consider again a selection of common N, P, K fertilizer draw solutions and a diluted feed solution with low concentration 0.16 g/l of the draw solute, when supplied to a CTA membrane. The properties of the fertilizer draw solutions are summarized in Table 5.1 and the membrane properties and process conditions are summarized in Table 5.3.

Figure 5.18 shows the resulting concentration profile normal to the membrane surface, for the start of fertilizer osmosis batch process (that is for a nearly saturated fertilizer solution). As shown a remarkable drop in concentration is observed across the boundary layers and especially the membrane support layer, such that the effective concentration difference across the active membrane layer remains only a small fraction of the difference between the bulk draw and feed solutions. For example, in the case of $\text{Ca}(\text{NO}_3)_2$ fertilizer, the effective concentration difference $\Delta c = 55.6$ g/l is less than 5 % of the bulk difference. Such severe polarization is associated with the initially super concentrated nature of the fertilizer draw solutions, although as the osmosis batch process advances the relative severity of polarization can be shown to decrease as fertilizer is diluted. In any case, the importance of considering the effects of concentration polarization in fertilizer osmosis are clearly illustrated. Figure 5.18 also illustrates the important effect that membrane orientation has on polarization, showing both cases where the active membrane layer is oriented (a) towards the feed and (b) towards the draw. In general, we observe nearly twice the effective concentration difference with the active membrane facing the draw. This suggests that the severity of polarization can be mitigated by orienting the active membrane layer towards the draw, thereby generating higher flux.

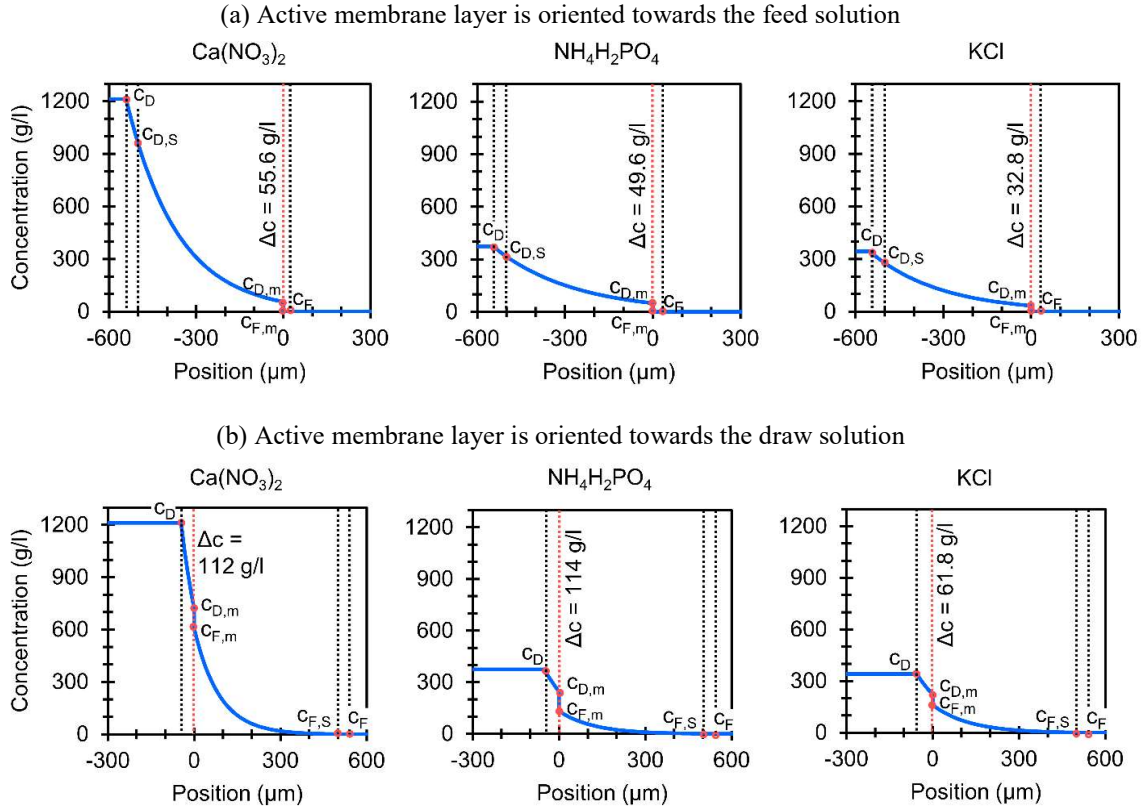


Figure 5.18. Concentration across the active membrane, its support structure and boundary layers. Fertilizer properties are summarized in Table 5.1, and the CTA membrane properties and process conditions are summarized in Table 5.3. In (a) the active membrane layer is oriented towards the feed, and in (b) it is oriented to the draw.

The vast majority of the literature however suggests that for forward osmosis applications such as fertilizer osmosis, membrane orientation with the active layer facing the feed is actually preferred [65,113,114]. This apparent contradiction can be understood after consideration of non-ideal fouling, and on the . Therefore, in this chapter, we followed the consensus recommendation and have oriented the membrane towards the feed. This is also consistent with other fertilizer osmosis studies [20,28,31,34,43,46,47,60,70,71].

5.7.4 Supplementary Note 5.4: MATLAB Codes for Generating Heat Maps

This MATLAB code uses fertilizer properties, feed concentration and feed recovery ratio as inputs and generates heatmaps for maximum theoretical volume and practical water limits shown in Figures 5.4 and 5.7.

```
clear;
iD=3; %Draw number of ions [unitless]
MD=164.1; %Draw molar mass [g/mol]
cD0=1212; %Draw maximum solubility [g/l]

iF=2; %Feed number of ions [unitless]
MF=58.44; %Feed molar mass [g/mol]

Jwdoubleprime=5; %minimum required flux [lmh]
AA = 4.3; %membrane permeability lmh/bar
Jmin=(Jwdoubleprime/AA)*100; %Jw/A [J/l]

A = linspace(0,15,1000);
cF= repmat(A,1000,1); %feed concentration [g/l]
B=linspace(0,1,1000)';
theta=repmat(B,1,1000); %recovery ratio

R=8.314; %gas constant [J/mol/K]
T=293.15; %Temperature [K]

piD0=iD*R*T*cD0/MD; %initial draw osmotic pressure [J/l]
piF=iF*R*T*cF/MF; %feed osmotic pressure [J/l]

Vprime=(1./cD0).*((piD0.*(1-theta)./piF)-1); %theoretical
volume limit[l/g] *1000 [l/kg]
Vdoubleprime=(1./cD0).*(piD0./(Jmin+piF./(1-theta))-1);
%practical volume limit [l/g]
G=(piD0./cD0).*(log(1+cD0.*Vprime))-
(piF.*Vprime./theta.*log(1./(1-theta))); %Gibbs energy[J/g]
/3.6 [Wh/kg]
Vstar=(1./cD0).*((sqrt(piD0./piF).*(1-theta))-1); % [l/g]
practical volume for max work *1000 [l/kg]
Pstar=piD0.*(1./(1+cD0.*Vstar))-piF.*(1./(1-theta)); %[J/l]
practical pressure for maximum work /100 [bar]
Wstar=Pstar.*Vstar; %[J/g] /3.6 [Wh/kg]
```

```

h=imagesc(A,100*B,Vdoubleprime*1000);
colormap('jet');
caxis([0 400]);
set(gca,'YDir','normal')
set(gca,'FontName','Arial')
set(gca,'FontSize',16)
set(gca,'linewidth',1.2)

xlabel('Feed concentration c_F^0 (g/l)')
ylabel('Recovery ratio \theta')

```

5.7.5 Supplementary Note 5.5: MATLAB Codes for Variable Recovery Ratio Figures

This MATLAB code uses fertilizer properties as inputs and shows theoretical and practical water recovery limits as a function of feed concentration and recovery ratio θ .

Figures 5.15 and 5.16 are created with this code.

```

clear;
iD=2; %Draw number of ions [unitless]
MD=115.03; %Draw molar mass [g/mol]
cD0=374; %Draw maximum sollubility [g/l]

iF=2; %Feed number of ions [unitless]
MF=58.44; %Feed molar mass [g/mol]

Jwdoubleprime=10; %minumum required flux
AA = 4.3; %membrane permeability
Jmin=(Jwdoubleprime/AA)*100; %Jw/A [J/l]

cF= linspace(0.01,5,10000);

theta1=0.01;
theta2=0.10;
theta3=0.20;
theta4=0.30;
theta5=0.40;
theta6=0.50;
theta7=0.60;

```

```

theta8=0.70;
theta9=0.80;
theta10=0.90;
theta11=0.99;

R=8.314; %gas constant [J/mol/K]
T=293.15; %Temperature [K]

piD0=iD*R*T*cD0/MD; %initial draw osmotic pressure [J/l]
piF=iF*R*T*cF/MF; %feed osmotic pressure [J/l]

Vprime1=(1./cD0).*((piD0.*(1-theta1)./piF)-1); % [l/g]
*1000 [l/kg]
Vdoubleprime1=(1./cD0).*(piD0./(Jmin+piF./(1-theta1))-1);
G1=(piD0./cD0).*(log(1+cD0.*Vprime1))-
(piF.*Vprime1./theta1.*log(1./(1-theta1))); % [J/g] /3.6
[Wh/kg]
Vstar1=(1./cD0).*((sqrt(piD0./piF).*(1-theta1))-1); % [l/g]
*1000 [l/kg]
Pstar1=piD0.*(1./(1+cD0.*Vstar1))-piF.*(1./(1-theta1));
% [J/l] /100 [bar]
Wstar1=Pstar1.*Vstar1; % [J/g] /3.6 [Wh/kg]

Vprime2=(1./cD0).*((piD0.*(1-theta2)./piF)-1); % [l/g]
*1000 [l/kg]
Vdoubleprime2=(1./cD0).*(piD0./(Jmin+piF./(1-theta2))-1);
G2=(piD0./cD0).*(log(1+cD0.*Vprime2))-
(piF.*Vprime2./theta2.*log(1./(1-theta2))); % [J/g] /3.6
[Wh/kg]
Vstar2=(1./cD0).*((sqrt(piD0./piF).*(1-theta2))-1); % [l/g]
*1000 [l/kg]
Pstar2=piD0.*(1./(1+cD0.*Vstar2))-piF.*(1./(1-theta2));
% [J/l] /100 [bar]
Wstar2=Pstar2.*Vstar2; % [J/g] /3.6 [Wh/kg]

Vprime3=(1./cD0).*((piD0.*(1-theta3)./piF)-1); % [l/g]
*1000 [l/kg]
Vdoubleprime3=(1./cD0).*(piD0./(Jmin+piF./(1-theta3))-1);
G3=(piD0./cD0).*(log(1+cD0.*Vprime3))-
(piF.*Vprime3./theta3.*log(1./(1-theta3))); % [J/g] /3.6
[Wh/kg]
Vstar3=(1./cD0).*((sqrt(piD0./piF).*(1-theta3))-1); % [l/g]
*1000 [l/kg]
Pstar3=piD0.*(1./(1+cD0.*Vstar3))-piF.*(1./(1-theta3));
% [J/l] /100 [bar]
Wstar3=Pstar3.*Vstar3; % [J/g] /3.6 [Wh/kg]

```

```

Vprime4=(1./cD0).*((piD0.*(1-theta4)./piF)-1);    %[1/g]
*1000 [1/kg]
Vdoubleprime4=(1./cD0).*(piD0./(Jmin+piF./(1-theta4))-1);
G4=(piD0./cD0).*(log(1+cD0.*Vprime4))-
(piF.*Vprime4./theta4.*log(1./(1-theta4))); %[J/g]    /3.6
[Wh/kg]
Vstar4=(1./cD0).*((sqrt(piD0./piF).*(1-theta4))-1); % [1/g]
*1000 [1/kg]
Pstar4=piD0.*(1./(1+cD0.*Vstar4))-piF.*(1./(1-theta4));
%[J/l]    /100 [bar]
Wstar4=Pstar4.*Vstar4; %[J/g]    /3.6 [Wh/kg]

Vprime5=(1./cD0).*((piD0.*(1-theta5)./piF)-1);    %[1/g]
*1000 [1/kg]
Vdoubleprime5=(1./cD0).*(piD0./(Jmin+piF./(1-theta5))-1);
G5=(piD0./cD0).*(log(1+cD0.*Vprime5))-
(piF.*Vprime5./theta5.*log(1./(1-theta5))); %[J/g]    /3.6
[Wh/kg]
Vstar5=(1./cD0).*((sqrt(piD0./piF).*(1-theta5))-1); % [1/g]
*1000 [1/kg]
Pstar5=piD0.*(1./(1+cD0.*Vstar5))-piF.*(1./(1-theta5));
%[J/l]    /100 [bar]
Wstar5=Pstar5.*Vstar5; %[J/g]    /3.6 [Wh/kg]

Vprime6=(1./cD0).*((piD0.*(1-theta6)./piF)-1);    %[1/g]
*1000 [1/kg]
Vdoubleprime6=(1./cD0).*(piD0./(Jmin+piF./(1-theta6))-1);
G6=(piD0./cD0).*(log(1+cD0.*Vprime6))-
(piF.*Vprime6./theta6.*log(1./(1-theta6))); %[J/g]    /3.6
[Wh/kg]
Vstar6=(1./cD0).*((sqrt(piD0./piF).*(1-theta6))-1); % [1/g]
*1000 [1/kg]
Pstar6=piD0.*(1./(1+cD0.*Vstar6))-piF.*(1./(1-theta6));
%[J/l]    /100 [bar]
Wstar6=Pstar6.*Vstar6; %[J/g]    /3.6 [Wh/kg]

Vprime7=(1./cD0).*((piD0.*(1-theta7)./piF)-1);    %[1/g]
*1000 [1/kg]
Vdoubleprime7=(1./cD0).*(piD0./(Jmin+piF./(1-theta7))-1);
G7=(piD0./cD0).*(log(1+cD0.*Vprime7))-
(piF.*Vprime7./theta7.*log(1./(1-theta7))); %[J/g]    /3.6
[Wh/kg]
Vstar7=(1./cD0).*((sqrt(piD0./piF).*(1-theta7))-1); % [1/g]
*1000 [1/kg]

```

```

Pstar7=piD0.*(1./(1+cD0.*Vstar7))-piF.*(1./(1-theta7));
%[J/l]    /100 [bar]
Wstar7=Pstar7.*Vstar7; %[J/g]    /3.6 [Wh/kg]

Vprime8=(1./cD0).*((piD0.*(1-theta8)./piF)-1); %[1/g]
*1000 [l/kg]
Vdoubleprime8=(1./cD0).*(piD0./(Jmin+piF./(1-theta8))-1);
G8=(piD0./cD0).*(log(1+cD0.*Vprime8))-
(piF.*Vprime8./theta8.*log(1./(1-theta8))); %[J/g]    /3.6
[Wh/kg]
Vstar8=(1./cD0).*((sqrt(piD0./piF).*(1-theta8))-1); %[1/g]
*1000 [l/kg]
Pstar8=piD0.*(1./(1+cD0.*Vstar8))-piF.*(1./(1-theta8));
%[J/l]    /100 [bar]
Wstar8=Pstar8.*Vstar8; %[J/g]    /3.6 [Wh/kg]

Vprime9=(1./cD0).*((piD0.*(1-theta9)./piF)-1); %[1/g]
*1000 [l/kg]
Vdoubleprime9=(1./cD0).*(piD0./(Jmin+piF./(1-theta9))-1);
G9=(piD0./cD0).*(log(1+cD0.*Vprime9))-
(piF.*Vprime9./theta9.*log(1./(1-theta9))); %[J/g]    /3.6
[Wh/kg]
Vstar9=(1./cD0).*((sqrt(piD0./piF).*(1-theta9))-1); %[1/g]
*1000 [l/kg]
Pstar9=piD0.*(1./(1+cD0.*Vstar9))-piF.*(1./(1-theta9));
%[J/l]    /100 [bar]
Wstar9=Pstar9.*Vstar9; %[J/g]    /3.6 [Wh/kg]

Vprime10=(1./cD0).*((piD0.*(1-theta10)./piF)-1); %[1/g]
*1000 [l/kg]
Vdoubleprime10=(1./cD0).*(piD0./(Jmin+piF./(1-theta10))-1);
G10=(piD0./cD0).*(log(1+cD0.*Vprime10))-
(piF.*Vprime10./theta10.*log(1./(1-theta10))); %[J/g]
/3.6 [Wh/kg]
Vstar10=(1./cD0).*((sqrt(piD0./piF).*(1-theta10))-1); %[1/g]
*1000 [l/kg]
Pstar10=piD0.*(1./(1+cD0.*Vstar10))-piF.*(1./(1-theta10));
%[J/l]    /100 [bar]
Wstar10=Pstar10.*Vstar10; %[J/g]    /3.6 [Wh/kg]

Vprime11=(1./cD0).*((piD0.*(1-theta11)./piF)-1); %[1/g]
*1000 [l/kg]
Vdoubleprime11=(1./cD0).*(piD0./(Jmin+piF./(1-theta11))-1);
G11=(piD0./cD0).*(log(1+cD0.*Vprime11))-
(piF.*Vprime11./theta11.*log(1./(1-theta11))); %[J/g]
/3.6 [Wh/kg]

```

```

Vstar11=(1./cD0).*((sqrt(piD0./piF).*(1-theta11))-1); %
[1/g]      *1000 [1/kg]
Pstar11=piD0.*(1./(1+cD0.*Vstar11))-piF.*(1./(1-theta11));
%[J/l]      /100 [bar]
Wstar11=Pstar11.*Vstar11; %[J/g]   /3.6 [Wh/kg]

plot(cF,Vdoubleprime1*1000,'color','[0,0.4,1]','LineWidth',
3)
hold on
plot(cF,Vdoubleprime2*1000,'color','[0,0.4,1]','LineStyle',
'--','LineWidth',3)
hold on
plot(cF,Vdoubleprime3*1000,'color','[0,0.4,1]','LineStyle',
'-.','LineWidth',3)
hold on
plot(cF,Vdoubleprime4*1000,'color','[0,0.4,1]','LineStyle',
'-.','LineWidth',3)
hold on
plot(cF,Vdoubleprime5*1000,'color','[0,0.4,1]','LineStyle',
'-.','LineWidth',3)
hold on
plot(cF,Vdoubleprime6*1000,'color','[0,0.4,1]','LineStyle',
'-.','LineWidth',3)
hold on
plot(cF,Vdoubleprime7*1000,'color','[0,0.4,1]','LineStyle',
':','LineWidth',3)
hold on
plot(cF,Vdoubleprime8*1000,'color','[0,0.4,1]','LineStyle',
':','LineWidth',3)
hold on
plot(cF,Vdoubleprime9*1000,'color','[0,0.4,1]','LineStyle',
':','LineWidth',3)
hold on
plot(cF,Vdoubleprime10*1000,'color','[0,0.4,1]','LineStyle',
':','LineWidth',3)
hold on
plot(cF,Vdoubleprime11*1000,'color','[0,0.4,1]','LineStyle',
':','LineWidth',3)

%red [1,0.314,0.314]
%blue [0,0.4,1]

set(gca, 'FontName', 'Times new roman')
set(gca,'FontSize',12)
set(gca,'TickDir','both')
set(gca,'FontSize',18);

```

```
set(gca,'linewidth',1.6)

xlabel('Feed concentration c_F^0 (g/l)')
```

5.7.6 Supplementary Note 5.6: MATLAB Codes for Including Non-ideal Effects

This MATLAB code uses fertilizer properties and membrane transport constants A,B and S as inputs to generate permeate flux vs permeate volume and time by including non-ideal effect such as polarization and using effective concentration eq. 5.8. Figures 5.9, 4.5 and 5.10 are created with this code.

```
clear all
clc

% FERTILIZER DRIVEN OSMOSIS

% CONSTANTS
R=8.314; % [J/K/mol] gas constant
T=20+273.15; % [K] temperature
i=2; % [unitless] number of salt ions
M=0.07455; % [kg/mol] molar mass of salt

% INITIAL BATCH PREP
VFo=10; % [m^3] volume of water
cFo=0.1; % [kg/m^3] feed concentration
mFo=cFo*VFo; % [kg] mass of salt

VDo=0.0003; % [m^3] volume of water
cDo=342; % [kg/m^3] draw concentration
mDo=cDo*VDo; % [kg] mass of salt in feed

% OPERATING CONDITIONS
VFlpm=0.275;% [lpm] feed flow
VFdot=VFlpm/1000/60; % [m3/s] feed flow
VDlpm=0.275; % [lpm] draw flow
VDdot=VDlpm/1000/60; % [m3/s] draw flow
dp=35e5; % [Pa] applied pressure difference
```

```

% FLUID PROPERTIES
rhoF=1000; % [kg/m^3] feed density
rhoD=1030; % [kg/m^3] draw density
vF=0.001; % [Pa*s] feed viscosity
vD=0.001; % [Pa*s] draw viscosity

% MEMBRANE MODULE
l=0.107; % [m] membrane length
w=0.039; % [m] membrane width
a=w*l; % [m^2] membrane area
t=0.0023; % [m] channel height
tshim=0.0014986; % [m] shim thickness
heff=t-tshim; % [m] effective channel height
pspacer=0.89; % [unitless] spacer porosity ...based on
what? this should be available from Sterlitech...
dD=2*heff; % [m] draw hydraulic diameter
dF=4*pspacer/((2/heff)+((1-pspacer)*(8/heff))); % [m] feed
hydraulic diameter

% MEMBRANE PROPERTIES
Almh=0.418; % [l/m^2/h/bar] water permeability
A=Almh/10^5/1000/3600; % [m^3/s/m^2/Pa] water permeability
Blmh=1.125; % [l/m^2/h] salt permeability
B=Blmh/1000/3600; % [m^3/s/m^2] salt permeability
S=0.000496147; % [m] structure parameter

% SOLVE BATCH PROCESS AT t=1
deltat=60*30; % [s] time step
tt=3*24*60*60/deltat; % range of variable
for t=1:tt; % variable
ts(1)=deltat; % [s] time
ts(t+1)=t*deltat; % [s] time
th(1)=ts(1)/60/60; % [h] time
th(t+1)=ts(t+1)/60/60; % [h] time

% DEFINE FLOW AT t=1
mFt(1)=mFo; % [kg] feed solute mass
mDt(1)=mDo; % [kg] draw solute mass
VFt(1)=VFo; % [m^3] feed volume
VDt(1)=VDo; % [m^3] draw volume
cFt(1)=cFo; % [kg/m^3] feed concentration
cDt(1)=cDo; % [kg/m^3] draw concentration

% REDEFINE FLOW
mF=mFt(1); % [kg] feed solute mass
mD=mDt(1); % [kg] draw solute mass

```

```

VF=VFt(1); % [m^3/s] feed volume
VD=VDt(1); % [m^3/s] draw volume
cF=cFt(1); % [kg/m^3] feed concentration
cD=cDt(1); % [kg/m^3] draw concentration

% BOUNDARY LAYERS
uF=VFdot/heff/w/pspacer; % [m/s] feed velocity
uD=VDdot/heff/w; % [m/s] draw velocity
ReF=dF*uF*rhoF/vF; % [unitless] feed Reynolds
ReD=dD*uD*rhoD/vD; % [unitless] draw Reynolds
DF=6.725e-6*exp(1.546e-4*cF-2513/T); % [m^2/s] feed
diffusion
DD=9.04e-10;
ScF=vF/rhoF/DF; % [unitless] feed Schmidt
ScD=vD/rhoD/DD; % [unitless] draw Schmidt
ShF=0.46*ReF^0.36*ScF^0.36; % [unitless] feed Sherwood
ShD=1.85*ReD^0.33*ScD^0.33*(dD/l)^0.33; % [unitless] draw
Sherwood
kF=ShF*DF/dF; % [m/s] feed diffusion transfer coefficient
kD=ShD*DD/dD; % [m/s] draw diffusion transfer coefficient
yF=DF/kF; % [m] feed boundary thickness
yD=DD/kD; % [m] draw boundary thickness

% SOLVE CONCENTRATION PROFILE
    dcguess(1)=cDo-cFo; % [kg/m^3] guess concentration
    for n=1:1:1000000; % [unitless] iterations for
numerical solution of system of equations
        dOn(n)=i*R*T*dcguess(n)/M; % [Pa] osmotic pressure
difference
        Jwn(n)=A*(dOn(n)-dp); % [m^3/(m^2*s)] water permeate
flux
        dcn(n)=(cD*exp(-Jwn(n)*yD/DD)-
cF*exp((S+yF)*Jwn(n)/DF))/(1+B/Jwn(n)*(exp((S+yF)*Jwn(n)/DF)
)-exp(-Jwn(n)*yD/DD)); % [kg/m^3] effective concentration
difference
        if (abs(dcguess(n)-dcn(n))>0.1);
            dcguess(n+1)=dcguess(n)-0.01;
        else
            break
        end
    end

% EFFECTIVE RESULTS GIVEN POLARIZATION EFFECT
dO=dOn(n); % [Pa] effective osmotic pressure difference
Jw=Jwn(n); % [m^3/s/m^2] effective water permeate flux
dc=dcguess(n); % [kg/m^3] effective salinity difference

```

```

cFS=(cF+B*dc/Jw)*exp(Jw*yF/DF)-B*dc/Jw; % [kg/m^3]
concentration at feed side of support structure
cFm=(cF+B*dc/Jw)*exp(Jw*(S+yF)/DF)-B*dc/Jw; % [kg/m^3]
concentration at feed side of membrane
cDm=(cD+B*dc/Jw)*exp(-Jw*yD/DD)-B*dc/Jw; % [kg/m^3]
concentration at draw side of membrane
dcm=cDm-cFm; % [kg/m^3] check concentration difference

% BASED ON SOLUTION DEFINE VALUES FOR t=1

% REDEFINE BOUNDARY LAYERS
uFt(1)=uF; % [m/s] feed velocity
uDt(1)=uD; % [m/s] draw velocity
ReFt(1)=ReF; % [unitless] feed Reynolds
ReDt(1)=ReD; % [unitless] draw Reynolds
DFt(1)=DF; % [m^2/s] feed diffusion
DDt(1)=DD; % [m^2/s] draw diffusion
ScFt(1)=ScF; % [unitless] feed Schmidt
ScDt(1)=ScD; % [unitless] draw Schmidt
ShFt(1)=ShF; % [unitless] feed Sherwood
ShDt(1)=ShD; % [unitless] draw Sherwood
kFt(1)=kF; % [m/s] feed diffusion transfer coefficient
kDt(1)=kD; % [m/s] draw diffusion transfer coefficient
yFt(1)=yF; % [m] feed boundary thickness
yDt(1)=yD; % [m] draw boundary thickness

% OUTPUT RESULTS
Jwt(1)=Jw; % [m^3/s/m^2] water permeate flux
Jwlmh(1)=Jw*1000*3600; % [l/m^2/h] water permeate flux
deltaV(1)=Jw*a*deltat; % [m^3] water permeate volume
Vt(1)=deltaV(1); % [m^3] cumulative water permeate volume
phit(1)=Vt(1)/VFo; % [unitless] recovery ratio

Wdott(1)=Jw*dp; % [W/m^2] power density
deltaE(1)=Wdott(1)*a*deltat; % [J] energy recovered
Et(1)=deltaE(1); % [J] cumulative energy recovery

Jst(1)=B*dc; % [kg/s] salt permeate flux
deltam(1)=B*dc*a*deltat; % [kg] salt permeate mass

dct(1)=dc; % [kg/m^3] effective concentration difference
dcmt(1)=dcm; % [kg/m^3] check concentration difference
dOt(1)=dO; % [Pa] effective osmotic pressure difference
cFSt(1)=cFS; % [kg/m^3] concentration at feed side of
support structure

```

```

cFmt(1)=cFm; % [kg/m^3] concentration at feed side of
membrane
cDmt(1)=cDm; % [kg/m^3] concentration at draw side of
membrane

% SOLVE CONCENTRATION POLARIZATION AT t=2

% FLOW PARAMETERS FOR i=2
mFt(2)=mFt(1)+deltam(1); % [kg] feed salt mass
mDt(2)=mDt(1)-deltam(1); % [kg] draw salt mass
VFt(2)=VFt(1)-deltaV(1); % [m^3] feed volume
VDt(2)=VDt(1)+deltaV(1); % [m^3] draw volume
cFt(2)=mFt(2)/VFt(2); % [kg/m^3] feed concentration
cDt(2)=mDt(2)/VDt(2); % [kg/m^3] draw concentration

% REDEFINE FLOW PARAMETERS
mF=mFt(t+1); % [kg] feed salt mass
mD=mDt(t+1); % [kg] draw salt mass
VF=VFt(t+1); % [m^3] feed volume
VD=VDt(t+1); % [m^3] draw volume
cF=cFt(t+1); % [kg/m^3] feed concentration
cD=cDt(t+1); % [kg/m^3] draw concentration

% BOUNDARY LAYERS
uF=VFdot/heff/w/pspacer; % [m/s] feed velocity
uD=VDdot/heff/w; % [m/s] draw velocity
ReF=dF*uF*rhoF/vF; % [unitless] feed Reynolds
ReD=dD*uD*rhoD/vD; % [unitless] draw Reynolds
DF=6.725e-6*exp(1.546e-4*cF-2513/T); % [m^2/s] feed
diffusion
DD=9.04e-10;
ScF=vF/rhoF/DF; % [unitless] feed Schmidt
ScD=vD/rhoD/DD; % [unitless] draw Schmidt
ShF=0.46*ReF^0.36*ScF^0.36; % [unitless] feed Sherwood
ShD=1.85*ReD^0.33*ScD^0.33*(dD/1)^0.33; % [unitless] draw
Sherwood
kF=ShF*DF/dF; % [m/s] feed diffusion transfer coefficient
kD=ShD*DD/dD; % [m/s] draw diffusion transfer coefficient
yF=DF/kF; % [m] feed boundary thickness
yD=DD/kD; % [m] draw boundary thickness

% SOLVE CONCENTRATION PROFILE
dcguess(1)=cDo-cFo; % [kg/m^3] guess concentration
for n=1:1:1000000; % [unitless] iterations for
numerical solution of system of equations

```

```

        dOn(n)=i*R*T*dcguess(n)/M; % [Pa] osmotic pressure
difference
        Jwn(n)=A*(dOn(n)-dp); % [m^3/(m^2*s)] water permeate
flux
        dcn(n)=(cD*exp(-Jwn(n)*yD/DD)-
cF*exp((S+yF)*Jwn(n)/DF))/(1+B/Jwn(n)*(exp((S+yF)*Jwn(n)/DF)
)-exp(-Jwn(n)*yD/DD)); % [kg/m^3] effective concentration
difference
        if (abs(dcguess(n)-dcn(n))>0.1);
        dcguess(n+1)=dcguess(n)-0.01;
        else
        break
        end
        end

% EFFECTIVE RESULTS GIVEN POLARIZATION EFFECT
dO=dOn(n); % [Pa] effective osmotic pressure difference
Jw=Jwn(n); % [m^3/(m^2*s)] effective freshwater permeate
flux
dc=dcguess(n); % [kg/m^3] effective salinity difference
cFS=(cF+B*dc/Jw)*exp(Jw*yF/DF)-B*dc/Jw; % [kg/m^3]
concentration at feed side of support structure
cFm=(cF+B*dc/Jw)*exp(Jw*(S+yF)/DF)-B*dc/Jw; % [kg/m^3]
concentration at feed side of membrane
cDm=(cD+B*dc/Jw)*exp(-Jw*yD/DD)-B*dc/Jw; % [kg/m^3]
concentration at draw side of membrane
dcm=cDm-cFm; % [kg/m^3] check concentration difference

% BASED ON SOLUTION DEFINE VALUES FOR i=t+1

% REDEFINE BOUNDARY LAYERS
uFt(t+1)=uF; % [m/s] feed velocity
uDt(t+1)=uD; % [m/s] draw velocity
ReFt(t+1)=ReF; % [unitless] feed Reynolds
ReDt(t+1)=ReD; % [unitless] draw Reynolds
DFt(t+1)=DF; % [m^2/s] feed diffusion
DDt(t+1)=DD; % [m^2/s] draw diffusion
ScFt(t+1)=ScF; % [unitless] feed Schmidt
ScDt(t+1)=ScD; % [unitless] draw Schmidt
ShFt(t+1)=ShF; % [unitless] feed Sherwood
ShDt(t+1)=ShD; % [unitless] draw Sherwood
kFt(t+1)=kF; % [m/s] feed diffusion transfer coefficient
kDt(t+1)=kD; % [m/s] draw diffusion transfer coefficient
yFt(t+1)=yF; % [m] feed boundary thickness
yDt(t+1)=yD; % [m] draw boundary thickness

```

```

% OUTPUT RESULTS
Jwt(t+1)=Jw; % [m^3/m^2/s] water permeate flux
Jwlmh(t+1)=Jw*1000*3600; % [l/m^2/h] water permeate flux
deltaV(t+1)=Jw*a*deltat; % [m^3] water permeate volume
Vt(t+1)=Vt(t)+deltaV(t+1); % [m^3] cumulative water
permeate volume
phit(t+1)=Vt(t+1)/VFo; % [unitless] recovery ratio

Wdott(t+1)=Jw*dp; % [W/m^2] power density
deltaE(t+1)=Jw*dp*a*deltat; % [J] energy recovered
Et(t+1)=Et(t)+deltaE(t+1); % [J] cumulative energy recovery

Jst(t+1)=B*dc; % [kg/m^2/s] salt permeate flux
deltam(t+1)=B*dc*a*deltat; % [kg] salt permeate mass

dct(t+1)=dc; % [kg/m^3] effective concentration difference
dcmt(t+1)=dcm; % [kg/m^3] check concentration difference
dOt(t+1)=dO; % [Pa] effective osmotic pressure difference
cFSt(t+1)=cFS; % [kg/m^3] concentration at feed side of
support structure
cFmt(t+1)=cFm; % [kg/m^3] concentration at feed side of
membrane
cDmt(t+1)=cDm; % [kg/m^3] concentration at draw side of
membrane

% FLOW PARAMETERS FOR i=t+2
mFt(t+2)=mFt(t+1)+deltam(t+1); % [kg] feed salt mass
mDt(t+2)=mDt(t+1)-deltam(t+1); % [kg] draw salt mass
VFt(t+2)=VFt(t+1)-deltaV(t+1); % [m^3/s] feed volume
VDt(t+2)=VDt(t+1)+deltaV(t+1); % [m^3/s] draw volume
cFt(t+2)=mFt(t+2)/VFt(t+2); % [kg/m^3] feed concentration
cDt(t+2)=mDt(t+2)/VDt(t+2); % [kg/m^3] draw concentration

% REDEFINE FLOW PARAMETERS
mF=mFt(t+2); % [kg] feed salt mass
mD=mDt(t+2); % [kg] draw salt mass
VF=VFt(t+2); % [m^3] feed volume
VD=VDt(t+2); % [m^3] draw volume
cF=cFt(t+2); % [kg/m^3] feed concentration
cD=cDt(t+2); % [kg/m^3] draw concentration

end

xlswrite('K1cta.xls', th, 'Sheet 1', 'b1')
xlswrite('K1cta.xls', Jwlmh, 'Sheet 1', 'b2')
xlswrite('K1cta.xls', Vt*1000/mDo, 'Sheet 1', 'b3')

```

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xlswrite('K1cta.xls', Et/3600/mDo, 'Sheet 1', 'b4')
xlswrite('K1cta.xls', Wdott, 'Sheet 1', 'b5')
xlswrite('K1cta.xls', phit*100, 'Sheet 1', 'b6')
xlswrite('K1cta.xls', (dOt-dp)/10^5, 'Sheet 1', 'b7')

```

5.8 List of Symbols in Chapter 5

A	membrane water permeability ($\text{m s}^{-1} \text{Pa}^{-1}$)
a	membrane surface area (m^2)
B	membrane salt permeability (m s^{-1})
c	concentration (g l^{-1})
D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
d_h	hydraulic diameter (m)
i	number of ions
J_w	permeate flux ($\text{l m}^{-2} \text{s}^{-1}$)
J_s	solute flux ($\text{g m}^{-2} \text{s}^{-1}$)
k	diffusion transfer coefficient (m s^{-1})
m	mass (kg)
$\dot{m}$	mass flow rate (kg s^{-1})
p	pressure (Pa)
R	gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
Re	Reynolds number
S	structure parameter (m)
Sc	Schmidt number
Sh	Sherwood number
R	gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
T	absolute temperature (K)
V	volume (m^3)

Greek symbols:

π	osmotic pressure (Pa)
δ	boundary layer thickness (m)

θ recovery ratio

Subscripts/Superscripts:

D draw

F feed

o initial

' osmotic limit

" practical limit

5.9 Acknowledgments

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CHAPTER SIX

CONCLUSIONS

6.1 Contributions

6.1.1 A New Concept

Water based farming techniques such as hydroponic systems have been used widely inside and around large cities to preserve space, water, and energy. Energy and water efficiency of such systems can yet be improved with new and innovative methods. One of these methods is fertilizer osmosis which works on the concept of osmotic pressure differences between concentrated fertilizer draw solutions and a source of feed water. Fertilizer solutions can extract clean water from wastewater sources and produce energy via processes such as forward osmosis and pressure retarded osmosis. In Chapter 2 we contributed a new concept to the literature, namely the first-ever introduction of converting fertilizer energy to mechanical work by PRO. We present preliminary performance analysis of these systems and show estimates of water recovery and energy recovery amount from fertilizer osmosis.

6.1.2 Experimental Validation

In Chapter 3, we experimentally demonstrated the use of fertilizer to generate useful mechanical work via pressure retarded osmosis (PRO). This is only the second time in the literature that the novel concept of power generation from fertilizer osmosis is demonstrated and experimentally validated. A number of common single solute and

blended fertilizer were analyzed using both experimental and numerical methods. Laboratory test trials showed energy recovery of up to 5 Wh per kg of fertilizer, and power of up to 6 W per m² of membrane area given commercial cellulose triacetate membranes. A drop in power is demonstrated throughout the fertilizer PRO batch process, and the resulting tradeoffs between energy recovery and power density are discussed. Simulation results suggest that high performance membranes can be used to maintain elevated power above 5 W/m² throughout the batch process, while recovering approximately 5 Wh/kg energy. The loss of valuable fertilizer via leakage to the feed stream is found to be less than 1 % of the initial fertilizer mass, suggesting that this non-ideal dynamic can be reasonably minimized. Implications at the food, energy, and water nexus are discussed.

6.1.3 Limits of Energy Recovery

In Chapter 4, a combination of analytical, numerical, and experimental methods is used to establish the thermodynamic and process limits of fertilizer energy conversion via PRO. This is the first time that the potential and significance of this energy source compared to farms requirements is demonstrated. The results indicate that up to 125 Wh/kg of energy is released from fertilizer when it is diluted in water. PRO process dynamics including operation at constant applied pressure, and the need to maintain high power levels throughout the batch process, limit the conversion to work to up to 14.9 Wh/kg. Further, experimentally-calibrated simulation results suggest that only up to 6.8 Wh/kg can be anticipated when considering non-ideal transport dynamics such as reverse solute flux and concentration polarization. The effect of feed source concentration and

recovery ratio on batch process dynamics are investigated, and it is found that using wastewater as feed may be comparable to scenarios where high recovery of clean irrigation feed is used. The potential of common hydroponic plant crops is evaluated, and results indicate that advances in membrane technology may allow energy recovery to approach 5 % of typical greenhouse electricity consumption.

6.1.4 Limits of Water Recovery

The quantities of water that can be recovered from batch processes remains a question, and how significant recovery volumes are relative to the overall water balance of crops. In Chapter 5, we establish the thermodynamic and practical limits of recovering water from a fertilizer osmosis batch process, and thereby provide insights into the future prospects of this concept. It is shown that common fertilizers can recover between 112-138 l/kg via fertilizer osmosis from a municipal wastewater feed source while maintaining practical flux of at least 5 lmh. The effects of membrane type, feedwater concentration, and permeate to feed recovery ratio are analyzed with a combination of analytical, numerical, and experimental methods. Water recovery limits are compared against the irrigation requirements of hydroponic crops. Between 32-99 % of a plant's irrigation water can be supplied by fertilizer osmosis at competitive flux levels, provided that low concentration feed such as municipal or hydroponic wastewater is available. Such recovery volumes represent a significant portion of the plant water balance and should justify future research in the area of fertilizer osmosis.

6.2 Future Work

In this dissertation, we have established the limits of energy and water recovery from fertilizer by considering different types of fertilizers, feed sources, membranes, and operating conditions. Some technical questions remain however, that we present in this chapter as proposed future work. Answering these questions would contribute to the fertilizer osmosis literature that is still an active field of research by several other groups such as University of Technology, Sydney (UTS) and Columbia University. We also introduce the novel concept of using fertilizer solution as liquid desiccant for dehumidification and present the preliminary results.

6.2.1 Modeling of Multispecies Solutions

The present model has limited ability to predict solute transport given multi-ion draw solutions. We observed this in Section 3.3.2, when we compared simulation and experimental data for Hoagland solution. The typical method of modeling solute transport in to assume only one solute in feed and draw solutions. For example, our model approximates wastewater and urine feed sources with a constant sodium chloride NaCl concentration. This simplification can be misleading while studying multi-ion solutions because every ion has a unique behavior such as diffusivity and osmotic pressure and every membrane has different permeability to each solute. The effective concentration difference that was previously shown in eqs, (4.12) and (5.8) that predict the polarization effects is also based on a single solute concentration gradient. In order to accurately understand these transport phenomena, we need to develop a new model that can predict the behavior of multi-ion solutions. We also assume a linear osmotic pressure function

with concentration gradient that is not accurate especially for higher concentration.

Therefore, the development of a complex model that can predict different ions interaction and considers non-linearity of osmotic pressure is proposed as future work.

6.2.2 Other Applications: Using Fertilizer as a Liquid Desiccant for Greenhouse

Dehumidification

In future work we propose the novel concept of using fertilizer solution as liquid desiccant for greenhouse dehumidification. Like fertilizer FO and PRO, the dehumidification takes place within a semi-permeable membrane that separates concentrated fertilizer draw solution and humid air. The driving force of this process is the water vapor pressure difference between humid air and fertilizer solution and the product is a clean fertigation solution that can be delivered to the plants.

We follow the previous chapter's pattern, by introducing the new concept and showing the preliminary analysis of developing the thermodynamic limits to fertilizer dehumidification. This limit is defined by partial pressure equilibrium. Similar to FO, water vapor permeates into fertilizer draw solution until there is no vapor pressure gradient across the membrane. We define this equilibrium as the thermodynamic limit to dehumidification. An analytical solution for the equilibrium permeate mass $\Delta m'$ per unit mass of fertilizer can be obtained in terms of initial conditions and recovery ratio.

$$\frac{\Delta m'}{m_D^0} = -M_D \left(\frac{1}{c_D^0} + \frac{i}{\ln \left[\left(\frac{n_{F,H_2O}^0}{n_F^0} - \theta' \right) \left(\frac{p_F}{p_{D,0}} \right) \right]} \right) \quad (6.1)$$

Where m_D^0 and c_D^0 are the initial mass and concentration of the fertilizer, respectively. M_D is the molar mass of fertilizer, θ' is the equilibrium recovery ratio, $\frac{n_{F,H_2O}^0}{n_F^0}$ is the mole fraction of water vapor to total moles of air, $p_{D,0}$ is the saturation pressure of water and p_F is partial pressure of air. Similarly, the equilibrium recovery ratio θ' is a measure of the feed that is made available for the fertilizer dehumidification process.

To illustrate, we refer to the same N, P, K fertilizers listed in table 5.1. Figure 6.1 shows the dehumidification process for each of the fertilizer draw solutions as they recover water permeate from air that approximates actual greenhouse, and with sufficient air volume so that equilibrium recovery ratio $\theta' = 0$. As shown, potential for water recovery per unit fertilizer $\Delta m'/m_D^0$ ranges from 19.4 – 18.5 g H₂O/kg, with the greatest potential among the three sample fertilizers shown for KCl. The partial pressure relation is shown in Eq. 6.11 as a function of concentration, recovery ratio, temperature, and relative humidity RH.

$$\Delta p_{H_2O} = p_{D0}(T) \exp \left[\frac{-i}{\frac{1}{c_D^0} + \frac{\Delta n'}{n_D^0}} \right] - \left(\frac{n_{F,H_2O}^0}{n_F^0} - \theta \right) p_F \quad (6.2)$$

Where $\Delta n'$ is the permeate moles of water at equilibrium.

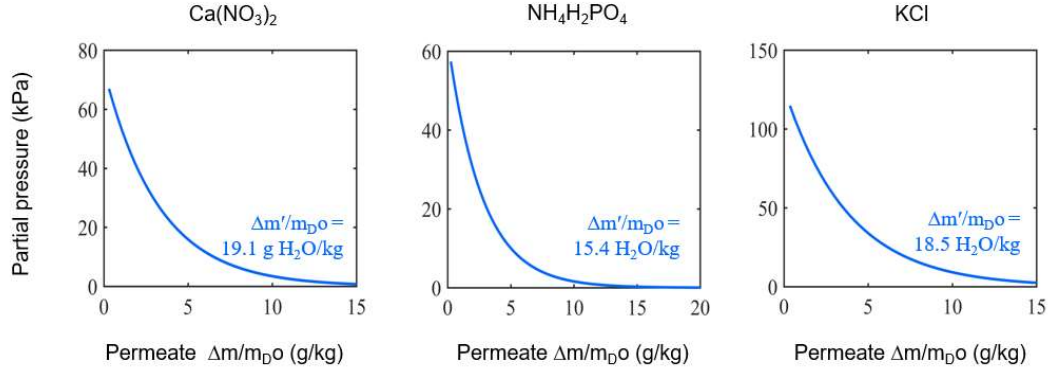


Figure 6.1. Partial pressure difference Δp between concentrated N, P, K fertilizer draw solutions and humid air feed solution (given $T = 25^\circ\text{C}$ and $\text{RH} = 100\%$ $\theta = 0$) as permeate volume Δm is recovered by the fertilizer. Equilibrium limits are identified by $\Delta m'$ and normalized per unit moles of fertilizer m_{D^0} .

This equilibrium limit will be largely a function of the relative humidity, temperature, and target recovery ratio. Figure 6.2 shows the normalized equilibrium permeate volume $\Delta V'/m_{D^0}$ for each of the fertilizers as a function of RH and recovery ratio. At equilibrium the partial pressure of water in feed and draw side are equal, $p_{D,\text{H}_2\text{O}} = p_{F,\text{H}_2\text{O}}$. As shown, an increase in either of these variables significantly reduces the potential for water recovery. To illustrate, each of the three cases are highlighted. In the case where 50% RH is available and given a high recovery target (large greenhouse with $\theta' = 0$) water recovery is limited to 15.5 l/kg. For the case where $\text{RH} = 80\%$ water recovery is limited to 17.3 l/kg. Comparing these two cases suggests that limits are much more sensitive to recovery ratio than RH.

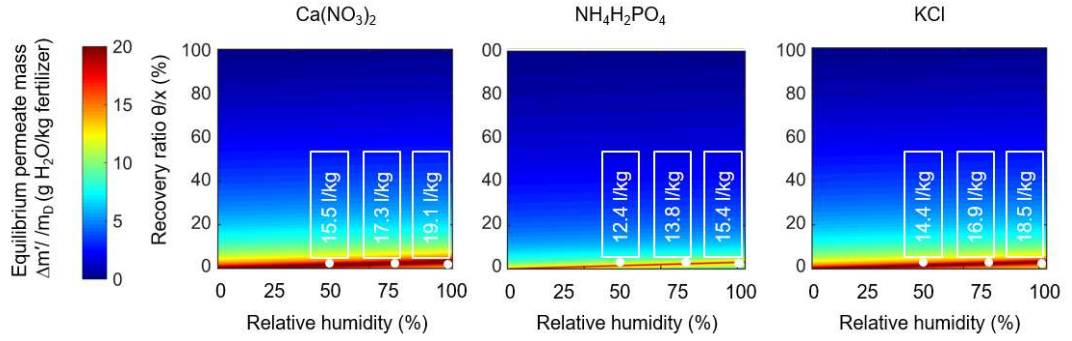


Figure 6.2. Equilibrium limits of water recovery $\Delta m'$ per unit mass of fertilizer m_D° for N, P, K fertilizers during dilution with various air humidity RH and given various target recovery ratios θ' . Values for 50, 80, 100 % RH at $\theta=0$ are show cased.

The amount of energy that can be saved is directly proportional to water recovery limits. The energy savings can be presented in terms of Wh/kg and are shown in Fig.6.3. The limits are show cased for three different RH at zero recovery ratio (very large greenhouse).

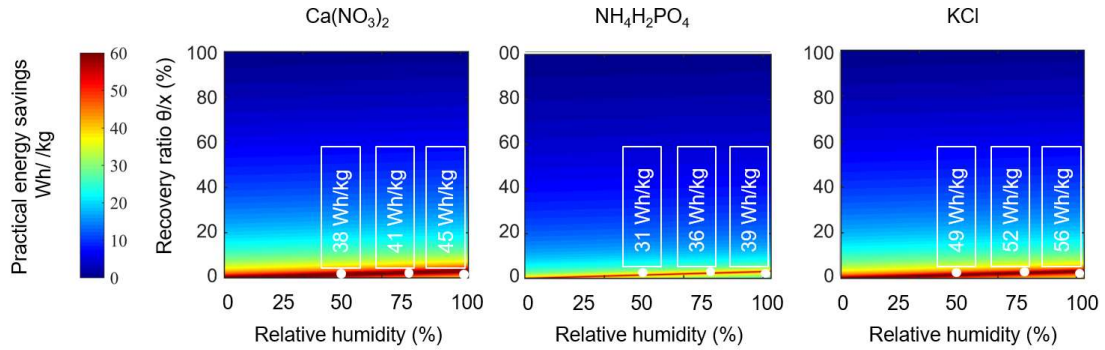


Figure 6.3. Energy saved while replacing by replacing conventional dehumidifier Wh/kg fertilizer for N, P, K fertilizers during dilution with various air humidity RH and given various target recovery ratios θ' . Values for 50, 80, 100 % RH at $\theta=0$ are show cased.

KCl shows the highest limits with 56 Wh/kg followed by $\text{Ca}(\text{NO}_3)_2$ with maximum of 45 Wh/kg. Same as water volume, the energy savings are more sensitive to RH than recovery ratio.

These preliminary results only show the maximum thermodynamic limits to fertilizer dehumidification. The next steps to complete this study will be developing the limits for practical dehumidification while including phase change and heat transfer dynamics.

6.3 Publications

6.3.1 Journal Papers

1. P. Pourmovahed, M. Lefsrud and J. Maisonneuve, “Thermodynamic Limits of Using Fertilizer to Produce Clean Fertigation Solution from Wastewater via Forward Osmosis” *Journal of Membrane Science* 647 (2022).
2. P. Pourmovahed and J. Maisonneuve, “Thermodynamic limits of using fertilizer osmosis to produce mechanical work via pressure retarded osmosis,” *Journal of Membrane Science* 629 (2021).
3. P. Pourmovahed and J. Maisonneuve, “Demonstration of power generation from fertilizer via pressure retarded osmosis,” *Transactions of the ASABE* 64, 495-505 (2021).
4. P. Pourmovahed and J. Maisonneuve, “Using fertilizer drawn osmosis to produce irrigation water and energy for hydroponic farming,” *Proceedings of the ASABE Annual International Meeting*, Detroit, MI, July 2018.
5. Maisonneuve, P. Pourmovahed, L. Zhu, and M. Dong, “Analysis and performance of a residential indoor vertical plant production unit,” *proceedings of the ASHRAE General Winter Meeting*, Chicago, IL, January 2018.

6.3.2 Conference Presentations

1. P. Pourmovahed and J. Maisonneuve, “Limits of using fertilizer osmosis to produce clean fertigation solution from wastewater,” poster presentation at the North American Membrane Society Annual Meeting, Estes Park, CO, August 2021.
2. P. Pourmovahed and J. Maisonneuve, “Limits of using fertilizer osmosis to generate mechanical work and produce irrigation water,” presentation at the International Congress on Membranes and Membrane Processes (online), December 2020.

3. P. Pourmovahed and J. Maisonneuve, “Using fertilizer to power and irrigate controlled plant environments,” presentation at the ASABE Annual International Meeting (online), July 2020.
4. P. Pourmovahed and J. Maisonneuve, “Experimental demonstration of power generation from fertilizer via pressure retarded osmosis,” presentation at the North American Membrane Society Annual Meeting (online), May 2020.
5. P. Pourmovahed and J. Maisonneuve, “Power from fertilizer using an osmosis cell,” presentation at the ASABE Annual International Meeting, Boston, MA, July 2019.
6. P. Pourmovahed and J. Maisonneuve, “Using fertilizer drawn osmosis to produce irrigation water and energy for hydroponic farming,” presentation at the ASABE Annual International Meeting, Detroit, MI, July 2018
7. J. Maisonneuve, P. Pourmovahed, L. Zhu, and M. Dong, “Analysis and performance of a residential indoor vertical plant production unit,” presentation at the ASHRAE General Winter Meeting, Chicago, IL, January 2018.
8. J. Maisonneuve and P. Pourmovahed, “Thermal modeling and simulation of a photovoltaic greenhouse prototype,” poster presentation at the ASABE Annual International Meeting, Spokane, WA, July 2017.

6.4 List of Symbols in Chapter 6

c	concentration (g l^{-1})
m	mass (kg)
M	molar mass (mol g^{-1})
n	number of moles
$p_{D,0}$	water saturation pressure (Pa)
p_F	partial pressure of air (Pa)
θ	recovery ratio

Subscripts/Superscripts:

D	draw
F	feed
o	initial
'	osmotic limit

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