

INVESTIGATION ON PRESSURE RETARDED OSMOSIS PROCESS OPERATION, OPTIMIZATION, AND HYBRID SYSTEMS

by Nahawand AlZainati

Thesis submitted in fulfilment of the requirements for
the degree of

Doctor of Philosophy

under the supervision of **Dr Ali Altaee**

Prof Jhon Zhou

Prof Senthilmurugan Subbiah

University of Technology Sydney
Faculty of Engineering and Information Technology

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Certificate of Original Authorship

I, *Nahawand AlZainati*, declare that this thesis is submitted in fulfilment of the requirements for the award of *Doctor of Philosophy, in the Faculty of Engineering and Information Technology* at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

This research is supported by the Australian Government Research Training Program.

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Dedication

I dedicate this dissertation to my parents Abdualwahhab AlZinati and Zain AlGhzawi for being supportive and good listeners, they believed in me, and helped me to follow my dream, thank you for being the best parents in this world.

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Statement of Contribution of Authors

More than 85% of the chapters in this thesis has been conducted by me. This includes writing the original draft, the computational framework, the models' design, the models' validation, and the representation of the results, in addition to the analysis and discussion of the results. The authors who contributed to the published papers are acknowledged in each chapter below. I declare that I'm the first author of the papers prepared in this thesis through my study in a higher degree by research.

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Abbreviations

Abbreviation	Definition
ANN	Artificial neural network
CatBoost	Categorical boosting
CLPRO	Closed loop pressure retarded osmosis
CTA	Cellulose triacetate
CNT	Carbon nanotube
CQDs	Carbon quantum dots
DCMD	Direct contact membrane distillation
DI	Deionized water
DS	Draw solution
DS mentioned in Chapter Three and Chapter Six	Dead Sea water
DSPRO	Dual stage pressure retarded osmosis
ERD	Energy recovery device
FO	Forward osmosis
FS	Feed solution
GWO	Grey wolf optimisation
HF	Hollow fiber
HfMs	Hollow fiber membranes
HNTs	Halloysitr-nanotubes
HPP	High pressure pump
ICCP	Internal concentrative concentration polarization
LPP	Low pressure pump
MAE	Mean absolute error
MD	Membrane distillation
MSDSPRO	Multistage pumping dual stage pressure retarded osmosis
MSE	Mean squared error
MVMD	Multistage vacuum membrane distillation
NOF	Number of the fibers in the hollow fiber pressure retarded osmosis module
NSEC	The net specific energy consumption in kWh/m ³
NSEG	The net specific energy generation in kWh/m ³
PA	Polyamide
PAN	Polyacrylonitrile nanofiber
PDA	Polydopamine
PEI	Polyetherimide
PES	Polyethersulfone
PRO	Pressure retarded osmosis
PX	Pressure Exchanger
QSPRO	Quaternary stage pressure retarded osmosis
Ra	The mean roughness of the membrane
Rms	The mean square ridge elevation of the membrane
RO	Reverse osmosis
ROB mentioned in Chapter Three and Chapter Six	Reverse osmosis brine

RW	River water
SGR/s	Salinity gradient resource/s
SW mentioned in Chapter Two	Spiral wound
SW mentioned in Chapter Three and Chapter Six	Sea water
SWM	Spiral wound membrane
TEM	Transmission electron microscopy
TFC	Thin-film composite
TFNC	Thin-film nanocomposite
TSPRO	Ternary stage pressure retarded osmosis
WW mentioned in Chapter Three and Chapter Six	Waste water
XGBoost	Extreme gradient boosting

Nomenclature

Symbol	Definition
A_1	The membrane area at the first PRO stage
A_2	The membrane area at the second PRO stage
$A / A_w / A_w / A_{w,PRO}$	The water permeability of the PRO in $m^3/m^2.s.bar$
A_{ERD}	The inlets side energy recovery device cross sectional area in m^2
$A_{m,PRO}$	The PRO membrane surface area in m^2
$A_{m,RO}$	The RO membrane surface area in m^2
A_s	The cross-section area of the membrane
$A_{w,RO}$	The water permeability of the RO in $m^3/m^2.s.bar$
B	The split points set for the internal nodes of the tree
B / B_{PRO}	The salt permeability coefficient of the PRO in m/s
B_{RO}	The salt permeability coefficient of the RO in m/s
$C_{Di} / C_{Di,PRO}$	The draw inlet concentration of the PRO in mg/L
$C_{Di,PRO1}$	The draw inlet concentration of the PRO1 in mg/L
$C_{Di,PRO2}$	The draw inlet concentration of the PRO2 in mg/L
$C_{Di,x}$	The initial molar concentrations of the draw stream at the distance x along the membrane length in mg/L
$C_{D,m}$	The PRO draw concentration at the membrane surface in mg/L
$C_{Dm,PRO}$	The draw membrane side concentration of the PRO in mg/L
C_{Do}	The draw outlet concentration of the PRO in mg/L
$C_{Do,PRO1}$	The draw outlet concentration of the PRO1 in mg/L
$C_{Do,PRO2}$	The draw outlet concentration of the PRO2 in mg/L
C_F	The feed concentration of the PRO in M
$C_{F,b}$	The feed concentration at the bulk in mg/L
$C_{F,RO}$	The concentration of the feed solution of the RO in mg/L
$C_{F,RO1}$	The feed concentration of the RO1 in mg/L
$C_{F,RO2}$	The feed concentration of the RO2 in mg/L
$C_{Fi} / C_{Fi,PRO}$	The feed inlet concentration of the PRO in mg/L
$C_{Fi,PRO1}$	The feed inlet concentration of the PRO1 in mg/L
$C_{Fi,PRO2}$	The feed inlet concentration of the PRO2 in mg/L
$C_{Fi,x}$	The initial molar concentrations of the feed stream at the distance x along the membrane length in mg/L
$C_{Fm,PRO}$	The feed membrane side concentration of the PRO in mg/L
$C_{Fm,RO}$	The feed membrane side concentration of the RO in mg/L
C_{Fo}	The feed outlet concentration of the PRO in mg/L
$C_{Fo,PRO1}$	The feed outlet concentration of the PRO1 in mg/L
$C_{Fo,PRO2}$	The feed outlet concentration of the PRO2 in mg/L
$C_{Fs,PRO}$	The feed concentration at the membrane support layer of the PRO in mg/L
C_{hi}	The high pressure brine inlet concentration of the ERD in mg/L
C_{ho}	The low pressure brine outlet concentration of the ERD in mg/L
$C_{i,e}$ and $C_{o,g}$	The inlet and outlet concentration of each stream in the mixer or the splitter in mg/L
C_{li}	The low pressure feed inlet concentration of the ERD in mg/L
C_{lo}	The high pressure feed outlet concentration of the ERD in mg/L
$C_{p,RO}$	The product concentration of the RO in mg/L
$C_{p,RO1}$	The product concentration of the RO1 in mg/L
$C_{p,RO2}$	The product concentration of the RO2 in mg/L
$C_{R,RO}$	The reject solution concentration of the RO in mg/L
$C_{R,RO1}$	The reject concentration of the RO1 in mg/L

$C_{R,RO2}$	The reject concentration of the RO2 in mg/L
$\Delta P / \Delta P_{PRO}$	Applied hydraulic pressure difference of the PRO in bar
$\Delta P_{D,x}$	The pressure drop at the draw side at x membrane length in bar
$\Delta P_{D,xj}$	The pressure drop at the draw side at distance x in j DPRO stage
$\Delta P_{F,x}$	The pressure drop at the feed side at x membrane length in bar
$\Delta P_{F,xj}$	The pressure drop at the feed side at distance x in j DPRO stage
ΔP_{RO}	Applied hydraulic pressure difference of the RO in bar
ΔP_x	Applied hydraulic pressure at point x of the PRO in bar
$\Delta P_{x,j}$	The effective pressure difference between the draw and feed solutions at distance x in j DPRO stage
D / Diff	The diffusion coefficient of the solute in m ² /s
D_F mentioned in Chapter Three	The diffusion coefficient at the support layer in m ² /s
D_F mentioned in Chapter Four	The darcy's law constant at feed side of the RO in bar.s/m ⁴
d_h	The hydraulic diameter of the flow through the feed spacer of the PRO membrane in m
D_i	Inner fiber diameter in the HF PRO module in m
D_i	Inner diameter of the shell in the HF PRO module in m
D_o	Outer fiber diameter in the HF PRO module in m
D_o	Outer diameter of the shell in the HF PRO module in m
D_{T2}	The diffusion coefficients at T ₂ (25°C) in m ² /s
e and g	The number of inlet and outlet streams in the mixer or the splitter
EC_{RO}	Energy consumption of the RO in kW
E_{o1}	The specific power generation at stage one of the DSPRO in kWh/m ³
E_{o2}	The specific power generation at stage two of the DSPRO in kWh/m ³
$E_{o\ tot}$	The total specific power generation of the DSPRO in kWh/m ³
$E_{ox,j}$	The specific power generation along the stage j of the DSPRO in kWh/m ³
E_{Pump}	The energy consumed through pumping in Kw
$E_{Turbine}$	The energy generated through the turbines in kW
$FibL$	The length of the fiber in the HF PRO module in m
$FibN_n$	The number of the fibers at certain radial n subsection in the HF PRO membrane
F_o	The basis function
i mentioned in Chapter Four	The Van't Hoff factor
$ICCP_j$	The average internal concentrative concentration polarization in the j membrane module in each PRO stage of the multistage PRO scenarios
$ICCP_{n,avg}$	The average internal concentrative concentration polarization in each PRO stage (n) of the multistage PRO scenarios
J mentioned in Chapter Three	Represents the PRO stag number
J_W / J_{PRO}	The water flux in the PRO in m ³ /m ² .h or in L/m ² .h
J_{wi}	The water flux in stage i of the multistage PRO scenario in L/m ² .h
J_{Wj}	The water flux in the j membrane module in L/m ² .h

$J_{wn,avg}$	The average water flux of each PRO stage of multistage PRO scenarios in $L/m^2.h$
J_{wtot}	The total water flux of the multistage PRO scenarios in $L/m^2.h$
J_{RO}	The product water flux of the RO in m/s
J_s	The salt flux of the PRO in $g/m^2.s$
k mentioned in Chapter Two	The mass transfer coefficient in m/s
K mentioned in Chapter Three and in Chapter Four	The solute diffusion resistivity of the PRO membrane in h/m
$k_d / k_{D,PRO}$	The mass transfer coefficient of the PRO draw side in m/s
$k_{F,PRO}$	The mass transfer coefficient of the PRO feed side in m/s
K_{FL}	The coefficient of the friction loss in the ERD in m
k_{RO}	The mass transfer coefficient of the RO feed side in m/s
K_x	The solute diffusion resistivity through the membrane porous layer at distance x of the membrane length in h/m
l_{PRO}	The length of the HF PRO membrane module in m
L_{RO}	The length of the pressure vessel of the RO in m
l_{RO}	The length of the RO membrane module in m
Lub_{flow}	The lubricant flow in the ERD in m^3/h
$Lub_{flowRatio}$	The lubricant flow ratio in the ERD
Mwt	The solute molecular weight in g/mol
%Mix _{ERD}	The mixing percentage of the ERD
m and n mentioned in Chapter Four	The subsection in the PRO membrane module in the axial and radial directions, respectively
M mentioned in Chapter Six	The number of the membrane modules in each PRO stage of the multistage PRO scenarios
M_{PRO}	Number of PRO membranes in a single pressure vessel
M / M_{RO}	The number of RO membrane's modules in a single pressure vessel
mT	The total number of sections in the axial direction of the PRO module
Mx	Mixer
N mentioned in Chapter Five	The number of data points
N mentioned in Chapter Six	The number of the PRO stages
NOP_{RO}	The number of pressure vessels of the RO
nT	The total number of sections in the radial direction of the PRO module
PackD	Packing density of the PRO membrane
$P_{d,D,PRO}$	the pressure drop in the draw (shell) side of the PRO membrane in bar
$P_{d,F,PRO}$	The pressure drop in the feed (lumen) side of the PRO membrane in bar
$P_{Di,PRO1}$	The draw inlet pressure of the PRO1 in bar
$P_{Di,PRO2}$	The draw inlet pressure of the PRO2 in bar
$P_{Do,PRO}$	The draw outlet pressure of the PRO in bar
$P_{Do,PRO1}$	The draw outlet pressure of the PRO1 in bar

$P_{Do,PRO2}$	The draw outlet pressure of the PRO2 in bar
P_{dRO}	The pressure drop in the RO pressure vessel in bar
$P_{F,RO}$	The hydraulic feed pressure of the RO in bar
$P_{F,RO1}$	The feed pressure of the RO1 in bar
$P_{F,RO2}$	The feed pressure of the RO2 in bar
$P_{Fi,PRO1}$	The feed inlet pressure of the PRO1 in bar
$P_{Fi,PRO2}$	The feed inlet pressure of the PRO2 in bar
$P_{Fo,PRO}$	The feed outlet pressure of the PRO in bar
$P_{Fo,PRO1}$	The feed outlet pressure of the PRO1 in bar
$P_{Fo,PRO2}$	The feed outlet pressure of the PRO2 in bar
P_{hi}	The high brine inlet pressure of the ERD in bar
P_{ho}	The low brine outlet pressure of the ERD in bar
P_i	The output predicted from the machine learning model
P_{li}	The low feed inlet pressure of the ERD in bar
P_{lo}	The high feed outlet pressure of the PX in bar
PN	The number of pumps
$P_{p,RO}$	The product pressure of the RO in bar
$P_{p,RO1}$	The product pressure of the RO1 in bar
$P_{p,RO2}$	The product pressure of the RO2 in bar
$P_{Pump,H}$	The head pressure of the pump in bar
$P_{Pump,i}$	The pressure of the inlet stream of the pump in bar
$P_{Pump,o}$	The pressure of the outlet stream of the pump in bar
$P_{R,RO1}$	The reject pressure of the RO1 in bar
$P_{R,RO2}$	The reject pressure of the RO2 in bar
$PRO1$	The first PRO unit
$PRO2$	The second PRO unit
$P_{Turbine,i}$	The pressure of the inlet stream of the turbine in bar
$P_{Turbine,o}$	The pressure of the outlet stream of the turbine in bar
PWD	The power density in W/m^2
Q_{Di}	The draw inlet flow rate of the PRO in m^3/h
$Q_{Di,1} / Q_{Di,PRO1}$	The draw inlet flow rate of the PRO1 in m^3/h
$Q_{Di,2} / Q_{Di,PRO2}$	The draw inlet flow rate of the PRO2 in m^3/h
$Q_{Di,x}$	The inlet flow rate of the draw solution to section x of the membrane in m^3/h
Q_{Do}	The draw outlet flow rate of the PRO in m^3/h
$Q_{Do,PRO1}$	The draw outlet flow rate of the PRO1 in m^3/h
$Q_{Do,PRO2}$	The draw outlet flow rate of the PRO2 in m^3/h
$Q_{Do,x}$	The outlet flow rate of the draw solution in m^3/h
$Q_{F,RO1}$	The feed flow rate of the RO1 in m^3/h
$Q_{F,RO2}$	The feed flow rate of the RO2 in m^3/h
Q_{Fi}	The feed inlet flow rate of the PRO in m^3/h
$Q_{Fi,1} / Q_{Fi,PRO1}$	The feed inlet flow rate of the PRO1 in m^3/h
$Q_{Fi,2} / Q_{Fi,PRO2}$	The feed inlet flow rate of the PRO2 in m^3/h
$Q_{Fi,x}$	The inlet flow rate of the feed solution in m^3/h
Q_{Fo}	The feed outlet flow rate of the PRO in m^3/h
$Q_{Fo,PRO1}$	The feed outlet flow rate of the PRO1 in m^3/h
$Q_{Fo,PRO2}$	The feed outlet flow rate of the PRO2 in m^3/h
$Q_{Fo,x}$	The outlet flow rate of the feed solution in m^3/h
Q_{hi}	The high pressure brine inlet flow rate of the ERD in m^3/h
Q_{ho}	The high pressure brine outlet flow rate of the ERD in m^3/h
$Q_{i,e}$ and $Q_{o,g}$	The inlet and outlet flow rate of each stream in the mixer or the splitter in m^3/h

Q_{li}	The low pressure feed inlet flow rate of the ERD in m^3/h
Q_{lo}	The low pressure feed outlet flow rate of the ERD in m^3/h
Q_P mentioned in Chapter Four	The final product water flow rate in m^3/h
Q_{pj}	The permeation rate in the j membrane module
Q_{pn}	The permeation rate of each PRO stage in the multistage PRO scenarios
$Q_{p,RO1}$	The product flow rate of the RO1 in m^3/h
$Q_{p,RO2}$	The product flow rate of the RO2 in m^3/h
$Q_{Pump,i}$	The flow rate of the inlet stream of the pump in m^3/h
$Q_{Pump,o}$	The flow rate of the outlet stream of the pump in m^3/s
$Q_{Px,j}$	The permeate flow rate at distance x in the membrane module along the stage j of the DSPRO
$Q_{R,RO1}$	The reject flow rate of the RO1 in m^3/h
$Q_{R,RO2}$	The reject flow rate of the RO2 in m^3/h
Q_{tot}	The draw and feed solutions' total inlet flow rate in m^3/h
$Q_{Turbine,i}$	The flow rate of the inlet stream of the turbine in m^3/h
$Q_{Turbine,o}$	The flow rate of the outlet stream of the turbine in m^3/h
R	The universal gas constant in $m^3.bar/mol.K$
R^2	The coefficient of determination
Re	Reynold number
$RecV_{PRO}$	The recovery rate of the PRO
$RecV_{RO}$	The recovery rate of the RO
RO1	The first RO unit
RO2	The Second RO unit
S	The PRO membrane structural parameter in m or μm
Sc	Schmidt number
SEC_{RO}	Specific energy consumption of the RO in kWh/m^3
Sh	Sherwood number
Sp	Splitter
T	Temperature in K
TN	The turbines number in the system
u_D	The draw solution velocity of the PRO in m/s
u_F	The feed solution velocity of the PRO in m/s
V	The solution velocity in m/s
W mentioned in Chapter Two and in Chapter Five	The PRO power density in W/m^2
W mentioned in Chapter Four	The energy generation of the PRO in kW
W_i	The power density resulting in stage i in the multistage PRO scenarios in W/m^2
W_j	The power density in the j membrane module
$W_{n,avg}$	The power density of each PRO stage in the multistage PRO scenarios
$W_{Pump} / W_{Pump,Consumed}$	The energy consumed of the pump in kW
W_{tot}	The total power density of the multistage PRO scenarios in W/m^2
$W_{Turbine}$	The energy generation of the turbine in kW
X	The input variable
X_{H2O}	The mass fraction of the water in the solution

X_{NaCl}	The mass fraction of the salt in the draw solution
x_{PRO}, y_{PRO}	Constants in mass transfer coefficient correlation of the PRO
x_{RO}, y_{RO}	Constants in mass transfer coefficient correlation of the RO
$\bar{y}_i$	The mean of the sample data
ρ_D	The draw solution density of the PRO in kg/m ³
ρ_{water}	The density of the feed water in ERD in g/m ³
$\Delta\pi / \Delta\pi_{PRO}$	Osmotic Pressure difference of the PRO in bar
$\Delta\pi_{RO}$	Osmotic Pressure difference of the RO in bar
$\pi_{D,b}$	The osmotic pressure of the PRO draw solution at the bulk in bar
$\pi_{F,b}$	The osmotic pressure of the PRO feed solution at the bulk in bar
ϵ	The porosity of the HF PRO module
η_{ERD}	The ERD efficiency
η_{Pump}	The pump efficiency
$\eta_{Turbine}$	The turbine efficiency
μ	The solute molecular weight in g/mol
μ_D	The draw solution viscosity of the PRO in kg/m.s
μ_F	The feed solution viscosity of the PRO in kg/m.s
Σ	The reflection coefficient

Abstract

An enormous amount of power is stored in the earth's waters due to the salinity variations between freshwater and seawater. Globally, around 37,300 km³ per year is the amount of river discharge, which can produce around 2 TW of renewable energy when mixed with seawater. One of the technologies employed to harvest salinity gradient energy is the Pressure Retarded Osmosis (PRO) process. Pressure retarded osmosis employs membrane technology for power generation from a pair of solutions of different salinity concentrations. It is not affected by weather conditions. Recently, more research has been published on this subject. Nevertheless, no one could successfully commercialize the PRO process to our knowledge. This study aims to determine the exact appraisal of PRO for technology feasibility and determination of the main impact of the optimum parameters on the process efficiency. Some of the objectives of this study are to build a computer model to predict the specific energy generation in a single-stage PRO system and a multistage PRO system to point out the advantages of the multistage PRO systems over conventional single-stage PRO systems.

The results reveal that the maximum specific energy generation (the total energy generated by the total initial feed and draw flow rates) in the dual stage pressure retarded osmosis (DSPRO) process with Dead Sea-Sea water salinity resources was 0.83 kWh/m³, showing a 71% increase in the maximum specific power generation at optimum operating conditions compared to the conventional operating conditions of equal flow rates and hydraulic pressure half of the osmotic pressure difference. Additionally, it has been suggested that utilizing the suggested hybrid system of two-pass reverse osmosis combined with DSPRO of 45000 mg/L seawater showed an 18% energy saving over the two-pass reverse osmosis model with the same conditions. Moreover, machine learning algorithms investigated and provided significant predictive power for the membrane's intrinsic parameters and power density based on the input parameters without doing any experiments. Furthermore, it has been noticed that the water flux and the power density boosted with the number of the PRO stages for all the investigated multistage PRO systems. The highest water flux and power density resulted in four PRO stages of values equal to 6 L/m².h and 15 W/m², respectively. The Dead Sea and wastewater salinity gradients produced the highest net specific energy generation of 0.82 kW.h/m³ over the other investigated types of salinity gradients.

Chapter One: Introduction

1.1 Introduction

Energy resources are depleting rapidly due to fast urban and industrial growth. The expected rise in energy demand for the next 30 years is more than one-third (37%) [1], forcing humanity to save energy and think of renewable sources as an alternative way of producing power. Common renewable energy sources are hydropower, solar, wind, marine energies, biomass, and geothermal. The most mature technology of all is hydropower [2]. Over the past 30 years, both hydropower and geothermal technologies have been stabilized. Wind, solar, and biomass research has increased since 1991 [2]. Hydropower, biomass, and geothermal are approaching parity with fossil fuels as contenders for electricity generation. [3]. Simultaneously, the costs of utilizing solar PV and wind technologies are continuously reduced due to their implementation enhancement [3].

The cost of producing electricity from renewable sources varies by technology, country, and time. It has been mentioned that the levelized expense of producing electricity by PV solar in 2014 was around 0.08 USD /kWh and 0.05 USD/kWh by using wind technology. The cost of producing electricity by biomass in the OECD countries 2014 was around USD 0.06/kWh, while it was USD 0.03/kWh in developing countries [3]. Differently, the price of geothermal plants ranged between 0.05 and 0.1 USD/kWh, and that of concentrated solar power (CSP) was between 0.17 and 0.35 USD/kWh.

Different countries around the world have various potentials for these renewable sources. For instance, the Kingdom of Saudi Arabia has an average value of more than 2200 kWh/m³ annually based on solar radiation limits [4]. Therefore, KSA is trying to lower its energy consumption using solar and nuclear power systems [5].

Energy consumption around the world varies in different countries as well. For instance, China was at the top of the list of energy-consuming countries in 2016, with around 23% of the world's total energy consumption. India is another big energy consumer in the world. It handled about 10% of the global increase in energy demand in 2013. Japan and the USA also consume much energy annually [5]. In 2014, the total world elementary energy consumption was around 160.310×10^9 MWh. This number could be forecasted to jump to $\sim 240.3 \times 10^9$ MWh in 2040 [6]. The practical prospect of sustainable energy is multiplied by 18 of the total global elementary power spent in 2015 [3]. However, renewable energy sources provided only 18% of the global energy need in 2015 [3]. A 30-80% increase in the share of renewable energy supply of the global power need is expected in 2100 [2]. For instance, the USA produces and consumes renewable

energy from various sources. As shown in **Fig. 1.1**, it consumed around 1461 million kWh by biomass in 2019 [7].

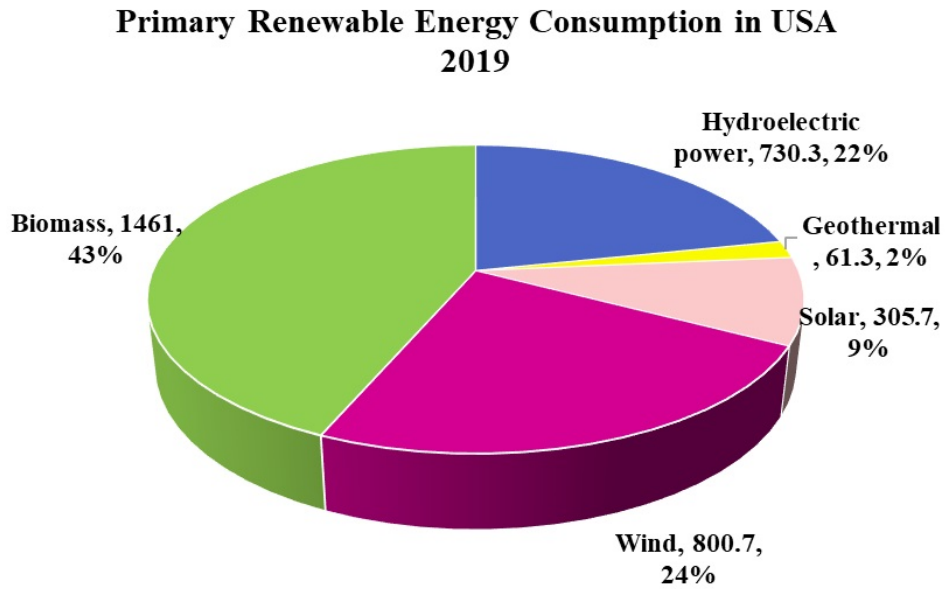


Fig. 1.1: The primary renewable energy consumption in the USA 2019. Sustainable energy sources include biomass, hydroelectric power, geothermal, solar, and wind. The values of the consumed energy are in millions of kWh. Figure adapted from Ref [7].

Around 260 billion USD was channelled annually in 2011 in the USA for renewable energy technologies [3]. Renewable energy sources are the most rapidly increasing and developing sources of electricity globally. The installed renewable electricity capacity worldwide has multiplied by two within around ten years from 2000 to 2011, with around 1000 GW of produced electricity by renewable sources globally in 2007 and 1560 GW in 2013. **Fig. 1.2** shows some renewable energy sources' capacity for power production in 2013. The diagram shows that the hydropower resources had the maximum power capacity over the other renewable sources included in the figure.

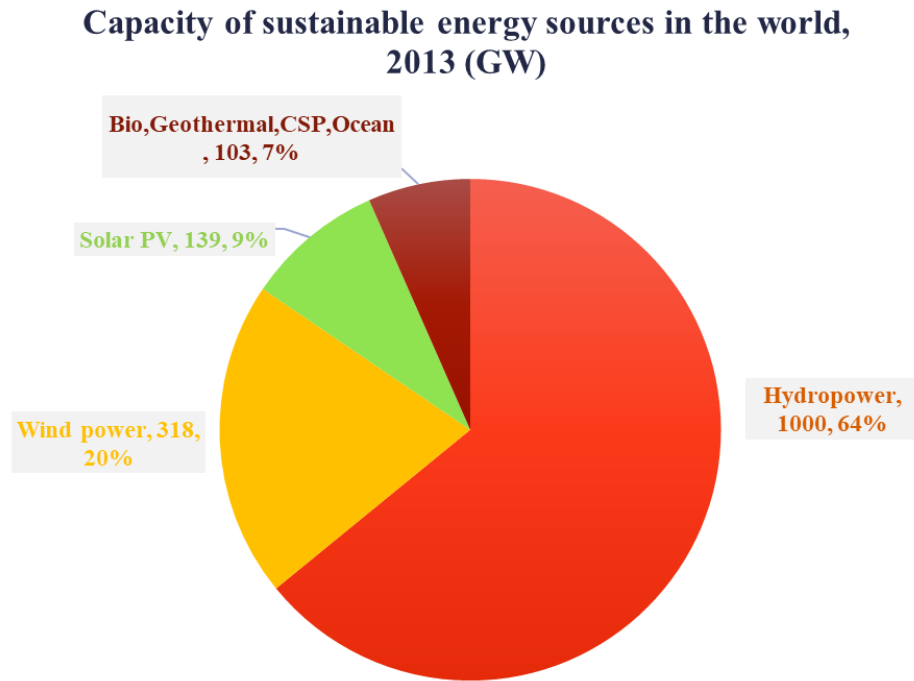


Fig. 1.2: Capacity in GW of sustainable energy sources worldwide, 2013. Figure modified from Ref [3].

Sustainable energy is acquired from everlasting sources; these sources are naturally reproduced. The most significant attribute of renewable energy, being clean, is infinite. It has much lower negative environmental impacts than conventional fossil energy [8]. Further, productizing and capitalizing on renewable energy sources would improve the world's energy security, lower conventional fuel prices, and save fossil fuel reserves for future generations. It would also reduce pollution and possibly minimize greenhouse gas emissions to levels that will settle greenhouse gases in the atmosphere. It might also decrease the reliance on imported fuels, support economic development, and offer new jobs [9].

Despite the considerable potential of existing renewable energy sources, their drawbacks should be mentioned. For instance, the hydropower technology necessitates the storage of huge amount of water, which results a damage to the nearby ecosystems [10]. On the other hand, solar energy technology suffers from the high initial cost of the solar panels in addition to the need of large area for installation [11]. Moreover, the scarce of the suitable project areas and the emissions drawbacks are some of the challenges that the geothermal energy production faces [12].

Following the discussion on the available renewable energy sources and the challenges they entail, the study will now introduce another renewable energy source under consideration. Pressure Retarded Osmosis (PRO) is considered a potential source of sustainable power, and it is found to be a higher power density and is more efficient than reverse electrodialysis [13]. It

produces hydraulic pressure from the osmotic pressure of a saline mixture (**Fig. 1. 3**). The main difference between the PRO and the forward osmosis (FO) is that in the PRO system the active layer of the membrane is facing the high saline solution, which eliminate the impact of the internal concentration polarization and enhance the specific power generation [14]. The major benefit of the dependence on the PRO for power production is that it will not inversely affect the environment [15-17]. Moreover, this source of sustainable power uses saline water sources [18-20] which additionally benefits the environment [21, 22] . Furthermore, PRO technology utilized in hybrid systems as coupling with reverse osmosis systems for the reduction of the consumed power through the desalination process [23, 24].

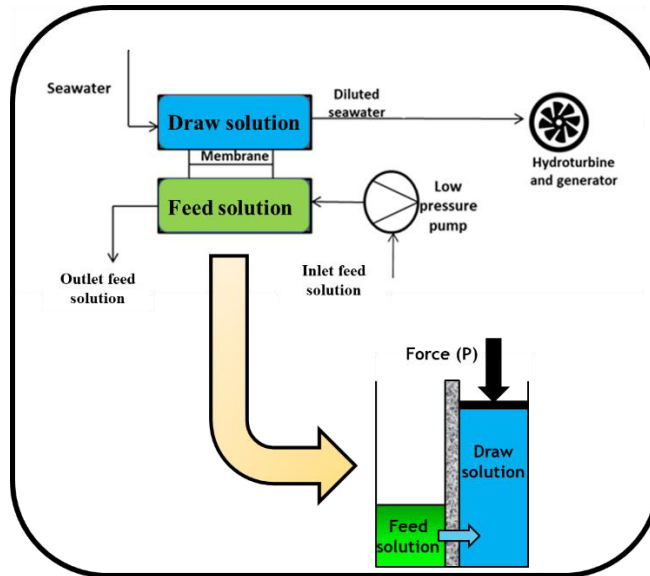


Fig. 1. 3: Schematic diagram of PRO process. Figure adapted from Ref [25].

1.2 Problem statement

The pressure retarded osmosis process suffers from the problem of concentration polarization [26, 27], which impacts the power produced by the salinity gradient sources. The concentration polarization in the PRO process at the feed solution side compromised water flux towards the pressurized draw solution [28]. To lessen the influence of concentration polarization in the PRO system, multistage PRO has been suggested as a new feed solution is pumped to each PRO stage. Another benefit of relying on the multistage PRO as a dual-stage PRO (DSPRO) system is that the second DSPRO stage will recover the remaining osmotic power in the draw solution out from stage one of the second DSPRO stage. Hence, a higher specific power will be generated [29]. Also, the exact osmotic driving force of the PRO system was not accurately calculated in the

previous work. The dilution of the draw solution and the concentration of the feed solution throughout the PRO module will affect the mass transfer coefficient, solute diffusion resistivity, and concentration polarization factors in the PRO system. Nevertheless, there is still a need to address the following PRO aspects:

- 1) There is a need better to understand the exact appraisal of PRO for technology feasibility and determine the main impact of the optimum parameters on the process performance, such as the draw and the feed solutions flow rates and the applied hydraulic pressure. Moreover, to the author's knowledge, no study has yet addressed the impact of the variations in the hydrodynamic condition, such as the mass transfer, solute resistivity coefficient, and a full-scale membrane module.
- 2) Additionally, the possibility of combining the DSPRO process with desalination processes in a hybrid system has not been investigated yet, and more studies are necessary to focus attention on the efficiency and feasibility of such hybrid systems, which have been pointed out in the PRO process.
- 3) Applying artificial intelligence to determine the PRO membrane's intrinsic parameters for optimum power generation needs further investigation.
- 4) Furthermore, the advantage of using multistage PRO on the system's performance with the possibility of investigating various salinity gradients is not widely addressed in the literature. It will help choose the best membrane module configuration for the highest energy generation.

1.3 Research questions

- 1) Yet, there is minimal number of studies evaluating the behaviour of the PRO system at optimum operating parameters. Previous research investigated the performance and energy generation in the PRO process at conventional testing conditions, i.e., equal flow rates for the feed and the draw solution and hydraulic pressure difference is half of the osmotic pressure difference ($\Delta P = \Delta \pi / 2$). Additionally, most previous studies assume constant mass transfer and solute resistivity coefficients. How do the pressure drop, mass transfer, and solute resistivity coefficient variation in a full-scale PRO module affect the process's performance?
- 2) What is the DSPRO performance at optimum operating parameters in comparison to a single-stage or the conventional PRO system? The contribution of the second DSPRO stage to the total specific energy generation in the DSPRO system at optimum operating conditions should be reported.

- 3) What is the feasibility of coupling DSPRO with desalination systems such as reverse osmosis (RO)? The specific power generation of the DSPRO hybrid system and its impact on the brine concentration should be investigated.
- 4) Would the multistage PRO be preferable over the conventional single-stage PRO for energy generation? What are the best possible salinity gradient resources and the operating conditions for higher energy generation?

1.4 Aim of the research

The main aim of this work is to comprehensively investigate the pressure retarded osmosis process for energy generation in order to define the optimal parameters and the best possible configuration for maximizing the production of the renewable energy.

1.5 Research objectives

The primary objective of this work of this work is to investigate the feasibility of the PRO process for energy generation. Many parameters influence the behaviour of the PRO system, and to accomplish the best process behaviour, these parameters must be studied. Accordingly, the main objectives behind this work are as follows:

- 1) To develop a computer model to anticipate the energy generation in the PRO system, power density, and the water flux where the salinity gradient concentrations the applied pressure on the draw solution side and the feed solution side will be the required inputs. The model will apply to various membrane areas and can be adjusted and used for variation of membrane module number or arrangement inside the single PRO stage, the two stages of the DSPRO, and all stages in the multistage PRO.
- 2) To determine the optimum parameters that govern the DSPRO system performance using a full-scale PRO membrane. The study will investigate the effect of the hydrodynamic conditions, including flow rates of feed and draw solutions, the pressure drop in the element, and variation in mass transfer and solute resistivity coefficients on the system performance.
- 3) To evaluate the feasibility of combining the DSPRO system with desalination processes for minimizing the desalination energy consumption and the brine's effect on the seawater.
- 4) To employ the artificial neural networks and Boosting-based tree models to predict the intrinsic parameters of the pressure retarded osmosis membrane based on the

minimum theoretical power density that could be predetermined and was presumed to be 5 W/m² in this study.

- 5) To compare the process performance of single and multistage PRO systems at optimum operating parameters, salinity gradients, and membrane module configurations.

1.6 Thesis outline

The thesis includes seven chapters.

Chapter One is the “Introduction”, including the problem statement, research questions, objectives, and thesis outline.

Chapter Two is the “Literature review” where detailed information regards pressure retarded osmosis, and all of the parameters that affect it can be found.

Chapter Three is the “Impact of Hydrodynamic Conditions on Optimum Power Generation in Dual Stage Pressure Retarded Osmosis using Spiral-Wound Membrane.”. In this chapter, a spiral wound PRO model was conducted, and the DSPRO system was determined to evaluate the optimum power generation.

Chapter Four is the “Experimental and Theoretical Work on Reverse Osmosis - Dual Stage Pressure Retarded Osmosis Hybrid System”. This chapter uses experimental data to design and validate a hollow fibre PRO plug-flow model. Then, it was used with an RO model to evaluate the energy enhancement through the hybrid system.

Chapter Five is “Machine Learning for Intrinsic Membrane Parameters and Power Density Prediction in Pressure Retarded Osmosis”, where machine learning algorithms are employed to predict the PRO membrane’s intrinsic parameters.

Chapter Six is “Multiple staging of pressure retarded osmosis: impact on the energy generation”, where the multistage PRO performance is investigated via various salinity gradients and membrane modules configurations.

And, Chapter Seven is the “Findings and Future Work”.

Chapter Two: Literature review

This chapter has been published in a review paper: Nahawand AlZainati, Haleema Saleem, Ali Altaee, Syed Javaid Zaidi, Marwa Mohsen, Alaa Hawari, Graeme J. Millar, Pressure retarded osmosis: Advancement, challenges and potential. *J. Water Process. Eng.*, 2021. 40 DOI: 10.1016/j.jwpe.2021.101950.

2.1 Introduction

Conventional energy production methods utilizing non-renewable fossil-fuel resources possess numerous weaknesses [30-33]. For example, power plants operated by fossil fuels generate greenhouse gases which can cause environmental damage [34-36]. Consequently, the demand for eco-friendly, as well as sustainable energy production systems is rising [37, 38]. 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 [39, 40]. Furthermore, fuel cell systems still need the development of the membrane to meet the complex operational conditions [41, 42]. Pattle et al. [43] and Loeb et al. [44, 45] initially presented the pressure retarded osmosis (PRO) definition as generating electrical power using water flux brought about by the osmotic power gradient 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 [15-17]; 2) the compact size of the membrane-based system lessens 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 [18-20]; 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 [21, 22].

Despite its numerous benefits, the pressure retarded osmosis system experiences several issues which inhibit commercialization. This situation is because of factors such as not only the deficiency of exceptional membranes which can function at increased pressure but also fouling issues, which diminish the water flux across the membrane [46-50]. Additionally, adverse phenomena like internal concentration polarization can remarkably decrease the effective osmotic gradient applied to the membrane; therefore 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 [51]. Several researches have been conducted to perceive 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 [52]. 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 [53, 54]. **Table 2.1** 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 [55, 56]. Hence, the minimum energy requirements, inclusive of pretreatment energy and power losses, must be recognized. In a study performed by Anthony et al. [56], an examination of the process feasibility for the production of power from the seawater-river water salinity gradient was reported. This work confirmed that the power produced by the pressure retarded osmosis process was lesser relative to the energy needed for the pretreatment in addition to the pumping of the draw and feed solutions. The highest energy produced by seawater-river water was 0.250 kWh/m³. In contrast, the highest available 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/m³, which can be greater relative to the maximal energy generation of the seawater-river water salinity resources [57].

Table 2.1: 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 [16, 58-61], some of these studies did not mentioned the PRO hybrid systems [58] or the DSPRO process[61]. While other papers did not include the maximum power generated by various salinity gradients in detailed manner. Other's focused only on the PRO membranes [60]. Therefore, the focus of this work is to furnish comprehensive information on all aspects concerning PRO systems, as outlined below.

This review paper explores various commercial PRO membranes, such as Toyoba, HTI, Toray, etc., provides insights into laboratory-developed membranes, discusses dual-stage PRO, and

dives into the energy of pretreatment. Until now, only a limited number of studies have addressed the ongoing advancements, diverse simulation analyses, and potential future applications of the pressure retarded osmosis process [61-64]. Nevertheless, based on our current understanding, there is a scarcity of studies that have explored commercial PRO membranes, laboratory-fabricated membranes, salinity gradient resources, the energy involved in pretreatment and inputs, the process design including the potential integration of 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.

2.1 Pressure retarded osmosis membranes

2.1.1 Commercial pressure retarded osmosis 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 [65]. Hollow-fiber forward osmosis membranes developed by Toyobo Co. Ltd. have a large active area that spreads 700 m² and operates with feed pressures of up to 30.0 bar; which makes these membranes appropriate for treating a salinity resources of osmotic pressure difference 60 bar. Saito et al. [66] 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 influence of the concentration polarization effect next to the membrane's surface 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/m² 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 in addition to 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 cm² [67],

20.02 cm² [68], and 18.75 cm² [25]. 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/m².h in the forward osmosis mode and 49.0 L/m².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/s 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) [69]. This pilot plant test confirmed the significance of feed water pretreatment for preventing the fouling of the membrane. Primarily, microfiltration and reverse osmosis processes were 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 system have been moreover diminished by adding a fourth port on the membrane feed side [66]. The Megaton venture effectively demonstrated an osmotic power plant model with 10.0 W/m² 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 power. 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 m² membrane area, fiber of internal diameter (ID) 0.2 mm), HFFO2 (2.3 m² membrane area, fiber ID 0.2 mm), HFFO.6 (0.6 m² 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 shown in **Table 2.2**. Pressure retarded osmosis mode test results are provided in this table for a more extensive comparison. In the Megaton Water project [69, 70], the maximum membrane power density per surface area attained was 13.50 W/m² 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 represented the feed solution and concentrated brine represented the 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 feed solutions, 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 2.2: 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	[70]
Toyobo 10-inch HFM module Polymer: Cellulose triacetate	1 M sodium chloride	30	13.3	[70]
Toyobo 10-inch HFM module Polymer: Cellulose triacetate	1 M sodium chloride	29	4.4	[66]
Toyobo 10-inch HFM module Polymer: Cellulose triacetate	1 M sodium chloride	25	7.7	[66]
HTI OsMem Spiral-wound membrane (SWM) module Polymer: Cellulose triacetate	1.03 M sodium chloride	4.0	1.10	[71]
HTI OsMem SWM module Polymer: Polyamide	0.60 M sodium chloride	9.8	1.00	[72]
Toray Chemical Korea 8040 SWM pressure retarded osmosis module Polymer: Polyamide	0.60 M sodium chloride	10.4	1.77	[73]
HTI OsMem SWM module Polymer : Cellulose triacetate	0.52 M sodium chloride	4.0	0.57	[71]

As per HTI, the membrane element used in the study [71] 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 m². 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 Kim et al. [72] research, 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 m², and twenty membrane envelopes were designed in 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. [73], 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 m² of membrane area with a

coating of polyamide. As per Toray, a distinct spacer for the feed solution was utilized for reducing the pressure resistance of the feed channel. The draw channel spacer had a thickness of about 0.80 mm and 97 cm² cross-section area.

2.1.2 Laboratory fabricated membranes

The best pressure retarded osmosis membrane need to be mechanically robust in order to withstand increased pressures, exhibit supreme water permeability, as well as low salt permeability [74, 75]. Advancement of the pressure retarded osmosis technology has been inhibited by the scarcity of effective membranes until the latest developments in PRO studies. Similar to other TFC-based membranes, the pressure retarded osmosis membrane support layers were developed in the form of 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 aforesaid 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 2.3**, together with its efficiency.

Table 2.3: Comparison of different polymer pressure retarded osmosis membrane modifications and their efficiency.

PRO membrane modification	Feed solution/Draw solution	Water Flux, (L/m².h)	Power Density, (W/m²)	Ref.
Polyethersulfone thin-film composite membranes with magnesium chloride	Deionized water / 1.20 M sodium chloride solution	38.0	27.4	[76]
Polyethersulfone thin-film composite membranes with Lithium chloride	Deionized water / 1.20 M sodium chloride solution	46.0	32.4	[76]
Polyethersulfone thin-film composite membranes with Calcium chloride	Deionized water / 1.20 M sodium chloride solution	50.0	34.7	[76]
Active layer etching using 1000 mg/L sodium hypochlorite	River water / Synthetic seawater	53.0	10.2	[17]
Active layer etching using 1000 mg/L sodium hypochlorite	Brackish water/ Synthetic seawater	40.0	7.9	[17]
Zwitterion coating at the bottom of the polyethersulfone substrate	Wastewater from municipal recycling plant / Synthetic seawater brine	Not applicable	7.2	[77]

2.1.2.1 Flat-sheet pressure retarded osmosis 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 [78]. They reported a power density of 2.60 W/m² 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. In work by Wei et al. [79], 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 as well as stability. In the study by Cui et al. [80], TFC membranes were developed which 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/m²). 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. [81], and the support was tiered using nanofiber layers of various diameters for better withstanding the hydraulic pressure. The membranes effectively handled 11.5 bar applied hydraulic pressure and showed a performance that could generate an equivalent peak power density of almost 8 W/m² in practical conditions. Moon et al. [82] prepared two electrospun membrane types utilizing: 1) an inherently strong thermally rearranged poly(benzoxazole-co-imide), 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. 2.1** presents the PRO performance of the membranes as a function of the various hydraulic pressures. Kim et al. [51] 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/m²). **Table 2.4** shows the behavior of various flat sheet membranes stated in the literature.

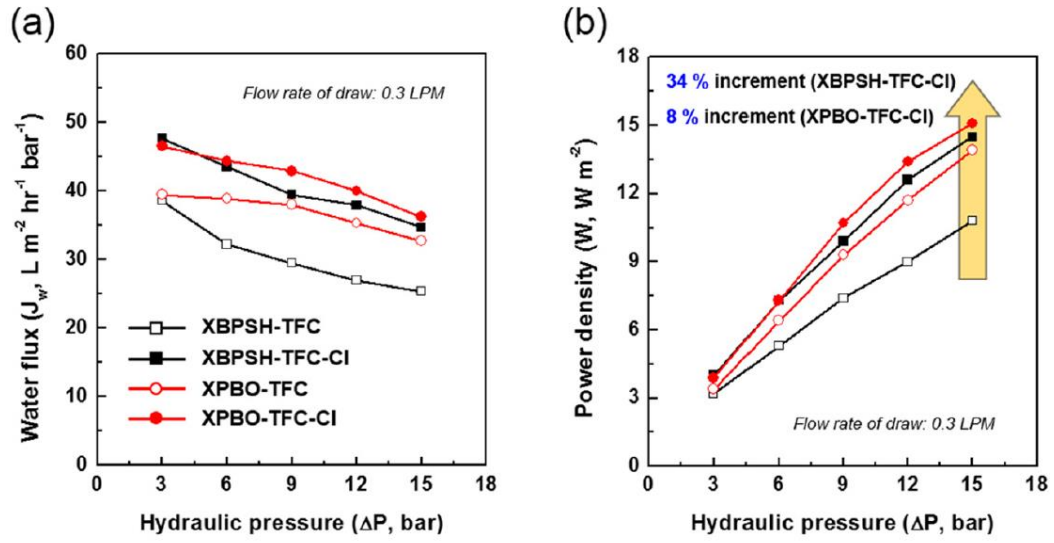


Fig. 2.1: (a) Water flux as well as (b) power density of Crosslinked Sulfonated poly (aryleneether sulfone) (XBPSH)-TFCs and Crosslinked poly (benzoxazole-co-imide) (XPBO)-TFCs as per the various hydraulic pressures. Reproduced from Ref [82].

Table 2.4: Performance of different flat-sheet membranes discussed 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	[83]
Polyamide-polysulfone	1 M Sodium chloride	Deionized water	12.9	22	[79]
Polyamide-polyimide	1 M Sodium chloride	Deionized water	18.09	22	[80]
Polyamide-polyacrylonitrile nanofiber	0.5 M Sodium chloride	Deionized water	8.0	11.5	[81]
Polyamide- Sulfonated poly(arylene ethersulfone), poly(benzoxazole-co-imide)	1 M Sodium chloride	Deionized water	26.6	21	[82]
Polyamide-polybenzoxazole-co-imide	2000 ppm Sodium chloride	Deionized water	40	15	[51]
Polyamide-polyamide-imide	3.5 % Sodium chloride	Deionized water	2.84	6	[84]
Polyamide-Matrimid	1 M Sodium chloride	Deionized water	6	15	[85]

When comparing the performance of different flat-sheet laboratory-fabricated membranes with the commercially available membranes, it is worth mentioning 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/m². In spite of this, the fact that the laboratory membranes require to have extensive field test and their long-term performance should also be proved. Moreover, maintaining the superior performance of membranes from small-scale membranes to modules can be regarded as a significant problem.

2.1.2.2 Hollow-fiber pressure retarded osmosis membranes

An advanced integral PRO hollow-fiber membrane (HFM) was fabricated by Li et al. [86] 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/m² 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) toward feed solution (FS) orientation (forward osmosis mode) conferred a substantial benefit over the active layer toward 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. [46], 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 having water solubility, increased hydrophilicity, along with exclusive chemistry, was molecularly prepared through a single-stage free-radical polymerization process. Due to the exceptional hydrophilicity, exclusive anionic and cationic groups as well as electrical neutrality of the zwitterionic brush, this advanced membrane showed increased resistance against organic fouling and inorganic scaling in the pressure retarded osmosis processes.

In general, a power density value of 5.0 W/m² 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. [87] stated that a power density value of 5.70 W/m² 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 [88]. This highly efficient thin-film nanofiber composite-PRO membrane could accomplish a power density of almost 15.20 W/m^2 as well as 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 draw and feed solutions, respectively. Zhao et al. [77] 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. [89] accomplished a power density of almost 20.90 W/m^2 at 15 bar pressure, using 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. [76] highlighted advanced techniques for designing an inner-selective TFC pressure retarded osmosis HFM with increased operating pressure and a superior power density by the addition of 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 high economical among other renewable sources of energies. **Table 2.5** presents the behaviour of various hollow-fiber membranes reported in different literature.

Table 2.5: Efficiency of various hollow-fiber membranes reported in the literature.

Material	Draw Solution	Feed solution	W (W/m²)	ΔP (bar)	Ref.
Polyamide-imide	1.0 M sodium chloride	Real wastewater	4.3	13	[86]
Polyamide-polyethersulfone	Synthetic RO brine (1 M sodium chloride)	40.0 mM sodium chloride	10.6	12	[87]
Polyamide-Polyacrylonitrile (PAN) nanofiber support	1.06 M sodium chloride	80.0 mM sodium chloride	15.2	15.2	[88]
Polyamide-polyetherimide	1.0 M sodium chloride	1 mM sodium chloride	20.9	15	[89]
Polyamide-polyethersulfone	1.2M sodium chloride	Deionized water	38	30	[76]
Polyamide-polyethersulfone	0.6M sodium chloride	Deionized water	2.98	7	[90]
Polyamide-polyethersulfone	1M sodium chloride	Deionized water	8	18	[91]
Cellulose acetate	1M sodium chloride	Deionized water	5.5	18	[92]
Polyamide-polyethersulfone	1M sodium chloride	Deionized water	10.05	22	[93]
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	[77]

The present laboratory-fabricated pressure retarded osmosis membranes, both hollow-fiber and flat-sheet types are typically eligible for meeting the economically feasible power density of 5 W/m². Demo research has been extensively performed in several countries from laboratory-scale to pilot-scale and has proved to be practicable. Conversely, there exist several challenges that must be addressed for additionally activating the advancement in pressure retarded osmosis technology for accomplishing the commercial stage. Moreover, there must be 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 are cautiously considered. Several studies for evaluating the commercial feasibility of the pressure retarded osmosis process typically have a serious limitation, that is, exclusion of the pretreatment costs. For increasing the consistency of feasibility studies, the models should be wisely taken into account with the inclusion of different components such as membrane modules, pumps, pre-treatments, hydro-turbine, and pressure exchangers.

2.1.3 Emerging membranes with nano-materials

Nanomaterials are considered to be very promising materials and different studies have been performed to examine the application of nanomaterials in various fields and also its related environmental impact [94-100]. 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 [101-107]. The addition of nanomaterials into pressure retarded osmosis membranes to develop thin-film nanocomposite (TFNC) membranes has demonstrated improvement in its hydrophilicity as well as the porosity, resulting in increased water flux along with osmotic power in the course of PRO process [108]. **Table 2.6** presents the performance of different nanomaterial incorporated membranes reported in the literature.

Table 2.6: Performance of some of the nanomaterial incorporated membranes reported in the literature.

Material	Nanomaterial used	Feed solutions	Draw Solutions	Power density in W/m²	Pressure bar	Ref.
Polyamide-polyethersulfone	Graphene oxide	Deionized water	Sodium chloride (1.0 M) solution	14.6	16.5	[101]
Polyamide-polysulfone	Graphene oxide	Deionized water	Sodium chloride (1.0 M) solution	16.7	21	[102]
Graphene oxide	Graphene oxide	0.017 M sodium chloride solution	Sodium chloride (1.0 M) solution	24.62	6.90	[109]
Polyamide-polyethersulfone	Carbon nanotubes	Deionized water	Sodium chloride (0.5 M) solution	1.6	6	[103]
Polyamide-polyetherimide	Carbon nanotubes	Deionized water	Sodium chloride (1M) solution	17.3	16.9	[110]
Polyamide-polyethersulfone	Carbon quantum dots	Deionized water	Sodium chloride (1M) solution	34.2	23	[111]
Polyamide-imide	Schiff base network-1	Deionized water	Sodium chloride (1M) solution	12.1	24	[112]
Polyamide-polyethersulfone	Carbon quantum dots	High alginate concentration (1 g/L)	0.81 mol/L NaCl	11	15	[113]
Polyacrylonitrile (PAN) nanofiber support membrane	Nano-silicon dioxide	80 mM NaCl synthetic brackish water	Seawater brine (1.06 M) solution	21.3	15.2	[88]

2.1.3.1 Graphene-oxide based pressure retarded osmosis 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 [114, 115]. 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 examined.

Park et al. [101] emphasized the development of TFC PRO membranes for increased osmotic power utilizing hollow fiber PES support framework modulated by the addition of hydrophilic

GO nanosheets. The concentration of graphene oxide in the hollow fiber substrates was altered to upgrade 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 salinity gradient solutions, respectively (**Fig. 2.2**). The test results indicated that the pressure retarded osmosis hollow fiber support layer modification by the incorporation of nanomaterials like graphene oxide nanosheet could be a beneficial tool for improving the PRO efficiency.

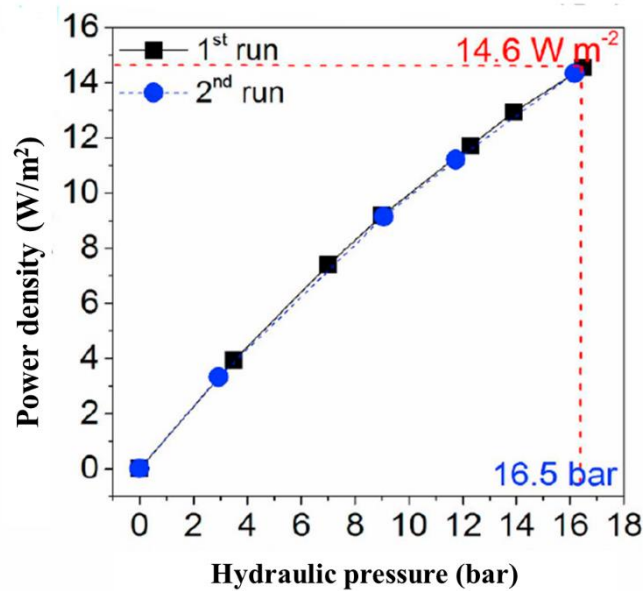


Fig. 2.2: Power density versus hydraulic pressure of THF-GO-0.2 with 1M sodium chloride (NaCl) as the draw solution and deionized (DI) water as the feed solution. Reproduced from Ref [101].

Lim and coworkers manufactured a TFC membrane with a double-layered nanocomposite substrate, prepared utilizing a double-blade casting method; to utilize in osmotic power production by the PRO method [102]. 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. 2.3** 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 considered to be 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.

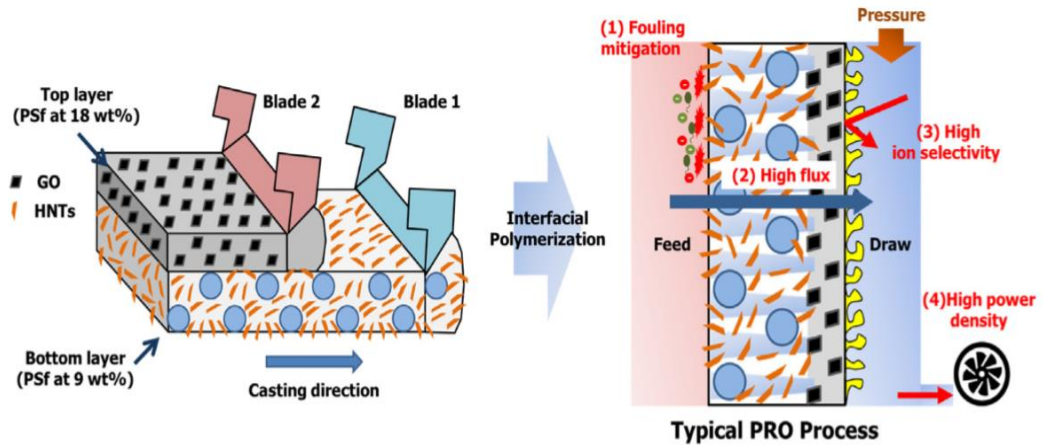


Fig. 2.3: Hypothetical model of the double-layered thin-film composite PRO membranes with halloysite nanotubes and graphene oxide incorporated in the bottom and topmost substrate layer, respectively. Reproduced from Ref [102].

2.1.3.2 Carbon nanotube (CNT) based pressure retarded osmosis 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 which are differentiated based on whether they comprise of a single graphene wall (Single-walled CNTs), or of 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 to be a very effective nanomaterial for increasing membrane hydrophilicity, porosity, as well as the negative membrane charge, leading to superior membrane performance concerning fouling resistance, selectivity, and permeability [116]. Son et al. [103] suggested the utilization of a carbon nanotube-integrated support layer for TFNC membranes in the pressure-retarded osmosis process for energy production using saltwater. The aforementioned thin-film nanocomposite membrane takes benefit of the improved porosity along with hydrophilicity brought about by functionalized-CNT in addition to the chemical etching of the polyamide selective layer for additionally increasing water flux. By the approach above, the maximum power density was improved by 110.0 %, relative to the results attained utilizing pristine thin-film composite membranes using deionized water and artificial seawater (0.5 M NaCl) which was utilized 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 layer materials of commercially used pressure retarded osmosis membranes vary, the carbon nanotubes could enhance the hydrophilicity along with the porosity of the support layer, leading to improved power density. Tian et al. [110] created tiered structured polyetherimide (PEI) nanofiber supports comprising of 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 inclusion of 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. 2.4A**) 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 opened multiwalled CNTs. The magnified TEM image in **Fig. 2.4B** confirmed the hollow structure of the multiwalled carbon nanotubes with an opened tip. This optimized membrane showed the ability to tolerate a transmembrane 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.

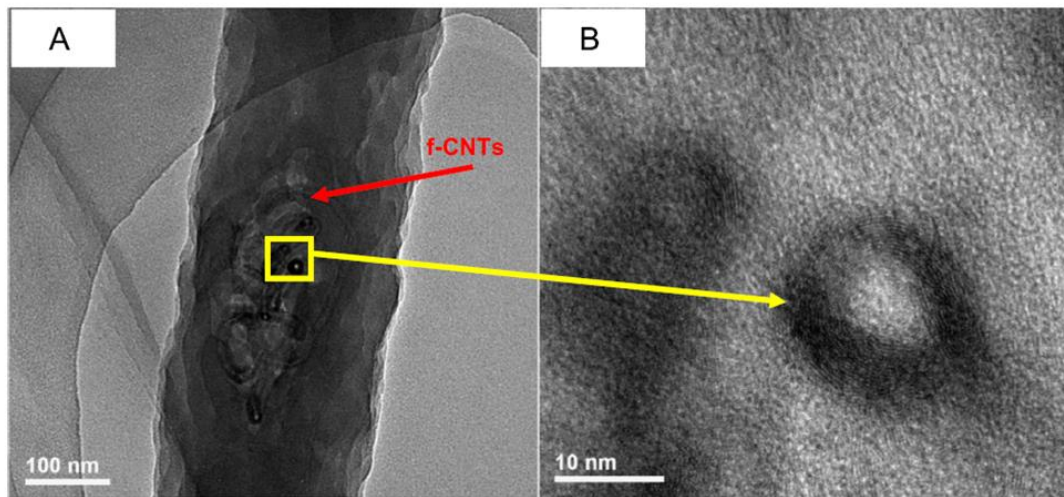


Fig. 2.4: (A) TEM image of f-CNTs inside the PEI nanofiber; (B) enlarged. Reproduced from Ref [113].

2.1.3.3 Carbon quantum dots-based pressure retarded osmosis 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 [117]. Gai et al. [111] 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/m² 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. [113] 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 modulated membranes showed an increased power density (11.0 W/m² versus 8.8 W/m²) and water recovery after back-washing (94.0 % versus 89.0 %) as compared to the unmodified membrane.

2.1.3.4 Silica nanomaterial-based pressure retarded osmosis 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. [118] 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/(m²h) while using 10.0 mM sodium chloride as a feed solution and 1.0 M sodium chloride draw solution. When compared with the thin-film composite membrane without incorporated zeolite, it demonstrated a water flux of just 21.50 L/(m²h) 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. [119], 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 due to the increased osmotic pressure gradient. While tested utilizing the 2.0 M sodium chloride solution as DS 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/(m²h). A zeolite-embedded thin-film nanocomposite membrane was also developed and examined in a

study performed by the work of Salehi et al. [120] for PRO utilization. The influence of nanostructured zeolite on the features of a polyether sulfone 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/(m²h).

Niksefat et al. [121] prepared an advanced type of thin-film nanocomposite membrane by the addition of silicon dioxide nanoparticles into PA active layer. The efficiency of the resulting membrane 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 water flux of the thin-film nanocomposite membrane was enhanced from 15.50 to 36.50 L/(m²h) as the silicon dioxide concentration rised from 0.0 to 0.1% (w/v). The pristine thin-film composite membrane demonstrated just 15.0 L/(m²h) under similar test conditions. Silicon dioxide consisting thin-film nanofiber composite PRO membranes were fabricated by Song et al. [88] 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/m² 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.

2.1.3.5 Metal nanomaterial-based pressure retarded osmosis membranes

Titanium dioxide is considered to be 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. [122] customized 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 feed solution and 2.0 M sodium chloride solution as draw solution. The leading performing membrane, with 0.5% titanium dioxide, was noted to have a water flux of 56.27 L/(m²h), which was almost 87.0 % greater relative to the pristine thin-film composite membrane.

Kim et al. [123] 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 as compared to a commercially available thin-film composite membrane in the existence of humic acid foulants. Consequently, high-performance as well as fouling resistant pressure retarded osmosis membrane may be developed using a titanium dioxide sol-gel-derived spray coating technique.

2.1.3.6 Covalent organic framework -based pressure retarded osmosis 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. [112]. 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 existence 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. 2.5** 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 (Ra), as well as root, mean square ridge elevation (Rms) is also shown. The mean roughness values were noted to enhance with the concentration of the nanomaterial.

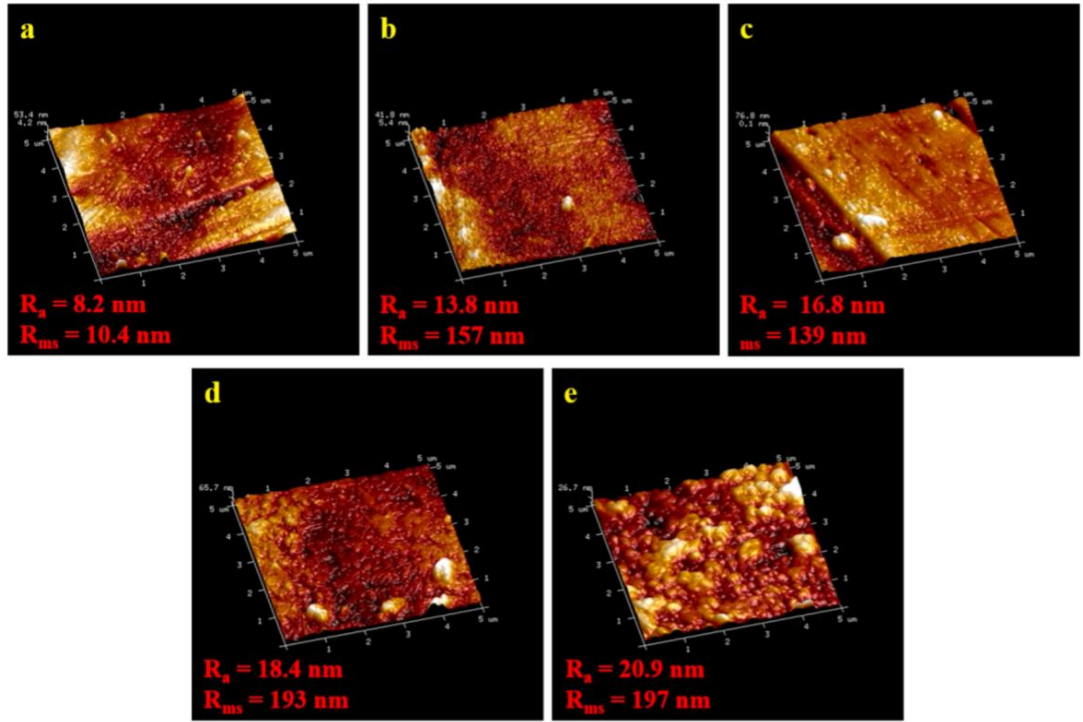


Fig. 2.5: Surface roughness of thin-film composite and thin-film nanocomposite membranes attained by atomic force microscopy analysis of (a) thin-film composite, (b) thin-film nanocomposite-0.01, (c) thin-film nanocomposite-0.02, (d) thin-film nanocomposite-0.05, and (e) thin-film nanocomposite-0.1 pressure retarded osmosis membranes. Reproduced from Ref [112].

Testing with 1 M sodium chloride draw solution, the thin-film nanocomposite membrane having 0.020 wt.% nanomaterial concentration reached a power density of 12.10 W/m^2 and the greatest water flux of $42.50 \text{ L/m}^2/\text{h}$, 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 for improving both energy harvesting ability and osmotic performance of the PRO process.

2.1.3.7 Other nanomaterial-based pressure retarded osmosis membranes

Layered double hydroxide/GO hybrid was used as nanofillers for polysulfone substrate for the development of thin-film nanocomposite membrane, as reported by Lu et al. [124]. 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 $23.60 \text{ L/(m}^2\text{h)}$ under the PRO mode.

Zirconium (IV)-carboxylate metal-organic framework UiO-66 nanomaterials have been efficiently prepared by Ma et al. [125] 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 amalgamation 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 PRO 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 that is generated by the existing nanomaterial-incorporated thin-film nanocomposite membranes varies.

2.2 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.

2.2.1 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 gradient 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 [126]. PRO feed solutions of low salinity could be: brackish water, river water [127] or wastewater, while the high salinity and pressurized draw solutions could be: seawater [64, 127] or brine [128]. Seawater or brine from RO systems and freshwater or wastewater effluent were suggested as salinity gradients for PRO systems [25, 29, 66, 87, 129-132]. The most well-known PRO salinity gradients are river water and seawater [133]. On the other hand, a maximum power density of 7.7 W/m² resulted from a pilot-scale study using seawater concentrate and wastewater effluent resources [66]. A high power density of 230 W/m² resulted when Dead Sea water was utilized with seawater (35

g/L), this value dropped to 70 W/m² when concentration polarization effects were considered [29]. Soltani [28] proposed that using RO brine instead of seawater as a draw solution caused improvement in specific energy values.

By 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 [134]. It is noteworthy that the available power, which can be extracted from the mixing process of river water with seawater in the PRO system, is determined to be around 1.4-2.6 TW [135]. However, practically the extractable energy may deviate. Researchers [136] 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/m³. 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/hm², respectively [137].

A huge power amount is stored in the earth's waters as a result of the salinity variations between freshwater and seawater [138]. Globally, around 37,300 km³ per year is the amount of river discharge, which can produce around 2TW renewable energy when mixing with seawater [136]. **Fig. 2.6** represents the available extracted energy from varied feed resources on a theoretical basis [139].

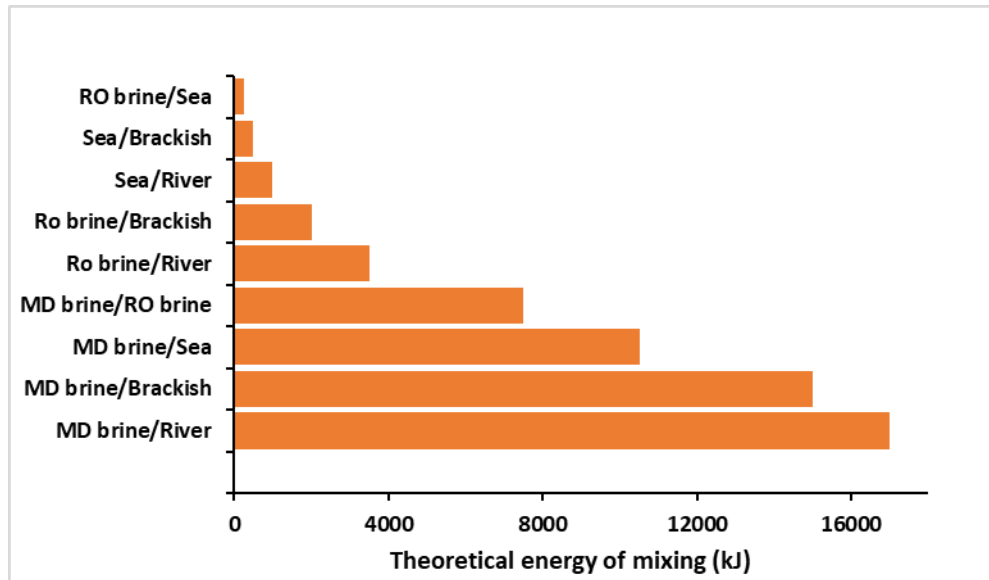


Fig. 2.6: The energy produced theoretically through mixing various feed sources: 10^{-5} , 10^{-4} , 5×10^{-4} , 10^{-3} , 5×10^{-3} mM NaCl of river water, brackish water, seawater, reverse osmosis (RO) brine and membrane distillation (MD) brine, respectively. Each of brine and seawater was determined as HCC solution. Figure adapted from Ref [139].

As shown in **Fig. 2.6**; 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 [139]. 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 [139]. 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/m³ as shown in **Table 2.7** [61]. Nevertheless, by changing the draw solution to such a higher salinity one like the seawater reverse osmosis (SWRO) brine (13 M salinity) then the net extractable work can reach 0.66 kWh/m³. This explains the importance and effectiveness of the used salinity gradients on the PRO process and that because of the corresponding osmotic pressure difference.

Table 2.7: Draw solution salinity effect on theoretical producible power per draw solution volume in m³. Table adapted from Ref [61].

	Seawater-River water PRO kWh/m ³	SWRO Brine-River water PRO kWh/m ³
Calculated ΔG_{mix}, 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 [140]. 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 applied pressure for the various operating modes. The used salinity gradients are presented in **Fig. 2.7**.

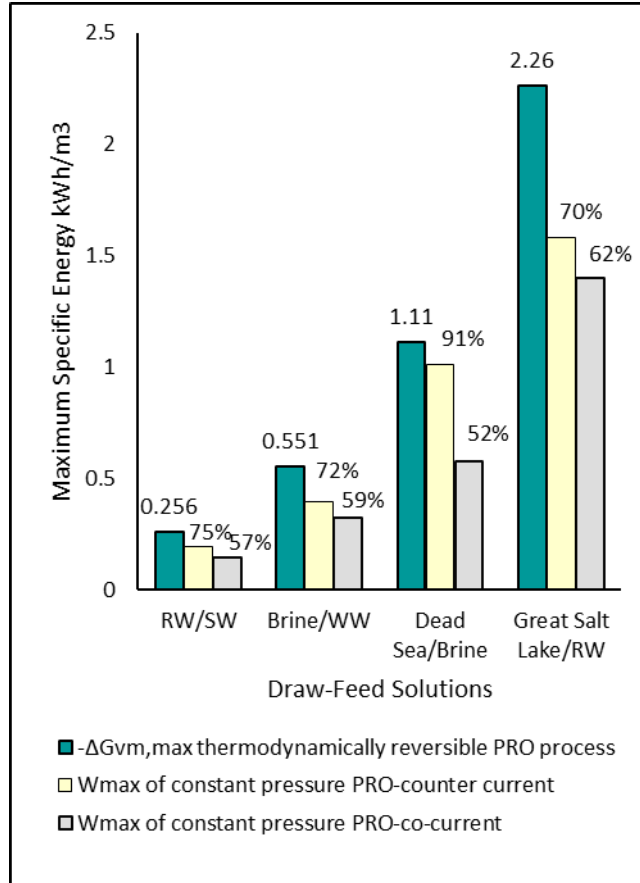


Fig. 2.7: The theoretical achievable maximum specific energy in three PRO system's modes for various solutions. The percentage of the maximum specific energy for counter and co-current PRO is referred to the maximum thermodynamically reversible PRO system. The figure adapted from Ref [140].

As shown in **Fig. 2.7**, for the case of river water (RW) of 0.015 M sodium chloride and seawater (SW) of 0.6 M sodium chloride as the salinity resources for constant pressure-counter current PRO mode; the theoretical maximum specific energy was around 0.192 kWh/m³; which was 75% of the maximum specific Gibb's free energy of mixing (0.256*0.75). Combining a draw solution of high salinity like the Great Salt Lake of approximate 4.6 M sodium chloride with RW as feed solution in a counter-current PRO system yielded a theoretical maximum specific energy of 1.6 kWh/m³. Mixing Dead Sea water of approximate 5.7 M sodium chloride and RO brine of 1.2 M sodium chloride, can produce around 1.0 kWh/m³ maximum specific energy for case of counter-current flow [140].

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 [141]. Optimization of one to four PRO systems was implemented, and the power generated was compared. Optimization included the draw and feed fractions in addition to 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 research proposed that the optimal applied 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 applied 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 enhancement in the maximum specific energy. The study found that changing the feed solution fraction in the salinity gradient had more effect on the PRO system's behaviour compared to the draw solution.

2.2.2 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 [26]. Energy losses through the process from streams circulation, inadequate power recovery, and pretreatment; as well as the pumping energy for feed and draw streams, are considered as the input energy, which should be calculated [26, 142]. 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. [142] on a counter-current PRO system calculated the net specific power utilizing seawater and river water as the input solutions [142]. 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% [142]. Around 0.017 kWh/m³ was the possible amount of power loss through pressure exchanger with 98% efficiency when 32 bar was the PRO hydraulic pressure [26]. Brine reject and wastewater were the salinity gradients in one study [26] where both input and output energies were calculated for various membranes. The energies of pretreatment, pumping from source or in the module, and loss in pressure exchanger were: 0.05, 0.03, 0.05 and 0.017 kWh/m³, respectively; which resulted in total input

energy of 0.147 kWh/m³. The maximum energy output was for Oasys-TFC membrane (0.194 kWh/m³) and the net power generation was 0.047 kWh/m³ [26].

Pretreatment processes, water pumping and membranes are considered as the main components that affect the capital, maintenance, and operating costs in PRO systems [143]. The high expense and significant amounts of energy may be required for the pretreatment process of PRO systems [143]. The pretreatment facility may consume around 20% of the energy unit rate for a PRO power plant of 200 MW capacity [144]. For PRO systems, pretreatment to reduce fouling is very important in some cases [22, 140]. It is considered as one of the prime elements which maximize the cost of generating energy by the PRO process and possibly make it infeasible financially [145]. However, pretreatment and process optimization could control membrane fouling [145-148]. Sand filtration and ultra-filtration are two methods employed in literature as pretreatment technologies for reducing the PRO membranes fouling [146]. 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 [146]. In one reported study, the consumed energy by ultra-filtration was 0.02-0.03 kWh/m³ with an estimated cost of 0.18-0.20 US \$/kWh with a capacity of 38000 m³/d [146].

The cost of the pretreatment depends on the employed salinity gradients. For instance; using seawater instead of SWRO draw solution will increase the cost of pretreatment [61]. Researchers mentioned that the required energy for pretreating wastewater effluent before entering the PRO membrane was around 0.1 kWh/m³ [26]. 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/m³) 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 [142].

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 [149]. 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/m² at 25 bar hydraulic pressure [149]. Another study performed by Altaee et al. [65] estimated the PRO feasibility for energy production without ignoring the

system losses and the amount of energy inputs. Four different salinity sources were utilized as represented in **Fig. 2.8**. 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.

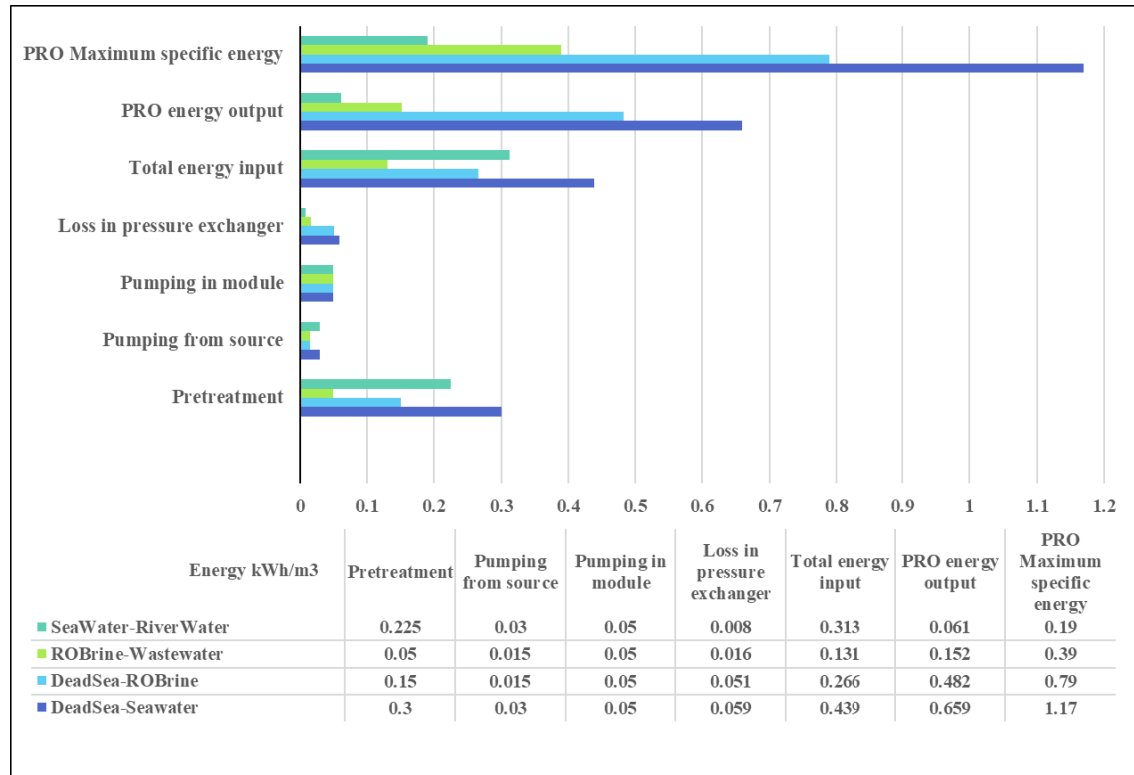


Fig. 2.8: Energy inputs, outputs and losses in a PRO system for four various salinity gradient sources. Energy values are in kWh/m³. Figure adapted from Ref [65].

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 60% of the total energy input, which suggested that using seawater-river water in the PRO process was not promising in regards to energy generation 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/m³ 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. 2.9** [150].

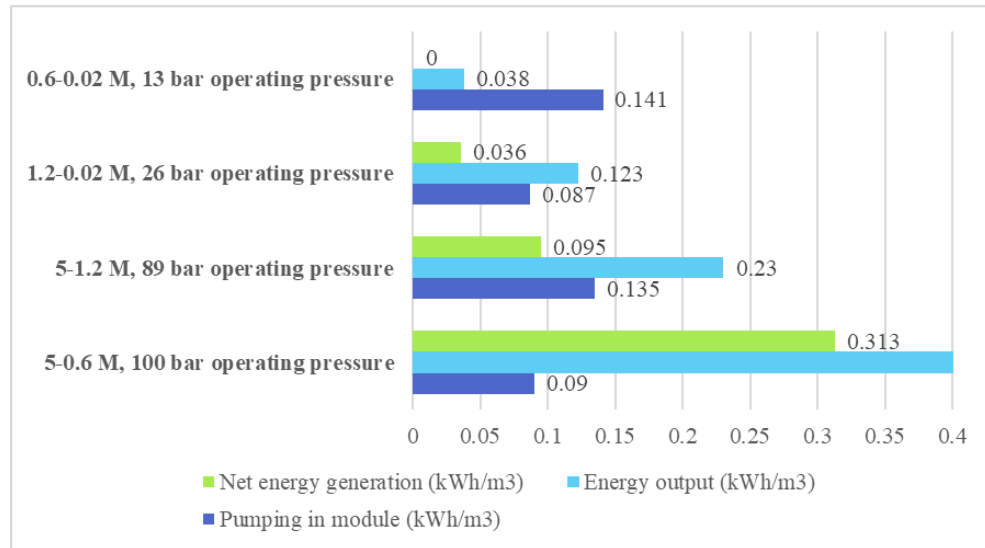


Fig. 2.9: The values of net energy generation, energy output and pumping energy in the module of various salinity gradient sources for the PRO model study where NaCl was the used salt in the solutions. Figure adapted from Ref [150].

As demonstrated in **Fig. 2.9** 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 energy necessary for pumping 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 [143]. For instance, Sharif et al. [151] 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 [151]. 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 [58]. 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 ($\frac{Revenue}{Membrane\ area \cdot year} = Power\ density * Energy\ price$). For instance, if talking about Australia specially New South Wales, the average electricity rate in 2020 is around 27.56c/kWh [152]. Assuming that the accomplishable power density is around 7 W/m² based on some previous studies [66, 85]. Then that results around 0.022 \$/m²yr. PRO revenue-boosting takes place by improving the process efficiency, and thus increase its power density, increase the membrane lifetime and/or lower the cost of the membrane [58]. 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 and that due to their naturalistic mechanical stability and the availability of a high active surface through the operation [153]. Hydration Innovation Technology (HTI) and Oasys Water- United States are the commercial companies which provide PRO membranes. Around USD 104 per m² is the cost of CTA or TFC membranes. Nevertheless, some pilot plants relied on modified membranes as Toyobo in their processes [154].

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/m² power density [144] as shown in **Fig. 2.10**.

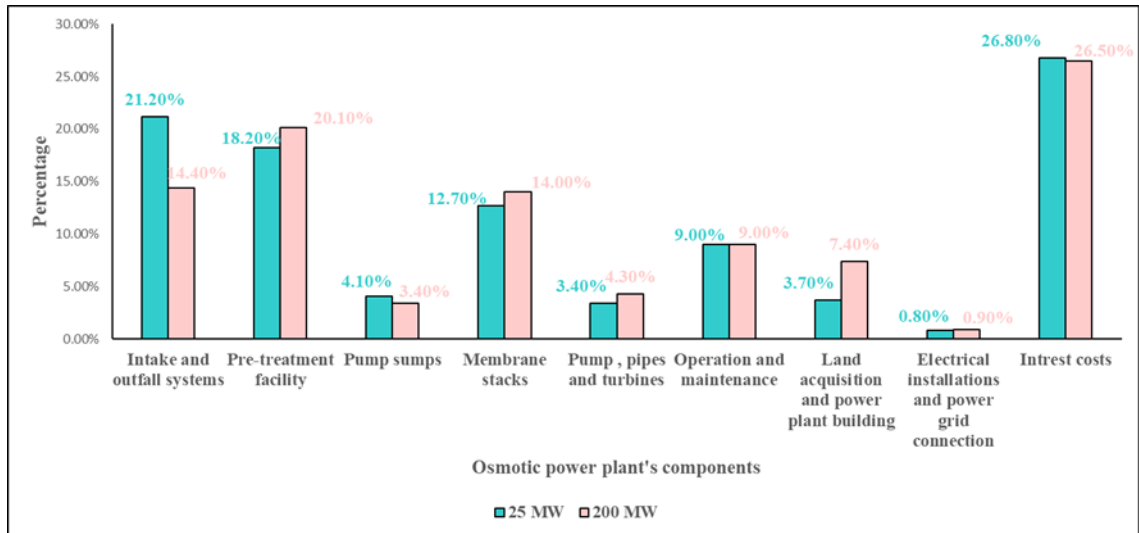


Fig. 2.10: Percentage distribution of energy unit rate of two PRO power plants with various capacities of the main plant's components. The various capacities of the two power plants are 25 MW (shows in green) and 200 MW (shows in pink). Figure updated from Ref [144].

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 capacity of the plant increase, the availability of the freshwater decrease and therefore the net power production is decreased [144]. 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 [1].

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 [61] that utilize SWRO in PRO hybrid systems cause an increase in the capital cost of around 30-50% [61]. 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 [61].

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 [61]. 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% [61].

2.2.3 Membrane fouling

One of the obstacles that facing the PRO process is membrane fouling [155-157]. Generally, water treatment as well as desalination systems suffers from membrane fouling issue. However, PRO is consider as the osmotic process that faces the most critical membrane fouling compared to RO and FO systems [67, 158]. This issue is responsible about reducing the systems productivity just like lower the rate of water transport through the membrane [159] and demanding higher power [59] as well as shortening the membrane lifetime [159]. 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 [59].

In PRO systems; the membrane faces a pair of solutions of different concentrations. For instance, the membrane active layer is expose to the draw solution while the support layer is expose to the feed solution as mentioned previously [58]. Generally, fresh water could have some foulants as organic matters and that is the reason behind fouling formation on the membrane support layer

[159]. When the feed solution contain foulants in a PRO system; these foulants have a high possibility to reach the porous substrate and thereafter, hold in the membrane active layer which responsible about lumping the pores and forming external fouling [60].

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. [159] 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 [159]. In another study done by Yip et al. [158] for the purpose of investigate the effect of organic fouling in 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 that responsible about the power of fouling in PRO. Thelin et al. [160] discovered that CA membrane compared to four various 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 [161] where the authors represented that a draw solution with high concentration of divalent cations (as Calcium and Magnesium ions) showed high organic fouling in PRO system which related to the reverse salt diffusion. Moreover, in 2015 a group of researchers notified that a drop in the water flux of a hybrid PRO-RO system was happened due to the inorganic fouling in the support layer of the PRO membrane [162]. Backwashing and flushing did not solve the problem while antiscaling pretreatment did. Another study done by Zhang et al. [163] 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 the optimization of the operating parameters, performing feed pretreatment and enhancing the structural parameters of the utilized membrane [60]. For instance, antifouling feed pretreatment and alkaline cleaning of the membrane were two reliable techniques for reduce membrane fouling in a PRO system with a high results of water permeation and power density [164]. In another hand, silica scaling in a PRO system was solved in a research by adjusting the chemistry of the solutions through by pH feed solutions modification [165].

2.3 Process design

Work performs, and thence energy produces in the PRO system by using the variance of osmotic pressure among a pair of water sources with variation in their salinities [133, 155]. 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 [139]. Accordingly, in a PRO system, 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 [128]. A hydroturbine is used to depressurize a portion of the diluted draw solution to procure the power [29] (**Fig. 2.11**).

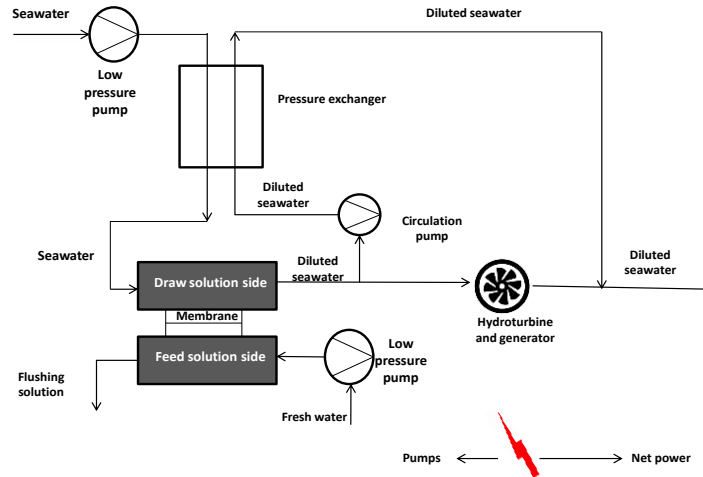


Fig. 2.11: Graphical diagram of a PRO energy facility. Figure adapted from Ref [25].

Before entering the PRO membrane, the draw stream is usually pressurized to a point lower than its osmotic pressure [13, 29]. During the time that freshwater crosses the PRO membrane, chemical potential transforms to hydraulic pressure as a consequence of 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 consequently produces positive net energy [13]. Generally, a pair of primary methods are available to collect energy in the PRO process. One is to place a turbine which is revolved by the outlet draw stream while the other utilizes an energy recovery device just like a pressure exchanger [166]. The great advantage of using a rotating turbine is that the produced energy is freely utilized [166].

PRO and FO as membrane processes based on salinity gradients can be used for the treatment of hypersaline solutions and capabilities to present an economically feasible system instead of using vapour-compression or thermal distillation. However, PRO is more favorable [167] in these

treatments than FO due to the unnecessary of additional regeneration stage [168, 169] to separate the produced water from the draw solutes [167]. 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 [167]. 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) [167]. Furthermore, single and dual closed-loop PRO systems produces more energy than what needed as a consumed electrical power for a multi-effect distillation (MED) plant [170]. 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 [170]. 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, the potential of coupling the PRO system with desalination systems or adding another stage to the system; will additionally affect the process outputs and its economic feasibility. These parameters and number of relevant researches are discussed next in order to clarify the significance of these factors on the PRO process.

2.3.1 Combining pressure retarded osmosis 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 [22, 171]. PRO could alleviate these problems by combining with desalination processes to produce energy, and this is because of its flexibility and high efficiency [166, 170, 172-174]. Various modules and hybrid processes were introduced in the literature to increase the PRO produced power [175, 176]. 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. As a consequence; the PRO osmotic pressure rises, and the total harvested power from the MED-PRO system rises too [166]. Some studies have shown that energy consumption in desalination processes could lessen by combining SWRO with PRO systems [170, 172, 177].

One study demonstrated the benefit of combining PRO with a desalination plant, as evidenced by reduced energy consumption [22]. The seawater of the desalination plant of Tampa Bay was utilized in a simulation study to anticipate the economical and energy behaviour of a full-scale

PRO process [22]. The research 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 [22]. 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 [1]. Process performance, economic feasibility and fouling effect were investigated in this research. Irrigation water was produced through NF by treating municipal wastewater effluent. Drinking water was produced by the SWRO subsystem. The feed stream of the PRO was the NF concentrate, while the draw solution was the SWRO brine, as shown in **Fig. 2.12**. 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. 2.12**, the less concentrated inlet stream was separated before introduction to 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 also separated into two streams: the first one pressurized by the high-pressure pump, while the other one 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 $\$5/\text{m}^2$ with the actual performance of the PRO membrane. While a membrane price over $\$15/\text{m}^2$ desired enhancement in the performance of the membrane [1].

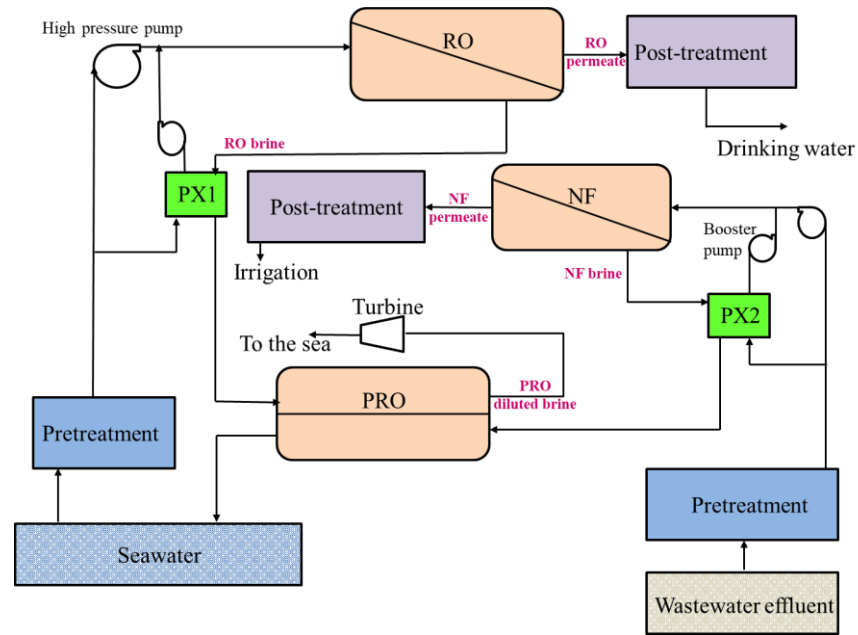


Fig. 2.12: Schematic diagram of process combines SWRO-PRO-NF for potable water, power and irrigation water output. Figure adapted from Ref [1].

Combining PRO with thermal desalination plant of multi-stage flashing (MSF) was examined for power generation and brine dilution [26]. The highly concentrated stream discharged from a thermal desalination plant and tertiary sewage effluent (**Fig. 2.13**) were the 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/m³, 31 L/m²h and 17 L/m²h, 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.

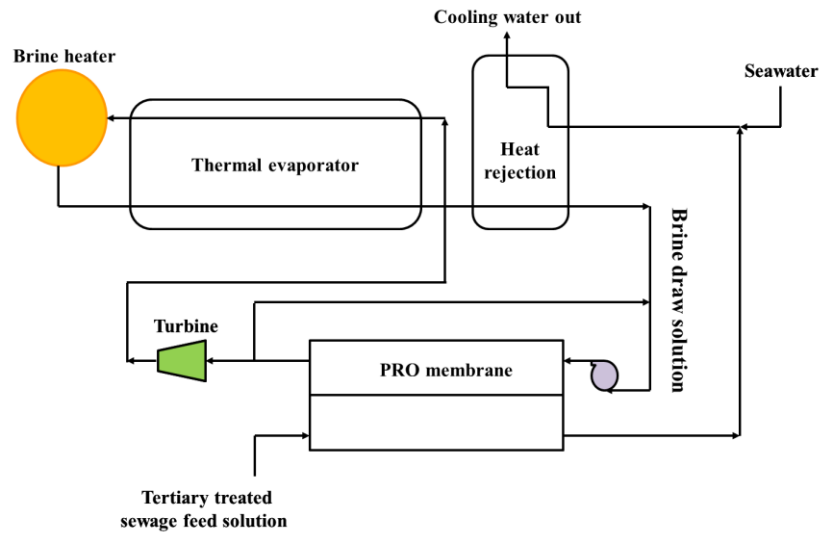


Fig. 2.13: Schematic diagram of hybrid process combines MSF-PRO for energy production. Figure adapted from Ref [26].

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 power among the concentrate (draw solution) and a low salinity feed stream [48]. SWRO concentrate has been used as a PRO draw stream, and that is a result of its relatively high concentration [65, 178-181]. RO concentrate can locate in one side of a semipermeable membrane, and 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. In the case of applying a hydraulic pressure on the concentrated solution that 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 [182]. 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 [69, 70]. Additionally, Altaee et al. [183] proposed an RO-PRO hybrid system that showed success to alleviate the RO brine reject and maximize 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 high-saline solution and 46% RO recovery rate; 28 W/m² PRO power density was achieved. Moreover, a PRO process was employed in one study [184] 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 favourable results and was theoretically verified [184].

PRO feed temperature could be an important factor that affects the process performance while combining with desalination plants. The coupling of RO with PRO has been studied for the aim of reducing the specific power consumption of the hybrid system by determining the feed temperature effect on the PRO performance [185]. The system was a combination of RO unit, PRO unit and two pressure exchangers, as shown in **Fig. 2.14**. 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 M NaCl was the draw solution [185].

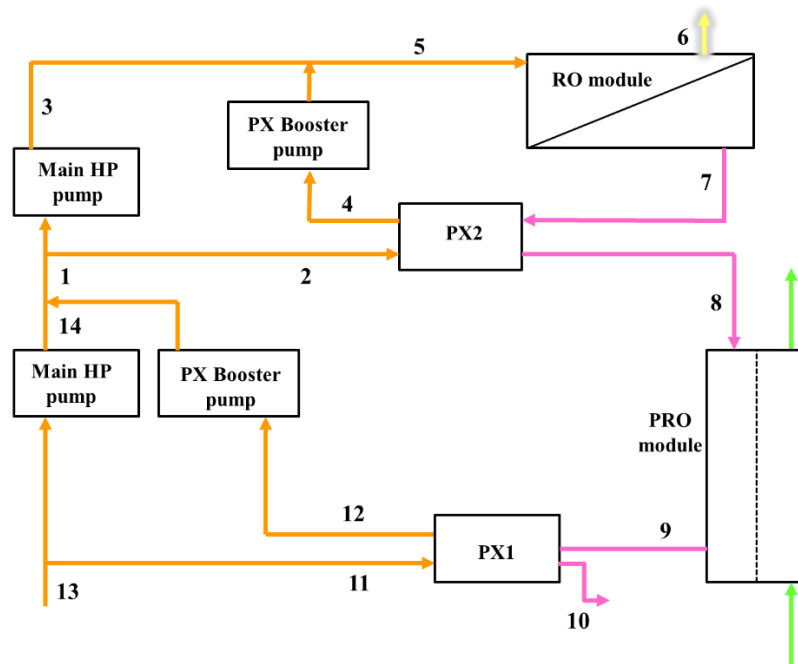


Fig. 2.14: Illustration figure for a combined system of RO-PRO with two pressure exchangers. Seawater or diluted seawater is the feed and appears in orange, the green lines are for freshwater, concentrated brine appears in pink, and the yellow line is for the RO permeate. Figure adapted from Ref [185].

Additionally, PRO systems can be combined with membrane distillation processes for power generation and water production at low heat energy [60, 186, 187]. The primary benefits of the PRO- membrane distillation (MD) systems that they are preferable to improve the generation of the osmotic energy, increase the fresh water recovery, and restrain the membrane fouling [188]. One type of these combinations is joining PRO with the direct contact membrane distillation

(DCMD) as shown in **Fig. 2.15**. In 2017 Park et al. [189] 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 demonstrated in **Fig. 2.15**. 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.

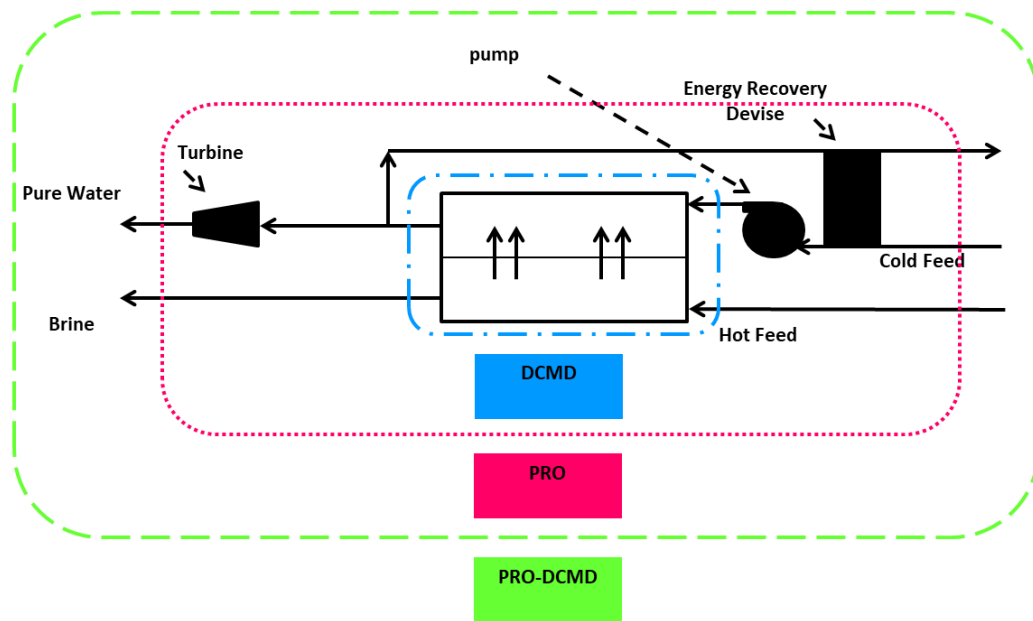


Fig. 2.15: Illustration figure for a combined system of PRO-DCMD. Figure adapted from Ref [189].

In another study, Lee et al. [190] did add a PRO unit with a multistage vacuum membrane distillation system (MVMD). Brine and distilled water were continuously generated by recycling flows. In the proposed 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 amongst 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 [190]. Moreover, some researchers in United State [191] 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; in addition to the need for feed solution pretreatment and its high energy consumption [55, 192].

2.3.2 Dual-stage pressure retarded osmosis

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 [29, 166, 193]. Dual-stage PRO (DSPRO) is more efficient with regards to 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 [29]. This is as 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 [29]. Furthermore, DSPRO technology has the superiority of diminished membrane fouling [29, 170]. Adding a second stage can renew the variance in chemical potential through the membrane and could minimize the feed side concentration polarization [28, 29]. DSPRO is slightly different than a single-stage PRO by streaming a portion of the draw stream to the second PRO stage (**Fig. 2.16**).

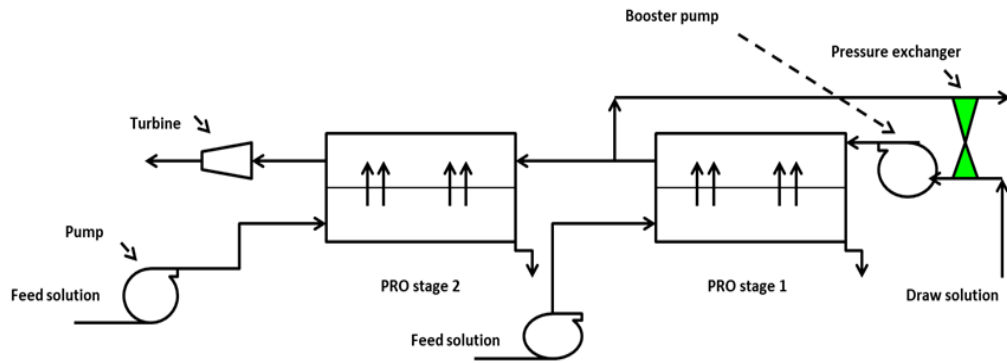


Fig. 2.16: Illustration figure of DSPRO. Figure adapted from Ref [29].

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 [29]. Additionally, introducing less concentrated draw solution to the second stage may cause extra water permeation within the membrane which caused an increase the power density. Adding a second PRO membrane increased energy by 18% as found by Altaee et al. [29, 170]. 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 [154].

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 between single and DSPRO systems, model calculations were performed on both single and dual closed-loop PRO (CLPRO) systems to figure out the difference of power generation on both processes in one of these studies [170]. The main advantages of using a CLPRO unit is that the PRO membrane fouling is possibly reduced. The impact 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 process, 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 [170]. A summary for some of the results shows in **Table 2.8**.

Table 2.8: Summary of some results for a DSPRO study [170].

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
J_w (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	-	-
J_w (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. [178]. 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/m³. For that subsystem, at recovery rates around 40-50%, the resultant power ranged between 110-190 Wh/m³. For subsystem two RO-two PRO, when RO recovery was 50%, then the specific power of the first PRO was around 150 Wh/m³ and for the second PRO was around 570 Wh/m³. For that subsystem, at recovery rates around 40-50%, the resultant power ranged between 700-930 Wh/m³. 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 [28]. 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 [29]. RO brine or Dead Sea water and wastewater effluent or seawater were the used salinity gradients. In the case of 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 2.9**).

Table 2.9: Summary of some results for a conventional and DSPRO study [29].

Modules arrangements in stage one and two respectively	Specific Power Generation kWh/m³				
	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. Additionally, 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 effect of wastewater fouling on the behaviour 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. [131] utilized different feed solution resources in the DSPRO system operating in

a counter-current mode to assess the effect of the feed salinity on the system effectiveness [131]. 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 [131].

The amount of power generated and brine concentration was investigated in a multistage pumping DSPRO process (MSDSPRO) [138]. 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/m², 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 stage one.

Moreover, different configurations of DSPRO systems were pointed out in the literature. For instance, the conventional DSPRO configuration shown in **Fig. 2.16** was compared to a different design (**Fig. 2.17**) in one study [154]. 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 [154]. 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 QR 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 [154].

gradient power plant, but there are no experiments performed to confirm. Future work should focus on the behaviour and efficiency of the DSPRO process.

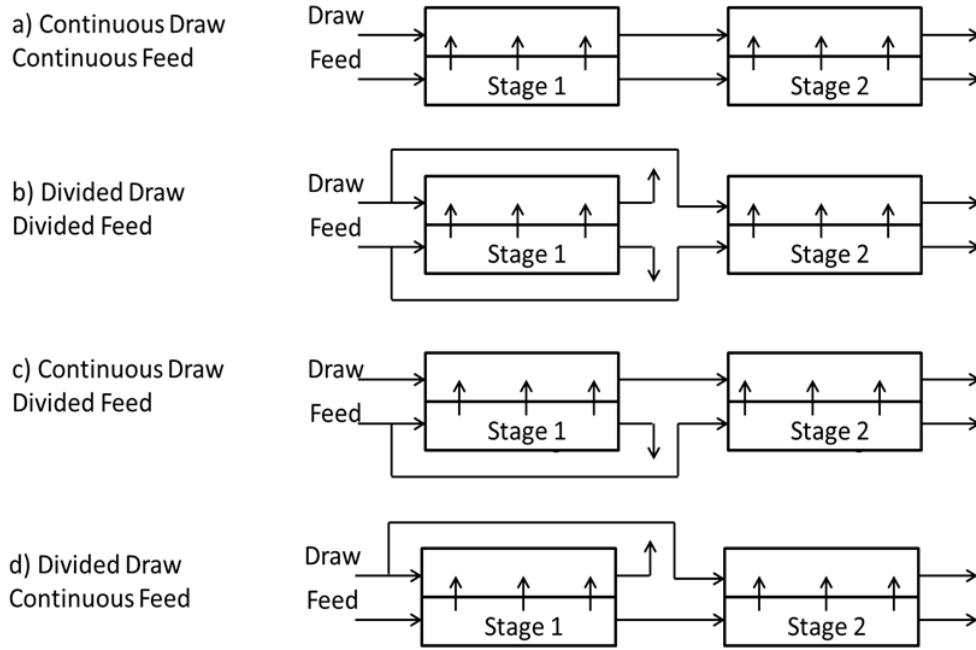


Fig. 2.18: Representation figure of proposed configurations of a DSPRO unit. Figure adapted from Ref [193].

2.3.3 The numerical models of pressure retarded osmosis

The first PRO model was proposed by Loeb in 1976 [195], 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 [156, 180, 196-198]. For instance, a study done by Kim et al. [180] 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 PRO system the draw stream is affected by operating pressure just as in RO system, but the direction of the net water flow is remaining toward the concentrated draw mixture like in FO process. Generally, water transition in FO, RO and PRO is described by **Equation 2.1**:

$$Jw = A(\Delta\pi - \Delta P) \quad (2.1)$$

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 [25, 48]. 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 refers to the power density (W) is shown in **Equation 2.2**:

$$W = J_w \Delta P = A(\Delta\pi - \Delta P) \Delta P \quad (2.2)$$

Equation 2.2 decisive that the most significant parameter for the PRO system 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) as a consequence of water passing the membrane. The dilutive external concentration polarization happens as water moves of the feed stream to the draw stream and produces its dilution at the membrane surface. Furthermore, the concentrative internal concentration polarization happens as a consequence of the membrane porous support layer resistance to mass transfer. This phenomenon occurs when the solute accumulates inside the support layer on the feed side [139]. As a conclusion of the reverse diffusion by the solute particles, the feasible osmotic pressure variance decreases through the membrane [199].

Asymmetric membranes used for osmotic processes are generally encompassing of two different layers, an extremely thin and relatively dense selective layer on a porous support layer [25, 200]. 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 [201-203] (**Fig. 2.19**). The membrane dense active layer generally towards the draw stream while the porous support layer towards the feed stream in PRO applications [25, 48] 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 [170].

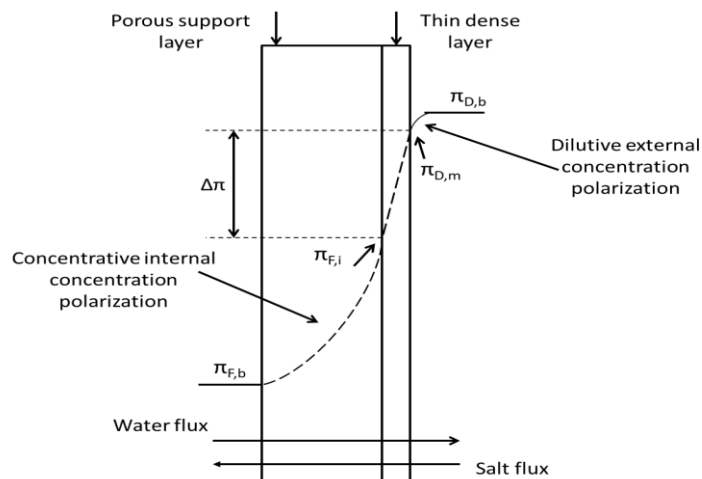


Fig. 2.19: Illustration figure of osmotic driving force profile for an asymmetric membrane for PRO system when the dense layer towards the draw stream. Figure adapted from Ref [156].

The water flux in PRO process with the effect of internal concentration polarization only [190] is introduced next:

$$J_w = A(\pi_{D,m} \frac{1 - \frac{C_{F,b}}{C_{D,m}} \exp(JwK)}{1 + \frac{B}{J_w}(\exp(JwK) - 1)} - \Delta P) \quad (2.3)$$

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 impact of internal, external concentration polarization and the reverse salt flux with only measurable quantities in the PRO [29]:

$$J_w = A \left(\frac{\pi_{D,b} \exp\left(-\frac{J_w}{k}\right) - \pi_{F,b} \exp(JwK)}{1 + \frac{B}{J_w}(\exp(JwK) - \exp\left(-\frac{J_w}{k}\right))} - \Delta P \right) \quad (2.4)$$

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 .

2.4 Summary and Gap Identification

A proper assessment of renewable energy sources is extremely significant 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 methods and is considered to be advantageous as compared to the other renewable energy technologies. Despite a large number of laboratory-scale experiments of the PRO system, there are a limited number of pilot plant trials. More pilot plants need to be investigated to clarify the potential capability of the PRO system for energy 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). Also, 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, it is strongly recommend that

more investment should be on fabricating a commercial PRO membrane. Moreover, the PRO systems also have serious reliance on the selection of draw and feed solutions. An increased concentration gradient could increase the possibility of practical operation of this process. Also, it is recommended to focus more on the environmental impact as well as benefits of PRO process especially when using waste stream for power generation. For example, RO brine-wastewater and Dead Sea-RO brine salinity gradient has environmental benefits in addition to 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 reducing the 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 system. One significant solution to enhance the PRO performance is developing better membranes by the means of handling higher pressure values, lowering the chance of fouling occurrence, increasing water permeation and reducing reverse salt flux [204]. Accordingly, it is very important to focus on the progress of 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.

Table 2.10 summarized 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 2.10: 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 ² h	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	[54]
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	[66]

10 mM NaCl	1M NaCl	11.0	CTA-FO supported by a woven fabric *	1/Lab scale	11.0	3.8	N/A	[67]
0-5 g/L NaCl	35 g/L NaCl 60 g/L NaCl	0-9.7	Flat sheet CTA-FO, custom made	1/Bench scale	0-25	≥ 2.7 ≥ 5.1	N/A	[25]
0.5 g/L NaCl	30 g/L NaCl	3.8	FO spiral wound	1/Lab scale	~6.3	0.57	N/A	[71]
DI water	1.0M NaCl (Seawater brine)	<15.0	TFC-PRO*	1/Lab scale	N/A	7-12	N/A	[85]
0 mol/m³ 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 *	[28]
Distilled water	1st stage: ~0.85 mol/L NaCl 2nd stage: ~0.49 mol/L NaCl	15.0	Flat sheet	2	1st stage= 11 2nd stage= 4	1st stage=5.67 2nd stage= 2.11	N/A	[170]
F1: 200mg/L, freshwater F2: 200mg/L wastewater effluent	45g/L Seawater to first stage	14.0	FO-CTA	2	N/A	W1= ~4.4 W2= ~3.0	N/A	[154]
DI water	4.6M NH ₃ -CO ₂	~101.3	Cross flow CA-FO	1	N/A	~170	N/A	[205]
10 mM NaCl	1.0 M NaCl	15	Dual layer Hollow fiber	1/Bench scale	13.0	5.10	N/A	[206]
DI water	3.0 M NaCl	48.0	Flat sheet TFC	1/Bench scale	N/A	60.0	N/A	[207]
DI water	1.0M NaCl	20.0	TFC Hollow Fiber	1/Lab scale	~14.0	7.6	N/A	[208]
10 mol/m³ River water	600 mol/m ³ Seawater	~9.0	Flat sheet	1/Module scale	2.3	N/A	0.1*	[209]
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	[210]

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

Chapter Three: Impact of hydrodynamic conditions on optimum power generation in dual stage pressure retarded osmosis using spiral-wound membrane

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3.1 Objectives

This chapter aims to specify the influence of the hydrodynamic conditions on the DSPRO system performance in full-scale membrane modules. The main objectives of this chapter are:

- 1) To determine the impact of various salinity gradients in the specific power generation in a DSPRO system.
- 2) To consider the impact of the draw solution dilution and the increase in the feed solution concentration in a DSPRO system along membrane modules in the specific power generation.
- 3) To determine the impact of the optimum parameters of the DSPRO system based on the specific power production in a spiral-wound membrane.
- 4) To determine the impact of the hydrodynamic conditions in a DSPRO system along membrane modules.

3.2 Introduction

The dual-stage pressure retarded osmosis (DSPRO) process was suggested for maximizing power generation from a salinity gradient resource [29, 193]. Adding a second stage to the PRO system helps recover the un-extractable osmotic power that remained in the diluted draw stream in the first stage of the PRO process [27, 29, 166, 193]. In the DSPRO system, a portion of the diluted draw solution flows out from the first PRO and stage sends it out to the second PRO stage (**Fig. 3.1**), where that flow is equal to the permeated flow rate in the first stage. A new feed solution is entered to the stage two of the DSPRO process to rejuvenate the chemical potential by reducing the feed side concentration polarization [29, 211]. Recent studies showed that PRO power generation could be enhanced by 18% when a second stage is added [27]. Another study investigating PRO membrane arrangements in the DSPRO process revealed that the highest

specific power generation was when couple of modules were used in stage one and single PRO module in the second DSPRO stage [29]. The studies assumed an operating pressure of half of the osmotic pressure difference ($\Delta P = \Delta \pi / 2$) and a feed to draw solution flow rate ratio equal to one in the DSPRO system. These optimum conditions in laboratory-scale systems are not valid in the PRO process using a full-scale module due to the concentration and dilution of feed and draw solutions along the membrane module [150]. In a PRO process using a full scale, the power generation could be increased by optimizing the hydrodynamic parameters of flow rates and pressure, leading to ~54% more energy output [150]. Unfortunately, there is no study yet, investigating power generation in the optimized DSPRO process and considering the impact of hydrodynamic parameters on mass transfer and solute resistivity to diffusion coefficients.

Soltani and Struchtrup [211] showed a preferable performance of the DSPRO process over a single PRO system. The hydraulic pressure, the changes in flow rates, and the concentration variations through the membrane length were investigated. However, the hydrodynamic parameters were assumed constant and did not change along the membrane. He et al. [193] found that power generation could be enhanced by including a second stage in the PRO process. The study did optimize the main operating conditions, but it did not investigate the changes in the feed or the draw solutions concentrations in a full-scale module. The PRO process was also investigated through theoretical analysis and optimization of extractable osmotic power from brine solution proposing a model-based optimization to maximize the normalized specific energy production (NSEP) [128]. In this study, the power generation optimization from a counter-current and constant pressure DSPRO has taken place by applying some dimensionless parameters in the model to identify the coupled performance through membrane characteristics and feed and operating conditions. The outcomes manifested that the multistage PRO process is more productive than single-stage PRO in generated power [128]. Nevertheless, the study ignored the pressure drop and did not include the effect of concentration polarization. Another study performed by Altaee et al. [212] showed the preferences of a DSPRO system over a single PRO system; however, it did not evaluate the changes of the operating parameters along the membrane module, examine the optimization of the operating parameters and did not point the impact of the solutions flow rates. In 2013, a full-scale hollow-fiber membrane module was employed in a PRO pilot plant system [69]. The power density was 4.4 W/m² from RO brine-sewage water (4.7% sodium chloride) salinity gradient with the same flow rates. The work did not consider the ratio of the flow rates of the feed and the draw solutions or the optimum applied pressure. In another PRO pilot plant study [213], RO brine and wastewater were the salinity gradients, and the utilized membrane was a Toyobo membrane where 7.7 W/m² power density was accomplished. However, the study did not consider the impact of feed and draw solution flow rates on the process performance. A full-scale PRO system was optimized by a machine learning algorithm based on

non-ideal operating parameters [19]. The study represented that the optimum applied pressure in a full-scale PRO is lower than $\Delta\pi/2$. Nevertheless, the effect of the variation of the mass transfer coefficient and the solute resistivity through the membrane length was not considered.

It has also been noticed that only a few studies focused on the DSPRO modelling [214, 215], despite that, no studies are available to define the optimum hydraulic pressure, the ratio of the inlet flow rates, and the pressure drop in the feed and draw sides in a full-scale DSPRO system. Moreover, several studies in the literature investigated the effect of utilizing higher draw and feed flow rates in PRO or DSPRO systems. Recently Habtom et al. [216] studied the importance of optimization of PRO process operating conditions and module dimension to achieve maximum energy output while mixing seawater - Indian river water. Also, they concluded that the optimization PRO process based on power density or net power density alone might lead to a suboptimal solution for the PRO-energy recovery device (ERD) integrated system. Further, to avoid a suboptimal solution, they recommended using net energy generation per river water unit as an optimization function. Still, the optimum hydrodynamic parameters for both PRO and DSPRO systems and for various salinity gradient resources are not reported in the literature [140, 212, 217]. Regardless that some studies in the literature consider the optimization of bench-scale PRO prototype systems [218, 219], optimization of the key operating parameters of a full-scale DSPRO module is still unavailable.

Although several studies investigated the effect of utilizing higher draw and feed flow rates on power generation in the DSPRO systems, determining the optimum key operating parameters in the DSPRO process using a full-scale module is still unavailable. Therefore, this study investigated the optimum operating parameters in a DSPRO system using a full-scale module, considering the effect of the feed and the draw solutions flow rates on solute resistivity and mass transfer conditions in the PRO module. In addition, the study considered the pressure drop in the draw and feed solution sides every 0.1 m of the membrane length. In Accordance to our knowledge, no study is available yet investigating the variations of the hydrodynamic parameters of the DSPRO process along the membrane length to understand the changes inside the membrane module. Four sets of SGRs were investigated in the current work, which are 5M-0.6M, 5M-1.2M, 1.2M-0.02M, and 0.6M-0.02M. These salinity gradients are widely investigated in the literature and represent Dead Sea-Sea water (DS-SW), Dead Sea-RO brine (DS-ROB), RO brine-Wastewater (ROB-WW), Sea water-Wastewater (SW-WW), respectively, and available in the environment for use in the DSPRO process.

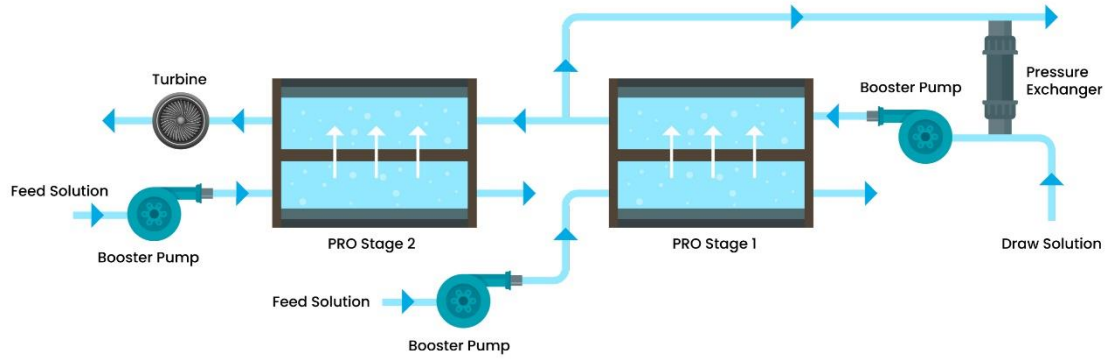


Fig. 3.1: Illustration figure of DSPRO process for power generation from SGR.

3.3 Methodology

3.3.1 Spiral-wound forward osmosis membrane characteristics

An FO Cellulose TriAcetate (CTA) membrane from the Hydration Technology Innovation Company (HTI) (an OsMem 8040FO-FS-P module) that was tested by Madsen et al. [220] in the PRO system was chosen in this research. The membrane active area is 16.5 m², the module length is 1.0 m, the feed temperature is 20°C, and the number of membrane leaves is 11. The membrane parameters are the water permeability coefficient (A_w) is 0.76 L/m².h.bar, the salt permeability (B) is 0.44 L/m².h and the structural parameter (S) is 655 μm [220].

3.3.2 The mass transfer coefficient and the solute diffusion resistivity

The mass transfer coefficient (k_d) varies along the membrane length (e.g., at every x (m) distance of the membrane) as the draw solution flow rate, Re number, the concentration of the draw solution as well as the diffusivity varies along the membrane length. The mass transfer coefficient, k_d , was calculated by the next equations.

$$k_d = Sh * D / d_h \quad (3.1)$$

Where Sh is Sherwood number, D is the diffusion coefficient in m²/s, and d_h is the hydraulic diameter of the flow through the feed spacer (twice the thickness of the feed spacer ($2 * 0.0025 = 0.005$ m)). The flow has been assumed turbulent at all flow rates, and under that condition, the Sh number can be found by the following expression.

$$Sh = 0.2 Re^{0.57} Sc^{0.40} \quad (3.2)$$

Where Re is Reynold number, and Sc is Schmidt number. Reynold number is calculated using **Equation 3.3**.

$$Re = \rho_D V d_h / \mu \quad (3.3)$$

Where ρ_D is the solution density in Kg/m^3 , V is the solution velocity in m/s and μ is the viscosity of the draw solution in kg/m.s . The draw solution viscosity was calculated at each concentration at 20°C and 25°C by interpolation of data from literature [221]. The density of the draw solution was calculated based on **Equation 3.4**.

$$\rho_D = \frac{1}{\left(\frac{X_{NaCl}}{\rho_{NaCl}}\right) + \left(\frac{X_{H2O}}{\rho_{H2O}}\right)} \quad (3.4)$$

Where X_{NaCl} is the mass fraction of the salt in the draw solution and X_{H2O} is the mass fraction of the water in the solution. The solution velocity is calculated as.

$$V = Q_{Di,x} / A_s \quad (3.5)$$

where, A_s is the cross-section area of the membrane, which is equal to the multiplication of the thickness of the spacer (0.0025 m) multiplied by the width of the channel (0.66 m); $A_s = 0.00165\text{ m}^2$. $Q_{Di,x}$ is the inlet flow rate of the draw solution to section x of the membrane. Next, the Schmidt number (Sc) can be given by the following equation.

$$S_c = \frac{\mu}{\rho_D D} \quad (3.6)$$

The diffusivity of NaCl at different concentrations at 25°C was found by interpolation of data found in the literature [222]. These values were used to calculate the diffusivity of the draw solutions at 20°C as follows.

$$\frac{D}{D_{T2}} = \frac{T}{T_2} \frac{\mu}{\mu_{T2}} \quad (3.7)$$

Where D and D_{T2} are the diffusion coefficients at T (20°C) and T_2 (25°C), respectively, while μ and μ_{T2} are the viscosities of the draw solution at T (20°C) and T_2 (25°C), respectively. After finding D at 20°C ; Sc , Sh , and k_d can be calculated at every 0.1 m of the membrane length.

The solute diffusion resistivity (K) will vary along the PRO module because of changing the viscosity of the feed solution, and the following equation measures it.

$$K = \frac{S}{D_F} \quad (3.8)$$

Where S is the membrane structural parameter and D_F is the diffusion coefficient at the support layer at 20 °C.

3.3.3 The numerical model of pressure retarded osmosis

The water flux in both DSPRO stages was predicted by the mathematical model of a one-meter long membrane module developed by Altaee et al. [65] which considers the impact of concentration polarization and the external resistivity on the support layer and represented in the next equation.

$$J_{w,x} = A_w \left(\frac{\left(\frac{nRTC_{Di,x} \left(1 + \frac{Q_{Di,x}}{Q_{Do,x}} \right)}{2} \right) \exp\left(\frac{-J_{w,x}}{k_{d,x}}\right) - \left(\frac{nRTC_{Fi,x} \left(1 - \frac{Q_{Fi,x}}{Q_{Fo,x}} \right)}{2} \right) \exp(J_{w,x}K_x)}{1 + \frac{B}{J_{w,x}} \left(\exp(J_{w,x}K_x) - \exp\left(\frac{-J_{w,x}}{k_{d,x}}\right) \right)} - \Delta P_x \right) \quad (3.9)$$

where A_w is the water permeability coefficient, n is the number of the ions in solution, R is the universal gas constant, T is the temperature (K), $C_{Di,x}$, $C_{Fi,x}$ are the initial molar concentrations of the draw and feed streams at the distance x along the membrane length, $Q_{Di,x}$, $Q_{Do,x}$, $Q_{Fi,x}$, $Q_{Fo,x}$ are the inlet and outlet flow rates of the draw and feed solutions, respectively, $k_{d,x}$ are the mass transfer coefficient of the draw solution at distance x , ΔP_x is $((P_{Di,x} - \Delta P_{D,x}) - (P_{Fi,x} - \Delta P_{F,x}))$ where $P_{Di,x}$, $P_{Fi,x}$ are the inlet draw and feed hydraulic pressure at point x , respectively, $\Delta P_{D,x}$ and $\Delta P_{F,x}$ are the pressure drop at the draw and feed sides at x membrane length, respectively, and K_x is the solute diffusion resistivity through the membrane porous layer at distance x of the membrane length. This model is used to predict the water flux value in the two DPRO stages. k_d and K were changing along the membrane length. It has been assumed that the pressure exchanger efficiency is 98% and the leakage of the solute in the pressure exchanger is neglected. The specific power generation ($E_{ox,j}$) along the two DPRO stages was calculated, as shown in **Equation 3.10**.

$$E_{ox,j} = \frac{\Delta P_{x,j} * Q_{P,x,j}}{Q_{Di,j} + Q_{Fi,j}} \quad (3.10)$$

Where j represents the stage number ($j=1$ for the first DSPRO stage and $j=2$ for the second DSPRO stage), $\Delta P_{x,j}$ $((P_{Di,j} - \Delta P_{D,x,j}) - (P_{Fi,j} - \Delta P_{F,x,j}))$ is the effective pressure difference between the two solutions at distance x in j DPRO stage through considering the pressure drop at the draw side ($\Delta P_{D,x,j}$) and the pressure drop at the feed side ($\Delta P_{F,x,j}$) and $Q_{P,x,j}$ is the permeate flow rate at distance x in the membrane module. In the second DPRO stage, the feed and draw flow rates equal the permeate flow rate in stage one ($Q_{Di,2} = Q_{Fi,2} = Q_{P,1}$). The membrane area in the stage two of the DSPRO was determined as follows.

$$A_2 = A_1 * \frac{Q_{Di,2}}{Q_{Di,1}} \quad (3.11)$$

Where, A_2 and A_1 are the membrane area at the second and first stages, respectively, while $Q_{Di,2}$ and $Q_{Di,1}$ are the inlet draw flow rates in the second and first stages, respectively.

The net specific power generation is equal to the summation of the specific power generation in the DSPRO stages. More details about the water flux can be found in the literature [170]. All the previous calculations were done by the built MatLab Code at every x (m) of the membrane length. The systematic simulation-based optimization study of the DSPRO was done by varying the main operating parameters: the draw flow rate, the feed flow rate, and the applied hydraulic pressure [217, 218]. The study of determining the optimum parameters of the DSPRO is divided into three main parts (**Fig. 3.2**), where the results from all cases are compared to the conventional scenario:

- Determining the optimum feed flow rate (Q_F) at fixed Q_D and $P_{Di,1} = \Delta\pi/2$
- Determining the optimum draw flow rate (Q_D) at fixed Q_F and $P_{Di,1} = \Delta\pi/2$
- Determining the optimum $P_{Di,1}$ at constant $Q_D = Q_F$

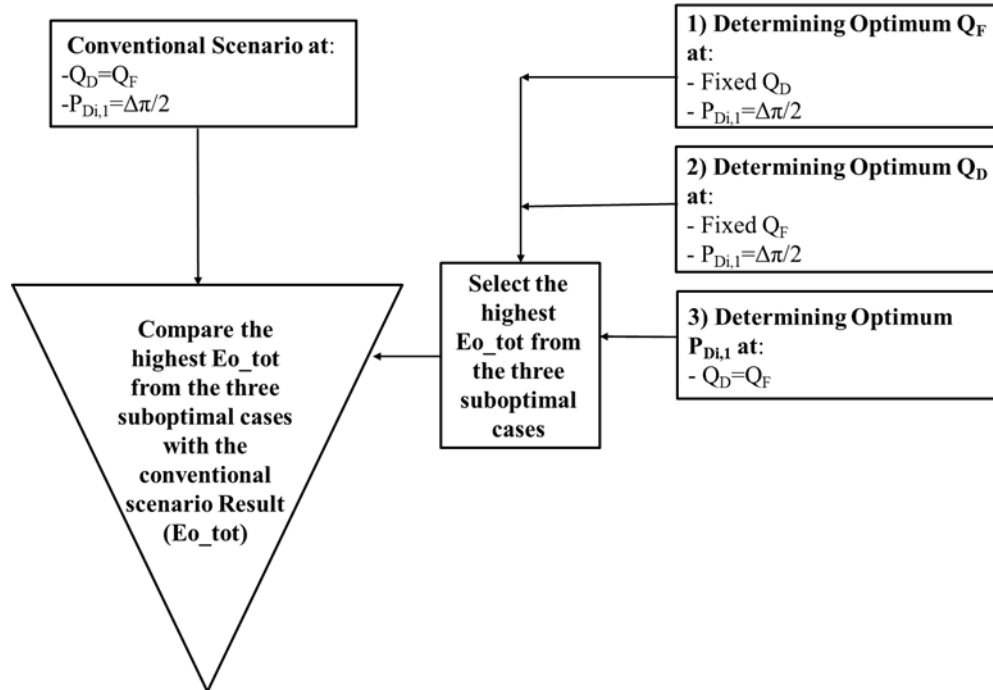


Fig. 3.2: Schematic diagram of the systematic simulation of the DSPRO system for process optimization.

In each scenario, various pressure or various flow rates of the draw solution or the feed solution were assumed. The specific power generated was calculated for the four different sets of SGRs.

At the end, the maximum specific power generated was compared with the specific power generated by the conventional DSPRO system. The three cases will demonstrate which parameter is the most dominant in the DSPRO performance. The parameter that governs the behaviour of the DSPRO process in this study is the produced specific power.

3.3.4 The model validation

The pilot plant experimental data performed by Tanaka et al. [176] of a full-scale FO membrane is considered to validate the model of water flux in this work. In the experimental study, 70.5 m^2 is the membrane area, A_w is $0.27 \text{ L/m}^2\text{h bar}$, B is $0.035 \text{ L/m}^2\text{h}$, the membrane module length is 0.682 m , the cross section area is 0.008 m^2 and S is $1024 \text{ }\mu\text{m}$ [176]. Tap water was the feed solution in the experimental study, and 1.0 M NaCl was the draw solution. The applied pressure ranged from 5 to 30 bar, and the flow rate was 8 L/min for both the feed and the draw solution [176]. **Fig. 3.3** shows a significant agreement between the experimental from the pilot study and the model results. The model validation result shows more than 92.3% agreement between the model results and the experimental study results [176].

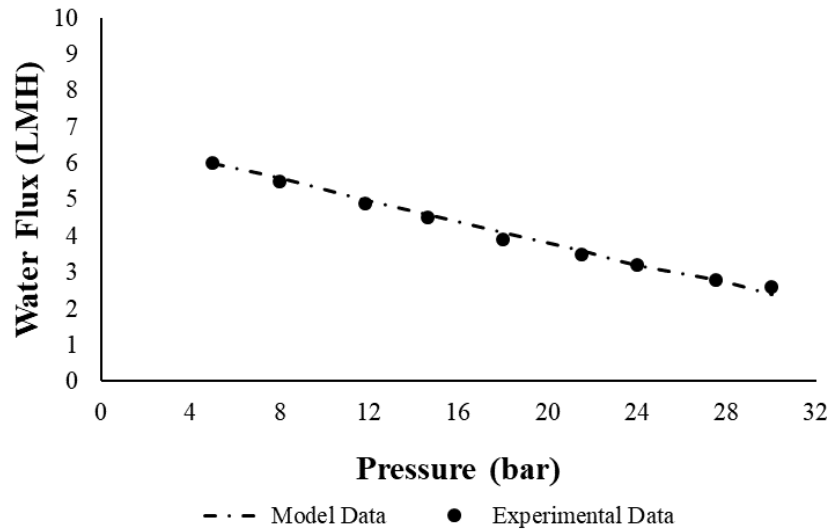


Fig. 3.3: The water flux vs. the applied hydraulic pressure in the draw side for the experimental results (Experimental Data) from the pilot study [176] and the model (Model Data) used in this study where; $Q_{Di}=Q_{Fi}=8 \text{ L/min}$.

3.3.5 The pressure drop calculations

The pressure drop was calculated on the feed and the draw solution sides. **Equation 3.12** was suggested by the HTI Company to determine the pressure drop in the feed solution side of the PRO element at 20°C.

$$[0.097 * (Q_{Fi,1} \text{ in LPM/ (total leaves)}) + 5.9] * (Q_{Fi,1} \text{ in LPM/ (total leaves)}) = \Delta P_F \text{ (in kPa/element)} \quad (3.12)$$

The pressure drop from **Equation 3.12** represents the pressure drop in one membrane module. To find the pressure drop in the feed side at every 0.1 m of the membrane length, the resulting value from the equation was multiplied by 0.1 since the length of the membrane is 1.0 m with 10 sections of 0.1 m length. On the draw solution side, the pressure drop at 20°C was calculated from **Equation 3.13**.

$$95 * [Q_{Di,1} \text{ in LPM/ (total leaves)}] = \Delta P_D \text{ (in kPa/element)} \quad (3.13)$$

Likewise, the pressure drop in the draw side was calculated at every 0.1 m of the membrane by multiplying the resulting value from **Equation 3.13** by 0.1. The suggested **Equations 3.12** from the HTI Company, are used only for water at 20°C. When different solutions are used, the resulting pressure drop from the equations is multiplied by the solution viscosity at 20°C.

3.4 Results and discussion

3.4.1 The impact of the pressure retarded osmosis membranes arrangement on the process performance

The influence of the membrane arrangement on the DSPRO system behaviour is examined at 5M-0.6M SGR, representing the DS-SW salinity gradient often used in the PRO process [29]. Previous studies suggested three PRO elements to evaluate the specific power generation at different membrane arrangements [2]. Water flux drops significantly at the end of the third PRO element, and the pressure vessel of the HTI membrane accommodates up to 3 elements in the pressure vessel. Considering these practical limitations, the following three different configurations of the DSPRO system were simulated (**Fig. 3.4**) i) three modules in a single PRO stage ii) a DSPRO system with one module stage one and two modules in stage two iii) while the last configuration was DSPRO system with two modules in stage one and one module in the stage two.

The hydraulic pressure is half of the osmotic pressure of the DS-SW salinity gradient, and each module is 1 meter long, with a 16.5 m² membrane active area. The specific power generation was calculated for each case and used to identify the best performance configuration. As shown in

Fig. 3.4, the PRO system with three modules in series had the lowest specific power generation (0.606 kWh/m^3) compared to the other configurations. Using a DSPRO system with one module in stage one and two modules in stage two caused an increase of the power generated by up to 0.646 kWh/m^3 compared to the PRO process with three membrane modules in series. The maximum power generated (0.676 kWh/m^3) occurred at the DSPRO system with two modules in stage one and one module in stage two, and hence this configuration was selected in this study. These results support the previous results found by Alanezi and Altaee [214] in which a preferable performance of the DSPRO system was with two modules in stage one and one module in the stage two.

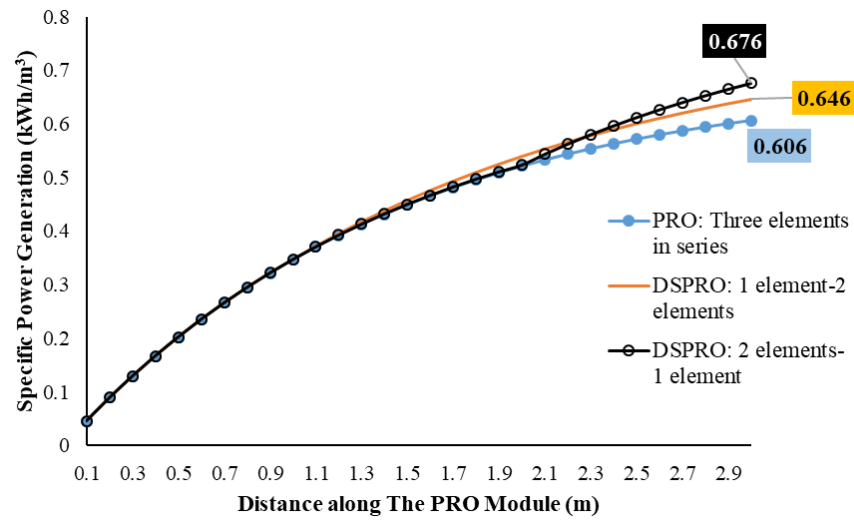


Fig. 3.4: The specific power generation along the membrane module of a PRO system of three elements in series and two configurations of a DSPRO system (1element in stage one-2 elements in stage two, and 2 elements in stage one-1 element in stage two). The feed and the draw solutions flow rates are 500 L/h, 5M-0.6M NaCl are the salinity gradient sources, and the applied pressure is half of the osmotic pressure.

3.4.2 The pressure drop through the membrane module

The pressure drop in the HTI membrane was calculated at the feed and the draw stream sides at a 0.1 m distance along the module. **Equations 3.12** and **3.13** show that mass transfer across the membrane will influence the pressure drop of the PRO membrane. Technically, the hydrodynamic conditions of the feed and the draw solutions change due to the permeation flow, affecting the pressure drop in the PRO membrane. Equal flow rates of the both feed and draw solutions (1000 L/h) were utilized to determine the pressure drop along the membrane modules in the DSPRO

process and $\Delta P = \Delta\pi/2$. For instance, the pressure drop at the end of the third PRO module for 5M-0.6M was 4.2 bar, as shown in **Fig. 3.5**. The results show a higher pressure drop in the SGRs of higher osmotic pressure gradients. The pressure drop for the 5M-0.6M was slightly higher than the other SGRs because of the higher permeation flux and flow rate along the PRO module.

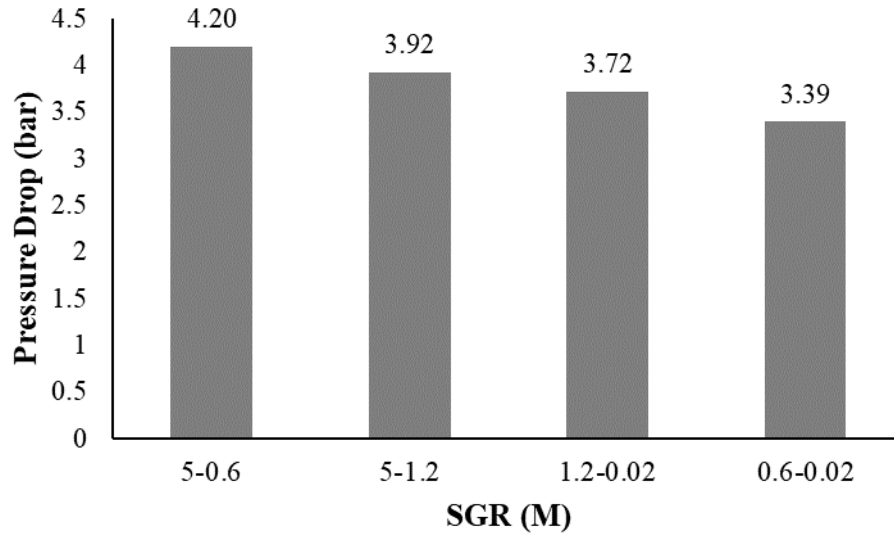


Fig. 3.5: The pressure drop of the DSPRO process includes two membrane modules in stage one and one membrane module in stage two of equal feed flow rates (1000 L/h) and hydraulic pressure of half of the osmotic pressure difference for various SGRs.

3.4.3 Determining the optimum hydraulic pressure

Previous laboratory-size studies pointed out that the optimum hydraulic pressure in the PRO system and equal to $\Delta\pi/2$ is not applicable for large scale systems and could be lower than this value [19, 212]. Accordingly, this work investigated the impact of the applied pressure on the DSPRO system behaviour; the optimum hydraulic pressure ($P_{Di,1}$) was determined at 1000 L/h flow rates of the feed and draw solutions. At 1000 L/h flow rates, the pressure drop on the draw and feed sides was calculated at every 0.1 m of the membrane length in all membrane modules as the salinity gradient resources flow rates and concentrations changed. It should be mentioned that 1000 L/h is within the flow rate recommended by the HTI Company. The membrane area in the second stage was calculated using **Equation 3.11**. It was found that the optimum applied pressure of the optimized DSPRO system is higher than $\Delta\pi/2$ for all SGRs (**Fig. 3.6A**). The optimum hydraulic pressure was 0.76% higher than $\Delta\pi/2$ for 5M-0.6M, 1.36% higher than $\Delta\pi/2$ for 5M-1.2M, 1.41% higher than $\Delta\pi/2$ for 1.2M-0.02M and 14.16% higher than $\Delta\pi/2$ for 0.6M-0.02M.

Even though the increase in pressure is not more than 14.16%, it will increase operating and maintenance costs. Using higher hydraulic pressure will also increase the need for membranes to handle higher pressure and requires higher mechanical stability [167].

Additionally, **Fig. 3.6A** show the membrane area in stage two of the DSPRO system. The ratio of A_2/A_1 is higher in the conventional DSPRO systems than in the systems operating at optimum pressure due to the slightly higher hydraulic pressure in the latter systems, i.e., $> \Delta\pi/2$, resulting in a drop in the water flux in the (**Fig. A1-Appendix**). The ratio of A_2/A_1 in the conventional systems was between 16.34%-33.53%, while in the systems operating at optimum pressure was between 16.14%-33.05%.

The specific power generation was calculated for optimized and conventional DSPRO systems (**Fig. 3.6B**). The generated specific power was calculated in the first DSPRO stage (E_{o1}), the second DSPRO stage (E_{o2}), and the entire DSPRO system (E_{tot}). In stage one of the DSPRO process, the results showed a slight increase in the specific power generation in the DSPRO process operated at optimum hydraulic pressure compared to the conventional DSPRO system because of the higher applied pressure in the former process. In stage two, E_{o2} in the DSPRO process at optimum applied pressure was lower than in the conventional DSPRO process for 5M-0.6M, 5M-1.2M, and 1.2M-0.02M SGRs, and higher for 0.6M-0.02M SGR (**Fig. 3.6A**). The reduction in E_{o2} for 5M-0.6M, 5M-1.2M, and 1.2M-0.02M could be due to the effect of the concentration polarization, which would reduce the permeation rate in the first stage, and that would cause a drop in the flow rates of the feed and draw solutions entering the second stage, and in consequence, reduce E_{o2} . The influence of concentration polarization in 0.6M-0.02M was insignificant due to the low water flux, and hence the E_{o2} was higher in the DSPRO system operating at optimum pressure.

The total specific power (E_{tot}) was between 0.007%-2.45% higher in the DSPRO process operating at optimum hydraulic pressure, and the highest increase was for 0.6M-0.02M. Generally, using optimum hydraulic pressure caused only a slight increase in the specific produced power. Compared to a single-stage PRO process, using the DSPRO process caused 33.8%, 35%, 31% and 34.7% increases in E_{tot} for 5M-0.6M, 5M-1.2M, 1.2M-0.02M, and 0.6M-0.02M, respectively.

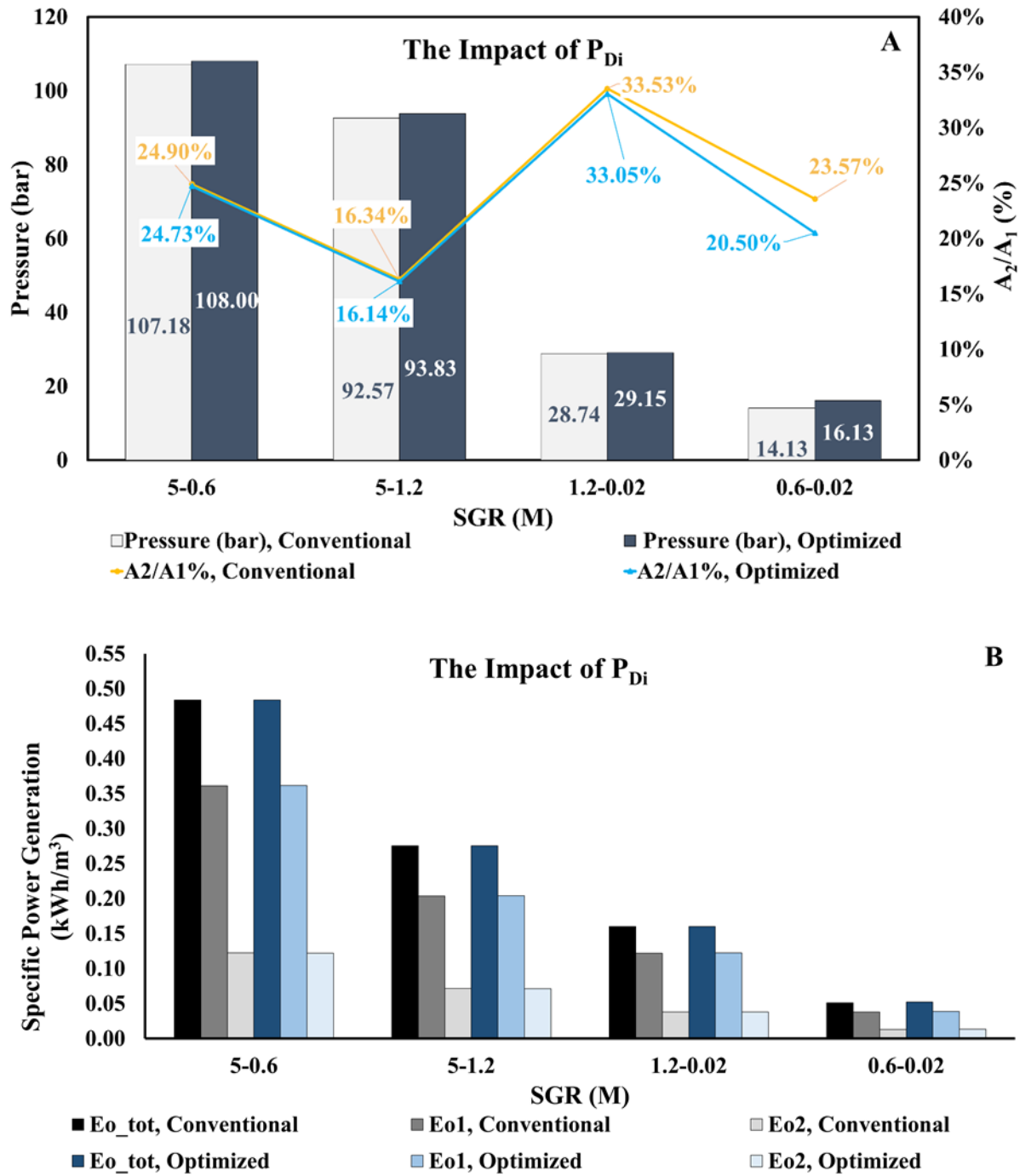


Fig. 3.6: The impact of the optimum hydraulic pressure of the DSPRO system on the specific power generation for various SGRs. **A:** The hydraulic pressure and the membrane area ratio (A_2/A_1 %), and **B:** specific power generation in the conventional and optimized DSPRO systems for all SGRs at stage one (Eo1), stage two (Eo2), and the total amount at both stages (Eo_tot).

3.4.4 Determining the optimum draw flow rate

The draw solution flow rate is one of the key parameters affecting the behaviour of the DSPRO systems [170, 193]. Determination of the optimum value of the draw solution flow rate in the DSPRO system was performed in this study at $P_{Di,1} = \Delta\pi/2$ and $Q_{Fi,1} = 1000$ L/h. The flow rates ratio in the first DSPRO stage (Q_D/Q_F) and the membranes' areas (A_2/A_1) for the optimized and conventional DSPRO systems are shown in **Fig. 3.7A**. Equal flow rates were used in conventional DSPRO systems [65]. The optimum ratio of the draw to the feed solution flow rate was different for each SGR. For instance, the optimum flow rate ratio of Q_D/Q_F was 57% for 5M-0.6M, 48.7% for 5M-1.2M, 56.9% for 1.2M-0.02M and 36.7% at 0.6M-0.02M. The Q_D/Q_F is a function of the permeation flow which relies on the concentration polarization phenomena in osmotically driven membrane processes. For example, Q_D/Q_F ratio 5M-0.6M was higher than in 5M-1.2M salinity gradient due to the higher flux in the former salinity gradient that required a higher draw solution flow rate to reduce the impact of concentration polarization on the draw dilution side. Likewise, the lowest Q_D/Q_F ratio was for 0.6M-0.02M which exhibited low water flux.

The percentage of A_2/A_1 in **Fig. 3.7A** show some difference between the ratio of membrane areas in stages one and two of the optimized and the conventional systems. For example, the A_2/A_1 ratio in the 0.6M-0.02M was 45.06% and 23.57% in the optimized and conventional DSPRO systems, respectively. There is a 91.17% increase in the A_2/A_1 in the optimized DSPRO system; this is because of the lower draw solution flow rate in the first stage ($Q_{Di,1}$) of the optimized DSPRO process. According to **Equation 3.11**, A_2 is a function of the draw solution flow rates in stage one and stage two ($Q_{Di,1}$ and $Q_{Di,2}$) of the process, but it is more affected by the draw solution flow rate in the first stage of the system. On the contrary, for 5M-0.6M salinity gradient, A_2 increased by 47.25% in the DSPRO process operated at optimum draw solution flow rate compared to the conventional process; this is due to the low draw solution flow rate in the first stage ($Q_{Di,1}$) of the optimized DSPRO process, which confirms the finding mentioned above. A_2/A_1 ratios were between 16.34%-33.53% for the different SRGs at the conventional systems and varied between 27.19%-47.42% when the optimum draw solution flow rate was used.

The specific power generation was calculated for all SGRs at the optimum draw solution flow rate and compared to the conventional DSPRO systems (**Fig. 3.7B**). The Eo_{tot} was 9.1%, 13.93%, 8.05%, and 24.22% higher for salinity gradients 5M-0.6M, 5M-1.2M, 1.2M-0.02M, and 0.6M-0.02M, respectively, in the DSPRO process operating at the optimum Q_D flow rate compared to the conventional DSPRO process. At optimum Q_D , there was an increase between 5% and 12% in the Eo_1 and between 13%-61% in the Eo_2 . Using optimum Q_D caused an increase in Eo_1 and Eo_2 due to the lower Q_D in the DSPRO process (**Equation 3.10**). The impact of using an optimum draw flow rate on the DSPRO process performance was higher than the impact of

using an optimum hydraulic pressure. The specific power generated improved by 9.1% to 24.22% after determining the optimum Q_D , but it was 0.007% to 2.45% after determining the optimum hydraulic pressure, P . The results also revealed an increase in the specific power generation between 35.6% and 49.4% due to adding a second PRO stage to the DPSRO process compare single-stage PRO process.

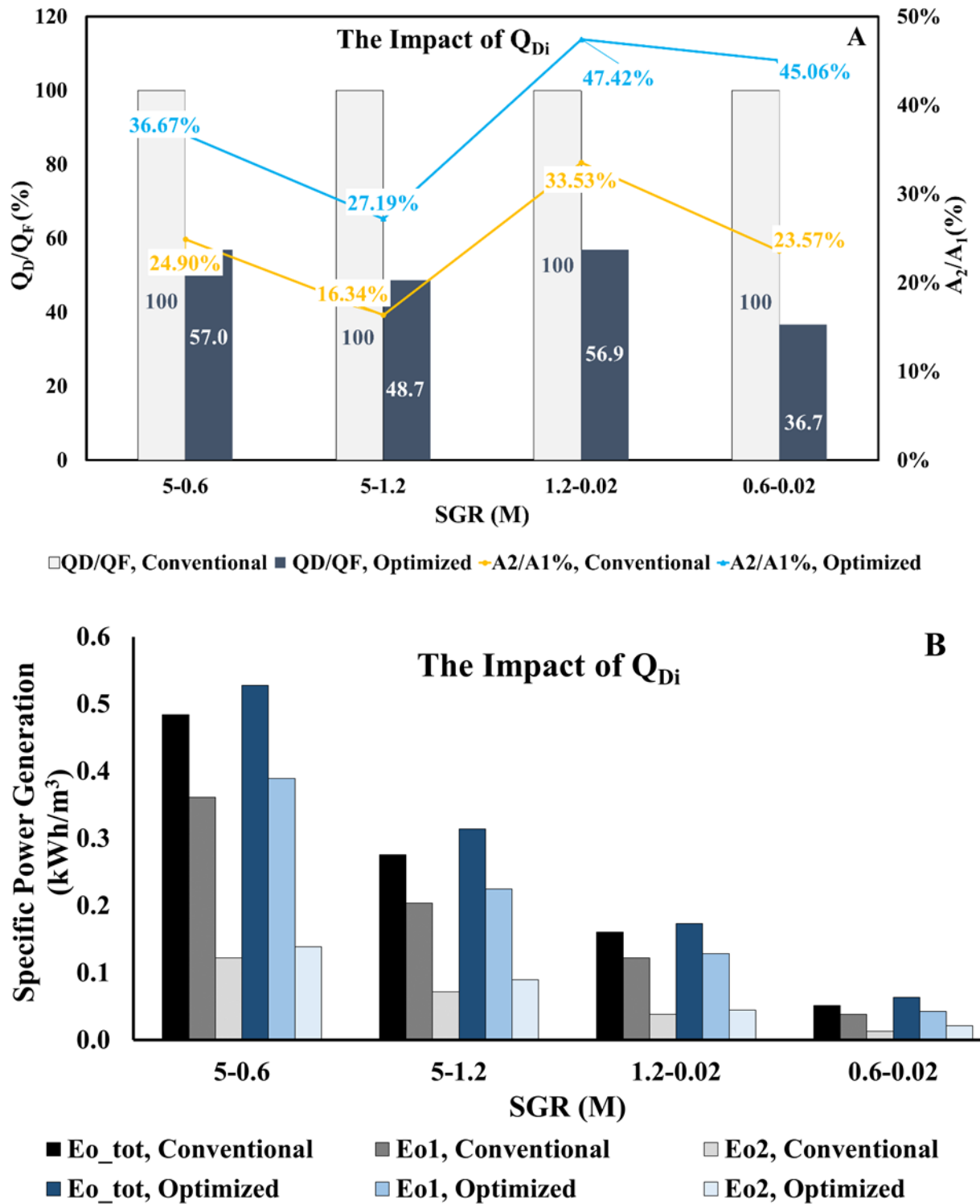


Fig. 3.7: The effect of the optimum draw solution flow rate of the DSPRO system on the specific power generation for various SGRs. **A:** The ratio of the draw solution flow rate to the feed solution flow rate in the first DSPRO stage (Q_D/Q_F %) and the membrane area ratio (A_2/A_1 %). **B:** Specific power generation in the conventional and optimized DSPRO systems for the SGRs at stage one ($Eo1$), stage two ($Eo2$) and the total amount at both stages (Eo_{tot}).

3.4.5 Determining the optimum feed flow rate

Another important parameter that affects DSPRO performance is the flow rate of the feed solution. The optimum feed flow rate and its impact on the produced specific power were performed in this study at $P_{Di,1} = \Delta\pi/2$ and $Q_{Di,1} = 1000$ L/h. **Fig. 3.8** shows the Q_F/Q_D ratio, A_2/A_1 ratio, and Eo_{tot} of the optimized and conventional DSPRO processes. Results show lower Q_F/Q_D ratios in the optimized systems compared to the conventional systems for all SGRs (**Fig. 3.8A**). The inlet feed to draw solution flow rate ratios for the optimized systems were 28 %, 42.4%, 27.8%, and 25.8% for 5M-0.6M, 5M-1.2M, 1.2M-0.02M, and 0.6M-0.02M, respectively. The highest optimum flow rates ratio (Q_F/Q_D) was 42.4% for 5M-1.2M, which is expected as a result of the high feed concentration. The effect of the internal concentration polarization increases with increasing the feed concentration, and hence high feed solution flow rate will minimize the concentrative CP effect [139]. The severity of the internal concentration polarization for 1.2M-0.02M and 0.6M-0.02M is lower than the other salinity gradients as a result of the low feed concentration. Consequently, the Q_F/Q_D values were lower for 1.2M-0.02M and 0.6M-0.02M. In effect, the flow rate of the feed solution and the ratio of Q_F/Q_D is a function of the feed concentration; the lower the feed concentration, the lower the feed solution flow rate is required.

Fig. 3.8A also shows the A_2/A_1 ratio of the optimized and conventional DSPRO systems. Contrary to the optimum Q_D impact, the A_2/A_1 ratios were lower in the optimized DSPRO systems than in the conventional systems. The A_2/A_1 ratios for the conventional systems were 24.9%, 16.34%, 33.53% and 23.57% for 5M-0.6M, 5M-1.2M, 1.2M-0.02M and 0.6M-0.02M, respectively. The corresponding results in the optimized DSPRO processes were 20.76%, 13.88%, 26.42%, and 21.45% for 5M-0.6M, 5M-1.2M, 1.2M-0.02M and 0.6M-0.02M, respectively. Therefore, a smaller membrane area for the second DSPRO stage was required in the optimized DSPRO processes compared to the conventional processes. Based on the DSPRO process design shown in **Fig. 3.1**, lower water flux in the optimized process required a smaller membrane area in the second DSPRO stage. The results pointed out around 9% to 21% reduction in the stage two membrane area after determining the optimum Q_F (**Fig. 3.8A**).

Determination of the optimum value of the feed flow rate displayed a higher enhancement in the specific power generation than the optimum value of the applied pressure or the draw solution flow rate. The increase in the specific power generation in stage one (Eo_1) when the DSPRO system operated at optimum feed solution flow rate was 31% for 5M-0.6M, 19% for 5M-1.2M, 24% for 1.2M-0.02M and 46% for 0.6M-0.02M (**Fig. 3.8B**). While the increase in Eo_2 was 6% for 5M-0.6M, 4% for 5M-1.2M, 8% for 1.2M-0.02M and 2% for 0.6M-0.02M. For all salinity gradient resources, the increase in Eo_1 was higher than the increase in Eo_2 due to the higher water flux in stage one compared to stage two of the DSPRO system. It is also due to the lower flux in

stage two of the DSPRO process caused by the draw solution dilution. The percentage enhancement in the total specific power generation (E_{tot}) was 24.39%, 15.44%, 20.58%, and 34.54% for 5M-0.6M, 5M-1.2M, 1.2M-0.02M, and 0.6M-0.02M, respectively, when the DSPRO operated at optimum feed solution flow rate. The Eo_{tot} as a result of optimizing the feed solution flow rate was 0.602, 0.318, 0.193, and 0.069 kWh/m³ for 5M-0.6M, 5M-1.2M, 1.2M-0.02M, and 0.6M-0.02M, respectively. Compared to a single-stage PRO process, Eo_{tot} increased by 27.6%, 30.7%, 27.1%, and 23.9% for 5M-0.6M, 5M-1.2M, 1.2M-0.02M, and 0.6M-0.02M, respectively when a second stage was added to the DSPRO process.

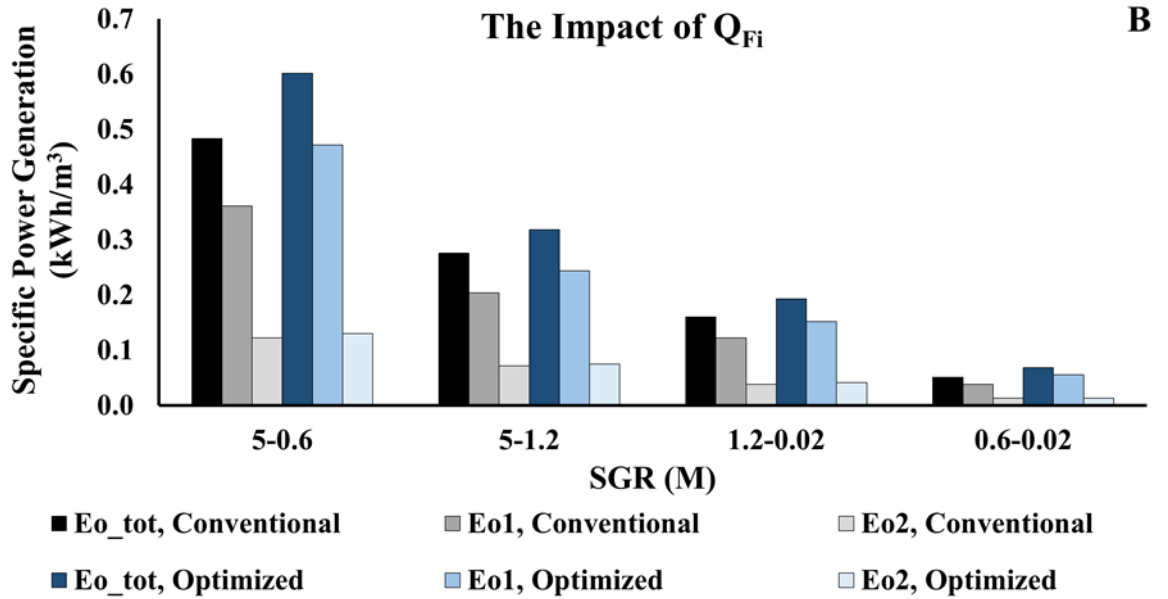
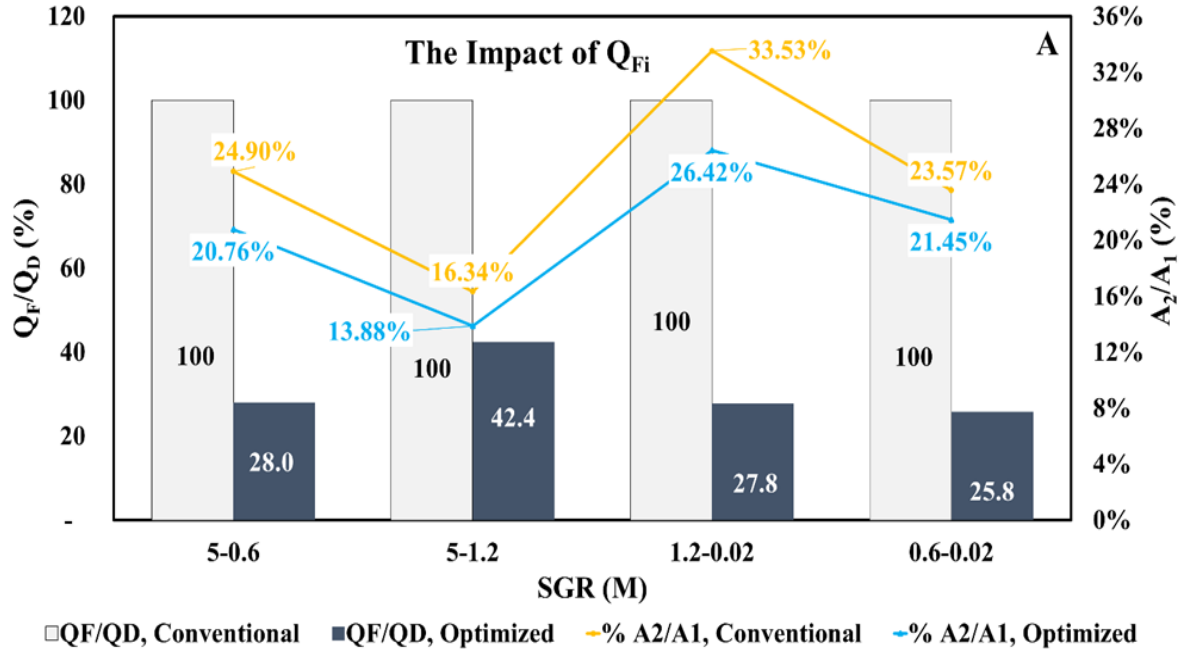


Fig. 3.8: The effect of the optimum feed solution flow rate of the DSPRO system on the specific power generation for various SGRs. **A)** The ratio of the feed solution flow rate to the draw solution flow rate in the first DSPRO stage (Q_F/Q_D %) and the membrane area ratio (A_2/A_1 %), and **B)** specific power generation in the conventional and optimized DSPRO systems for the SGRs at stage one ($Eo1$), stage two ($Eo2$) and the total amount at both stages (Eo_{tot}).

Table 3.1 shows the percentage rise in the specific power generation in the DSPRO system due to the optimum parameters. The maximum increase in the specific power occurred at the optimum feed solution flow rate, followed by the optimum draw solution flow rate and the hydraulic

pressure. As such, the systematic simulation-based optimization of the feed flow rate at the optimum values of the applied pressure and the draw solution flow rate is considered next to determine the percentage rise in the specific power generation due to the systematic simulation-based optimization in the DSPRO systems for the SGRs.

Table 3.1: The percentage increase in total specific power generation in the DSPRO processes resulting from the systematic simulation-based optimization of the main process parameters.

Salinity gradient resources (M)	The percentage increase in the total specific power generation at an optimum applied pressure	The percentage increase in the total specific power generation at an optimum draw flow rate	The percentage increase in the total specific power generation at an optimum feed flow rate
5-0.6	0.007%	9.10%	24.39%
5-1.2	0.022%	13.93%	15.44%
1.2-0.02	0.025%	8.05%	20.58%
0.6-0.02	2.45%	24.22%	34.54%

3.4.6 Systematic simulation-based optimization of feed flow rate at optimum draw flow rate and pressure

In this simulation case, the optimum draw solution flow rate and hydraulic pressure parameters are obtained from the simulation process of the DSPRO process and presented in **Table 3.2**. The optimum feed solution flow rate was found for all the SGRs, and the Q_F/Q_D ratio, A_2/A_1 ratio, and Eo_{tot} of the optimized and conventional DSPRO processes are shown in **Fig. 3.9**. The Q_F/Q_D ratio influenced by the salinity gradient resource, which determines water flux across the membrane and tends to increase with increasing water flux to overcome the impact of concentrative CP. For example, the Q_F/Q_D ratio increased from 35.11% for 5M-1.2M salinity gradient to 46.32% for 5M-0.6M salinity gradient due to higher water flux in the latter salinity gradient. A similar observation was found with 1.2M-0.02M and 0.6M-0.02M salinity gradients. A higher feed to draw flow rates ratio is required in the 0.6M-0.02M salinity gradient to overcome the impact of dilutive CP when using low concentration draw solution such as seawater (0.6M) compared to RO brine (1.2M). The membrane area used in the second DSPRO stage was larger in the optimized process compared to the conventional process (**Fig. 3.9A**) due to the lower draw

solution flow rates in the first DSPRO stage (**Equation 3.11**). A_2/A_1 ratio of the optimized processes was 33.81%, 25.54% 41.96%, and 36.64% for 5M-0.6M, 5M-1.2M, 1.2M-0.02M, and 0.6M-0.02M, respectively. While the A_2/A_1 ratio of the conventional processes was 24.9%, 16.34%, 33.53% and 23.57% for 5M-0.6M, 5M-1.2M, 1.2M-0.02M, and 0.6M-0.02M, respectively.

The specific power generation was higher in the optimized DSPRO processes than in the conventional processes (**Fig. 3.9B**). Although a significant improvement in the specific power generation was achieved in the optimized processes, the specific power generation increase was more in the first DSPRO stage. It could be related to the higher permeation flow in the first DSPRO stage compared to the second DSPRO stage. The osmotic pressure driving force in the second DSPRO stage is lower than in the first stage, leading to a lower water flux. The maximum enhancement in the specific power generation due to the optimization was 133.54% for 0.6M-0.02M, followed by 108.8% for 5M-1.2M, 71.07% for 5M-0.6M, and 63.18% for 1.2M-0.02M salinity gradient resource. Results in **Fig. 3.9B** reveal that using a low concentration feed solution, such as 0.02M wastewater, would result in a higher improvement in the DSPRO process after systematic simulation-based optimization as a result of the negligible internal concentration polarization on the feed solution side. There was a considerable increase in the specific power generation of the DSPRO processes with 5M-0.6M, 5M-1.2M, and 0.6M-0.02M salinity gradients. **Fig. 3.9** revealed that the specific power generation could be increased by 22% when a second PRO system was added to the DSPRO process. The rise in the energy output due to adding a second PRO stage was 21.5%, 19.1%, 22.4%, and 20.5% for 5M-0.6M, 5M-1.2M, and 0.6M-0.02M salinity gradient resources, respectively. The results showed the advantages of DSPRO over the single-stage PRO process in increasing the energy output from salinity gradient resources.

Table 3.2: The optimum values of the hydraulic pressure and the draw flow rate at the systematic simulation-based optimization of the DSPRO process with the maximum percentage of the specific power generation.

SGR (M)	The Optimum Values of P (bar)	The Optimum Values of Q_D (L/h)
5-0.6	108	570
5-1.2	93.83	487
1.2-0.02	29.15	569
0.6-0.02	16.13	367

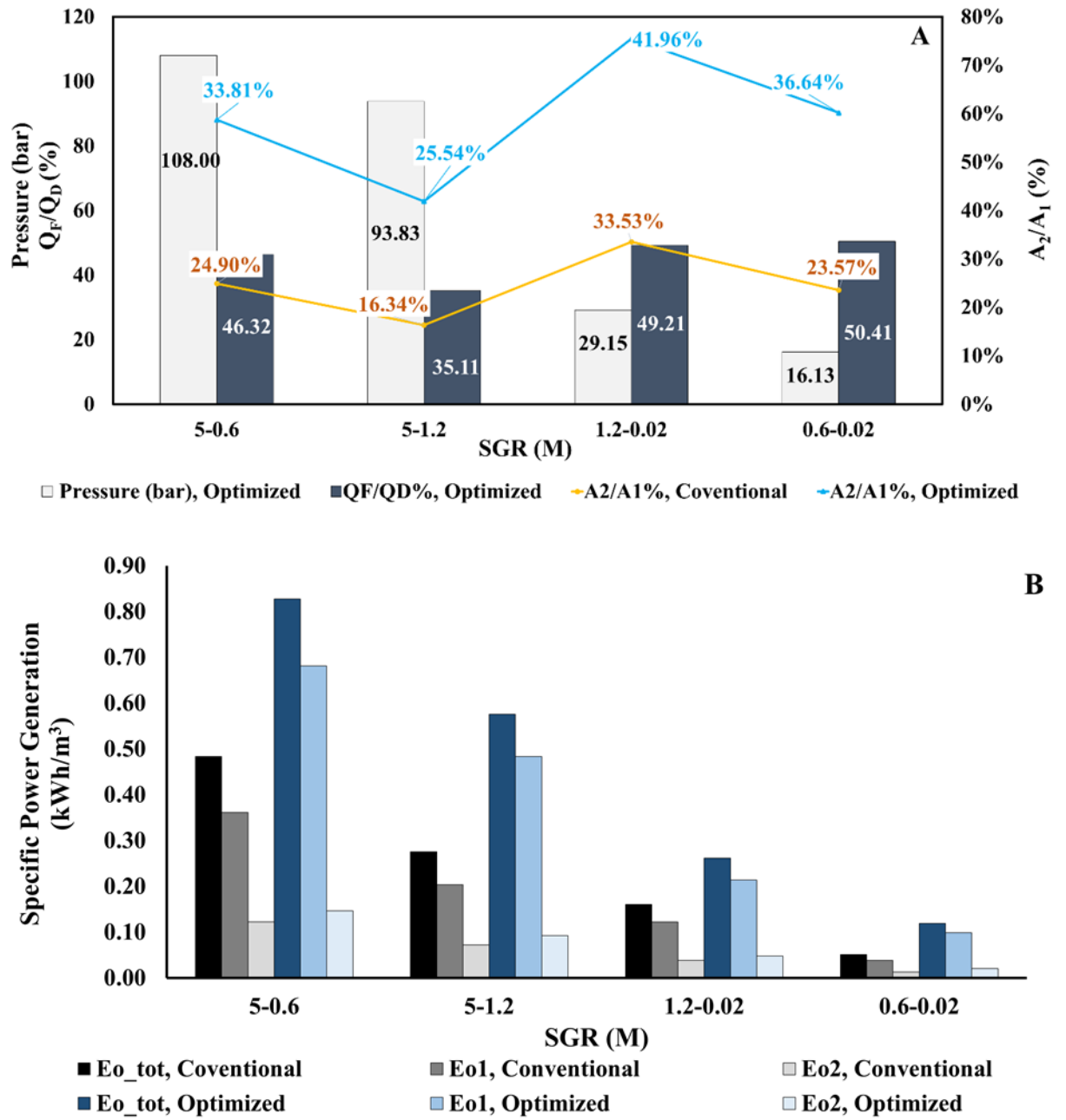


Fig. 3.9: The effect of the optimum feed solution flow rate at the optimum values of the hydraulic pressure and the draw flow rates of the DSPRO system on the produced power generation for various SGRs. **A:** The ratio of the feed solution flow rate to the draw solution flow rate in the first DSPRO stage (Q_F/Q_D %) and the membrane area ratio (A_2/A_1 %), and **B:** specific power generation in the conventional and optimized DSPRO systems for the SGRs at stage one (Eo1), stage two (Eo2) and the total amount at both stages (Eo_tot).

3.4.7 Mass transfer, solute resistivity and pressure drop impact on dual stage pressure retarded osmosis performance

The previous DSPRO simulation scenarios considered the impact of hydrodynamic conditions on the mass transfer coefficient (k_d) and the solute diffusion resistivity (K) along the full-scale PRO module. Three scenarios are investigated to study the DSPRO process performance using i) case 1, k_d and K are variables with pressure drop in the PRO membrane module ii) case 2, k_d and K are constants with pressure drop in the PRO membrane module, and iii) case 3, k_d and K are constants without pressure drop in the PRO module (**Table 3.3**). In the comparison study, case 1 vs case 2 shows the effect of k_d and K on the process performance, case 2 vs case 3 shows the influence of pressure drop on the process behaviour, and case 3 vs case 1 shows the impact of k_d , K , and pressure drop on the process performance.

Table 3.3: The effect of considering the variation of k_d , K , and the pressure drop along the membrane modules in the DSPRO systems for the SGRs in the total specific power generation.

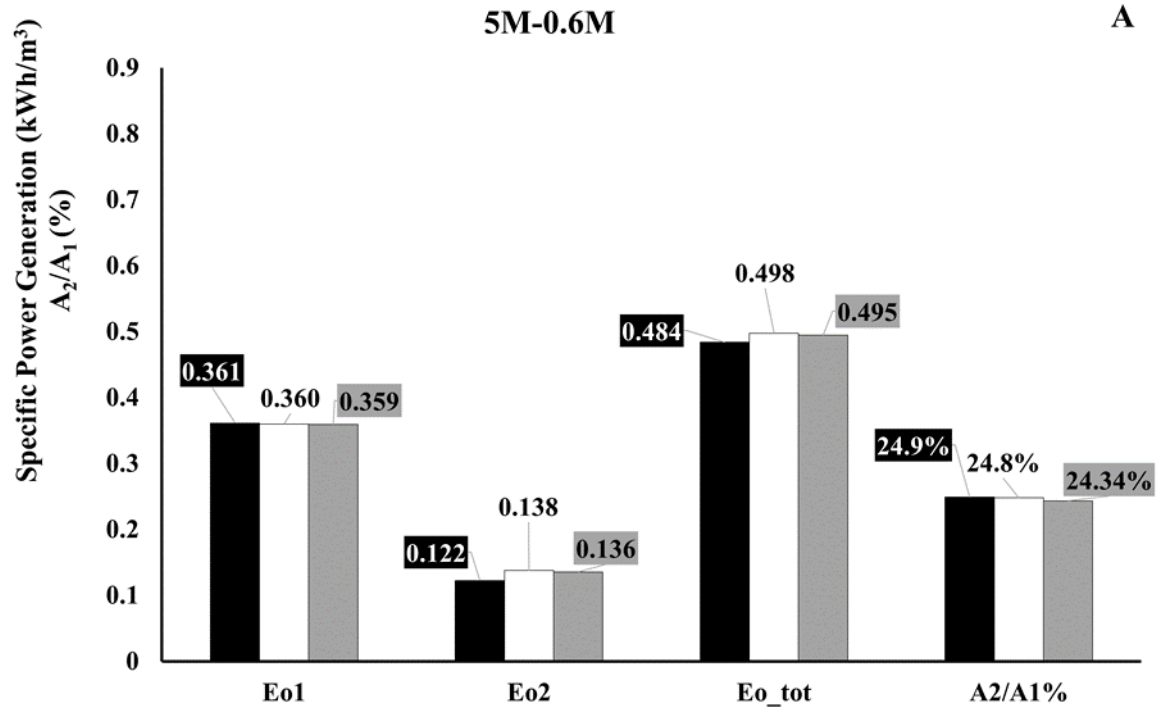
Scenarios	Parameters	SGRs NaCl (M)	Comparison	% Difference in Eo1	% Difference in Eo2	% Difference in Eo_tot
Case 1	k_d and K are variables with pressure drop	5-0.6	Case 1 Vs. Cas2	0.39	-11.14	-2.8
		5-1.2		0.57	-13.04	-3.37
		1.2-0.02		0.78	-9.2	-1.78
		0.6-0.02		0.39	-8.82	-2.13
Case 2	k_d and K are constants with pressure drop	5-0.6	Case 2 Vs. Case 3	0.25	1.66	0.63
		5-1.2		0.25	1.07	0.49
		1.2-0.02		1.04	5.98	2.27
		0.6-0.02		-0.79	-1.63	-1.03
Case 3	k_d and K are constants without pressure drop	5-0.6	Case 3 Vs. Case 1	-0.63	10.7	2.24
		5-1.2		-0.81	13.77	2.99
		1.2-0.02		-1.8	3.92	-0.44
		0.6-0.02		0.41	11.49	3.23

The results were obtained at standard testing conditions of the DSPRO process, i.e., 1000 L/h flow rate of feed and draw solutions and a hydraulic pressure equal to $\pi/2$ to determine the impact of these parameters under the same experimental conditions. **Fig. 3.10** explains the specific power generation in stage one and stage two (Eo1 and Eo2), total specific power generation (E_tot), and

A_2/A_1 ratio in DSPRO processes. In the first DSPRO stage, the specific power generation for 5M-0.6M was 0.361 kWh/m³, 0.360 kWh/m³, and 0.359 kWh/m³ in case 1, case 2, and case 3, respectively. The results indicated that the DSPRO performance was subtly higher in case 1 (**Fig. 3.10A**). The same trend was noticed for 5M-1.2M, and 1.2M-0.02M (**Fig. 3.10B** and **Fig. 3.10C**), where E_{o1} was highest at case 1. For 0.6M-0.02M, E_{o1} was slightly higher (0.0382 kWh/m³) in case 3 (**Fig. 3.10D**) due to the combined effect of the hydraulic pressure and water permeation rate on the specific power generation (**Fig. A3B - Appendix**). In the second DSPRO stage, the highest specific power generation was in case 2, followed by case 3, then case 1 for 5M-0.6M, 5M-1.2M, and 1.2M-0.02M. Compared to case 2, there was an 11.14%, 13.04%, 9.2%, and 8.82% reduction in the second stage power generation for 5M-0.6M, 5M-1.2M, 1.2M-0.02M, and 0.6M-0.02M, respectively, due to changing k_d and K in case 1. The increase in E_{o2} in case 2 is as a results of increasing the water flux in stage two of the DSPRO system (**Fig. A2-Appendix**). Nevertheless, the highest percentage increase in E_{o2} for 0.6M-0.02M was in case 3 (**Fig. 3.10D**). The variation in the specific power generation of the DSPRO system at constant k_d and K and ignoring the pressure drop in the membrane is influenced by water flux and hydraulic pressure. For 0.6M-0.02M SGR, water flux is higher in case 1 than in case 3 (**Fig. A2D-Appendix**), but E_{o2} was higher in case 3 due to the higher hydraulic pressure since pressure drop was neglected in case 3 (**Fig. A3B - Appendix**). The total specific power generation (E_{o_tot}) was higher in case 2 for 5M-0.6M, 5M-1.2M, and 1.2M-0.02M, than E_{o_tot} in case 1. For instance, there was a 2.8%, 3.37%, 1.78% and 2.13% reduction in the E_{o_tot} for 5M-0.6M, 5M-1.2M, 1.2M-0.02M, and 0.6M-0.02M, respectively, in case 1 compared to in case 2. Comparing case 3 to case 1, 2.24%, 2.99%, and 3.23% increase in E_{o_tot} occurred for 5M-0.6M, 5M-1.2M, and 0.6M-0.02M, respectively, due to the variation in k_d , K and considering the pressure drop across the membrane modules. In contrast, a reduction of 0.44% for 1.2M-0.02M (**Table 3.3**) occurred due to the reduction in the permeation flow and applied pressure in case 1 compared to case 3 (**Fig. A3A - Appendix**).

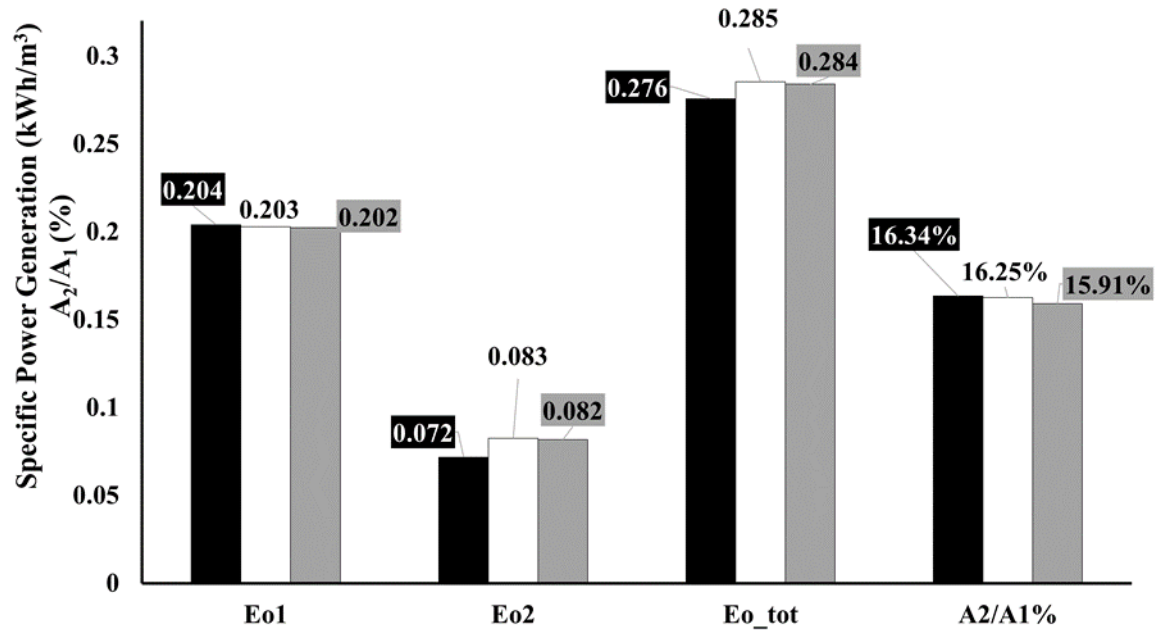
There was also a subtle difference in the A_2/A_1 ratio in case 1, case 2, and case 3. A_2/A_1 ratio was slightly higher in the DSPRO processes performed in case 1 followed by case 2, and then case 3 due to the higher permeation flow rate in the first DSPRO stage (**Fig. A2-Appendix**). A_2 is affected by the permeate flow rate (**Equation 3.11**); the more the permeation rate in the first DSPRO stage, the higher the A_2/A_1 ratio. The variation of k_d , K and considering the pressure drop across the membrane modules generated a higher permeation flow rate in the first DSPRO stage, which is the draw solution in the second DSPRO stage, increasing the membrane area of the second DSPRO stage.

Practically, k_d and K parameters and the pressure drop will change in the full-scale module due to the variation in feed and draw solution flow rates. Overlooking variation in k_d and K parameters will overestimate Eo_{tot} , as shown in case 2 compared to case 1. Likewise, ignoring the pressure drop along the PRO membrane will subtly affect Eo_{tot} , as shown in case 3 compared to case 2. Overall, results in **Fig. 3.10** showed the impact of k_d and K parameters on Eo_{tot} (case 1 vs case 2) is higher than the impact of pressure drop on the Eo_{tot} (case 2 vs case 3). In effect, the DSPRO performance would be closer to real field conditions when pressure drop and variation in hydrodynamic conditions are included in calculating the specific power generation.



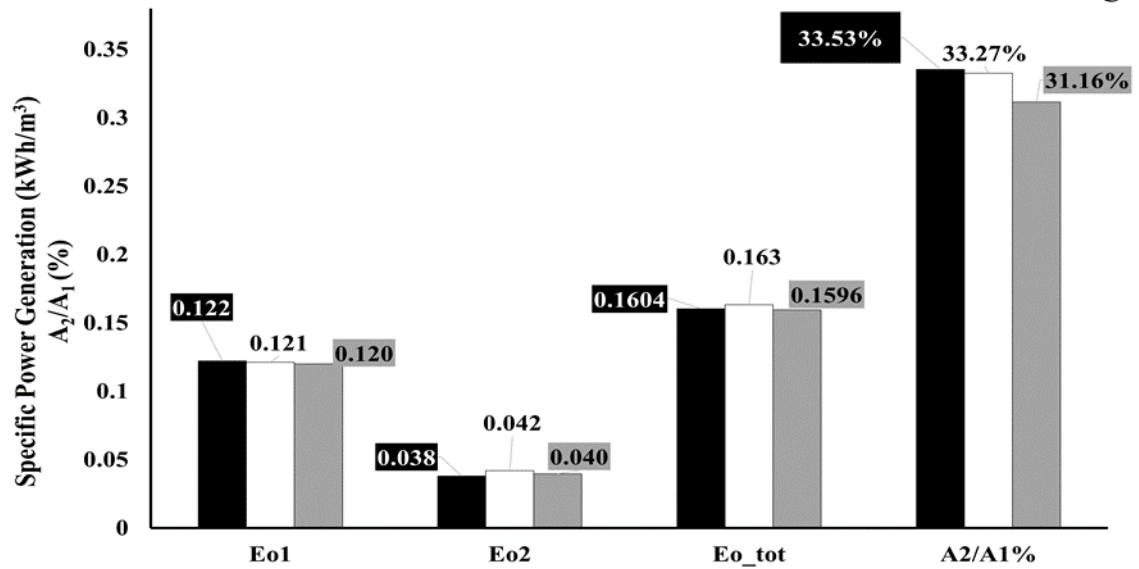
5M-1.2M

B



1.2M-0.02M

C



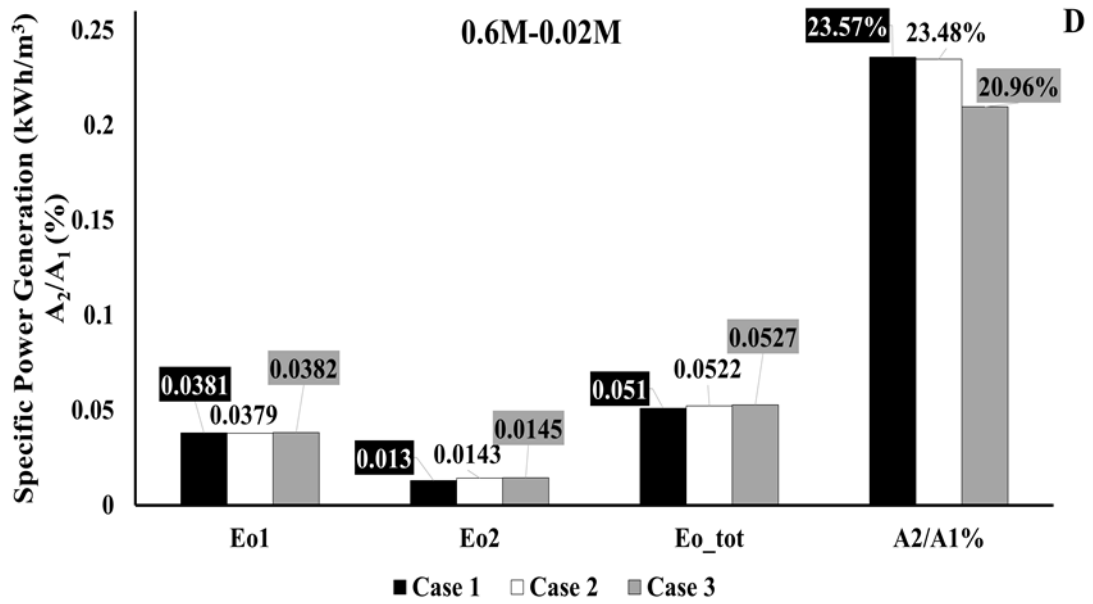


Fig. 3.10: The impact of changing k_d and including the pressure drop in the DSPRO processes on the produced power generation in stage one and stage two, and the total amount at case 1, case 2, and case 3 on 5M-0.6M, 5M-1.2M, 1.2M-0.02M, and 0.6M-0.02M (A, B, C, and D, respectively).

3.5 Conclusion

DSPRO system was suggested for higher power generation from salinity gradient resources. However, the determination of the optimum operating parameters would further enhance process performance. Process systematic simulation would improve the specific energy output and reduce the cost of energy input. The study results revealed that the optimum ratio of feed to draw solution flow rate is less than in the conventional process and equal unity. Results also revealed that the feed solution flow rate is the most dominant parameter affecting the DSPRO process performance, followed by the draw solution flow rate, then hydraulic pressure. The DSPRO system total power generation could be increased by 71.07%, 108.8%, 63.18%, and 133.54% for DS-SW, DS-ROB, ROB-WW, and SW-WW SGRs, respectively, after optimizing the operating parameters. For the first time, the study evaluated the influence of hydrodynamic parameters, such as k_d and K coefficients, in process simulation. The study found that k_d and K coefficients affect the DSPRO process performance, and overlooking these parameters may overestimate the total specific power generation in the DSPRO system. This study showed 2.8% more power generation occurred in the DSPRO system using the DS-SW salinity gradient when k_d and K were considered constants. Moreover, the total power generation was increased by 0.63% for DS-SW when the pressure drop was ignored in the DSPRO process while ignoring k_d and K variations and pressure drop in the process resulted in 2.24% higher energy output. Accordingly, the results showed that k_d and K

variations in the DSPRO process would have more impact than ignoring pressure drop on the energy output and these parameters should be considered in estimating the energy output from a salinity gradient resource.

Chapter Four: Experimental and theoretical work on reverse osmosis - dual stage pressure retarded osmosis hybrid system

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4.1 Objectives

This chapter aims to develop modelling and optimization of reverse osmosis – dual-stage pressure retarded osmosis hybrid system. The main objectives of this chapter are:

- 1) To provide a suggested model of two-pass reverse osmosis with dual-stage pressure retarded osmosis hybrid system.
- 2) To compare the results of a two-pass reverse osmosis model with two-pass reverse osmosis –dual-stage pressure retarded osmosis model.
- 3) To determine the impact of the energy generated by the dual-stage pressure retarded osmosis on the net specific energy consumption of the hybrid model.
- 4) To minimize the net specific energy consumption of the suggested hybrid models.

4.2 Introduction

Reverse osmosis (RO) has been recognized as the common technology for seawater treatment as the most efficient and affordable technology compared to other desalination processes [223-225]. The theoretical specific energy consumption for seawater desalination is 1.06 kWh/m³ for seawater of 35 g/L total dissolved solids (TDS) and a 50% recovery rate [226]. For an RO plant with an energy recovery device, the specific power consumption depends on seawater TDS, which is less than 2.0 kWh/m³ for 35 g/L seawater [227, 228]. Compared to thermal desalination, RO technology is more energy-efficient and has higher recovery rates [229]. Nevertheless, it is still considered an energy-intensive desalination process, limiting its affordability in countries with high energy prices [230]. There were attempts to reduce RO energy consumption by coupling it with renewable energy sources such as solar energy [231, 232], geothermal [233, 234], wind energy [235, 236], and wave energy [237, 238]. Integrating the RO plant with renewable energy is constrained by their availability throughout the day; therefore, additional energy sources may be necessary to power the desalination plant. A new kind of renewable power, pressure retarded

osmosis (PRO), was recommended for coupling with RO desalination to lessen energy consumption [239-242]. The PRO system is a salinity gradient-operated technology that uses a slightly pressurized RO brine to convert a chemical potential to hydraulic energy [243-245]. The high-pressure RO brine will be pumped into the PRO membrane module for freshwater extraction from a lower salinity feed solution in the RO-PRO hybrid system. The diluted RO brine (the PRO draw solution) will be depressurized in a hydro turbine system for energy recovery. Previous studies demonstrated that the power consumption of RO desalination could be reduced by 14 to 40% when coupled with the PRO process [185].

Several studies considered combining the PRO system with the RO desalination plant to lessen energy consumption and brine discharge to the sea. For instance, Altaee et al. [217] studied the behavior of the RO-PRO hybrid system for energy generation. The study underlined the advantage of coupling the RO with the PRO system to lessen the energy consumption of the RO plant by 31%. Results also revealed that reducing the draw solution flow rate reduced the RO plant energy consumption. In another study, Quan et al. (2019) [185] determined the effect of feed temperature on the energy harvested from an RO brine using a PRO unit. The study revealed a 14.41% to 17.93% reduction in the specific energy consumption could be achieved by increasing the PRO operating temperature from 25 °C to 50 °C. Moreover, it was noticed that the PRO operating pressure has an inverse relationship with the specific energy consumption of the RO-PRO hybrid system.

Another RO-PRO hybrid study determined the RO recovery rate and feed concentration influence on the PRO membrane area, feed pressure, and draw solution concentration [183]. Using 35 g/L seawater feed solution in the RO plant at a 52% recovery rate produced a maximum power density of 24 W/m². However, using higher salinity of the seawater of 45 g/L and reducing the recovery rate to 46% increased the PRO power density to 28 W/m². The study also reported that adding the PRO system to the RO system caused an 18% increase in the RO recovery rate. He et al. [246] demonstrated that a standalone RO desalination system with an energy recovery device required an optimum net specific energy consumption of around 1.6 kWh/m³ at a 50% RO recovery rate. At the same recovery rate, coupling the RO desalination system with a PRO unit and energy recovery device caused a 1 kWh/m³ drop in the optimum net specific energy consumption of the RO plant. The results suggest that adding the PRO system to the RO system could reduce the optimum net specific energy consumption to around 38%.

Touati et al. [178] proposed a hybrid system of two RO units (2RO), an energy recovery device, a pressure exchanger, a turbine, and two PRO units. Each RO membrane unit was coupled individually with a PRO system. The specific energy generation of PRO stage one at a 50%

recovery rate and 80% draw stream dilution was 0.15 kWh/m^3 . In the second PRO system operating under the same conditions, the specific energy consumption was 0.57 kWh/m^3 . Results also revealed that energy generation had an inverse relationship with the RO recovery rate. Nevertheless, the study did not include optimization of the specific energy consumption. It should be noted that the 2RO plant is a common design for optimizing the quality of the product water [247]. A dual-stage PRO (DSPRO) process would be suitable for optimizing the performance of the 2RO plant in a fully integrated RO-PRO hybrid system. However, studies that considered the coupling of the DSPRO with the 2RO plant and hybrid system optimization are scarce [178, 218]. In the DSPRO system, the draw solution from the PRO stage one is coupled with a fresh feed solution in the PRO stage two to reduce the concentration polarization effect and improve the harvested energy from the salinity gradient resource [27, 29].

This research discussed the behavior of the 2RO-DSPRO based on the RO specific energy consumption and PRO net specific energy generation as objective functions. Furthermore, model-based optimization will enable the plant to create a hybrid 2RO-DSPRO system. Accordingly, this study evaluated the energy efficiency of the 2RO-DSPRO hybrid system (**Fig. 4.1**). In the 2RO-DSPRO system, RO1 brine is partially depressurized in the ERD2 before going to the PRO1 for freshwater extraction from the wastewater feed solution. When leaving the PRO1, the diluted draw solution fed to ERD1 to partially pressurize a seawater feed solution. A partially depressurized diluted draw solution will leave ERD1 and enter the PRO2 unit for freshwater extraction from a wastewater feed solution before splitting it into two streams. The first stream fed to a hydro turbine for power generation, and the second stream goes to ERD3 to depressurize the RO1 permeate that forms the RO2 feed solution. The study developed separate models for the RO and PRO processes using the “Modelica” modelling language through the Dymola software. The RO and the PRO models were validated using experimental data. The performance of the 2RO plant was compared with the 2RO-DSPRO plant at different recovery rates and seawater salinities of 40 g/L and 45 g/L. To the best of the authors' knowledge, no study is yet available about the 2RO-DSPRO hybrid system and system optimization to minimize the specific energy consumption of the desalination process.

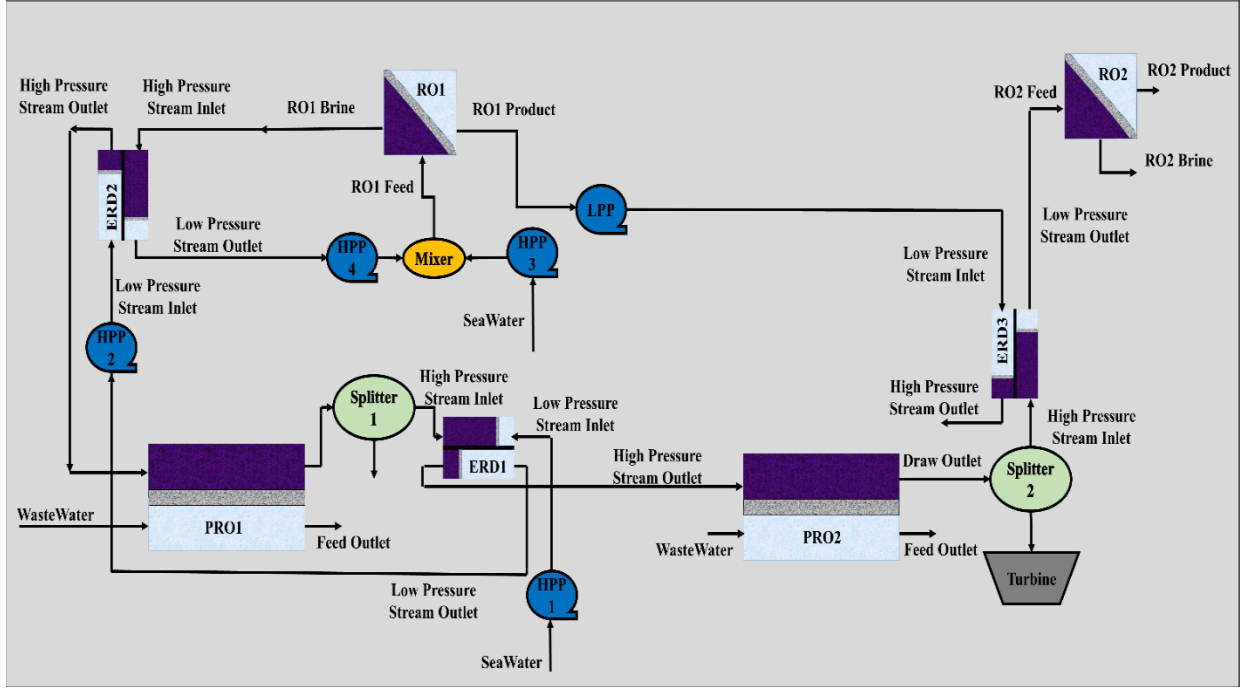


Fig. 4.1: The 2RO-DSPRO hybrid system.

4.3 Methodology

The hybrid system of the two-pass RO-DSPRO (2RO-DSPRO) includes a turbine, high-pressure pump (HPP), low-pressure pump (LPP), and an energy recovery device (ERD) (**Fig. 4.1**). Mathematical models were separately defined in Dymola software for the RO and PRO systems. Accordingly, the other processes' mathematical models will be introduced in this section. The modelling language Modelica is used to model and simulate the RO and the PRO processes by Dymola software and system components such as turbines, pumps, and energy recovery devices. Simulations were performed on the RO and PRO models to determine the applicable range of operating variables.

4.3.1 The reverse osmosis model

The water flux in the RO unit is calculated based on the following equation.

$$J_{RO} = Aw_{RO}(\Delta P_{RO} - \sigma \Delta \pi_{RO}) \quad (4.1)$$

where J_{RO} is the water flux in the RO process, Aw_{RO} is the water permeability, ΔP_{RO} is the difference in the applied pressure, σ is the reflection coefficient, and $\Delta \pi_{RO}$ is the difference in the osmotic pressure which is calculated by the next equation.

$$\Delta\pi_{RO} = \left(\frac{i^*R^*T}{Mwt}\right)(C_{Fm,RO} - C_{p,RO}) \quad (4.2)$$

Where, i is the Van't Hoff factor, R is the real gas constant, T is the feed solution temperature, Mwt is the molecular weight of the solute, $C_{Fm,RO}$ is the feed membrane side concentration, and $C_{p,RO}$ is the product concentration. To determine the product concentration, the equation of the concentration polarization is included with the flux of the solute by the SK model [218] in the RO model and these are described next.

$$\frac{(C_{Fm,RO}-C_{p,RO})}{(C_{F,RO}-C_{p,RO})} = e^{\frac{J_{RO}}{k_{RO}}} \quad (4.3)$$

Equation 4.3 represents the film theory's concentration polarisation, where $C_{F,RO}$ is the concentration of the feed solution, and k_{RO} is the mass transfer coefficient. **Equation 4.4** represents the flux of the solute by the SK model.

$$\frac{C_{p,RO}}{C_{F,RO}} \left(1 + \left(\frac{\sigma}{1-\sigma}\right) \left(1 - e^{-J_{RO}(1-\sigma)/B_{RO}}\right)\right) = e^{\frac{J_{RO}}{k_{RO}}} \quad (4.4)$$

where B_{RO} is the solute permeability. Darcy's model is used to determine the pressure drop along the spiral wound membrane as the hydraulic pressure could be varied through the length of the membrane as a function of the feed solution flow rate [248]. The pressure and the flow rate are taken to average inlet and outlet conditions for simplicity. Thus, the pressure drop (Pd_{RO}) in the pressure vessel is calculated as follows.

$$Pd_{RO} = L_{RO} * D_F \frac{Q_{F,RO} + Q_{R,RO}}{2} \quad (4.5)$$

where L_{RO} is the pressure vessel length which is equal to the multiplication of the length of one membrane module (l_{RO}) times the number of the membrane modules in one pressure vessel (M), D_F is Darcy's law constant for the feed solution, $Q_{F,RO}$, and $Q_{R,RO}$ is the flow rate of the feed and reject solutions, respectively. It is presumed that the pressure of the product solution is 1.5 bar, and the pressure drop in both the feed and permeate sides is negligible. The difference in the hydraulic pressure across the RO membrane (ΔP_{RO}) is given as follows.

$$\Delta P_{RO} = P_{F,RO} - \frac{Pd_{RO}}{2} - P_{p,RO} \quad (4.6)$$

where $P_{F,RO}$ is the hydraulic feed pressure, and $P_{p,RO}$ is the product pressure. The mass transfer coefficient (k_{RO}) is determined by the following correlation with “ x_{RO} ” and “ y_{RO} ” are empirical constants.

$$k_{RO} = x_{RO} \left(\frac{Q_{F,RO} + Q_{R,RO}}{2} \right)^{y_{RO}} \quad (4.7)$$

The product flow rate is calculated from the following equation.

$$Q_{p,RO} = J_{RO} * Am_{RO} * M \quad (4.8)$$

where Am_{RO} is the RO membrane area and M is the number of membrane modules in a pressure vessel. The mass balance equations are included in the model too and added below.

$$Q_{F,RO} = Q_{R,RO} + Q_{p,RO} \quad (4.9)$$

$$Q_{F,RO} * C_{F,RO} = Q_{R,RO} * C_{R,RO} + Q_{p,RO} * C_{p,RO} \quad (4.10)$$

Where, $C_{R,RO}$ is the reject solution concentration. The last equation of the RO model is the one of the recovery rate ($Recv_{RO}$), and it is found as follows.

$$Recv_{RO} \% = \frac{Q_{p,RO}}{Q_{F,RO}} * 100\% \quad (4.11)$$

4.3.2 The pressure retarded osmosis model

The water flux in the PRO unit (J_{PRO}) is determined based on the following equation [25, 176].

$$J_{PRO} = Aw_{PRO} (\Delta\pi_{PRO} - \Delta P_{PRO}) \quad (4.12)$$

where Aw_{PRO} is the water permeability, ΔP_{PRO} is the difference in the applied pressure, $\Delta\pi_{PRO}$ is the difference in the osmotic pressure which is calculated by the next equation.

$$\Delta\pi_{PRO} = \left(\frac{i * R * T}{Mwt} \right) (C_{Dm,PRO} - C_{Fm,PRO}) \quad (4.13)$$

where i is the Van't Hoff factor, R is the real gas constant, T is the feed/draw solution temperature, Mwt is the molecular weight of the solute, $C_{Fm,PRO}$ is the feed concentration at

the membrane surface, and $C_{Dm,PRO}$ is the draw concentration at the membrane surface. The salt flux (J_s) is found as follows.

$$J_s = B_{PRO}(C_{Dm,PRO} - C_{Fm,PRO}) \quad (4.14)$$

In **Equation 4.14**, B_{PRO} is the salt permeability.

The mass transfer coefficients for the feed and the draw solutions ($k_{F,PRO}$ and $k_{D,PRO}$, respectively) are calculated by the following correlations with “ x_{PRO} ” and “ y_{PRO} ” are empirical constants.

$$k_{F,PRO} = x_{PRO} \left(\frac{Q_{Fi,PRO} + Q_{Fo,PRO}}{2} \right) y_{PRO} \quad (4.15)$$

$$k_{D,PRO} = x_{PRO} \left(\frac{Q_{Di,PRO} + Q_{Do,PRO}}{2} \right) y_{PRO} \quad (4.16)$$

The dilutive and the concentrative concentration polarization at the draw and feed sides [143, 249], respectively, are given below.

$$\frac{C_{Dm,PRO} - C_{Fi,PRO}}{C_{Di,PRO} - C_{Fi,PRO}} = e^{(-J_{PRO}/k_{D,PRO})} \quad (4.17)$$

$$\frac{C_{Fs,PRO} - C_{Di,PRO}}{C_{Fi,PRO} - C_{Di,PRO}} = e^{(-J_{PRO}/k_{F,PRO})} \quad (4.18)$$

where $C_{Fs,PRO}$ is the feed concentration at the membrane support layer, and $C_{Di,PRO}$, and $C_{Fi,PRO}$ are the initial concentration of the draw and feed solutions, respectively. The internal concentration polarization with the impact of the solute resistivity in the support layer (K) is given as follows.

$$C_{Fm,PRO} = C_{Dm,PRO} \left(\frac{J_{PRO} * \frac{C_{Fs,PRO}}{C_{Dm,PRO}} * e^{(J_{PRO} * K)} + B_{PRO}(e^{(J_{PRO} * K)} - 1)}{B_{PRO}(e^{(J_{PRO} * K)} - 1) + J_{PRO}} \right) \quad (4.19)$$

The solute resistivity is calculated as follows:

$$K = \frac{S}{Diff} \quad (4.20)$$

where S is the membrane structural parameter and $Diff$ is the solute diffusivity in the solution.

The chosen PRO model in this study is a plug flow model, where feed and the draw solutions flow rates in the radial and the axial directions, respectively. The membrane module suggested is a hollow fiber membrane. Accordingly, the pressure drop in the feed (lumen) side ($Pd_{F,PRO}$) is calculated by the Hagen-Poiseuille equation, while the pressure drop in the draw (shell) side ($Pd_{D,PRO}$) is determined by the Ergun equation [216] as given below.

$$Pd_{F,PRO} = \left(\frac{FibL}{mT}\right) * \frac{32 * \mu_F * u_F}{di^2} \quad (4.21)$$

$$Pd_{D,PRO} = \left(\frac{(Do-Di)/2}{nT}\right) * \left(\frac{150(1-\varepsilon)^2 \mu_D u_D}{\varepsilon^3 (1.5do)^2} + \frac{1.75(1-\varepsilon) \rho_D u_D^2}{\varepsilon^3 (1.5do)}\right) \quad (4.22)$$

where $FibL$ is the fiber length, mT is the total number of sections in the shell side of the module, μ_F is the feed solution viscosity, u_F is the feed solution velocity, di is the inner fiber diameter, Do , and Di are the outlet and inlet diameter of the shell of the HF module, nT is the total number of the sections in the radial direction, ε is the porosity of the membrane module, μ_D is the draw solution viscosity, u_D is the draw solution velocity, ρ_D is the draw solution density, and do is the outlet fiber diameter. The feed and draw velocities in the fiber and shell sides, respectively, need to be predicted to solve the pressure drop equations. The feed solution velocity inside the fiber can be found by dividing the feed flow rate by the area of the fibers as follows.

$$u_F = \frac{Q_{Fi,PRO}}{FibNn * \frac{\pi di^2}{4}} \quad (4.23)$$

where $FibNn$ is the number of the fibers at a certain “ n ” subsection, as the radial side is divided by “ n ” subsections, where each “ n ” has a different number of fibers. The next equation is used to determine the number of the fibers at a certain “ n ” section in the radial direction by multiplying the area of each “ n ” subsection by the total number of the fibers divided by the total area of the membrane module.

$$FibNn = \frac{\frac{\pi}{4} [(Do-Di) \frac{n}{nT} + Di]^2 - Di^2 * NOF}{\frac{\pi}{4} (Do^2 - Di^2)} \quad (4.24)$$

where NOF is the total number of fibers in the HF PRO module. Similarly, the draw solution velocity is required for determining the pressure drop at the shell side and can be found by dividing the inlet flow rate of the draw solution by the available area for the draw solution to flow. Based on the “ m ” and “ n ” subsections, this area will vary in axial and radial module directions. The velocity of the draw solution in the shell side is calculated as follows.

$$u_d = \frac{Q_{Di,PRO}}{\frac{\pi}{2} \left(\left[(D_o - D_i) \frac{n}{nT} + D_i \right] * \frac{l_{PRO}}{mT} * (1 - PackD) \right)} \quad (4.25)$$

Where l_{PRO} is the length of the HF PRO module and $PackD$ is the packing density of the membrane. After calculating the pressure drop at both sides, the following equations are used to determine the outlet pressure of the feed and draw sides ($P_{Do,PRO}$, and $P_{Fo,PRO}$), respectively.

$$P_{Fo,PRO} = P_{Fi,PRO} - Pd_{F,PRO} \quad (4.26)$$

$$P_{Do,PRO} = P_{Di,PRO} - Pd_{D,PRO} \quad (4.27)$$

The difference in the applied pressure is then found as the difference between the average pressure in the draw side and the average pressure in the feed side as follows.

$$\Delta P_{PRO} = \frac{(P_{Di,PRO} + P_{Do,PRO})}{2} - \frac{(P_{Fi,PRO} + P_{Fo,PRO})}{2} \quad (4.28)$$

The outlet flow rates of the draw and feed solutions are then calculated.

$$Q_{Fo,PRO} = Q_{Fi,PRO} - (J_{PRO} * \left(\frac{Am_{PRO}}{mT * nT} \right)) \quad (4.29)$$

$$Q_{Do,PRO} = Q_{Di,PRO} + (J_{PRO} * \left(\frac{Am_{PRO}}{mT * nT} \right)) \quad (4.30)$$

where Am_{PRO} is the membrane surface area of the PRO. The total energy generation (W), the power density (PWD), and the recovery rate ($Recv_{PRO}$) of the PRO are determined by the next equations [249].

$$W = (Q_{Do,PRO} * P_{Do,PRO}) - (Q_{Di,PRO} * P_{Di,PRO}) \quad (4.31)$$

$$PWD = \frac{W}{\frac{Am_{PRO}}{mT * nT}} \quad (4.32)$$

$$Recv_{PRO} = \frac{Q_{Do,PRO} - Q_{Di,PRO}}{Q_{Do,PRO}} * 100\% \quad (4.33)$$

4.3.3 The pump model

The pumps were used in the models for pumping the feed seawater to the RO unit at a fixed pressure. The mass balance of the pump is given below.

$$Q_{Pump,i} = Q_{Pump,o} \quad (4.34)$$

Where, $Q_{Pump,i}$, and $Q_{Pump,o}$ are the inlet and outlet flow rates, respectively. The next equation is the momentum balance of the pump.

$$P_{Pump,o} = P_{Pump,i} + P_{Pump,H} \quad (4.35)$$

where $P_{Pump,o}$, $P_{Pump,i}$, $P_{Pump,H}$ are the outlet, inlet, and head pressures, respectively. The power consumed of the pump ($W_{Pump,Consumed}$) is determined as follows.

$$W_{Pump,Consumed} = \frac{Q_{Pump,i} * P_{Pump,H}}{\eta_{Pump}} \quad (4.36)$$

where η_{Pump} is the pump efficiency.

4.3.4 The energy recovery device (ERD) model

Two streams are entering the ERD, the high-pressure one and the low-pressure one, as shown in **Fig. 4.2**. The high-pressure stream will leave the device at lower pressure (P_{ho}) compared to its inlet pressure (P_{hi}), while the low-pressure stream will leave at higher pressure (P_{lo}) compared to its inlet pressure (P_{li}). The mass balance equations in the ERD are given below.

$$Q_{ho} - Q_{hi} = Q_{li} - Q_{lo} \quad (4.37)$$

$$Q_{li}C_{li} + Q_{hi}C_{hi} = Q_{lo}C_{lo} + Q_{ho}C_{ho} \quad (4.38)$$

where Q_{hi} , Q_{ho} , Q_{li} , and Q_{lo} is the inlet flow rate of the high-pressure stream, the high-pressure outlet stream, the low-pressure inlet stream, and the low-pressure outlet stream, respectively, C_{hi} , C_{ho} , C_{li} , and C_{lo} is the concentration of the high-pressure inlet stream (brine inlet), of the high-pressure outlet stream (feed outlet), of the low-pressure inlet stream (feed inlet), and the low-pressure outlet stream (brine outlet), respectively.

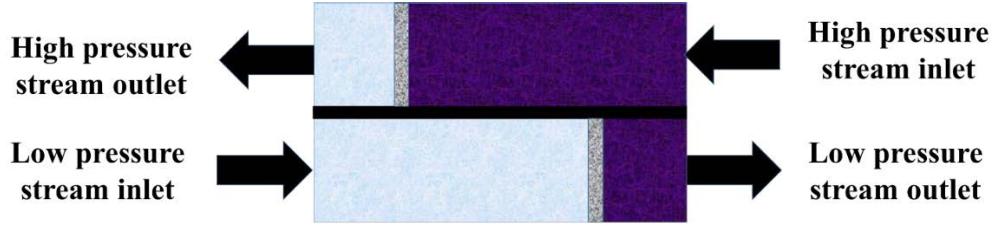


Fig. 4.2: Representative figure of energy recovery device.

As two streams of different pressures fed to the ERD, the outlet concentrations of these streams will vary accordingly and can be estimated by defining the mixing percentage ($\%Mix_{ERD}$) in the ERD as the following.

$$\%Mix_{ERD} = \frac{C_{lo} - C_{li}}{C_{hi} - C_{ho}} * 100\% \quad (4.39)$$

The following correlation is used to determine the outlet pressure of the low-pressure stream (P_{lo}) based on Bernoulli's equation [250].

$$P_{lo} = \frac{\eta_{ERD}(Q_{hi}P_{hi} - Q_{ho}P_{ho}) + Q_{li}P_{li} - K_{FL}(\eta_{ERD}Q_{ho}\rho_{water}(\frac{Q_{hi}^2}{A_{ERD}^2}) - Q_{lo}\rho_{water}(\frac{Q_{li}^2}{A_{ERD}^2}))}{Q_{lo}} \quad (4.40)$$

where, η_{ERD} is the ERD efficiency, P_{hi} , P_{ho} , P_{li} , and P_{lo} is the pressure of the high-pressure inlet stream, of the high-pressure outlet stream, of the low-pressure inlet stream. The low-pressure outlet stream, respectively, ρ_{water} is the density of the feed water, K_{FL} is the coefficient of the friction loss, and A_{ERD} is the inlets side cross-sectional area of energy recovery device. Next is the lubricant flow (Lub_{flow}) equation in the ERD as a small amount of the high-pressure stream will flow towards the low-pressure stream.

$$Lub_{flow} = Lub_{flowRatio} * Q_{hi} \quad (4.41)$$

$Lub_{flowRatio}$ is the ratio of the lubricant flow and the inlet flow of the high-pressure stream.

4.3.5 The mixer and the splitter models

The mixer is used to mix the multiple streams, while the splitter is used to split one stream into multiple streams. The pressure drop in both models is suggested to be neglected for simplicity. The mass balance for both models is given next.

$$\sum_1^e Q_{i,e} = \sum_1^g Q_{o,g} \quad (4.42)$$

where e and g are the number of inlet and outlet streams in the corresponding model, $Q_{i,e}$, and $Q_{o,g}$ are each stream's inlet and outlet flow rate in the corresponding model. The outlet concentration of all streams leaving the splitter will be equal to the concentration of the inlet stream. On the other hand, the concentration of the outlet stream in the mixer will be determined by the solute balance as the following.

$$\sum_1^e Q_{i,e} C_{i,e} = \sum_1^g Q_{o,g} C_{o,g} \quad (4.43)$$

where $C_{i,e}$, and $C_{o,g}$ are the inlet and outlet concentration of each stream in the corresponding model.

4.3.6 The turbine model

The turbine is utilized to produce the energy from the inlet pressure head. The next equations are the mass balance and the pressure head for the turbine.

$$Q_{Turbine,i} = Q_{Turbine,o} \quad (4.44)$$

$$P_{Turbine,o} = P_{Turbine,i} - P_{Turbine,H} \quad (4.45)$$

where $Q_{Turbine,i}$, and $Q_{Turbine,o}$ are the flow rate of the inlet and the outlet streams of the turbine, $P_{Turbine,i}$, and $P_{Turbine,o}$ are the pressure of the inlet and the outlet streams of the turbine and $P_{Turbine,H}$ is the head pressure used in the turbine to produce the energy ($W_{Turbine}$) which is determined as next,

$$W_{Turbine} = \eta_{Turbine} * Q_{Turbine,i} * P_{Turbine,H} \quad (4.46)$$

Where $\eta_{Turbine}$ is the turbine efficiency.

4.3.7 Reverse osmosis- pressure retarded osmosis hybrid system

The performance of S1-C1 (2RO) and S2-C1 (2RO-DSPRO) was carried out at 40 g/L seawater salinity to compare recovery rate, permeate concentration, and the net specific energy consumption (NSEC). In the S1-C1 system, the permeate from the RO1 membrane will form the feed to the RO2 membrane to provide high-quality freshwater (

Fig. 4.3). For the S2-C1 system, the RO1 permeate, and brine will be the feed to the RO2 and the draw solution to the PRO1, respectively (**Fig. 4.1**). Then, the diluted draw solution from the PRO1 will form the draw solution of the PRO2 system, using a new wastewater feed solution. The performance of S1-C2 (2RO) and S2-C2 (2RO-DSPRO) was also carried out at 45 g/L seawater salinity to compare recovery rate, permeate concentration, and the net specific energy consumption (NSEC) with S1-C1 and S2-C1 systems. The systems' performance was evaluated at recovery rates between 30 and 46% to determine the net specific energy consumption for desalination.

The permeate from the RO1 membrane in the S1-C2 system will form the feed of the RO2 membrane (

Fig. 4.3). For the S2-C2 system, the RO1 permeate, and brine will be the feed to the RO2 and the draw solution to the PRO1, respectively (**Fig. 4.1**). Then, the diluted PRO1 draw solution will form the inlet draw solution of the PRO2 system, using a new wastewater feed solution. The seawater feed flow rate to the HPP4 (

Fig. 4.3) in S1-C2 and the HPP3 (**Fig. 4.1**) in S2-C2 was fixed at 172.8 m³/h and 162 m³/h, respectively.

4.4 Results and discussion

Two scenarios are determined in this study i) two-pass reverse osmosis system (2RO) (

Fig. 4.3) and ii) two-pass reverse osmosis-dual stage pressure retarded osmosis system (2RO-DSPRO) (**Fig. 4.1**). The first system consists of 2RO units, with one ERD proposed for freshwater production. The 2RO-DSPRO system will produce freshwater and benefit from the energy generation by the DSPRO.

The seawater is pumped by the high-pressure pump (HPP1) and introduced to the ERD in the 2RO system (

Fig. 4.3) as the low-pressure stream inlet, while the RO1 brine will be the high-pressure stream inlet. The energy will be exchanged in the ERD from the RO1 brine to the seawater, which after leaving the ERD, goes to pump HPP3 and is mixed with another high-pressure seawater stream. The RO1 feed stream represents the outlet stream of the mixer. The RO1 product stream will be

pressurized in the low-pressure pump (LPP) and sent to the RO2 for freshwater production (RO2 product), and the RO2 brine goes to a turbine for energy recovery.

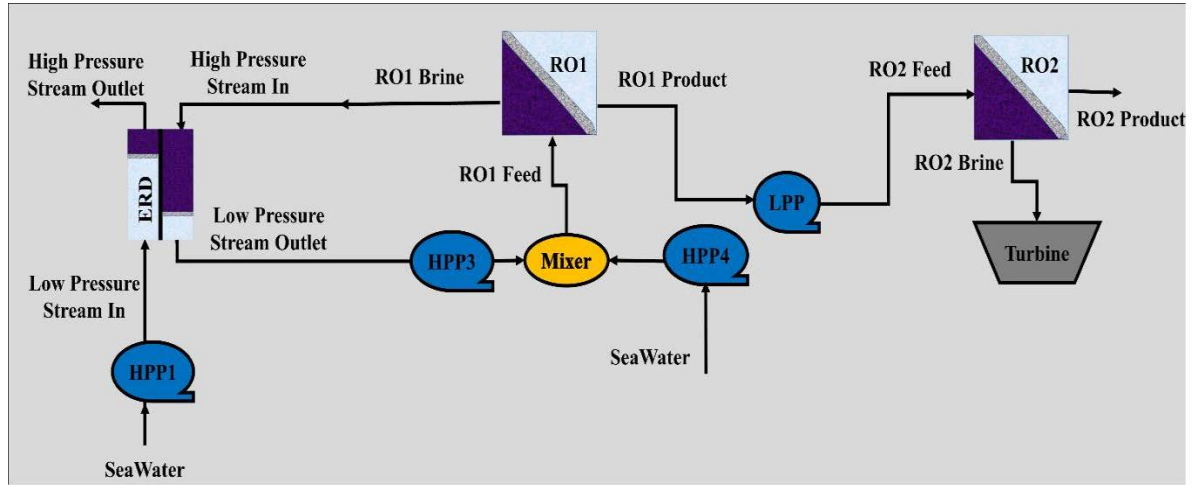


Fig. 4.3: Schematic diagram of the two-pass RO system for seawater desalination.

The other proposed 2RO-DSPRO hybrid system consists of two RO units (RO1 and RO2) and a DSPRO system (PRO1 and PRO2) (**Fig. 4.1**). The system includes three ERDs (ERD1, ERD2, and ERD3) to exchange energy between various streams of different flow rates, concentrations, and pressures. Initially, seawater is pressurized by pump HPP3 and mixed with the low-pressure stream outlet from ERD2 to form the feed stream of the RO1 unit. The RO1 brine stream will be sent to ERD2 to exchange its energy with the low-pressure stream inlet coming from the low-pressure stream outlet from ERD1 (**Fig. 4.1**). The high-pressure stream outlet from ERD2 will be the draw solution inlet of the PRO1, in which wastewater solution will be the feed inlet stream. The draw solution outlet of the PRO1 will be sent to ERD1 to exchange energy with the low-pressure seawater inlet of ERD1. In the second DSPRO stage, wastewater is the feed inlet stream, while the high-pressure stream outlet of ERD1 forms the draw solution inlet. Then, the draw outlet stream of PRO2 will go to the ERD3 to exchange energy with the product stream of the RO1. The low-pressure stream outlet of the ERD3 will be the feed stream of the second RO unit, i.e., RO2, for further treatment and freshwater production.

As shown in **Fig. 4.1** and

Fig. 4.3, the main difference between the two systems is the addition of the DSPRO in the second system. The DSPRO will be responsible for energy generation to minimize the net specific energy consumption of the RO plant. The efficiency of HPP, LPP, and ERD is 80%, 80%, and 96%, respectively. Four scenarios of 2RO and 2RO-DSPRO were investigated in this study with 40 g/L

and 45 g/L seawater salinities (**Table 4.1**). Scenarios S1-C1 and S1-C2 are for the 2RO system without the DSPRO process, and scenarios S2-C1 and S2-C2 with the DSPRO process. The salinity of the feed solution of DSPRO stages one and two was fixed at 1 g/L, while the pressure of the feed solutions was fixed at 1.5 bar, and the feed solution flow rate was fixed at 163 m³/h. Moreover, the inlet pressures of the draw solution of the first and second DSPRO stages are fixed at 39 and 26.5 bar, respectively.

Table 4.1: Type of investigated RO and RO-PRO systems and seawater salinities.

System and Case Number	Abbreviation	RO Units	PRO Units	Seawater Salinity (g/L)
System 1-Case 1	S1-C1	2	-	40
System 2-Case 1	S2-C1	2	2	40
System 1-Case 2	S1-C2	2	-	45
System 2-Case 2	S2-C2	2	2	45

This section will include the RO model validation, the PRO model validation, the comparison of systems net specific energy consumption, the total energy consumed, the total energy generated, the net energy consumed, and the final product concentration.

4.4.1 The reverse osmosis model validation

The developed RO model in Dymola has been validated using experimental data from literature [218] where seawater of 32000 mg/L was the feed stream, and the validation results are shown in **Table 4.2**. The main parameters of the model as x_{RO} , y_{RO} , A_{WRO} , B_{RO} , σ , and D_F were determined by using the experimental data to tune the model. The table shows that the absolute percentage error, the difference between the model results, and the experimental data divided by the experimental data were between 0.13-10.47 %.

Table 4.2: The validation results of the RO model.

Feed flow rate (m³/h)	Feed operating pressure (bar)	Parameter	Experimental Result	Model Result	Error %
1047.6	50.47	Product Flow Rate (m ³ /h)	336.24	351.00	4.39
		Product Concentration (mg/L)	44	41.49	5.71
		Reject Pressure (bar)	48.23	49.39	2.40
1047.96	55.81	Product Flow Rate (m ³ /h)	417.60	420.48	0.7
		Product Concentration (mg/L)	49	44.20	9.79
		Reject Pressure (bar)	54.72	54.79	0.13
1047.96	60.28	Product Flow Rate (m ³ /h)	460.80	475.20	3.12
		Product Concentration (mg/L)	52	46.56	10.47
		Reject Pressure (bar)	59.22	59.30	0.14

4.4.2 The pressure retarded osmosis model validation

The PRO model chosen for this study is plug flow with feed solution flows in the radial direction while the draw solution flows in the axial direction. The proposed model considers the impact of concentration polarization, the transportation of the solute and solvent through the membrane, and the pressure drop in the radial and axial directions. The used membrane module is hollow fiber (HF)-FO, and it is divided among the model into (nxm) sections as shown in **Fig. 4.4**. Here “n” represents the subsections in the radial direction, and “m” represents the subsections in the axial direction. Both solutions' concentrations and flow rates will vary across the membrane module's radial and axial directions as represented by the module subsections. The pressure drop in the radial (lumen) side is predicted by the Hagen-Poiseuille equation, while the pressure drop in the axial (shell) side is determined by the Ergun equation [216].

Nevertheless, it has been noticed that there is a variation in the predicted pressure drop compared to the experimental one, which can be attributed to the fact that the fibers reshaped within high pressure, which may increase the experimental pressure drop. The model has been

calibrated and validated by the Dymola software, and the parameters are evaluated by minimizing the error. It has been assumed that the variation in the pressure, flow rate, and concentration in the radial (lumen) side is only taking place in the radial direction. A similar assumption is made in the axial (shell) side, where the variables only vary in the axial direction. Additionally, the flow inside the radial direction is assumed to be laminar, so using the Hagen-Poiseuille equation to determine the lumen side pressure drop is applicable [251]. According to the Ergun equation, the flow inside the shell side is assumed to equal the flow through a structured packed bed to determine the pressure drop in the shell side [251]. Moreover, it is suggested that the membrane structure is held constant throughout its module. The feed and draw solutions are assumed to consist of water and sodium chloride only.

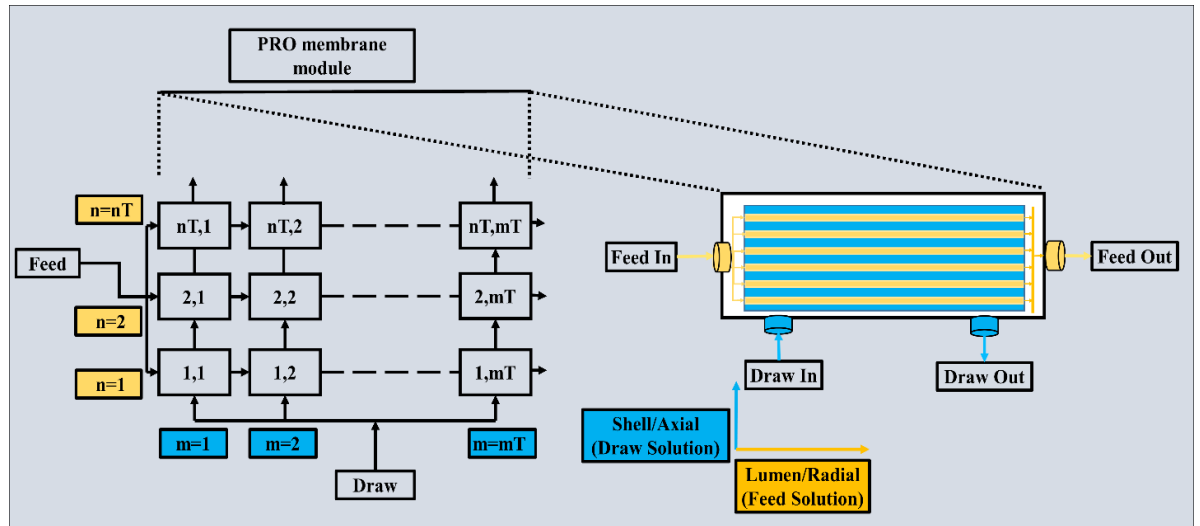


Fig. 4.4: Schematic diagram of the suggested PRO HF membrane module.

One significant point in modelling the PRO is to predict the number of subsections the membrane module will be divided into (e.g., $n \times m$). The outlet flow rate of the draw solution was the element that governed the chosen number of the subsections. Five sets of $n \times m$ were determined and they are (1x1, 1x3, 2x6, 3x9, and 4x12) and the inputs were: $C_{Fi,PRO}=45$ mg/L, $P_{Fi,PRO}=1$ bar, $Q_{Fi,PRO}=0.2$ m³/h, $C_{Di,PRO}=25000-35000$ mg/L, $P_{Di,PRO}=3$ bar, and $Q_{Di,PRO}=0.2$ m³/h. It was noticed that the outlet draw flow rate was decreasing by around 0.5% for all different draw concentrations, as shown in **Table 4.3** when having 4x12 subsections compared to 3x9, and that is why the 4x12 set is chosen for the rest of the study.

Table 4.3: The flow rate of outlet draw solution variation at various nxm subsections with various draw concentrations.

Draw inlet concentration (mg/L)	Draw outlet flow rate (m ³ /h)					Difference % in draw outlet flow rate (3x9 Vs. 4x12)
	1x1	1x3	2x6	3x9	4x12	
25000	0.357	0.360	0.349	0.346	0.345	0.45%
26000	0.362	0.365	0.354	0.351	0.349	0.47%
27000	0.367	0.370	0.358	0.355	0.354	0.49%
28000	0.371	0.375	0.363	0.360	0.358	0.48%
29000	0.375	0.380	0.367	0.364	0.362	0.48%
30000	0.378	0.384	0.370	0.368	0.366	0.51%
31000	0.381	0.387	0.374	0.372	0.370	0.49%
32000	0.384	0.390	0.378	0.375	0.374	0.45%
33000	0.386	0.392	0.382	0.379	0.377	0.48%
34000	0.388	0.394	0.386	0.383	0.381	0.49%
35000	0.389	0.395	0.389	0.386	0.384	0.48%

The validation of the PRO plug flow model was performed using Dymola software. The water permeability ($A_{W,PRO}$), the salt permeability coefficient (B_{PRO}), the membrane structural parameter (S), and the mass transfer coefficients for the feed (x_{PRO} and y_{PRO}) were estimated by the calibration of the model using experimental data with NaCl and water as the feed and the draw streams, respectively. The experiments were performed in India by the Indian Institute of Technology Guwahati. The conditions of the experiments are shown in **Table 4.4**, where different initial conditions were used at the same temperature (293 K) for the experiments. The validation results of the PRO model are shown in **Fig. 4.5** for each experiment. The validation results showed a maximum error of 15% between the experimental water flux results and the PRO model water flux results.

Table 4.4: The initial conditions of the PRO experiments.

Experiment's number	Feed inlet flow rate (m ³ /h)	Feed inlet concentration (mg/L)	Feed inlet pressure (bar)	Draw inlet flow rate (m ³ /h)	Draw inlet concentration (mg/L)	Draw inlet pressure (bar)
1	0.205	45	1.37	0.197	30000	3.92
2	0.208	45	1.35	0.202	30000	5.26
3	0.207	45	1.34	0.194	30000	6.04
4	0.211	110	1.39	0.105	20000	6.30
5	0.215	110	1.34	0.185	20000	6.24
6	0.215	110	1.24	0.332	20000	6.32
7	0.211	110	1.20	0.422	20000	6.24
8	0.206	100	1.48	0.194	15000	6.85

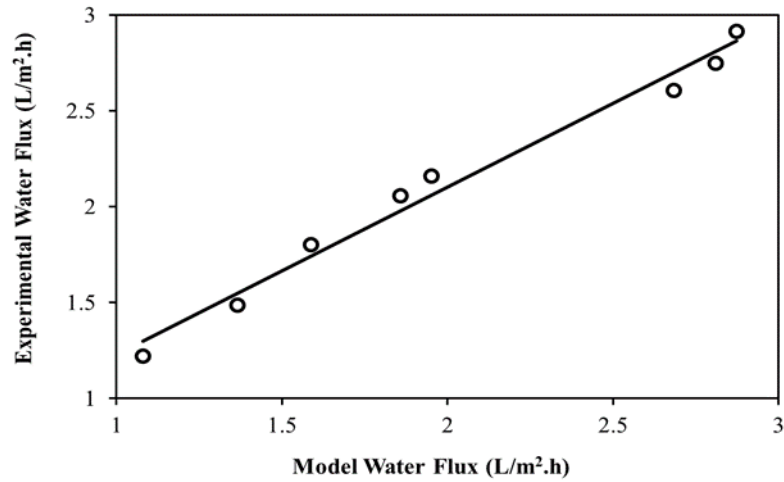


Fig. 4.5: The model water flux versus the experimental water flux of the PRO system.

The validated model is later used for simulation and optimization. Through the validation of the PRO model, it has been noticed that the salt permeability is a function of the draw inlet concentration at low values, as seen in **Fig. 4.6** and mentioned in the literature [252]. It is revealed that the solute permeability is a function of the draw inlet concentration till 30000 mg/L. At higher concentrations, it is assumed that the B_{PRO} value will be constant and equal to 6.235×10^{-9} m/s.

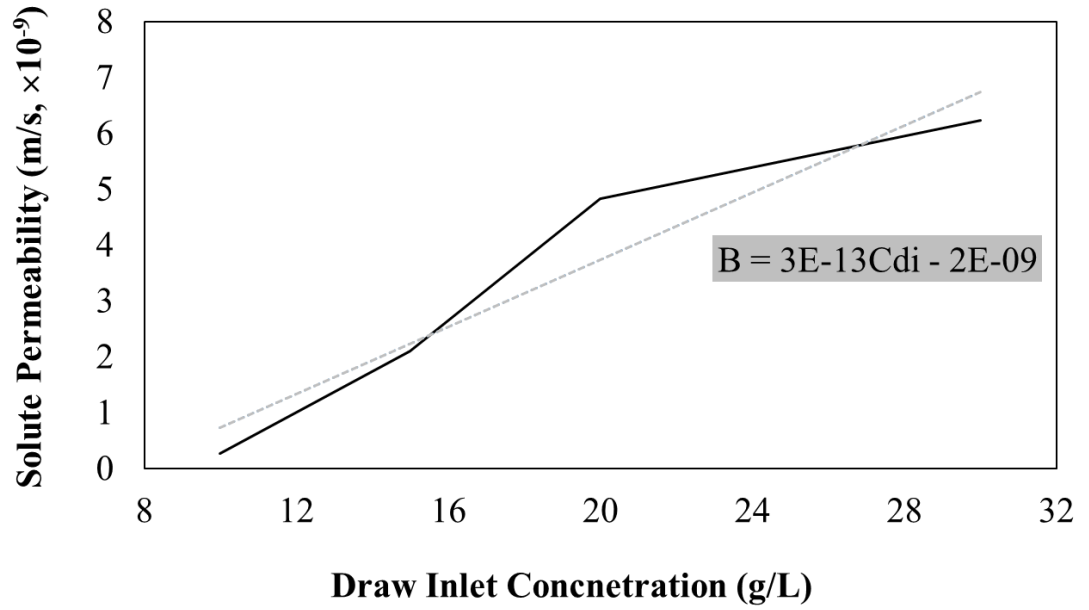


Fig. 4.6: The variation in the solute permeability with the draw inlet concentration. The straight gray line represents the intersection line, and the black curve represents the trend line of the solute permeability coefficient with the draw inlet concentration.

4.4.3 2RO and 2RO-DSPRO systems of 40 g/L seawater

The 2RO and 2RO-DSPRO systems' performance was evaluated at recovery rates between 26 and 49%, and the net specific energy consumption was determined from the following expression.

$$NSEC = \frac{1}{Q_p} * (\sum_1^{PN} W_{Pump} - \sum_1^{TN} W_{Turbine}) \quad (4.47)$$

where, NSEC is the net specific energy consumption in kW.h/m³, PN is the number of pumps in the system, TN is the turbines number in the system, W_{Pump} is the consumed energy by the pump in kW, $W_{Turbine}$ is the generated energy by the turbine in kW, and Q_p is the final product water flow rate in m³/h.

The seawater feed flow rate to the HPP4 (

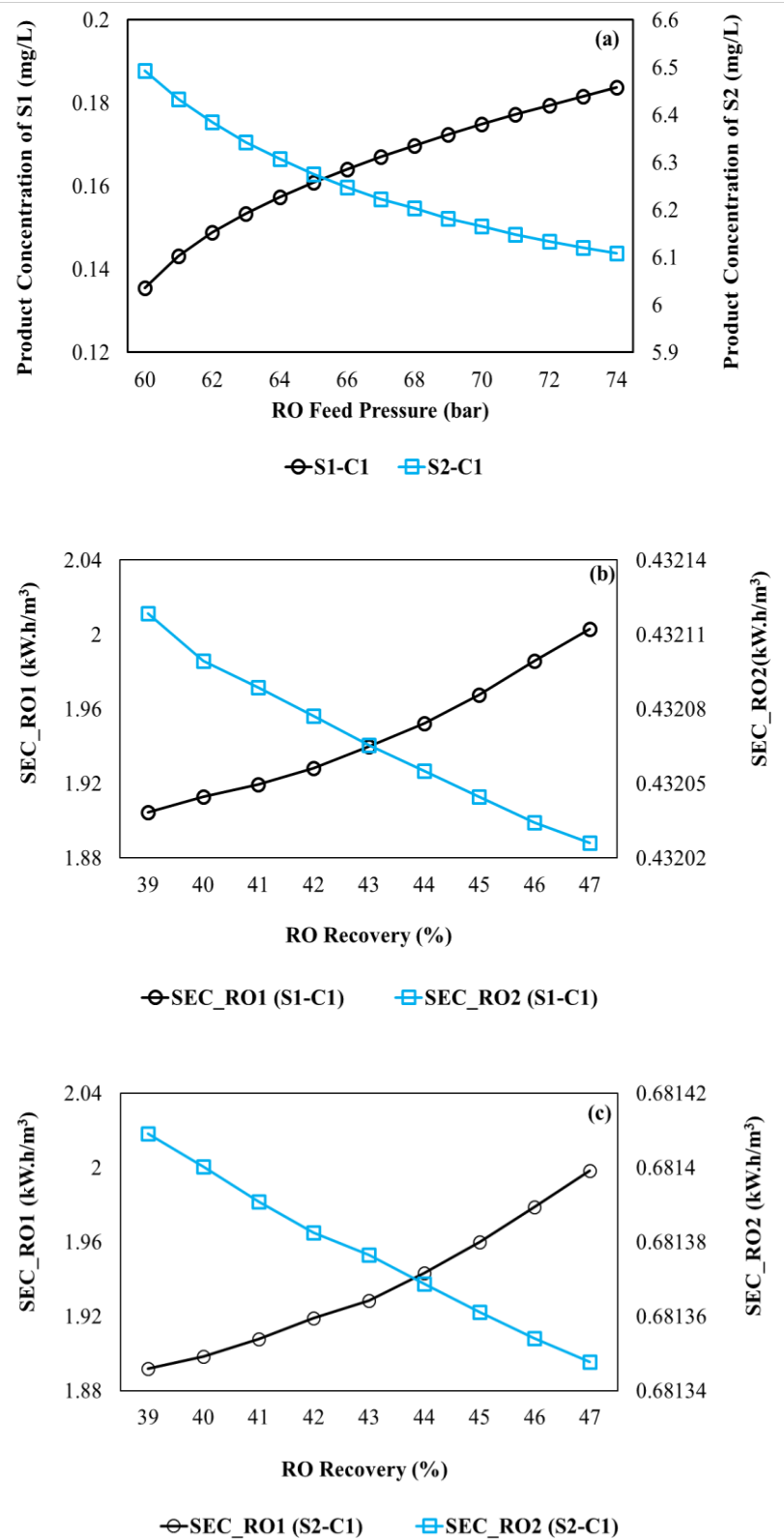
Fig. 4.3) in S1-C1 and the HPP3 (**Fig. 4.1**) in S2-C1 was fixed at 172.8 m³/h and 162 m³/h, respectively. **Fig. 4.7a** shows that the RO2 permeate concentration (the final product stream) was higher in S2-C1 compared to S1-C1. The reason for this is that the feed stream of the RO2 unit in S1- C1 represents the product stream of RO1 (

Fig. 4.3), while, in S2-C1, it is the low-pressure stream outlet of ERD 3 (**Fig. 4.1**), which is more concentrated than the RO1 product stream in S1-C1. Nevertheless, the final product concentration of both systems shows exceptionally low salinity compared to the allowable drinking water limits (0.25 g/L) [253]. Interestingly, the product concentration of S1-C1 slightly increased with the RO1 feed pressure due to the recovery rate increase; hence, the bulk concentration of feed solution in the RO1 increased. For the S2-C1, the product concentration decreased with higher the RO1 feed pressure due to the RO1 feed flow rate increase. As feed pressure increases, the RO1 recovery rate and brine concentration increase, increasing the PRO1 permeation flux and, hence, the ERD1 low-pressure flow rate that composes the feed stream to the RO1 unit (**Fig. 4.1**). Moreover, **Fig. 4.7b** and **Fig. 4.7c** show an increase in the SEC of the RO1 with the increase in the RO recovery rate of S1-C1 and S2-C1 as a result of the greater feed pressure necessary to overcome the brine osmotic pressure [218]. The RO1 energy consumption of the S1-C1 and S2-C1 systems is the same, while the RO2 energy consumption was higher in the S2-C1 system due to higher feed salinity.

The NSEC of S1-C1 and S2-S1 was calculated for the recovery rates ranging from 26 to 49% by varying the RO feed pressure (**Fig. 4.7d**). The NSEC decreased with increasing the feed pressure, then increased again at 66 bar for S1-C1 and 69 bar for S2-C1. However, NSEC was lower in the S2-C1 system than in the S1-C1 system, indicating the role of PRO in reducing desalination energy consumption. For example, at 60 bar, the NSEC of the S2-C1 system was 0.34% lower than that of the S1-C1 system and increased to 15.3% at 74 bar. Comparable results were found in the literature [218]. The authors suggested that utilizing a hybrid SWRO-PRO system at 32 g/L draw solution and 1 g/L feed solution saved 16% of the net energy consumption compared to the SWRO system. In general, the profile of NSEC on S1-C1 and S2-C1 agrees with the literature findings that the RO energy consumption reaches an optimum value at a certain recovery rate and then increases due to the increased bulk feed concentration [254].

The RO1 membrane system is responsible for the most desalination energy consumption due to high seawater feed salinity (**Fig. 4.7e**). In the S1-C1 system, the RO1 was responsible for 93.5 and 89.8% of total energy consumption at 60 and 74 bar feed pressure. The corresponding values for the S2-C1 system are 89.9 and 85.1% of the total energy consumption at 60 and 74 bar feed pressure. In contrast, 6.5 to 10.2% of the total energy consumption was in the RO2 of the S1-C1 system and 10.1 to 14.9% in the RO2 of the S2-C1 system. The difference between the RO1 energy consumption of S1-C1 and S2-C1 systems is 7.4% at 60 bar feed pressure and decreased to 5.2% at 74 bar feed pressure. For the RO2 membrane, the energy consumption in the S1-C1

system was lower than in the S2-C1 system. The RO2 energy consumption of the S2-C1 system was 49% higher than that of the S1-C1 system at 60 bar and 46.4% at 74 bar.



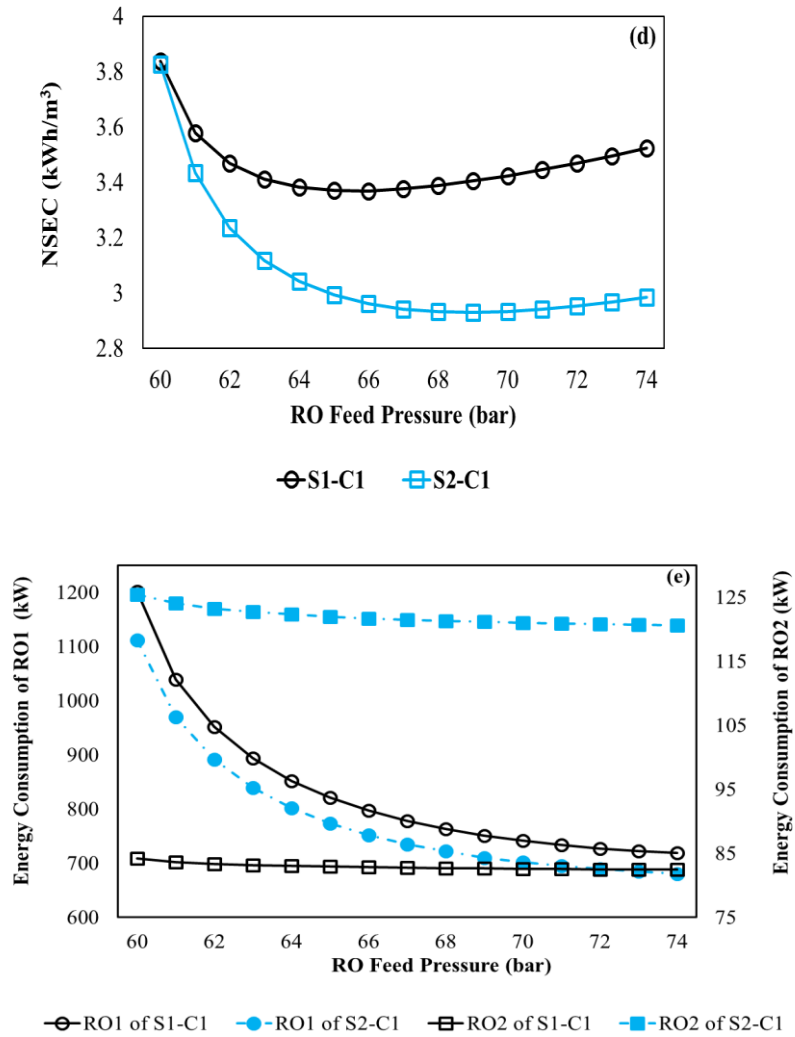
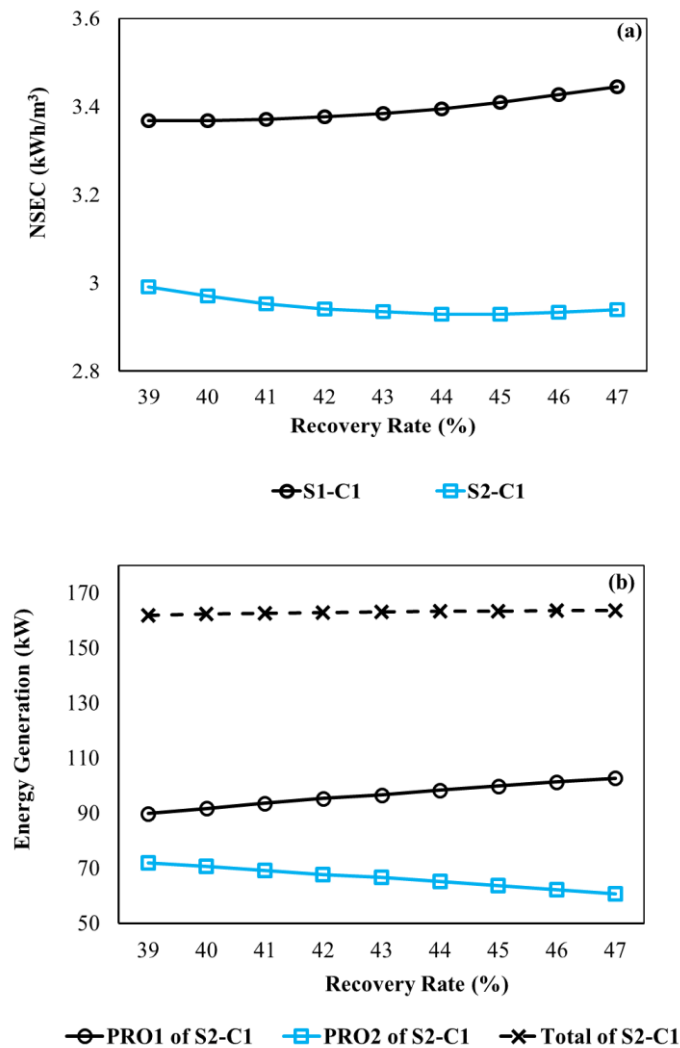


Fig. 4.7: (a) The product concentration of S1-C1 and S2-C1 with the variation of the RO feed pressure, (b) the SEC of RO1 and RO2 of S1-C1 with the variation of the RO recovery rate, (c) the SEC of RO1 and RO2 of S2-C1 with the variation of the RO recovery rate, (d) the NSEC of S1-C1 and S2-C1 with the variation of the RO feed pressure, and (e) the energy consumption of RO1 and RO2 of S1-C1 and S2-C1 with the variation of the RO feed pressure.

Moreover, **Fig. 4.8a** display the energy efficiency of S1-C1 and S2-C1 systems at 39-47% recovery rates. There is an 11.2 to 14.7% decrease in the NSEC of the S2-C1 compared to the S1-C1 system (**Fig. 4.8a**). The NSEC of the S1-C1 system increased by increasing the recovery rate from 39 to 47%. In comparison, the NSEC of the S2-C1 system decreased with the recovery rate and reached the lowest value of 2.9 kWh/m³ at a 45% recovery rate before it increased again. The NSEC of the S1-C1 system at a 45% recovery rate is 3.4 kWh/m³, which is 14.7% higher than that of the S2-C1 system.

Fig. 4.8b and **Fig. 4.8c** show the energy generation and water flux of the DSPRO process in the S2-C1 system. The energy generation of the PRO stage one (PRO1) increased with increasing the recovery rate of the RO system (**Fig. 4.8b**) due to the increased water flux (**Fig. 4.8c**). Overall, the PRO water flux is directly proportional to the net pressure difference in the PRO [218]. The net pressure difference in PRO2 ($\Delta\pi - \Delta P$) has dropped with the increase of the recovery rate (**Fig. A4**), and that causes the drop in the energy generation and the water flux of the PRO2, as shown in **Fig. 4.8b** and **Fig. 4.8c**, respectively.

The maximum energy generation of the PRO1 in the S2-C1 system was 102.7 kW. For the PRO stage two (PRO2) of the DSPRO system, the energy generation decreased with increasing the RO recovery rate (**Fig. 4.8b**) due to the decreased water flux (**Fig. 4.8c**). The higher energy generation of the PRO2 was 71.9 kW at a 39% recovery rate. The maximum energy generation of the PRO1 is 40.9% higher than that of the PRO2, underlining the fact that PRO1 is responsible for the most energy generated in the DSPRO system.



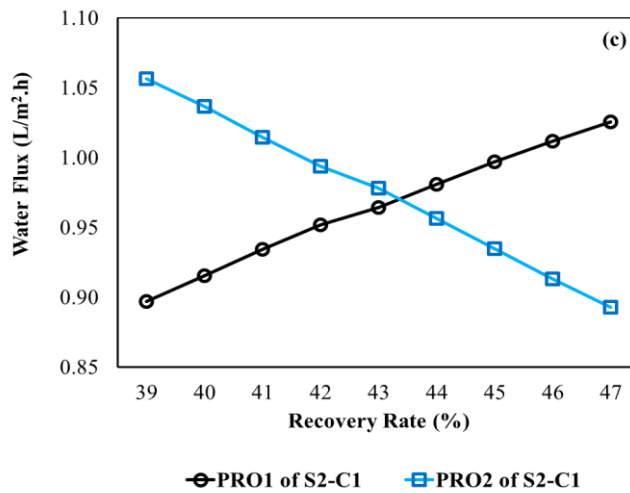


Fig. 4.8: (a) The NSEC of S1-C1 and S2-C1 with the variation of the recovery rate, (b) the energy generation of PRO1, PRO2, and the total energy generation with the variation of the recovery rate of S2-C1, and (c) the water flux of PRO1 and PRO2 with the variation of the recovery rate of S2-C1.

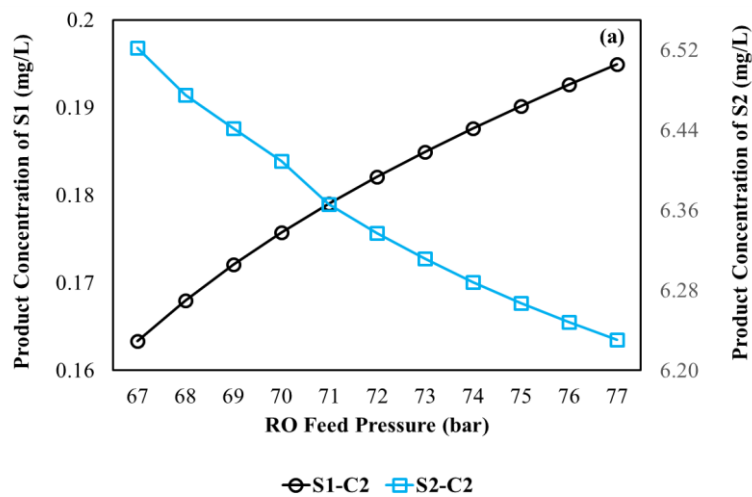
4.4.4 2RO system and 2RO-DSPRO system of 45 g/L seawater

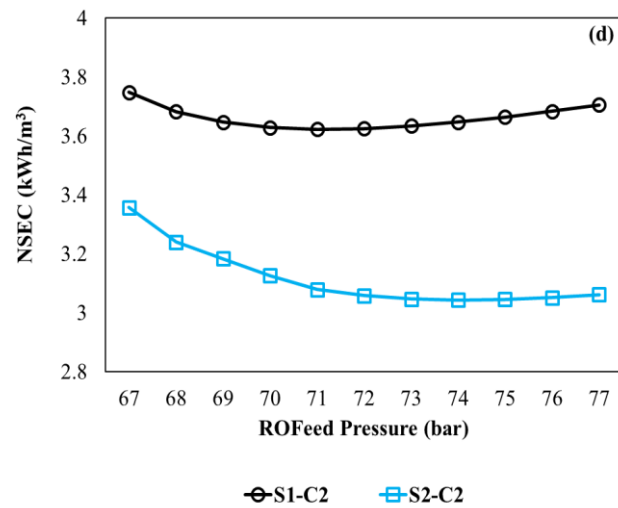
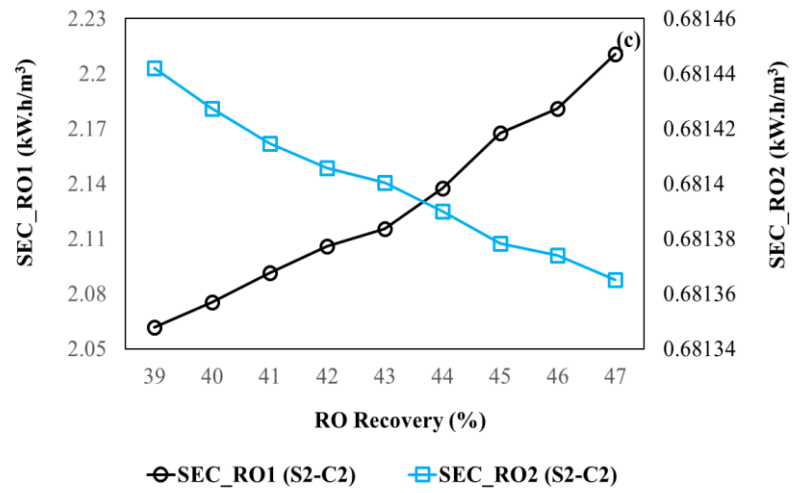
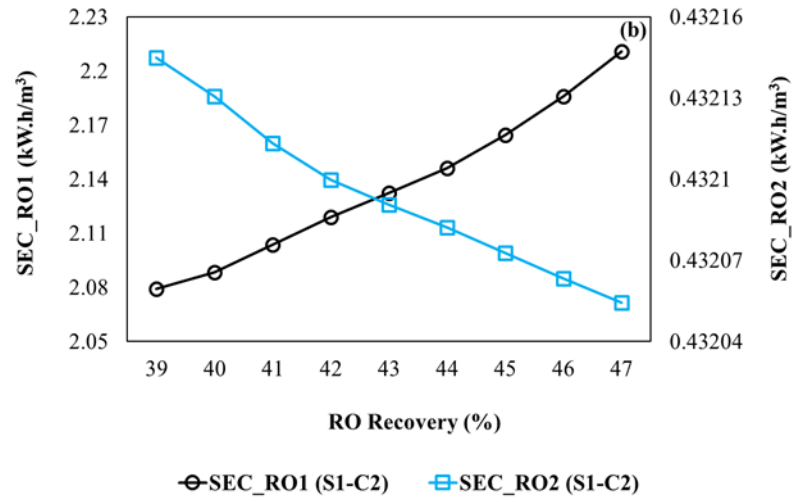
The permeate concentration (the RO2 product) was higher in the S2-C2 system than in the S1-C2 system (**Fig. 4.9a**). This is because the feed stream of the RO2 unit in the S1-C2 system is the RO1 product (

Fig. 4.3), while it is the low-pressure outlet stream of ERD 3 in the S2-C2 system (**Fig. 4.1**). The latter stream is more concentrated than the RO1 product stream in the S2-C2 system. The final product concentration of S1-C2 and S2-C2 systems are much lower than the allowable drinking water limits (0.25 g/L) [253]. Results also showed that the product concentration of the S1-C2 system slightly increased with the RO1 feed pressure due to the recovery rate increase, which in turn increased the bulk concentration of feed solution in the RO1. For the S2-C2 system, the product concentration was reduced with the rise of the RO1 feed pressure due to the increase of the RO1 feed flow rate. As feed pressure increases, the RO1 recovery rate and brine concentration increase, increasing the PRO1 permeation flux and, hence, the ERD1 low-pressure flow rate that forms the feed stream to the RO1 membrane (**Fig. 4.1**). Furthermore, **Fig. 4.9b** and **Fig. 4.9c** show an increase in the SEC of the RO1 with the rise of the RO recovery rate of S1-C2 and S2-C2, respectively [218]. The energy consumption of RO1 was similar in the S1-C2 and S2-C2 systems, but the RO2 energy consumption was higher in the S2-C2 system than in the S1-C2 system due to the higher feed salinity.

The NSEC of S1-C2 and S2-C2 systems was calculated for the recovery rates ranging from 30 to 46% by varying the RO feed pressure (**Fig. 4.9d**). The NSEC decreased with increasing the feed pressure, then increased again at 71 bar for the S1-C2 system and 74 bar for the S2-C2 system. However, NSEC was lower in the S2-C2 system than in the S1-C2 system, emphasizing the PRO's merit in reducing desalination energy consumption. For example, at 67 bar, the NSEC of the S2-C2 system was 10.43% lower than that of the S1-C2 system and increased to 17.37% at 77 bar. In general, the profile of NSEC for S1-C2 and S2-C2 systems agrees with the literature findings that the RO energy consumption reaches an optimum value at a certain recovery rate and then increases due to the increased bulk feed concentration [254].

The RO1 membrane system is responsible for the most desalination energy consumption due to high seawater feed salinity (**Fig. 4.9e**). In the S1-C2 system, the RO1 was responsible for 94.1 and 91.0% of total energy consumption at 67 and 77 bar feed pressure. The corresponding values for the S2-C2 system are 89.1 and 86.5% of the total energy consumption at 67 and 77 bar feed pressure. In contrast, 5.9 to 8.9% of the total energy consumption was in the RO2 of the S1-C2 system and 10.9 to 13.5% in the RO2 of the S2-C2 system. The difference between the RO1 energy consumption of S1-C2 and S2-C2 systems is 24.9% at 67 bar feed pressure and decreased to 7.5% at 77 bar feed pressure. For the RO2 membrane, the energy consumption in the S1-C2 system was lower than in the S2-C2 system. The RO2 energy consumption of the S2-C2 system was 46.7% higher than that of the S1-C2 system at 67 bar and 46.4% at 77 bar.





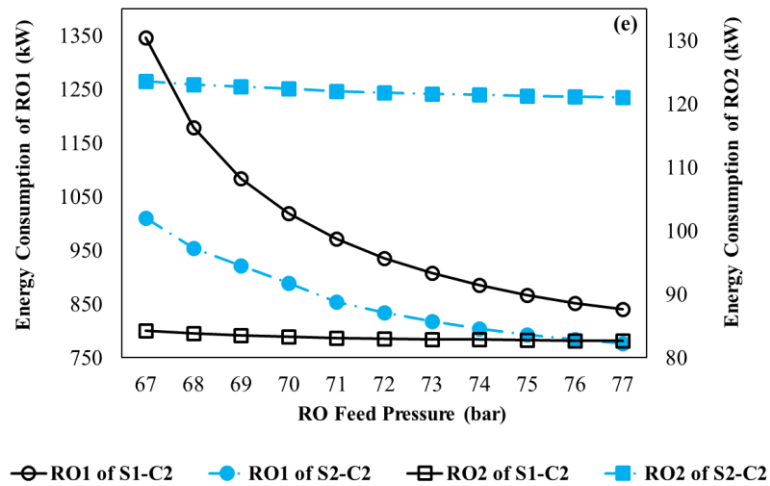


Fig. 4.9: (a) The product concentration of S1-C2 and S2-C2 with the variation of the RO feed pressure, (b) the SEC of RO1 and RO2 of S1-C2 with the variation of the RO recovery rate, (c) the SEC of RO1 and RO2 of S2-C2 with the variation of the RO recovery rate, (d) the NSEC of S1-C2 and S2-C2 with the variation of the RO feed pressure, and (e) the energy consumption of RO1 and RO2 of S1-C2 and S2-C2 with the variation of the RO feed pressure.

Furthermore, **Fig. 4.10a** display the energy efficiency of S1-C2 and S2-C2 systems at 39-47% recovery rates. There is a 15.03 to 17.53% decrease in the NSEC of the S2-C2 compared to the S1-C2 system (**Fig. 4.10a**). The NSEC of the S1-C2 system increased by increasing the recovery rate from 39 to 47%. In comparison, the NSEC of the S2-C2 system decreased with the recovery rate and reached the lowest value of 3.04 kWh/m³ at a 43% recovery rate before it increased again. The NSEC of the S1-C2 system at a 43% recovery rate is 3.7 kWh/m³, which is 17.8% higher than that of the S2-C2 system.

The energy generation of the DSPRO system was calculated; **Fig. 4.10b** and **Fig. 4.10c** show the energy generation and water flux of the DSPRO process in the S2-C2 system. The energy generation of the PRO1 increased with increasing the recovery rate of the RO system (**Fig. 4.10b**) due to the increased PRO1 water flux (**Fig. 4.10c**). Overall, the PRO water flux is directly proportional to the net pressure difference in the PRO [218]. The net pressure difference in PRO2 ($\Delta\pi - \Delta P$) has dropped with the increase of the recovery rate (**Fig. A2 - Appendix**), and that causes the drop in the energy generation and the water flux of the PRO2 (**Fig. 4.10b** and **Fig. 4.10c**).

The maximum energy generation of the PRO1 in the S2-C2 system was 126.7 kW. For the second PRO2 unit, the energy generation decreased with increasing the RO recovery rate (**Fig. 4.10b**) due to the decreased water flux (**Fig. 4.10c**). The highest energy generation of the PRO2 was 79.3 kW at a 39% recovery rate. The maximum energy generation of the PRO1 is 47.7% higher than

that of the PRO2, underlining the fact that PRO1 is responsible for the most energy generated in the DSPRO system.

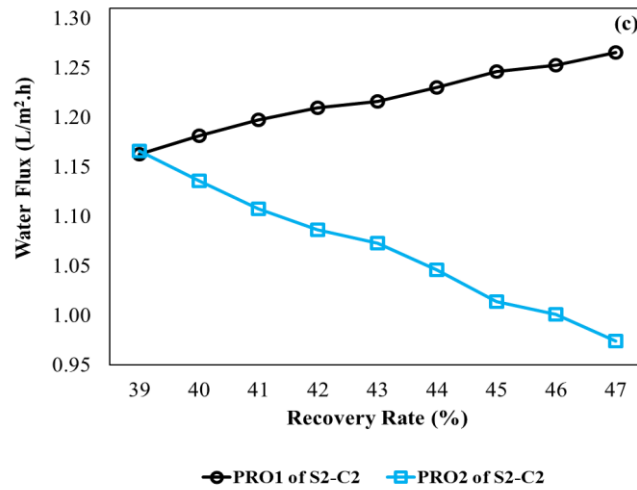
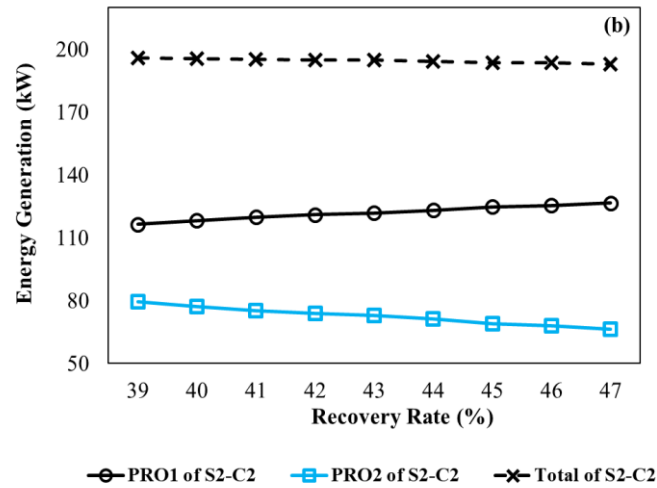
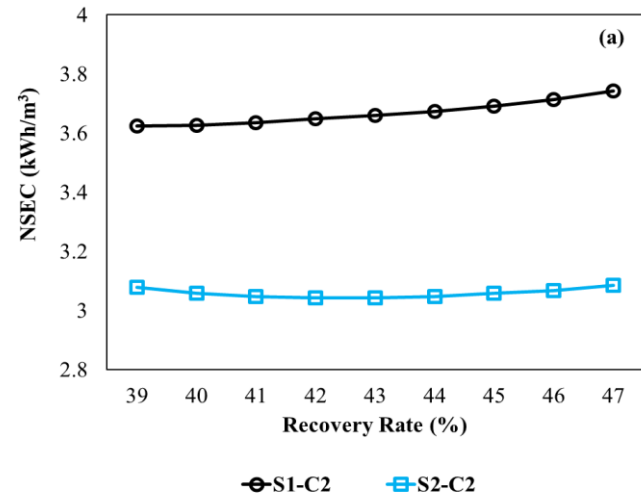
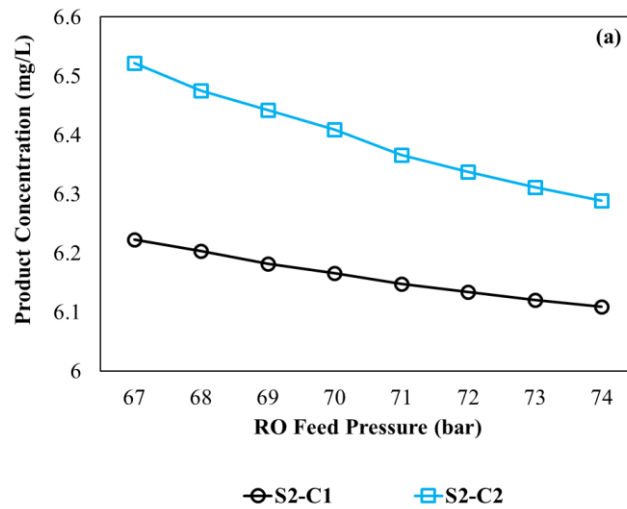


Fig. 4.10: (a) The NSEC of S1-C2 and S2-C2 with the variation of the recovery rate, (b) the energy generation of PRO1, PRO2 and the total energy generation with the variation of the recovery rate of S2-C2, and (c) the water flux of PRO1 and PRO2 with the variation of the recovery rate of S2-C2.

4.4.5 Comparison between S2-C1 and S2-C2

The performance of the S2-C1 system was compared with that of the S2-C2 system. The difference between the systems is that they use 40 g/L and 45 g/L seawater salinity in the S2-C1 and S2-C2 systems. **Fig. 4.11a** show that the permeate water salinity of the S2-C2 system was greater than that of the S2-C1 system due to the higher seawater salinity. The increase in seawater salinity from 40 g/L in S2-C1 to 45 g/L in the S2-C2 system led to a decrease in the recovery rate of the latter system. For example, at 67 bar feed pressure, the recovery rate was 42% and 31% in the S2-C1 and S2-C2 systems, respectively (**Fig. 4.11b**). The NSEC for seawater desalination of the 2RO-DSPRO systems was 2.94 kWh/m³ for the S2-C1 system and 3.36 kWh/m³ for the S2-C2 system (**Fig. 4.11c**). The higher NSEC in the S2-C2 system is due to the higher energy requirements for desalination in the RO membrane using 45 g/L seawater salinity.



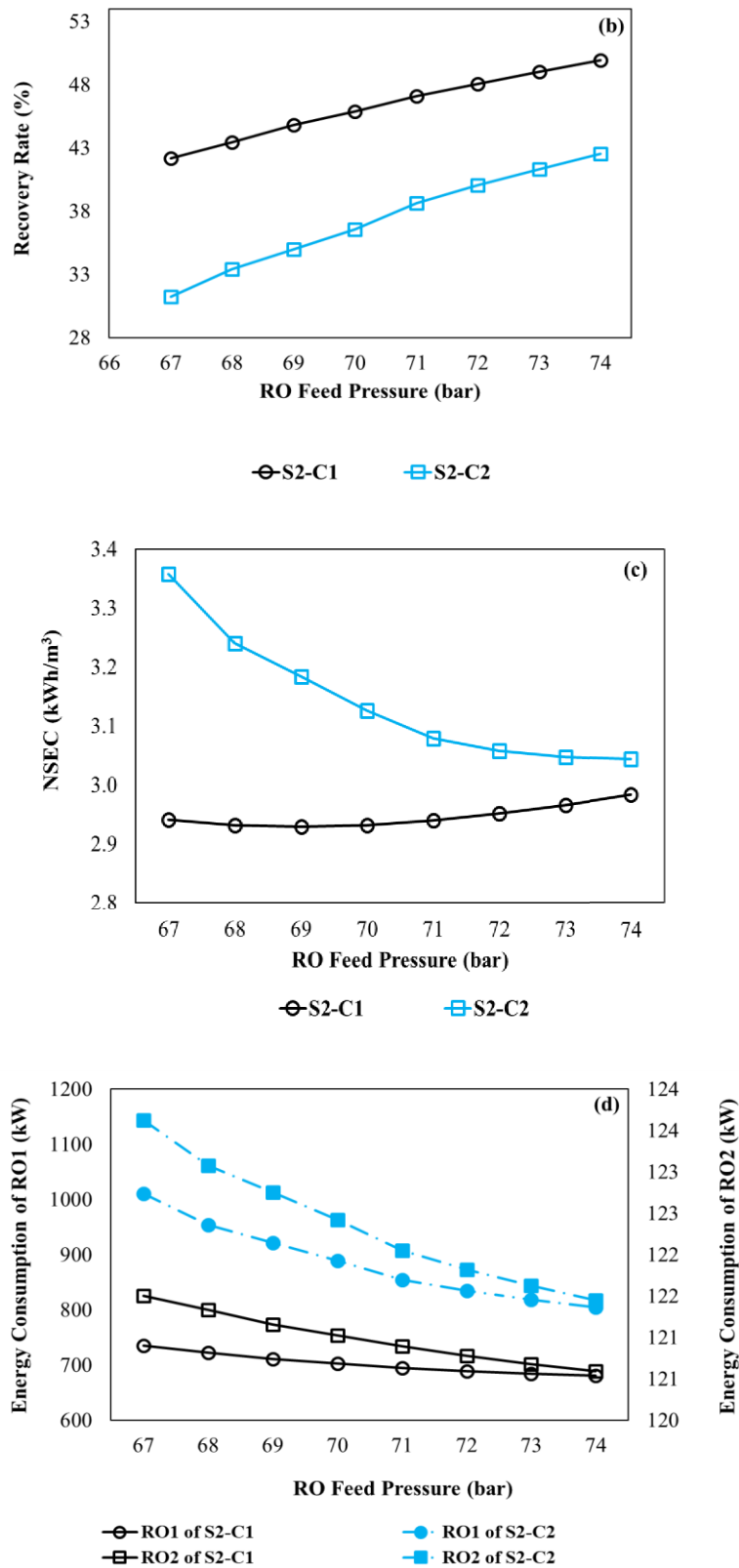
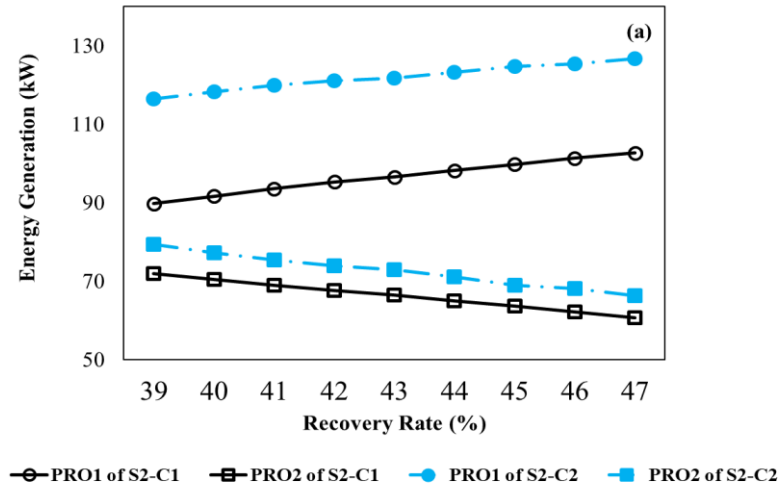


Fig. 4.11: (a) The product concentration of S2-C1 and S2-C2 with the variation of the RO feed pressure, (b) the recovery rate of S2-C1 and S2-C2 with the variation of the RO feed pressure, (c) the NSEC of S2-C1 and S2-C2 with the variation of the RO feed pressure, and (d) the energy consumption of RO1 and RO2 of S2-C1 and S2-C2 with the variation of the RO feed pressure.

Fig. 4.12a show the energy generation in the PRO1 and PRO2 of S2-C1 and S2-C2 systems. Results reveal that the energy generation of PRO1 and PRO2 in the S2-C2 system was greater than in the S2-C1 system due to the higher seawater salinity that generated more concentrated brine. The more concentrated brine in the S2-C2 system increased the osmotic pressure gradient in the PRO1 and PRO2, increasing the water flux and energy generation in the DSPRO system (**Equation 4.31**). As shown in **Fig. 4.12b**, the osmotic pressure difference in the PRO1 and PRO2 of the S2-C2 system was higher than that of the S2-C1 system. The total desalination energy consumption is equal to the energy consumption in the RO1 and RO2 membranes. In contrast, the net energy consumption is determined as the difference between the total energy consumption and the total energy generation in the PRO1 and PRO2 systems. Despite the higher energy generation in the S2-C2 system, **Fig. 4.12d** shows that the net energy consumption was higher in the S2-C2 system than in the S2-C1 system. This is related to the higher seawater salinity in the S2-C2 system.



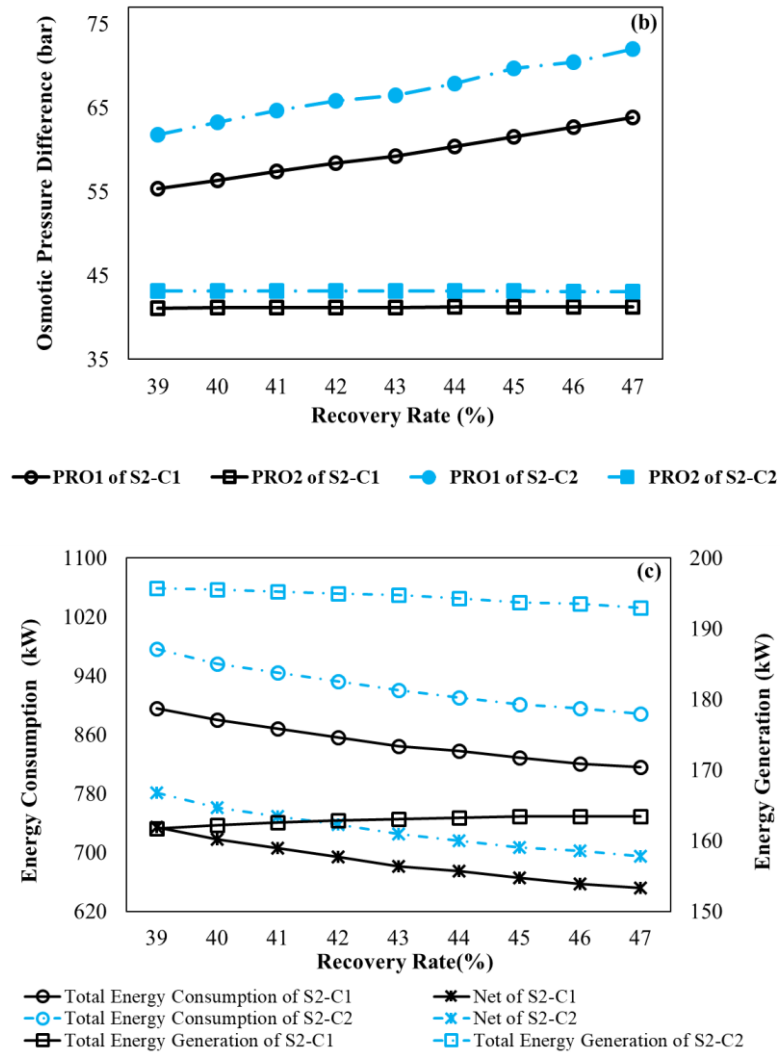


Fig. 4.12: (a) The energy generation of the PRO1 and PRO2 of S2-C1 and S2-C2 at various recovery rates, (b) the osmotic pressure difference of the PRO1 and PRO2 of S2-C1 and S2-C2 at various recovery rates, and (c) the total energy consumption, the total energy generation, and the net energy consumption of S2-C1 and S2-C2 at various recovery rates.

4.4.6 Optimization problem formulation

The NSEC is optimized using the “Modelica” modelling language for 158.4 m³/h capacity two-pass RO desalination plants with and without PRO systems. The main constraints were decided before the simulation of the hybrid systems, where parameters that showed a strong impact on the NSEC were selected as the constraints in the optimization problem formulation of the hybrid systems, such as feed and draw solutions flow rate, draw solution pressure, and seawater flow rate [217]. The systems constraints (ranges of the output parameters) and the tuner parameters

(input parameters) are illustrated in **Table 4.5**, knowing that the tuning parameters related to the PRO system are not applicable for the standalone 2RO plant.

In the case of 40 g/L and 45 g/L seawater TDS, S2-C1 and S2-C2 systems, respectively, the outlet stream of the LPP is sent to ERD3 (**Fig. 4.1**), and the other inlet stream to the ERD3 is the draw outlet from the PRO2. The optimization process will change the pressure of the draw solution outlet in the PRO2. Dymola software suggests that the ERD model should fix the pressure of one of the inlet streams; hence, the pressure of the outlet stream of the LPP was fixed in this study. Accordingly, this stream is not included in the optimization problem formulation (**Table 4.5**).

Table 4.5: Constraints and tuner parameters for the 2RO and 2RO-DSPRO systems at 40 g/L and 45 g/L seawater salinity.

Constraints	S1-C1	S2-C1	S1-C2	S2-C2
Minimized constraint	NSEC	NSEC	NSEC	NSEC
Equality constraints	$Q_{p,RO2} = 158.4$ (m ³ /h)	$Q_{p,RO2} = 158.4$ (m ³ /h)	$Q_{p,RO2} = 158.4$ (m ³ /h)	$Q_{p,RO2} = 158.4$ (m ³ /h)
Inequality constraints	$Recv_{RO1} \leq 45$	$Recv_{RO1} \leq 45$	$Recv_{RO1} \leq 45$	$Recv_{RO1} \leq 45$
		$Recv_{RO2} \leq 95$		$Recv_{RO2} \leq 95$
		$Recv_{PRO1} \leq 45$		$Recv_{PRO1} \leq 45$
	$Recv_{RO2} \leq 95$	$Recv_{PRO2} \leq 45$	$Recv_{RO2} \leq 95$	$Recv_{PRO2} \leq 45$
		$\frac{Q_{Di,PRO1}}{Q_{Fi,PRO1}} \leq 2$		$\frac{Q_{Di,PRO1}}{Q_{Fi,PRO1}} \leq 2$
		$\frac{Q_{Di,PRO2}}{Q_{Fi,PRO2}} \leq 2$		$\frac{Q_{Di,PRO2}}{Q_{Fi,PRO2}} \leq 2$
Tuner Parameter	S1-C1	S2-C1	S1-C2	S2-C2
Seawater flow rate	$72 \leq Q_{SW} \leq 324$ (m ³ /h)	$72 \leq Q_{SW} \leq 324$ (m ³ /h)	$72 \leq Q_{SW} \leq 324$ (m ³ /h)	$72 \leq Q_{SW} \leq 324$ (m ³ /h)
Pressure of the LPP	$10 \leq P_{LPP} \leq 22$ (bar)	N/A	$10 \leq P_{LPP} \leq 22$ (bar)	N/A
Pressure of the HPP3	$45 \leq P_{HPP3} \leq 85$ (bar)	$45 \leq P_{HPP3} \leq 85$ (bar)	$45 \leq P_{HPP3} \leq 85$ (bar)	$45 \leq P_{HPP3} \leq 85$ (bar)
Feed inlet flow rate of PRO1	N/A	$72 \leq Q_{Fi,PRO1} \leq 324$ (m ³ /h)	N/A	$72 \leq Q_{Fi,PRO1} \leq 324$ (m ³ /h)

Feed inlet flow rate of PRO2	N/A	$72 \leq Q_{Fi,PRO2} \leq 324 \text{ (m}^3/\text{h)}$	N/A	$72 \leq Q_{Fi,PRO2} \leq 324 \text{ (m}^3/\text{h)}$
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After defining the main constraints and the tuner parameters, the optimum NSEC for S1-C1, S2-C1, S1-C2, and S2-C2 systems are determined (**Table 4.6**). **Fig. 4.13** shows that the NSEC for the optimized S1-C1, S2-C1, S1-C2, and S2-C2 systems is lower than that for the unoptimized systems. There is a difference between 2.68% and 3.59% in the NSEC in favour of the optimized S1-C1, S2-C1, S1-C2, and S2-C2 systems. The maximum NSEC difference is 3.59% for the S1-C2 system, while the minimum difference is 2.68% for the S2-C1 system. The optimum NSEC of S1-C1 and S2-C1 systems are 3.25% and 2.91 kWh/m³, respectively (**Table 4.6**). At 40 g/L seawater salinity, the energy-saving due to the optimization of the 2RO-DSPRO hybrid system is 10.46% higher than that of the 2RO system. In contrast, the optimum NSEC of S1-C2 and S2-C2 are 3.49 and 2.97 kWh/m³ (**Table 4.6**). The results indicate that at 45 g/L seawater salinity, the energy-saving due to the optimization of the 2RO-DSPRO hybrid system is 14.92% higher than that of the 2RO system. The increase in energy-saving in the 2RO-DSPRO hybrid systems has highlighted the significance of coupling the DSPRO with the RO plant to minimize desalination energy consumption.

It is noteworthy that the PRO performance is a function of the osmotic pressure difference of the salinity gradient resource; the higher the osmotic pressure difference, the higher energy extracted in the PRO system. Utilizing the same wastewater feed solution, power generation in the PRO1 and PRO2 from 40 g/L seawater was lower than that from PRO1 and PRO2 from 45 g/L (**Fig. 4.12a**). For the same feed solution concentration, power generation in the PRO system increases with the concentration of the seawater. Therefore, the power generation will be lower at 35 g/L seawater than at 40 g/L and 45 g/L seawater salinity.

Table 4.6: The NSEC for the optimized 2RO and 2RO-DSPRO systems at 40 g/L and 45 g/L seawater salinity.

Results	S1-C1	S2-C1	S1-C2	S2-C2
NSEC	3.25 (kWh/m ³)	2.91 (kWh/m ³)	3.49 (kWh/m ³)	2.97 (kWh/m ³)
Product flow rate	158.4 (m ³ /h)	158.36 (m ³ /h)	158.4 (m ³ /h)	158.47 (m ³ /h)
Recovery Rate	Recv _{RO1} = 40%	Recv _{RO1} = 43%	Recv _{RO1} = 39%	Recv _{RO1} = 42%
		Recv _{RO2} = 93%		Recv _{RO2} = 94%
		Recv _{PRO1} = 29%		Recv _{PRO1} = 35%
	Recv _{RO2} = 95%	Recv _{PRO2} = 30%	Recv _{RO2} = 95%	Recv _{PRO2} = 31%
		$\frac{Q_{Di,PRO1}}{Q_{Fi,PRO1}} = 1.3$		$\frac{Q_{Di,PRO1}}{Q_{Fi,PRO1}} = 0.73$
		$\frac{Q_{Di,PRO2}}{Q_{Fi,PRO2}} = 0.86$		$\frac{Q_{Di,PRO2}}{Q_{Fi,PRO2}} = 0.74$
Tuner Parameter	S1-C1	S2-C1	S1-C2	S2-C2
Seawater flow rate	164.16 (m ³ /h)	162.60 (m ³ /h)	164.12 (m ³ /h)	162.68 (m ³ /h)
Pressure of the LPP	17 (bar)	N/A	17 (bar)	N/A
Pressure of the HPP3	65 (bar)	67 (bar)	71 (bar)	73 (bar)
Feed inlet flow rate of PRO1	N/A	172.44 (m ³ /h)	N/A	313.20(m ³ /h)
Feed inlet flow rate of PRO2	N/A	252.04 (m ³ /h)	N/A	309.60 (m ³ /h)

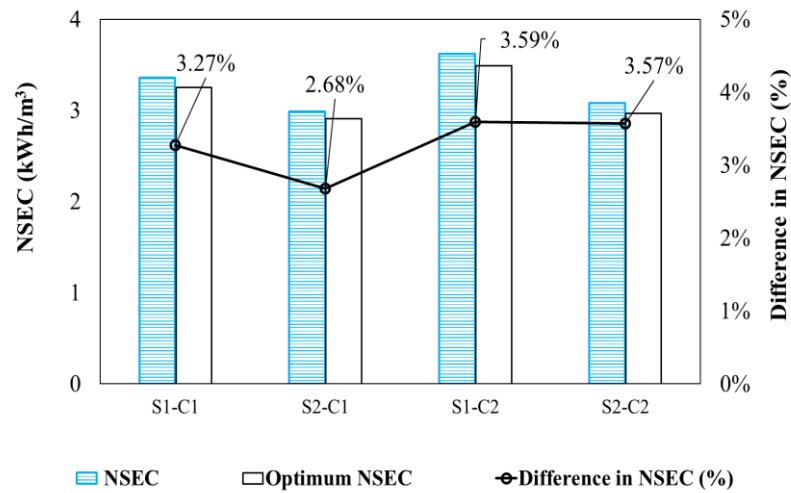


Fig. 4.13: The NSEC, the optimum NSEC, and the percentage difference in the NSEC of S1-C1, S2-C1, S1-C2, and S2-C2.

4.4.7 Membrane and energy costs

The cost and area of the hollow fibre PRO element in stages one and two were provided by Toyobo Company (Japan), and the spiral wound RO element in stages one and two from the literature [218]. The active membrane and cost of the PRO element are 63 m² and \$ 5193 US/element, i.e., \$ 82 US/m². The RO element has 30.5 m² of active membrane area and \$ 600 US/element, \$ 15 US/m². The membrane area and cost for two-stage RO and two-stage RO-DSPRO plants of 3801.6 m³/d capacity were calculated (**Table 4.7**). It is worth noting that the reported cost of PRO membranes is the retail cost, and it is expected that this cost will be reduced with increased demand and supply of PRO membranes. The membrane cost is reported based on the retail price for the 70 m² PRO membrane model, even though the 650 m² PRO model is less expensive. However, the PRO membrane cost is expected to reduce in the future or when there is a large market for the PRO technology.

The cost of RO1 in S2-C1 and S2-C2 systems is 5% more expensive than in S1-C1 and S1-C2 systems. The same trend is noticed for RO2, where the cost of RO2 in S2-C1 and S2-C2 systems is 10% more expensive than in S1-C1 and S1-C2 systems due to the higher salinity of feed solution in the former systems, which requires the higher salinity of feed solution larger membrane areas. The required PRO1 membrane area for the S2-C1 system was 23% higher than that for the S2-C2 system due to the higher draw solution concentration in the S2-C2 system using 45 g/L seawater salinity. The higher seawater salinity increased the osmotic pressure of the PRO1 draw solution and the water flux, reducing the required PRO membrane. Similarly, the required PRO2 membrane area for the S2-C1 system was 9% higher than that for the S2-C2. The cost of

S2-C1 and S2-C2 systems with PRO units for energy generation is higher than the S1-C1 and S1-C2 systems with RO units only. Toyobo hollow fibre PRO membranes are modified from the RO membrane with a water permeability coefficient of about 0.36 L/m²h.bar, which is less than the TFC membranes with a water permeability coefficient of about 1.25 L/m²h.bar [220]. The PRO membrane cost could be reduced by i) applying an improved PRO membrane with a higher water permeability coefficient and ii) reducing the cost of the PRO membrane when there is a big market for the technology. For example, the cost of the PRO membrane could be decreased 6 times when buying a large hollow fibre PRO membrane module.

However, the NSEC of the 2RO-DSPRO system is lower than that of the 2RO system. The NSEC in the S2-C1 system was 9.55% lower than that of the S1-C1 system. For 45 g/L seawater salinity, the NSEC of the S2-C2 was 15% lower than that of the S1-C2 system. The annual energy saving in the 2RO-DSPRO systems S2-C1 and S2-C2 is 471779 and 721544 kWh per year, respectively. 53% more energy-saving was achieved for 45 g/L seawater salinity because of the higher RO brine salinity, underlining that the 2RO-DSPRO system generates more energy than seawater salinity increases.

Table 4.7: The membrane cost of RO and PRO processes based on the current study.

Process	Parameter	System type			
		S1-C1	S2-C1	S1-C 2	S2-C2
RO1	Membrane Area (m ²)	5943	6240	5941	6237
	Cost (US\$)	89,145	93,600	89,115	93,555
RO2	Membrane Area (m ²)	5813	6419	5819	6429
	Cost (US\$)	87,195	96,285	87,285	96,435
PRO1	Membrane Area (m ²)	-	176624	-	136215
	Cost (US\$)	-	14,483,168	-	11,169,630
PRO2	Membrane Area (m ²)	-	149914	-	135841
	Cost (US\$)	-	12,292,948	-	11,138,962
Total NSEC	kWh/m ³	3.25	2.91	3.49	2.97
Energy Saving	kWh/year		471779		721544
Total cost	(\$US)	176,340	26,966,001	176,400	22,498,582

4.5 Conclusion

The study evaluated the feasibility of coupling the DSPRO with a two-pass RO plant, 2RO-DSPRO, for 40 g/L and 45 g/L salinity seawater treatment. The behaviour of the 2RO plant was compared with that of the 2RO-DSPRO plant to study the impact of system hybridization on the permeate quality and NSEC. The study showed that 2RO systems provided a higher quality desalinated water than the 2RO-DSPRO system. However, both systems could generate desalinated water that meets the drinking water quality of $\text{TDS} < 0.25 \text{ g/L}$. The advantage of coupling DSPRO with the 2RO plant was evidenced in reducing the NSEC of the desalination process. At 40 g/L seawater and recovery rates between 39% and 47%, the NSEC of the S2-C1 system was 11.2%-14.7% lower than that of the S1-C1 system (RO plant only).

Interestingly, the reduction in the NSEC of desalination further increased at 45 g/L seawater salinity. At 45 g/L seawater salinity, the NSEC of the S2-C2 system was 15.03%-17.53% lower than that of the S1-C2 system. Furthermore, the optimization of the NSEC showed preferred minimization results. For instance, the NSEC of S1-C2 decreased from 3.62 kWh/m^3 to 3.49 kWh/m^3 after the optimization. The energy generated by the DSPRO will cover part of the energy required for powering the 2RO system, reducing the reliance on fossil fuels and the environmental impact of CO_2 gas emissions. Another significant benefit of the 2RO-DSPRO system is that it would reduce the RO brine concentration due to dilution in the PRO process. Consequently, this will reduce the negative environmental impact of the high concentrated brine on the sea. It should be noted that the cost of the 2RO-DSPRO was around \$US 27 million compared to \$US176 thousand for the 2RO plant, due to the cost of the PRO membrane. However, the cost of the PRO membrane is expected to decrease when there is a market for the technology.

One of the main obstacles in commercializing the PRO system is finding a suitable membrane and the cost of membranes. Toyobo CTA PRO membrane is about $1.0 \times 10^{-7} \text{ m/s.bar}$ is low compared to $1.69 \times 10^{-7} \text{ m/s.bar}$ for HTI CTA membrane and $3.25 \times 10^{-7} \text{ m/s.bar}$ for HTI TFC membrane and $5.25 \times 10^{-7} \text{ m/s.bar}$ for Porifera TFC membrane. A membrane with higher water permeability is desirable to improve the PRO performance [255]. Also, the cost of the PRO membrane should be dropped to be affordable, knowing that the Toyobo membrane costs less than HTI and Poreifera membranes [217].

Chapter Five: Machine learning for intrinsic membrane parameters and power density prediction in pressure retarded osmosis

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5.1 Objectives

This chapter aims to use machine learning algorithms to predict the pressure-retarded osmosis membrane's intrinsic parameters and power density. The main objectives of this chapter are:

- 1) To collect factual PRO experimental data, to be fed to a diversity of machine learning algorithms to predict the intrinsic parameters of the membrane and the power density.
- 2) To employ artificial neural networks and Boosting-based tree models to predict the intrinsic parameters of the pressure retarded osmosis membrane based on the minimum theoretical power density that could be predetermined and was suggested to be 5 W/m² in this study.
- 3) To compare the predictive power of the different machine learning algorithms for the determination of the membrane's intrinsic parameters and the power density.
- 4) To use the machine learning algorithms with the highest predictive power to evaluate the feature importance of each input parameter affecting the power density of the pressure retarded osmosis membrane.

5.2 Introduction

Pressure retarded osmosis (PRO) is one of the blue energy techniques for sustainable energy generation from salinity gradient solutions. The osmotic pressure variation between the two PRO feed solutions is responsible for the water permeation from the low salinity to the high salinity of the PRO semipermeable membrane, where the hydraulic power is generated through the hydro-turbine [27, 29, 170]. Recently, the availability and development of promising PRO membranes for producing higher power density of the PRO process have been broadly investigated [17, 85, 87, 89, 256]. A PRO membrane of satisfactory water permeability and good salt rejection would ensure the cost-effectiveness of the process.

The membrane efficiency in osmotically driven systems is usually related to the membrane characteristics like the membrane water permeability coefficient, the salt permeability coefficient, and the membrane structural parameter [17, 257]. The membrane's intrinsic parameters highly

influence the PRO process performance. For example, Zhang et al. [74] revealed that the reduction of the salt permeability coefficient caused an enhancement of 58.5% of the PRO power density. Moreover, the salt permeability coefficient points out the severity of the reverse solute diffusion from the high concentrated side to the low concentrated side. Nevertheless, the analytical model in PRO studies [87, 127, 190, 258, 259] ignored the influence of the reverse salt flux on the system behaviour for simplicity. The reverse salt diffusion can intensify the membrane's internal concentration polarization [161, 196, 260-262] and the possibility of enhancing the membrane fouling [261, 262]. These phenomena involve controlling the behaviour of the PRO system and cannot be underestimated. Consequently, the PRO process's effectiveness is governed by precisely determining the membrane parameters.

The accurate determination of the membrane's intrinsic parameters with the variation of the operating conditions is necessary for the precise cost estimation of the osmotically driven membrane processes. Determining the membrane parameters affected by the process operating conditions has been challenging. Many studies in the literature [190, 198, 220, 263-265] assumed constant values of these parameters, which is not the real case. Nevertheless, the variation in the applied hydraulic pressure of the PRO membrane cannot be ignored. Undoubtedly, the applied pressure will affect the membrane performance, and it could produce a lower permeation rate or enhance the reverse salt flux [266-268]. The water and salt permeability coefficients cannot be constants in this case. For instance, She et al. [202] compared the PRO process outputs with two scenarios predicting the water and solute permeability coefficients. The first scenario relied on the conventional RO method. In contrast, the second scenario used a new technique in which the membrane transport parameters varied within the applied hydraulic pressure changes. The results showed a preferable prediction of the experimental PRO-specific solute reverse flux when the second scenario determined the membrane transport properties. This method clarifies the significance of using specific values for the membrane parameters based on the actual process conditions.

Moreover, analytical PRO models assumed a constant membrane structural parameter [25, 269]. Technically, the membrane structural parameter can provide reasonable knowledge of the internal concentration polarization, a significant incident in osmotically driven membrane systems. For instance, the occurrence of internal concentration polarization in the PRO system will attenuate the osmotically driving force at the membrane sides, decreasing the PRO power density [87]. Accordingly, the variation of the membrane structural parameter within the operating conditions of the PRO system should be considered. Another shortcoming of analytical is that the effect of high salinity is often ignored when estimating membrane intrinsic parameters [270]. For instance, one study [271] reported that the membrane salt permeability coefficient increased up to 10 times when 100% increase in the salinity of the solute occurred.

Alternatively, to assume constant intrinsic membrane parameters, the determination of these parameters should be addressed. Usually, the conventional RO and the FO processes determine the PRO process membrane parameters [67, 68, 88, 257, 267]. The water and salt permeability coefficients are predicted using the RO process, where the feed solution is pressurized. On the contrary, the FO test defines the membrane structural parameter. However, this method is inaccurate according to the differences between the RO, FO, and PRO systems [67, 68]. Performing RO tests to predict the membrane properties relies on using flat porous support or filling the permeation channel with a carrier to support the membrane to eliminate its deformation. Unfortunately, this method does not resemble the actual operating conditions in the PRO process [67, 68, 272]. For instance, the high pressure applied on the PRO process's draw solution may progressively cause membrane deformation [87, 267], leading to different A_w , B and S values, which the physical models usually ignore.

Additionally, physical, or analytical modelling studies neglect the reverse salt diffusion in the PRO system. Consequently, some studies [67, 68, 88, 273-275] presented different experimental results compared to the modelled results based on predicting the membrane parameters using the conventional technique. This information is not obtainable through traditional analytical models [273]. Several researchers have utilized numerical techniques, such as Computational Fluid Dynamics (CFD) [276], to examine the hydrodynamics and mass transfer within a PRO channel; however, CFD is not practical for large-scale analysis due to its high computational costs [277]. Leveraging machine learning (ML) technology to predict PRO power density using an actual PRO database can minimize the required PRO experimental work, saving the researcher's time and reducing the PRO process's operational cost. It could also be used as a prior experimental step to choose better input conditions for the best power density needed for the PRO system. Notably, the actual economically viable PRO power density deviates according to the process design, including the system capacity, feed solutions salinity, and applied pressure on the feed solutions. Additionally, the consumed energy through the pumping and treatment of the PRO feed solutions should be contemplated to evaluate the net energy generation of the PRO system. The net energy generation would present the best view of the viability of the PRO process. ML models can also aid researchers in exploring novel PRO configurations, materials, and operational strategies by rapidly analyzing and generating insights from vast amounts of experimental and theoretical data. This study aims to utilize machine learning to predict the intrinsic membrane properties to achieve the threshold power density of 5 W/m^2 for an economic PRO system depends on input operating conditions, which can subject the membrane's intrinsic parameters to change. The membrane characteristics, i.e., water and salt permeabilities and the structural parameter, and the power density should be built by techniques that employ factual PRO operating conditions, such as the applied pressure, the osmotic pressure of the feed and the draw solutions, the feed and the draw

solution type, and the membrane type. A PRO database will be arranged using the experimental data available in the literature, followed by collecting the membrane parameters by assuming a theoretical 5 W/m^2 power density to achieve an economic PRO system [27, 131]. It should be pointed out that the theoretical power density threshold could be adjusted to achieve an economic PRO process. The machine learning program will predict the membrane power density based on the membrane characteristics and operating parameters to allow researchers to select or fabricate PRO membranes with A_w , B , and S factors recommended to generate a power density equal to or more than the 5 W/m^2 threshold. These parameters will be predicted by four different machine learning algorithms, namely Artificial Neural Network, CatBoost, XGBoost, and Random Forest, where the results will be compared. The predicted membrane parameters and PRO power density will be compared to the published data.

5.3 Methods

5.3.1 The pressure retarded osmosis dataset collection

Pressure retarded osmosis data, termed the PRO dataset, is a comprehensive and systematic collection of data for pressure retarded osmosis. The dataset is provided along with the study. The PRO dataset in this study is higher than one thousand points, which is higher than the dataset points of other studies where machine learning modelling applications have been applied [278]. The PRO dataset includes 1190 instances and 24 features. The dataset was collected from 47 published papers of the literature. Notably, the conclusion will be ranged with these studies; however, the experimental work of the PRO system is limited, and most studies are from modelling works due to the PRO's expensive infrastructure. The figures were collected from the literature (Data and references provided in supplementary information, S.1). Then the online software "WebPlotDigitizer" was applied to extract the data from the figures and plots. The dataset visualized in **Fig. 5.1** shows the membrane's intrinsic parameters at a power density less than and more than the economically viable 5 W/m^2 at various values of the applied pressure difference of the PRO. For instance, **Fig. 5.1a** show the power density lower than 5 W/m^2 in one of the y-axis (black) and the water permeability coefficient in the other y-axis (pink) at different hydraulic pressure values. Also, at a power density of more than 5 W/m^2 , the A_w values are shown in **Fig. 5.1b**. It is worth noting that around 52% of the collected power density data are less than 5 W/m^2 . The water permeability coefficient, the salt permeability coefficient, and the membrane structural parameter were reported in the studies and were considered as it is in the modelling. The data's maximum, minimum, average, median and standard division were extracted using Python and tabulated in **Table 5.1**. The applied pressure difference ranges from 0.41 to 70.04 bars (**Table 5.1**). Theoretically, modelling higher pressures of more than 70.04 bar can be simulated,

requiring less time and no infrastructure. The maximum recorded power density value is 120 W/m², while the highest osmotic pressure difference is 176 bars.

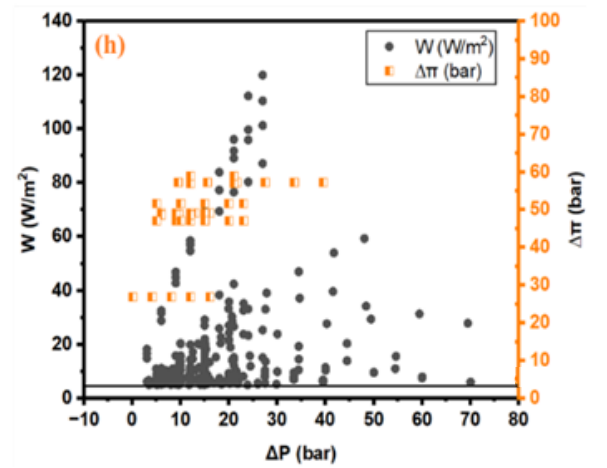
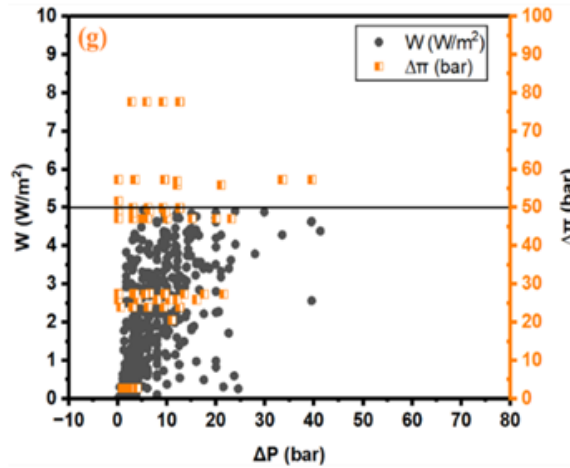
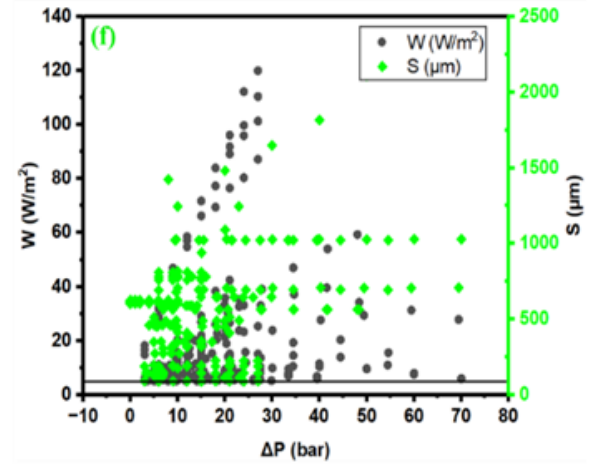
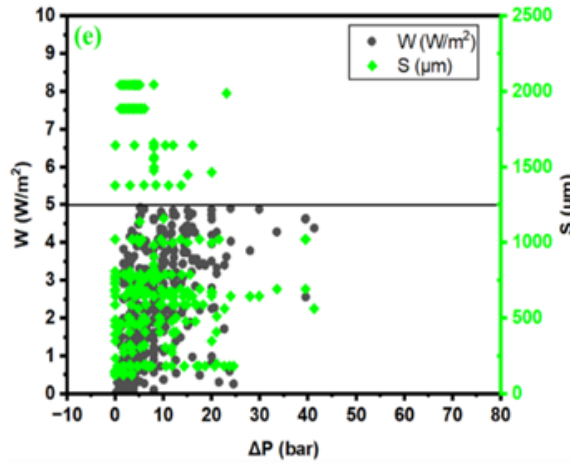
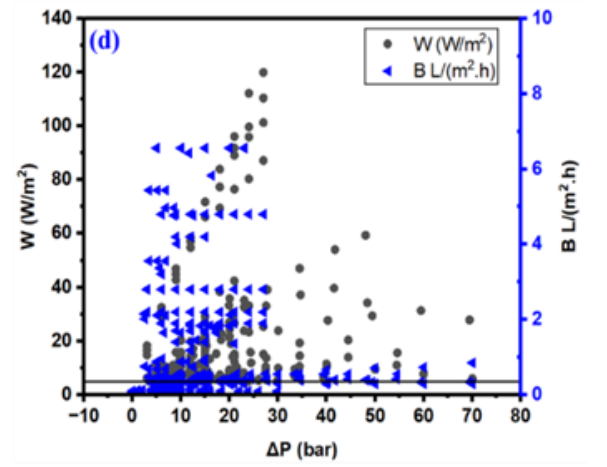
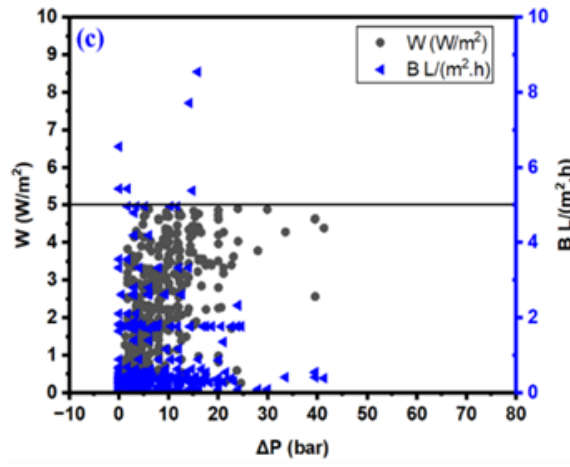
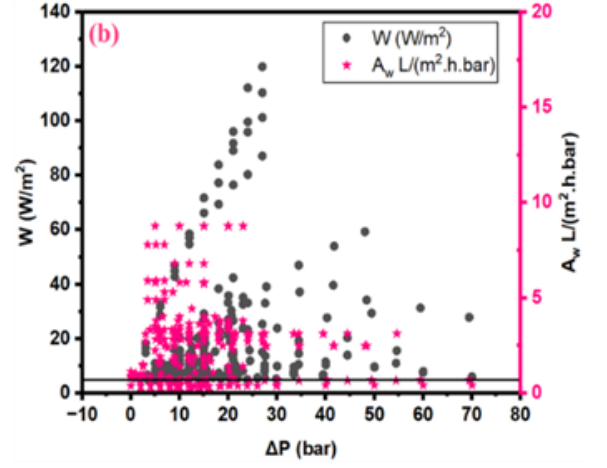
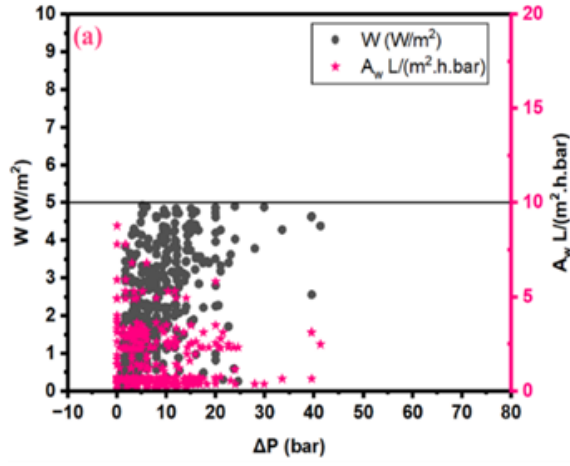


Fig. 5.1: (a), (b) The A_w values at W lower and higher than 5 W/m^2 , respectively, with the variation of the applied hydraulic pressure difference, (c), (d) the B values at W lower and higher than 5 W/m^2 , respectively, with the variation of the applied hydraulic pressure difference, (e), (f) the S values at W lower and higher than 5 W/m^2 , with the variation of the applied hydraulic pressure difference, and (g), (h) the osmotic pressure difference at W lower and higher than 5 W/m^2 , with the variation of the applied hydraulic pressure difference.

Table 5.1 provides an overview of the collected data.

Table 5.1: The maximum, minimum, average, median, and standard division of the numerical database.

		Maximum	Minimum	Average	Median	Standard deviation
Collected data						
Inputs	Draw flow rate (L/min)	40.00	0.03	2.18	0.50	5.00
	Feed flow rate (L/min)	27.58	0.02	1.33	0.50	2.81
	Applied pressure on the draw side (bar)	29.48	0.72	9.88	8.93	6.33
	Applied pressure on the feed side (bar)	6.63	0.10	1.42	0.50	1.59
	Draw salinity (M)	3.00	0.07	1.00	1.00	0.63
	Feed Salinity (M)	1.00	0.00	0.04	0.01	0.12
	Membrane thickness (m)	0.40	0.000059	0.03	0.00	0.10
	Membrane area (m^2)	650.00	0.00005	9.88	0.00	44.97
	Draw temperature (K)	343.00	283.00	298.18	297.00	8.37
	Feed temperature (K)	343.00	283.00	298.80	298.00	8.58
	The osmotic pressure difference (bar)	176.00	2.80	50.58	49.20	30.72
	The applied pressure difference (bar)	70.04	0.41	10.83	8.62	10.31
	Water flux ($\text{L/m}^2\cdot\text{h}$)	148.40	0.11	24.30	16.47	23.47
	Reverse salt flux ($\text{L/m}^2\cdot\text{h}$)	459.77	0.00	30.28	0.00	77.08
Outputs						
	Power density (W/m^2)	120.00	0.02	7.68	3.77	14.27
	Water permeability coefficient ($\text{L/m}^2\cdot\text{h}\cdot\text{bar}$)	8.78	0.08	2.14	2.27	1.77
	Salt permeability coefficient ($\text{L/m}^2\cdot\text{h}$)	8.55	0.01	0.78	0.32	1.21
	Membrane structural parameter (μm)	2877.81	90.00	729.07	645.94	473.51

5.3.2 Determination of A_w , B and S in the literature

In the PRO studies, determining the membrane water permeability requires the water flux, the applied hydraulic pressure difference, and the osmotic pressure difference along the membrane (**Equation 5.1**). These were taken directly from the experimental data for accuracy, where the water flux was determined according to **Equation 5.1** in the experimental studies.

$$J_w = A_w(\Delta\pi - \Delta P) \quad (5.1)$$

where J_w is the water flux, A_w is the membrane permeability coefficient ($L/(m^2 \cdot h \cdot bar)$), $\Delta\pi$ is the osmotic pressure difference (bar), and ΔP is the applied hydraulic pressure difference (bar), respectively. Power density (W) in W/m^2 , the energy generated in the PRO system by the membrane area, is reported in the studies or determined by the following equation.

$$W = J_w \Delta P = A_w(\Delta\pi - \Delta P) \Delta P \quad (5.2)$$

Traditionally, in all the data, **Equation 5.1** estimates the A_w based on the RO test when $\Delta\pi$ is zero [25]. On the other hand, B is estimated by the following equation [25].

$$B = \frac{A \left(\frac{C_P}{C_F} \right) (\Delta P - \Delta\pi)}{\left(1 - \frac{C_P}{C_F} \right)} \quad (5.3)$$

where A is the membrane area in (m^2), C_P (M) is the permeate concentration, and C_F (M) is the feed concentration. All the points for B were collected from the literature for the given studies. The membrane structural parameter (S) was also collected from the studies. Data pre-processing will remove any outliers from the data before machine learning modelling can be applied to minimize error due to different estimation methods for A_w , B , S , and power density.

5.3.3 Machine learning study design and algorithms

5.3.3.1 Study design

The data attached (**Supplementary information, S.1**) was collected from PRO studies using figures and Tables. The extracted data was tabulated in Excel from the figures and tables and then exported to Python. After cleaning, pre-processing, and transforming the data, feature engineering was conducted to drop less relevant features in the collected data (**Fig. 5.2**). The data was subsequently fed into the ANN or gradient boosting models and evaluated with the evaluation metrics.

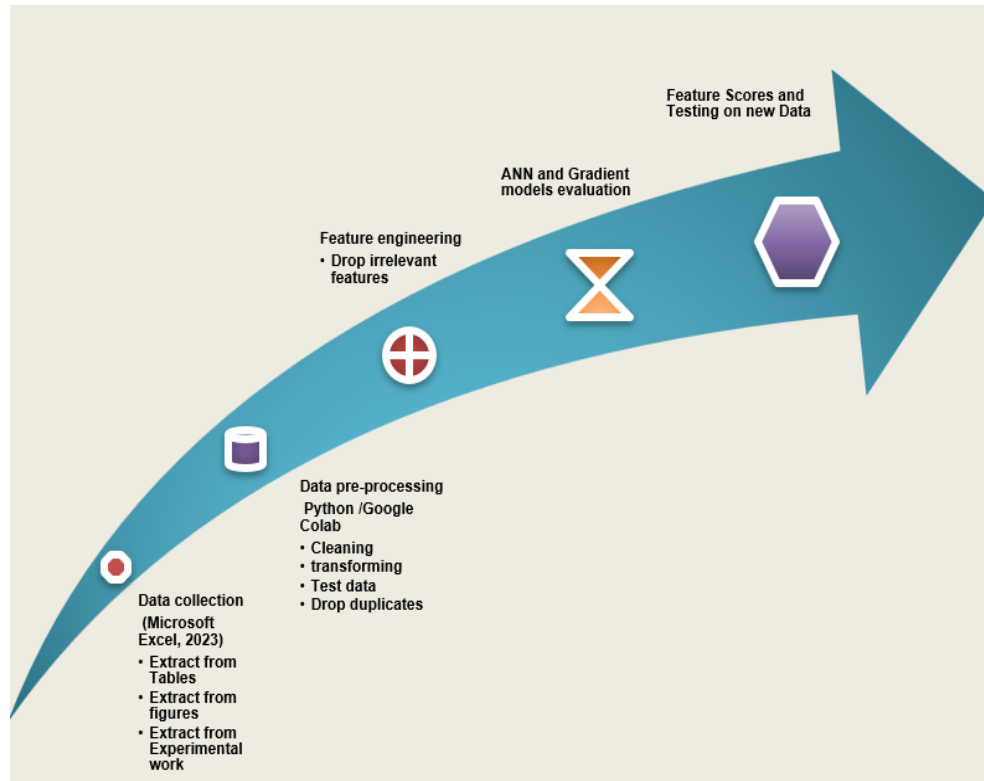


Fig. 5.2: Study design for machine learning models.

5.1.1.1 Artificial neural network (ANN) architecture

A built-in library in Python called "Keras" was employed to scheme a neural network. An artificial neural network (ANN) is a deep learning algorithm built to imitate the human brain's neural networks by developing multi-connections between artificial neurons [279]. It is a subset of machine learning algorithms designed to process and learn from data. The basic processing elements of neural networks are called artificial neurons or nodes, representing features of raw input data. Each neuron in the network is a computational unit that takes the inputs, performs a weighted sum, applies a non-linear function, and generates an output.

The ANN model has been conducted with a specific architecture. The training model comprised six dense layers with different numbers of neurons (512, 512, 128, 128, 128, and 64) to learn and represent complex patterns (as shown in **Table 5.2**). Rectified Linear Unit (ReLU) is an activation function for the introduction of the non-linearity into the network. Furthermore, regularization has been applied using dropouts to prevent overfitting and improve the model's generalization ability.

Table 5.2: ANN model architecture.

Layer Type and activation	Output (Shape)	Number of Parameters
dense (Dense)	(None, 512)	6656
activation (ReLU)	(None, 512)	0
Dense_1 (Dense)	(None, 512)	262656
Activation_1 (ReLU)	(None, 512)	0
Dense_2 (Dense)	(None, 128)	65664
Activation_2 (ReLU)	(None, 128)	0
Dense_3 (Dense)	(None, 128)	16512
Activation_3 (ReLU)	(None, 128)	0
Dropout (Dropout 0.3)	(None, 128)	0
Dense_4 (Dense)	(None, 128)	16512
Activation_4 (ReLU)	(None, 128)	0
Dense_5 (Dense)	(None, 64)	8256
Activation_5 (ReLU)	(None, 64)	0
Dropout_1 (Dropout 0.2)	(None, 64)	0
Dense_6 (Linear)	(None,1)	65
Total Parameters		
376,321		
Trainable Parameters		
376,321		
Non-trainable parameters		
0		

The dropout rate of 0.3 in the first Dropout layer means that during training, 30% of the input units (neurons) will be randomly set to 0 at each update, which helps prevent the model from relying too heavily on any subset of neurons. Similarly, the dropout rate of 0.2 in the second Dropout layer means that 20% of the input units will be randomly set to 0 during training. The ANN model can become more robust and generalize better to unseen data by using dropout. It helps prevent overfitting by forcing the network to learn more robust representations by not relying too much on specific neurons. Finally, the model ends with a dense layer containing a single neuron and an activation layer with a linear activation function suitable for regression tasks.

5.3.3.2 ANN training procedure and hyperparameters

The ANN model was trained using the Adam (Adaptive moment estimation) optimizer with a learning rate of 0.001. The learning rate is a crucial hyperparameter determining the step size

during gradient descent optimization. The Adam optimizer adapts the learning rate during training, helping the model converge faster and potentially escape local minima. The ANN model was trained for 500 epochs (i.e., 500 passes through the entire training dataset), and the batch-size parameter was set to 256, indicating that the training data will be divided into batches of 256 samples during each training iteration. This approach helps in optimizing memory usage and accelerating training. The MSE was used as a loss function. In general, L2 loss (MSE) tends to provide more precise gradient information for optimization. The pre-trained ANN model was loaded to make predictions with ANN, and the new test data was pre-processed similarly to the PRO dataset. Finally, predictions were obtained for the new test data and exported.

5.3.3.3 Gradient boosting method

Three gradient boosting models were processed in the current study: Categorical Boosting (CatBoost), Extreme Gradient Boosting (XGBoost), and the Random Forest. These models combine multiple decision trees, which leads to strong predictive power. These models are well-known for faster training and improved generalization and have been successfully used in many regression problems. For instance, CatBoost is considered a significant method for the high accuracy of the generalization [280]. Moreover, Random Forest is determined as a significantly accurate method and fast learning without being affected by the nature of the original dataset [281]. Random Forest as an ML method is a variety of classifiers processed in decision trees, created based on a couple of randomization sources. The decision trees' forming relies on choosing the best split points to minimize the loss [282]. The input variables are the PRO process parameters that impact the water permeability coefficient, the salt permeability coefficient, the membrane structural parameter, or the power density. Furthermore, the output variable is one of the membrane's intrinsic parameters or the power density. A single tree in the gradient boosting models is utilized to build a basis function [283, 284] as follows.

$$Fo(x) = \arg \min_{\beta} \sum_{i=1}^n \text{Loss}(y_i, \beta) \quad (5.4)$$

where x is the input variable, Fo is the basis function, $\text{Loss}(y_i, \beta)$ is the loss function, and β is the split points set for the internal nodes of the tree. The best β value that guarantees to minimize the loss function is decided using the training data.

5.3.3.4 Gradient Boosting models architecture and hyperparameters

Gradient Boosting is a well-known machine-learning technique utilized for prediction tasks. It is an ensemble learning technique that builds multiple weak learners (i.e., decision trees) where each weak learner is trained sequentially to correct the errors occurred by the previous ones. CatBoost

and XGBoost are powerful gradient-boosting models used in our experiments. Random Forest Regressor is an ensemble learning technique that uses a collection of decision trees (forest) to perform regression tasks. Each tree in the forest independently predicts the output, and the final prediction is obtained by averaging (for regression) the predictions of all trees. The hyperparameters of CatBoost, XGBoost and Random Forest regression are listed in **Table 5.3**. The parameters iterations (CatBoost) or n_estimators (XGBoost and Random Forest), respectively, are similar and control the number of boosting rounds or iterations, which corresponds to the number of base learners (decision trees) built in the ensemble.

Table 5.3: Hyperparameters used in Gradient boosting models.

Model Name	Iterations/n_estimators	Learning rate	Depth	Verbose	Booster
CatBoost	3000	0.001	10	False	gbtree
XGBoost	10	0.01	15	None	gbtree
Random Forest	100	N/A	15	0	N/A

The learning rate hyperparameter controls the step size at which the models (CatBoost and XGBoost) are updated during each boosting iteration. A smaller learning rate allows the model to make more conservative updates, which can improve stability during training. For instance, the learning rate is set to 0.001 for CatBoost, which means the model will make small updates to the parameters at each iteration. The Mean squared error (MSE) was used as a loss function for all the models. In Random Forest, there is no iterative boosting procedure, and the model's parameters are not updated with a learning rate. The trees are trained independently, and their predictions are combined directly without any iterative optimization process. The depth hyperparameter specifies the maximum depth of each decision tree in the ensemble. A deeper tree can capture more complex relationships in the data but may also lead to overfitting. For instance, by setting the depth to 15 for the XGBoost, the code limits each decision tree to a maximum depth of 15 levels. Finally, by setting verbose to False or 0, no progress messages are revealed during training, making the training process silent.

5.3.3.5 The metrics evaluation of the model performance

Models for the water permeability, the salt permeability, the structural parameter, and the PRO power density were built and evaluated. The main metrics used to evaluate the ML models are the coefficient of determination (R^2), the mean square error (MSE), and the mean absolute error

(MAE). The performance of the proposed machine learning models is examined by the coefficient of determination (R^2), between 0 and 1. The highest the value of the R^2 is, the more efficient the model.

$$R^2 = \frac{\sum_{i=1}^n (P_i - \bar{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y}_i)^2} \quad (5.5)$$

where n is the number of data points, P_i is the output predicted from the machine learning model, $\bar{y}_i$ is the mean of the sample data, and y_i is the real output value. To determine how much the model fitting line is close to the collected data, the mean square error was evaluated as the following.

$$MSE = \frac{1}{n} \sum_{i=1}^n (y_i - P_i)^2 \quad (5.6)$$

In **Equation 5.6**, MSE is the mean square error used to evaluate the machine learning model's performance. It has been suggested that the MSE of the testing data governs the machine learning model's predictive performance. However, the importance of the MSE of the training data is to clarify and point out the reliability of the machine learning models in digging for the abnormality in the dataset. The mean absolute error (MAE) of the testing data is also included as the summation of the absolute error between the predicted data and the real output data as follows.

$$MAE = \frac{1}{n} \sum_{i=1}^n |y_i - P_i| \quad (5.7)$$

The Google Colaboratory platform, through Python 3.9 software and the built-in libraries, was operated for building and running the models. The input data present the independent variables of the machine learning models, while the output layer would be the water permeability, salt permeability, structural parameter, or power density.

5.3.3.6 Testing the models on new unseen data

Model performance was predicted using unseen data, and a comparison was made to illustrate the predictive powers of the best models for intrinsic membrane parameters and power density.

5.4 Results

Four machine learning algorithms predict the intrinsic parameters of the PRO membrane. Furthermore, the PRO output represented by the power density is also predicted. The prediction of these parameters and output will be discussed in this section.

5.4.1 Prediction of the membrane's intrinsic parameters and the pressure retarded osmosis power density using ANN

Neural networks are powerful deep learning algorithms that can find hidden patterns in data and accurately predict a process's output. Python was used for designing the artificial neural network (ANN) algorithm to predict the water permeability coefficient, the salt permeability coefficient, the structural parameter, and the PRO power density. The PRO dataset was loaded into the software. The categorical variables, such as the types of the salinity gradient solutions, the membrane types, or the membranes manufacturing companies, were converted to numerical data by one-hot encoding to form binary variables. Through the design of the ANN algorithm, the layers number, the algorithm learning rate, and the training epochs number were decided precisely (Epochs = 500, learning rate = 0.01) because the PRO input parameters have no direct impact on the process outputs. First, the number of hidden layers was assigned to one, and then through trial and error, the appropriate number of hidden layers was decided. The optimal number of epochs was determined by plotting the loss function of the training data and validation data against the number of epochs, starting from 100. The input parameters, such as the draw and the feed solutions type, salinity, flow rate, temperature, hydraulic pressure, membrane type, and membrane area, were considered while designing the ANN model. The built ANN model had one input layer, three hidden layers, and one output layer to predict A_w , B , S , and power density. The RELU (Rectified linear Unit) activation function was applied to the output of each neuron from the dense layer.

A significant predictive power of the designed ANN model was displayed for the water permeability coefficient, the salt permeability coefficient, and the structural parameter but not for the power density. The categorical data were encoded to numbers with the help of the "LabelEncoder" transformer in Python. Early stopping occurred to prevent the model's overfitting and enhance the learning rate. **Fig. 5.3a** represents the hierarchy of the ANN model, and multiple hidden layers make the relation between the inputs and outputs complex. A correlation matrix through a heat map for the water permeability, the salt permeability, the structural parameter, and the power density was prepared (**Fig. 5.3b**) to investigate further how the input parameters influenced them.

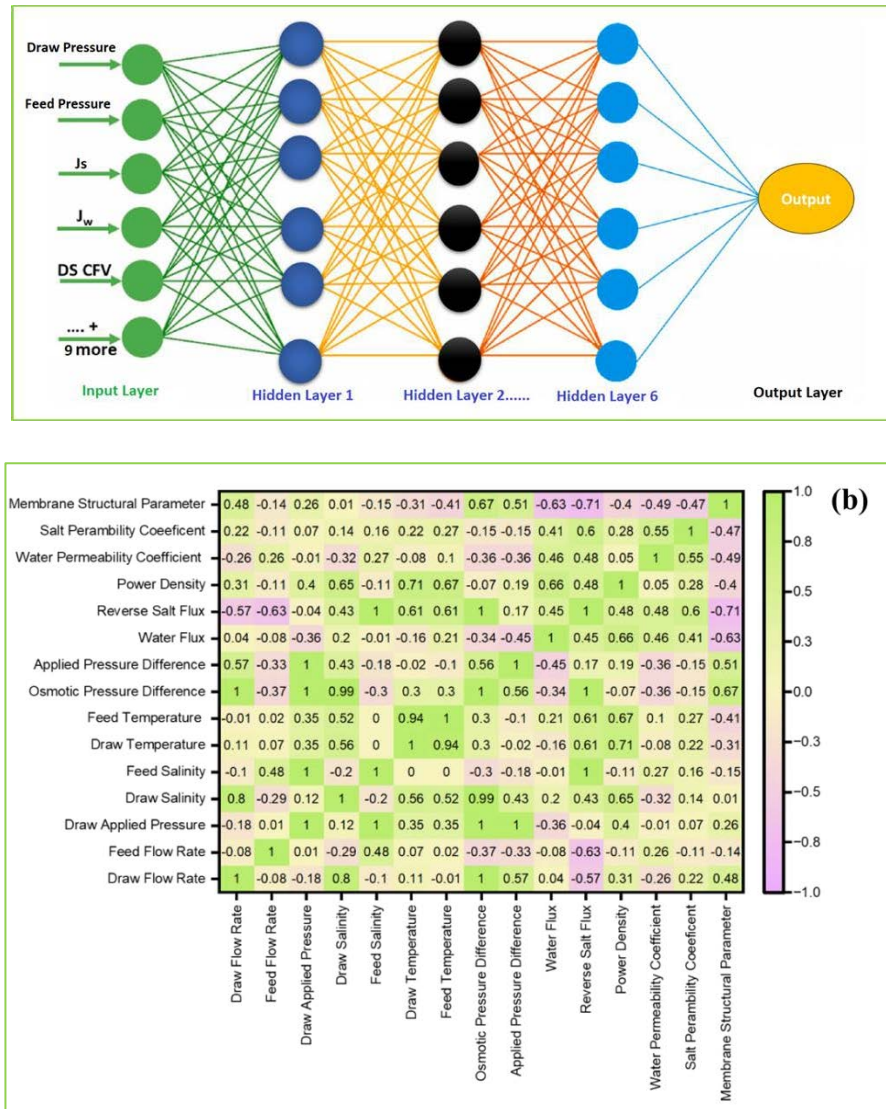


Fig. 5.3: **a)** ANN hierarchy, and **b)** the correlation matrix of the impact of the PRO input parameters of the water permeability coefficient, the salt permeability coefficient, the structural parameter, and the power density.

A correlation factor of value close to 1 means the parameters have a high correlation and impact each other strongly. Conversely, a correlation factor of a value close to -1 means that the parameters have no or weak impact on each other. A high correlation factor of "1" was found to relate the osmotic pressure gradient to the draw flow rate and the reverse salt flux with the feed salinity (**Fig. 5.3b**). The training set was around 80% of the collected input data. In contrast, the remaining 20% of the data was used to test the ANN model and predict the output parameters. Some input data were classified as categorical; the type of PRO feed solutions, the membranes type, and the manufacturers. These were encoded with one-hot encoding in Python and normalized.

The ANN model was simulated using the Adam optimizer and the learning rate of 0.001. The R^2 value was found for the training and testing data, as shown in **Fig. 5.4** for A_w , B, S and W, and the optimization of the ANN was done using the loss function for the training set against the validation set. The loss function against the number of epochs plot is presented in **Figure S1 (Supplementary information S1)**. The R^2 of the training data for the A_w is 0.9988, while the R^2 for the testing data for the water permeability coefficient is 0.9882 (**Fig. 5.4a** and **Fig. 5.4b**). The high R^2 value exhibits the significant performance of the ANN model for the prediction of A_w and no signs of overfitting. A high R^2 value indicates that the ANN can accurately predict the A_w based on the input conditions. Excellent results of the simulation of the ANN model for the training and testing data are shown for the salt permeability coefficient, B, with R^2 of 0.9977 for the training data (**Fig. 5.4c**). Furthermore, the R^2 of the salt permeability coefficient for testing the ANN model is 0.9501 (**Fig. 5.4d**). Smaller R^2 values, compared to other output parameters, can be noticed for both training and testing data of the membrane structural parameter of 0.7789 and 0.7119, respectively, as shown in **Fig. 5.4e** and **Fig. 5.4f**. The coefficient of determination for the training and testing data of the power density is equal to 0.9959 and 0.9858, respectively, which again shows excellent predictive ability.

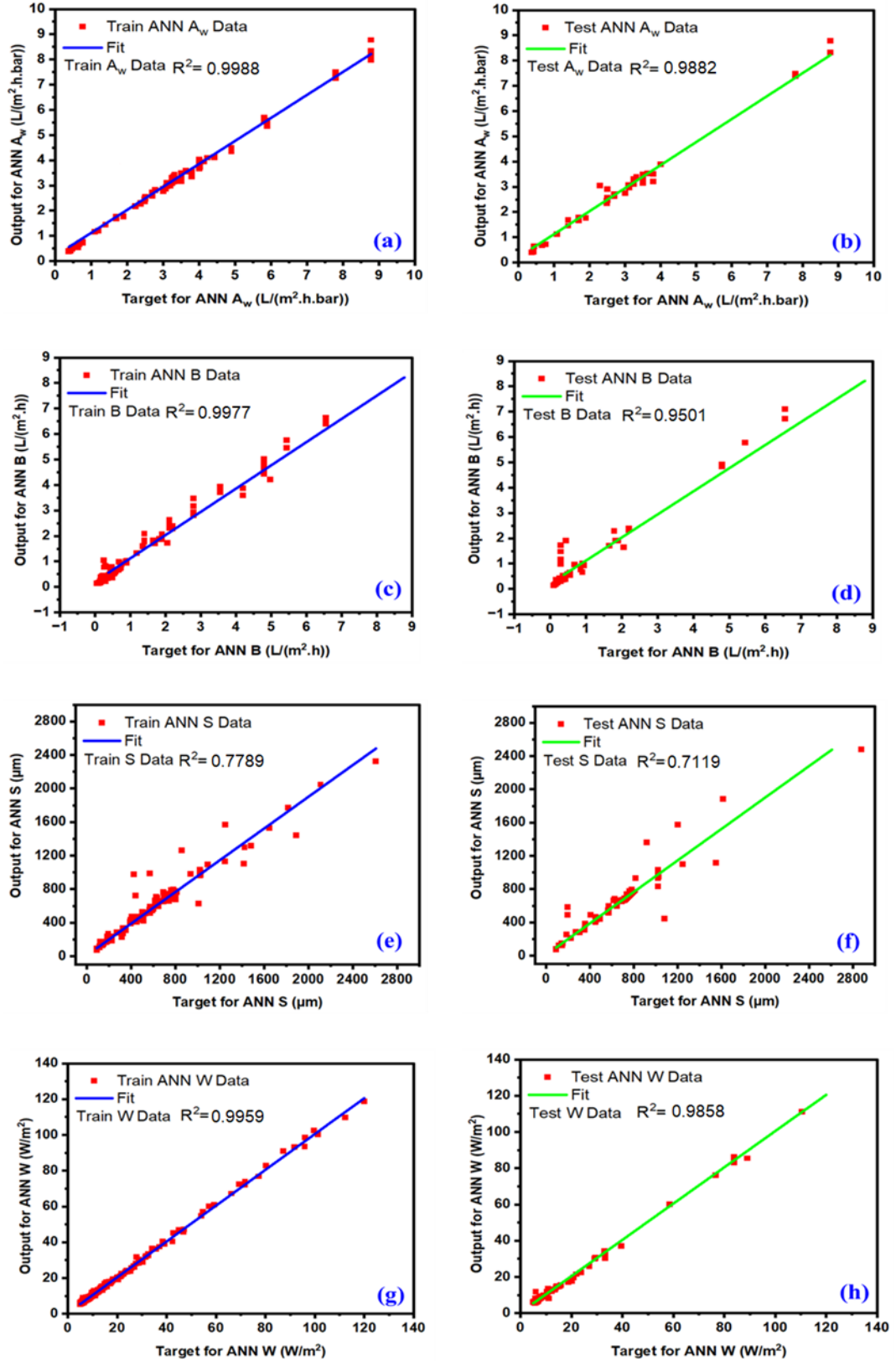


Fig. 5.4: The ANN R^2 predictive power for the prediction of the training and the testing data of (a) and (b) of the water permeability coefficient, (c) and (d) of the salt permeability coefficient, (e) and (f) for the membrane structural parameter, and (g) and (h) for the PRO power density, respectively.

The R^2 metric is insufficient to evaluate a machine learning model; therefore, the MSE and MAE metrics were also evaluated. The MSE results are based on the ANN model for the water permeability coefficient, salt permeability coefficient, structural parameter, and power density are 0.03 L/m².h.bar, 0.07 L/m².h, 8.78E-8 m, and 3.02 W/m², respectively. The results show good predictive power for the ANN testing data using the ANN model of the water and salt permeability coefficients but not for the membrane structural parameter (S) and the power density. Moreover, the MAE results were also evaluated for all the models. The MAE for the models were $A_w = 0.1$ L/m².h.bar, $B = 0.06$ L/m².h, structural parameter = 0.0002 m, and power density = 0.90 W/m². According to the results, the ANN model predicts the water permeability coefficient, salt permeability coefficient, and power density.

The ANN program for the prediction of S was also investigated using the AdamW optimizer instead of the Adam and a variable learning rate instead of a fixed learning rate [285]. AdamW (W stands for "Weight Decay") is a variant of the popular Adam optimizer that introduces weight decay during optimization, which helps with stabilizing training and reducing overfitting. The R^2 value after AdamW optimization increased slightly to 0.7199 compared to 0.7119 for Adam using 500 epochs. The learning rate for the S model has been changed to a variable learning rate coupled with AdamW, and the R^2 was improved to 0.86 and MSE to 4.07E-08 m.

5.4.2 Prediction of the membrane's intrinsic parameters and the pressure retarded osmosis power density with the Gradient Boosting models

In the Gradient Boosting model, the previous predictions are updated based on the residual values at every single iteration, which leads to optimizing the loss function [286]. The CatBoost, the XGBoost, and the Random Forest are evaluated in this study to predict the water permeability coefficient, the salt permeability coefficient, the structural parameter, and the power density. The main benefit of using the CatBoost model is that this machine learning algorithm improves its prediction power by learning from its mistakes through simulation. Moreover, it is considered an easy algorithm, stable, requires minimum computations, and has high accuracy [287]. Additionally, it does not require addressing the categorical variables. Generally, boosting models depend on gathering several weak models to design one model with high predictive power in a greedy manner. Accordingly, there is no need for a large dataset for boosting machine learning models to learn from [288]. 80% of the dataset was used for the training data, while the remaining data points were utilized to validate and test the Gradient Boosting models. The dataset used in the Gradient Tree Boosting models was the same as the one used for the ANN model. The CatBoost model was fitted to the training data, and the input features and target variables (A_w , B,

S, and W) were specified. The model iteratively builds an ensemble of decision trees based on the gradient-boosting algorithm. The loss function against the number of iterations plot is presented in **Figure S2 (Supplementary information S1)**. The R^2 and MSE are determined to present the predictive power of the CatBoost model for the various output parameters.

Fig. 5.5 displays the performance of the CatBoost model for predicting the water permeability coefficient, the salt permeability coefficient, the structural parameter, and the power density. The R^2 of the training data for the water permeability coefficient is 0.9785, while the R^2 for the testing data for the water permeability coefficient is 0.9012 (**Fig. 5.5a** and **Fig. 5.5b**). A less significant fitting of the CatBoost model for the training data is shown of the salt permeability coefficient with R^2 of 0.9248 (**Fig. 5.5c**). Moreover, the R^2 of the salt permeability coefficient for testing the CatBoost model is 0.8420 (**Fig. 5.5d**). Higher R^2 values can be noticed for both training data of the membrane structural parameter of 0.9740 and the R^2 of the testing data is 0.7903, as shown in **Fig. 5.5e** and **Fig. 5.5f**, respectively. A significant prediction through the CatBoost model resulted in a power density with R^2 of 0.9772 for the training data and 0.9522 for the testing data. Accordingly, the CatBoost model can predict the power density with high accuracy. Nevertheless, the MAE value of the membrane structural parameter (100.68) and the MSE and MAE values of the PRO power density (23.6 and 3.44, respectively) are high. Based on these results, the CatBoost model presents reasonable prediction behaviour for the water and salt permeability coefficients with the lower predictive power of the membrane structural parameter and the PRO power density. Further investigation through additional ML models should occur for better prediction power.

The predictive power of the membrane's intrinsic parameters regarding R^2 value is higher for the ANN model than the CatBoost model. For instance, the predictive power for the salt permeability coefficient based on the training data related to the ANN model is around 7.31% higher than the CatBoost model. A similar trend can be noticed for the PRO power density, as its predictive power is around 1.88% higher for the ANN model compared to the CatBoost model.

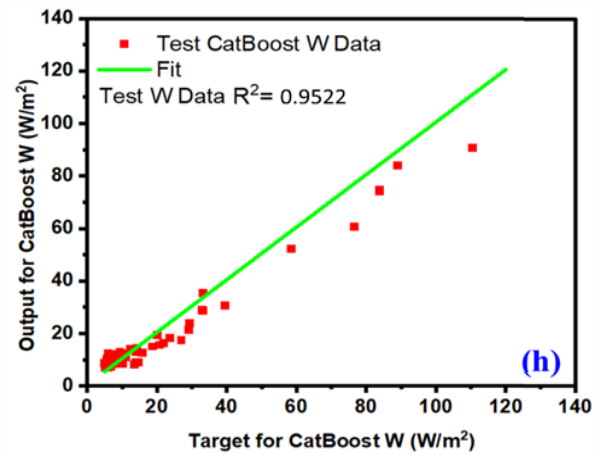
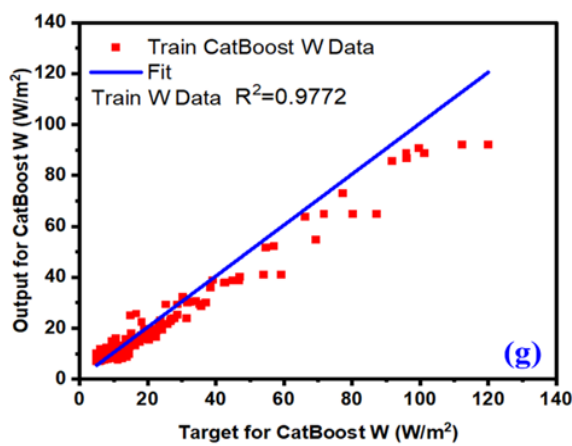
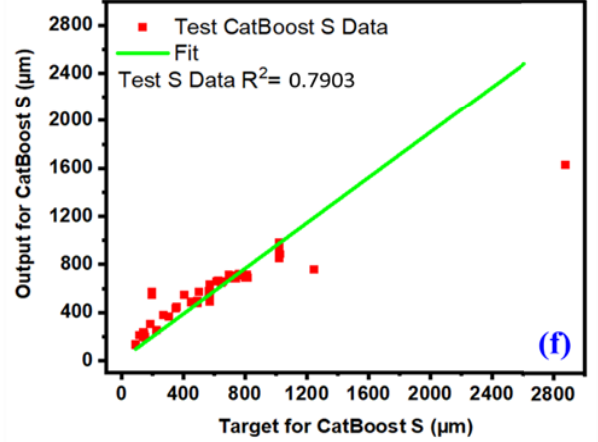
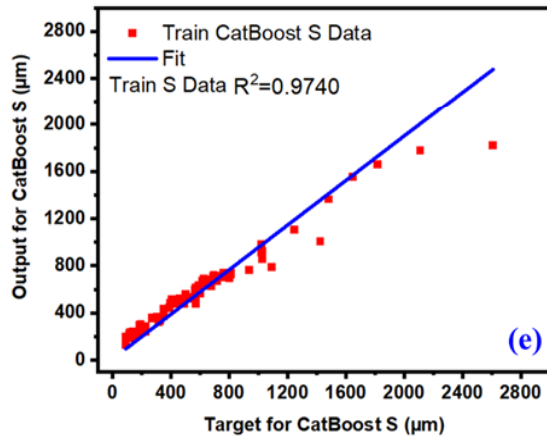
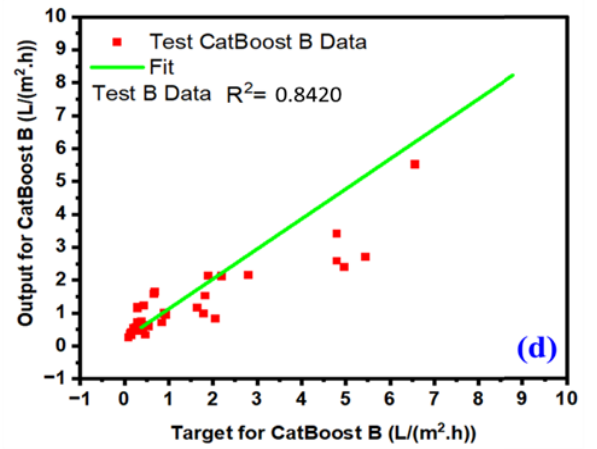
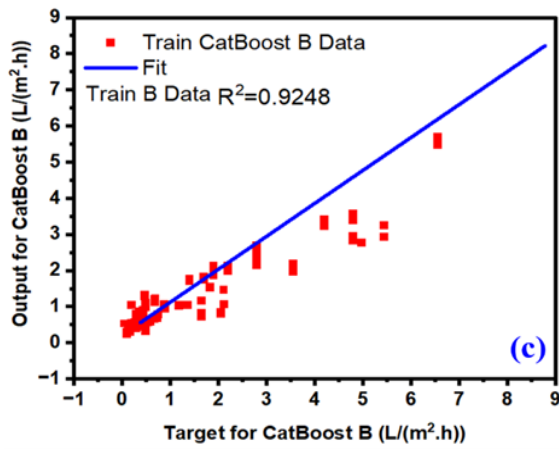
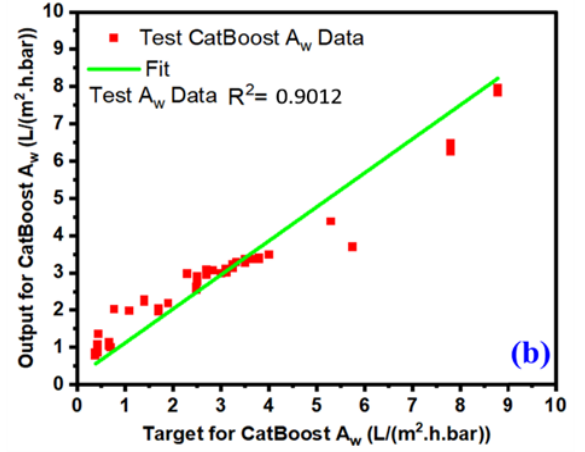
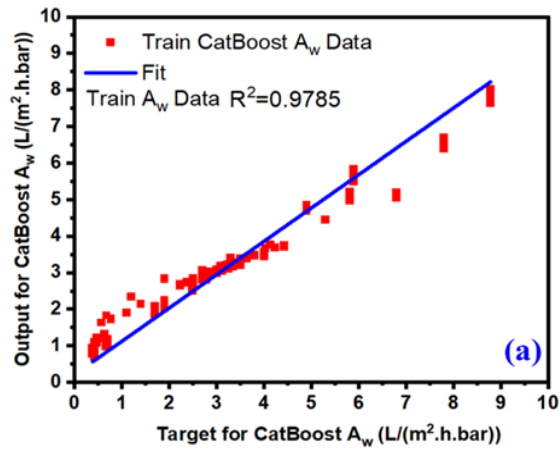


Fig. 5.5: The CatBoost R^2 predictive power for the prediction of the training and the testing data of (a) and (b) of the water permeability coefficient, (c) and (d) of the salt permeability coefficient, (e) and (f) for the membrane structural parameter, and (g) and (h) for the PRO power density, respectively.

The MSE results for the water permeability coefficient, the salt permeability coefficient, the structural parameter, and the power density were 0.31, 0.35, 3.43E-08, and 23.6, respectively.

In contrast, the MAE results for the water permeability coefficient, the salt permeability coefficient, the structural parameter, and the power density were 0.43, 0.41, 100.68, and 3.44, respectively. A similar trend was observed for the MSE results of the power density using the CatBoost to the ANN model, where the MSE values are high. Nevertheless, the R^2 , MSE, and MAE values of the water permeability and salt permeability coefficients present significant fitting of the CatBoost model to the testing data but not the membrane structural parameter and the PRO power density.

The Extreme Gradient Boosting model is also investigated to evaluate the membrane's intrinsic parameters and the PRO power density. XGBoost is an algorithm that relies on the boosted trees, and due to the learning, the boosting procedure is accelerated, which enhances the fitting behaviour of the data [289]. The XGBoost model is beneficial by pointing out the influence of the different input parameters on the membrane's intrinsic parameters and the PRO power density. The XGBoost model can benefit from its low-time processing compared to the ANN model. Additionally, it has other advantages, such as cross-validation and not highly suffering from overfitting [290]. For this model, the data was trained by 80% of the data, and the rest 20% was used for testing. The predictive power was assigned by determining the R^2 values. **Fig. 5.6** displays the performance of the XGBoost model for predicting the water permeability coefficient, the salt permeability coefficient, the structural parameter, and the power density. The R^2 of the training data for the water permeability is 0.9989, while the R^2 for the testing data for the water permeability coefficient is 0.9404 (**Fig. 5.6a** and **Fig. 5.6b**). The fitting of the XGBoost model for the training data shows the salt permeability coefficient with R^2 of 0.9978 (**Fig. 5.6c**). Furthermore, the R^2 of the salt permeability coefficient for testing the XGBoost model is 0.9845 (**Fig. 5.6d**). Similar R^2 values can be noticed for both training and testing data of the membrane structural parameter of 0.9926 and 0.8016, respectively, as shown in **Fig. 5.6e** and **Fig. 5.6f**. A significant prediction through the XGBoost model resulted in the power density with R^2 of 0.9953 for the training data and 0.9736 for the testing data. Accordingly, the XGBoost model can predict power density with high accuracy. The loss function against the number of iterations plot is presented in **Figure S3 (Supplementary information S1)**.

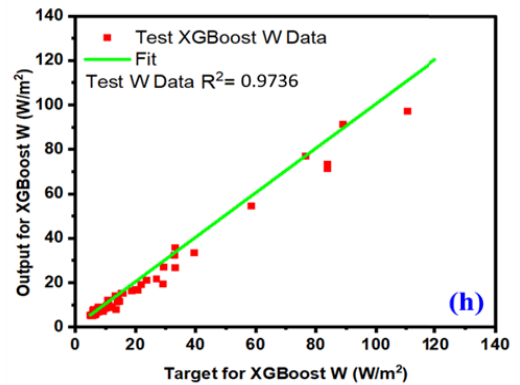
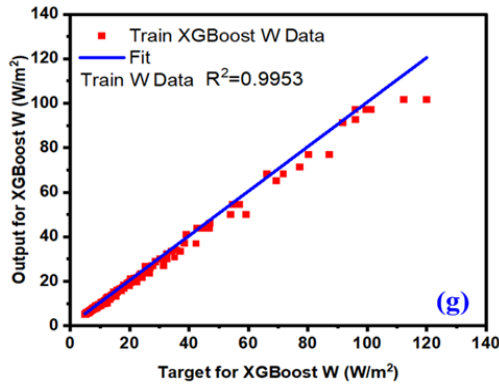
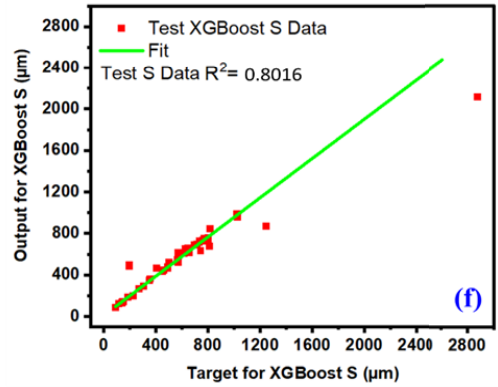
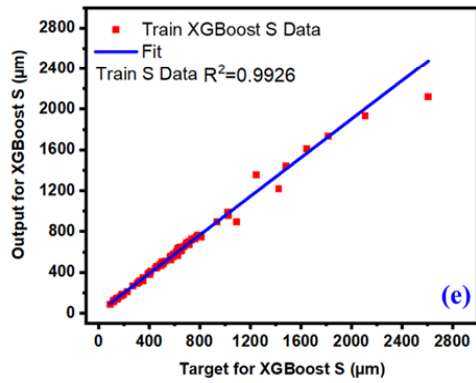
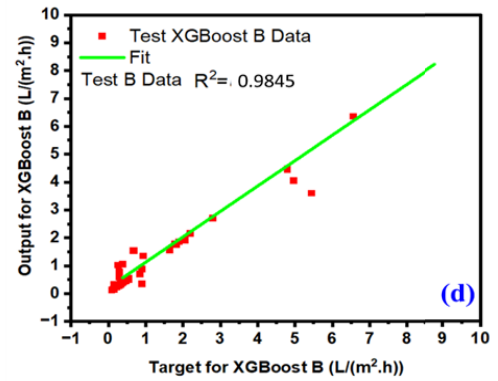
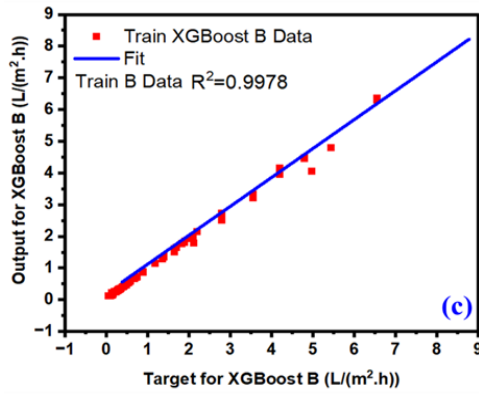
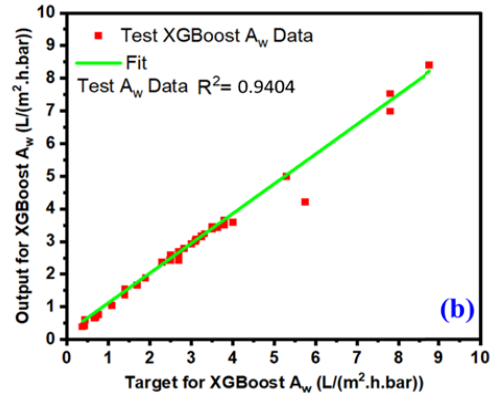
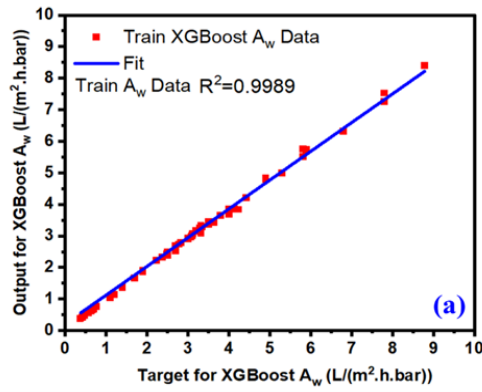


Fig. 5.6: The XGBoost R^2 predictive power for the prediction of the training and the testing data of (a) and (b) of the water permeability coefficient, (c) and (d) of the salt permeability coefficient, (e) and (f) for the membrane structural parameter, and (g) and (h) for the PRO power density, respectively.

The MSE results based on the XGBoost model for the water permeability coefficient, salt permeability coefficient, structural parameter, and power density are 0.18, 0.01, 5.49E-08, and 7.08, respectively. Furthermore, the MAE results based on the XGBoost model for the water permeability coefficient, salt permeability coefficient, structural parameter, and power density are 0.16, 0.05, 0.00016, and 1.80, respectively. The prediction power of the XGBoost model shows good behaviour for determining the membrane's intrinsic parameters.

The Random Forest algorithm was also considered in this study, where Random Forest work on multiple decision trees to evaluate single output, valid for the classification and the regression by using the bagging technique [291]. The output of the Random Forest model was one of the investigated parameters in the current study. The main advantages of the Random Forest model are the possibility of utilizing it for large datasets and its capability of estimating the missing data and averting overfitting, which gives the model better prediction values of the outputs [291]. When using the training data, the Random Forest regression model was trained by calling the ".fit()" function [292]. This process involves adjusting the model's internal settings to find the best patterns and relationships between the input and target variables. The "n_estimators" parameter was set to 100 in this case. It determines the number of decision trees the model will build before calculating the average prediction. Each decision tree is a separate model contributing to the final prediction; setting "n_estimators" to 100 means that the Random Forest model will construct 100 decision trees and then combine their predictions to obtain an average value. This averaging helps to enhance the accuracy and stability of the predictions made by the model. The higher the tree number, the better the model performance and the higher the prediction stability of the outputs.

Fig. 5.7 displays the Random Forest model's performance for predicting the water permeability coefficient, the salt permeability coefficient, the structural parameter, and the power density. The R^2 of the training data for the water permeability coefficient is 0.9958, which is 0.3% lower than its corresponding value resulting from the ANN model. The R^2 for the testing data for the water permeability coefficient is 0.9536 (**Fig. 5.7a** and **Fig. 5.7b**). The fitting of the Random Forest model for the training data is shown of the salt permeability coefficient with R^2 of 0.9953 (**Fig. 5.7c**). It can be noticed that the R^2 of the training data for the salt permeability coefficient by the Random Forest model is higher than its corresponding values by the CatBoost model of around 7.19%. Moreover, the R^2 of the salt permeability coefficient for testing the Random Forest model

is 0.9830 (**Fig. 5.7d**), which shows the great predictive power of the Random Forest for the prediction of B. The R^2 values for the training and testing data of the membrane structural parameter are 0.9945 and 0.9749, respectively, as shown in **Fig. 5.7e** and **Fig. 5.7f**. A significant prediction through the Random Forest model resulted in the power density with R^2 of 0.9792 for the training data and 0.9748 for the testing data (slightly less than the training data). One can notice that the Random Forest model presents significant prediction behaviour for the water permeability coefficient, the salt permeability coefficient, the structural parameter, and the power density, with R^2 higher than 0.95 value.

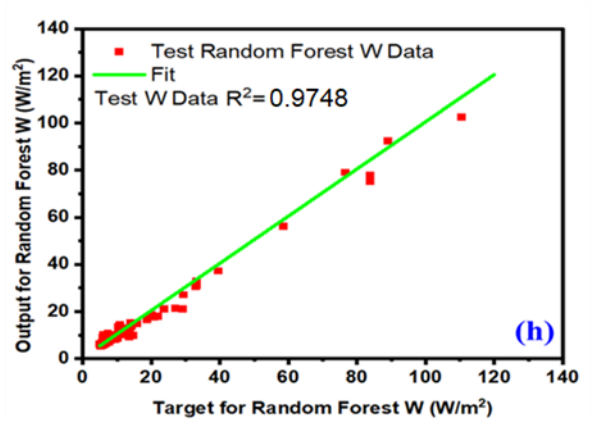
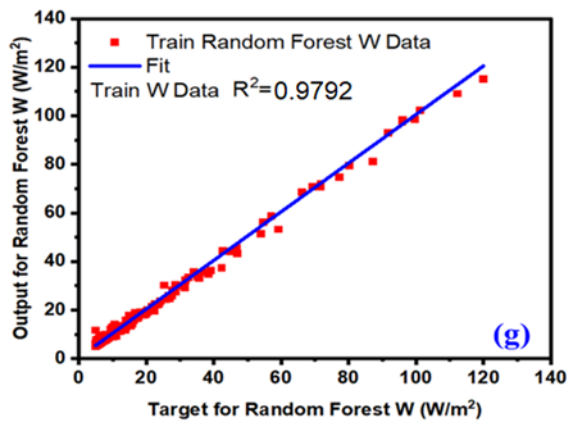
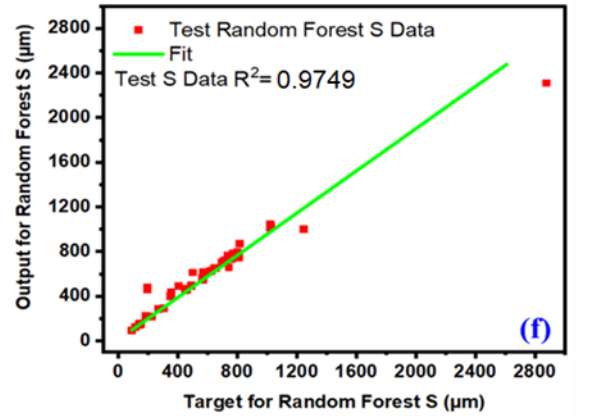
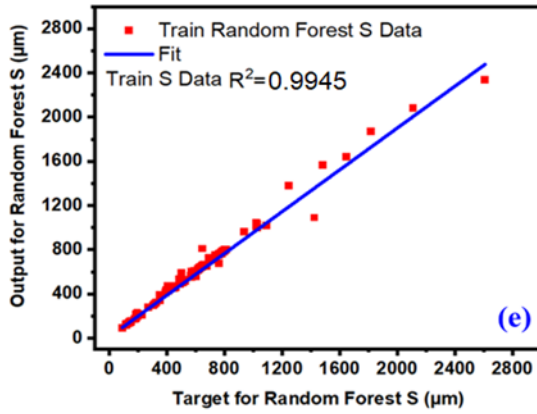
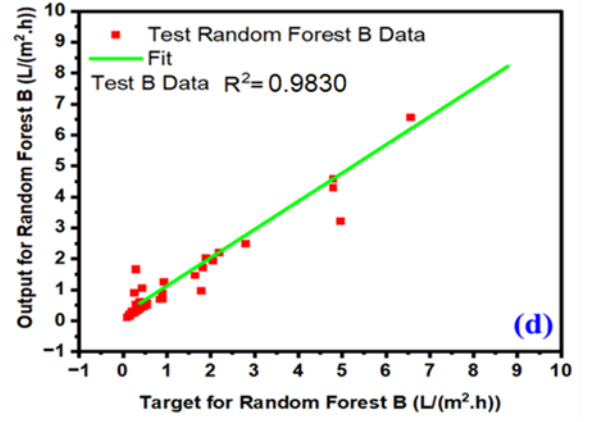
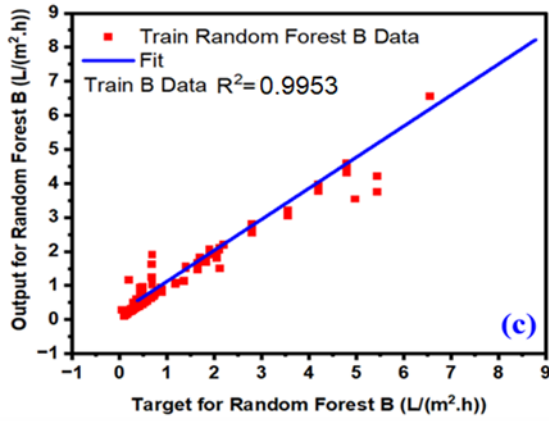
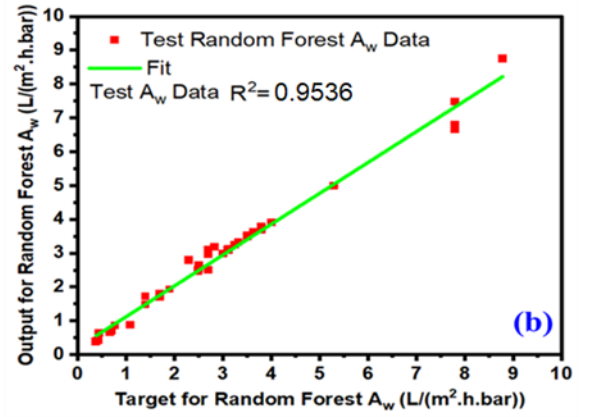
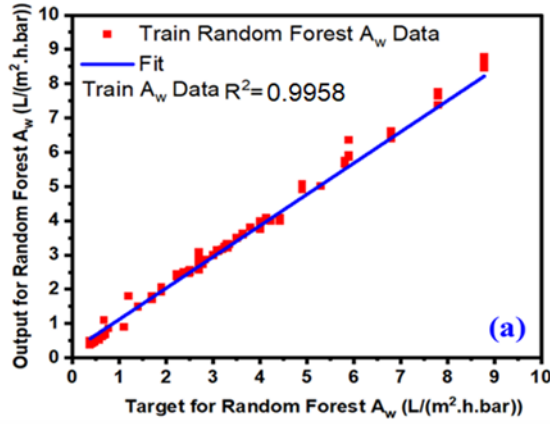


Fig. 5.7: The Random Forest R^2 predictive power for the prediction of the training and the testing data of (a) and (b) of the water permeability coefficient, (c) and (d) of the salt permeability coefficient, (e) and (f) for the membrane structural parameter, and (g) and (h) for the PRO power density, respectively.

The MSE results based on the Random Forest model for the water permeability coefficient, salt permeability coefficient, structural parameter, and power density are 0.15, 0.02, 7.1E-09, and 6.06, respectively. Furthermore, the MAE results based on the Random Forest model for the water permeability coefficient, salt permeability coefficient, structural parameter, and power density are 0.13, 0.05, 0.00028, and 1.09, respectively. The Random Forest model's prediction power shows good behaviour for determining the membrane's intrinsic parameters.

The R^2 of the training and the testing data of the ML algorithms evaluated in this study and the MSE and MAE results are summarised in **Table 5.4** and discussed more in the following subsection.

5.4.3 Comparison of the ML models

Four ML models were determined to predict the membrane's intrinsic parameters and the PRO power density, where the R^2 , the MSE, and the MAE values of testing data are summarized in **Table 5.4**. The higher the R^2 and the lower the MSE and the MAE values, the more significant the model's predictive power. The most significant model to predicate the water permeability coefficient is the ANN model. As seen in **Table 5.4**, the ANN model achieved the highest R^2 (0.98), the lowest MSE (0.3), and the lowest MAE (0.1). The situation is different for predicting the salt permeability coefficient, in which the Random Forest and the XGBoost models showed the two best predictive behaviours. The resulting MSE value is lower by the XGBoost model compared to the Random Forest model. Variations in trends are depicted when forecasting the structural parameter of the membrane. The XGBoost and the Random Forest models show the best prediction power; however, the R^2 is higher for the Random Forest, while the MSE is lower for the Random Forest model. Accordingly, the Random Forest model is preferable for predicting the membrane structural parameter. Moreover, the ANN model shows the lowest predictive power of the membrane structural parameter over the other three ML models. To summarize the results, the Random Forest model shows the best predictive power of the salt permeability coefficient and the membrane structural parameter. In contrast, the XGBoost model shows a significant predictive power of the membrane's intrinsic parameters and power density. Accordingly, the two models will be further discussed in the following subsections.

Table 5.4: The R^2 , MSE, MAE, execution time and size comparison of the ML algorithms.

Parameter	Metrics/ Training parameters	ANN	CatBoost	XGBoost	Random Forest
A_w (L/m².h.bar)	R^2	0.98	0.90	0.94	0.95
	MSE	0.03	0.31	0.18	0.15
	MAE	0.10	0.43	0.16	0.13
	Execution Time (seconds)	86.8	77.1	0.36	1.04
	Model Size (Megabytes)	4.36	44.7	0.01	1.39
B (L/m².h)	R^2	0.95	0.84	0.98	0.98
	MSE	0.07	0.35	0.01	0.02
	MAE	0.06	0.41	0.05	0.05
	Execution Time (seconds)	90.3	60.09	0.04	0.47
	Model Size (Megabytes)	4.38	45.90	0.07	1.39
S (m)	R^2	0.71	0.79	0.80	0.97
	MSE	8.78E-08	3.43E-08	5.49E-08	7.1E-09
	MAE	0.0002	100.68	0.00016	0.00028
	Execution Time (seconds)	148	55.3	0.04	0.41
	Model Size (Megabytes)	4.38	44.79	0.01	1.40
Power Density (W/m²)	R^2	0.98	0.95	0.97	0.97
	MSE	3.02	23.6	7.08	6.06
	MAE	0.90	3.44	1.80	1.09
	Execution Time (seconds)	85.5	56.1	0.10	0.55

Model Size (Megabytes)	4.38	45.8	0.01	1.39
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The execution times and mode sizes for all the programs were also compared. It should be noted that model training time, data manipulation and cleaning were not considered in execution time. Amongst all the programs, XGboost, followed by Random Forest, was the lightest and fastest (**Table 5.4**). CatBoost was the slowest due to many iterations (3000); however, for smaller iterations, CatBoost did not return any satisfactory results.

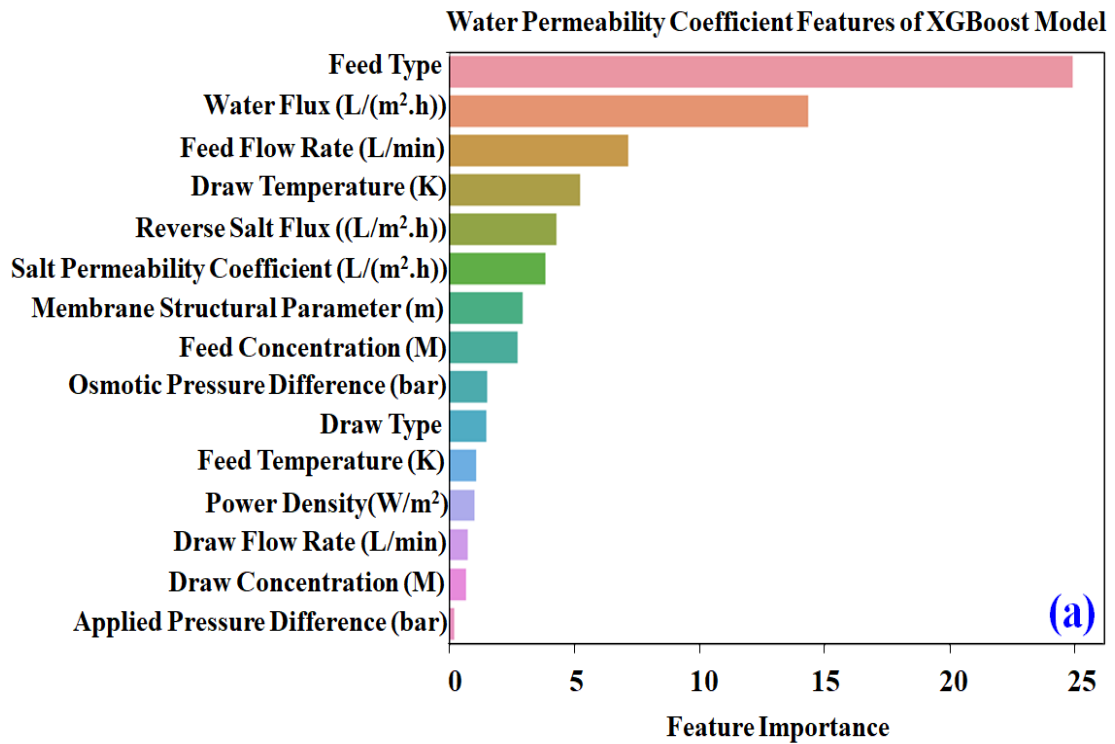
5.4.4 Features importance

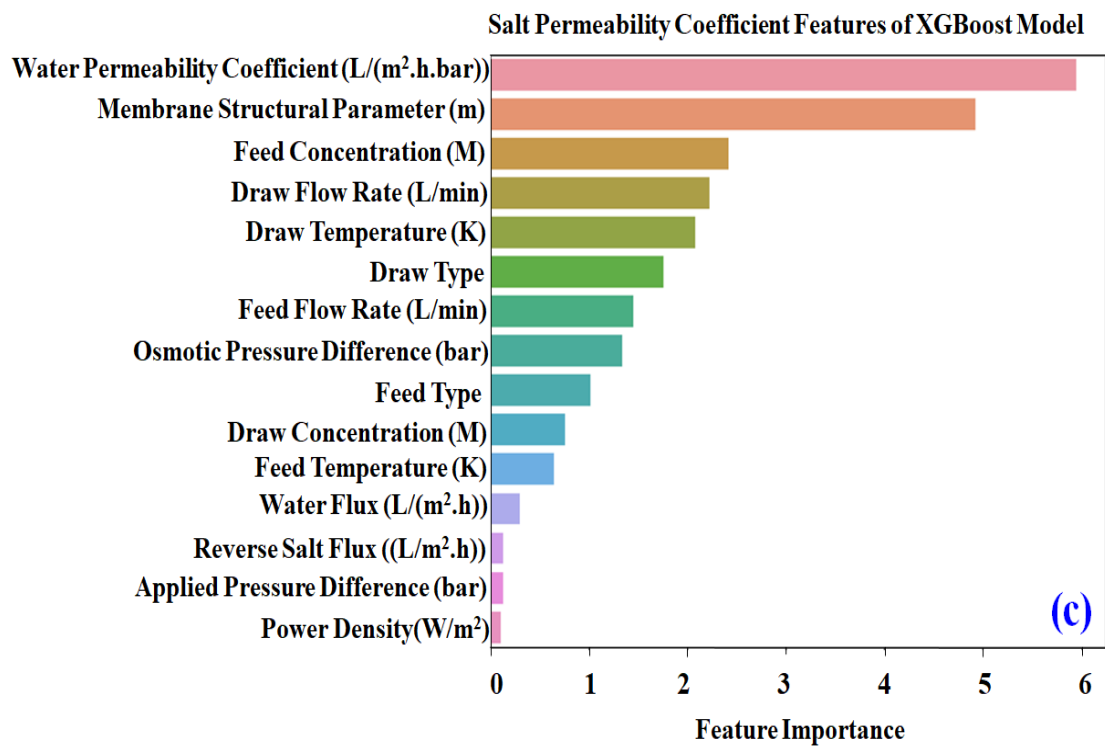
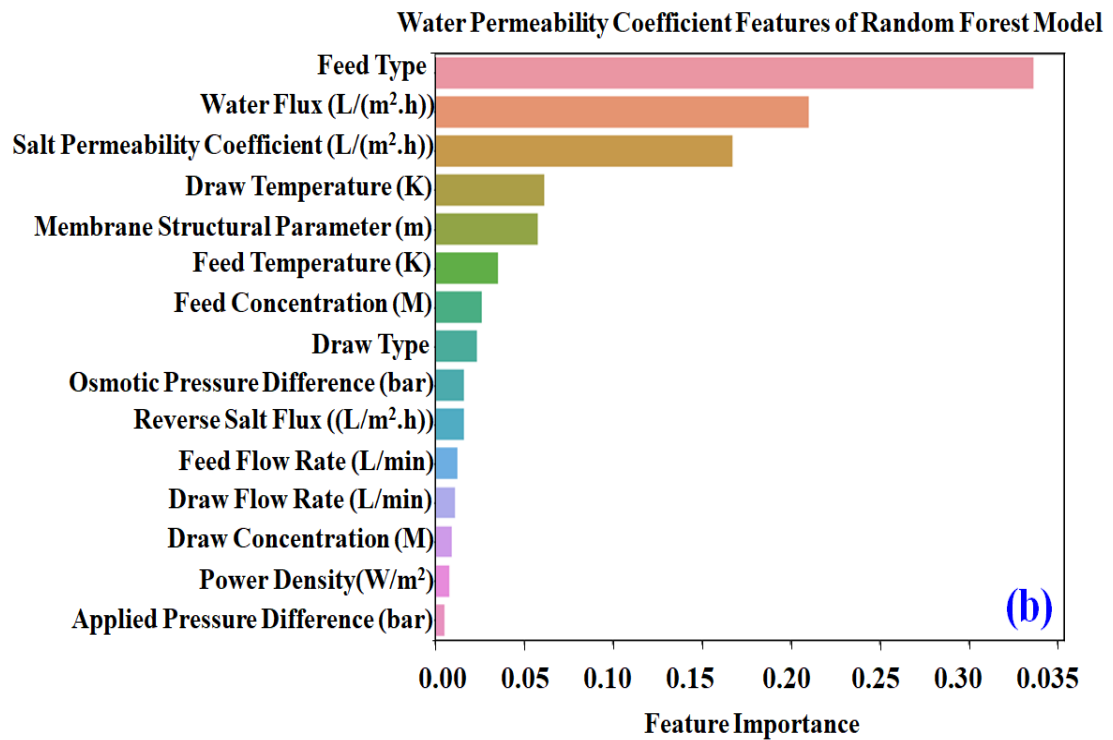
The Feature importance is a metric parameter that can be estimated in the tree-based algorithms to evaluate further the importance of the input parameters for modelling the outputs. Features with high scores impact the output more than features with low scores. The importance of the different PRO operating parameters can be evaluated with ML models to predict the membrane's intrinsic parameters and the PRO power density. Determining the feature importance and selecting the best features can enhance the predictive power of the model and its performance by including the most significant input parameters. Here, the feature importance is defined for the XGBoost and the Random Forest models only since these models exhibited the best predictive powers compared to the CatBoost and the ANN models. **Fig. 5.8** represents the XGBoost, and the Random Forest features the importance of the training data for (a) and (b) the water permeability coefficient, (c) and (d) the salt permeability coefficient, (e) and (f) the structural parameter, and (g) and (h) the PRO power density, respectively. The highest feature importance of the water permeability coefficient is feed type and equal to 25 for the XGBoost (**Fig. 5.8a**) and 0.035 for the Random Forest (**Fig. 5.8b**), followed by water flux, which is 15 for the XGBoost (**Fig. 5.8c**) and 0.20 for the Random Forest (**Fig. 5.8d**). This observation can reveal the high impact of the feed type and the water flux on the evaluation of the water permeability coefficient. Further, the lowest feature importance resulted in the applied pressure difference, which clarifies that this parameter has the least impact on the water permeability coefficient.

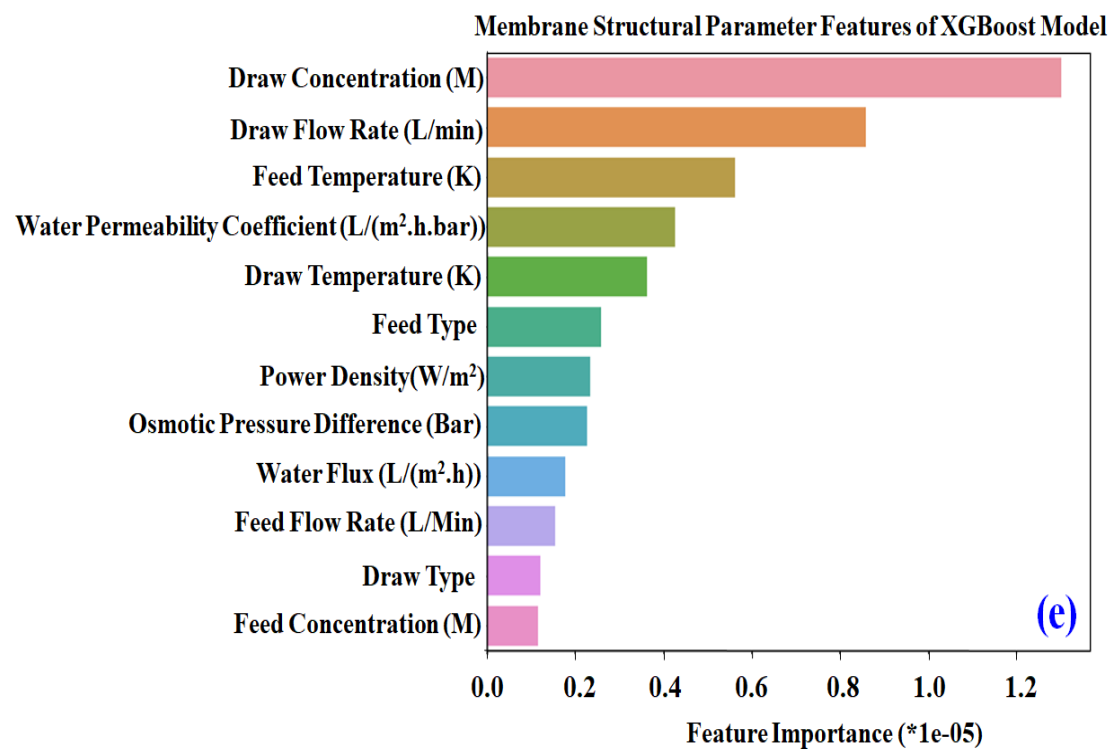
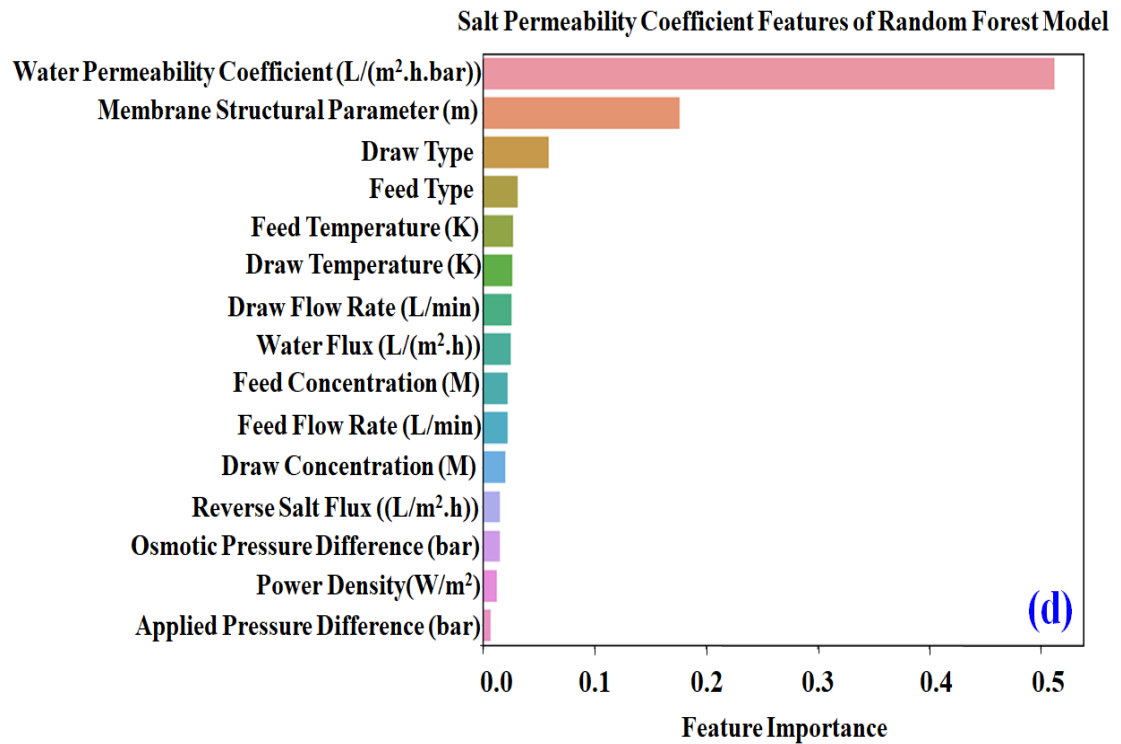
It can be noticed that the highest feature importance of the salt permeability coefficient is the water permeability coefficient; this can be related to the fact that the water permeability coefficient usually affects the water flux. In return, the water flux impacts the amount of water that permeates through the membrane, affecting the reverse salt flux and the salt permeability coefficient. For instance, Xiaoxiao et al. suggested a direct correlation between the permeability coefficients of the water and the salt for several thin film nanofiber composite membranes [293]. The lowest feature importance is for the power density and the applied pressure difference (**Fig. 5.8c** and **Fig. 5.8d**).

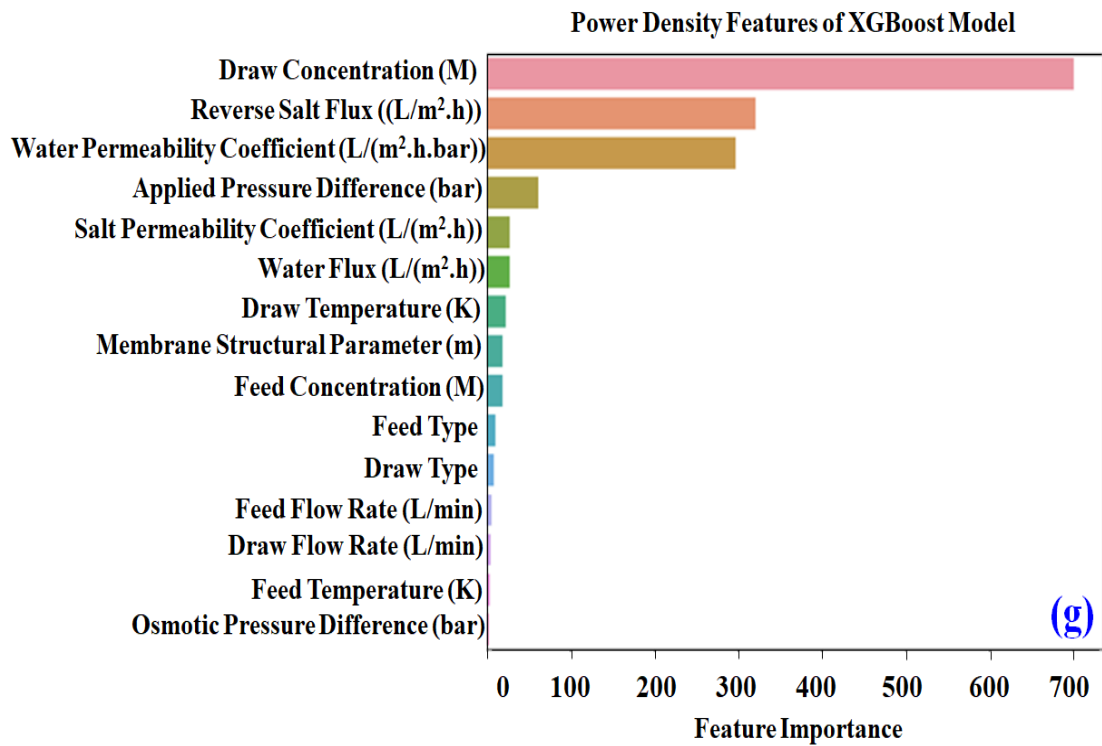
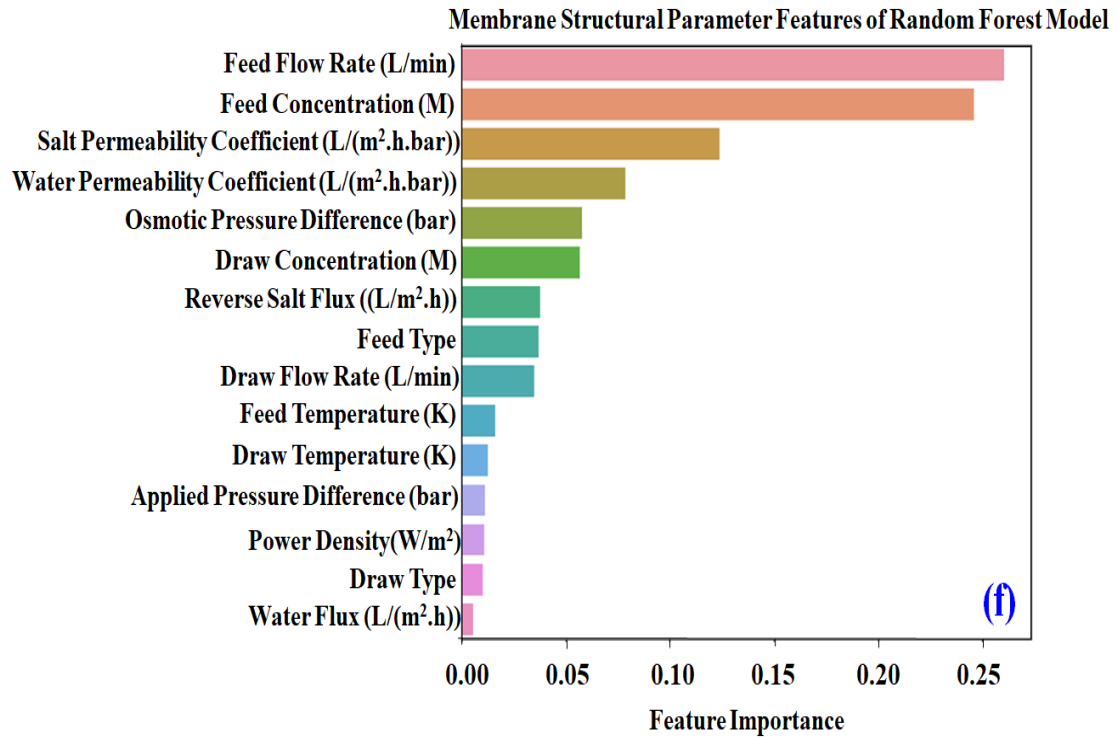
The situation is different regarding the membrane structural parameters of the XGBoost and Random Forest models. The XGBoost model shows the highest feature importance for the draw concentration (Fig. 5.8e). The salinity of the draw solution influences the diffusivity of the solution through the membrane. As the membrane structural parameter is governed by the equation of the solute diffusion resistivity (solute diffusion resistivity = membrane structural parameter/diffusion coefficient of the support layer) [294], then it is affected by the modification of the draw salinity, as presented in Fig. 5.8e. Interestingly different, the highest feature importance of the membrane structural parameter found by the Random Forest model is the feed flow rate (Fig. 5.8). The feed solution flow rate affects the water flux and the permeation rate. Accordingly, the feed flow rate also impacts the solute resistivity to diffusion and the membrane structural parameter [294].

Fig. 5.8g and Fig. 5.8h show that the draw concentration is the most significant parameter affecting the PRO power density because the salinity of the draw solution governs the variance in the osmotic pressure along the membrane, and the latter relates to the water flux [295]. Thus, the power density, in its turn, is directly impacted by the water flux, which explains the feature importance of the draw concentration on the PRO power density.









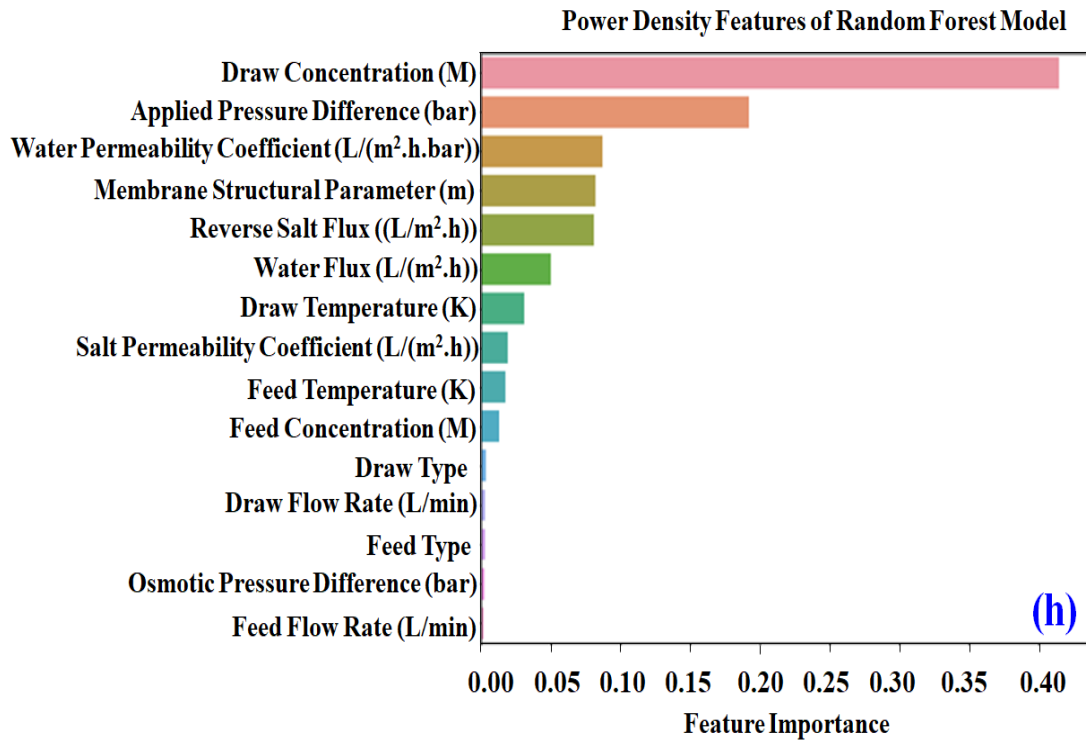


Fig. 5.8: (a) and (b): The feature importance of the water permeability coefficient of the XGBoost model, and the Random Forest model, respectively, (c) and (d): the feature importance of the salt permeability coefficient of the XGBoost model, and the Random Forest model, respectively, (e) and (f): the feature importance of the membrane structural parameter of the XGBoost model, and the Random Forest model, respectively, and (g) and (h): the feature importance of the PRO power density of the XGBoost model, and the Random Forest model, respectively.

5.4.5 New insights for power density modelling

The Random Forest regression is the optimal model to predict power density with high accuracy. The feature importance scores can provide new insights into unexpected relationships between the input and output parameters. As shown in **Fig. 5.8h**, the top six key features for power density predictions are the draw solution concentration, applied pressure difference, water permeability coefficient, membrane structural parameter, reverse salt flux and water flux. The influence of draw solution salinity and applied pressure difference is well-established in the PRO literature [296]. The impact of the water permeability coefficient on power density is also substantial and agrees with previous work done by Andrea Achilli, Tzahi Y Cath [297]. However, according to our current results, the draw solution concentration and applied pressure difference affect the power density more than the pure water permeability value. The reverse salt flux (a feature often neglected by analytical models) has a similar feature importance score as the membrane structural parameter, slightly less than the pure water permeability of the PRO membrane, and a surprisingly

higher feature importance score than the water flux of the PRO membrane. Membrane scientists often emphasize improving membrane water permeability and structural parameters, ignoring reverse salt diffusion's impact. The accumulation of draw solution on the membrane surface due to the reverse salt flux may also lead to membrane deformation [298], leading to different A_w , B and S values for the PRO membrane than predicted with RO tests in analytical models. Accordingly, an ideal draw solution in the PRO applications should have high osmotic pressure along with low reverse salt flux. As evident from the PRO dataset (e-component file, supplementary), most researchers have investigated NaCl draw solution, which has high reverse salt flux and can impact the output power density. Furthermore, the draw solution temperature has a higher feature score than the feed solution temperature. Brines discharged from desalination or wastewater plants usually have higher temperatures [299], and can be potentially utilized as a draw solution in the PRO system to optimize the power density in future applications.

5.4.6 Testing the models on new data

The PRO water flux is determined through the solution diffusion model in the literature. For further consideration, the machine learning models predicted the efficiency of the machine learning prediction power of the water permeability coefficient, the salt permeability coefficient, the membrane structural parameter, and the PRO power density. Then, the prediction results were compared to the experimental results in the literature for different lab-fabricated and commercial membranes. **Fig. 5.9** presents the percentage difference between the experimental data and the predicted data by the machine learning models of the membrane's intrinsic parameters and the power density. **Fig. 5.9** compares the ANN model, the XGBoost model, and the Random Forest model. The testing data here differs from the original dataset used for training the models. The highest percentage error of prediction A_w by the ANN, the XGBoost, and the Random Forest models is 4.01%, 5.09%, and 2.36%, respectively (**Fig. 5.9a**). Higher percentage error noticed for the prediction of B using the ANN, and the Random Forest model of maximum error 7.75% and 3.5%, respectively, compared to the XGBoost model of highest error 0.75% (**Fig. 5.9b**). The Random Forest model shows the best prediction of S compared to the other models with percentage error of less than 1.82% (**Fig. 5.9c**).

Overall, the agreement between the modelled water permeability coefficient, the salt permeability coefficient, the membrane structural parameter, and the predicted ones is high by the Random Forest model with a maximum percentage error of around 6.61%, compared to 6.86% and 15.4% when using the XGBoost model and the ANN mode, respectively. This emphasizes the reliability of the Random Forest model and its significant fitting with the additional testing data. On the other hand, the ANN model and the XGBoost model show better behaviour than the Random Forest model for predicting the PRO power density (**Fig. 5.9d**).

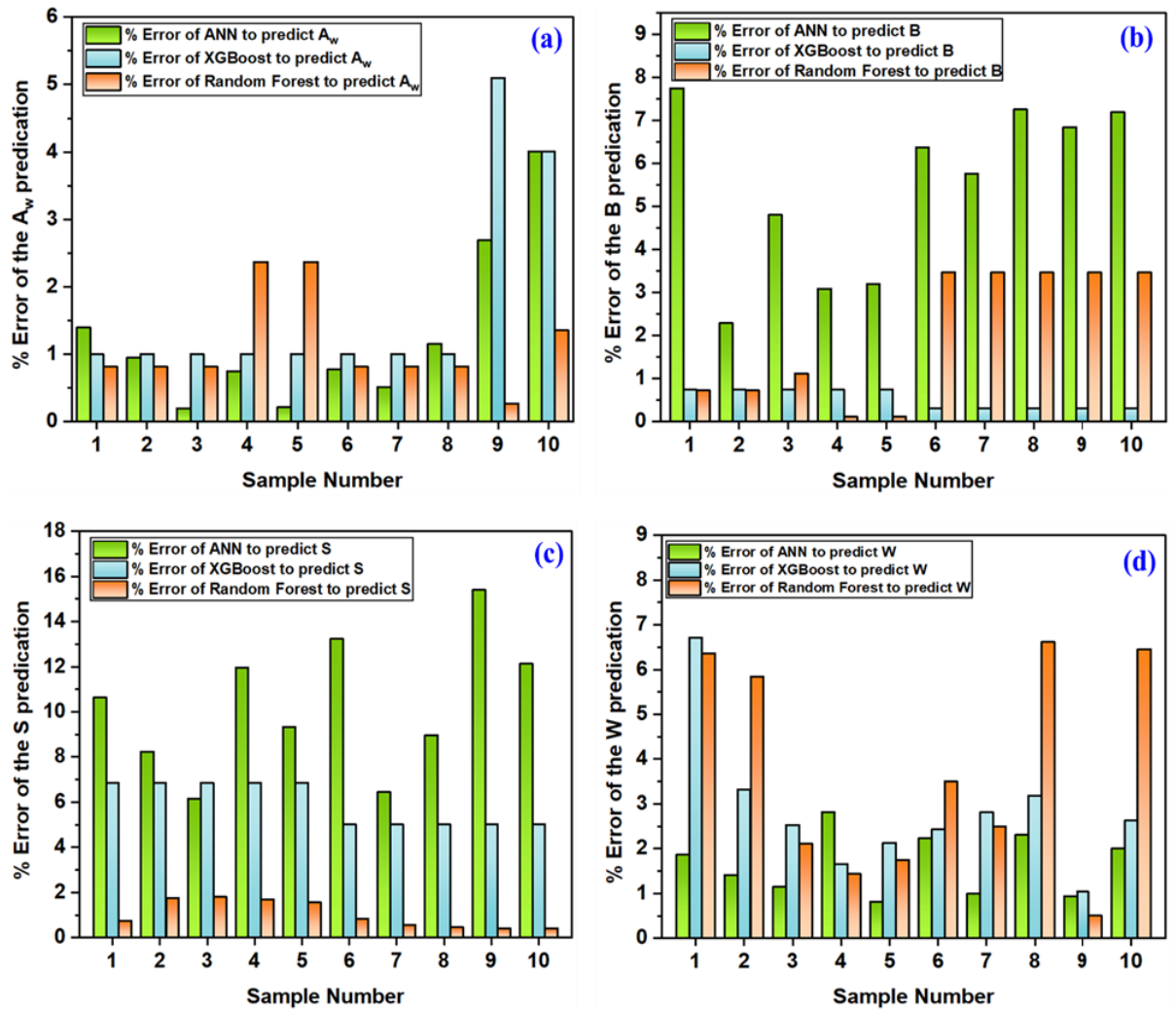


Fig. 5.9: The predictive power of the XGBoost and the Random Forest models for validation data of (a) the water permeability coefficient, (b) the salt permeability coefficient, (c) the membrane structural parameter, and (d) the power density.

5.5 Conclusion

While PRO experiments require a lot of infrastructure, modelling studies are abundant in the literature. However, few models have considered the impact of all input parameters on the power density. Thanks to machine learning algorithms, intrinsic membrane parameters can be predicted and checked if the power density is viable without doing any experiments. The characterization of the PRO membrane transport parameters and the PRO power density has been presented in the current study through a new technique. The prediction of the behaviour of the PRO system has been conducted through collected PRO experimental data with multiple physical and chemical operating conditions, such as the applied hydraulic pressure and the diverse types of PRO feed

solutions. Four machine learning models were performed to predict the membrane's intrinsic parameters and the PRO power density. The investigated ML models show a high predictive power of the outputs based on the PRO operating conditions. The XGBoost and Random Forest models revealed the best predictive power over the other models for predicting the membrane's intrinsic parameters and the PRO power density. The XGBoost and the Random Forest models achieved a significant R^2 value of 0.97 for the prediction of the power density. The user can predict the membrane's intrinsic parameters and the PRO power density with the membrane's characteristics and input operating conditions, which enhances the design of the PRO membranes with no requirement of performing PRO experiments. It should be mentioned that the more accurate the collected data, the more precise the predictive power of the ML models. Accordingly, the data collection should occur with high accuracy to guarantee the best prediction behaviour through the ML models. Moreover, certain machine learning studies may necessitate a larger volume of data collection and could be susceptible to inadequate or biased data, leading to erroneous outcomes. Future work should investigate machine learning algorithms for energy optimization and design optimization of pressure retarded osmosis.

Chapter Six: Multiple staging of pressure retarded osmosis: impact on the energy generation

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6.1 Objectives

This chapter is focusing on studying the impact of utilizing multi-stage pressure retarded osmosis on net energy generation. The primary goals of this chapter are:

- 1) To create models of single, dual, tertiary, and quaternary pressure retarded osmosis through Dymola software.
- 2) To evaluate the net energy consumed, the net energy generated, and the net specific energy generation through the different investigated models.
- 3) To investigate the variation of the membrane modules arrangement on the amount of the net specific energy generation of the PRO.
- 4) To determine the impact of the variation of the main operating conditions on the best PRO multi-stage system.

6.2 Introduction

In nonideal pressure retarded osmosis (PRO), the energy of mixing a salinity gradient source is partially converted to hydraulic energy [300, 301]. The draw solution gets diluted whilst the feed solution concentration intensifies after leaving the PRO unit. The simultaneous decrease and increase in the draw and feed solutions during the osmotically driven membrane systems will adversely impact the water flux and process efficiency [302]. For example, in a single PRO stage (SSPRO), only a part of the draw solution osmotic energy will be harvested due to the feed solution concentration increase caused by freshwater transport through the PRO membrane [29]. Increasing the salinity of the feed solution will compromise the osmotic driving power, and the permeation flux enters the turbine unit for energy generation. Therefore, a multistage PRO scenario was suggested to improve the PRO efficiency compared to the SSPRO [27, 29, 166]. The multistage PRO scenario uses a new feed solution in each stage to eliminate the effect of increased feed solution concentration in the previous stage on the osmotic driving force [170, 295]. In the single-stage PRO, the draw solution undergoes pressurization and is introduced into the PRO membrane for freshwater extraction from the feed solution (**Fig. 6.1a**). The pressurized flow divides into two segments after exiting the PRO membrane; the initial portion is directed to a pressure exchanger (PX) to pressurize the seawater feed whereas the second portion is routed to

turbine for power generation. In the dual PRO, the first stage resembles the single-stage PRO process, except that the pressurized draw solution from the first PRO module is directed to a second PRO module, where it merges with a new feed solution (**Fig. 6.1b**). A considerable freshwater permeation from the feed to the draw solution is expected in the second PRO stage due to the osmotic pressure gradient restoration across the membrane (**Fig. 6.1c**). After leaving the second PRO module, the entire seawater flow goes to a turbine system for power generation. This arrangement will facilitate harvesting the remaining draw solution osmotic energy in subsequent PRO stages. Due to the intense concentration polarisation at the feed side, the performance of the multistage PRO scenario becomes more efficient at high draw solution concentrations. Accordingly, using new feed water in each stage will alleviate the vestige of concentration polarization and the fouling phenomena on the membrane [170]. Besides, pumping a new feed solution in each stage will regenerate the osmotic driving power across the membrane and the water flux [27, 295].

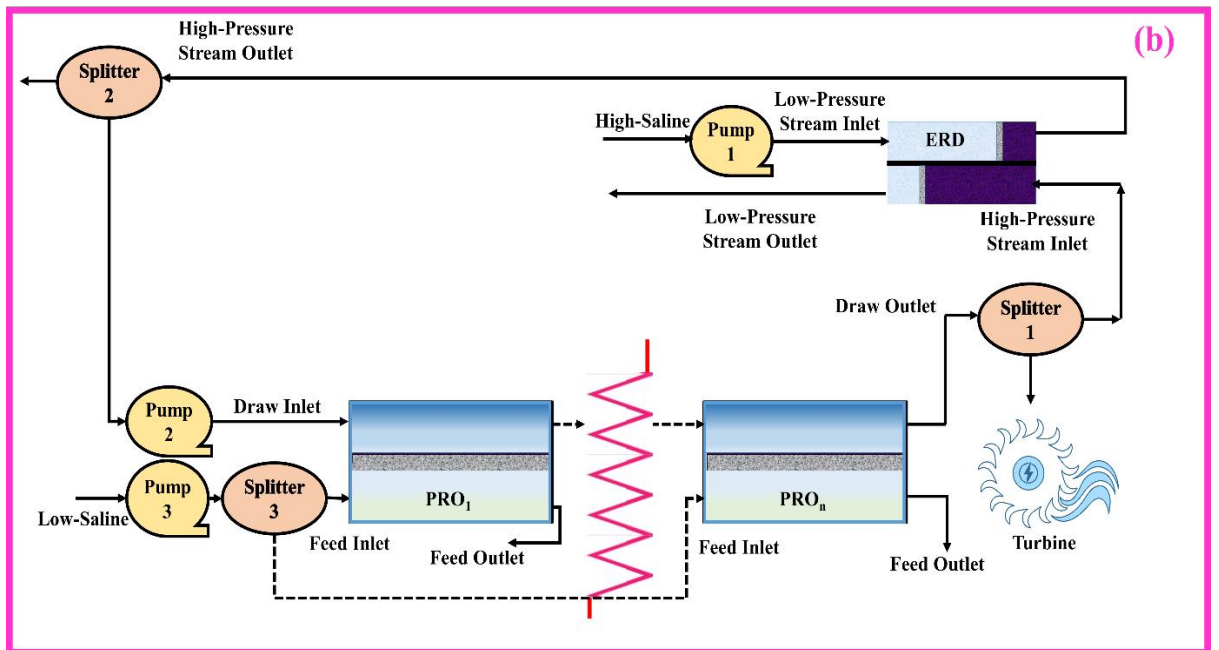
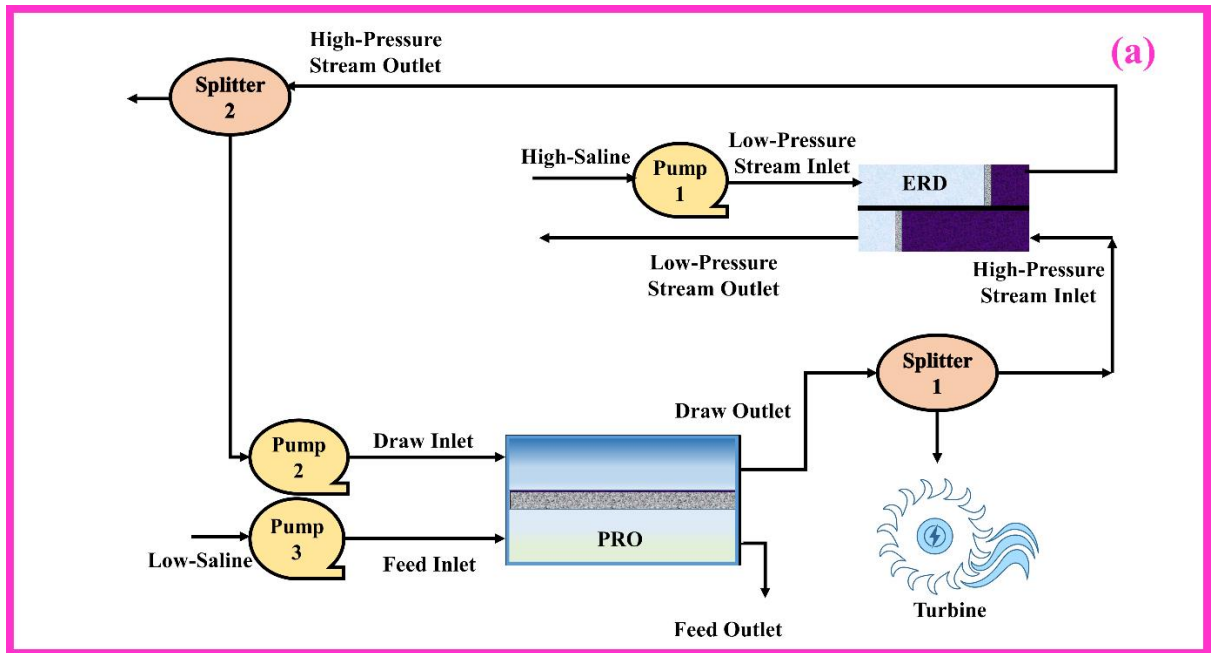
The dual-stage PRO (DSPRO) system is investigated broadly in the literature [29, 128, 131, 138, 154, 170, 211, 212, 214, 215, 294] due to the possibility of utilizing the DSPRO system with a variety of feed solution nature and applying different membrane types in each stage [154]. Altaee et al. [170] reported an 18% increase in energy generation and a 43% increase in the power density by a DSPRO compared to an SSPRO. Additionally, the authors noticed a reduction in the impact of concentration polarization when dealing with DSPRO. Unfortunately, these studies did not determine net energy generation [154, 170]. Another study implied that the specific energy of the DSPRO system was 8% higher than the corresponding one of the SSPRO system [211]. Nevertheless, the study did not investigate a higher number of PRO stages. In another study, four different designs of the DSPRO system were introduced for power generation [193]. The first design was similar to the SSPRO system, as the feed solution was fed from stage one to stage two. New feed and draw solutions were sent to the second stage in the second design. In the third design, a new feed solution was utilized in stage two, while the less concentrated draw solution leaving stage one was sent to stage two. The results revealed that the second design's power density was below the SSPRO system's power density. It has been suggested that the mean power density of the first and third designs was elevated at a higher dimensionless flow rate. Nevertheless, the power density is a good indicator of the performance of the PRO. Still, it is not the best factor to describe the net available energy of the PRO system [150]. The power density relates to the maximum power harvested per membrane unit area. Nevertheless, the net specific power is calculated as the variance between the energy output and the energy input. Using PRO requires pumping energy, whereas ignoring this fact would overestimate the efficiency of the PRO process. Also, utilizing multistage PRO with the exact amount of pumping energy compared to the single-stage is promising for generating higher net specific energy. A recent study [303]

reported an extremely high power density of around 90 W/m^2 ; however, the study did not consider the net available energy.

Madsen et al. [304] also reported the advantages of utilizing a dual-stage PRO system when coupled with a geothermal heat system for energy generation. Two configurations were suggested; the first used lower applied pressure for the draw solution of the second PRO stage, while the second configuration used the same applied pressure for the draw solution of both PRO stages. The generated energy increased to 46% when using the first dual-stage PRO configuration. A double energy generation was noticed when using the second dual-stage PRO configuration compared to a single PRO system. However, optimization was not considered in the study to determine the maximum energy generated through the different PRO systems.

Sarp et al. [167] examined the impact of the variation of the feed solution pressure of a multistage PRO system on the process performance. Four PRO stages were designed in series with fresh feed solutions for each PRO stage. The optimum power recovery was obtained by varying the feed solution's hydraulic pressure in each stage of the PRO, where the draw solution was a hypersaline solution of up to 300 g/L . Even though the study optimized feed solution hydraulic pressure, the evaluation of the net energy generation was not included. A multistage PRO design was investigated in one research [305], where hydro-turbines were included in each stage for energy production. Single, dual, and three PRO stages were studied. The results conducted higher net specific energy generation for the three PRO stages, followed by the DSPRO and the SSPRO. The driving force represented by the salinity gradient among the osmotic pressure and the hydraulic pressure was elevated in the three PRO stages than in dual or single PRO stages. Bharadwaj and co-workers optimized energy recovery through a multistage PRO system [306]. The authors reported that the multistage PRO system could collect higher energy than the single PRO. The highest energy recovered occurred when using one membrane module, followed by three membrane modules in DSPRO. The results reported that the enhancement of the energy recovery was reduced when the number of stages was increased to more than three PRO stages. Multiple PRO stages were added in series in another study [245], where a new feed solution was added in each stage, and the draw solution was sent from one stage to another. This system configuration was compared to a single PRO stage with multiple modules, where the final outlet draw solution was partially circulated to the initial draw solution. The outcomes reported that the variation of the proportion of the feed outlet flow rate to the draw inlet flow rate did not influence the specific energy of the multistage PRO system. In contrast, the variation in the flow ratio affected the specific energy of the single-stage PRO process. A 10.71% increase in the generated specific energy was reported when using the multistage PRO system over the single-stage PRO process.

To date, the advantage of utilizing a multistage PRO system for maximizing net energy generation is not reported. As mentioned earlier, some studies did not determine the evaluation of net energy generation [167, 214], other studies only compared SS PRO to DS PRO [29, 170, 193], and some studies did not consider the variation of the multistage PRO system parameters for the maximum energy generation [304, 305]. The pumping energy consumed in the multistage PRO should not be ignored. Increasing the number of PRO stages could boost the total energy generation and the total energy consumed by the pumps, signifying the importance of investigating the multistage PRO system by evaluating the net-specific energy generation, where the total energy used is considered. The influence of salinity gradient resources on energy generation should be examined. Besides the PRO stage configuration, the operating conditions, such as the feed and draw flow rates and the applied pressure on the draw side, of the single and multistage PRO are critical in maximizing the net energy generation and process performance. The study assessed the net specific energy generation (NSEG) of the multistage PRO compared to a single-stage PRO. The PRO membranes in the single, dual, ternary, and quaternary PRO stages (SS PRO, DS PRO, TS PRO, and QS PRO, respectively) were four, arranged in the configurations illustrated in **Table 6.1**. For instance, the TS PRO scenario has three designs for stage configurations (**Table 6.1**). TS PRO [1,1,2] represents three PRO stages, where one membrane module is in the first and the second stage, while two membrane modules are used in the third stage. The NSEG of the best PRO stage configuration will be evaluated for several salinity gradient resources. The research questions are i) What is the effect of PRO multistaging on power generation, and ii) What is the net energy generation by the single and multistage PRO scenarios? The study hypothesized that the NSEG of multistage PRO designs (**Table 6.1**) is the variation between the energy generation by the hydro turbine and pump energy consumption, assuming that the feed and draw solution flow rates are equal, thus the pretreatment energy. The study also hypothesized the potential for custom-designing the PRO membrane to withstand elevated feed pressures, given the absence of any existing commercial PRO membrane. According to the authors' knowledge, there is no study yet in the literature that has investigated the net-specific energy generation of a multistage PRO scenario with different module arrangements and various salinity gradients by studying the operating parameters' variation on the best multistage PRO model.



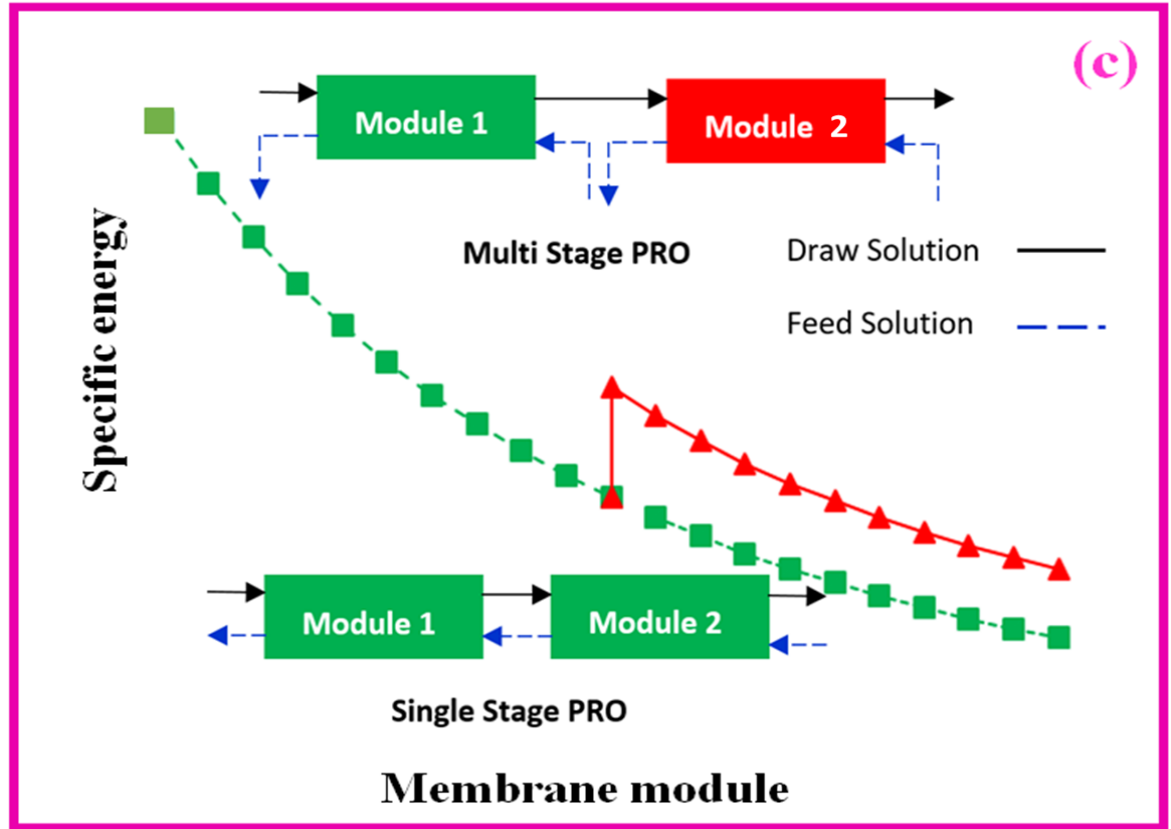


Fig. 6.1: (a) Single-stage PRO (SSPRO) for energy generation, (b) multistage PRO for energy generation, where PRO_1 represents the first PRO stage, and PRO_n represents the last PRO stage, and (c) the specific energy of the Dead sea-wastewater salinity gradients of Dual-stage PRO (DSPRO) design with the membrane module.

6.3 Methodology

The four PRO designs with the possible membrane modules' configurations are shown in **Table 6.1**. It's worth noting that the SSPRO and the QSPRO have one arrangement only, as the SSPRO has four membrane modules in one stage, while the QSPRO has a single membrane module for each of its four stages. The suggested model of SSPRO and multistage PRO scenarios, including the PRO unit/s, pumps, turbines, splitters, and energy recovery device (ERD), are presented in **Fig. 6.1**. The mathematical models for the pump, splitter, turbine, and energy recovery device were separately built and designed by Dymola software and discussed in detail in our previous study [295]. The pumps' efficiency is 80%, and the ERD efficiency is 96%. The PRO system model was built and validated using the Modelica language through Dymola software, where more details about it are included in our previous study [295]. The PRO system has been modelled and simulated through Dymola, and a brief explanation is introduced next.

Table 6.1: The membrane module arrangement in the various stages of the multistage PRO scenario.

PRO stages	Abbreviation	Membrane modules in stage one	Membrane modules in stage two	Membrane modules in stage three	Membrane modules in stage four
SSPRO	SSPRO	4	0	0	0
DSPRO	DSPRO [3,1]	3	1	0	0
	DSPRO [1,3]	1	3	0	0
	DSPRO [2,2]	2	2	0	0
TSPRO	TSPRO [2,1,1]	2	1	1	0
	TSPRO [1,2,1]	1	2	1	0
	TSPRO [1,1,2]	1	1	2	0
QSPRO	QSPRO	1	1	1	1

6.3.1 The Mathematical model of the PRO

A radial plug flow model is selected to define the flow of the PRO unit in this study. The feed solution moves in the radial direction, whereas the draw solution moves in the axial direction. A hollow fibre (HF) membrane is the used module. The mathematical approach for the HF membrane module is described in reference [216], where more details can be found. The solution-diffusion model represents the feed and draws solutions flow among the membrane. The internal and external concentration polarization effects are determined in the PRO mathematical model [216]. The reverse salt flux (J_s) and the pressure drop in both the radial and the axial directions are also included in the model. The mass transfer coefficient for the feed solution (k_F) and for the draw solution (k_D) are considered through the model [216, 295]. The following equation can find the PRO water flux (J_w).

$$J_w = A_w \left(\frac{\left(\frac{nRTC_{Di} \left(1 + \frac{Q_{Di}}{Q_{Do}} \right)}{2} \right) \exp\left(\frac{-J_w}{k_D}\right) - \left(\frac{nRTC_{Fi} \left(1 + \frac{Q_{Fi}}{Q_{Fo}} \right)}{2} \right) \exp\left(J_w \left(K + \frac{1}{k_F} \right)\right)}{1 + \frac{B}{J_w} \left(\exp\left(J_w \left(K + \frac{1}{k_F} \right)\right) - \exp\left(\frac{-J_w}{k_D}\right) \right)} - \Delta P \right) \quad (6.1)$$

where A_w is for the water permeability coefficient, n is for the number of the ions in the salt solution, R is for the universal gas constant, T is for the temperature, C_{Di} , and C_{Fi} are for the initial salinity of the draw solution and the feed solution, respectively, Q_{Di} , Q_{Do} , Q_{Fi} , and Q_{Fo} are for the initial and outlet flow rates of the draw and feed solutions, respectively, B is for the salt permeability coefficient, K is the solute resistivity in the membrane support layer, k_F is the mass transfer on the feed side, and ΔP is for the applied pressure difference of the draw and the feed

solutions. In this study, the draw solution pressure was equal to the average osmotic pressure difference across the membrane, $\Delta P = \Delta \pi / 2$, to maximize the power density [11].

The overall mass balance for the draw and the feed solutions is given below:

$$Q_{Fo} = Q_{Fi} - (J_w * A_m) \quad (6.2)$$

$$Q_{Do} = Q_{Di} + (J_w * A_m) \quad (6.3)$$

where A_m is the membrane surface area of the PRO membrane. The solute mass balances for the feed and the draw solutions are given below:

$$Q_{Fo} C_{Fo} = Q_{Fi} C_{Fi} - (J_w * A_m) \quad (6.4)$$

$$Q_{Do} C_{Do} = Q_{Di} C_{Di} + (J_w * A_m) \quad (6.5)$$

Simulation results of a single PRO membrane module using the suggested model are included in **Appendix**.

The power density (W) is calculated from the membrane flux multiplied (J_w) by the hydraulic pressure difference across the PRO membrane (ΔP):

$$W = J_w \Delta P \quad (6.6)$$

The permeation rate (Q_p) is determined for a single PRO system as follows.

$$Q_p = J_w * A_m \quad (6.7)$$

where A_m is the area of a single PRO membrane in m^2 .

The significance of the internal concentrative concentration polarization (ICCP) with mass transfer on the feed side on the system behaviour is also included and explained through the following expression [216].

$$ICCP = \exp \left(J_w \left(K + \frac{1}{k_F} \right) \right) \quad (6.8)$$

The water flux of each PRO stage ($J_{wn,avg}$) in the multistage PRO scenarios is determined as the average value of the water flux of each membrane module in that stage, as follows.

$$J_{wn,avg} = \frac{\sum_{j=1}^m J_{wj}}{m} \quad (6.9)$$

where J_{wj} is the water flux in the j membrane module, m is the number of the membrane modules in each PRO stage of the multistage PRO scenarios, and n is the number of the PRO stages.

The power density of each PRO stage ($W_{n,avg}$) in the multistage PRO scenarios is determined as the average value of the power density of each membrane module in that stage, as follows.

$$W_{n,avg} = \frac{\sum_{j=1}^m W_j}{m} \quad (6.10)$$

where W_j is the power density in the j membrane module, m is the number of the membrane modules in each PRO stage of the multistage PRO scenarios, and n is the number of the PRO stages.

The internal concentrative concentration polarization, including mass transfer on the feed side, is determined for each membrane module in each PRO stage in the multistage PRO scenarios. After that, the average internal concentrative concentration polarization ($ICCP_{n,avg}$) in each PRO stage (n) of the multistage PRO scenarios is calculated as follows.

$$ICCP_{n,avg} = \frac{\sum_{j=1}^m ICCP_j}{m} \quad (6.11)$$

where $ICCP_j$ is the average internal concentrative concentration polarization in the j membrane module in each PRO stage of the multistage PRO scenarios.

The permeation rate of each PRO stage (Q_{pn}) in the multistage PRO scenarios is calculated as the summation of the permeation rate in each membrane module in that stage, as follows.

$$Q_{pn} = \sum_{j=1}^m Q_{pj} \quad (6.12)$$

where Q_{pj} is the permeation rate in the j membrane module. This study used Hagen-Poiseuille and Ergun equations to determine the pressure drop in the feed and the draw side of the PRO module. More information about the pressure drop models is found in the literature [8]. Generally, the pressure drop in the PRO module was insignificant, which agrees with the findings [8].

The model used in this study is based on the performance of a commercial Toyobo PRO module instead of a laboratory-made membrane. The water permeability of commercial PRO membrane is about (1×10^{-7} m/bar.s), slightly lower than FO membranes such as Aquaporin and Porifera, affecting the power generation by the module.

Furthermore, experimental data validated the PRO model for a Toyobo HF module utilizing Dymola. The experiments were conducted in the Water and Energy Nexus Laboratory, Indian Institute of Technology Guwahati. The effective length of the membrane module is 0.78 m, and 63 m^2 is the membrane area. The agreement between the modelled and experimental water flux was high, with an error of no more than 15% [295]. The evaluated membrane parameters are 3.6×10^{-4} m/bar.h for the water permeability coefficient, 6.2×10^{-9} for the salt permeability coefficient, and 880 μm for the membrane structural parameter. Moreover, the model has been validated by another experimental data for the Toyoboo hollow fiber membrane module of 70.5 m^2 area, with tap water as the feed solution and 1 M NaCl draw solution [176]. The hydraulic pressure on the draw side ranged between 5 and 30 bar, while the pressure on the feed side ranged between 3 and 7 bar. The feed and draw solutions' flow rates were set between 0.48 to 0.72 m^3/h . The agreement between the modeling and experimental results is shown in **Fig. 6.2**, where no more than 14% error was found.

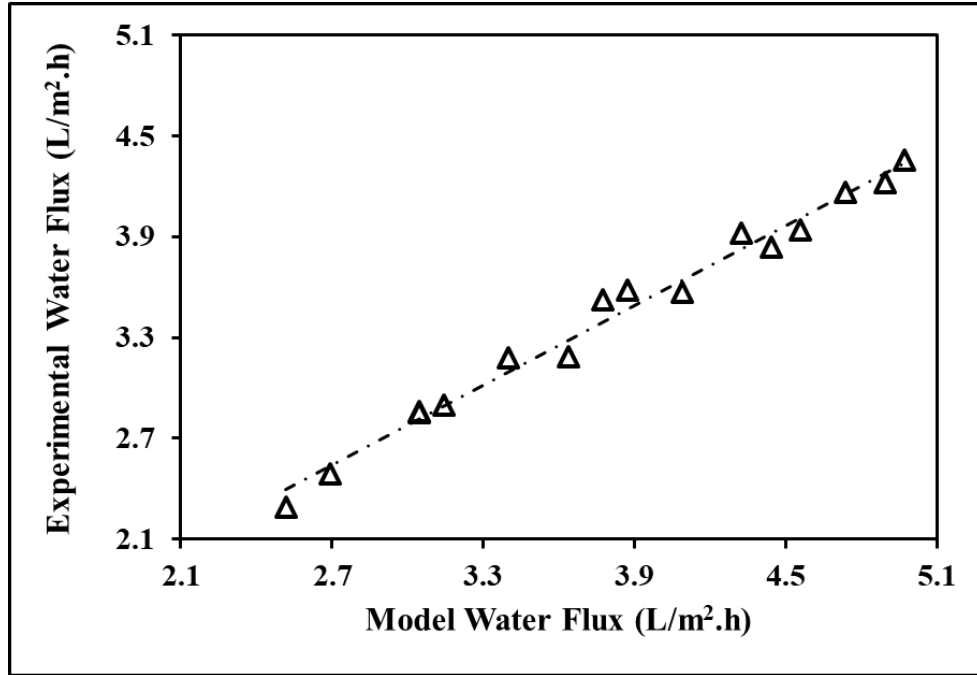


Fig. 6.2: The model water flux versus the experimental water flux of the PRO model.

6.3.2 The multistage PRO system design

In membrane processes driven by osmosis, the osmotic driving force undergoes attenuation through the module due to the dilution of the draw solution and the increase in the intensity of the feed solution concentration. Increased feed solution concentration results from freshwater transport to the draw solution, compromising the process efficiency. Previous studies demonstrated the effectiveness of multistaging the PRO to reduce the influence of the rise in the feed solution concentration on energy generation [29]. Unlike the SSPRO process, a new feed solution is fed for each stage of the multistage PRO system. Combining the initial draw solution with a new feed solution will partially restore the osmotic gradient through the PRO membrane, leading to a higher water flux (**Fig. 6.1a**).

The SSPRO scenario for energy generation is shown in **Fig. 6.1a**. A part of the less concentrated draw stream leaving the PRO unit is sent to the ERD. The energy of the less concentrated draw solution is extracted through the ERD when the pressurized high-saline is used as the low-pressure feed stream for the ERD. Then, the high-pressure stream leaving the ERD is fed to the PRO system to represent the inlet draw solution. The low-saline stream is pressurized through a pump (Pump 2) and utilized as the feed solution of the PRO unit. The other portion of the diluted draw stream and a limited portion ($< 0.5\%$) of the high-pressure stream-out from the ERD are sent to turbines for energy generation. The flow layout of the multistage PRO for energy generation is shown in **Fig. 6.1b**. PRO_1 represents the first PRO stage, while PRO_n represents the last PRO

stage. PRO_n would be PRO_2 for DSPRO, PRO_3 for TSPRO, and PRO_4 for QSPRO. A similar flow path is noticed for the multistage PRO scenario compared to the single PRO scenario.

Fig. 6.1c shows the significance of utilizing a DSPRO scenario compared to a SSPRO scenario of producing higher specific energy. Adding fresh feed solution to the second stage in the DSPRO causes a sudden increase in the specific energy compared to the SSPRO of the same number of membrane modules, highlighting the advantage of considering multistage PRO designs for the specific energy rise.

Nevertheless, the multistage PRO consists of more than one PRO stage. Additionally, pump 3 is used to pressurize the low-saline feed stream, and then splitter 3 is responsible for dividing the stream equally into the PRO stages. This proposed design of the multistage PRO scenario is utilized to fix equal flow rates of the draw inlet stream sending to the first PRO stage and the low-saline stream (**Fig. 6.1**).

The multistage PRO would have two, three, or four stages in this study. The multistage PRO scenario is designed to send the less concentrated draw solution from the previous stage to present the inlet draw solution of the following PRO stage. Furthermore, the feed solution is freshly supplied at each PRO stage (**Fig. 6.1b**) to regenerate the osmotic power gradient among the PRO membrane. At the last PRO stage (PRO_n), the diluted draw solution will be divided and sent to a turbine and an ERD. The diluted draw stream will exchange energy with a pressurized high-saline solution in the ERD. After that, more than 99% of the pressurized stream leaving the ERD will present the draw solution inlet to the first PRO stage, while the rest will be sent to another turbine to gather the unused left energy.

The design of the multistage PRO of sending the entire less concentrated draw stream to the next stage is preferable to enhance the water flux in the following PRO stage. Altaee and Hilal [154] reported that utilizing such a design for DSPRO increased the power density by 17.4% compared to splitting the diluted draw stream and sending a portion to the next stage, sending the rest to an ERD. Additionally, the authors noticed a reduction in the specific energy consumption while utilizing the discussed DSPRO design. Recharging the feed solution for each PRO stage in the multistage PRO causes a boost in the permeation rate and, consequently, the dilution in the draw side [245].

6.3.3 The design operating conditions

The power density and net specific energy generation of the SSPRO and the multistage PRO scenarios were investigated through the use of Dead Sea water of 292.20 g/L and RO Brine of 70.13 g/L as the high-saline and low-saline solutions (**Fig. 6.1**). It is noteworthy that Dead Sea has been suggested in many studies as the draw solution in the PRO system because of its high osmotic pressure and relevance to combine with myriad feed solutions such as combined with

wastewater, seawater, or even RO brine [29, 145]. The draw solution of PRO stage one is the high-pressure outlet stream from the ERD (**Fig. 6.1b**). Each PRO stage uses a fresh feed solution. The pressure on the draw solution is 90 bar, while the feed solution pressure is 1 bar. The draw and feed solutions' total inlet flow rate (Q_{tot}) is fixed at 2 m³/h for the SSPRO and the multistage PRO designs. For instance, in the SSPRO, the draw inlet flow rate and the feed inlet flow rate are equal (1 m³/h each). In contrast, for DSPRO, the draw inlet flow rate is equal to 1 m³/h, which is equivalent to the summation of the feed inlet flow rate to the first and the second PRO stages, where the feed inlet flow rate of each stage is 0.5 m³/h. The solution's temperature is assumed to be room temperature (298 K). The net energy generation (NSEG) (kWh/m³) is the difference between the energy generated in the turbine and the energy consumed for pumping the draw and feed solution. NSEG is calculated and compared for each PRO scenario.

$$NSEG = \frac{1}{Q_{tot}} * (\sum_1^{TN} E_{Turbine} - \sum_1^{PN} E_{Pump}) \quad (6.13)$$

where $E_{Turbine}$ and E_{Pump} are the energy generated through the turbines in kW and energy consumed through pumping in kW, TN is the number of turbines in the PRO scenario, and PN is the pumps' number in the PRO scenario. $E_{Turbine}$ is the energy out and is equal to the permeate flow in the PRO module multiplied by the hydraulic pressure of the draw solution. The energy consumed by the pumps, E_{Pump} , presents the input energy required for feed and draw solution pumping into the PRO system, and it is equal to the feed or the draw solution flow rate multiplied by the feed pressure. Besides, the pump efficiency was assumed to be 0.8 in this study. The pump head loss was accounted for in the model and calculated as the difference between pressure out and pressure in. Then, the power consumed was calculated as = (inlet flowrate*head loss)/efficiency.

Fixing the total feed and the draw solution initial flow rates is critical for major comprehension of the advantage of the PRO system with the highest NSEG. Moreover, the total water flux and the total power density of the multistage PRO scenarios are defined as follows.

$$J_{wtot} = \sum_{i=1}^{i=n} J_{wi} \quad (6.14)$$

$$W_{tot} = \sum_{i=1}^{i=n} W_i \quad (6.15)$$

J_{wi} is the water flux in stage i of the multistage PRO scenario, and W_i is the power density resulting in stage i.

It should be noted that The SSPRO and multistage PRO costs are not significantly different since they use the same number of PRO elements. There may be a slight cost difference between SSPRO and multistage PRO pressure vessels; however, it will not significantly impact overall costs since pressure vessels typically last the plant's lifetime.

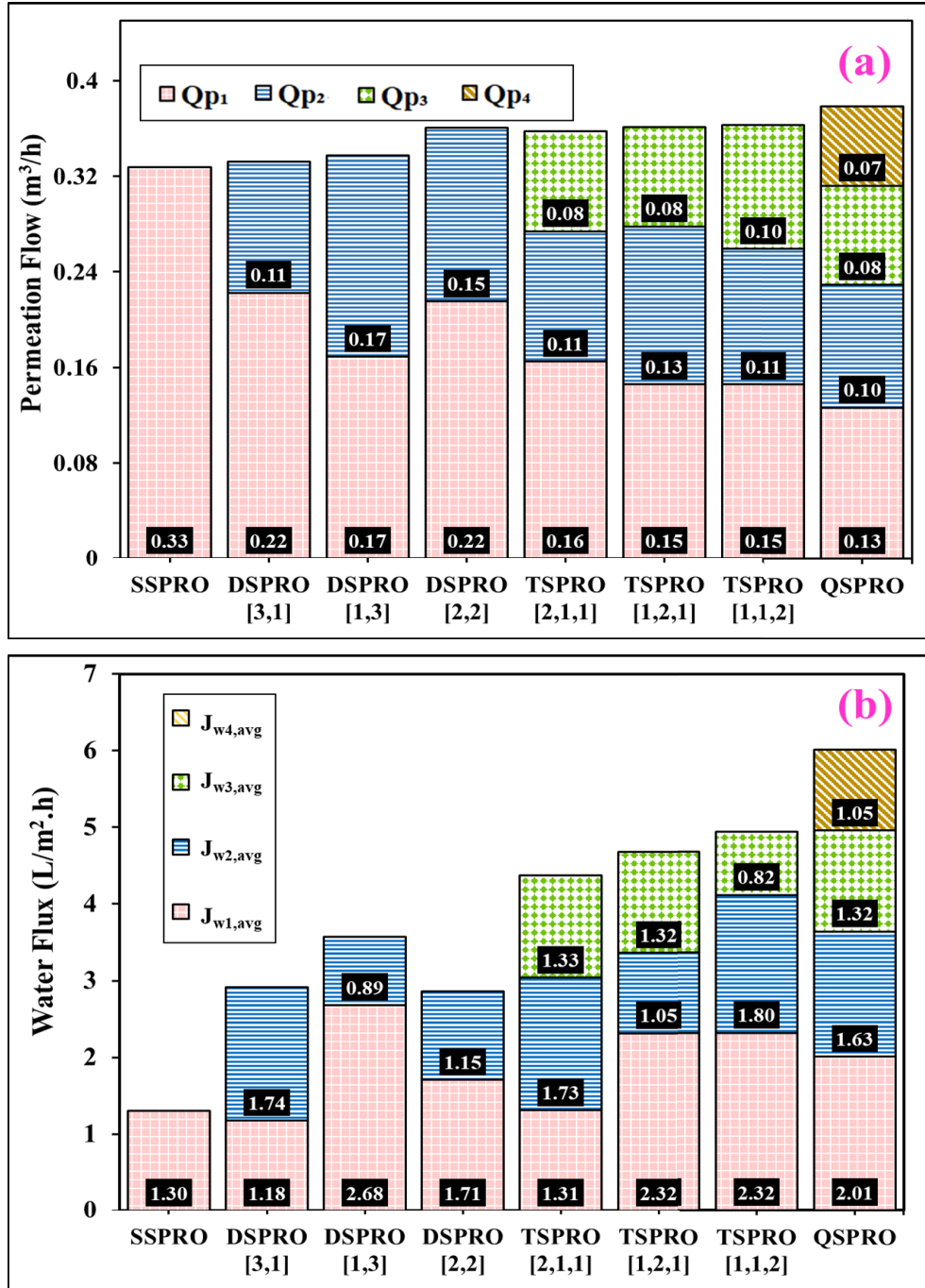
6.4 Results and discussion

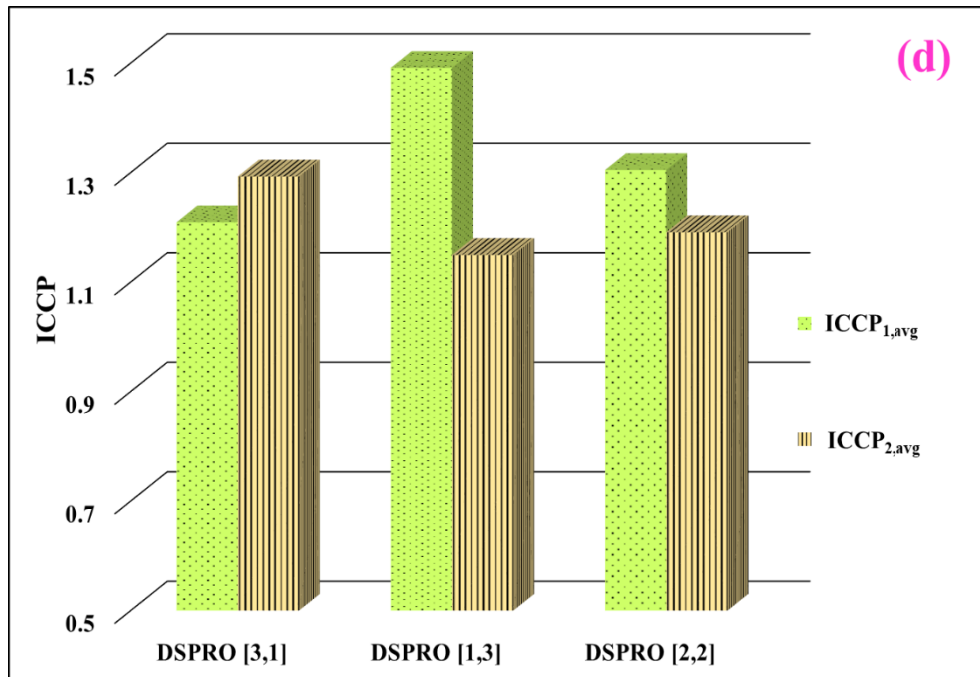
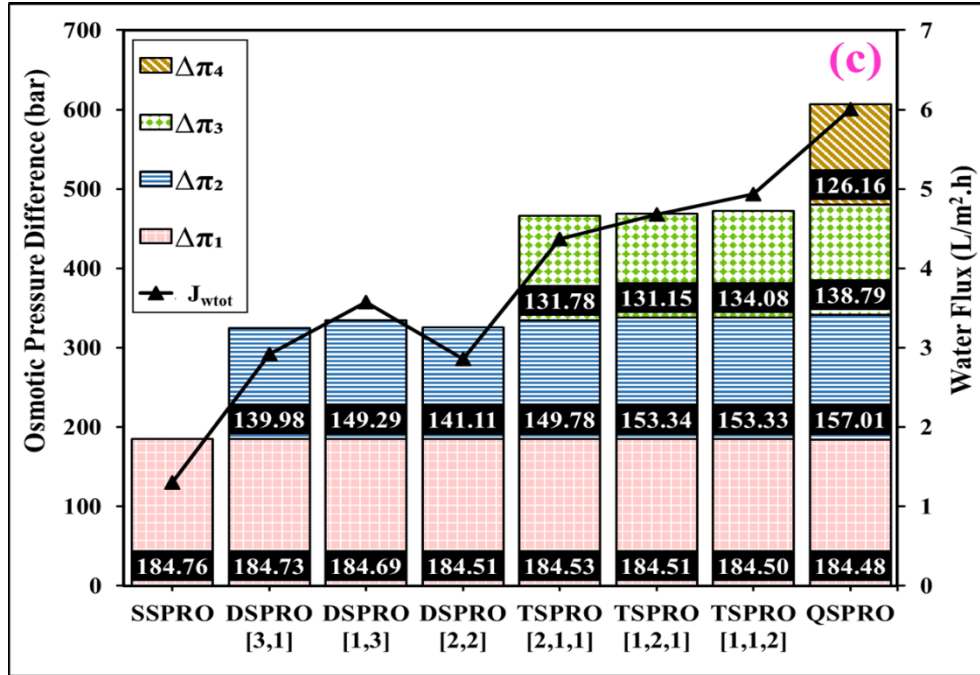
Four scenarios of PRO systems are investigated in the current study, with eight PRO designs (**Table 6.1**). SSPRO scenario with four membrane modules is the first scenario. The second and third scenarios of the DSPRO and the TSPRO have three designs, each to investigate different membrane module arrangements. The fourth QSPRO scenario has one design with a single membrane module in each stage. The same type of high-saline and low-saline solutions were used for all designs but with different numbers of PRO stages in each design. For the multistage PRO scenarios, an extra pump is necessary to pump the fresh feed solution to each stage. However, the multistage PRO scenarios maximize the energy harvested from the draw solution when paired with a new feed stream in the subsequent PRO stages. The water flux (J_w), power density (W), and NSEG were calculated for each of the eight PRO designs and compared in this section.

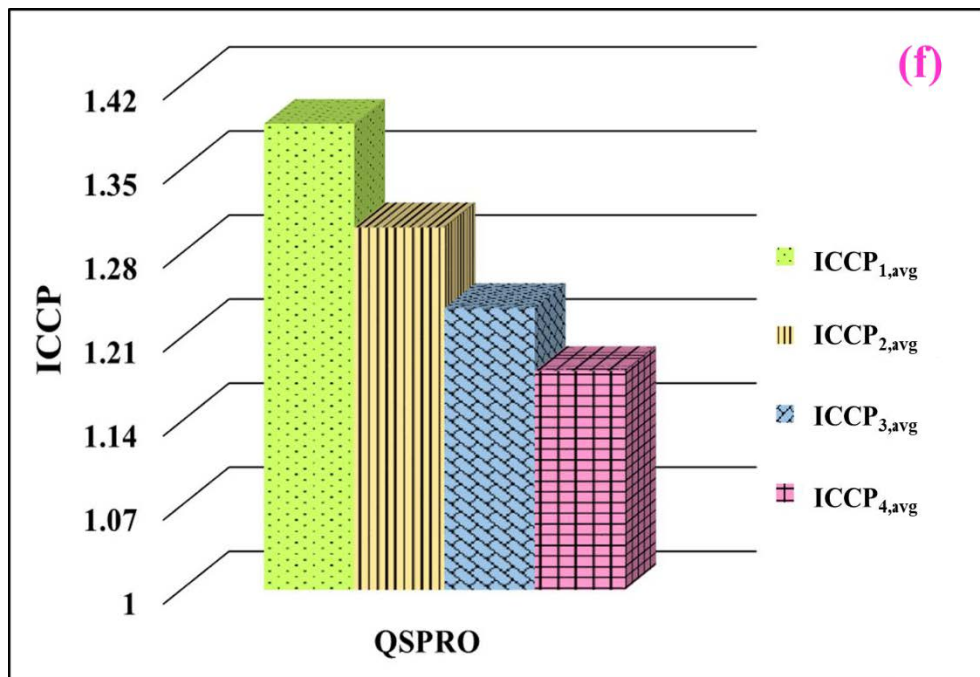
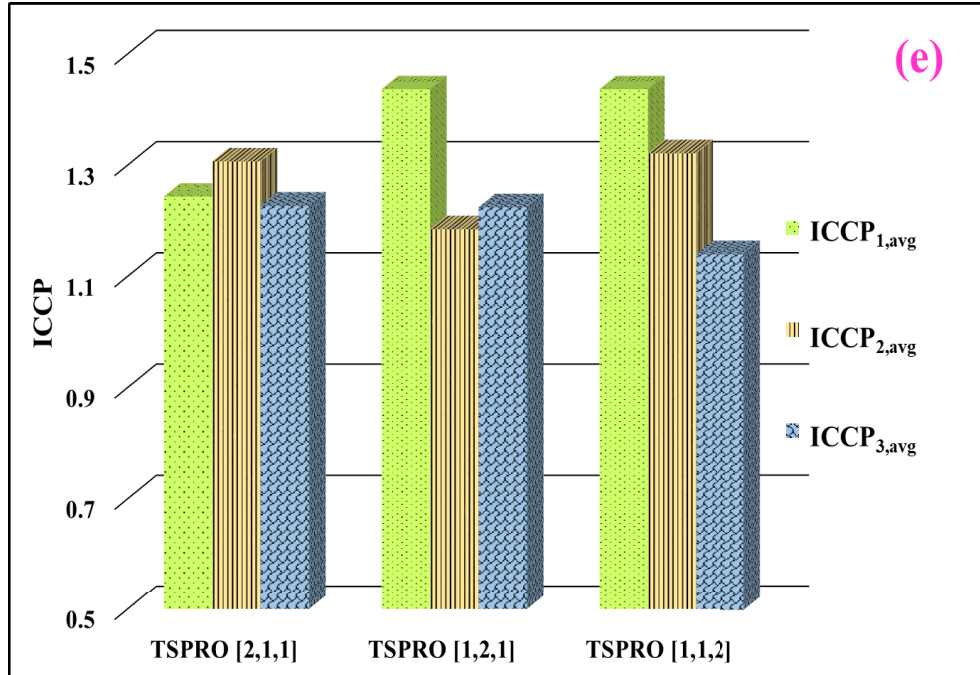
6.4.1 The comparison of the SSPRO and multistage PRO scenarios

6.4.1.1 Water flux and power density

The impact of adding more stages to the PRO system compared to the SSPRO is investigated and discussed here. The hydraulic pressure in the SSPRO and multistage PRO systems was equal to $\Delta\pi/2$. Although the draw solution osmotic pressure changes along the PRO module and from one PRO module to another, the hydraulic pressure remains constant to reduce energy losses. Therefore, the designed hydraulic pressure of the SSPRO and multistage PRO will be carried from the first to the tail PRO module without modification. The permeation flow is the parameter influenced by the variation in the number of PRO stages and membrane module configuration in the stages. **Fig. 6.3a** shows the permeation flow at each PRO stage of the SSPRO and the multistage PRO scenarios. As can be noticed, the permeation flow increased with the PRO stages in the multistage PRO scenarios. Increasing the PRO stages, with a new feed at each stage, enhances the permeation flow. Compared to the SSPRO configuration, the percentage increase in the total permeation flow in the DSPRO [2,2], TSPRO [1,2,1], and QSPRO designs is 9.96%, 10.15%, and 15.53%, respectively. The permeation flow varied depending on the PRO configurations (**Fig. 6.3a**); for instance, the DSPRO [2,2] design produces 0.37 m³/h permeation flow compared to 0.33 m³/h and 0.34 m³/h for the DSPRO [3,1] and DSPRO [1,3] designs.







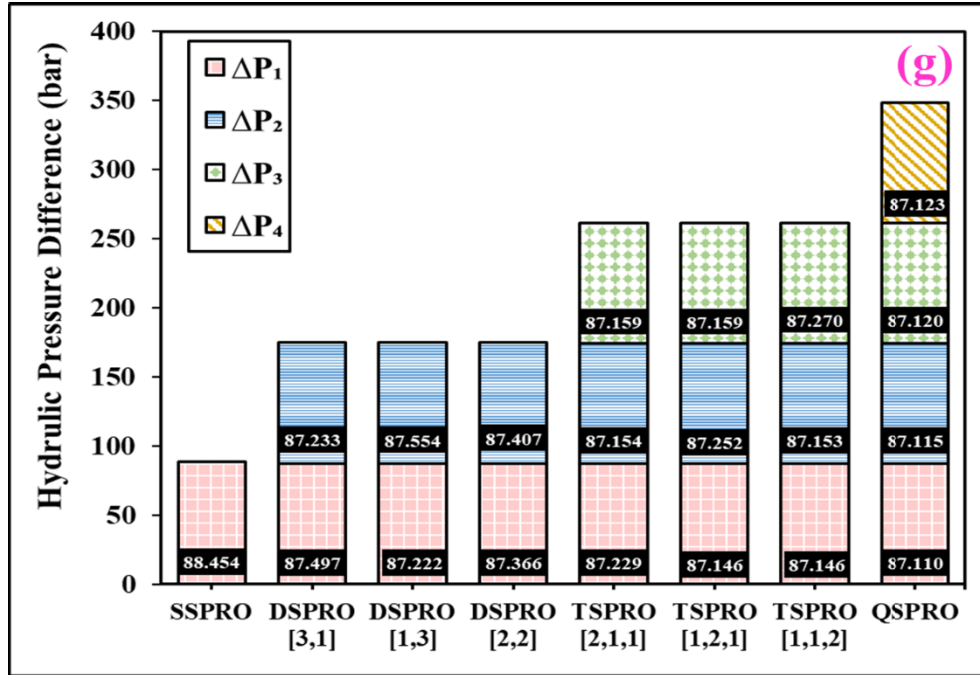


Fig. 6.3: (a) The permeation flow in the first, second, third, and fourth PRO stages (Q_{p1} , Q_{p2} , Q_{p3} , and Q_{p4} , respectively) in the single-stage PRO (SSPRO) and the multistage PRO scenarios, (b) the average water flux in the first, second, third, and fourth PRO stages ($J_{w1,avg}$, $J_{w2,avg}$, $J_{w3,avg}$, and $J_{w4,avg}$, respectively) in the single-stage PRO (SSPRO) and the multistage PRO scenarios, (c) the total water flux ($J_{w,tot}$) and the osmotic pressure difference in the first, second, third, and fourth PRO stages ($\Delta\pi_1$, $\Delta\pi_2$, $\Delta\pi_3$, and $\Delta\pi_4$, respectively) of the SSPRO and the multistage PRO scenarios, (d) the average internal concentrative concentration polarization in the first and the second PRO stages ($ICCP_{1,avg}$ and $ICCP_{2,avg}$, respectively) in the dual-stage PRO (DSPRO) scenarios, (e) the average internal concentrative concentration polarization in the first, the second, and the third PRO stages ($ICCP_{1,avg}$, $ICCP_{2,avg}$, and $ICCP_{3,avg}$, respectively) in the ternary-stage PRO (TSPRO) scenarios, (f) the average internal concentrative concentration polarization in the first, the second, the third, and the fourth PRO stages ($ICCP_{1,avg}$, $ICCP_{2,avg}$, $ICCP_{3,avg}$, and $ICCP_{4,avg}$ respectively) in the quaternary-stage PRO (QSPRO) scenario, and (g) the hydraulic pressure difference in the first, second, third, and fourth PRO stages (ΔP_1 , ΔP_2 , ΔP_3 , and ΔP_4 , respectively) of the SSPRO and the multistage PRO scenarios.

Fig. 6.3b shows the average water flux at each PRO stage of the SSPRO and the multistage PRO scenarios. $J_{w1,avg}$, $J_{w2,avg}$, $J_{w3,avg}$, and $J_{w4,avg}$ is the water flux at the first, the second, the third, and the fourth PRO stage, respectively. The figure shows that the amount of water flux increased with the PRO stages. For instance, the DSPRO scenarios produce higher water flux than the SSPRO scenario, which agrees with the literature [170]. The percentage increase in the water flux by using DSPRO [3,1], DSPRO [1,3], and DSPRO [2,2] compared to the SSPRO scenario is 124%,

175%, and 120%, respectively. Nevertheless, the water flux of each DSPRO design varied with the membrane modules' configurations. The DSPRO [1,3] attained the highest $J_{w1,avg}$ and the lowest $J_{w2,avg}$ compared to the DSPRO [3,1] and the DSPRO [2,2] scenarios. The DSPRO [1,3] exhibited the highest total water flux compared to the DSPRO [3,1] and [2,2] due to the highest osmotic pressure difference (**Fig. 6.3c**). The osmotic pressure gradient in stage two of DSPRO [1,3] is 149.3 bar, whilst in stage two of DSPRO [3,1] and DSPRO [2,2] is 139.9 bar and 141.1 bar, respectively. In the PRO stage one of the DSPRO [1,3], the internal concentrative concentration polarization ($ICCP_{1,avg}$) was greater than in the DSPRO [3,1] and DSPRO [2,2] due to higher water flux, then decreased in the PRO stage two ($ICCP_{2,avg}$) of the DSPRO [1,3] compared to the DSPRO [3,1] and DSPRO [2,2] (**Fig. 6.3d**) as water flux decreased.

Interestingly, adding a third PRO stage caused a further improvement in the water flux. For instance, the percentage rise in the water flux of the TSPRO [2,1,1], TSPRO [1,2,1], and TSPRO [1,1,2] compared to the SSPRO scenario is 236%, 260%, and 280%, respectively (**Fig. 6.3b**). Over the three TSPRO designs, the TSPRO [1,2,1] design shows the highest $J_{w1,avg}$, while the TSPRO [1,1,2] shows the highest $J_{w2,avg}$ and the TSPRO [2,1,1] shows the highest $J_{w3,avg}$. The variation in the water flux occurred due to the change in the membrane configurations of the TRSPRO scenario. For instance, it has been noticed that having one membrane module in stage one of the TSPRO produced higher $J_{w1,avg}$, and having one membrane module in stage two of the TSPRO produced higher $J_{w2,avg}$ (**Fig. 6.3b**). Additionally, the results present that the highest the water flux in a PRO stage of the TSPRO of any configuration is the highest the $ICCP_{avg}$ of that stage. As shown in **Fig. 6.3e**, the $ICCP_{1,avg}$ is higher than the $ICCP_{2,avg}$ and $ICCP_{3,avg}$ of the TSPRO [1,1,2], as a result of $J_{w1,avg}$ is higher than $J_{w2,avg}$ and $J_{w3,avg}$ of the TSPRO [1,1,2] (**Fig. 3b**). The TSPRO [1,1,2] design is preferable over the TSPRO [2,1,1], and TSPRO [1,2,1] designs for producing greater water flux (**Fig. 6.3b**) and having the highest permeation flow (**Fig. 6.3a**). The better water flux in the TSPRO [1,1,2] configuration can be attributed to the greater osmotic pressure difference compared to the other TSPRO configurations (**Fig. 6.3c**), where higher osmotic pressure difference causes an increase in the PRO water flux [307]. For instance, the percentage increase in $\Delta\pi_3$ of TSPRO [1,1,2] compared to TSPRO [2,1,1] and TSPRO [1,2,1] is 1.7%, and 2.2%, respectively.

Finally, the QSPRO shows the highest permeation flow of 0.38 m³/h, around a 15.53% greater permeation flow than the SSPRO scenario. Additionally, it has the highest amount of water flux of 6.01 L/m².h, around 362% higher than the water flux from the SSPRO scenario. The QSPRO design achieved greater water flux due to the higher osmotic pressure gradient than the other PRO designs (**Fig. 6.3c**). The QSPRO design shows higher $\Delta\pi_2$ (2.4%-12.2) and $\Delta\pi_3$ (3.5%-5.8%) in comparison to the DSPRO designs and the TSPRO designs (**Fig. 6.3c**). The internal concentrative concentration polarization results in the first, second, third, and fourth PRO stages of the QSPRO

are shown in **Fig. 6.3f**. It can be noticed that the internal concentrative concentration polarization values are decreasing gradually from stage one to stage four in the QSPRO design. The finding points out the advantage of adding more PRO stages, where each stage will face less ICCP, and it agrees with the behaviour of the permeation flow and water flux of the QSPRO, where the permeation flow and the water flux decreased gradually from stage one to stage four. The higher the water flux, the higher the permeation from the feed side to the draw side, increasing the concentration at the membrane's feed side and consequently increasing the ICCP [308].

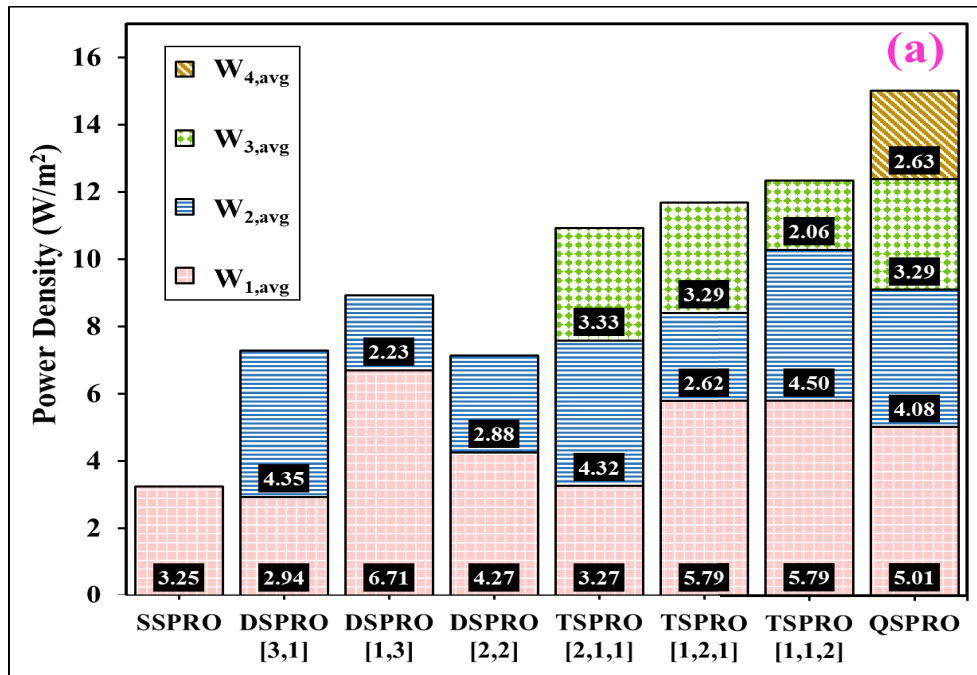
Fig. 6.3c shows the advantage of utilizing multistage PRO in increasing the osmotic pressure gradient. The osmotic pressure difference increases due to the fresh feed introduced to the additional PRO stages. For instance, using the DSPRO [1,3] design caused an 81% rise in the osmotic pressure gradient compared to the SSPRO. Having TSPRO [1,1,2] enhanced the osmotic pressure difference of around 155% compared to the SSPRO. The highest rise in the osmotic pressure difference was for the QSPRO, 228% compared to the SSPRO. Different membrane modules' arrangements showed different osmotic pressure differences. For instance, the osmotic pressure difference of the second stage of the DSPR [3,1] is lower than that of the other dual-stage configurations (DSPRO [1,3] and DSPRO [2,2]), as demonstrated in **Fig. 6.3c**. This can be explained by the further draw solution dilution in the three membrane modules in the first stage of the DSPRO [3,1] design compared to the other two PRO configurations (DSPRO [1,3] and DSPRO [2,2]). Draw solution dilution in the second stage of the DSPRO [3,1] reduced the osmotic pressure difference in this stage.

Fig. 6.3g represents the hydraulic pressure difference in each stage of the SSPRO and the multistage PRO scenarios. It is worth noting that the applied pressure difference in each stage is determined by the difference between the average hydraulic pressure on the draw side and the average hydraulic pressure on the feed side, where the pressure drop on both sides is considered. It can be noticed that the hydraulic pressure variation between the multistage scenarios and the SSPRO scenario is less than 1.5%. This is because the applied hydraulic pressure on the draw and the feed side were fixed for all of the scenarios.

The PRO process operates with consistent hydraulic pressure [167], yet the freshwater transport causes fluctuations in the driving force within the PRO module. These fluctuations in draw and feed solution concentration ultimately impact the power density of the PRO process. The variation in the number of PRO stages and the membrane modules' configuration in the stages influence the power density. **Fig. 6.4a** displays the average power density of the first, second, third, and fourth PRO stages ($W_{1,avg}$, $W_{2,avg}$, $W_{3,avg}$, and $W_{4,avg}$, respectively) of the SSPRO and the multistage PRO scenarios. The power density of the SSPRO scenario is 3.25 W/m². A higher power density was obtained in the multistage PRO scenarios. The DSPRO design [1,3] shows the highest W_1 and the lowest W_2 compared to the DSPRO design [3,1] and the DSPRO design [2,2].

The profile of the total power density results follows the total water flux trend in the PRO designs (**Fig. 6.4b**). Generally, the power density is controlled by the water flux and the difference in the applied pressure (**Equation 6.6**).

Furthermore, adding a third PRO stage caused a rise in the power density. For instance, the percentage rise in the average power density of the TSPRO design [2,1,1], TSPRO design [1,2,1], and TSPRO design [1,1,2] compared to the DSPRO design [1,3] is 22%, 31%, and 38%, respectively (**Fig. 6.4a**). The TSPRO [1,1,2] is preferable over the other TSPRO designs for producing higher power density. Over the three TSPRO designs, the TSPRO design [1,2,1] shows the highest $W_{1,avg}$, while the TSPRO design [1,1,2] shows the highest $W_{2,avg}$, and the TSPRO design [2,1,1] shows the highest $W_{3,avg}$. The variation in the total power density through the different TRSPRO designs was affected by the variation in the total water flux (**Fig. 6.4b**). It can be noticed (**Fig. 6.4b**) that the power density increases with more PRO stages, which agrees with Chung et al. [13] study. Finally, the QSPRO shows the highest total power density of 15.02 W/m^2 , around 362% more than the power density produced through the SSPRO scenario.



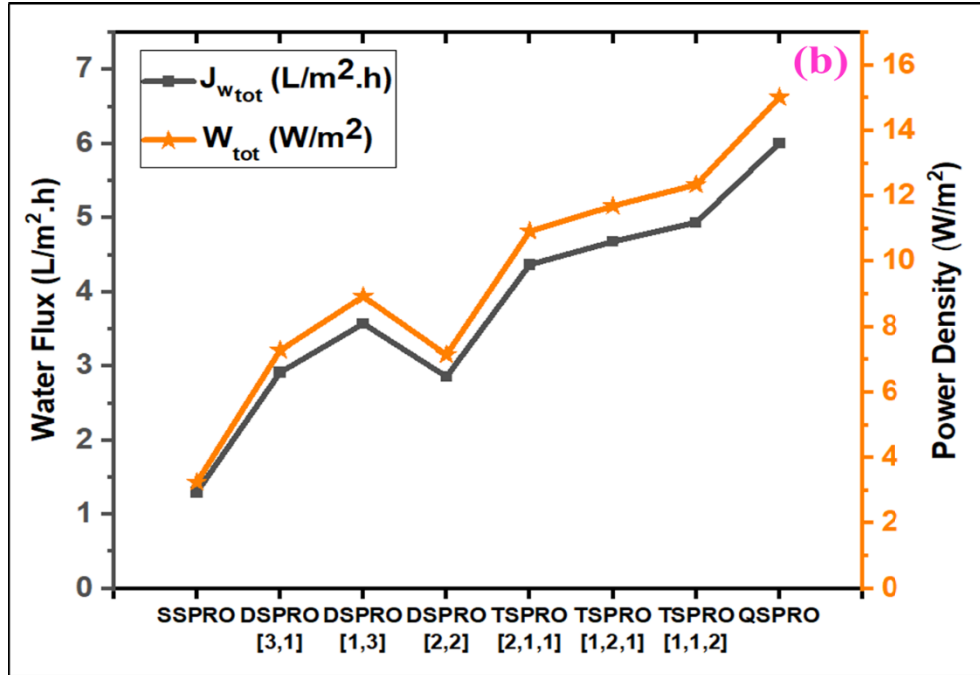


Fig. 6.4: (a) The power density in the first, second, third and fourth PRO stages (W_1 , W_2 , W_3 , and W_4 , respectively) of the single-stage PRO (SSPRO) and the multistage PRO scenarios, and (b) the total water flux ($J_{w_{tot}}$) and the total power density (W_{tot}) of the single-stage PRO (SSPRO) and the multistage PRO scenarios.

6.4.1.2 The NSEG results

Taking into account various flow rates for single and multistage PRO designs would yield varying requirements for pretreatment energy, consequently affecting the cost of pretreatment. Such a scenario would not be conducive to highlighting the variation in NSEG based on the number of stages in PRO. Accordingly, the single and multistage PRO designs used the same draw and feed solution flow rates; therefore, the required pretreatment energy of the draw and feed solutions is equal. **Fig. 6.5** represents the energy generated through the turbines, the energy consumed through pumping, and the net specific energy generation of the SSPRO and the multistage PRO scenarios. $E_{Turbine}$ ranges between 0.63 kW and 0.77 kW for the SSPRO and the QSPRO scenarios, respectively. As the PRO stages increased, the amount of energy generated also increased according to the higher permeation flow and power generation in the PRO process. Further, the amount of energy consumed through pumping is fixed for the investigated designs because all scenarios utilize the exact amount of the inlet feed and draw solution flow rates. Accordingly, the NSEG will be enhanced with adding more PRO stages (**Fig. 6.5**). The NSEG for SSPRO, DSPRO design [3,1], DSPRO design [1,3], DSPRO design [2,2], TSPRO design [2,1,1], TSPRO design [1,2,1], TSPRO design [1,1,2], and QSPRO design are 0.209, 0.230, 0.235, 0.257, 0.258, 0.261,

0.263, and 0.279 kW.h/m³, respectively. Presenting two membrane modules in each PRO stage of the DSPRO scenario caused a 23.41% rise in the NSEG compared to the NSEG of the SSPRO (Table 6.2). The NSEG increase in the DSPRO compared to an SSPRO ranged from 10% to 23%. A similar result is reported in the literature [29], where the authors reported that around 12% to 16% was the increase in the specific energy due to using a DSPRO scenario. It is worth pointing out that the PRO module configuration of the DSPRO directly affected the NSEG. For instance, using the DSPRO design [3,1] instead of the DSPRO design [2,2] reduces the NSEG by around 11.98%. As mentioned above, different membrane modules' configurations affected the permeation flow in the PRO stages (Fig. 6.3a). For instance, it was noticed that the DSPRO design [2,2] produced the highest permeation compared to the DSPRO design [1,3] and the DSPRO design [3,1] (Fig. 6.3a), explaining why the DSPRO design [2,2] produced higher NSEG. Additionally, the same trend is noticed for the TSPRO designs, where a 26.10% increase in the NSEG (Table 6.2) was achieved in the TSPRO design [1,1,2] compared to the SSPRO (Fig. 6.5). Results showed that having two membrane modules in PRO₁, one membrane module in PRO₂, and one membrane module in PRO₃ (i.e., TSPRO design [2,1,1]) is the less favourable configuration over the other two TSPRO designs (Fig. 6.5). By changing the modules' configuration to TSPRO design [1,1,2], higher water flux, power density (Fig. 6.4b), and permeation rate (Fig. 6.3a) was achieved, causing an increase in the NSEG. Furthermore, it has been noticed that the water flux and the membrane area govern the permeation flow along the PRO system. For instance, having more membrane modules in one PRO stage increases the permeation flow of that stage (Fig. 6.3a). The best-performance membrane configuration was in the QSPRO; a 33.96% increase in the NSEG was attained compared to the SSPRO (Table 6.2).

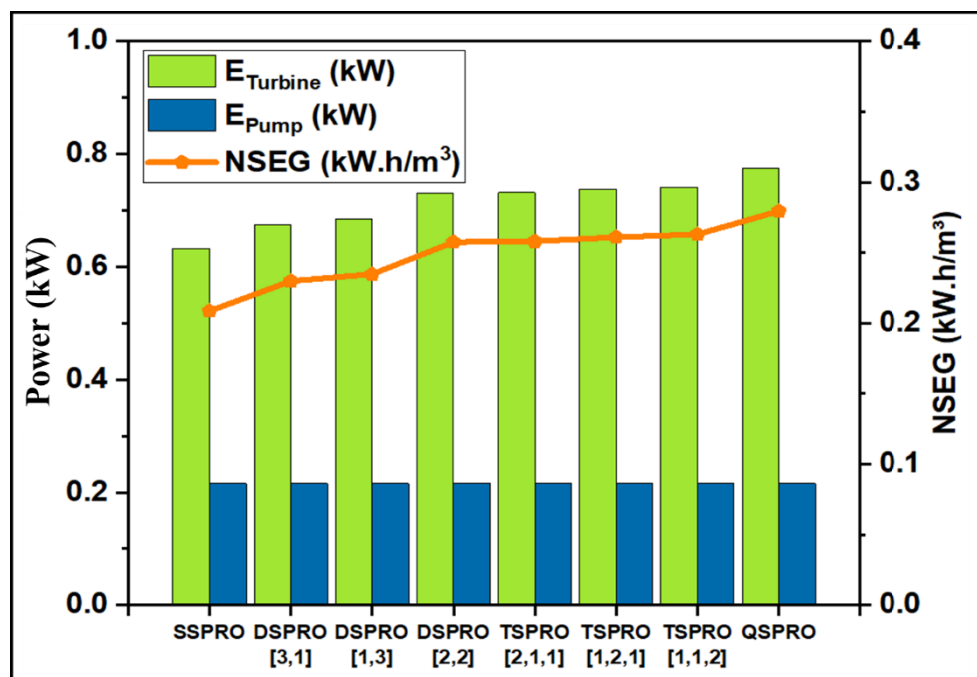


Fig. 6.5: The energy generated by the turbines (E_{Turbine}), the energy consumed by the pumps (E_{Pump}), and the net specific energy generation (NSEG) of the single-stage PRO (SSPRO) and the multistage PRO scenarios.

Table 6.2: The percentage increase in the NSEG using the multistage PRO scenarios compared to the single-stage PRO (SSPRO) scenario.

Multistage PRO scenario		% Increase in the NSEG
Dual-stage PRO	DSPRO [3,1]	10.20
	DSPRO [1,3]	12.51
	DSPRO [2,2]	23.41
Ternary-stage PRO	TSPRO [2,1,1]	23.69
	TSPRO [1,2,1]	25.12
	TSPRO [1,1,2]	26.10
Quaternary-stage PRO	QSPRO	33.96

Permeation flow, water flux, and internal concentrative concentration polarization are the key parameters that impact the amount of NSEG produced in the PRO. These parameters are affected by the number of PRO stages in the system and the membrane modules' configuration. For instance, although the power density in the DSPRO design [2,2] was not the best-performing PRO design, it produced the highest NSEG in the DSPRO scenario. The situation differed for the three TSPRO designs, where the TSPRO design [1,1,2] showed the highest permeation flow, water flux, and internal concentrative concentration polarization than the other two TSPRO designs. That explains why the TSPRO design [1,1,2] has the highest NSEG than the two TSPRO designs. It is worth noting that the membrane cost will be equal for all of the investigated multistage PRO scenarios, as they all contain four membrane modules. The HF membrane module (HP5230SI) PRO's price, as Toyoboo gave and mentioned in our previous study [295], equals \$5,193 US/membrane element. Then, the cost of the four membranes will be \$20,772 US.

Besides the advantages of employing multistage PRO systems, it is important to consider their main limitations. For instance, a balance between the number of the PRO stages and the feed and the draw initial flow rates should be investigated. Adding more than four PRO stages would require an increase in the feed and draw solutions' initial flow rates. On the other hand, increasing the flow rates would increase the total consumed energy, impacting the net-specific energy generation. Moreover, the capital cost of the multistage PRO systems would vary based on the number of used PRO units. For instance, the cost of the PRO membrane module's pressure vessel

will impact the system's cost analysis. The QSPRO will be more expensive than the TSPRO, the DSPRO, and the SSPRO systems. Therefore, a critical cost analysis determining the capital and operational costs should occur before choosing how many PRO stages would be used. A power plant of a multistage PRO system would have turbines, pumps, pressure vessels, and water tanks. Accordingly, the availability of empty land should also be considered based on the number of the PRO stages that would be used. Accordingly, a commercial power plant with PRO technology is not available yet, and further optimization and cost analysis of a full-scale plant are required [309, 310].

After comparing the PRO designs' permeation flow, water flux, internal concentrative concentration polarization, and power density, the QSPRO scenario is the best-performance scenario for NSEG (**Table 6.2**). Consequently, this scenario will be further investigated with different salinity gradients.

6.4.2 Impact of the salinity gradient resource

The salinity gradient resource is one of the significant parameters that dominate the process efficiency of the PRO process [145, 311]. It presents the driving force behind the water flow from the feed solution to the draw solution in the PRO according to the osmotic pressure gradient between the two solutions. Accordingly, this section studies the influence of the salinity gradient resource on the NSEG in the QSPRO scenario. Five salinity gradient resources were considered: Dead Sea-wastewater (DS-WW), Dead Sea-seawater (DS-SW), RO brine-wastewater (ROB-WW), seawater-wastewater (SW-WW), and Dead Sea with RO brine (DS-ROB). The selected feed and draw solutions represent the most available water bodies for energy generation by the PRO system [59, 61, 67, 75]. The inlet feed and the draw solutions' flow rates were 1 m³/h, the applied pressure on the feed side (1 bar) and the solutions' temperature (298 K) and the same as the used ones for the DS-ROB (Subsection 6.3.3). **Table 6.3** shows the salinity gradient resources, the resources' salinity concentration, and the applied pressure on the draw side. The applied pressure on the draw side for the DS-WW is half the osmotic pressure of the salinity gradient resource [139].

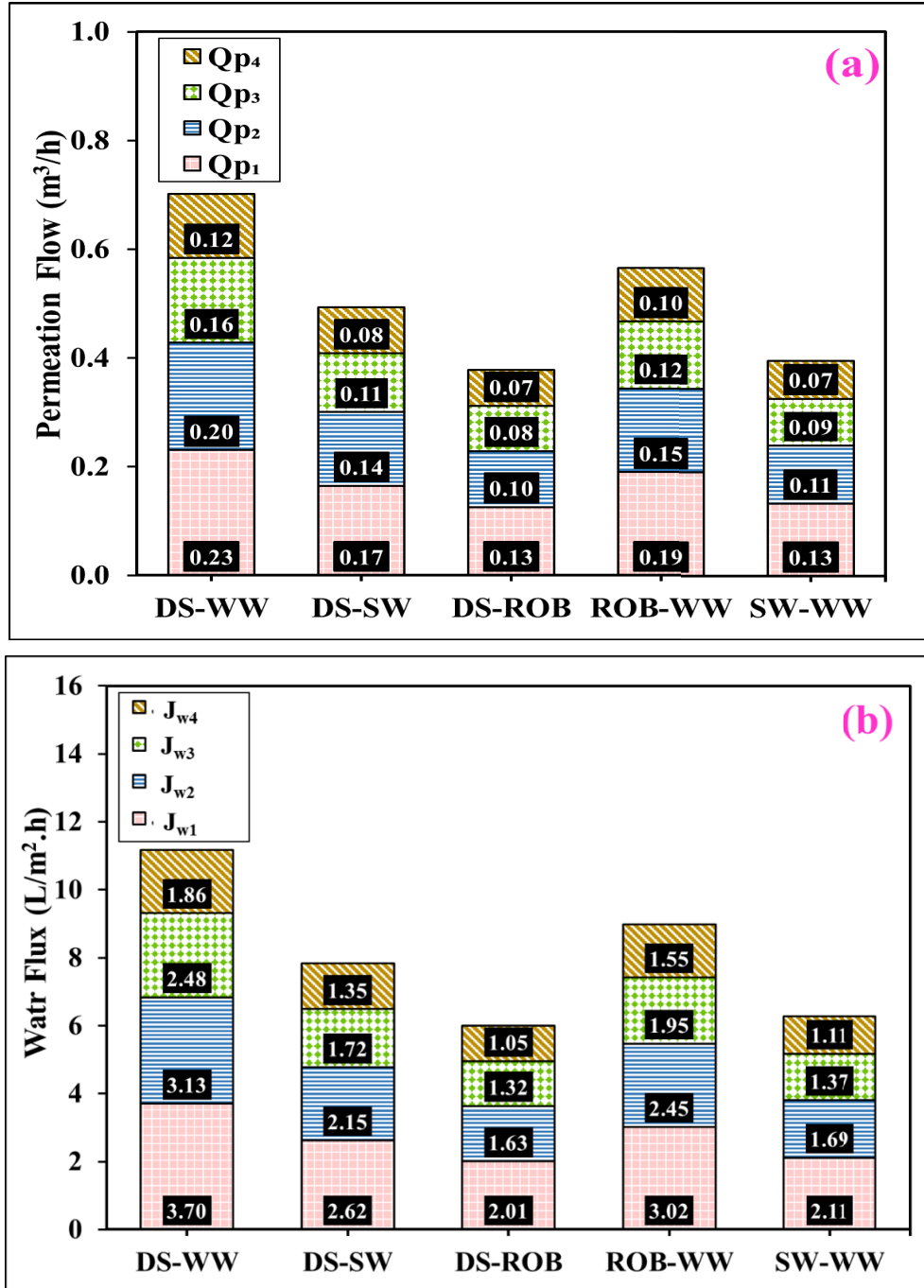
Table 6.3: The salinity and the applied pressure on the draw side of the investigated salinity gradient resources.

Salinity gradient resources	Abbreviation	Resources' salinity (g/L)	Applied pressure on the draw side (bar)
Dead Sea-Wastewater	DS-WW	292.20-1.16	121
Dead Sea- Seawater	DS-SW	292.20-35.06	108
Dead Sea-RO Brine	DS-ROB	292.20-70.13	90
RO Brine-Wastewater	ROB-WW	70.13-1.16	29
Sea Water-Wastewater	SW-WW	35.06-1.16	16

As the salinity gradient resources change, the performance of the QSPRO scenario changes.

Fig. 6.6a shows the permeation flow of the investigated salinity gradient resources' PRO1, PRO2, PRO3, and PRO4 designs. The DS-WW salinity gradient shows the highest Q_{p1} , Q_{p2} , Q_{p3} , and Q_{p4} compared to the other salinity resources (**Fig. 6.6a**). Compared to the DS-WW, the percentage drop in the permeation flow is 29.66%, 46.03%, 19.41%, and 43.55% for the DS-SW, DS-ROB, ROB-WW, and SW-WW salinity gradient resources. Additionally, the DS-WW has the highest water flux (**Fig. 6.6b**) and the highest osmotic pressure difference (**Fig. 6.6c**), potentially maximising the energy output.

Fig. 6.6b displays the water fluxes (J_{w1} , J_{w2} , J_{w3} , and J_{w4}) for the PRO1, PRO2, PRO3, and PRO4 for the investigated salinity gradient resources. The highest total water flux is for the DS-WW, followed by ROB-WW, DS-SW, SW-WW, and DS-ROB. The DS-WW shows the highest J_{w1} , J_{w2} , J_{w3} , and J_{w4} compared to the other salinity resources (**Fig. 6.6b**) because of its highest osmotic pressure-driven force (**Fig. 6.6c**). The highest osmotic pressure gradient across the membrane, the highest water flux [29, 170]. Compared to the DS-WW, the percentage drop in the total water flux is 29.91%, 46.22%, 19.69%, and 43.75% for the DS-SW, DS-ROB, ROB-WW, and SW-WW salinity gradient resources. At the same time, the internal concentrative concentration polarization is also affected by the permeation flow across the membrane. For instance, as shown in **Fig. 6.6b**, the ROB-WW shows the second-highest water flux compared to the DS-SW, DS-ROB, and SW-WW, which is responsible for the severe ICCP of ROB-WW compared to DS-SW, DS-ROB, and SW-WW salinity gradients (**Fig. 6.6d**).



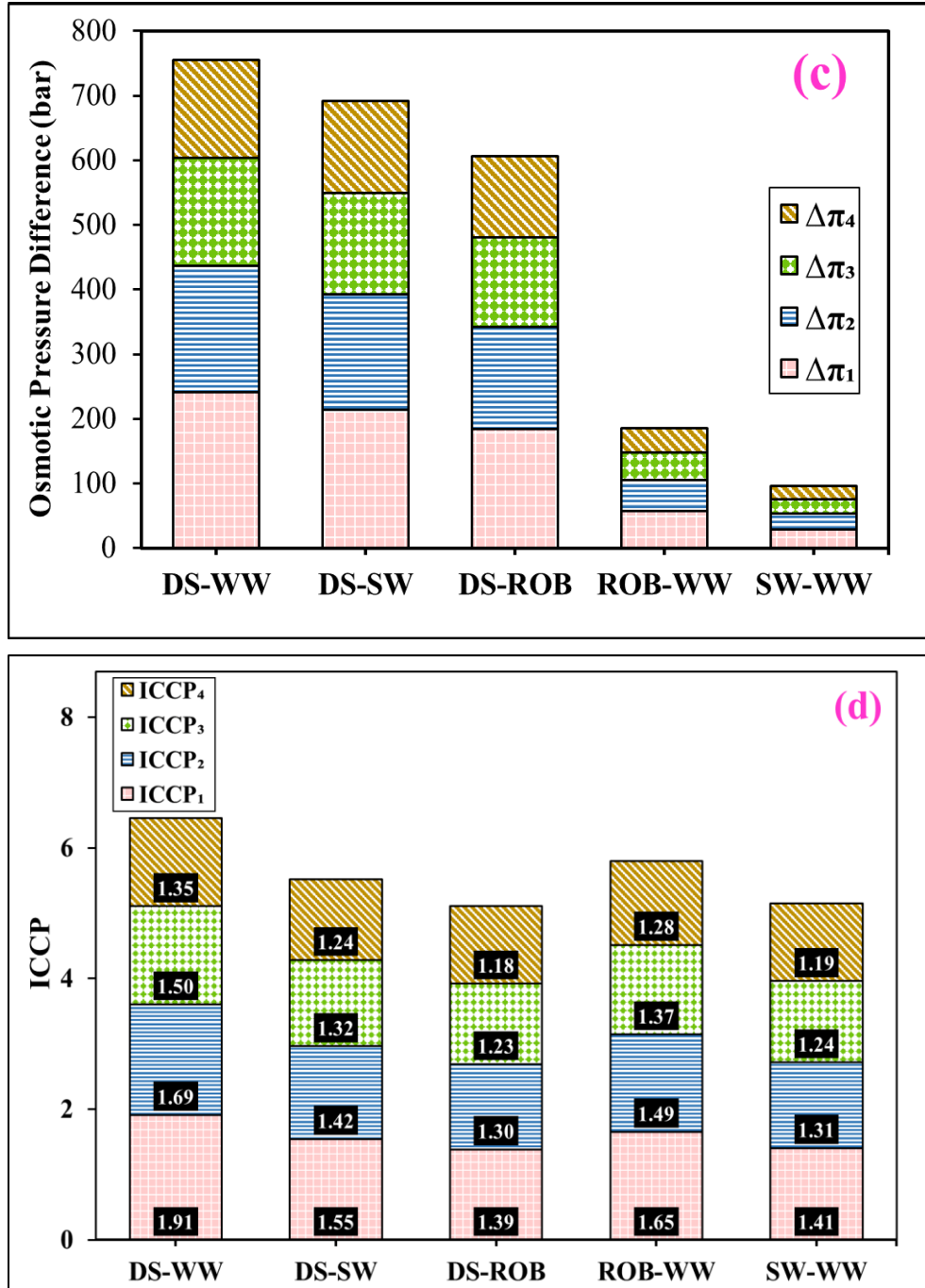
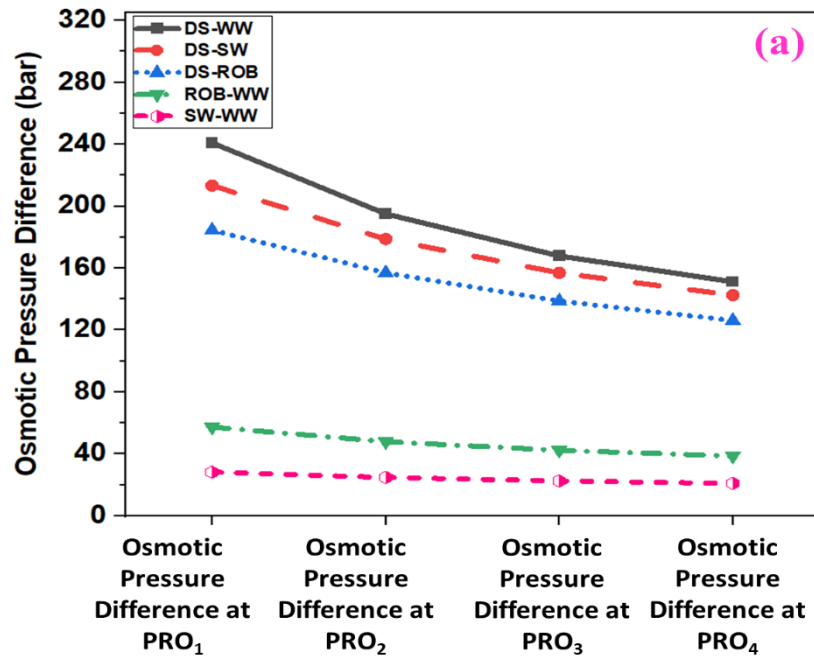


Fig. 6.6: (a) The permeation flow in the first, second, third and fourth PRO stages (Q_{p1} , Q_{p2} , Q_{p3} , and Q_{p4} , respectively) in the quaternary-stage PRO (QSPRO) scenario for DS-WW, DS-SW, DS-ROB, ROB-WW, and SW-WW salinity resources, (b) the water flux in the first, second, third and fourth PRO stages (J_{w1} , J_{w2} , J_{w3} , and J_{w4} , respectively) in the quaternary-stage PRO (QSPRO) scenario for DS-WW, DS-SW, DS-ROB, ROB-WW, and SW-WW salinity resources, (c) the osmotic pressure difference in the first, second, third and fourth PRO stages ($\Delta\pi_1$, $\Delta\pi_2$, $\Delta\pi_3$, and $\Delta\pi_4$, respectively) of the quaternary-stage PRO (QSPRO) scenario for DS-WW, DS-SW, DS-ROB, ROB-WW, and SW-WW salinity resources, and (d) the internal concentrative polarization in the first, second, third and fourth PRO stages (ICCP₁, ICCP₂, ICCP₃,

and ICCP₄, respectively) of the quaternary-stage PRO (QSPRO) scenario for DS-WW, DS-SW, DS-ROB, ROB-WW, and SW-WW salinity resources.

The PRO system's osmotic pressure gradient across the membrane significantly impacts the produced energy. **Fig. 6.7a** displays the osmotic pressure gradient across the membrane of the QSPRO scenario for the five salinity gradient resources. The highest osmotic pressure gradient is for the DS-WW resource, while the lowest is for the SW-WW resources. The variance between the osmotic pressure of the feed and the draw solution explains the results in **Fig. 6.7a**. The energy generated, consumed by the pumps, and the NSEG of the QSPRO scenario for the investigated salinity gradient resources are shown in **Fig. 6.7b**. The energy consumed by the pumps depends on the salinity gradients. It ranges between 0.269 kW for the DS-WW and 0.205 kW for the SW-WW salinity gradient. The maximum energy generated through turbines is 1.91 kW for the DS-WW salinity gradient. The highest osmotic pressure gradient (**Fig. 6.7a**) and the highest applied pressure on the draw side (**Table 6.2**) resulted in the highest NSEG. Around 0.82 kWh/m³ is the NSEG produced in the QSPRO scenario using the DS-WW salinity gradient (**Fig. 6.7b**). The NSEG decreased by 41.73%, 65.97%, 86.44%, and 99.15% when DS-SW, DS-ROB, ROB-WW, and SW-WW salinity gradients were used instead of the DS-WW salinity gradient.



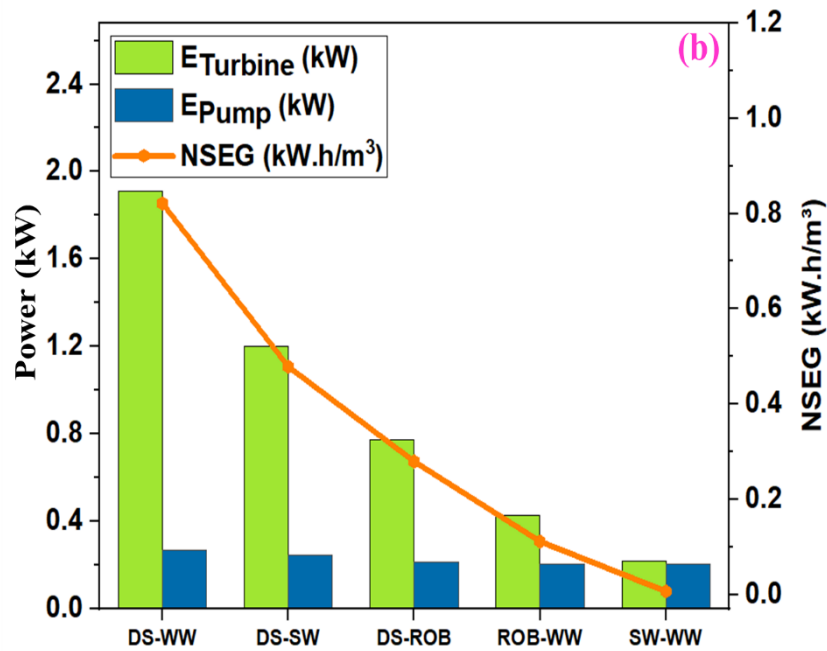


Fig. 6.7: (a) The osmotic pressure difference at PRO₁, PRO₂, PRO₃, and PRO₄ of the quaternary-stage PRO (QSPRO) scenario for DS-WW, DS-SW, DS-ROB, ROB-WW, and SW-WW salinity resources, and (b) the energy generated by the turbines (E_{Turbine}), the energy consumed by the pumps (E_{Pump}), and the net specific energy generation (NSEG) of the quaternary-stage PRO (QSPRO) scenario for DS-WW, DS-SW, DS-ROB, ROB-WW, and SW-WW salinity resources.

6.4.3 Impact of operating parameters on DS-WW QSPRO performance

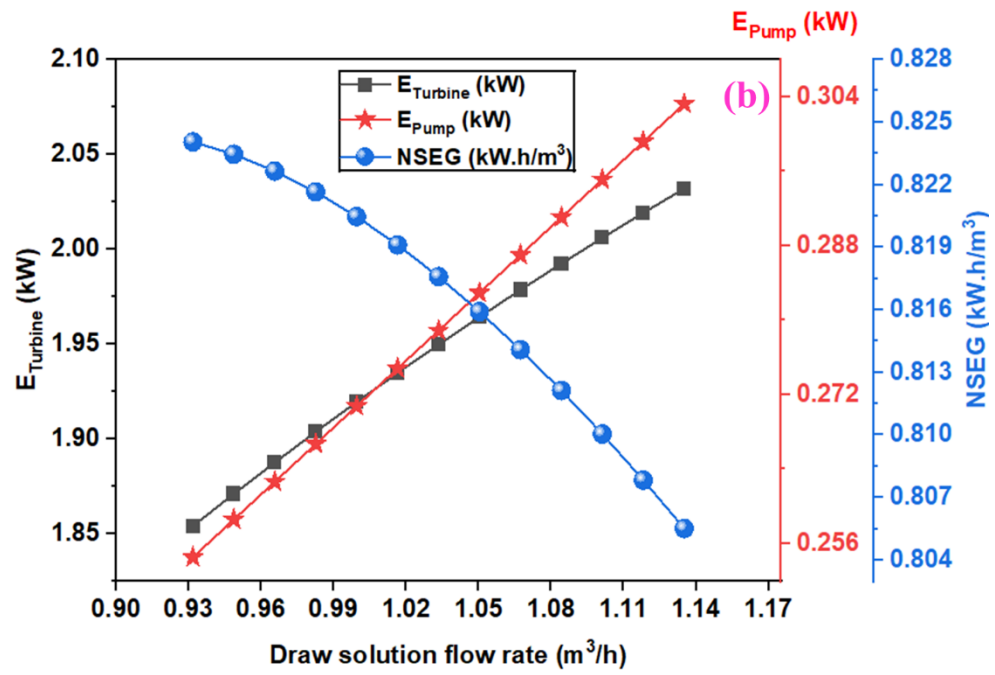
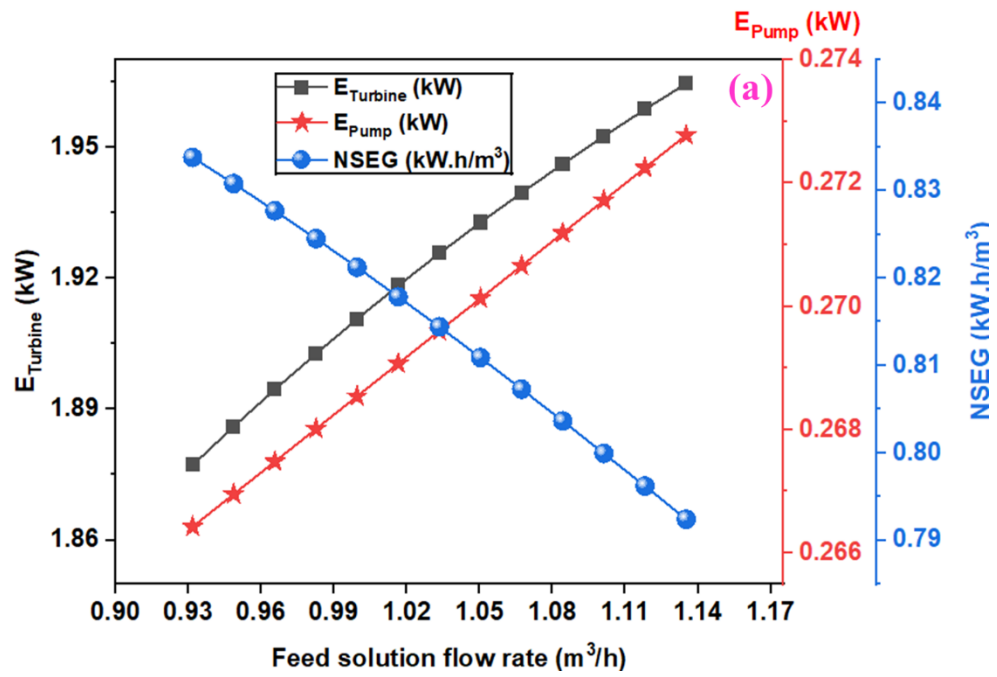
According to Subsection 6.4.2, the QSPRO scenario with DS-WW showed the highest NSEG of around 0.82 kWh/m³. To further enhance the QSPRO system performance, this subsection investigated the impact of the feed and the draw solutions flow rates and the applied draw solution pressure (**Fig. 6.1b**) on the energy generated by the turbines (E_{Turbine}), the energy consumed in the pumps (E_{Pump}), and the NSEG. The feed and draw solutions flow rates and the applied draw solution pressure govern the energy generation and consumption in the PRO process [217, 312, 313].

Fig. 6.8a shows the E_{Turbine} , E_{Pump} , and NSEG of the QSPRO scenario at different feed solution (WW) flow rates. Increasing the feed solution flow rate from 0.93 to 1.14 m³/h caused an increase in the energy generated by the turbines from 1.88 kW to 1.96 kW, about 5%. Increasing the feed flow rate in the QSPRO scenario was responsible for the rise in the water flux at each PRO stage since water flux in the PRO system rises with the feed solution flow rate [176] as more water would be available for the permeation. Therefore, increasing the feed flow rate explains the boost in the water flux and, consequently, the increase in the energy generated by the turbines.

Besides, E_{Pump} increased by 2% due to the feed flow rate increase from 0.93 to 1.14 m³/h, since the higher the flow rate, the higher the energy consumed through pumping [314]. Even though the energy consumed through pumping was increased, the net energy, **Equation 6.13**, increased due to the considerable increase in the energy generated compared to the energy consumed. **Fig. 6.8a** shows that the NSEG dropped due to the increased feed solution flow rate. The decrease in the NSEG can be explained by **Equation 6.13** since the NSEG is inversely related to the total feed and draw flow rates (Q_{tot}). There was a 22% increase in the feed solution flow rate when the feed solution flow rate increased from 0.93 to 1.14 m³/h. Thus, the lower the feed solution flow rate is, the higher the NSEG (**Table 6.4**).

The profile of NSEG followed the same trend when the draw solution flow rate increased from 0.93 to 1.14 m³/h. The E_{Turbine} and the E_{Pump} increased with the draw solution flow rate (**Fig. 6.8b**). A 22% rise in the draw solution flow rate caused a 10% increase in the E_{Turbine} and a 19% increase in the E_{Pump} . The higher the draw solution flow rate, the lower the impact of the draw dilution effect on the water flux [315]. The increased water flux improved the E_{Turbine} generated in the PRO process. Previous research reported a direct relation between the draw solution flow rate and the water flux of the PRO system [176, 308, 316, 317]. However, the NSEG decreased from 0.824 kWh/m³ to 0.806 kWh/m³ (**Fig. 6.8b**) due to the rise in the total draw solution flow rate, as shown in **Equation 6.13**. Enhancing the net specific energy harvested by the PRO required less draw solution flow rate (**Table 6.4**).

Fig. 6.8c displays the impact of varying the applied pressure on the draw side (Pump 2, **Fig. 6.1b**) on the QSPRO system performance. Undoubtedly, increased E_{Pump} was noticed with the increased applied pressure. A 37% increase in the applied pressure caused a rise in E_{Pump} from 0.258 kW to 0.330 kW (**Fig. 6.8c**). In contrast, the results showed a 16% drop in the E_{Turbine} with the increased applied pressure (**Table 6.4**) due to the drop in the water flux in the PRO stages of the QSPRO [87, 196, 318]. Additionally, the higher the applied pressure on the PRO membrane, the greater the membrane fouling [319, 320], impacting the PRO water flux. Approximately 23% reduction in the NSEG occurred with increased draw solution pressure. It can be noticed that the variation of the applied pressure on the draw side has the highest impact on the QSPRO system performance compared to the feed and draw solutions flow rates.



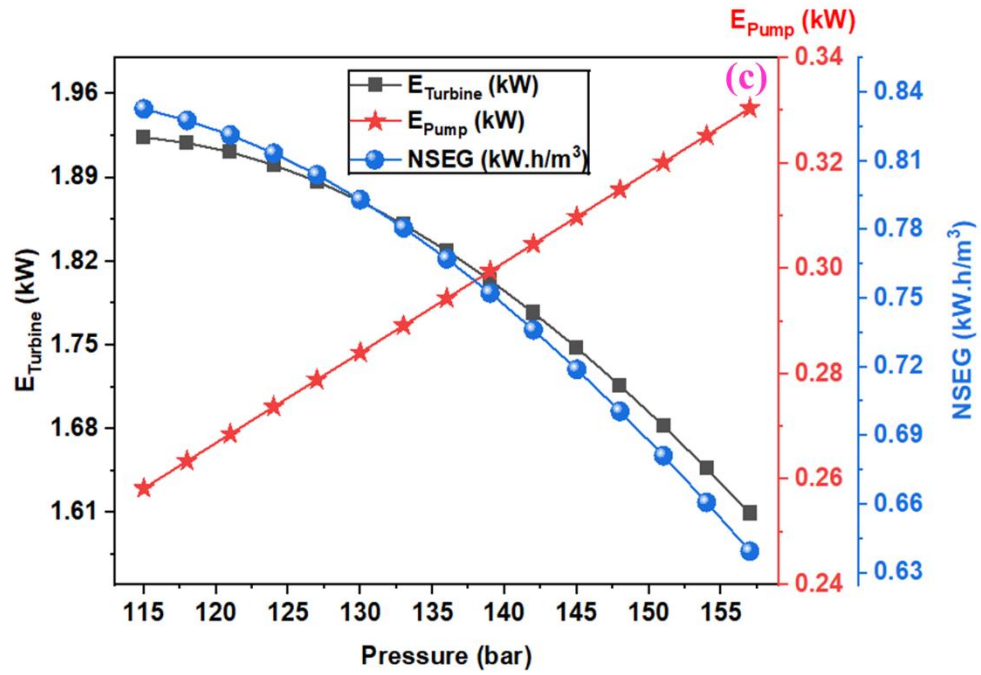


Fig. 6.8: (a), (b), and (c) The impact of the variation of the feed solution flow rate, the draw solution flow rate, and the applied pressure on the draw side on the energy generated by the turbines (E_{Turbine}), the energy consumed by the pumps (E_{Pump}), and the net specific energy generation (NSEG) of the quaternary-stage PRO (QSPRO) scenario for DS-WW salinity resources, respectively.

Generally, multistage PRO scenarios are more efficient than single-stage PRO due to the lower ICCP on the feed side in the additional stages. Dividing the feed solution into the PRO stages attenuates the impact of ICCP, improving water flux and, eventually, energy generation. The QSPRO configuration achieved the highest energy generation due to the greater permeation flow caused by using a fresh feed solution in each stage (**Fig. 6.3**). Dead Sea-wastewater salinity gradients exhibited the highest osmotic pressure driving force and NSEG compared to other salinity gradients. **Table 6.4** shows the results of the variation of the operating conditions on the QSPRO system using DeadSea-wastewater as the salinity gradient resources. Varying the feed and draw solution flow rates and draw solution pressure led to an insignificant drop in the NSEG. Therefore, using a feed-to-draw flow rate ratio of less than 1 and a draw solution pressure slightly lower than the average osmotic pressure difference of the salinity gradient offers the best operating condition in the multistage PRO process (**Table 6.4**). For instance, reducing $\frac{Q_{Fi}}{Q_{Di}}$ from 1 to 0.93 (reducing the feed flow rate and using a draw flow rate was 1 m³/h) caused a 1.53% increase in the NSEG. A similar trend was noticed when $\frac{Q_{Di}}{Q_{Fi}}$ was reduced from 1 to 0.93 by reducing the draw flow rate and using 1 m³/h feed flow rate caused a 0.44% increase in the NSEG.

In contrast, a 1.39% increase in the NSEG occurred when the applied hydraulic pressure was 0.95 of the average osmotic pressure difference (**Table 6.4**). However, the highest impact on the NSEG was noticed when the applied pressure increased from $\frac{\Delta\pi}{2}$ to $1.30 * \frac{\Delta\pi}{2}$, causing a 22.14% drop in the NSEG. Accordingly, the applied hydraulic pressure is the most influential parameter on the NSEG, and it is preferred to be equal to or slightly less than $\Delta\pi/2$.

Table 6.4: The percentage change in the E_{Turbine} , E_{Pump} , net energy, and NSEG as the quaternary-stage PRO (QSPRO) scenario parameters changed.

Parameter changed	Range	% Change in the E_{Turbine}	% Change in the E_{Pump}	%Change in the net energy	% Change in the NSEG
Feed flow rate	$1 > \frac{Q_{Fi}}{Q_{Di}} > 0.93$	-1.75	-0.79	-1.91	1.53
	$1 < \frac{Q_{Fi}}{Q_{Di}} < 1.14$	2.82	1.58	3.03	-3.51
Draw flow rate	$1 > \frac{Q_{Di}}{Q_{Fi}} > 0.93$	-3.41	-6.00	-2.98	0.44
	$1 < \frac{Q_{Di}}{Q_{Fi}} < 1.14$	5.87	11.99	4.86	-1.82
Hydraulic pressure on the draw side	$\frac{\Delta\pi}{2} > \Delta P > 0.95 * \frac{\Delta\pi}{2}$	0.65	-3.84	1.39	1.39
	$\frac{\Delta\pi}{2} < \Delta P < 1.30 * \frac{\Delta\pi}{2}$	-15.79	23.04	-22.14	-22.14

6.5 Conclusion

This study focuses on determining the NSEG of SSPRO, DSPRO, TSPRO, and QSPRO of DS-ROB as salinity gradients. The results showed that the NSEG of the QSPRO scenario is 33.96% higher than its corresponding SSPRO scenario. Moreover, it has been noticed that the water flux and the power density are increasing by adding more PRO stages to the system. For instance, the QSPRO scenario will produce 362% higher water flux than the SSPRO scenario. Adding more PRO stages lessens the inverse impact of the internal concentration polarization on the multistage PRO performance. It will enhance the multistage PRO systems' water flux, power density, and NSEG.

Five salinity gradients are investigated using the QSPRO scenario. The DS-WW salinity gradients of the QSPRO scenario presented the highest produced water flux over the DS-SW, DS-ROB, ROB-WW, and SW-WW. Additionally, the DS-WW has the highest osmotic pressure gradient and the applied pressure on the draw side. These results clarify that the DS-WW of the QSPRO scenario produced the highest NSEG of about 0.82 kW.h/m³.

The variation of the feed solution flow rate, the draw solution flow rate, and the applied pressure on the QSPRO system productivity are also evaluated. The results show that the applied pressure has the most dominant impact on the behaviour of the QSPRO scenario compared to the feed solution and the draw solution flow rates. A 37% increase in the applied pressure caused a 23% drop in the NSEG. On the other hand, the reduction in the NSEG was 5% and 2%, with a 22% rise in the feed solution flow rate and the draw solution flow rate, respectively, indicating the significance of choosing the best parameters for maximizing the NSEG of the QSPRO scenario. It has been concluded that the highest impact on the NSEG was noticed when the applied pressure increased from $\frac{\Delta\pi}{2}$ to $1.30 * \frac{\Delta\pi}{2}$, causing a 22.14% drop in the NSEG. Accordingly, the applied hydraulic pressure is the most influential parameter on the NSEG, and it is preferred to be equal to or slightly less than half of the osmotic pressure difference. The outcomes of this study aim to enhance comprehension among researchers and scientists regarding the merits of employing a multistage PRO instead of a single-stage PRO in water treatment. Conducting a pilot plant investigation is essential for interpreting the advantages associated with the multistage PRO process, and it is strongly advised that such studies be undertaken to verify the findings of this study.

Chapter Seven: Findings and future work

7.1 Findings

This thesis investigated the developments and applications of the PRO system and the available energy that can be collected from salinity gradient resources in single-stage and multi-stage PRO systems. In Chapter Three, the Dual Stage Pressure Retarded Osmosis (DSPRO) technique is considered for power generation. For the first time, the influence of feed flow rates, hydraulic pressure, and pressure drop on mass transfer and solute diffusion in a full-scale membrane model was investigated to maximize power generation. Dead Sea-seawater (DS-SW), Dead Sea-Reverse Osmosis brine (DS-ROB), Reverse Osmosis brine-wastewater (ROB-WW), and seawater-wastewater (SW-WW) salinity gradient resources (SGRs) were investigated for power generation. Results revealed a 71.07% increase in the specific power generation due to the DSPRO system optimization using DS-SW SGR. The enhancement in the specific power generation due to the DSPRO optimization was 108.8%, 63.18%, and 133.54%, respectively, for DS-ROB, ROB-WW, and SW-WW SGRs. At optimum operating conditions, the DSPRO process, as an alternative to the single Pressure Retarded Osmosis (PRO) process, achieved up to a 22% rise in the energy output. The optimum ratio of the feed to draw solution flow rates was less than in the conventional process of equal flow rates. Additionally, it has been noticed that the feed solution flow rate is the most dominant parameter affecting the DSRO process performance, followed by the draw solution flow rate and then the hydraulic pressure.

Interestingly, the hydraulic pressure at optimum operating conditions was slightly higher than the average osmotic pressure gradients in the DSPRO system. The study also clarified that power generation in the DSPRO process operating at constant mass transfer and solute resistivity parameters was overestimated by 2.8%. Results presented that the effect of the hydrodynamic conditions on the total specific power generation was higher than the effect of the pressure drop on the specific power generation in the DSPRO system.

Moreover, a distributed system model of a two-dimensional radial flow Hollow Fibre Pressure Retarded Osmosis (HFPRO) module is implemented using the object-oriented modelling (OOM) approach of Modelica language and the Dymola software tool. In the modelling approach discussed in Chapter four, the single membrane module is divided into ($n \times m$) control volumes, where “ n ” represents the number of grids in the axial direction and “ m ” represents the number of grids in the radial direction. All $n \times m$ control volumes are interconnected using Modelica’s OOM flowsheet modelling approach to get an integrated model of a single radial flow hollow fibre module. The mass and momentum balance equation is coupled with the membrane transport and concentration polarization model for water and solute flux terms in each control volume. The

integrated model equations are solved using a nonlinear solver (DASSL) in the Dymola software. The optimal size of the grid in both radial and axial directions is calculated from the grid-independent test for the given module and fibre dimension. Finally, PRO experiments are performed in the pilot plant using Toyobo's radial flow HFPRO module with feed solution in the fibre lumen side (axial direction) and draw solution in the shell side (radial direction). The model was validated with experimental data and showed a maximum error of 9.4%. The validated radial flow HFPRO model calculates the net optimal energy generation of the PRO system integrated with ERD, turbine, and pumps. The calculated optimum net energy generated from the PRO process is 0.15 kW.h/m^3 at a 42% PRO recovery rate, much higher than the calculated energy generation by the axial flow module of 0.0015 kW.h/m^3 at a 50% PRO recovery rate.

Next, an investigation of the significance of the energy generated by the dual-stage pressure retarded osmosis (DSPRO) from the reverse osmosis (RO) brine stream was considered. The main units of the DSPRO-RO hybrid system are RO, pressure retarded osmosis (PRO), and energy recovery device, and their models are considered. Dymola software, using Modelica modelling language, was utilized to solve the hybrid system models. Two different flowsheets were built; the first included a two-pass RO, while the second was a hybrid of a two-pass RO (2RO)-DSPRO system. Seawater salinities of 40 and 45 g/L were the RO feed solution, and 1 g/L tertiary treated wastewater was the feed solution of the DSPRO system. The net specific energy consumption was calculated for the 2RO and 2RO-DSPRO systems for 40 and 45 g/L salinities. At a 47% recovery rate and 40 g/L seawater salinity, the 2RO-DSPRO system was 14.7% more energy efficient than the 2RO system. The corresponding energy saving at a 47% recovery rate and 45 g/L seawater salinity was 17.5%. The desalination energy for the 2RO system was between 3.25 and 3.49 kWh/m^3 , and the 2RO-DSPRO system was between 2.91 and 2.97 kWh/m^3 . The reduction of energy consumption was higher at higher seawater salinity gradients. The results demonstrate the great potential of integrating the 2RO with the DSPRO to lessen desalination's energy consumption and environmental impacts. Furthermore, employing a commercially available hollow fiber PRO element manufactured by Toyobo Company (Japan), boasting a substantial membrane area of 63 m^2 , and demonstrating noteworthy energy savings of 18%, is poised to incentivize further investment in the PRO process within the industrial sector.

The experimental work on the PRO requires expensive infrastructure, is time-consuming, and is affected by environmental and technical parameters. Laboratory work is necessary to determine the membrane's intrinsic parameters, such as the membrane water permeability, the salt permeability, and the structural parameter, that impact the process performance. High PRO pressures lead to membrane deformity and dynamically changing membrane intrinsic parameters. Determining the membrane's exact intrinsic parameters in a full-scale PRO module is challenging

and time-consuming, and assuming constant parameters will compromise the accuracy of the results and power generation in the PRO system. Therefore, Chapter Five in the thesis reported the usage of the artificial neural networks and Boosting-based tree models to predict the intrinsic parameters of the pressure retarded osmosis membrane based on the minimum theoretical power density that could be predetermined and was assumed to be 5 W/m^2 in this research. The Random Forest and XGBoost algorithms demonstrate superior predictive power ($R^2 = 0.97$) compared to the other examined machine learning algorithms. The results reveal that machine learning algorithms can provide significant predictive power for the membrane's intrinsic parameters and power density based on the input parameters. Additionally, the algorithms were used to evaluate the feature importance of each input parameter affecting the power density of the pressure retarded osmosis membrane. The highest feature importance of the water permeability coefficient was feed type equal to 25 for the XGBoost and 0.035 for the Random Forest, followed by water flux, which is 15 for the XGBoost and 0.20 for the Random Forest. Pointing out the high impact of the feed type and the water flux on evaluating the water permeability coefficient. On the other hand, the feature importance results showed that the lowest feature importance was in the applied pressure difference, which clarifies that this parameter has the most negligible impact on the water permeability coefficient.

Interestingly, the water permeability was the parameter with the highest impact on the salt permeability. The XGBoost model shows the highest feature importance on the membrane structural parameter, the draw concentration. In contrast, the feed flow rate was the highest feature importance of the membrane structural parameter found by the Random Forest model. The draw concentration was the most critical parameter affecting the PRO power density because the salinity of the draw solution governs the osmotic pressure difference along the membrane, and the latter directly relates to the water flux and, consequently, the power density.

Furthermore, applying a multiplestage PRO scenario is one suggestion to boost the generated energy in the PRO process. Accordingly, Chapter Six in the thesis evaluated the benefit of multiple stages of pressure retarded osmosis on specific energy generation. Single, dual, ternary, and quaternary pressure retarded osmosis stages were investigated for power generation using four membrane modules in the PRO process. Eight designs were proposed to cover the arrangement of the membrane modules in a single, dual, ternary, and quaternary PRO process and estimate the net-specific energy generation of pressure retarded osmosis. For each design, the variation in the total energy input and the total energy output of single and multistage pressure retarded osmosis processes were calculated. The water flux and the power density enhanced with the number of stages for the investigated multistage PRO scenarios. For instance, the QSPRO scenario will produce 362% higher water flux than the SSPRO scenario. The maximum water

flux and power density resulted in four PRO stages of values equal to 6 L/m².h and 15 W/m², respectively. For the Dead Sea-reverse osmosis brine salinity gradient, a 33.96% rise in the net specific energy generation is observed in the quaternary-stages pressure retarded osmosis scenario. The Dead Sea and wastewater salinity gradients produced the highest net specific energy generation of 0.82 kW.h/m³ over the other investigated types of salinity gradients. The outcomes revealed that the applied pressure has the most dominant impact on the behaviour of the QSPRO scenario compared to the feed solution and the draw solution flow rates, and it is preferred to be equal to or slightly less than $\Delta\pi/2$. The net specific energy generation increased with reduced applied pressure in the QSPRO scenario.

7.2 Future work

Pressure retarded osmosis would have a bright future in the renewable energy field if more research is conducted. A few points need to be further addressed in the future research. For instance, one of the existing obstacles for the PRO technique is discovering a commercial membrane with the forward osmosis membrane's characteristics (for diminishing the phenomenon of concentration polarization, superior rejection, and increased permeability) and the reverse osmosis membrane's characteristics (for handling high hydraulic pressure with minimal structural parameter). Laboratory and pilot scale experiments would be highly recommended to compare the behaviour of the commercial PRO membranes and the promising laboratory-fabricated PRO membranes. To date, the benchmark for the membrane characteristics required for PRO to be economically viable has not been reported. This may be attributed to variations in the membrane characteristics depending on the type of membranes used in the PRO process, the salinity gradients employed, and differences in the operating conditions of the PRO system. For instance, it has been reported that the use of thermally rearranged thin-film composite membranes could yield remarkably high power density, reaching approximately 40 W/m². This is attributed to the elimination of the internal concentration polarization's impact on the PRO process. [51]. However, it is worth mentioning that there are commercial membranes available for the PRO system, such as the 5-inch and 10-inch HF Cellulose triacetate (HF-CTA) membranes manufactured by Toyobo Co Ltd, spiral-wound Polyamide thin-film composite (PA-TFC) membranes manufactured by Hydration Technology Innovations (HTI), spiral-wound Cellulose triacetate (CTA) membranes manufactured by Hydration Technology Innovations (HTI), and spiral-wound Polyamide membranes manufactured by Toray Chemical [27].

Additionally, a DSPRO-thermal plant hybrid model could be examined. As the concept of coupling single-stage PRO with a thermal plant has been addressed previously [26, 191], using DSPRO through modelling would have promising results. The primary purpose of the DPRO with

a multistage flashing hybrid system is to reduce the impact of brine reject before discharge to sea and power generation. The brine from the multistage flashing unit will be sent to the first DPRO stage for dilution and pressurization, and then the diluted draw stream out from that stage will be sent to stage two. The outlet draw stream from the second DSPRO stage will be sent to an energy recovery device for power generation.

Pump storage technology is one of the most common techniques for energy storage. This technique uses water flowing through a turbine to produce and use electricity on demand. Power is stored as water is pumped to an elevated reservoir from a lower reservoir through low electricity demand and stored till needed in the power facility [321]. The stored hydropower will be utilized throughout high electricity demand by ejecting the water in the upper reservoir through turbines as a conventional hydropower unit. The pump storage technology is efficient due to the variations in the electricity prices at peak and off-peak times and its advantage as an auxiliary part for providing power as needed. This leads to combining a multistage PRO system and a hydroelectric storage unit. Freshwater and seawater could be the feed and draw solutions, respectively, of the first PRO stage. Due to the increase in the draw solution volume as the freshwater permeates across the PRO membrane, the hydroelectric power will be enhanced. The pressurized draw solution will be stored in the upper reservoir as a pumped head, which can be utilized throughout high electricity demand. The operating parameters include the feed and draw solutions flow rates. The applied hydraulic pressure and the membrane type could be investigated and optimized to determine the hydroelectric storage's best configuration. Despite the existence of hybrid systems coupling photovoltaics, wind energy, or bioenergy with pumped storage technology as reported in the literature [322, 323], to the best of our knowledge there has been no study demonstrating the possibility of integrating PRO with the pump storage technology up to the present date.

Combining DSPRO with thermal plants holds greater potential compared to energy storage, as thermal power technology has undergone extensive development. Conversely, energy storage through PRO is still in its nascent stage and requires further research before transitioning to the pilot scale.

Finally, a pilot-scale PRO plant operation is necessary to realize the advantages of the multiplestage PRO system over a single stage. The lack of multiplestage PRO plant test will rise questions about the design benefit's CAPEX and OPEX, such as lower membrane fouling and higher water flux and power generation.

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Appendix

A.1: The impact of the optimum hydraulic pressure

Water flux of the DSPRO system reduces across the membrane modules due to the lessening of the osmotic power through the membrane length. In stage two of the DSPRO, a fresh feed solution was used, increasing the osmotic pressure and water flux. Determination of the optimum value of the applied pressure in the DSPRO system showed a reduction in the water flux for 5M-1.2M SGR (**Fig. A1**). The optimum applied pressure was higher than the applied pressure in the conventional DSPRO system, reducing the amount of water permeation through the membrane modules in both DSPRO stages. This explains the drop in the water flux due to the usage of the optimum hydraulic pressure.

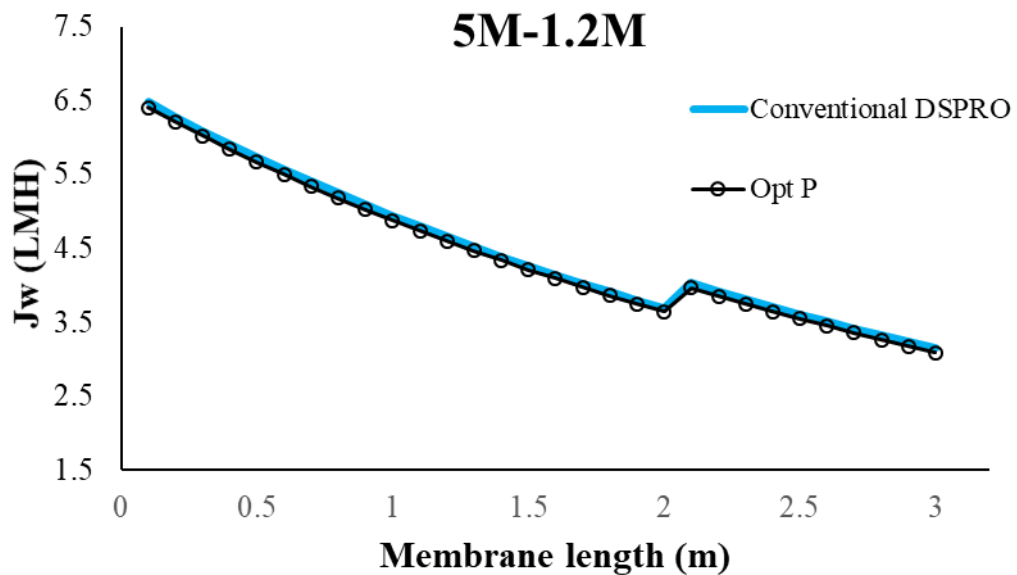


Fig. A1: Water flux along the membrane modules in the DSPRO system where two modules in stage one and one module in stage two for 5M-1.2M SGR. $P_{Di,1}$ is 92.57 bar and equal flow rates of 1000 L/h of the feed and the draw solutions in the conventional case. While $P_{Di,1}$ is 93.83 bar at 1000 L/h feed flow rate and 1000 L/h draw flow rate for the DSPRO process at optimum pressure.

A.2: The impact of variation of mass transfer, solute resistivity and pressure drop on water flux

The impact of variation in mass transfer, solute resistivity, and pressure drop along the membrane modules in DSPRO processes was considered for 5M-0.6M, 5M-1.2M, 1.2M-0.02, and 0.6M-0.02M. **Fig. A2** shows the variation in the water flux along the membrane modules of the DSPRO processes performed in case 1, case 2, and case 3 for all SGRs. For all SGRs; higher water flux in the first DSPRO stage was obtained in case 1 followed by case 2 and case 3, which means that considering the variation in k_d , K , and the pressure drop in the DSPRO processes improves the water permeation through the membrane in the first DSPRO stage. Higher water flux at the second DSPRO stage performed in case 2 resulted for all SGRs, representing that ignoring the variation of k_d and K along the DSPRO membrane modules will overestimate the water flux at the second DSPRO stage. Ignoring the pressure drop at the DSPRO processes performed in case 3 displayed lower water flux for all SGRs than the DSPRO processes performed in case 2. The figure shows that the water flux is influenced by k_d , K and the pressure drop in the DSPRO processes for all SGRs, and their impacts cannot be ignored.

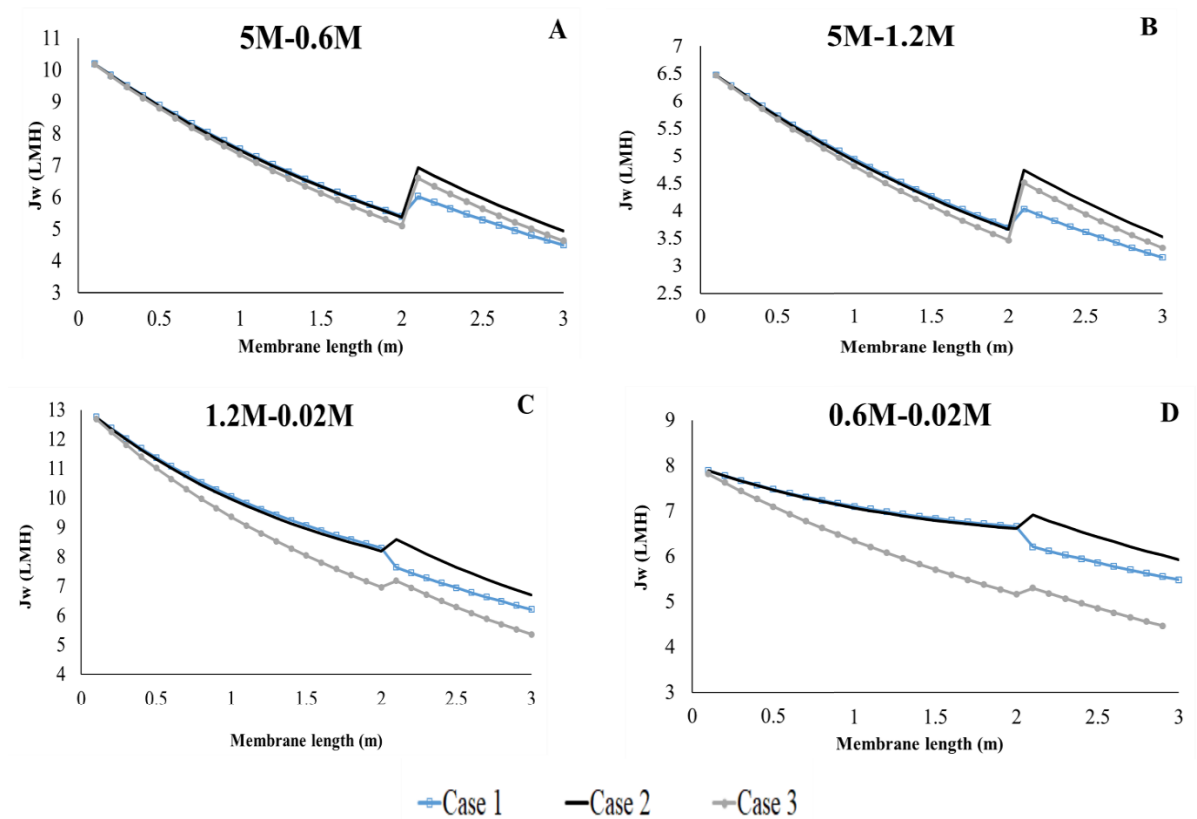


Fig. A2: The variation in the water flux along the membrane modules in the DSPRO processes performed at case 1, case 2, and case 3 for 5M-0.6M (**figure A**), 5M-1.2M (**figure B**), 1.2M-0.02M (**figure C**), and 0.6M-0.02M (**figure D**).

A.3: The impact of variation of mass transfer, solute resistivity and pressure drop on permeation rate and the hydraulic pressure

As discussed earlier, the variation of k_d , K , and the pressure drop affect the DSPRO process's performance represented by the specific power generation. The applied hydraulic pressure controls the specific power generation, permeation flow rate, feed, and draw solutions flow rates. Since the feed and the draw solutions flow rates are the same for all the cases presented in section 3.4.7; then the difference in specific power generation between the SGRs was governed by the permeation flow rate and the applied hydraulic pressure. Accordingly, the combined effect of the permeation rate (Q_p) and the applied hydraulic pressure (P) was studied and shown in **Fig. A3**. The figure shows the permeate flow rate times the applied pressure for the DSPRO processes of 1.2M-0.02M and 0.6M-0.02M performed at case 1 and case 3. $Q_p \cdot P$ is higher for the DSPRO process performed at case 1 for 1.2M-0.02M than in case 3. The water flux of the DSPRO process of 1.2M-0.02M performed in case 1 showed higher values than the water flux of the DSPRO process performed in case 3 (**Fig. A2C - Appendix**). For the DSPRO process performed in case 3, the pressure drop was ignored, and then the optimum applied pressure was higher than the DSPRO process performed in case 1.

Nevertheless, the combined effect of the lower permeate flow rate and higher applied pressure caused a reduction in $Q_p \cdot P$ for the DSPRO process at case 3 compared to case 1, which explains that Eo_{tot} for the DSPRO process of 1.2M-0.02M was lower in case 3 compared to case 1 (**Fig. 3.10C**). The scenario was the opposite of the DSPRO process of 0.6M-0.02M. $Q_p \cdot P$ is lower for the DSPRO process performed at case 1 for 0.6M-0.02M than in case 3. The water flux of the DSPRO process of 0.6M-0.02M performed in case 1 showed higher values than the water flux of the DSPRO process performed in case 3 (**Fig. A2D - Appendix**). For the DSPRO process performed in case 3, the pressure drop was ignored, and then the optimum applied pressure was higher than the DSPRO process performed in case 1. Then, the combined effect of the lower permeate flow rate and higher applied pressure caused enhancement in $Q_p \cdot P$ for the DSPRO process at case 3 compared to case 1, which explains that Eo_{tot} for the DSPRO system of 0.6M-0.02M was higher in case 3 compared to case 1 (**Fig. 3.10D**).

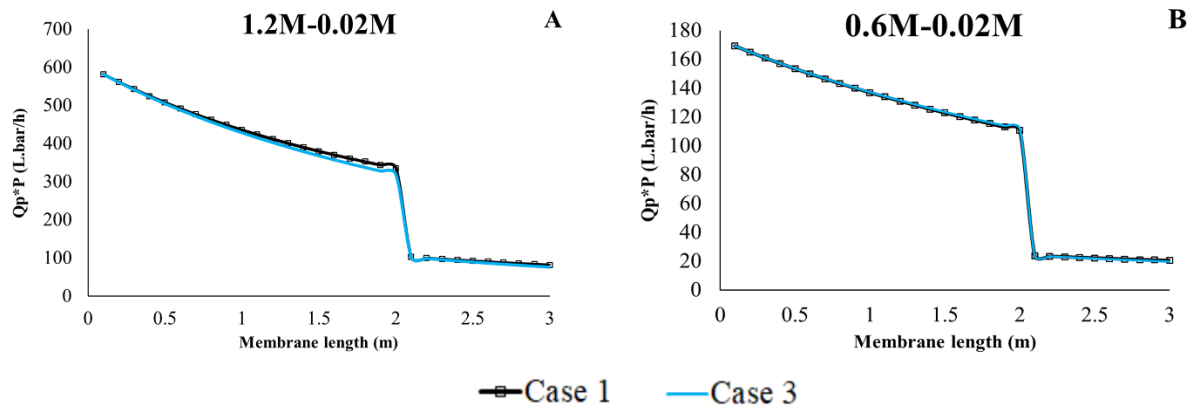


Fig. A3: The variation in the permeated flow rate times the effective applied pressure along the membrane modules in the DSPRO processes performed at case 1 and case 3 for 1.2M-0.02M (figure A) and 0.6M-0.02M (figure B).

A.4: The impact of recovery rate on the DSPRO net pressure difference

The net pressure difference between stage one and stage two of the DSPRO system is calculated as $(\Delta\pi - \Delta P)$ and shown in **Fig. A4** concerning the RO1 recovery rate. As shown in the figure, for the PRO2 of the S2-C2 system, there was a sharp drop in the net pressure difference along the membrane with the recovery rate increase. In contrast, for the PRO1 of the S2-C2 system, the net pressure difference across the membranes increased with the recovery rate increase. Technically, the RO brine concentration increases with recovery rates increase, leading to an increase in the osmotic pressure of the PRO1 draw solution. Nevertheless, the PRO2 draw solution is the high-pressure outlet stream of ERD1 (**Fig. 4.1**). The concentration of this stream decreases with the increase of the RO recovery rate. Therefore, the net pressure difference of the second DSPRO stage of these two systems decreases with the recovery rate. In general, the concentration of the PRO 1 draw solution is higher at elevated RO1 recovery rates, increasing the performance of the PRO1.

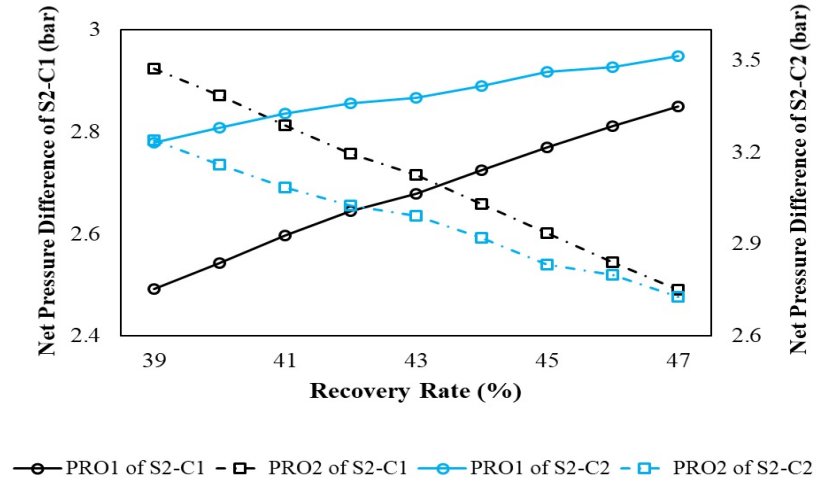


Fig. A4: The net pressure difference of the PRO1 and PRO2 of System 2 with the variation of the recovery rate.

A.5: The plug flow PRO model simulation results

The following table represents the results of the simulation of the suggested PRO model used in Chapter Six.

Table A.1: The outputs and the parameters of the PRO process simulation.

Input	Value
Feed inlet flow rate, Q_{Fi} (m ³ /h)	1
Feed inlet concentration, C_{Fi} (g/L)	70.13
Feed inlet pressure, P_{Fi} (bar)	1
Draw inlet flow rate, Q_{Di} (m ³ /h)	1
Draw inlet concentration, C_{Di} (g/L)	292.20
Draw inlet pressure, P_{Di} (bar)	90
Parameter	Value
Area of the single membrane, A_m (m ²)	63
Vont's Hoff factor, i	2
Universal gas constant, R (m ³ .bar/(mol.K))	0.00008314
Molecular weight of NaCl, M_{wt} (g/mol)	58.5
Constant in mass transfer coefficient relation, x (bar.s/m ⁴)	0.002068

Constant in mass transfer coefficient relation, y	0.501
Membrane water permeability, A_w (m/(bar.s))	$1 \cdot 10^{-7}$
Membrane salt permeability, B (m/s)	$6.235 \cdot 10^{-9}$
Membrane structural parameter S (m)	$880 \cdot 10^{-6}$
Output	Value
Feed outlet flow rate, Q_{F0} (m ³ /h)	0.76
Feed outlet concentration, C_{F0} (g/L)	880.01
Draw outlet flow rate, Q_{D0} (m ³ /h)	1.24
Draw outlet concentration, C_{D0} (g/L)	243.116
Feed outlet pressure, P_{F0} (bar)	0.81
Draw outlet pressure, P_{D0} (bar)	89.89

Supplementary information S1

Plots of loss vs Epochs or iterations for all models.

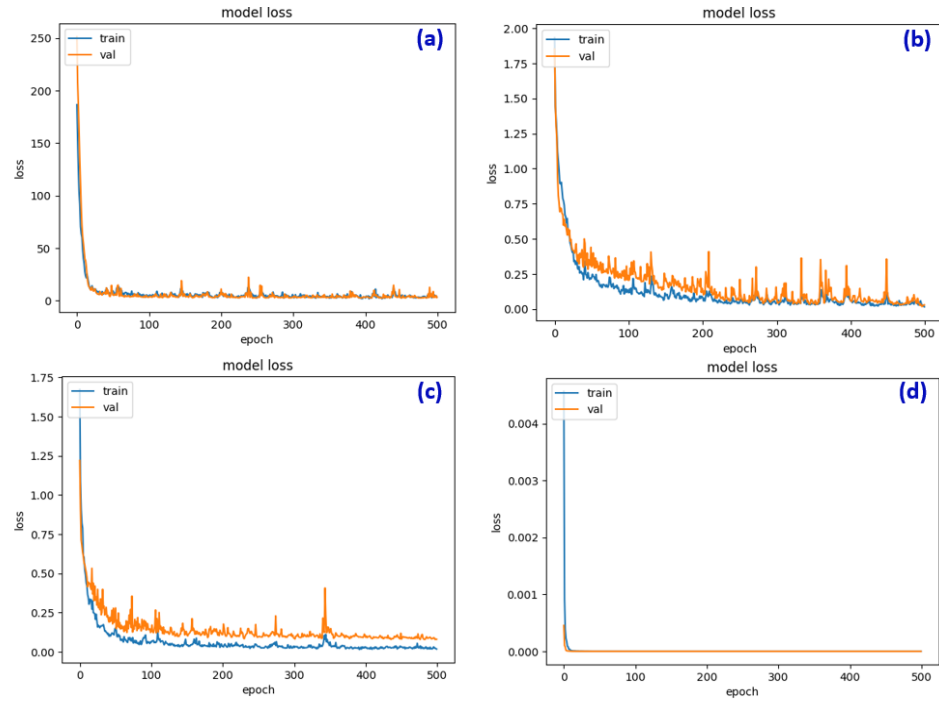


Figure S1: Number of epoch vs loss for artificial neural networks, **a)** power density **b)** pure water permeability A_w , **c)** salt permeability B , and **d)** structural parameter S .

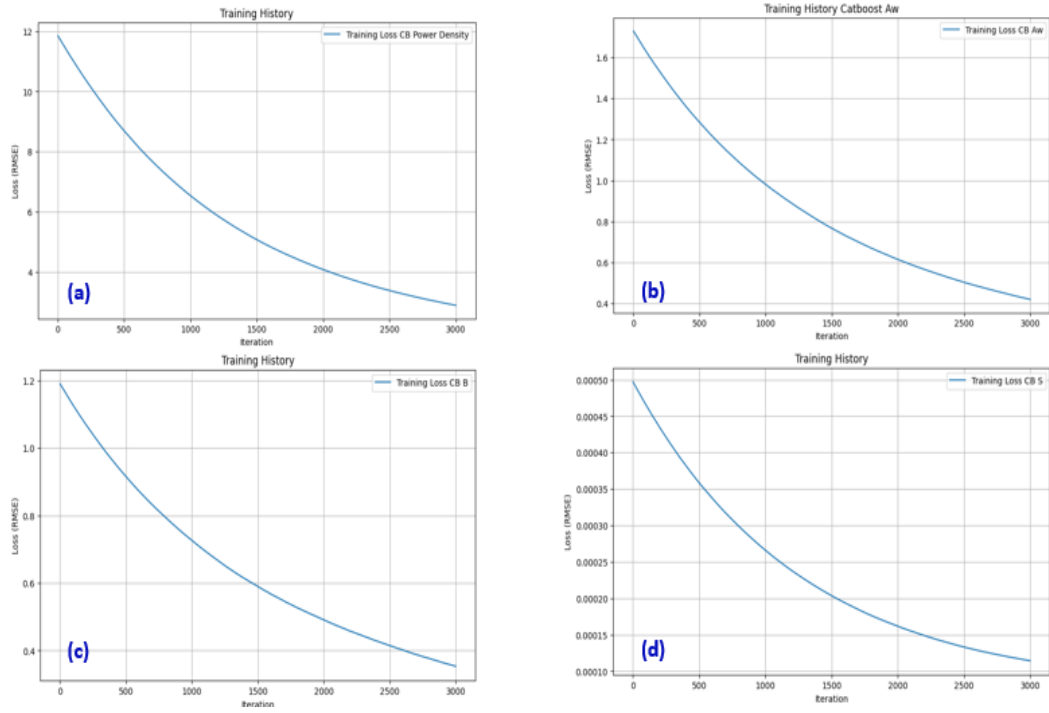


Figure S2: Loss and iteration curves for CatBoost, **a)** power density, **b)** pure water permeability A_w , **c)** salt permeability B , and **d)** structural parameter S .

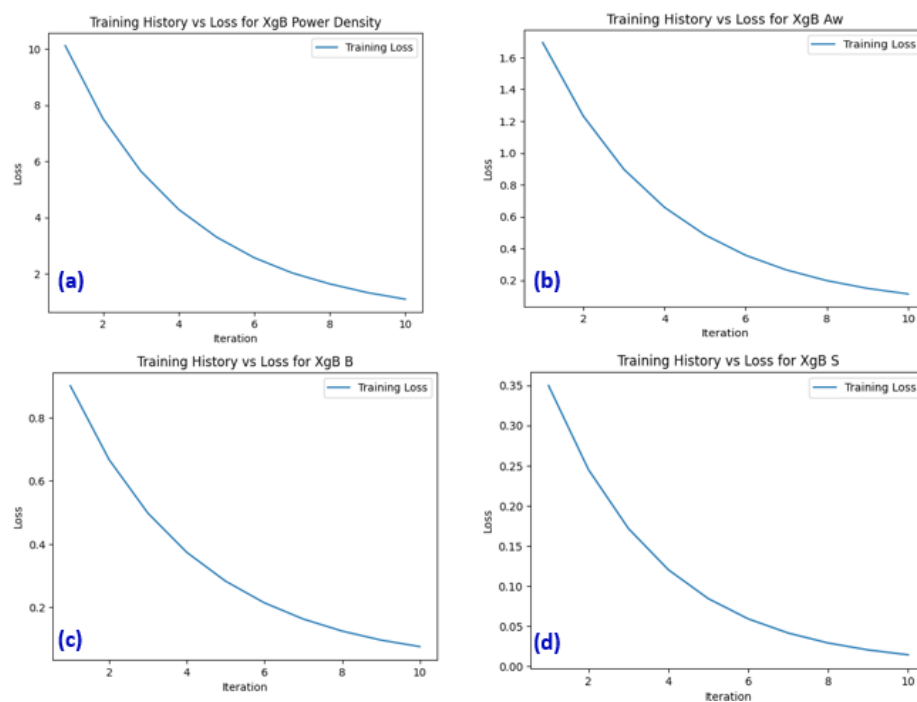


Figure S3: Loss and iteration curves for XgBoost, **a)** power density, **b)** pure water permeability A_w , **c)** salt permeability B, and **d)** structural parameter S.