UNIVERSITY OF TECHNOLOGY SYDNEY

POTENTIAL APPLICATIONS OF GRAPHENE-BASED MEMBRANE IN SOLUTION PURIFICATION PROCESSES

by Sudesh Yadav

Thesis submitted in fulfilment of the requirements for
the degree of

Doctor of Philosophy

under the supervision of **Dr. Ali Altaee (Prinicipal Supervisor)**
Prof. John Zhou (Co-supervisor)

University of Technology Sydney
Faculty of Engineering and Information Technology

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CERTIFICATE OF ORIGINAL AUTHORSHIP

I, **Sudesh Yadav** declare that this thesis, is submitted in fulfilment of the requirements for the award of **Doctor of Philosophy**, in the **School of Civil and Environmental Engineering/Faculty of Engineering and Information Technology** at the **University of Technology Sydney** (UTS).

I certify that the work in this thesis is my own and the literature used is appropriately acknowledged.

This thesis has not been submitted to any other academic institution for accreditation.

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Signature: Production Note: Signature removed prior to publication.

Date: 22nd June 2022

DEDICATION

This doctoral thesis is dedicated to:

My teacher **Dr. Ali Altaee** and my father **Mr. Ranbeer Singh Yadav**,

who taught me the power of patience and perseverance,

And

My brother **Mr. Sanoj Kumar**,

for having my back, and motivating me.

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LIST OF PUBLICATIONS

- This list includes journal articles that have been prepared during the Ph.D. candidature, which are **part** of the report.

1. **S. Yadav**, H. Saleem, I. Ibrar, O. Naji, A.A. Hawari, A.A. Alanezi, S.J. Zaidi, A. Altaee, J. Zhou, Recent developments in forward osmosis membranes using carbon-based nanomaterials, Desalination, 482 (2020) 114375.
2. P. Bhol[†], **S. Yadav**[†], A. Altaee, M. Saxena, P.K. Misra, A.K. Samal, Graphene-based membranes for water and wastewater treatment: a review, ACS Applied Nano Materials, 4 (2021) 3274-3293. [†] P.B. and S.Y. contributed equally.
3. **S. Yadav**, I. Ibrar, A. Altaee, A.K. Samal, R. Ghobadi, J. Zhou, Feasibility of brackish water and landfill leachate treatment by GO/MoS_2-PVA composite membranes, Science of the Total Environment, (2020) 141088.
4. **S. Yadav**, I. Ibrar, A. Altaee, A.K. Samal, E. Karbassiyazdi, J. Zhou, P. Bartocci, High-Performance Mild Annealed CNT/GO-PVA Composite Membrane for Brackish Water Treatment, Separation and Purification Technology, (2021) 120361.
5. **S. Yadav**, I. Ibrar, A. Altaee, S. Déon, J. Zhou, Preparation of novel high permeability and antifouling polysulfone-vanillin membrane, Desalination, 496 (2020) 114759.
6. **S. Yadav**, I. Ibrar, A.K. Samal, A. Altaee, S. Déon, J. Zhou, N. Ghaffour, Preparation of fouling resistant and highly perm-selective novel PSf/GO-vanillin nanofiltration membrane for efficient water purification, Journal of Hazardous Materials, (2021) 126744.
7. **S. Yadav**, I. Ibrar, A. Altaee, A.K. Samal, J. Zhou, Surface modification of nanofiltration membrane with kappa-carrageenan/graphene oxide for leachate wastewater treatment, Journal of Membrane Science, (Manuscript Number: MEMSCI-D-21-0295; Under Review).

- This list includes journal articles that have been prepared during the PhD candidature, which are **not part** of the report.

1. **S. Yadav**, I. Ibrar, S. Bakly, D. Khanafer, A. Altaee, V. Padmanaban, A.K. Samal, A.H. Hawari, Organic Fouling in Forward Osmosis: A Comprehensive Review, Water, 12 (2020) 1505.
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3. I. Ibrar, **S. Yadav**, A. Altaee, A.K. Samal, J.L. Zhou, T.V. Nguyen, N. Ganbat, Treatment of biologically treated landfill leachate with forward osmosis: Investigating membrane performance and cleaning protocols, Science of The Total Environment, 744 (2020) 140901.
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5. I. Ibrar, **S. Yadav**, N. Ganbat, A.K. Samal, A. Altaee, J.L. Zhou, T.V. Nguyen, Feasibility of H_2O_2 cleaning for forward osmosis membrane treating landfill leachate, Journal of Environmental Management, 294 (2021) 113024.
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15. O. Naji, R.A. Al-juboori, A. Khan, **S. Yadav**, A. Altaee, A. Alpatova, S. Soukane, N. Ghaffour, Ultrasound-assisted membrane technologies for fouling control and performance improvement: A review, Journal of Water Process Engineering, 43 (2021) 102268.
16. S. Swarnalata, B.M. Shenoy, P. Bhol, **S. Yadav**, S.R. Jena, G. Hegde, A. Altaee, M. Saxena, A.K. Samal, Facet dependent catalytic activity of Pd nanocrystals for the remedy of organic Pollutant: A mechanistic study, Applied Surface Science, 570 (2021) 150775.
17. R. Ghobadi, A. Altaee, J. Zhou, P. McLean, **S. Yadav**, Copper removal from contaminated soil through electrokinetic process with reactive filter media, Chemosphere, 252 (2020) 126607.

- This list includes book chapters that have been prepared during the PhD candidature, which are **not part** of the report.

1. M.B. Bhavya, S. Swain, P. Bhol, **S. Yadav**, A. Altaee, M. Saxena, P.K. Misra, A.K. Samal, Functionalized nanomaterials (fnms) for environmental applications, Functionalized Nanomaterials for Catalytic Application, (2021) 109-134.
2. S. Swain, P. Bhol, M.B. Bhavya, **S. Yadav**, A. Altaee, M. Saxena, P.K. Misra, A.K. Samal, Synthesis of functionalized nanomaterial (fnm)–based catalytic materials, Functionalized Nanomaterials for Catalytic Application, (2021) 135-168.
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5. S.R. Jena[†], **S. Yadav**[†], A. Yadav, M.B. Bhavya, A. Altaee, M. Saxena, A.K. Samal, Advanced functional materials for the detection of perfluorinated compounds in water, Polymer-Based Advanced Functional Materials for Energy and Environmental Applications (Energy, Environment, and Sustainability) Springer, Singapore, (2022) 257-269. [†] S.R.J. and S.Y. contributed equally.

PREFACE

This doctoral thesis is prepared in a "Thesis by compilation" format according to the "Graduate Research Candidature Management, Thesis Preparation and Submission Procedures, 2019" of the University of Technology Sydney. It comprises of the articles that have been published or submitted for publication.

This thesis contains two published review paper in Chapter 2 and five original research articles in Chapters 3 to 7, four of which are published, and another one is under review for publication. The authorship of these works has been decided after discussing with the supervisory team. Lastly, Chapter 8 includes conclusions and future recommendations.

Chapter 2 comprises of the following article:

S. Yadav, H. Saleem, I. Ibrar, O. Naji, A.A. Hawari, A.A. Alanezi, S.J. Zaidi, A. Altaee, J. Zhou, Recent developments in forward osmosis membranes using carbon-based nanomaterials, Desalination, 482 (2020) 114375.

P. Bhol[†], **S. Yadav**[†], A. Altaee, M. Saxena, P.K. Misra, A.K. Samal, Graphene-based membranes for water and wastewater treatment: a review, ACS Applied Nano Materials, 4 (2021) 3274-3293. [†] P.B. and S.Y. contributed equally.

Chapter 3 includes the following technical article:

S. Yadav, I. Ibrar, A. Altaee, A.K. Samal, R. Ghobadi, J. Zhou, Feasibility of brackish water and landfill leachate treatment by GO/MoS_2-PVA composite membranes, Science of the Total Environment, (2020) 141088.

Chapter 4 includes the following technical article:

S. Yadav, I. Ibrar, A. Altaee, A.K. Samal, E. Karbassiyazdi, J. Zhou, P. Bartocci, High-Performance Mild Annealed CNT/GO-PVA Composite Membrane for Brackish Water Treatment, Separation and Purification Technology, (2021) 120361.

Chapter 5 includes the following technical article:

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Chapter 6 includes the following technical article:

S. Yadav, I. Ibrar, A.K. Samal, A. Altaee, S. Déon, J. Zhou, N. Ghaffour, Preparation of fouling resistant and highly perm-selective novel PSf/GO-vanillin nanofiltration membrane for efficient water purification, Journal of Hazardous Materials, (2021) 126744.

Chapter 7 includes the following technical article:

S. Yadav, I. Ibrar, A. Altaee, A.K. Samal, J. Zhou, Surface modification of nanofiltration membrane with kappa-carrageenan/graphene oxide for leachate wastewater treatment, Journal of Membrane Science, (Manuscript Number: MEMSCI-D-21-0295; Under Review).

Chapter 8 includes the conclusions and future recommendations.

STATEMENT OF CONTRIBUTION OF AUTHORS

The research papers reported on original research I conducted during the period of my Higher Degree by Research candidature and is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in this thesis. I have contributed more than 80% to all the papers reported in this thesis including conceptualization, methodology, software, validation, formal analysis, investigation, data curation, visualization, writing - original draft, - review and editing. I am the primary author of all the papers reported in this thesis.

Signature: Production Note: Signature removed prior to publication.

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LIST OF ABBREVIATIONS

NF	Nanofiltration
RO	Reverse osmosis
1D	One-dimensional
2D	Two-dimensional
GO	Graphene oxide
rGO	Reduced graphene oxide
MrGO	Mild annealed reduced graphene oxide
CNT	Carbon nanotubes
MWCNT	Multiwalled carbon nanotubes
SWCNT	Single-walled carbon nanotube
GO-ZnO	Graphene oxide–zinc oxide
MoS_2	Molybdenum disulphide
PSf	Polysulfone
PES	Polyethersulfone
PVP	Polyvinyl pyrrolidone
PVA	Polyvinyl alcohol
PEI	Polyethyleneimine
PVC	Polyvinyl chloride
PAN	Polyacrylonitrile
PVDF	Polyvinylidene fluoride
CA	Cellulose acetate
MCE	Mixed cellulose esters
NMP	1-Methyl-2-pyrrolidone
B14DBA	Benzene-1,4-diboronic acid
BCP)	block copolymers
kGN	kappa carrageenan
BSA	Bovine serum albumin
R_r	Reversible fouling
R_{ir}	Irreversible fouling
R_t	total fouling

FRR	Flux recovery ratio
K	potassium
Ca	calcium
Th	thorium
Pb	lead
Ag	silver
Zn	zinc
Fe	iron
Cr	chromium
Al	aluminium
Mg	magnesium
NaCl	Sodium chloride
Na_2SO_4	Sodium sulfate
$MgSO_4$	Magnesium sulfate
$MgCl_2$	Magnesium chloride

NOMENCLATURE

Meaning and symbol	Unit
Transmembrane pressure (ΔP)	Pa
Brunauer, Emmett and Teller (BET)	m^2/g
Molecular weight	g/mol
Active membrane surface area (A)	m^2
Permeated water volume (V)	L
Time interval (Δt)	h
Solute concentrations of feed solution (C_f)	g/ L
Solute concentrations of permeate solution (C_p)	g/ L
Water flux (J_w)	$L.m^{-2}.h^{-1}$ (LMH)
Maximum value of membrane surface roughness (R_{max})	nm
Root mean square value of membrane surface roughness (R_q)	nm
Turbidity	NTU
Total dissolved solids (TDS)	mg/L
Total organic carbon (TOC)	mg/L
Conductivity	mS/cm
Salinity	ppt

ABSTRACT

Climate change with industrial and environmental pollution are among the reasons for water quality deterioration. Unfortunately, conventional polymeric membranes have inherent limitations, such as low separation or rejection rate, fouling, limited water flux, and high energy consumption. Two-dimensional (2D) based layered materials with tunable chemical functionalities and surface charge properties have emerged for on-demand applications, including membrane technology. However, the instability of graphene oxide (GO) membranes during operation is one of the biggest challenges for its practical applications. Therefore, it is important to improve the stability of GO membranes without losing their physiochemical properties.

This thesis aims to develop advanced performance GO membranes for water purification. Initially, research was conducted to investigate the pressure-assisted method for fabricating a GO membrane using polyvinyl alcohol (PVA) as adhesive materials for swelling control and molybdenum disulfide (MoS_2) as nanospacer. The next study evaluated synergistic ionic complexation between 1D-CNT (carbon nanotubes), 2D-GO, and PVA to overcome the permeability-selectivity trade-off. Thermal treatment of GO membranes was also investigated in this study. Later, part of this thesis is focused on developing a proof of concept of preparing an antifouling GO membrane using a non-solvent induced phase separation method for a highly selective membrane. The potential of vanillin and GO for various model foulants and landfill leachate wastewater was investigated in this study. Finally, a surface modification technique was used to modify the commercially available loose nanofiltration (NF) membrane. In this study, kappa-carrageenan (κ-CGN)/GO composite has been used to modify a commercial NF membrane to improve salt rejection antifouling properties when landfill leachate wastewater is the feed solution.

The techniques presented in this thesis demonstrates are not only simple and effective but can also be applied to a wide range of membrane substrates and even large-scale membrane development. GO membranes' mechanical integrity and structural stability are evaluated for 72 hours of operation; however, low water permeability is still challenging. Therefore, studies should prepare an efficient GO membrane of high permeability without compromising its rejection rate and stability. At the same time, the mechanical properties and stability of the GO membrane should be explored to understand its potential applications better.