

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 (Principal Supervisor)**

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June 2022

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.

This research is supported by the UTS President's Scholarship (UTSP) and UTS International Research Scholarship (UTS IRS) Program.

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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.

ACKNOWLEDGEMENTS

How do I acknowledge my teacher Dr. Ali Altaee who has stood by me throughout my Ph.D. journey? My simple answer is to dedicate this doctoral thesis to my principal supervisor Dr. Ali Altaee, for his unwavering support and encouragement throughout my Ph.D. study. I would like to express my heartfelt gratitude to Prof. John Zhou for the enlightening discussions throughout my doctoral studies.

Apart from my supervisors, I'd like to express my gratitude for the assistance I received from the external collaborators (Prof. Akshaya K. Samal, Prof. Sébastien Déon and Prof. Juin-Yeh Lai) who allowed me to work with them. I am grateful to all laboratory staff and friends in UTS for their support especially Elika Karbassiyazdi, Ibrar Ibrar, and Nahawand AlZainati, Namuun Ganbat and Dr. Niren Pathak.

I'd like to express my gratitude to my mother (Mrs. Roshni Devi) and sister-in-law (Deepika), whose love and guidance accompany me in whatever endeavour I undertake. Their unwavering trust, timely encouragement, boundless patience, and love resurrected me when I became weary. I'd also like to thank my daughters (Innaya and Parisha) for providing me with endless joy and happiness.

Finally, I thank with love to my friends Ajay Gill, Dr. Akash S. Rasal, Dr. Anchal Yadav, Arpit Pandey, Deepika Matta, Dixi S. Patel, Divya Prasad, Pooja M. Suresh, Poorvika Agarwal and Uttam Kumar. They have always loved, supported, encouraged, entertained, and helped me get through this agonizing period in the most positive way. Thank you to my wife (Rekha Kumari) for her patience and friendship.

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/MoS₂-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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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.
 3. I. Ibrar, D. Khanafer, **S. Yadav**, S. Bakly, J. A. Khan, A. Altaee Solar co-generation of electricity and water, large scale photovoltaic systems - Desalination by Forward Osmosis: Failure, Success, and Future Expectations, UNESCO-EOLSS.
 4. M.B. Bhavya, **S. Yadav**, A. Altaee, M. Saxena, P.K. Misra, A.K. Samal, Role of surfactants in facet dependent synthesis of anisotropic nanostructures, *Chemical Modifications of Solid Surfaces by the Use of Additives*, (2021) 1-20.

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/MoS₂-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:

S. Yadav, I. Ibrar, A. Altaee, S. Déon, J. Zhou, Preparation of novel high permeability and antifouling polysulfone-vanillin membrane, Desalination, 496 (2020) 114759.

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.

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Signature: Signature removed prior to publication.

Date: 22nd June 2022

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Table 7.1 Characteristics of landfill leachate wastewater obtained from Hurstville Golf Centre in Sydney, Australia.

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Table 7.3 Analytical instruments used to characterize UA-60- κ -CGN-GO composite membranes.

Table 7.4 Water contact angle and surface zeta potential measurements for UA-60, UA-60- κ -CGN, and UA-60- κ -CGN-GO membranes.

Table 7.5 Initial concentration and rejection percentage of various ions and total organic carbon of landfill leachate wastewater using UA-60, UA-60- κ -CGN, and UA-60- κ -CGN-GO membranes.

Table 8.1 Performance summary of the optimal prepared membranes reported in this thesis.

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

<i>FRR</i>	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 ₂ SO 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)	$\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (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.