

MSF Brine Reject Dilution in the Forward Osmosis Process: Performance Analysis

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Certificate of Original Authorship

I, Daoud, declare that this thesis is submitted in fulfilment of the requirements for the award of the 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.

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Yadav, S., Ibrar, I., Bakly, S., **Khanafer, D.**, Altaee, A., Padmanaban, V., Samal, A.K. and Hawari, A.H. 2020. Organic fouling in forward osmosis: A comprehensive review. *Water* 12(5), 1505.

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Abbreviations

<i>A</i>	Pure water permeability
AL	Active layer
<i>B</i>	Solute permeability
CP	Concentration polarization
CTA	Cellulose triacetate
DI	Deionized
DS	Draw solution
EDS	Energy Dispersive X-ray Spectroscopy
FO	Forward Osmosis
FS	Feed solution
FTIR	Fourier transform infrared
GCC	Gulf Cooperation Council
ICP	Internal Concentration polarization
J_w	Water flux
MSF	Multi-Stage Flashing
NF	Nanofiltration
PAFO	Pressure-assisted forward osmosis
RO	Reverse Osmosis
<i>S</i>	Structural parameter
SEM	Scanning electron microscopy
SL	Support layer
TBT	Top brine temperature
TDS	Total dissolved solids
TFC	Thin Film Composite
TSE	Tertiary sewage effluent

Abstract

One of the largest global risks is freshwater scarcity. In countries with limited natural water resources, water reclamation and desalination have become a strategic source of clean and usable water. Specifically, seawater desalination is a sustainable flow of fresh water in the Gulf Cooperation Council (GCC) countries located in the driest part of the world. Multi-Stage Flashing (MSF) desalination has been proved to be the most reliable thermal desalination technology in the GCC countries, mainly considering Qatar's MSF plants. Despite its efficiency and high-quality water production, MSF technology suffers major drawbacks affecting its performance. Scale formation, specifically the non-alkaline scale, has been a serious issue from thermodynamic and economic perspectives. Pretreatment of the feed solution to the MSF plants was proposed and investigated in the literature to tackle the scale issue. The current project's novelty is to design and test the FO-MSF hybrid system for seawater pretreatment by the FO process for the MSF desalination plant. Several commercial FO and NF membranes were applied for recycling the MSF brine reject within the FO system using the brine as a draw solution.

Selecting the appropriate membrane and the ideal draw solution is essential for an efficient FO process. Since the brine reject solution is the only DS used in all the experiments conducted in this study, the variables included the membrane and the feed solution. TFC and CTA FO membranes with fresh seawater feed solution were used in the FO system for the MSF plant. Pressure-assisted FO (PAFO) process was introduced, and experimental results showed 50% more permeation flux by increasing the feed pressure from 1 to 4 bar. When tertiary sewage effluent (TSE) was proposed as a feed solution using TFC membranes, a considerably high water flux of 35 L/m²h was achieved. Under the same operating conditions in the FO mode using fresh seawater on the feed side, commercial NF membranes were tested for the first time in the FO system. A more feasible membrane selection can be the NF membranes as they demonstrated better results than FO membranes. However, higher performance was achieved when TSE and NF were combined in the FO process.

Experimentally, this combination recorded a maximum water flux of 39.5 L/m²h and achieved up to 42% divalent ions dilution. While the outcome of this study is still preliminary, the results are promising and can highlight the potential of using the FO system for MSF brine dilution.