



Faculty of Resource Science and Technology

**Synthesis and Application of Graphene Oxide@ZIF-8/Alumina Hollow
Fibre Membrane for Oily Wastewater Treatment**

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Synthesis and Application of Graphene Oxide@ZIF-8/Alumina Hollow Fibre Membrane for Oily Wastewater Treatment

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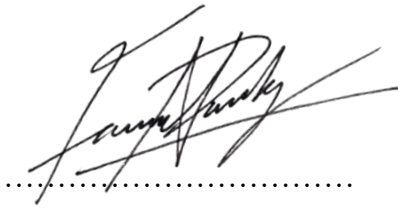
Faculty of Resource Science and Technology

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.



Signature

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ABSTRACT

Oily wastewater pollution primarily harms drinking water and groundwater resources, endangers marine life and threatens human health. Therefore, the use of membrane filtration technology for water reclamation from oily wastewater is one of the effective ways for the removal of oil from industrial wastewater. Hence a promising approach is by microfiltration using membrane-based graphene oxide (GO). The pristine alumina hollow fibre membrane is modified with a graphene oxide (GO) sheet which was inserted with Zeolitic Imidazolate Framework-8 (ZIF-8) crystals to form a stable nanocomposite membrane with a high surface area and rich with oxygen functional groups. This significantly improved the adsorption capacity because it provides more site for oil adsorption. Therefore, this research aims to synthesize the graphene oxide (GO) and to fabricate the GO@ZIF-8 nanocomposites onto the alumina hollow fibre membrane (Al_2O_3) to produce hybrid graphene oxide@ZIF-8/alumina hollow fibre membrane (GO@ZIF-8/ Al_2O_3). In brief, GO is prepared by the oxidation of graphite using KMnO_4 as a strong oxidizing agent based on the modified Hummers' method, then followed by the fabrication of crosslinked GO@ZIF-8 composites on the alumina hollow fibre membrane via *in-situ* solvothermal assembly method. The GO@ZIF-8/ Al_2O_3 composites structure is explored by Fourier-Transform Infrared Spectrophotometer (FTIR), Ultraviolet–visible spectroscopy (UV-Vis), Field Emission Scanning Electron Microscope (FE-SEM) and X-Ray Diffraction (XRD). Successively, the removal of oil from water by GO@ZIF-8/ Al_2O_3 membrane performance was evaluated through the batch adsorption study and crossflow filtration system. The effects of several adsorption factors, such as initial oil concentration and response time, were investigated. To determine the adsorption mechanism, different kinetic models including Pseudo-First Order and Pseudo-Second Order and isotherms

models such as Freundlich and Langmuir were used. Adsorption isotherm is best suited by the Freundlich model ($R^2=0.98046$), whereas adsorption kinetics is best fit by the pseudo-second order ($R^2=0.98247$), indicating that the adsorption process involves chemisorption. According to the crossflow filtration study, the membranes could remove up to 96.32% of the oil from the aqueous solution. Additionally, the reusability analysis revealed that 90.08% of the oil was rejected after 6 reusability cycles. The better separation performance could be attributed to the well dispersion of ZIF-8 nanoparticles in the GO onto the alumina hollow fibre support membrane. Hence, a straightforward scalable approach for producing reliable GO@ZIF-8 based membranes with an efficient oil removal capability is shown.

Keywords: Graphene oxide (GO), Zeolitic Imidazolate Framework-8 (ZIF-8), oil removal, membrane reusability

Sintesis dan Aplikasi Membran Gentian Berongga Grafena Oksida@ZIF-8/Alumina untuk Rawatan Air Sisa Berminyak

ABSTRAK

Pencemaran air sisa berminyak memudaratkan terutamanya air minuman dan sumber air bawah tanah, membahayakan hidupan marin dan mengancam kesihatan manusia. Oleh itu, penggunaan teknologi penapisan membran untuk penambakan air daripada air sisa berminyak adalah salah satu cara yang berkesan untuk penyingkiran minyak daripada air sisa industri. Oleh itu pendekatan yang menjanjikan adalah dengan penapisan mikro menggunakan membran berasaskan grafena oksida (GO). Membran gentian berongga alumina tulen diubah suai dengan kepingan grafena oksida (GO) yang dimasukkan dengan kristal Kerangka Zeotic Imidazoalate-8 (ZIF-8) untuk membentuk membran nanokomposit yang stabil dengan luas permukaan yang tinggi dan kaya dengan kumpulan fungsian oksigen. Hal ini meningkatkan kapasiti penyerapan dengan ketara kerana ia menyediakan lebih banyak tapak untuk penyerapan minyak. Oleh itu, penyelidikan ini bertujuan untuk mensintesis grafena oksida (GO) dan untuk menghasilkan nanokomposit GO@ZIF-8 pada membran gentian berongga alumina (Al_2O_3) untuk menghasilkan membran hybrid gentian berongga grafena oksida@ZIF-8/alumina. Secara ringkasnya, GO disediakan melalui pengoksidaan grafit menggunakan KMnO_4 sebagai agen pengoksidaan kuat berdasarkan kaedah Hummers yang diubah suai, kemudian diikuti dengan fabrikasi nanokomposit GO@ZIF-8 bersilang pada membran gentian berongga alumina melalui kaedah pemasangan in-situ solvothermal. Struktur nanokomposit GO@ZIF-8/ Al_2O_3 diterokai oleh Spektrofotometer Inframerah Transformasi Fourier (FTIR), Spektroskopi Ultraungu-nampak (UV-Vis), Mikroskop Elektron Pengimbasan Pelepasan Medan (FE-SEM) dan Difraksi Sinar-X (XRD). Setelah itu, prestasi penyingkiran minyak daripada air oleh

GO@ZIF-8/Al₂O₃ membran gentian berongga akan dinilai melalui kajian penjerapan kelompok dan sistem penapisan aliran silang. Kesan daripada beberapa faktor penjerapan seperti kepekatan minyak pada awal dan masa tindak balas telah disiasat. Untuk menentukan mekanisme penjerapan, model kinetik yang berbeza termasuk Perintah Pseudo-Pertama dan Perintah Pseudo-Kedua dan juga model isoterma seperti Freundlich dan Langmuir telah digunakan. Isoterma penjerapan paling sesuai ialah model Freundlich ($R^2=0.98046$), manakala kinetik penjerapan paling sesuai ialah Pseudo-Second Order ($R^2=0.98247$), menunjukkan bahawa proses penjerapan melibatkan kemisorpsi. Berdasarkan kajian ini, penapisan aliran silang membran boleh mengeluarkan sehingga 96.32% minyak daripada larutan akueus. Selain itu, analisis kebolegunaan semula mendedahkan bahawa 90.08% minyak telah dikeluarkan selepas enam kitaran kebolegunaan semula. Prestasi pemisahan yang lebih baik boleh dikaitkan dengan seberapa baik penyebaran nanopartikel ZIF-8 dalam GO ke membran sokongan gentian berongga alumina. Oleh itu, pendekatan berskala mudah untuk menghasilkan membran berasaskan GO@ZIF-8 yang boleh dipercayai dengan keupayaan penyingkiran minyak yang cekap ditunjukkan.

Kata kunci: *Grafena oksida (GO), Kerangka Zeotic Imidazoalate-8 (ZIF-8), penyingkiran minyak, kebolegunaan semula membran*

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LIST OF ABBREVIATIONS

AGMD	Air Gap Membrane Distillation
Al	Aluminium
Al ₂ O ₃	Alumina/ Aluminium Oxide
AMs	Adsorptive Membranes
AOPs	Advanced Oxidation Processes
APTES	3-Aminopropyltriethoxysilane
BaCl ₂	Barium Chloride
BDC	1,4-benzene dicarboxylate
BET	Brunauer-Emmett-Teller
bpy	4,4-Bipyridine
BSA	Bovine Serum Albumin
C	Carbon
Ca	Calcium
Cd	Cadmium
CDs	Carbon Dots
CF	Cotton Fabric
CG	cMCNTs/GO
CH ₄	Methane
Cl	Chloride
cMCNTs	carboxylated multiwalled CNTs
CNTs	Carbon Nanotubes
COD	Chemical Oxygen Demand
COOH	Carboxylic Acid

CTS	Chitosan
Cu	Copper
Cu ₂ O	Copper (I) Oxide
DAF	Dissolved Air Flotation
DI	Deionized
DMF	N, N-Dimethylformamide
EDTA	Ethylenediaminetetraacetic Acid
EDX	Energy Dispersive X-Ray
FESEM	Field-Emission Scanning Electron Microscopy
FO	Forward Osmosis
FTIR	Fourier Transform Infrared Spectroscopy
G	Graphene
GNA	Graphene/Nanofiber Aerogels
GO	Graphene Oxide
GO@ZIF-8/Al ₂ O ₃	Graphene Oxide@ZIF-8/Alumina
GS	Gravity Separation
HCl	Hydrochloric Acid
HCN	Hydrophilic Crosslinking Network
HCOONa	Sodium Formate
HDTMS	Hexadecyltrimethoxysilane
HF	Hollow Fiber
HNO ₃	Nitric Acid
H ₂ O ₂	Hydrogen Peroxide
H ₃ PO ₄	Phosphoric Acid
H ₂ SO ₄	Sulphuric Acid

Im	Imidazolate
KOH	Potassium Hydroxide
KMnO ₄	Potassium Permanganate
2-MeIm	2-Methylimidazole
MeOH	Methanol
MB	Methyl Blue
MD	Membrane Distillation
MF	Microfiltration
MgO	Magnesium Oxide
MF	Microfiltration
MIm	2-Methylimidazole
MMMs	Mixed Matrix Membranes
MnO ₂	Magnesium Dioxide
MNPs	Magnetic Nanoparticles
MOFs	Metal Organic Frameworks
MWCO	Molecular Weight Cut Off
N	Nitrogen
NaNO ₃	Sodium Nitrate
NF	Nanofiltration
Ni	Nickel
NOM	Natural Organic Matter
O	Oxygen
O/W	Oil-In-Water
PAN	Poly(Acrylonitrile)
Pb	Lead

PCPs	Porous Coordination Polymers
PDA	Polydopamine
PE	Polyethylene
PEI	Poly(Ethyleneimine)
PES	Polyethersulfone
PFO	Pseudo-first order
PFOES	Perfluorooctyltriethoxysilane
pH	Potential of Hydrogen
PHFMs	Polysulfone Hollow Fibre Membranes
PMs	Polymeric Membranes
POMs	Polyoxometalates
POME	Palm Oil Mill Effluent
PP	Polypropylene
Ppm	Parts Per Million
PSA	Polysulfonamide
PSf	Polysulfone
PSO	Pseudo-second order
PTFE	Poly(Tetrafluoroethylene)
PVA	Poly(Vinyl Alcohol)
PVC	Polyvinyl Chloride
PVDF	Polyvinylidene Fluoride
PVP	Polyvinylpyrrolidone
rGO	Reduced Graphene Oxide
RO	Reverse Osmosis
RSM	Response Surface Methodology

S	Sulphur
SCWO	Supercritical Water Oxidation
SDS	Sodium Dodecyl Sulphate
SEM	Scanning Electron Microscope
SGA	Superhydrophobic Graphene Aerogel
Si	Silicon
SiO ₂	Silicon Dioxide
TA	Tannic Acid
TiO ₂	Titanium Dioxide
TMP	Transmembrane Pressure
TCPP	Tris(Chloropropyl) Phosphate
UF	Ultrafiltration
UV-Vis	Ultraviolet–Visible Spectroscopy
V	Vanadium
WHO	World Human Organization
XRD	X-Ray Diffraction
Zeo	Zeolite
ZIFs	Zeolite Imidazolate Frameworks
ZIF-8	Zeolite Imidazolate Framework-8
ZGO	ZIF-8@Graphene Oxide
Zn	Zinc
ZnCl ₂	Zinc Chloride
Zn(NO ₃) ₂ •6H ₂ O	Zinc Nitrate Hexahydrate
ZnO	Zinc Oxide
Zr	Zirconium

ZrO₂

Zirconium Dioxide

CHAPTER 1

INTRODUCTION

1.1 Background of study

Oily wastewater is a broad term that encompasses any water contaminated with oil, and it can originate from various sources. The contamination can be a result of natural processes, such as stormwater runoff carrying oils from roads or other surfaces, or it can be generated as a byproduct of industrial activities. One of the major contaminants is the discharged of oily wastewater mainly from palm oil industries, oil fields, and automobiles. Produced water from the oil and gas extraction process is the world's greatest source of oily wastewater (Chen et al., 2021). Oily wastewater can affect drinking water sources, such as rivers and lakes, that are used by people downstream or harm marine life. Furthermore, if the contamination is not identified and appropriately remedied, it may have an impact on crop productivity later on. Oily wastewater is very hard to be treated because it comprises of a dispersed (suspended droplets of oil and water) and continuous phase (medium suspension) (Paixão & Balaban, 2018). Simple physical processes can readily remove suspended or free oil from the aqueous phase (de Medeiros et al., 2022). However, emulsions may include significant levels of mineral oil, which is very resistant to breakdown by biological processes. These complex emulsions are stabilised chemically and comprise water, oil, and additives such emulsifiers and antifoaming agents. Therefore, the separation of the oil and other immiscible components is important whether the purpose is to recover the oil for economic gain or to remove the oil phase for ecologically friendly disposal (Tanudjaja et al., 2019).

The process of treating wastewater involves eliminating impurities from it before it enters natural water sources such lakes, rivers, seas, and aquifers (Mohsenpour et al., 2021). Numerous techniques are anticipated for cleaning oily wastewater and are categorised into chemical, physical, mechanical, and biological approaches. Due to the limitations of conventional methods, a few modern approaches have been created based on scientific and technology advancements.

In comparison to common technologies such as solvent extraction, coagulation and dissolved air flotation (DAF), one of the most promising techniques for treating oily wastewater is membrane separation, particularly for oil-water emulsion separation where the oil droplets are smaller than 20 μ m (Chen et al., 2021). A membrane separates and restricts the transit of numerous substances by acting as a selective barrier between two phases. The membrane separation technique is more efficient at removing oil, has a more compact design, and requires less space than traditional methods (Drouin et al., 2022). Membrane-based filtration can treat oily wastewater with a much wider compositional range and at the same time are managed to ensure a high removal of oil in wastewater (Ikhsan et al., 2020). Therefore, membrane-based separation technology is one of the most potential alternatives for wastewater treatment, offering benefits such as environmental preservation, ease of operation, and energy savings (Ahmad et al., 2020). The two types of membranes that were commonly used for the treatment of oily wastewater are polymeric membrane and ceramic membrane. Ceramic membranes offer a variety of advantages over polymeric membranes including the cleaning simplicity, long lifespan, high mechanical, chemical and thermal stability making them particularly suitable for oily wastewater treatment (Abdullayev et al., 2019; Motta Cabrera et al., 2021). However, fouling and low

separation efficiency remain two major obstacles to the continued use of ceramic membranes (Kang et al., 2019).

One excellent technique to alter surface wetting behaviour and improve oil-water separation and anti-fouling performance is by applying nanoparticles to the surface of ceramic membranes (Kang et al., 2019). Graphene oxide (GO) nanosheet has a remarkable potential for excellent separation performance because of its atomic layer thickness and oxygen-rich functional groups (Yang et al., 2018). Nonetheless, there are still certain drawbacks to using GO as an independent adsorbent, including a slightly larger preparation cost and a longer cycle with insufficient capacity for separation and recovery (Li & Xu, 2021). A growing number of researchers are looking towards changing GO in order to address these limitations. For instance, GO can be used with other materials to improve removability and reduce costs (Avornyo & Chrysikopoulos, 2024; Xuan et al., 2023). Therefore, researchers utilize nanostructures and functional groups to improve the GO surfaces to optimize the effects of GO on membrane performance. Metal organic frameworks (MOFs) are a common nanostructure that is applied to GO surfaces. Zeolitic imidazolate frameworks (ZIFs) are one of the MOF that presents more adaptability as well as hydro stability (Ahmed et al., 2019). The coupling of N-atoms in imidazolate anions with metal ions forms ZIFs which are permeable in nature such as Co^{2+} or Zn^{2+} . The ZIFs have a structure like zeolites, which are made up of four-connected webs of tetrahedral components. ZIFs have improved membrane properties such as surface roughness and hydrophilicity resulting in increased antifouling capabilities and solute rejection and water flux (Makhetha & Moutloali, 2020).

The preferred support membrane is an alumina hollow fibre membrane, which is constructed of alumina, a natural substance. The remarkable optical, chemical, thermal, mechanical, and electrical properties of aluminium oxide (alumina) have attracted a lot of interest (Chauhan & Kumar, 2020). Performance of the alumina membrane is anticipated to be enhanced by embedding the GO@ZIF-8 layer on the membrane surface.

At the same time, hybrid nanocomposites are being used by researchers to effectively incorporate fillers in membranes to improve membrane performance aspects. For example, Makhetha & Moutloali (2020) used an *in-situ* growing approach to synthesis several ZIF-8@GO composites with varied volumes of evenly dispersed ZIF-8 on GO support. Then, employing the phase inversion method, a series of ZIF-8@GO/PES ultrafiltration membranes was created by implanting ZIF-8@GO composites into the PES matrix (Makhetha & Moutloali, 2020). According to Li et al. (2020), the composite membrane's separation factor and permeate flux were improved due to the preferential adsorption and mass transfer of ZIF-8 modified GO laminate (ZGO). These findings demonstrated that ZGO/PEBA membranes may recover bio-butanol from aqueous solution. In a similar study, Xie et al. (2021) effectively synthesized a ZIF-8-ERGO nanocomposite by mixing pre-synthesized ZIF-8 and GO at ambient temperature, followed by electrochemical reduction (Xie et al., 2021). For the first time, the ZIF-8-ERGO modified electrode was created and used as a sensor for the electrochemical detection of the dangerous industrial contaminant hydrazine.

According to studies, MOFs can successfully adsorb pollutants such as heavy metal ions, organic dyes, phenols, heavy metal ions, and oil droplets from aqueous solutions (Dhaka et al., 2019). The shape, chemical and physical properties, stability, and potential

applications of MOFs can be dramatically enhanced by combining them with suitable substances. Graphene oxide (GO) is an ideal material for developing MOF composites because in addition to altering the characteristics of the MOF such as shape and structure, graphene oxide (GO) also inhibits MOF aggregation (Wang et al., 2020; Zheng et al., 2018). Therefore, the composite made of GO@MOFs is most likely to show great potential in the role of adsorbent for the treatment of wastewater. As a result, the focus of this study is on the development of a graphene oxide ZIF-8 membrane for oily wastewater treatment. Hence, the objectives of this research were to synthesize, characterize, and evaluate the oil removal ability of the prepared nanocomposite membrane.

1.2 Problem statement

One of the potential solutions to address the challenge of oil-contaminated wastewater treatment is the innovation of membrane-based technologies. Membrane filtration, particularly using alumina hollow fibre ceramic membranes has shown promise due to its straightforward operational processes and high efficiency. However, a significant challenge in this approach lies in achieving effective separation of alumina membrane which is critical for filtering oil from wastewater. Poor separation efficiency can lead to incomplete removal of oil pollutants, while membrane integrity may be compromised by inadequate adhesion or compatibility between the oil molecules and alumina. Additionally, the absence or insufficient presence of functional groups on the membrane surface impairs its ability to attract and adsorb oil contaminants, posing another key challenge.

To enhance the performance of membranes in oily wastewater treatment, the integration of carbon nanomaterials, particularly graphene oxide (GO) has gained

significant attention. GO is highly valued for its unique properties, including its large surface area and hydrophilicity, which make it an ideal candidate for improving the filtration efficiency of membranes. By incorporating GO into membranes, it is possible to enhance the adsorption of oil molecules. This improvement is attributed to the increased surface energy and hydrophilic nature of GO which facilitates better interaction between the membrane and oil particles. Additionally, the presence of oxygen-containing functional groups on GO allows for enhanced chemical interactions, improving the overall adsorption capacity of the membrane.

Despite these advantages, one of the main challenges with using GO in aqueous environments is its poor long-term stability. In aqueous solutions, GO tends to delaminate or disaggregate, losing its structural integrity within a few hours (Thebo et al., 2018). This instability diminishes the membrane's effectiveness over time, limiting its practical application in continuous or long-term wastewater treatment processes. To address this issue, researchers have explored hybridization strategies that combine GO with other materials such as metal-organic frameworks (MOFs) to create more stable and efficient membrane structures. ZIF-8 is a type of MOFs characterized by its well-defined nanoporous structure, large surface area, and tuneable pore size, making it highly suitable for filtration applications. The incorporation of ZIF-8 with GO enhances the membrane's overall performance by forming a composite nanostructure that not only prevents GO delamination but also significantly improves the adsorption capacity of the membrane. This is achieved through the formation of strong interactions between ZIF-8 and GO, including hydrogen bonding, ionic bonding, and coordination bonding (Cao et al., 2021). Moreover, the uniform dispersion of ZIF-8 onto GO nanosheets effectively reduces ZIF-8 agglomeration in the membrane's active layers, combining the advantages of both

materials. By combining GO with ZIF-8, the resulting composite membrane can benefit from the synergistic properties of both materials.

Therefore, this research focuses on synthesizing a graphene oxide@ZIF-8 composite nanomaterial supported on an alumina hollow fibre membrane. A simple, rapid, room-temperature procedure was used to synthesize the GO@ZIF-8 hybrid nanocomposite, which outperforms traditional solid adsorbents like mesoporous silica and activated carbon because of its varied pore sizes, active sites, and high specific surface areas.

1.3 Objectives

The objectives of this study:

- i. To determine the effect of graphene oxide loading on the physicochemical properties of GO@ZIF-8/Al₂O₃ membrane
- ii. To evaluate the effects of graphene oxide loading on the adsorption efficiency, adsorption mechanism and filtration performance of the GO@ZIF-8/Al₂O₃ membrane
- iii. To determine the reusability potential of the GO@ZIF-8/Al₂O₃ membrane

1.4 Scope of the study

- i) To determine the effect of graphene oxide loading on the physicochemical properties of GO@ZIF-8/Al₂O₃ membrane:

- a) Modifying alumina membrane by using the GO and ZIF-8 to produce the GO@ZIF-8/Al₂O₃ membrane.
 - b) Characterizing the structure and surface morphology of the modified membrane by using scanning electron microscopy (SEM), X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR).
- ii) To evaluate the effects of contact time, pH and initial concentration on the adsorption efficiency and mechanism of the GO@ZIF-8/Al₂O₃ membrane:
- a) Examining the influence of contact time on the adsorption efficiency of the GO@ZIF-8/Al₂O₃ membrane by adsorption experiments at different time intervals.
 - b) Analysing the impact of pH on the adsorption behaviour of the GO@ZIF-8/Al₂O₃ membrane by adjusting the pH of the oily water and conducting the adsorption experiments at different pH levels (3,7 and 10).
 - c) Evaluating the adsorption efficiency of GO@ZIF-8/Al₂O₃ membrane at different initial concentrations of oily water.
- iii) To evaluate the effects of GO loading on the filtration performance of the GO@ZIF-8/Al₂O₃ membrane:
- a) Determining the optimal loading concentration of graphene oxide that maximizes the filtration performance by using a different amount of GO loading.
 - b) Evaluating the filtration ability of the GO@ZIF-8/Al₂O₃ membrane by using the crossflow filtration system study.

iv) To determine the reusability potential of the GO@ZIF-8/Al₂O₃ membrane:

- a) Measuring the reusability of the GO@ZIF-8/Al₂O₃ membrane from multiple cycles of filtration.
- b) Regenerating used membrane by soaking in the prepared 2% wt. sodium dodecyl sulphate (SDS) solution.

CHAPTER 2

LITERATURE REVIEW

2.1 Oily wastewater

The term "oily wastewater" refers to wastewater that contains significant concentrations of dissolved organic and/or inorganic compounds in suspension together with oils, greases and fats (Adetunji & Olaniran, 2021). The oil mixed with water contains fats, hydrocarbons, and petroleum fractions like petrol, kerosene, and diesel oil. As shown in Table 2.1, the contaminants found in oily wastewater are divided into two groups: organic and inorganic (Ikhsan et al., 2020).

Table 2.1: Classification of oily wastewater pollutants (Ikhsan et al., 2020).

Properties	Organic Pollutant	Inorganic pollutants
Major component	Petroleum hydrocarbons	Inorganic oils
Types	Asphaltenes, aromatic, aliphatic,	Motor oil, lubricating, turbine, hydraulic
Major element	Sulphur, nitrogen, Oxygen,	—
Accompanying element	Organometallic complexes, vanadium (V), lead (Pb), cadmium (Cd), Nickel (Ni)	Particulate matters, solvents, oily sludge, heavy metals, gasoline
Distribution in oily wastewater	Dissolved, emulsified, or dispersed,	Settleable or floatable

At present, a great deal of companies produces large amounts of oily wastewaters, which have a number of detrimental consequences on the ecosystem, including pollution of the air from hydrocarbons and oil evaporating into the atmosphere. By establishing new economic and social opportunities, industrial advancements have substantially contributed to the advancement of human civilization. However, untreated wastes released by businesses have a negative impact on ecological systems, human health, and the environment, with oil polluted wastewater becoming one of the most urgent issues (Barambu et al., 2021). Figure 2.1 shows the three typical types of oil-water emulsion.

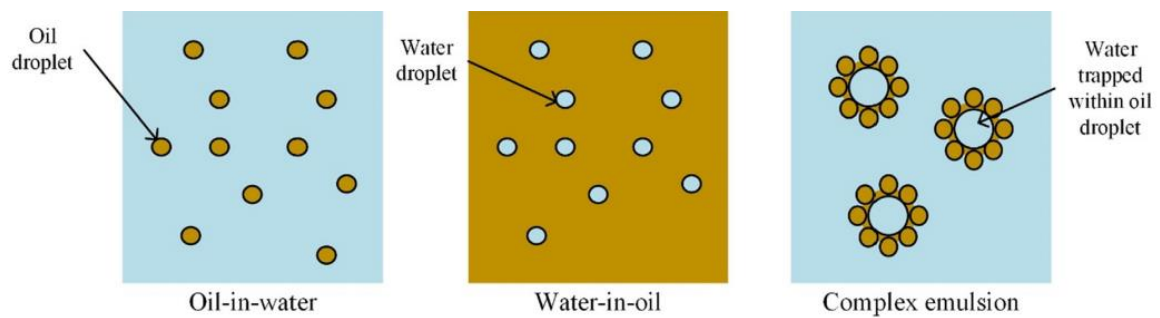


Figure 2.1: Classification of oil-water emulsion (Barambu et al., 2021).

The different forms of oil-water emulsions are water-in-oil, oil-in-water, and complex emulsions (Tian et al., 2022). Figure 2.2 illustrates a few examples of the negative effects of improperly disposing of oily wastewater.

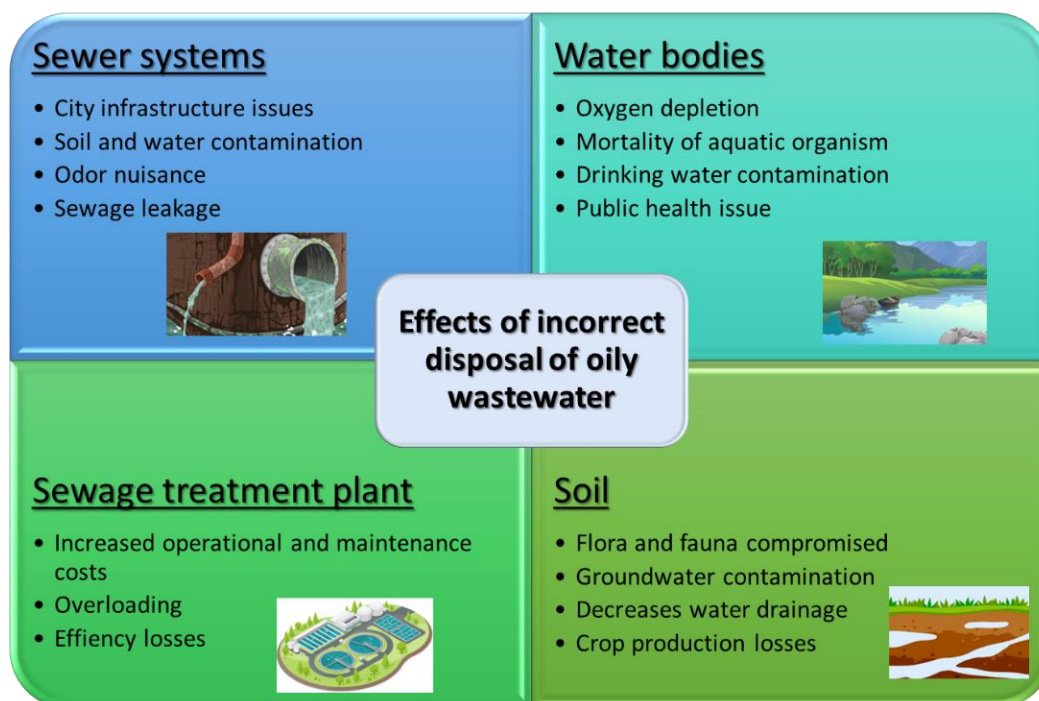


Figure 2.2: Effects of incorrect disposal of oily wastewater (Mulinari et al., 2020).

The pollution caused by oily wastewater affects a number of things, including sources of water, the health of people, the atmosphere, agriculture production, the environment, and the survival of living things. Oily effluent is created during numerous industrial operations, including those related to food, ships, petrochemicals, oil refineries, leather, and metal polishing. Reusing water or discharging it into surface waterways and sewer systems requires the removal of oils and greases (Yalcinkaya et al., 2020). The discharge limit for mineral and synthetic oils and grease is 10–15 mg/L, whereas the limit for oils and grease derived from animals and vegetables is 100–150 mg/L (Adetunji & Olaniran, 2021). The content of the oil can be categorized according to their physical form as shown in Table 2.2.

Table 2.2: Characterization of oil based on physical form (Yalcinkaya et al., 2020).

Type of oil	Descriptions
Free (floating) Oil	When conditions are stable, it rises swiftly to the water's surface. There are droplets larger than 150 microns in size.
Dispersed oil	Tiny droplets stabilized by the presence of surfactants and carry an electric charge. The droplets range in size from 20 to 150 microns. Polyaromatic hydrocarbons and a few alkyl phenols that are less soluble in water make up dispersed oil (Jiménez et al., 2018).
Emulsified oil	Surfactants are used to create a more stable dispersion, even though it resembles dispersed oil. There are droplets that are smaller than 20 microns.
Dissolved oil	Transparent and translucent oil soluble in water. The droplet size is smaller than 5 microns.

To clean oil effluent, an appropriate treatment process (or methods combined) must be used. These techniques can demonstrate variations that depend on the physical form. The treatment approach is described together with its benefits and drawbacks in the next section.

2.2 Oil removal technologies

Oil pollution in wastewater poses significant risks to ecosystems, human health, and resource recovery (Zhang et al., 2019). A variety of techniques are used to treat oily wastewater, including membrane separation, coagulation, flotation, and biological methods. While each method offers distinct advantages, many face limitations related to

efficiency, cost, and the potential generation of secondary pollutants. Conventional methods, such as gravity separation and dissolved air flotation (DAF), have been widely adopted, but advancements in technology have introduced more effective modern solutions.

Gravity separation (GS) is one of the most basic physical methods used for oily wastewater treatment. This approach relies on the density difference between oil and water, allowing oil to rise and water to settle. While gravity separation is straightforward and cost-efficient, it struggles with separating emulsified oil and requires long residence times, which makes it less suitable for treating complex wastewater (Douglas et al., 2022). As a result, GS is typically used as a preliminary treatment step to remove dispersed oil and large particles from the water (Abuhasel et al., 2021). Dissolved air flotation (DAF) is another conventional method that introduces air bubbles into the wastewater, which bond with oil particles, causing them to rise to the surface where they can be skimmed off. DAF is effective, with separation rates reaching up to 80%, and it operates efficiently under a variety of wastewater conditions (Rocha e Silva et al., 2020). However, limitations in microbubble production can affect its overall efficiency, particularly when treating wastewater containing small-diameter colloidal oil particles (Brasileiro et al., 2021).

Coagulation and flocculation are also widely used in the treatment of oily wastewater. In this method, chemical coagulants destabilize oil droplets in the water, and flocculation encourages the formation of larger aggregates that can be more easily removed. The efficiency of coagulation and flocculation depends on factors such as coagulant dosage, the pH of the wastewater, and the concentration of oil present (C. Zhao et al., 2021).

More modern methods have emerged to address the limitations of these conventional approaches. Biological treatments, both aerobic and anaerobic, have proven to be highly effective and environmentally friendly for treating oily wastewater. In biological processes, microorganisms break down oil and other pollutants into non-toxic byproducts, offering a sustainable and cost-efficient treatment option (Sanghamitra et al., 2021). Anaerobic systems, in particular, are energy-efficient and can produce methane from organic pollutants, reducing both energy consumption and pollutant levels (Ibrahim et al., 2022). By combining aerobic and anaerobic processes, treatment efficiency can be further enhanced without the need for extensive pre-treatment. Figure 2.3 illustrates the schematic diagram depicting advanced technologies for the treatment of industrial oily wastewater. Figure 2.3 illustrates the schematic diagram depicting advanced technologies for the treatment of industrial oily wastewater.

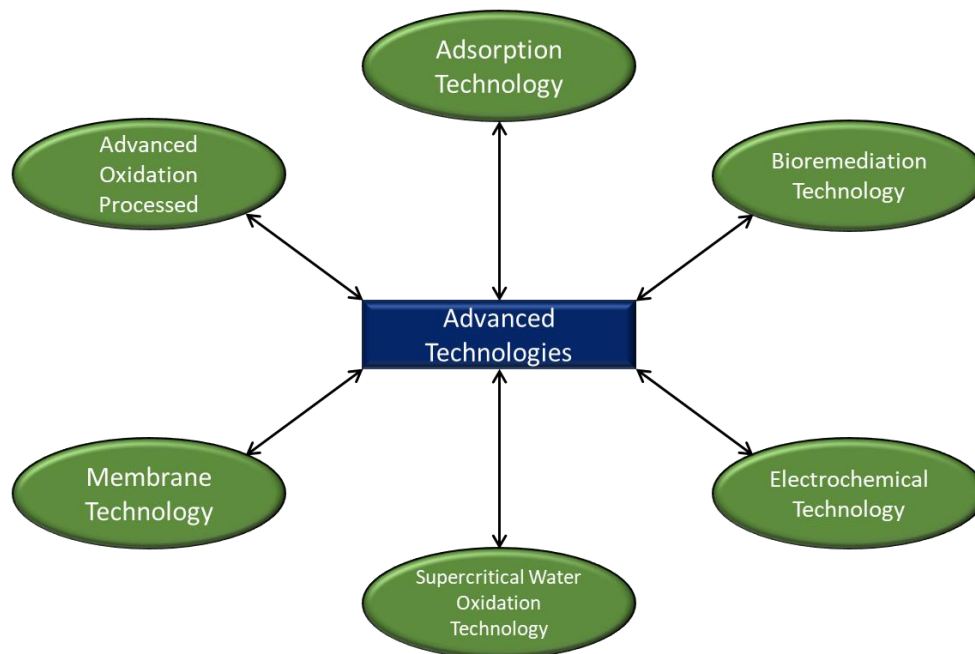


Figure 2.3: Advanced technologies for the treatment of industrial oily wastewater (Adetunji & Olaniran, 2021).

Advanced oxidation processes (AOPs) represent another modern approach to oily wastewater treatment. These processes rely on chemical reactions to generate hydroxyl radicals that break down complex organic pollutants into simpler, less harmful compounds. AOPs, such as photocatalysis, Fenton reactions, and supercritical water oxidation (SCWO), have been shown to be highly effective in treating recalcitrant pollutants that are resistant to conventional treatments (Gul et al., 2021). SCWO, in particular, excels at decomposing toxic substances under high pressure and temperature, resulting in harmless byproducts such as CO₂, water, and nitrogen (Li et al., 2020). Despite the high costs associated with AOPs, their ability to degrade harmful compounds makes them a promising solution for the treatment of complex wastewater streams. Table 2.3 provides the comparison of the various methods for oily wastewater treatment, summarizing their mechanisms, advantages, and limitations.

Table 2.3: Different methods for oily wastewater treatment.

Treatment Method	Mechanism	Advantages	Limitations
Gravity Separation (GS)	Separates based on density differences.	Simple, low energy.	Inefficient for emulsified oil, slow process.
Dissolved Air Flotation (DAF)	Air bubbles lift suspended particles.	High separation efficiency.	Limited microbubble production.
Coagulation & Flocculation	Destabilizes particles using chemicals.	Cost-effective, widely used.	Chemical usage, dependent on dosage.
Biological Treatment	Microorganisms degrade oil.	Eco-friendly, low-cost.	Requires control, longer process.
Advanced Oxidation (AOPs)	Uses radicals to break down pollutants.	Effective on complex pollutants.	High cost, toxic byproducts.
Supercritical Water Oxidation (SCWO)	Oxidizes contaminants at high temperature/pressure.	Breaks down toxic substances completely.	High energy and equipment costs.

2.3 Membrane separation technology

When it comes to separation techniques, membrane technology provides a more efficient approach. Though it is still in its early phases of development, membrane-based technology for treating oily wastewater is predicted to overtake other options in the near future (Tanudjaja et al., 2019). Membrane-based separation is indeed an effective and often cost-efficient solution for removing oil droplets smaller than approximately 10 micrometres (μm).

A membrane is a barrier between two phases, which separates and limits the transport of many chemicals selectively. Membranes can be classified as heterogeneous, homogeneous, asymmetric or symmetric depending on their structural makeup. Membranes can be neutral or bipolar, have a positive or negative charge, and separate solids from liquids. Both functions of the membrane are fulfilled, and the separation is simple. Membrane filtration involves the use of semi-permeable membranes to separate and remove contaminants from water as illustrated in Figure 2.4, producing a treated effluent of higher quality. The efficiency of the membranes is dependent on the membrane itself.

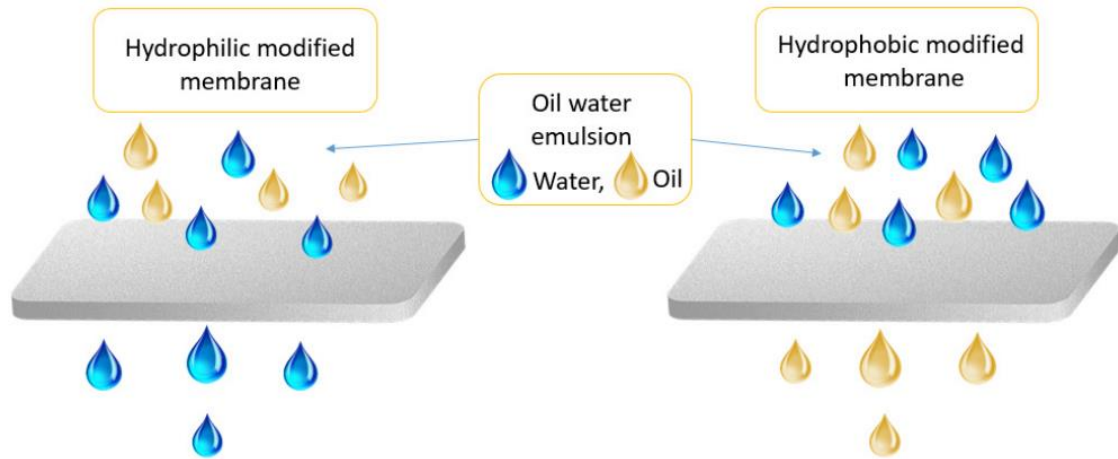


Figure 2.4: Membrane filtration process (Elhenawy et al., 2021).

Membrane filtration technology has become increasingly prevalent in both municipal and industrial wastewater treatment due to its effectiveness in improving the quality of filtered water (Yang et al., 2021). However, a downside of membrane technology is fouling, which results in increased operational and membrane replacement costs. Membrane filtration is characterized the periodic transition between filtration and reverse flushing is known as backwashing, and it is an essential part of maintaining the performance and longevity of the membrane system particularly when hollow fibre membranes are employed in submerged applications.

In this size range, various membrane processes, such as microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF), can effectively separate and remove oil droplets, suspended solids, and other contaminants from water as shown in Figure 2.5.

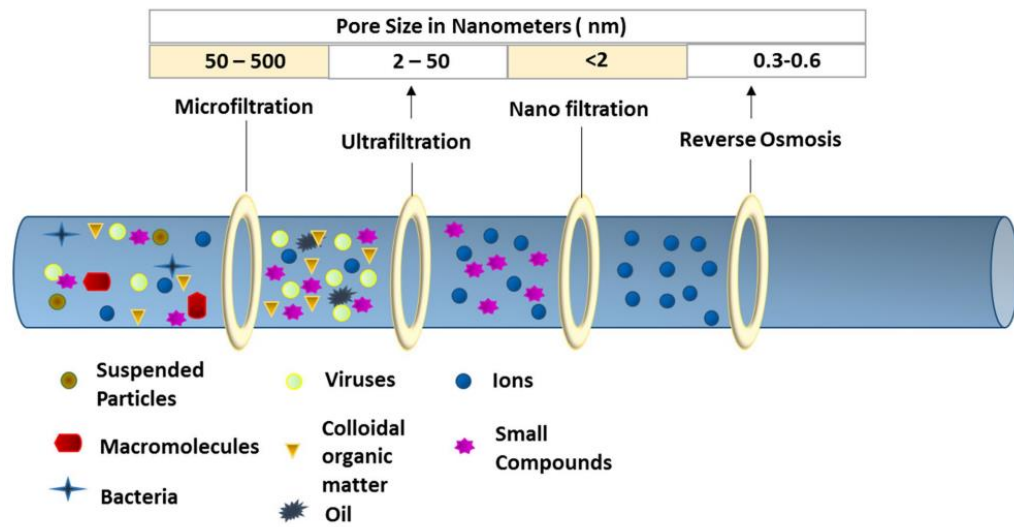


Figure 2.5: Membrane filtration driven by pressure (Rezazazemi et al., 2018).

Due to its benefits, including its ability to remove oil droplets from wastewater with high effectiveness, low energy consumption, and mid-temperature requirements, membrane technology is receiving a lot of attention in this area (Bolto et al., 2020). Water will travel through the membrane more easily and oil droplets will be repelled by hydrophilic surfaces (Bolto et al., 2020). Figure 2.6 summarize the process of membrane separation.

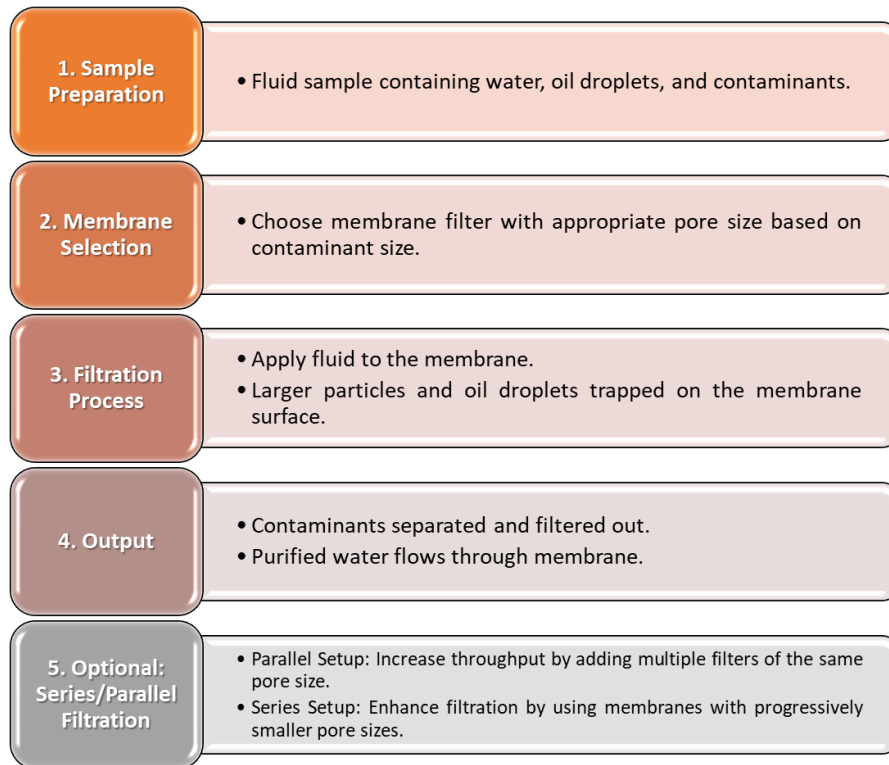


Figure 2.6: Flowchart on the membrane filtration process.

Membranes are classified as polymeric or ceramic based on their composition. Water filtration has been the subject of substantial research on both kinds of membranes. In addition to having outstanding mechanical strength and temperature tolerance, inorganic membranes are extremely durable and resistant to corrosive substances including strong acids, bases, and oxidants. Since inorganic membranes are less susceptible to bacterial deterioration, they are also better for maintenance than polymeric membranes. High temperature chemical cleaning is a viable method for achieving high flux recovery and removing biofouling (Wen et al., 2019).

2.3.1 Polymeric membrane

Membranes made of polymeric materials are highly flexible. Their pore diameters are controllable within a certain range. By changing the coagulation bath conditions, additives, casting conditions, monomer molecules and concentrations, and so on, the properties of the membrane can be altered (Al Harby et al., 2022). Nevertheless, polymeric membranes also offer a number of significant disadvantages. Polymeric membranes' main shortcomings are their inclination to foul and their vulnerability to chlorine (Li et al., 2020). The purpose of membrane cleaning is to preserve or repair the permeability or selectivity of a membrane, which can change as a result of membrane fouling (Gul et al., 2021). Another challenge is the significant trade-off between selectivity and permeability. With the existing polymeric membrane, it is challenging to enhance one without sacrificing the other.

Polyethersulfone (PES), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), and polyethylene (PE) are the most widely used polymeric membranes (Bolto et al., 2020). They are employed in ultrafiltration and microfiltration (Ismail et al., 2020). Compared to hydrophobic membranes, hydrophilic polymeric membranes provide more effective treatments. The combination of super hydrophilic and underwater super oleophobic properties is desirable for membranes used in water treatment. Fouling is a significant problem with the application of polymeric membranes, as it causes a progressive reduction in the permeation flow and separation efficiency while the membrane is operating. Chemical cleaning using potent oxidants and photocatalysis are the methods used to regenerate fouled polymer membranes. These techniques cause membrane material to photodegrade, decrease membrane wettability and service life, and result in membrane corrosion (Nascimbén Santos et al., 2020). One possible solution to fouling

issues is the calcination of polymer membranes to break down organic materials. But to do the calcination, the polymer membrane must be made of thermally stable engineering polymers like polysulfonamide (PSA).

Recent research has focused heavily on using membrane modification techniques to reduce fouling and improve the hydrophilic characteristics of polymer membranes. Techniques for modifying membranes can be divided into three categories which are mixing, surface grafting, and coating. Graphene oxide, copper(I) oxide (Cu_2O) nanoparticles, silica nanoparticles, and nanosized zirconium dioxide (ZrO_2) are examples of nanomaterials that are frequently employed to change membranes through all three of these approaches because of their high number of functional groups and huge surface area (Yalcinkaya et al., 2020). Nanomaterials can modify the hydrophilicity, decrease membrane fouling, create homogenous coatings, alter the pore structure, and alter the surface morphology of the membrane.

2.3.2 Ceramic membrane

A membrane controls the movement of components or contaminants and functions as a selective barrier between two stages in a separation process. Narrower pore size distribution polymeric membranes can be produced at a cheap cost. On the contrary hand, they are easily fouled and cannot survive high temperatures or acidic environments. In this regard, ceramic membranes outperform polymeric membranes, offering superior corrosive resistance, ease of cleaning, and extended lifetime in addition to good thermal and chemical stability (Sandhya Rani & Kumar, 2021). When compared to polymeric membranes, ceramic membranes provide several benefits, such as narrower and more

precisely defined pore size distribution, increased porosity, improved separation and flux, higher hydrophilicity, higher fluxes at low pressure, and reduced fouling. By using calcination, the ceramic membrane may be recovered with ease. In addition, compared to polymeric membranes, ceramic membranes are unlikely to degrade due to bio-fouling caused by microorganisms (Abuhasel et al., 2021). The fragile structure of this membrane makes handling it difficult. Other drawbacks include fouling and expensive fabrication costs (Nguyen et al., 2019).

As shown in Figure 2.7, ceramic membranes are often composed of multiple layers that form an asymmetric structure. These layers are typically constructed of zirconia (ZrO_2), alumina (Al_2O_3), titania (TiO_2), and silica (SiO_2). Nevertheless, these raw ingredients are expensive, and high sintering temperatures (1300–1500°C) are necessary (Sandhya Rani & Kumar, 2021). For ceramic membranes to be commercially viable, the cost of the raw ingredients and the sintering temperature should be kept to a minimum. Nonetheless, there is a great deal of potential to create ceramic membranes with inexpensive basic materials and still preserve their benefits. Lowering the sintering temperatures can also be accomplished with inexpensive ceramic material (Gu et al., 2021; Zou et al., 2020; Zou et al., 2019).

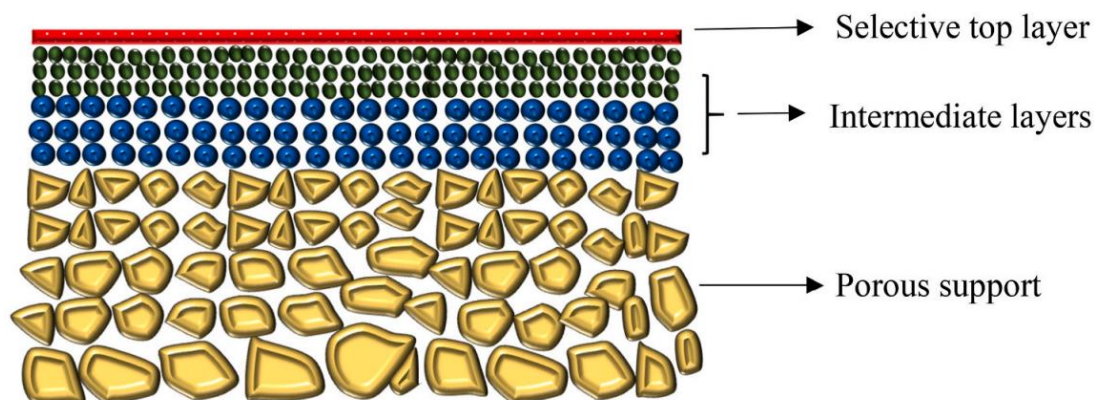


Figure 2.7: Multilayer asymmetric membrane (Sandhya Rani & Kumar, 2021).

Four important steps are involved in the production of ceramic membranes. Firstly, high-quality raw materials are chosen based on the desired characteristics of the ceramic membranes. Common materials include alumina (aluminium oxide), zirconia (zirconium oxide), and titania (titanium dioxide). Raw materials are processed to achieve the desired composition and particle size distribution. This may involve grinding, milling, and mixing to create a homogenous powder. Next, the prepared ceramic powder is formed into the desired shape of the membrane. This can be achieved through various methods, including extrusion, slip casting, tape casting, or injection moulding. Afterwards, the green membrane is subjected to a high-temperature sintering process (Sandhya Rani & Kumar, 2021). Sintering involves heating the ceramic material to a temperature below its melting point, causing the particles to bond and form a solid, dense structure. Lastly, in some cases, the ceramic membrane may undergo additional treatment or coating to enhance its performance. For example, a selective layer may be added to improve the membrane's rejection properties for specific contaminants. Surface modifications or treatments may be applied to make the membrane more hydrophilic or to impart specific properties that enhance its performance in the intended application.

The type of fabrication techniques used determines the final ceramic support/membrane geometry. As a result, different preparation techniques produce different membrane microstructure and morphological characteristics. Ceramic membranes are typically manufactured in two main shapes: tubular and flat. There are further intricate configurations that are variations of tubular-shaped membranes, such as multi-channel monoliths and hollow fibre membranes. Tubular-shaped membranes are frequently made via the extrusion process, while flat-shaped (circular) membranes are typically manufactured by pressing, paste casting, and tape casting processes. A few research explained the way ceramic membranes were made via the use of phase inversion, slip casting, and freeze casting techniques (Zou & Fan, 2021). Among the various geometries, ceramic membranes with tubular and hollow fibres are excellent choices for wastewater treatment applications. In comparison to flat-sheet ceramic membranes, the geometries and structure of ceramic membranes such as tubular and hollow-fibre ceramic membrane modules offer stronger mechanical strength, packing density, and superior handling capabilities against high crossflow velocities (Asif & Zhang, 2021).

2.3.3 Alumina membrane

Alumina membranes are a type of ceramic membrane that is predominantly made from alumina, which is aluminium oxide (Al_2O_3). Looking back on history, the boehmite sol-gel method was used to successfully create the first crack-free alumina films with ultra-fine pores in 1984 (Wang et al., 2022). Afterwards, in 1994, metallic cation retention was made possible by the preparation and application of nanofiltration alumina membranes, and in 2002, multilayer configurations of $\alpha\text{-Al}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ (also known as anatase)/anatase

were made to improve the retentions for relatively tiny organic molecules. Prior research on this topic mostly concentrated on the alumina membrane's preparation and filtration capabilities. Today's alumina membrane development involves surface modification, filtration performance optimisation, enrichment of function and shape, cost-effective production, and preparation. Alumina can be used as the substrate, intermediate layer, and active layer in ceramic membranes because of its simple manufacturing and inherent qualities of high strength, superior chemical stability, and thermal stability (He et al., 2019). Alumina membranes have been used in water and wastewater microfiltration, ultrafiltration, and nanofiltration, depending on the range of pore sizes. For alumina membrane, common ceramic processing techniques included dip coating, sintering, and sol-gel (He et al., 2019).

In general, the development of alumina membranes has encompassed surface modification, optimal filtering performance, enrichment of morphology and function, preparation, and cost-effective manufacturing (Wang et al., 2022). The effectiveness and operational capabilities of Al_2O_3 membranes for water filtration are strongly correlated with their geometries. Alumina membranes are commercially available in three shape which are hollow, tubular, and flat sheet fibre geometries (Rahman et al., 2023). Flat sheet alumina membranes are mostly used as immersed units in plate and frame modules. Their hollow plate structure suggests that the membranes are formed like thin, flat plates with hollow spaces inside. Tubular alumina membranes possess an asymmetric structure that provides exceptional mechanical strength and stability (de la Rocha et al., 2021). Hollow fibre membranes are primarily prepared using the spinning-phase inversion method. In the spinning-phase inversion process, a polymer solution is extruded through a spinneret into a nonsolvent bath. The exchange of solvents induces the formation of a porous structure,

creating the hollow fibres. The smaller channel diameters make these membranes suitable for applications requiring fine filtration and separation of smaller particles. However, for large-scale practical applications, the intrinsic brittleness of hollow fibre membranes needs to be carefully evaluated and handled. Furthermore, in recent years, certain unique geometries have arisen, such as flexible nano-fibre membranes.

Alumina (Al_2O_3) membranes have indeed found applications primarily in microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) processes (Younssi et al., 2018). The use of alumina membranes in reverse osmosis (RO) or forward osmosis (FO) has been limited compared to other membrane materials. Alumina MF membranes are mostly utilised for the separation of suspended particles because their pore diameters are < 2 nm, 2–50 nm, and 0.1–10 μm , respectively. Alumina NF membranes are primarily used to reject salts and ions with molecular weight cut-off (MWCO) between 300 and 1000 Dalton under suitable pressure driven force. Alumina UF membranes are well suited for the separation of proteins, high-salinity dye wastewater treatment, and decolorization of vinegar fermentation wastewater.

2.4 Adsorptive membrane for removal of oil

Adsorptive membranes effectively extract and remove oil pollutants from water by combining the principles of conventional adsorption with membrane technology. To improve their affinity for hydrophobic substances like oils, these membranes are usually made of particular materials or have had their surfaces modified. The process by which oil molecules adhere to the solid adsorbent surface upon contact is known as adsorption (Teow et al., 2023). Adsorbent is a key component of adsorption because different

adsorbents may use various adsorption methods, which can influence adsorption efficiency (Emenike et al., 2022). The efficiency, adaptability, and relatively simple operation of this technology make it a common option for environmental remediation and water treatment. Natural and non-natural adsorbents are the two general categories into which adsorbents are classified (Teow et al., 2023). On the other hand, non-natural adsorbents include commercial adsorbents and adsorbents synthesised in laboratories. Natural adsorbents are further divided into earth crust and bio-adsorbents. However, the ability to remove oil from water is hindered by the materials' low adsorption selectivity towards oils. Oils from water can be effectively removed by using an adsorbent based on graphene that has both hydrophobic and oleophilic qualities (Olabintan et al., 2022). The unique properties of graphene, such as its high chemical stability, high flexibility, low weight, great mechanical strength and huge surface area have made it a preferred choice for adsorbents (Teow et al., 2023). Graphene can be utilised to treat OW because of its remarkable adsorption capacity.

Adsorption, sieving, and electrostatic processes are some of the mechanisms that the adsorptive membrane for oil removal uses to operate as intended. The structure and characteristics of the membrane are critical to the process of separating oil from water. For example, the membrane's structure and surface energy have an impact on the adsorption and accumulation of oil droplets. Additionally, the ability of the membrane to separate oil from water is dependent on the size and configuration of its pores. Because the membrane surface has functional groups, hydrophobic interactions, and electrostatic attractions, oil molecules attach to it as part of the adsorption mechanism. On the other hand, sieving is a process that retains oil molecules according to their size and form.

The best adsorbent is chosen based on a number of criteria, including availability, affordability, and particular wastewater treatment needs. For oil/water separation, a variety of membrane materials have been reported, including foamed, natural, nanogel, hybrid membranes, MOFs, inorganic, organic, metallic, novel responsive/switchable, and additive materials. To effectively treat oily wastewaters, these membranes must have adjustable permeability, antifouling, and mechanical qualities. Adsorptive membranes are employed to extract soluble micropollutants that are eluded by conventional water treatment techniques because they are exceptionally difficult to eliminate. The development of adsorptive membranes has made it possible to effectively remove contaminants from water. Table 2.4 shows the adsorptive membranes of other related studies.

Table 2.4: Summary of adsorptive membrane studies for oil/water separation.

Type of adsorbent	Type of oil	Adsorption Capacity	Remarks	References
CNTs/POTS-modified PVDF nanofibre	Sunflower, avocado, motor and engine oils	111.4 g/g	High adsorption efficiency (~99%); can be reused for 37 cycles	(Mofokeng et al., 2020)
PAN- UiO-66-NH ₂ -coated composite membrane	Colleseed oil, Kerosene, Methylbenzene, Methyl silicone oil, Dichloromethane	19.9 to 39.9 g/g	Oil flux: 2286 L/m ² h, retains 1568 L/m ² h after 10 cycles; effective in gravity-based separation	(Chen & Jiang, 2020)

WSD@Fe ₃ O ₄ NPs/SA	Used motor oil, Crude oil	28.32 g/g (Motor oil), 41.22 g/g (Crude oil)	High oil removal capacity due to hydrocarbon chain of SA and elongation by additional three carbon members.	(Soliman et al., 2020)
STAB-Sep and DDAB-Sep	Crude oil	0.957 mg/g (STAB-Sep), 1.032 mg/g (DDAB-Sep)	High efficiency after 8 cycles.	(Zheng et al., 2020)
Mixed Adsorbents (Activated Carbon + Silica Gel), PAC, GAC, Zeolite, Silica Gel	Produced Water	108.38 mg/g	Removal decreases in order: Mixed Adsorbents > PAC > Silica Gel > GAC > Zeolite	(Khader et al., 2021)

2.4.1 Adsorption mechanism

An adsorptive membrane for oil removal utilizes adsorption as the primary mechanism to capture and separate oil or hydrophobic contaminants from water. Adsorptive membranes for oil removal, such those made of ZIF-8 and graphene oxide (GO), work by combining several physicochemical mechanisms. The main mechanisms of

adsorption are the presence of functional groups on the membrane surface, hydrophobic interactions, and electrostatic attractions. The wettability of graphene-based materials by oil is closely associated with their oil adsorption efficiency. An oil droplet would spread instantly on an oleophilic porous surface, and if the surface is hydrophobic as well, oil may be absorbed from an oil/water mixture selectively. Van der Waals interactions, however, predominate over all other interactions, and their strength is influenced by the size, polarizability, and electric charge of the molecules (Anjum et al., 2019). These forces are caused by affinities between electron-rich and electron-deficient regions of uncharged molecules. However, these nonspecific interactions are not the sole factors that leads to improved oil adsorption in scenarios including donor-acceptor contacts, dipole-induced dipole forces, dipole-dipole forces, and hydrogen bond interactions.

Hydrophobic interactions between the oil molecules and the hydrophobic groups on the membrane surface accelerate the adsorption process. This hydrophobicity can be achieved through the incorporation of hydrophobic functional groups or materials. Oil is removed from the wastewater as a result of the interactions that allow the oil molecules to attach to the membrane surface (Emenike et al., 2022). For oil adsorption, attempts have been made to create superhydrophobic and superoleophilic materials. The measurement of the water contact angle is typically done to assess the hydrophobicity of the adsorbent surface. The graphene-based adsorbent produced by Xiao et al. (2018) in their study shows a water contact angle of 159° for GO-cellulose nanofiber hexadecyltrimethoxysilane (HDTMS) aerogel (Xiao et al., 2018). After chemical modification and crosslinking via vapor deposition of HDTMS, Graphene/nanofiber aerogels (GNA) turns to be a superhydrophobic and superelastic material that can adsorb organic liquids with an adsorption capacity of 230 to 734 g/g, being superior to most of known adsorbents.

Meanwhile, a study by Wang et al. (2019) demonstrate a water contact angle of 156.6° for rGOPDA-1H,1H,2H,2H-perfluorooctyltriethoxysilane (PFOES) aerogel (Wang et al., 2019). This work produced the superhydrophobic graphene aerogel (SGA) by hydrothermal functionalization of graphene aerogel (GA) with polydopamine (PDA) and then modifying it hydrophobically with fluoroalkylsilane by vapor-liquid deposition. Figure 2.8 shows the PVDF/GO@PDA@HNTs oil/water emulsion separation and surface-wetting mechanism.

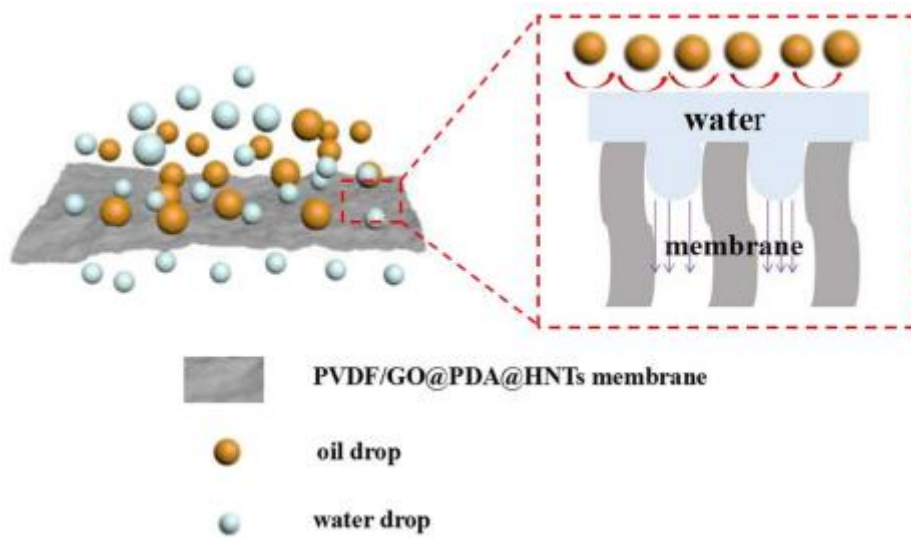


Figure 2.8: Adsorption mechanism of PVDF/GO@PDA@HNTs for oil/water emulsion (Wang et al., 2019).

The adsorption process is also influenced by electrostatic forces. Adsorption can be further enhanced by the membrane's surface having a negative charge that draws in positively charged oil molecules (Emenike et al., 2022). Electrostatic interactions, also called coulombic interactions, are considered as "electric" at the atomic level and have been used to explain whether the sorption capacity decreases as the pH of the solution increases. The interaction involving the oil and the adsorbent surface can be impacted by

the existence of electrostatic forces. Such as in the context of oil-water separation membranes, charged oil droplets are drawn to the oppositely charged surface of the membrane by electrostatic forces, which can also play a role in hydrophobic interactions and the adsorption mechanism (Emenike et al., 2022; Liu et al., 2022). Furthermore, the stability and order of the system might be affected by electrostatic forces at the oil-water interface, which can also have an impact on the behaviour of nearby particles. However, the effect of electrostatic forces on the adsorption of oil from water might differ based on the particular system and the makeup of the components involved. Zhang et al. (2022), developed an ultrahigh-performance oil-water emulsion separation using an ultrathin *in-situ* silicification layer created by an electrostatic attraction force method. The SiO₂-d-PK membrane was equipped with an ultrathin silicification layer that allowed for a high rejection rate of almost 99.9%, improved emulsion separation qualities for high oily emulsion fluxes for hexane-based oily emulsions (5329 Lm⁻¹h⁻¹bar⁻¹), and a comparable water permeance of 7533 Lm⁻¹h⁻¹bar⁻¹ (Zhang et al., 2019).

Adsorption can be accelerated by the presence of functional groups like carboxylate and hydroxyl groups on the membrane surface. By forming hydrogen bonds and engaging in other interactions with the oil molecules, these groups can increase the efficacy of adsorption (Emenike et al., 2022). The interaction between the oil molecules and the charged surfaces of the adsorbent can be facilitated by the functional groups. The adsorption of heavy metals, including Pb(II), Cr(VI), Hg(II), Cd(II), and Ni(II) ions, onto the carbon surface has been reported to be significantly influenced by oxygen-containing functional groups on activated carbon (Neolaka et al., 2023). Among the most prevalent functional groups, the hydroxy and carboxyl groups have been shown to play a significant role in the adsorption of heavy metals (Yang et al., 2019). Similar to this, activated carbons

feature hydrophilic surface oxygen functional groups that serve as the main sites for adsorption of water vapour and hydrophobic surface groups that serve as the main sites for adsorption of organic molecules. Oil-water separation membranes with improved antifouling capabilities have been shown to result from the introduction of hydrophilic chains onto graphene oxide surfaces, which decrease the adhesive force of oil droplets. Thus, functional groups on the membrane surface may have an impact on the adsorption process used for removing oil from water. Figure 2.9 shows the example of the adsorption mechanisms by using zeolite-Fe/AC adsorbent to treat the palm oil mill effluent (POME).

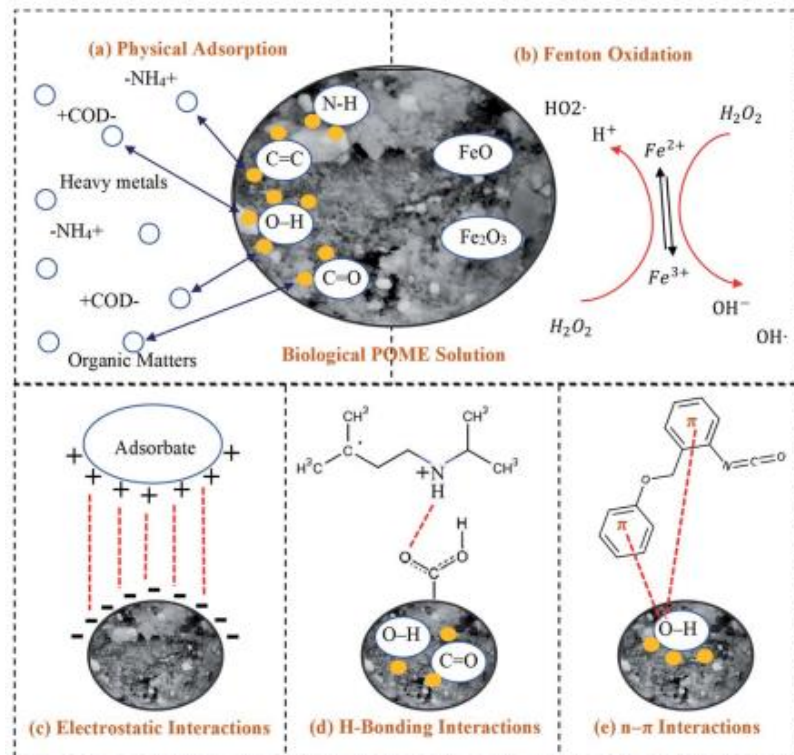


Figure 2.9: Adsorption process of zeolite-Fe/AC adsorbent for biological POME (Jun et al., 2020).

2.5 Oil-water emulsion treatment using ceramic membranes

Ceramic membranes are currently widely utilised for treating oily wastewater because of their numerous benefits. The permeate flux and rejection in crossflow microfiltration experiments are significantly influenced by several operating parameters, such as transmembrane pressure (TMP), the starting concentration of oil in the feed, and crossflow rate. Permeate flux rises with increasing applied pressure and crossflow rate, but the proportion of rejection falls (Sandhya Rani & Kumar, 2021).

The mechanical, chemical, and thermal properties of ceramic membranes make them a reliable choice for treating oily wastewater in various industrial applications (Motta Cabrera et al., 2021; Zou et al., 2019; Zou et al., 2019). The combination of narrow pore size distribution, high porosity, and hydrophilicity in ceramic membranes, especially in hybrid-ceramic membrane processes like ceramic membrane bioreactors, provides several performance advantages over polymeric counterparts. These advantages contribute to higher efficiency, pollutant removal, and operational reliability in water treatment applications (Asif & Zhang, 2021). Organic substances and bacteria are less likely to contaminate a hydrophilic surface (water contact angle $< 90^\circ$) because a coating of water molecules forms on the surface to block interaction with pollutants from the solution. Therefore, one of the keyways to increase membrane hydrophilicity and reduce membrane fouling is to improve the surface hydrophilicity of ceramic membranes through process modifications. Additionally, increasing the emulsion's interfacial tension can also help (Tummons et al., 2020). The surface exhibits greater water affinity when it is more hydrophilic (Pichardo-Romero et al., 2020). Modification can significantly enhance the performance of ceramic membranes by considering permeate flux, oil rejection, and fouling resistance. coating ceramic membranes, such as $\alpha\text{-Al}_2\text{O}_3$ membranes, with nano-

sized metal oxides like TiO_2 , ZrO_2 , $\gamma\text{-Al}_2\text{O}_3$, Fe_2O_3 , and SiO_2 has been found to be an effective strategy for enhancing permeate flux. The key factor contributing to this enhancement is the improved surface hydrophilicity resulting from the presence of these metal oxide coatings (Chen et al., 2021).

Nonetheless, the applied pressure does not cause the permeate flux to change linearly. A greater drop in flux occurs when the oil layer on the membrane forms quickly at high pressures. Conversely, a higher initial feed oil concentration results in a decrease in the permeate flux and an increase in the rejection rate because the size and density of the oil droplets increase. Both the crossflow rate and the surface wettability of the membrane can significantly influence the permeate flux in membrane filtration processes. Oil is selectively absorbed by the hydrophobic/oleophilic surface whereas water is able to pass through the hydrophilic/oleophobic surface. Ceramic membranes naturally absorb water molecules and have a higher concentration of hydrophilic groups (Usman et al., 2021). A few researchers have further altered the surface of ceramic membranes to increase their hydrophilicity and obtain an increased permeate flux.

2.6 Membrane surface modification method

Membrane surface modification is a technique used to alter the properties of a membrane's surface, enhancing its performance in specific applications. The goal is often to improve characteristics such as hydrophilicity, fouling resistance, selectivity, and chemical stability. Metal oxides make up the majority of ceramic membranes, which are produced through high-temperature sintering. Since the membrane surface contains hydroxyl ($-\text{OH}$) groups, they are hydrophilic in theory. These days, there are a lot more

methods for modifying membranes, including grafting, hydrothermal synthesis, blending/doping, and dip-coating. The choice of surface modification method depends on the specific requirements of the application and the properties desired for the membrane. Different methods offer unique advantages in terms of cost, ease of implementation, and the extent of modification achievable.

2.6.1 Dip-coating

The dip coating method is the most widely used approach for producing ceramic-polymer composite membranes, mostly in laboratory and industrial scale (Sawunyama et al., 2023). To increase a desired property, dip-coating is an easy and efficient method of fabricating composite membranes (Madalosso et al., 2021). The coating solution has a significant impact on the final composite membrane properties. In this approach, three basic steps make up the dip-coating process, solution or suspension containing the desired coating material is prepared. This solution may include polymers, nanoparticles, or other functional materials. The substrate, such as a membrane, is dipped into the coating solution, ensuring complete wetting of the substrate surface. The substrate is slowly withdrawn from the coating solution at a controlled rate enabling the membrane surface to absorb a layer of suspension or sol due to the capillary forces. Lastly, the produced membrane being were dried. The coating layer's thickness is typically determined by the coating solution's viscosity, which is affected by temperature, solution grouping, and other materials. As the solution's viscosity is decreased at lower concentrations, the coating solution will penetrate into the substrate pores (Siddique et al., 2021).

Using a dip-coating technique, Mousavi et al. (2021) successfully increase the porous PEI hollow fibre membrane's surface hydrophobicity for the air gap membrane

distillation (AGMD) process of treating methylene blue (MB) solution (Mousavi et al., 2021). Using a dry-wet spinning technique, the hydrophobic 2-(Perfluoroalkyl) ethanol (Zonyl® BA) was employed as the coating material to create the porous PEI membrane. During the first 500 minutes of the AGMD operation for the treatment of the MB solution, a reduced flux reduction was noted in comparison to the pristine PEI membrane because of the improved characteristics of the PEI-Zonyl hollow fibre membrane. The PEI-Zonyl membrane demonstrated a permeate flux of 6.5 kg/m² h and an MB rejection of 98% for the course of the AGMD operation, which lasted 76 hours.

In a different work, Wenten et al. (2020) used the dip-coating approach to coat a Polypropylene (PP) hollow fibre membrane with a layer of PSf/PEG400/ZnO to create a polypropylene-based membrane with a reduced organic fouling tendency (Wenten et al., 2020). The FTIR and SEM examination results demonstrate that the straightforward dip-coating process was effectively used to deposit a PSf/PEG400/ZnO layer on the surface of the PP membrane. Relative flux reduction falls from 53% to 44% while the flux recovery ratio rises from 63% to 66%. M-ZnO-40% composite PP membrane can remove approximately 70% of humic compounds from peat water. The study's findings demonstrate that adding a PSf/PEG400/ZnO layer to a PP hollow fibre membrane can significantly increase its permeability, selectivity, and resistance to organic fouling.

2.6.2 Surface grafting

Surface grafting is a membrane modification method that involves attaching polymer chains or functional groups onto the surface of a membrane. The process of polymer grafting is used to enhance the morphology, chemical composition, and physical characteristics of polymers (Purohit et al., 2023). This method can increase the solubility,

nano-dimensional shape, biocompatibility, bio-communication, and other properties of parent polymer by improving the current conduction and properties of polymers other than charge transport (Purohit et al., 2023). Polymer chains are joined by a chemical reaction process to create a solid surface for surface grafting, forging a robust covalent connection between the polymer brushes and the surface (Rezakazemi et al., 2018). As a result, the grafting layer maintains its chemical stability over time. Membrane surfaces can be prepared with chemicals, UV light, plasma, or enzymes to start the grafting process (Chen et al., 2021).

Depending on the type of grafting polymer used, the membrane's properties can be changed from superhydrophilic to superhydrophobic, expanding its possible range of uses. For example, to increase the hydrophilicity of a membrane, polyethylene glycol was added. Furthermore, surface-grafted membranes are an important alternative for adding hydrophilic functional groups to membrane surfaces (Rezakazemi et al., 2018). Surface grafting is mostly used to modify hydrophilic ceramic membranes which have great mechanical strength and a high tolerance to chemicals and oxidants to make them superhydrophobic or hydrophobic for use in membrane distillation applications. For the treatment of oily wastewater, it can also be utilised to modify ceramic membranes to strengthen their anti-fouling properties.

Qi et al. (2019) modified a novel high selective separation membrane by using 2-chloro-1-methylpyridine as an active agent to graft polyimide polymer onto the membrane surface through covalent bonding with carboxylic groups on the membrane surface. High selectivity for multivalent anions and low capacity for multivalent cations and heavy metal ions are the distinguishing features of nanofiltration (NF) membrane performance (Qi et al., 2019). The pore size screening effect and charge repulsion of the

membrane contribute to its good selectivity. For instance, the membrane has remarkable selectivity for the screening of inorganic salts and rejects more than 96% of heavy metal ions and dyes. Only 32% of monovalent ions (Li^+) are rejected, compared to a significant percentage of polyvalent ions (Mg^{2+} ; Ca^{2+}). Furthermore, the covalently produced grafted membrane exhibited superior alkali stability while retaining its original rejection capacity, which was up to 93%.

2.6.3 Blending

Incorporating inorganic nanoparticles into the membrane matrix through doping or blending is another technique for modifying membranes (Siddique et al., 2021; Yuan et al., 2020). This approach involves physically mixing the nanoparticles with membrane precursors, followed by solid-state processes that sinter them at optimal temperatures. By altering the blending of additives, it is possible to enhance the hydrophilicity of these membranes and potentially enhance their resistance to fouling during the process of oil/water separation (Alammar et al., 2020). This method has also been extensively applied to the development of hybrid organic/inorganic membranes. Various inorganic material types, such as metal–organic framework (MOF) as fillers for mixed-matrix membranes (MMMs) and metal oxides, including graphene, graphene oxide (GO), carbon nanotubes, silica, zinc oxide (ZnO), zeolite (Zeo), iron oxides (Fe_2O_3 , Fe_3O_4), titania (TiO_2) (Siddique et al., 2021). The surface functionality of ceramic membranes can also be enhanced by doping or blending.

Ayyaru et al. (2019) combined graphene oxide (GO) and zinc oxide (ZnO) to create a blended GO-ZnO nanocomposite additive for a polyvinylidene fluoride (PVDF) membrane with high hydrophilicity (Ayyaru et al., 2020). Blending the GO-ZnO

nanocomposite greatly increased the membrane's porosity and wettability, or hydrophilicity. Additionally, the GO-ZnO/PVDF membrane exhibited a 48% increase in water flux in comparison to the basic PVDF membrane, and its anti-fouling characteristics were significantly enhanced. The flux of the GO-ZnO-containing polymer matrix membrane was higher than that of the PVDF membrane in its pure form.

Koulivand et al. (2020) improved the performance of nanofiltration, permeation, and antifouling by developing polyethersulfone membranes enhanced with carbon dots. In the study, a polyethersulfone (PES) matrix and carbon dots (CDs) were blended to create a unique mixed matrix nanofiltration membrane (Koulivand et al., 2020). A solution of bovine serum albumin (BSA) was filtered through the produced nanocomposite membranes to assess their fouling resistance. Through successive increases in the dosage of CDs from 0.05 to 0.50 wt%, the membrane permeability was raised to a maximum value of 76.5 kg/m²h, which is nearly double that of bare PES. Significant antifouling characteristics were also demonstrated by the 0.50 wt% PES/CDs membrane, with total and irreversible fouling values of 35.6 and 20.3%, respectively, in contrast to 54.7 and 46.3% for the bare PES.

2.6.4 Hydrothermal

The most widely utilised technique for producing ZIF-8 membranes is *in-situ* hydrothermal synthesis because it can produce high-quality crystals under regulated growth conditions (Choi et al., 2023). A precursor synthesis solution is applied to the porous support's surface during *in-situ* synthesis. Hydrothermal synthesis has been used extensively to generate inorganic materials and to fabricate zeolite membranes (Chen et al., 2021; Yang & Park, 2019). In an autothermal reaction, an aqueous mixture of precursors is

typically heated to 80–230°C for a few hours or even days (Chen et al., 2021). In order to modify the membrane, the autoclave is placed in an oven for the hydrothermal process after the membrane support has been submerged in a solution containing a combination of precursors. The membranes are then cleaned, dried, and calcined. Numerous benefits, including low cost, easy setup, and high yield, are provided by this technology (El Bojaddayni et al., 2023). Consequently, a number of studies have improved the oil separation effectiveness of ceramic membranes by modifying them using the hydrothermal process.

Green hydrothermal reduction was used by Fan et al. (2020) to generate reduced graphene oxide (rGO), and vacuum filtering was used to prepare rGO membranes on polyvinylidene fluoride (PVDF) supporting membranes (Fan et al., 2020). Hydrothermal reduction leads to the transportation of water molecules in a considerably smaller interlayer space because of the disorder and defects of rGO nanosheets, their reduced oxygen-containing functional group, and their increased hydrophobicity. For methyl blue, Congo red, and crystal violet, the synthesised rGO membrane rejects more than 99% of the sample. Additionally, Paimen et al. (2020) prepared an *in-situ* growth of α -Fe₂O₃ by a hydrothermal method on an asymmetric Al₂O₃/YSZ hollow fibre (Paiman et al., 2020). The increased surface hydrophilicity of the deposited α -Fe₂O₃ layer enhanced the membrane's permeate flux. Pure water permeation, porosity, and structure were assessed for pristine hollow fibre and hollow fibre with α -Fe₂O₃.

Choi et al. (2023) investigate the way the temperature and humidity in the chamber affect the ZIF-8 layer's structure after it is created using the hydrothermal process (Choi et al., 2023). The study emphasised on ZIF-8 growth and the impact of growth environment parameters, particularly the chamber's temperature and relative humidity, while

maintaining constant growth circumstances for all other parameters. In order to prevent the solvent effect from affecting ZIF-8 nucleation and growth, water was employed as a solvent. The temperature and relative humidity were controlled between 50°C and 70°C and 20% and 100% using a thermos-hygrostat chamber. The number of ZIF-8 nuclei changed according to temperature and relative humidity in the early phases of ZIF-8 nucleation seen during the *in-situ* growth in this chamber. Different kinds of ZIF-8 films or particles were created as a result. It is crucial to adjust the heating rate or relative humidity for different applications because the heating rates of the reactive solutions vary appropriately. Controlling humidity and temperature may be crucial in other fabrication techniques, even though the observed growth conditions are restricted to the hydrothermal process. Table 2.5 summarizes the membrane surface modification methods.

Table 2.5: Membrane surface modification methods.

Modification Method	Process Description	Materials Used	Membrane Type	Improved Properties
Dip-coating	Membrane dipped into a coating solution and dried to form a thin layer.	Polymers, nanoparticles, ZnO, PSf/PEG400	Polypropylene (PP) hollow fibre, PEI membrane	Increased hydrophobicity, reduced fouling, increased flux
Surface grafting	Polymer chains or functional groups grafted onto the membrane	Polyimide, PEG, chlorinated agents	Ceramic membranes, nanofiltration (NF) membranes	Increased hydrophilicity, antifouling, high selectivity

	surface via chemical reactions.			
Blending	Inorganic nanoparticles blended into membrane precursors to enhance surface properties.	GO, ZnO, Carbon Dots, PES	PVDF, PES	Enhanced hydrophilicity, improved permeability, antifouling properties
Hydrothermal	Membrane submerged in a precursor solution and heated to induce crystal growth.	ZIF-8, rGO, α -Fe ₂ O ₃	Ceramic membranes, PVDF, Al ₂ O ₃ /YSZ hollow fibre	Enhanced oil separation, hydrophobicity, high rejection rates

2.7 Graphene oxide synthesis

Since graphite oxide was discovered to be capable of converting into graphene oxide/graphene as the readily available precursor, scientists from all over the world have made major advances in understanding the chemistry of graphite oxide (Wang et al., 2021). A strong acid and an oxidising species are used to treat graphite to synthesize graphene oxide (GO), which delaminates the crystal structure of the material and introduces oxygen

functional groups (Ikram et al., 2020). By oxidising graphite with potassium chlorate and fuming nitric acid in 1859, Brodie established the basis for the synthesis of graphene oxide. Staudenmaier followed about 40 years later, slightly modifying Brodie's method by oxidising the graphite in steps in a solution of sulfuric acid and nitric acid (Ikram et al., 2020). Small amounts of potassium chlorate were added to prevent explosive reactions in an environment that were more acidic (Adetayo & Runsewe, 2019). A safer method of producing GO was developed and implemented in 1957 by Hummers and Offeman. By adding KMnO_4 and NaNO_3 to concentrated sulfuric acid, graphite was oxidised (Chen et al., 2022). This synthetic approach is still used presently with minor adjustments and greater concentrations of oxidising chemicals for a faster rate of material oxidation (Kong et al., 2019).

2.7.1 Hummers' method

Almost a century after Brodie's original discovery, Hummers and Offeman made the most significant advancement in the field of graphite exfoliation by oxidative chemicals. They invented a safe and quick conventional method for producing Hummers' graphene oxide (GO-HU), with a carbon-to-oxygen (C/O) ratio of 2.25 that is very equivalent to Brodie's graphene oxide (GO-BR), which C/O ratio of 2.2 (Brisebois & Siaj, 2020). The impact of sulfuric acid, a small amount of sodium nitrate and the excess of potassium permanganate on graphite served as the basis for their approach. The development of explosive ClO_2 was prevented, making their process far safer than chlorate-based ones (Kumar et al., 2021). Additionally, the extra KMnO_4 was conveniently neutralised using a weak solution of H_2O_2 to produce non-toxic manganese sulphate salts and gaseous oxygen that was simple to remove during the purifying processes (Kumar et

al., 2021; Sridhar et al., 2022). Nevertheless, certain hazardous gases (NO_2 , N_2O_4) and nitric acid were still formed on-site because of the acidification of sodium nitrate. As of now, GO created by the Hummers, Staudenmaier or Brodie processes exhibit many weaknesses such as holes, creases, irregular shapes, and the presence of impurities than those created by micromechanically cleaving graphite (Brisebois & Siaj, 2020). Hummers' approach is still of great interest since it is a straightforward reaction that can provide significant amounts of graphite oxide that can be completely delaminated into GO utilising liquid exfoliation methods. The covalently linked nitrates and sulphates or adsorbed nitric and sulfuric acids are most likely to blame for the GO that is produced, which contains traces of sulphur (up to 6%) and nitrogen (Brisebois & Siaj, 2020; Rady & Naij, 2022).

2.7.2 Tours' method

The GO is often produced via the modified Hummers process, which oxidises graphite while aggressively stirring or sonicating a solution of sulfuric acid, sodium nitrate and potassium permanganate (Jiříčková et al., 2022). After the suspension has been diluted with water and hydrogen peroxide has been added to enhance the degree of oxidation, the mixture has been rinsed with water. However, the lengthy processing times and hazardous gas (NO_2 and N_2O_4) production are the disadvantages of this method. Therefore, Tour and coworkers updated their method to address these problems by replacing sodium nitrate with phosphoric acid in a mixed $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ (9:1) ratio while raising the concentration of KMnO_4 (Benzait et al., 2021; Jiříčková et al., 2022). Phosphoric acid (H_3PO_4), a dispersive and etching agent, was used in place of sodium nitrate to aid in the oxidative chemical exfoliation of graphite to produce GO with a higher yield (Rady & Naij, 2022).

The benefit of this procedure is that hazardous gas production is prevented. The drawbacks consist of time-consuming sifting, filtration, centrifugation, and washing processes, as well as the usage of a lot of KMnO_4 . In comparison to GO-BR and GO-HU, The GO produced by the Tour method (GO-TO) is more uniformly structured, with less defects in the basal plane, and has a higher level of oxidation (Huang, 2018; Hummers & Offeman, 1957). The development of five-membered cyclic phosphate groups between the phosphoric acid and two vicinal diols produced on the graphite basal plane accounts for the more regular structure (Huang, 2018). After Brodie, Staudenmaier, and Hummers, this method is frequently regarded as the "fourth" main method to make GO. A thorough examination of the intercalation process reveals how sulfuric acid, potassium permanganate, and other compounds intercalate into the inter-galleries of graphite. Nevertheless, there are also several different methods to synthesize GO as summarized in Table 2.6.

Table 2.6: Summarization of the GO synthesis method.

Method	Year	Oxidants	Solvents	References
Brodie	1859	KClO_3	HNO_3	(Brodie, 1859)
Staudenmaier	1898	KClO_3	HNO_3 (Fuming), H_2SO_4	(Staudenmaier, 1898)
Hummers	1958	NaNO_3 , KMnO_4	H_2SO_4	(Hummers & Offeman, 1958)
Modified Hummers	1999	$\text{K}_2\text{S}_2\text{O}_8$, P_2O_5 , KMnO_4	H_2SO_4	(Kovtyukhova et al., 1999)
Tours	2010	KMnO_4	H_2SO_4 , H_3PO_4	(Marcano et al., 2010)

2.8 Membranes surface modification with GO

Graphene oxide (GO) has several advantages over graphene (G), including facile processing, large-scale synthesis, and inexpensive production costs. Recent research on GO has revealed that it possesses exceptional qualities as well, including an abundance of active oxygen-containing functional groups (Yu et al., 2020). The graphene oxide interlayer gap is likewise widened by the presence of oxygen-containing groups. It can be functionalized by small molecules or polymer intercalations. At present, great progress has been achieved in the functionalization of graphene oxide. It has been used in the desalination, medication delivery, oil-water separation, solar cell, immobilisation catalysis, energy storage, and healthcare industries (Kumar et al., 2019; Shetti et al., 2019; Yu et al., 2020). In order to meet the treatment requirements, membrane filtration technology needs to be improved on a regular basis (Januário et al., 2021). It has been observed that membrane surface modification improves oil separation at high flux and increases the membrane's resistance to fouling problems (Bolto et al., 2020). The surface deposition of particular materials can alter the microporous membrane's structure and physicochemical properties, including its affinity for water, potentially enhancing selectivity, permeate flux, and antifouling capabilities (Diogo Januário et al., 2020). A growing number of GO nanosheets have been used recently to modify the surface of membranes because of their special electrical, mechanical, optical, and chemical properties as well as their two-dimensional, one-atomic-thickness structure.

Graphene oxide (GO) sheets are a particularly interesting candidates since graphene can now be produced in large quantities using existing methods. This graphene derivative can be used to create laminates, which are collections of GO crystallites that are micron in

size and form an interlocking layered structure. This structure exhibits exceptional mechanical strength and flexibility, resembling nacre even for films with submicron thickness. In terms of practical applications, atomically thin GO films are superior to other membranes due to how easily they can be converted into membranes. In general, graphene prevents everything from passing through. With its excellent membrane characteristics and vast potential for practical uses, graphene oxide (GO) is showing signs of promise. Nanocomposite materials made of graphene oxide and silicone-silicone may both bind waste in water. Thus, adding them to nanodispersed solutions will increase the quantity of waste bonded to the appropriate surface area. As the surface area to volume ratio increases, so will the adsorption capacity.

Researchers are actively working on surface-modifying commercial microfiltration and ultrafiltration membranes using graphene oxide (GO) nanosheets and other chemicals like polyethyleneimine (PEI), titanium dioxide (TiO_2), tannic acid (TA), and *Moringa oleifera* Lam. Modi and Bellare (2019) conducted a study whereby they embedded a nanohybrid made of graphene oxide nanosheets and carboxylated carbon nanotubes (CNTs/GO) in polysulfone hollow fibre membranes (PHFMs) to enhance their physicochemical properties. These properties included surface functionality, hydrophilicity, mechanical strength, and surface charge, as well as separation performance, which includes antifouling property, water permeation flux, and oil-water separation (Modi & Bellare, 2019). These membranes also shown exceptional antifouling properties (flux recovery $\sim 90.5\%$), a remarkably high oil rejection rate ($98.7 \pm 1.2\%$), and a significantly high water penetration flux ($487.9 \pm 25.4 \text{ mL/m}^2/\text{h/mmHg}$). These findings clearly revealed that the carboxylated multiwalled CNTs (cMCNTs) and GO nanosheets working together as a cMCNTs/GO (CG) nanohybrid had a beneficial influence on improving the

physiochemical characteristics and separation efficacy of the Psf-CNTs/GO composite HFMs.

Another study by Kang et al. 2019, using a modified Hummer technique, graphene oxide was synthesised and subsequently bonded to β -SiAlON via dip coating (Kang et al., 2019). The outcome demonstrates that although surface modification had minimal effect on the membrane's morphology, it did fairly reduce the pore size. Larger applied pressure led to a larger flow flux and a lower rejection rate, while higher flow velocity resulted in a higher flow flux and rejection, according to the oil/water emulsion separation experiment. The results of the stability test showed that at constant flow rate and flux, the β -SiAlON/GO membrane performed better against fouling. By modifying the concentration and volume of the GO suspensions, the filtration-assisted process's membrane thickness can be changed (Wei et al., 2018). It was proven that when the GO laminates were thicker, the water flux would decrease exponentially. Compared to hydrophobic porous GO membranes, more water can pass through the pores due to their hydrophilic modification (Sun & Li, 2018). Moreover, in environments with mild ionic strength, charged group modification such as carboxylate pores offers robust free-energy barriers for high flux and ion rejection (Sun & Li, 2018).

2.9 Graphene-oxide/metal–organic framework composites

The synthesis of high-quality graphene oxide (GO) in large quantities is indeed of great importance for various applications in research, industry, and technology (Benzait et al., 2021). Many studies have been conducted on graphene oxide (GO), either in isolation for the construction of various devices, as an additive to improve the performance of

materials, or even as a precursor to synthesise graphene by chemical or physical reduction. However, the application of graphene is severely limited by the single component graphene material's shortcomings, which include weak electrochemical activity, simple agglomeration, and challenging processing. Thus, increasing the applications of graphene oxide requires functional modification. Graphene oxide's functionalization is predicated on additional alterations to its inherent structure.

Graphene oxide (GO) membranes have attracted a great deal of attention across various disciplines because to their easy and large-scale fabrication, and they exhibit exceptional separation performance because of their internal 2D nanochannels (Meng et al., 2018). Nevertheless, the limited 2D nanochannels in GO-based membranes result in a poor penetration flux, which significantly impedes their use in wastewater treatment (Xie et al., 2020). The surface characteristics of the GO nanosheets and the distance between neighbouring GO layers are the two main elements influencing the permeability and selectivity of the GO membranes. To enhance the separation performance of the laminated GO membrane, a great deal of research has been done on adjusting the GO interlayer spacings and the GO nanosheet surface features (Zhang et al., 2019). For GO membranes to simultaneously attain increased permeation flux and separation efficiency, viable transport nanochannels are therefore required. As of right now, nano-intercalation has shown to be a viable method for improving the transport nanochannels in GO membranes. To modify the permeability and selectivity of membranes, a variety of nanomaterials have been intercalated into GO/RGO nanosheets, including polymers, SiO₂, natural minerals, carbon nanotubes and MOFs (Liu et al., 2019; Luo et al., 2019). The GO/RGO membranes that have been intercalated demonstrate a higher penetration flux and suitable selectivity.

By fusing metal ions with organic ligands, a novel class of crystalline porous materials known as metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) are produced. Their pore topologies are constant and easily tuned, making them intriguing materials for a variety of applications. MOFs are three-dimensional ordered porous materials composed of inorganic clusters (metal ions or clusters) connected by organic ligands. The unique combination of metal ions and organic linkers results in a highly porous structure with well-defined pores and channels. MOFs exhibit exceptional surface areas and are known for their record-setting internal surface areas among various porous materials (Wang et al., 2018). Metal–organic frameworks, or MOFs, are three-dimensional hollow materials with a wide range of uses in catalysis, adsorption, and separations. They have a relatively large specific surface area and pore volume. The distance between GO layers can be changed by combining GO with MOFs to influence the transport and screening of molecules. This means that composites have a wide range of possible uses in industries like water and gas treatment.

Single-layer graphene, while possessing exceptional mechanical strength in its pristine form, can become quite weak when it is in the form of individual sheets or monolayers. This weakness is attributed to the absence of interlayer interactions, which play a crucial role in the outstanding mechanical properties of bulk graphene. Graphene oxide (GO), a derivative of graphene, is known to exhibit spontaneous aggregation in most solvents. This behavior is due to the presence of oxygen-containing functional groups on the basal plane and edges of GO sheets. The functional groups introduce hydrophilicity to GO, causing sheets to attract each other through Van der Waals forces and hydrogen bonding, resulting in aggregation. The tendency of GO to aggregate makes it challenging to achieve effective dispersion in many solvents. MOFs, on the other hand, are relatively

unstable while having high specific surface area, high porosity, and high crystallinity. Their significant instability made their practical use restricted. By combining the best qualities of both material types, GO/MOF composites can be created that have improved physical properties.

MOFs are a class of coordination polymers that consist of metal centres or clusters connected by multitopic organic ligands. Figure 2.10 shows the illustrations of some important reported MOFs. These ligands typically contain multiple coordination sites, such as carboxylate groups, which can form strong covalent or coordinate bonds with metal ions. The combination of metal nodes and organic linkers results in the formation of a three-dimensional framework structure with well-defined pores (Annamalai et al., 2022). Many MOFs with high porosity, superior adsorption performance, and other favourable physical and chemical properties can be constructed by using various metal centres and ligands as molecular constructions (Hu et al., 2019; Seidi et al., 2020). However, there were some disadvantages that prevented MOFs from having effective and superior functional features and applications, such as low electrical conductivity and poor thermal and chemical durability (Annamalai et al., 2022).

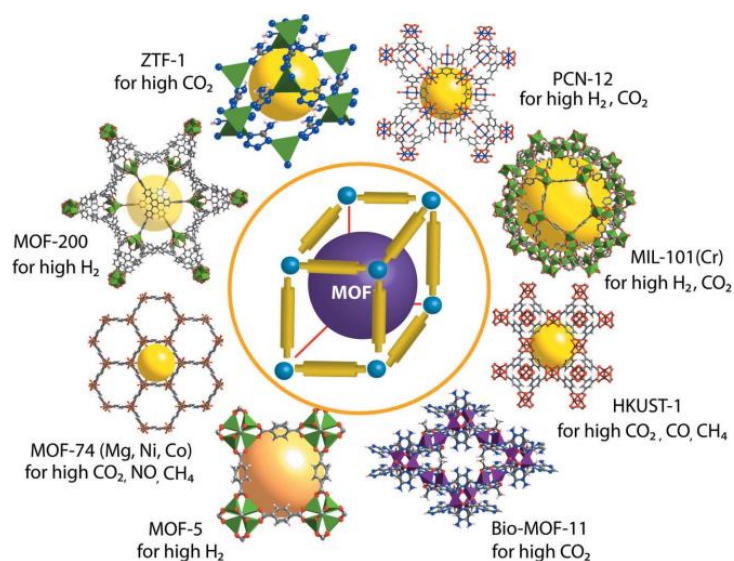


Figure 2.10: Schematic representation of important reported MOFs (Dey et al., 2014).

To increase MOF stability, carbon-based materials such as carbon nanotubes and graphene oxide are frequently employed as MOF supports, and positive property outcomes have been obtained (Jeon et al., 2023). Graphene oxide (GO) is recognised as one of the most promising carbon-based materials for MOF composites (Janakiram et al., 2020). GO/MOF composites increase MOFs' adaptability and have led to innovative applications in a variety of industries (Wei et al., 2020) GO/MOF composites materials have been synthesized and widely used in various fields.

2.9.1 Preparations of GO@MOF

In addition to having numerous surface functional groups and a high atom density, GO can initiate the crystallisation of MOF at room temperature. Consequently, the conditions and driving forces used in the synthesis process have a significant impact on the nature of the interaction between GO and MOF in GO/MOF composite materials (Muschi

& Serre, 2019). There may be a formation of some free MOF particles due to competitive interaction between the oxygen atoms of the MOF ligand and the oxidised groups on GO with the metal cation. This could lower the density of MOF particles and lessen the GO/MOF composites' ability to boost performance and have synergistic properties (Muschi & Serre, 2019). Additionally, by having GO participate in the crystallisation process, MOF development may be directed in specific directions to create oriented MOF structures, which favour consistent pore and crystal architectures that are beneficial for a variety of applications (Mazlan et al., 2022). The *in-situ* synthesis method, where metal-organic frameworks (MOFs) are formed directly within the graphene-based components, is often preferred over physical mixing methods. This preference arises from the advantages associated with *in-situ* synthesis, including the utilization of defects and functional groups on the graphene surface as nucleation sites for MOF crystallization (Jayaramulu et al., 2022). Combining the MOF precursor with GO is the most convenient method for creating GO/MOF composites when GO is present. This is an easy and quick way to prepare (Jayaramulu et al., 2022; Qu et al., 2021). Additionally, by keeping the GO sheet in close contact with the MOF component, the *in-situ* approach promotes the development of additional pores.

A simple and scalable *in-situ* synthesis approach for GO/ZIF-8 blended with a CO₂-philic comb copolymer was proposed by Chen et al. (2019). This process produced a series of mixed matrix membranes (MMMs), which were assessed for their effectiveness in CO₂/N₂ separation (Chen et al., 2019). The reaction time in the synthesis of ZIF-8@GO composites play a crucial role in determining the crystal size, structure, and properties of the resulting material. Therefore, the gas separation performance of ZIF-8@GO composites can be adjusted by controlling the reaction time. Figure 2.11 (a) shows that

there is low coverage of ZIF-8 crystals on the GO nanosheets for a short reaction time (3 h), indicating that a small number of ZIF-8 are forming on the surface of GO. The ZIF-8 crystals progressively cover the GO surface after the reaction time is increased to 6 hours (Figure 2.11 (b)). On the surface of GO, the ZIF-8 crystals that were formed show a good distribution. On the other hand, aggregation occurs and the generated ZIF-8 crystals fully cover the GO surface when the reaction time is increased to 12 hours (Figure 2.11 (c)). As predicted, the gas separation performance of the resulting MMMs is significantly influenced by the ZIF-8@GO reaction time. The synergistic impact of ZIF-8 and GO allows ZIF-8@GO to have the greatest CO₂ adsorption capacity, with an optimal reaction time of 6 hours.

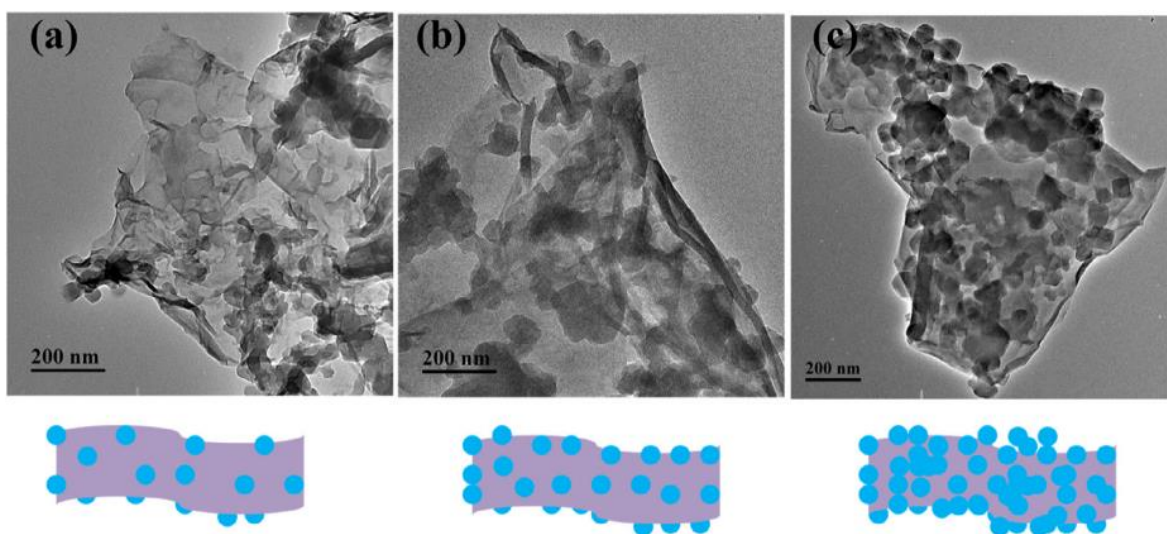


Figure 2.11: TEM images of ZIF-8@GO composites with different reaction times: (a) 3 h, (b) 6 h and (c) 12 h. The cartoons show the different densities of ZIF-8 on the GO surface respectively (Chen et al., 2019).

In addition to *in-situ* growth, self-assembly techniques are also possible to produce GO@MOF composite membranes. Cheng et al. (2018) created a hybrid membrane for the removal of Cs⁺ ions by electrostatically assembling a 2D MOF with GO (Cheng et al., 2018). This study presents the fabrication of novel self-assembled membranes made of

graphene oxide (GO) and two-dimensional (2D) metal–organic frameworks (MOFs) using a simple filtration method that can effectively absorb Cs^+ from aqueous solutions. The 2D CoMOF $\text{Co}_2(\text{TCPP})(\text{bpy})$ was prepared by gradually combining a DMF/ethanol solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, polyvinylpyrrolidone (PVP), and 4,4-bipyridine (bpy) with a solution of Tris(chloropropyl) phosphate (TCPP) in DMF/ethanol. Centrifugation was used to collect the cobalt porphyrin MOF from the reaction mixture after it had been heated to 80°C and sonicated. The product was then stored in DMF. The next step involved adding a GO suspension in DMF to the Co-MOF dispersion and magnetically stirring the reaction mixture. Finally, this solution was vacuum filtered across an organic membrane, and the sample was peeled off the organic membrane to obtain the hybrid membrane.

Yang et al. (2019) created graphene@MOF hybrid-based 2D membranes using MOF-2(Cu) self-assembly with GO assisted by hydrogen bonds (Yang et al., 2019). Diffusion-mediated method of synthesising MOF-2(Cu) involved layering solutions of 1,4-benzene dicarboxylate (BDC) and $\text{Cu}(\text{NO}_3)_2$ in a test tube. Following the creation of MOF-2(Cu) nanosheets, a combination of GO and MOF-2(Cu) dispersions were sonicated to create a mixed dispersion. The resultant mixed dispersion was then vacuum-filtered onto an Al_2O_3 substrate to create a MOF-2(Cu)-GO membrane. Cu-O coordination, π – π interactions, and hydrogen bonding propelled MOF-2(Cu) to hybridise with GO nanosheets, filling the gaps between MOF-2(Cu) nanosheets with GO nanosheets.

2.9.2 Applications of GO@MOF

GO is deposited layer by layer to create filtration membranes with great hydrophilicity, excellent chemical stability, and molecular selectivity (Thebo et al., 2018). In order to achieve superior separation performance and selectivity, MOF materials can be

used to modify the GO layer spacing, increase the composite material's hydrophilicity, and create efficient channels and driving forces that improve water transport through the membrane. Thus, the application of GO/MOF membranes in water treatment has become popular (B. M. Jun et al., 2020). Numerous techniques for modifying the GO base film with MOF have been researched till now. A number of modelling studies have demonstrated that a considerable shift in the layered GO base film's water permeability will occur if the layer spacing varies (Sui et al., 2019).

Ventura et. al. (2020), developed a series of highly efficient adsorbents using $\text{Ni}_3(\text{BTC})_2$ and $\text{Co}_3(\text{BTC})_2$ metal-organic frameworks (MOFs) and Fe_3O_4 magnetic nanoparticles (MNPs) to functionalize graphene oxide (GO) (Ventura et al., 2020). The synthesised composite micro adsorbents were employed to sorb common ions (Na^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , SiO_3^{2-}) from a brackish water model and Methylene Blue (MB), a model for common organic pollutants in water. In comparison to the MOFs parent materials, the adsorbed concentration of the produced composite nano adsorbents increases by an average of 30.52 and 13.75 mg/g for the Co and Ni composite, respectively, at equilibrium of MB. When compared to graphene oxide, the adsorbed amount of sulphate ions increases by 112.1 mg/g for the Ni composite and 92.1 mg/g for the Co composite. This increase in adsorption is explained by the following: the presence of GO inhibits aggregation by increasing dispersive forces in the MOFs; the MOFs create nanoscale MOFs over the GO platform; and the MOFs prevent the graphene layers from stacking. The *in-situ* synthesis of the MOFs on the GO support contributes for the higher adsorption at equilibrium of the composite nano adsorbents. This is because the formation of MOFs increases the dispersive forces, which prevents the stacking of GO sheet layers and increases the number of accessible adsorption sites.

In 2019, Jiahui Gu and colleagues created a novel form of wrinkled micro spherical MOF/rGO composite that is both superhydrophobic and super-oleophilic (Gu et al., 2019). A novel pleated 3-D microsphere MOF/rGO composite was prepared by embedding MOF nanoparticles between GO nanosheets and following high-temperature reduction and self-assembly. This mechanism differs greatly from the widely documented 3D MOF/graphene composites made by grafting MOF onto developing GO nanosheets (Qu et al., 2021). After ZIF-8/rGO is loaded onto a polyurethane sponge and the sponge is submerged in water while an external force is applied, the sponge will immediately float on the water's surface without absorbing any water. When silicone oil drops on the sponge, it is instantly absorbed. This demonstrates the superhydrophobic and superoleophilic characteristics of the MOF/rGO composite.

2.10 Zeolitic imidazolate framework

MOFs (metal-organic frameworks) are a class of crystalline porous materials with a variety of uses. The large surface area and pore size tunability of these MOF materials make them especially attractive (Awang Chee et al., 2022). The Zeolitic imidazole framework-8 (ZIF-8) is one of the subclasses of MOF. ZIF-8 has showed a great performance to remove various types of pollutants for instance the heavy metals (Awang Chee et al., 2021; Li et al., 2021) organic matter (Yoo et al., 2020; Zhang et al., 2021) and dyes (Zhang et al., 2019; Zhang et al., 2021). ZIF-8 is a promising material because of its high stability. They consist of tetrahedral metal ions (Zn, Co, etc.) coupled by imidazolate (Im), forming a novel class of porous crystal with extended three-dimensional structures. Along with the well-known aluminosilicate zeolites, many other zeolite-like inorganic

compounds were also found in the 1980s and 1990s, including aluminophosphates and transition metal phosphates.

A subfamily of MOFs known as M–Im–M (where M is for Zn, Co cation, and Im is for the imidazolate linker) was produced by the self-assembly process. ZIFs have geometries that resemble those of conventional aluminosilicate zeolites. Zn^{2+} ions function similarly to silicon (Si) in zeolites in ZIFs, whereas imidazolate anions act as a bridge between the metal ions to mimic the function of oxygen in zeolites. In ZIFs, including ZIF-8, the metal–imidazole–metal (M–Im–M) angle is defined as 145 degrees. ZIF-8 has a sodalite structure and is expressed as $\text{Zn}(\text{mim})_2$ (Hmim = 2-methylimidazolate). The ZIF-8 pore window size is reported to be 0.34 nm. In summary, ZIF-8 is characterized by its sodalite structure and a specific metal–imidazole–metal angle. The pore size of ZIF-8 is designed to be suitable for the selective adsorption of gases such as CO_2 and N_2 . This structural design and selective adsorption capability make ZIF-8 and similar ZIFs promising materials for applications in gas separation, storage, and related fields.

2.10.1 Synthesis method of ZIF-8 composites

ZIF-8 has been synthesised using a variety of techniques, including hydrothermal, solvothermal, ultrasonic/sonochemical, mechanochemical, microwave heating, and room temperature synthesis (Feng et al., 2021). Nevertheless, the *in-situ* technique of synthesis is fairly simple, however it has strict requirements for the properties of the substance. The fundamental idea is to leverage certain functional groups or surface properties of the constituent materials to enable various groups distribute biological reactions or interactions in order to accomplish binding without the need for any kind of treatment

(Keshvardoostchokami et al., 2021; Sharsheeva et al., 2019). ZIF-8 combined with two additional materials has also been effectively utilised with the *in-situ* approach.

In the experiment of Ran group, involved evenly dispersing TiO₂/ZIF-8 particles over cotton fabric (CF) (Ran et al., 2021). Polydopamine was used as a pretreatment for CF because its phenolic hydroxyl functional groups could chelate zinc, which significantly aided in the *in-situ* development of TiO₂/ZIF-8 on CF. When ZIF-8 films are synthesised *in-situ*, the carrier is typically placed in the reaction system under hydrothermal conditions, and a continuous ZIF-8 film is obtained on the surface of the carriers by using the carriers' surface qualities or other auxiliary techniques. The reverse diffusion method is another *in-situ* synthesis technique. It works by attaching two precursor solutions to either end of the porous matrix which is the zinc source and a 2-methylimidazole ligand. These two solutions have different concentrations, which will cause them to diffuse through the substrate's pores in the opposite direction. When they encounter one another on the substrate's surface, they will nucleate and create a film. While *in-situ* growth offers advantages in terms of controlling crystal size, enhancing interface interactions, and promoting nucleation on substrates, challenges may arise in achieving high film density (Jiang et al., 2019).

Another synthesis technique is surface modification, which involves applying surfactants, coupling agents, or crystal seeds to the nuclear particle surface to increase the adsorption and binding force between the nanoparticles and ZIF-8 and ultimately produce a close combination of them. The advantages of this method are its strong applicability and easy operation (Li et al., 2020; Yang et al., 2019). By using nanoscale ZIF-8 seed particles rather than chemical reagents to load and modify the carrier particles' surface, the

secondary growth method of seed crystals is a type of surface modification technique that speeds up the growth of ZIF-8 crystals due to the seed crystals' structural guiding effect, ultimately forming a dense and continuous ZIF-8 shell that covers the carrier. This approach can efficiently reduce ZIF-8 crystals' sensitivity to the synthesis conditions while also effectively preventing crystals from precipitating out of solution.

In order to successfully separate propylene from propane by molecular sieving, Tran et al. (2019) prepared a microporous ZIF-8 membrane using this technique. Employing the secondary growth seeding technique, they were able to successfully create ZIF-8 membranes that are defect-free (Tran et al., 2019). ZIF-8 membrane that is continuously intergrown in all directions on α -Al₂O₃ support can be produced by sodium formate. Hence, sodium formate with its uniquely discovered rapid recrystallization property, plays a role in steadily removing defects formed by crack formation in membranes. This property offers a promising avenue for the development of membrane materials with improved durability and resilience against damage. The application of sodium formate in membrane technology may provide a novel solution for addressing structural issues and enhancing the overall performance of membranes in various separation processes.

2.10.2 Applications of ZIF-8 composites for oily water treatment

ZIF-8 composite is a novel sewage treatment material that has endless potential for use in the field of wastewater regeneration. Its exceptional qualities allow it to effectively remove a wide range of wastewater contaminants as both an adsorbent and a photocatalyst. Adsorption is an impressive wastewater treatment method because of its straightforward

operation, inexpensive cost, and lack of hazardous effects. Developing effective sorbents is one of the main requirements for the adsorption process. Once an adsorbent has been determined, modifying its shape and structure to increase the number of reaction sites will improve its adsorption capacity. ZIF-8 possesses a high porosity and large specific surface area, which enable it to adsorb big molecules larger than its pore size thanks to its revolving door effect.

Anisi et al. (2021) reported that they removed olive oil from an aqueous solution using the ZIF-8 adsorbent (Anisi et al., 2021). In the study, the ZIF-8 adsorbent was optimised by response surface methodology (RSM) to facilitate batch adsorption studies for the separation of olive oil and water emulsion. By optimising the ligand to salt ratio to 10.37, the solvent to salt ratio to 702.7, and the temperature to 52.91°C, the ideal synthesis conditions were achieved for the highest production of ZIF-8 and the capacity of olive oil adsorption. With a large surface area of 1672.8 m²/g and a total pore volume of 0.7055 cm³/g, the optimised ZIF-8 was demonstrated. The largest amount of olive oil (1120 mg/g) was found to be adsorbed at a temperature of 25°C, a ZIF-8 dosage of 2.5 g/l, an initial oil concentration of 400 ppm, and a contact time of 120 minutes. The models that best suit the data to describe sorption equilibria and adsorption kinetics are the pseudo-first order model and the Freundlich isotherm model, respectively.

Another study by Rodrigues et al, ZIF-8 was prepared via the solvothermal method and it is used for the removal of emulsion oil/water (Rodrigues et al., 2020). A combination of methods (XRD, BET, IR) demonstrated that the solvothermal process was successful in obtaining the ZIF-8's crystalline phase. ZIF-8 uses adsorption to separate emulsified oil droplets from water. According to the oil removal test, the ZIF-8 demonstrated good process efficiency, eliminating up to 99.82% of the pollutant. A total of

2811.1 mg of oil were eliminated for every gram of ZIF-8 in the test conducted with a 500 mg/L concentration, yielding the best result. Lastly, ZIF-8 may also be regenerated using the solvent-washing method, and after three cycles, the regenerated ZIF-8 showed more than 98% regeneration efficiency.

2.11 Reusability of membrane for water treatment

The economic viability and sustainability of the water treatment process are directly impacted by the reusability potential of membranes, making it an important factor to consider. Hence, membranes employed in water treatment operations must have an excellent reusability potential, which makes them ideally suited for water reuse applications requiring high-quality water (Devaisy et al., 2023). Furthermore, a number of studies have shown that deactivated membranes, such zeolite membranes, and abandoned ceramic membranes, can be regenerated and reused, preventing their disposal in landfills (Karatas et al., 2023). Overall, research on the regeneration and reusability of membranes is ongoing, having a particular emphasis on the possible applications of these materials for reuse and sustainable water treatment.

Membrane fouling is the primary obstacle to the effective application of membrane processes (Balcik, 2021). Given the interactions with different components in the feed solution, the problem is defined by an irreversible drop in the flux throughout time and an increase in the hydraulic resistance. Particulate matter can bind to the surfaces of membranes and/or accumulate within membrane holes during the mass transport process. The contaminants are hydrophobic, meaning that they have a tendency to repel water. The membrane materials' low surface energy and hydrophobic properties are the reason for the fouling (Du et al., 2020). Due to the advantageous interactions, the hydrophobic

contaminants are likely to adhere to the membrane surface (Du et al., 2020). The effectiveness and quality of the membrane can be affected by severe fouling.

There are two types of membrane fouling: reversible and irreversible. We also ascribe these fouling categories to specific mechanisms, namely chemisorption and pore clogging. On the membrane surface, a cake layer development or concentration polarisation of materials is seen in the reversible fouling. Reverse fouling refers to the fouling that occurs on the permeate side of the membrane, affecting the clean side rather than the feed side. Reverse fouling can reduce the efficiency of the membrane by impeding the flow of permeate (El Batouti et al., 2022). There are two types of reverse fouling which are back washable and non-back washable. Back-washable fouling is fouling that can be removed or cleaned through a backwashing process. Fouling materials are loosely attached, allowing them to be dislodged and flushed away with the reverse flow of water. On the other hand, non-back-washable fouling is fouling that cannot be easily removed by backwashing. Fouling materials are more tenaciously attached, making them resistant to removal through standard backwashing procedures (Alsawafthah et al., 2021). The use of disinfectants like hydrogen peroxide (H_2O_2) or chemicals such as hydrogen chloride (HCl), and nitric acid (HNO_3) is a standard practice to remove foulants and restore membrane performance. Fouling is irreversible when the membrane is being used for a long period of time (Alsawafthah et al., 2021). The irreversible membrane fouling rises with the number of filtration cycles. As a result, increasing the membrane's hydrophilicity will help to reduce fouling and improve membrane flux.

2.11.1 Physical cleaning

Physical cleaning is the process of eliminating foulants from the membrane surface using mechanical or hydraulic forces. The most popular physical cleaning techniques are mechanical (sponge ball and fluidized particle cleaning) and hydraulic (forward and reverse flushing, backwashing, membrane relaxation, and air flushing). Novel and inventive cleaning methods are being created, even as the methods that have already been discussed are being improved. Ultrasound technology has recently been proposed and demonstrated as a viable method for controlling membrane fouling (Aghapour Aktij et al., 2020). These techniques are based on mechanical procedures that are used to clean the membrane surface of impurities. Physical cleaning takes no more than two minutes and is a faster method than chemical cleaning. Chemicals are not needed, and no chemical waste is produced. A lesser amount of damage is done to the membrane. However, in comparison to chemical cleaning, it is a less successful technique (Gul et al., 2021). Chemical cleaning is necessary for non-reversible contamination, but physical cleaning is only an option for reversible contamination (Abdel-Karim et al., 2021).

Another physical cleaning method is the use of vibration techniques like ultrasound, which operate by passing an electrical current through a transducer that generates high frequency vibrations. The production of tiny bubbles or voids filled with vapour in the surrounding liquid is known as cavitation, and it is caused by these vibrations. These cavities have the ability to collapse or implode, producing shockwaves that have the physical power to push loosely connected particles away from surfaces. This method has several benefits, such as chemical-free operation, *in-situ* treatment appropriateness, and the ability to clean and improve flux at the same time.

The application of ultrasound in the recovery of hydrophobicity in hollow fibre polyvinylidene fluoride (PVDF) membranes during intermittent membrane distillation (MD) operation, particularly to simulate solar-powered operation was found to be effective (Hejazi et al., 2019). After immersing the membranes in an ultrasonic bath for half an hour, the contact angle increased from 77° to 98°. The researchers pointed out that when the membrane module was not in use, it was crucial to leave the feed water in there because partial dry out caused subsequent wetting and crystal formation. This method needs to be used cautiously in pilot systems since any remaining heat in the module's feed side will allow evaporation to continue even after the feed flow has stopped. Without this flow, polarisation of temperature and concentration can rise, and there are no longer any shear forces produced by the fluid flow to remove or stop the formation of scale. Consequently, there might be a higher chance of crystal formation on the membrane. Smaller lab-based modules are less vulnerable to this problem because they have a faster cooling rate.

Naji et al. (2020) showed promising results using in-line low power (8–23 W) ultrasound to efficiently eliminate calcium (Ca) and silica scaling on PTFE and PVDF membranes. The increased mass transfer also resulted in an over 50–70% increase in flux (Naji et al., 2020). They used AGMD to treat both natural groundwater and RO reject water. Lower-power ultrasound not only conserved the membrane but also used less energy because, although greater power ultrasound further increased the flux, the authors pointed out that this can cause the membrane to deteriorate.

2.11.2 Chemical cleaning

Chemical cleaning is the process of using chemical agents to remove contaminants and restore membrane flux (Gul et al., 2021). The most significant factors influencing membrane efficacy are permeability and selectivity, which are necessary for optimal flux performance and product quality control. Chemical cleaning can assist in getting the membrane back to its original performance and in eliminating the foulants (Gokulakrishnan et al., 2021). Consequently, in order to restore the membrane's permeate flux properties, chemical cleaning must be effective in removing the various types of foulants from the membrane.

Liu et al. (2021) investigated the use of hydrophilic crosslinking network (HCN)-modified Polytetrafluoroethylene (PTFE) hollow fibres for hollow fibre microfiltration to remove soybean oil (Liu et al., 2021). This study demonstrated the great desirability of hydrophilic PTFE hollow fibre membranes, particularly those with strong resistance to chemical cleaning. For artificially accelerated cleaning, the hydrophilic modified C-PTFE membrane was submerged in strong oxidant solutions of NaOH (pH = 12), HCl (pH = 2), and NaClO (2000 ppm) for a period of two weeks. For up to 14 days, the C-PTFE membrane maintains its exceptional wettability even rigorous cleaning with bases, acids, and oxidants. Strong instantaneous wettability is demonstrated by the C-PTFE membrane's water contact angle, which dropped from 120° to 0° in 1.6 seconds. This is because the hydrophilic crosslinking network (HCN) is firmly anchored in the membrane matrix. It was thought that the crosslinking network was essential for fending off the strong chemical attack.

The impact of chemical cleaning on a microfiltration ceramic membrane contaminated by natural organic matter (NOM) source water was examined by Bazin et al. (2018). To treat NOM source water, a microfiltration membrane constructed from *Sayong* ball clay was employed that use the uniaxial dry compaction method (Bazin et al., 2018). The flux improved and up to 50% flux recovery was achieved after chemical cleaning. This demonstrated that the foulant can be eliminated from the membrane surface using NaOH. The flow rate increased by 1.8 times following chemical cleaning with 0.1M NaOH, as predicted. Nevertheless, the membrane demonstrated a sharp decrease in flux over time during the first 15 minutes of filtering, both before and after cleaning. The flux value remained almost unchanged after an hour of filtration. When particles in lake water clogged and fouled the membrane pores, a rapid decline in flow occurred. After the cleaning technique, the iron peak was eliminated. Once the chemical cleaning operation was completed, the lake's water quality also improved.

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Preparation of Graphene Oxide: Graphite powder (Sigma-Aldrich). Concentrated sulphuric acid (98% H_2SO_4), Sodium nitrate (NaNO_3), Potassium permanganate (KMnO_4), hydrogen peroxide solution (30% H_2O_2), and hydrochloric acid (35% HCl). The experiment's equipment and apparatus were cleaned with soap solution and rinsed with deionized (DI) water.

Modification of APTES: Toluene (ACS reagent, Merck), 3-(aminopropyl) triethoxysilane (APTES) (99%), Sigma-Aldrich).

Preparation of GO@ZIF-8/ Al_2O_3 Membrane: N, N-Dimethylformamide (ACS reagent, Merck) 2-methylimidazole (99%, Sigma-Aldrich), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%, Sigma-Aldrich), and sodium formate.

3.2 Research plan

The overall experimental procedure conducted in this study is illustrated in Figure 3.1. The research aimed to develop and evaluate the performance of GO@ZIF-8/ Al_2O_3 hollow fiber membranes for oil removal from wastewater. This include preparing the membrane, characterizing the membrane and evaluating the performance of the membrane through batch adsorption, cross-flow filtration, and reusability study.

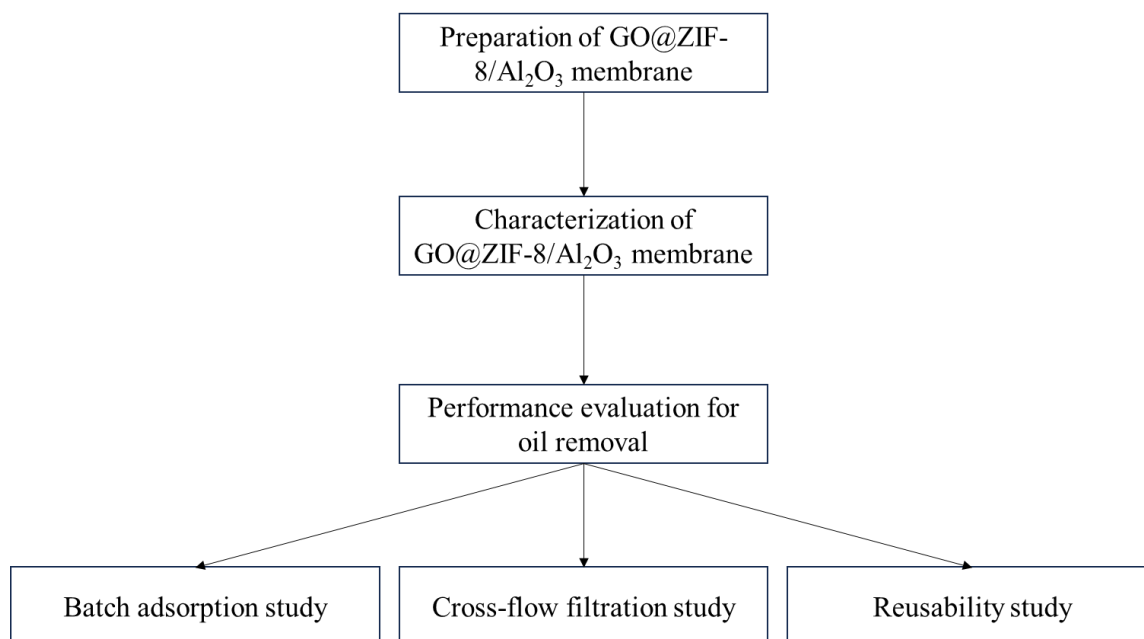


Figure 3.1: The research flowchart.

3.3 Preparation of graphene oxide (GO)

GO was synthesized from the graphite powder by the method of modified Hummer's method (Hu et al., 2016; Hummers & Offeman, 1957). Firstly, an ice bath was used to cool 23 mL of 98% concentrated H_2SO_4 below 0°C for 30 to 45 minutes. Separately, 0.5 g of NaNO_3 and 1 g of graphite were mixed. Then, this mixture was added to the chilled concentrated H_2SO_4 and stirred continuously for 45 minutes in ice bath to further mix the chemicals. Next, after slowly and gradually adding 3 g of KMnO_4 , the colour of the solution changed from black to greenish black, leading to oxidation. This was accomplished by keeping the solution's temperature below 20°C and stirring continuously for 15 minutes as shown in Figure 3.2.

After being taken out of the ice bath, the solution was left to warm until it reached room temperature. The solution is kept in an oil bath with constant stirring after reaching

room temperature, to the point the colour of the solution turns brown. Once the solution warmed to room temperature and turned brown while stirring in the oil bath, 140 ml of DI water was slowly added. Afterward, the reaction was stopped by adding 10 ml of 30% H_2O_2 followed by stirring the solution for 15 minutes. After filtering the resultant mixture, graphene oxide was washed with 5% HCl aqueous solution until 0.2 M BaCl_2 solution could not detect the presence of sulphate ions. The GO was rinsed using DI water until it achieves pH of 5 to 6.

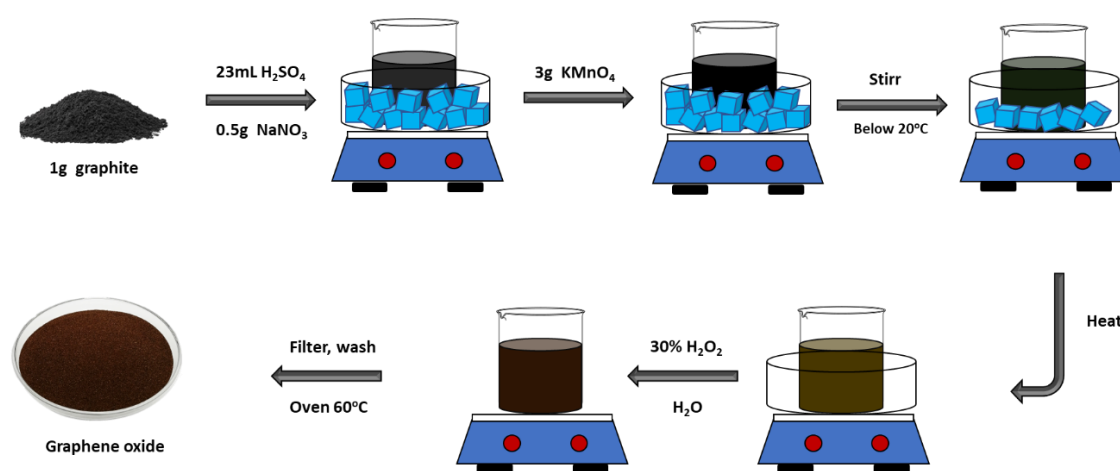


Figure 3.2: Schematic diagram of GO synthesis.

After that, the GO solution was ultrasonicated for one hour, and the big and incompletely exfoliated GO was removed by centrifuging the mixture for 2 hr at 4000 rpm. The GO was dried for 12 hours at 60°C in an oven. The dried GO was redissolved into a significant volume of acetone and aggressively agitated in order to further purify the material. Finally, the GO solution is filtered, and the resulting GO cake is dried for 6 hours at 60°C in a vacuum oven.

3.4 Preparation of GO@ZIF-8/ Al_2O_3 membrane

3.4.1 Preparation of GO@ZIF-8 nanocomposites

$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 2-MeIM, and sodium formate was mixed with N, N-Dimethylformamide (DMF) with the ratio of 1 : 2 : 1 : 313 respectively to make the ligand solution. Hence, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.3 g) was dissolved in DMF (31.3 ml) to make a metal salt solution. Then, to make the ligand solution, 2-MeIM (0.6 g) was dissolved in DMF (62.6 ml) with the addition of sodium formate (0.3 g). The ligand solution had been added with GO sheets in an amount based on the mass of the Zn salt and sonicated for 30 minutes (Ahmad et al., 2020). To improve GO dispersion, the ligand solution was agitated for 2 hours. After the ligand suspension was gradually added to a Zn salt solution, a cloudy solution appeared almost immediately and the mixture was vigorously stirred for 30 minutes as shown in Figure 3.3 (Ahmad et al., 2020).

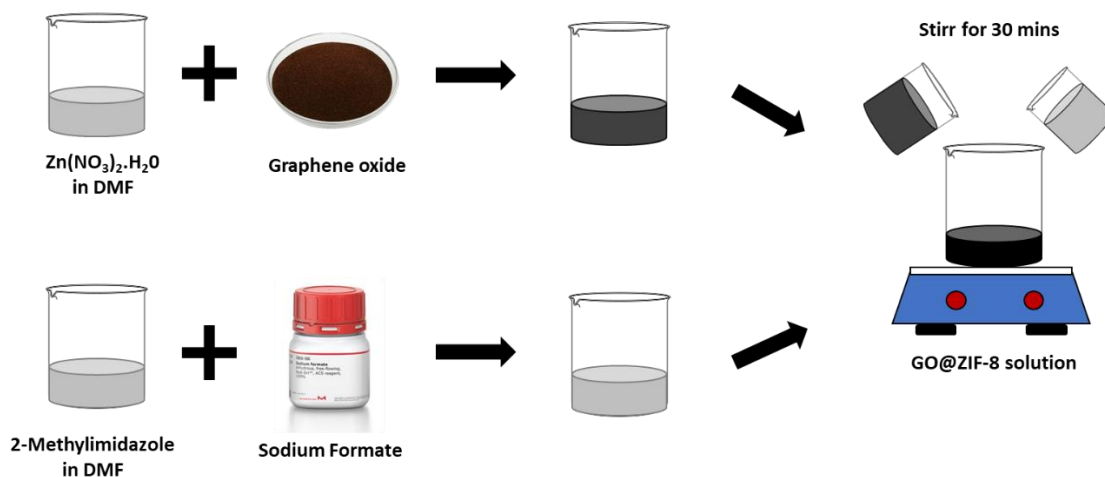


Figure 3.3: GO@ZIF-8 synthesis solution.

3.4.2 Alumina hollow fiber membrane modification using 3-aminopropyl triethoxysilane (APTES)

The alumina hollow fibre membrane underwent a 5 minute ultrasonic cleaning procedure while soaked in methanol, acetone, and deionized water. Then, 2% APTES solution in toluene was used to silanize the cleaned alumina hollow fibre membranes for 2 hours (Awang Chee et al., 2021). The modified membrane was then dried and cleaned with ethanol after the process. The membranes were heated in an oven at 60°C for 30 minutes to remove the solvent on their surface.

3.4.3 Fabrication of GO@ZIF-8 nanocomposite on alumina hollow fiber support

The GO@ZIF-8 synthesis solution was prevented from entering the lumens of the modified alumina hollow fibre by wrapping both ends of the membrane with PTFE before the synthesis procedure. The modified alumina hollow fibres were then added to a Teflon container containing the GO@ZIF-8 synthesis solution, which was then heated in an oven at 130°C for 24 hours as shown in Figure 3.4. The membrane was then dried in an oven for four hours at 60°C after being rinsed with DMF after the solvothermal process was completed.

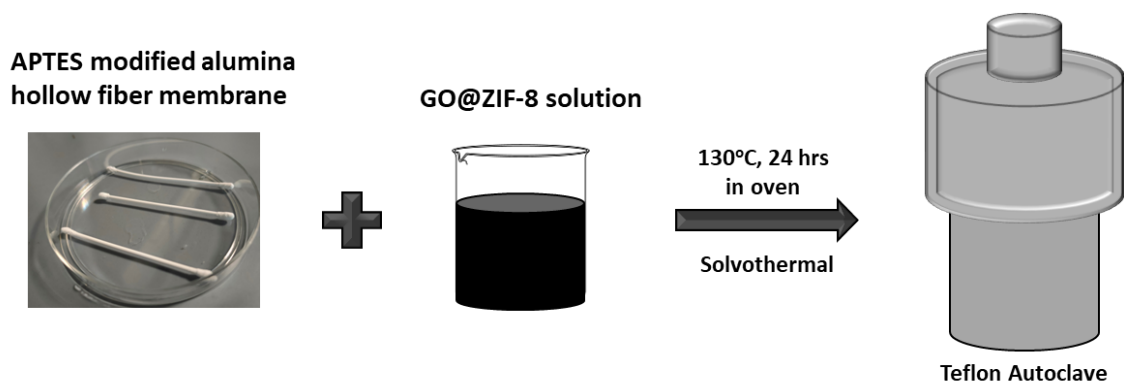


Figure 3.4: GO@ZIF-8/Al₂O₃ membrane *in-situ* solvothermal process.

3.5 Characterization of GO@ZIF-8/Al₂O₃ membrane

3.5.1 Field emission scanning electron microscopes (FE-SEM)

FESEM was utilized to observe the surface morphology and cross-sectional structure of the membranes. This helped determine the surface characteristics, layer thickness and porosity of the membrane. About 0.5 cm of the GO@ZIF-8/Al₂O₃ membranes were attached onto the 1 cm × 1 cm platinum plate holder. The surface morphologies of the GO@ZIF-8 deposited onto the alumina hollow fibre support were observed using FE-SEM (JOEL JSM-IT500HR) by coating the sample with gold/platinum mixture under vacuum condition for about 3 minutes at 20 mA. The purpose of gold/platinum coating on the samples was to reduce the charging effect before images were taken.

3.5.2 Fourier-transform infrared spectroscopy (FTIR)

FTIR was used to identify the functional groups present in the synthesized membranes. The analysis provided information about the chemical bonding and molecular

structure of the membrane materials. The samples were analysed using a pressed KBr pellet and a Thermo Nicolet IS10 Fourier Transform Infrared (FTIR) spectrophotometer. At wavelengths ranging from 400 to 4000 cm^{-1} , the spectra of the samples were scanned using the OMNIC Spectra software, which identified the individual components in any mixture from the single spectrum in a single step.

3.5.3 X-ray diffraction spectroscopy (XRD)

XRD was used to investigate the crystalline structure of the membrane materials. The analysis provided insights into the phase composition and the degree of crystallinity of the synthesized samples. The GO and GO@ZIF-8 powder were grounded into very small particles using mortar and pestle before performing the X-ray diffraction (XRD) characterization. About 2 g of the ground powder were analyzed using XRD. XRD is a non-destructive analysis to give information on the lattice parameters, phase identity, phase purity, crystallinity and crystal structure of the synthesized sample. The XRD (MiniFlex, Rigaku) emitted x-rays to the sample and the x-rays are diffracted at different angles and intensities by using $\text{CuK}\alpha$ radiation with a wavelength (λ) = 1.54Å at room temperature.

3.5.4 Ultraviolet–visible spectroscopy

UV-Vis spectroscopy was employed to analyse the optical properties and light absorbance of the materials. It also helped to evaluate the efficacy of the GO in absorbing specific wavelengths, which is relevant for applications of oil removal. UV-visible analysis was analysed using a Cary 60 UV-Vis spectrophotometer, which has a wavelength in the range of 200–800 nm. The GO sample was dissolved in deionized water and sonicated for

30 minutes to ensure the sample was well-dispersed and free from aggregates to allow light transmission. The GO solution was then placed into a cuvette suitable for UV-Vis measurements.

3.6 Performance of GO@ZIF-8/Al₂O₃ membrane for oil removal

3.6.1 Preparation of oil-water emulsion

Sorption experiments were conducted with oil that was dissolved in water, and then used as a model oily wastewater. The surfactant-stabilized synthetic oily wastewater emulsions were made by using motor oil (Shell Helix HX5 SN 10W-40) with distilled water as follows: To create a 1000 ppm stock solution, 1 mL of motor oil was mixed with 1 L of distilled water. Then, 200 mg of sodium dodecyl sulphate (SDS) as the anionic surfactant was added to the oil solution stirred for 12 hours initially (Raji et al., 2021). If the solution had not turned completely white and cloudy by then, stirring was extended up to 24 hours until it was well-mixed. The mixture was then sonicated using a water bath sonicator for 60 minutes to obtain stable oil–water emulsions (Zhong et al., 2021). Finally, distilled water was used to dilute the oily water to produce various concentrations (10-200 ppm) . Using a UV-vis spectrophotometer to measure absorbance at a wavelength of 235 nm, the amount of oil present in the feed and permeate samples was determined.

3.6.2 Batch adsorption study

In this experiment, the influence of several conditions on the adsorption experiment was examined using the controlled variable approach. Different variables including pH, contact time, and initial oil concentration as shown in Table 3.1. The pH range was

selected to explore the influence of acidity and alkalinity on the adsorption process. The pH 7 represents a neutral condition while the pH 3 and pH 10 represents acidic and alkaline conditions respectively (Li et al., 2022; Mottaghi et al., 2021). The contact time was varied to ensure optimal adsorption equilibrium. The contact time is a crucial factor for maximizing adsorption efficiency as longer contact times often lead to higher adsorption but after a certain point equilibrium is typically achieved (Awang Chee et al., 2021). The range of initial oil concentration was chosen to simulate different levels of oil contamination in water, allowing for the assessment of adsorption capacity under varying oil pollutant loads. The selected range is commonly used in oil–water separation studies and reflects practical concentrations found in industrial effluents, as noted in multiple studies on adsorption for wastewater treatment (Diraki et al., 2018, 2019; Ewis et al., 2020).

Table 3.1: Adsorption experiments conditions.

Experiments	Initial oil concentration (ppm)	Adsorbent dose (g)	Contact time (h)	pH
Effect of pH	60	0.2	8	3, 7, 10
Effect of contact time	60	0.2	0.5-8	3
Effect of initial oil concentration	10-130	0.2	8	3

Adsorption study was performed by soaking 0.2 g of GO@ZIF-8/Al₂O₃ hollow fibre membrane into 50 mL of oily water solution. This amount of adsorbent was chosen

based on studies that balance optimal adsorption efficiency with material economy. Previous works using GO-based composites have shown that this quantity is sufficient to provide maximum surface area exposure for pollutant interaction while preventing saturation (Li et al., 2022). Using 0.2 g helps achieve effective oil adsorption without needing excessive adsorbent, thus making it cost-effective for experimental replication (Masibi et al., 2022). Next, the solution was shaken using an orbital shaker set at 150 rpm for 8 hours.

Finally, a UV-Vis spectrophotometer operating at a wavelength of 235 nm was used to determine the oil concentration. A calibration curve was made using known concentrations, and the concentration of the oil solution was calculated from it. The amount of oil adsorbed at equilibrium was calculated using q from Equation 3.1 and Equation 3.2 was used to obtain the oil removal effectiveness (percent of adsorption) (Nikou et al., 2021).

$$\text{Adsorption capacity (mg/g), } q_e = \frac{(C_o - C_e)v}{m} \quad \text{Equation 3.1}$$

$$\text{Removal efficiency (\%)} = \frac{C_o - C_t}{C_o} \times 100 \quad \text{Equation 3.2}$$

Where C_0 (mg/L) represent the initial concentration of oil in an aqueous solution, C_t indicates the oil concentration over time, the oil concentration at equilibrium was denoted by C_e (mg/L), the volume of oil solution used was V (L), and the mass of adsorbent was m (g).

The adsorption equilibrium isotherms and kinetic models was applied for describing the mechanism of adsorption as shown in Table 3.2. The Freundlich and Langmuir isotherms explain the amount of material adsorbed per unit mass of adsorbent,

whereas pseudo-first order and pseudo-second order kinetic models indicate the adsorption rate (Khan et al., 2018; Simonin, 2016).

Table 3.2: Adsorption isotherms and kinetics models (Khan et al., 2018; Simonin, 2016).

Isotherms models	Equations
<i>Langmuir</i>	$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$ Equation 3.3
	$R_L = \frac{1}{(1-K_L C_0)}$ Equation 3.4
<i>Freundlich</i>	$q_e = K_F C_e^{1/n}$ Equation 3.5
Kinetics models	Equations
Pseudo-first order	$\ln(q_e - q_t) = \ln q_e - k_1 t$ Equation 3.6
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$ Equation 3.7

3.6.3 Cross-flow filtration study

A system of crossflow filtering was applied to calculate the oil rejection and solute permeate (Awang Chee et al., 2021). The feed for the filtering process was produced using an oil solution with concentration of 100 ppm. To get a significant oil rejection, the experiments were carried out at 1 bar. The concentration of oil in the permeate and in feed solution were measured using the UV-vis spectrophotometer. Firstly, the water was allowed to penetrate the inner side of the membrane by pumping the water of the feed solution from the outer side. Then it enters via the lumen of the hollow fibre membrane to

travels to the other end of the membrane which is unsealed as shown in Figure 3.5. Before being collected for the purpose of determining the flux and rejection, the permeates were stabilized for around 3 min. Equation 3.8 was used to calculate the permeate flux (Awang Chee et al., 2021):

$$J_w = \frac{V}{t \times A} \quad \text{Equation 3.8}$$

For oil rejection study, 100 ppm of diluted oil solution was used. The oil rejection was determined by using the equation used in Equation 3.9 (Awang Chee et al., 2021):

$$\text{Oil removal (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad \text{Equation 3.9}$$

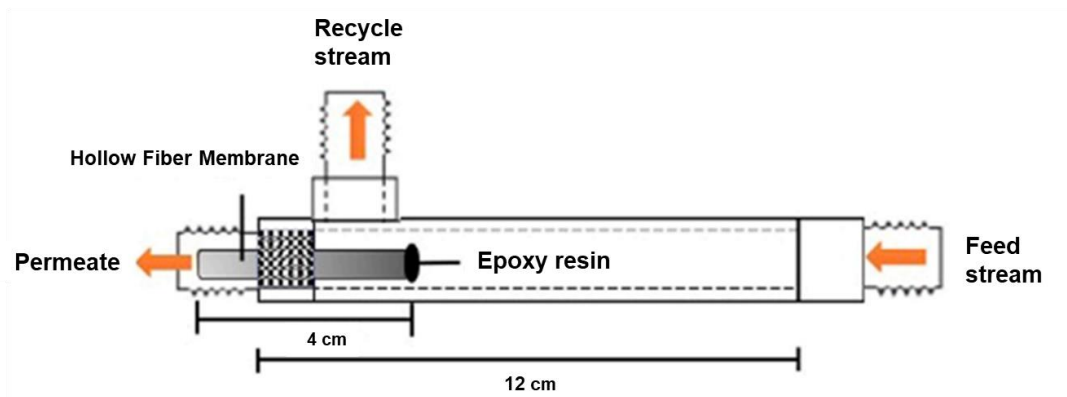


Figure 3.5: Hollow fiber module specifications (Awang Chee et al., 2021).

3.6.4 Regeneration study

The membrane's ability to regenerate and be reused is crucial for long-term applications. In this study, after a 5-hour filtration period, the membrane was regenerated

using a 2% wt. sodium dodecyl sulphate (SDS) solution (Gruskevica & Mezule, 2021; Lv et al., 2023). The used membrane was soaked in the SDS solution for 30 minutes and sonicated for 15 minutes before further use. The regenerated membrane was reused for 5 additional filtration cycles, making a total of 6 cycles. The rejection efficiency was tested after each cycle to assess the membrane's long-term performance (Avornyo et al., 2023).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Graphene oxide characterization

Chemical studies of graphite and GO were carried out using the Fourier transform infrared spectroscopy (FTIR) and UV-Vis spectroscopy. The obtained FTIR spectra which is displayed in Figure 4.1 comprises the entire wavenumber range of 4000-400 cm^{-1} . The various oxygen functional group presence in GO has been determined at 3438 cm^{-1} from stretching vibrations of O-H, at 1704 cm^{-1} from the stretching vibrations of C=O, at 1640 cm^{-1} from unoxidized graphitic domains' skeletal vibrations, and at 1117 cm^{-1} from C-O stretching vibrations. These functional groups with hydrophilic oxygen give GO sheets good dispersibility in water and many other solvents (Junaidi et al., 2021). The carboxylic acid groups should still be present in the graphene materials since reduction of these groups was not anticipated (Sastry et al., 2021). Graphite is transformed into graphite oxide through the attachment of oxygen-containing functional groups to its surface during an oxidation process (Tiwari et al., 2020). These results demonstrated that functional groups containing oxygen were present on the graphene oxide surface (Yu et al., 2020). When graphite powder was exposed to potassium permanganate and concentrated sulphuric acid for oxidation, the extended conjugated *p*-orbital system of the material is destroyed. The functional group containing oxygen such as carboxyl, carbonyl and hydroxyl groups are substituted into the carbon skeleton.

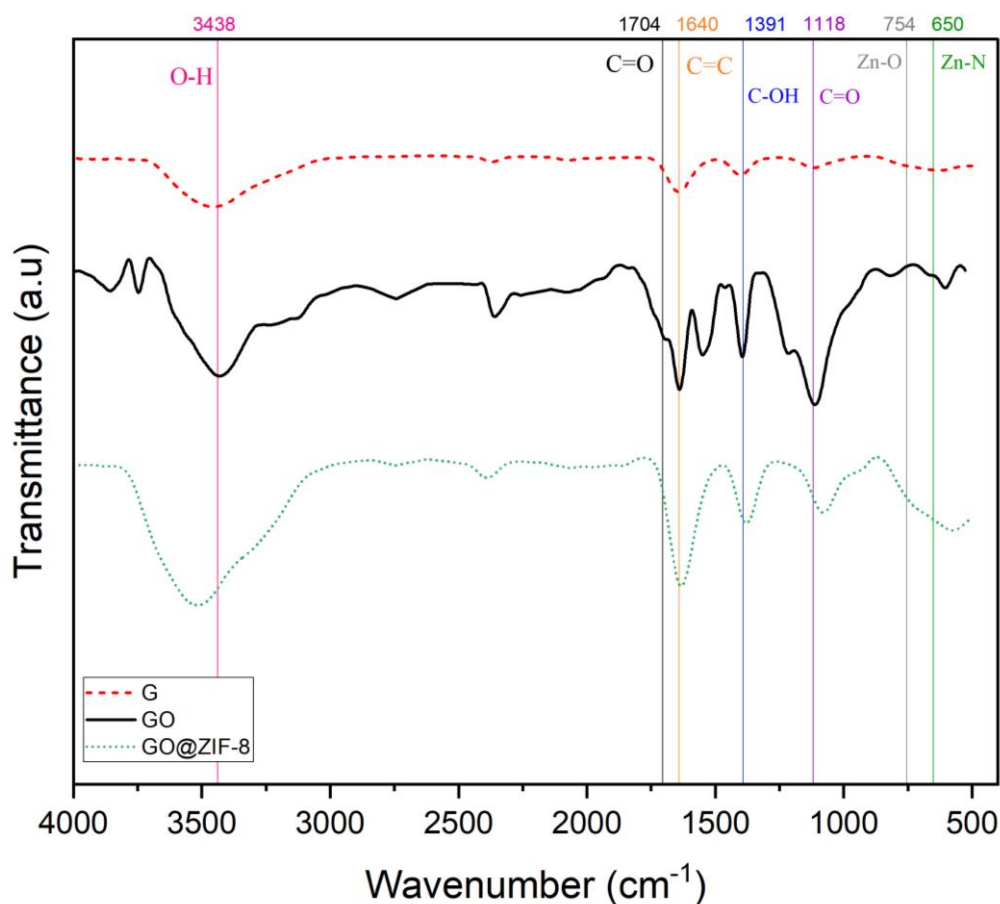


Figure 4.1: FTIR spectra of graphene, GO and GO@ZIF-8 composite.

In graphite, there were two distinct peaks that were very prominent. The structural OH groups and the stretching of the O-H vibrations that absorbed water molecules contributed to the peak at 3452 cm^{-1} , while the graphene oxide peak at 1110 cm^{-1} was attributed for the C-O (Monteiro et al., 2020). In addition, peaks like C=C at 1639 cm^{-1} , which was attributed to the skeletal vibrations of unoxidized graphitic domains or the contribution of the stretching deformation vibration of intercalated water (Nebol'sin et al., 2020).

Figure 4.2 shows the UV-visible spectrum of the aqueous dispersion of GO. The UV-Vis analysis was performed to confirm the optical properties and identify the functional groups of graphene oxide (GO) by detecting characteristic absorption peaks.

Graphene oxide (GO) exhibits a maximum peak absorption around 230 nm and a shoulder peak at about 300 nm. These distinctive absorption peaks are indicative of specific molecular transitions. The strong peak at 230 nm corresponds to the $\pi \rightarrow \pi^*$ transitions in aromatic C=C bonds, while the less energetic shoulder peak at 300 nm is associated with $n \rightarrow \pi^*$ transitions in C=O bonds (Trikkaliotis et al., 2021). These transitions occur when p-orbitals are either in phase or out of phase, allowing for combined transitions between low-energy π and high-energy π^* orbitals (Figure 4.2). Hence, the GO spectrum has these two distinctive peaks: an intense peak at 230 nm that corresponds to the sp^2 C=C ($\pi \rightarrow \pi^*$) transition, and a shoulder peak at 300 nm showing the C=O ($n \rightarrow \pi^*$) transition (Chen et al., 2019; Trikkaliotis et al., 2020).

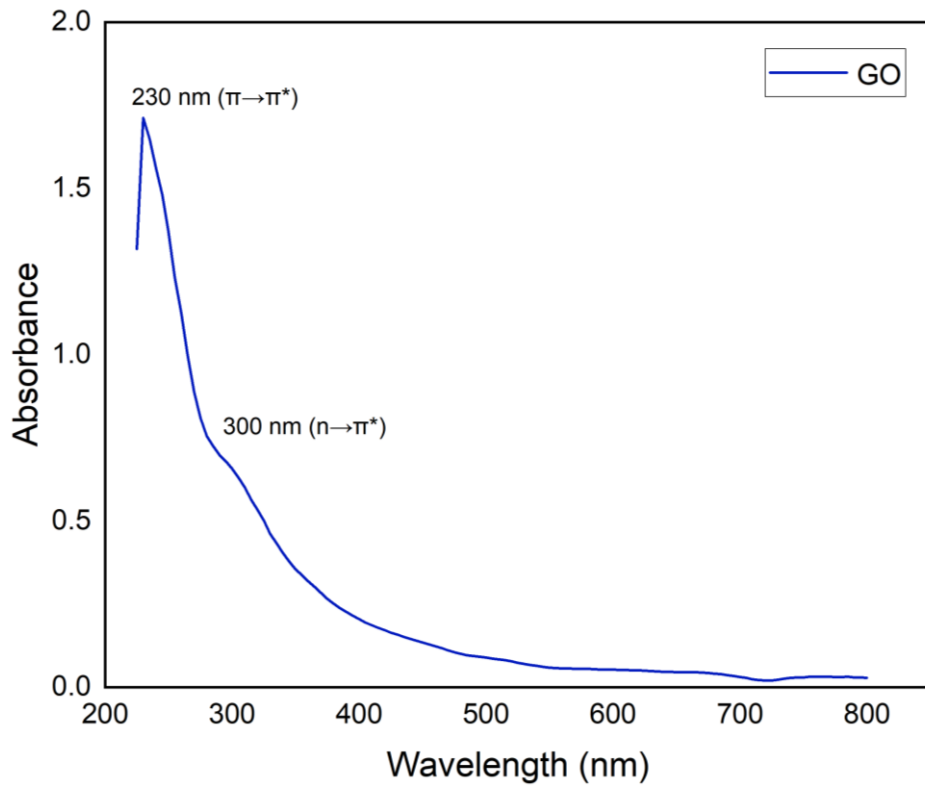


Figure 4.2: The UV-Vis spectrum of GO.

The X-ray diffraction spectrophotometer (XRD) analysis was used to further examine the structure of graphene oxide produced by the modified Hummers method. Figure 4.3 shows the XRD patterns of the prepared graphene oxides, which are consistent with earlier studies (Abaszade, 2022; Guliyeva et al., 2023; Nikou et al., 2021). The GO has a strong diffraction peak identified at $2\theta = 9.51^\circ$ on the (001) plane, corresponding to a d-spacing of 9.29 Å, assigned to the hexagonal plane of the graphene oxide crystalline structure. A smaller peak at 42.21° on the (100) plane, corresponding to a d-spacing of 2.14 Å, further confirms the crystalline structure of GO, which is in agreement with published data (Ain et al., 2019; Al-Gaashani et al., 2019; Kumar et al., 2019). The change in d-spacing can be attributed to the intercalation of oxygenated functional groups which leads to structural disorder after the oxidation process.

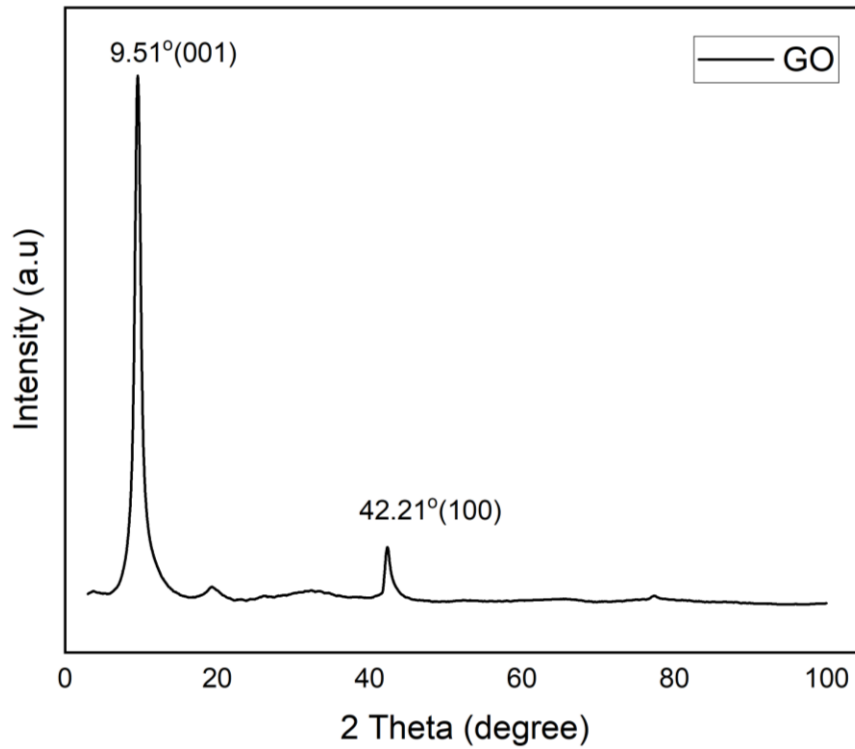


Figure 4.3: The XRD pattern of GO.

Figure 4.4 shows the surface morphology of pure graphite powder compared to graphene oxide. The graphite microstructure exhibits structural deterioration. The microstructure particles not only feature an irregular and lamellar structure, but also a rough surface with numerous microscopic asperities and long graphitic nanostructured sheets (Zhang et al., 2020). Meanwhile, graphene oxide has a layered structure, allowing for the production of homogenous and ultrathin graphene films which is similar to the literature from (Abaszade, 2022; Adetayo & Runsewe, 2019; Benzait et al., 2021; X. Chen et al., 2022).

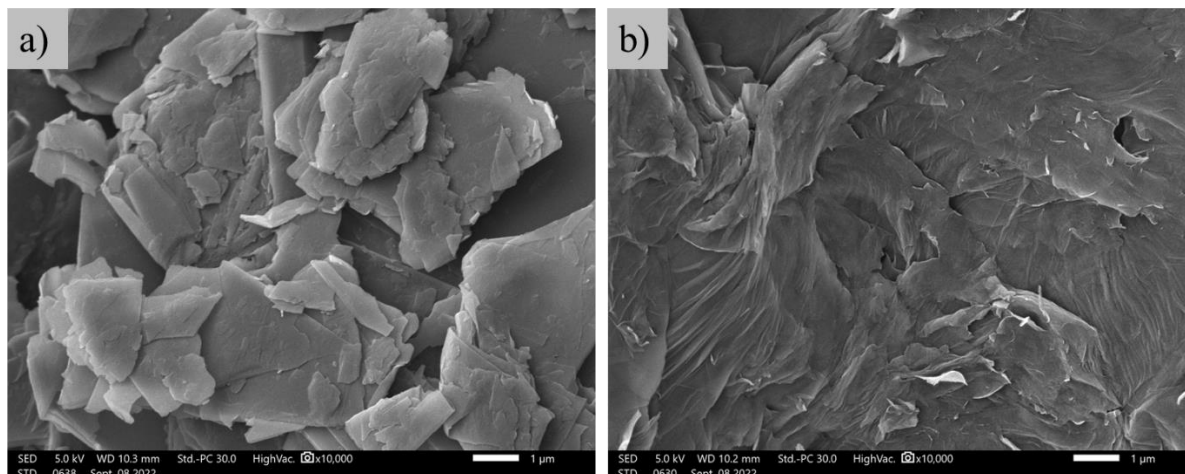


Figure 4.4: The SEM images of pure (a) graphite and (b) graphene oxide.

Figure 4.5 present a flakes-like structure from SEM micrographs of synthesized GO with different scale bars. From the figure, these films are sometimes folded or continuous and the individual sheets' edges can be seen along with any wrinkled or kinked regions. Moreover, the EDX analysis which shows the elemental chemical compositions of the GO exhibits the presence of element carbon (C), oxygen (O) and sulphur (S) as shown in Figure 4.5 (b). The oxygen and sulphur present in the GO is due to the usage of oxidizing agent H_2SO_4 and KMnO_4 during oxidation process (Abaszade et al., 2021). This proves the formation of GO where graphene layer is decorated with oxygen containing groups. To summarize, Figure 4.4 (a) shows a SEM image of plain graphite powder with an unclear surface structure, whereas Figure 4.5 shows a well-cleared surface with flakes-like structures on graphene oxide.

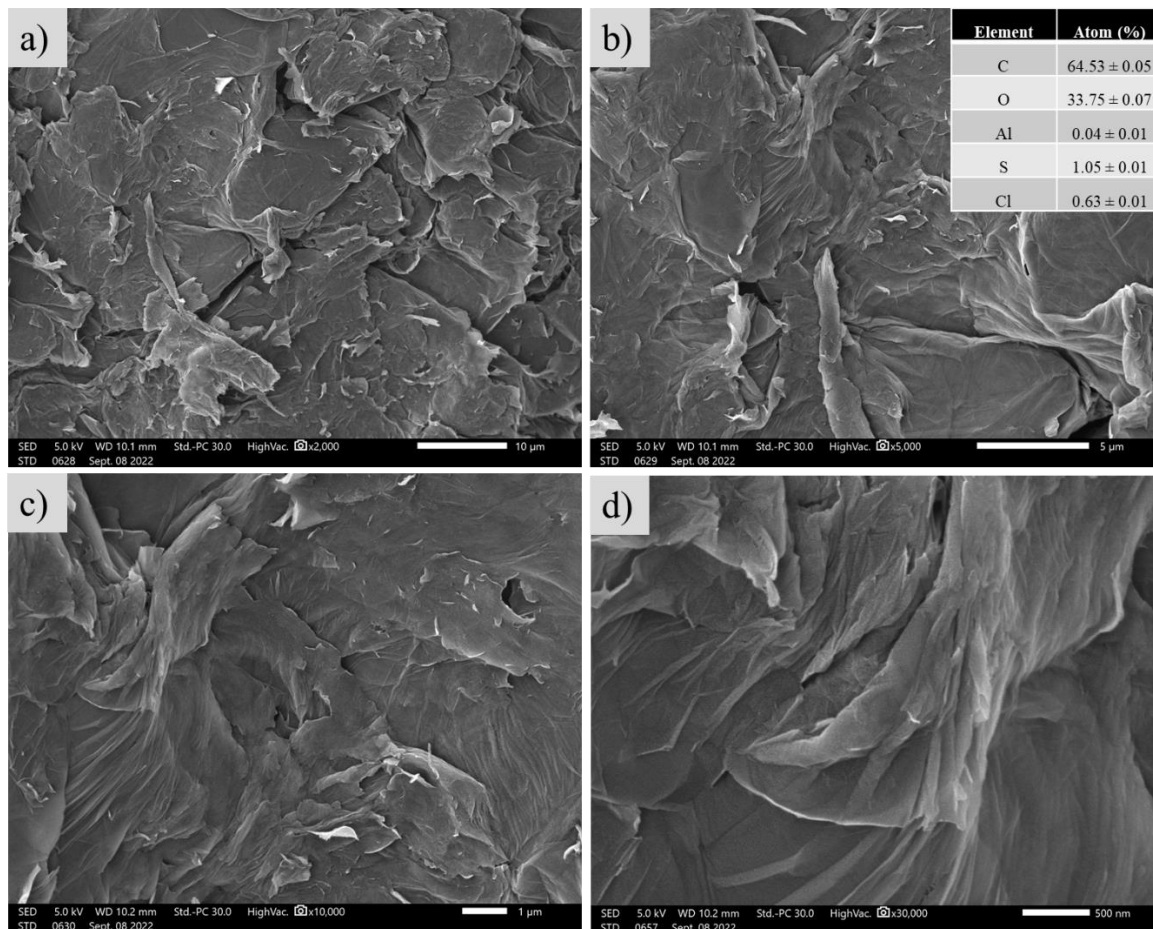


Figure 4.5: SEM micrograph of graphene oxide at magnification (a) x2000, (b) x5000, (c) x10 000 and (d) x30 000.

4.2 GO@ZIF-8 nanocomposites characterization

The FTIR spectra of GO@ZIF-8 and GO is shown in the Figure 4.1. The distinctive peaks for GO sheets were identified at 3438 cm^{-1} and 1704 cm^{-1} , and were assigned to the -OH and C=O of the GO sheets (Huang & Feng, 2018). However, spectrum of GO@ZIF-8 demonstrated that the GO sheet's carboxyl group was coordinated with Zn^{2+} through the elimination of the peak at 1704 cm^{-1} (Yang et al., 2018). As a result, the peak at 1640 cm^{-1} is widened and its intensity is increased as the ZIF-8 content in GO@ZIF-8 composites decreases (Zhu et al., 2020). The coordination of Zn^{2+} with the carboxylic of GO sheet also supported by the existence of the new Zn-O peak at 754 cm^{-1} .

The surface chemistry of GO@ZIF-8 composites shows that the composites were successfully synthesized because it contains recognised peaks from both GO and ZIF-8. Additionally, due to ZIF-8 particles that had distributed extensively on the GO layers, the GO@ZIF-8 infrared spectra and the GO infrared spectra were nearly identical (Zhu et al., 2018). Given that GO surfaces contain epoxy and carboxylic groups, zinc clusters may be able to adhere to them. It was further demonstrated that GO@ZIF-8 was successfully synthesised when the ZIF-8 diffraction peaks interfered with the weak GO characteristic peaks.

The comparison between the XRD pattern of GO and GO@ZIF-8 composites is shown in the Figure 4.6. The distinct peak of GO was the wide peak at $2\theta = 9.51^\circ$ which was related to the formation of multiple functional groups with oxygen on graphitic planes and indicated an interlayer spacing of $9.29\text{\AA}$. Nevertheless, the previously prominent peak for GO were now dominated by ZIF-8 peaks for the synthesised GO@ZIF-8 composites spectra (Hoseinzadeh et al., 2021; Makhetha et al., 2020). Based on Figure 4.6, GO@ZIF-8 has characteristic peaks at $2\theta = 8.38^\circ, 18.94^\circ, 23.04^\circ, 27.92^\circ, 28.90^\circ, 32.02^\circ$ and 33.74° , which are consistent with the peaks of the ZIF-8 (Li et al., 2019; Nikou et al., 2021; Tuncel & Ökte, 2021). The disappearance of GO peak at 9.51° is attributed to either exfoliation or distortion of GO stacking sheets, indicating the presence of metal-organic frameworks (MOFs) between the GO sheets and a modification of the interlayer spacing (Makhetha et al., 2020). The results of the XRD indicate that ZIF-8 produced on GO sheets successfully prevents the stacking of the GO sheets, showing that the required structure was obtained in conformity with the other techniques, particularly the FTIR data.

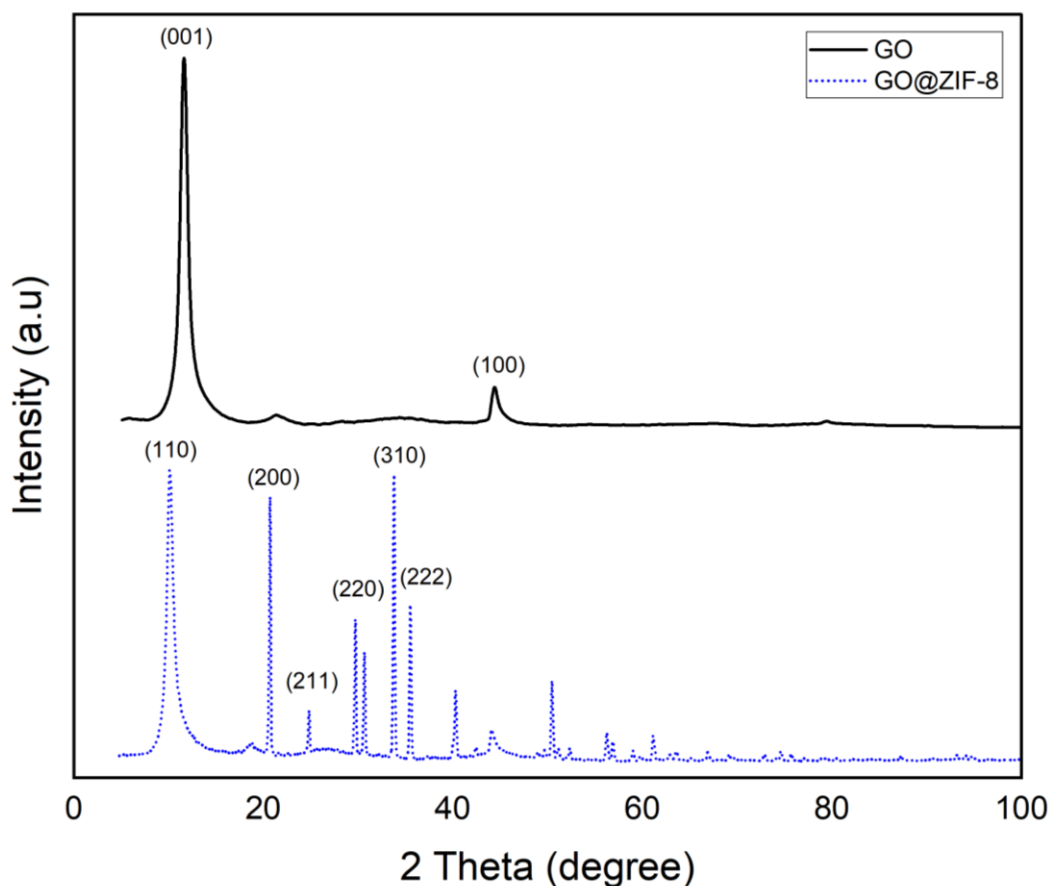


Figure 4.6 The XRD pattern of GO and GO@ZIF-8 composites.

The changes in the morphology of the nanocomposites were examined using field emission scanning electron microscopy (FESEM) images as shown in Figure 4.7 for the modified GO@ZIF-8 nanomaterials. The GO nanosheets incorporation affects the nanocrystals formation and growth since it becomes a platform for growth of crystal (Li & Xu, 2021). Moreover, the functional groups containing oxygen on the GO nanosheets hindered the ZIF-8 particles growth by way of coordination, as a result with the addition of GO will decrease the size of ZIF-8 particles (Li & Xu, 2021; Zhu et al., 2018). Figure 4.7 shows the two-dimensional lamellar structure of the GO@ZIF-8 composite. Due to coordination interactions between the Zn^{2+} and carboxyl groups of GO, ZIF-8 was uniformly spread on the GO surface via *in-situ* growth. This increased the anti-biofouling

performance of the GO@ZIF-8-incorporated membrane (Wang et al., 2018). Thus, the synthesis of the GO@ZIF-8 laminates was successful.

As illustrated in Figure 4.7, a dense GO layer forms between firmly adhered ZIF-8 crystals. The GO layer is defect-free and does not have any obvious fractures, tiny holes, or other flaws. Adjusting the concentration of GO suspensions will change the extent to which the GO layer is covered. However, greater GO coverage results in increased ZIF-8 crystals coated by the GO layer, which lowers the GO@ZIF-8 membrane permeance and reduces the "real membrane area" for flux permeation. The EDX analysis shown in Figure 4.7 (c) exhibits the composition of elements in GO and ZIF-8 such as the carbon (C), oxygen (O), sulphur (S), nitrogen (N), chloride (Cl) and zinc (Zn) confirming the formation of GO@ZIF-8 nanocomposites.

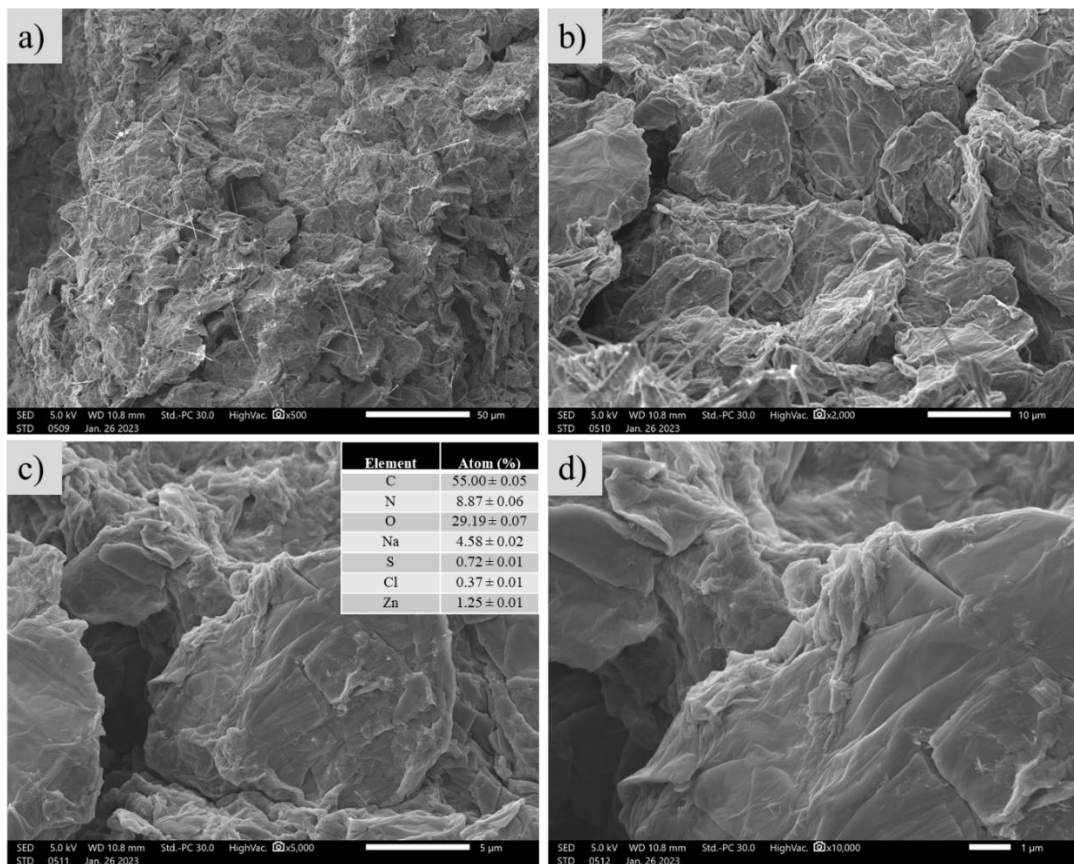


Figure 4.7: SEM micrograph of GO@ZIF-8 at magnification (a) x500, (b) x2000, (c)

x5000 and (d) x10 000.

4.3 GO@ZIF-8/Al₂O₃ membrane characterization

The GO@ZIF-8 nanocomposites were embedded to the alumina hollow fiber membrane support via solvothermal *in-situ* approach. Figure 4.8 depicts the results of an FTIR analysis of GO@ZIF-8 membranes. The functional group present in the pristine alumina, ZIF-8/Al₂O₃, and GO@ZIF-8/Al₂O₃ membrane prepared with APTES was compared. Based on Figure 4.8, the GO@ZIF-8/Al₂O₃ composites membrane spectrum exhibited similarities to the ZIF-8/Al₂O₃ spectrum. When ZIF-8 was deposited and grown on the GO surface for the composites, the O-H band at 3454 cm⁻¹ and the C=C band at 1627 cm⁻¹ was suppressed (Makhetha & Moutloali, 2020). The broad band seen for the GO@ZIF-8/Al₂O₃ membrane with the APTES modification demonstrated that the ZIF-8 layer had developed on the support alumina membrane. The peak at 1384 cm⁻¹ at the ZIF-8/Al₂O₃ membrane was assigned to the fingerprint of complete ring stretching, while 1588 cm⁻¹ was identified for the C=N stretching (Awang Chee et al., 2021). There were also other bands seen between 1380 cm⁻¹ and 960 cm⁻¹, which were attributed to the imidazole ring's in-plane bending mode (Tuncel & Ökte, 2021) and the bands at 740-609 cm⁻¹ were associated to aromatic *sp*² C-H bending (Biata et al., 2022; Tuncel & Ökte, 2021). The stretching of Zn-N is detected at a wavenumber 439 cm⁻¹.

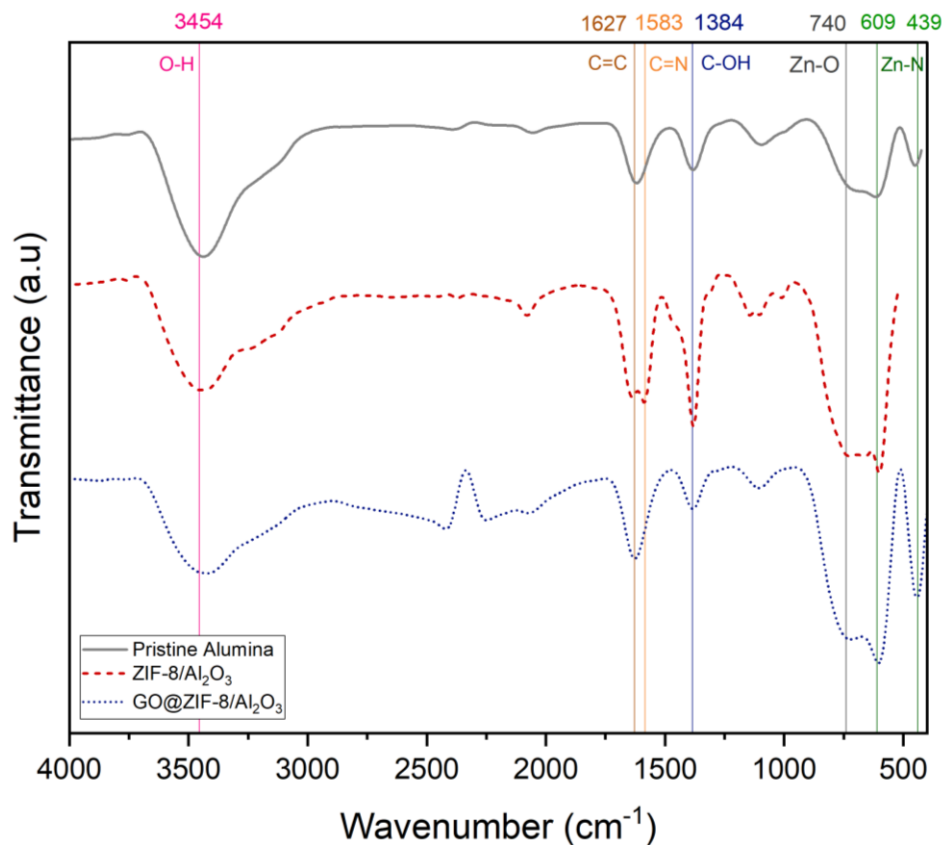


Figure 4.8: FTIR spectra of pristine alumina, ZIF-8/Al₂O₃ and GO@ZIF-8/Al₂O₃.

FESEM was used to determine the composite membranes' cross-section and surface morphologies. For further comparison, the morphologies of pristine alumina and GO@ZIF-8/Al₂O₃ membrane were examined. Figure 4.9 depict the cross-section and surface morphologies of a pristine alumina hollow fibre membrane created using the sintering and phase-inversion process. The membrane has a thickness of 419.26 μm measured from the outer surface to the inner surface as shown in the Figure 4.9 (c). The membrane FESEM images shows a huge finger-like configuration on both the lumen and shell sides. At the top of the huge finger-like arrangement is a thin layer of structures resembling sponges. This morphology is favourable because the top of the membrane was deposited with the layer of ZIF-8 because of the small holes and sponge-like structure.

Consequently, it can aid in preventing ZIF-8 particle infiltration into the membrane's inner layer. The surface image of the alumina hollow fibre (Figure 4.9) also showed that the membrane had a large amount of porosity. To improve the effectiveness of the membrane for removing oil molecules, additional modification to the support membrane's surface is needed to minimise the porosity of the surface.

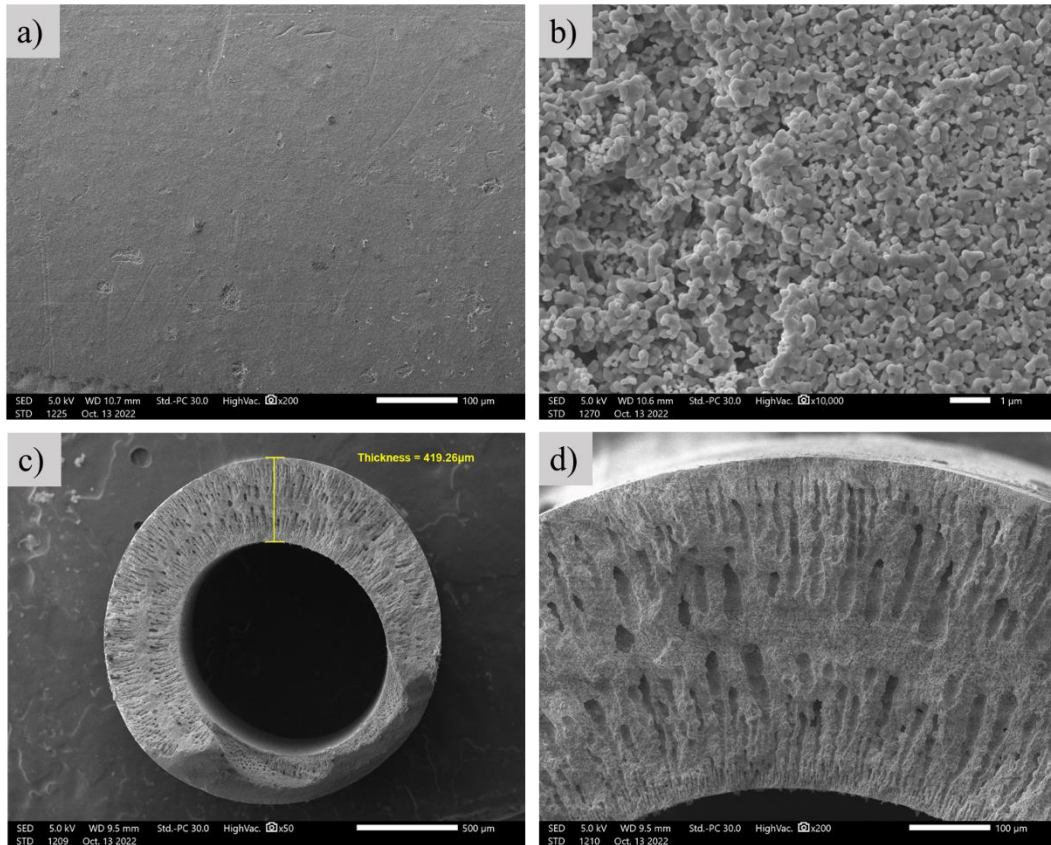


Figure 4.9: SEM images of pristine alumina hollow fiber surface at magnification (a) x200, (b) x10 000 and cross-section at magnification (c) x50, (d) x200.

According to Figures 4.10 and 4.11, the pores surface of the hollow fiber ceramic membrane was coated when it was deposited by the GO@ZIF-8 nanocomposites. The membrane's surface has a shape like a dodecahedron and few randomly placed irregular rectangles that are covered and anchored between the GO sheets (Ahmad et al., 2021). The

presence of GO sheets causes the surface of the GO@ZIF-8 nanocomposite membrane to have typical wrinkles (Makhetha et al., 2020). Moreover, the cross-section morphology reveals a brick-and-mortar structure (Yang et al., 2018). Figures 4.11 (a) and 4.11 (b) illustrate the surface morphologies and cross-section of the composite membrane GO@ZIF-8. The aggregation of ZIF-8 particles caused an exceptionally rough surface to emerge on the composite membrane as the nanoparticle content increased (Chen et al., 2020). The slight disintegration of the crystal during the amine functional modification revealed the irregular dodecahedron shape of the crystal after APTES functionalization (Wei et al., 2019). The cross-sectional images of the composite membranes allow us to see the ZIF-8 particles as well. The polyhedron-shaped ZIF-8 was coated on the veil-like GO nanosheet, maintaining the same morphology as the ZIF-8 in the as-prepared GO@ZIF-8 (Figure 4.10 (d)), demonstrating that ZIF-8 was quite stable during this process. The preparation of GO@ZIF-8 using the *in-situ* growing approach was successfully demonstrated by these results (Li et al., 2019).

When GO was added to the precursor solution for ZIF-8 in different weight ratios, a dense ZIF-8 layer was formed by multiple ZIF-8 crystals due to capillary forces and covalent bonding between the GO layer, as shown in Figure 4.10 (c) and 4.10 (d) (Zhu et al., 2018). Furthermore, not just a single layer of ZIF-8 but multiple ZIF-8 particles were adsorbed onto the GO. The use of different weight ratios of GO was intended to optimize the interaction between GO and ZIF-8 as GO content can significantly affect the dispersion and adhesion of ZIF-8 particles. Figure 4.10 demonstrates that the dispersion of ZIF-8 particles on the support membrane increases as the GO content increases. This variation in GO content was critical for achieving uniform particle distribution and enhancing the formation of a stable separation layer structure. Higher GO content also creates more

functional sites, which strengthens the interaction between ZIF-8 and GO, leading to improved membrane performance (Yang et al., 2018). In layered GO membranes, guest molecules move along stacked nanochannels between adjacent nanosheets to accomplish effective separation (Su et al., 2020).

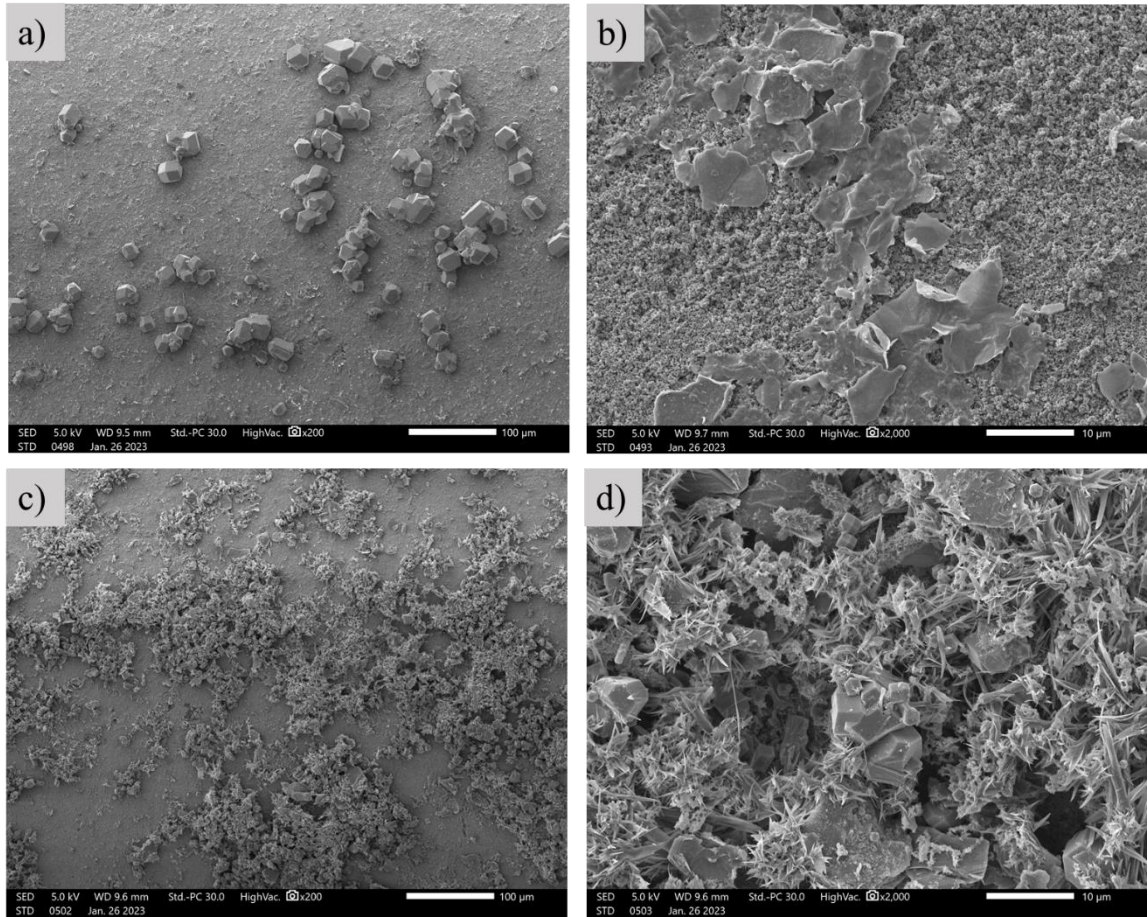


Figure 4.10: FESEM images of the membrane surface, $\text{GO}_{(1:1)}@ZIF-8/\text{Al}_2\text{O}_3$ at magnification (a) x200, (b) x2000 and $\text{GO}_{(2:1)}@ZIF-8/\text{Al}_2\text{O}_3$ at magnification (c) x200, (d) x2000.

FESEM analyses were conducted as well on the $\text{GO}@ZIF-8/\text{Al}_2\text{O}_3$ composite membrane's surface and cross-sectional morphologies. The surface of the composite membrane also has a thick separating layer as shown in Figures 4.11 (b) and 4.11 (d). The thickness of the $\text{GO}_{(1:1)}@ZIF-8/\text{Al}_2\text{O}_3$ separating layer on the surface of the membrane is

13.32 μm while for the $\text{GO}_{(2:1)}@\text{ZIF-8}/\text{Al}_2\text{O}_3$ is 15.12 μm as shown in the figure. There were less agglomerated and wrinkles particles visible on the $\text{GO}_{(1:1)}@\text{ZIF-8}/\text{Al}_2\text{O}_3$ composite membrane surface. In comparison to the other composite membrane, the separating layer is also thinner. The surface of the composite membrane becomes thicker as the $\text{GO}@\text{ZIF-8}$ loading increases from 0.3 g to 0.6 g. The increased of the separation layer thickness is an important factor that could influence the composite membrane separation ability (Wang et al., 2020).

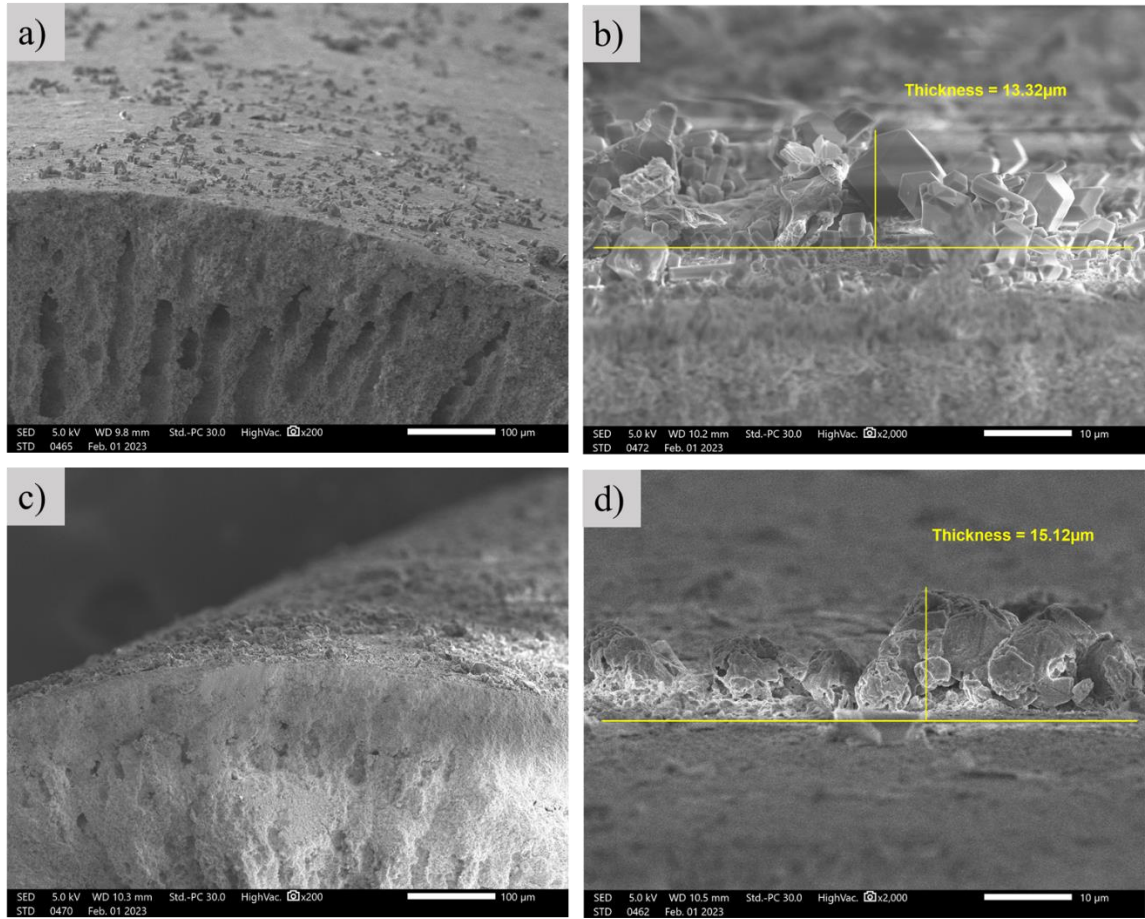


Figure 4.11: FESEM images of the membrane cross-section, $\text{GO}_{(1:1)}@\text{ZIF-8}/\text{Al}_2\text{O}_3$ at magnification (a) x200, (b) x2000 and $\text{GO}_{(2:1)}@\text{ZIF-8}/\text{Al}_2\text{O}_3$ at magnification (c) x200, (d) x2000.

4.4 Batch adsorption study

4.4.1 Effect of contact time

Figure 4.12 depicts the change in the adsorption capacity over time, showing a gradual increase as time progresses. The adsorption achieved equilibrium at around 7 hours. The presence of GO in the ZIF-8 composite played a significant role in this process. As the GO concentration increased, the adsorption capacity of the GO@ZIF-8 composites also increased. This is primarily because higher GO loadings result in a larger surface area and more available functional groups, which in turn provide additional adsorption sites. The porous structure of GO and the increased surface area contributed by the ZIF-8 crystals further enhance the oil adsorption efficiency (Kubra et al., 2021; Ni et al., 2021).

Figure 4.12 shows the percentage of oil removal from modified ZIF-8@GO over time, demonstrating that the oil removal percentage increased with GO loading. In the initial 4 hours, the rapid adsorption can be attributed to the large number of free adsorption sites available on the surface of the membrane. This correlates with the increased porosity and surface area provided by higher GO concentrations. The GO nanosheets also introduce oxygenated functional groups such as hydroxyl, carboxyl, and epoxy, which facilitate the interaction between oil molecules and the membrane surface enhancing adsorption (Mo et al., 2022). As time progressed, the adsorption sites became gradually occupied, leading to a plateau in the adsorption capacity and oil removal percentage at around 7 hours. The increase in adsorption capacity with higher GO loadings can be explained by the enhanced accessibility of these functional groups and the increased surface area for oil molecules to interact with. The final equilibrium adsorption capacity and oil removal percentage at 7 hours were 62.5 mg/g and 41.7%, respectively, which reflects the saturation of available adsorption sites on the GO@ZIF-8 membrane (Kubra et al., 2021; Ni et al., 2021).

The differences in adsorption behavior between varying GO loadings can be attributed to the structure of the composite membrane. Membranes with higher GO content exhibited better oil removal due to the increased availability of active sites and the formation of layered structures that facilitate the diffusion of oil molecules. This suggests that optimizing GO content in the membrane structure plays a critical role in enhancing the adsorption performance (Mo et al., 2022).

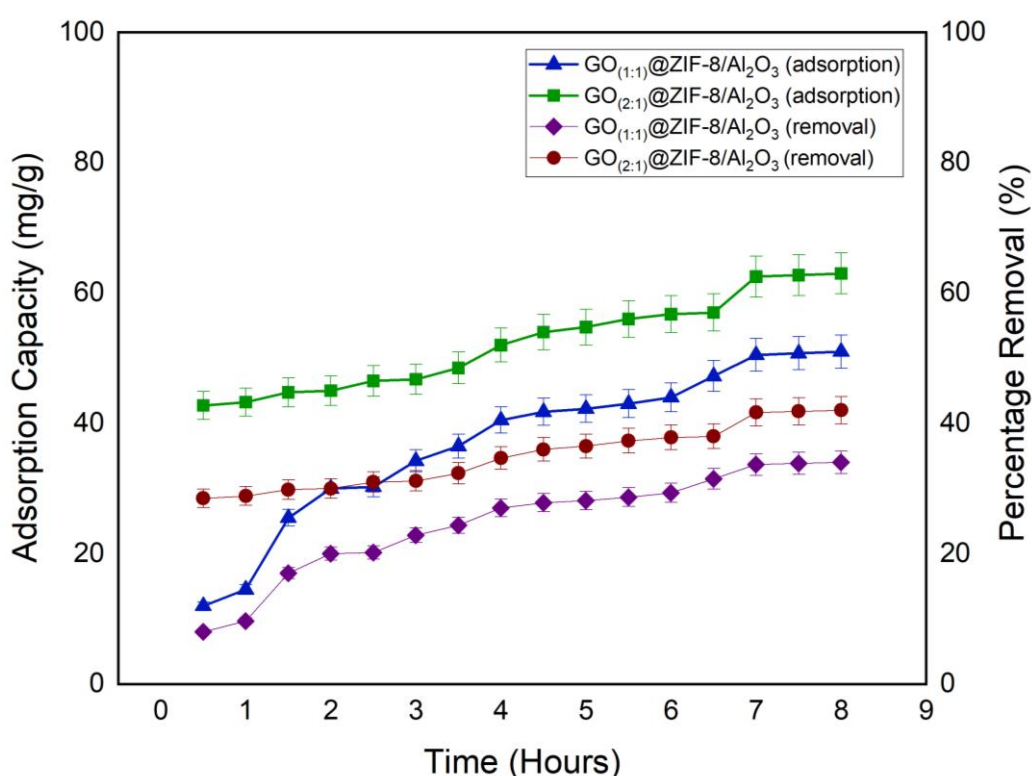


Figure 4.12: Effect of contact time on the oil adsorption capacity and removal percentage.

4.4.2 Effect of pH

To adjust the pH for the most effective removal, experiments were run at pH 3, 7, and 10. GO could be characterized as an amphiphile or a surfactant due to its hydrophilic

edges and hydrophobic basal plane (McCoy et al., 2019). Therefore, the effect of pH value on the removal of oil emulsion by GO@ZIF-8/Al₂O₃ membrane was investigated at pH 3, 7 and 10. The GO was found to work effectively in neutral or acidic environments (Bhattacharjee et al., 2023; Reynosa-Martínez et al., 2020). The amount of residual oil in the separated water at various pH levels as a function of GO nanosheet dose was measured to conduct a quantitative study. The influence of pH on the adsorption of oil of GO_(1:1)@ZIF-8/Al₂O₃ and GO_(2:1)@ZIF-8/Al₂O₃ membranes at pH 3, pH 7 and pH 10 was shown in Figure 4.13.

The results demonstrate that the removal of oil emulsions by the GO@ZIF-8/Al₂O₃ membrane was highly influenced by the pH of the solution, with the maximum adsorption capacity observed at pH 3. At this acidic condition, the highest percentage of oil removal was achieved, with 45.83% oil removed by the GO_(2:1)@ZIF-8/Al₂O₃ membrane (Figure 4.13). This can be explained by the emulsion breaking process which occurs more readily in acidic environments. Emulsion breaking leads to enhanced interaction between oil molecules and the adsorbent allowing oil to be adsorbed more effectively (Mottaghi et al., 2021). The increased oil removal at pH 3 can also be attributed to the thicker GO@ZIF-8 layer formed on the membrane, which provides more available adsorption sites. Multiple studies confirm that a thicker membrane structure generally correlates with increased adsorption capacity due to the higher number of active sites for interaction (Cao et al., 2018; Efome et al., 2019). Hence, GO_(2:1)@ZIF-8/Al₂O₃ membrane have more adsorbents which allows it to accommodate more adsorption sites.

This is further supported by the fact that, as GO concentration increases, the available surface area and adsorption sites also increase, leading to improved oil adsorption performance (Abu-Nada et al., 2021). The role of functional groups is also important in

understanding the behavior of the membrane at low pH. In acidic environments, the functional groups (-OH and -COOH) on the GO@ZIF-8 nanosheets are ionized, which decreases the hydrophilicity of the nano-demulsifiers, allowing them to interact more effectively with the oil phase (Javadian et al., 2019). As a result, the GO@ZIF-8 nanosheets proliferate in the oil phase, enhancing the oil-water separation process.

As the pH increases to neutral (pH 7) and alkaline (pH 10) conditions, the oil removal efficiency decreases. At higher pH, the adsorption capacity of the membrane decreases because fewer functional groups are ionized, reducing the affinity between the membrane surface and oil molecules (Mottaghi et al., 2021). Additionally, in highly alkaline conditions, the GO@ZIF-8 membrane's performance further declines as the membrane's surface charge alters, making it less effective in capturing oil molecules. The membrane behavior in alkaline conditions shows poor oil-water separation, especially at pH 10, where the adsorbent's ability to bind oil is significantly reduced. In conclusion, the GO@ZIF-8/Al₂O₃ membrane demonstrates optimal oil adsorption performance at acidic pH levels, primarily due to the emulsion-breaking process and the ionization of functional groups that promote stronger interactions with oil molecules. In contrast, higher pH levels result in reduced adsorption efficiency due to changes in membrane surface behavior, demonstrating that low pH is favorable for effective oil-water separation.

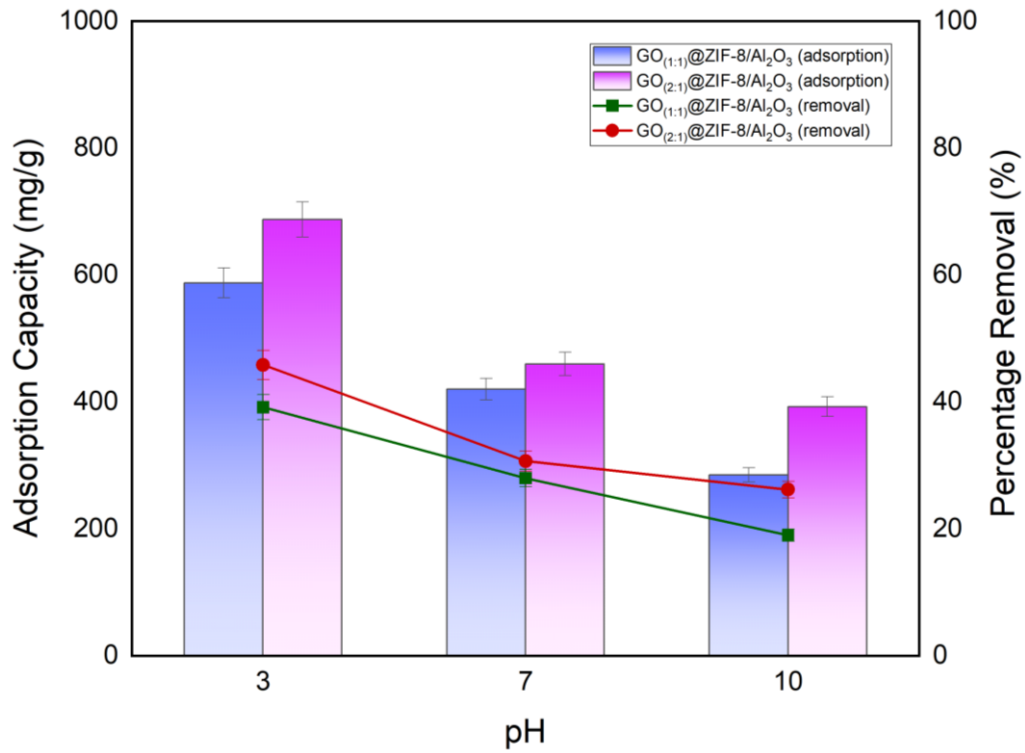


Figure 4.13: Effect of pH on adsorption capacity and percentage of oil removal.

4.4.3 Effect of initial concentration

Studying the initial concentration is crucial because the adsorption kinetics, the process that regulates the overall kinetic coefficient, can be greatly influenced by the initial concentration of the oil residue in the solution. Figure 4.14 show that the rate of oil adsorption increases with initial oil content up to a certain point and then tends to attain equilibrium. Adsorbed oil gradually starts to clog the membrane pores close at the outer surface over time, preventing oil from diffusing to the active areas in the interior surface (Abadikhah et al., 2018; Khalifa et al., 2019). As shown in Figure 4.14, the removal rate reached its peak at 53.73% as the oil concentration rose from 10 mg/L to 130 mg/L and the adsorption capacity also increased. Therefore, the GO@ZIF-8 membrane used in this work can successfully treat wastewater that contains oil.

The effect of initial concentrations on the adsorption capacity of oil removal was investigated at 10, 30, 50 ,70 110 and 130 ppm oil concentrations over the respective optimum time interval of 30 mins. Figure 4.14 shows the result of the test. When the starting concentration increased, adsorption increased at the binding sites until it reached to the point the adsorption capacity dropped or maintained because the deposited pollutants induced repulsion (Uddin et al., 2021). A membrane's adsorption capacity usually grows with the initial concentration of oil in the solution. This is because there is a greater amount of driving force for adsorption at higher starting concentrations. The number of oil molecules that can interact with the membrane's adsorption sites has increased. The oil concentration and accessible adsorption regions on the surface of the adsorbent determine the maximum adsorption capacity because oil molecules compete for adsorption sites on the surface of the adsorbents (Katheresan et al., 2018).

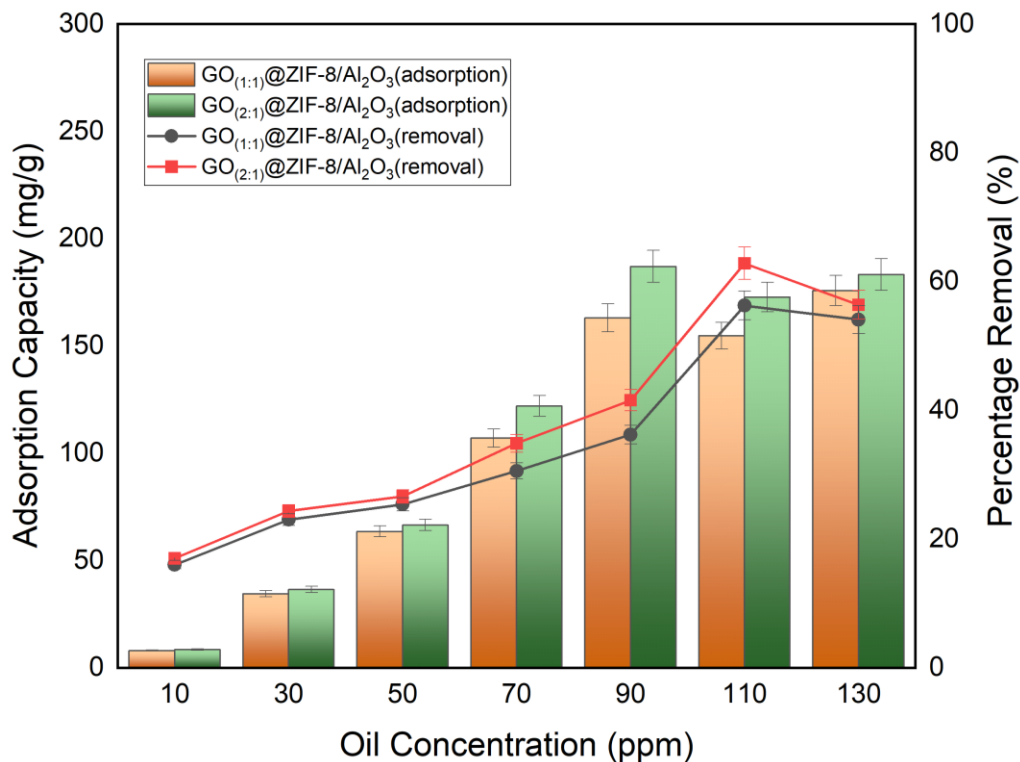


Figure 4.14: Effect of initial concentration on adsorption capacity and percentage of oil removal.

The adsorption capacity may increase with concentration in the beginning but it may eventually be plateaued which indicates saturation. The adsorption sites in the membrane can get filled up completely at high starting concentrations, and further concentration increases such as 200 ppm or more could not result in a proportionate increase in adsorption. Thus, the absorption of oil onto the GO@ZIF-8 started to become equilibrium with further increases in the concentrations. These findings show that initial oil concentration affects the oil adsorption because it acts as the primary driving force in overcoming mass transfer restrictions between the adsorbate and the surface of the adsorbent (Fathy et al., 2018).

4.5 Adsorption mechanisms

4.5.1 Adsorption isotherms

Adsorbate is transferred from the solution phase to the adsorbent phase under equilibrium circumstances, as shown by the mathematical equation known as the adsorption isotherm (Abdi & Abedini, 2020). The Freundlich isotherm is used for multilayer adsorption on heterogeneous sites while the Langmuir isotherm is used for monolayer adsorption on homogeneous sites (Kalam et al., 2021). Comparative effectiveness outcome (CEO) studies frequently employ Freundlich and Langmuir isotherms as the two parameters for adsorption. Two non-linear versions of the Langmuir and Freundlich models were used to examine the experimental isotherm data. Once the adsorbent surface have equal amount of oil adsorbed and the amount of oil desorption on the adsorbent surface, adsorption equilibrium has been reached (Hoseinzadeh et al., 2021). The degree of compatibility and adaptation of each isotherm was measured by the correlation coefficient R^2 . As a result, the isotherm with the higher R^2 coefficient that is compatible with the adsorption process was chosen (Hoseinzadeh et al., 2021).

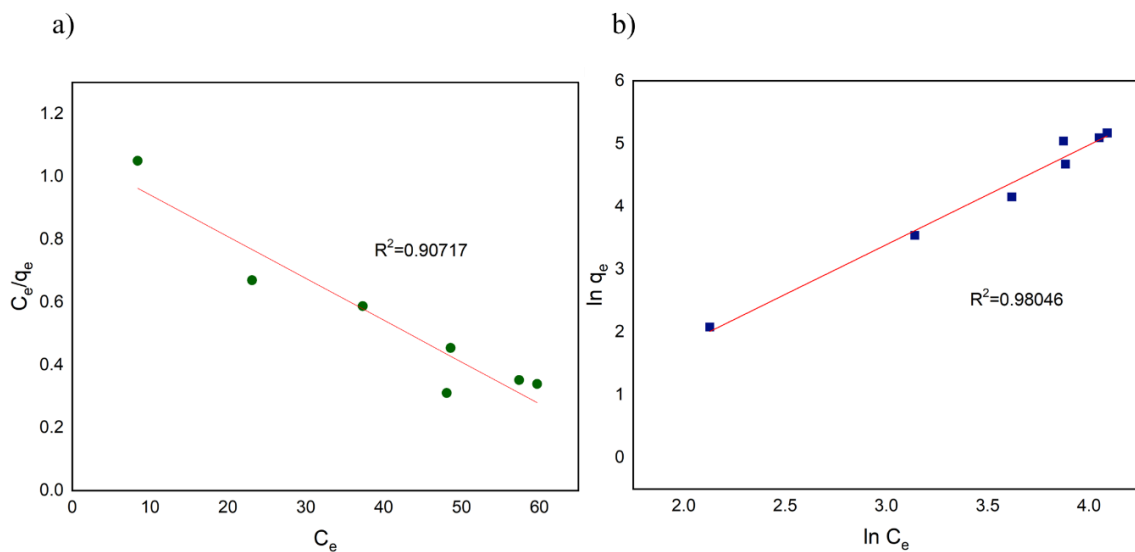


Figure 4.15: The (a) Langmuir isotherm and (b) Freundlich isotherm for oil adsorption

on GO@ZIF-8/Al₂O₃.

There are three hypotheses in the Langmuir model. Adsorbed molecules are bound to specific surface active sites, only one molecules can be adsorbs by each sites, and adsorption takes place uniformly and in one layer on active surface sites (Hoseinzadeh et al., 2021; Mahmoodi et al., 2019). The Langmuir linear model (Equation 3.3) is as shown in Table 3.2. The Langmuir constants K_L (l/mg) and q_m (mg/g) are parameters that relate to adsorption energy and adsorption capacity in the relationship shown above. Additionally, q_e (mg/g) refer to the equilibrium adsorption capacity, while C_e (mg/L) represents the equilibrium concentrations of the solution. The specific adsorption (C_e/q_e) against equilibrium concentration (C_e) is plotted linearly in Figure 4.15 (a), where the q_{max} and constants K_L refer to the maximum adsorption capacity and energy of adsorption, respectively. The values are derived from the interception and slope of the plot as shown in Table 4.1. The regression coefficient (R^2) of the Langmuir isotherm is 0.90717 while the Langmuir adsorption constant (K_L) is -0.00124, and the theoretical adsorption capacity (q_m) is calculated to be -75.1315 mg/g.

Moreover, by employing the separation factor or equilibrium parameter (R_L) known as a dimensionless constant represented by Equation 3.4 in Table 3.2, the crucial components Langmuir isotherm can be used to calculate the adsorption affinity between the sorbent and sorbate (Ragadhita & Nandiyanto, 2022), where C_0 is the initial concentration and K_L is the Langmuir constant. The value of R_L determined whether the Langmuir isotherm was favourable ($0 < R_L < 1$) or unfavourable ($R_L > 1$), irreversible ($R_L = 0$) and linear ($R_L = 1$) (Musah et al., 2022). In this study, the R_L value was discovered to be

1.12562, indicating that the oil molecules adsorption onto the membrane was not favourable.

The Freundlich isotherm is represented as an empirical model (Equation 3.5) in Table 3.2, where C_e stands for the equilibrium concentration (mg/L), q_e stands for the equilibrium adsorbed quantity per amount of adsorbent (mg/g), n and K_f stand for parameters that depend on the adsorbent and adsorbate. The Freundlich empirical isotherm model explains the concept of heterogeneous adsorption sites of the adsorbent with the adsorption of organic pollutant on the surface (Mahmoodi et al., 2019). Table 3.2 shows the linearized Freundlich adsorption isotherm where n and K_f are Freundlich constants which are correlated with intensity and adsorption capacity, respectively. Based on the linear version of the Freundlich equation (Figure 4.15 (b)), the values for the equilibrium constants of Freundlich were obtained from the plot of $\ln q_e$ vs $\ln C_e$. The n value represents the degree of nonlinearity between adsorption and solution concentration as follows: if $n > 1$, adsorption is a physical process; if $n = 1$, adsorption is linear; and if $n < 1$, adsorption is a chemical process (Alasadi et al., 2019; Awwad et al., 2020). According to Table 4.1, the n value for the Freundlich equation is 0.62983. As a result, the process of oil molecules interacting with the GO@ZIF-8 membrane might be referred to as chemisorption.

Figure 4.15 illustrate Freundlich and Langmuir graphs for the adsorption of oil molecules onto GO@ZIF-8/Al₂O₃, and Table 4.1 lists the correlation coefficients (R^2) and adsorption constants for these two types of plots. To identify the ideal model for the adsorption of the oil molecules, data were fitted to Freundlich and Langmuir isotherm models. The results showed that the Freundlich model, which had an R^2 value of 0.98046 provided the best fit for the oil adsorption mechanism.

Table 4.1: Langmuir and Freundlich isotherm parameters for oil adsorption on GO@ZIF-8/Al₂O₃.

Adsorption Isotherm	Isotherm Constants	Value
<i>Langmuir</i>	q_m	-75.1315
	K_L	-0.00124
	R_L	1.12562
	R^2	0.90717
<i>Freundlich</i>	n	0.62983
	K_F	0.25373
	R^2	0.98046

4.5.2 Adsorption kinetics

The adsorption kinetics demonstrate the way the adsorption process has changed over time. The adsorption process in the treatment of aqueous solutions depends on various experimental parameters like texture of adsorbents, pH, solute concentration, sorbent dose, and temperature that affect the kinetics of adsorption of an adsorbate onto any adsorbent (Moussout et al., 2018). Therefore, these factors must be used to establish the contact time at which the adsorption process reaches a real equilibrium. In batch adsorption systems, a variety of models including the Mixed Order model (MO), The Ritchie's Equation, The Elovich model, and the Pseudo-nth-Order (PNO) model, have been developed in order to explain solute diffusion at the surface and in the pores of the adsorbent (Wang & Guo, 2020). However, pseudo-first order (PFO) and pseudo-second

order (PSO) models were used extensively to characterise the rate of adsorption in liquid solid interactions (Son & An, 2022).

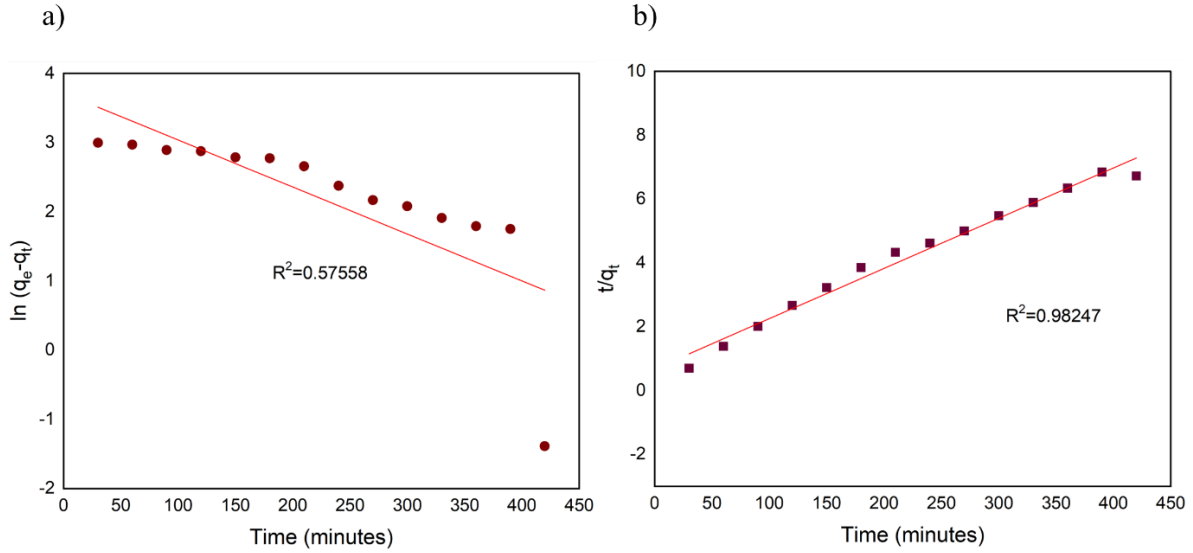


Figure 4.16: The plots of (a) pseudo-first order and (b) pseudo-second order kinetics for the adsorption of oil at 60 ppm on GO@ZIF-8/Al₂O₃ at room temperature and pH 3.

In general, the initial stage of an adsorption process is suitable to the pseudo-first order model where it assumes that the difference in the concentration and rate at which the adsorbate is removed with time is directly proportional to the rate of change in the absorption of adsorbate at a particular reaction time (Musah et al., 2022; Sahoo & Prelot, 2020). The Equation 3.6 in Table 3.2 for the model, also referred to as the Lagergren model, states that k_t is the rate constant for pseudo-first order adsorption, q_e is the adsorbent's adsorption capacity at equilibrium and q_t is its adsorption capacity at time t (Revellame et al., 2020). The value of k_t and q_e can be calculated from the slope and intercept of the plot of the graph $\ln(q_e - q_t)$ vs t that provides a linear relationship. Table 3.2 presents the Equation 3.7 for the pseudo-second order adsorption kinetics rate equation, where the rate constant of the pseudo-second order adsorption is denoted as k_2 . The slope

and intercept of the plot (t/q_t) and t in equation in Table 3.2 is used to determine k_2 and q_e respectively (Edet & Ifelebuegu, 2020). The pseudo-second-order model assumes that chemisorption is the rate-limiting mechanism as opposed to the pseudo-first-order model, which assumes that physisorption limits the rate at which particles adsorb onto the adsorbent (Revellame et al., 2020).

An adsorption test with a 60 ppm oil concentration was used to examine the kinetics of oil adsorption utilising GO@ZIF-8/Al₂O₃. The samples were collected during an 8 hours period at 30 minutes intervals. Data from the experiment was plotted using the pseudo-first order and pseudo-second order equations. Figure 4.16 depicts the pseudo-first order and pseudo-second order for batch kinetics of GO@ZIF-8/Al₂O₃ with plots of $\ln(q_e - q_t)$ vs time and t/q_t vs t respectively. The correlation coefficient (R^2) displayed the consistency of the experimental data with the value predicted by the model. Figure 4.16 depicts in graph form the pseudo-first order and pseudo-second order models of the GO@ZIF-8 adsorption process. Table 4.2 displays the calculated correlation coefficients and adsorption kinetic parameters using the kinetic equation.

The correlation coefficient (R^2) value of 0.98247 showed that the pseudo-second order model fits the kinetics of the adsorption of GO@ZIF-8/Al₂O₃ membrane more suitable than the pseudo-first order model. The experimental capacity, q_e (exp.) was 62.50 mg/g, which was closer to the maximal capacity, q_e (cal.), of pseudo-second order which was 63.5324 mg/g. According to these data, it is concluded that the pseudo-second order kinetic equation is more suited for the oil adsorption by GO@ZIF-8.

Table 4.2: Pseudo-first and pseudo-second order parameters for oil adsorption on GO@ZIF-8/Al₂O₃ at 60 mg/L.

Adsorption kinetics	Concentrations	Kinetic Constants	Value
Pseudo-First Order	60 mg/L	q_e	41.1120
		k_1	0.00679
		R^2	0.57558
Pseudo-Second Order	60 mg/L	q_e	63.5324
		k_2	3.653e-4
		R^2	0.98247

Other similar works on the oil removal are presented in Table 4.3. The adsorption capacity of the present study is comparable with other reported composites membrane. The GO@ZIF-8 modified alumina membrane also have a comparable adsorption capacity in comparison with other available alumina-based membrane.

Table 4.3: Comparison of GO@ZIF-8/Al₂O₃ hollow fiber membrane adsorption capacities with reported study for oil removal.

Adsorbent	Type of oil	Adsorption capacity (q_{max})	References
PVDF/GE	Engine oil	64.1 g/g	(Zhang et al., 2021)
rGO@MF	Crude oil	5.6 g/g	(Ahmed et al., 2021)
PCLM	Motor oil	15.93 g/g	(Zhang et al., 2020)
polytetrafluoroethylene (PTFE)	Crude oil	11.7 $\mu\text{g}/\text{cm}^2$	(Zhang et al., 2020)

TiO ₂ /Al ₂ O ₃ -PVDF	Oil solid	18.57 $\mu\text{g}/\text{cm}^2$	(Yi et al., 2018)
GO@ZIF-8/Al ₂ O ₃	Motor oil	62.50 mg/g	Present study

When comparing the adsorption capacities of the GO@ZIF-8/Al₂O₃ hollow fiber membrane with other adsorbents listed in Table 4.3, it is evident that the capacity of the present study's membrane (62.5 mg/g for motor oil) appears lower than many other reported adsorbents, which show capacities in the range of g/g. However, it is important to contextualize these values based on the unique properties and dimensions of the membrane used in this study.

The GO@ZIF-8/Al₂O₃ membrane utilized in this work is a hollow fiber with a length of 4 cm, a diameter of 1.80 mm, and a mass of only 0.2 g. Due to its small size, the overall surface area available for adsorption is relatively limited compared to larger planar membranes or bulk adsorbents like PVDF/GE, which has an adsorption capacity of 64.1 g/g for engine oil (Zhang et al., 2021). The cylindrical tube-like structure of the hollow fiber membrane inherently restricts the volume available for oil adsorption, but its design is optimized for filtration processes, where both adsorption and permeation are utilized in synergy. In contrast, the larger, flat-sheet membranes or adsorbents designed solely for adsorption tend to have much greater surface areas, contributing to their higher capacity.

Additionally, the distribution of GO@ZIF-8 particles on the surface of the membrane plays a crucial role in determining its adsorption performance. The uniform distribution of these nanocomposites ensures a higher number of active adsorption sites on the membrane's surface, which facilitates oil removal. However, if the distribution is uneven, areas of the membrane may become less effective at adsorbing oil, leading to a

reduction in overall adsorption capacity. In the case of hollow fiber membranes, the surface area per unit mass is generally lower compared to larger, bulkier membranes, which may partly explain the lower adsorption values in mg/g compared to other materials.

Moreover, the structure of GO@ZIF-8 itself provides both adsorption sites and a porous framework, which aids in separating oil from water during filtration. However, as a multi-functional material, the GO@ZIF-8/Al₂O₃ membrane focuses not only on adsorption but also on maintaining high water flux, making it a more versatile option for continuous oil-water separation processes. While the adsorption capacity may be lower than some bulk adsorbents, the ability to integrate adsorption with water permeation through a hollow fiber membrane offers a different advantage, especially for industrial applications where both oil removal and water filtration are necessary.

Therefore, although the membrane used in this study demonstrates a lower adsorption capacity in mg/g, its small size and dual-functionality should be taken into account. The GO@ZIF-8/Al₂O₃ hollow fiber membrane provides a promising solution for combined adsorption and filtration, particularly where space constraints and continuous separation are priorities. Furthermore, optimizing the distribution of GO@ZIF-8 nanocomposites on the membrane surface could potentially enhance the adsorption performance, as these particles significantly contribute to the adsorption mechanism.

4.6 Oil-water separation performance

4.6.1 Crossflow filtration study

A crossflow filtering system operating at 1 bar was used to conduct further testing on the ability of the membranes to separate oil emulsions. Figure 4.17 shows the

performance of each membrane in terms of oil removal capacity and water flux. The $\text{GO}_{(1:1)}@\text{ZIF-8}/\text{Al}_2\text{O}_3$ shows the highest permeate flux among the other membranes, with $98.268 \text{ Lm}^{-2}\text{h}^{-1}$, while the $\text{GO}_{(2:1)}@\text{ZIF-8}/\text{Al}_2\text{O}_3$ membrane has a slightly lower permeate flux at $92.147 \text{ Lm}^{-2}\text{h}^{-1}$. However, the lowest flux was recorded by the pristine membrane, at $33.652 \text{ Lm}^{-2}\text{h}^{-1}$, nearly three times lower than the modified membranes. These results demonstrate that membranes modified with $\text{GO}@\text{ZIF-8}$ nanocomposites exhibited significantly higher water flux compared to the pristine alumina membrane.

This higher water flux is attributed to the synergistic properties of both GO and ZIF-8 in the composite structure. The $\text{GO}_{(1:1)}@\text{ZIF-8}/\text{Al}_2\text{O}_3$ and $\text{GO}_{(2:1)}@\text{ZIF-8}/\text{Al}_2\text{O}_3$ membranes showed a reduction in tortuosity due to the hydrophilic nature of GO and the porous framework of ZIF-8, which facilitated additional flow channels for water molecules (Makhetha & Moutloali, 2020). ZIF-8, as a metal-organic framework (MOF), possesses an intrinsic porous structure that allows for greater fluid permeability by reducing the physical resistance to water flow. These MOFs also offer specific pore sizes that enable selective separation, improving the membrane's overall performance (Zhao et al., 2021). The inclusion of ZIF-8 reduces the membrane's tortuosity, providing more efficient pathways for water flow while maintaining robust mechanical properties (Masibi et al., 2022).

The increased hydrophilicity of the $\text{GO}@\text{ZIF-8}$ nanocomposite promotes water absorption, enhancing the water flux. Water molecules are more easily pulled in and can flow through the membrane efficiently due to the strong interaction between water molecules and the hydrophilic functional groups present on GO sheets. High surface hydrophilicity membranes allow for more water to pass through in a given time, which is critical for applications such as water filtration and wastewater treatment. The addition of

ZIF-8's porous structure further enhances the flux, offering more routes for water transport, thus lowering the mass transfer resistance.

To evaluate the impact of nanocomposite materials on oil selectivity, oil rejection experiments were performed (Figure 4.17). Results show that all the modified composite membranes effectively rejected oil molecules, with rejection rates exceeding 90%. The alumina hollow fiber membranes exhibited improved oil rejection performance with the inclusion of GO@ZIF-8 nanocomposites compared to the pristine alumina. As shown in Figure 4.17, the pristine membrane had the lowest rejection of oil molecules (84.38%), while the $\text{GO}_{(1:1)}@ZIF-8/\text{Al}_2\text{O}_3$ and $\text{GO}_{(2:1)}@ZIF-8/\text{Al}_2\text{O}_3$ membranes had oil rejection rates of 90.64% and 96.32%, respectively.

The oxygenated functional groups found on the edges of GO sheets, responsible for their hydrophilic qualities, were the main contributors to the modified membrane's high oil removal performance (Elhenawy et al., 2021). The abundance of oxygen-containing functional groups on the GO surface not only enhances the stability of the membrane in polar solvents but also improves its oil rejection capacity by increasing the surface's interaction with water molecules, preventing oil from passing through.

Additionally, the GO@ZIF-8 hybrid nanocomposites offer tunable surface areas and pore volumes, which can be adjusted by altering the amount of GO (Yang et al., 2018). Increasing the concentration of GO provides more active sites for oil adsorption, enhancing the membrane's ability to separate oil molecules. The structure of the GO@ZIF-8 composite provides more opportunities for interaction between the oil molecules and the available adsorption sites on the surface. However, excessive GO concentration can lead to the formation of barriers that obstruct water flow if ZIF-8 is not adequately dispersed, as discussed by Yang et al. (2018).

From the outcomes depicted in Figure 4.17, it can be concluded that the $\text{GO}_{(2:1)}@\text{ZIF-8}/\text{Al}_2\text{O}_3$ membrane offers the best performance for oil removal. As the GO concentration increased from 1:1 to 2:1, the membrane flux slightly decreased from $98.268 \text{ Lm}^{-2}\text{h}^{-1}$ to $92.147 \text{ Lm}^{-2}\text{h}^{-1}$, while the oil rejection rate increased from 90.64% to 96.32%. This trade-off is explained by the increase in the separation layer thickness, which adds mass transfer resistance as the GO concentration increases. Although the membrane flux decreased slightly, the increased number of adsorption sites for oil molecules significantly improved the oil rejection performance.

If the GO concentration becomes too high, however, excess GO sheets without sufficient separation channels can act as barriers that obstruct solvent flow, leading to a further reduction in flux. Similarly, when the GO concentration is too low, ZIF-8 particles may agglomerate, resulting in poor separation performance due to insufficient interaction between the oil molecules and the membrane surface. Thus, there is a delicate balance in optimizing the GO concentration for the most effective separation efficiency.

In conclusion, the $\text{GO}_{(2:1)}@\text{ZIF-8}/\text{Al}_2\text{O}_3$ membrane demonstrated the highest oil rejection and overall separation efficiency in this study. While the permeate flux slightly decreased with increased GO concentration, the improved oil rejection illustrates the membrane's capacity to achieve high separation efficiency, making it suitable for applications that require effective oil-water separation.

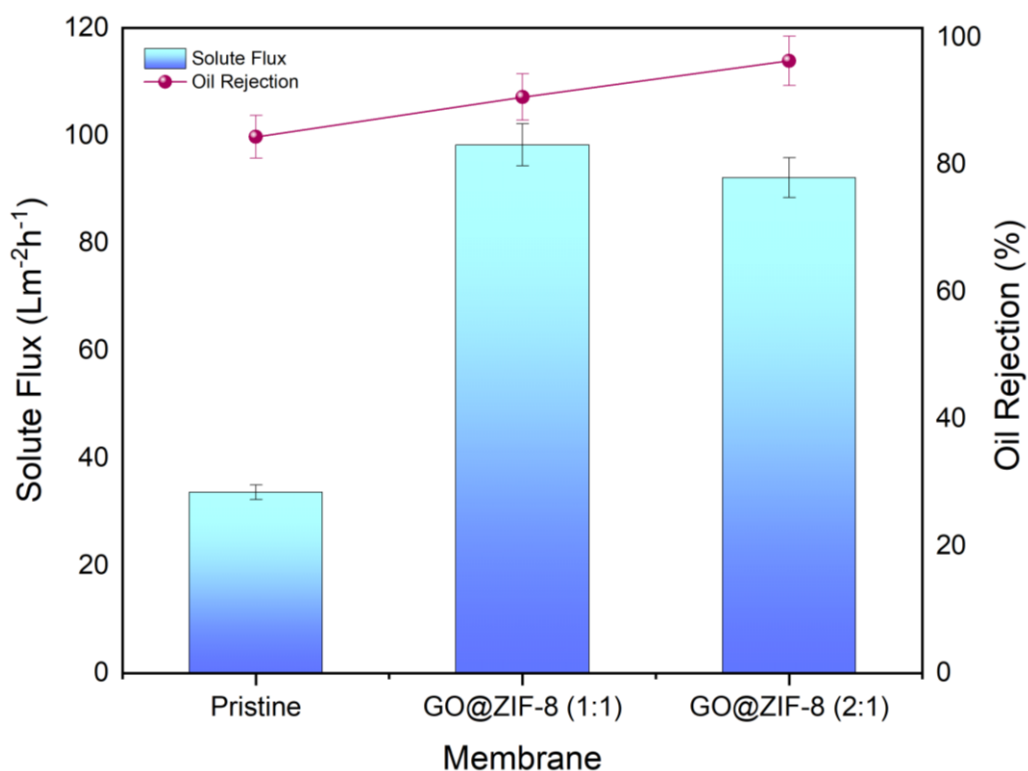


Figure 4.17: The solute flux and oil rejection of pristine and GO@ZIF-8 membranes.

Other similar works on the oil removal are presented in Table 4.4. The solute flux and removal efficiency of the present study is comparable with other reported composite membrane. The GO@ZIF-8/Al₂O₃ hollow fiber membrane also exhibited higher solute flux and removal efficiency in comparison with the other type of alumina membrane.

Table 4.4: Comparison of GO@ZIF-8/Al₂O₃ hollow fiber membrane solute flux and removal efficiency with reported study for oil removal.

Type of Membrane	Type of oil	Flux (Lm ⁻² h ⁻¹)	Removal efficiency (%)	References
MTES coated kaolin	Crude oil	80	90	(Usman et al., 2020)

TiO ₂ /Al ₂ O ₃	Kerosene	41.8	99.1	(Zhang et al., 2018)
Fenton-AC/CM	Crude oil	82	97	(Mu et al., 2021)
Ag-CuO-TiO ₂ /ZrO ₂	Synthetic oil	303.63	97.8	(Avornyo et al., 2023)
GO- Al ₂ O ₃	Crude oil	42	90	(Othman et al., 2017)
Al ₂ O ₃ /AC	Vegetable oil	Not mentioned	99.02	(Fard et al., 2018)
Al ₂ O ₃ /AC	Synthetic oil	60	98.8	(Manawi et al., 2022)
GO@ZIF-8/Al ₂ O ₃	Motor oil	92.147	96.32	Present study

The comparative data presented in Table 4.4 provides insights into the performance of various membrane technologies, focusing on their flux and removal efficiency. When comparing the GO@ZIF-8/Al₂O₃ membrane to other technologies, it is evident that it exhibits a competitive flux of 92.147 Lm⁻²h⁻¹ and a high oil removal efficiency of 96.32% for engine oil. This suggests that the GO@ZIF-8/Al₂O₃ membrane is highly effective for separating oil emulsions from water, particularly when dealing with heavier oils like motor oil, which pose significant challenges in water treatment applications.

The MTES coated kaolin membrane (Usman et al., 2020) and the Fenton-AC/CM membrane (Mu et al., 2021), both tested with crude oil show lower fluxes of 80 Lm⁻²h⁻¹

and $82 \text{ Lm}^{-2}\text{h}^{-1}$ respectively, with moderate removal efficiencies between 90% and 97%. While these membranes are effective in oil removal, the GO@ZIF-8/ Al_2O_3 membrane demonstrates superior flux and comparable or higher removal efficiency indicating its potential advantage in high-efficiency separations.

In contrast, membranes like Ag-CuO- $\text{TiO}_2/\text{ZrO}_2$ (Avornyo et al., 2023) show higher fluxes of $303.63 \text{ Lm}^{-2}\text{h}^{-1}$, but these results were obtained using synthetic oil which may behave differently compared to heavier oils like engine oil or crude oil. Synthetic oil tends to have lower viscosity which could lead to higher flux values. However, the GO@ZIF-8/ Al_2O_3 membrane performs impressively even with more viscous oils which suggests it could be more suitable for practical industrial applications involving oily wastewater.

The $\text{TiO}_2/\text{Al}_2\text{O}_3$ membrane (Zhang et al., 2018) tested with kerosene, a lighter oil, demonstrates high removal efficiency at 99.1% but the flux ($41.8 \text{ Lm}^{-2}\text{h}^{-1}$) is significantly lower than that of the GO@ZIF-8/ Al_2O_3 membrane. This further highlights the superior balance of both flux and removal efficiency offered by the GO@ZIF-8/ Al_2O_3 composite. Overall, while other membranes demonstrate strong removal capabilities for specific oils, the GO@ZIF-8/ Al_2O_3 membrane shows excellent all-around performance particularly for challenging oils like motor oil. This makes it a promising candidate for advanced oil/water separation technologies.

4.6.2 Regeneration study

One important aspect of GO@ZIF-8/ Al_2O_3 membranes operational capabilities is their capacity to be reused for water filtration (Sutrisna et al., 2022). To possibly reuse the

membrane, membrane regeneration is important. For this study, the $\text{GO}_{(2:1)}@\text{ZIF-8}/\text{Al}_2\text{O}_3$ membrane was chosen to be reuse because it has the best removal efficiency in term of permeate flux and oil rejection based on the result of the crossflow filtration study. After regeneration by SDS solution, the same settings with the pressure of 1 bar and 100 ppm oil feed solution were used for the crossflow filtrations. The rejection percentage after six cycles of reusability with the 2% wt. SDS solution was 90.08% as illustrated in Figure 4.18. The membrane's rejection efficiency only fell by 6.24% from the optimum results. Throughout the six cycles, the membrane continued to exhibit a stable performance in terms of oil rejection and permeate flux.

At the first cycle, the oil removal efficiency reached 97.42%, with a high permeate flux of $125.798 \text{ Lm}^{-2}\text{h}^{-1}$ the removal efficiencies of the membrane were reduced to 91.63% and 90.08% in the fifth and sixth cycle, respectively. The permeate flux decreased to $64.064 \text{ Lm}^{-2}\text{h}^{-1}$ at the sixth cycle of reusability. According to these findings, the synthesised composite exhibits significant possibilities and high recoverability for reuse. This proved that $\text{GO}@\text{ZIF-8}$ composite is simple to regenerate, which considerably lowers the cost of materials and synthesis procedure. The membrane surface desorbs the attached oil molecules following the surfactant treatment and the membrane once more shown its potential (Sutrisna et al., 2022). To conclude, the results of the regeneration study imply that SDS solution have successfully regenerated the membrane.

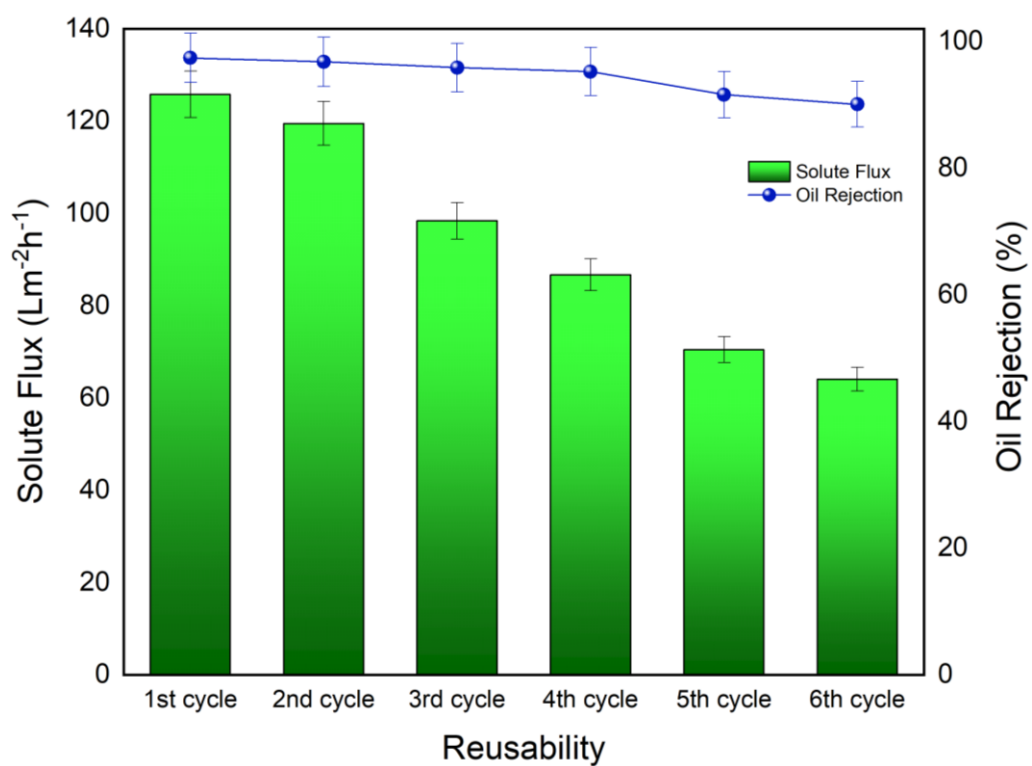


Figure 4.18: The solute flux and oil rejection of $\text{GO}_{(2:1)}/\text{ZIF-8}/\text{Al}_2\text{O}_3$ membrane for six cycles of reusability.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This study successfully synthesized GO@ZIF-8 composites via an in-situ solvothermal process using APTES as a linker and supporting the composites on alumina hollow fiber membrane. Through characterization techniques such as FESEM, FTIR, XRD, and UV-Vis, it was observed that increasing the GO loading significantly influenced the physicochemical properties of the GO@ZIF-8/Al₂O₃ composite membrane. The enhanced surface area and increased porosity facilitated better interaction with oil molecules thus improving the membrane's adsorption capabilities. GO_(2:1)@ZIF-8/Al₂O₃ demonstrated the highest surface uniformity and structural integrity leading to optimal adsorption performance. The study revealed that the adsorption efficiency of the membrane increased with higher GO content. The maximum oil adsorption capacity reached 62.50 mg/g and the oil removal efficiency was as high as 96.32% with a flux of 92.147 Lm⁻²h⁻¹. The adsorption mechanism followed the Freundlich isotherm and pseudo-second-order kinetics, indicating multilayer adsorption and chemisorption as the controlling mechanisms. This demonstrates that the composite membrane effectively traps oil molecules through both physical and chemical interactions making it an efficient material for oil-water separation. The membrane exhibited strong reusability over multiple cycles, retaining up to 90.08% of its oil removal capacity after six cycles. This performance highlights the robust structural stability of the GO@ZIF-8/Al₂O₃ membrane which coupled with its high separation efficiency makes it a promising candidate for long-term use in

practical wastewater treatment applications. In summary, this study demonstrated that the GO@ZIF-8/Al₂O₃ composite membrane shows high adsorption capacity, strong separation performance, and excellent reusability, making it a viable and effective solution for treating oil-rich wastewater.

5.2 Recommendations

Future research can examine several topics to improve our comprehension and maximize the performance of the graphene oxide@ZIF-8/alumina hollow membrane for the treatment of oily wastewater. Firstly, the adsorption mechanisms at the molecular level can be analysed using technologies like advanced spectroscopic techniques or molecular dynamics simulations. This could provide information on the atomic-level interactions between oil molecules and the GO@ZIF-8/alumina membrane. Furthermore, surface analysis techniques such as scanning tunnelling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) can be employed to investigate how the membrane's surface chemistry changes because of sorption. Also, it is recommended to determine the optimal conditions for improved adsorption performance by methodically optimizing variables including feed concentration, temperature, and pressure.

To ensure long-term efficiency, it is important to explore ways to regenerate and reuse the GO@ZIF-8/Alumina membrane. Hence, examining the areas where environmental factors such as salinity and pH have an impact on membrane performance is crucial to reduce their effects on the membrane. For larger-scale applications, it is essential to evaluate the scalability of the membrane. Subsequently, the efficiency in handling actual industrial oily wastewater treatment should be assessed. An analysis should be conducted

to determine whether GO@ZIF-8/alumina membrane technology can be implemented economically on an industrial scale, considering expenses related to maintenance, energy usage, and material costs. These future studies may further our comprehension about the graphene oxide@ZIF-8/alumina hollow membrane and its possibilities for efficient and long-lasting treatment of oily wastewater by tackling those issues.

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