GreenPRO: A novel fertilizer-driven osmotic power generation process for fertigation

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Abstract

This study introduces and describes GreenPRO, a novel concept involving fertiliser-driven osmotic energy generation via pressure retarded osmosis (PRO). The potential of GreenPRO was proposed for three objectives: (a) power generation, (b) water pressurization for fertiliser-based irrigation, and (c) water treatment, as a holistic water-energy-food nexus process. Three pure agricultural fertilisers and two commercial blended fertiliser solutions were used as the draw solution and irrigation water as feed to test this concept for power generation. Theoretical thermodynamic simulation of the maximum extractable Gibbs energy, was first performed. After which, a series of bench-scale experiments were conducted to obtain realistic extractable energy data. The results showed that concentrated fertilisers potentially have 11 times higher energy than seawater. Even after accounting for the irreversibility losses due to constant pressure operation, the investigated pure fertilisers were found to have between 2.5 – 4.6 Wh/kg of energy. The outcomes from the flux and power density modelling were then validated with real experimental data. This study has successfully demonstrated that concentrated fertilisers can release a substantial amount of chemical potential energy when diluted for fertigation. This energy could be harnessed by transforming it into electric energy or pressure energy via PRO.

Keywords: Pressure Retarded Osmosis; Fertigation; GreenPRO; Salinity Power.

1 Introduction

The exponential increase in the world population and urbanization leads to alarming crises in global water scarcity, energy availability, and food security. These could potentially affect global economies. Thus a surge in interest in energy-water-food nexus research and scientific discovery is seen in recent years as a response to optimise the use of water and energy resources to provide food [1]. Water-energy-food nexus is a concept mostly used when sustainable development is discussed, providing a holistic approach to examine the demands of a growing society and how these demands are met.

Water and energy are highly essential in ensuring global food supply, through agriculture. The agriculture sector is one of the largest consumers of the world's total fresh water supply, with over 70% of fresh water supply consumed for agriculture alone [2]. Furthermore, food production consumes more than a quarter of the total global energy, and around 90% of global energy production requires water [3, 4]. Agricultural chemicals, such as fertilisers, are important indirect energy inputs in agriculture and food production; in fact, global fertiliser consumption has increased exponentially over the past five decades [4]. It was reported that, from 2015 to 2018, the global demand for nitrogen-, phosphorus-, and potassium-based fertilisers increase 1.8% annually [5]. These fertilisers make up to around 60% of the fertilisers used on-farm for high yield crop production. The continuous global nutrient requirement is expected to affect both raw material availability, as well as greenhouse gas emissions and eutrophication [6]. One of the forms by which nitrogen is delivered through fertilisers is ammonia (NH_3). Approximately 2% of the world energy consumption is used for producing ammonia (NH_3) fertiliser by Haber-Bosch process that required very high temperature and pressure [7, 8], and this process also produces significant amount of carbon dioxide (CO_2) as a by-product. The production of a certain amount of NH_3 leads to the two- to three-fold production of CO_2 as a by-product [8, 9]. NH_3 production alone contributes to 0.93% of the greenhouse gas emission worldwide [8].

As irrigation water quality is not always available for agriculture, desalination of seawater and saline aquifers is currently employed through a number of technologies, which include thermal distillation and membrane-based processes [10]. The conventional membrane-based process, reverse osmosis (RO) is an energy-intensive process. Thus the large-scale implementation of RO to provide fresh water supply for agricultural consumption can be costly. This leads to the exploration of other less energy-intensive processes for seawater desalination, such as forward osmosis (FO) and pressure retarded osmosis (PRO). FO and PRO are both osmotically-driven process, such that these utilize the osmotic pressure difference between two streams of different osmotic potential or concentrations separated by a semipermeable membrane to desalinate water of high salinity [11]. Aside from desalination, PRO also uses the chemical potential for osmotic power generation, wherein the osmotic energy obtained between the two solutions is converted into mechanical energy through a water turbine [12, 13].

One of the challenges in osmotically-driven processes is the separation and recovery of the highly concentrated draw solution from the desalinated water. Desalination is mainly reliant on the efficiency of draw solution recovery and separation unless there is no need to separate and recover the draw solution. This was the concept of the fertiliser-driven FO (FDFO) process, which was primarily applied for agricultural purposes via fertilised irrigation, or fertigation, wherein the fertilisers are supplied through an irrigation network system. While this process has yet to be fully commercialized, the concept of FDFO has since been the subject of a number of extensive work on fertigation, osmotically-driven processes, and hydroponics [14-23].

Hydroponics, or greenhouse farming, is an agricultural system which maintains a controlled environment suitable for cost-effective and profitable crop production [24]. This particular method, also known as protected cultivation, is advantageous over open field agriculture due to its self-reliance and robustness, such that food production is ongoing throughout the year, unaffected by heavy rainfall, wind, and other anthropological conditions. Opting for greenhouse-based agriculture can potentially save a large amount of fresh water and fertiliser compared to open field agriculture, but this process would entail higher energy requirements. Such high energy requirements may not possibly be met by electrical power supply, especially for rural farms; thus, a need for a decentralized, and possibly, off-the-grid, energy supply in farms arises with the emergence of efficient agriculture practices. This then leads us to the novel combination of fertigation via FDFO and osmotic power generation using PRO, in a process, we call GreenPRO.

GreenPRO aims to harvest the Gibbs free energy of mixing between concentrated fertilisers and irrigation water for fertigation to obtain situ generation of useful energy while performing water purification simultaneously. GreenPRO is therefore a perfect example of the water-energy-food nexus concept, having a process wherein water is desalinated, and fertiliser is delivered for irrigation while producing energy at the same time. Through this process, concentrated fertilisers are used as the draw solution to extract pure water from the feed solution and produce electric or potential energy. If irrigation-quality water is used as feed solution, (i) membrane fouling is not expected to significantly reduce the process performances and (ii) the loss of nutrients due to reverse fertiliser diffusion, and optimal fertiliser dilution are not a concern as the concentrated feed can be merged with the partially diluted draw. On the other hand, if impaired water sources are used, this process is expected to suffer the same limitations as FDFO. In that case, the system could be coupled with other treatment processes, such as RO, to provide the remaining water. In such a system, a pressure exchanger could be used to harness the energy generated by the GreenPRO to power the RO. This, however, has to be validated in future studies.

In this study, a theoretical analysis of the maximum extractable Gibbs free energy from commercially available agricultural chemicals was initially performed. The theoretical investigation was then backed up by experiments using single and blended commercial fertilisers under different operating conditions. Finally, the outcomes were used to outline the opportunities and challenges of GreenPRO, as well as suggesting future research.

2 Methodology

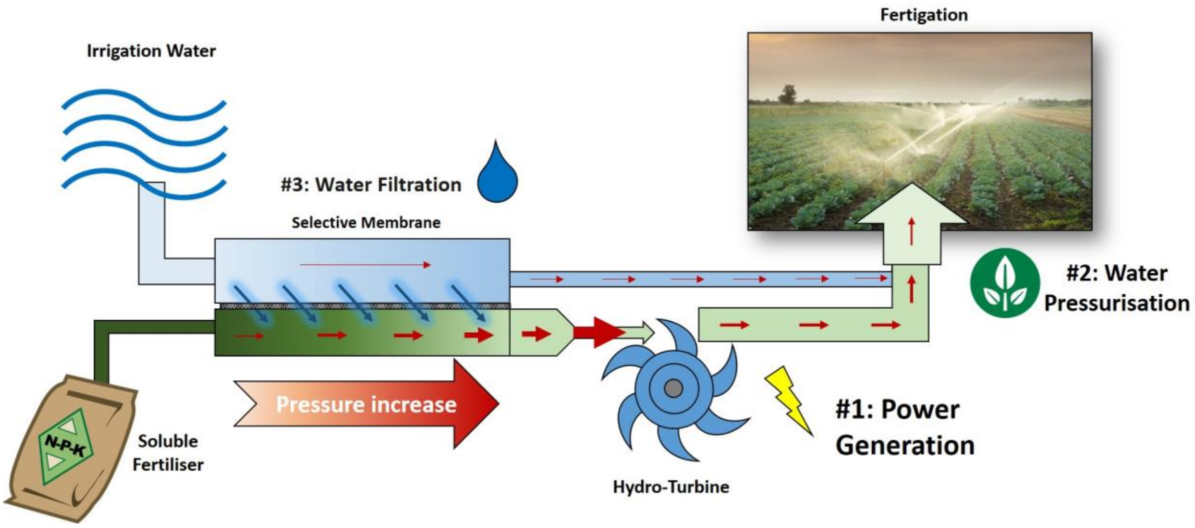

Figure 1 Conceptual design of the GreenPRO process.

2.1 Process descriptions

Figure 1 shows the whole concept of the GreenPRO process. Irrigation water and fertiliser solution are used as the feed solution and draw solution, respectively. The two solutions are separated by a selective and semi-permeable PRO membrane, whose active layer faces the draw solution (i.e., AL-DS, PRO mode). The osmotic gradient between the two solutions will allow the permeation of water to the draw channel, whose volume is fixed, thereby causing an increase in pressure. The hydraulic pressure build-up in the draw channel can then be transformed into electric energy, via a hydro turbine, or used deliver the pressurised fertigation water to the crops. Similar to FDFO, draw solution recovery is not performed in this process, as it is mixed with the irrigation water stream for direct fertigation. If water treatment is not targeted, the economic impact of reverse nutrient diffusion is also negligible as the concentrated feed solution can be merged with the diluted draw to reach full draw dilution and to close the nutrients mass balance.

2.2 Specific energy extractable from fertilisers

The thermodynamic extractable energy upon the mixing of two solutions with different salinity is extensively investigated and reported in the literature, for the dilution of seawater/RO brine with river water/wastewater [25-27]. In this work, however, the extractable Gibbs free energy of mixing is investigated for the dilution of blended fertilisers or pure agricultural chemicals with fresh water for irrigation. To fully elucidate the theoretical maximum extractable energy from concentrated fertilisers, a thermodynamic analysis is required.

The Gibbs free energy of mixing per volume of total mixed solution, i.e. ΔG_V, was calculated using Eq. 1 and 2 [25]:

$$\frac{\Delta G_V}{\nu RT} = c_M \ln(c_M) - \phi c_F \ln(c_F) - (1-\phi) c_D \ln(c_D) \quad (1)$$

$$\pi(c) = \nu RTc \quad (2)$$

where the concentration of feed (c_F), draw (c_D) and a mixed solution (c_M) are used. The feed volume fraction (ϕ) can be approximated by the quotient of the initial feed volume and the initial volume of the mixing solution $\left[\phi_i = \frac{(V_{D,i} - V_{D,i-1})}{V_{D,i}}\right]$ [25]. In Eq. 2, ν is the van't Hoff factor for strong electrolytes, R is the ideal gas constant, and T is the absolute temperature. By combining Eq. 1 and 2, ΔG_V can be obtained as a function of the osmotic pressure of the mixing solutions.

For this study, several simplifications of these equations were made. First, it was assumed that the osmotic pressure $\pi(c)$ follows the van't Hoff equation (Eq. 2). Also, the feed and draw were assumed to behave like an ideal solution, whose activity coefficient is unity and solute effect contribution on the volume is negligible [26]. Lin et al. showed that for seawater/river water or RO brine/river water mixing, this simplification caused a ΔG_V overestimation of less than 10%. It should be noted, however, that in the case of highly concentrated fertiliser solutions, the van't Hoff equation is expected to overestimate the real osmotic pressure of the solution, which might also not behave ideally. To cope with this, an experimental investigation was also performed in this work.

The maximum specific energy extractable from the fertiliser can, therefore, be obtained by solving the equation $d(\Delta G_V)/d\phi=0$. The result is shown in Eq. 3.

$$\Delta G_{V,max}\left[\frac{kWh}{m^3}\right] = \frac{\pi_D \pi_F}{\pi_D - \pi_F}(\ln(\pi_D) - \ln(\pi_F)) - \exp\left(\frac{\pi_D \ln(\pi_D) - \pi_F \ln(\pi_F)}{\pi_D - \pi_F} - 1\right) \quad (3)$$

In this work, three pure fertilisers $NH_4H_2PO_4$, KCl, and $(NH_4)_2SO_4$, and two commercial liquid blended fertiliser solutions were used for the analysis. Additionally, NaCl was also employed as a reference salt. The osmotic pressure of the fertiliser solutions was estimated using OLI Studio Analyser (Version 9.5, Oli Systems Inc., USA). The OLI Studio Analyser software uses Eq. 2 to calculate the osmotic pressure of a solution. Equation 4 was used to calculate the theoretical maximum energy extractable from a solid fertiliser:

$$\Delta G_{s,max}\left[\frac{Wh}{Kg}\right] = \frac{\Delta G_{V,max}}{C_{D,max}} \qquad (4)$$

where $C_{D,max}$ is the maximum solubility of the pure fertiliser in water at 20 ℃, or the concentration of the commercial liquid fertiliser. Table 1 shows the maximum solubility and relative osmotic pressure of the fertiliser solutions considered in this study. Finally, the theoretical of extractable energy (SE_{max}) in a constant-pressure, counter-current membrane module was also calculated with Eq. 5.

$$SE_{max} = \frac{(\pi_D - \pi_F)^2}{4\,(\pi_D - \pi_F)} \qquad (5)$$

Table 1 Maximum solubility and relative osmotic pressure of pure and commercial blended fertilisers. OLI Studio Analyser (Version 9.5, Oli Systems Inc., USA) was used for the estimation of C_D and π_D. The C_D, π_D, and D of commercial liquid fertilisers (Blend A, B) were calculated based on the composition provided by the manufacturer.

	$C_{D,max}$ (in H_2O at 20 ℃) [g/L]	Osm. Pressure, π_D [bar]
$NH_4H_2PO_4$	404	174
KCl	340	227
$(NH_4)_2SO_4$	754	275
Blend A	216	95
Blend B	128	66

2.3 Bench-scale FD-PRO experiments

Thermodynamic analysis is a useful tool to investigate the theoretical maximum extractable energy. However, in reality, PRO membranes are not perfectly selective, and occurrence of concentration polarisation significantly reduces the actual driving force in the membrane boundary layer. The non-ideal property of commercial membrane would then lessen the real maximum ΔG_{mix}. In order to investigate this, actual PRO experiments with commercial pure and blended fertilisers were performed. The materials used and the experimental protocol are presented in this section.

2.3.1. Materials

Three pure agricultural fertilisers, $NH_4H_2PO_4$, KCl, and $(NH_4)_2SO_4$, and two commercial liquid blended fertiliser solutions (Optimum Grow - twin pack hydroponic nutrient) were used in this PRO study. NaCl was also used as the reference draw solute for process standardization. All pure chemicals were obtained from Merck and used as received. The commercial liquid blended fertilisers used in this study were obtained from Fernland Agencies Pty Ltd (Queensland, Australia). This is a hydroponic nutrient solution usually employed in plant nurseries and commercial greenhouses. Their composition can be found in the literature [28]. This nutrient solution comes with two parts (i.e., A and B) to be diluted separately and then mixed. De-ionised water was used as feed solution. Commercial PRO thin film composite membrane (Toray Chemical Korea Inc., South Korea) was used as the semipermeable membrane.

2.3.2. Bench-scale PRO experiments

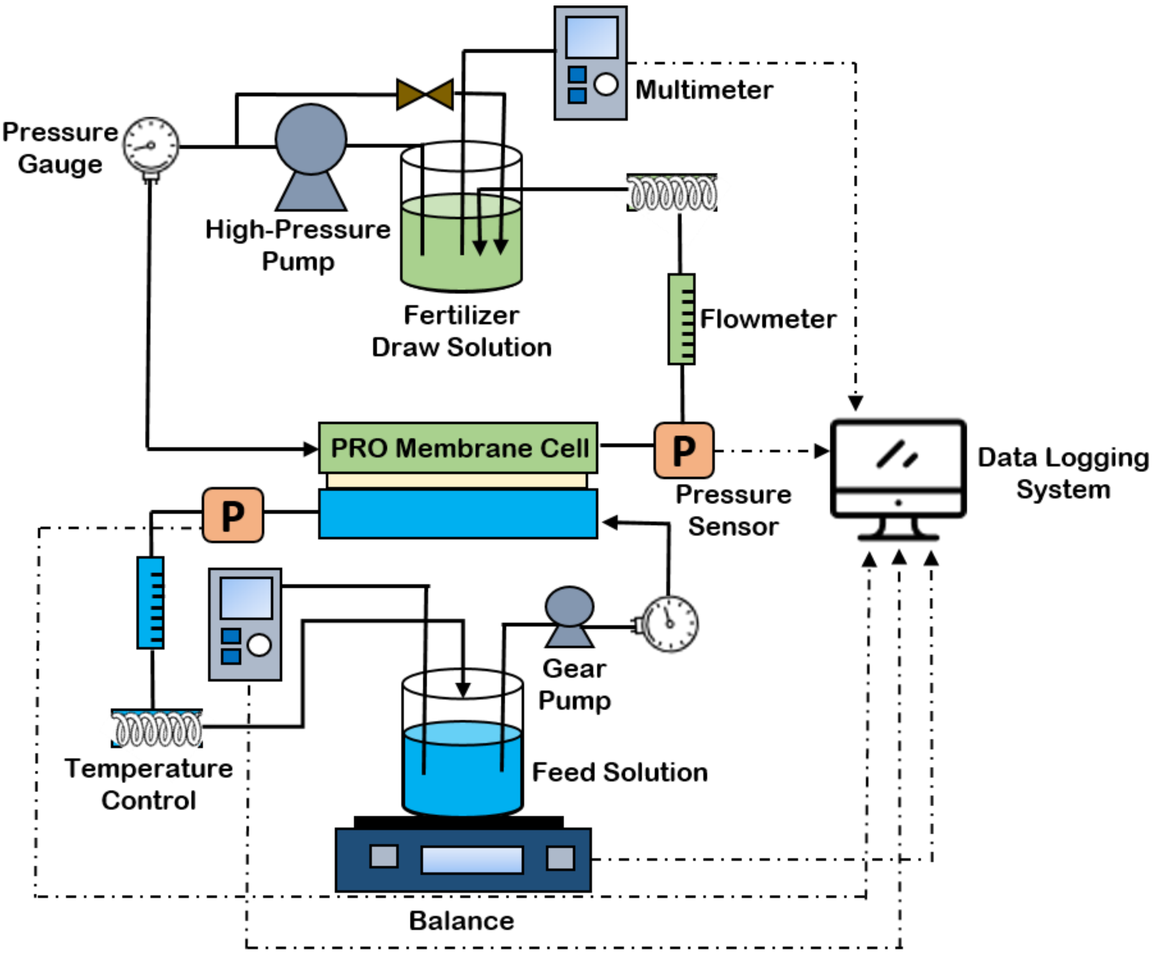

Figure 2 Experimental set-up used for the PRO tests.

The PRO experiments were carried out using a bench-scale system, as shown in Figure 2 (Cheon Ha Heavy Industries Co. Ltd., Gwangju, South Korea). The system consists of stainless-steel based membrane test cell containing two water channels allowing for counter-current operation. A gear pump (Cole Parmer, USA) was used to flow the feed solution while a high-pressure plunger pump (BM-4.18, BTLN, China) was used for the flow and pressurisation of the draw solution. Behind the high pressure pump, the customized buffer chamber (Chunha heavy industry, Republic of Korea) was installed in the PRO unit in order to alleviate the pulsation produced from the pump, so that the applied pressure was constantly maintained under the lab-scale PRO experiments [29]. The channel on the feed solution side had the following dimensions: 77 mm length, 26 mm width, and 2.5 mm depth. The feed solution flowed tangential to the membrane, which had an active area of 20.02 cm^2. A fixed flow rate of 200 mL min^{-1} was set for both the draw and feed streams. Mesh spacers were placed on the feed channel to support the membrane. The feed solution was contained in a vessel, whose weight is measured using a top-loading balance (CAS CUW4200HX, CAS, South Korea) and monitored using the PRO data auto-logging system. The feed solution is recirculated using a gear pump (Cole Parmer, USA). The draw solution, on the other hand, was recirculated using a high-pressure positive displacement pump. Conductivity measurements were monitored by a conductometer (Horiba LAquaact D-74, Horiba Scientific, Japan), while volume changes of the permeated water and applied pressures were observed and recorded by the data auto-logging system connected to the lab-scale PRO system.

The membrane was firstly stabilized and pre-compacted at 10 bar for 30 min. After pre-compaction, each fertiliser solutions was tested from 0 bar stepwise till 25 bar (which is the maximum pressure stated by the manufacturer). All experiments were performed at a fixed system temperature of 23.0 ± 1.0 °C. The water flux (J_w, L m^{-2} h^{-1}) was calculated based on the permeated volume over time. The power density (W, W m^{-2}) was obtained from Eq. 6, where ΔP is the pressure difference across the PRO membrane [30, 31].

$$W = J_W \cdot \Delta P \qquad (6)$$

2.4 Water flux and power density modelling

Water flux and power density of the pure and blended fertilisers were modelled using Eq. 6 and 7, respectively [32, 33].

$$J_W = K \cdot \ln\left(\frac{\pi_D - \left(\frac{J_W}{A}\right)\cdot\left(1+\left(A\frac{\Delta P}{J_W}\right)\right)+\left(\frac{B}{A}\right)\cdot\left(1+\left(A\frac{\Delta P}{J_W}\right)\right)}{\pi_F + \left(\frac{B}{A}\right)\cdot\left(1+\left(A\frac{\Delta P}{J_W}\right)\right)}\right) - \text{AL-DS orientation} \qquad (7)$$

Eq. 7 specifically accounts for the internal concentration polarisation (ICP) occurring during the osmotic process, as well as the applied hydraulic pressure. The mass transfer coefficient K was calculated with Eq. 9 as a ratio of the solute diffusivity D and the structural parameter of the porous membrane support S [34].

The A in eq. 7 value was calculated as the average of the transmembrane flux as a function of the applied hydraulic pressure, ranging from 5 to 10 bar, i.e. $\mathbf{A} = \frac{J_w}{\Delta P}$. To measure the salt rejection, necessary for the B value calculation (eq. 8), the rejection of a 500 mg/L solution of each salt was measured under 10 bar operating pressure [31]. Finally, the diffusivity coefficient of each salt was calculated with OLI Studio Analyser (Version 9.5, Oli Systems Inc., USA). The input data for the modelling can be seen in Table 2.

$$B = \left(\frac{1-R}{R}\right) \cdot (\Delta P - \Delta\pi) \cdot (A) \quad (8)$$

where ΔP is the trans-membrane pressure difference (bar), R the solute rejection and Δπ the osmotic pressure difference across the membrane.

$$S = \frac{D}{K} \quad (9)$$

Table 2 Input parameters used for the modelling of water flux and power density. Osmotic pressure and diffusivity were estimated using OLI Studio Analyser (Version 9.5, Oli Systems Inc., USA) while rejection, A and S are based on experimental data.

	C_D exp. [M]	Osm. Pressure, π_D [bar]	Diffusivity, D [$m^2.s^{-1}$]	Rejection, R [%]	Selectivity, B [$L.m^{-2}.h^{-1}$]
$NH_4H_2PO_4$	0.5	22.8	6.70×10^{-10}	97.9	0.84
KCl	0.5	22.3	9.04×10^{-10}	96.4	1.46
$(NH_4)_2SO_4$	0.5	24.3	9.45×10^{-10}	97.6	0.96
NaCl	0.6	27.8	1.48×10^{-9}	96.5	1.25
Blend A	As provided	95.2	3.60×10^{-10}	98.1	0.76
Blend B	As provided	66.3	3.60×10^{-10}	98.8	0.46
A [$L.m^{-2}.h^{-1}.bar^{-1}$]		3.94			
S [μm]		520			

J_W and W were estimated for the concentrated fertiliser solutions using the model, and the results were first validated with the PRO data from the diluted pure agricultural fertiliser solutions presented in Table 2. After the validation, the model was used to predict the flux and power density of the more concentrated commercial liquid fertiliser blends at higher applied hydraulic pressures.

3 Results and Discussion

3.1 Maximum Gibbs free energy from single and blended fertilisers

A theoretical investigation of the upper limit of the thermodynamic specific extractable energy from the pure and blended fertilisers was first performed. In a thermodynamically reversible system, the applied pressure ΔP variation is always infinitesimally smaller than the osmotic pressure $\Delta\pi$ difference across an ideal perfectly selective and semipermeable membrane [26, 27]. Figure 3 compares the Gibbs free energy, as a function of the feed volume fraction ϕ, of seawater-river water mixing with the energy from mixing commercial liquid fertiliser blends with river water. It can be seen that ΔG_{mix} of the commercial fertilisers is about 3.8 times (for Blend A) and 2.6 times (for the Blend B) compared to the ΔG_{mix} of seawater.

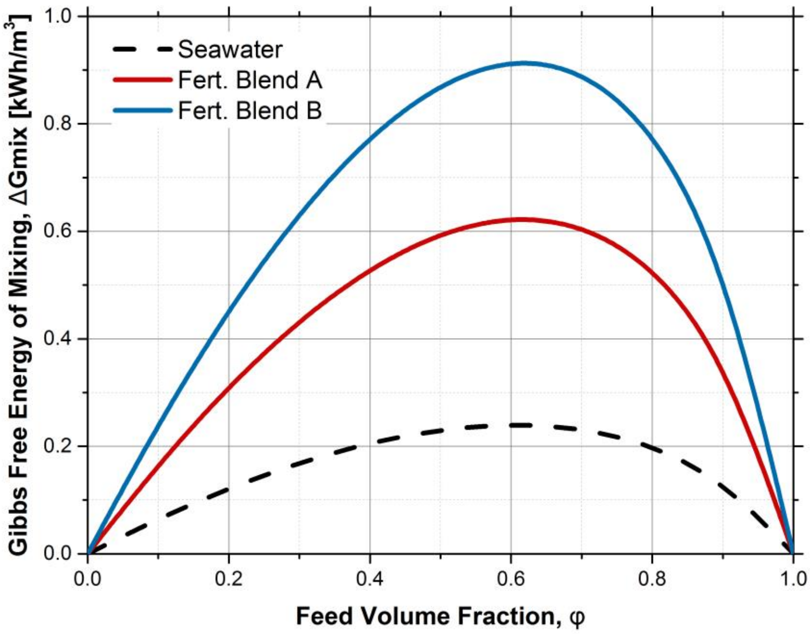

Figure 3 Comparison of the specific Gibbs free energy of mixing seawater (black, dashed), commercial liquid fertilisers blend A, B with river water as a function of the mixing ration of feed and draw (ϕ). Equation 1 was used for the calculation. It was assumed that river water has an osmotic pressure of π_r = 0.71 bar (0.015 M NaCl), seawater has π_{SW} = 27.84 bar (0.6 M NaCl), fertiliser blend A $\pi_{Fert.\ Blend\ A}$ = 95.2 bar and fertiliser blend B $\pi_{Fert.\ Blend\ B}$ = 66.3 bar. The osmotic pressure of the solutions was calculated via OLI Studio Analyser (Version 9.5, Oli Systems Inc., USA).

Nonetheless, in full-scale operation, the GreenPRO system would likely operate under constant pressure, thereby decreasing the maximum extractable energy [27]. In fact, throughout the module, water would permeate from the feed to the draw (i.e., ΔQ); however, this cannot result in a situation where $\Delta\pi < \Delta P$. Therefore, at constant pressure, there is a limit to the permeation flow rate ΔQ which results in a lower extractable energy limit $\Delta G_{V,\,max}$ [26, 27]. In a previous study, Straub et al. [35] demonstrated that the countercurrent operation would result in the maximum theoretical extractable energy limit (Eq. 5).

By looking at Figure 4, it can be seen that between 20-30% of the specific extractable energy is lost under constant pressure operation, in accordance with the literature data [27]. It is also noticeable that pure fertilisers have $\Delta G_{V,\,max}$ values considerably higher than that of seawater. This is because of its high solubility in water that results in very high theoretical osmotic pressure (i.e., 275 bar for SOA, Table 1). Figure 5 shows that KCl held the highest $\Delta G_{S,\,max}$ due it's high osmotic pressure even at relatively low concentration.

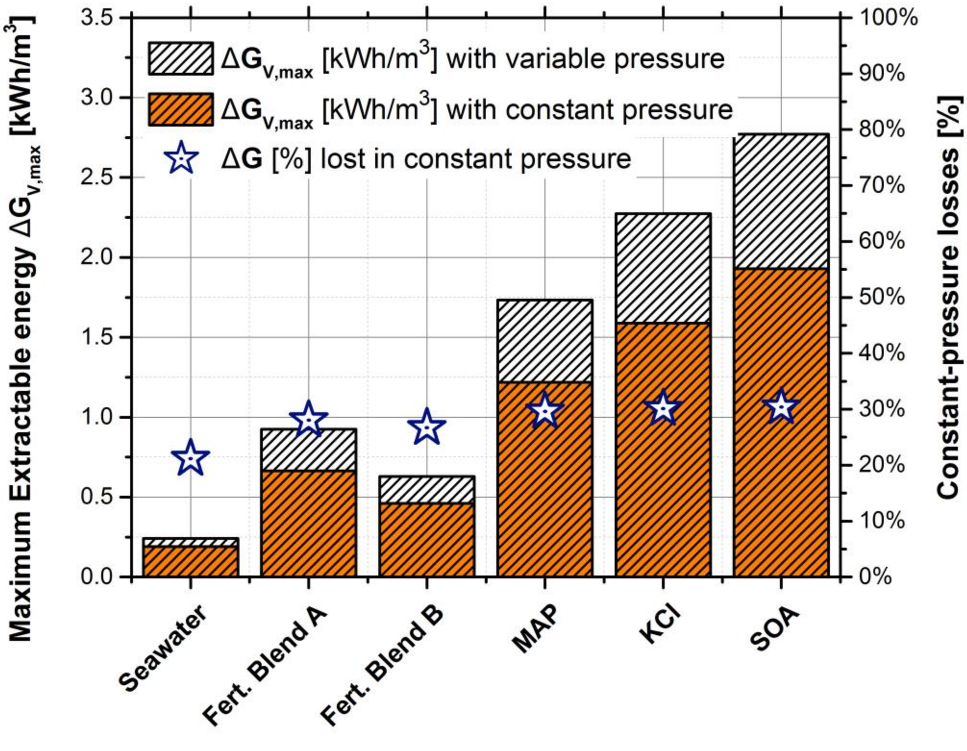

Figure 4 Comparison between the maximum specific energy $\Delta G_{V,\,max}$ of pure fertilisers (eq. 1), at their maximum concentration in water at 20℃, commercial liquid fertiliser blends, and seawater. The losses due to constant-pressure, counter-current mode operation, were accounted for in the orange histogram (eq. 5). The percentage of $\Delta G_{V,max}$ is plotted as blue stars on the right-Y axis. The osmotic pressure of the solutions, used for the calculation, was calculated via OLI Studio Analyser (Version 9.5, Oli Systems Inc., USA).

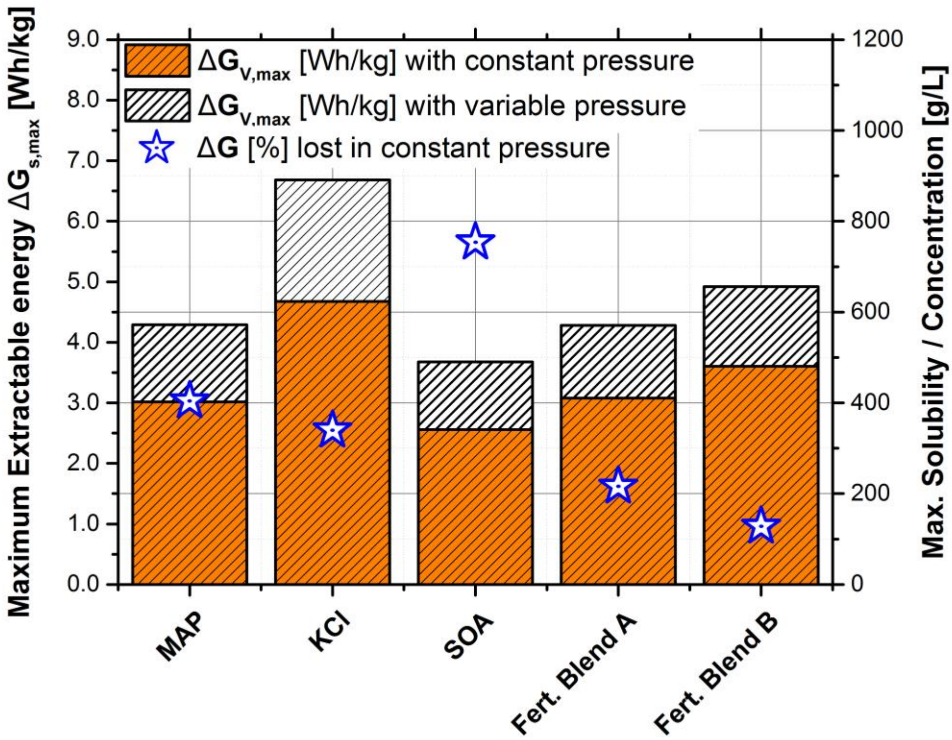

Figure 5 Plot of the maximum extractable energy from pure $NH_4H_2PO_4$ (MAP), KCl, $(NH_4)_2SO_4$ (SOA), and liquid fertilisers A and B dissolved in water at 20℃. The losses due to constant-pressure, counter-current mode operation, were accounted for in the orange histogram (eq. 5). Equation 4 was used for the calculation, where $C_{D,max}$ is displayed as blue stars on the right-Y axis. The osmotic pressure of the solutions, used for the calculation, was calculated via OLI Studio Analyser (Version 9.5, Oli Systems Inc., USA).

Based on the specific maximum extractable energy modelling, it can be concluded that soluble fertilisers held an energy of mixing ranging from 3.7 – 6.7 Wh/kg. This is because of their high solubility and speciation. This is particularly true for the pure fertilisers. In the case of commercial liquid blended fertilisers, as a marketing strategy, the value is lower since the fertiliser solutions have probably not reached saturated conditions. It can be then considered as an already partially diluted solution. Therefore, it expected that, when concentrated solutions are mixed with irrigation water, a maximum of 1.7 – 2.6 kWh/m^3 could be extracted. These values decrease by about 30% when the constant-pressure operation losses are accounted for. Still, these values are overestimating the actual extractable energy as they assume a perfectly selective semipermeable membrane with no occurrence of ICP. To account for the losses with the use of a commercially-available membrane (about an additional 15% in the case of seawater-river water mixing [27]), a full-scale module analysis should be performed. To lay the foundation for this future analysis, a model to predict the flux and power density of real commercial fertilisers was developed and validated experimentally. The results are presented in the following sections.

3.2 Performances of pure and commercial fertilisers under constant pressure

Water flux and power density values were plotted as a function of the applied hydraulic pressure for the fertiliser solutions used in this study, as shown in Figure 6. 0.6 M NaCl, the average seawater concentration [36], was used as the standard draw solution for comparison. The pure agricultural chemicals ($NH_4H_2PO_4$, KCl, and $(NH_4)_2SO_4$) were dissolved in 0.5 M aqueous solutions, while the commercial fertiliser blends were used as received. Due to the dilute nature of the pure agricultural chemical solutions, a lower water flux and power density were observed, compared to the seawater-like draw solution standard. The water flux of these solutions was also observed to be similar; at 0 bar, $NH_4H_2PO_4$, KCl, and $(NH_4)_2SO_4$ exhibited 26.2, 23.4, and 25.9 L m^{-2} h^{-1}, respectively. On the contrary, since the commercial fertiliser blends were used directly without dilution, the overall concentration was expected to be higher than that of seawater; at 0 bar, fertiliser blends A and B exhibited water flux values of 45.3 and 41.8 L m^{-2} h^{-1}, respectively, compared to seawater's 38.1 L m^{-2} h^{-1}.

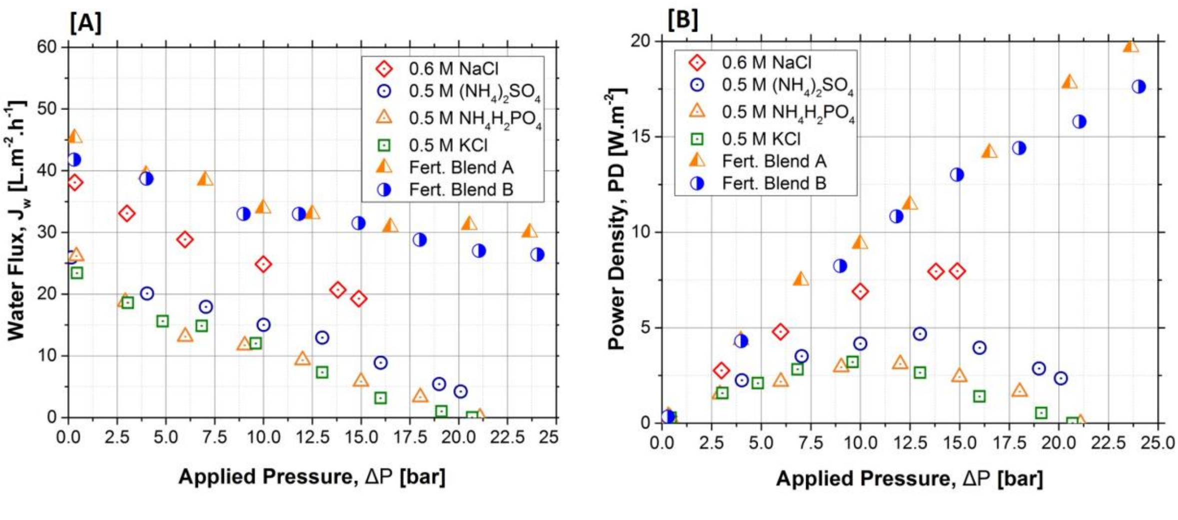

Figure 6 Experimental results of the measured water flux [A] and power densities [B] achieved with 0.5 M single fertilisers, simulated seawater (0.6 M NaCl) and commercial liquid fertiliser blends. Toray PRO membrane was used with an applied hydraulic pressure up to 25 bar.

It can also be seen in Figure 6 that as the applied hydraulic pressure increases, water flux decreases as well. For the pure agricultural chemical solutions, water flux decreased until reaching zero at approximately 21 bar. Moreover, the power density reached a maximum when the applied hydraulic pressure is approximately half of the pressure at which water flux reaches zero. Maximum power densities of 3.1 W m^{-2} (at 12 bar), 3.2 W m^{-2} (at 9.6 bar), and 4.7 W m^{-2} (at 13 bar) for $NH_4H_2PO_4$, KCl, and $(NH_4)_2SO_4$, respectively. For the fertiliser blend solutions, sufficient hydraulic pressure to decrease the water flux to 0 was not applied in this study, due to limitations of the bench-scale facility, yet the gradual decrease of water flux and increase of the power density values were observed in this study. During the PRO process, the draw solution is diluted simultaneously as the feed concentration increases. This leads to a reduction of the osmotic pressure gradient between the draw and feed solutions, that, the maximum power density can only be achieved at a certain applied hydraulic pressure value.

3.3 Water flux and power density modelling

Evaluation of the performances of commercial state-of-the-art PRO membranes is essential to estimate the real maximum extractable energy from a fertiliser solution. Straub et al. [27] estimated that approximately 15% of energy loss occurs due to reverse salt flux and concentration polarisation when NaCl is used as draw solution. However, it is clear from Table 2 that the diffusivity D (main factor in the ICP effect) and rejection R of fertilisers can differ quite substantially from the diffusivity and rejection of pure NaCl. Thus, the ΔG losses when fertilisers are used as draw solution using a real membrane needs to be evaluated. In this paper, we have focused the attention on the validation of a water flux and power density model to predict the performances of the selected fertilisers. This model can be then used for future analysis of the realistic amount of energy extractable from the concentrated fertiliser solution.

Eq. 6 and 7 were used for the calculations, and the input of the equations are displayed in Table 2. Real experimental data were used to validate the modelling results. Figure 7 and Figure 8 show the theoretical and experimental water flux and power density data. It can be seen that even under the assumptions regarding the osmotic pressure and average diffusivity, the model was able to predict closely the flux and power density of liquid commercial fertiliser blends. Figure 8 shows that, theoretically, the high osmotic pressure of the fertiliser blends can lead to power densities between 24 to 29.5 W/m^2 however, there is no commercial osmotic or PRO membranes that can withstand hydraulic pressure between 40 to 50 bars and hence this shows the prospects of the need to develop PRO membranes with significantly enhanced mechanical strength compared to the existing osmotic membranes. There is a trade-off between structural parameters (S) and mechanical strength, and increasing the membrane strength can likely result in increasing also the S value which, in turn, could aggravate the ICP effect. This therefore opens up opportunities to explore other material composites for improving the mechanical strength of the PRO membrane without significantly impacting the structural parameters.

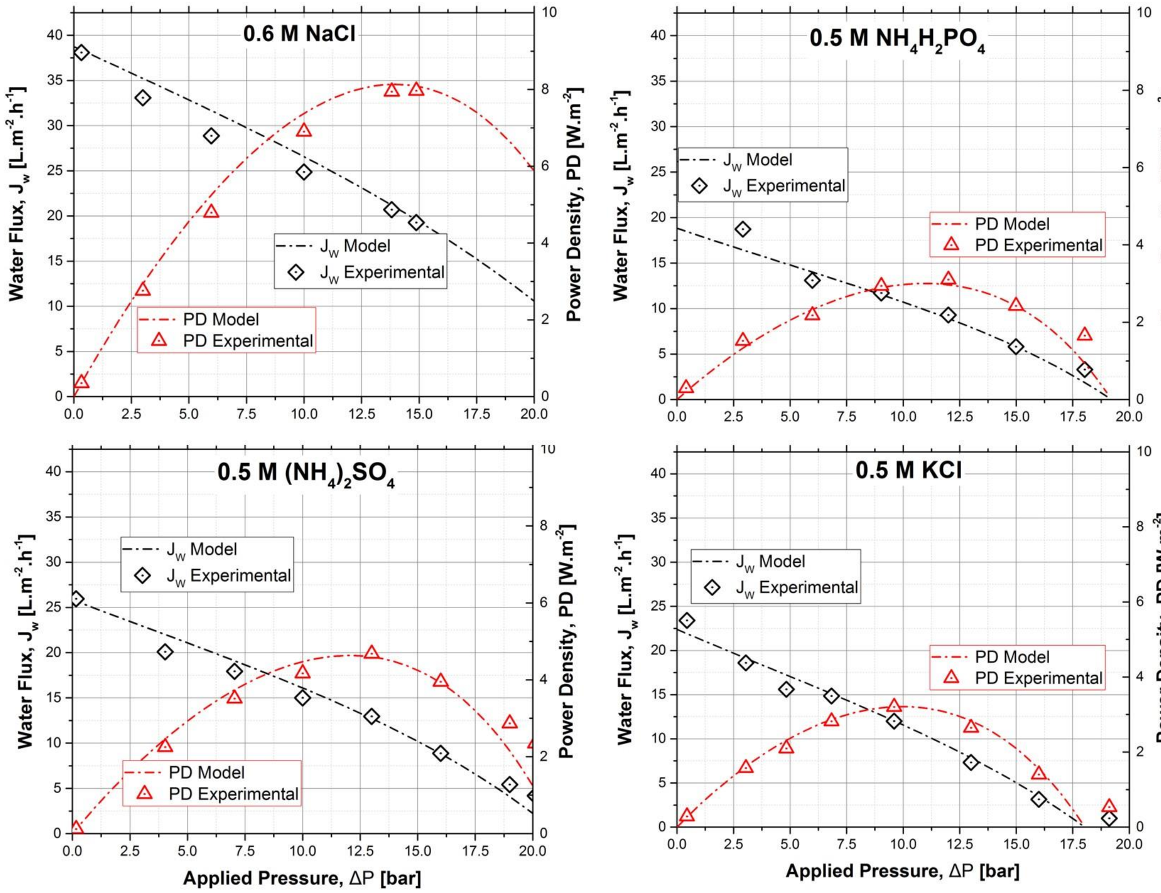

Figure 7 Experimental and modelled water flux and power density at different applied pressures using pure single fertilisers. A 0.6M NaCl solution was also tested and used as a benchmark. Equations 6 and 7 were used for the calculations, and the input for the equations are displayed in Table 2.

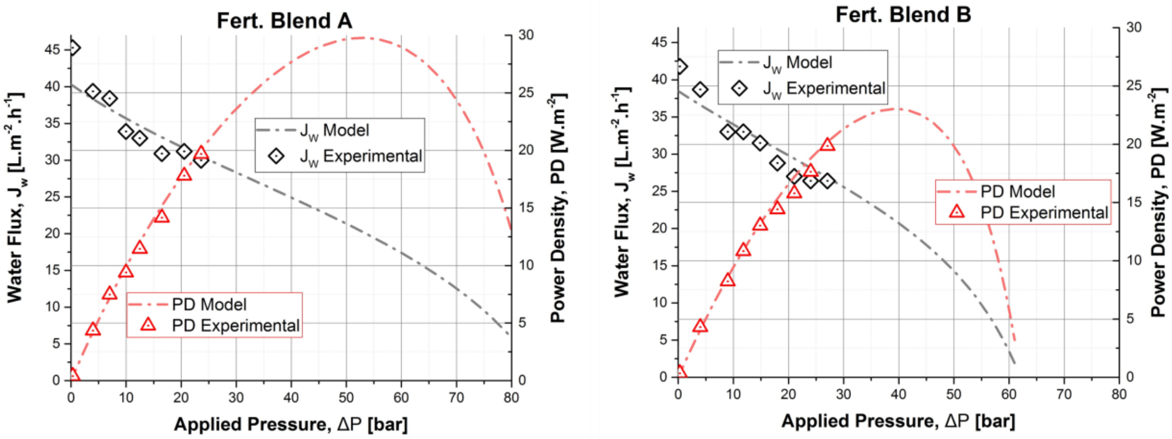

Figure 8 Experimental and modelled water flux and power density at different applied pressures using liquid commercial fertiliser blends. Equations 6 and 7 were used for the calculations, and the input for the equations are displayed in Table 2.

3.4 Future perspective of GreenPRO

In this section, the potential challenges and opportunities for FD-PRO are outlined, and some research questions are likewise proposed.

First, to better understand the realistic amount of extractable energy from fertilisers, a full-scale module PRO simulation should be performed. This could help in quantifying the energy losses due to membrane non-ideality [35, 37].

Another important investigation is to quantify the amount of fertiliser used by open farms or greenhouses to understand the volume of draw solution available. This is crucial in performing a cash flow analysis and calculate the return on investment for a GreenPRO plant. Additionally, this would also help in understanding how much energy from pump use can be lowered with this PRO system. Power generation using a hydraulic turbine is, however, not the only possible application for GreenPRO. In fact, as mentioned in the earlier sections, the harvested osmotic energy in the form of hydraulic pressure, could be used directly to distribute the diluted fertiliser to the field, which could effectively reduce the energy expenses for pumping. Nonetheless, this concept needs to be carefully analysed to understand its viability. Especially from the engineering point of view, when accounting for the pressure drops during the process. A combination of power generation, when the fertiliser is highly concentrated, and water pressurisation, when it is more diluted, could also be investigated to exploit the chemical energy released during fertiliser dilution fully.

As previously mentioned PRO membranes are highly selective toward ions and high molecular weight compound, therefore this process could also be used for simultaneously water purification and power generation, and pressure generation. Brackish water or secondary wastewater effluent could be used as feed solution. In this case, however, the effect of constant pressure in the retention of fertiliser in the draw solution (i.e., reverse salt flux) needs to be carefully evaluated as it might jeopardise the economic feasibility of such process. In fact, one of the advantages in using irrigation water as feed is that the fertiliser lost during reverse permeation during the process can be reintroduced in the diluted draw, thereby ensuring a closed system with no loss of nutrients.

Additionally, other salinity gradient processes such as reverse electrodialysis (RED), capacitive mixing (CapMix) and mixing entropy battery should be investigated as a mean to harness the energy diluting concentrated fertiliser solutions [38-41]

To conclude, several research questions still need to be addressed to understand the viability of this new concept. However, if the economics would be found favourable, it could be a new approach to reduce the energy consumption and, possibly, improve water reclamation for decentralised farms or greenhouses.

4 Conclusions

A common practice in agriculture is to dilute soluble fertilisers to produce a nutrient solution able to supply both the water and nutrient needs for plants. In the dilution process, a large amount chemical potential energy (i.e., osmotic potential energy) is produced due to the high concentration gradient between the fertiliser salt solution and the irrigation water. In this work, pressure retarded osmosis (PRO) was proposed as a means to harness this chemical potential energy and transform it into electric or pressure energy, through a novel process known as GreenPRO.

The thermodynamic maximum Gibbs free energy of mixing single or blended fertiliser salts with irrigation water was initially investigated. The results show that concentrated fertilisers, such as $(NH_4)_2SO_4$ or KCl, can reach $\Delta G_{V,max} > 2$ kWh.m^{-3}, which can be over 11 times higher than that produced during seawater/river water mixing. Higher energy was also found to be achieved for solutes with higher solubility and speciation. However, these values decrease by about 30% during constant-pressure operation due to thermodynamic irreversibility losses. In order to have a realistic power density value, the non-ideal nature of the available PRO membranes needs to be accounted for. To do so, water flux and power density model, which accounts for concentration polarisation effect and non-ideal solute rejection, was employed. The model was then fed with the characteristics (i.e., A, B, S) of a commercial PRO membrane, as well as the chemical proprieties of the employed fertilisers, and then validated with real experimental data. The model proved to converge closely to flux values similar to the experimentally measured ones. Based on these data, a full-scale simulation can be later investigated to assess the realistic extractable energy from commercial pure or blended fertilisers.

Future efforts should be directed in understanding the economic feasibility of this concept by coupling the measurements of the extractable energy and power density from concentrated fertilisers with the amount of fertilisers normally used in agriculture. This way, a realistic cash flow analysis can be performed.

Finally, this study showed the potential of GreenPRO in harnessing fertiliser potential energy for fertigation water pressurisation and/or water treatment. This would hopefully augment high energy requirements typical for most agricultural processes.

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