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**SYNTHESIS AND CHARACTERIZATION OF POLYETHER-ETHER KETONE
SUPPORTED TpPa-1 COVALENT ORGANIC FRAMEWORK MEMBRANE FOR
ORGANIC SOLVENT NANOFILTRATION**

by

Rahul Sampat Khandge

A Thesis Submitted in
Partial Fulfilment of the
Requirements of the Degree of

Master of Science

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The University of Wisconsin-Milwaukee

December 2021

ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF POLYETHER-ETHER KETONE SUPPORTED TpPa-1 COVALENT ORGANIC FRAMEWORK MEMBRANE FOR ORGANIC SOLVENT NANOFILTRATION

by

Rahul Sampat Khandge

The University of Wisconsin-Milwaukee, 2021
Under the Supervision of Professor Xiaoli Ma

There is a lot of potential for energy-efficient separation in membranes made up of covalent organic frameworks (COF). It has been reported that COFs are able to separate dyes, salts, bacteria, and nanoparticles based on size-selective transport through ordered pore structure. They have recently emerged as promising membranes for separations involving organic liquids. In the last decade, organic solvent nanofiltration (OSN) has received a lot of attention since it is an energy- and waste-efficient method for separating mixtures down to the molecular level. Although the number of OSN publications has increased in recent years, there is a need to search for new membrane materials with a combination of excellent solvent stability and adequate separation performances. In this work, continuous TpPa-1 COF membranes were synthesized on polyether ether ketone (PEEK) supports via the interfacial polymerization (IP) method, in a similar way to the standard IP process used for the synthesis of polyamide (PA) membranes. A conformal TpPa-1 COF membrane was formed on the porous substrate within a minute owing to the fast reaction between amine and aldehyde monomers, which were dissolved in the aqueous and organic solutions, respectively. The separation performances of the TpPa-1 membranes were evaluated in water and organic solvent systems with ethanol as the polar organic solvent and with dye molecules as the model solutes. Anionic dyes such as methyl blue and fast green (FG) dye molecules were rejected at

a rate of 95% with a permeance of $229.88 \text{ L m}^{-2}\text{hr}^{-1}\text{bar}^{-1}$ and 86.55% with a permeance of $48 \text{ L m}^{-2}\text{hr}^{-1}\text{bar}^{-1}$ for aqueous system. The molecular weight cut off (MWCO) of the membranes for OSN in the ethanol system was $\sim 780 \text{ g} \cdot \text{mol}^{-1}$. The rejection mechanism of TpPa-1 COF membrane in the polar solvent has also been discussed. Moreover, solvothermal synthesis was used to synthesize TpPa-1 COF powder, and their structural stability was examined using polar and nonpolar solvents. Covalent organic framework materials along with highly stable polyether ether ketone substrate appear to have great potential for OSN applications.

Keywords: Covalent organic Framework (COF), Polyether Ether Ketone Substrate, Organic Solvent stability of COF, Organic Solvent Nanofiltration.

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Dedication
to
my late Mother and Brother,
Dad and my love.

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STRUCTURE OF THESIS

This thesis report results from a study of Organic Solvent Nanofiltration (OSN) using TpPa-1 Covalent Organic Framework selective layer synthesized on Polyether ether ketone (PEEK) substrate for a range of solvents that are polar-aprotic as well polar protic behaviour and reports rejection of various solutes in organic solvents.

Chapter I- Describes the structure of the thesis and the aims and objectives of the work. This chapter also includes an overview of nanofiltration (NF) and comparisons with Ultrafiltration (UF) and Reverse Osmosis (RO), their operating regimes, and the use of solvent resistant nanofiltration for aqueous and non-aqueous separations in applications such as petrochemical, pharmaceutical, wastewater treatment applications, etc.

Chapter II- The numerous types of membranes/substrates available for Organic Solvent Nanofiltration are explained. Discussion of the many polymeric materials that can create various selective layers. Nanoporous materials, a unique and forthcoming material for membrane technology, are also discussed in this chapter.

Chapter III- The experimental setup is described, including chemicals, COF-1 powder/membrane preparation and synthesis, and experiment designs.

Chapter IV- This section of the paper discusses the numerous characterization methods employed in this study and the results and discussion section.

Chapter V- The investigation comes to an end in this section, which also outlines future experimental that should be investigated.

CHAPTER I

1.1 Background

The elements of modern membrane science were developed in 1960, but membranes were used in small and specialized industrial applications. Four critical problems prevented their widespread use as a separation process: unreliable, sluggish, non-selective, and costly. In the chemical industry, the separation and purification of molecular mixtures into pure components is of crucial importance, and so far, a variety of practical techniques have been developed. A membrane is a thin barrier that enables selective mass transport. Membranes can be made from a wide variety of organic (e.g., polymers, liquids) or inorganic (e.g., carbons, zeolites, etc.) materials [1]. Membranes can regulate the rate of permeation of a chemical substance moving through. It allows the specific chemical material from one solution to be separated by membrane technology. Membrane technology usually includes chemical synthesis, material science, advanced characterization techniques, membrane processing and alteration, module design, and process engineering. As a result, developments in membrane technology will simultaneously improve separation techniques in practical industries and promote development in related research and manufacturing industries [2]. The overwhelming majority of industrial chemical syntheses are conducted in organic solutions. Solute concentration and solvent recovery consume ~50 percent of the energy required to manufacture chemicals and pose problems that are as important as the synthesis process itself. Separation and purification processes also require phase change and, as such, are extremely energy intensive. Solvent recycling is typically used in waste generation units such as pharmaceuticals, paint lacquer, metal finishing, and automotive coatings. This recycling principle has been implemented for several decades and is a standard in the pharmaceutical industry; it is used for the economic recovery of certain solvent waste. Membrane technology has recently been widely used in the

solvent recovery process due to its improved efficiency and low energy costs. On the other hand, membrane-based separations can be performed under mild conditions, which are cheap, convenient, environmentally friendly, and space-saving.

1.2 Traditional method for Separation

In recent years, manufacturing plants have placed a greater emphasis on process energy efficiency and mass efficiency. The recovery of solvents can give substantial advantages: lower acquisition cost, storage, and disposal, greater compliance with environmental law, and decreased greenhouse gas emissions. Distillation systems are energy and power intensive processes that contribute to emissions of greenhouse gasses (e.g., carbon dioxide) [3]. The distillation process, which is an energy-intensive process of the chemical industry, is thus the first to be tackled in the short- and long-term concerning energy-saving efforts. Distillation energy usage and atmospheric CO₂ gasses have essential links. The bigger the energy requirements, the bigger the CO₂ emissions to the air. Therefore, efforts should focus on energy-saving measures and changes to decrease CO₂ emissions from distillation systems.

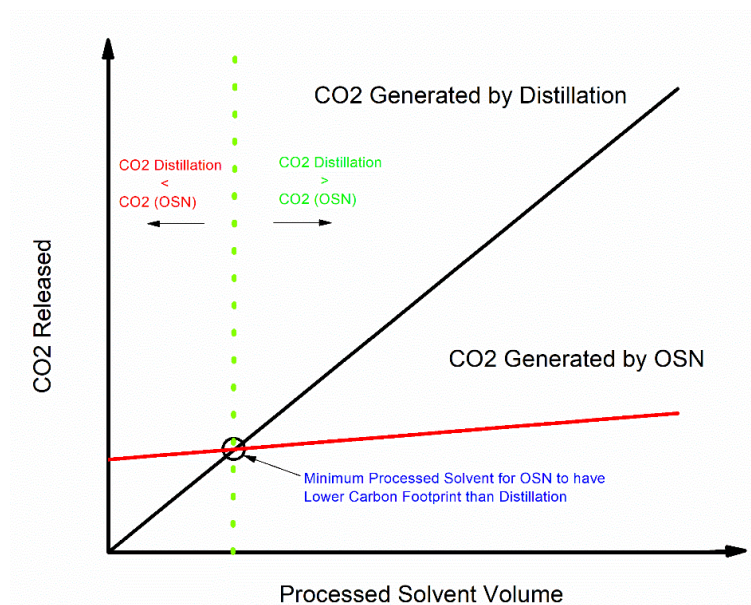


Figure 1. CO₂ production by OSN and distillation [4]

A paper by Raymond [5] reported a study done by Life cycle assessment (LCA), Life cycle assessment (also known as life cycle analysis, Eco balance, and cradle-to-grave analysis) is a strategy for evaluating environmental consequences associated with all phases of a product's life from conception to disposal (i.e., from raw material extraction through materials processing, manufacture, distribution, and use) [5]. This evaluation takes into account all steps of a process, from getting raw materials from the ground to disposing of pollutants/waste back into the earth. This provides a thorough knowledge of a process's real environmental consequences, allowing the analyst to spot issues and solutions that a single-issue approach might overlook. For example, according to the Toxic Release Inventory, the pharmaceutical industry in the United States created 88 million kg of waste in 2008. (Categorized by the US EPA as either priority pollutants or hazardous air pollutants). The top 10 solvents used in the pharmaceutical industry were responsible for 83 percent of the waste.

A life cycle assessment was performed on various common solvents, using EcoSolvent (Safety and Environmental Group, Zurich, Switzerland) and SimaPro 7.1 software packages [6]. In-process emissions were ignored to show the environmental impact of solvent use on a larger scale. These emissions were ignored in the preliminary analysis because it was assumed that no solvent would be consumed during use. In-process emissions, such as fugitive emissions and emissions from pumping, mixing, and heating, would be insignificant compared to emissions from solvent production and waste treatment. Each life cycle inventory was created based on 1 kilogram of solvent. The findings of the life cycle assessment for the manufacture of 10 frequently used organic solvents are summarized in Table 1. SimaPro 7.1R was used to calculate the cumulative energy demand (CED) for manufacturing these ten solvents. The CED is the overall energy need for a component's life cycle as specified by the analyses' life cycle limits. The mass of wastes released to air, water, or soil is defined as air, water, and soil

emissions, respectively, in Table 1. The sum of air, water, and soil emissions is the total emissions value.

Table 1. Life cycle analysis for the production of 1 kg of various organic solvents, [6].

Emission							
Solvent	Raw Kg	Air	Water	Soil	CO2 Kg	Total Kg	CED MJ-Eq
Acetone	1.53E+00	1.83E+00	2.56E-02	7.23E-07	1.80E+00	1.86E+00	6.73E+01
Acetonitrile	1.54E+00	1.97E+00	1.44E-01	6.80E-04	1.95E+00	2.12E+00	6.15E+01
Diethyl Ether	1.17E+00	1.09E+00	1.66E-02	1.95E-04	1.08E+00	1.111E+00	4.80E+01
Ethanol	1.17E+00	1.09E+00	1.66E-02	2.00E-04	1.08E+00	1.111E+00	4.80E+01
Hexane	1.59E+00	8.84E-01	1.75E-01	5.93E-03	8.55E-01	1.06E+00	6.17E+01
IPA	1.55E+00	1.66E+00	5.42E-01	3.18E-04	1.63E+00	2.20E+00	6.52E+01
MeOH	1.53E+00	6.47E-01	6.39E-03	1.27E-04	6.44E-01	6.54E-01	3.78E+01
THF	1.53E+00	5.52E+00	2.31E-03	2.31E-03	5.46E+00	5.65E+00	1.28E+02
Toluene	1.53E+00	1.21E+00	3.87E-03	3.46E-07	1.19E+00	1.21E+00	6.34E+01
Generic Solvent	1.53E+00	1.78E+00	1.22E-01	1.56E-04	1.75E+00	1.91E+00	6.51E+01

This waste might be significantly reduced by introducing an on-site solvent recovery system. A variety of separation methods can be utilized to achieve these goals, including classical distillation and more creative techniques like pervaporation and nanofiltration. For higher solvent savings, this might be paired with a move to continuous rather than batch production techniques [4].

1.3 Solution for reduction of Carbon due to Distillation

Organic solvent nanofiltration (OSN), also known as solvent-resistant nanofiltration (SRNF), is an emerging technology for the molecular separation and purification of organic substances. OSN membranes are the core component of the OSN technology, which should ensure high solvent permeability and rejection and provide strong solvent resistance. As a result, organic Solvent Nanofiltration enables size exclusion-based separations of solutes ranging from 50 to

2000 $g \cdot mol^{-1}$, solvent exchange, and solvent recovery in organic media simply by introducing a pressure gradient [7] Fig 2.

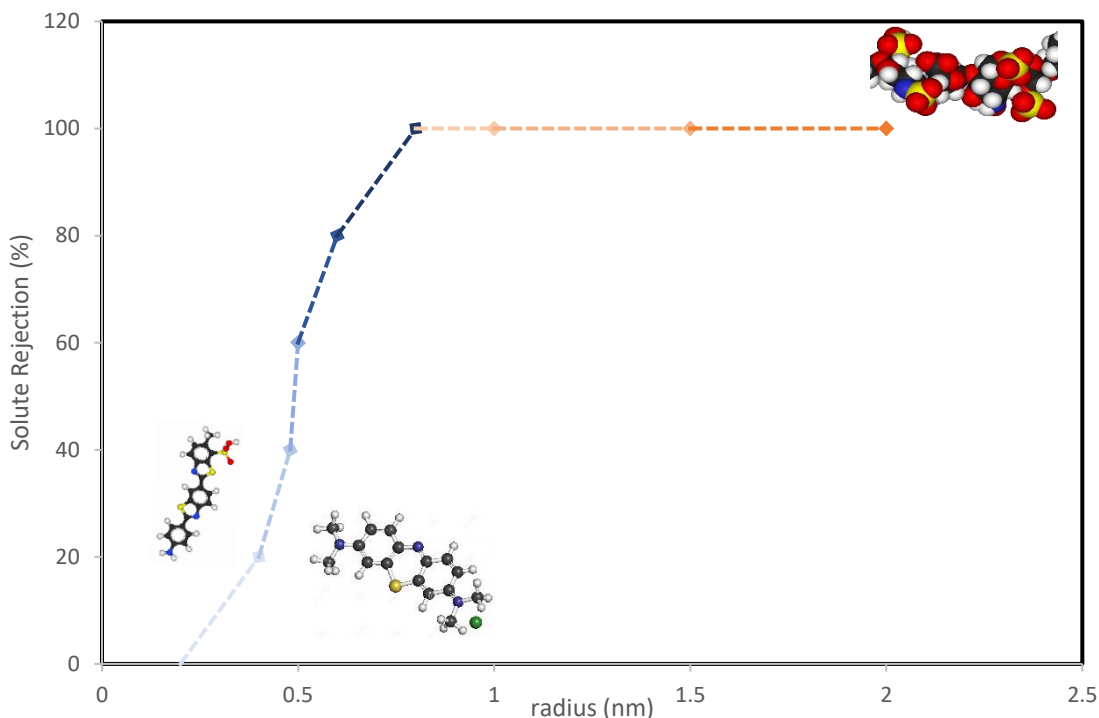


Figure 2. Solute rejection as a function of molecule size and weight for OSN.

OSN needs solvent resistance membranes with defect-free morphology and a regulated molecular weight cut-off that maintain separation properties while processing a variety of solvents. As a first step of the target product concentration, nanofiltration is sometimes used in conjunction with other separation processes (distillation, extraction, pervaporation, and others). Furthermore, organic solvent nanofiltration may be the sole option to separate thermally unstable systems in some instances (the separation of intermediates during replacement of organic solvents in the course of a multistage organic synthesis can be given as an example). While saving energy is crucial for developing sustainable processes, the more solvent is separated employing the OSN cascade, the higher the required membrane area [7]. Especially the price of OSN membranes is an uncertain parameter because only a few industrial

applications are available so far. However, due to the high potential of OSN processes for greener and more sustainable methods [6]] an increasing application in the future will likely result in improved manufacturing and reduced membrane prices.

1.4 Application of Organic Solvent Nanofiltration

Reduced energy usage and simplicity of solvent-based processes might help industries ranging from oil refining to medicines, much as reverse osmosis membranes have benefited the desalination sector.

1.4.1 Petrochemical Industry:

The inclusion of long-chain saturated hydrocarbons (paraffin) in motor oils is well-known for increasing the solidification temperature. Solvent dewaxing is one method of extracting paraffin from motor oil. This method involves chilling a motor oil solution in an organic solvent (or a combination of solvents) to -20 C to crystallize paraffin, followed by filtering via a drum filter. However, at such a low temperature, the presence of an organic solvent encourages the system's viscosity to drop. Therefore, distillation is typically used to replenish the solvent after filtering to save energy, and the cost application of Organic Solvent Nanofiltration at the stage of motor oil concentration before the distillation stage is preferred [8].

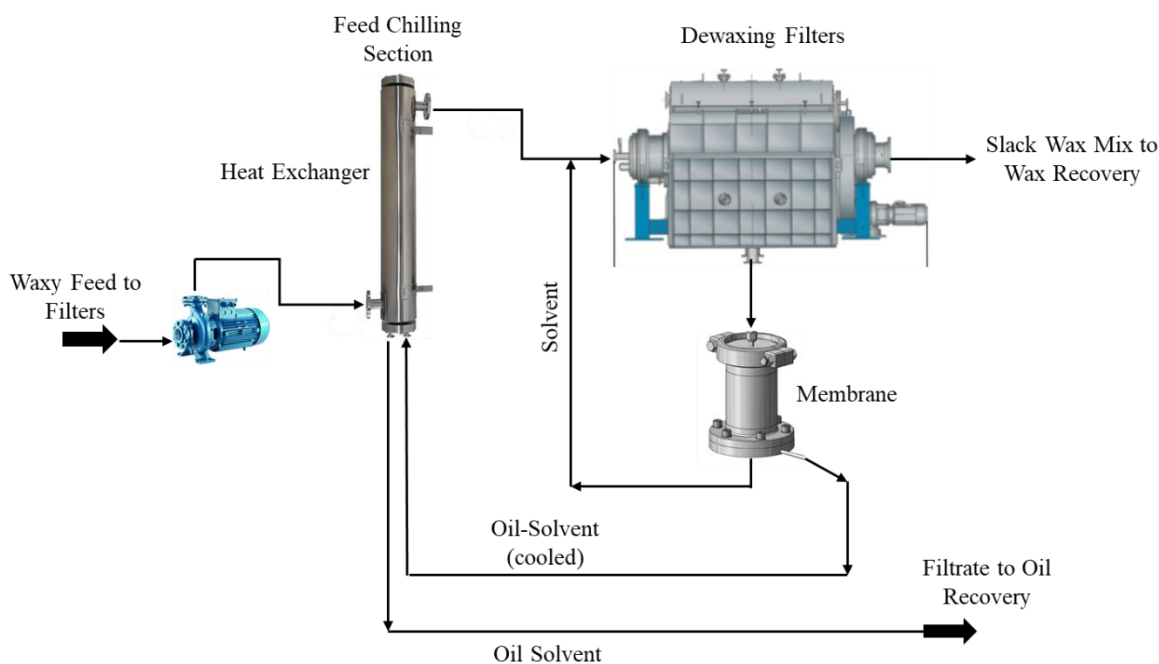


Figure 3. Cold solvent separation from lubricant oil filtrate through Membrane Technology [9]

The first development goals were to provide a membrane with a sufficient flow and a rejection of oil, recover 25% of its solvent in the filtrate with less than 300 m² of membrane from the 160-cubic meter feed/day (1000-barrel feed/day) membrane unit. As a result, energy and operational expenses and capital investment might be lower than traditional debottlenecking with a higher oil output and higher wax quality [9].

1.4.2 The Application of Nanofiltration in homogenous catalysis:

Many catalytic methods in essential organic, petrochemical, and fine organic synthesis employ transition metal complexes (Pt, Pd, Ru, Rh, and others) with organic ligands as homogeneous catalysts. Hydroformylation, hydrocarboxylation, hydrocarbalkoxylation, carbonylation, hydrogenation, alcoholises, positional isomerization of an unsaturated carbon link, hydrocyanation, hydrosilylation, and other processes involving carbon monoxide are examples of such methods. The technology of such procedures necessitates a step of product separation from a costly catalyst and a recycling stage for continuous modes, both of which are linked

with significant investments and energy costs in many situations. For example, in the oxo synthesis of butyl alcohols using a homogeneous cobalt-containing catalyst (120-160°C, 270-300 atm), the cost of the catalyst recycling stage accounts for a large portion of the total investment and operational expenses. Rhodium-containing catalytic systems that possess the high activity and selectivity and ensure mild conditions of the process (90 ± 100 °C, 15 ± 17 atm) are wholly or partially deactivated at the recycling stage [10]. The only method to organize a homogeneous catalytic process and enhance the lifespan of the metal complex catalyst is to efficiently separate the catalyst from the reaction products, reactivate, and recycle it. The challenge of homogeneous catalyst recycling is addressed in several ways [11][12][13]. Ultra- or nanofiltration can be used to separate soluble catalytic complexes. This method, however, has yet to find a commercial application.

Organic solvent nanofiltration enables the efficient retention of homogeneous catalysts, such as organometallic complexes, with 300-1200 Da molecular weights while simultaneously removing reaction products and solvent. This method has the benefit of allowing the optimized transition metal catalytic complex to be utilized without further modification. The utilization of a chemical reactor paired with a nanofiltration separation unit (fig is an efficient approach to tackle the problem of homogenous catalyst recycling without deactivation.

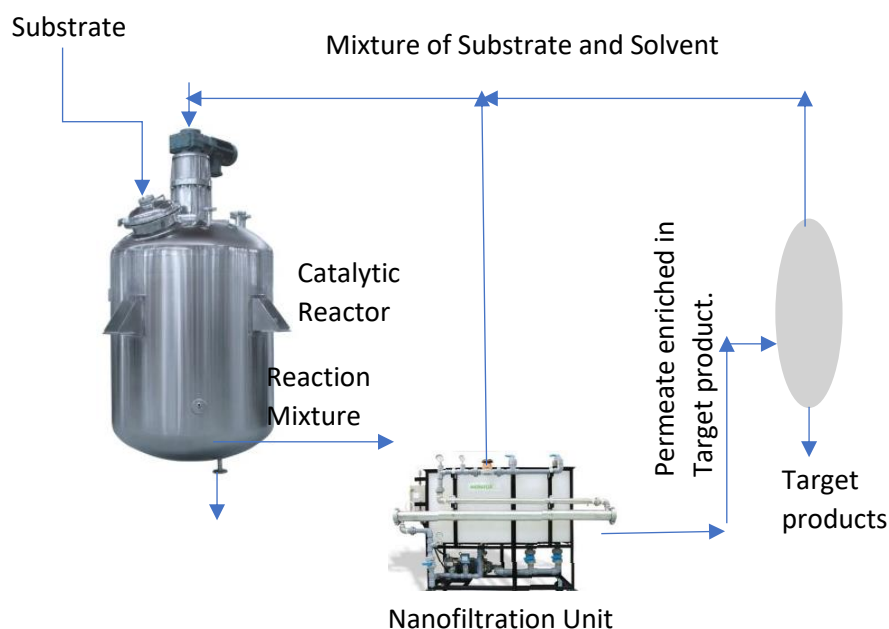


Figure 4. Catalyst Recycling from Organic Solvent

The patent literature may find several baromembrane techniques of separating homogeneous catalysts from non-aqueous fluids utilizing various polymeric membranes. Baromembrane methods were used to separate homogeneous catalysts from reaction mixtures almost half a century ago. American Oil patented a technique of membrane separation (reverse osmosis) of acid catalysts used in hydrocarbon conversion processes in 1959, utilizing hydrophobic continuous polyethylene membranes. (US P. 2913507 (1959)). British Petroleum patented an ultrafiltration technique using cellulose acetate membranes to separate transition metal (rhodium, nickel, vanadium, etc.) complexes from olefin dimerization and propylene hydroformylation products 1971. (US P. 3617553) (1971). Many other applications of using Nanofiltration membranes, such as using a membrane-based on silicon rubber ranging at a temperature of 0-200C and pressure up to 277 atm was used by British petroleum in 1974. (US P. 3645891 (1972)), E I du Pont de Nemours patented the use of asymmetric membranes based on aromatic polyamides and polyimides for the reverse osmosis separation of organ element catalysts from organic media including compounds with nitrile groups in 1974 (US P. 3853754 (1974)).

In 1993, Membrane Products Kiryat Weitzman Ltd received patents for MPF series nanofiltration membranes that are stable in organic solvents and are based on silicon rubbers [e.g., polydimethylsiloxane (PDMS)] for the isolation of various solutes from organic media, such as catalysts, organic element compounds, pigments, oils, and so on. (US P. 5205934 (1993) US P. 5265734 (1993)). The separation of homogeneous catalysts based on rhodium complexes and non-bonded organophosphorus ligands from the reaction mixture, including enantiomeric aldehydes (a patent of Union Carbide Chemicals and Plastics Technology' 22), was one of the first practical applications of such membranes. After the hydroformylation process was completed, the authors decreased the catalyst concentration in the combination of aldehydes (30%) and acetone as a solvent (70%) from 389.3 to 5.6 ppm using MPF-50

membranes in three steps. A patent (US P. 5681473 (1997) for the technique of membrane isolation of homogeneous catalysts was obtained in 1997 because of research into the same catalytic system based on rhodium complexes and a mixture to be separated with comparable composition (aldehydes in a solution of acetone or butyric aldehyde). At a pressure of 27.5 atm, the retention of a rhodium catalyst in polydimethylsiloxane membranes MPF-50 in the shape of a helical unit (unit active area 0.25 m²) is 92.8 percent, according to the patent.

Richard R. Schrock, Robert H. Grubbs, and Yves Chauvin shared the Nobel Prize for Chemistry in 2005 for their contributions to the field of metathesis research (Grubbs-type catalyst). Grubbs-type catalysts, which were created by Grubbs' research group and are well-defined, commercially accessible, homogenous ruthenium carbene complexes, are one of the major reasons for their widespread usage. Despite the benefits that Grubbs-type catalysts may provide, such as high activity and selectivity, they still have several flaws that prevent them from being widely used in industry. The difficulty in isolating these catalysts for re-use in an active state from post-reaction mixtures is a major drawback, aside from the expense. Heterogenization (using inorganic, dendrimer, and polymer supports), biphasic extraction, scavengers (such as lead tetra-acetate, DMSO, and phosphine additives), and membrane technology have all been offered as ways to overcome the disadvantage of recovering homogeneous catalysts [14].

One of the most actively developed membrane technology fields is the chemical reactor's coupling with nanofiltration separation. The effective recycling of a homogeneous catalyst allows for lower consumption and, as a result, lower end product costs. Furthermore, in the pharmaceutical sector, a considerable reduction in catalyst levels in the post-reaction mixture is critical for further purification of the end product from by-products.

1.4.3 Pharmaceutical Industry:

In the pharmaceutical manufacturing process, organic solvents are always present. The pharmaceutical sector is one of the significant users of organic solvents in terms of finished product volume. They are commonly employed at any stage of the active ingredient or excipient manufacturing route and during the medicinal product formulation process. Production techniques such as drying at a high temperature under low pressure or lyophilization cannot entirely remove organic solvents due to physical and chemical obstacles (freeze-drying). As a result, small solvents are usually left in the finished product. Residual solvents (RS), sometimes known as volatile organic impurities, are residual solvents (OVI). Manufacturers strive to reduce the quantity and volume of solvents used in medication manufacturing for toxicological reasons. Aside from the fact that they have no medicinal effect and may be harmful, they may also hasten the product's disintegration. For instance, there are directions provided by European medicine agencies; for the patient's safety, appropriate levels of residual solvents in medicines are required. It suggests the use of less hazardous solvents and specifies the toxicologically acceptable amounts of residual solvents. For many years, the United States Pharmacopoeia was the only pharmacopeia that specified limitations for residual solvents in pharmaceutical goods [15]. The ICH released its guidance for industry Q3C in December 1997, and it went into effect in March 1998. Regulatory authorities from Europe, Japan, and the United States and representatives from the research-based pharmaceutical sector developed the ICH guideline. ICH guidelines suggest that solvents are divided into three classes starting with the first class containing known human carcinogens compounds. Class II solvents ought to be limited because they are non-genotoxic animal carcinogens or substances that may cause irreversible toxicity, such as neurotoxicity or teratogenicity. They are also suspected of having other serious, reversible side effects [15].

Table 2. Class I Solvents, ICH

Solvents	Concentration Limit (ppm)	Concern
Benzene	2	Carcinogen
Carbon tetrachloride	4	Toxic and environmental hazard
1,2-Dichloroethane	5	Toxic
1,1-Dichloroethene	8	Toxic
1,1,1-Trichloroethane	1500	Environmental hazard

Table 3. Class II Solvents.

Solvent	PDE (mg/day)	Concentration limit (ppm)
Acetonitrile	4.1	410
Chlorobenzene	3.6	360
Chloroform	0.6	60
Cyclohexane	38.8	3880
1,2-Dichloroethene	18.7	1870
Dichloromethane	6	600
1,2-Dimethoxyethane	1	100
N,N-Dimethylacetamide	10.9	1090
N,N-Dimethylformamide	8.8	880
1,4-Dioxane	3.8	380
2-Ethoxyethanol	1.6	160
Ethylene glycol	6.2	620
Formamide	2.2	220
Hexane	2.9	290
Methanol	20	2000
2-Methoxyethanol	0.5	50
Methylbutylketone	0.5	50
Methylcyclohexane	11.8	1180
N-methylpyrrolidone	48.4	4840
Nitromethane	0.5	50
Pyridine	2	200
Sulfolane	1.6	160
Tetralin	1	100
Toluene	8.9	890
1,1,2-Trichloroethylene	0.8	80
Xylene	21.7	2170

Daily doses of 50 mg (0.5 percent) or less are permitted for Class 3 solvents (corresponding to 5000 ppm or 0.5 percent per day). No solvent has been identified as a human health concern in this category at levels commonly used in medicines. In addition, they are less hazardous in acute or short-term tests, and in genotoxicity studies, they are negative [15].

OSN can be used in the pharmaceutical business, especially in the API (Active Pharmaceutical Ingredient) production process, to bridge the gap between various reaction stages and in downstream processing, such as separations (extraction, distillation) and particle forming unit activities (crystallization, filtration, drying). OSN can be used to either hold a target molecule (retentate stream) or allow the target molecule to pass through while the impurity is retained (permeate stream) [16].

1.5 Aim and Objective of Research

Based on the background provided above, the concept of sustainability has become more relevant as environmental concerns have grown. Environmental restrictions are becoming more stringent, and enterprises are increasingly utilizing membrane technology to increase the sustainability of their processes. The organic solvent nanofiltration (OSN) process has capabilities to discriminate nanometer-sized molecules in organic solvents with less energy to be consumed with a greener side for carbon emission. This research aims to develop a membrane that can be stable in harsh organic solvents without swelling and can provide higher permeances for organic solvents that are commercially used. 2D Covalent organic frameworks (COFs) are a new class of crystalline porous materials. Intrinsic structures and customizable organic linkers provide low density, large surface areas, tuneable pore size and structure, and easy-to-tailor functionality, attracting increasing interest in the field of membrane separations. In this study, the objective is to synthesize 2D COF onto porous polymer support (polyether-ether ketone) via interfacial polymerization technique, which is scalable, unlike other synthesis

processes such as vacuum filtration to form COF layer for the retention of nanosized molecules in organic solvents. COF as a selective layer has the potential to create stable, antifouling OSN membranes for use in the pharmaceutical, oil, and gas, and food industries.

CHAPTER II

2.1 Membranes for organic solvent nanofiltration

Membranes are generally categorized based on the material, the membrane structure, and the purpose for which they are to be used. The structure-based description of the membrane is typically symmetrical and asymmetrical, either transparent or solid and porous or dense membranes, figure 4. For this article, we focus on membranes used for the recovery of organic solvents or the separation of organic solvents, so the membranes used for this separation are typically made up of organic or inorganic materials. Organic materials include polymeric membranes, both natural and synthetic. Inorganic membranes comprising ceramic, metallic, and zeolite are available. However, due to their thick, densified, and separating layers, commercially available polymeric or ceramic OSN membranes are still insufficiently permeable to meet the industrial requirements for large quantities of organic solvents. In order to achieve a high solvent permeation, the separating layer of the OSN membrane should be as thin as possible without sacrificing its mechanical strength or inducing defects such as pinholes and cracks. The properties of polymers depend on several variables, such as polymer chain length and conformation, chain cross-linking, polar interactions, and size and type of side-group relation. Modifying polymers will improve the membrane's selectivity and increase the range of properties required for separation. Polymers such as polyethylene (PE), polyvinyl chloride (PVC), and polypropylene (PP) are commonly used in membrane processing.

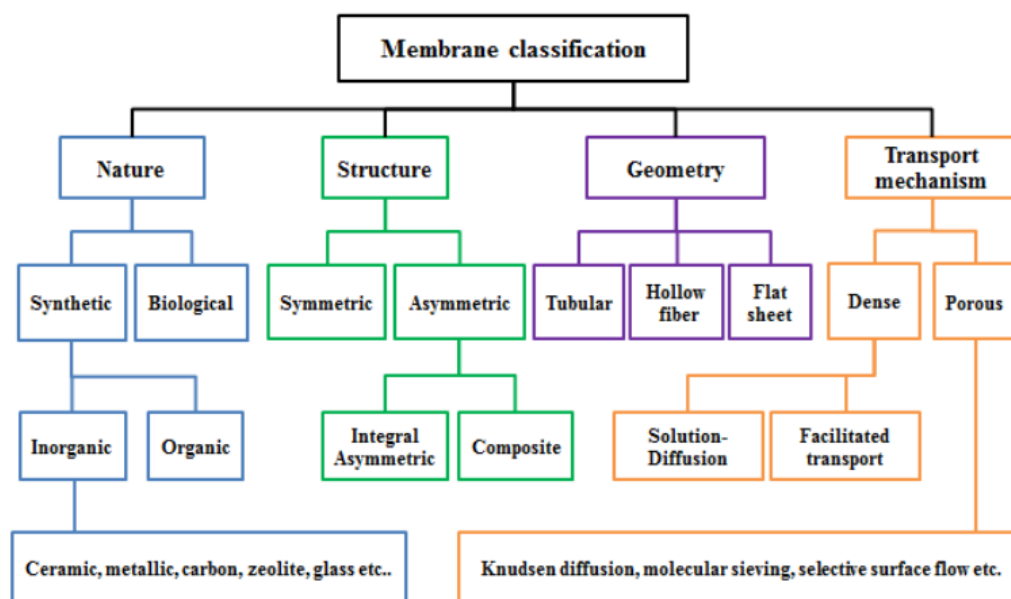


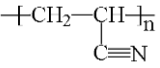
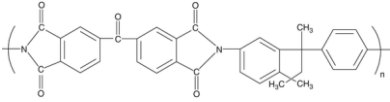
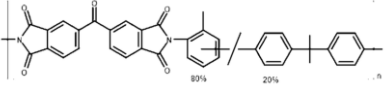
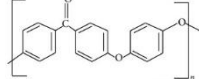
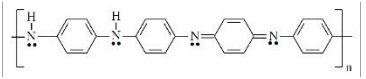
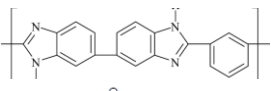
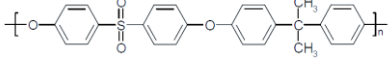
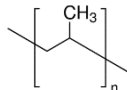
Figure 5. Classification of membranes

Source: Adapted from [17]

The composition of the membrane, from the selective layer – the most discriminating layer of the membrane – to the supporting layer(s), can be divided into one of three classes of materials: either polymer (organic), ceramic (inorganic), or hybrid. Polymers commonly used in polymeric OSN substrate include polyamide-imides, polydimethylsiloxane (PDMS), polyacrylonitrile (PAN), polyether ether ketone (PEEK), polysulfone, polyaniline (PANI), polybenzimidazole (PBI), and mixtures of the above. These membranes can be categorized as isotropic, asymmetric, dense, and porous membranes. Anisotropic surfaces have strong directionality, differ considerably in roughness, and the properties of the materials are not the same at all points. Isotropic surfaces have the same topography, regardless of the direction of measurement, and the physical properties are the same at every point/location of the substance. Membranes with symmetrical pores are more uniform, while asymmetric pores have variable pore diameters. Most polymeric membranes are formed on a nonwoven backing material to provide mechanical stability. As we know, OSN is size dependent separation; to achieve high selectivity, the pores on the membrane should be comparatively smaller than the particles in the mixture for one part of the mixture to stay and the other to permeate. Membrane fouling is

the drawback of a porous membrane that causes the flux to decrease over time. The table shows polymer substrates/membranes used in OSN.

Table 4. Structure and properties of Organic Solvent Nanofiltration substrate, [18].

Polymer	Structure	Glass Transition Temperature T _g , (C°)	Membrane Type
Polyacrylonitrile (PAN)		143 °C	NF, UF
Polyimide Matrimid (PI)		302 °C	NF, UF
Polyimide (PI) P84		315 °C	NF, UF
Poly(Ether-Ether) Ketone		143 °C	UF
Polyaniline (PANI)		104.85 °C	NF
Polybenzimidazole (PBI)		425 °C	NF
Polysulfone (PSf)/sulfonated poly(ether ether ketone)		230 °C	NF
Polypropylene (PP)		-20 °C	UF

The membranes employed in this technology must fulfil the following criteria in order to achieve successful and efficient organic solvent nanofiltration. They should be resistant to organic solvents mechanically and chemically, have a good retention potential for the target product, and transfer organic solvent effectively.

2.2 Commercially Available Polymer Membranes

Puramem S380 from Evonik (MET Ltd., UK), designed for filtrations with hydrophobic solvents such as alkanes, is commercially available composite polydimethylsiloxane (PDMS)-based membrane that consists of a cross-linked PDMS layer on crosslinked polyimide (PI), [16]. Solsep series (some Solsep membranes were proven to have a silicon top layer) and other commercially available membranes [16]. GMT-ONF-2 (GMT Membrantechnik GmbH, Rheinfelden, Germany) commercially available composite membrane with an active layer of PDMS (Polydimethylsiloxane) on a PAN(Polyacrylonitrile) support was used by Zeidler. In contrast, the manufacturer reports a 75% rejection for tetracosane (They are primarily used in applications for which isoalkanes are not acceptable for biological reasons, e.g., the production of detergents or proteins. /Higher n-Alkanes/) with a molecular weight of $338 \text{ g} \cdot \text{mol}^{-1}$ in toluene.

The studies employed by J. Geens and team [19] used three membranes from the StarMem (Membrane Extraction Technology, London, UK) series (120, 122, and 228) with polyimide top layer and cut-off values of 200, 220, and 280, respectively to determine the solute rejection of five API's with molecular weights of 189, 313, 435, 531, and 721 present in organic solvents of Janssen Pharmaceutica-Johnson & Johnson (Company) chemical manufacturing operations (Geel, Belgium).

Limited commercial membranes are still available on the market, and most rely on polyimide (PI) or polyacrylonitrile (PAN) polymers. Polyimides are unstable in some amines, however, and have overall poor stability and performance in polar-aprotic (Tetrahydrofuran (THF), dimethyl-formamide (DMF) and n-methyl-pyrrolidone (NMP)) solvents and chlorinated

(MCM) solvents in which the majority of polyimides are soluble [20]. The DuramemTM (crosslinked PI, Evonik MET, UK) line of PI OSN membranes offer long-term stability in most polar aprotic solvents (acetone, tetrahydrofuran, dimethylformamide) but are still not advised in the presence of chlorinated solvents, strong amines, and strong acids and bases, [21].

Apart from commercially available membranes, many additional materials are available for the OSN. The durability of surface crosslinked chitosan/polyacrylonitrile composite NF membranes has been demonstrated in a variety of organic solvents and at basic pH. However, only aqueous media were used to establish acid/base resistance [22]. An intensive study is being carried out with commercially accessible glassy polymers that were not explicitly designed as OSN membrane materials. The chemical stability and mechanical strength of polybenzimidazole (PBI) and polyether (ether ketone) (PEEK) have drawn attention among these polymers.

2.2.1 Polyether Ether Ketone Substrate

PEEK is an intriguing material for OSN membranes since it has a low or no solvent solubility but is slightly soluble in sulphuric acid (SA) and methane sulphonic acid (MSA), although it dissolves in high boiling point esters, benzophenone, and diphenyl sulphone at temperatures around the melting point. It is a high-performance semi-crystalline thermoplastic with a stiff aromatic backbone structure made up of hydroquinone and a benzophenone segment. In a paper by Peeva, [23] the Pd catalyst was retained by a polymeric (PEEK) OSN membrane in a one-pot, long-term continuous Heck coupling process conducted in DMF at 80 °C with organic base concentrations $>0.9 \text{ mol}\cdot\text{L}^{-1}$ for the first time.

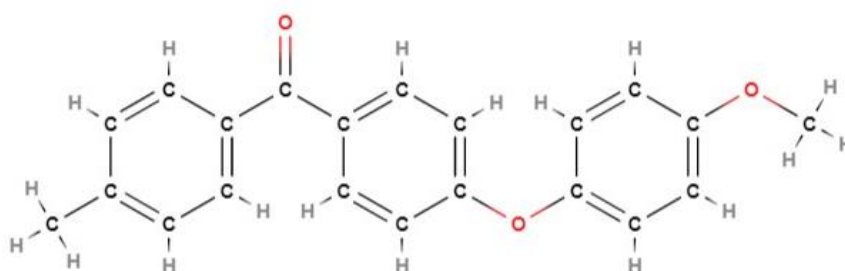


Figure 6. Structure of Polyether ether ketone (PEEK).

Only the PEEK membrane appeared to have no influence on the reaction rate compared to PBI and aminopropyl triethoxysilane (APTS) cross-linked PI membranes: the usage of APTS crosslinked PI membrane lowered the reaction rate. In contrast, the PBI membrane seemed to block the process (via Pd catalyst inhibition).

Ceramics are also utilized in Solvent Resistant NF, although they are far more costly and brittle, making large-scale synthesis and module manufacturing more difficult. Metal oxides such as alumina (Al_2O_3), zirconia (ZrO_2), and titania (TiO_2) make up the majority of current ceramic nanofiltration membranes (TiO_2). Porous ceramics for nanofiltration consist of oxide materials with either symmetrical or asymmetrical architecture, different pore size distributions, porous structures, and overall different geometries. Inorganic membranes are usually categorized by structure and morphology; based on these two factors, the inorganic membranes are classified as porous and non-porous (dense) membranes, as seen in Figure 7,

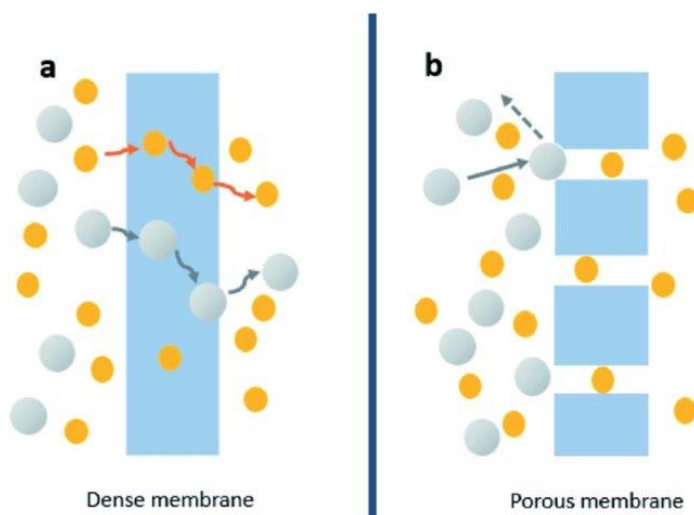


Figure 7. Inorganic membranes, (a) Non-porous Membrane, (b) Porous Membrane

Source Adapted from: [24]

Glass, metal, alumina, zirconia, zeolite, oil, cordierite, silicon carbide, titanium, mullite, tin oxide, and mica silicon nitride are examples of porous inorganic membranes. The properties of the supporting layer are primarily important because selectivity and permeability are both important for the separation process. The support layer materials are typically chosen based on the criteria for mechanical strength and other factors such as chemical resistance and durability. A membrane with over two layers, where the separating layer is connected to more than one sheet, the thin middle sheet functions like a pressure drop controlling layer by preventing a large volume of particles from being transported through the pores of the underlying layers. Recent advancement uses selective MOF and COF layers on both the ceramic and polymers membranes for selective rejection based on the molecular size (Da). As we focus more on inorganic membranes, Covalent Organic Framework (COF) is a new class of covalently extended, crystalline porous network structures with tuning characteristics. In recent years, COF's have intrigued researchers because of their enormous potential as selective membranes and catalyst support.

As we focus more on inorganic membranes, Covalent organic framework (COF) is a new class of covalently extended, crystalline porous network structures with tuning characteristics. COFs have intrigued researchers in recent years because of their enormous potential as selective membranes and catalyst support.

2.3 Nanoporous materials

Nanoporous materials are well recognized for their technological use in a wide range of applications such as gas purification, organic liquid separation, pervaporation, etc. Despite the fact that amorphous polymers with semirigid chemical structures are naturally microporous, pore uniformity remains poor. To obtain high porosity and porous uniformity, several highly rigid crystalline materials, including zeolites, activated carbon, metal organic frameworks

(MOF), covalent organic frameworks (COF), ceramics, and silicates, were typically constructed by many research groups. Later in this part, we will go into metal organic frameworks (MOFs) and covalent organic frameworks (COFs).

2.3.1 Metal organic framework

Metal organic frameworks (MOFs) are an intriguing family of solid crystalline materials that may be easily self-assembled by connecting metal ions or clusters with organic ligands. The structure and hence the characteristics of the MOF are determined by the metal and linker used. The propensity for metal coordination, for example, impacts the size and form of the pores by regulating how many ligands may bind to the metal and in which direction.

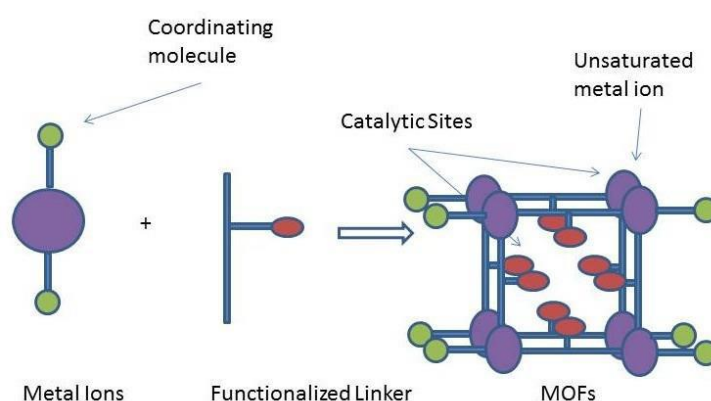


Figure 8. Metal Organic Framework.

MOFs have gotten a lot of interest for several industrial applications, including membrane separation, because of their intrinsic porosity properties, chemical flexibility, and abundance of functionality. The study of MOFs was developed from the study of zeolite. Except for the use of preformed ligands, MOFs and zeolites are produced almost exclusively by hydrothermal or solvothermal techniques, where crystals are slowly grown from hot solutions. In contrast to zeolites, MOFs are made of organic bridging ligands that remain intact throughout the

synthesis. Exciting research activities have emerged, ranging from manufacturing strategies to separation applications of MOF-based membranes. Pure MOFs or a combination of MOF particles and conventional polymers have garnered a lot of interest in membrane separations [25]. For example, Li and colleagues [26] used in situ solvothermal systems to construct defect-free UiO-66 MOF membranes on a porous alumina substrate. With enhanced permeability, this membrane was able to reject multivalent ions considerably. MOF nanoparticles are frequently employed as fillers in nanocomposite membranes, such as the mix matrix membrane, for further separations. However, realizing the full potential of MOF-based membranes is problematic due to limited adherence to polymeric support, partly organic composition, and potential flaws between crystals. For the fabrication of improved separation membranes, the research and design of novel porous crystalline polymers with ordered pore architectures and tuneable pore sizes is critical [27].

2.3.2 Covalent organic framework

Covalent organic frameworks (COFs) are two-dimensional and three-dimensional organic solids with extended structures in which strong covalent bonds interlink the building blocks. Covalent organic frameworks (COFs), made of organic compounds, are a new class of crystalline porous materials. Intrinsic structures and customizable organic linkers provide low density, large surface areas, tuneable pore size and structure, and easy-to-tailor functionality, attracting increasing interest in the various fields, including membrane separations [28][29][30]. New membranes made of porous crystalline materials with uniform pore channels have significant advantages in selectivity and porosity.

The first kind of COF described by Yaghi and Co-worker in 2005 is the boron ester COF, which is produced via reversible reactions between phenyl diboronic acid and hexahydroxy triphenylene that result in periodic crystalline structures. The crystalline structures provide rigid porous frameworks for this material, with pore diameters ranging from sub-nanometres to several nanometres [25]. The application of COF has gradually increased from gas adsorption to membrane separation, covering a wide range of areas such as water purification/treatment, nanofiltration of organic solvents, pervaporation, and fuel cells the membranes are exposed to various mild/harsh environments. This makes the synthesis of appropriate COFs for membrane separations more complicated than other applications, requiring rational selection criteria for manufacturing COF-based membranes. COFs can be 2D porous crystalline structures or three dimensional (3D). The covalently bonded framework in 2D COFs is limited to 2D sheets, which stack to produce a layered eclipsed structure with regularly aligned columns. This columnar stacking structure offers a one-of-a-kind way to generate ordered pore systems that are difficult to achieve using traditional covalent and noncovalent methods. 3D COFs, on the other hand, have high specific surface areas (in some cases greater than 4000 m²/g), numerous open sites, and low densities because they expand this framework three dimensionally through a building block containing sp³ carbon or silane atom (as low as 0.17 g/cm³). Because of these characteristics, 3D COFs are excellent candidates for gas storage.

With the advancement of porous materials, particularly microporous materials, several of these materials have been included in the membrane matrix to improve membrane permeance. Examples include metal-organic frameworks (MOFs), zeolites, and covalent organic frameworks (COFs). These porous materials are generally included as additives into polymeric matrixes to produce a more pronounced performance, giving extra molecular transport channels with increased permeance.

2D COFs are believed to have a great potential for usage as OSN membrane materials. However, the synthesis of continuous and defect-free COF membranes remains tricky, and there have been few reports of their use in OSN. On the other hand, in order to address the increased need for precise molecular sieving, the pore size must be rationally tuned. Despite the fact that this is regarded as one of the most significant advantages of COF materials, experimental demonstrations are still rare. Schiff base chemistry, which involves a number of reversible processes, is a popular method for forming amorphous polymeric networks [31]. Recently, a few works on the interfacial synthesis of the water/organic interface to generate imine-linked COF thin films for dye separation have been published. For example, Marias. [32], Dichtel [33] and Banerjee [34] all employed interfacial synthesis to create free-standing COF films that could then be transferred to porous substrates in various ways to build composite membranes. Although these technologies can manufacture thin COF films and the resulting composite membranes have good performance, they face substantial challenges in the efficient and up-scale production of COF membranes, such as COF stability in aggressive solvents, longer durations for synthesis (typically, the reaction takes several days) affecting the production efficiency. Moreover, adhesion between the COF layer and the substrate could also be an issue.

In this research, PEEK100 was selected as the substrate because it shows higher permeation capability than another substrate available commercially for OSN. PEEK substrates are stable in harsh organic solvents (e.g., DMF, THF, Toluene). TpPa-1 COF was employed as the selective layer to accomplish dye nanofiltration separation as the structures of TpPa-1 series COFs are very stable. TpPa-1 is one representative COF in the group of TpPa COFs. The solvent stability of COF powders is a crucial factor, TpPa-1 stability was investigated in solvents ranging in viscosity from low to high, including methanol (MeOH), acetone, ethanol (EtOH), isopropyl alcohol (IPA), chloroform, tetrahydrofuran (THF), dichloromethane

(DCM), hexane, and dimethylformamide (DMF). A known amount of TpPa-1 COF powder was immersed in the aforementioned solvents. The powders were tested for colour change after being added and then dried for X-ray Diffraction to see if the crystal structure of the powders altered after being exposed to solvents. Later, the resilience of the 2D TpPa-1 layer was tested by immersing it in Dimethylformamide (DMF), although no X-ray Diffraction was performed on it. Other characterization techniques were performed, such as Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Microscope (SEM) for membrane topology.

CHAPTER III

3.1 EXPERIMENTAL

3.1.1 Chemicals and materials:

The chemicals used in this research work are PEEK100K substrate (Sterlitech, Novamem), 1,3,5 triformylphloroglucinol (Tp, 95%), p-phenylenediamine (Pa, 97%), acetic acid (AA, 99.5%), Hexane (99%), Ethyl alcohol (EtOH) (99%), Methyl Orange, pure indicator (MO), Primuline, Congo Red (CR), Methyl Blue (MB), Fast Green dye (FG), Reactive Red 120 (RR), were purchased from Sigma Aldrich. All chemicals were used as received without any further purification.

3.1.2 Preparation of Tp and Pa monomer solution:

The synthesis of the TpPa-1 COF layer was performed as follows: first, the porous substrate (PEEK100K) was submerged in ethyl alcohol (EtOH) for 24 hours before synthesizing the COF layer. In 20 mL hexane, various quantities of 1,3,5 triformylphloroglucinol (Tp) were dissolved, ranging from 0.025 wt% to 0.057 wt%. After sonication, the mixture was agitated for another 0.3 hours on a vibrating shaker. The P-phenylenediamine solution was prepared by dissolving a range of Pa concentrations (2wt % - 5wt %) in 20 mL DI containing 200 mL acetic acid (AA), sonicated, and agitated in the same way as Tp solution.

3.1.3 Synthesis of TpPa-1 membrane:

To begin, set the substrate on a glass slab/PVDF board and dry off any remaining EtOH from the top layer without entirely drying the support. Then, using a pipette, pour the required amount of Pa concentration monomer solution into the support layer for the specified duration (20sec-110sec). Before continuing, remove any excess Pa monomer from the surface, and then

pour as desired Tp monomer solution to the surface of the Pa coated substrate for the same amount of time as the Pa solution. After the Tp monomer has been introduced for the appropriate period, wash the membrane with hexane. Submerge the membrane in methanol (MeOH) for 0.3 hours before placing it in DI water. The DI water is replenished during the first two hours to avoid contamination. The process for synthesizing the TpPa-1 membrane can be seen in fig 9.

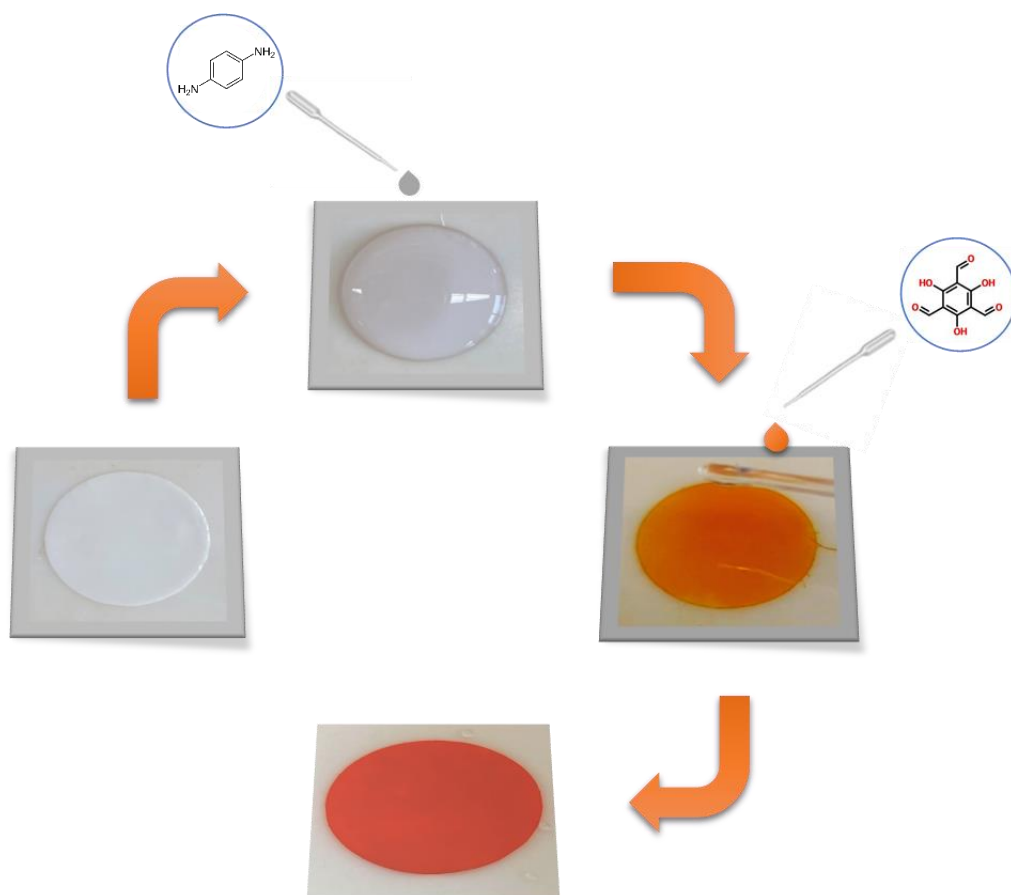


Figure 9. Synthesis of TpPa-1 COF membrane.

3.1.4 Synthesis of TpPa-1 powders:

The TpPa-1 powders were made utilizing the conventional solvothermal synthesis method, the same as the TpPa-1 membrane. Specifically, 0.3 mmol Tp and 0.45 mmol Pa were mixed in a combination of 7.5 mL 1, 4-dioxane, and 7.5 mL mesitylene, followed by 1 mL AA (12 M) and nitrogen bubbling for 5 minutes, then the autoclave containing COF monomers were heated at 120 °C for 72 hours. Before further characterizations, the powders were extensively washed with 1, 4-dioxane, and ethanol and dried at 100 °C overnight.

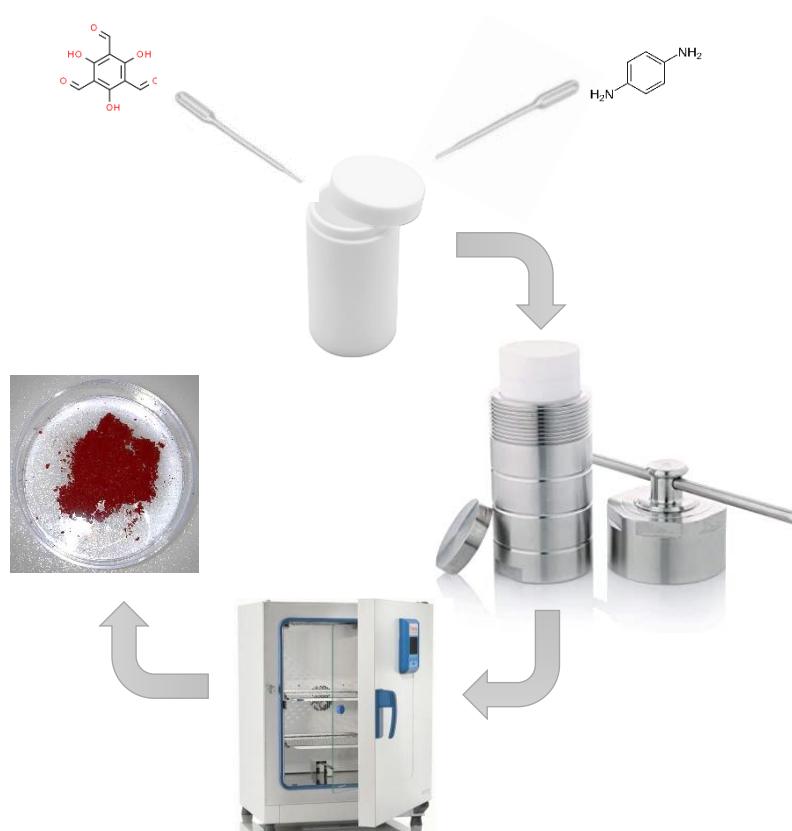
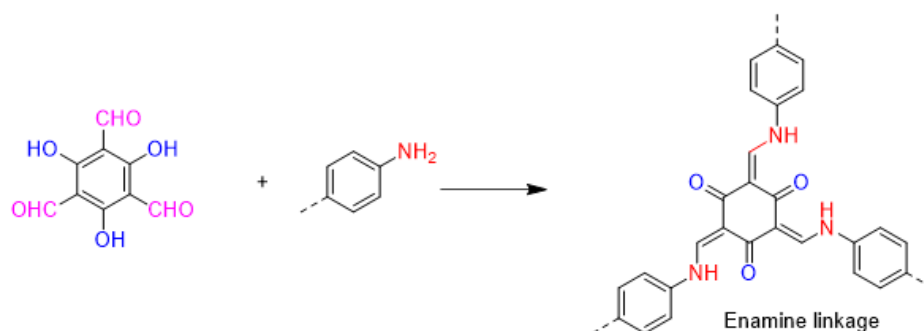


Figure 10. Synthesis of Tp-Pa1 COF powder.

a



b

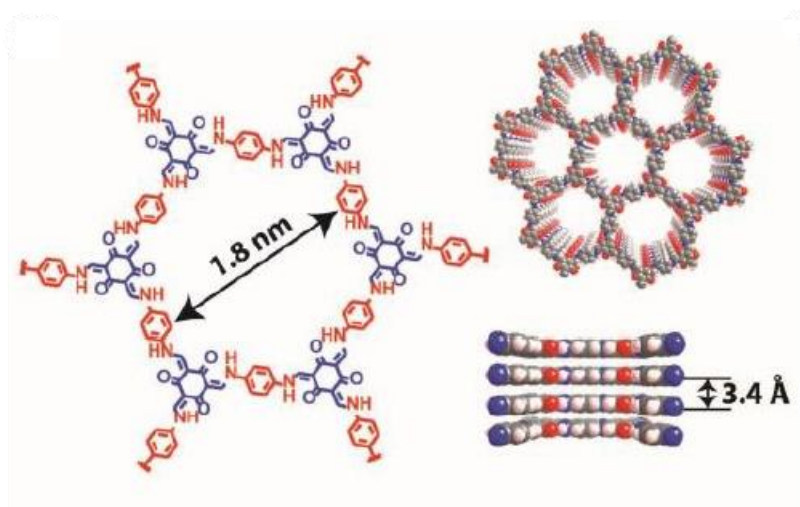


Figure 11. Schematic illustration of the synthesis of TpPa-1 COF (a), pore structure, and chemical structure of TpPa-1 COF

3.2 Experimental Setup:

3.2.1 Aqueous System:

First, the dye rejection of the membrane was tested in a water system to its performance. The rejection capability of the membrane was determined using a crossflow arrangement comparable to the OSN setup. A 50ppm dye solutions made by dissolving respective dye into DI water.

3.2.2 Organic Solvent System:

The organic solvent experiments were carried out with lab-built organic solvent nanofiltration (OSN) system, which included a stainless-steel crossflow cell that was stable in organic solvents and PTFE tubing that transported the solvents from the feeding tank to the cell and back to the tank. A Viton fluor elastomer O-ring was used to insert the constructed TpPa-1 membrane into the cell. After an hour of operating the system at constant pressure with a flow rate of 25 mL/min, the extract phase was collected. RB, CR, and Primuline dyes were prepared in concentrations of 50ppm in EtOH solvent.

3.2.3 Organic Solvent Nanofiltration Setup:

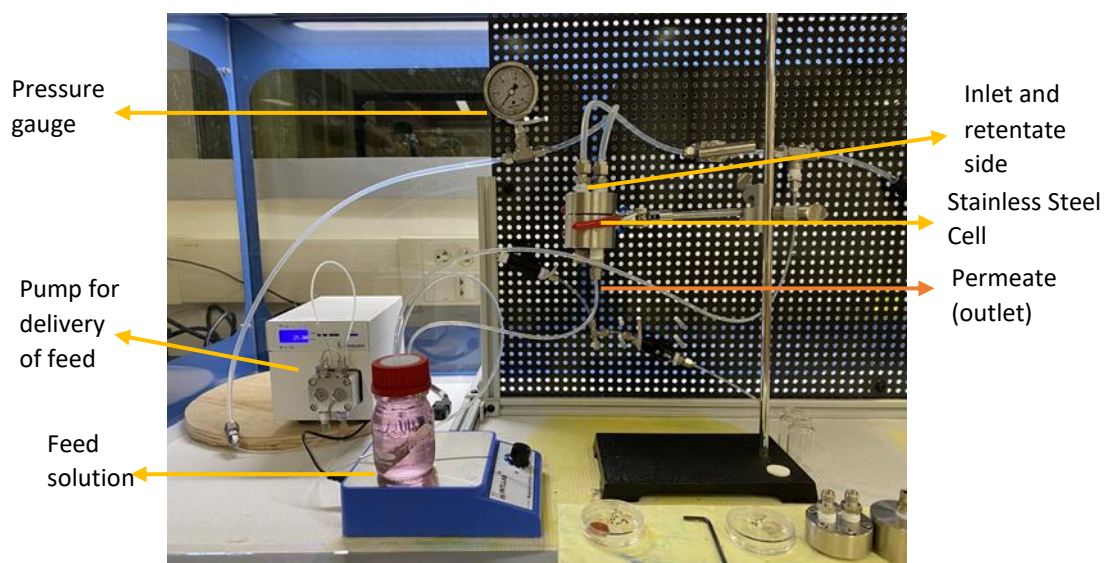


Figure 12. Organic Solvent Nanofiltration setup was used for this research.

3.2.4 Stability Test

The TpPa1 COF powder composite's long-term stability was tested for eight months in various organic solvents commonly used in the industry for Active Pharmaceutical Ingredients (APIs). After that, X-ray Diffraction and Fourier transform infrared spectroscopy were used to characterize the powder in comparison to TpPa-1 COF powder without any solvent treatment

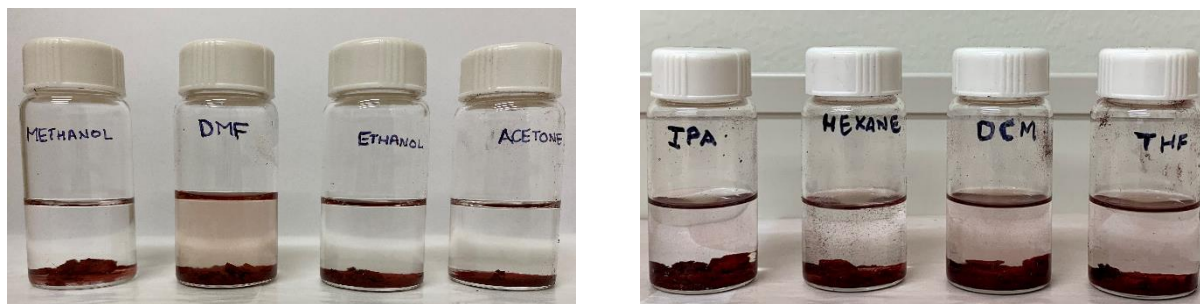


Figure 13. TpPa-1 COF powder synthesized using the solvothermal method and soaked in various Organic Solvents.

CHAPTER IV

4.1 Characterization:

Morphologies and elemental analysis of the membranes were performed on a field-emission scanning electron microscope (SEM). The TpPa-1 COF powder's X-ray diffraction (XRD) patterns at ambient temperature were observed using Bruker X-ray Diffractometer (Bruker XRD) operating at 2θ range of $0-45^\circ$. UV spectrophotometer (UV-Vis) was used to determine the presence of dye molecules in the permeance phase of the experiment. A Fourier transform infrared spectroscopy spectrophotometer (FTIR, Shimadzu IRTracer-100) was employed to investigate the chemical structure of the surface of the resultant membrane and COF powders with a scanning wavelength from 4000 cm^{-1} to 600 cm^{-1} .

4.2 Filtration and separation test:

The membranes performance was assessed in water first with two dyes.

1. Methyl Blue (MW-799)
2. Fast Green (MW-808.86)

Followed by testing the best performing membrane from the water system into organic solvents with dyes such as:

(1)

1. Methyl Orange, pure indicator (MW- 327.32)
2. Primuline (MW- 475.54)
3. Congo Red (MW- 696.6)
4. Methyl Blue (MW- 799)
5. Reactive Red (1469.98)

The permeance and rejection data were obtained using the lab made OSN setup mentioned earlier. Pure solvent permeance (P) and various dyes permeance were calculated by the following expression:

$$Permeance = \frac{v}{A \cdot T \cdot P}$$

Where,

Permeance, ($L \cdot m^{-2} \cdot hr^{-1} \cdot bar^{-1}$)

v = Volume, L

A = Area exposed for separation, m^2

T = Time, hr

P = Pressure that is used to supply feed to the crossflow cell, Bar

A UV–vis detector (NanoDrop 2000c, Thermo) was used to measure the concentrations of feed (C_F), permeate (C_P), and retention (C_R) at each dye's maximum absorption wavelength. The following equation was used to determine the rejection (R , %) of the different dyes:

$$R = (1 - C_P / C_F) \times 100\% \quad (2)$$

4.3 RESULTS AND DISCUSSION

4.3.1 TpPa-1 COF POWDER CHARACTERIZATION

TpPa-1 COF powder stability analysis was conducted over 6-8 months. Fig 14(A) shows TpPa-1 COF powder dispersed into respected solvents. The dispersion rates of Dichloromethane (DCM) and Tetrahydrofuran (THF) seem to be higher than those of other solvents. COF powder settles well at the bottom in organic solvents as shown in Fig 14(B). THF is the only solvent that offers very little dispersion. After soaking in solvents, further characterizing of COF powder was conducted using X-ray Diffraction.

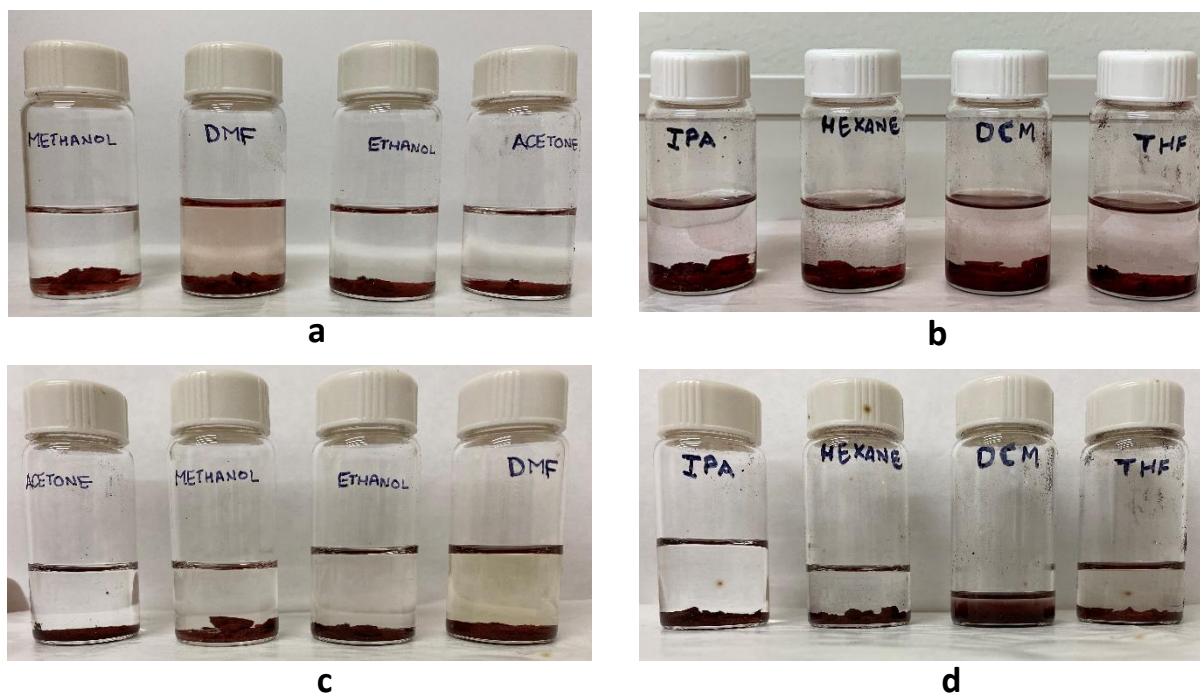


Figure 14. (a,b) Before and (c,d) after images of TpPa-1 COF powder soaked in organic solvents.

The trend for Tp-Pa1 COF powder was studied under XRD. Figure (15) shows COF powders soaked in various organic solvents. The XRD patterns for TpPa-1 COF powders are consistent with those reported in the literature [35]. After soaking the powders for months, the XRD data show no major changes in TpPa-1 COFs crystal structure, except powders in THF solvent,

which showed decrease in the peak intensity. THF is a moderately polar solvent capable of dissolving various nonpolar and polar chemical substances. It is worth noting that the COF powders appear to show good structural stability even in DMF, as indicated by the strong COF peaks after the stability test.

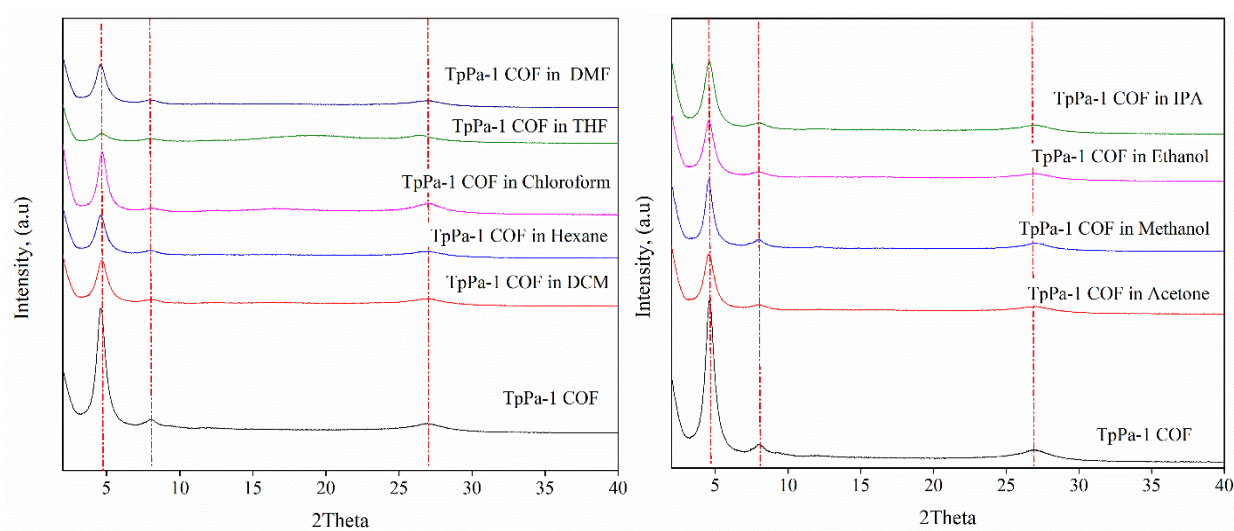


Figure 15. XRD patterns for TpPa-1 COF powders after stability test; (A) Acetone, Methanol, Ethanol, Isopropyl alcohol (IPA), (B) Dichloromethane (DCM), Hexane, Chloroform, Tetrahydrofuran (THF) and Dimethylformamide (DMF)

4.3.2 X-Ray Diffraction (XRD) of TpPa-1 COF Membrane:

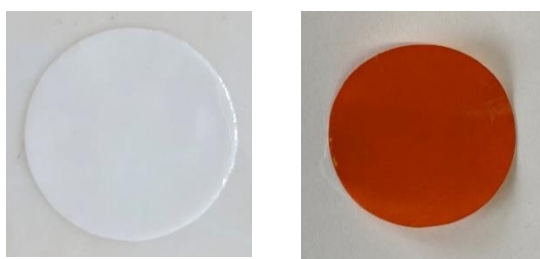


Figure 16. Shows the PEEK support (Left) and synthesized TpPa-1 COF membrane (Right). The colour change confirms that a layer of TpPa-1 is formed onto the PEEK support.

To confirm the structure of TpPa-1 COF formed onto the PEEK substrate, X-ray diffraction (XRD) was performed on bare PEEK support and synthesized TpPa-1 COF membrane. Fig 17 shows XRD patterns for simulated TpPa-1 COF, PEEK substrate, TPA-2 membrane, and TPA-3 membrane (see table 7 for a description of membranes). As shown, COF peaks were not

observed in the two COF membranes. COFs synthesized in the open environment are thought to have imperfections on their surfaces because active ingredients such as oxygen in the open environment may engage in the process, resulting in low crystallinity or even amorphous COFs, [36]. In addition, when compared to TpPa-1 COF powders, the COF membrane layer formed on the PEEK substrate is relatively thin, resulting in no evident peak in XRD data.

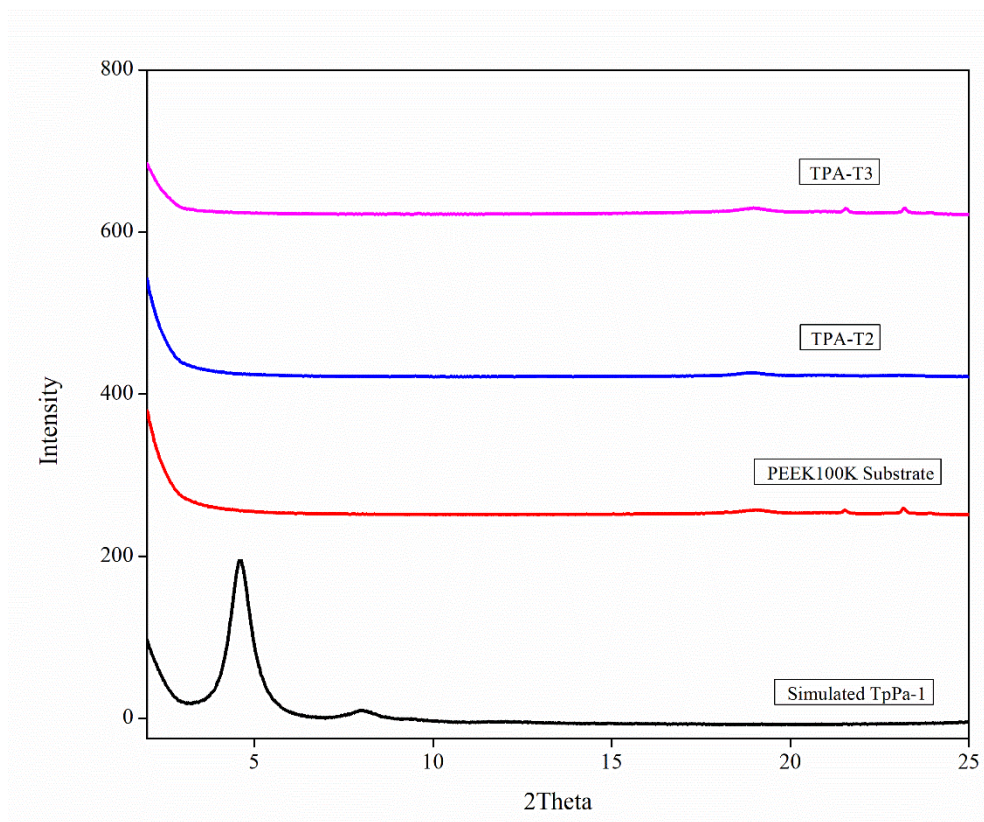


Figure 17. XRD data for simulated TpPa-1 COF membrane compared to the membranes used in these studies.

X-ray-Diffraction pattern for covalent organic framework membranes are classified into two types based on their crystallinity. Thin films (<500 nm) shows little or no apparent crystallinity made by polymerizing monomers at liquid-liquid, liquid-solid, or liquid-air interfaces [37]. The second type of COF made by solvothermal synthesis generated as thick films or solids/powders using traditional processes shows higher crystallinity. XRD patterns in figure 15 for COF powders suggest that TpPa-1 COF powders fall into the second category, whereas TpPa-1 COF

membranes fall into the first category. To determine the thickness of the TpPa-1 COF layer synthesized on PEEK support scanning electron microscope was used.

4.3.3 Scanning Electron Microscopy

TpPa-1 membrane morphologies were studied by SEM. In order to confirm the successful synthesis of TpPa-1 COF onto PEEK substrate, magnified images were taken for the PEEK substrate and TpPa-1 COF membrane.

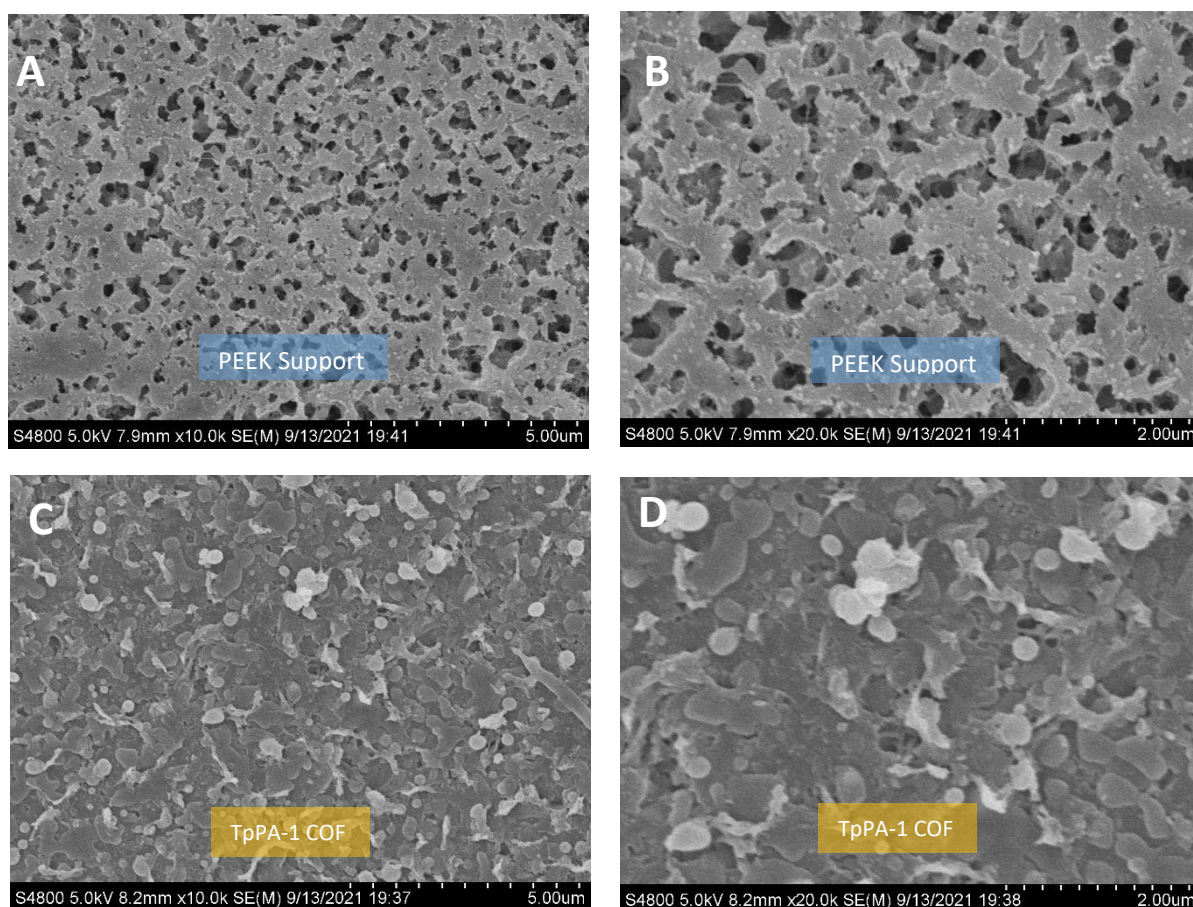
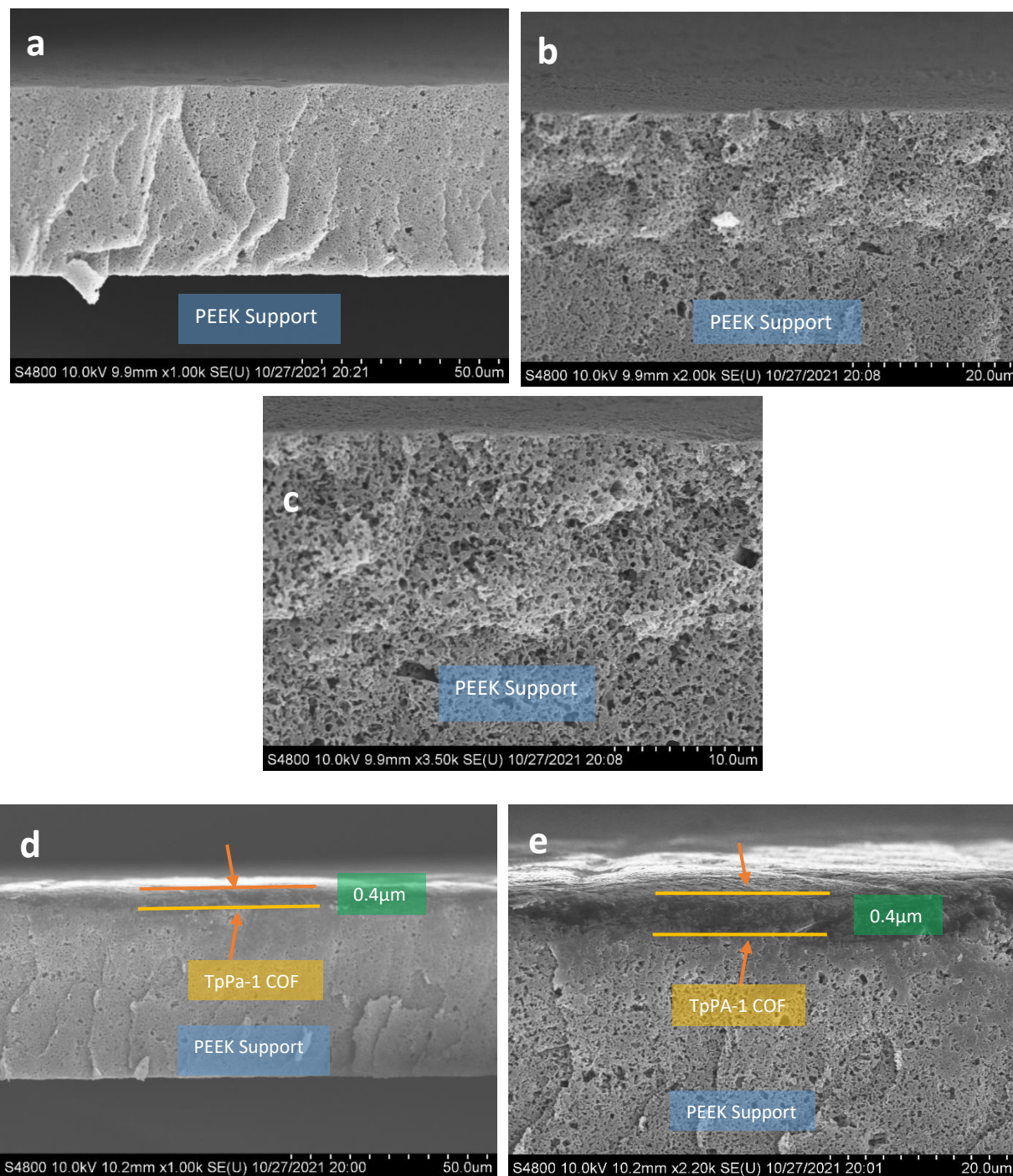


Figure 18. Surface SEM images of (A, B) PEEK100k Substrate, (C, D) TpPA-1 synthesized PEEK100k Substrate.

As shown in Fig. 18A and 18B, the open pore surface of PEEK substrate can be seen; the scale in Fig 18B suggests that the pores of PEEK support range from 0.1 μ m-0.2 μ m. In Fig. 18C and 18D, the pores of the PEEK support are covered by a layer of TpPa-1 COF. To confirm the difference in PEEK support and the TpPa-1 layer, cross-section SEM images were gathered for the PEEK substrate and COF membrane. Fig. 19 shows the cross-sectional images of PEEK

substrate and TpPa-1 synthesized on the PEEK membrane. TpPa-1 COF layer of 0.4 μm can be seen in fig. 19 (d, e, f and g). The surface SEM images, and cross-sectional images of PEEK and synthesized TpPa-1 COF membrane confirms the successful growth of TpPa-1 COF layer that covers the pores of the PEEK substrate.



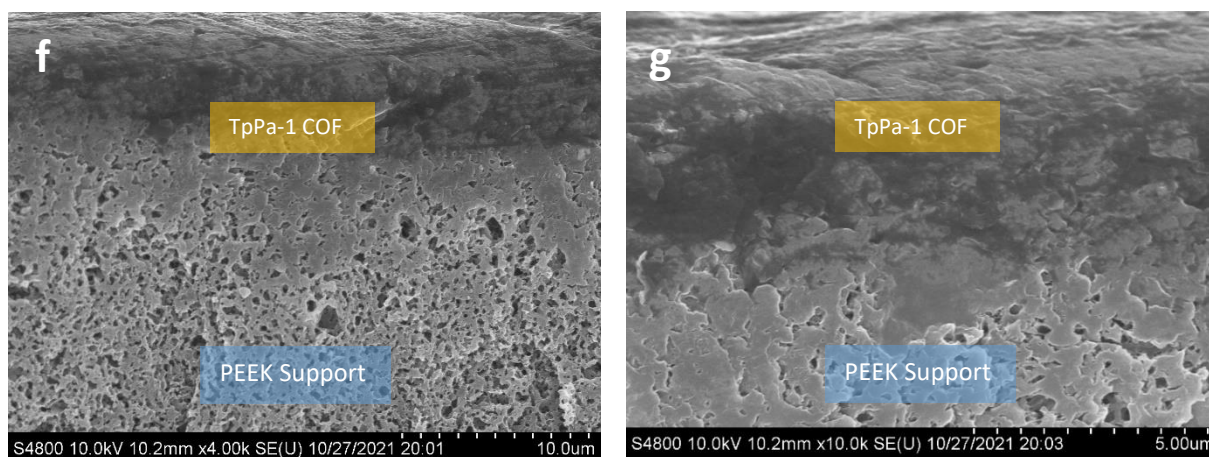


Figure 19. SEM insights of PEEK support and TpPa-1 COF membrane synthesized on PEEK substrate. (a, b, c) PEEK substrate cross sectional view at various magnifications, (d, e, f, g) TpPa-1 synthesized COF membrane on PEEK substrate (cross sectional view).

4.3.4 FTIR OF TpPa-1 MEMBRANE:

The formation of TpPa-1 COFs was studied using FT-IR. Figure 22 shows FT-IR data for Tp and Pa monomer. The monomer Tp, shows CH=O bond peak at around $2900-3100\text{ cm}^{-1}$, whereas Pa monomer peaks (N-H bond) show up in the range of $3250-3500\text{ cm}^{-1}$. PEEK support and TpPa-1 membranes (TPA-T2 and TPA-T3) FT-IR wavelengths were analysed, figure 20 shows the wavelengths for PEEK and TpPa-1 COF membranes, the peak at 1640 cm^{-1} corresponds to the typical absorption of C=O, which is combined with the peak of the C=C stretching band at 1583 cm^{-1} , peaks at 1454 cm^{-1} and 1225 cm^{-1} are caused by the C=O and C-N stretching. After comparing Pa monomer (N-H) and TpPa-1 COF membrane peaks for N-H bond at wavelength of about $3500-3200\text{ cm}^{-1}$ it was suggested that the wavy curve in the region of N-H for TpPa-1 COF membrane resembles a water molecules peak. PEEK support, and COF membranes were stored in water to maintain their integrity, and this

could be a reason for the water peak to show up in the region of $3250\text{-}3500\text{ cm}^{-1}$ instead of the N-H group. The CH=O group resembling Tp monomer seems to disappear for TPA-2 membrane, TPA-3 membrane. This suggests that the Tp monomer is fully reacted during the synthesis of the membrane.

PEEK substrate exhibits same peak wavelength as the TpPa-1 COF membrane from region $3000\text{-}1000\text{ cm}^{-1}$. To confirm that the FT-IR spectrum peaks seen in figure 20 are generated from TpPa-1 COF membrane, we performed an experiment by synthesizing a free standing TpPa-1 COF layer (fig 21) onto a glass. FT-IR was performed on the free standing TpPa-1 COF membrane.

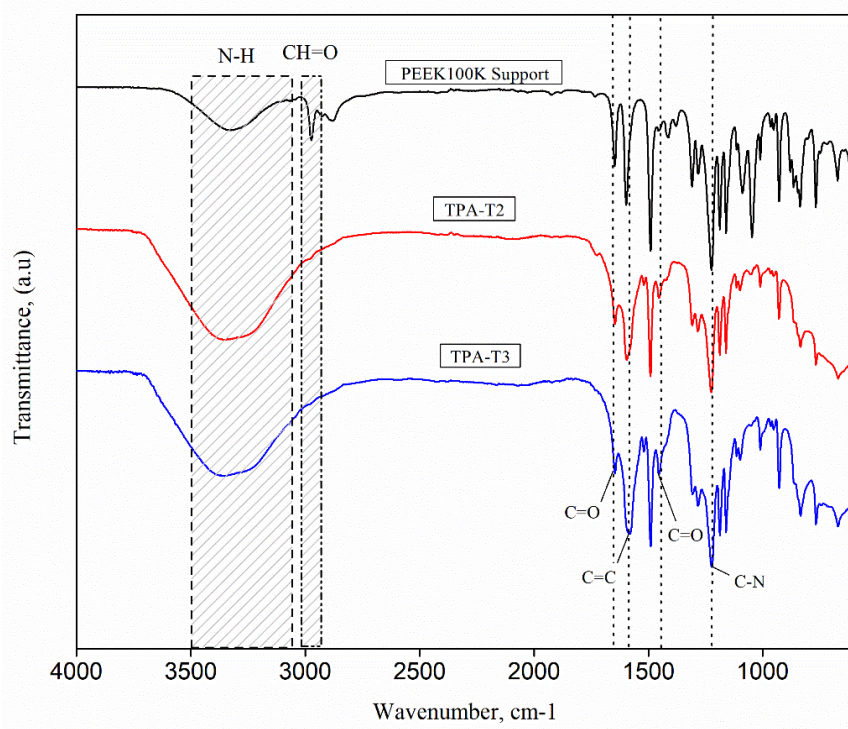


Figure 20. FTIR Data for PEEK support and TpPa-1 COF membrane



Figure 21. Free standing TpPa-1 COF layer.

TpPa-1 COF FT-IR peaks (Fig 23) from glass closely resembles to the peaks reported in literature [39]. The N-H stretching in the region of $3250\text{--}3500\text{ cm}^{-1}$ resemble the Pa monomer. This peak was missing for TPA series membrane but visible for thin film TpPa-1 COF layer on glass it can be understood that the Pa monomer have been reacted for TPA-T2 and TPA-T3 membrane and might have few unreacted Pa monomer for thin film made on glass. The CH=O peaks from Tp monomer is visible for the free-standing COF film.

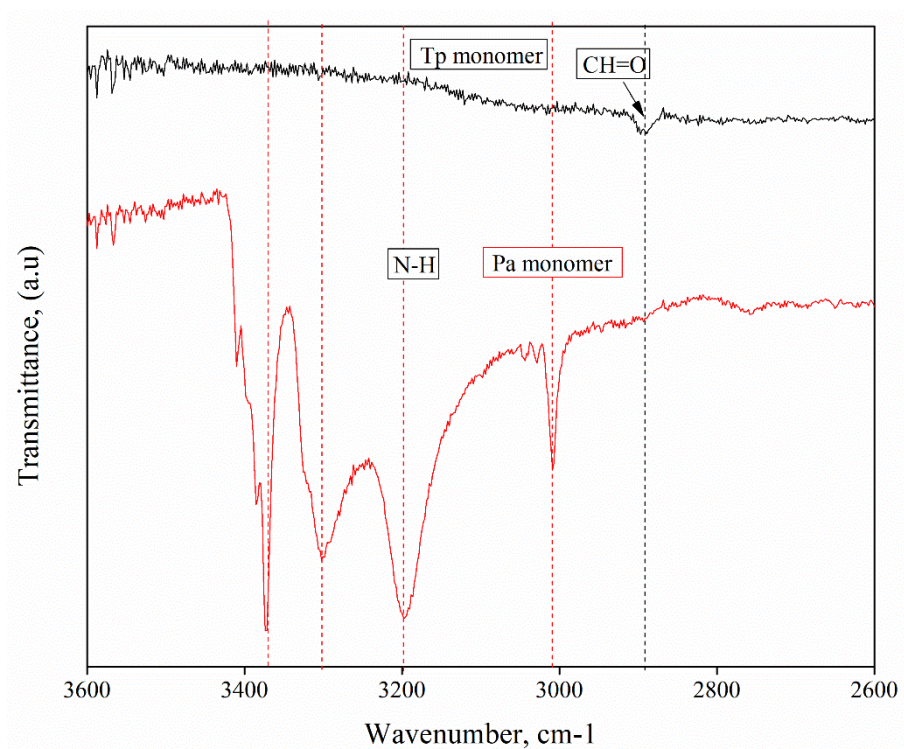


Figure 22. FT-IR spectrum for Tp and Pa monomer.

The C=O obtained at 1670 cm^{-1} and 1604 cm^{-1} for the TpPa-1 COF layer (Fig. 23) and membranes (Fig. 20) have reduced wavelength intensity than PEEK support. The peaks obtained at 1593 cm^{-1} , 1444 cm^{-1} , and 1253 cm^{-1} are caused by the stretching of C=C, C=O, and C-N groups. These data suggest successful synthesis of the TpPa-1 COF layer on PEEK support.

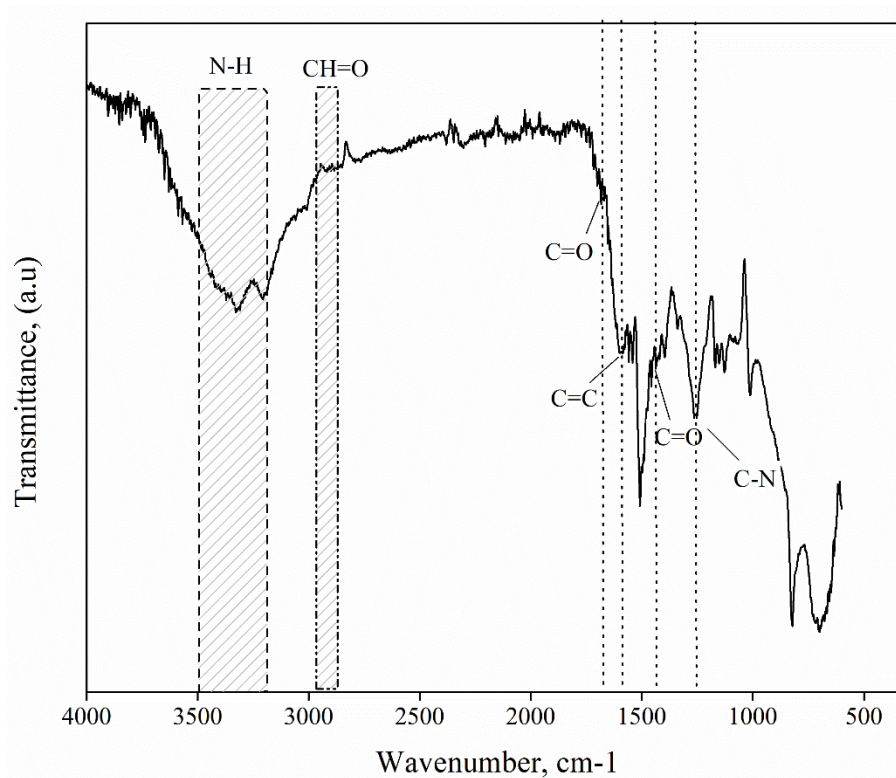


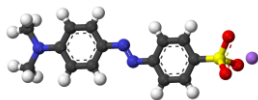
Figure 23. FT-IR spectrum for Free standing TpPa-1 COF layer.

Table 5. Shows common properties of solvent used in this study.

Solvent	Molecular weight ($g \cdot mol^{-1}$)	Kinetic diameter (nm)	Viscosity (cP)	Surface tension (dyne/cm)	Dielectric Constant
MeOH	32.04	0.38-0.41	0.55	22.6	33.00
EtOH	46.07	0.44	1.10	21.9	24.90
THF	72.11	0.48	0.55	28.8	7.58
DMF	73.09	~0.55	0.8	36.4	36.7

4.3.5 FILTRATION TEST:

Methyl Orange

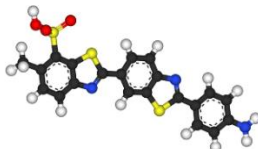


MW- 327.32

Charge: (-)

MD: 1.13nm x 0.42nm

Primuline

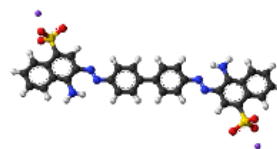


MW- 475.54

Charge: (-)

MD: 1.02nm x 0.51nm

Congo Red

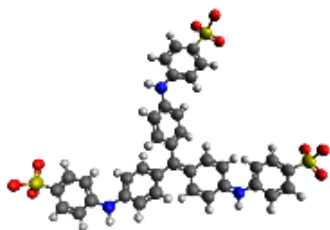


MW- 696.6

Charge: (-)

MD: 2.56nm x 0.73nm

Methyl Blue

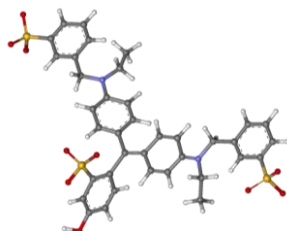


MW- 799

Charge: (-)

MD: 1.74nm x 2.36nm

Fast Green

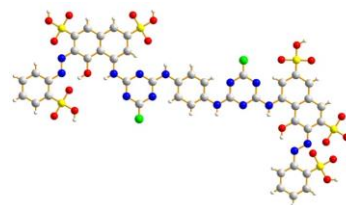


MW- 808.86

Charge: (-)

MD: -

Reactive Red 120



MW- 1469.98

Charge: (-)

MD: 1.355 nm x 0.981nm

Figure 24. Properties of dyes used in Nanofiltration studies.

4.3.5.1 WATER SYSTEM DYE REJECTION TEST

The COF membranes synthesized were first tested in water to evaluate their quality and performance. The table below shows the first sets of membranes made for the water system test. The membranes were synthesized by varying the Tp monomer concentration while keeping other synthesis parameters (e.g., Pa monomer concentration and reaction time for each monomer) constant. These prepared membranes were then tested against two dyes.

Table 6: Change in Tp concentration membranes.

Membrane	Tp conc, mg	Pa conc, g	Time, s
TPA-C1	2	0.5	30
TPA-C2	3	0.5	30
TPA-C3	4	0.5	30
TPA-C4	5	0.5	30

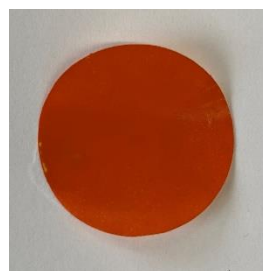
1. Change in Tp concentration:



TPA-C1



TPA-C2



TPA-C3



TPA-C4

Figure 25. TpPa-1 COF membrane made by varying the concentration of Tp monomer. A colour shift can be noted as the Tp concentration is increased. This indicates that the coating becomes visibly thicker.

The prepared membranes were tested for two dyes, as mentioned in the experimental section.

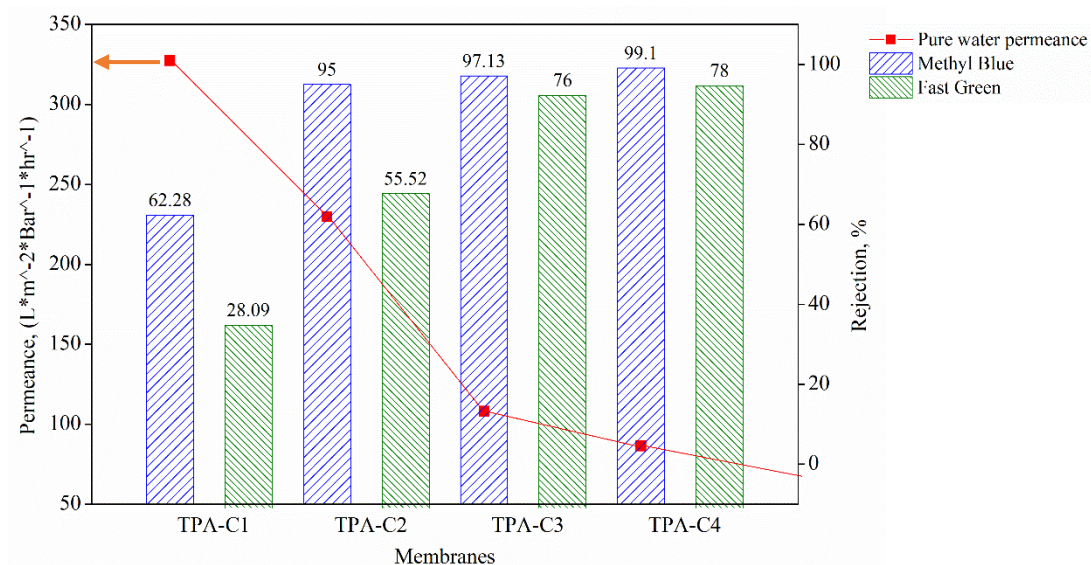


Figure 26, Nanofiltration performance of the membrane.

In a water system, the effect of changing Tp monomer concentration on rejection and permeance was investigated using four membranes with varied Tp-conc (Fig. 26). As the concentration of Tp monomer is increased, rejection of both dyes increases while the permeance decreases. TPA-C1 membrane has a pure water permeance of $327.48 \text{ L m}^{-2} \text{ hr}^{-1} \text{ bar}^{-1}$ which is higher compared to TPA-C4 membrane with a permeance of $86.46 \text{ L m}^{-2} \text{ hr}^{-1} \text{ bar}^{-1}$. TPA-C1 showed a rejection of 62 % and 28 % for methyl blue and fast green, respectively, whereas TPA-C4 showed a rejection of 99.1 % and 78 % for methyl blue and fast green, (fig 26). This demonstrates that if the Tp monomer concentration is increased during synthesis, the permeance of the membrane reduces, but on the other hand, the rejection of the membrane will increase. The rejection data and permeance data support the statement that with an increase in Tp conc, the COF membrane layer becomes thicker (fig 25), which in turn affects the permeance and rejection of TpPa-1 COF membrane.

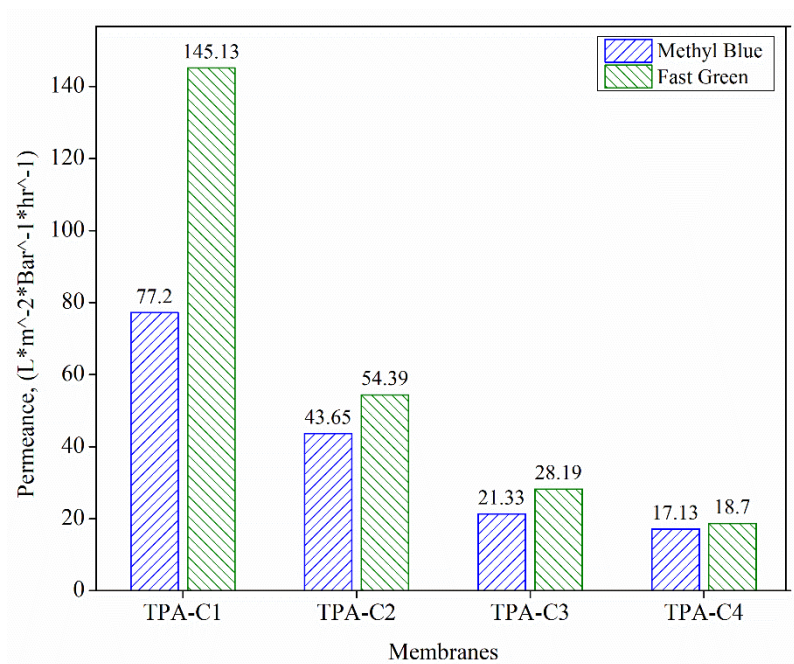


Figure 27. Permeance data for TpPa-1 COF membranes tested for Methyl Blue and Fast Green.

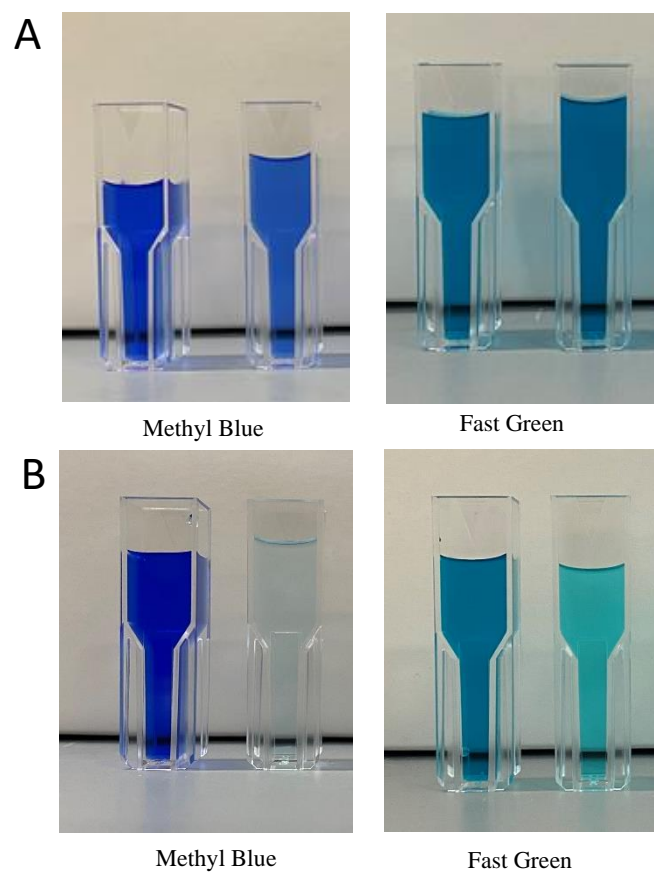


Figure 28. Visual rejection analysis for Methyl blue and Fast green dye for (a) TPA-C1 membrane, (B) TPA-C3 membrane.

After analyzing the first test results, the second condition for the membrane was determined. TPA-C3 was chosen since it has a higher rejection and a better permeance.

Table 7: Change in synthesis time for each monomer (Tp and Pa)

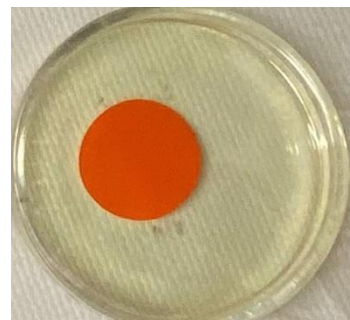
Membrane	Tp conc, mg	Pa conc, g	Time, s
TPA-T1	4	0.5	20
TPA-T2	4	0.5	40
TPA-T3	4	0.5	60



TPA-T1



TPA-T2



TPA-T3

Figure 29. TpPa-1 COF membrane made by varying synthesis time for each monomer.

Table 7 illustrates the time difference between each TpPa-1 COF membrane synthesized. The colour of the membrane darkens as we increase the synthesis time, and comparable outcomes were observed when the Tp monomer concentration was changed. Similar dyes were used to determine the membrane performance.

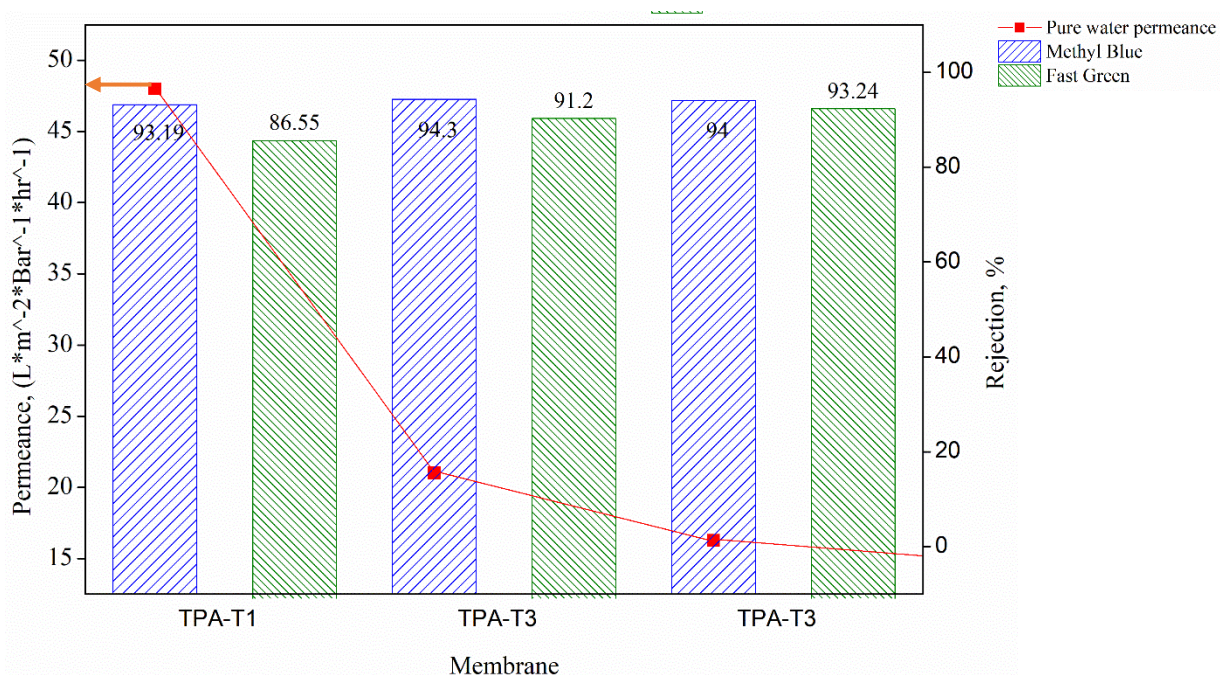


Figure 30. Nanofiltration performance of TpPa-1 COF membranes synthesized by hinging time for each monomer.

Figure 30 shows rejection data for membranes that were synthesized by changing synthesis time. A similar retention and permeation trend was observed when membranes were made by change in Tp monomer concentration. TPA-T1 membrane has a comparatively higher permeance of water, $48 \text{ L m}^{-2} \text{ hr}^{-1} \text{ bar}^{-1}$ compared to TPA-T3 membrane synthesized at 60s with a permeance of $16.27 \text{ L m}^{-2} \text{ hr}^{-1} \text{ bar}^{-1}$. After increasing the synthesis time, a shift in rejection was also observed. This confirms that as the monomer concentration or synthesis time for COF membrane increases, a thicker layer of TpPa-1 COF membrane is formed. The thickness of membrane leads to a continuously formed (integrity) TpPa-1 COF membrane.

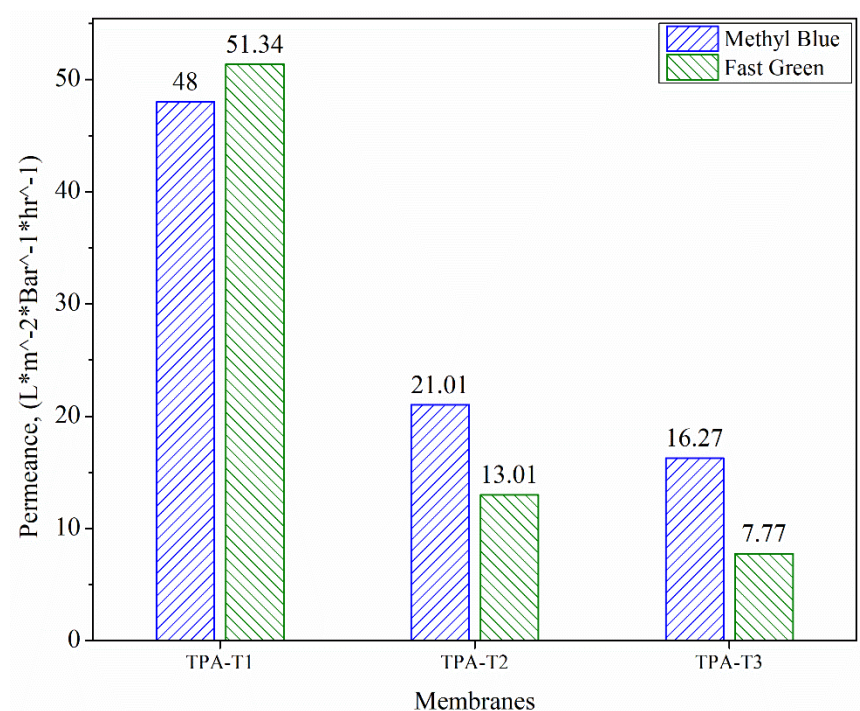


Figure 31. Permeance data for TpPa-1 COF membranes tested for Methyl Blue and Fast Green.

The increased thickness of TpPa-1 COF membrane can also lead to higher degree of adsorption in aqueous system. In support of the adsorption theory [32], the possibility of rejection due to charges between the solutes and the membrane maximizes.

After evaluating the membranes in water and validating the optimal conditions for synthesis of TpPa-1 COF membrane, we examined membranes tagged as TPA-T2 and TPA-T3 in an organic solvent system. Dye solutions (50ppm) were made by dissolving five dyes in polar solvent (ethanol). It is known that dye molecules tend to become neutral in organic solvents.

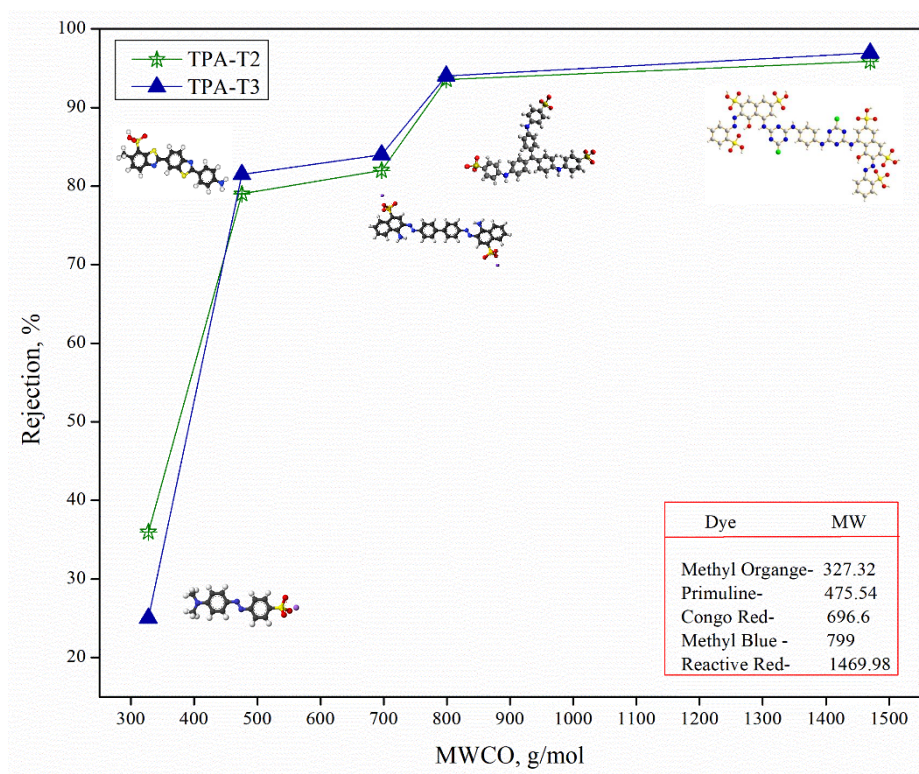


Figure 32. Organic Solvent Nanofiltration rejection performance of TpPa-1 COF membranes.

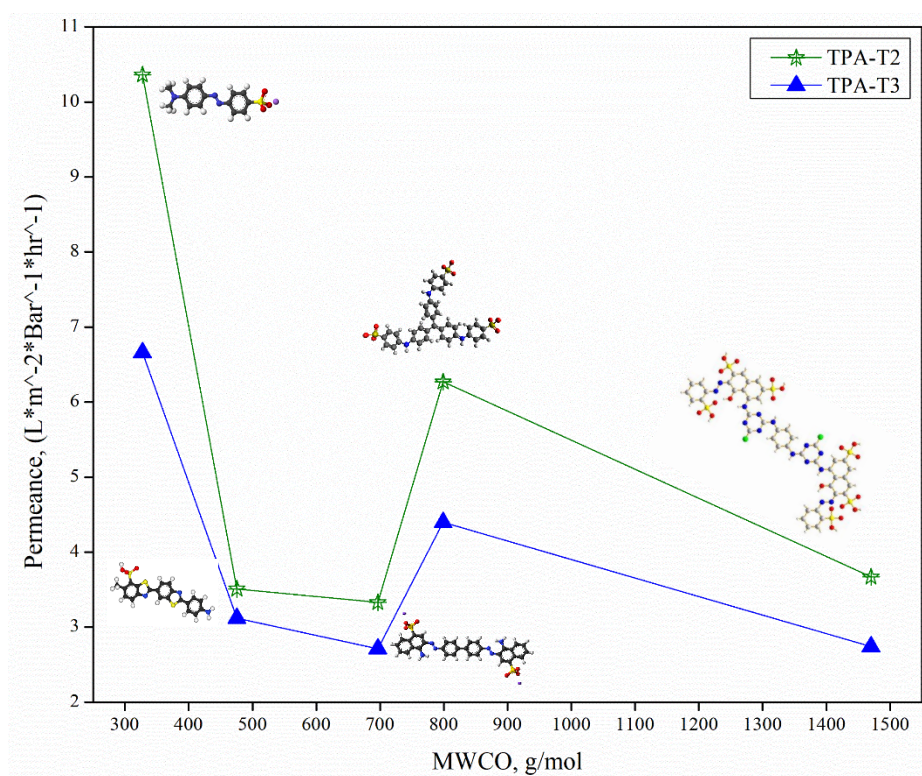


Figure 33. Organic Solvent Nanofiltration permeance data for TpPa-1 COF membrane.

Fig. 32 shows the molecular weight cut off for TPA-T2 membrane and TPA-T3 membrane. A molecular weight retention trend was observed for TpPa-1 COF membrane. We could see that

methyl orange with a molecular weight of $327.32 \text{ g mol}^{-1}$ has a rejection value of 26.12% and 35.51% for TPA-2 membrane and TPA-3 membrane, whereas for the same set of membranes the reactive red 120 rejection is almost 95.86% and 96.93% with a molecular weight of $1469.98 \text{ g mol}^{-1}$. It confirms that the difference in molecular weight causes the rejection of dye solutes in ethanol. Secondly, if we consider the molecular shape/molecular size, methyl orange is comparatively smaller in structure than methyl blue and reactive red 120. This theory suggests that the rejection could be due to the molecular size of the solute. The charge effect, which can be seen in a water system (methyl blue rejection is higher than fast green rejection), is not visible in an organic solvent system because the dye solutes become neutral [41]. Figure 34 shows TpPa-1 COF membrane used for dye rejection in water system and organic solvent system. Solute particles can be seen adsorbed on TpPa-1 COF membrane (A) in the water system, whereas very few solute particles are seen on the membrane used in the organic solvent system.

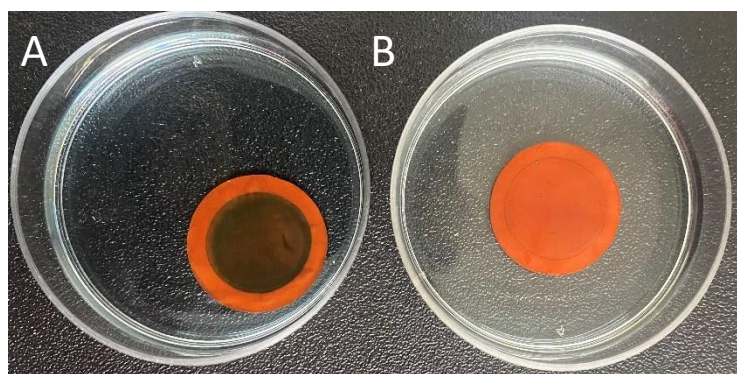


Figure 34. Shows PEEK substrate and TpPa-1 COF membrane, (A) TpPa-1 COF membranes tested in water system and (B) organic solvent system (right).

Because of the differences in the properties of the solvents and solutes used (structure, size, charge, concentration, etc.) and the experimental filtration conditions (transmembrane pressure, temperature) used in most studies, filtration data, including MWCO-values, from

different experiments are difficult to compare [41]. When evaluating filtration results, the varying properties of given solutes must be taken into account. The molecular shape is the first thing to alter.

Figure 35 depicts the pure solvent permeance of the TpPa-1 COF membrane employed in the organic solvent nanofiltration system.

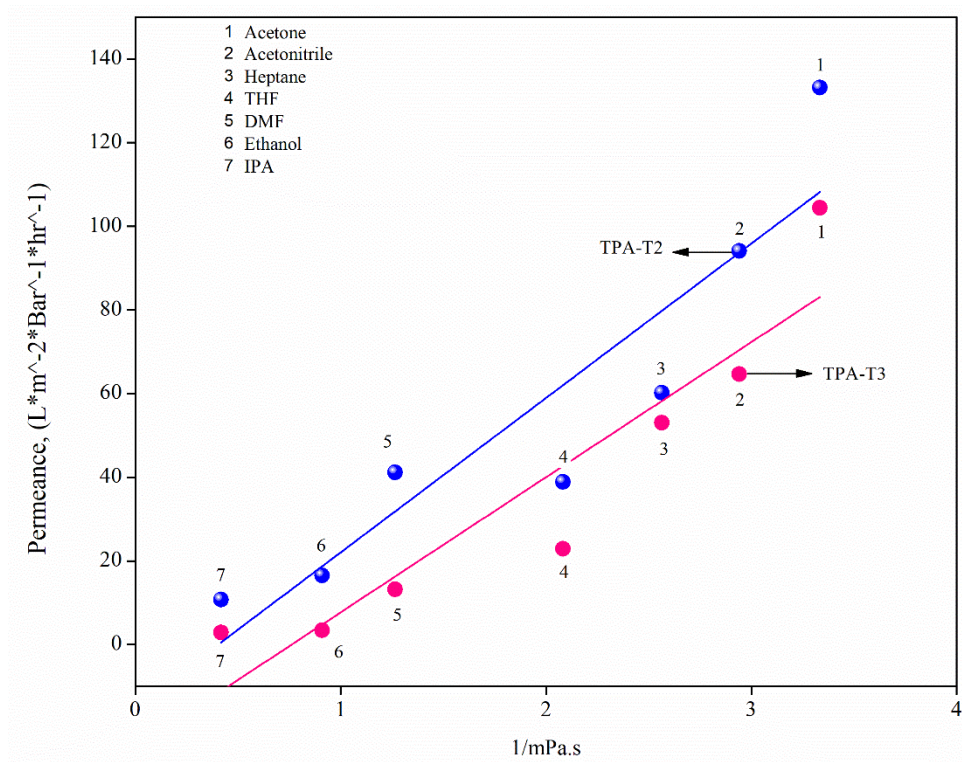


Figure 35. The permeances of polar and nonpolar organic solvents through TpPa-1 COF membranes plotted against inverse of their viscosity.

The plot of permeance versus the inverse of viscosity ($1/\text{mPa.s}$) is shown in figure 35. Many researchers [40], have reported linear curves for OSN membrane, suggesting that the TpPa-1 COF membrane has definite pores where the liquid permeation obeys the pore flow theory. The pore-flow model was built on the assumption that all membrane pores are straight and cylindrical, with an effective length penetrating through the selective layer of the membrane, and that all pores are operating in an isothermal state. Inside the membrane, stable pores are assumed to exist, and the driving force for transport is the pressure differential across the

membrane. In figure 35, a gradual decrease in solvent permeance can be seen based on viscosity change from solvent to solvent. There is considerable debate about whether pore-flow or solution-diffusion models should be used to describe OSN transport. Some authors propose that molecules dissolve in the membrane and then diffuse through it as a result of an activity gradient. Others believe that pressure-driven viscous flow through nanopores is accountable for solute transport.

The solvent permeability, solute rejection, and filtration recovery all contribute to the overall performance of an OSN process. There was no special interest in understanding the interactions between the solute and the water molecules in aqueous; however, putative membrane–solvent–solute interactions may be considerably more relevant for OSN since changing the solvent can produce an extensive range of different interactions.

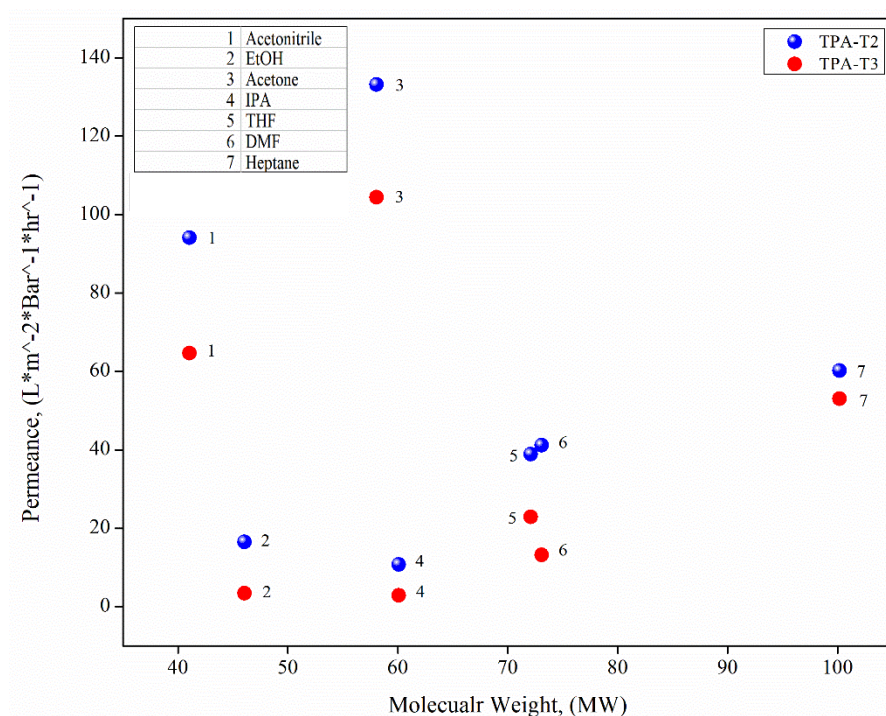


Figure 36. Pure solvent permeance plotted against molecular weight of solvents for TPA-T2 and TPA-T3 COF membrane.

The graph above (Fig 36) does not follow a linear trend of permeance. This confirms that the permeance of TpPa-1 COF membranes is not dependent on molecular weight because the pore

size is much larger than the molecular dimensions of the solvent molecules. The MWCO of TpPa-1 COF membrane studied in this research is found to be $780\text{ g} \cdot \text{mol}^{-1}$ which is much larger than the solvent molecular weight.

CONCLUSION

The work presented in this study illustrates the synthesis of continuous covalent organic framework membranes on solvent-resistant polymer (polyether ether ketone) substrates by the scalable interfacial polymerization method. SEM characterization revealed the formation of a continuous COF layer with a thickness of around 400nm, completely covering the pores of PEEK support. The FT-IR data of the membranes suggested that the layer formed on PEEK support is TpPa-1 COF, but a detailed study is needed. X-ray Diffraction results indicated that TpPa-1 COF powder has a good crystalline structure, however, there are no observable peaks for TpPa-1 COF membrane, implying low crystallinity for the COF made via interfacial polymerization.

The results from nanofiltration measurement in water and organic solvent system suggest that the rejection of charged dyes in water system is due to electrostatic/adsorption whereas, in organic solvents its due to size exclusion by membrane pores (fig. 34). The adsorption effect is largely inhibited in organic solvents system. Therefore, the rejection of solute dissolved in organic solvent (e.g., ethanol) is mainly due to size exclusion effect offered by the TpPa-1 COF pores. For TPA-T3 COF membrane a retention of >95% and >93% was achieved for reactive red dye and methyl blue with a solvent permeance of $56.1 \text{ L m}^{-2}\text{hr}^{-1}\text{bar}^{-1}$ and $15.83 \text{ L m}^{-2}\text{hr}^{-1}\text{bar}^{-1}$, respectively.

To date, COF membranes synthesized by interfacial polymerization do not possess the ideal 2D COF structures observed in COF powders made by solvothermal synthesis. It is difficult to explain how an unaligned structure can exhibit very high apparent size selectivity and permeability.

Additional work is needed to improve the performances of COF membranes and to better understand their structures, including:

1. The first and foremost is to make COF layer more crystalline with defined arrangement of COF structures for the rejection of solutes of similar molecular weights or sizes.
2. More study is needed to learn about the interactions of solute, solvent, and solute-solvent interactions with membrane.
3. Experiments with active pharmaceutical ingredient (API) and catalysts used industrially need to be explored.
4. The membrane pore size and molecular weight cut off in OSN need to be further evaluated using neutral solutes such as polyethylene glycol (PEG) and polystyrene (PS).
5. The swelling and stability of COF membranes in harsh organic solvents need to be investigated by material characterization and long-term permeation measurement.

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