Pressure Retarded Osmosis: advancement, Challenges and Potential

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Abstract

An excessive amount of renewable energy could be possibly produced when solutions of dissimilar salinities are combined simultaneously in a semipermeable membrane. The aforestated energy harnessing for transformation into power could be achieved through the pressure retarded osmosis (PRO) process. The PRO system utilizes a semipermeable membrane for separating a low concentration solution from a pressurized-high concentrated solution. This work examines the recent developments and applications of the PRO process and potential energy that could be conceivably harvested from salinity gradient resources in a single-stage and multi-stage PRO processes. One of the existing challenges for this process is finding a commercial membrane that combines characteristics of the forward osmosis membrane (for reducing the phenomenon of concentration polarization) and the reverse osmosis membrane (to withstand high hydraulic pressure). For addressing this challenge, details about the commercial PRO membranes and the innovative laboratory fabricated PRO membranes are introduced. The potential of the PRO process is presented by elucidating salinity gradient resources, the energy of Pretreatment, the process design, PRO-desalination systems, and dual-stage PRO (DSPRO). It is anticipated that this paper can assist in widely understanding the PRO process and thus deliver important data for activating additional research and development.

Keywords: pressure retarded osmosis, renewable energy, salinity gradient, dual-stage pressure retarded osmosis, membrane

1. Introduction

Conventional energy production methods utilizing non-renewable fossil-fuel resources possess numerous weaknesses [1-4]. For example, power plants operated by fossil fuels generate greenhouse gases which can cause environmental damage [5-7]. Consequently, the demand for eco-friendly, as well as sustainable energy production systems, is rising [8, 9]. Even though several renewable technologies like solar, wind and tidal generation have been advanced in the last few years, there exist significant concerns that the aforementioned renewable energy production systems are non-sustainable because of various power source features [10, 11]. Furthermore, fuel cell systems still need to develop a membrane to meet complex operational conditions [12, 13]. Pattle et al. [14] and Loeb et al. [15, 16] initially presented the pressure retarded osmosis (PRO) concept: generating electrical power using water flux brought about by the osmotic pressure difference between two different saline components. This pressure retarded osmosis system has been the subject of considerable research due to its inherent advantages: 1) It will not generate dangerous waste to the surroundings [17-19]; 2) the compact size of the membrane-based system reduces the size requirement of the treatment plant needed, hence, is less damaging to the ecology; 3) this is a sustainable energy production method utilizing saline water sources [20-22]; 4) this technology has application as a high-efficiency hybrid system, while utilized with commercialized reverse osmosis (RO) [23, 24]; and 5) PRO system has an extensive range of uses such that different sources of water in the globe might be utilized [25, 26].

Despite its numerous benefits, the pressure retarded osmosis system experiences several issues which inhibit commercialization. This situation is because of factors such as the deficiency of exceptional membranes that can function at increased pressure and fouling issues, which diminish the water flux across the membrane [27-31]. Additionally, adverse phenomena like internal concentration polarization can remarkably decrease the effective osmotic difference applied to the membrane; thus hindering efficient power generation. As an illustration, asymmetric cellulose acetate (CA) membrane from the company Hydration Technology Innovation (HTI, USA) accomplished just the nominal power densities due to serious internal concentration polarization problems [32]. Several studies have been conducted to understand the process performance as well as membrane effectiveness for the generation of power from a salinity-gradient energy technology. The PRO procedure was also verified in a pilot-scale plant for demonstrating its practicability as well as performance in real-world applications [33]. The test results of the pilot-scale studies, as well as bench-scale studies, confirm that the PRO process could be a renewable energy source, particularly after the PRO membrane commercial development [34, 35]. Table 1 presents the currently available different commercial PRO membranes. In recent times, a thermodynamic analysis of the pressure retarded osmosis process demonstrated that the input energy might be greater than the output energy. This outcome was due to inadequate salinity gradient osmotic energy as well as power losses because of the drawback of the membrane [36, 37]. Hence, the minimum energy requirements, inclusive of pretreatment energy and power losses, must be recognized. In a study performed by Anthony et al. [37], an examination of the process feasibility for the production of power from the seawater-river water salinity gradient was reported. This study confirmed that the power produced by the pressure retarded osmosis process was lesser relative to the energy needed for the Pretreatment as well as the pumping of the draw and feed solutions. The highest energy produced by seawater-river water was 0.250 $kWh.m^{-3}$. In contrast, the maximum extractable energy by the pressure retarded osmosis process was less than that due to the membrane inefficiency and energy loss. Additionally, the energy necessary for the pumping and Pretreatment has been indicated to be between 0.170 and 0.50 $kWh.m^{-3}$, which can be greater relative to the maximal energy generation of the seawater-river water salinity gradient [38].

Table 1: Currently available different commercial PRO membranes.

Membrane	Manufacturer	Configuration
5-inch and 10-inch Cellulose triacetate (CTA) membrane	Toyobo Co., Ltd. Osaka City, Japan	Hollow fiber
Polyamide thin-film composite (TFC) membrane	Hydration Technologies Innovations	Spiral-wound membrane

Cellulose triacetate (CTA) membrane	Hydration Technologies Innovations	Spiral-wound membrane
Polyamide membrane	*Toray* Chemical Korea	Spiral-wound membrane

In comparison with the recently published review papers [18, 39-42], some of these studies did not mention the PRO hybrid systems [39] or the DSPRO process[42]. At the same time, previous studies did not include the maximum power generated by various salinity gradients in a detailed manner. Other's focused only on the PRO membranes [41]. As a result, this work emphasises to provide detailed information on all aspects related to the PRO systems as follows.

In this review paper, we discuss the different commercial PRO membranes available (Toyoba, HTI, Toray, etc.), details about some laboratory-developed membranes, dual-stage PRO and the energy of Pretreatment. So far, only a few studies discussed the current developments, different simulation studies, and future applications of pressure retarded osmosis process [42-45]. However, to the best of our knowledge, few studies have discussed the commercial PRO membranes, laboratory fabricated membranes, salinity gradient resources, the energy of pretreatment and energy inputs, and the process design, including the possibility of combining PRO with desalination plants, and dual-stage PRO. This review is thus aimed to contribute new understanding and information for the scientific community in this field.

2. PRO membrane

2.1 Commercial PRO membranes

Toyobo Co. is considered to be one of the innovative companies which have effectively developed as well as tested pressure retarded osmosis membranes for a large-scale pilot plant trial [46]. Hollow-fiber forward osmosis membranes developed by Toyobo Co. Ltd. have a large active area that spreads 700 m^2 and operates with feed pressures of up to 30.0 bar; which makes these membranes appropriate for treating a salinity gradient of osmotic pressure difference 60 bar. Saito et al. [47] performed a small bench-scale pressure retarded osmosis permeation experiment utilizing three-inch modules obtained from Toyobo Co., Ltd. Standard modules consisting of the reverse osmosis membrane elements typically have 3 open ports; namely, a seawater inlet, reject stream outlet, and product water outlet (three-orifice module). In the event the element mentioned above was used for the pressure retarded osmosis process, each port was used as a product water inlet, reject stream inlet, and product water flux outlet. In the outlined study, an amended module, which possessed 4 open ports, was developed for the pressure retarded osmosis process (four-orifice module). Each of the ports functioned as a reject stream inlet, brine and product water mixture outlet, product water inlet and the final one functioned as a permeate water outlet; whereby the non-permeating freshwater left. This arrangement minimized the impact of the concentration polarization effect close to the surface of the membrane on the freshwater side. The experimental conditions of the PRO system were: the brine (3.20 wt% sodium chloride solution) side pressure was about 0.90 MPa, whereas the freshwater side was pressurized at 0.50 MPa. The prototype pressure retarded osmosis plant demonstrated 7.70 $W.m^{-2}$ maximal output power density at 2.50 MPa hydraulic pressure difference, and pure water permeation of 38.0 % into the brine.

Recently, Hydration Technology Innovation (HTI) manufactured and commercialized flat-sheet cellulose triacetate forward osmosis membranes as well as thin-film composite (TFC) forward osmosis membranes. As such, several scientists employed forward osmosis membrane coupons for lab-scale pressure retarded osmosis research using effective membrane areas of 140 cm^2 [48], 20.02 cm^2 [49], and 18.75 cm^2 [50]. The advanced TFC membrane of HTI exhibited superior rejection and increased permeability. In addition to a pH tolerance in the range of 2.0 to 12.0 the membrane tolerated the high pressure encountered in different PRO operating conditions. The flat sheet flux of manufactured membrane averaged 20.0 $L/m^2/h$ in the forward osmosis mode and 49.0 $L/m^2/h$ in pressure retarded osmosis mode at a testing condition of deionized (DI) water as the feed solution and 1.0 M sodium chloride as the draw solution at 23.0 °C and 30.0 cm/sec cross-flow velocity.

In recent times, the Megaton project was performed with Toyobo hollow-fiber membranes utilizing salinity gradient resource of reverse osmosis brine (RO)-tertiary treated wastewater effluent (TSE) [51]. This pilot plant test confirmed the significance of feed water pretreatment for preventing the fouling of the membrane. Microfiltration and reverse osmosis processes were primarily carried out for the tertiary treated wastewater treatment; however, reverse osmosis fouling was noticed. For this reason, the wastewater effluent underwent Pretreatment using microfiltration, which has been noted to be satisfactory for removing the fouling material from the feed solution to the pressure retarded osmosis process. The fouling phenomena of the membrane in the PRO process have been diminished by adding a fourth port on the membrane feed side [47]. The Megaton venture effectively demonstrated an osmotic power plant model with 10.0 W/m^2 average power density. The stated value was practically twofold the threshold stated by Statkraft Company and needed for a cost-effective pressure retarded osmosis process.

Aquaporin developed as well as commercialized Aquaporin Inside hollow-fiber forward osmosis (FO) biomimetic membranes for improved water reuse and concentration processes, with low back diffusion and employing just osmotic pressure. These membranes could concentrate natural compounds present in liquids with no pressure or heat, thereby conserving the natural and nutritional quality. Different module sizes such as HFFO14 (13.8 m^2 membrane area, fiber of internal diameter (ID) 0.2 mm), HFFO2 (2.3 m^2 membrane area, fiber ID 0.2 mm), HFFO.6 (0.6 m^2 membrane area, Fiber ID 0.2 mm) are available. These modules consist of a selective thin-layer of polyamide thin-film composite with integrated aquaporin proteins.

To allow comparison of the membrane module efficiencies, the efficiencies of different commercial hollow-fiber membranes (HFMs) and flat-sheet membranes (FSMs) are presented in Table 2. Pressure retarded osmosis mode test results are provided in this table for a more extensive comparison. In the Megaton Water project [51, 52], the maximum membrane power density per surface area attained was 13.50 W/m^2 by employing ten-inch modules at the prototype pressure retarded osmosis plant in Fukuoka, and 17.10 W/m^2 in the lab-scale experimental set up employing five-inch module with pure water as feed solution and concentrated brine as draw solution. The data confirmed that the net output was estimated at 13.50 W/m^2 and 17.1 W/m^2 of power density in the prototype plant and the lab-scale plant. The difference reflected the use of spiral wound and hollow-fiber configurations while utilizing the brine from seawater reverse osmosis facility and less-saline water from a wastewater treatment plant as a draw solution and feed solution, respectively. It was noted that the power density obtained from Toyobo's HFM module was relatively high, as compared to the SWM modules of other manufacturers. Even though SWM modules and HFM modules have been investigated relatively equally till date, study trends have confirmed that the HFM modules are probably more promising in the pressure retarded osmosis process because of its easy design modification, superior packing density, and pressure-tolerant structure.

Table 2: Efficiency of different commercial-size PRO hollow-fiber membrane (HFM) modules and Spiral-wound membrane (SWM) modules.

Membrane	Concentration of draw solution	Pressure of draw solutions in bar	Power density expressed in $W.m^{-2}$	Ref.
Toyobo 5-inch Hollow-fiber membrane(HFM) module Polymer: Cellulose triacetate	1 M sodium chloride	30	17.1	[52]
Toyobo 10-inch HFM module Polymer: Cellulose triacetate	1 M sodium chloride	30	13.3	[52]
Toyobo 10-inch HFMmodule Polymer: Cellulose triacetate	1 M sodium chloride	29	4.4	[47]
Toyobo 10-inch HFM module Polymer: Cellulose triacetate	1 M sodium chloride	25	7.7	[47]
HTI OsMem Spiral-wound membrane (SWM) module Polymer: Cellulose triacetate	1.03 M sodium chloride	4.0	1.10	[53]
HTI OsMem SWM module Polymer: Polyamide	0.60 M sodium chloride	9.8	1.00	[54]
Toray Chemical Korea 8040 SWM pressure retarded osmosis module Polymer: Polyamide	0.60 M sodium chloride	10.4	1.77	[55]
HTI OsMem SWM module Polymer : Cellulose triacetate	0.52 M sodium chloride	4.0	0.57	[53]

As per HTI, the membrane element used in the study [53] can tolerate solution in the range of 3–8 pH, 110 °F (43 °C) maximum operating temperature, and 5 bar maximum hydraulic pressure. The HTI Company rated salt (sodium chloride) rejection for the module as 99.0 %. The active membrane area was noted to be 0.50 m^2. The membrane length and width was 0.520 and 0.480 m, respectively. The membrane element employed a diamond type feed spacer to provide a steady permeate flux and a permeate spacer for permitting an increased draw flow rate as well as support the membrane. To facilitate operation of the module at increased hydraulic pressure as required for pressure retarded osmosis tests; the spiral membrane element was located in polyvinyl chloride (PVC) pressure vessel with a maximum tolerable hydraulic pressure of 15.0 bar. In the study by Kim et al. [54], the prototype seawater pressure retarded osmosis membrane module of 0.20 m diameter and 1.0 m length, was employed for the pressure retarded osmosis analysis. The effective membrane area of the pressure retarded osmosis module was ca. 29.0 m^2, and twenty membrane envelopes were rolled into a spiral-wound configuration. As per HTI, the membrane developed for pressure retarded osmosis was a thin-film composite polyamide-based membrane. In research by Lee et al. [55], the 8040 pressure retarded osmosis module was provided by Toray Chemical Korea. This module had a similar size as the 8040 RO module and was 0.20 m diameter and 1.0 m length. This pressure retarded osmosis module had 17.90 m^2 of membrane area with a coating of polyamide. As per Toray, a distinct spacer for the feed solution was used for reducing the pressure resistance of the feed channel. The draw channel spacer had a thickness of about 0.80 mm and 97 cm^2 cross-section area.

2.2. Laboratory fabricated membranes

The best pressure retarded osmosis membrane needs to be mechanically robust to withstand increased pressures, exhibit supreme water permeability, and low salt permeability [56, 57]. Advancement of the pressure retarded osmosis technology has been inhibited by the scarcity of effective membranes until the latest developments in PRO studies. Like other TFC-based membranes, the pressure retarded osmosis membrane support layers were developed in a hollow fiber or flat-sheet configuration using phase separation method. However, the selective polyamide (PA) layer was prepared by the interfacial polymerization (IP) technique. The aforestated characteristic 2 stage process generated a TFC membrane which had an extensive field of uses in different separation processes. Till now, the TFC polyamide membranes manufactured utilizing interfacial polymerization demonstrated promising possibilities. Numerous approaches, as well as modifications on the polymer membranes, have been made during the advancement of pressure retarded osmosis for energy generation, and these have been summarized in Table 3, together with its efficiency.

Table 3: Comparison of different polymer pressure retarded osmosis membrane modifications and their efficiency.

PRO membrane modification	Feed solution/Draw solution	Water Flux, (L/(m^{2}h)	Power Density, (W/m^2)	Ref.
Polyethersulfone thin-film composite membranes with magnesium chloride	Deionized water / 1.20 M sodium chloride solution	38.0	27.4	[58]
Polyethersulfone thin-film composite membranes with Lithium chloride	Deionized water / 1.20 M sodium chloride solution	46.0	32.4	[58]
Polyethersulfone thin-film composite membranes with Calcium chloride	Deionized water / 1.20 M sodium chloride solution	50.0	34.7	[58]
Active layer etching using 1000 mg/L sodium hypochlorite	River water / Synthetic seawater	53.0	10.2	[19]
Active layer etching using 1000 mg/L sodium hypochlorite	Brackish water/ Synthetic seawater	40.0	7.9	[19]
Zwitterion coating at the bottom of the polyethersulfone substrate	Wastewater from municipal recycling plant / Synthetic seawater brine	Not applicable	7.2	[59]

2.2.1. Flat-sheet PRO membranes

For the manufacture of flat-sheet pressure-retarded osmosis membranes, several developments have been accomplished. In a study by Zhang and coworkers, the group prepared TFC flat-sheet membranes on polyacrylonitrile (PAN) support using various post-treatments [60]. They reported a power density of 2.60 W/m^2 at 10 bar pressure utilizing the draw solution 3.5 wt% sodium chloride. Very thin polyamide selective layers of this TFC membranes demonstrated superior efficiency in a majority of liquid-separation uses. Wei et al. [61] found that flat-sheet TFC pressure-retarded osmosis membranes with reinforced support layer were manufactured. The membrane characteristics were optimized by combining high molecular weight poly (vinylpyrrolidone) with the polysulfone-based casting solution. The different test results established that the reinforced thin-film composite membrane showed superior mechanical strength and stability. In the study by Cui et al. [62], TFC membranes were developed, comprised of a selective PA thin-film layer prepared using an IP process and macrovoid-free polyimide-based support. For improving water flux and power density, three various treatments were analyzed. Consolidation of the post-treatments and pretreatments on the membranes cooperatively improved the power density generated (almost 18.09 W/m^2).

Nanofibers were considered to be favorable support materials for TFC membranes utilized in osmotic processes. Nanofiber mats as the support layer of thin-film composite pressure retarded osmosis membranes fabricated by the electrospinning technique; contribute significant benefits like less tortuosity, increased porosity, and very thin membrane thickness. Ultimately the described features consequently reduced the S value. An advanced electrospun nanofiber supported TFC pressure retarded osmosis membrane was prepared by Bui et al. [63], and the support was tiered using nanofiber layers of various diameters for better withstanding the hydraulic pressure. The membranes effectively withstood 11.5 bar applied hydraulic pressure and showed a performance that could generate an equivalent peak power density of almost 8 W/m^2 in practical conditions. Moon et al. [64] prepared two electrospun membrane types utilizing: 1) thermally rearranged poly(benzoxazole-co-imide), which is inherently strong, and 2) sulfonated poly(arylene ethersulfone), that requires chemical cross-linking to increase the mechanical properties. The fabricated chlorine-modified TFC membranes demonstrated remarkable pressure retarded osmosis efficiency. The modifications applied to the support layer (polyvinyl alcohol coating or chemical cross-linking) and the PA layer (sodium hypochlorite treatment) brought forth thin-film composite membranes with upgraded water permeability, good hydrophilicity, as well as physical robustness. Fig. 1 presents the PRO performance of the membranes as a function of the various hydraulic pressures. Kim et al. [32] described the preparation of a thermally rearranged TFC membrane comprising of a very-thin selective PA layer and a thermally rearranged nanofiber polymeric support coated using polydopamine; particularly for the utilization in PRO for sustainable power production. This membrane showed reduced internal concentration polarization, which resulted in superior pressure retarded osmosis performance for producing electricity (40 W/m^2). Table 4 shows the performance of various flat sheet membranes stated in the literature.

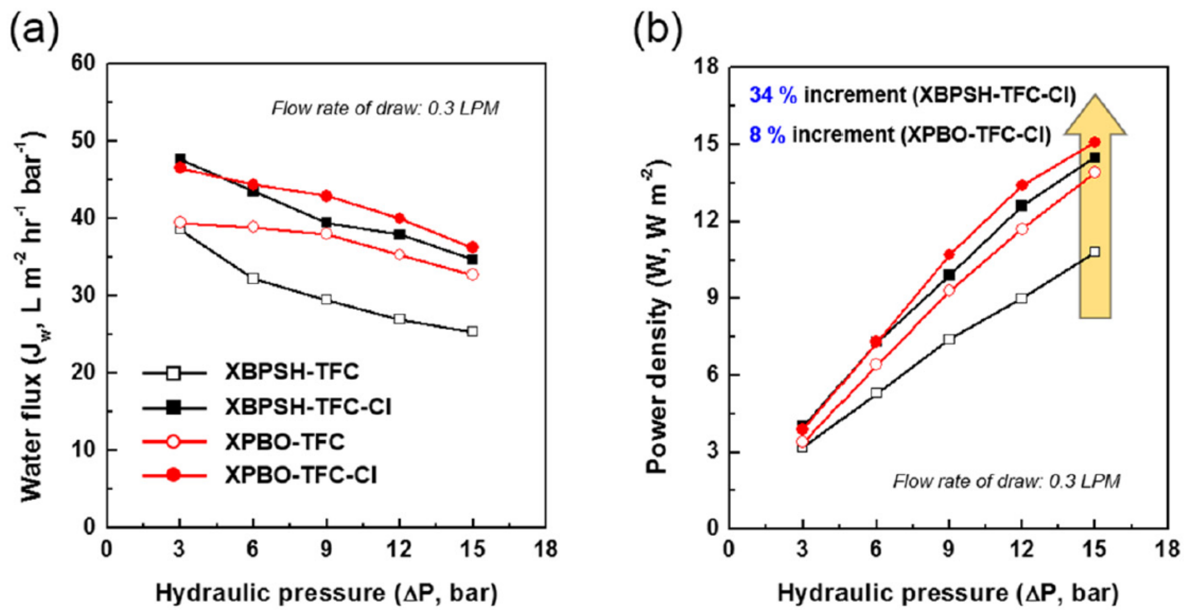


Fig. 1: (a) Water flux as well as (b) Power density of Crosslinked Sulfonated poly (aryleneether sulfone) (XBPSH)-TFCs and Crosslinked poly (benzoxazole-co-imide) (XPBO)-TFCs as per the various hydraulic pressures. Reproduced from Ref [64].

Table 4: Performance of different flat-sheet membranes reported in the literature.

Material	Draw Solution	Feed solution	W (W/m^2)	ΔP (bar)	Ref.
Polyamide-polysulfone	3 M Sodium chloride	Deionized water	60	48	[65]
Polyamide-polysulfone	1 M Sodium chloride	Deionized water	12.9	22	[61]
Polyamide-polyimide	1 M Sodium chloride	Deionized water	18.09	22	[62]
Polyamide-polyacrylonitrile nanofiber	0.5 M Sodium chloride	Deionized water	8.0	11.5	[63]
Polyamide- Sulfonated poly(arylene ethersulfone), poly(benzoxazole-co-imide)	1 M Sodium chloride	Deionized water	26.6	21	[64]
Polyamide-polybenzoxazole-co-imide	2000 ppm Sodium chloride	Deionized water	40	15	[32]
Polyamide-polyamide-imide	3.5 % Sodium chloride	Deionized water	2.84	6	[66]
Polyamide-Matrimid	1 M Sodium chloride	Deionized water	6	15	[67]

When comparing the performance of different flat-sheet laboratory-fabricated membranes with the commercially available membranes, it can be noted that the flat-sheet laboratory-fabricated membranes superior pressure retarded osmosis performance for producing electricity (up to 60 W/m^2). However, for the commercial pressure retarded osmosis membranes, the maximum power density obtainable was 17.10 W/m^2. Despite this, we should consider that the laboratory membranes require extensive field tests, and their long-term performance should also be proved. Moreover, maintaining the membranes' superior performance from small-scale membranes to modules can be regarded as a significant problem.

2.2.2. Hollow-fiber PRO membranes

An advanced integral PRO hollow-fiber membrane (HFM) was fabricated by Li et al. [68] utilizing the phase inversion approach and succeeded by a simple cross-linking post-treatment process. Two cross-linking steps produced a membrane with a reduced pore size on the external surface which demonstrated increased rejection towards different inorganic salts. This advanced membrane accomplished 4.3 W/m^2 stable power density output at almost 12 to 13 bar hydraulic pressure, utilizing 1.0 M sodium chloride and real wastewater reverse osmosis retentate as the draw and feed streams, respectively. These test results confirmed that the PRO process in the active layer (AL) facing feed solution (FS) orientation (forward osmosis mode) conferred a substantial benefit over the active layer facing draw solution orientation (pressure retarded osmosis mode); by eradicating the feed water pretreatment and/or additional steps related to fouling control of membrane in the PRO mode. In a study by Han et al. [27], a simple, as well as a versatile method, was confirmed for the manufacture of less-fouling PRO HFMs for osmotic power production from extremely contaminated wastewater. A zwitterionic random copolymer with water solubility increased hydrophilicity, and exclusive chemistry was molecularly designed and prepared through a single-stage free-radical polymerization process. Due to the exceptional hydrophilicity, exclusive anionic and cationic groups, and electrical neutrality of the zwitterionic brush, this advanced membrane demonstrated increased resistance against organic fouling and inorganic scaling in the pressure retarded osmosis processes.

In general, a power density value of 5.0 W/m^2 is needed for commercializing the pressure retarded osmosis process utilizing river water and seawater, as feed solution and draw solution, respectively. On the other hand, because of the deficiency of extremely efficient pressure retarded osmosis membranes, the harvested power has been much less than the standard value. Chou et al. [69] stated that a power density value of 5.70 W/m^2 could be generated by a hollow-fiber composite PA membrane from river water as well as artificial seawater. Song and his coworkers introduced a modification technique for nanofiber support membranes which resulted in thin-film nanofiber composite PRO membranes having improved mechanical properties as well as enduring a lesser S value, which has been considered to be crucial for increased power density pressure retarded osmosis processes [70]. This highly efficient thin-film nanofiber composite-PRO membrane could accomplish a power density of almost 15.20 W/m^2 and maximum energy recovery of about 0.860 kWh/m^3, utilizing 1.06 M sodium chloride seawater brine and 80 mM sodium chloride artificial brackish water, as a draw solution and feed solution, respectively. Zhao et al. [59] modified 2-methacryloyloxyethylphosphorylcholine (MPC) and grafted it onto polydopamine (PDA) coated PES hollow fiber substrate, to decrease the fouling propensity.

Both the preparation as well as the surface coating of 2-methacryloyloxyethylphosphorylcholine were simple and easy for scale-up. Relative to the pure polyethersulfone and polyethersulfone-polydopamine substrates, the MPC modified substrate (polyethersulfone- polydopamine-2-methacryloyloxyethylphosphorylcholine) displayed superior resistance to bacteria adhesion and protein adsorption. The thin-film composite HFM prepared by Chou et al. [71] accomplished a power density of almost 20.90 W/m^2 at 15 bar pressure, utilizing artificial river water (1.0 mM sodium chloride) as the feed water and synthetic saltwater brine (1.0 M sodium chloride as the draw solution. Wan et al. [58] highlighted advanced techniques for designing an inner-selective TFC pressure retarded osmosis HFM with increased operating pressure and a superior power density by adding an inorganic salt, calcium chloride, to the dope solution and fine-adjustment of the spinning conditions. The upgraded performance developed the pressure retarded osmosis technology nearer to commercialization and made the osmotic energy more economical among other renewable sources of energies. Table 5 presents the behavior of various hollow-fiber membranes reported in different literature.

Table 5: Efficiency of various hollow-fiber membranes reported in the literature.

Material	Draw Solution	Feed solution	W (W/m^2)	ΔP (bar)	Ref.
Polyamide-imide	1.0 M sodium chloride	Real wastewater	4.3	13	[68]
Polyamide-polyethersulfone	Synthetic RO brine (1 M sodium chloride)	40.0 mM sodium chloride	10.6	12	[69]
Polyamide-Polyacrylonitrile (PAN) nanofiber support	1.06 M sodium chloride	80.0 mM sodium chloride	15.2	15.2	[70]
Polyamide-polyetherimide	1.0 M sodium chloride	1 mM sodium chloride	20.9	15	[71]
Polyamide-polyethersulfone	1.2M sodium chloride	Deionized water	38	30	[58]

Polyamide-polyethersulfone	0.6M sodium chloride	Deionized water	2.98	7	[72]
Polyamide-polyethersulfone	1M sodium chloride	Deionized water	8	18	[73]
Cellulose acetate	1M sodium chloride	Deionized water	5.5	18	[74]
Polyamide-polyethersulfone	1M sodium chloride	Deionized water	10.05	22	[75]
Polyamide-Polydopamine (PDA) coated poly (ether sulfone) (PES)	Artificial seawater brine (0.81 mol/L sodium chloride)	Wastewater from municipal recycle plants	7.2	15	[59]

The present laboratory-fabricated pressure retarded osmosis membranes, both hollow-fiber and flat-sheet types are typically eligible for meeting the economically viable power density of 5 W/m^2. Demo research has been extensively performed in several countries from laboratory-scale to pilot-scale and has proved to be practicable. Conversely, several challenges must be addressed for additionally activating the advancement in pressure retarded osmosis technology for accomplishing the commercial stage. Moreover, there must be a proper selection of satisfactory pretreatments, considering the characteristics of feed water. For the industrial-scale facilities, satisfactory pretreatment process related to the feed water quality is cautiously considered. Several studies for assessing the commercial feasibility of the pressure retarded osmosis process typically have a serious limitation, excluding the pretreatment costs. For increasing the consistency of feasibility studies, the models should be wisely considered with the inclusion of different components such as membrane modules, pumps, pre-treatments, hydro-turbine, and pressure exchangers.

2.3 Emerging membranes with Nano-materials

Nanomaterials are considered very promising materials and different studies have been performed to examine the application of nanomaterials in various fields and its related environmental impact [76-82]. Several polymer-based materials (for example, modified polyethersulfone, polyetherimide, polyamide-imide) and nanomaterials like graphene oxide, carbon nanotubes (CNTs), etc. have been utilized in membranes for reducing membrane structural deformation; while maintaining increased water flux under enhanced-pressure pressure retarded osmosis process [83-89]. The addition of nanomaterials into pressure retarded osmosis membranes to develop thin-film nanocomposite (TFNC) membranes has demonstrated improvement in its hydrophilicity and porosity resulting in increased water flux along with osmotic power in the course of PRO process [90]. Table 6 presents the performance of different nanomaterial incorporated membranes reported in the literature.

Table 6: Performance of some of the nanomaterial incorporated membranes reported in the literature.

Material	Nanomaterial used	Feed solutions	Draw Solutions	Power density in W/m^2	Pressure bar	Ref.
Polyamide-polyethersulfone	Graphene oxide	Deionized water	Sodium chloride (1.0 M) solution	14.6	16.5	[83]
Polyamide-polysulfone	Graphene oxide	Deionized water	Sodium chloride (1.0 M) solution	16.7	21	[84]
Graphene oxide	Graphene oxide	0.017 M sodium chloride solution	Sodium chloride (1.0 M) solution	24.62	6.90	[91]
Polyamide-polyethersulfone	Carbon nanotubes	Deionized water	Sodium chloride (0.5 M) solution	1.6	6	[85]
Polyamide-polyetherimide	Carbon nanotubes	Deionized water	Sodium chloride (1M) solution	17.3	16.9	[92]
Polyamide-polyethersulfone	Carbon quantum dots	Deionized water	Sodium chloride (1M) solution	34.2	23	[93]
Polyamide-imide	Schiff base network-1	Deionized water	Sodium chloride (1M) solution	12.1	24	[94]

Polyamide-polyethersulfone	Carbon quantum dots	High alginate concentration (1 g/L)	0.81 mol/L NaCl	11	15	[95]
Polyacrylonitrile (PAN) nanofiber support membrane	Nano-silicon dioxide	80 mM NaCl synthetic brackish water	Seawater brine (1.06 M) solution	21.3	15.2	[70]

2.2.3.1 Graphene-oxide based PRO membranes

Due to the exceptional characteristics of graphene oxide (GO) nanomaterial like 1-2 nm atomic thicknesses with a 2-dimensional single layer as well as hydrophilic characteristics with the existence of hydrophilic functional groups; graphene oxide nanosheets have increased possibility for manufacturing composite polymer membranes having an exceptional antifouling propensity, superior hydrophilicity, and enhanced structural properties [96, 97]. Despite the substantial enhancement in the TFC-forward osmosis membrane performance gained with the incorporation of nanomaterials, the manufacture of mixed matrix hollow-fiber support for TFC-pressure retarded osmosis membranes has still not been completely investigated.

Park et al. [83] emphasized the development of TFC PRO membranes for increased osmotic power utilizing hollow fiber PES support framework modified by the addition of hydrophilic GO nanosheets. The concentration of graphene oxide in the hollow fiber substrates was altered tom improve the water flux performance with no compromise in the mechanical properties. Graphene oxide incorporated (≤ 0.20 wt%) polyethersulphone hollow fiber supports demonstrated clear enhancement in freshwater permeability, upgraded structural morphologies, and hydrophilicity inside the support layer, with no deterioration in the mechanical strength. The maximum power density of about 14.60 W/m^2 was accomplished at 16.5 bar operating pressure under the condition of 1M sodium chloride and deionized water as draw and feed solutions, respectively [Fig. 2]. The test results indicated that the pressure retarded osmosis hollow fiber support layer modification by incorporating nanomaterials like graphene oxide nanosheet could be a beneficial tool for improving the PRO efficiency.

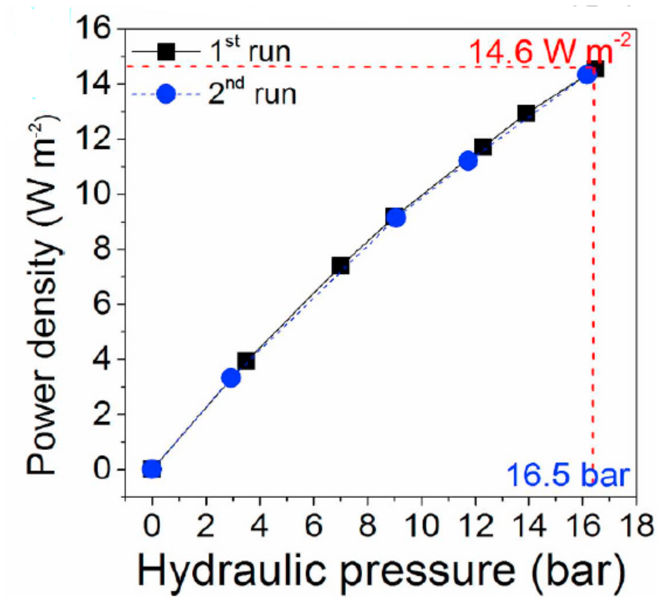


Fig. 2: Power density versus hydraulic pressure of THF-GO-0.2 with 1M sodium chloride (NaCl) as the draw solution and deionized (DI) water as the feed solution. Reproduced from Ref [83].

Lim and coworkers fabricated a TFC membrane with a double-layered nanocomposite substrate, using a double-blade casting method for the PRO process [84]. In this method, halloysite-nanotubes (HNTs) were incorporated within the lowest polymeric substrate layer and GO on the topmost layer substrate; whereupon, a very-thin selective PA layer was developed. Fig. 3 is the hypothetical model of the double-layered thin-film composite PRO membranes with halloysite nanotubes and graphene oxide incorporated in the bottom and topmost substrate layer, respectively. The membrane substrate synthesized demonstrated excellent membrane substrate properties like open-bottom surface, superior porosity, appropriate topmost-skin surface structure for future active layer development and increased mechanical properties; that have been important for extremely efficient PRO processes. This research contributed to an advanced alternate method for preparing PRO membranes with increased fouling resistance as well as power density.

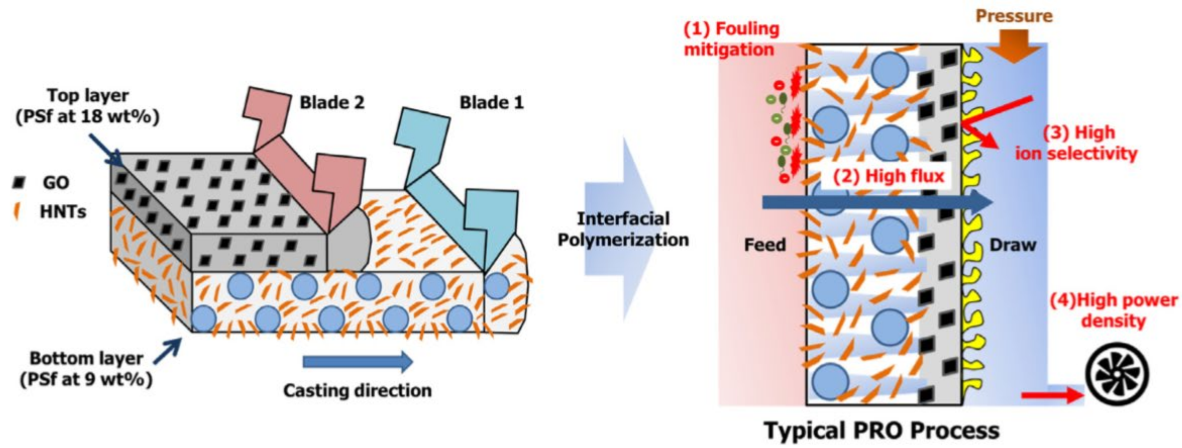


Fig. 3: Hypothetical model of the double-layered thin-film composite PRO membranes with halloysite nanotubes and graphene oxide incorporated in the bottom and topmost substrate layer, respectively. Reproduced from Ref [84].

2.2.3.2 Carbon nanotube (CNT) based PRO membranes

CNTs are molecular carbon allotropes, and its structure can be envisioned as cylinders composed of rolled graphene layers. There are 2 types of carbon nanotubes differentiated based on whether they comprise a single graphene wall (Single-walled CNTs) or multiple-walls concentrically organized (Multi-walled CNTs,). Due to the presence of C-C bonds, the carbon nanotubes are anticipated to be very strong along their axes and possess a high Young's modulus in their axial direction. Functionalized carbon nanotubes have been considered a very effective nanomaterial for increasing membrane hydrophilicity, porosity, and the negative membrane charge, leading to superior membrane performance concerning fouling resistance selectivity, and permeability [98]. Son et al. [85] suggested utilising a carbon nanotube-incorporated support layer for TFNC membranes in the pressure-retarded osmosis process for energy production using saltwater. The thin-film nanocomposite membrane mentioned above takes benefit of the improved porosity and hydrophilicity brought about by functionalized-CNT and the chemical etching of the polyamide selective layer for additional increasing water flux. The maximum power density was improved by 110.0 % by the approach above, relative to the results attained utilizing pristine thin-film composite membranes using deionized water and artificial seawater (0.5 M sodium chloride) as the feed and draw solution, respectively. Addition of functionalized-CNT represents an alternative method for commercial modification of pressure retarded osmosis membranes for maximizing the efficiency of their polymeric-based membranes with the least possible cost rise. Even though the structures and support later materials of commercially used pressure retarded osmosis membranes vary, the carbon nanotubes could enhance the hydrophilicity and the porosity of the support layer, leading to improved power density. Tian et al. [92] created tiered structured polyetherimide (PEI) nanofiber supports comprising a coarse fiber layer at the bottom and a thin fiber layer on the top with both reinforced utilizing functionalized multi-walled carbon nanotubes. By including functionalized-CNTs into both nanofiber layers, concurrent enhancement in the porosity and mechanical properties of the supports was observed. Transmission electron microscopy (TEM) micrographs (Fig. 4A) confirmed the effective incorporation of carbon nanotubes within the polyetherimide nanofibers while conserving the polyetherimide nanofibrous morphology. The multi-walled carbon nanotubes used had a diameter of 11.0 nm and average length of 10.0 µm. Subsequent to the dispersion using a probe sonicator, the functionalized-CNTs were shortened with some of the tips of the multi-walled carbon nanotubes opened. The enlarged TEM image in Fig. 4B confirmed the hollow structure of the multi-walled carbon nanotubes with an opened tip. This optimized membrane showed the ability to tolerate a trans-membrane pressure up till 24.0 bar and developed a peak power density of 17.30 $W.m^{-2}$ at 16.90 bar utilizing deionized water as the feed solution and artificial seawater brine (1.0 M sodium chloride) as the draw solution.

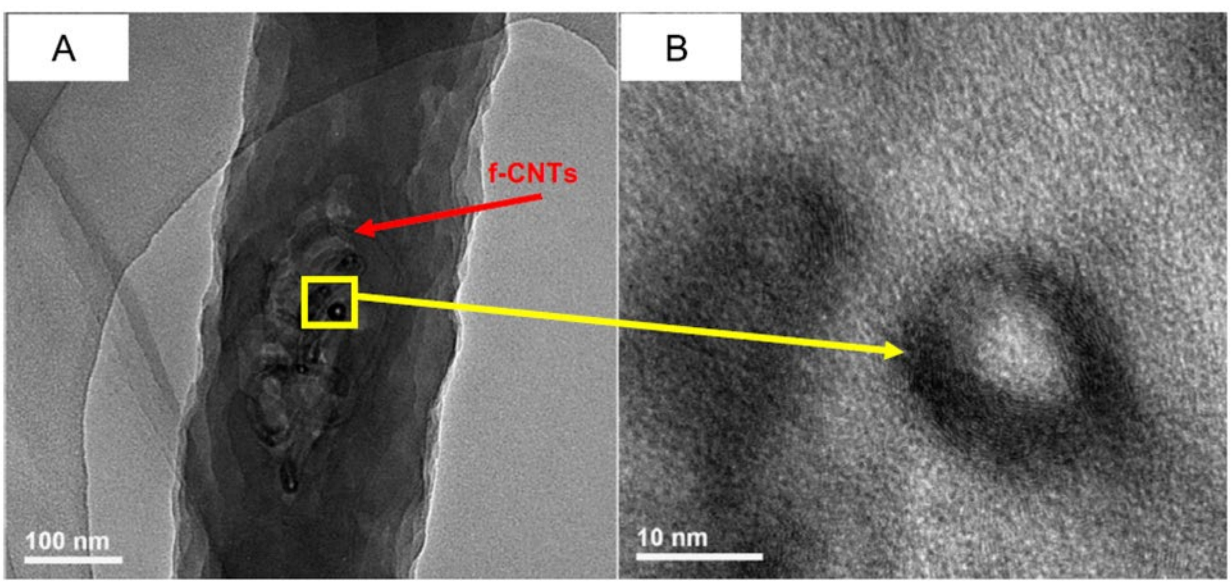


Figure 4: TEM image of f-CNTs inside the PEI nanofiber; (B) enlarged. Reproduced from Ref [95].

2.2.3.3. Carbon quantum dots-based PRO membranes

Carbon quantum dots (CQDs) are an advanced class of carbon-based nanomaterials developed in the past decade. In addition to its interesting optical properties, these materials may be low cost, eco-friendly, less toxic, and of excellent hydrophilicity [99]. Gai et al. [93] prepared CQDs inclusive of the pristine CQDs, and Na± functionalized CQDs, as included into the PA selective layers for developing advanced TFC membranes for pressure retarded osmosis applications. As per the membrane structure and PRO efficiency of the developed TFC membranes with various CQDs, it was possible to conclude that the m-phenylenediamine solution pH remarkably affected the interfacial polymerization process. The advanced TFC membranes developed consisting of 1.0 wt % Na± functionalized carbon quantum dots demonstrated a peak power density of about 34.2 $W.m^{-2}$ at 23 bar utilizing DI water as the feed solution and artificial seawater brine (sodium chloride 1M) as the draw solution for the generation of osmotic power.

Zhao et al. [95] immobilized CQDs onto the polydopamine layer of a pressure retarded osmosis membrane to improve its power capability as well as its antifouling resistance. Pressure retarded osmosis operation at 15 bar demonstrated that the CQD modified membranes showed an increased power density (11.0 W/m^2 versus 8.8 W/m^2) and water recovery after back-washing (94.0 % vs 89.0 %) as compared to the unmodified membrane.

2.2.3.4. Silica nanomaterial-based PRO membranes

Silica nanoparticles possess benefits such as increased hydrophobicity, superior biocompatibility, systemic stability, good resistance against pH variation, and also large multifunctionality. Zeolites, as well as mesoporous silica nanoparticles, are aluminosilicate or silicate nanomaterials with well defined porous networks. A zeolite-incorporated PA layer was effectively developed by Ma et al. [100] on a polysulfone membrane substrate; and employed in a pressure retarded osmosis process. By incorporating only 0.1 w/v % of zeolite, the resulting thin-film nanocomposite membrane demonstrated a water flux of 30.70 $L/(m^2h)$ while using 10.0 mM sodium chloride as a feed solution and 1.0 M sodium chloride draw solution. Compared with the thin-film composite membrane without incorporated zeolite, it demonstrated a water flux of just 21.50 L/(m^2h) under similar test conditions. This substantial improvement in the water flux of the thin-film nanocomposite membrane also indicated the increased power density, which could be generated. In another study by Ma et al. [101], the influence of DS concentration (0.5, 1.0, and 2.0 M sodium chloride) on the efficiency of a zeolite-incorporated thin-film nanocomposite membrane for the pressure retarded osmosis operation was examined. The test results confirmed that a higher DS concentration resulted in higher water flux because of increased osmotic pressure difference. While tested utilizing the 2.0 M sodium chloride solution as draw solution and DI water as FS, the resulting thin-film nanocomposite membrane demonstrated almost 2.5 times greater water flux relative to the control thin-film composite membrane, recording 86.0 L/(m^2h). A zeolite-embedded thin-film nanocomposite membrane was also developed and examined in a study performed by Salehi et al. [102] for pressure retarded osmosis utilization. The influence of nanostructured zeolite on the features of a polyethersulfone substrate and subsequently, the thin-film nanocomposite membrane was analyzed. The results confirmed that the thin-film nanocomposite membrane prepared from optimized nanocomposite substrate (0.40 wt%) could be enhanced by almost 50% of the water flux of the pristine membrane (with no zeolite) while tested under a pressure retarded osmosis mode (10.0 mM sodium chloride solution as FS and 2.0 M sodium chloride solution as DS), leading to water flux of 33.10 L/(m^2h).

Niksefat et al. [103] prepared an advanced type of thin-film nanocomposite membrane by adding silicon dioxide nanoparticles into PA active layer. The resulting membrane's efficiency has been determined to utilize a 10.0 mM sodium chloride solution as FS and a 2.0 M sodium chloride solution as DS in pressure retarded osmosis mode. The thin-film nanocomposite membrane's water flux was enhanced from 15.50 to 36.50 L/(m^2h) as the silicon dioxide concentration increased from 0.0 to 0.1% (w/v). The pristine thin-film composite membrane demonstrated just 15.0 L/(m^2h) under similar test conditions. Silicon dioxide containing thin-film nanofiber composite pressure retarded osmosis membranes were fabricated by Song et al. [70] to enhance the membrane power density. PAN nanofiber embedded with silicon dioxide was fabricated, followed by PA layer formation using an IP method. The resulting thin-film nanofiber composite membrane was additionally post-treated before it was utilized for pressure retarded osmosis. Test results confirmed that the thin-film nanofiber composite pressure retarded osmosis membrane could accomplish a power density of about 15.20 W/m^2 utilizing artificial brackish water (80.0 mM sodium chloride) as FS and seawater brine (1.06 M sodium chloride) as DS. The aforementioned two solutions had osmotic pressure of about 3.920 and 51.80 bar, respectively.

2.2.3.5. Metal nanomaterial-based PRO membranes

Titanium dioxide is considered the most commonly utilized material for the manufacture of photocatalytic membranes because of its high chemical stability, non-toxicity, and low cost. Emadzadeh et al. [104] modified the polysulfone substrate of a thin-film nanocomposite membrane by adding varying amounts of titanium dioxide nanomaterials into the substrate matrix. The quantity of titanium dioxide changed from 0 to 1.0 wt% and its impact on the thin-film nanocomposite membrane was analyzed in pressure retarded osmosis mode utilizing 10.0 mM sodium chloride as FS and 2.0 M sodium chloride solution as DS. With 0.5% titanium dioxide, the best performing membrane was noted to have a water flux of 56.27 $L/(m^2h)$, which was almost 87.0 % greater relative to the pristine thin-film composite membrane.

Kim et al. [105] reported an advanced surface coating technique that increased the water flux as well as organic fouling resistance of pressure retarded osmosis membranes. The support layer of a commercially used thin-film composite membrane was coated using titanium dioxide nanoparticles by a sol-gel-derived spray coating technique. This titanium dioxide nanoparticle coating contributed hydrophilic characteristics along with a negative charge to the surface of the membrane. The titanium dioxide nanoparticle-coated membrane displayed a 25.0 % rise in water flux and a 50.0 % reduction in reverse salt flux. The flux loss of the titanium dioxide nanoparticle-coated membrane was almost 32.0 % less than a commercially available thin-film composite membrane in the existence of humic acid foulants. Consequently, high-performance and fouling resistant pressure retarded osmosis membrane may be developed using a titanium dioxide sol-gel-derived spray coating technique.

2.2.3.6. Covalent organic framework -based PRO membranes

Schiff base network-1, a melamine-based covalent organic framework, was integrated into the PA selective layer of an advanced thin-film nanocomposite PRO membrane by Gonzales et al. [94]. The deposition of Schiff base network-1 was done on an open-mesh fiber-reinforced polyamide-imide support substrate using IP process. Substantial improvement was noted in the membrane hydrophilicity after the selective PA layer development on the polyamide-imide substrate and the subsequent addition of nanomaterials. The comparative hydrophobicity, as well as less surface energy of polyamide-imide, resulted in an increased contact angle measurement noted for the substrate. The enhancement in the surface hydrophilicity after the addition of Schiff base network-1 was because of the secondary amine functional groups left unreacted with trimesoyl chloride. The surface roughness of the membrane was characterized by atomic force microscopy analysis. Fig. 5 presents the 3-dimensional atomic force microscopy images of the surfaces of the membrane for the thin-film composite and thin-film nanocomposite membrane samples. The mean roughness (R_a) and root, mean square ridge elevation (Rms) are also shown. The mean roughness values were noted to enhance with the concentration of the nanomaterial.

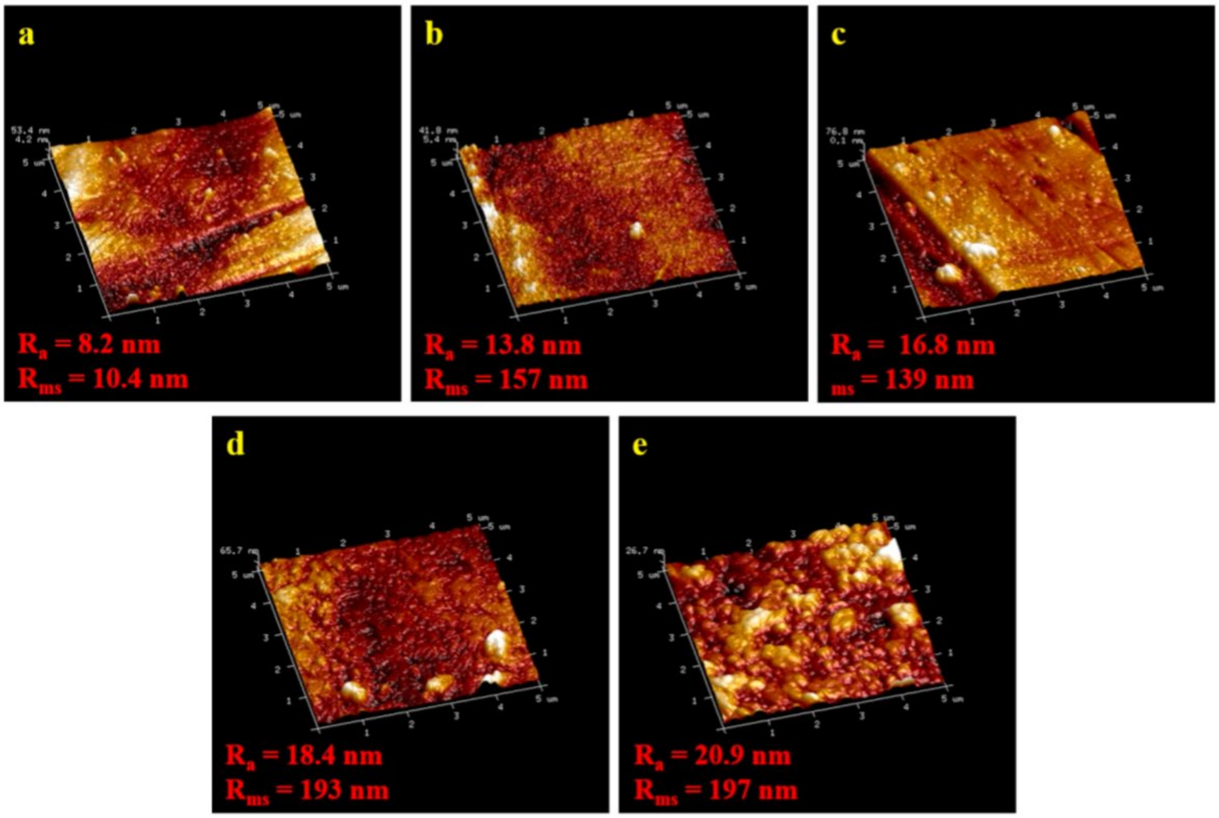


Figure 5: Surface roughness of thin-film composite and thin-film nanocomposite membranes atatined by atomic force microscopy analysis of (a) thin-film composite, (b) thin-film nanocomposite-0.01, (c) thin-film nanocomposite-0.02, (d) thin-film nanocomposite-0.05, and (e) thin-film nanocomposite-0.1 pressure retarded osmosis membranes. Reproduced from Ref [94].

Testing with 1 M sodium chloride draw solution, the thin-film nanocomposite membrane having 0.020 wt.% nanomaterial concentration showed a power density of 12.10 W/m^2 and the greatest water flux of 42.50 L/m^2/h, whereas withstanding almost 24.0 bar hydraulic pressure. The outlined study suggested that covalent organic framework addition could be a potential technique in pressure retarded osmosis membrane fabrication to improve both energy harvesting ability and the osmotic performance of the PRO process.

2.2.3.7. Other nanomaterial-based PRO membranes

Layered double hydroxide/GO hybrid was used as nanofillers for polysulfone substrate to develop thin-film nanocomposite membrane, as reported by Lu et al. [106]. By utilizing 1.0 M sodium chloride as the DS and deionized water as FS, the water flux of the thin-film nanocomposite membrane with a 2.0 wt% layered double hydroxide/GO dosage, was high as 23.60 L/(m^2h) under the PRO mode.

Zirconium (IV)-carboxylate metal-organic framework UiO-66 nanomaterials have been efficiently prepared by Ma et al. [107] and embedded in the PA layer to develop advanced thin-film nanocomposite membranes. As compared to the pure polyamide TFC membranes, the addition of UiO-66 nanomaterials remarkably changed the membrane structure as well as chemistry, resulting in an enhancement in the intrinsic separation properties because of the molecular sieving as well as the super hydrophilic nature of the nanoparticles. Addition of 0.1 wt.% to the nanoparticle generated a maximum water flux enhancement of 40% over the thin-film composite control under PRO mode; when 1.0 M sodium chloride was used as the DS against DI as the feed solution.

Thus, it is clear that the efficiency of the pressure retarded osmosis membrane can be enhanced by the incorporation of nanomaterials either into the PA top selective layer or membrane support layer. Numerous research has effectively illustrated the improved efficiency of nanomaterial-added thin-film nanocomposite membranes for pressure retarded osmosis process, as compared to the pristine thin-film composite membrane; in terms of power density and water flux. Contingent upon the test conditions (for example, DS property, FS property, and operating pressure), the power density generated by the existing nanomaterial-incorporated thin-film nanocomposite membranes varies.

3. Salinity gradient resources and Membrane Fouling

After introducing some of the commercial membranes as well as the advanced laboratory-developed membranes of PRO, the salinity gradient resources and the PRO process design will be pointed in the next section, to emphasize the effect and importance of these factors on the PRO performance.

3.1 Salinity gradient resources: maximum power generation and availability

Salinity gradient resources play an important role in PRO processes due to their responsibility for creating sufficient driving force across the membrane. A higher osmotic pressure difference between feed and draw solutions produces higher water flux and an increase in workable power. Hence an improvement in the PRO process economic feasibility occurs [108]. PRO feed solutions of low salinity could be: brackish water, river water [109] or wastewater, while the high salinity and pressurized draw solutions could be: seawater [45, 109] or brine [110]. Seawater or brine from RO systems and freshwater or wastewater effluent were suggested as salinity gradients for PRO systems [47, 50, 69, 111-115]. The most popular PRO salinity gradients are river water and seawater [116]. On the other hand, a maximum power density of 7.7 W/m^2 resulted from a pilot-scale study using seawater concentrate and wastewater effluent resources [47]. A high power density of 230 W/m^2 resulted when Dead Sea water was coupled with seawater (35 g/L), this value dropped to 70 W/m^2 when concentration polarization effects were taken into account [113]. Soltani [117] proposed that using RO brine instead of seawater as a draw solution caused improvement in specific energy values.

In the case of assuming 40% PRO energy conversion efficiency, the action of land water runoff to the ocean in the United States has a possibility for electrical energy production of 55GW [118]. It is noteworthy that the potential power, which can be exploited from the mixing process of river water with seawater in the PRO system, is determined to be around 1.4-2.6 TW [119]. However, practically the extractable energy may deviate. Researchers [120] showed that mixing high saline water (600 mM) of a near-infinite volume with low saline water (1.5 mM) of an infinitesimal volume, produced theoretically extractable work of a maximum value of 0.77 kWh/m^3. A study showed that changing feed solution from DI water to a 3.5% by weight NaCl solution with the same draw solution of 2 M NaCl utilizing the same TFC-FO modified membrane; caused a change in the resultant water flux from 33.0 to 15.0 L/hm^2, respectively [121].

A huge power amount is stored in the earth's waters due to the salinity variations between freshwater and seawater [122]. Globally, around 37,300 km^3 per year is the amount of river discharge, which can produce around 2TW renewable energy when mixing with seawater [120]. Fig.6 represents the available extracted energy from varied feed resources on a theoretical basis [123].

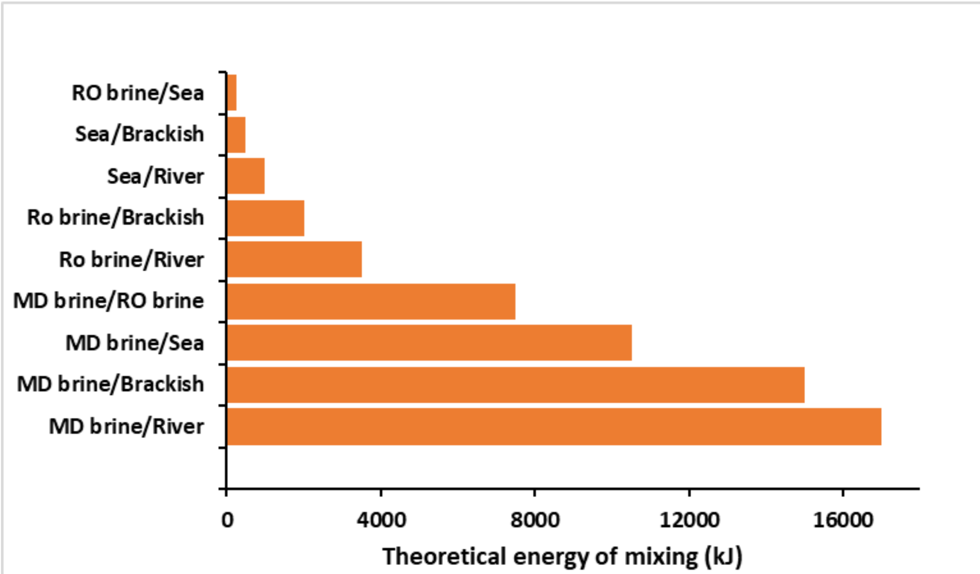


Fig. 6: The energy produced theoretically through mixing various feed sources: 10^{-5}, 10^{-4}, $5x10^{-4}$, 10^{-3}, $5x10^{-3}$ mM NaCl of river water, brackish water, seawater, reverse osmosis (RO) brine and membrane distillation (MD) brine, respectively. Each of brine and seawater was determined as HCC solution. Figure adapted from Ref [123].

As shown in Fig. 6; combining one cubic meter of each seawater and river water could produce up to 1400 kJ power, which corresponds to power produced by falling water from a height of 280 m [123]. Mixing RO brine with seawater shows lower produced energy, around 420 kJ. 10500 kJ could be produced by mixing membrane distillation (MD) brine with seawater. Interestingly; mixing MD brine with river water produced around 17000 kJ of energy [123]. These numbers may additionally impact the effectiveness of the employed technology to extract energy.

Sarp et al. indicated that when considering some factual circumstances as system inefficiencies (membranes and turbines) and pretreatment processes, the net produced power can be significantly dropped to 0.22 kWh/m^3 as shown in Table 7 [42]. Nevertheless, in changing the draw solution to such a higher salinity one like the seawater reverse osmosis (SWRO) brine (13

M salinity), the net extractable work can reach 0.66 kWh/m^3. This explains the importance and effectiveness of the used salinity gradients on the PRO process due to the corresponding osmotic pressure difference.

Table 7: Draw solution salinity effect on theoretical producible power per draw solution volume in m^3. Table adapted from Ref [42].

	Seawater-River water PRO kWh/m^3	SWRO Brine-River water PRO kWh/m^3
Calculated ΔGmix, VoLC*	0.61	1.35
Membrane and hydraulic inefficiencies (40% loss)	-0.24	-0.54
Pretreatment_ultrafiltration	-0.15	-0.15
Net producible power kWh/m3	0.22	0.66

*: Mixing Gibb's free energy per unit volume of the final solution.

Different salinity gradients with various operating modes were used in one study to evaluate the thermodynamic limits of the PRO system by determining the achievable specific energy or the extracted energy per unit volume of the solution [124]. An ideal reversible PRO system, including constant pressure with counter-current flow and constant pressure with the co-current flow; were the analyzed modes of operation in this study. An analytical model was derived from measuring the maximum producible specific energy and correlative optimal percentage of the feed flow rate and hydraulic pressure for the various operating modes. The used salinity gradients are illustrated in Fig. 7.

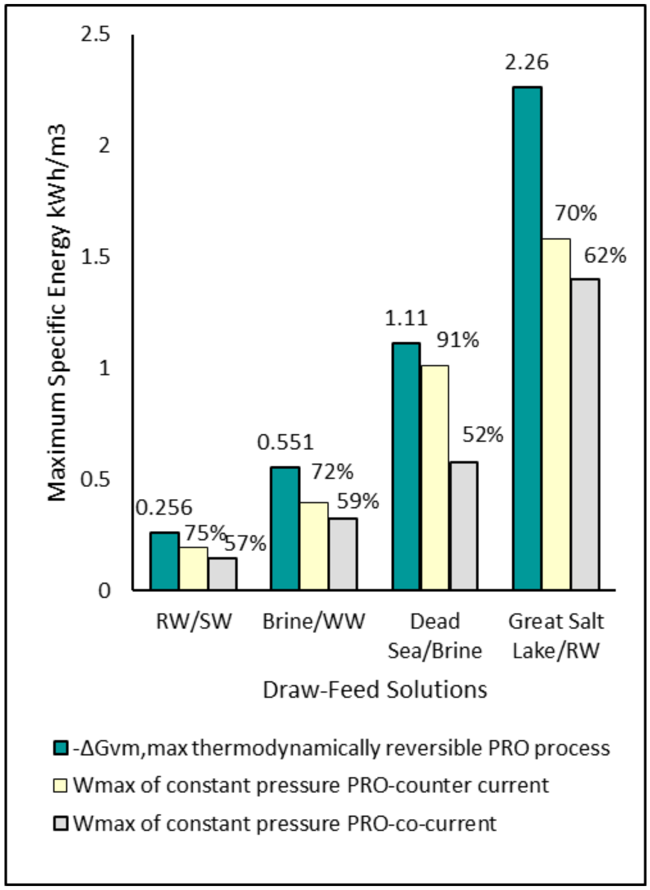


Fig. 7: The theoretical achievable maximum specific energy in three modes of the PRO process for various salinity gradients. The percentage of the maximum specific energy for both counter and co-current PRO is referred to the maximum thermodynamically reversible PRO process. Fig adapted from Ref [124].

As shown in Fig. 7, for the case of river water (RW) of 0.015 M NaCl and seawater (SW) of 0.6 M NaCl as the salinity resources for constant pressure-counter current PRO mode; the theoretical maximum specific energy was around 0.192 kWh/m^3; which was 75% of the maximum specific Gibb's free energy of mixing (0.256*0.75). Combining a draw solution of high salinity such as the Great Salt Lake of approximate 4.6 M NaCl with RW as feed solution in a counter-current PRO system yielded a theoretical maximum specific energy of 1.6 kWh/m^3. Mixing Dead Sea water of approximate 5.7 M NaCl and RO brine of 1.2 M NaCl, can produce around 1.0 kWh/m^3 maximum specific energy for case of counter-current flow [124].

Different salinity gradient resources were utilized in a recent study based on non-ideal operating conditions. Grey Wolf Optimization (GWO) algorithms were introduced to optimize a full-scale PRO process by applying a machine learning method to determine the effect of concentration polarization [125]. Optimization of one to four PRO systems was implemented, and the power generated was compared. Optimization included the draw and feed fractions as well as the operating pressure for different salinity gradient resources. Four sources of various salt concentration were used: Dead Sea-seawater, Dead Sea-RO concentrate, seawater-wastewater effluent and RO concentrate-wastewater effluent. The research divulged that the recommended draw or feed fraction to the total solution (~0.5) and operating pressure ($\Delta P = \Delta\pi/2$) in laboratory-scale are unfounded in a full-scale non-ideal PRO unit. This study proposed that the optimal hydraulic pressure was lower than what was suggested formerly ($\Delta P = \Delta\pi/2$). The optimum operating pressure for 0.6-0.02 M salinity gradient was 12 bar, and it was unaffected largely by the PRO modules number in the pressure vessel. While for the other salinity gradients, increasing PRO modules caused a drop in the optimum hydraulic pressure. The process of hydraulic pressure optimization caused an increase of 4.4% of the PRO output energy. Furthermore, optimization of the feed portion in the solution produced an increase in the power production in a single PRO membrane module of 28 to 70% and an increase of 9 to 54% of the power production in a PRO unit containing four modules. The results also showed that increasing PRO membrane modules caused an increase in the maximum specific energy. The study found that changing the fraction of the feed solution in the salinity gradient had more impact on the performance of the PRO process compared to the draw solution.

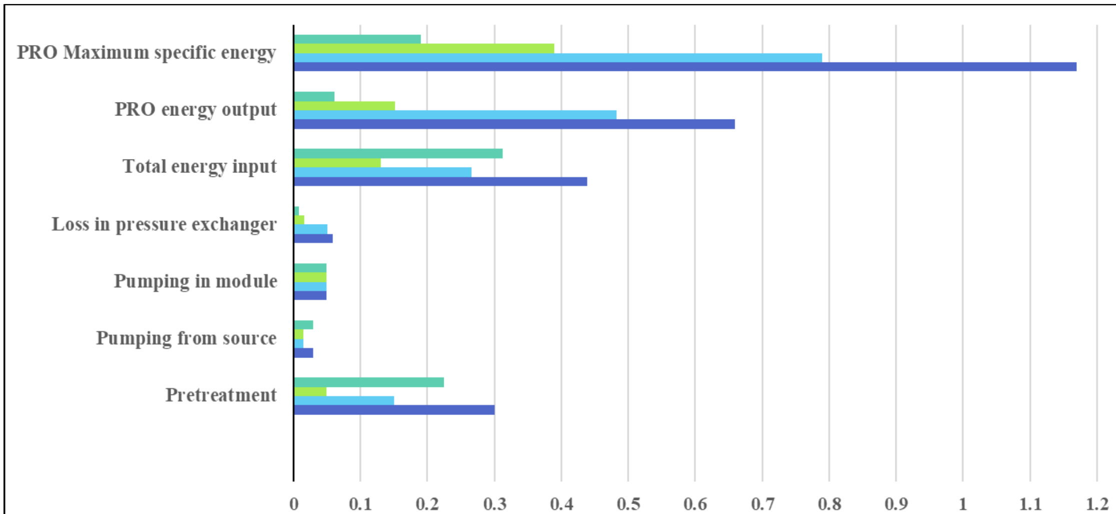
3.2 The energy of pretreatment and energy Inputs

Some studies did not consider determining the net generated power instead of power density and gross energy. The net generated power is the difference between the amount of input and output energy of the system [126]. Energy losses through the process from streams circulation, inadequate power recovery, and Pretreatment and the pumping energy for feed and draw streams are considered the input energy, which should be calculated [126, 127]. The economic feasibility of PRO is highly affected by these losses as well as the amount of energy input. A study performed by Wang et al. [127] on a counter-current PRO system calculated the net specific power using seawater and river water as the input solutions [127]. They proposed that the pressure drop was not remarkably impacting the output energy. It also was suggested to minimize the power dissipation in the pressure exchanger to increase system effectiveness. Very low energy loss will be caused by a pressure exchanger with an efficiency of around 98% [127]. Around 0.017 kWh/m^3 was the possible amount of power loss through pressure exchanger with 98% efficiency when 32 bar was the PRO hydraulic pressure [126]. Brine reject and wastewater were the salinity gradients in one study [126] where both input and output energies were calculated for various membranes. The energies of Pretreatment, pumping from source, pumping in the module, and loss in pressure exchanger was: 0.05, 0.03, 0.05 and 0.017 kWh/m^3, respectively; which resulted in total input energy of 0.147 kWh/m^3. The maximum energy output was for Oasys-TFC membrane (0.194 kWh/m^3) and the net power generation was 0.047 kWh/m^3 [126].

Pretreatment processes, water pumping and membranes are considered the main components affecting the capital, maintenance, and operating costs in PRO systems [128]. The high expense and significant amounts of energy may be required for the pretreatment process of PRO systems [128]. The pretreatment facility may consume around 20% of the energy unit rate for a PRO power plant of 200 MW capacity [129]. For PRO systems, pretreatment is very important in some cases to reduce fouling [26, 124]. It is considered one of the prime elements that maximise the cost of generating energy by the PRO process and possibly makes it infeasible financially [130]. However, pretreatment and process optimization could control membrane fouling [130-133]. Sand filtration and ultra-filtration are two methods employed in literature as pretreatment technologies for reducing the PRO membranes fouling [131]. It has been shown that ultra-filtration has preferable results for controlling hardness, turbidity and total organic carbon compared to sand filtration for the PRO process [131]. In one reported study, the consumed energy by ultra-filtration was 0.02-0.03 kWh/m^3 with an estimated cost of 0.18-0.20 US $/kWh with a capacity of 38000 m^3/d [131].

The cost of the Pretreatment depends on the employed salinity gradients. For instance; using seawater instead of SWRO draw solution will increase pretreatment cost [42]. Researchers mentioned that the required energy for pretreating wastewater effluent before entering the PRO membrane was around 0.1 kWh/m^3 [126]. Furthermore, pretreatment functions a significant role in the net power generation. Assuming the same amount of energy for the SWRO treatment (0.2-0.4 kWh/m^3) is consumed in the pretreatment of seawater/river water system; a positive net power production will be unlikely to result. Therefore, it was suggested to use RO brine and wastewater effluent salinity gradient or couple the PRO with thermal distillation systems to improve the system performance [127].

Producing freshwater from saline water as river water, for the feed solution of the PRO process, without adding extra cost is one of the obstacles that confront the technical feasibility. SWRO and treated wastewater were the salinity resources of a prototype system which used CTA hollow fiber membrane to reduce the energy of the SWRO [134]. An ultra-filtration unit and chemicals were used to remove foulants of the membranes from the wastewater stream before entering the PRO. Using these techniques was enough to keep the same permeate flow for 14 days and achieve power density equal to 13.5 W/m^2 at 25 bar hydraulic pressure [134]. Another study performed by Altaee et al. [46] estimated the PRO feasibility for energy production without ignoring the system losses and energy inputs. Four different salinity sources were utilized as represented in Fig. 8. The maximum specific energy values shown in the figure were calculated for an ideal PRO system, assuming 98% pressure exchanger efficiency and ignoring the pressure exchanger solute leakage. Pretreatment, pumping in the module and pumping from the sources were assumed based on previous studies.



Energy kWh/m3	Pretreatment	Pumping from source	Pumping in module	Loss in pressure exchanger	Total energy input	PRO energy output	PRO Maximum specific energy
SeaWater-RiverWater	0.225	0.03	0.05	0.008	0.313	0.061	0.19
ROBrine-Wastewater	0.05	0.015	0.05	0.016	0.131	0.152	0.39
DeadSea-ROBrine	0.15	0.015	0.05	0.051	0.266	0.482	0.79
DeadSea-Seawater	0.3	0.03	0.05	0.059	0.439	0.659	1.17

Fig. 8: Energy inputs, outputs and losses in a PRO system for four various salinity gradient sources. Energy values are in kWh/m^3. Figure adapted from Ref [46].

Comparing the calculated maximum specific energy with the total energy input could give a clear idea of whether the PRO process of the utilized sources was feasible with regards power generation or not. As can be seen in the figure for Dead Sea-RO brine and RO brine-wastewater sources, the maximum specific energy was around three times higher than the total energy input. While in the case of using seawater-river water sources; the maximum specific energy was only 60% of the total energy input, which suggested that using seawater-river water in the PRO process was not promising in regards to energy production compared to using Dead Sea-RO brine or RO brine-wastewater. Additionally, the pretreatment energy was varied among the different salinity gradients. The highest pretreatment energy was 0.3 kWh/m^3 for Dead Sea-Seawater resources.

A computer model was performed on a full-scale PRO system. The net energy production for various salinity gradient sources was calculated as the difference between the energy output and the energy input, Fig. 9 [135].

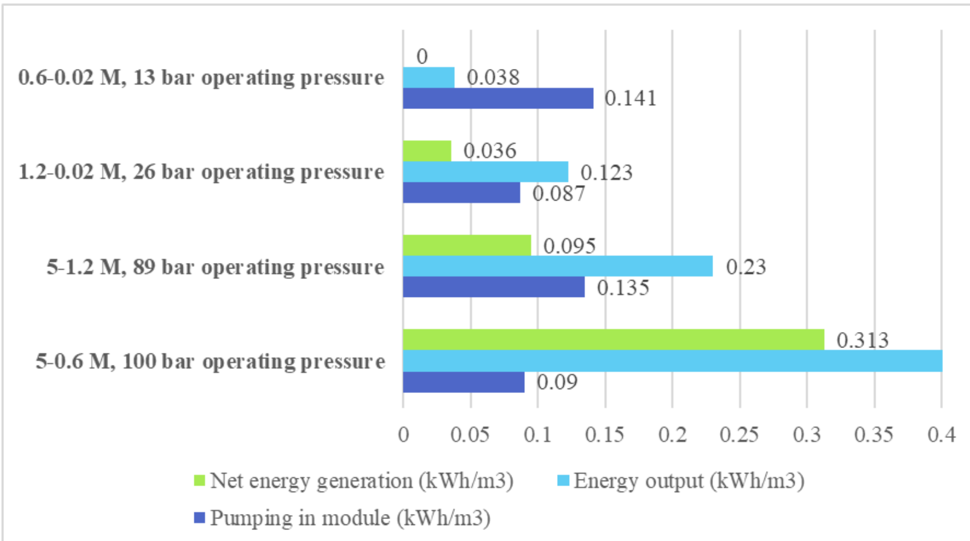


Fig. 9: The values of net energy generation, energy output and pumping energy in the module of various salinity gradient sources for the PRO model study where NaCl was the used salt in the solutions. Figure adapted from Ref [135].

As demonstrated in Fig. 9 the maximum net energy generation (0.313 kWh/m^3) was for 5-0.6 M NaCl, and it was 0.095 kWh/m^3 for the sources of 5-1.2 M NaCl. The pumping energy in the module which represented the energy input was higher than the energy output for the salinity gradient sources of 0.6-0.02 M, indicating such source had an insufficient driving force to produce power through the PRO system.

According to the deficiency of large-scale power plants of PRO, the cost of energy generation is still open to question. The only thing to do at this stage is to relay on the available knowledge in literature and postulate the progress of the main process components, then use this information to estimate the process cost [128]. For instance, Sharif et al. [136] showed that 50-80% of the expense of the hydro osmotic power plant depends on membranes, where these values affected by the solutions salinity difference [136]. Therefore, enhancing PRO feasibility can occur through additional progress in membrane manufacturing and determining the best PRO membranes. Membranes cost, longevity and performance effectiveness are the main elements to consider while estimating the PRO process cost. Low priced membrane with poor performance is not recommended. One study showed that a membrane which can last for 10 years has almost 10 times higher revenue than a membrane which can last only for 1 year [39]. This study suggested that the economic feasibility estimation of the PRO process can be found by determines the PRO system revenue per area of membrane per year as ($\frac{Revenue}{Membrane\ area.year} = Power\ density * Energy\ price$). For instance, if talking about Australia specially New South Wales, the average electricity rate in 2020 is around 27.56c/kWh [137]. It assumes that the accomplishable power density is around 7 W/m^2 based on some previous studies [47, 67]. Then that results around 0.022 \$/m^2yr. PRO revenue-boosting takes place by improving the process efficiency and increasing its power density, increasing the membrane lifetime and/or lowering the cost of the membrane [39]. However, as mentioned previously, the net power generation should consider.

Different membranes of different properties have a different effect on the process cost. Hollow fiber membranes are much preferable over flat sheet membrane for the PRO system due to their naturalistic mechanical stability and the availability of a high active surface through the operation [138]. Hydration Innovation Technology (HTI) and Oasys Water- United States are the commercial companies which provide PRO membranes. Around USD 104 per m^2 is the cost of CTA or TFC membranes. Nevertheless, some pilot plants relied on modified membranes as Toyobo in their processes [139].

It has been noticed that the price of energy production is affected by another factor which is the power plant capacity. Unit energy and capital costs were analyzed by Kleiterp for two PRO power plants with different capacities (25 MW and 200 MW) in the Netherlands in 2012 utilizing a membrane with 2.4 W/m^2 power density [129] as shown in Fig. 10

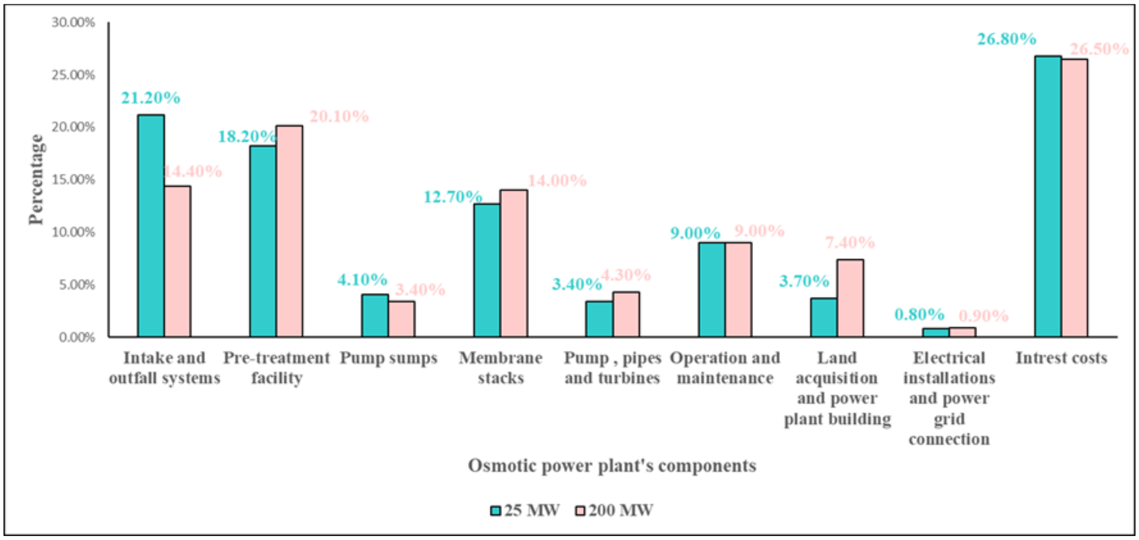


Fig.10: Percentage distribution of energy unit rate of two PRO power plants with various capacities of the main plant's components. The various capacities of the two power plants are 25 MW (shows in green) and 200 MW (shows in pink). Figure updated from Ref [129].

As displays in the figure, the intake and outfall systems, as well as the pretreatment facility, are the main components that caused the high unit rate of energy. The research estimated that the unit power price of the 25 MW plant is 1.15 €/kWh, and 3.71 €/kWh from the 200 MW plant. Increasing the capacity didn't show decreasing in the energy unit rate, which is attributed to the fact that as the plant's capacity increases, the availability of the freshwater decreases and the net power production is decreased [129]. Another study showed that increasing input flows results in an enhancement of the process economics. That system was a combination of SWRO, NF and PRO [140].

Both capital and operational cost should be contemplated when inspecting the PRO profitability analysis. It mentioned previously in this section that the membrane cost affected by the salinity gradients solutions. It also has been proposed by Sarp, and Saththasivam [42] that utilize SWRO in PRO hybrid systems cause an increase in the capital cost of around 30-50% [42]. Using SWRO as a draw solution for PRO processes has a higher potential to produce power using seawater. The high cost of the membrane module and high capital cost of pretreatments may exceed the economic profit of power generation when thinking about scaling up a seawater-river water PRO system [42].

Another element that may affect the PRO economic feasibility is the decision of choosing hydroturbine or pressure exchanger to convert the resulted power to electricity [42]. Sarp and Saththasivam proposed that using a pressure exchanger instead of a hydroturbine for SWRO-PRO hybrid system may enhance the rate of using the hydraulic pressure up to 97%. Accordingly, reduce energy utilization of the desalination process for the SWRO to 25% [42].

3.3 Membrane Fouling

One of the problems that face the PRO process is membrane fouling [141-143]. Generally, water treatment, as well as desalination systems, suffers from membrane fouling issue. However, PRO is considered the osmotic process that faces the most critical membrane fouling compared to RO and FO systems [48, 144]. This issue is responsible about reducing the productivity of the system just like lower the rate of water transport through the membrane [145] and demanding higher power [40] as well as shortening the membrane lifetime [145]. Accordingly, the operating and maintenance costs of the membrane will be increased due to the fouling and that will affect the PRO feasibility. Fouling can be organic, inorganic, bio-fouling or colloidal fouling. Fouling could shrink the pore size, totally plug the pore or form a cake layer on the membrane surface [40].

In PRO systems; the membrane faces two solutions of different concentrations. For instance, the membrane active layer is exposed to the draw solution, while the support layer is exposed to the feed solution mentioned previously [39]. Generally, freshwater could have some foulants as organic matters, which is the reason behind fouling formation on the membrane support layer [145]. When the feed solution contains foulants in a PRO system; these foulants can reach the porous substrate and thereafter, hold in the membrane active layer responsible for lumping the pores and forming external fouling [41].

Many factors can affect the membrane fouling in PRO systems and one of these factors is the type of the used salinity gradients. Choi et al. [145] represented that the relationship between the fouling possibility of the feed and the draw solutions and the power density of the process is reversely proportional. Pretreatment was reported as a solution for fouling problems [145]. In another study done by Yip et al. [144] for investigating the effect of organic fouling on the PRO energy production. Their results showed a reduction of less than 50% in water flux by the foulants from the feed river water to the support layer of the membrane. The foulants successfully removed from the support layer by osmotic backwash.

The membrane type is another factor responsible for the power of fouling in PRO. Thelin et al. [146] discovered that CA membrane compared to four different types of TFC membranes was the least vulnerable to the occurrence of natural organic matter fouling. While organic foulants were the investigated material in another study [147], the authors represented that a draw solution with a high concentration of divalent cations (as Calcium and Magnesium ions) showed high organic fouling in the PRO system which related to the reverse salt diffusion. Moreover, in 2015 a group of researchers notified that a reduction in the water flux of a hybrid PRO-RO system happened due to inorganic fouling in the support layer of the PRO membrane [148]. Backwashing and flushing did not solve the problem while antiscaling pretreatment did. Another study done by Zhang et al. [149] delineated that internal concentration polarization- induced gypsum scaling was the reason behind a complete reduction in the water flux in a PRO system.

Generally, membrane fouling can be reduced by optimizing the operating conditions, performing feed pretreatment and enhancing the structural parameters of the utilized membrane [41]. For instance, antifouling feed pretreatment and alkaline cleaning of the membrane were two reliable techniques for reducing membrane fouling in a PRO system with a high water permeation and power density [150]. On the other hand, silica scaling in a PRO system was solved in a research by adjusting the solutions' chemistry through by pH feed solutions modification [151].

4. Process design

Work performs, and thence energy produces in the PRO process by using the variance of osmotic pressure among a pair of water sources with variation in their salinities [116, 141]. Salinity disparity is the motive power behind water flowing from the low concentrated stream to the high concentrated stream in PRO processes. This flow pressurizes the draw solution and causes an increase in its flow rate [123]. Accordingly, in a PRO process, water permeates from a feed solution of low salt concentration towards a higher salinity and pressurized draw solution through a membrane. The generated power is equivalent to the rate of water permeation times the operating pressure [110]. A hydroturbine is used to depressurize a fraction of the diluted draw solution to procure the power [113] (Fig. 11).

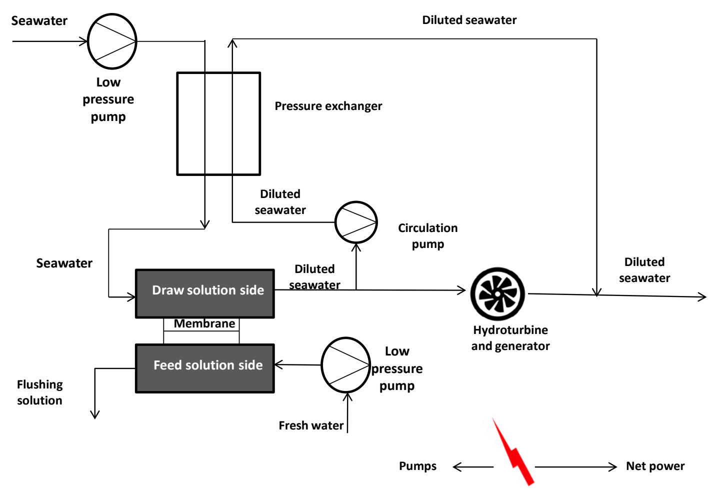


Fig. 11: Graphical diagram of a PRO energy facility. Figure adapted from Ref [50].

Before entering the PRO membrane, the draw stream is usually pressurized to a point lower than its osmotic pressure [113, 152]. When freshwater crosses the PRO membrane, the chemical potential transforms to hydraulic pressure due to the osmotic pressure variation. After the diluted pressurized draw solution leaves the membrane it goes into two lines; the first one proceeds into the pressure exchanger to pressurize the raw draw stream while the second one is used to produce electricity from the hydraulic energy by a turbine as mentioned earlier. The energy required to pressurize the draw stream can be lower than what is extracted from the turbine due to the flow rate increase and produces positive net energy [152]. Generally, a pair of primary methods are available to collect energy in the PRO process; either by a turbine on the draw solution outlet or using an energy recovery device such as a pressure exchanger [153]. The great advantage of using a rotating turbine is that the produced energy is freely utilized [153].

PRO and FO as membrane processes based on salinity gradients can be used to treat hypersaline solutions and capabilities to present an economically feasible system instead of using vapourcompression or thermal distillation. However, PRO is more favorable [154] in these treatments than FO due to the unnecessity of additional regeneration stage [155, 156] to separate the produced water from the draw solutes [154]. Another benefit of using the PRO process in general, that it considers as a near isobaric system. That means the draw solution pressure does not change greatly through the process [154]. Additionally, a volume change during the PRO process occurs due to water drawing from the feed solution. As a result of both a near-constant pressure and a volume increase in PRO systems, the extractable work increases (Energy=Pressure * Volume) [154]. Furthermore, single and dual closed-loop PRO systems prodcuces more energy than what needed as a consumed electrical power for a multi-effect distillation (MED) plant [157]. The power generated from a dual-stage closed-loop PRO was proposed to be 95% more than the electrical energy utilization by a multi-effect distillation plant [157]. The thing that makes it possible to produce electricity by employing low-grade heat of salinity gradient sources.

Some of the parameters that govern the effectiveness of the PRO process are the salinity gradient resources, the energy of pretreatment and energy inputs and the chosen energy recovery device. Moreover, combining the PRO system with desalination plants or adding another stage to the system; will also affect the process outputs and its economic feasibility. These parameters and number of relevant researches are discussed next to clarify the significance of these factors on the PRO process.

4.1 Combining PRO with desalination plants

The extractable energy of the PRO system is controlled by whether the PRO unit is standing-alone or combined with desalination systems. The benefits of combining PRO with desalination plants and research on hybrid systems are discussed in this sub-section. Desalination processes like reverse osmosis (RO) have some drawbacks such as the high cost of energy as well as brine discharge effects on the environment [26, 158]. PRO could alleviate these problems by combining with desalination processes to produce energy, and this is because of its flexibility and high efficiency [153, 157, 159-161]. Various modules and hybrid processes were introduced in the literature to increase the PRO produced power [162, 163]. Thermal desalination with the PRO system has one strong benefit; the high temperature of the MED brine stream, which is the highly concentrated stream of the PRO. The heat of the concentrate would be exchanged to the PRO feed solution through the heat exchanging process. Consequently, the PRO osmotic pressure rises, and the total harvested power from the MED-PRO system rises too [153]. Some studies have shown that energy consumption in the desalination processes could be lessened by combining SWRO with PRO systems [157, 159, 164].

One study demonstrated the benefit of combining PRO with a desalination plant, as evidenced by reduced energy consumption [26]. The seawater of the Tampa Bay desalination plant was utilized in a simulation study to anticipate the economical and energy behaviour of a full-scale PRO process [26]. The study proposed that 9% of the consumed energy for each m^3 permeate can be saved in the case of combining the PRO system with the desalination plant, as well as brine dilution to 41 ppt instead of 66 ppt. The study suggested-based on the net present value evaluation that the most significant factors affecting the performance of the PRO system were membrane properties (permeability of salt and water and the structural parameter) in addition to the price of energy and the size and length of the pipe for water transmission [26]. Another study performed by Touati et al. pointed out the advantages behind combining the PRO with a desalination system. They amalgamated SWRO, PRO and nanofiltration (NF) for potable water, irrigation water and power production [140]. Process performance, economic feasibility and fouling effect were investigated in this research. Irrigation water was produced through NF by treating municipal wastewater effluent. The SWRO subsystem produced drinking water. The feed stream of the PRO was the NF concentrate, while the draw solution was the SWRO brine, as shown in Fig. 12. The advantages of coupling the PRO with the RO membrane using RO brine as draw solution are low operating cost since no chemicals are required for preparing the draw solution, RO brine does not require Pretreatment, and reducing the environmental impact of desalination due to brine disposal. As manifested in Fig. 12, the less concentrated inlet stream was separated before introducing the RO membrane. The first pressure exchanger (PX1) was used to: regain the SWRO brine pressure by depressurizing it and using it as a PRO draw solution; pressurizing a portion from the feed seawater to the RO subsystem. The wastewater effluent was also separated into two streams: the first one pressurized by the high-pressure pump, while the other was introduced to the second pressure exchanger (PX2). PX2 lowered the NF brine pressure to the feed stream for the PRO system and increased the pressure of one portion of the wastewater effluent (as a feed for the NF). Results demonstrated that around 0.38 kWh/m^3 produced energy from the system was recovered after considering the total energy consumed. The study proposed that the system was economically feasible in the case of using membranes costing \$5/m^2 with the actual performance of the PRO membrane. Simultaneously, a membrane price > \$15/m^2 is the desired enhancement in the membrane's performance [140].

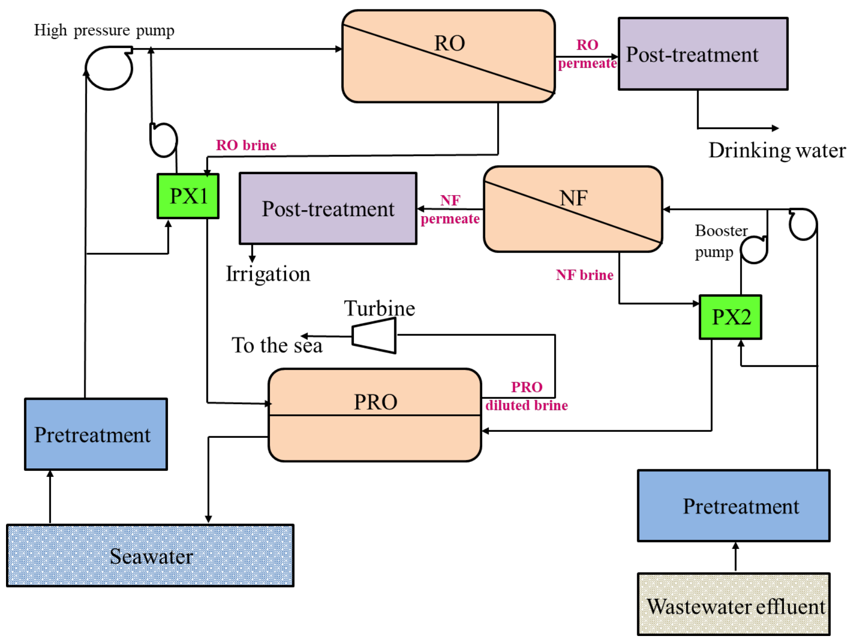


Fig. 12: Schematic diagram of process combines SWRO-PRO-NF for potable water, power and irrigation water output. Figure adapted from Ref [140].

Combining PRO with thermal desalination plant of multi-stage flashing (MSF) was examined for power generation and brine dilution [126]. The highly concentrated stream discharged from a thermal desalination plant and tertiary sewage effluent (Fig. 13) utilized salinity gradients in the PRO unit. Generally, divalent ions with a high concentration in the feed stream of the MSF system have undesirable effects on the process performance due to scaling. This issue may be solved by combining MSF to PRO to dilute the feed solution by making it the PRO draw solution. Additionally, PRO could lower the energy of pumping to the MSF unit by the osmotic power of the diluted brine out from the PRO. Sundry FO membranes were employed in the PRO unit to find out the amount of energy produced. The specific power production, the water flux and the average water flux for Oasys FO membrane were: 0.194 kWh/m^3, 31 L/m^{2}h and 17 L/m^{2}h, respectively. The specific power production of the brine discharge-the tertiary sewage effluent salinity sources was 0.41 and 0.28 of the maximum Gibbs free energy for Oasys membranes and Hydration Technology Innovation CTA membrane, respectively.

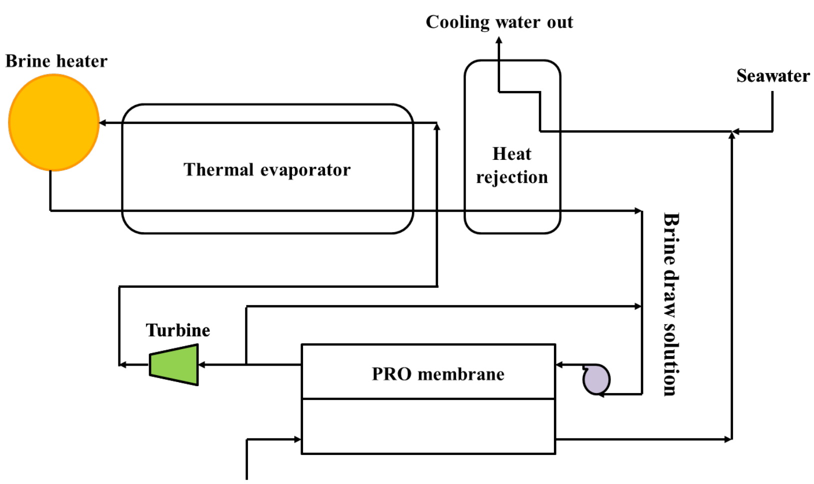


Fig. 13: Schematic diagram of hybrid process combines MSF-PRO for energy production. Figure adapted from Ref [126].

Another example of PRO-desalination combination systems is the RO-PRO scenario, which has been suggested as an effective way to dilute RO concentrate and gather the energy of the variation of osmotic pressure among the concentrate (draw solution) and a low salinity feed stream [29]. SWRO concentrated brine has been used as a PRO draw stream because of its high osmotic pressure [46, 165-168]. RO concentrate can be located on one side of a semipermeable membrane. The other side could be a low concentrated feed solution like effluent from the wastewater treatment plant; causing water flow to relieve the pressure variation. Applying a hydraulic pressure on the concentrated solution exceeds the osmotic pressure between the two solutions; an excess of the diluted and pressurized solution will result. This solution possibly divided into two lines and used for power production in a hydroturbine and in a pressure exchanger to pressurize the inlet concentrate or the draw solution [169]. Pairing wastewater with RO concentrate was utilized in some projects as Mega-ton Water System in Japan and a plant in South Korea (Global MVP). These two projects are at their pilot-scale phase, and there is a possibility for a full-scale application [51, 52]. Additionally, Altaee et al. [170] proposed an RO-PRO hybrid system that showed success in alleviating the RO brine reject and maximising the desalination recovery rate by 18% based on the salinity of the used seawater. These results showed that at 45 g/L seawater, 5 mol/L NaCl as a draw solution and 46% RO recovery rate; 28 W/m^2 PRO power density was achieved. Moreover, a PRO system was employed in one study [171] to supply an RO plant with the required power. The study represented two subsystems: desalination of seawater by RO unit and energy production based on a PRO system where the draw solution was the RO pressurized brine. At high flow rates and low recovery of RO process; the combined system of the PRO with the RO has favorable results and was theoretically verified [171].

PRO feed temperature could be an important factor that affects the process performance while combining with desalination plants. The combination of RO with PRO has been studied to reduce the specific power consumption of the hybrid system by determining the feed temperature effect on the PRO performance [172]. The system was a combination of RO unit, PRO unit and two pressure exchangers, as shown in Fig. 14. The results revealed that maximizing the temperature reduced the specific energy consumption of the system. 17.93% was the reduction in the specific energy consumption of the system by doubling the operating temperature of the PRO unit from 25 ˚C to 50 ˚C where 1.2 mol/L NaCl was the draw solution [172].

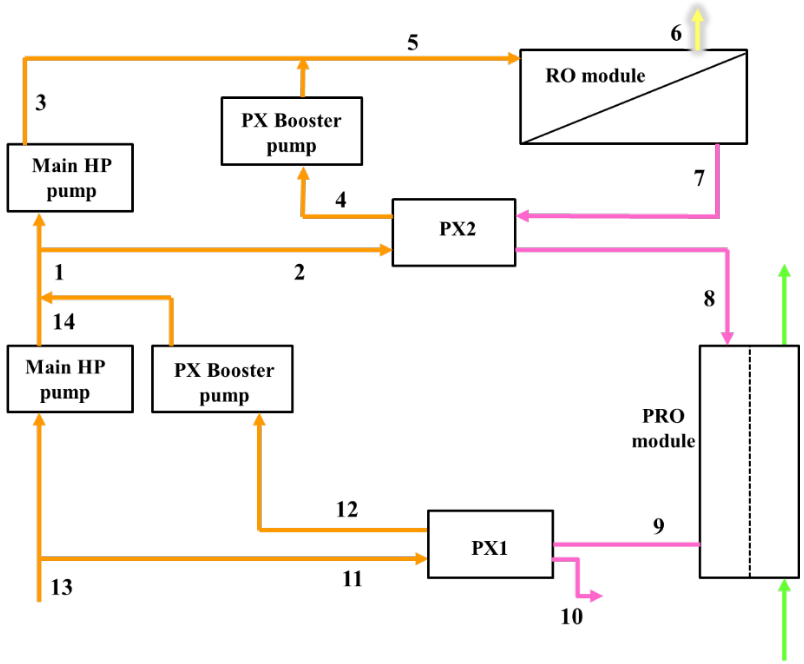


Fig. 14: Illustration figure for a combined system of RO-PRO with two pressure exchangers. Seawater or diluted seawater is the feed and appears in orange, the green lines are for freshwater, concentrated brine appears in pink, and the yellow line is for the RO permeate. Figure adapted from Ref [172].

Additionally, PRO systems can be combined with membrane distillation processes for power generation and water production at low heat energy [41, 173, 174]. The main advantages of the PRO- membrane distillation (MD) systems that they are preferable to improve the generation of the osmotic energy, increase the freshwater recovery, and restrain the membrane fouling [175]. One type of these combinations is joining PRO with the direct contact membrane distillation (DCMD) as shown in Fig.15. In 2017 Park et al. [176] did study a PRO-DCMD system theoretically in one membrane module by developing a mathematical model to predict the power and water production and compared the results within DCMD and PRO systems separately. The suggested system included a cold draw solution and a hot feed solution came in contact through a hydrophobic membrane, as shown in Fig.15. As in a DCMD process; water permeates as a vapour from the hot feed solution to the cold draw solution. Then as in PRO systems; the power is produced through the turbine. The researchers figured out that adding PRO to DCMD system is responsible about reducing the consumed energy (saved around 0.1738 kWh/m^3) as a result of power production from the PRO; however, they got less water flux.

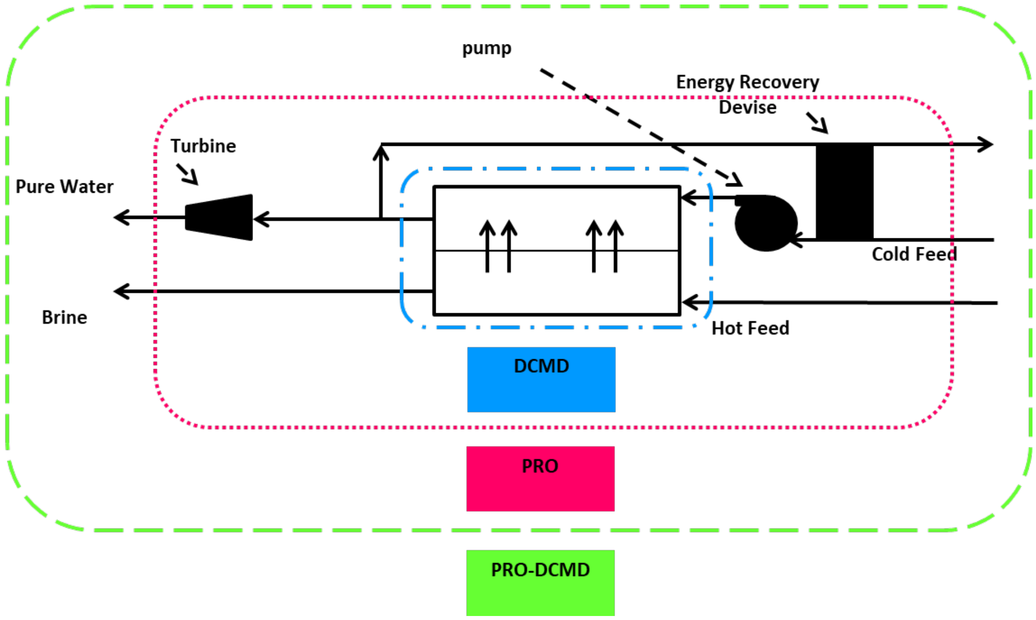


Fig. 15: Illustration figure for a combined system of PRO-DCMD. Figure adapted from Ref [176].

In another study, Lee at. al [177] did add a PRO unit with a multistage vacuum membrane distillation system (MVMD). Brine and distilled water were contentiously generated by recycling flows. In this system, the PRO draw solution was the concentrated brine from the MVMD recycle stream. The distillate generated and the amount of power produced were evaluated theoretically based on the feed flow rate and the flow ratio in the recycling process. They found an inverse relationship between the recycling flow ratio and the amount of the distillate produced at fixed feed rate. A maximum of 1.9 M of brine concentration was achieved at feed flow rate of 50 g/s and 90% recycle ratio. A value of 9.7 W/m^2 power density was resulted in the PRO unit when the feed solution was river water at 13 bar applied pressure [177]. Moreover, some researchers in United State [178] presented a closed loop process which joined MD with PRO together for the purpose of operating low thermal power as a heat engine. The pure distilled water and the concentrated streams out from the thermal separation unit were the feed and draw solutions, respectively for the PRO unit. Their study showed that 1 M of Sodium Chloride with 20 and 60 ˚C of cold and hot solutions, respectively in this PRO-MD system could theoretically produce 9.8% energy efficiency.

Some studies in literature did not represent a successful outcome of combining PRO with desalination plants. For example, various studies professed that SWRO-PRO integration is not economically valuable. The main reasons behind this outcome were the low osmotic pressure difference between the draw solution as the SWRO brine and the feed solution as the wastewater effluent or river water and high energy requirements for feed solution pretreatment [36, 179].

4.2 Dual-stage PRO

The recovered power in non-ideal PRO systems is only a portion of the salinity gradient energy available. The remaining portions are discharged as a non-returnable power stays in the salinity gradient source. Accordingly, PRO-single stage efficiency is minimized, and its applications become less productive, which triggered the idea of including a second stage to the system to collect the remaining osmotic energy in the diluted draw stream before discharge [113, 153, 180]. Dual-stage PRO (DSPRO) is more efficient in power generation than a single PRO system; may diminish the losses of irreversible energy. Additionally, researchers proposed that DSPRO can perform better than conventional PRO when dealing with salinity resources of high feed concentration [113]. This is a consequence of the serious concentration polarization generated on the feed side, which can be minimized by introducing raw feed stream for the second PRO stage [113]. Furthermore, DSPRO technology has the superiority of diminished membrane fouling [113, 157]. Adding a second stage can renew the variance in chemical potential through the membrane and could minimize the feed side concentration polarization [113, 117]. DSPRO is slightly different than a single-stage PRO by streaming a portion of the draw stream to the second PRO stage (Fig. 16).

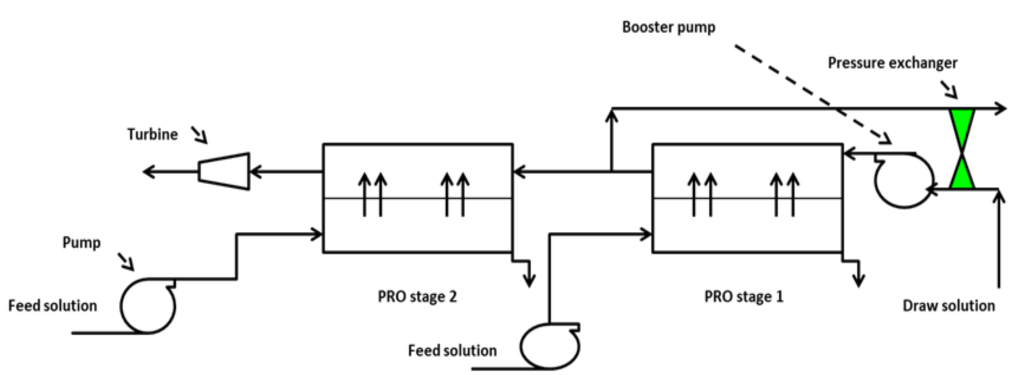


Fig. 16: Illustration figure of DSPRO. Figure adapted from Ref [113].

The DSPRO process has some benefits over a single-stage PRO process which are due to the chemical potential that occurs in the second PRO stage by applying fresh feed solution to that stage and as a consequence, elevates the water flux [113]. Additionally, introducing less concentrated draw solution to the second stage may cause extra water permeation within the membrane and as a result, increase the power density. Adding a second PRO membrane increased energy by 18%, as Altaee et al. [113, 157]. The DSPRO process can operate with feed solutions of different types, capable of alleviating the feed salt concentration effect on the system efficiency and has the potential of using different membrane types in each stage [139].

Several studies focused on studying the difference between single and dual PRO systems or multi-stages systems. Other studies demonstrated different salinity gradients and their effect on the performance of DSPRO systems. While some researchers showed different DSPRO configurations. To compare single and DSPRO systems, model calculations were performed on both single and dual closed-loop PRO (CLPRO) systems to determine the difference of power generation on both processes in one of these studies [157]. The main advantages of using a CLPRO unit is that the PRO membrane fouling is possibly reduced. The effect of draw solution flow rate and pressure in addition to the membrane area on the power generation was studied. The study demonstrated that the draw stream pressure was the most dominant criteria affect the first stage performance. The flow rate of the draw stream was the most effective parameter in the second stage. As a result, optimization of draw solution pressure is a requirement for the design of a DSPRO process. For the case of a single PRO system, increasing the membrane area caused a rise in the water inflow, and that was due to the enlargement of the permeate flow. The power generated by the two stages-CLPRO was 18% more than that generated by a single PRO system. Furthermore, DSPRO power density was 43% more than that of a single-stage PRO. Lower effect of concentration polarization was noted when using DSPRO system [157]. A summary for some of the results shows in Table 8.

Table 8: Summary of some results for a DSPRO study [157].

Results	200 m^2 membrane area	300 m^2 membrane area	10 bar Draw solution hydraulic pressure	16 bar Draw solution hydraulic pressure	2500 L/h Draw solution flow rate	5000 L/h Draw solution flow rate
Jw (First stage)(L/m²hr)	11.2	11.6	7.2	11.6	-	-
Inlet draw solution concentration (First stage) (mol/L)	0.86	0.92	0.5	0.9	-	-
Jw (Second stage)(L/m²hr)	5.0	4.0	3.2	4.1	1.6	4.2
π_D (Second stage)(bar)	26	23.7	-	-		
Inlet draw solution concentration (Second stage) (mol/L)	0.58	0.52	-	-	0.42	0.52
External concentration polarization ($e^{-J_w/k}$) (Second stage	0.98	0.99	-	-	-	-
Recovery rate (First stage)	45%	70%	-	-	70%	70%
Recovery rate (Second stage)	27%	51%	-	-	14%	51%
Total recovery	60%	85%	58%	85%	-	-
Power density (First stage) (W1) (W/m²)	6.0	6.5	2.5	6.46	-	-
Power density (Second stage) (W2) (W/m²)	2.8	2.3	1.1	2.3	0.9	2.3
W2/W1	45%	35%	45%	35%	20%	70%

Another study that clarified the difference of single and DSPRO was performed by Touati et al. [165]. Researchers have applied SWRO in addition to PRO for single and double stages. The suggested DSPRO showed preferred performance. Two RO, two RO-one PRO and two RO-two PRO were the proposed systems. For subsystem two RO-one PRO, when RO recovery was 60%, then the PRO specific power was around 280 Wh/m^3. For that subsystem, at recovery rates around 40-50%, the resultant power ranged between 110-190 Wh/m^3. For subsystem two RO-two PRO, when RO recovery was 50%, then the specific power of the first PRO was around 150 Wh/m^3 and for the second PRO was around 570 Wh/m^3. For that subsystem, at recovery rates around 40-50%, the resultant power ranged between 700-930 Wh/m^3. It was noted that as the dilution rate increased, the osmotic pressures of the second PRO increase too. Moreover, the produced energy decreases as the recovery rate of the RO unit increases. Another study that compared between the single and the dual stages of the PRO system was done by Soltani [117]. The productivity of DSPRO in terms of specific energy and work per freshwater drawn was higher than the single stage. The study found that the overall system performance of a DSPRO improved up to 8% in term of specific energy. Enhancing the membrane features as lessening the solute rejection coefficient for DSPRO system caused an increase in specific energy up to 14%.

Suggestions of different membrane module arrangements and a simulation study of energy comparison between single and DSPRO systems were introduced [113]. RO brine or Dead Sea water and wastewater effluent or seawater were the used salinity gradients. In a single PRO unit, they found a proportional relationship between the number of used modules and the generated specific power. The power generation of single-stage PRO process was increased by 70% when three membrane modules were used rather than one module for the Dead Sea water-wastewater salinity ingredients (Table 9).

Table 9: Summary of some results for a conventional and DSPRO study [113].

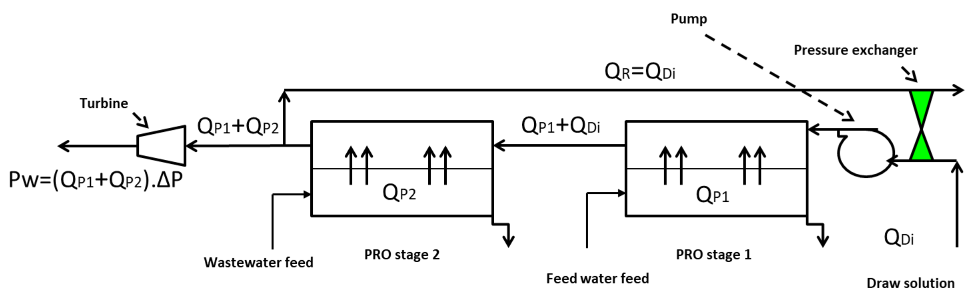
Modules arrangements in stage one and two respectively	Specific Power Generation kWh/m^3				
	Dead Sea-Sea Water	Dead Sea-Waste Water	Dead Sea-RO Brine	RO Brine-Waste Water	Sea Water-Waste Water
1-0	0.40	0.75	0.24	0.07	0.02
2-0	0.58	1.10	0.35	0.13	0.04
3-0	0.65	1.28	0.40	0.16	0.05
1-1	0.64	1.07	0.40	0.13	0.04
1-2	0.74	1.21	0.46	0.16	0.05
2-1	0.75	1.28	0.47	0.16	0.05

Results of a DSPRO process when Dead Sea-seawater were the salinity gradients showed an increase of the maximum power generation ranging between 10 and 13% depending on the design configuration. These values were 12 to 16% when Dead Sea-RO brine was the used salinity gradients for DSPRO. Theoretically, adding a second stage, PRO of Dead Sea-wastewater and RO brine-wastewater did not affect the maximum specific energy although the simulation study did not consider the impact of wastewater fouling on the performance of the process. However, this was not the case for the higher concentrated solutions as Dead Sea-seawater when using DSPRO as mentioned earlier. DSPRO would be favorable for highly concentrated solutions, as shown in this study.

Regards utilizing various salinity gradients and their effect on DSPRO system; a study performed by Altaee et al. [114] utilized different feed solution resources in the DSPRO system operating in a counter-current mode to assess the impact of the feed salinity on the process effectiveness [114]. They investigated using brackish water (1-5 g/L) or freshwater (0.2 g/L) as feed solution for the first module and wastewater effluent (0.2 g/L) for the second module. The best system performance resulted while utilizing brackish water for the first module and wastewater for the second module. They proposed that the energy generated in DSPRO unit was more than what generated in the PRO unit by the total value of energy produced in the second stage [114].

The amount of power generated and brine concentration was investigated in a multistage pumping DSPRO process (MSDSPRO) [122]. The MSDSPRO process achieved high energy production efficiency and high brackish water brine concentration. Significant power generation efficiency of MSDSPRO was noticed even at low concentration of the draw stream. Power density in stages one and two were found to be 4 and 6.25 $W/m^{2,}$ respectively, when the concentration of the draw stream was 0.073 kg/L. A directly proportional relationship was found between reverse salt diffusion and draw stream concentration, and it was noticed to be more in the second stage than the first stage.

Moreover, different configurations of DSPRO systems were pointed out in the literature. For instance, the conventional DSPRO configuration shown in Fig. 16 was compared to a different design (Fig. 17) in one study [139]. The new DSPRO configuration was based on sending an undivided seawater stream of stage one completely to stage two according to improve membrane flux in stage two [139]. Researchers also scrutinized the effect of draw solution concentration by testing a range of seawater salinities (32-45 g/L) on process performance. They found that the process performed better with increased seawater salinity. The power density was 17.4% higher in the new DSPRO Q_R configuration in comparison to the old one. The outcomes also displayed that the specific energy consumption in the modified layout of DSPRO was less compared to the previous layout by about 8%. Finally, they proposed that the capital cost was lower for the new design since it needed fewer membrane elements [139].



Q_{Di}: Flow rate of inlet draw solution in m^3/hr

Q_{P1},Q_{P2}: Permeate flow rate in stage 1 and stage 2 respectively in m^3/hr

Q_R: Recycle flowrate in m^3/hr

ΔP: Hydraulic pressure difference in bar

Pw: Power in KW/day

Fig. 17: Schematic diagram of different design used in one study of dual-stage pressure retarded osmosis. Figure adapted from Ref [139].

He et al. proposed four different flow configurations of two PRO stages in their study, as shown in Fig. 18 and compared to a single PRO system [180]. The four various configurations are continuous draw-continuous feed, continuous draw-divided feed, divided draw-divided feed and divided draw-continuous feed. Average power density and produced power were chosen as the factors to compare between the dual's PRO and the PRO of one stage. In this study, researchers used the same membrane area and same salinity gradients in a two PRO system to compare with the single PRO. The extractable power of the first design (a) was higher than that of the single PRO. Therefore higher hydraulic pressure was required, and in consequence, consideration of the membrane mechanical strength was a necessity in such a case. They also found that in all the possible operations, the energy capacity, as well as the average power density of divided draw divide feed configuration (d), were less than that of the single PRO. Better performance of the remaining two configurations was noticed by differentiating their results to the one-stage PRO unit in terms of extractable power. They also proposed that configurations (a) and (c) were better according to the membrane average power density at a high dimensionless flow rate [180]. Several studies discussed the variation of the net power density of multistage PRO systems [152, 181]. For example, Chung et al. categorized various configurations of multistage PRO systems and investigated these systems thermodynamically [152]. The results showed that using a 10 stage PRO system caused an increase of 9% of the net power density than a single-stage unit. DSPRO concept, in general, seems to have a great potential to improve the performance of the salinity gradient power plant, but there are no experiments performed to confirm. Future work should focus on the performance and efficiency of the DSPRO process.

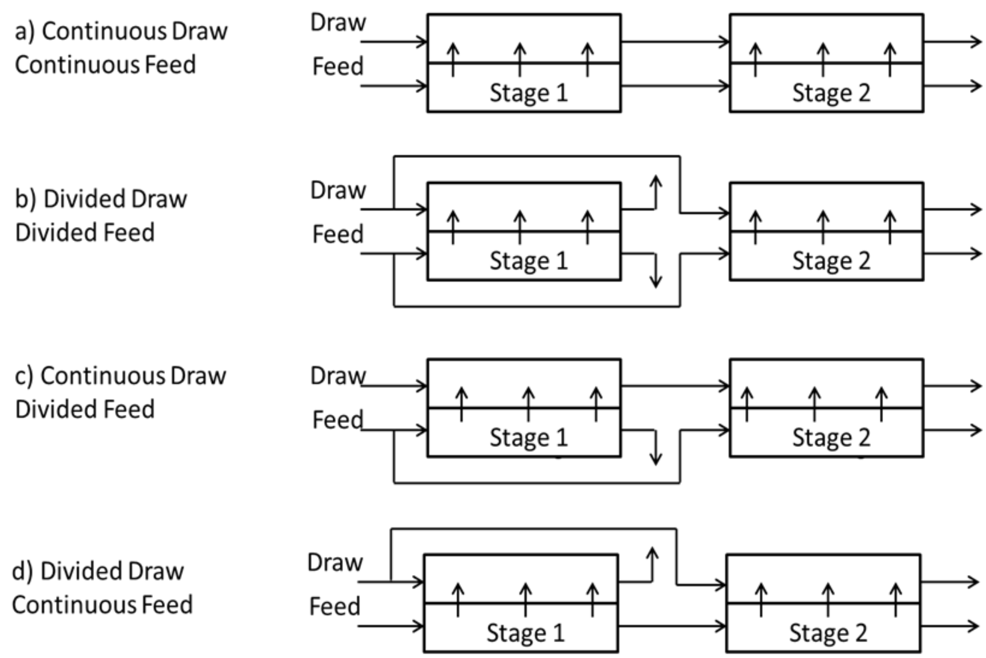


Fig. 18: Representation figure of proposed configurations of a DSPRO unit. Figure adapted from Ref [180].

4.3 The Numerical Models of PRO

The first PRO model was proposed by Loeb in 1976 [182], after that more models were developed to include the effects of: internal concentration polarization, dilutive external concentration polarization, reverse salt flux, the concentration changes through the membrane module length or even for various membrane types [142, 167, 183-185]. For instance, a study done by Kim *et al.* [167] updated the flux model to investigate the changes in the concentration and the flow rates along the membrane length for a pilot PRO system.

In the PRO system, the draw stream is affected by operating pressure just as in the RO system, but the direction of the net water flow remains toward the concentrated draw mixture like in the FO process. Generally, water transition in FO, RO and PRO is described by equation 1:

$$Jw = A(\Delta\pi - \Delta P) \quad (1)$$

where Jw: the water flux $L/m^2.h$, A: membrane water permeability coefficient $L/m^2.h.bar$, $\Delta\pi$: the osmotic pressure difference in bar and ΔP: the hydraulic pressure difference in bar [29, 50]. If $(\Delta\pi - \Delta P) > 0$ then theoretically water flux is positive. Nevertheless, at specific pressure difference, the flux result may be less feasible for applications. The energy might be produced in PRO to membrane area, which is known as the power density (W) is shown in equation 2:

$$W = Jw\Delta P = A(\Delta\pi - \Delta P)\Delta P \quad (2)$$

Equation 2 decisive that the most important parameter for the PRO process is the membrane permeability. Nevertheless, and as mentioned earlier, more factors affect the performance of PRO. One of these factors is the concentration polarization effect. Concentration polarization is the presence of concentration gradients at an interface. The solute concentration becomes higher on the feed solution-membrane interface (concentrative internal concentration polarization) and lower concentration on the permeate side (dilutive external concentration polarization) due to water passing the membrane. The dilutive external concentration polarization happens as water moves from the feed stream to the draw stream and produces dilution at the membrane surface. Furthermore, the concentrative internal concentration polarization happens due to the membrane porous support layer resistance to mass transfer. This phenomenon occurs when the solute accumulates inside the support layer on the feed side [123]. As a conclusion of the reverse diffusion by the solute particles, the feasible osmotic pressure variance decreases through the membrane [186].

Asymmetric membranes used for osmotic processes generally encompass two different layers, an extremely thin and relatively dense selective layer on a porous support layer [50, 187]. Concentration polarization happens internally (in the porous support layer), and externally-which considers as minor compared to the internal- (on the dense layer side) on membrane layers at dense layer-draw solution interface [188-190] (Fig.19). The membrane dense active layer generally towards the draw stream while the porous support layer towards the feed stream in PRO applications [29, 50] to help the membrane to maintain the hydraulic pressure presence on the draw solution side, to lower the impact of internal concentration polarization and to reduce the aggregation of solute particles in the porous support layer [157].

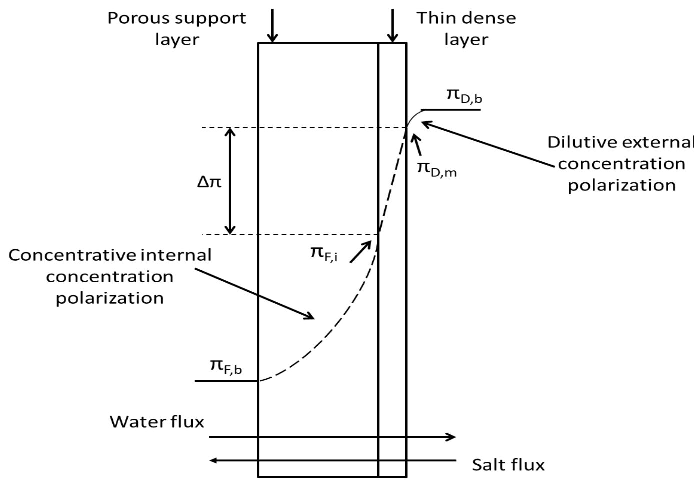


Fig.19: Illustration figure of osmotic driving force profile for an asymmetric membrane for PRO system when the dense layer towards the draw stream. Figure adapted from Ref [142].

The water flux in the PRO process with the effect of internal concentration polarization only [177] is introduced next:

$$J_w = A(\pi_{D,m} \frac{1-\frac{C_{F,b}}{C_{D,m}}\exp(JwK)}{1+\frac{B}{Jw}(\exp(JwK)-1)} - \Delta P) \quad (3)$$

Where $C_{F,b}$ is the feed concentration at the bulk, $C_{D,m}$ is the draw concentration at the membrane surface, K is the solute diffusion resistivity in the porous support layer, and B is the active layer salt permeability coefficient.

The next model is an analytical model for permeate flux that includes the effect of internal, external concentration polarization and the reverse salt flux with only measurable quantities in the PRO [113]:

$$J_w = A(\frac{\pi_{D,b}\, exp\left(-\frac{Jw}{k}\right) - \pi_{F,b}\exp(JwK)}{1+\frac{B}{Jw}\left(\exp(JwK) - exp\left(-\frac{Jw}{k}\right)\right)} - \Delta P) \quad (4)$$

where the osmotic pressure of the draw solution at the bulk is $\pi_{D,b}$, the osmotic pressure of the feed solution at the bulk is $\pi_{F,b}$, and the mass transfer coefficient is k.

5 Conclusions

A proper assessment of renewable energy sources is extremely important for meeting the growing global energy requirements resulting from population growth and rapid industrialization. Utilizing the salinity gradient between low-saline and high-saline solutions, pressure retarded osmosis could overpower the limitations of conventional energy production technologies and is considered advantageous compared to the other renewable energy technologies. Despite many laboratory-scale experiments of the PRO system, there are a limited number of pilot plant trials. More pilot plants need to be investigated to understand the PRO process's potential capability for power generation of different salinity gradients. For example, there is no PRO plant tested in the Middle East, where seawater salinity reaches 1.5 times more than the standard seawater (35 g/L). More investigation should be on the PRO-thermal desalination hybrid system due to the great potential of brine reject of thermal plants that can be combined with treated wastewater as a salinity gradient resource. There is also an opportunity for dual-stage PRO technology trial as a promising concept for increasing the energy harvested from salinity resources.

It is a fact that there is no membrane dedicated for the PRO process yet, apart from Toyobo hollow fiber membrane that is modified from the RO membrane. Hence, we strongly recommend that more investment should be on fabricating a commercial PRO membrane. Moreover, the PRO processes also have a serious dependence on the selection of draw and feed solutions. An increased concentration gradient could increase the possibility of the practical operation of this process. It is also recommended to focus more on the environmental impact and benefits of the PRO process, especially when using the waste stream for power generation. For example, the RO brine-wastewater and Dead Sea-RO brine salinity gradient have environmental benefits and power generation. Research should also focus on the availability and potential of salinity gradient resources. Studies confirmed that thermal plant brine reject coupled with wastewater has great potential for power generation and reduces thermal and high salinity impact on seawater.

Some issues should not be ignored while investigating the PRO systems, and these include the internal concentration polarization, external concentration polarization, reverse salt penetration and membrane fouling. Accordingly, more studies and effort are still necessary to enhance DSPRO efficiency, power density, and net power production instead of the power generated in the PRO process. One and best solution to enhance the PRO performance is developing better membranes by handling higher pressure values, lowering the chance of fouling occurrence, increasing water permeation and reducing reverse salt flux [191]. Accordingly, it is very important to focus on developing new membranes, specifically for large scale PRO applications and consider the reduction of membrane fouling. Cost calculations should also be considered for large scale systems to study the process feasibility. Additionally, more studies on the PRO process efficiency related to the net power production instead of the power density are required.

Appendix

Table 10 summarised some of the conditions and results for PRO systems discussed in the literature. As shown in the table; some of the studies did not consider the net power generation instead of the power density as discussed previously.

Table 10: Summary of some results of PRO studies discussed in the literature.

Feed solution/s	**Draw solution/s**	**Operating pressure bar**	**Type of used membrane/s**	**PRO stages**	**Water flux L/m^2h**	**Power density W/m^2**	**Net power generation kWh/m^3**	**Source**
Seawater 0.5 M NaCl	2.0 M NaCl	12.5	Flat sheet CTA	1/Bench scale	~14.0	4.7	N/A	[35]
Pure water	SWRO Brine (~1.0M NaCl)	25.0	Toyobo 10 inch Hollow fiber module	1/Large scale	42% permeation of pure water to draw	7.7	N/A, Ideal situation was assumed	[47]
10 mM NaCl	1M NaCl	11.0	CTA-FO supported by a woven fabric *	1/Lab scale	11.0	3.8	N/A	[48]
0-5 g/L NaCl	35 g/L NaCl	0-9.7	Flat sheet CTA-FO, custom made	1/Bench scale	0-25	≥2.7	N/A	[50]
	60 g/L NaCl					≥5.1		
0.5 g/L NaCl	30 g/L NaCl	3.8	FO spiral wound	1/Lab scale	~6.3	0.57	N/A	[53]
DI water	1.0M NaCl (Seawater brine)	<15.0	TFC-PRO*	1/Lab scale	N/A	7-12	N/A	[67]
0 mol/m^3 NaCl	600 mol/m^3 NaCl	15.0	Spiral wound	2/Large scale	*	2.98	Extracted work per L of drawn freshwater= 0.94 kJ/L *	[117]
Distilled water	1st stage: ~0.85 mol/L NaCl	15.0	Flat sheet	2	1st stage= 11	1st stage= 5.67	N/A	[157]
	2nd stage: ~0.49 mol/L NaCl				2nd stage= 4	2nd stage= 2.11		

F1: 200mg/L, freshwater	45g/L Seawater to first stage	14.0	FO-CTA	2	N/A	W1= ~4.4	N/A	[139]
F2:200mg/L wastewater effluent						W2= ~3.0		
DI water	4.6M NH_3-CO_2	~101.3	Cross flow CA-FO	1	N/A	~170	N/A	[192]
10 mM NaCL	1.0 M NaCl	15	Dual layer Hollow fiber	1/Bench scale	13.0	5.10	N/A	[193]
DI water	3.0 M NaCl	48.0	Flat sheet TFC	1/Bench scale	N/A	60.0	N/A	[194]
DI water	1.0M NaCl	20.0	TFC Hollow Fiber	1/Lab scale	~14.0	7.6	N/A	[195]
10 mol/m^3 River water	600 mol/m^3 Seawater	~9.0	Flat sheet	1/Module scale	2.3	N/A	0.1*	[196]
0.21 g/L River water (Magdalena River)	33.7 g/L Sea water (Caribbean Sea)	11.5	Flat sheet*	1	N/A	6.45	6.0 MW	[197]

*: More information can be found in the corresponding reference.

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