UTS UNIVERSITY OF TECHNOLOGY SYDNEY

VOLATILE FATTY ACID AND WATER EXTRACTION FROM RUMEN FLUID BY FORWARD OSMOSIS

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Thesis submitted in fulfilment of the requirements
for the degree of

Doctor of Philosophy

under the supervision of Professor Long D. Nghiem and
Professor Hokyong Shon

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This thesis is dedicated to my wife

Dr Shabana Ghaffar

For her priceless love and consistent support

Certificate of Original Authorship

I, **Jamshed Ali Khan** declare that this thesis is submitted in fulfilment of the requirements of the award of **Doctor of Philosophy**, in the School of Civil and Environmental Engineering at the University of Technology Sydney.

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

This thesis is wholly my own work unless otherwise reference or acknowledged. Any help that I have received in my research and preparation of the thesis has been acknowledged. Besides, I certify that all information sources and literature used are indicated in the thesis. This research is supported by the Australian Government Research Training Program.

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Research Outcome Summary

Journal papers

1) **Khan JA**, Shon HK, Nghiem LD. From the Laboratory to Full-Scale Applications of Forward Osmosis: Research Challenges and Opportunities. Current Pollution Reports. 2019;5(4):337-52.
2) **Khan JA**, Nguyen LN, Duong HC, Nghiem LD. Acetic acid extraction from rumen fluid by forward osmosis. Environmental Technology & Innovation. 2020;20:101083.
3) **Khan JA**, Vu MT, Nghiem LD. A preliminary assessment of forward osmosis to extract water from rumen fluid for artificial saliva. Case Studies in Chemical and Environmental Engineering. 2021:100095.

In-preparation Journal Paper

4) **Khan JA**, Nguyen AQ, Vu MT, Shon HK, Nghiem LD. Biofouling characterization and evaluation of membrane cleaning techniques in a forward osmosis process to dewater rumen fluid. Journal of Membrane Science (in preparation)

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List of Abbreviations

Abbreviation	Meaning
AOC	Assimilable organic carbon
CFV	Cross flow velocity
CTA	Cellulose triacetate
DI	Deionized
ECP	External concentration polarization
EDTA	Ethylene diamine tetra-acetic acid
EDX	Energy dispersive X-ray
EPS	Extracellular polymeric substances
FO	Forward osmosis
FTIR	Fourier transformed infrared
gMH	$g/m^2.h$
ICP	Internal concentration polarization
IP	Interfacial polymerization
LMH	$L/m^2.h$
MBR	Membrane bioreactor
MD	Membrane distillation
MED	Multi-effect distillation
MF	Microfiltration
mgMH	$mg/m^2.h$
MPD	M-phenylenediamine
MSF	Multi-stage flash
NF	Nanofiltration
NMP	N-methyle-2-pyrrolidone

PA	Polyamide
PAI	Polyamide-imide
PcoA	Principal coordinates analysis
PEI	Polyethyleneimine
PES	Polyethersulfone
PET	Polyethylene terephthalate
PRO	Pressure retarded osmosis
PSF	Poysulfone
RO	Reverse osmosis
RSF	Reverse solute flux
SEM	Scanning electron microscopy
SRSF	Specific reverse solute flux
TDS	Total dissolved solids
TFC-PA	Thin-film composite polyamide
TMC	Trimesoyl chloride
UF	Ultrafiltration
VFAs	Volatile fatty acids
VS	Volatile solids

Abstract

Nature offers elegant, efficient, and sustainable solutions to most of our problems. One such problem is to convert the most abundant natural resource of lignocellulosic biomass into a fermented solution for subsequent biochemicals extraction. An efficient, economical and eco-friendly technique or system has not been developed yet to address this problem. Nature has offered a robust solution to this problem in the form of ruminant's digestive system where a fermented solution (rumen fluid) is produced from the digestion of biomass in the fore-stomach (or rumen) with the help of diverse microbiota followed by volatile fatty acids (VFAs) absorption from the rumen fluid in the small intestine along with water absorption in the omasum and large intestine. This study aims to replicate the two important processes taking place inside the ruminant's digestive system with a membrane-based forward osmosis (FO) process. First is the use of FO for acetic acid extraction from rumen fluid by mimicking the VFAs absorption in the small intestine and second is employing FO for dewatering of rumen fluid by simulating the water absorption in the omasum and the large intestine. Besides, this study also covers the membrane biofouling that can occur as a result of resource recovery from rumen fluid in a long term FO operation and evaluates the various membrane cleaning strategies for flux recovery.

Unlike other FO applications to extract water and reduce the feed water volume, this study used FO to mimic the ruminant’s small intestine for extracting acetic acid from rumen fluid to a clean matrix with a minimum water flux. Membrane characterisation results showed better separation performance by the thin-film composite polyamide (TFC-PA) membrane in terms of pure water permeability, solute rejection, and structural parameter compared to the cellulose triacetate (CTA) membrane. This was further endorsed by the higher acetic acid transport through the CTA membrane than the TFC-PA membrane.

Increasing the stripping solution pH from 5.5-6.5 to 9.0-10.0 increased the acetic acid transport through both the CTA and TFC-PA membranes. On the other hand, the membrane orientation had no discernible effect on the transport of acetic acid. Under the optimum conditions, the FO process using the CTA membrane exhibited negligible water flux and extracted 27% of the maximum attainable acetic acid from the synthetic solution within 8 hours of operation. The optimised conditions were used to elaborate the FO extraction of acetic acid from a real rumen fluid. Considerably lower extraction rate from the real rumen fluid was observed compared to the synthetic solution.

This study also explored the use of FO for extracting water from the rumen fluid by replicating the dewatering function of the large intestine and omasum in ruminant animals. The reference artificial saliva solution was determined by comparing its osmotic pressure to that of the rumen fluid. The concentrated saliva showed good pH buffering capacity with no significant pH changes during FO operation. High water flux and a low reverse solute flux (RSF) were observed using concentrated artificial saliva as a draw solution and clean water as the feed. However, the water flux decreased and the RSF increased significantly when rumen fluid was used as the feed. Membrane fouling was observed with the deposition of mainly biomolecules from the rumen fluid on the membrane surface and the high temperature of feed solution further exacerbated membrane fouling. Membrane fouling was evidenced by visual examination as well as scanning electron microscope (SEM), energy dispersive X-ray (EDX), and Fourier transformed infrared (FTIR) analysis of the membrane surface.

Membrane biofouling was investigated in a long term FO operation for water extraction from rumen fluid. Three of the possible membrane module configurations were used to assess their effect on the membrane fouling. In the horizontal membrane module configurations, the circulation of the feed solution on top of the membrane cell led to

more severe fouling compared to that from the bottom of the membrane module. The best resistance to fouling was observed in the vertical configuration of the membrane module. The results suggest that fouling is driven mostly by the gravity-driven deposition of foulants on the membrane surface. This was evidenced by the SEM-EDX and FTIR analyses of the fouling layers. The biofouling phenomenon was further characterized using the bioinformatics analysis of the inoculum, feed solution, and fouling layer microbial communities. A distinct biofilm microbial community with lower diversity and different composition from other samples were observed when feed solution was on top in the membrane module, due to the thick and more mature fouling layer. Aerobic and facultatively anaerobic microbial species such as *Pseudomonadaceae, Xanthomonadaceae* and *Arcobacteraceae* that were not detected in the inoculum emerged in the feed and thrived in biofilms under all membrane module configurations. Among these species, *Pseudomonadaceae* and *Xanthomonadaceae* were the most abundant, and both have been previously reported to possess superior attachment and biofilm-forming capacity. Different membrane cleaning techniques including hydraulic cleaning, osmotic backwashing, and chemical cleaning were applied to remove membrane fouling. A combination of chemical cleaning using 0.1% NaOCl and osmotic backwashing using NaCl 1M solution was found to be most effective with 70.0% flux recovery while hydraulic cleaning was the least effective that could only recover 14.1% flux. While the results are still preliminary, they highlight the potential for effective control of membrane fouling during water extraction from rumen fluid by FO.