Water–energy nexus for estuarine systems with seasonal salinity variations: a thermodynamic feasibility analysis of reverse osmosis (RO)–pressure retarded osmosis (PRO) combinations

Arijit Chakraborty and Anirban Roy

ABSTRACT

The underlying philosophy of pressure retarded osmosis (PRO)–reverse osmosis (RO) hybrid technology is the assumption of the availability of 'fresh' water for the purpose, which gets severely affected once the fresh-water streams undergo seasonal salinity variations. In the present article, the authors have tried to understand the overall feasibility of PRO-RO combination in such estuarine systems with appreciable variation of seasonal salinity. The article first discusses the feasibility of pretreating the feed of PRO using RO and later understanding the feasibility of PRO as supplemental technology to existing RO units. It was found that pretreating the PRO feed in such estuarine systems was energetically infeasible. However, PRO as supporting technology was found to produce energy of around 0.0994 kWh for 50% recovery. It was also concluded that with a fraction of RO permeate used for PRO, energy savings increase for estuarine systems with seasonal salinity variations.

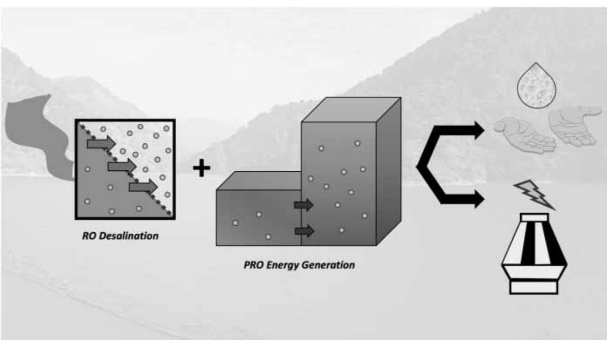
Key words | estuaries, Gibbs free energy, pressure retarded osmosis, reverse osmosis, salinity gradient energy

Arijit Chakraborty
Anirban Roy (corresponding author)
Department of Chemical Engineering,
Goa Campus, BITS Pilani,
Goa 403726,
India
E-mail: *anirbanr@goa.bits-pilani.ac.in*

HIGHLIGHTS

- Pressure retarded osmosis (PRO) feasibility is challenged in estuaries.
- Reverse osmosis (RO) reject disposal is a waste of osmotic energy.
- Salinity variations in rivers challenge RO-PRO combination.
- PRO-RO combination is practical when RO acts as supplement to PRO.

GRAPHICAL ABSTRACT



doi: 10.2166/ws.2020.144

INTRODUCTION

Pressure retarded osmosis (PRO) and reverse osmosis (RO) are two technologies which perform analogous to each other. In RO, hydraulic pressure is used to overcome osmotic pressure to desalinate saline water, whereas in PRO osmotic pressure is utilized to salinate fresh water thereby producing hydraulic pressure. Thus, while RO consumes power to desalinate water, PRO consumes fresh water to produce power. This technology was first explored by Pattle (1954) in 1954 and the first experimental PRO results were published by Loeb *et al.* (1976) in 1976. The last decade has witnessed sustained efforts by scientists and technologists worldwide to explore and address the challenges in order to make this a viable source of sustainable energy.

For the present article, it is of utmost importance to understand the challenges associated with PRO. The first roadblock was the low efficiency of continuous flow terrestrial plant configuration as pointed out by Loeb *et al.* (1990). Later with more research and technological development it was overcome (with pressure exchangers) but a new challenge was posed, which was the low power densities of membranes as well as challenges due to internal and external concentration polarization. There was considerable research conducted to understand the concentration polarization effect in various layers of anisotropic membranes employed for PRO (Lee *et al.* 1981). Such studies demonstrated the fact that internal concentration polarization was more severe and reduced power densities (Reali *et al.* 1990; de Vilhena 1992; Achilli *et al.* 2009). It was proven in earlier studies as well as further investigated later that power densities of membrane modules should be at minimum 4–6 W/m^2 (Loeb *et al.* 1976; Lee *et al.* 1981; Loeb *et al.* 1990; Reali *et al.* 1990; de Vilhena 1992; Gerstandt *et al.* 2008; Achilli *et al.* 2009).

After almost three decades from the first conception of PRO, the first osmotic power plant was installed by Statkraft to generate 10 kW of power in 2009, with plans to build a full-scale 25 MW unit by 2015 (Achilli & Childress 2010). However, as it turned out Statkraft discontinued investment in PRO technology in 2014. The decision was primarily due to the insufficient power densities of commercial membranes (1 W/m^2) and to economics (availability of 5 W/m^2 membranes at less than \$20/m^2). Thus, this was a huge challenge posed to the research and manufacturing sectors of membrane technologies worldwide. However, in this article, the authors investigate a challenge of entirely different nature – the salinity variation of rivers.

It is evident that PRO consumes fresh water to generate hydraulic power. Fresh water available in huge quantities is obtained from rivers and of course such plants can be envisaged as being located at the confluence of rivers and the sea. However, in order to make PRO really versatile, the challenge of river salinity and its seasonal variations have not been investigated. Recently, the authors have investigated this and found that PRO in estuarine systems can be infeasible (Chakraborty & Roy 2018). The authors have investigated the effect of river salinities, which can vary from approximately 0 mM (1 mM = 0.001 M) to almost that of sea water over a 12-month period and which results in fluctuating energy generation. The present effort is an extension to understand this challenge to a deeper extent. In the present article, it is first investigated whether an RO can precede a PRO in order to guarantee 'fresh' water salinity throughout the year and at the same time deem the overall configuration energetically feasible. The second configuration is that of an RO being supplemented by a PRO to make up for the energetics of desalination. These analyses have been carried out for estuarine systems where salinity variations are appreciable throughout the year. The authors believe that salinity variations are most important to understand and address simply because this is not in anybody's control and the whole principle of mixing energy harvesting is challenged once the 'fresh' water stream is not so any more.

The primary focus of this research paper is addressing the core of the water–energy nexus – using novel PRO energy generation method to minimize energy demand for a conventional RO desalination system. A reasonable range of RO input as well as achievable RO permeate concentration values have been considered for the purpose of the calculation of energy saved as well as net energy required in the combined process. The use of the PRO system alongside a conventional RO desalination system is an add-on whose energetics have been studied for two purposes – firstly, to evaluate the energetics if no RO permeate leaves the system and secondly, to evaluate the energetics based on the fraction of RO permeate leaves the system. These have been compared and can help provide a reasonable estimate of the energy savings when such hybrid systems are implemented. This work addresses the need of the hour in terms of issues pertaining to the water–energy nexus – a comprehensive assessment of both has been carried out through the discussed strategies of the RO-PRO hybrid module.

METHODS

It is important to appreciate at this juncture that there have been reports of various configurations of RO-PRO combinations. The authors thus have concentrated on recent literature (Senthil & Senthilmurugan 2016; Tanioka 2016; Wang *et al.* 2016; Touati *et al.* 2017; Tran *et al.* 2017; Xiong *et al.* 2017; Altaee *et al.* 2018; Arias 2018; Cheng *et al.* 2018; Wan *et al.* 2018) to understand the differences and salient features of the present effort. This is detailed later. The focal points to understand the energetics of PRO are: (i) the feed solution should ideally be of zero salinity and (ii) the draw solution should be as saline as possible and probably even hypersaline (Tran *et al.* 2017). Figure 1 depicts the RO-PRO combination used for the present study and for estuarine systems where river-water salinities vary appreciably over a year. The two combinations which are considered are depicted in Figures 1 and 2.

RO pretreating water for PRO (RO-PRO 1)

A novel configuration was envisioned in an attempt to make the pressure retarded osmosis (PRO) process feasible for locations where the river-water properties such as salinity, and thus osmotic pressure vary seasonally, in Figure 1. The configuration involved setting up a reverse osmosis (RO) desalination unit before the PRO unit, such that the input for the desalination process shall be brackish river water. The output from the RO desalination unit consists of two streams – a very low-salinity potable water stream, and a brine stream of salinity much higher than the input. The brackish water of the river shall be pretreated using the RO unit, and the resulting permeate will be used as the feed solution of the PRO unit. The hypersaline brine reject of the RO unit shall be used as the PRO unit's draw solution.

Such a configuration involves pretreatment of brackish water to generate greater energy than the conventional PRO unit. Based on the work of Chakraborty & Roy (2018), this could provide a solution for those geographies where river-water properties vary significantly for several reasons.

For such conditions, the thermodynamic limits were evaluated such as the maximum energy emanated by the mixing of streams in the PRO unit, which translates to the maximum energy that can be obtained from such a unit, as well as the minimum energy of desalination. If the

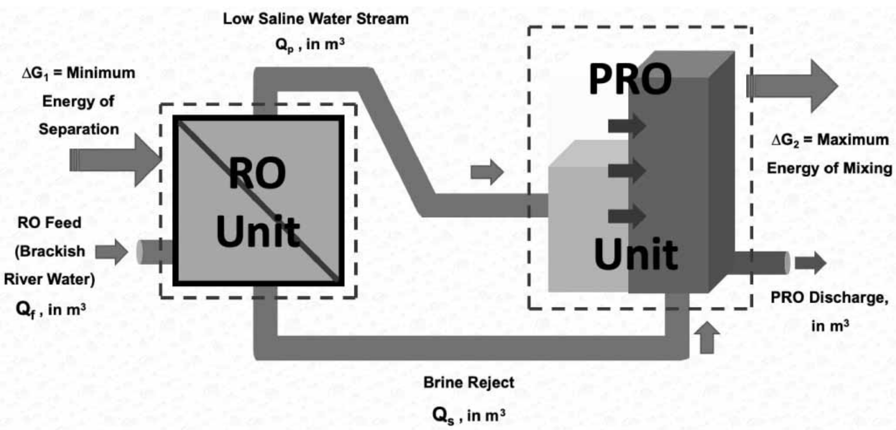


Figure 1 | PRO-RO hybrid configuration for excess energy generation.

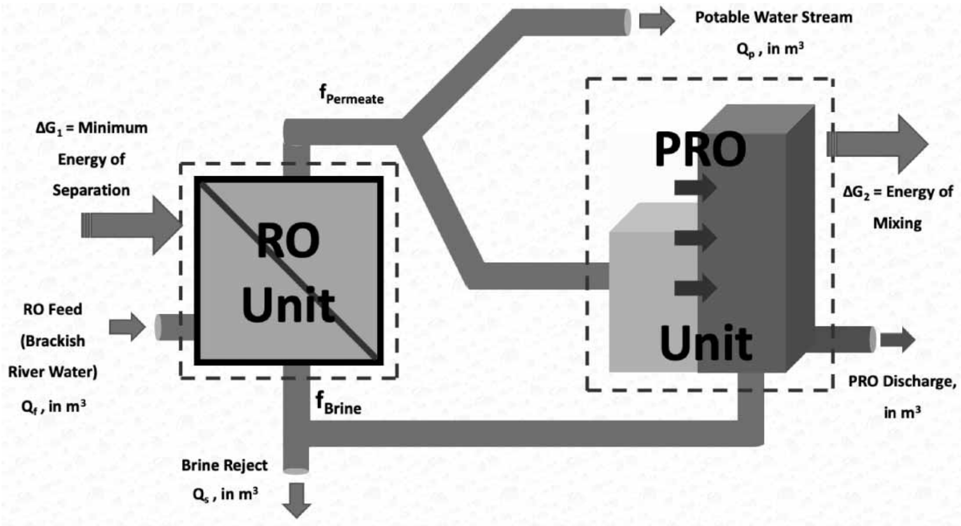


Figure 2 | PRO–RO hybrid configuration for potable water.

difference between the energy input to the desalination unit exceeded the maximum energy generated by the PRO unit, then the PRO unit, from an energy generation standpoint, would be thermodynamically infeasible. This is tantamount to saying that the net energy input to the PRO-RO hybrid system exceeds the energy output.

However, if the energy output is more than that input to the system, then such a system can be used for power generation. For varying salinities of the river water, for a multitude of reasons, different values of the net energy input or output shall result.

PRO supplementing energy for RO (RO-PRO 2)

In the configuration illustrated in Figure 2, the focus for the previously proposed hybrid PRO-RO system (Figure 1) is shifted from power generation through salinity gradient mixing, to one of producing potable water from brackish river water – with reduced energy requirements. Since producing potable water is the objective here, the permeate stream, which results from the RO unit, in its entirety cannot be fed into the PRO unit as the feed stream. The brine reject need not be completely fed into the PRO unit as the draw solution either.

A trade-off must be made between the quantity of water that needs to be sent to the PRO unit for producing energy and the potable water that can be removed without being sent to the PRO unit. The fraction of the RO permeate that is removed without being further sent to the PRO unit is denoted by f_{permeate}. The fraction of the RO brine reject stream that is sent to the PRO unit is denoted by f_{Brine}.

An optimum quantity must be calculated to find the maximum energy that can be saved while also obtaining potable water from the RO unit. The objective of such a setup is to minimize the energy requirements of the conventional RO desalination unit such that the reduced energy requirements translate into reduced cost per cubic metre of potable water.

Modelling of pressure retarded osmosis (PRO) process

When two solutions of different concentrations are mixed, the Gibbs free energy of mixing is released. For a binary system of aqueous strong electrolyte solutions pertinent to this study, we evaluate the Gibbs free energy emanated when two such solutions of known concentrations and activity coefficients mix. Gibbs free energy represents the maximum amount of reversible work that can be extracted from a closed system (Smith *et al.* 2005). As the definition suggests, this is the work that can only be obtained during a reversible process. If a solution is considered (containing two or more species) then the Gibbs free energy is expressed as (Smith *et al.* 2005):

$$\bar{G}_i = G_i(T, P) + RT \ln(\gamma_i x_i) \tag{1}$$

where $\bar{G}_i$ represents free energy per mole of species i in the solution, $G_i(T, P)$ is the molar Gibbs energy of pure species i at temperature T (in K) and pressure P (in Pa), R (in J/mol-K) is the gas constant, x_i is the mole fraction of species i in solution and γ_i is the activity coefficient of species i in solution. Total molar Gibbs free energy (G) of a solution composed of i species is the sum of the weighted contribution of each of the species (Yip & Elimelech 2012).

When we consider the mixing of two streams, say A and B, each with individual Gibbs free energy G_A and G_B and the ratios of the total moles of A and B in solution are φ_A and φ_B respectively, there is irreversible mixing which results in a mixture of Gibbs free energy (G_M) (Yip & Elimelech 2012). The difference between the Gibbs free energy of the resultant mixture and the sum of the weighted components of individual streams is termed the Gibbs free energy of mixing, denoted by ΔG_{mix}. Thus,

$$-\Delta G_{mix} = G_M - (\varphi_A G_A + \varphi_B G_B) \quad (2)$$

The negative sign indicates that energy is released from the system due to mixing.

From fundamental material balance, we know that the species must be conserved even after the mixing process.

The Gibbs free energy per unit volume of mixed solution (M) released during mixing of two solutions (A and B) can be calculated as follows (Yip & Elimelech 2012):

$$-\Delta G_{mix} = RT\left\{\left[\sum x_i \ln(\gamma_i x_i)\right] - \varphi_A\left[\sum x_i \ln(\gamma_i x_i\right]_A - \varphi_B\left[\sum x_i \ln(\gamma_i x_i)_B\right]\right\} \quad (3)$$

It is well known that the activity coefficient and mole fraction for water at relatively low salt concentrations can be approximated to unity (Robinson & Stokes 1960). Applying salt mass balance and further simplifying, the following equation is generated (Yip & Elimelech 2012):

$$-\frac{\Delta G_{mix}}{vRT} = \frac{C_M}{\varphi}\ln(\gamma_{s,M}C_M) - C_A\ln(\gamma_{s,A}C_A) - \frac{(1-\varphi)}{\varphi}C_B\ln(\gamma_{s,B}C_B) \quad (4)$$

In Equation (4), φ is defined as the ratio of moles of feed solution (solution A for a binary mixture) to the moles of feed and draw solution, while C_M is the molar concentration of the mixture. An inspection of Equation (4) reveals that the Gibbs Free Energy of Mixing is dependent on the relative proportion of the initial solutions and the composition of the solutions for a mixing process at constant temperature and pressure.

For calculation purposes, C_A is the molar concentration of the feed solution in the PRO unit, C_B is the molar concentration of the draw solution in the PRO unit, while C_M is the molar concentration of the mixture, which is given by:

$$C_M = \varphi C_A + (1-\varphi)C_B \quad (5)$$

Equation (4) can be approximated (Yip & Elimelech 2012) for highly dilute solutions as:

$$-\frac{\Delta G_{mix}}{vRT} = \frac{C_M}{\varphi}\ln(C_M) - C_A\ln(C_A) - \frac{(1-\varphi)}{\varphi}C_B\ln(C_B) \quad (6)$$

The activity coefficients were adopted from the literature (Robinson & Stokes 1960; Pitzer *et al.* 1984) and a linear interpolation function was used to find intermediate values (Yip & Elimelech 2012).

Modelling of reverse osmosis (RO) process

Cerci *et al.* (2003) developed a general relation for the minimum work input required for desalination processes using the Second Law of Thermodynamics. This relation determines the minimum work input per unit mass of fresh water produced for various feed saline water and produced fresh-water salinities. It is shown that the minimum energy consumption for the separation of a saline solution into pure water and concentrated brine is independent of the process and configuration of the desalination technology used for the separation.

Particular attention must be paid to the modelling of the pressure vessel of the RO module where the saline feed water is separated in two streams – the drinkable permeate and the rejected brine. The performance of an RO membrane depends on several operating parameters such as temperature, pressure and salinity of the feed water. The membrane is considered as a porous environment (Al-Zahrani *et al.* 2012).

Specific energy consumption is an important parameter in RO. It is defined as pump energy consumption per unit amount of produced permeate water. The minimum specific energy (SE) represents the energy needed to produce a unit volume of permeate, when the applied hydraulic pressure is equal to the brine osmotic pressure at the exit of the membrane module. Consequently, SE can be expressed using the initial osmotic pressure (of feed), π_{feed}, and the recovery ratio, R. At the theoretical limit of constant pressure operation, the RO system operates with an applied hydraulic pressure that is equal to the final osmotic pressure of the brine exiting the RO module. Therefore, the minimum specific energy of desalination for an RO process, $SE_{\text{RO, desal}}$, is expressed as follows (Al-Zahrani *et al.* 2012; Straub *et al.* 2016; Touati *et al.* 2017):

$$SE_{\text{RO,desal}} = \frac{\pi_{\text{feed}} - \pi_{\text{permeate}}}{1 - R} \quad (7)$$

where π_{feed} is the osmotic pressure of the RO feed solution, π_{permeate} is the osmotic pressure of the RO permeate solution and R is the recovery ratio of the RO module.

RESULTS AND DISCUSSION

Infeasible PRO-RO hybrid system

The configuration depicted in Figure 1 is a hybrid system involving an RO desalination unit, which pretreats brackish water and sends the lower-salinity permeate and hypersaline brine reject to the PRO unit for the purpose of generating energy, such that the energy would be greater than that needed to operate the RO unit. For the one-stage RO desalination system, it has been shown in the literature that the optimal recovery rate for an RO unit is around 40–50% (Touati *et al.* 2017). Hence, for the purpose of calculations, the recovery has been considered to be 50%, while the temperature has been considered to be constant at 298 K. Also, it is important to consider that the volume of RO feed is constant at 2 m^3, such that the volume of water entering the PRO module is 1 m^3 (at 50% recovery).

Figure 3 shows the variation of energy required to operate the PRO-RO hybrid system with the RO feed concentration, for different RO permeate concentrations. The graph shows that with an increase in RO feed concentration, greater energy is required to operate the hybrid system. From Figure 3, with higher RO feed concentrations, the PRO unit generates more energy. For 50% recovery of the RO unit, for RO feed concentration of 150 mM and RO permeate concentration as 40 mM, the energy required to operate the hybrid PRO-RO system is 0.2524 kWh. Similarly, for 40% recovery (not presented in the paper due to limited space), the energy required is 0.2197 kWh. This implies that the energy required to run the RO desalination unit exceeds the energy generated by the PRO unit, thus rendering it infeasible. Another drawback of such a system is that the entire low-salinity potable water stream is fed into the PRO unit for producing energy, thus trading off the possibility of using that water for drinking or other such purposes.

The inset of Figure 3 shows the variation of energy generated through the PRO unit in Figure 1, with RO feed concentration, for different RO permeate concentration values. It can clearly be inferred from the graph that with a rise in the RO feed concentration, the energy generated through the PRO process rises, as with a rise in the RO feed concentration, the brine reject is correspondingly high. The greater the difference in salinity between the feed and draw solutions of the PRO unit, the greater will be the energy generated. Hence the graph slopes upwards as RO feed concentration increases. For constant salinity, higher permeate concentration is higher concentration of feed solution for the PRO unit. This results in lower energy generated through the PRO process for higher-salinity permeate, as compared with that for lower salinity. The energy generated at 50% recovery, for 200 mM of RO feed and 20 mM RO permeate, is 0.1245 kWh. The same calculation at 40% recovery results in 0.0902 kWh energy generated (not presented in the paper).

Feasible PRO-RO hybrid system

For the calculations done below, recovery of the RO desalination unit is considered to be 50% – in accordance with the optimal recovery rate for an RO unit being around

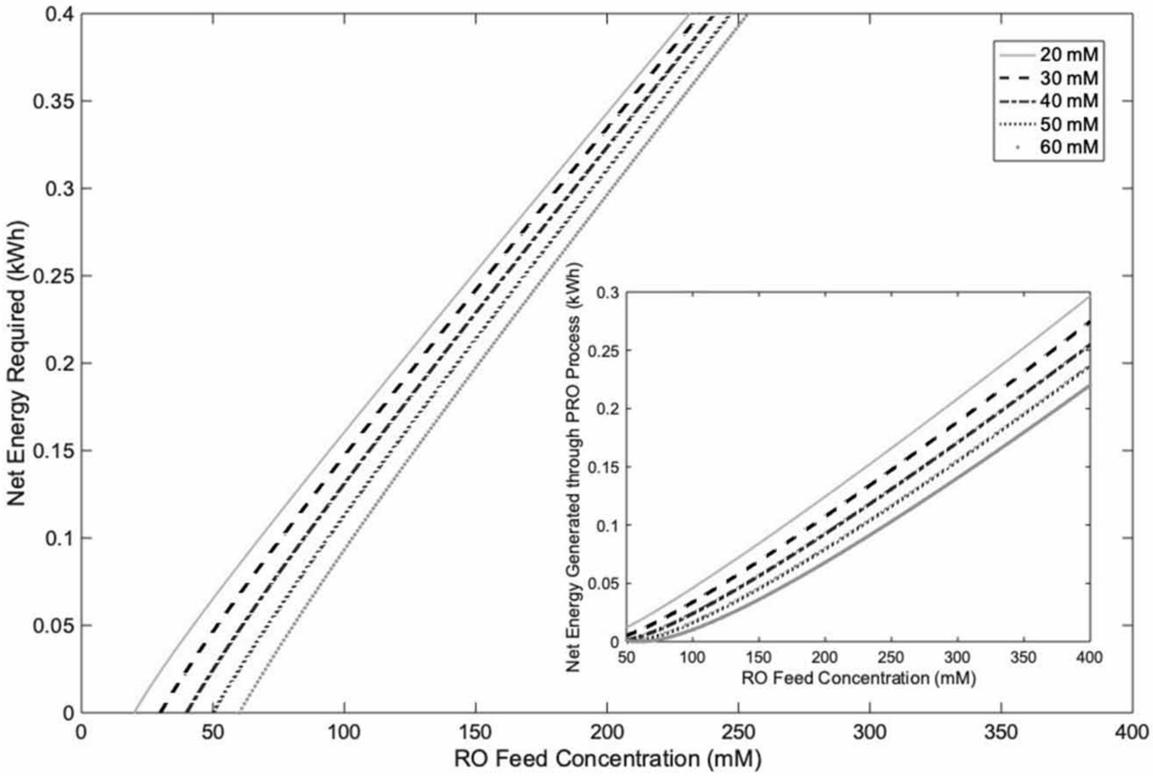


Figure 3 | Variation of energy generated with RO feed concentrations, for different RO permeate concentrations.

40–50% (Touati *et al.* 2017), while the temperature is considered to be 298 K.

The variation of net energy required by the whole process against the fraction of the RO permeate entering the PRO unit, for different recoveries of the RO desalination unit, is shown in Figure 4. For this calculation, the RO permeate is assumed to be 2 mM, while the RO feed concentration is considered to be 250 mM. For 50% recovery and only half of the RO permeate entering the PRO unit, the energy required is 1.0566 kWh, while that for 40% recovery is 0.8958 kWh (not presented in the paper). This can be explained by the increased energy demand of the RO unit due to higher recovery. It is also observed that the energy required to operate the RO-PRO hybrid system decreases with an increase in the fraction of RO permeate entering the PRO unit.

The inset of Figure 4 depicts the variation of the net energy saved by the whole process as a result of using the PRO unit for supplementing some of the energy requirement, against the fraction of the RO permeate entering the PRO unit, for different recovery values. For this calculation, the RO input concentration is assumed to be 250 mM while the RO permeate concentration is assumed to be 2 mM. For 50% recovery and half of the RO permeate entering the PRO feed, the energy saved is 0.2343 kWh, while that for 40% recovery is 0.1799 kWh (not presented in the paper).

As can be observed, the greater the fraction of the RO permeate entering the PRO unit, the greater the energy saved by the whole RO-PRO process as compared with the regular RO desalination process without the PRO unit. Another observation is that the greater the recovery, the greater is the energy produced by the PRO unit or energy saved, by the whole process. This is intuitive because the greater the recovery, the greater the volume of low-salinity permeate. This implies a higher-salinity brine reject stream being produced from the RO desalination unit which is ultimately increasing the driving force in the PRO unit, and thus increasing the energy generated by the PRO unit.

Figure 5 depicts the variation of the net energy required by the whole process against the fraction of the RO permeate entering the PRO unit, for different RO feed

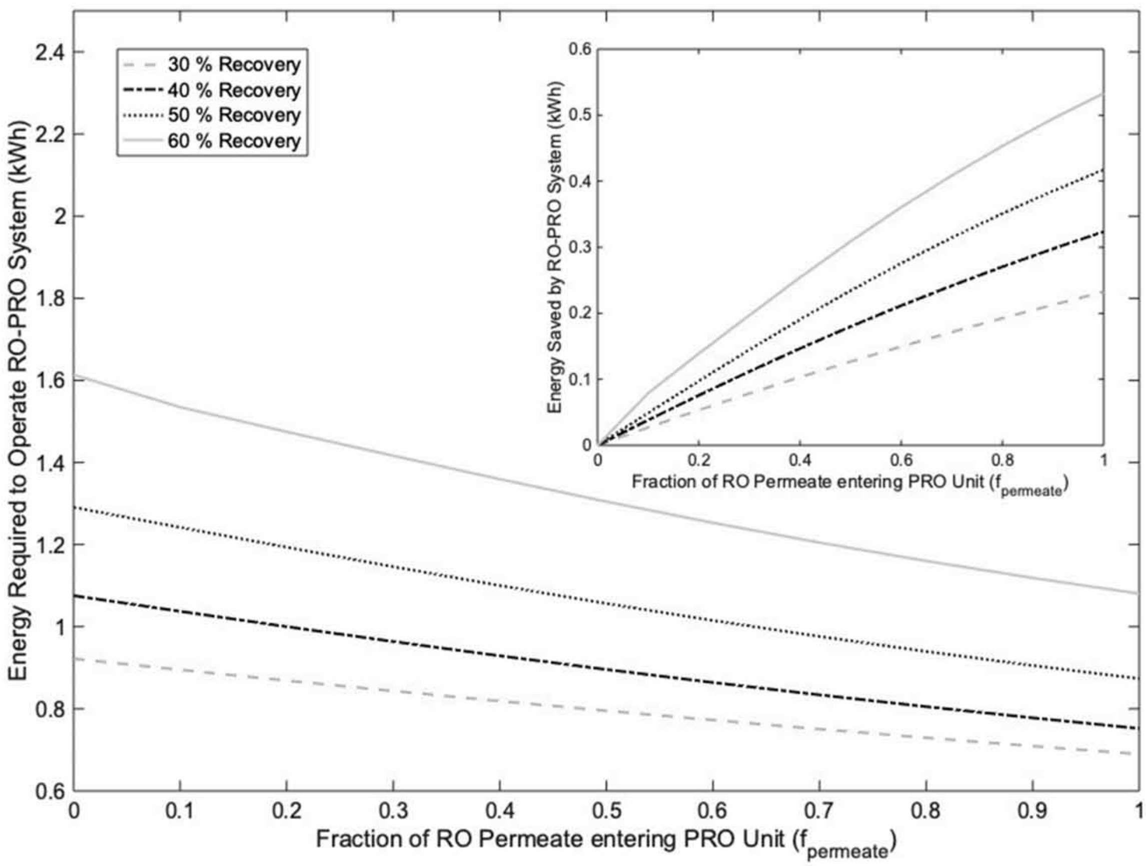


Figure 4 | Variation of energy required, with fraction of RO permeate entering the PRO unit, for different recoveries.

concentrations. For this calculation, the RO permeate concentration is assumed to be 2 mM. As can be observed, the lower the fraction of RO permeate entering the PRO unit, the greater the energy requirement of the whole process. The energy required for 50% recovery when the RO feed concentration is 200 mM and only half of the RO permeate enters the PRO unit is 0.8205 kWh, while that for 40% recovery is 0.7055 kWh (not presented in the paper). Although the lowest energy is required when the entire RO permeate is fed to the PRO as the feed solution, this defeats the purpose of such a setup. The objective is to reduce energy such that the cost of drinking water is reduced.

The inset of Figure 5 shows the variation of the net energy saved by the whole process against the fraction of the RO permeate entering the PRO unit, for different RO feed concentrations. The energy saved is essentially the energy generated by the PRO unit for the given specifications. For this calculation, the RO permeate concentration is assumed to be 2 mM. The energy saved for an RO feed of 200 mM concentration, at 50% recovery and only half of the RO permeate entering the PRO feed, is 0.1616 kWh, while that at 40% recovery is 0.1157 kWh (not presented in the paper).

As can be observed, the greater the fraction of the RO permeate entering the PRO unit, the greater the energy saved by the whole RO-PRO process as compared with regular RO desalination process, without the PRO unit. Another observation is that the greater the RO feed concentration, the greater the energy produced by the PRO unit or energy saved by the whole process.

Figure 6 illustrates the variation of the net energy required by the whole process against the fraction of the RO permeate entering the PRO unit, for different RO permeate

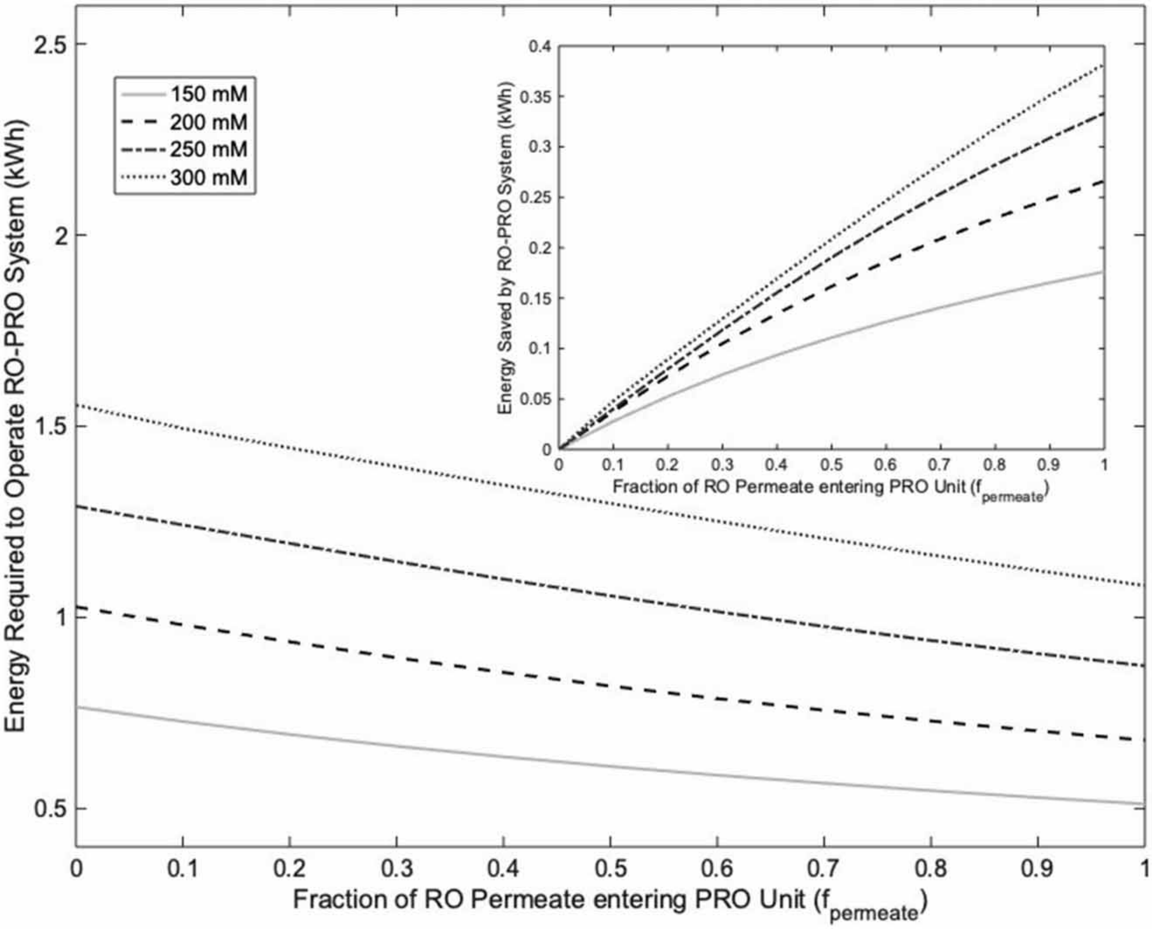


Figure 5 | Variation of energy required, with fraction of RO permeate entering the PRO unit, for different RO inputs.

concentrations. For this calculation, the RO input concentration is assumed to be 250 mM. As can be observed, the lower the fraction of RO permeate entering the PRO unit, the greater the energy requirement of the whole process. Another observation is that the greater the concentration of the RO permeate, the lower the energy requirement of the overall process. This is intuitive, as the energy required for desalination is significantly reduced along with the energy generated through the PRO process. The net energy required for a permeate of 40 mM, 50% recovery and where only half of the RO permeate is fed as PRO feed solution is 0.9397 kWh, while that for 40% recovery is 0.7958 kWh (not presented in the paper).

The inset of Figure 6 illustrates the variation of the net energy saved by the whole process (as a result of using the PRO unit for supplementing some of the energy requirement), against the fraction of the RO permeate entering the PRO unit, for different RO permeate concentrations. The energy saved is essentially the energy generated by the PRO unit for the given specifications. For this calculation, the RO feed concentration is assumed to be 250 mM. At 50% recovery, an RO permeate concentration of 60 mM and only half the RO permeate entering the PRO feed, the energy saved is 0.1272 kWh, while that for 40% recovery is 0.0944 kWh (not presented in the paper).

As can be observed, the greater the fraction of the RO permeate entering the PRO unit, the greater the energy saved by the whole RO-PRO process as compared with the regular RO desalination process, without the PRO unit. Another observation is that the greater the RO permeate concentration, the lower the energy produced by the PRO unit, or energy saved by the whole process.

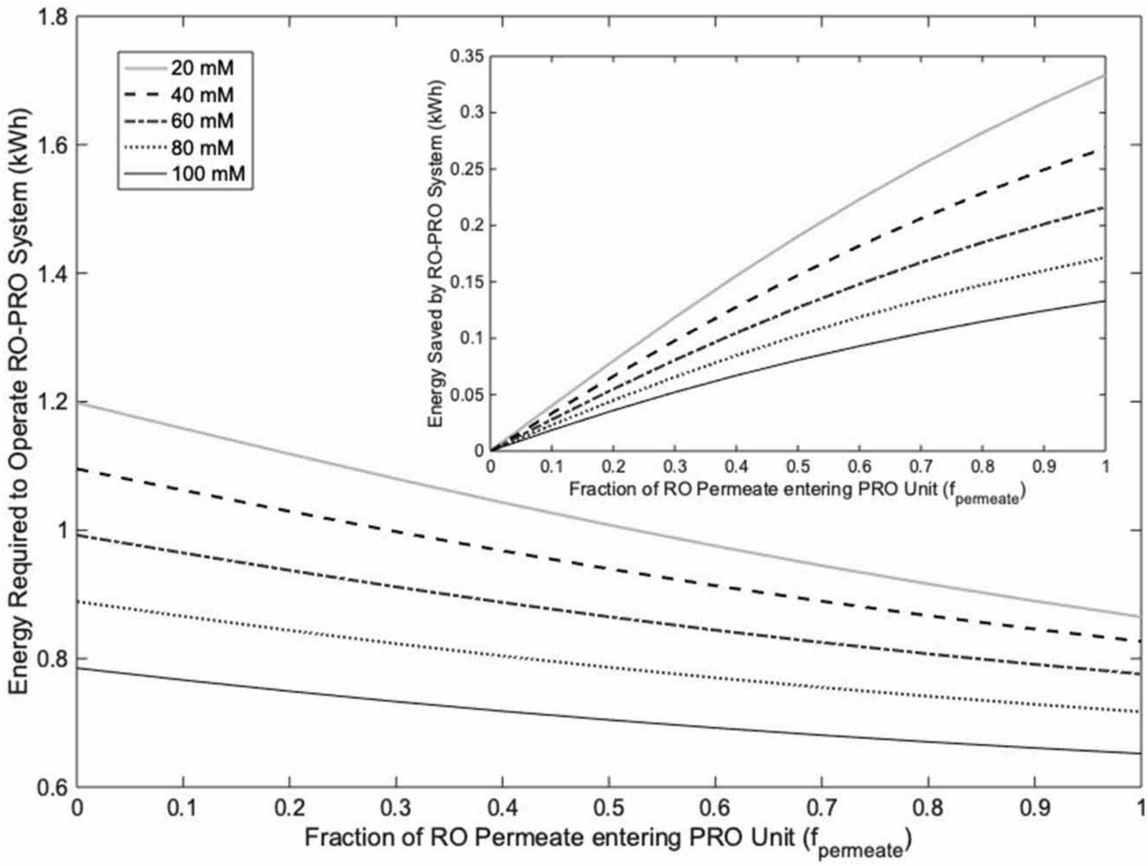


Figure 6 | Variation of energy required with fraction of RO permeate entering the PRO unit, for different RO permeate concentrations.

Having previously discussed the effects of the concentrations of the RO feed stream and the RO permeate stream, it is essential to delve into a detailed comparison between the present work and recent reported literature.

The present work emphasizes two separate configurations of PRO – one being a hybrid in conjunction with an RO desalination unit, with the focus on maximizing the energy generated through the PRO process, while the other is also a hybrid with the RO unit but the focus is on reducing the energetics of a conventional RO unit by usage of a PRO unit. The works of Tran *et al.* (2017), Xiong *et al.* (2017), Altaee *et al.* (2018) and Wang *et al.* (2016) indicate research on the configuration illustrated in Figure 1. The works of Touati *et al.* (2017), Senthil & Senthilmurugan (2016) and Chung *et al.* (2017) indicate research on the configuration illustrated in Figure 2.

It is evident from Tables 1 and 2 that the stark difference between the present work and that of other researchers is that the seasonal variation of river- or fresh-water concentration has been accounted for in the present work. This has often been overlooked when studying PRO processes – especially in estuarine geographies, where the river-water properties vary significantly for a multitude of reasons such as sea-water intrusion and precipitation. The actual setting up of a PRO process plant demands that such an analysis be carried out for the purpose of estimating the cost-effectiveness of the setup. Approximations may result in over- or under-estimation of energy generated. This could lead to huge losses in capital expenditure.

The works considered in Table 1, along with the present work, discuss the hybrid combination in Figure 1. The river-water concentration was considered to be varying seasonally in the other works, with the exception of Altaee *et al.* (2018) where discrete values were considered – some as high as the average concentration of sea-water itself

Table 1 | Significance of discussed PRO-RO hybrid combination (Figure 1) in contrast with state-of-the-art literature

PRO-RO combination 1 (Figure 1)

	Is river-water (PRO feed) concentration varying?	Variation of river-water concentration considered (mM)	Net specific energy generation estimated (kWh/m^3)	Is it thermodynamically feasible?
Present work	Yes	~0–400	0.1605–1.0597	No
Tran *et al.* (2017)	No	N/A	4.5	Yes
Xiong *et al.* (2017)	No	N/A	0.42	Yes
Altaee *et al.* (2018)	Yes	10, 600 & 700 mM were considered with different draw solutions	0.54–1.2	Yes
Wang *et al.* (2016)	No	N/A	0–0.4	Yes

Table 2 | Significance of discussed PRO-RO hybrid combination (Figure 2) in contrast with state-of-the-art literature

PRO-RO combination 2 (Figure 2)

	Is river-water (PRO feed) concentration varying?	Variation of river-water concentration considered (mM)	Net specific energy estimated (kWh/m^3)	Is it thermodynamically feasible?
Present work	Yes	~0–400	0.1786–1.2538	Yes
Touati *et al.* (2017)	No	N/A	0.11–0.19, 0.7–0.93	Yes
Senthil & Senthilmurugan (2016)	Yes	1–100	1.21–2.73	Yes
Chung *et al.* (2017)	No	N/A	0.42–0.43	Yes

(600 mM). Based on the authors' previous work (Chakraborty & Roy 2018), the river-water concentration in some parts of the world varies from nearly 0 mM to that of sea water. Realistically, the energy output was obtained to lie within a range 0.1605–1.0597 kWh/m^3.

The present work considering the configuration in Figure 1 has deemed it thermodynamically infeasible as the focus was to produce excess energy through the PRO process, such that the energy requirements of the RO desalination unit could be supplemented through the PRO unit and there would be excess energy left to be sent to the grid. Based on the calculations, the PRO unit falls short of these energy requirements. Hence, it has been termed thermodynamically infeasible. For the other works listed in the table, the focus is not on generating excess energy through PRO such that the RO unit's energy requirements can be supplemented through the excess energy generated.

The works considered in Table 2, along with the present work, discuss the hybrid combination in Figure 2. The river-water concentration was not considered to be varying seasonally in the other works, with the exception of Senthil & Senthilmurugan (2016). The energy estimated here is for the concentration range of 1–100 mM, with the energy output being 1.21–2.73 kWh/m^3.

As previously discussed, the focus of the configuration in Figure 2 is on reduction of the energy demand of the conventional RO desalination unit. The energy savings by introduction of a PRO unit in conjunction with the RO unit has previously been graphically illustrated in the insets of Figures 4–6 and discussed in the above sections.

The thermodynamics of the hybrid process–whilst accounting for the salinity variations – to the best of the authors' knowledge has not been discussed previously in great detail. The membrane module properties and optimization have been researched in great detail, however, the thermodynamics dictates the limits of the processes. The implication of accurate estimation of the energy requirements of the hybrid process is a necessity, and approximations cannot be relied upon. Furthermore, the energy savings due to the PRO unit lead to a reduced operating cost of the PRO process plant.

CONCLUSION

The following conclusions were drawn in the context of the present study:

i. Pretreating the feed to a PRO using an RO was found to be energetically infeasible.
ii. The energy required to operate the RO-PRO hybrid decreases with increase of RO permeate entering the PRO.
iii. Greater recovery results in higher energy savings from a RO-PRO hybrid than just a standalone RO.
iv. The current research proves the necessity of establishing hybrid RO-PRO systems in estuarine geographies.

ACKNOWLEDGEMENTS

Anirban would like to thank the Research Initiation Grant (BPGC/RIG/2017-2018, dt. 01/08/2017) and OPERA award (FR/SCM/230117/CHE, dt. 19/08/2017) by BITS Pilani Goa for carrying out the work. Anirban also would like to thank DST – SERB for the research grant (CRG/2018/001538 dt. 28/01/2020) for partially supporting the work.

AUTHOR DISCLOSURE AGREEMENT

No competing financial interests exist.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Achilli, A. & Childress, A. E. 2010 Pressure retarded osmosis: from the vision of Sidney Loeb to the first prototype installation – review. *Desalination* **261** (3), 205–211.

Achilli, A., Cath, T. Y. & Childress, A. E. 2009 Power generation with pressure retarded osmosis: an experimental and theoretical investigation. *J. Membr. Sci.* **343** (1–2), 42–52.

Altaee, A., Zhou, J., Zaragoza, G. & Sharif, A. O. 2018 Impact of membrane orientation on the energy efficiency of dual stage pressure retarded osmosis. *J. Water Process Eng.* **30**, 100621.

Al-Zahrani, A., Orfi, J., Al-Suhaibani, Z., Salim, B. & Al-Ansary, H. 2012 Thermodynamic analysis of a reverse osmosis desalination unit with energy recovery system. *Procedia Eng.* **33**, 404–414.

Arias, F. J. 2018 A first estimate for a pressure retarded osmosis-driven thermosyphon. *Sol. Energy* **159**, 962–965.

Cerci, Y., Cengel, Y., Wood, B., Kahraman, N. & Karakas, E. S. 2003 *Improving the Thermodynamic and Economic Efficiencies of Desalination Plants: Minimum Work Required for Desalination and Case Studies of Four Working Plants*. Desalination and Water Purification Research and Development Program Final Report No. 78, Bureau of Reclamation, US Department of the Interior, Denver, CO, USA.

Chakraborty, A. & Roy, A. 2018 Seasonal variations in river water properties and their impact on mixing energies and pressure retarded osmosis. *Environ. Eng. Sci.* **35** (10), 1075–1086.

Cheng, Z. L., Li, X. & Chung, T. S. 2018 The forward osmosis–pressure retarded osmosis (FO-PRO) hybrid system: a new process to mitigate membrane fouling for sustainable osmotic power generation. *J. Membr. Sci.* **559**, 63–74.

Chung, H. W., Nayar, K. G., Swaminathan, J., Chehayeb, K. M. & Lienhard V, J. H. 2017 Thermodynamic analysis of brine management methods: zero-discharge desalination and salinity-gradient power production. *Desalination* **404**, 291–303.

de Vilhena, M. T. 1992 An analytical solution of the steady state convective-diffusion equation with space dependent diffusion coefficient. *J. Membr. Sci.* **71** (1–2), 51–56.

Gerstandt, K., Peinemann, K.-V., Skilhagen, S. E., Thorsen, T. & Holt, T. 2008 Membrane processes in energy supply for an osmotic power plant. *Desalination* **224** (1–3), 64–70.

Lee, K. L., Baker, R. W. & Lonsdale, H. K. 1981 Membranes for power generation by pressure-retarded osmosis. *J. Membr. Sci.* **8** (2), 141–171.

Loeb, S., Van Hessen, F. & Shahaf, D. 1976 Production of energy from concentrated brines by pressure-retarded osmosis: II Experimental results and projected energy costs. *J. Membr. Sci.* **1**, 249–269.

Loeb, S., Honda, T. & Reali, M. 1990 Comparative mechanical efficiency of several plant configurations using a pressure-retarded osmosis energy converter. *J. Membr. Sci.* **51** (3), 323–335.

Pattle, R. E. 1954 Production of electric power by mixing fresh and salt water in the hydroelectric pile. *Nature* **174** (4431), 660.

Pitzer, K. S., Peiper, J. C. & Busey, R. H. 1984 Thermodynamic properties of aqueous sodium chloride solutions. *J. Phys. Chem. Ref. Data* **13** (1), 1–102.

Reali, M., Dassie, G. & Jonsson, G. 1990 Computation of salt concentration profiles in the porous substrate of anisotropic membranes under steady pressure-retarded-osmosis conditions. *J. Membr. Sci.* **48** (2–3), 181–201.

Robinson, R. A. & Stokes, R. H. 1960 *Electrolyte Solutions,* 2nd revised edn. Dover Publications, New York, USA.

Senthil, S. & Senthilmurugan, S. 2016 Reverse osmosis–pressure retarded osmosis hybrid system: modelling, simulation and optimization. *Desalination* **389**, 78–97.

Smith, J. M., Van Ness, H. C. & Abbott, M. M. 2005 *Introduction to Chemical Engineering Thermodynamics*. McGraw-Hill, New York, USA.

Straub, A. P., Deshmukh, A. & Elimelech, M. 2016 Pressure-retarded osmosis for power generation from salinity gradients: is it viable? *Energy Environ. Sci.* **9** (1), 31–48.

Tanioka, A. 2016 Preface to the special issue on 'Pressure Retarded Osmosis in Megaton Water System Project'. *Desalination* **389**, 15–17.

Touati, K., Tadeo, F. & Elfil, H. 2017 Osmotic energy recovery from reverse osmosis using two-stage pressure retarded osmosis. *Energy* **132**, 213–224.

Tran, T. T. D., Park, K. & Smith, A. D. 2017 System scaling approach and thermoeconomic analysis of a pressure retarded osmosis system for power production with hypersaline draw solution: a Great Salt Lake case study. *Energy* **126**, 97–111.

Wan, C. F., Yang, T., Gai, W., Lee, Y. D. & Chung, T. S. 2018 Thin-film composite hollow fiber membrane with inorganic salt additives for high mechanical strength and high power density for pressure-retarded osmosis. *J. Membr. Sci.* **555**, 388–397.

Wang, Z., Hou, D. & Lin, S. 2016 Gross vs. net energy: towards a rational framework for assessing the practical viability of pressure retarded osmosis. *J. Membr. Sci.* **503**, 132–147.

Xiong, J. Y., Cai, D. J., Chong, Q. Y., Lee, S. H. & Chung, T. S. 2017 Osmotic power generation by inner selective hollow fiber membranes: an investigation of thermodynamics, mass transfer, and module scale modelling. *J. Membr. Sci.* **526**, 417–428.

Yip, N. Y. & Elimelech, M. 2012 Thermodynamic and energy efficiency analysis of power generation from natural salinity gradients by pressure retarded osmosis. *Environ. Sci. Technol.* **46** (9), 5230–5239.

First received 20 May 2019; accepted in revised form 19 June 2020. Available online 1 July 2020