Synthesis of composite membrane using Melamine modified Zeolitic imidazolate framework for CO_2/CH_4 separation

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A thesis submitted to the National University of Sciences and Technology, Islamabad, in partial fulfillment of the requirements for the degree of

Master of Science in
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Supervisor: Dr. Zaib Jahan

School of Chemical and Materials Engineering

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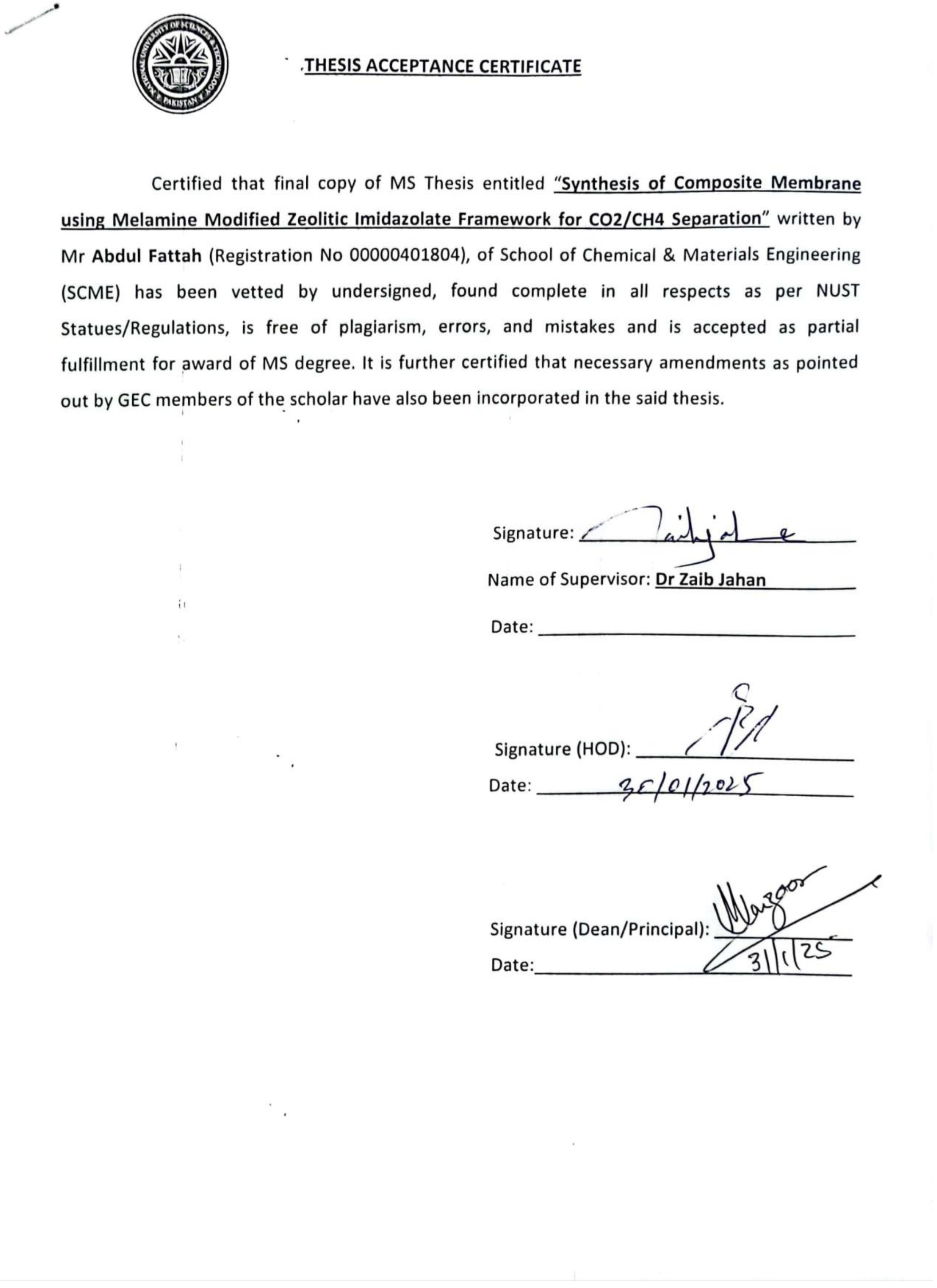

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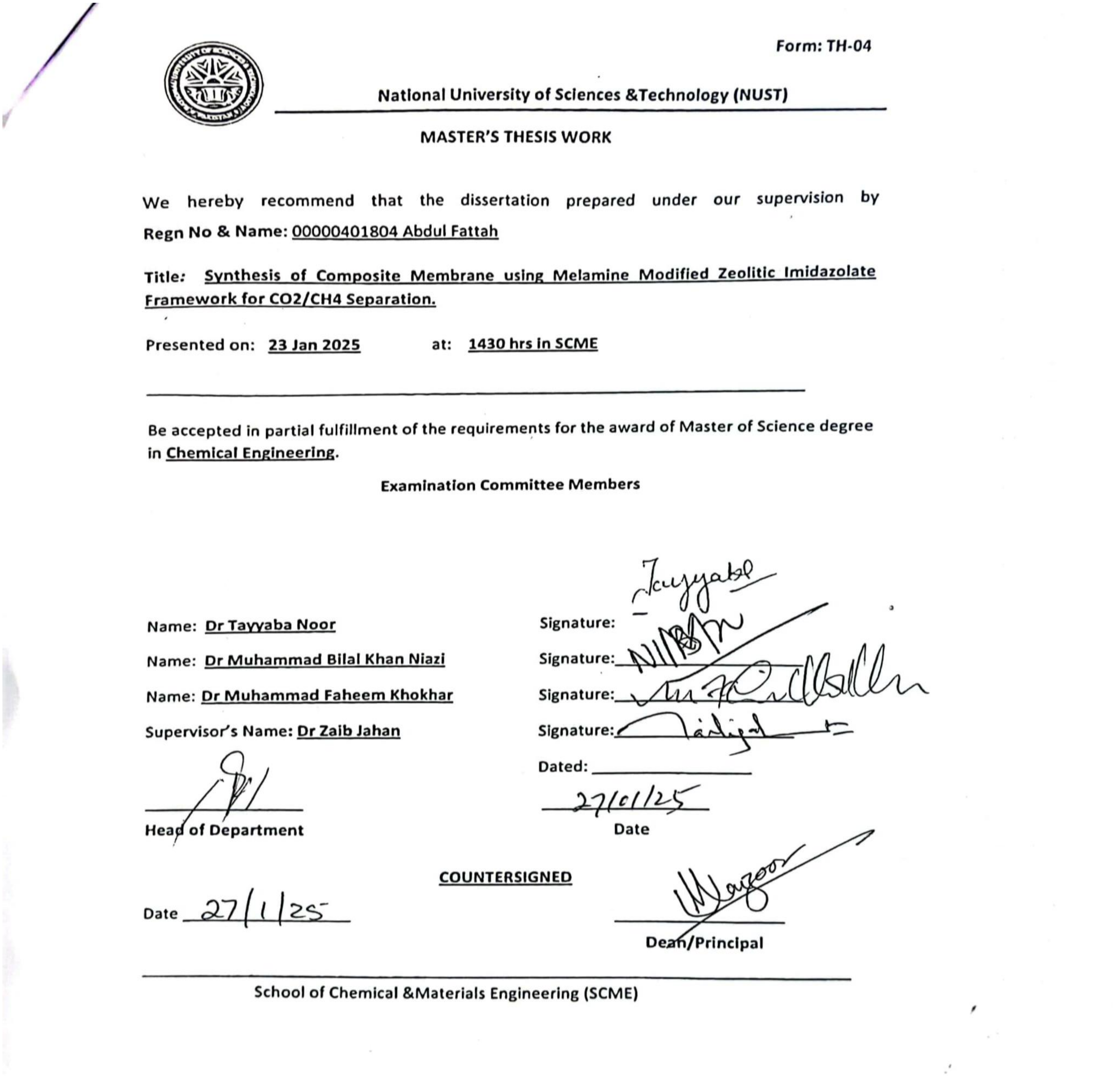

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DEDICATION

To my **Father** whose wisdom and love shaped the foundation of my life. Though you are no longer with us, your spirit continues to guide me every day. This thesis is a tribute to your sacrifices and the lessons you imparted, which I carry with me always.

To my **Mother**, whose boundless love and support have been my anchor. You’ve been my rock through every challenge, your resilience a constant reminder that no matter what the obstacles, we are never alone. I owe everything to your encouragement and faith in my dreams.

This is for both of you, the ones who made me who I am today.

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LIST OF ACRONYMS

CA	Cellulose acetate
PSf	Polysulfone
FTM	Facilitated transport membranes
CNTs	Carbon nano tubes
MOFs	Metal Organic Framework
MMMs	Mixed matrix membranes
CNCs	Cellulose nano crystals
Nm	nano meters
μm	micro meter
SEM	Scanning electron microscopy
XRD	X Ray diffraction
FTIR	Fourier Transform Infrared Spectroscopy
DI water	De-ionized water
ZIF-8	Zeolitic imidazolate framework-8
CO_2	Carbon Dioxide
CH_4	Methane

ABSTRACT

The study involves cellulose acetate (CA) as the primary polymeric matrix, dissolved in acetone, and reinforced with melamine modified zeolitic imidazolate framework-8 (ZIF-8) nanoparticles. Development and characterization of composite membranes for the separation of carbon dioxide (CO_2) from methane (CH_4), specifically tailored for enhanced gas separation performance. These composite membranes are supported on a robust Poly-sulfone ultrafiltration layer, which provides mechanical strength while allowing for selective gas permeation. The research focuses on varying the weight percentage of ZIF-8 nanoparticles within the CA matrix, examining concentrations ranging from 1% to 3% by weight. Performance was evaluated across a range of operational conditions by evaluating under different pressures (4 bar, 6 bar, and 8 bar).Permeability at low ZIF-8 loadings (1 wt%) is slightly higher than for the pure CA membrane, while exhibiting negligible effect on CH_4 permeability resulting in significant improvement in the selectivity of CO_2 over CH_4. CO_2 permeability increases with increasing ZIF-8 content and selectivity increases as densely packed ZIF-8 nanoparticles are formed as content increases to 2 wt% and 3 wt%. Membrane morphology and functional performance are analyzed by advanced characterization techniques involving scanning electron microscopy (SEM) and gas permeation testing. The contribution of this thesis to gas separation technology is to bring understanding in the way that metal organic framework (MOF) nanoparticles such as melamine modified ZIF-8 can further increase the gas separation ability of polymeric membranes while having excellent mechanical stability. We demonstrate that selectivity and efficiency of membranes for CO_2/CH_4 separation can be greatly improved through a favorable optimal loading of the nanoparticle, which may lead to more energy efficient membrane processes during natural gas purification and greenhouse gas management.

CHAPTER # 1 INTRODUCTION

1.1 Importance of Gas Separation

Gas separation technologies form the backbone of key industrial processes dependent on energy generation, environmental protection and manufacturing. In addition to lowering the amount of CO_2 emissions in the atmosphere, separating natural gas from CO_2 is also necessary to increase the fuel's calorific value, prevent pipeline corrosion, and lower the amount of gas that must be delivered via pipelines(Othman et al., 2009). As a foundation to enhance such industries' efficiency and sustainability, the capability of selective separation of individual gases from a mixture is essential. The first commercial CA membrane process for CO_2 removal from natural gas was developed some few years later in the mid 1980s, and since then, the CO_2 membrane separation market is dominated by this process. (Baker, n.d.).

1.2 Overview of Gas Separation Technologies and Their Applications

Gas separation is the separation of one or more gases out of a gas mixture using physical or chemical differences among the individual components of the gas mixture. The primary technologies employed for gas separation include Cryogenic Distillation ,Absorption , Adsorption and Membrane Separation. Every year, 30 billion tons of CO2 is released to the atmosphere, mainly contributed by combusted gases and burning of fuels(Mubashir et al., 2016). CAs success is based on the fact that they are easy to obtain, cheap, and stable (both mechanically and chemically). It is currently the most widely used commercial polymer for CO2 separation. Up to 80 percent of the natural gas processing market membrane technology market was CA in 2012(Scholes et al., 2012).

1.3 Membrane Separation

Membrane Separation is one of highest selectivity’s forms of separation, since it uses selective permeability of a certain gas through a membrane material. Scientists had estimated that the CO_2 concentration would be increased to 970 ppm in the atmosphere by next century (Friebe et al., 2016). The application of this technology is in natural gas purification and hydrogen production. Therefore, membrane separation is energy-efficient, operationally simple and constitutes it as a viable option for different industrial applications. Membrane separation technologies, however, often suffer from a trade-off of permeability with selectivity. Furthermore, membranes are prone to fouling, and can degrade their performance over time, requiring continued maintenance. However, depending on the geological location, raw natural gas varies significantly in composition and may contain 10–40 mole% CO_2 (Separation et al., 2021).

Despite this, each of these technologies has its own unique advantages and is selected based on the specific needs of the application including the purity levels desired, throughput desired and economic considerations envisioned. An economically viable technology for CO2 separating from flue gas and natural gas is necessary(He et al., 2014).

1.4 Specific Emphasis on CO_2 and CH_4 Separation

CO_2 and CH_4 separation is of particular importance because they possess both arrows and benefits for energy efficiency improvement and environmental management.

- **Natural Gas Processing:** Often natural gas extracted from wells already includes large amounts of CO_2, and these CO_2 must be removed before the gas meets pipeline specifications and prevents corrosion in. CO_2 also lowers heating value of natural gas and its removal is economically. Natural gas is separated by efficient separation technologies, so it is suitable for end use applications, such as residential heating, electricity generation and as a feedstock for chemical synthesis.
- **Carbon Capture and Storage (CCS):** Capturing CO_2 emissions from sources like power plants and storing them underground away from the atmosphere (totally below it) to prevent them from entering into the air is the basic concept of CCS; simply separating CO_2 from industrial flue gases is a crucial part of the CCS process. CO_2 separation with membrane technologies provides a scalable and energy efficient solution for at least reducing greenhouse gas emissions
- **Biogas Upgrading:** Generally, a biogas produced from anaerobic digestion of organic matter contains CH_4 and CO_2. To use biogas as a renewable energy source, it should be upgraded to biomethane, removing CO_2 to increase the CH_4. Since membrane-based separation is an attractive approach when it comes to biogas

upgrading based on its operational simplicity and modularity, membrane was chosen as the core technology for biogas upgrading.

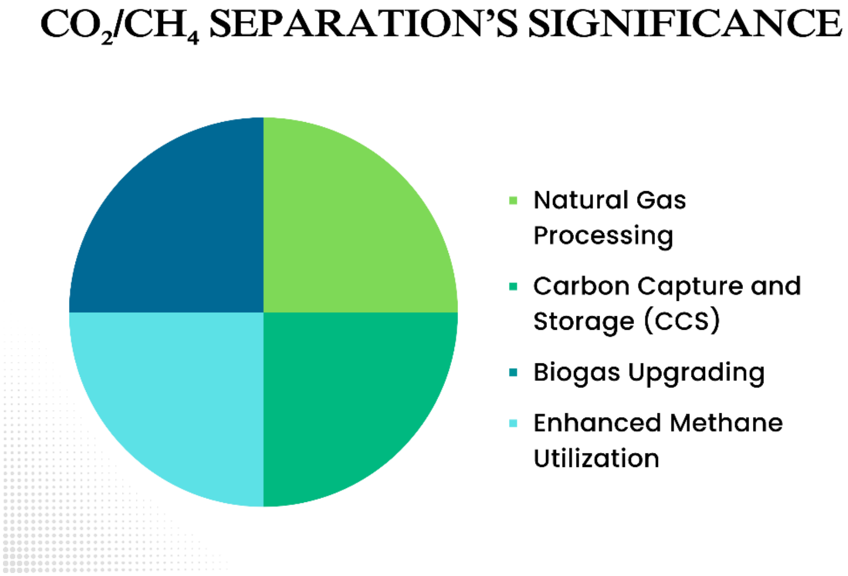


Figure 1: CO2/CH4 Separations Significance

- **Enhanced Methane Utilization:** Methane is a particularly strong greenhouse gas with a global warming potential of up to 72 times that of CO2 in a 100 year basis. Utilization and separation of CH_4 are efficient and valuable energy resource and help mitigate its environmental impact.

1.5 Technological Challenges and Innovations

Such separation is important yet separation of CO_2 and CH_4 remains challenging to both achieve and be cost and energy efficient. These include:

- **Selectivity and Permeability Trade-off:** The selectivity (the ability to prudentially separate one gas from another) versus permeability often represents a tradeoff in the case of membranes. Consequently, membrane design is a very challenging task: enhancing one particular property usually entails a compromise in the other.
- **Fouling and Stability:** However, membrane materials are often prone to fouling degradation as the time goes by especially in harsh industrial environments. For

practical applications , developing robust membranes with long term stability is crucial.

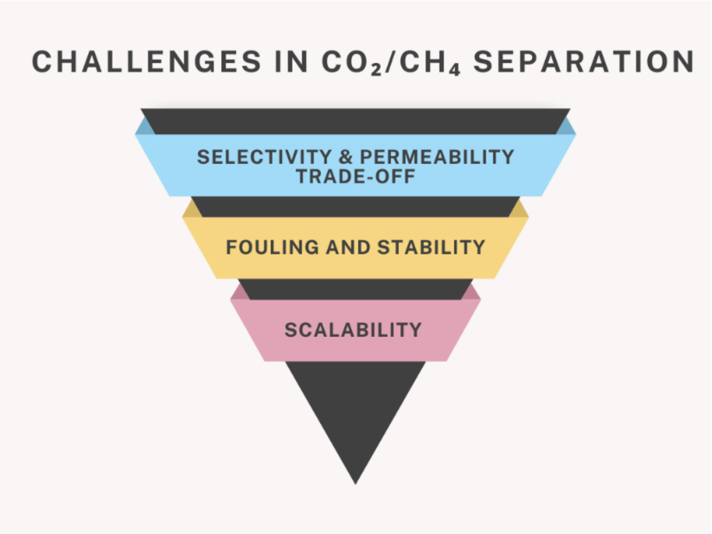


Figure 2: Challenges in CO2/CH4 Separation

- **Scalability and Cost:** Membrane technologies remain a hurdle in scaling from laboratory to industrial scale while maintaining performance and low costs. It is demonstrated that these barriers(Othman et al., 2009) can be overcome by innovations in materials science and manufacturing processes.

1.6 Impact of CO_2 Emissions on Climate Change

Global warming and climate change are matters of serious concern in which carbon dioxide is a main greenhouse gas. Since the Industrial Revolution, atmospheric CO_2 concentration has jumped up sharply, with most of that increase caused by the burning of fossil fuels, deforestation, and other industrial processes. CO_2 in the atmosphere can be elevated, which results in a stronger greenhouse effect and thus global warming, altered weather patterns, rising sea levels, and a range of other negative impacts on the system.CA is a material of choice because of its hydrophilic and biocompatible surface, low nonspecific adsorption, and plenty of hydroxyl ions. The features provide an opportunity to develop much better affinity for CO2, thereby enhancing the separation of CO2 from a gas mixture (Sanaeepur et al., 2015).

To meet global climate targets, like those in the Paris Agreement, mitigating the impacts of CO_2 emissions is essential. CO_2 capture and sequestration is an essential component of an approach to abolishing atmospheric CO_2 concentrations .Membrane based separation technologies can be used to separate CO_2 from point sources like coal plants and industrial facilities as a means to reduce emissions and fight climate change .As green energy source for modern power plants, natural gas is replacing fossil fuel(Lin & Yavari, 2023).

1.7 Necessity for Effective CO_2 Capture Methods

To address the urgency of climate change it is necessary to develop and implement efficient CO_2 capture methods. However, traditional methods, like amine scrubbing, are effective but have high energy costs and environmental concern — solvent degradation and possible toxicity. 42.However, these membranes are facing challenges such as high cost and complicated fabrication process (Mohamed et al., 2017).These membrane technologies have the potential to overcome these energies requirements since they are modular, non-expensive, and can be integrated to existing industrial processes.CO2 present in flue gases is the main contributor to climate change and ocean acidification (Moghadam et al., 2017).

Membrane materials have advanced through embodiments of the incorporation of fillers i.e metal organic frameworks that have increased membrane performance for CO_2 capture. High surface areas, tunable pore structures and these materials can selectively transport CO_2 and improved overall separation Reducing Greenhouse Gas Emissions . Metal organic framework (MOF) material is a new type of porous nanomaterial, consisting of organic framework connecting to metal ions or metal clusters as the centre. (Zhao et al., 2018).

The two major greenhouse gas contributors, CO_2 and CH_4, are addressed with its dual approach of a carbon capture and utilization of CH_4. By developing advanced membrane technologies for CO_2/CH_4 separation, the following benefits can be achieved:

- **Enhanced Carbon Capture:** The improved membrane performance allows CO_2 to be captured from industrial emissions, as a part of measures to reduce carbon footprints and meet emission reduction targets

- **Methane Management:** CH_4 separation and utilization are energetically efficient preventing its release into the atmosphere and eliminating its potent greenhouse effect. In sectors such as agriculture, waste management, and fossil fuel extraction, methane emissions are prevalent and this is especially important.
- **Economic Incentives for Sustainable Practices:** Efficient gas separation offers economic benefits encouraging industries to adopt energy saving strategies. CO_2 capture and CH_4 utilization can provide support to the transition towards greener technologies and the development of low carbon economies at a relatively low cost

1.8 Basic Mechanisms of Membrane Separation

1.9 Solution-Diffusion Mechanism:

For dense, non-porous membranes, the solution diffusion model is most applicable. Here we show that gas molecules dissolve into the membrane material on the feed side, permeate through the membrane matrix, and finally desorb on the permeate side. The solubility and diffusivity of the gas species in the membrane material determines the overall permeation rate. membrane technology has been widely studied as an alternative for CO2 removal processes since it is energy efficient and involved low cost(Jomekian et al., 2016).

- **Solubility:** Affinities toward the membrane material are governed differently by polarity, molecular size and chemical interactions for different gases. Permeation rates of higher solubility are further enabled.
- **Diffusivity:** After dissolution, the gas molecules rate of diffusion through the membrane is controlled by the mobility of gas molecules within the membrane matrix. For smaller and less polar molecules, diffusivity is thus found to be higher.

1.10 Pore Sieving Mechanism:

Porous membranes with characteristic pore sieving mechanisms, where physical size exclusion is an important part of separation. Thus, in this scenario, gas molecules pass through the membrane's pores only, and mostly with the passage of high, molecules pass with the pace set by size of pore on kinetic diameter of the gas molecules.

- **Size Exclusion:** Permeability occurs due to molecules that are smaller than the pore size, and they are allowed to pass, and molecules that are larger than pore size are retained. For separating gases with large size disparities, this mechanism is very effective.
- **Knudsen Diffusion:** Gas transport within membranes with pore size comparable to the mean free path is also possible by Knudsen diffusion, in which lighter gas molecules have higher velocity than heavier gas molecules, thus, they diffuse faster

1.9. Comparison with Traditional Separation Methods

Membrane separation technologies present several benefits over conventional ways such as absorption, adsorption, and cryogenic distillation. They benefit from the inherent characteristics: energy efficiency, scalability.

- **Energy Efficiency:**

  The separation based on boiling points is accomplished using equipment sizes which are often large with high heat load, and this requires a lot of energy, so the separation based on boiling points can prove to be very expensive. Unlike membrane processes, the latter are operated at ambient or moderate temperatures and do not require phase changes, causing much lower energy consumption
- **Operational Simplicity and Scalability:**

  Typically, membrane systems require less complexity (fewer moving parts), and don’t require extensive heat integration or solvent regeneration. Such simplicity also makes scaling from lab to industrial easier to scale by modules and flexibly by engineering deployment to satisfy different separation requirements. Traditional separation technologies demonstrated the disadvantages such as high capital cost, equipment corrosion, low CO2 loading capacity and weight requirement (Yeo et al., 2012).
- **Environmental Impact:**

  Membrane technologies often have a smaller environmental footprint than solvent-based methods, using chemicals that can be both toxic and generate hazardous waste, this tends to be the case. Furthermore, membranes can be developed that use minimum amounts of solvent or zero solvent during their operation, consistent with green chemistry

- **Selective Permeability:**
  Enhanced selectivity and efficiency are provided with the ability to tailor membrane materials for specific separations. For example, polymeric membranes can be designed to select for certain gas hybrids, such as CO_2/CH_4, by varying their chemical composition and structure to enhance specific interactions with target molecules .

1.10. Types of Membranes

There are mainly two structural categories and 7 functional attributes by which gas separation membranes can be divided. Dense membranes, porous membranes and mixed matrix membranes (MMMs) are the main categories. There are advantages of each type and therefore it's best suited for each different.

Table 1:Comparison of Membrane Types for Gas Separation

Membrane Type	Mechanism	Advantages	Limitations	Examples
Dense Membranes	Solution-Diffusion	High selectivity; ease of fabrication; compatibility with various processes.	Trade-off between selectivity and permeability.	Cellulose Acetate (CA), Polyimides
Porous Membranes	Size Exclusion, Knudsen Diffusion	High permeability; ability to separate based on molecular size.	Lower selectivity for certain gas pairs; fouling susceptibility.	Ceramic, Polymeric porous membranes

Mixed Matrix Membranes (MMMs)	Combination of Solution-Diffusion and Pore Sieving	Enhanced selectivity and permeability; tunable properties.	Challenges in filler dispersion and interfacial bonding.	CA + ZIF-8, PES + Zeolites
Thin Film Composite (TFC) Membranes	Layered selective and support layers	High selectivity and permeability; mechanical robustness.	Complex fabrication; potential layer adhesion issues.	CA/ZIF-8 on polysulfone support

1.11. Composite Membranes

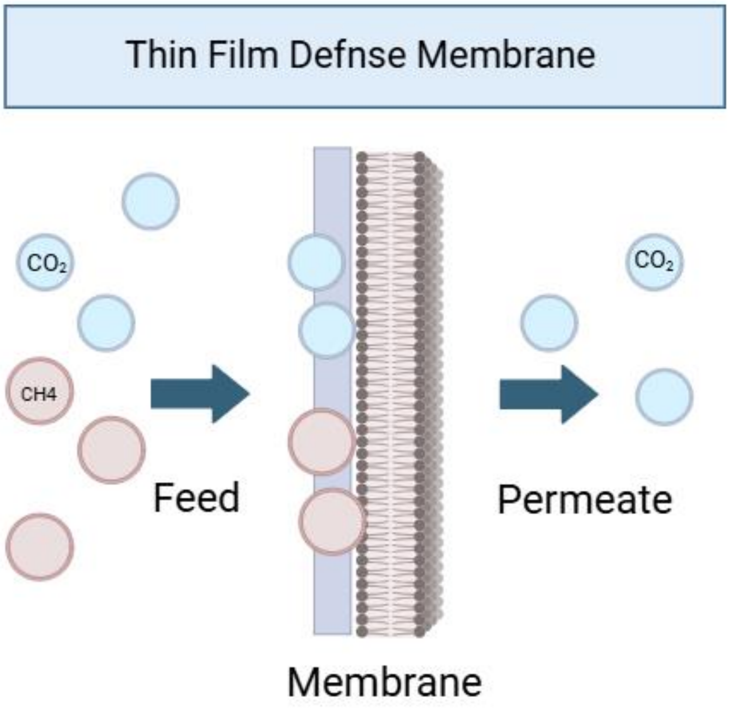


Figure 3:TFC Membrane Mechanism

Thin Film Composite (TFC) membranes are engineered with a distinct layered structure, comprising primarily a selective layer and a support layer. This design facilitates high-performance gas separation while ensuring mechanical robustness and operational stability.

- **Selective Layer:** The topmost layer of the TFC membrane is called the selective layer, which is generally very thin (tens to hundreds of nanometers in thickness and is selective. The selective permeation of target gas molecules to this membrane is dictated by this layer and hence the membrane's separation performance. This includes polymeric materials like Cellulose Acetate (CA), polysulfone (PSf) or polyimides, depending upon your choice based on certain solubility, chemical and gas permeability characteristics(Lin & Freeman, 2004).
- **Support Layer:** The support layer, below the selective layer, provides the mechanical strength required by the membrane structure. A porous support layer, generally comprised of porous materials such as polysulfone (PSf), polyethersulfone (PES), or ceramic substrates, with high porosity, low thickness, and to further minimize mass transfer resistance (Baker et al., 2018)(Lin & Freeman, 2004).

1.12. Advantages of Composite Membranes

1.12.1. Enhanced Selectivity and Permeability:

Composite membranes have a layered architecture which allows the high selectivity layer to be engineered at the expense of permeability without affecting the quality of the selective layer. The support layer supports a stable framework that does not slow carrier gas transport significantly, while the selective layer allows for the transport of gas via an ultrathin selective layer at rapid rates.

- **Selective Layer Optimization:** TFC membranes are able to achieve tailored separation properties by precisely controlling the composition and thickness of the selective layer. In this case, when melamine ZIF 8 is incorporated into a Cellulose Acetate matrix, the CO2 selectivity is improved by providing additional adsorption sites and allowing facilitated transport mechanisms
- **Permeability Enhancement:** The thin selective layer minimizes the resistance to gas diffusion providing higher permeation rates. This is very beneficial in large-scale industrial applications where the throughput is very high

1.12.2. Flexibility in Material Incorporation:

Owing to its flexibility with regard to material and the ability to modify it, Composite membranes are promising. Typically, the selective layer can be made from many different types of polymers, and also includes a range of fillers and other additives to target specific applications.

- **Incorporation of Fillers:** Membrane properties can be customized by the capability of integrating fillers such as melamine ZIF-8, metal organic frameworks (MOF), and other nanomaterials. However, these fillers may provide additional separation mechanisms, such as transport aided by adsorption, facilitated transport or molecular sieving, which can also Overall membrane performance can be improved. as a material, MOF has been attracting wide interest and used in catalysis due to its mature existing advantages, such as high specific surface area, adjustable pore size (Hao et al., 2020).
- **Chemical and Physical Modifications:** Chemical and physical modifications of the selective layer (e.g., crosslinking, surface functionalization, blending with other polymers) are possible to improve selectivity, permeability and stability. The membranes can be made tailor made to specific gas separation challenge.

1.12.3. Improved Mechanical Stability and Durability:

Composite membranes require the support layer for mechanical support to prevent deformation or damage to the membrane under operational pressures and physical stress. Composite membranes have enhanced durability which allows for consistent performance over long use, making Composite membranes well suited for operating in demanding industrial environments. However, selection of poor material may cause the formation of interfacial voids, .which affects the performance of MMMs. Thus, selection of an appropriate polymer and filler is quite challenging and complicated(Chung et al., 2007).

1.12.4. Resistance to Fouling and Degradation:

On the other hand, the robust support layer provides the selective layer from physical damage and fouling agents, retaining membrane performance and reducing the demand of significantly frequent maintenance or replacement

1.12.5. Scalability and Integration:

Composite membranes are ideally suited for production on a large scale, and can easily be incorporated into existing gas separation systems. The membrane module design is modular such that they can be scaled to meet the characteristics of different applications

- **Ease of Fabrication:** Compared to other thin film deposition techniques, dip-coating and other thin film deposition techniques used in TFC membrane fabrication are compatible with industrial manufacturing processes and enable mass production and quality control .
- **Modular Design:** Typically, Composite membranes can be incorporated into a number of module configurations including spiral wound, hollow fiber, and flat sheet modules, giving design and operating flexibilities in a system.
- **Energy Efficiency:**Composite membranes have high permeability and selectivity and can thus help reduce the energy consumed in gas separation processes. Composite membranes make more efficient operation possible compared to conventional methods by reducing pressure drop and increasing gas flux which results in lower operational cost and a more sustainable system. Subsequently, CO2 present in natural gas reduces its energy and cause equipment corrosion in the presence of water (Jiao et al., 2017).

1.13. Acetone as a Solvent

Acetone is normally incorporated in preparative techniques for preparation of membranes, especially for polymers such as Cellulose Acetate (CA). It is versatile and it performs a number of functions linked with the dissolving of CA, forming of uniform films and the quality of the membrane.

1.13.1. Dissolution of CA:

The experiments revealed that acetone efficiently dissolved CA due to its capacity to eliminate the hydrogen bond within the polymer matrices. The solvent dissolves the CA and weakens the inter and intramolecular forces of the acetyl groups preparing it for membrane casting . This dissolution is important to obtain a uniform polymer solution that is important for perfect free-standing membrane. CA membranes were applied in the 1970s to gas separation, mostly for CO2 removal from natural gas and hydrogen purification(Kelley, 1989).

1.13.2. Facilitation of Membrane Formation:

In fabrication of the membrane through dip-coating or casting, acetone serves as a solvent through which CA is uniformly applied on the substrate. Its high volatility is important for the solvent evaporation process through which the selective layer is formed, whereas the solvent diffusion out of the polymer film is rapid and maintaining an even polymer film thickness

1.13.3. Control of Membrane Morphology:

It also observed that Boiling point, viscosity, and evaporation rate of acetone as a solvent affects morphology of the CA membrane. In this way, the main parameters including the concentration of the solvent, temperature, and rate of evaporation are used by researchers to define the thickness, porosity and the outer layer of the membrane to meet the efficiency required for certain types of gas separation

1.14. Challenges Associated with Acetone Use:

- Handling and Safety:
- Solvent Residue:
- Environmental Regulations:

1.15. Melamine- ZIF-8 as a Filler

Zeolitic Imidazolate Framework-8 (ZIF-8) is a prominent member of the metal-organic frameworks (MOFs) family, distinguished by its crystalline structure comprising zinc ions coordinated with 2-methylimidazole ligands. ZIF-8 exhibits a zeolite-like topology, characterized by high surface area and porosity, making it highly suitable for various applications, including gas storage, catalysis, and membrane separations.ZIF-8 is a kind of pore MOF zeolite material composed of a zinc ion and 2-methylimidazole ligand(Perez et al., 2009).

1.15.1. Impact of ZIF-8 on the Overall Performance and Stability of the Membrane

Incorporating ZIF-8 into the CA selective layer profoundly enhances the membrane's performance and stability in several key areas:

Table 2:Impact of ZIF-8 on the Overall Performance and Stability of the Membrane

Impact Area	Description	Effect on Membrane Performance	Reference
Enhanced Selectivity	ZIF-8 increases the membrane's selectivity for CO_2 over CH_4 by exploiting size and affinity differences.	Improves the separation factor by allowing selective diffusion of CO_2 while hindering CH_4 passage.	Zhang et al., 2018
Increased Permeability	Provides additional adsorption sites and transport channels for CO_2 molecules.	Increases overall permeation rate of CO_2 without significantly affecting selectivity.	Li et al., 2009
Mechanical Stability	Acts as reinforcement within the CA matrix.	Enhance tensile strength and resistance to deformation under operational pressures, improving durability.	Bakkali et al., 2020
Thermal and Chemical Stability	Contributes to the membrane's structural integrity under varying temperatures and chemical exposures.	Maintains consistent performance and longevity in diverse operational environments.	Park et al., 2006

Resistance to Fouling	Provides a smoother, more hydrophobic surface that reduces contaminant adhesion.	Minimize performance degradation and extend operational lifespan.	Miyajima et al., 2011
Scalability and Fabrication Efficiency	Enhances uniform membrane production on a larger scale due to improved dispersion and compatibility.	Ensure consistent performance across different membrane batches, supporting commercial viability.	Robeson, 2008

1.15.2. Challenges and Considerations

Despite the numerous benefits of incorporating ZIF-8 into CA-based TFC membranes, several challenges must be addressed to optimize membrane performance:

Efficient membranes for CO_2/CH_4 separation present significant challenges in their development as the inherent physical and chemical properties of these membranes require innovative optimization strategies to minimize performance degradations and to enable practical application. Dispersing, and interfacial compatibility of fillers; membrane thickness and loading, cost and scalability, and membrane stability are among the main challenges. Compared with other MOF materials, ZIF-8 has a superior thermal stability, chemical stability and large specific surface area(T. Li et al., 2018).

The uniform distribution of ZIF-8 nanoparticles within CA matrix is achieved by means of Filler Dispersion. Agglomeration and defect formation occur due to poor dispersion and can cause compromise in membrane integrity and performance. In order to do this, researchers have used ultrasonication methods in order to ensure fillers are evenly distributed throughout the polymeric matrix. In addition, melamine functionalization of ZIF-8 improves its compatibility with the CA matrix, preventing particle aggregation.CO2 separation using polymeric membranes is attractive due to its lower cost as well as operation simplicity(Nejad et al., 2016).

Maintaining membrane integrity and preventing defects are dependent on interfacial compatibility between ZIF-8 and the CA matrix. This mechanical stability and effective gas separation is supported by strong bonding at the interface. Several interfacial compatibility strategies are used to enhance interfacial compatibility, including the substitution of ZIF-8 with groups compatible with other materials, addition of compatibilizers or coupling agents, and optimization of fabrication parameters to improve adhesion.

1.16. Objectives

The objectives for which the research will be used as well as the significance of the same for gas separation technologies and environmental sustainability are detailed. The present study seeks to push the field of membrane-based gas separation forward by improving and optimizing Composite membranes.

The research is driven by several key objectives, each targeting specific aspects of membrane fabrication, performance evaluation, and optimization:

1. Synthesis of composite membrane using melamine ZIF 8
2. Characterization of composite membranes using different techniques like SEM, XRD,FTIR , Mechanical testing etc.
3. Fabricated membranes will be tested for the CO_2 separation performance using gas permeation setup.

CHAPTER # 2 LITERATURE REVIEW

With the global rise in energy demand and the rising concerns about greenhouse gas emissions, there are pressing requirements for efficient technologies for carbon dioxide (CO_2) capture and separation. The selective separation of CO_2 from methane (CH_4) is one of the many gas separation processes that are important for biogas upgrading, natural gas quality improvement, and environmental mitigation. CO_2 present in natural gas reduces its calorific value and can cause pipeline corrosion, so it must be removed to meet industry standards. In biogas, the removal of CO_2 makes it a more energetic and useful renewable energy source. Cryogenic distillation and amine absorption are conventional separation technologies that are energy intensive and environmentally taxing. In contrast, membrane based separation technologies provide a more sustainable and cost effective approach to separation with lower energy consumption, scalability and continuous operation. (Miller et al., 1989)(Lin & Freeman, 2004).

2.1. Membrane Materials

Gas separation membranes are composed of a large variety of materials, including polymers, inorganic substances and hybrid composites. The most commonly used are polymeric membranes, which are low cost, easy to fabricate, and have well understood gas transport properties. While they come with inherent limits, such as the Robeson's upper bound tradeoff between permeability and selectivity. However, these limitations can be overcome by the use of mixed matrix membranes (MMMs), which utilize polymers with inorganic fillers(Scholes et al., 2012)(Chen, 2014).

2.2. Cellulose Acetate (CA)

CA, a cellulose derivative, is a gas separation membrane material that has been used for a long time. Good film forming ability, mechanical strength, thermal stability and intrinsic selectivity for CO_2 over CH_4 are among its favorable properties. Thin, defect free membranes can also be fabricated using a variety of casting techniques in organic solvents such as acetone, making CA also soluble (Kelley, 1989)(Sanaeepur et al., 2015).

CA specifically interact with acetate groups of CA, increasing CO_2 molecules' solubility and permeation through the membrane. Nevertheless, the poor permeability of pure CA membranes requires incorporating fillers to enhance their gas transport properties without sacrificing selectivity. Further adjustments of the degree of acetylation can further optimize CA's performance by increasing permeability with lower acetylation levels and lower CO_2/CH_4 selectivity with higher acetylation levels (Mohammadi et al., 2008).

2.3.Metal-Organic Frameworks (MOFs)

Crystalline, porous MOFs, such as Zeolitic Imidazolate Framework 8 (ZIF-8), have been attracting attention as fillers in MMMs. MOFs are highly surface area, have tunable pore sizes and exhibit excellent thermal and chemical stability. In particular, ZIF-8 possesses uniform pores (0.34 nm) and a strong affinity for CO_2, which make it a good candidate for CO_2/CH_4 separation. When placed into CA matrices, ZIF-8 enhances permeability through additional gas transport pathways while retaining selectivity via size exclusion and preferential adsorption of CO_2 molecules(Slater & Cooper, n.d.)(Caro, 2011).

More functionalization of MOFs, such as amine or PEG modification, further enhances their interaction with CO_2 and thus, the permeability and selectivity. These modifications improve the compatibility with polymer matrices and reduce the problem of filler agglomeration(Zhao et al., 2018)(Separation et al., 2021).

2.4.Membrane Fabrication Techniques

2.4.1. Fabrication Methods

Fabrication of membranes has a great influence on their structural and functional properties. Membranes with tailored properties are created with various techniques including phase inversion, interfacial polymerization, electrospinning and dip coating. Among these, dip coating is particularly advantageous for the manufacture of thin film composite (TFC) membranes because it is simple, scalable, and allows for control of membrane thickness and morphology (Liu et al., 2020)(Rezakazemi & Ebadi, 2014).

2.4.2. Dip-Coating Method

The formation of a thin polymer film is via dip-coating, in which a substrate is immersed into a polymer solution and withdrawn at a controlled speed. The advantages of this technique include the production of defect free membranes, industrial scalability and flexibility in adjusting fabrication parameters. The thickness and uniformity of the membrane can be controlled precisely by varying parameters such as withdrawal speed, solution concentration and number of coating cycles. Dip coating offers the integration of a selective thin layer in a porous support, resulting in high selectivity, but mechanical robustness for composite membranes(Houde et al., n.d.; Rezakazemi & Ebadi, 2014).

2.5. Enhancements and Current Developments

2.5.1. Mixed Matrix Membranes (MMMs)

MMMs take advantage of the strengths of polymers and fillers to enhance gas separation performance. It has been found that the incorporation of ZIF-8 into CA matrices has greatly enhanced CO_2 permeability and selectivity, while overcoming the tradeoff constraints of pure polymer membranes. However, filler loading optimization is crucial. Agglomeration and defects can occur at excessive loading and can affect mechanical strength and selectivity (Muhammad et al., 2015)(Friebe et al., 2016).

2.5.2. Functionalization of Fillers

CO_2 adsorption and selectivity can be improved by post-synthetic modification of ZIF-8, for example by amine functionalization. Unmodified fillers were inferior to functionalized ZIF8 in cellulose triacetate (CTA)/cellulose diacetate (CDA) blend membranes in terms of CO_2 permeability and selectivity. Functional groups, like amines, add to the interaction strength of CO_2 molecules and improve gas separation performance(Liu et al., 2020; Separation et al., 2021).

2.5.3. Advances in Fabrication and Modeling

Recent work has focused on hybrid membranes with a view to understanding gas transport mechanisms through computational modeling. These approaches allow for the design of membranes with improved performance characteristics precisely. For example, gas permeability was greatly increased by decreasing the thickness of CDA films while CO_2/CH_4 selectivity was maintained(C. Li et al., 2021).

2.6.Challenges and Limitations

- Although much has been learned about the scaling up and durability of MMMs, there is still much work to be done. Key issues include:
- **Agglomeration**: ZIF-8 particles tend to agglomerate under high filler loading, resulting in defects and uneven gas transport. Mechanical strength and selectivity are often compromised due to this problem(O et al., 1999; Rasekh & Raisi, 2021).
- **Long-term Stability**: Membrane stability and resistance to fouling and degradation under operating conditions is essential for practical applications (Separation et al., 2021; Zhao et al., 2018).
- **Cost and Scalability**: However, translating laboratory scale synthesis to large scale production is challenging. It is critical for commercialization to maintain consistent membrane quality while minimizing costs(Lin & Freeman, 2004; Muhammad et al., 2015).

2.7.Case Studies and Research Highlights

Under optimized conditions, amine functionalized ZIF-8 in CTA/CDA blend membranes show remarkable CO_2 permeability (17.32 Barrer) and selectivity (18.55). Further, studies have also shown that functionalizing ZIF-8 improves CO_2 adsorption capacity, making it a critical strategy to improve membrane performance(Separation et al., 2021)(Liu et al., 2020).

2.7.1. Thickness and Morphology Control

Nguyen et al. (2019) showed that reducing film thickness to submicron levels resulted in 130% increase of gas permeability while maintaining CO_2/CH_4 selectivity. Such control over membrane morphology is critical to achieve high performance separation, which is underscored by this (Liu et al., 2020).

2.8.Future Directions

The future of membrane technology for CO_2/CH_4 separation lies in the development of hybrid systems and advanced fabrication techniques. Research priorities include:

- **Filler Functionalization**: Further exploration of functional groups to enhance compatibility with polymers and improve gas separation performance.
- **Durability and Scalability**: Developing membranes with long-term stability and cost-effective production methods to enable industrial adoption.
- **Computational Modeling**: Leveraging simulations to gain deeper insights into gas transport mechanisms and optimize membrane design (Separation et al., 2021)(Chen, 2014).

The dense composite membranes composed of CA/acetone with melamine modified ZIF-8 are promising for efficient CO_2/CH_4 separation. However, challenges like filler agglomeration, and scalability, still exist, however, fabrication techniques, functionalization strategies, and computational modeling have made significant strides towards future innovations. Sustainable membrane technologies have the potential to contribute to the solution of global energy and environmental challenges(Rasekh & Raisi, 2021; Separation et al., 2021).

CHAPTER # 3 MATERIALS AND METHODS

The materials used for this study were cellulose acetate (CA), that has become the polymers of choice for membrane fabrication due to the ease of their film formation and good mechanical stability. Cellulose acetate was dissolved in acetone, and an organic solvent with high volatility, to form the polymer matrix. In house synthesized melamine substituted Zeolitic Imidazolate Framework-8 (ZIF-8) nanoparticles were synthesized by modified procedure of established protocols using melamine and tetracarboxylic acid fields.

Table 3: List of Chemicals and Materials

Sr. No.	NAME	CATALOGUES	SOURCE
01	Cellulose Acetate	CAS NO. 9004-35-7	Sigma Aldrich
02	Acetone	CAS NO. 67-64-1	Sigma Aldrich
03	PSF Sheet	CAS NO. 25154-01-2	Alfa Laval
04	Aluminum Tape	CAS NO. 7429-90-5	Sigma Aldrich

Polysulfone (PSF) membranes with mechanical strength and stability under operating conditions were used as porous support for the membranes. Chemicals of analytical grade were all used and purchased from well-known chemical suppliers. The cleaning and washing procedures were performed with deionized (DI) water, to assure the removal of impurities.

3.1. Substrate Preparation

Substrates were prepared from the selection of high-quality glass slides as a stable substrate for membrane preparation. To ensure proper adhesion of membrane layers to these slides, the slides were thoroughly cleaned, since any contamination or residue would destroy the uniformity and integrity of the final membrane. The first step involved rinsing the glass slides with running deionized (DI) water to remove loose particles, visible impurities, and allowing the slides to dry overnight. Then followed ultrasonic cleaning in

DI water for 30min to remove microscopic contaminants. High frequency sound waves used in ultrasonic cleaning cause cavitation bubbles in the cleaning solution which dislodge particles from the glass surface without physical damage.

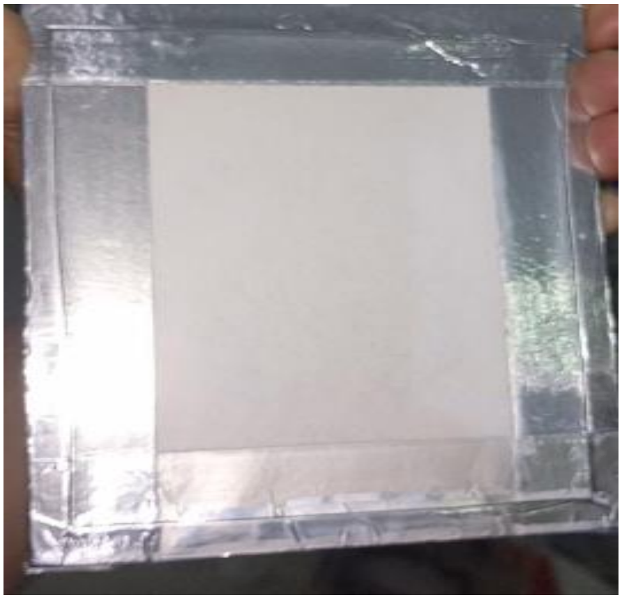


Figure 4: PSF Sheet wrapped in Aluminum Tape

The slides were cleaned with ultrasonic and carefully dried at room temperature for 30 minutes. This step was very important to avoid water spots as they could act as defects to the coating during the coating process. After cleaned and dried slides were stored in a clean environment to avoid contamination, slides were used in later steps.

3.2. Pretreatment of Polysulfone (PSF) Membranes

PSF membranes were pretreated prior to the application of the selective layer to improve their compatibility with the polymer matrix, and structural stability during the dip-coating process. Dimensions of the cut membranes were slightly larger than the target area of the membrane in order to enable proper handling and attachment during fabrication.

They were mounted on glass plates using adhesive backed aluminum tape to give a stable platform for subsequent coating. 0.28 ml of each of these mounted membranes were placed in a water bath maintained at 25°C for 30 minutes. This step relaxed the polymer chains in the PSF membrane and made it more flexible and free of surface defects for coating.

After immersion, the membranes were washed with distilled water for 5 minutes to remove any residues or loose particles that might have accumulated during handling. Finally, the membranes were dried in a fume hood for 30 minutes to eliminate any remaining moisture. This thorough pretreatment process ensured that the PSF membranes were in optimal condition for the application of the selective layer.

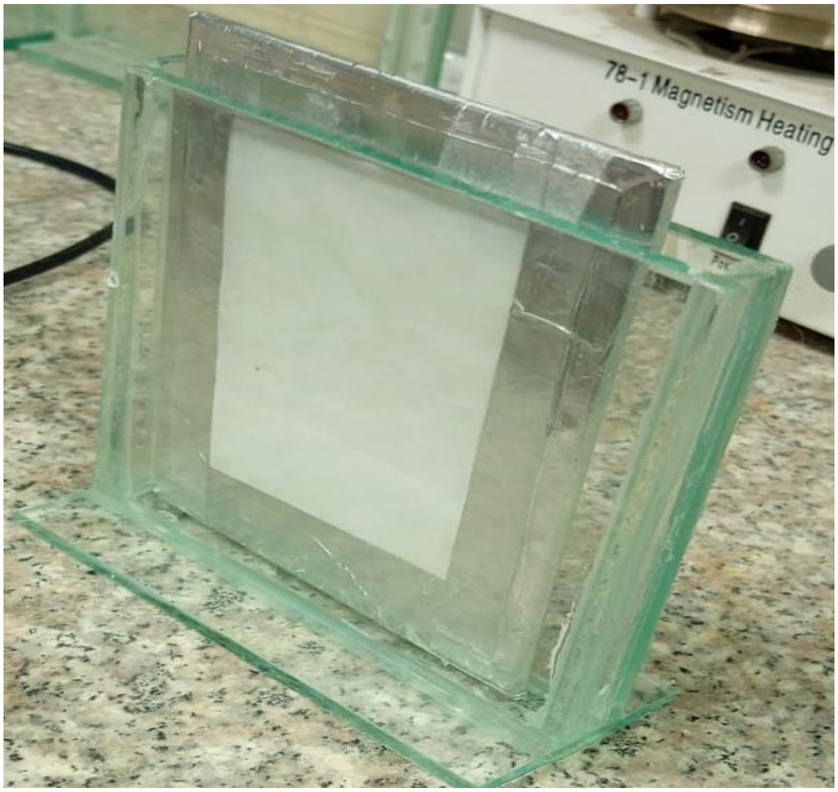


Figure 5: Pretreatment in DI water before TFC casting

3.3. Preparation of CA/Acetone-ZIF-8 Casting Solution

The casting solution was obtained by dissolving cellulose acetate (CA) in acetone to produce a polymer solution for uniform phase. Three percent (3 wt.%) of CA was added to obtain the right viscosity and to enhance its film-forming characteristic. To this solution, the calculated amount of CA was added slowly and gradually to acetone while stirring at 350 rpm. The solution was stirred for 24 hrs. at room temperature between 28-30 °C, to allow the polymer to fully dissolve in the solution.

In order to incorporate the melamine modified ZIF-8 nanoparticles to the polymer matrix, different concentrations (1 wt.%, 2 wt.%, 3 wt.%) of the nanoparticles were added to the CA/acetone solution. The nanoparticles were added slowly, under continuous stir, to avoid the formation of clumps. The nanoparticles were dispersed into the polymer matrix with overnight stirring to allow the uniform distribution of the nanoparticles into the polymer matrix.

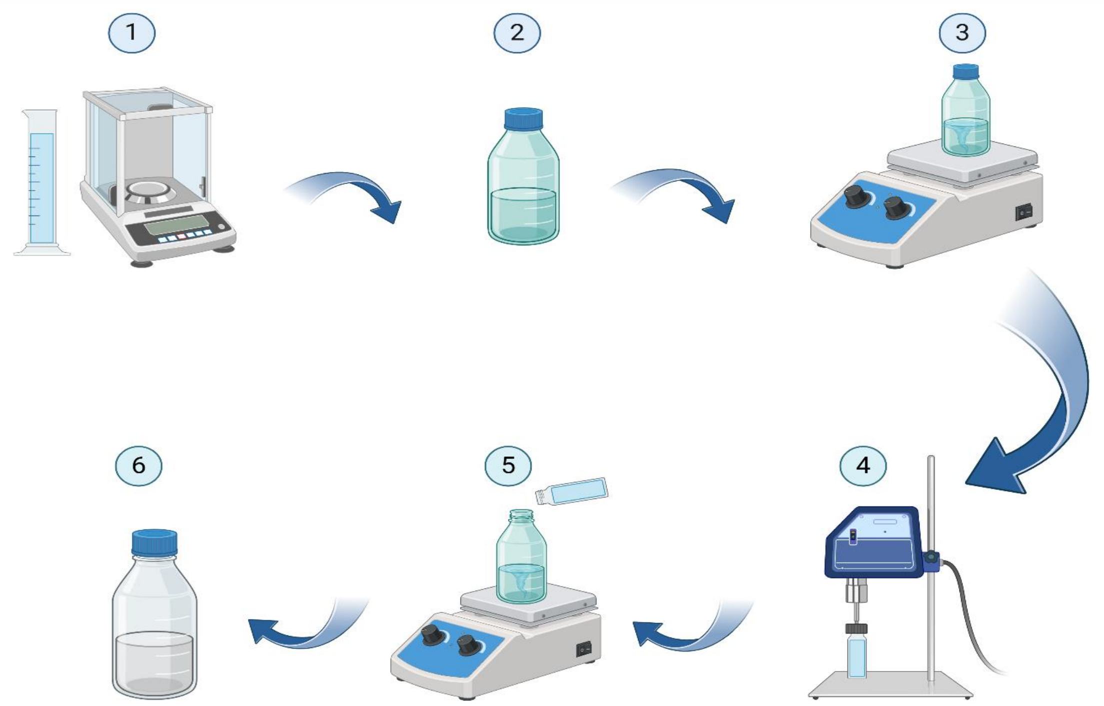


Figure 6: Casting Solution Preparation steps

The suspensions were sonicated in a probe sonicator for 2 hours to improve dispersion and reduce nanoparticle agglomeration. High frequency vibrations caused by the sonication fragment nanoparticle clusters and maintained the dispersion in a fine, uniform state. After sonication the suspensions stood for 2 hours at room temperature to allow the release of entrapped air bubbles. Essential to prevent defects in the final membrane structure, this degassing step was necessary.

3.4. Dip-Coating Process

The fabrication of the thin film composite membranes was carried out using a custom-designed dip-coating apparatus. This apparatus was specifically calibrated to ensure precise control over the dipping speed, residence time, and withdrawal rate, which are critical parameters for achieving a uniform coating.

To avoid introducing air bubbles, careful pouring of the prepared CA/acetone-ZIF-8 casting solution into the dip coating chamber was performed. The solution was to stand for 15 minutes, then was free of visible air bubbles and ready to be coated. The solution was hooked onto a pretreated PSf membrane that was mounted on a glass plate and was introduced into the solution at a controlled rate of 1.5 cm/sec. After 30 seconds, when enough time was allowed for the solutions interaction with the substrate, the membrane was placed in the solution.

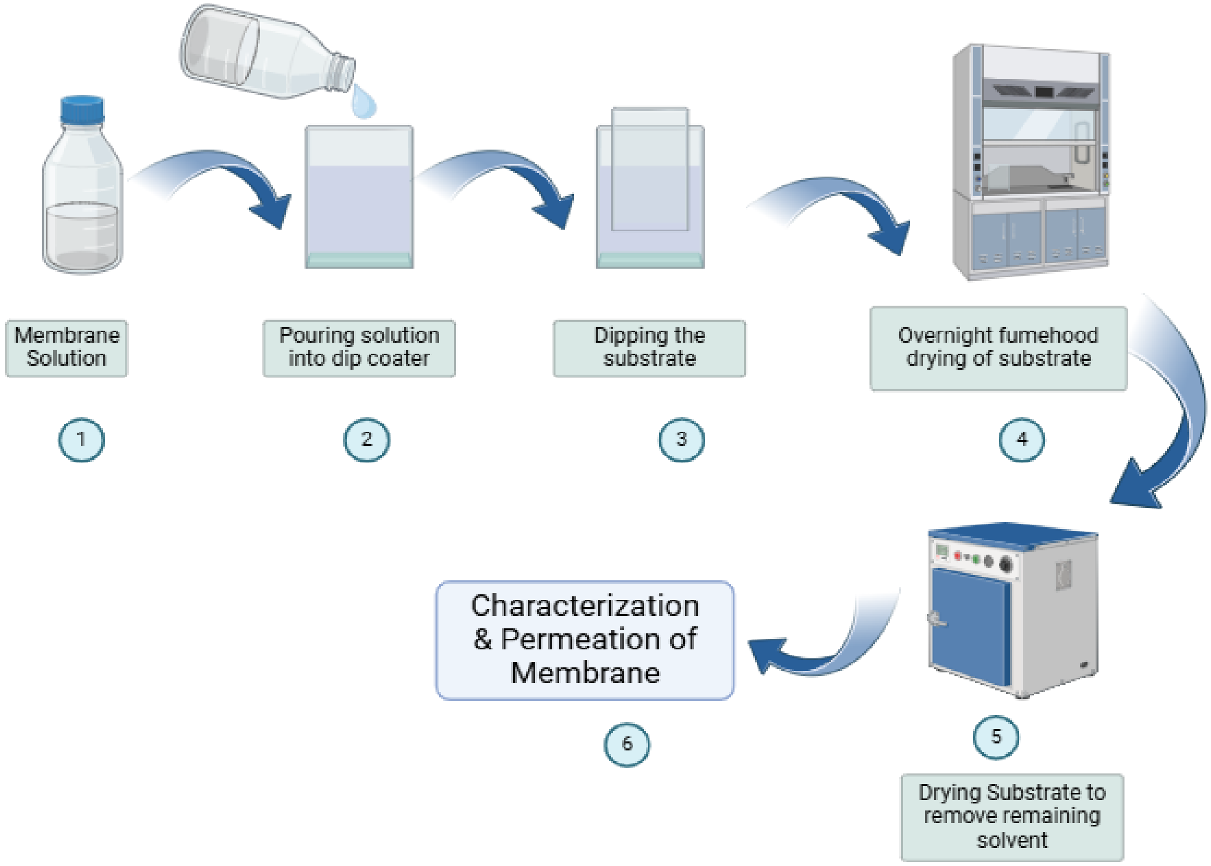


Figure 7: Dip Coating procedure step wise to cast a composite membrane

The edges of the membrane were sealed by adhesive backed aluminum tape to prevent solution from passing through the backside of the PSf support. The membrane was then slowly withdrawn and positioned vertically overnight at room temp to dry. The membrane was rotated by 180° to produce even coats on both sides in the repeat of the dip coating process.

Fume hood drying of the final coated membranes overnight allowed the solvent to evaporate completely. The membranes were then dried in an oven at 60degC for 2 hours for enhanced structural stability. By drying the composite membrane in this dual process after solvent removal, defect free, stable composite membranes were obtained.

3.5. Characterization of Composite Membranes

Complete characterization of the fabricated thin film composite membranes was performed through a variety of characterization techniques including physical, chemical, and functional properties. Insights about the structural integrity, morphological features, chemical interactions and performance of CO_2/CH_4 gas separation were obtained by these membrane-based approaches.

3.5.1. Fourier Transform Infrared Spectroscopy (FTIR)

In this study, composite membranes were analyzed by Fourier transform infrared (FTIR) spectroscopy, a technique to identify functional groups and to study molecular interactions. FTIR gave a molecular fingerprint to the materials, measuring infrared absorption spectra to give a specific vibrational transition that gave a fingerprint of functional groups. Dried membrane samples were prepared as KBr pellets and analyzed using a Nicolet 6700 spectrophotometer with a wavenumber range of 4000–400 cm^{-1} and a resolution of 4 cm^{-1}. Characteristic peaks at ~1730 cm^{-1} (carbonyl (C=O) stretching) and ~1225 cm^{-1} (C–O stretching) confirmed the presence of cellulose acetate, while peaks at 1580 cm^{-1} and 1140 cm^{-1} corresponded to the imidazolate linkages of ZIF-8 nanoparticles. These peaks shifted, implying strong interactions, e.g., hydrogen bonding or van der Waals forces, between cellulose acetate matrix and ZIF-8, indicating the successful integration and chemical compatibility of the components.

3.5.2. Scanning Electron Microscopy (SEM)

Surface morphology and cross-sectional structure of the composite membranes were investigated by Scanning Electron Microscopy (SEM). This method plays an essential role in understanding the uniformity of the selective layer, the distribution of the nanoparticles, and the total structural integrity of the membrane. And SEM imaging offers insights into the defects of the membrane, i.e., cracks or agglomerations, which can impact gas separation performance

Clean cross-sectional surfaces were obtained from membrane samples fractured in liquid nitrogen and sputter coated with a thin layer of gold for SEM analysis to improve conductivity. Surface and cross-sectional features were imaged at different magnifications. It was found that a dense and uniform selective layer resulted from the dip coating process. The integration of ZIF-8 nanoparticles demonstrated minimal sign of aggregation, which indicated good dispersion of them throughout the cellulose acetate matrix.

The thickness of the selective layer and its firm adhesion to the polysulfone substrate were confirmed by cross-sectional images. The morphology that was observed led to the validation of the structural integrity of the composite membranes, and also proved their suitability as composite membranes for CO_2/CH_4 gas separation applications.

3.5.3. X-Ray Diffraction (XRD)

To analyze the crystalline structure of the composite membranes and to determine retaining the crystallinity of the ZIF-8 nanoparticle crystallinity on the cellulose acetate matrix, XRD was used. This is a technique based on diffraction of X rays by atomic lattice of a material for determining information about its phase composition and extent of crystallinity.

XRD patterns were recorded using an X-ray diffractometer equipped with Cu Kα radiation ($\lambda = 1.5406$ Å) under the following conditions: 40 kV, 30 mA scanning range ($\theta = 5°–40°$) with a step of 0.02°. Dried samples under ambient conditions were mounted onto glass slides for membrane preparation.

Characteristic diffraction peaks of ZIF-8 at ~7.3°, 10.3°, and 12.7° were expected since the membrane also features the crystalline integrity of the nanoparticles present. These peaks were slightly broadened in the membrane samples and could be attributed to partial amorphization of ZIF-8 during fabrication or interactions between ZIF-8 and cellulose acetate matrix. The broad halo peak in the XRD pattern indicated that the cellulose acetate matrix had a semi crystalline nature. The success of incorporating ZIF-8 into the membrane and its structural stability were validated through these results, as both of these features are important to ensure improved gas separation performance.

3.6. Gas Permeance and Selectivity Testing

Single gas transport properties under control conditions were tested on the composite membranes using a custom-built gas permeation setup designed to evaluate the gas permeance and selectivity of the composite membranes. The experiments were conducted for CO_2 and CH_4 gases at five different feed pressures: Permeate side atmospheric pressure, 1, 2, 3, 4, 5 bar. A comprehensive assessment of the membrane performance over a range of driving forces was made possible with this range of pressures.

3.6.1. Membrane Preparation for Testing:

In order to reliably determine the gas transport properties, the selective layer of the composite membranes was mounted in a permeation cell with the feed gas side facing. The cell was sealed carefully to avoid leakage and to ensure uniform gas exposure to the membranes.

3.6.2. Gas Flux and Permeance Measurement:

The volumetric flow rate of gas at the membrane was measured using a calibrated mass flow meter and the gas flux (JJJ) through the membrane was determined accordingly. The permeance (PPP) of the gas was calculated using the equation:

$$P = \frac{J}{A \cdot \Delta P} \tag{1.1}$$

Where:

- P is the gas permeance ($mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$),
- J is the measured gas flux ($mol \cdot s^{-1}$),
- A is the effective membrane area (m^2), and
- ΔP is the pressure difference across the membrane (Pa).

The permeance of both CO_2 and CH_4 gases was measured at each of the five pressures to determine how the membrane's gas transport properties varied with pressure.

3.6.3. Selectivity Measurement:

The ideal selectivity (α\alphaα) of the membrane for CO_2 over CH_4 was determined by calculating the ratio of the permeances of the two gases: (T. Mohammadi et al., 2008)

$$\alpha = \frac{PCo2}{PCo4} \qquad (1.2)$$

3.6.4. Membrane Thickness Analysis

The thickness of the membrane was influenced by the concentration of the melamine modified ZIF-8 nanoparticles in the casting solution during the fabrication process. Here, the dip-coating process was directly affected by the mass concentration of ZIF-8 (1 wt.%, 2 wt.%, and 3 wt) and the variations of the membrane thickness.

To ensure consistency and evaluate the effect of thickness on membrane performance:

1. **Dip-Coating Parameters:**

Due to unpredictable uneven solution deposition, the residence time (30 seconds), withdrawal speed (1.5 cm/s) and rotation during the cycle were carefully controlled to minimize the variations in thickness.

2. **Measurement of Thickness:**

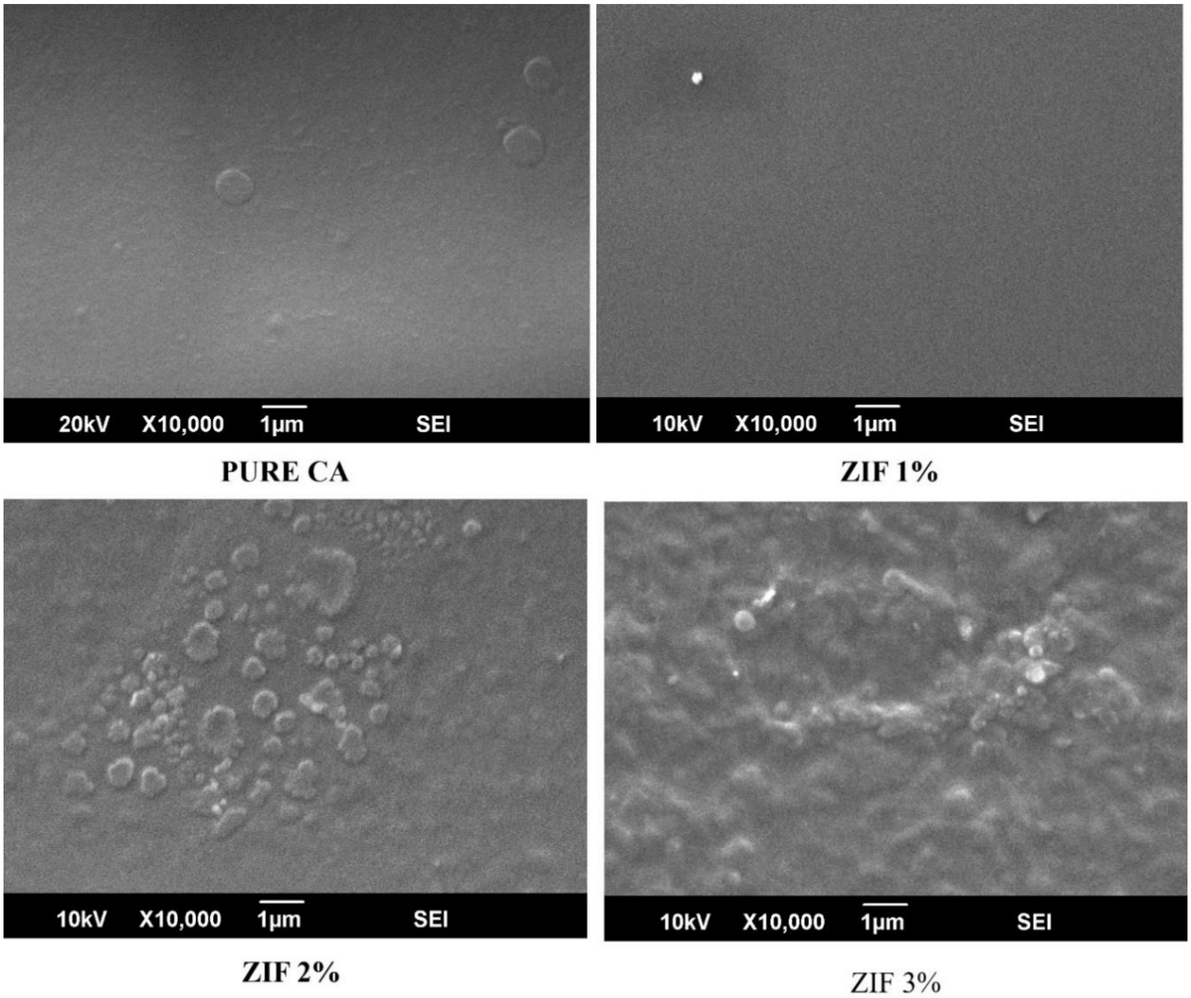
Cross sectional Scanning Electron Microscopy (SEM) was performed to measure the final thickness of the selective layer. Under high magnification the membrane samples were fractured and the resulting sample analyzed to measure thickness precisely at numerous points around the membrane sample.

3.7 Ultimate Tensile Strength Measurement

The SHIMADZU AGS-X series precision ultimate tensile tester was used to measure the ultimate tensile strength.The ASTM standard D882-02 was used to test each sample at a strain rate of 5 mm/min. Samples with Pure CA, 1%, 2%, and 3% ZIF in CA/Acetone membranes had their stress-strain behavior examined.

CHAPTER # 4 RESULTS AND DISCUSSIONS

4.1. Scanning Electron Microscopy (SEM)



PURE CA **ZIF 1%**

ZIF 2% ZIF 3%

Figure 8:SEM Image for membrane

To assess membranes prepared with 3 wt% cellulose acetate (CA) dissolved in acetone coated onto a polysulfone (PSF) ultrafiltration support, membranes were analyzed by scanning Electron Microscopy (SEM). The pure CA membrane also exhibited a uniform, defect free surface signifying excellent film formation and uniform solvent evaporation. The cross section showed a strong bond between dense CA layer and porous PSF support × with constant thickness and no defects. The structure of this form provides high mechanical stability while maintaining efficient ultrafiltration performance.

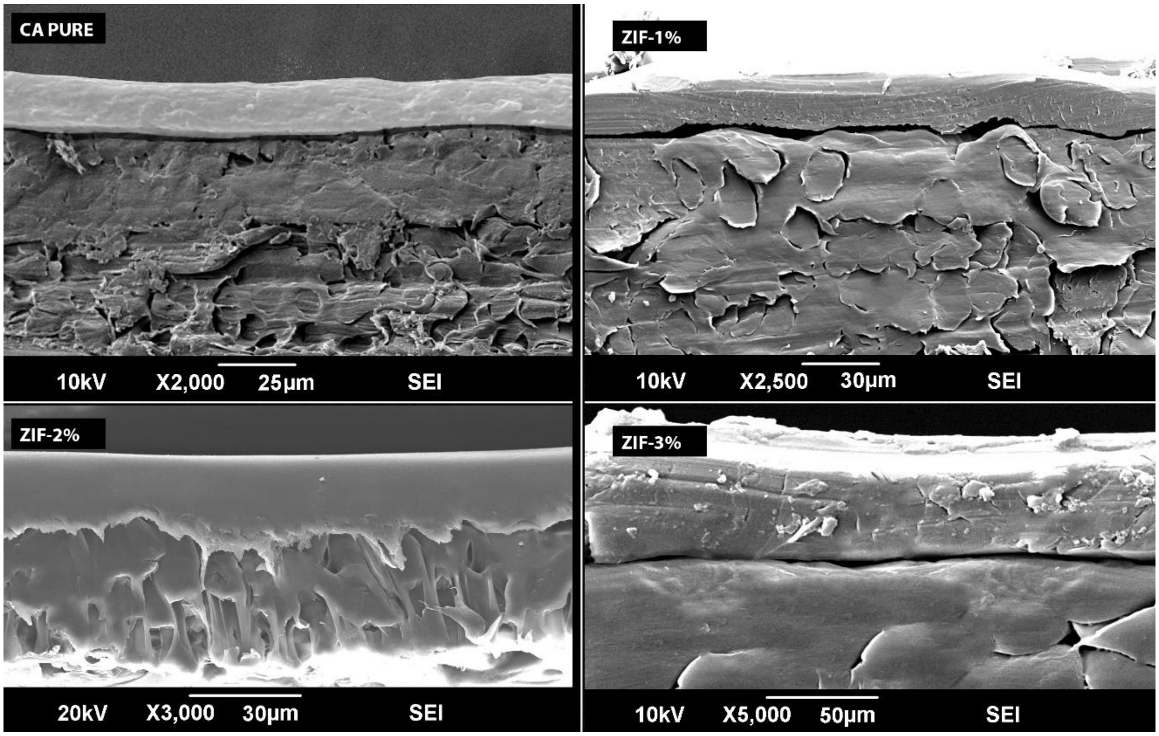


Figure 9:Cross Sectional SEM

The pure CA membrane retained its smooth and uniform surface even when 1 wt% melamine-modified ZIF-8 was added to the CA-acetone solution. The addition of ZIF-8 particles in the CA matrix improved porosity and facilitated additional solvent transport pathways. The improvement enhanced the membrane permeability and selectivity without losing structural integrity.

ZIF-8 content increased up to 2 wt% resulted in more visible ZIF-8 particles homogeneously distributed throughout the CA layer. Additional particles were added that did not non-interference with membrane structure, remained smooth, and defect free and improved filtration performance by enhancing porosity and creating more selective pathways.

Some particle agglomeration was seen at the highest ZIF 8 loading of 3 wt%, as larger crystalline domains within the CA matrix. Minor surface irregularities were introduced by the aggregated ZIF-8 particles, and the overall membrane structure remained intact with strong adhesion between the CA layer and the PSF support. This concentration may improve filtration property by forming more selective sites.

4.2. X-Ray Diffraction (XRD)

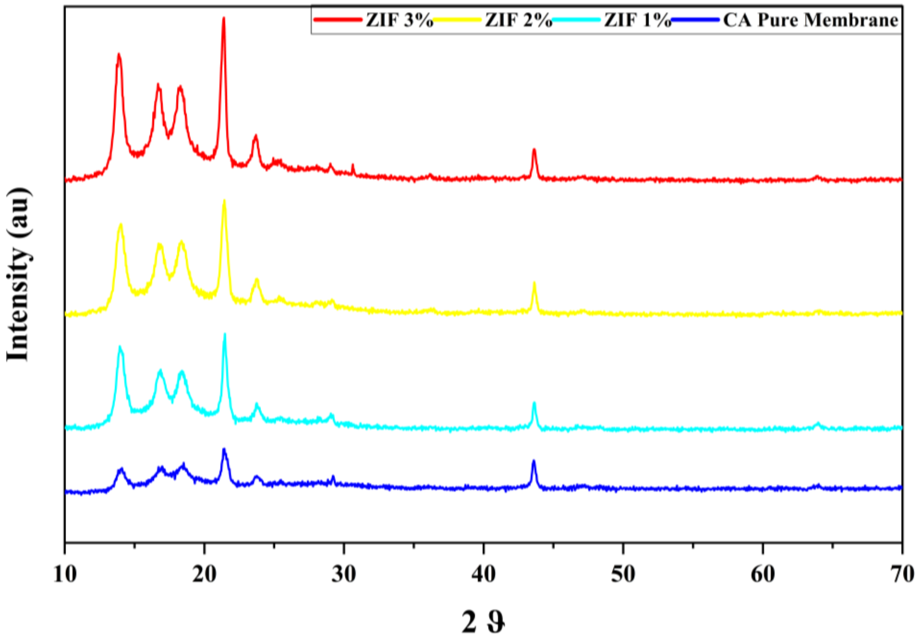


Figure 10:X-Ray Diffraction peaks of CA and ZIF-8

The graph shows XRD (X ray Diffraction) patterns on the crystalline structure of pure cellulose acetate (CA) membrane and its composite membranes with different concentration of ZIF-8 Nanoparticles (1 wt%, 2 wt%, and 3 wt%).In Pure CA Membrane (blue curve) , We observe the pristine CA membrane to have a broad amorphous hump around 2θ = 10°–25° in the XRD profile, consistent with its predominantly amorphous nature. We confirm that the pure membrane does not have a crystalline structure by the absence of sharp peaks. ZIF 1% (cyan curve)At the presence of 1 wt% ZIF-8, sharp diffraction peaks at specific 2θ values (about 10°, 20°, and 30°) are observed, which indicate that ZIF-8 has crystalline planes. These peaks reveal that ZIF-8 dispersed in the CA matrix without breaking the polymer’s structure integrity. ZIF 2% (yellow curve) The ZIF-8 nanoparticles induce higher degree of crystallinity at 2 wt% ZIF-8 as depicted by the increased intensity of the sharp peaks. Well defined crystalline domains within the membrane are suggested by the distinct peaks around 2θ = 15°, 20°, and 30°.ZIF 3% (red curve) The highest level of crystalline content is exhibited by the 3wt% ZIF-8 membrane as the most pronounced peaks in the XRD pattern of the 3wt% ZIF-8 membrane. Nevertheless, the increased intensity may further indicate aggregation of ZIF-8 molecules at higher concentrations, which in turn may affect the membrane performance. Generally, the crystalline portion imparts strength to the semicrystalline polymer, whereas the amorphous region is mainly responsible for flexibility. (Puleo et al., 1989)

The XRD analysis of membranes shows that the crystallinity of the membranes is gradually enhanced with the increasing amount of ZIF-8 nanoparticle addition. The incorporation and preservation of the intrinsic crystalline framework of ZIF-8 is evidenced by the distinct peaks in the CA matrix associated with ZIF-8. This structural enhancement can enhance mechanical strength, thermal stability and separation performance of the membranes.

4.3. Fourier Transform Infrared Spectroscopy (FTIR)

In the first graph, the Fourier transform infrared (FTIR) spectra for cellulose acetate (CA) membranes and colloidal composites of CA membranes with ZIF-8 nanoparticles at different concentrations (1 wt%, 2 wt%, and 3 wt%) show the characteristic peaks of the functional groups present in cellulose acetate (CA) membranes. This data essentially gives key insight into the interaction between ZIF-8 nanoparticles and the CA matrix. Characteristic absorption bands corresponding to the C-F stretch (<1100 cm^{-1}), N-H stretch (<3300 cm^{-1}) and other associated functional groups are observed for the spectrum of the pure CA membrane (blue curve). Second, the peaks serve as a baseline for comparison of the molecular structure of pristine cellulose acetate. Upon the addition of ZIF-8 nanoparticles, new peaks and shifts are observed. For instance, ZIF 1% (cyan curve) A clear O-H stretching band at 3200 – 3500 cm^{-1} and a notable peak at the region of C-Br stretching (~600 – 800 cm^{-1}) is observed in the spectrum. The changes observed here suggest that these ZIF-8 nanoparticles interact with the hydroxyl groups in the CA membrane matrix. ZIF 2% (yellow curve) The sharp O-H stretching peak and shifts in the C-F stretch are observed with 2 wt% ZIF-8 nanoparticles incorporated into the composite. The presence of C-Cl stretching (~700 cm^{-1}) implies a chemical environment modification from higher ZIF-8 concentration. ZIF 3% (red curve) The spectrum of 3 wt% ZIF-8 composite membrane has a more pronounced N-H bending (~1500 cm^{-1}) and broadening of the O-H stretching region suggesting hydrogen bonding between ZIF-8 and CA. The integration of ZIF-8 with the polymer matrix at the molecular level is evident from the emergence of new peaks.

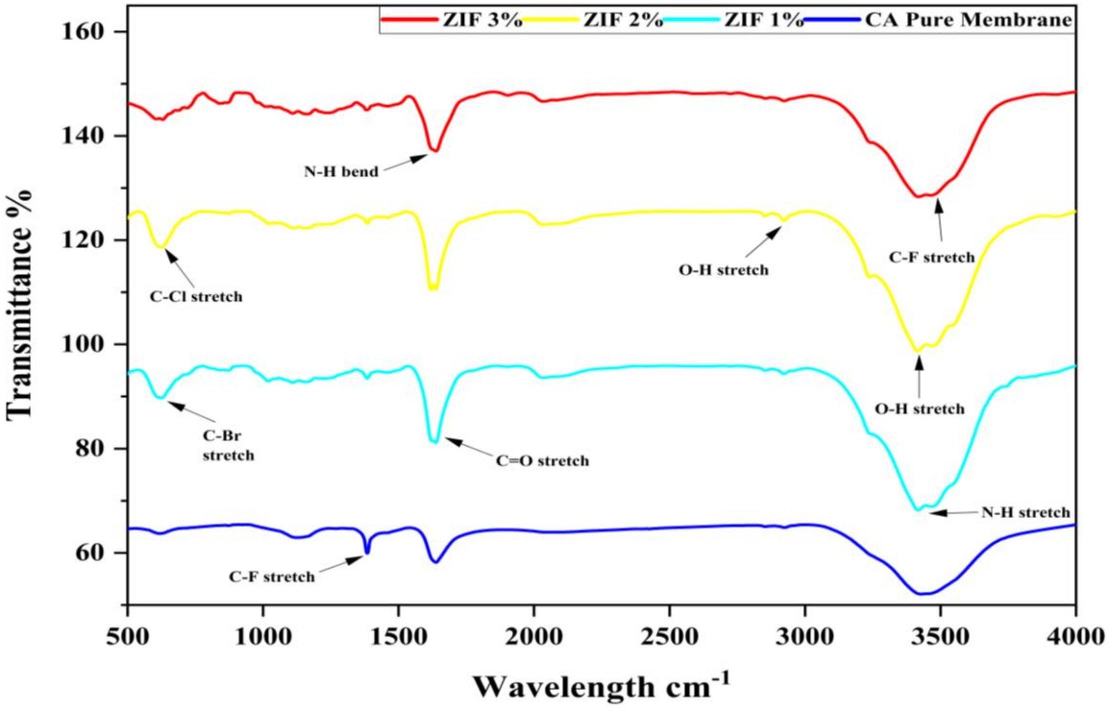


Figure 11:FTIR Spectra of ZIF-8 and CA Membrane

The FTIR data confirms the incorporation of ZIF-8 nanoparticles into the cellulose acetate membranes. Through analysis of the spectral shifts and appearance of new peaks, we observe chemical interactions between the ZIF-8 framework and the CA matrix, which may lead to improvements in the structural and functional properties of the membrane.

4.4. Membrane Thickness

The bar graph shows the thickness measurements of pure CA and its composites with ZIF-8 NPs at 1 wt%, 2 wt%, and 3 wt%. Results from the data show an increase in membrane thickness with the successful addition of ZIF-8.

The lowest thickness of approximately 0.0294 cm is seen from the CA membrane. The baseline thickness of the unmodified polymer membrane is this value. ZIF 1% Membrane thickness is slightly increased to 0.0297 cm when 1 wt% ZIF-8 is incorporated. It shows a small increase which is nearly a margin of the membrane structure under low ZIF-8 concentration impact. ZIF 2%With 2 wt% ZIF-8, the membrane thickness increases to 0.0300 cm, supporting a higher effect of the added nanoparticles.

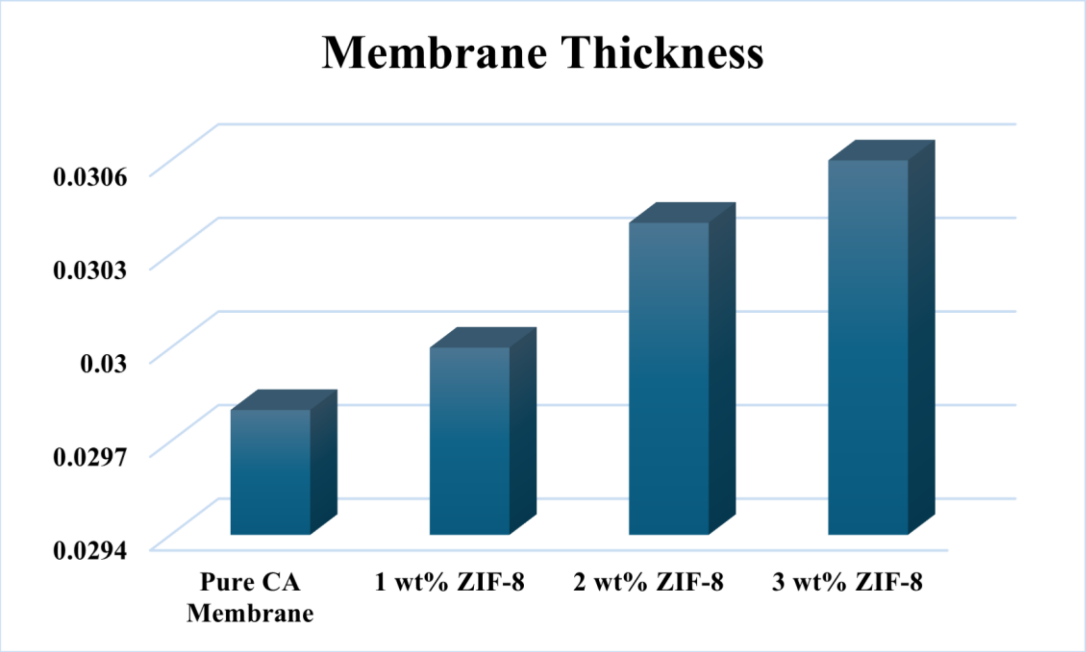


Figure 12:Thickness of Pure CA Membrane and ZIF 1wt%, 2 wt% and 3wt%

The likely source of this increase is the contribution of ZIF-8 to the overall membrane bulk due to the higher volume fraction of ZIF-8.Among the membranes, the membrane with 3 wt% ZIF-8 has the largest thickness of 0.0306 cm. This large increase is explained by the accumulation of ZIF-8 particles within the polymer matrix to create a denser, thicker membrane structure.

The physical presence of the nanoparticles in the membrane matrix results in increasing trend of the membrane thickness with the ZIF-8 concentration. The transport properties, mechanical stability and separation efficiency of the membranes can be influenced by this structural modification. Nevertheless, membrane design may be obliged to handle increased resistance to mass transfer due to excessive thickness. When the incorporation of ZIF-8 exceeded 0.6 wt%, the viscosity of the casting solution increased, and the thickness of the membrane increased (Rasekh et al., 2021)

4.5. Gas Permeation

4.5.1. Effect of ZIF-8 Concentration on CO_2 Permeability

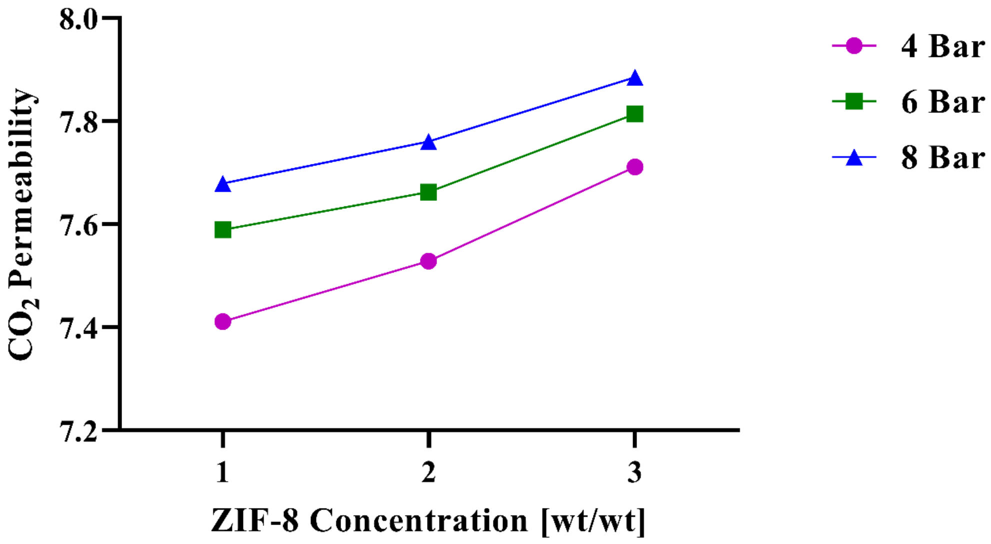


Figure 13:Effect of ZIF-8 Concentration on CO_2 Permeability

It is shown that at operating pressures of 4, 6, and 8 bar, ZIF-8 concentration is positively correlated with CO_2 permeability, indicating that ZIF-8 serves to increase CO_2 diffusion across membranes. CO_2 permeability is higher at 4 bar (7.4 at 1 wt% ZIF-8, 7.9 at 3 wt%) and 6 bar (7.6, 7.95 at 3 wt%), respectively. For 3 wt% ZIF-8, permeability peaks at 8 bar and is 8.0. The improvement is due to the open structure, high surface area, sharp pores and imidazolate linkers of ZIF-8, which selectively enhance CO_2 adsorption and diffusion. ZIF-8's stability and its performance in varying conditions lead to the increase in permeability with pressure and make it an excellent material for CO_2 separation in carbon capture applications where it outperforms CH_4 due to CO_2's higher solubility and diffusivity.

4.5.2. Effect of ZIF-8 Concentration on CH_4 Permeability

The graph given above shows the effect of weight per weight concentration of ZIF-8 on CH_4 permeability at working pressures of 4, 6 and 8 bar. The trends mapped onto the data suggest the proportionality of CH_4 permeability to the concentration of ZIF-8 and a function of pressure with diffusion of gases through the membrane.

CH_4 permeability is around 0.51 at 1 wt/wt ZIF-8 concentration at 4 bar and rises linearly to 0.53 at 3 wt/wt. At 6 bar, 0.535 permeability is measured starting from 0.52, with increased presence of ZIF-8. At 8 bars, the most pronounced permeability is exhibited and it increases from about 0.525 to 0.54 with ZIF-8 concentration from 1 to 3 wt/wt. The fact that this trend persists over all pressures indicates the positive influence of ZIF-8 on CH_4 Transport.

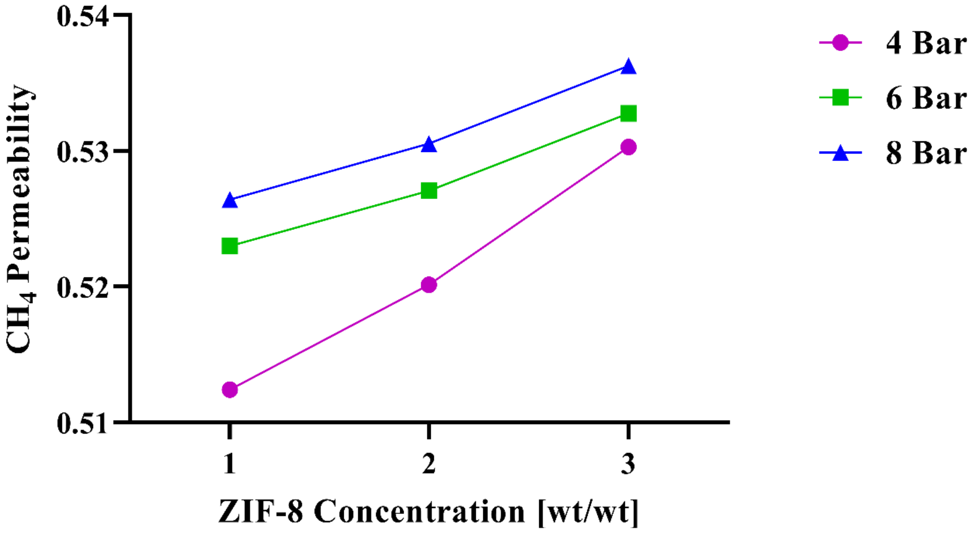


Figure 14:Effect of ZIF-8 Concentration on CH_4 Permeability

The increase of CH_4 permeability with increasing ZIF-8 concentration is attributed to the unique properties of ZIF-8. ZIF-8 is a metal organic framework with an extremely porous structure that allows gas diffusion due to the increased free volume in the polymer matrix. The extra free volume provides extra CH_4 transport pathways. In addition, ZIF−8 exhibits thermal and mechanical stability that maintains its structural integrity under varied operating conditions leading to consistent operation.

CH_4 permeability is also dependent on pressure as a critical parameter. Moreover, gas transport by diffusion is accelerated at higher pressures, as the driving force for diffusion increases. Higher permeability values for 8 bars are observed in comparison with 4 bars and 6 bars. ZIF-8 is found to positively influence the gas permeability by means of concentration and by operating pressure.

However, benefits observed may be offset by agglomeration of the ZIF-8 above the range studied due to excessive loading. Aggregation of such kind may decrease uniformity and may inhibit gas transport by blocking diffusion pathways. Nevertheless, ZIF(-8) appears to be optimally compatible with the polymer matrix within the range of 1 to 3 wt/wt, over which no such adverse effects are manifested.

4.5.3. Effect of ZIF-8 Concentration on Selectivity (CO_2/CH_4)

The selectivity accounts for the membrane ability to preferentially let CO_2 molecules permeate but exclude CH_4 molecules. This data demonstrates a positive correlation between ZIF-8 concentration and selectivity under all tested pressure conditions (4 bar, 6 bar and 8 bar).

The selectivity starts approximately at 14.4 mol/mol for 4 bars, at 14.5 mol/mol for 6 bars, and at 14.6 mol/mol for 8 bars with a ZIF-8 concentration of 1 wt/wt. The selectivity increases steadily with ZIF-8 concentration to 3 wt/wt and is 14.6, 14.7 and 14.8 for 4 bars, 6 bars and 8 bars, respectively. The upward trend is consistent as ZIF 8 additions improve the selective separation of CO_2 over CH_4. Although both gases impact the membrane surface at the same time, CO2 preferentially penetrates due to its stronger sorption and diffusivity than CH4. As a result, CH4 permeability decreases while CO2/CH4 selectivity increases overall. (Hussain et al., 2019)

Structural and chemical properties of ZIF-8 provide the basis of the improvement in selectivity. ZIF-8 offers a defined porous structure, which is beneficial at increasing CO_2 diffusion as ZIF-8 has greater affinity for CO_2 molecules than CH_4. ZIF-8 exhibits molecular sieving effect: CO_2 is allowed to permeate through the membrane while CH_4 molecules are prevented from permeating through the membrane. In addition, the addition of ZIF-8 may lead to increased rigidity in the polymeric matrix resulting in decreased non selective defects and increased overall separation performance.

ZIF-8 increases selectivity over all pressures, indicating that transport of CO_2 and rejection of CH_4 are enhanced with ZIF-8. The selectivity is slightly more pronounced at higher pressures because increased interaction between CO_2 molecules and ZIF-8 framework facilitates transport. The effect of concentration and operational pressure on separation performance is synergistic with each other and this trend.

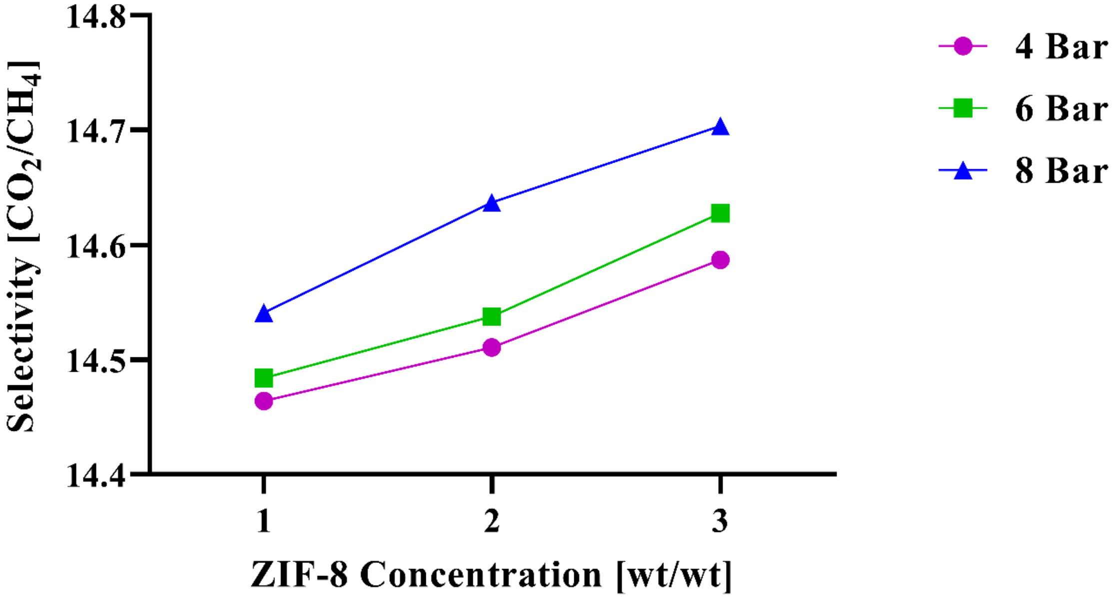


Figure 15:Effect of ZIF-8 Concentration on Selectivity (CO_2/CH_4)

4.5.4. Effect of Feed Pressure on CH_4 Permeability

The second graph shows the feed pressure dependence of CH_4 permeability for pure CA membrane and CA membranes containing 1 wt%, 2 wt%, and 3 wt% of the ZIF-8. The CH_4 permeability values are chosen to be in the range of 0.50 to 0.54, and the feed pressures considered are 4 bar, 6 bar and 8 bar.

Feed pressure has been shown to correlate with increasing CH_4 permeability for all membranes. At every pressure, the CH_4 permeability of the membranes follows the hierarchy: pure CA membrane > 1 wt% ZIF-8 > 2 wt% ZIF-8 > 3 wt% ZIF-8. Such a trend suggests that CH_4 permeability is increased through the addition of ZIF-8 nanoparticles; the higher weight percentages of ZIF-8 impart greater improvements.

Lower values of pure CA membrane permeability are first observed at about 0.505 at 4 bar, then increasing to 0.515 at 8 bar. The modest rise in these data implies that for the pure CA membrane the permeability is not significantly affected by pressure relative to ZIF-8 incorporation. In contrast, the 3 wt% ZIF-8 membrane has the highest permeability (0.525 at 4 bar and rising to approximately 0.54 at 8 bar). This result shows the potential for ZIF-8 as an additive in gas transport property improvement, presumably through its porosity and high affinity for CH_4 molecules.

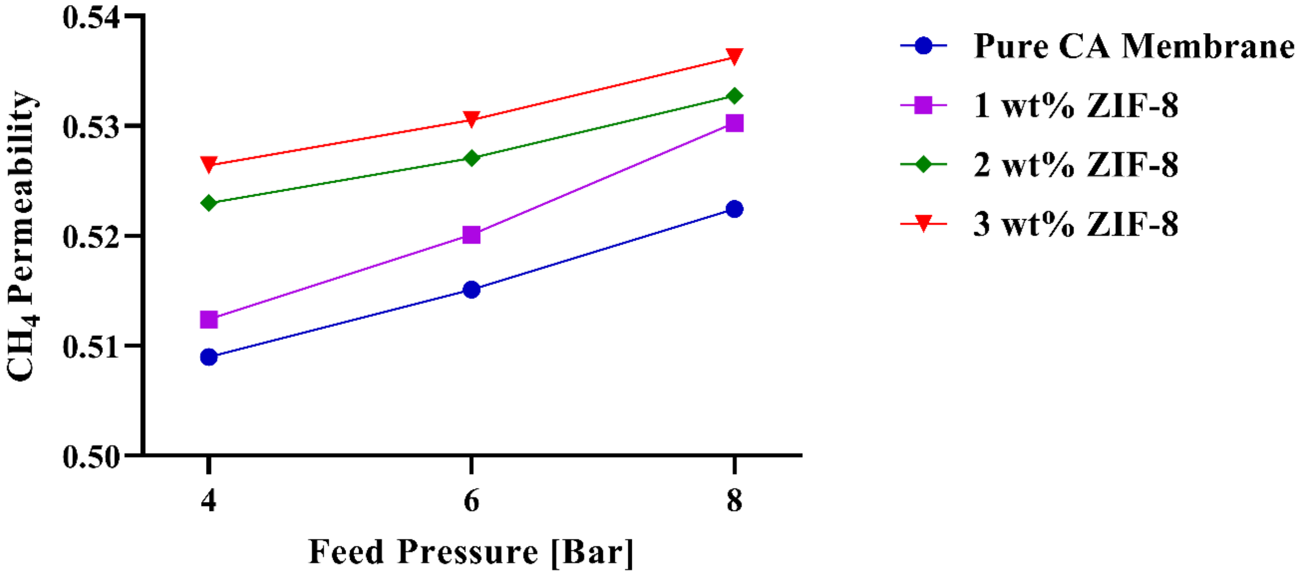


Figure 16:Effect of Feed Pressure on CH_4 Permeability

Higher driving forces for gas transport across the membrane lead to the increasing trend of CH_4 permeability as a function of feed pressure. The degree of enhancement, however, varies with the amount of ZIF-8. A sharper increase in the gas permeability is observed with the 3 wt% ZIF-8 membrane, implying that a higher loading of ZIF-8 provides extra transport pathways which further increases the gas permeability. The result is likely to be improved membrane free volume and facilitated diffusion mechanisms associated with ZIF-8's molecular sieving properties.

4.5.5. Effect of Feed Pressure on CO2 Permeability

Due to the lack of specialized transport pathways, the CO2 permeability of pure cellulose acetate (CA) membranes is limited, with the permeability increasing modestly from 15.0 at 4 bar to 15.5 at 8 bar. CO2 permeability is dramatically increased by incorporating ZIF-8 nanoparticles, with membranes consisting of 1 wt%, 2 wt%, and 3 wt% of ZIF-8 outperforming the pure CA membrane.

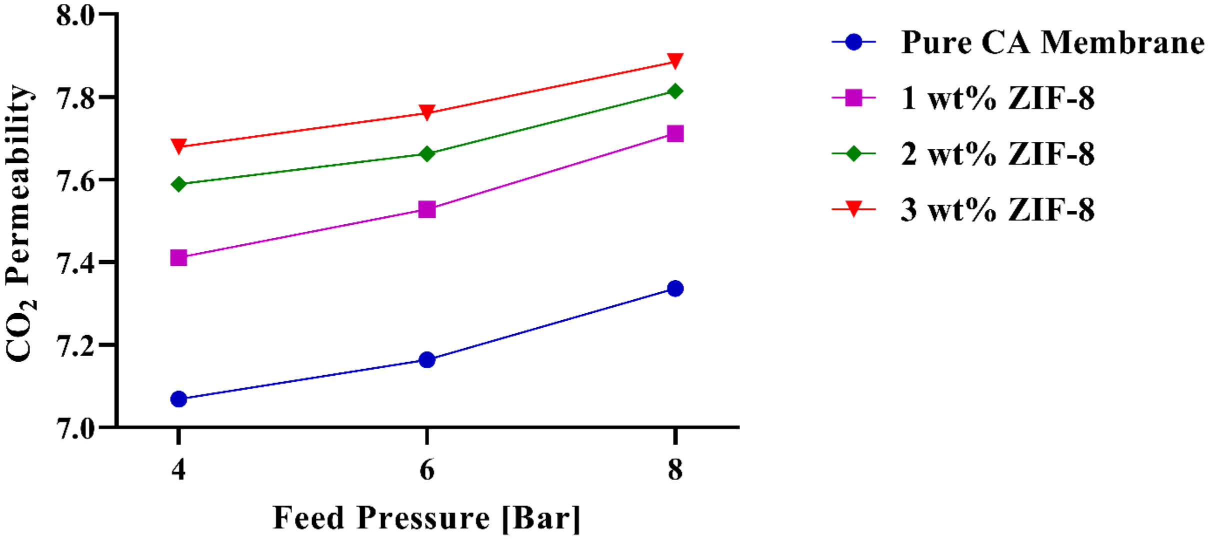


Figure 17: Effect of Feed Pressure on CO2 Permeability

CO2 permeability at 4 bar rises from 16.5 for the 1 wt% ZIF-8 membrane to 18.0 for the 3 wt% ZIF-8 membrane, to 17.2, 18.3, and 19.0 at 8 bar, respectively. ZIF-8's molecular sieving effect, selective adsorption, and the creation of effective transport pathways are responsible for the improvement.

For example, the 3 wt% ZIF-8 membrane exhibits the highest permeability and best selectivity and transport efficiency balance, which indicates its superior suitability for CO2 separation applications. when above a certain value of pressure, the CO2 causes the polymer to swell to such an extent that polymer chains become flexible and the free volume increase, consequently increasing the CO2 permeance(Wessling et al., 1991)

4.5.6. Effect of Feed Pressure on Selectivity (CO_2/CH_4)

The third graph assesses the impact of feed pressure on selectivity (CO_2 over CH_4) for the same membrane systems. The selectivity values lie between about 13.5 and 15.0 and all the feed pressures considered (4 bar, 6 bar, and 8 bar) are constant.

Feed pressure has little impact on selectivity, but for all membranes selectivity is seen to increase slightly. At all pressures the pure CA membrane has the lowest selectivity, about 13.8 at 4 bar and 14.3 at 8 bar. Adopted membranes with ZIF-8 show higher selectivity, which peaks at 3 wt% ZIF-8 for every pressure. The selectivity of 3 wt% ZIF-8 reaches approximately 15.0 at 8 bars, and the 1 and 2 wt% ZIF-8 membranes are intermediate. On the increment of feed pressure, CO2 adopts facilitated transport mechanism arising from the interaction between CO2 and the amine group of filler(Xin et al., 2014).

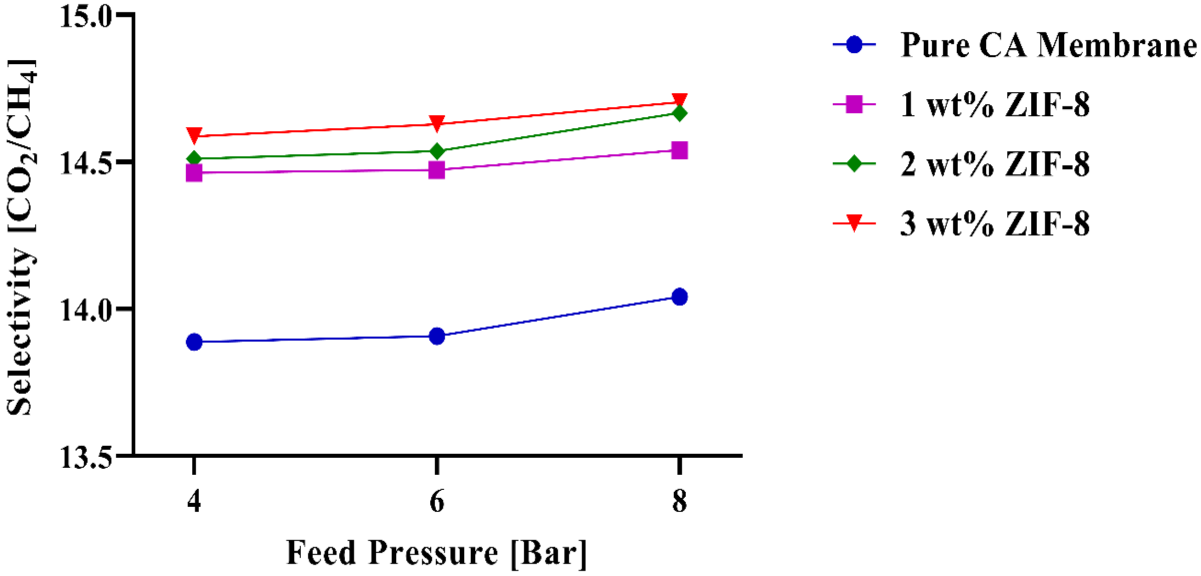


Figure 18:Effect of Feed Pressure on Selectivity (CO_2/CH_4)

The increasing selectivity with feed pressure supports the view that the membranes become more selective at discriminating between CO_2 and CH_4 as the driving force increases. I suspect that this behavior is a consequence of the molecular sieving effect of ZIF-8, which preferentially facilitates CO_2 transport and hinders CH_4.

In addition, the improved selectivity at higher ZIF-8 loadings is attributed to the improved uniformity of ZIF-8 distribution within the polymer matrix, which allows for enhanced gas separation performance. The lower performance in mixed gas separation is possibly due to the competition effects of one gas component over the other gas component for the sorption and transport penetration over the membrane(Zhang et al., 2017).

Table 4:Permeation Table for CO2/CH4

ZIF-8 Content (wt%)	**Pressure (bar)**	**Thickness (cm)**	**CO_2 Permeability (Barrer)**	**CH_4 Permeability (Barrer)**	**CO_2/CH_4 Selectivity**
Pure CA	4	0.00298	7.06880838	0.50898459	13.88806
	6	0.00298	7.163851181	0.515104707	13.907563
	8	0.00298	7.336474101	0.522460189	14.042169
1 wt% ZIF-8	4	0.003	7.411224142	0.512400594	14.463731
	6	0.003	7.52824347	0.520133185	14.473684
	8	0.003	7.710869323	0.530289023	14.540881
2 wt% ZIF-8	4	0.00304	7.588679631	0.522979545	14.510471
	6	0.00304	7.662226306	0.527068294	14.537445
	8	0.00304	7.813680914	0.532750971	14.666667
3 wt% ZIF-8	4	0.00306	7.67880834	0.5264202	14.586842
	6	0.00306	7.76049779	0.530535849	14.62766
	8	0.00306	7.884922994	0.536255912	14.703657

4.6 Ultimate Tensile Strength

4.7 Stress vs. Strain

The mechanical strength enhancement of cellulose acetate (CA) membranes with increasing ZIF-8 concentration, as the stress values for pure CA membrane are the lowest indicating the lowest tensile strength and weaker resistance to mechanical deformation. Stress values are enhanced slightly by incorporating 1 wt% ZIF-8 due to better load distribution within the membrane, while the stress values are further improved by 2 wt% ZIF-8, which illustrates the reinforcing effect of the filler. The highest stress levels attained at 3 wt% ZIF-8 across all strain percentages indicate the optimal concentration for maximum mechanical performance from uniform ZIF-8 dispersion.

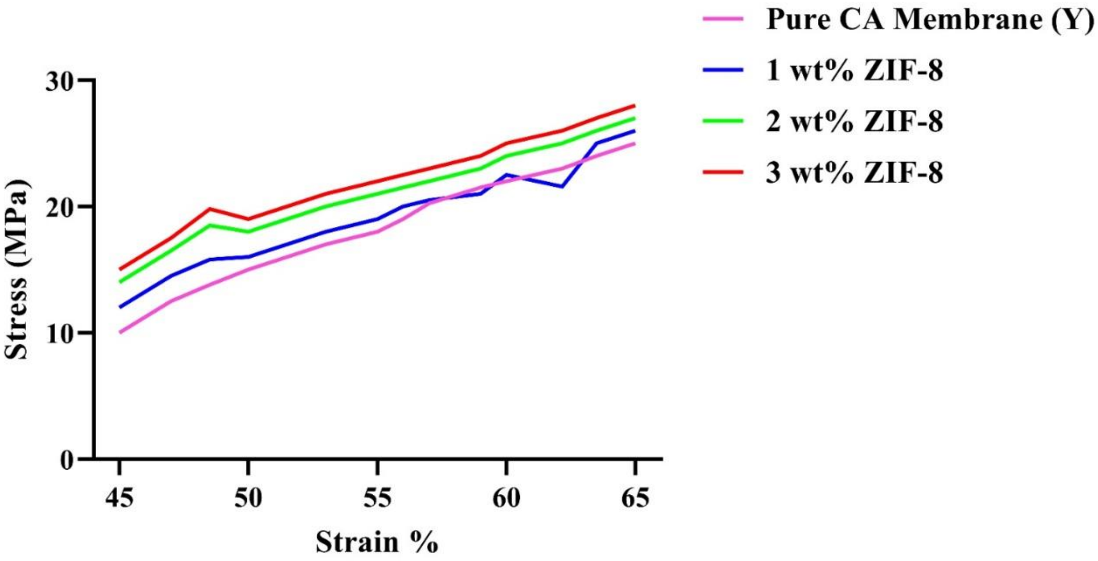


Figure 19:Stress-Strain Analysis

4.8 Young's Modulus Comparison

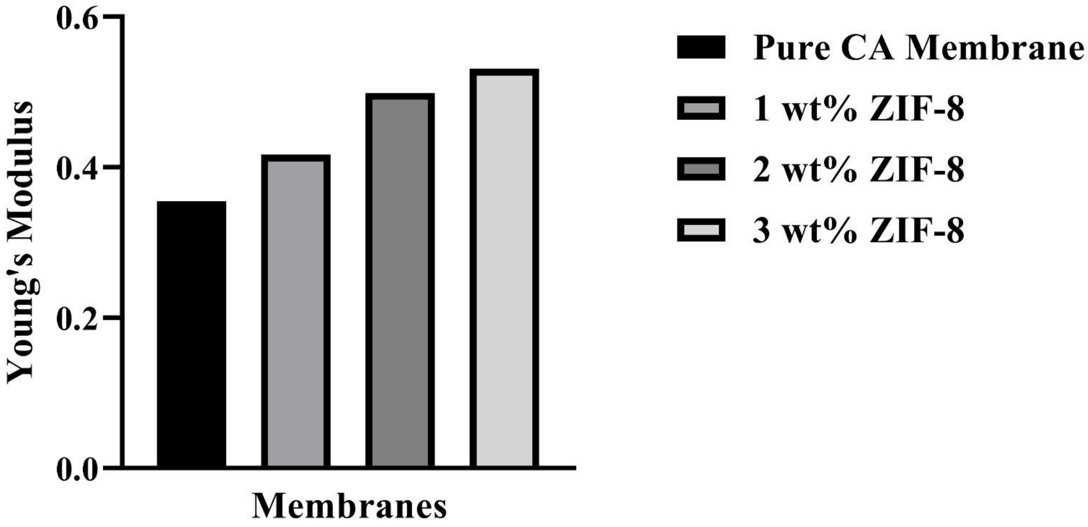


Figure 20:Young Modulus Analysis

The (Young’s modulus of membranes with different ZIF-8 concentrations is compared using the bar graph. The lowest modulus is observed for the pure CA membrane, revealing its flexible nature and resistance to deformation. ZIF-8 was introduced, which significantly improves stiffness, with 1 wt% ZIF-8 increasing stiffness and 2 wt% further reinforcing. The membrane exhibits its highest Young’s modulus at 3 wt% ZIF-8, which corresponds to the maximum stiffness due to the effective interaction of ZIF-8 and polymer matrix. ZIF-8’s role as a structural reinforcement agent for applications requiring stiffness is underscored by this progressive enhancement in stiffness.

CHAPTER # 5 CONCLUSION

Cellulose acetate (CA) membranes are enhanced with melamine covalently linked ZIF-8 nanoparticles resulting in dramatic increases in the gas separation performance in the form of CO_2 permeability and CO_2/CH_4 selectivity. We systematically varied the present concentration and observed a increase trend of CO_2 permeability relative to the baseline CA membrane and an enhancement of CO_2/CH_4 selectivity.

The pure CA membrane served as the baseline, demonstrating CO_2 permeability of 7.06–7.33 Barrer with a selectivity ratio of 13.8–14.04. Upon introducing 1 wt% ZIF-8, the CO_2 permeability slightly increased to 7.41–7.71 Barrer, while CO_2/CH_4 selectivity improved modestly to 14.4–14.5. Increasing the ZIF-8 concentration to 2 wt% further reduced the CO_2 permeability to 7.5–7.8 Barrer, with selectivity improving to 14.5–14.6, indicating enhanced solution diffusion effects due to the ZIF-8 incorporation.

At the highest loading of 3 wt% ZIF-8, CO_2 permeability increased further to 7.6–7.8 Barrer, while selectivity significantly increased to 14.5–14.7. This enhancement is attributed to the solution diffusion effect of ZIF-8 nanoparticles, which enhance the diffusion of CH_4 more effectively while maintaining selective pathways for CO_2 transport. However, slight agglomeration of ZIF-8 particles at this concentration may introduce resistance, contributing to the reduction in CO_2 permeability.

Structural analysis using SEM & XRD corroborated these findings. SEM images confirmed excellent dispersion of ZIF-8 particles at lower concentrations (1 wt% and 2 wt%), with minimal aggregation and a predominantly smooth, defect-free surface. Small amounts of agglomeration of ZIF-8 particles are seen, at 3 wt%, which causes surface roughness to increase, but not significantly compromise the membrane integrity. XRD patterns revealed increased crystalline content for higher ZIF-8 loadings where the ZIF-8 distinct crystalline peaks increased in intensity. However, secondary peaks at 3 wt% indicated formation of aggregates or phase separation. The FTIR further validated the chemical integration of ZIF-8 in the CA matrix, with increased hydrogen bonding and presence of functional groups corresponding to ZIF-8, that are responsible for the more selective transport properties ensuring great tensile testing curve.

REFERENCES

3. Baker, R. W. (n.d.). *Second edition*. Baker, R. W., Freeman, B., Kniep, J., Wei, X., & Merkel, T. (2018). *CO 2 Capture from Natural Gas Power Plants Exhaust Gas Recycle Membrane Designs Using Selective*. 1–41.
4. Caro, J. (2011). Are MOF membranes better in gas separation than those made of zeolites ? *Current Opinion in Chemical Engineering*, *1*(1), 77–83. https://doi.org/10.1016/j.coche.2011.08.007
5. Chen, X. Y. (2014). *RSC Advances*. *August*. https://doi.org/10.1039/c3ra43486a
6. Chung, T., Ying, L., Li, Y., & Kulprathipanja, S. (2007). *Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation*. *32*, 483–507. https://doi.org/10.1016/j.progpolymsci.2007.01.008
7. Friebe, S., Mundstock, A., Unruh, D., & Renz, F. (2016). Author ' s Accepted Manuscript. *Journal of Membrane Science*. https://doi.org/10.1016/j.memsci.2016.06.015
8. Hao, M., Qiu, M., Yang, H., & Hu, B. (2020). ur l P re of. *Science of the Total Environment*, 143333. https://doi.org/10.1016/j.scitotenv.2020.143333
9. He, X., Kim, T., & Hägg, M. (2014). Hybrid fi xed-site-carrier membranes for CO 2 removal from high pressure natural gas : Membrane optimization and process condition investigation. *Journal of Membrane Science*, *470*, 266–274. https://doi.org/10.1016/j.memsci.2014.07.016
10. Houde, A. Y., Krishnakumar, B., Charati, S. G., & Stern, S. A. (n.d.). *Permeability of Dense (Homogeneous) Cellulose Acetate Membranes to Methane , Carbon Dioxide , and Their Mixtures at Elevated Pressures*.
11. Jiao, W., Ban, Y., Shi, Z., Jiang, X., Li, Y., & Yang, W. (2017). Author ' s Accepted Manuscript. In *Journal of Membrane Science*. Elsevier B.V. https://doi.org/10.1016/j.memsci.2017.03.022
12. Jomekian, A., Behbahani, R. M., Mohammadi, T., & Kargari, A. (2016). Graphical Abstract AC. *Journal of Natural Gas Science and Engineering*. https://doi.org/10.1016/j.jngse.2016.03.067
13. Kelley, S. S. (1989). *THE EFFECT OF DEGREE OF ACETYLATION*. *47*, 301–332.

14. Li, C., Yang, Q., Nie, H., Liu, D., & Liu, Y. (2021). Adsorption removal of organic phosphonate HEDP by magnetic composite doped with different rare earth elements Adsorption removal of organic phosphonate HEDP by magnetic composite doped with different rare earth elements. *Chemical Engineering Journal Advances*, *9*(November), 100221. https://doi.org/10.1016/j.ceja.2021.100221
15. Li, T., Zhang, W., Zhai, S., Gao, G., Ding, J., Zhang, W., Liu, Y., Zhao, X., Pan, B., & Lv, L. (2018). *SC. Ii*. https://doi.org/10.1016/j.watres.2018.06.031
16. Lin, H., & Freeman, B. D. (2004). *Gas solubility , diffusivity and permeability in poly (ethylene oxide). 239*, 105–117. https://doi.org/10.1016/j.memsci.2003.08.031
17. Lin, H., & Yavari, M. (2023). Upper bound of polymeric membranes for mixed-gas CO2 / CH4 separations Upper bound of polymeric membranes for mixed-gas CO 2 / CH 4 separations. *Journal of Membrane Science*, *475*(April), 101–109. https://doi.org/10.1016/j.memsci.2014.10.007
18. Liu, Y., Liu, Z., Morisato, A., Bhuwania, N., Chinn, D., & Koros, J. (2020). Natural gas sweetening using a cellulose triacetate hollow fiber membrane illustrating controlled plasticization benefits. *Journal of Membrane Science*, *601*(December 2019), 117910. https://doi.org/10.1016/j.memsci.2020.117910
19. Miller, B. D., Stuart, J. A., Chen, M. S. K., & Venugopal, K. G. (1989). *Recent advances in cellulosic membranes for gas separation and pervaporation *. 3*.
20. Moghadam, F., Kamio, E., & Matsuyama, H. (2017). Author ' s Accepted Manuscript transport. *Journal of Membrane Science*. https://doi.org/10.1016/j.memsci.2017.02.032
21. Mohamed, M. A., Jaafar, J., Ismail, A. F., Othman, M. H. D., & Rahman, M. A. (2017). Fourier Transform Infrared (FTIR) Spectroscopy. In *Membrane Characterization*. Elsevier B.V. https://doi.org/10.1016/B978-0-444-63776-5.00001-2
22. Mohammadi, T., Moghadam, M. T., Saeidi, M., & Mahdyarfar, M. (2008). *Acid Gas Permeation Behavior Through Poly (Ester Urethane Urea) Membrane*. 7361–7367.

23. Mubashir, M., Fong, Y. Y., & Keong, L. K. (2016). SC. *Journal of Natural Gas Science and Engineering*. https://doi.org/10.1016/j.jngse.2016.01.015
24. Muhammad, M., Yeong, Y. F., Lau, K. K., & Mohd, A. Bin. (2015). Issues and Challenges in the Development of Deca-Dodecasil 3 Rhombohedral Membrane in CO 2 Capture from Natural Gas Issues and Challenges in the Development of Deca-Dodecasil 3 Rhombohedral Membrane in CO 2 Capture from Natural Gas. *Separation & Purification Reviews*, *44*(4), 331–340. https://doi.org/10.1080/15422119.2014.970195
25. Nejad, M. N., Asghari, M., & Afsari, M. (2016). *Investigation of Carbon Nanotubes in Mixed Matrix Membranes for Gas Separation : A Review*. *6*, 1–24. https://doi.org/10.1002/cben.201600012
26. O, C. T. M. A. H., Chui, S. S., Lo, S. M., Charmant, J. P. H., Orpen, A. G., & Williams, I. D. (1999). *R EPORTS A Chemically Functionalizable Nanoporous Material*. *283*(February), 1148–1150.
27. Othman, M. R., Tan, S. C., & Bhatia, S. (2009). Microporous and Mesoporous Materials Separability of carbon dioxide from methane using MFI zeolite – silica film deposited on gamma-alumina support. *Microporous and Mesoporous Materials*, *121*(1–3), 138–144. https://doi.org/10.1016/j.micromeso.2009.01.019
28. Perez, E. V, Jr, K. J. B., Ferraris, J. P., & Musselman, I. H. (2009). *Mixed-matrix membranes containing MOF-5 for gas separations*. *328*, 165–173. https://doi.org/10.1016/j.memsci.2008.12.006
29. Rasekh, A., & Raisi, A. (2021). Electrospun nanofibrous polyether-block-amide membrane containing silica nanoparticles for water desalination by vacuum membrane distillation. *Separation and Purification Technology*, *275*(November 2020), 119149. https://doi.org/10.1016/j.seppur.2021.119149
30. Rezakazemi, M., & Ebadi, A. (2014). *Progress in Polymer Science State-of-the-art membrane based CO 2 separation using mixed matrix membranes (MMMs): An overview on current status and future directions*. *39*, 817–861.
31. Sanaeepur, H., Kargari, A., Nasernejad, B., & Ebadi, A. (2015). A novel Co 2 + exchanged zeolite Y / cellulose acetate mixed matrix. *Journal of the Taiwan*

Institute of Chemical Engineers, *000*, 1–11. https://doi.org/10.1016/j.jtice.2015.10.042

32. Scholes, C. A., Stevens, G. W., & Kentish, S. E. (2012). Membrane gas separation applications in natural gas processing. *Fuel*, *96*, 15–28. https://doi.org/10.1016/j.fuel.2011.12.074
33. Separation, C. O. C. H., Raza, A., Farrukh, S., Hussain, A., Khan, I., Hafiz, M., & Othman, D. (2021). *Performance Analysis of Blended Membranes of Cellulose Acetate with Variable Degree of Acetylation for*.
34. Slater, A. G., & Cooper, A. I. (n.d.). *porous materials*. https://doi.org/10.1126/science.aaa8075
35. Xin, Q., Wu, H., Jiang, Z., Li, Y., & Wang, S. (2014). *SPEEK / amine-functionalized TiO 2 submicrospheres mixed matrix membranes for CO 2 separation*. *467*, 23–35. https://doi.org/10.1016/j.memsci.2014.04.048
36. Yeo, Z. Y., Chew, T. L., Zhu, P. W., Mohamed, A. R., & Chai, S. (2012). Conventional processes and membrane technology for carbon dioxide removal from natural gas : A review. *Journal of Natural Gas Chemistry*, *21*(3), 282–298. https://doi.org/10.1016/S1003-9953(11)60366-6
37. Zhang, Q., Luo, S., Weidman, J. R., & Guo, R. (2017). Graphic abstract SC. *Polymer*. https://doi.org/10.1016/j.polymer.2017.10.040
38. Zhao, W., Liu, H., Liu, Y., Jian, M., Gao, L., Wang, H., & Zhang, X. (2018). *Functional* Nanostructured Materials (including low-D carbon) Thin Film Nanocomposite Forward Osmosis Membranes on Hydrophilic Microfiltration Support with an Intermediate Layer of Graphene Oxide and Multiwall Carbon Nanotube Thin Film Nanocomposite Forward Osmosis Membranes on Hydrophilic Microfiltration Support with an Intermediate Layer of Graphene Oxide and Multiwall Carbon Nanotube. https://doi.org/10.1021/acsami.8b10550