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Energy Procedia 142 (2017) 4182–4197

Energy Procedia

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Enhanced Performance Dual Stage Pressure Retarded Osmosis

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Abstract

A dual stage PRO process has been proposed for power generation from a salinity gradient across a semi-permeable membrane. Both closed-loop and open-loop dual stage PRO system were evaluated using 2 M NaCl and Dead Sea as draw solutions, whereas the feed solution was either fresh water or seawater. The impact of feed salinity gradient resource and feed pressure on the net power generation and water flux were evaluated.

DSPRO can be combined with desalination plant using seawater brine as the draw solution either in closed-loop or open-loop. This hybridization has multiple applications such as reducing the impact of discharging concentrated brine to sea, energy storage, and increase the recovery rate of the desalination. Power generation by DSPRO will reduce the energy consumption by the desalination processes. Waste heat from power plants can be used for the regeneration of the draw solution in the closed-loop DSPRO. Process modelling has been performed and shown promising results for DSPRO application for power generation.

Keywords: Pressure Retarded Osmosis, Osmotic Power Plants, Salinity Gradients, Dual Stage Pressure Retarded Osmosis, Renewable Energy

1. Introduction

Pressure retarded osmosis (PRO) process has received a lot of attention because of its potential application for power generation from renewable resources [1-6].Two solutions of different salinities and osmotic pressure, known as feed and draw solution, are pumped into a semipermeable membrane module of relatively high

Peer-review under responsibility of the scientific committee of the 9th International Conference on Applied Energy .

rejection rate and water permeability [7]. Draw solution is normally pressurized before going to the PRO membrane. Chemical potential converts into hydraulic pressure as the fresh water transports across the PRO membrane due to the osmotic pressure gradient. The pressurized diluted draw solution splits into two streams after leaving the membrane; stream one goes back to a pressure exchanger to pressurize the raw draw solution while stream two goes to a turbine to convert hydraulic energy into electricity [Figure 1].

Finding a suitable membrane was one of the earliest challenges PRO process encountered for successful application; insufficient membrane flux has been reported due to the inability of the membrane to effectively alleviate the effect of concentration polarization [8-9]. Intensive concentration polarization in the earlier membrane generation caused a detrimental impact on membrane flux and power generation by the process [9]. Recent development in the membrane manufacturing industry has successfully improved the performance of PRO membrane through increasing the membrane flux [10-12]. Practically, the indicator for PRO membrane performance is power density, W (kW/m^2), which is the power generated per unit membrane area [13]. Theoretically, the threshold value of power density for an economical PRO process is about 5 W/m^2; this value, in fact has been recommended by several laboratory and pilot plant studies [14]. Recent pilot plant study with Reverse Osmosis (RO) concentrated brine and wastewater effluent as the draw and feed solutions, respectively, has demonstrated a promising membrane flux of 7.7 W/m^2 at 25 bar hydraulic pressure using a modified, four ports, Toyobo Hollow Fibre (THF) membrane in the POR process [11]. Mega-ton project is another successful example of osmotic power plant using RO brine-wastewater effluent salinity gradient resource and 30 bar hydraulic pressure [10]. Ten inch diameter Toyobo HF membrane was used in the membrane module yielding a membrane power density of 13.3 W/m^2. The successful implementation of Megaton pilot plants was mainly attributed to i) the considerable osmotic driving pressure generated by the salinity gradient resource and enabled 30 bar hydraulic pressure to be applied across the membrane and ii) the relatively high membrane permeability. In general, at fixed hydraulic pressure, power density can be increased by increasing the osmotic pressure gradient across the PRO membrane or by increasing the membrane permeability. Therefore, salinity gradient resource should be given more attention in the design of the osmotic power plant. The higher the osmotic pressure gradient across the PRO membrane is, the higher the power density generated by the PRO process.

Seawater, RO brine, inorganic metal salts, Dead Sea brine, Rift valley water, Jordan water, and Salt Lake water are some examples of the draw solutions proposed for the PRO process [15-17]. These draw solution can be paired with a feed solution of lower osmotic pressure such fresh water, wastewater effluent and seawater to create a sufficient driving pressure for water permeation across the PRO membrane. NaCl and Ammonium/carbon dioxide mixtures were proposed as the draw solutions in a number of studies [18]. In such case, the diluted draw solution is regenerated for recycling to minimize the operation and capital costs using a Closed-Loop PRO (CLPRO) process [3]. Open-Loop PRO (OLPRO) process has also been proposed for power generation using Dead Sea brine or Salt Lake water; the diluted draw solution returns to the Dead Sea to replenish evaporation rate [3, 16]. Using a very high concentration draw solution such as Dead Sea brine or concentrated inorganic salts has the advantage of increasing water flux across the PRO membrane and hence the power density of PRO process. This issue has been demonstrated experimentally when the power density increased from 3.8 W/m^2 to 6.7 W/m^2 as a result of NaCl draw solution concentration increase from 6% to 12% using 13 bar hydraulic pressure and 0.06% NaCl feed solution [19]. Power density, theoretically, exceeds 367 W/m^2 when 24% NaCl is coupled with 0.06 mol NaCl solution as the salinity gradient resources at 67.2 bar hydraulic pressure [16]. This power density is almost 70 times higher than the theoretical threshold to achieve an economical PRO process. Dead Sea brine, salt concentration ~ 30%, is a good example of high potential draw solution for osmotic power plant.

Interestingly, the concentration of draw solution remains high after dilution when a concentrated brine, such as Dead Sea or equivalent concentration, is applied as a draw solution of the PRO process [16, 20]. The diluted draw solution goes either to a regeneration system for recycling and reuse or discharged to sea. Alternatively, the remaining energy of the diluted brine can be harvested by a second stage PRO unit to maximize the performance of PRO process. A Dual-Stage PRO (DSPRO) process is suggested here to enhance the performance of conventional PRO process especially when concentrated brine is the draw solution. As shown in Figure 1, part of the diluted draw flow leaving the first stage of the DSPRO process returns to a Pressure Exchanger (PX) to pressurize the draw solution whereas the rest of diluted draw solution flow goes to a second stage POR process. The entire diluted draw solution from the second stage, which is equal to permeate flows of stage one and stage two of the DSPRO process, goes to a turbine for power generation. It should be noted that no additional pump is required for pumping the draw solution in the second stage. Yet, there is not a detailed study showing the advantages of using DSPRO and the impact of the operating parameters on the process performance. The current study evaluates the performance of DSPRO process and efficiency for power generation compared to a single stage conventional PRO process. A number of salinity gradient resources were investigated to evaluate the performance of DSPRO process. The impact of hydraulic pressure, concentration polarization, feed and draw solution concentrations, and membrane orientation on the process performance was also evaluated using a pre-developed computer model [2]. The impact of the membrane orientation was evaluated to understand the performance of first and second stage when feed solution is facing the porous or selective layer.

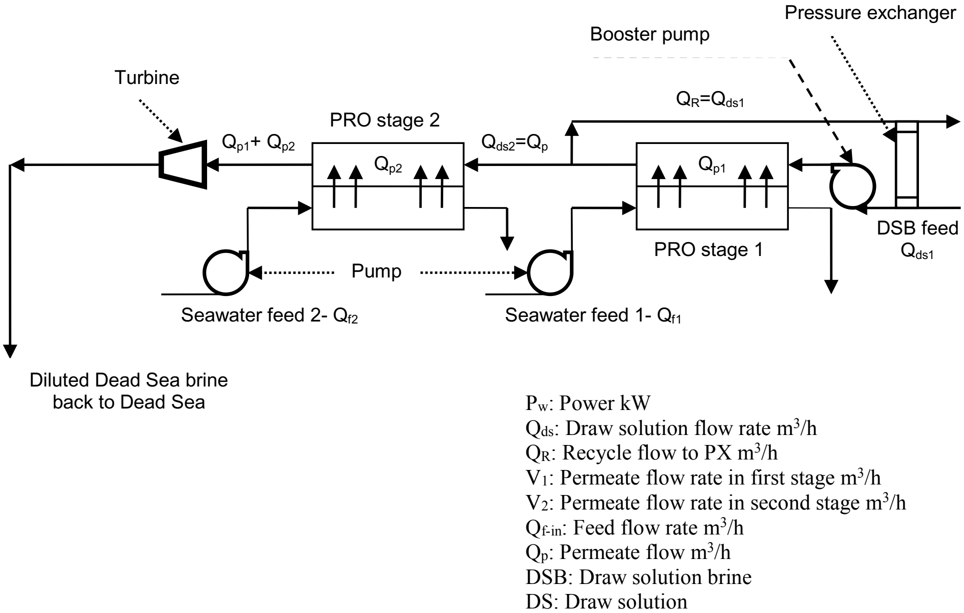


Figure 1: Schematic Diagram of Dual Stage PRO Process

2. Harvesting the osmotic energy of concentrated brine

Defined as the power generated per square meter of membrane (W/m^2), power density (W) has been used as an indicator of the PRO process performance [13]. Power density can be calculated from the expression shown in Equation 1:

Equation 1
$$W = \Delta P * J_w$$

Where, ΔP is the hydraulic pressure difference across the membrane (bar) and J_w is the PRO membrane flux (L/m^2h). The maximum specific power generated from a salinity gradient resource can be represented by free Gibbs energy [13]. For a PRO process operating on a counter-current mode, the maximum extractable specific energy from a salinity gradient resource is represented by the following equation [1]:

Equation 2
$$E_m = \frac{nRT(C_D - C_F)^2}{4(C_D - C_F)}$$

Where, E_m is the maximum specific power generation (kWh/m3), n is number of ionic species in solution, R is the gas constant (0.082 L atm/K mol), C_D and C_F are the concentrations of draw and feed solutions respectively (mol/L), and T is the temperature in Kelvin (273+°C). Following Equation 2, E_m increases with the increase of the draw solution concentration and the decrease of the feed concentration. Several salinity gradient resources have been proposed in literature for the power generation in the PRO process from mixing high with low salinity solutions; such as Dead Sea (DS), seawater (SW) or RO brine draw solution pairing with wastewater

(WW), seawater (SW) or RO brine feed solution [1, 2, 16]. For simplicity, the concentration of DS was assumed equal to 5 mol/L of NaCl solution whereas the concentration of WW was equal to 0.017 mol/L of NaCl solution. The maximum power generation from salinity gradient resources is explained in Figure 2. Ignoring the effects of internal and external concentration polarization and reverse salt diffusion, a maximum energy yield of 1.2 kWh/m^3 was achieved by pairing DS with 32 g/L seawater. Pairing DS with SW resulted in an E_m between 1.2 kWh/m^3 and 0.99 kWh/m^3, the lowest energy yield was for coupling DS with 50 g/L salinity SW. On the other hand, the E_m of SW-WW increased from 0.17 kWh/m^3 to 0.27 kWh/m^3 with the increase of seawater salinity from 32 g/L to 50 g/L. the maximum energy harvested from DS-SW salinity gradients was 4 to 7 times higher than that of SW-WW salinity gradients. The reason for that was the large driving force across the PRO membrane in the case of DS-SW salinity gradient resources. The driving pressure at $P=\Delta\pi/2$ was 105 bar in the case of DS-SW 32 g/L salinity [Figure 3]. The corresponding value for 32 g/L SW-WW was 11 bar; this is 9 times lower than the driving pressure for DS-SW at 32 g/L. Figure 3 also shows that the driving pressures of DS draw solution were about 6 to 9 times higher than those for the seawater draw solution.

Theoretically, the mixing energy of two solutions of different concentrations would result in a maximum specific energy of E_m but this would not necessarily result in equilibrium between the draw and feed solution concentrations at end of the PRO process. In other words, the process of energy extraction from the salinity gradient resource by the PRO process was incomplete. If not recovered, this energy will be wasted when the diluted draw solution is discharged to sea. There is also an extra energy embedded in the draw solutions associated with the pumping and pretreatment processes. Such energy could be harvested by a second stage PRO process by adding a second stage PRO process to harvest the energy of the relatively diluted DS solution. As shown in Figure 1, part of the pressurized diluted draw solution equal to the amount of permeate flow of the first stage of the DSPRO process, Q_{v1}, goes to the second stage of the DSPRO process for fresh water extraction from the second feed seawater. After that, the entire flow from the second stage of the DSPRO process goes to a hydro-turbine for power generation. It should be mentioned that the second stage PRO stage requires less membrane area due to the lower feeds flow. Furthermore, no pretreatment is required for the draw solution.

Adding a second stage PRO enhances the energy recovery from the salinity gradient resource and the gross power generation in the first and second stage of the dual stage PRO process is given as:

Equation 3 $$PW_1 = \Delta P_1 * Q_{v1}$$

Equation 4 $$PW_2 = \Delta P_2 * Q_{v2}$$

PW_1 and PW_2 are the gross power generation from single and dual stage PRO processes, respectively (kW), ΔP_1 and ΔP_2 is the hydraulic pressure difference across the membrane of first and second stage respectively (bar), and Q_{v1} and Q_{v2} are the permeate flow rates in stage one and stage two of the DSPRO process, respectively

(m^3/h). Assuming that hydraulic pressure losses in the first stage of the DSPRO process are negligible; i.e. $\Delta P_1 = \Delta P_2$, the total power generation, *PWt*, in the dual stage PRO process is given as:

Equation 5 $$PWt = \Delta P * (Q_{v1} + Q_{v2})$$

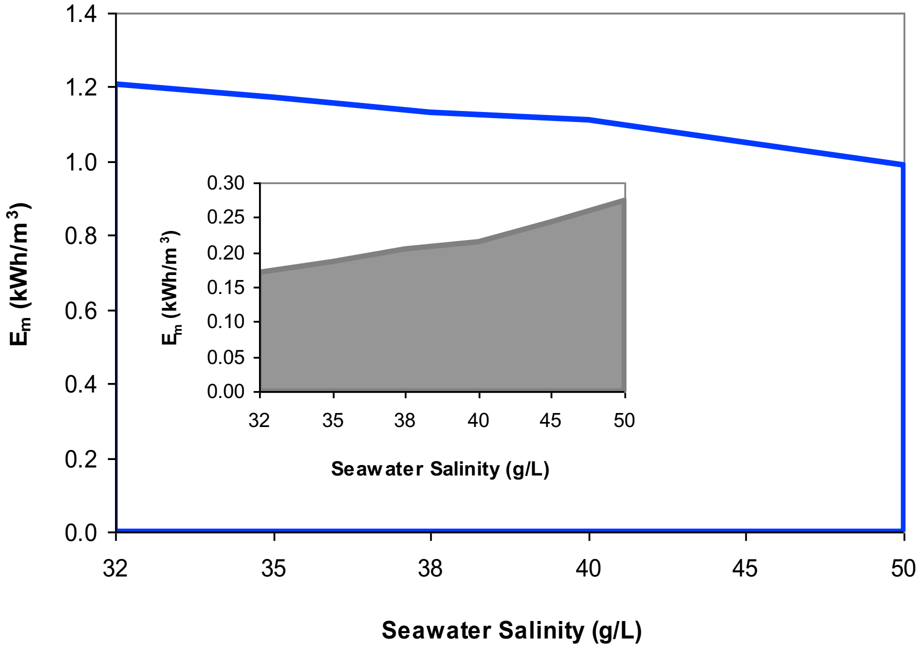


Figure 2: Maximum specific power generation from a number of salinity gradients made of coupling Dead Sea (DS) with seawater (SW) of salinities between 32 g/L and 50 g/L or coupling seawater (SW) with wastewater (WW).

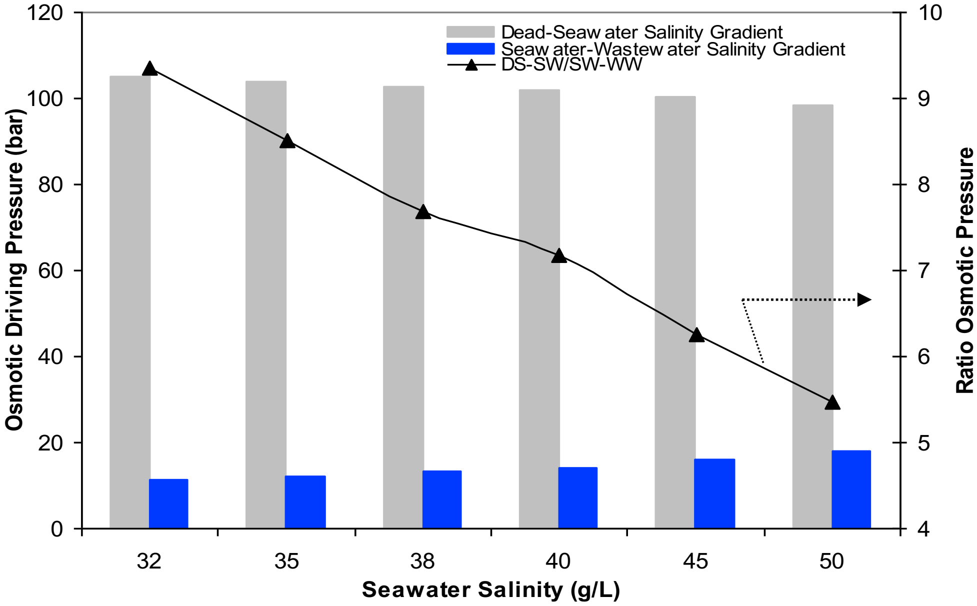


Figure 3: Osmotic driving pressure of different salinity gradient resources generated from coupling DS solution with seawater and seawater with wastewater

3. Process Modelling

The expression used to calculate the membrane flux, J_w, of the PRO process is given as: [11]

Equation 6
$$J_w = A_w\left(\frac{\pi_{Db}e^{(\frac{-J_w}{k})} - \pi_{Fb}e^{(J_w K)}}{1+\frac{B}{J_w}(e^{(J_w K)} - e^{(\frac{-J_w}{k})})} - \Delta P\right)$$

where, π_{Db} and π_{Fb} are the osmotic pressures of the bulk draw and feed solution, respectively, A_w is the water permeability coefficient, ΔP is the hydraulic pressure across the PRO membrane, k is the mass transfer coefficient, B is the solute permeability coefficient, K is the solute resistivity for diffusion within the porous support layer, and A is the membrane area. Equation 3 was experimentally developed to calculate J_w in a bench scale flat sheet membrane coupon. Yet, there is not any empirical formula to accurately calculate J_w in a full scale membrane module; hence equation 3 has been suggested for rough estimation of the membrane flux in a full scale membrane module. Membrane flux at distance x from the PRO module entry was calculated from the following equation:

Equation 7 $$J_{w-x} = A_w\left(\frac{nRTC_{Di-0}(1+\frac{Q_{Di-x}}{Q_{Do-x}})e^{\frac{-J_{w-x}}{k}} - nRTC_{Fi-0}(1-\frac{Q_{Fi-x}}{Q_{Fo-x}})e^{J_{w-x}K}}{1+\frac{B}{J_{w-x}}(e^{J_{w-x}K} - e^{\frac{-J_{w-x}}{k}})} - \Delta P\right)$$

The local maximum specific energy of salinity gradient resource, E_{o-x}, is defined as the maximum specific energy of the salinity gradient resource at distance x along the membrane module and can be calculated from the respective draw and feed concentrations as in the following equation:

Equation 8 $$E_{o-x} = \frac{nRT(C_{Do-x} - C_{Fo-x})}{(C_{Do-x} - C_{Fo-x})}$$

The local maximum specific energy is normalized by the maximum specific energy of the salinity gradient resource as in the following equation:

Equation 9 $$E_{x-N} = \frac{E_{o-x}}{E_{\max}}$$

where, E_{x-N} is the normalized local maximum specific energy. The normalized power generation by the PRO process is function of the hydraulic pressure, permeate flow, and feeds flow rate:

Equation 10 $$Es_{-x} = \frac{\Delta P Q_{p-x}}{Q_{FT-x}}$$

where, Es_{-x} is the specific power generation by the PRO process, ΔP is the hydraulic pressure of the draw solution, Q_{p-x} is the permeate flow rate normalized by the membrane area, and Q_{FT-x} is the total flow rate of feed and draw solutions normalized by the membrane area. In non-ideal system, the harvested specific energy by the PRO process is lower than the theoretical maximum specific energy estimated by equation 1 due to the reverse salt diffusion and effects of concentration polarization. However, the energy yield of PRO process can be maximized by adding extra modules to increase the membrane area.[15] The impact of membrane area on the energy efficiency of PRO process can be evaluated by calculating the local maximum specific energy, E_{x-N}, along the membrane module. At any point along the PRO module, E_{x-N} value represents the osmotic energy of the salinity gradient resource which is unrecovred by the PRO process. Typically, E_{x-N} decreases along the membrane module due to the dilution and concentration of the draw and feed solutions respectively.

4. Impact of Increasing Membrane modules

The effect of adding an extra PRO module was evaluated assuming the length of PRO module is 1 m and 2 PRO modules in the single PRO; Figure 4 shows a gradual decrease of the $E_{x\text{-}N}$ along the membrane modules due to the dilution and concentration of draw and feed solution, respectively. This caused a reduction of the chemical potential difference of the salinity gradient resource. Adding a second PRO module generated more reduction of $E_{x\text{-}N}$ due to the greater energy yield of the PRO process. The impact of salinity gradient resource type on the harvested specific energy by the PRO process is illustrated in Figure 4. $E_{x\text{-}N}$ of the salinity gradient resource at the outlet of first PRO module of a meter long represents the osmotic energy which has not been recovered by the process; the $E_{x\text{-}N}$ at the outlet of first PRO module was 55%, 58% and 68% for Dead Sea-Ro brine, DS-SW and DS-WW salinity gradients respectively. The corresponding values for RO brine-WW and SW-WW salinity gradients were 82% and 88% respectively; this refers to the low energy recovery by the first membrane module. Apparently, the increased $E_{x\text{-}N}$ refers to the low energy yield of the PRO process. Figure 4 also depicts that $E_{x\text{-}N}$ at the outlet of second PRO module was greater for DS-WW compared to the DS-SW and DS-RO brine salinity gradient resources. This was due to the larger chemical potential gradient across the PRO membrane for Dead Sea-wastewater salinity gradient resource. As such, more membrane area is needed for harvesting the energy of salinity gradient resource. One of the limitations for increasing the number of membrane modules is the inadequate membrane flux which decreases with the number of PRO modules [Figure 2B]. For example, membrane flux decreased from 23 L/m^{2}h to 5 L/m^{2}h at the end of PRO process for DS-RO brine.

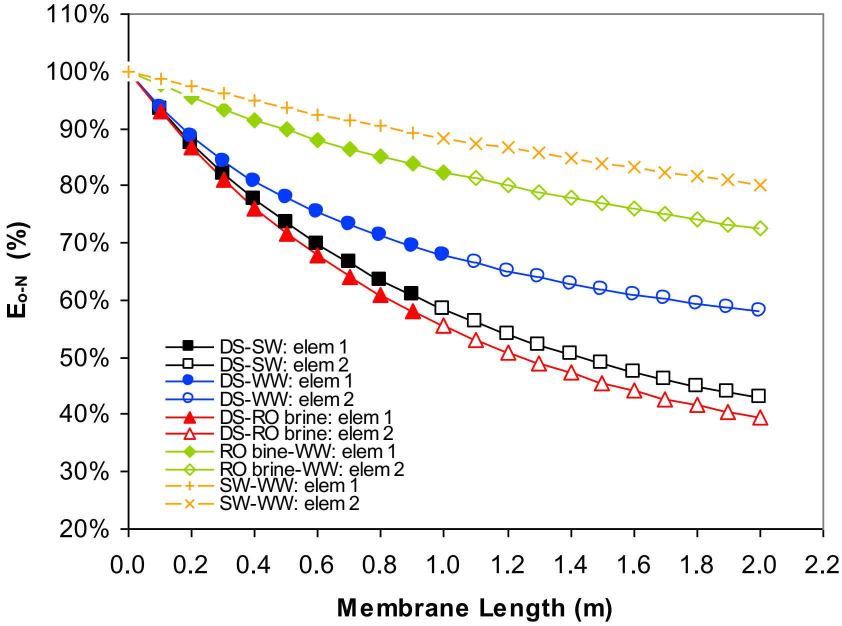


Figure 4: The specific energy along PRO modules in the pressure vessel. Dead Sea water (DS) is 5 M NaCl, RO brine is 1.2 M NaCl, seawater (SW) is 0.6 M NaCl, and wastewater (WW) is 0.017 M NaCl. The length of PRO module is 1.0 m and there are 2 modules in the pressure vessel.

5. Increasing PRO Stages

We investigated the $E_{o\text{-}N}$ along the PRO module for each stage of the DSPRO process for several PRO modules arrangement in the pressure vessel as illustrated in Table 1.

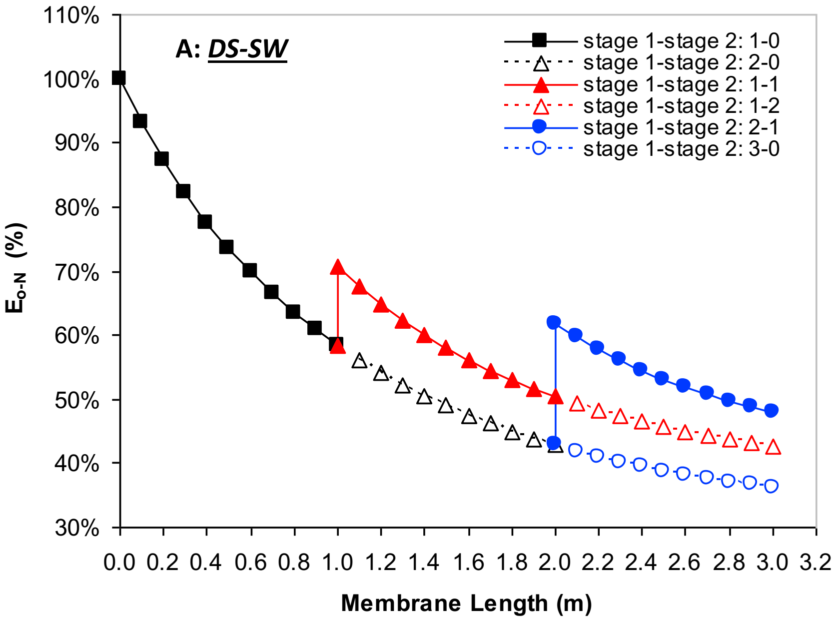
Table 1: PRO and DSPRO scenarios

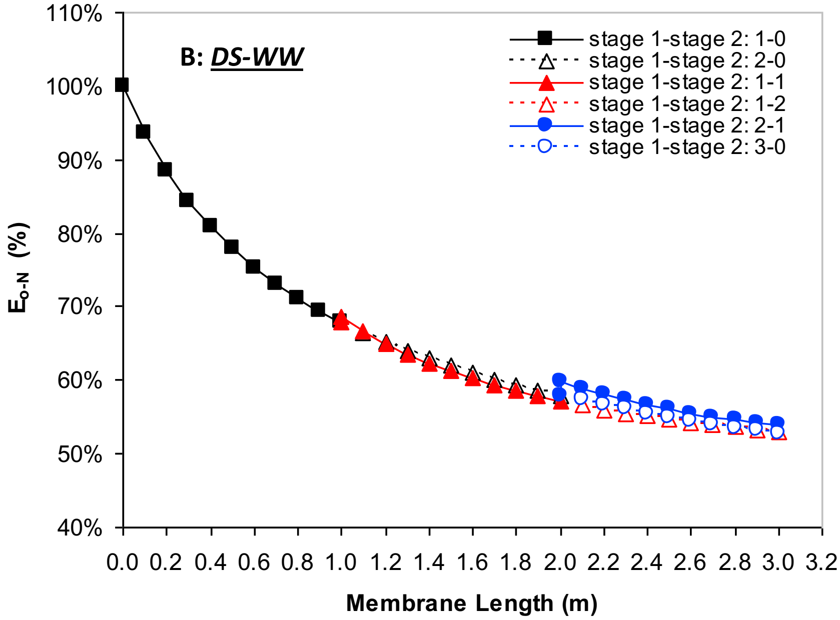
Scenario	Modules arrangement configurations	Symbol
1	One module in the first stage only	1-0
2	Two modules in the first stage only	2-0
3	Three modules in the first stage only	3-0
4	One module in the first stage and second stage	1-1
5	One module in the first stage and two modules in the second stage	1-2
6	Two modules in the first stage and one module in the second stage	2-1

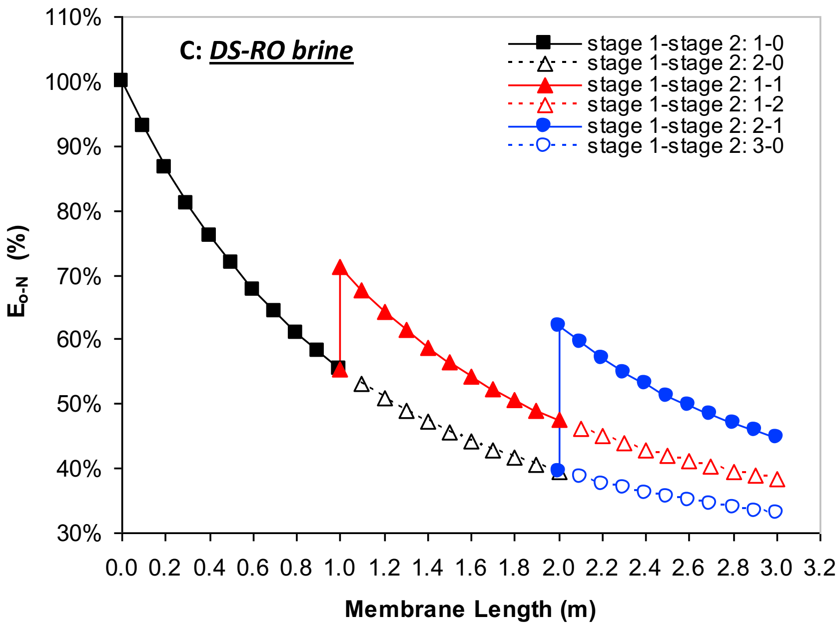
For DS-SW salinity gradient resource, scenario 1 shows a sharp drop of $E_{o\text{-}N}$ along the PRO module due to the dilution and concentration of draw and feed solutions respectively. Adding a second and third PRO module in scenarios 2 and 3 just caused a further decrease in $E_{o\text{-}N}$ and permeation flux dropped sharply that adding more PRO modules will not improve the process significantly. In scenario 4, one module in the first and second stage of the DSPRO process; this arrangement resulted in a tangible jump in $E_{o\text{-}N}$ mainly due to the replacement of concentrated feed brine from the first stage with a fresh feed solution of lower concentration. Using one module in the first stage and two modules in the second stage as in scenario 5 resulted in an increase of $E_{o\text{-}N}$ even higher than in scenario 4. In scenario 6 there were two modules in the first stage and one module in the second module caused a better performance than scenarios 1 to 5.

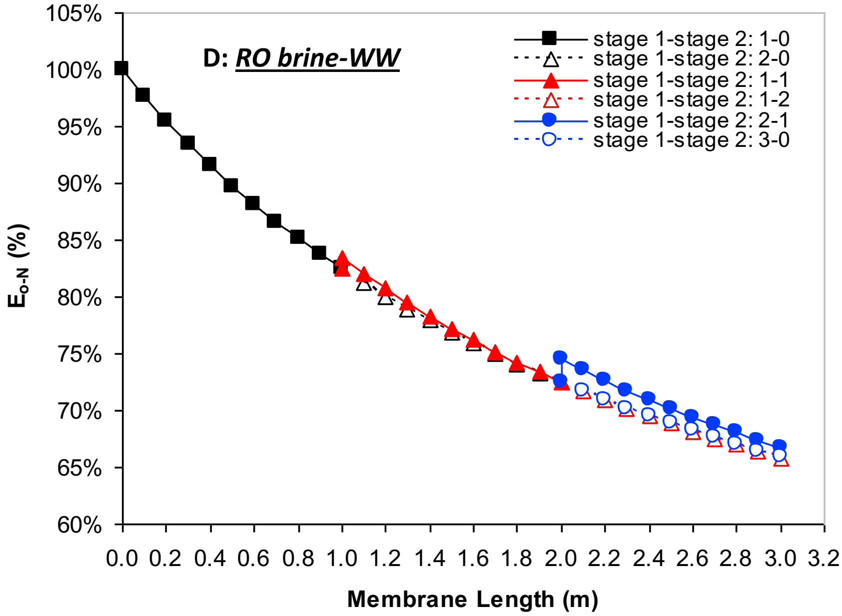
For DS-WW salinity gradient resources [Figure 5B], the increase of membrane modules in scenarios 1 to 3 resulted in higher energy yield of the RO process. Adding modules in the second stage as illustrated in scenario 4 to 6 did not result in a substantial increase of the energy yield of the DSPRO process. Similar observation was noticed in ROB-WW salinity gradient resource; adding more modules in the first stage increased the energy yield of the PRO process. However, there was not a considerable change in the energy yield of the DSPRO process when a second stage was added. This was probably due to low concentration of feed solution in these salinity gradients which resulted in a minimum change in the osmotic energy of the salinity gradient due to the replacement of the feed solution in the second stage. Iy should be noted that WW feed solution has relatively high concentration of organic matter which causes membrane fouling over time. The effects of these organic matter on the membrane performance was not been investigated in this study but has been referred to in previous studies. Therefore, DSPRO process may be required to reduce membrane fouling over time since fresh feed solution is used in the second stage; this will maintain the concentration of organics under the critical level.

Finally, DS-RO salinity gradient was evaluated for scenarios 1 to 6 in Table 1. Apparently, DSPRO process outperformed the conventional PRO process and more energy was harvested when a second stage PRO process was introduced [Figure 5C]. This was due to the replacement of the feed brine from the first stage with low concentration fresh feed solution in the second stage. As matter of fact, using fresh feed brine expanded the operating boundary of the salinity gradient. On the other hand, increasing number of the PRO modules in a single stage PRO process increased the energy yield of the process but that was still lower than that in the DSPRO process. furthermore, the performance of the DSPRO process was better in scenario 6 than scenarios 4 and 5 hence using 2 PRO modules in stage 1 followed by 1 module in the second stage provides the best results.




B: DS-WW
stage 1-stage 2: 1-0
stage 1-stage 2: 2-0
stage 1-stage 2: 1-1
stage 1-stage 2: 1-2
stage 1-stage 2: 2-1
stage 1-stage 2: 3-0
110%
100%
90%
80%
70%
60%
50%
40%
E_{o-N} (%)
0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0 3.2
Membrane Length (m)


C: DS-RO brine
stage 1-stage 2: 1-0
stage 1-stage 2: 2-0
stage 1-stage 2: 1-1
stage 1-stage 2: 1-2
stage 1-stage 2: 2-1
stage 1-stage 2: 3-0
110%
100%
90%
80%
70%
60%
50%
40%
30%
E_{o-N} (%)
0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8 3.0 3.2
Membrane Length (m)



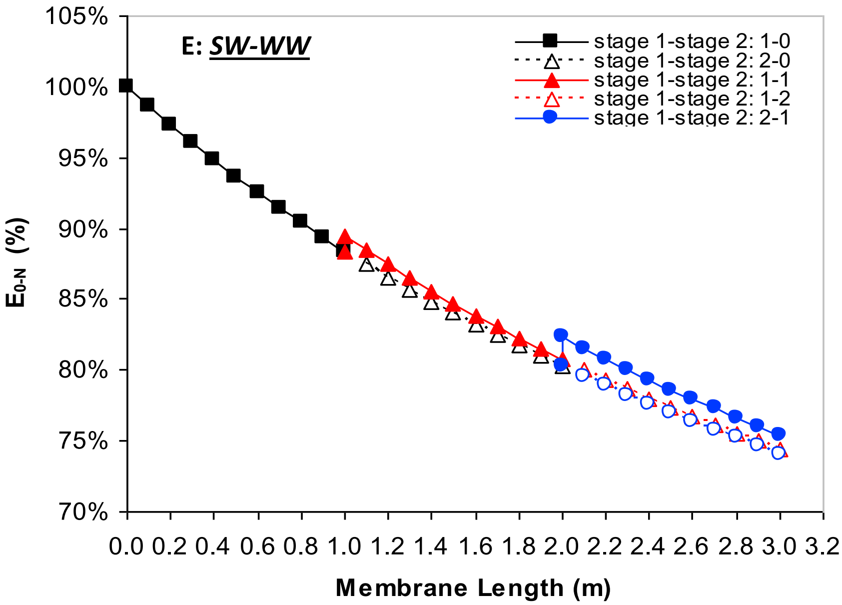


Figure 5: Specific energy in conventional (single stage) PRO and DSPRO modules in the pressure vessel A) Dead Sea-seawater B) Dead Sea-wastewater C) Dead Sea-RO brine D) RO brine-wastewater E) seawater-wastewater. The normalized membrane of the second stage $A_{2\text{-}norm}$ for scenario 5 is 27%, 11%, 45%, 19%, and 17% for Dead Sea-seawater, seawater-wastewater, Dead Sea-wastewater, Dead Sea-RO brine, and RO brine-wastewater respectively. The normalized membrane of the second stage $A_{2\text{-}norm}$ for scenario 6 is 40%, 20%, 66%, 27%, and 28% for Dead Sea-seawater,

seawater-wastewater, Dead Sea-wastewater, Dead Sea-RO brine, and RO brine-wastewater respectively.

6. Field Application

PRO has been proposed for power generation but apparently the performance has been overestimated, especially, for low concentration salinity gradient resources. Seawater coupling with river water has been questioned for energy efficiency since the energy requirements for feed and draw solution pretreatment exceeds the energy output from the PRO process. Substituting conventional PRO with DSPRO would not help in increasing the energy yield from seawater-wastewater salinity gradient since its maximum osmotic energy is less than the energy requirement for feeds treatment. However, there are many examples of lakes, industrial wastewaters, and brine lagoons which can be used as the draw solution in the DSPRO process while wastewater, seawater or river water would be the feed solution. For example, RO brine is one of the abundant resources in the Middle East and arid areas which, if coupled with properly treated wastewater, can be used in the DSPRO process. The advantage of staging the process is to reduce the PRO membrane fouling especially at high permeation flux. With osmotic pressure approaching 50 bar, RO brine can be generate around 8 W/m^2 power density when it is coupled with wastewater effluent. This energy can be tapped into to reduce the cost of desalination and also reduce the environmental impact desalination brine before discharge.

On the other hand, hypersaline solutions such Dead Sea, Salt Lake, hypersaline groundwater and saline lagoons which are abundant in the Middle East are potential source of draw solution. Such draw solution can be coupled with wastewater, seawater, and wastewater effluent for power generation in the DSPRO process. The advantage of using a second PRO stage is to reduce the energy losses due to the effects of CP at the feed side and fouling issues. The DSPRO process is only viable with feed solution replacement in the second stage but can be applied in open loop DSPRO or closed loop DSPRO process. Neither high pressure pump nor draw solution pretreatment is required in the second stage which reduces the capital and operating cost of the DSPRO process. Number of PRO modules in each stage should be optimized to enhance the process performance and reduces fouling problems but ultimately several PRO modules would be required.

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