FERTILIZER DRAWN HOLLOW FIBER FORWARD OSMOSIS FOR DESALINATION

Submitted by

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Certificate of Authorship

I certify that the work in 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 acknowledged within the text.

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DEDICATED TO ALL THOSE WHO SPENT THEIR LIFE FOR THE WELFARE OF THE HUMANITY

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Table of Contents

Abstract

Continuous increase in fresh water demand has underscored the importance of developing a low cost water desalination process. Fertilizer drawn forward osmosis (FDFO) presents a promising step forward for low cost desalination using the natural osmotic pressure of the fertilizer draw solution (DS) as a driving force. FDFO carries a distinct advantage over other FO processes because the final diluted draw solution requires minimal to no treatment processes and it can be easily used for any useful fertigation application. This helps to eliminate the energy intensive permeate recovery step for the FO process and represents an economical desalination option. However, the performance ratio outcome for the earlier FO studies has highlighted a number of areas that can be improved in relation to FO performance.

This study evaluated FDFO using eight commercial fertilizers as DS for the flat sheet FO membrane using sea water (SW) quality feed (35 g/L NaCl) and targeting the NPK fertilizer and water requirements for tomato crops. Diverse results were achieved as some of the fertilizers showed significant flux while others showed negative or very low flux outcomes. This indicated that all commercial fertilizers may not be effectively used as DS for the SW quality feed. The results with various quality feed solutions (FS) and DS concentrations indicated that the flux performance does not vary in a linear sense with the changes in $\Delta\pi$. Varying flux outcome for various individual or mixed fertilizer DS's carrying similar $\Delta\pi$ values reflects the involvement of some unknown interactions between the DS and membrane surfaces, both at the active layer (AL) and the support layer (SL), for these specific results. These results further highlighted the fact that the osmotic pressure of the DS alone may not be used as the main criteria for the DS selection but rather the association between the DS

solutes and the active and support layers of the membrane are also vital in terms of understanding the FO flux performances.

In addition, these outcomes revealed a number of limitations in relation to the FDFO e.g. reverse solute flux issues, higher nutrients concentration in the final DS and low recovery for osmotic equilibrium issues.

These fertilizer DS's were further assessed and their performance was compared for cellulose triacetate (CTA) flatsheet and polyamide (PA) hollow fiber FO (HFFO) membranes to understand the association between the DS properties and the membrane characteristics for the FO outcome. It was observed that at similar operating parameters, the PA hollow fiber showed a comparatively better outcome in terms of flux and reverse solute flux (RSF). HFFO was also evaluated for the effects of various operating conditions and markedly enhanced performances were found. It was observed that for 2 M NaCl as DS and DI water as FS, the HFFO successfully delivered water flux of 62.9 LMH at DS/FS Reynolds number (Re) of 3750/1500 whereas the same membrane in AL-FS orientation showed a flux of 9.67 LMH at DS/FS Re of 200/500. This indicated a flux increase of about 511% for a set of two operating conditions for the same FO membrane which further suggested that the changes in the operating conditions induce some indistinct changes in the membrane structure that can affect the water transport phenomenon through the membrane. It is therefore recommended that further studies be undertaken to investigate the real mechanism for the water transport through the membrane as this could contribute to the development of a higher performing membrane for the FO process. Results also indicate that cationic and anionic parts of the DS seriously affect the RSF outcomes. Further evaluation in this regard may contribute towards the creation of a better DS for the FO process with reduced RSF consequences.

The HFFO membrane was further evaluated for inorganic scaling and organic fouling issues using brackish ground water quality FS loaded with various model organic foulants such as humic acid, alginate and bovine serum albumine (BSA). During these FO fouling studies, it was noted that the commonly used FO fouling protocol which is similar to the RO fouling protocol may not be successfully used to evaluate FO fouling. The RO fouling was evaluated against a fixed driving force (hydraulic pressure) and any changes in the flux performance were referred to the fouling impact. However, in FO, as the driving force (net osmotic pressure difference between the FS and DS) kept changing constantly, it was really difficult to predict any flux change which was particularly associated with the scaling or fouling. For any two tests, at any particular time, the FO did not show the same driving force and hence for the evaluation of the fouling, the flux comparison for two different curves was not always useful. Accordingly, a new protocol is suggested for the FO fouling studies.

The fouling results indicated that FO, like the RO membrane, also posed potential operational risks in terms of scaling and fouling. The HFFO membrane indicated varying degrees of fouling potential for the membrane used in the AL-FS and AL-DS orientation and these were not related to membrane properties. Instead the hydrodynamic conditions employed for the process affected the fouling potential of the membranes used. Results indicated that the higher crossflow rate helped to keep the membrane clean from inorganic scale and the turbulence shear force did not allow scale build-up at the high Re.

It was also observed that the inorganic scaling was not fully reversed for the HFFO membrane used in the AL-FS and AL-DS orientations which employed hydraulic cleaning practices because the cleaning totally depended on how the flow shear forces using various cross flowrates were applied on the membrane surface. For the organic foulants, the turbulence shear force could not overcome the membrane–foulant interactions and foulants

layer deposited on the membrane surfaces and reduce the FO performance which was not recovered by hydraulic flushing. The chemical cleaning which used HCl, NaOH and EDTA was evaluated and it was found that the EDTA (pH 11) showed a better outcome for FO membrane cleaning.

Keywords: Fertilizer drawn forward osmosis, draw solute, desalination, sea water, hollow fiber FO membrane, EDTA cleaning.

Journal Articles Published

1) **T. Majeed**, S. Sahebi, F. Lotfi, J.E. Kim, S. Phuntsho, L.D. Tijing and H.K. Shon, (2014) *Fertilizer-drawn forward osmosis for irrigation of tomatoes*, Desalination and Water Treatment, 1-14.

2) **T. Majeed**, F. Lotfi, S. Phuntsho, J.K Yoon, K. Kim,& H.K. Shon, (2013). *Performances of PA hollow fiber membrane with the CTA flat sheet membrane for forward osmosis process*. Desalination and Water Treatment**,** 1-11.

3) **T. Majeed**, S. Phuntsho, S. Sahebi, J.E. Kim, J.K. Yoon, K. Kim,& H.K. Shon,. (2014). *Influence of the process parameters on hollow fiber-forward osmosis membrane performances*. Desalination and Water Treatment**,** 1-12.

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6) **T. Majeed**, A. Rafiq, M. Yaseen, M. Y. Malik, M. Q. Shahbaz and M. S. A. Taj, (2011). *Some comments on HE's homotopy- perturbation method for solving higher-order boundary value problems*. Nonlinear Analysis Forum *16*, 137–146.

Conference papers and presentations

1. **Tahir Majeed** , Sherub Phuntsho, Ho Kyong Shon; *Evaluation of the scaling and fouling potential with appropriate cleaning strategies for hollow fiber forward osmosis membrane*, Civil and Environmental Engineering Research Seminar (CEERS) April 4, 2014, UTS, Sydney.

2. **Tahir Majeed**, Sherub Phuntsho, Ho Kyong Shon; *Hollow fiber forward osmosis desalination using fertilizers as draw solutes*, 8th International Membrane Science and Technology Conference (IMSTEC 2013), 25-29 November 2013, Melbourne, Australia

3. **Fezeh Lotfi**, Tahir Majeed, Sherub Phuntsho, Ho Kyong Shon; *Membrane fouling during fertilizer drawn forward osmosis desalination*, 8th International Membrane Science and Technology Conference (IMSTEC 2013), 25-29 November 2013, Melbourne, Australia

4. **Tahir Majeed**, Sherub Phuntsho, HoKyong Shon, *Performances of the CTA flat sheet and PA hollow fiber forward osmosis forward osmosis membranes: using fertilizers as draw solutes*, Civil and Environmental Engineering Research Seminar (CEERS), August 16, 2013, UTS, Sydney.

5. **Tahir Majeed**, Sherub Phuntsho and Ho Kyong Shon, Innovative Hollow Fiber Forward Osmosis Desalination for Fertigation, FEIT Showcase 2013, June 12, 2013, Faculty of Engineering & Information Technology, University of Technology Sydney (UTS), Sydney, Australia.

6. **Tahir Majeed**, Sherub Phuntsho, Ho Kyong Shon, Fertilizer draw forward osmosis (FDFO) desalination for fertigation: Application to Tomato, The 5th annual conference on the challenges in environmental science and engineering (CESE) Conference, 9 - 13 September 2012, Melbourne, Australia

7. **Tahir Majeed**, Sherub Phuntsho, HoKyong Shon, A low-energy fertiliser drawn forward osmosis desalination- Possible application for Tomato, Civil and Environmental Engineering Research Seminar (CEERS), August 24, 2012, UTS, Sydney.

8. **Tahir Majeed**, Sherub Phuntsho and HoKyong Shon; Novel Fertilizer draw forward osmosis (FDFO) desalination for fertigation: Application to Tomato, FEIT Showcase 2012, 13 June 2012, School of Civil & Environmental Engineering, Faculty of Engineering & Information Technology University of Technology Sydney (UTS), Sydney, Australia.

9. **Tahir Majeed**, Sherub Phuntsho, Ibrahim El Saliby, Ganesh Sharma, HoKyong Shon, *Mixed ferilizers as draw solutes for the fertilizer drawn forward osmosis desalination*, Civil and Environmental Engineering Research Seminar (CEERS), 28 October 2011, UTS, Sydney.

10. **Tahir Majeed**, Sherub Phuntsho, HoKyong Shon, Ibrahim El Saliby; *Blended Ferilizers as Draw Solution for the Fertilizer Drawn Forward Osmosis Desalination*, 6^{th} IWA Specialist Conference on Membrane Technology for Water and Wastewater Treatment, 4-7 October, 2011, Aachen, Germany

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13. Sherub Phuntsho, Hokyong Shon and **Tahir Majeed**, (2011). *Performance of Commercial bulk Fertilizer as Draw Solution for forward Osmosis Desalination. Paper presented at The Fourth Annual Conference on the Chanllenges in Environmental Science & Engineering*, Tainan City, Taiwan

Nomenclature

TDS	:	Total dissolved solids
MF	:	Microfiltration
UF	:	Ultrafiltration
NF	:	Nanofiltration
RO	:	Reverse osmosis
FO	:	Forward osmosis
FS	:	Feed solution
DS	:	Draw solution
AL	:	Active layer
SL	:	Support layer
MBR	:	Membrane biological reactor
FDFO	:	Fertilizer drawn forward osmosis
CP	:	Concentration polarization
ECP	:	External concentration polarization
ICP	:	Internal concentration polarization
PR	:	Performance ratio
RSF	:	Reverse solute flux
AL-DS	:	Active layer – draw solution
AL-FS	:	Active layer - feed solution
DI	:	Deionized
MED	:	Multi-effect distillation
MSF	:	Multi-stage flash distillation
VCD	:	Vapor compression distillation
MD	:	Membrane distillation
CDI	:	Capacitive deionization
BWRO	:	Brackish water reverse osmosis
ED	:	Electrodialysis
EDR	:	Electro dialysis reversal
PRO	:	Pressure-retarded osmosis
PBI	:	Polybenzimidazole
PSf	:	Polysulfone
PES	:	Polyethersulfone
PA	:	Polyamide
CA	:	Cellulose acetate
CTA	:	Cellulose triacetate
TFC	:	Thin flim composite
IP	:	Interfacial polymerization
CPSFs	:	Carboxylated polysulfones
PSF	:	Polysulphone
TFN	:	Thin film nanocomposite
PAI	:	Poly (amide-imide)

OMBR	:	Osmotic membrane bioreactor
HF	:	Hollow fiber
FSFO	:	Flat sheet forward osmosis
HFFO	:	Hollow fiber forward osmosis
PAO	:	Pressure assisted osmosis
EPS	:	Extracellular polymeric substances
BW	:	Brackish water
SW	:	Sea water
BGW	:	Brackish ground water
SIS	:	Salt interception scheme
MDB	:	Murray Darling Basin
MFDS	:	Mixed fertilizer draw solutions
NPK	:	Nitrogen; phosphorous; potassium
MAP	:	Mono ammonium phosphate
DAP	:	Di ammonium phosphate
SOA	:	Sulphate of Ammonia
CAN	:	Calcium nitrate
AN	:	Ammonium nitrate
AC	:	Ammonium chloride
BSA	:	Bovine serum albumin
HA	:	Humic acid
NOC	:	Natural organic carbon
EDTA	:	Ethylene di amine tetra acetic acid
SEM	:	Scanning electron microscope
FDDS	:	Final diluted draw solutions
LMH	:	$L/m^2/h$
AN	:	Ammonium nitrate
AC	:	Ammonium chloride
PWP	:	Pure water permeability
SRSF	:	Specific reverse solute flux
Re	:	Reynolds number
HTI	:	Hydration Technology Innovations

List of Symbols

A	:	Water permeability coefficient (L .m^{-2} .h^{-1}.bar^{-1})
B	:	Salt permeability coefficient (m.s^{-1})
C	:	Solute number density (L^{-1})
c	:	Solute concentration
D/Ds	:	Diffusion coefficient (m^{2} s^{-1})
Dh	:	Hydraulic diameter (m)
I	:	Intrinsic membrane structural properties
J_s	:	Solute flux (g.m^{-2}.h^{-1})
J_w	:	Water flux (L m^{-2} h^{-1})
J_w, sp	:	Specific water flux (L m^{-2} h^{-1} bar^{-1})
k	:	Mass transfer coefficient
K	:	Solute diffusion resistance (s.m^{-1})
K	:	Boltzmann's constant (1.38x10^{-3} J.K^{-1})
M	:	Solute molar concentration (mol. L^{-1})
M	:	Molar concentration of the solution
Mw	:	Molecular weight (mol.g^{-1})
N	:	Moles of solute (mol)
N_A	:	Avogadro's number
n	:	Van't Hoff factor
P	:	Applied hydraulic pressure (bar)
R/R_g	:	Gas constant (0.08314 L bar mol^{-1} K^{-1})
Re	:	Reynolds number
Sc	:	Schmidt number
Sh	:	Sherwood number
T	:	Absolute temperature (in K)
t	:	Thickness of the membrane (m)
Δt	:	Time interval (h)
ΔV	:	Volume change (L)
ΔP	:	Pressure change (bar)

Superscripts/subscripts

w	:	Water
s	:	Solute
F	:	Feed
D	:	Draw
m	:	Membrane
i	:	Interface
D, b	:	Draw, bulk
F, b	:	Feed, bulk
F, m	:	Feed, membrane
D, m	:	Draw, membrane
W, sp	:	Water, specific

Greek letters

π	:	Osmotic pressure (bar)
φ	:	Osmotic pressure coefficient
σ	:	Reflection coefficient,
ε	:	Porosity
β	:	van't Hoff coefficient
τ	:	Tortuosity

List of Figures

List of Tables