Faculty of Engineering

# THE EFFECT OF ORGANOCLAY BASED MEMBRANE EMBEDDED VIA PHASE INVERSION FOR HEAVY METAL REMOVAL

NATALIE ANNE DURIE ANAK EDWARD DOLMAN

Bachelor of Engineering with Honours

(Chemical Engineering)

2022

**UNIVERSITI MALAYSIA SARAWAK**

Grade: ________________

**Please tick (✓)**

| | |
|---|---|
| Final Year Project Report | ✓ |
| Masters | |
| PhD | |

**DECLARATION OF ORIGINAL WORK**

This declaration is made on the 29th day of June 2022.

**Student's Declaration**:

I NATALIE ANNE DURIE ANAK EDWARD DOLMAN (66912), hereby declare that the work entitled THE EFFECT OF ORGANOCLAY BASED MEMBRANE EMBEDDED VIA PHASE INVERSION FOR HEAVY METAL REMOVAL is my original work. I have not copied from any other students' work or from any other sources except where due reference or acknowledgement is made explicitly in the text, nor has any part been written for me by another person.

3 JULY 2022
Date Submitted

NATALIE ANNE DURIE ANAK EDWARD DOLMAN (66912)
Name of student (Matric No.)

**Supervisor's Declaration:**

I hereby certifies that the work entitled THE EFFECT OF ORGANOCLAY BASED MEMBRANE EMBEDDED VIA PHASE INVERSION was prepared by the above named student, and was submitted to the "FACULTY" as a * partial/full fulfillment for the conferment of BACHELOR OF ENGINEERING WITH HONOURS (CHEMICAL ENGINEERING), and the aforementioned work, to the best of my knowledge, is the said student's work.

Received for examination by: Date: 2022

(Name of coordinator)

I declare this Project/Thesis is classified as (Please tick (√)):

| | | |
|---|---|---|
| | **CONFIDENTIAL** | (Contains confidential information under the Official Secret Act 1972) * |
| | **RESTRICTED** | (Contains restricted information as specified by the organization where research is done) |
| ✓ | **OPEN ACCESS** | |

**Validation of Project/Thesis**

I therefore duly affirmed with free consent and willingness declared that this said Project/Thesis shall be placed officially in the Centre for Academic Information Services with the abiding interest and rights as follows:

- This Project/Thesis is the sole legal property of Universiti Malaysia Sarawak (UNIMAS).
- The Centre for Academic Information Services has the lawful right to make copies for the purpose of academic and research only and not for other purposes.
- The Centre for Academic Information Services has the lawful right to digitize the content to for the Local Content Database.
- The Centre for Academic Information Services has the lawful right to make copies of the Project/Thesis for academic exchange between Higher Learning Institute.
- No dispute or any claim shall arise from the student itself neither third party on this Project/Thesis once it becomes sole property UNIMAS.
- This Project/Thesis or any other material, data and information related to it shall not be distributed, published or disclosed to any party by the student except with UNIMAS permission.

Student' signature: Natalie ( 3 JULY 2022)

Supervisor's signature: ____________________ (2022)

Current Address:

NO.72, S/L 173, LRG 2, TAMAN DESA MOYANG, JALAN TONDONG, BATU KAWA, 93250 KUCHING, SARAWAK.

Notes: * If the Project/Thesis is **CONFIDENTIAL** or **RESTRICTED**, please attach together as annexure a letter from the organisation with the period and reasons of confidentiality and restriction.

[The instrument is duly prepared by The Centre for Academic Information Services]

# APPROVAL SHEET

This final year project report, which entitled **THE EFFECT OF ORGANOCLAY BASED MEMBRANE EMBEDDED VIA PHASE INVERSION FOR HEAVY METAL REMOVAL** was prepared by Natalie Anne Durie anak Edward Dolman (66912) as a partial fulfillment for the Degree of Bachelor of Chemical Engineering is hereby read and approved by:

| | |
|---|---|
| ________________________________________ | _______________________ |
| MR. MOHAMED AFIZAL MOHAMED AMIN | Date |
| (Final Year Project Supervisor) | |

# THE EFFECT OF ORGANOCLAY BASED MEMBRANE EMBEDDED VIA PHASE INVERSION FOR HEAVY METAL REMOVAL

NATALIE ANNE DURIE ANAK EDWARD DOLMAN

A dissertation submitted in partial fulfilment

of the requirement for the degree of

Bachelor of Engineering with (Hons)

Chemical Engineering

Faculty of Engineering

Universiti Malaysia Sarawak

2022

# ACKNOWLEDGEMENT

First and foremost, I am indebted to my final year project supervisor, Mr. Mohamed Afizal Mohamed Amin, for his kindness, guidance and help in all aspects throughout this journey in completing this research. Personally, his constructive criticism, perceptive comments, and recommendations have made this research possible. My deep and sincere gratitude are dedicated to the respective examination panels, Dr. Nazeri Abdul Rahman, Dr. Khairul Anwar Mohd Said, and Dr. Ibrahim Yaakub for their invaluable suggestions, and productive comments which have helped me to improve my dissertation.

Heartfelt acknowledgements are extended to those assistant engineers in Analytical Laboratory, and Reaction Laboratory and Unit Operation Laboratory, especially, Mr. Airul Azhar Jitai, Ms. Dayang Fadhilatul Aishah Abang Abdul Hamid, and Mr. Mohd Hafiz Mafadi for all their help and tireless assistance throughout my research work in the laboratory. My sincere appreciation is extended to my close friends who have remained by my side since the beginning, offering help, companionship, motivation, and true friendship. The completion of this dissertation would not have been possible without the individuals who had participated and contributed with unwavering support, and mutual support, thus, I am extending my heartfelt thanks to every person that has joined this journey.

Finally, I am forever grateful to my parents, Mr. Edward Dolman anak Adrian Suji and Mdm. Sylvia Layam anak Bernard Lium, as well as to my brother, Jamie Ryan anak Edward Dolman, for all the love, constant support, and their encouragement ever since day one, because without them, I would not be the person I am today.

# ABSTRACT

Water scarcity is a global catastrophe which had become the world most recent focus due to the limitation of fresh water sources. The idea of treating wastewater is vital as wastewater is actually freshwater that is contaminated by pollutants where it can be considered as an alternative source of freshwater to reduce the scarcity of water worldwide. Pollutants which occurred from industrial and human activities had increases the present of harmful heavy metals in wastewater, hence membrane technology is introduced as one of the methods in treating wastewater, nevertheless, there are still limitations to this method as it has low commercial adsorbents and lack of appropriate adsorbents with high adsorption capacity. Hence, the incorporation of polymeric membrane with organoclay nanocomposite is introduced as this type of membrane enables the improvement of polymer matrices such as hydrophilicity and increases the polymer matrix's efficacy for pollutant removal in aqueous environments. This thesis aims to develop an organoclay-based membrane embedded via phase inversion technique and to analyse the effect of the developed membrane on the water separation performance. The experimentation setup for this thesis separated into three phases which includes fabrication, characterization, and testing. In the characterization of cloisite and membrane, several analyses is carried out using FTIR, SEM-EDX, PSA, AAS, pure water flux, and Water uptake. The result shows that the modified membrane projected uneven trend of pure water flux, and the rejection of lead is 7.36% for membrane with 7.5 wt% of Cloisite-15A.



***Keywords:*** *Water scarcity, heavy metals, polymeric membrane, organoclay nanocomposites, phase inversion technique*

# ABSTRAK

Kekurangan air merupakan sebuah bencana global yang telah menjadi tumpuan dunia baru-baru ini kerana batasan sumber air tawar. Idea untuk merawat air sisa kumbahan adalah penting kerana air sisa kumbahan merupakan air tawar yang tercemar oleh bahan pencemar di mana ia boleh dianggap sebagai sumber alternatif air tawar untuk mengurangkan kekurangan air di seluruh dunia. Pencemaran yang berlaku akibat daripada aktiviti perindustrian dan manusia telah meningkatkan kehadiran logam berat berbahaya di dalam air sisa kumbahan, oleh itu, teknologi membran diperkenalkan sebagai salah satu kaedah dalam merawat air sisa kumbahan, namun, masih terdapat batasan terhadap kaedah ini kerana ia mempunyai penyerap komersial yang rendah dan kekurangan penyerap yang sesuai dengan kapasiti penyerapan yang tinggi. Oleh itu, penggabungan membrane polimer dengan organoclay nanocomposite diperkenalkan kerana jenis membran ini membolehkan peningkatan matriks polimer seperti hidrofilik dan meningkatkan keberkesanan matriks polimer untuk penyingkiran pencemar dalam persekitaran berair. Tesis ini bertujuan untuk membangunkan membrane berasaskan organoclay yang tertanam melalui teknik penyongsangan fasa dan untuk menganilisis kesan membran yang dibangunkan pada prestasi pemisahan air. Persediaan percubaan untuk tesis ini dipisahkan kepada tiga fasa yang merangkumi fabrikasi, pencirian, dan ujian. Dalam pencirian cloisite dan membran, beberapa analisis dijalankan dengan menggunakan FTIR, SEM-EDX, PSA, AAS, fluks air tulen, dan pengambilan air. Membran yang diubahsuai menunjukkan trend fluks air tulen yang tidak sekata, dan penolakan plumbum adalah 7.36% untuk membran dengan 7.5wt% Cloisite-15A.

**Kata kunci:** *kekurangan air, logam berat, membran polimer, organoclay nanocomposite, teknik penyongsangan fasa*

# TABLE OF CONTENTS

# LIST OF FIGURES

# LIST OF TABLES

# ABBREVIATIONS

| | |
|---|---|
| AAS | Atomic Absorption Spectroscopy |
| $Al_2O_3$ | Aluminium oxide |
| As | Arsenic |
| C-15A | Cloisite 15A |
| CA | Cellulose Acetate |
| CAC | Cation Exchange Capacity |
| Cd | Cadmium |
| Co | Cobalt |
| CPS | Clay-polymer nanocomposites |
| Cr | Chromium |
| Cu | Copper |
| Cu (II) | Copper two |
| DMAc | Dimethylacetamide |
| DMF | Dimethylformamide |
| EIPS | Evaporation-induced phase separation |
| Fe | Iron |
| FTIR | Fourier transform infrared spectroscopy |
| GO | Graphene oxide |
| HFO | Hydrated ferric oxide |
| Hg | Mercury |
| HM | Heavy metal |
| HMO | Hydrous manganese oxide |
| IWMI | International Water Management Institute |
| LbL | Layer-by-layer |

| | |
|---|---|
| MF | Microfiltration |
| Mn | Manganese |
| NaCl | Sodium Chloride |
| NF | Nanofiltration |
| NFO | Nickel Ferrite |
| Ni | Nickel |
| NIPS | Non-solvent induced phase separation |
| NMP | N- methyl-pyrrolidone |
| PAN | Polyacrylonitrile |
| Pani-GO | Polyaniline-Graphene oxide |
| Pb | Lead |
| PC | Polycarbonate |
| PES | Polyethersulfone |
| PP | Polypropylene |
| PPEES | Poly-(1,4-phenylene ether) ether sulfone |
| PPS | Poly(p-phenylene sulphide) |
| PSA | Particle Size Analyzer |
| PSf | Polysulfone |
| PTFE | Polytetrafluoroethylene |
| PU | Polyurethane |
| PVC | Polyvinyl chloride |
| PVDF | Polyvinylidene Fluoride |
| RO | Reverse Osmosis |
| Se | Selenium |
| SEM-EDX | Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis |

| | |
|---|---|
| $SiO_2$ | Silicon dioxide |
| TFN | Thin Film Nanocomposites |
| $TiO_2$ | Titanium dioxide |
| TIPS | Thermal-induced phase separation |
| TPD | Ternary phase diagrams |
| UF | Ultrafiltration |
| UN | United Nations |
| USA EPA | US Environmental Protection Agency |
| VIPS | Vapour-induced phase separation |
| WHO | World Health Organization |
| ZIF | Zeolitic Imidazolate framework |
| Zn | Zinc |
| ZnO | Zinc Oxide |

# NOMENCLATURES

| | |
|---|---|
| °C | Degree Celsius |
| L | Litre |
| m | Metre |
| µm | Micrometre |
| % | Percentage |
| wt% | Weight Percent |
| J | Flux |
| mg/l | Milligram per liter |
| $l/m^2h$ | Liter per square meter hour |
| $cm^{-1}$ | Reciprocal centimeter |
| $cm^2$ | Cubic centimeter |
| ppm | Parts per million |

# CHAPTER 1

# INTRODUCTION

## 1.1 Research Background

Water supplies are under increasing demand all around the world due to the growth of population, pollutions, climate change, as well as changes in land use which brings an impact on the quality and the quantity of the water (Ghernaout, 2018). There are approximately 2.5 % of the water is fresh, but only 1% of it is drinkable and easily accessible to the world's 7.6 billion inhabitants even though the Earth is surrounded by 70% of the water (Sultana, 2018; Yalcinkaya et al., 2020). Hence, this had led to the most recent focus issue on the global water catastrophe known as "water scarcity". Teow *et al.* also defined water scarcity as a broad term that encompasses a variety of water-related difficulties such as shortage of water, water stress, as well as an existing water crisis (Teow et al., 2017). Furthermore, a massive decrease in the quality and quantity of available freshwater is raising concerns regarding the influences on human health, the environment as well as the world's economy (Tahreen et al., 2020). Sharma & Bhattacharya had mentioned that it is undeniable that developed countries are mostly affected by chemical discharge issues, whilst developing nations are affected by the agricultural runoff (Sharma & Bhattacharya, 2017). Ensuring safe drinking water to everyone is a tough challenge, thus, several processes, as well as technologies, have emerged as a result of decades of research in this area.

Additionally, massive industrial development has led to a rise in the amount of waste discharged in surface water systems (Ibrahim et al., 2020). As a result of increased weathering processes brought on by domestic sewage, industrial water pollution, population growth, pesticides and fertilisers, plastics and polythene bags, urbanisation, soil pollution, and agricultural water pollution, the quantity and quality of freshwater have further decreased (Bhagat & Giri, 2021). Metal contamination in freshwater habitats can come from direct atmospheric precipitation, geologic weathering, or the discharge of waste from industrial, municipal, or domestic (V. Kumar et al., 2019). Plus, heavy metal pollution in aquatic ecosystems has attracted major worldwide attention due to its potential to cause irreparable harm to human health. (Qu et al., 2018). As mentioned by Chai et al., heavy metals such as Cd, Pb, Fe, Hg, Ni, Mn, Cu, Zn, and Co, are typically present in trace level, yet they are nevertheless regarded as the most dangerous and pervasive elements in wastewater discharge. As a result of the body's inability to metabolise certain heavy metals, they are usually built up in soft tissues which endangered the human health. Furthermore, the United Nations (UN) has indicated that 80% of the world's wastewater is dumped into the environment, either untreated or with minor treatment (Chai et al., 2021). Ince & Kaplan Ince had stated that due to the capacity of heavy metal to accumulate in organism, diseases such as, organ damage, high blood pressure, impaired growth and development, sleep problems, fatigue, poor concentration, aggressive behaviour, irritability, depression, mood swings, increased allergic reactions, vascular occlusion, autoimmune diseases, oxidative stress, and memory loss are just a few of the symptoms that heavy metals can bring on. On top of that, they may also interfere with human biological enzymes (Ince & Kaplan Ince, 2017).

Moreover, Ezugbe & Rathilal had stated that the generation of wastewater is unavoidable because it is a necessary part of the supply chain in all sectors of society (Ezugbe & Rathilal, 2020). It is believed that the generated wastewaters are freshwater with the presence of pollutants. Therefore, freshwater resources may be augmented with the help of effective wastewater treatment where portable water is made accessible to everyone as this appears to be the most obvious method of coping with the scarcity of water. Among the several processes and technologies that have been adopted for the advancement of water purification, membrane technology had become the most popular method due to its ease of operation, energy-saving, highly efficient, scale-up, small footprint, and requires the least input of chemical (Ali et al., 2019; K. Wang et al., 2017; Zhu et al., 2018). In addition, the rising usage of membrane filtration is attributed to the improvements in membrane quality and its ability to reduce costs. Zhu *et al.* had also mentioned that in the last 30 years, both academia and industry have implemented purifying methods for the treatment of water (Zhu et al., 2018). Besides, the technology of membrane is described as a selective barrier that allows certain substances to pass through easily as compared to others and this technology is believed to outperform other high-energy separation systems (Cheng et al., 2018).

In the past few years, there has been a substantial surge in the interest in acquiring the new type of membranes that are differentiated by greater productivity and selectivity (Apel et al., 2019). According to Goh & Ismail, polymeric membranes are the center of attention in desalination and wastewater treatment, owing to their significant track records and well-established technology (Goh & Ismail, 2018). Correspondingly, the common types of polymers utilised by researches for the treatment of oily wastewater consists of cellulose acetate [CA], polypropylene [PP], polyurethane [PU], poly(p-phenylene sulphide) [PPS], polyacrylonitrile [PAN], polyethersulfone [PES], polytetrafluoroethylene [PTFE], polyvinylidene fluoride [PVDF], poly-(1,4-phenylene ether) ether sulfone [PPEES], and polysulfone [PSf] (N. H. Ismail et al., 2020). Undoubtedly, polymeric membranes have become increasingly popular in the industry of water treatment due to their economical manufacturing, ease of preparation and adjustability of porous structure, excellent product quality, convenience in scaling up, lower consumption of energy, and eco-friendliness (Ariono et al., 2017; Aryanti et al., 2017). Conversely, fouling formation, which adds to flux loss, increased trans-membrane pressure, and a change in membrane selectivity limits the membrane's applicability (Aryanti et al., 2017). Despite the drawbacks, polymeric membranes are favourable due to their ability to be altered according to the exact requirements of the process in which they are utilised, allowing the process of selective separation (Dickhout et al., 2017).

According to Zahid *et al.*, among the methods applied in the modification of polymeric membranes, surface grafting and surface coating are two of the most prevalent ways for improving antifouling properties and adding a hydrophilic character to the membrane (Zahid et al., 2018). Nevertheless, the stated methods utterly alter the membrane's exterior surface, not its internal pores, and membrane manufacture also necessitates post-treatment. Mousa *et al.* had elaborated innovative approaches and materials with improved surface hydrophilicity via interfacial polymerization or the addition of hydrophilic nanoparticles are required to overcome these constraints (Mousa et al., 2020). Therefore, recent studies have shown significant interest to incorporate the polymeric membranes with nanocomposite materials because of their synergistic effect in enhancing the character of the membranes for better oil-water separation (Modi & Bellare, 2019). As mentioned previously, there are various materials used for the development of polymeric membrane, however, the most important membrane materials are PSf and this due to its mechanical, thermal, and chemical stability, as well as its oxidation resistance, and anti-fouling properties (Alosaimi et al., 2017; Dong et al., 2018; Mousa et al., 2020; Zahid et al., 2018). Even so, membrane fouling is common with PSf membranes as this is due to their hydrophobic nature. Thus, in order to prevent membrane fouling, researchers have proposed to increase the hydrophilicity of membranes through surface or bulk alteration. The incorporation of inorganic nanoparticles into the polymer matrix of membranes is a type of bulk modification procedure used to improve the membrane's hydrophilicity and antifouling characteristics (Tizchang et al., 2019).

Apart from that, organoclay has gained attention in recent years due to its high adsorption capacity, abundant in nature, economical, and simplistic in incorporation with membranes. Hussain & Chakraborty had stated that the formation of organoclay nanocomposites from organic-inorganic (clay) minerals are gaining popularity and are being extensively researched in the material science field (Hussain & Chakraborty, 2017). Besides, it allows the creation of new functionalized materials with characteristics such as an easily changing layer-by-layer (LbL) structure, precisely controlled film thickness, or a variety of physical qualities not present in each of the specific elements. Due to the stated potential, thus, the detailed explanation, as well as comparison of the phase inversion technique, development of polymeric membrane incorporated with organoclay, and the water separation performance, will be further discussed in the next chapter.

## 1.2 Research Problems

Various water separation techniques have been established to treat contaminated water or also known as wastewater. The wastewater treatment methods are such as reverse osmosis, chemical precipitation, gravity, ion exchange, electrodialysis, adsorption, membrane filtration and etc. Li *et al*. have mentioned that the massive wastewater outflow from municipal, industrial, and agricultural may lead to substantial risk posed by toxic heavy metals that are found in wastewater. Moreover, if the concentration of heavy metals in wastewater exceeds the allowable discharge limits for aquatic ecosystems, the release into the environment is also dangerous to public health (H. Li et al., 2020). According to Khulbe & Matsuura, adsorption is thought to be the best way for treating wastewater, yet typical adsorbents including activated carbon, zeolites, and natural fibres have poor selective sorption, low adsorption capacities, and inadequate regeneration abilities. Nqombolo *et al.* have mentioned that adsorption is one of the broadly utilised methods in wastewater treatment as it is economical, provides a large range of adsorbents, and has ease of operation, but it is believed that there are some limitations to this method which are lack of suitable adsorbents with high adsorption capacity and poor commercial use of the adsorbents, hence, the polymeric membrane is introduced (Nqombolo et al., 2018).

According to Shen *et al.,* PSf is known for its high performance and stable characteristic but this technology is prone to membrane fouling because of its natural hydrophobicity that encouraged the adhesion of hydrophobic natural organic materials (Shen et al., 2020). In addition, Alosaimi had mentioned by incorporating polymer-clay nanocomposites, enables the improvement of polymer matrices such as hydrophilicity, even when added in small amounts and increases the polymer matrix's efficacy for pollutant removal in aqueous environments (Alosaimi, 2021a). However, the incorporation of inorganic nanoparticles, such as organoclay, into polymer matrices only leads to a minor improvement in characteristics. Dlamini et al. had also stated that it may not be best to change the polarity of the clay mineral because the negative charge on the clay mineral or clay is believed to be responsible for greater selectivity through anion repulsion (Dlamini et al., 2019). Clay mineral sheets, on the other hand, are impenetrable which prevent water from passing through. Besides, no research has been conducted regarding improvement of PSf membrane by incorporating the organoclay into the water bath as well as the study on its water separation performance in removing heavy metal. Hence, this study will be focusing on how to improve the performance of membranes by studying its water separation performance after incorporating the polymeric membrane with organoclay via phase inversion.

## 1.3 Research Questions

This research project will focus on the study of water separation performance by modifying polymeric membrane with organoclay embedded via phase inversion technique. Hence, the research questions are:

i. What is the significant effect of the membrane surface modification with organoclay via phase inversion technique in term membrane morphology?
ii. How will the chemical properties and the morphology influence the prepared membrane?
iii. What is effect of the modified membrane on water separation performance as well as the removal of heavy metal?