PRACTICAL CONSIDERATIONS FOR FULL-SCALE APPLICATION OF HYBRID FORWARD OSMOSIS SYSTEM:

ASSESSMENT THROUGH PILOT-SCALE EXPERIMENTS AND FULL-SCALE SIMULATIONS

by

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Doctoral of Philosophy

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CERTIFICATE OF AUTHORSHIP/ORIGINALITY

I certify that this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledge within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis. I also acknowledge that this study was supported by Australian Government Research Training Program.

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2. **Kim, J. E.;** Phuntsho S.; Shon H. K.,Fertiliser drawn forward osmosis process: Pilot-scale desalination of mine impaired water for fertigation, International Forward Osmosis Summit (IFOS), 2-4 December 2016, ***Awarded the Best Poster Presentation***.
3. **Kim, J. E.;** Phuntsho S.; Shon H. K., Fertiliser drawn forward osmosis process: Pilot-scale desalination of mine impaired water for fertigation, International Water Association (IWA), 9-13 October 2016, Poster Presentation.
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Presentations made during the Ph.D. candidature including oral and poster presentations.

LIST OF ABBREVIATIONS

AOP	Advanced oxidation process
BWRO	Brackish water reverse osmosis
CA	Cellulose acetate
CAPEX	Capital expense
CC	Membrane cleaning chemicals
CNT	Carbon nanotube
CP	Concentration polarization
CS	Corrugated spacer
CTA	Cellulose triacetate
DDS	Diluted draw solution
DI water	Deionized water
DS	Forward osmosis
EC	Electrical conductivity
EC	Energy
ECP	External concentration polarisation
ED	Electrodialysis
EDTA	Ethylenediaminetetraacetic acid
EP	Eutrophication
ET	Ecotoxicity
FDFO	Fertiliser driven forward osmosis
FMR	Fossil fuel and mineral resource
FO	Forward osmosis
FS	Feed solution
GAC	Granular activated carbon
GO	Graphene oxide
GW	Global warming
HF	Hollow fibre
HTI	Hydration technology innovations
HTI	Human toxicity
ICP	Internal concentration polarisation

IP	Interfacial polymerization
LCA	Life cycle assessment
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
LPRO	Low-pressure reverse osmosis
MBC	Membrane brine concentrator
MBR	Membrane bioreactor
MD	Membrane distillation
MDC	Microbial desalination cells
MED	Multi-effect distillation
MF	Microfiltration
MNPs	Magnetic nanoparticles
MR	Membrane replacement
MS	Medium spacer
MSF	Multi-stage flash
MW	Molecular weight
NF	Nanofiltration
OD	Osmotic dilution
OD	Ozone depletion
OMBR	Osmotic membrane bioreactor
OPEX	Operational expense
PA	Polyamide
PAA	Polyacrylic acid
PAFO	Pressure-assisted forward osmosis
PAO	Pressure-assisted osmosis
PAspNa	Poly aspartic acid sodium salt
PBI	Polybenzimidazole
PES	Polyethersulfone
PET	Polyethylene terephthalate
PRO	Pressure retarded osmosis
PSf	Polysulfone
PV	Photovoltaic
rGO	Reduced graphene oxide

RO	Reverse osmosis
ROSA	Reverse osmosis system analysis
RSF	Reverse solute flux
RSS	Red sea salt
SEC	Specific energy consumption
SOA	Ammonium sulphate or $(NH_4)_2SO_4$
SRSF	Specific reverse solute flux
SRT	Solids retention time
SWFO	Spiral wound forward osmosis
SWRO	Seawater reverse osmosis
TDS	Total dissolved solids
TFC	Thin-film composite
TFI	Thin-film inorganic
TFN	Thin-film nanocomposite
TMA	Trimethylamine
TOC	Total organic carbon
TREG	Triethyleneglycol
TrOCs	Trace organic compounds
UF	Ultrafiltration
VMD	Vacuum membrane distillation
WHO	World health organization
WPT	Wastewater treatment plant
ZLD	Zero-liquid discharge

LIST OF SYMBOLS

A	Pure water permeability coefficient	$Lm^{-2}h^{-1}bar^{-1}$
μ	Dynamic viscosity	
B	Salt permeability coefficient	ms^{-1}
C	Molar solute concentration	Moles or M
C_{D0}	Initial draw solution concentration	Moles or M
C_{Db}	Bulk draw solution concentration	Moles or M
C_{F0}	Initial feed solution concentration	Moles or M
C_{Fb}	Bulk feed solution concentration	Moles or M
D	Solute diffusivity	m^2s^{-1}
D_D	Diffusion coefficient of the draw solute	m^2/s
D_F	Diffusion coefficient of the feed solute	m^2/s
d_h	Hydraulic diameter	m
D_h	Diffusion coefficient of the feed channel	m^2/s
J_s	Salt flux	$gm^{-2}h^{-1}$ or $mmolesm^{-2}h^{-1}$
J_w	Water flux	$Lm^{-2}h^{-1}$
k	Mass transfer coefficient	
K	Solute resistivity	sm^{-1}
L	Length of channel	m
M	Molar concentration of the solution	Moles or M
M_w	Molecular weight	Mole/g
P	Applied pressure	Bar
Q_{D0}	Initial draw flow rate	L/min
Q_{F0}	Initial feed flow rate	L/min
Q_P	Permeate flow rate	L/min
R	Salt rejection	%
Re	Reynolds number	
RR_{FO}	Forward osmosis feed recovery	%
S	Structural parameter	m
Sc	Schmidt number	
Sh	Sherwood number	

Π	Osmotic pressure	bar
$\Delta\Pi$	Net osmotic pressure	
$\Pi_{D,b}$	Bulk draw osmotic pressure	bar
$\Pi_{D,m}$	Osmotic pressure at support layer	bar
$\Pi_{F,b}$	Bulk feed osmotic pressure	bar
$\Pi_{F,m}$	Osmotic pressure at active layer	bar
ρ	Solution density	

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ABSTRACT

Forward osmosis (FO) has recently emerged as one of the most promising low energy technologies for desalination and water reclamation. The FO process is based on the principle of natural osmotic process driven by the concentration difference between a concentrated draw solution (DS) and saline water (i.e. feed water, FS) across a semipermeable membrane. In the FO process, fresh water is extracted from the saline water using special osmotic membranes and the concentrated DS becomes diluted. The membrane fouling problem in FO process is less challenging than the reverse osmosis (RO) process mainly as the FO process operates in the absence of high hydraulic pressure, and this is one of the important operational benefits for FO process application in terms of energy. However, the lack of a desirable DS has limited the application of FO desalination for producing drinking water quality. When a normal inorganic salt solution is used as DS, the recovery of draw solutes from the diluted DS require additional subsequent processes that still require energy and this makes FO unattractive compared to the existing RO desalination technology.

The objectives of this study are therefore to investigate the performances of the hybrid FO systems mainly through pilot-scale operations and simulation for different applications, identify its limitations, evaluate its environmental impacts and conduct economic analysis. The Thesis has been presented in nine chapters that include an assessment of the performance of selected draw solutes under a closed-loop system, practical applicability of FO hybrid system through both simulation and module-scale experiments, and development of a simulation software to design FO process for optimum performance. Most of the chapters are in part or in whole already published during the course of this Ph.D. candidature as listed at the beginning of this Thesis.

Considering the challenges of the FO process for potable water desalination, a novel concept of fertilizer drawn forward osmosis (FDFO) has been introduced. In this process, a highly concentrated fertilizer solution is used as the DS to extract water from saline water sources or any impaired water source using a semi-permeable membrane by natural osmosis. The main advantage of the FDFO desalination process is that the final product water or the diluted fertilizer DS, can be used for direct fertigation and thus the separation

of draw solutes is not necessary. However, due to intrinsic process limitations, the diluted fertilizer DS may not meet the water quality standards for direct fertigation especially when feed water sources with high salinity are used. The final diluted DS may require additional dilution before it is suitable for the direct application and the dilution factor can be quite significant depending on the feed water salinity. To reduce the salt concentration of the diluted DS, the nanofiltration (NF) process has been suggested as one of the post-treatment process options to reduce fertilizer nutrient concentrations in the diluted fertilizer DS. The concept of the integrated FDFO desalination process with NF membrane has been evaluated in bench-scale experiments in the earlier studies. However, in this study, this concept has been demonstrated in a larger-scale in the field.

The pilot-scale FDFO and NF system was operated in the field for about six months for the desalination of saline groundwater from the coal mining activities. Although the FO flux can be significantly lowered when high turbidity feed water is used, however; our long-term operation of the FO pilot-scale indicates that simple hydraulic cleaning could effectively restore the water flux without the need for a rigid chemical cleaning. The NF post-treatment process did not experience any noticeable fouling or scaling issues due to the excellent quality of feed water produced by the FDFO process. Test fertigation of the turfgrass and potted tomato growth indicates that FDFO-NF desalination system can produce water quality that meets irrigation standard. However, FO membrane with higher reverse flux selectivity than the cellulose triacetate FO membrane used in this study is needed for scale-up operation of the FDFO desalination process. The reverse diffusion of draw solutes will be one of the biggest challenges of the FDFO process as the nitrogen concentration in the final concentrated brine may not satisfy the effluent discharge standards. Low FO feed rejection may also likely to result in the gradual build-up of feed solutes (such as Na^+ and Cl^-) in fertiliser draw solution during repetitive recycling of the draw solution by the subsequent NF process consequently affecting the final water quality in terms of Na^+ and Cl^- which can be detrimental to the whole process.

Based on the long-term operational data of the FDFO-NF desalination process, environmental and economic impacts of the FDFO-NF hybrid system were conducted and compared with conventional RO hybrid scenarios using microfiltration (MF) or ultrafiltration (UF) as a pre-treatment process. The results showed that the FDFO-NF hybrid system using thin film composite forward osmosis (TFC) FO membrane has a less environmental impact than the conventional MF or UF based RO hybrid systems due to lower consumption of energy and cleaning chemicals. The energy requirement for the treatment of mine impaired water by the FDFO-NF hybrid system was 1.08 kWh/m^3, which is 13.6% less energy than an MF-RO and 21% less than UF-RO hybrid system under similar feed conditions. In a closed-loop system, the FDFO-NF hybrid system using a TFC FO membrane with an optimum NF recovery rate of 84% had the lowest unit operating cost of AUD $\$0.41/m^3$. Given the current relatively high price and low flux performance of the cellulose triacetate (CTA) and TFC FO membranes, the FDFO-NF hybrid system still holds opportunities to lower the operating expenditure further in the future when high performance membranes are available in the market.

In addition, environmental and economic life cycle assessment (LCA) was carried through the simulation of a full-scale closed-loop FO and RO or NF hybrid system for selecting the most suitable DS. Baseline environmental LCA showed that the dominant components for energy use and global warming are the DS recovery processes (i.e., RO or NF processes) and FO membrane materials, respectively. When considering the DS replenishment in the FO process, the contribution of chemical use to the overall global warming impact was significant for all hybrid systems. Furthermore, from an environmental perspective, the FO-NF hybrid system with Na_2SO_4 shows the lowest energy consumption and global warming with additional considerations of final product water quality and FO brine disposal. From an economic perspective too, the FO-NF with Na_2SO_4 showed the lowest total operating cost due to its lower DS loss and relatively low solute cost. In a closed-loop system, FO-NF with NaCl and Na_2SO_4 as DS had the lowest total water cost at optimum NF recovery rates of 90 and 95%, respectively. Overall, draw solute performances and membrane cost in FO and recovery rate in RO/NF play a crucial role in determining the total water cost and environmental impact of FO hybrid systems in a closed-loop operation.

The operation of a large spiral wound forward osmosis (SW FO) module operation is essential to provide a better understanding and practical insight for a full-scale FO desalination plant. Therefore, two different 8” SW FO modules (i.e. 8040 CTA and TFC FO membrane modules) were investigated for their module-scale operations in terms of hydrodynamics, operating pressure, water and solute fluxes, fouling behavior and cleaning strategy. FO membrane module operation results indicated that, a significantly lower initial DS flow rate is essential in order to lower the pressure drop and also maintain lower pressure within the DS channel as exceeding the DS pressure above the feed pressure would undermine the integrity of the FO membrane. Under FO and pressure assisted osmosis (PAO, up to 2.5 bar) operations, the TFC FO membrane module featured higher water flux and lower reverse salt flux compared to the CTA FO membrane module. The fouling tests with both the FO membrane modules demonstrated that foulant deposition caused feed inlet pressure build-up, indicating that the FO fouling deposition likely occurred in the feed channel rather than on the membrane surface and the location of foulant deposition.

Performance of an FO hybrid system was evaluated for osmotic dilution of seawater using wastewater effluent as a feed source for simultaneous desalination and water reuse based on 8040 FO membrane module-scale experiments and the extrapolated empirical relationship. The main limiting criteria for module operation is to always maintain higher feed pressure than the draw pressure throughout for safe module operation. The study showed that a single membrane housing cannot accommodate more than 4 elements as the draw pressure exceeds the feed pressure. Six different FO modular configurations were proposed and simulated. A two-stage FO configuration with multiple housings (in parallel) in the second stage using same or larger spacer thickness reduces draw pressure build-up as the draw flow rates are reduced to half in the second stage thereby allowing more than 4 elements in the second stage housing. The lower values for feed pressure (pressure drop) and osmotic driving force in the second stage are compensated by operating under the pressure assisted osmosis (PAO) mode which helps enhance permeate flux and maintains positive pressure differences between the feed and draw chamber. The PAO energy penalty is compensated by enhanced permeate throughput, reduced membrane area, and plant footprint. The contribution of FO/PAO to total energy consumption was not significant compared to post RO desalination (90%) indicating that the proposed two-stage FO modular configuration is one way of making the full-scale FO operation practical for FO-RO hybrid system.

This thesis finally concludes with recommendations to develop high-performance membranes in terms of solute rejections, permeability and improved fouling resistance for its long-term performances. Improving the solute rejections in the form of low specific reverse solute flux is very important in order to eliminate the issue of brine contamination with the draw solutes especially containing fertilizer nutrients which becomes detrimental for brine management and discharge. High feed solute rejection is essential which otherwise would accumulate in the draw solution in a closed-loop FO-RO/NF hybrid system thereby undermining the product water quality. The current design of spiral wound FO membrane module also needs rethinking. There is a need to significantly improve the packing density of the FO membrane element in order to reduce its footprint and the capital cost since its current packing density is only about a third of the RO membrane element. The module also needs to improve its operational robustness as the current module has significant operational challenges in terms of pressure drop. Finally, the thesis recommends developing a simulation software that can be used for the full or module-scale FO process design and system analysis. A brief structural framework on the desing of the software also has been provided.