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A Review on Advanced Covalent Organic Framework Membranes: Design, Synthesis, Characterization, and Applications

Amira Hajri

Department of Chemistry, Alwajh College, University of Tabuk, Tabuk 71421, Saudi Arabia

Abstract

Membrane technology has received great interest in the past decades in diverse disciplines like chemistry, engineering, physics, and materials science. To handle current and upcoming scientific, technological, and social concerns, better and more effective membranes are required. For the manufacturing of such membranes, new materials with improved characteristics are requested. Covalent Organic Frameworks (COFs) are a novel type of crystalline porous materials, that has a vast surface area, tunable pore size, structure, and functionality; making them an ideal option for membrane fabrication. Several articles focusing on the production of membranes for various applications using COFs have been published recently. In this context, this article review examines the study that looked at the creation of COFs membrane and their various appliances in numerous fields. Firstly, this work seeks to give a comprehensive picture of the covalent organic framework membrane fabrication techniques, highlighting the basic parameters for their fabrication and also their weaknesses. The second goal was to present a thorough overview of the characterization techniques used for COF membranes. The third objective detailed the applications of these membranes in numerous processes, including molecular separation, gas separation, water purification, and energy storage. From our perspective, using this article review as a starting point to teach about the function of covalent organic frameworks membranes in diverse domains would be beneficial.

1. Introduction

Membrane technologies have been visualized as a disruptive and necessary technology to substitute the actual energy-intensive separation applications [1-4]; membranes are capable of reducing the amount of energy used worldwide for the chemical separation of crude materials and vigorously minimizing greenhouse gas emissions, also training the foundation for a sustainable future [5, 6]). Consequently, membranes-based technologies are one of the most suitable techniques from a scientific and practical standpoint [7, 8]. Due to its outstanding capacity to address energy threats, water scarcity, pollution, and carbon neutrality, membrane technology is actually playing a greater position in the durable improvement of our society [9, 10]. In fact, among the major challenges in the application of membranes, the permeability/selectivity trade-off problem has gathered increased scientific attention in currents years. Ultrathin membrane (downward to 300 nm) could be able to resolve this issue [11]. The foundation of membrane technology is the membrane materials that establish the selectivity, percolation flux, and effective steadiness of membranes [12-15]. Therefore, investigating novel materials and advanced strategies for compact, greatly systemically microporous membranes is a constant continuation [16-21]. Over the past decades, porous materials have drawn a huge agreement of attention in physics, chemistry, and materials science [22, 23]. In fact, in reason to their large specific surface area, intersecting channel structure, and excellent stability, porous materials have gained a lot of attention in scientific research. Many membrane materials, including zeolites, silicas, carbons, conjugated microporous polymers, metal-organic frameworks, polymers with intrinsic microporosity, and different sophisticated porous materials are used to achieve this goal [11, 24]. In theory, perfect membrane should have elevated channel density or porosity, thin thickness, and small tortuosity to deliver high permeance and have regular channel morphology and even channel size to deliver

tall selectivity [25-27]). Though, the permeability and the selectivity of the conventional polymer membrane, which at present represent for the greater part of the membranes promote, sometimes undergo from an inherent trade-off [28, 26]). In fact, the dense and amorphous structure of the polymer membranes makes them less than suitable for transport. These permeability-selectivity tradeoff problems of polymer membrane states that increasing the flux of amorphous polymer membrane without fail results in a loss of selectivity. On the other hand, in applications involving gas separation and water desalination, membranes composed of structured micro-porous materials, like zeolites and metal organic frameworks, have established efficiency greater to that of polymer membranes [29-33]. Despite the effectiveness of these membranes, ordered porous membranes have not yet been used to their complete capability. One contributing factor is the lack of structural and chemical stability most large-pore zeolites and MOFs display when used for liquid separation [30]. Hence, MOF membranes are typically unstable in the working media and are more expensive and difficult to scale up than zeolite membranes [26, 34, 35]). In reason their feasible use in water filtration, molecular separation, and desalination, precise molecular sieving and fast solvent permeation through graphene oxide membrane have recently garnered a lot of attention. However, the swell of interlayer channels makes it difficult to preserve the laminar graphene-oxide membrane pores when immersed in an aqueous solution. These difficulties hinder the potential use of laminar graphene oxide membrane in the actual separation process [36]. It appears that research has not yet been able to create the most effective membrane for application in a specific domain.

Porous organic materials are attracting more attention as a result of their appealing applications in a broad range of industries, including gas separation, biotechnology, adsorption, optoelectronics, desorption catalysis purification, etc. These porous materials have a multitude of distinctive qualities, including low mass densities, great porosity, and surface areas, consistent and constant pore sizes, and outstanding thermal and chemical durability. COF a new category of porous materials with predesignate structure, is one of these materials [37]. The combination of organic construction components into extremely ordered and periodic two-dimensional (2D) or three-dimensional (3D) network structures with atomic precision is known as a covalent organic framework (COF) [38, 39]). COF is a potential candidate for creating advanced membranes that work very well for molecular separation in reasons their properties such as persistent porosity, substantial specific surface area, and clearly defined pore aperture [36, 40, 41]. The first covalent organic framework described by Yaghi et al. in 2005 [42] where the manufacturer employs the reversible reaction of boronic acid trimerization to form boroxine COF (e.g. COF-1), or their condensation with catechols to form bornate ester COFs (e.g. COF-5) [6]. Up to date, the approaches ever explored for fabricating COF membranes involved solid-state mixing method, in situ growth, Langmuir-Blodgett strategy, polymerization, and vapor-assisted synthesis and assembly of COF nanosheets. Based to literature COF membranes demonstrated high potential application in numerous domains such as molecular separation, gas separation, water cleansing, and energy storage. As indicate in figure 1, in the last decade, the numeral of publications on covalent organic framework membranes has augmented exponentially. Nowadays, diverse review articles on other membranes such as MOF have been published. Unlike COF membrane, there are some overviews published, such as by Fang et al. in 2020 [43] and Li et al. in 2021 [44].

Given the great progress realized in recent years on the COF membranes, it is noble to summarize current developments in an appropriate and systematic manner; As such that it dish as a foundation for researchers novel to the subdue also as a rapid reveal for the specialist in the domain. In this research, we initially offer advanced strategies to fabricate COF membranes. Then the principal characterization methods used to determine membrane properties have been described. In the three-part, the design of COF membranes is discussed. Finally, recent advances in some emerging applications of COF have been discussed.
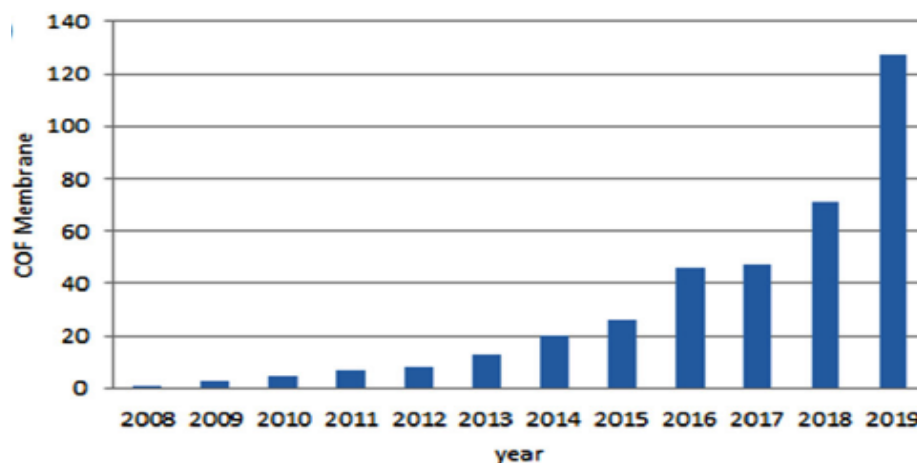
Figure 1: The sum of research per year COFs membranes (Data obtained from the Web of Sciences [43]

II Synthesis of covalent organic framework membranes

Covalent organic frameworks (COFs) are prepared by organic building elements through dynamic covalent bonds. Getting suitable conditions for the fabrication of COFs is a vital task to transplant the merits of COF into practical applications. In these contexts, researchers are making efforts to synthesize COF-based membranes with outstanding efficiency. Up to now, several approaches have been developed for fabricating excellent-performance COF membranes. In the next sections, different strategies have been developed for COF-based membranes are highlighted:

1. Polymerization

Interfacial polymerization has been renowned as one of the most impressive approach thanks to its outstanding designability, applicability, and scalability. For instance, recently Zhou and coworkers first fabricated a t-TpMa-COF membrane referring to interfacial polymerization at the liquid-liquid interface [45]. One of the most interesting awards of the prepared membrane is the different surface morphologies bent at the interface between the two solvents. In fact, the obtained t-TpMa-COF membrane showed a hydrophobic character on the side by linear Turing structure, whereas, the other side was super hydrophilic with a porous Turning structure. The bidirectional anisotropic properties of the membrane led to an increase in the water permeability of the hydrophilic boundary by 45 times in comparison to the hydrophobic side. Thus, this membrane realized dual rewards by improving the water permeability and preventing the reverse osmosis of water. Moreover, the phase-transfer polymerization process was used to fabricate COF-based membranes. A tight COFs membrane was successfully formed following molecular precursor engineering of COFs [46]. During this study, six quaternary ammonium-functionalized were fabricated by assembling functional hydrazides and various aldehyde precursors conferring the uppermost hydroxide ion conductivity reaching a value above 200 mS cm^{-1} at 800°C. Surface-initiated polymerization (SIP) is becoming a major area of interest within the field of surface modification as well as getting polymer coatings. In this view, [23] used SIP in the well-ordered building of a COF coating on initiator-immobilized silicone support. After the sacrificial layer withdrawal, a free-standing sulfonic COF was successfully developed. Wang and coworkers [47] drew a novel protocol for IP by direct synthesis of COF on polysulfone (PSF) substrates and obtained high perm-selective composite membranes. In particular, COF precursors of 1,3,5-triformylphloroglucinol (Tp) and p-phenylenediamine (Pa) molecules were consecutively dropped on PSF ultra filtration substrates. Owing to the adequate reaction rate between monomer pairs in corresponding organic and aqueous solutions, the development of COF crystallites is directly composited together with the substrate within 1 min.

2. Langmuir-Blodgett

The Langmuir-Blodgett (LB) method was perceived as a versatile way to make, at the air-water interface, monomolecular films of amphiphilic molecules with the precise organization [48]. The gained films are then conveyed onto solid substrates in order to get the looked-for number of layers of LB films. The said method can accurately adjust the membrane thickness to the molecular scale. Recently, there has been renewed interest in the Langmuir-Blodgett as a

prestigious way for fabricating COF thin films. For instance, a simplistic fabrication 2D covalent organic tinny film via imines bonding through the LB method has been reported by Gadwal et al [49]. More specifically, this film is prepared from two aromatic building blocks, hexaalkylatedtruxene based of triamine [Tru (NH$_2$)$_3$ and terephthalaldehyde (TPA). The obtained thin film showed a pore size of about 1.5 nm a compacted membrane with a thickness of around 2-3 molecular layers was effectively fabricated. With the aim to acquire 2D COFs with minor size, Meng et al reduced the two branches 'length and included two amine and aldehyde functional groups at a terphenyl core, a C$_2$ symmetric bifunctional A$_2$B$_2$ molecule, and pioneer the fabrication of 4,4-diamino-2'-5'-diformyl-1,1':4',1''-terphenyl [50]. Taking the advantage of monomer size, a terphenyl (TP) based COF with 0.99 nm pore size was developed via the LB method. Shinde and coworkers fabricated crystalline 2D COF membranes by the LB approach for the first time [32]. During this work, the COF membrane was formed by the β-ketoenamine assembly between the two precursors of 1,3,5-triformylphloroglucinol (TEP) and 9,9-dihexylfluorene-2,7-diamine (DHP), at the water-air interface. More recently, this working group worked on the development of two ultrathin COF-based membranes with the aim of sensibly tuning the pore size. Diamines, 9,9-dipropylfluorene-2,7-diamine (DPF) and 9,9-dinonylfuorene-2,7-diamine (DNF), were fabricated. The two mentioned COF displayed comparable framework structures to the previous TFP-DHF membrane however with dissimilar pore sizes and diverse lengths of carbon chains. The obtained COF membranes exhibited superior thermal and chemical stability associated with high crystal quality [44].

3. In situ growth

The in situ growth of COF on a porous substrate has been suggested as an efficient method for COF-based membrane fabrication consisting of mixing the metal ions/monomer and the organic ligands/monomer into a solution as a first phase and the immersion of porous substrates in a next step. The reaction interface occurs on the substrate surface. A great COF membrane maintained on the amine-functionalized porous ceramic α-Al$_2$O$_3$ substrate was obtained via in situ growth [51]. In fact, the CPF-300 membrane was developed by a one-step solvothermal

technique via the Teflon-lined autoclave and showed several advantages including superior specific surface area together with porosity. The characterizations of the prepared COF membrane confirmed that pre-grafting of 3-aminopropyltriethoxysilane (APTES) and terephthalaldehyde (TPA) operated as a surface anchor towards the linkers between the ceramic support and the membrane. Recently, an ultrathin suffocated imine-linked triformylphloroglucinol with 2,5-diaminobenzensulfonic acid (TPE-DABA) COF membrane on polyacrylonitrile (PAN) support was developed. The DABA served as an acid catalyst while the PAN proceeded as a molecular linker to attach and anchor COF building-monomers which in turn stimulated the nucleation of COFs on the support and the growth of the COF layer [26]. The blending of catalyst and monomers into a solution of polyacrylonitrile (PAN) constitutes a good approach for COF membranes. For instance, a cationic COF named TpEB was used to fabricate a high-quality TpEB-PAN membrane [52]. In fact, the TpEB cationic crystallites were restrained subsequent to the contact with negative PAN chains. This phenomenon led to the creation of a well-distributed and homogeneous TpEB-combined casting solution. Here the membrane was developed using the no solvent-induced phase separation (NIPS) process and the TpEB crystallites play the role of modulators to regulate the NIPS method as well as functional fillers. Moreover, a novel COF-based membrane named COF-LZU1 (LZU: Lanzhou University) was successfully developed by the in situ solvothermal method supported on a ceramic tubes. It was obtained by the condensation of 1,3,5-triformylbenzene (TFB) together with the phenylenediamine (PDA) and showed a 2D eclipsed layered sheet structure and a thickness of 400 nm [53].

4. Other methods

Owing to their good mechanical behavior and plentiful functional groups [54] coupled with Silk nanofibrils (SNF) and ionic liquid-soaked COFs to fabricate COF /SNF composite membranes. Firstly, a sulfonic acid-based COF (COF-SO3H) was firstly fabricated (COF-SO$_3$ H) and burdened with methylimidazolium tetrafluoroborate [Bmim] (BF$_4$) in order to obtain IL-COFSO$_3$H. Secondly, IL-COFSO$_3$H-SNF composite was prepared by combining IL-COFSO$_3$H and SNF by casting

technique. During this study, authors indicated that the impregnation of IL inside COF SO_3H delivered enormous proton hopping sites.

Layer-by-layer (LB) assembly has been viewed as an attractive and widespread method to fabricate nanofilms, resulting in well-regulated thickness and high surface chemistry using several substrates and applied in diverse fields.

In this context [36] succeeded to prepare a cationic EB-COF:Br nanosheets via the interfacial crystallization method. Subsequently, a LB restacking method was executed to prepare continuous 2D EB-COF:Br membrane using vacuum filtration of several quantities of nanosheets on the nylon 66 substrate. The fabricated COF-based membrane presented high porosity and thus great solvent permeability. Polyamide has the advantage of being mechanical and chemically stable confirming its high performance on membrane materials. For that reason, [55] combined polyamide and COF and pioneer the fabrication of amide-linked COF
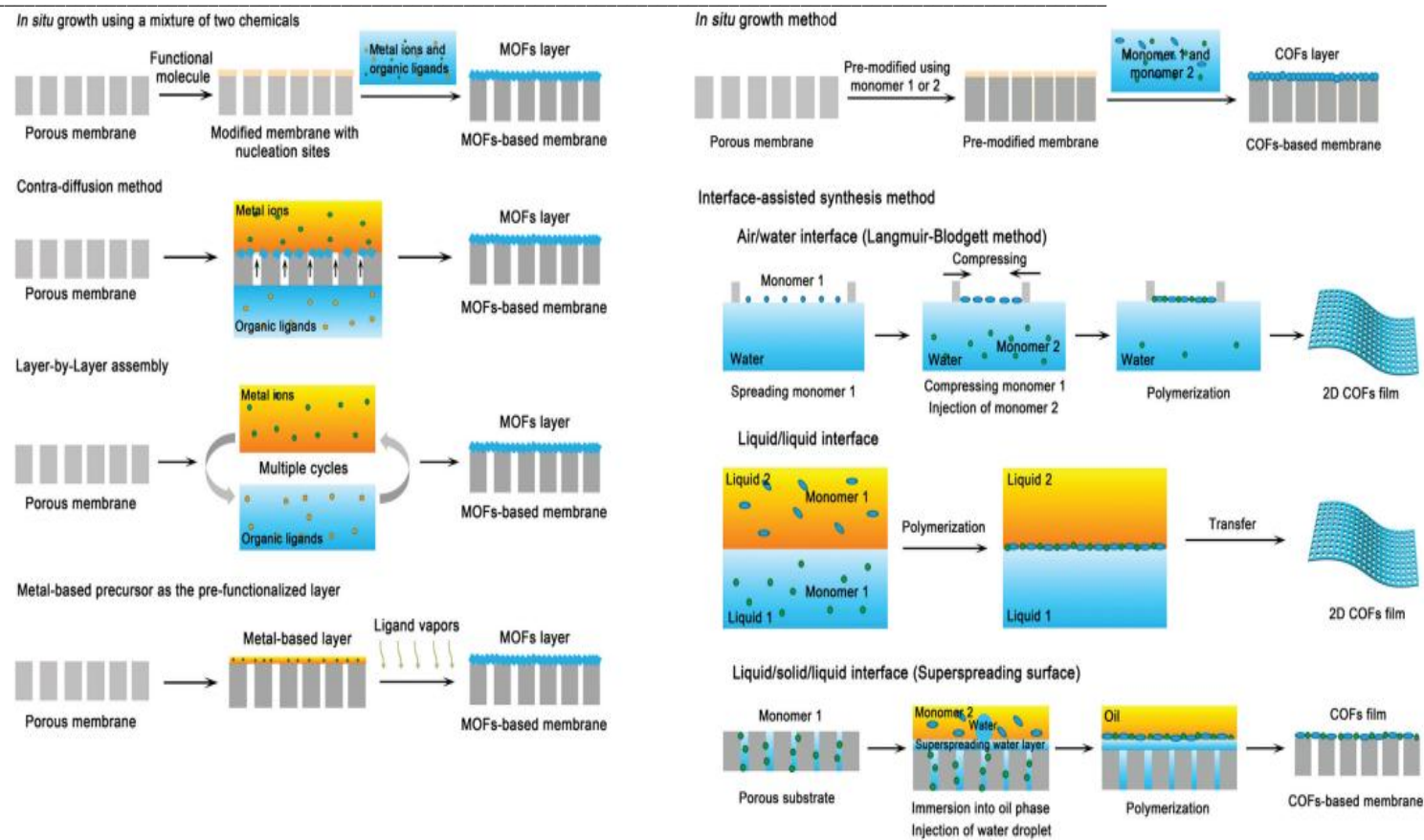
membranes. Firstly, COF layers were prepared by interfacial polymerization procedure. The amide-COF layers were obtained using the oxidation of imines COF layers with $KHSO_5$, while the amine-COF layers were reached by $NaBH_4$ reduction of imines COF layers. Afterward, COF membranes were made-up referring to the vacuum-assisted LB method. The prepared polyamide COF membrane presented a high crystalline property, which in turn makes order distribution of the inside process.

Each preparation methods have its one protocol and characteristics which are summarized in Figure 2. In particular, Figure 2 summarizes different COF synthetic aspects such as chemical structures, linkage and chemical conditions employed during each method.

Table 1 illustrated significant research in the late literature, demonstrating a great movement for the employment of these various methods to prepare covalent organic framework membranes.

Tableau 1: Recapitulation of covalent organic framework membranes

COF	Preparation Methods	Advantages	Disadvantages	Application	References
CPF-300	In situ growth	-Easy process -Worldwide tunable thickness	Require functional substrate surface	Selective Dye Separation	[51]
TpEB-PAN				nanofiltaration	[52]
COF-LZU1				Dye separation	[19]
COF-LZU1				Gas separation H_2/CH_4	[57]
-TFP–DPF -TFP–DNF	Langmuir-Blodgett:	-Transformation to several substrates -Turnablethinkness	Small scale	Organic solvent nanofiltration	[39]
TFP-DHF				Organic solvent nanofiltration	[30]
Tru $(NH_2)_3$ TPA				Molecular Sieving Nanofiltration	[49]
COF-QAswould	Polymerization	-Direct formation and scale -Tunable think		Anion transport	[46]
t-TpMa-COF				Water treatment Deacidification	[45]
SCOF				Proton conduction	[23]
EB-COF:Br	Layer-by-layer assembly	Control of thickness Ultra-thin layer	Extra exfoliation steps are required	Selective molecular sieving	[36]
Polyamide COF				Molecular sieving	[55]

**Figure 2:** Preparation methods of covalent organic framework membrane [56]

IΙΙ Characterization and Properties of covalent organic framework membrane

This section concentrates on the techniques for characterizing the COF membrane's qualities, including its stability, flexibility, thickness, permeability, and porosity. In fact, understanding of COF membrane structure is crucial for their practical applications. Two levels of characterization are available for membranes manufactured from COF material: characterization of the covalent organic framework particle and characterization of the membrane made from the particle. The characterization of COF materials is the subject of several leading papers. At this point, we will highlight the typical methods for characterizing covalent organic framework membranes based on their basic characteristics, like their structural, morphological properties, textural, etc. In literature, the COF membranes have been characterized using various techniques to understand their structure, pore size, crystallite size, and pores distribution. X-ray diffraction (XRD), Fourier transforms infrared (FTIR) electro micrographs (SEM), transmission electron microscopy (TEM), etc. are essential techniques for characterizing materials (Figure 3).

Figure 3: Characterization and properties of COF membrane
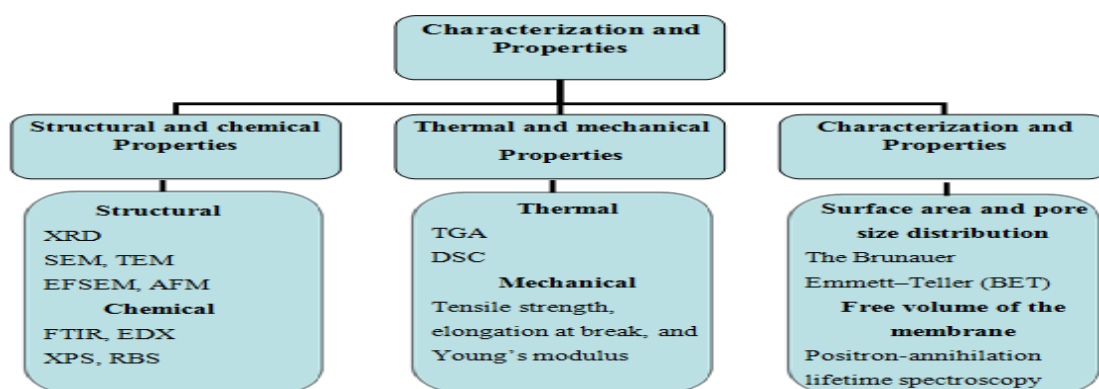
Given that COF is a crystalline porous material, crystalline structure in the membranes based on these materials is expected. The membrane structure would be confirmed and the effectiveness of the used approach would be demonstrated by a differentiation of the pattern of the membrane and the pattern of COF materials used. XRD was the mainly effective technique employed to determine the membrane's degree of crystallinity. In addition to crystallinity, XRD may identify the packing pattern and orientation of the COF particles that compose the membrane. As a result, XRD measurement has typically been employed to verify the success of COF membrane preparation.

The most crucial characteristics to establish for membranes are their morphological characteristics, which reveal their surface roughness and continuity are devoid of surface cracks that could contribute to preferential diffusion paths. In the literature microscopies imaging methods like scanning electron microscopy, field emission electron microscopy (FESEM), transmission electron microscopy, and atomic force microscopy (AFM) are employed to obtain perspicacity into the inner structure of the membrane. These methods have the benefit of providing clear and visible information about the membrane morphology. For instance, many publications have used cross-sections of covalent organic framework membranes under scanning electron microscopy, transmission electron microscopy, or atomic force microscopy analysis to provide details on the membrane thickness and the interface between the covalent organic framework layer and the matrix. The pore size and morphology of the covalent organic framework membrane are also determined using TEM or FESEM imaging.

Fourier transform infrared, X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy, and Rutherford backscattering spectrometry are effective methods for the chemical characterization of the covalent organic framework membrane. Chemical bonds and functions are revealed as vibration signals in an FTIR spectrum. It is a simple procedure to verify the emergence of covalent organic framework selective layers and

investigate membrane surface transformation. The binding energy of atoms, which can be employed to determine an element's degree of oxidation, is measured using XPS. Chemical composition analysis using XPS can rarely be carried out and compared with FTIR analysis. SEM or TEM imaging is frequently combined with EDX spectroscopy. According to the kind and intensity of the X-ray interaction with the various atoms and elements present inside the deducting region, a quantitative map of the elements might be constructed (observation window). To identify the various components included in a covalent organic framework membrane, EDX is an extremely practical instrument.

Thermogravimetric analysis (TGA) and differential scanning calorimetry can be employed to examine the thermal flexibility and stability of the COF membrane (DSC). This method is particularly helpful for determining the highest temperature the membrane can reach before decomposing. Examining the impact of applied pressure and mechanical stress on the membrane structure are be achieved by evaluating the mechanical resistance of the COF membrane. Tensile strength, elongation at break, and Young's modulus are frequently studied parameters.

The Brunauer-Emmett-Teller surface area was usually estimated using N_2 adsorption measured at 77Kand employed to determine the pore size distribution by applying various models as a function of the pore geometry. Zeta potential analysis was used to examine the charged nature of a composite membrane surface, one of the significant surface physico-chemical parameters, for a better understanding the impact of surface charge on rejection characteristics.

According to literature review, several researches have utilized these techniques to describe Covalent Organic Framework membranes:

By assembling two-dimensional COF nano sheets with one-dimensional cellulose nanofibers a mixed-dimensional structure, [58] were able to produce a multitude of COF membranes (CNFs).The pore size distribution and membrane stability were determined in this study. According to the results, TpTGCl's intrinsic pores account for the pore size distribution of 1.3 nm for all membranes. This indicates that varied molecular separations can be accomplished by successfully adjusting pore size

distribution in the membranes. The TpTGCl@CNFs-X membranes exhibit considerably higher elastic modulus and tensile strength (up to 108.3 MPa) (up to 3.62 GPa).The membranes architecture also resembles those of bee honeycombs, which include multilayered hexagonal cells and cell coverings that resemble fibers and are extremely strong mechanically. Thermogravimetric analysis curves demonstrate the membranes' great thermal stability, with weight loss as low as 5% at temperatures below 200 °C.

Lu and his team in 2015 [37] were developed a three dimensional Covalent Organic Framework-320 membrane on a surface modified porous α-Al_2O_3 substrate. Powder X-ray diffraction, Scanning Electron Microscopy, Fourier Transform Infrared spectroscopy, and TG-DSC were used to examine the crystallinity and the particle morphology of the tree dimension Covalent Organic Framework-320 powders that were extracted from the same reaction tube in which the supported three dimensional COF-320 membrane was synchronously generated. According to the findings, the 3D COF-320 powder's PXRD pattern had a significant crystallinity level. The production of the expected -CQN- bonds was further confirmed by the Fourier Transform Infrared Spectroscopy spectra of the three dimensions Covalent Organic Framework 320. Moreover, the 3D COF-320 powder exhibits considerable particle aggregation and a broad particle size range of 0.2-1.0mm as determined by Scanning Electron Microscopy.

Zhang et al. 2018 [36] reported the production of two dimensional (2D) cationic COF,EB-COF:Br nanosheets using a simple bottom-up interfacial crystallization method. Finally, using just vacuum filtration, a permanent and dense two dimensional ionic Covalent Organic Framework membrane with adjustable thicknesses created by layer-by-layer restacking. Several methods have been used to analyze the porosity and pore size of and to figure out the thickness of the EB-COF:Br nanosheets in order to obtain insight into the internal structure of the Covalent Organic Framework nanosheets and membrane.

The obtained results are as following:

-The EB-COF: Br nanosheets exhibit an excellent level of crystallinity, as shown by the TEM image.

-The EB-COF: Br membrane is continual and free of surface flaws, which is necessary for effective separation, according to the Scanning Electron Microscope pictures.

-The EB-COF: Br membrane's structure was confirmed using X-ray diffraction. The EB-COF: Br is a typical two dimensional layered hexagonal network as it has been synthesized according to structural resolution using the X-ray diffraction pattern and generated structure

-The membrane nitrogen adsorption-desorption experiment was performed at 77K, and the results show that a significant rise in gas absorption was noticed at deceased pressure, indicating the existence of micropores in the membrane.

-For EBCOF: Br, the surface area determined using the Brunauer-Emmett-Teller model is 554 $m^2 g^{-1}$.

-The concept of nonlocal density functional, caused by the model N_2 at 77 K on carbon was employed to calculate the distribution of pore size of the EBCOF: Br membrane. In EB-COF:Br, the 16.8 pore size is predominant.

The findings above confirmed that EB-COF: Br with uniform 1D channel, a porous two dimensional Covalent Organic Frameworks membrane is the Br membrane.

The Langmuir-Blodgett method was utilized by Shinde et al. in 2020 [39], to synthesize two ultrathin covalent organic framework membranes (TFP-DFP and TFP-DNF) 9.9 –diproyl uorene-2.7-diamine (DPF) and 9,9-dihexylfluorene-2,7-diamine (DNF). The powder X-ray diffraction pattern of TFP-DPF indicated peaks at 5.1 and 122.45, which were attributed to (100) and (001), respectively. The wide peak between 17 and 27, however, was most probably associated with the membrane's nodal structure. Both instances of nitrogen physiosorption 77K revealed a type II adsorption isotherm. TFP-DPF and TFP-DNF had Brunauer-Emmett-Teller surface areas of 336 and 172 $m^2 g^{-1}$, respectively. Both optical and scanning electron microscopies were used to examine the single-layer COF membranes' characteristics. The thin, smooth, and compact single layer covalent organic framework membranes and all observations have shown that they are defect-free. For precise Separations in difficult circumstances.

Shi et al. 2021 [59] created adaptable and reliable three-dimensional covalent organic framework (3D-OH-COF). Powder X-ray diffraction,
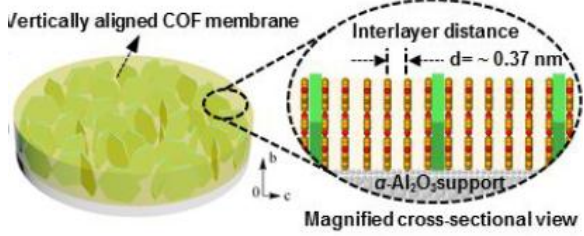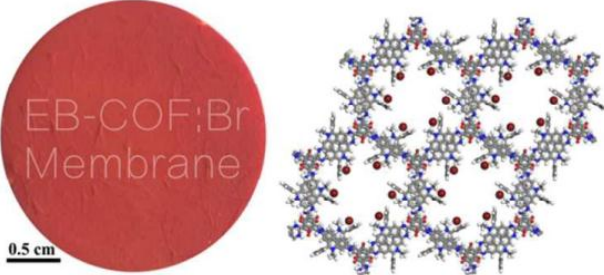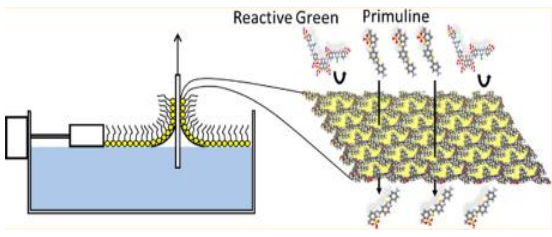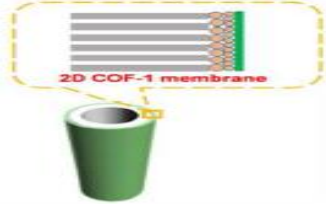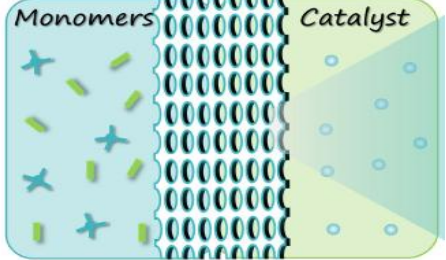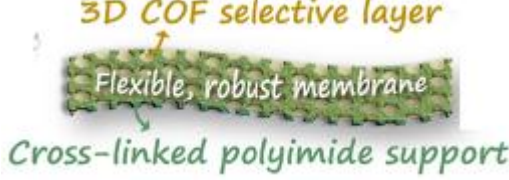
thermogravimetry, and measures of N_2 adsorption and desorption on the 3D-OH-COF have all been used to characterize these membranes. The resulting Powder X-ray diffraction pattern exhibits strong concordance with the modeling and the findings of numerous studies, which point to an excellent crystalline structure. According to a thermographimetric examination, three-dimensional-OH-COF can withstand thermal treatment up to 450 °C. A small range of pore sizes with a center of 0.88 nm is recognized by the fitting of the nonlocal density functional theory (NLDFT), and the area of the surface calculated by Brunauer-Emmett-Teller (BET) is found to be 843.4$m^2 g^{-1}$.

IV Design of membranes with a covalent organic framework

Applying the reticular chemistry design principles, covalent organic frameworks can be divided into two-dimensional (2D) and three-dimensional (3D) categories based on the dimensionality of linkages (Table 2). Until now, 2D COFs have made up more than 95% of COF membranes, resulting in efficient sieving pore size between 1 and 2.5 nm. Two-dimensional covalent organic framework are newly developed crystalline porous materials with carefully regulated pore size, functionalized pore surface, and nanochannels oriented In their vertical direction [36]. Specifically, because of their well organized, straight pores and remarkable stability under difficult chemical circumstances, two-dimensional covalent organic frameworks have demonstrated great potential as membrane materials [60].

The 2D COF membrane was created by ketoenamine linkages between TEP and DHF precursors resulting in a hexagonal with an inclined AA stack and pores that are around 1.41 nm in size. Shinde and his team in their work [30] developed the membrane for organic solvent nanofiltration using elevated flux according to the findings; the membrane was thermally stable up to 200 °C and has a water contact angle of 84.5°. The TFP-DHF two dimensional covalent organic framework membrane's well-defined porosity structure considerably increased solvent permeability by 100 times as compared with amorphous membranes constructed using the similar method, and it matched the best-reported polymer membranes in all aspects.

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Tableau 2: Summary of COF membrane Design and, characterization

COF membrane	Design	References
High-Flux Vertically Aligned 2D Covalent Organic Framework		[57]
Two dimensional (2D) cationic COF, EB-COF: B membrane		[36]
1,3,5-triformylphloroglucinol - 9,9-dihexylfluorene-2,7-diamine 2D COF membrane		[30]
2D exfoliated COF-1 nanosheets membrane.		[56]
3D tetrakis(4-formylphenyl)-methane - hydrazine hydrate / polyacrylonitrile membranes		[63]
3D-OH-COF		[59]

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By gradually controlling the development of imines-based covalent organic framework-LZUI and azine-based ACOF-1 layers using a solvothermal temperature-swing method, Fan et al. (2018) [61] establish a type of two-dimensional layered stacking COFCOF composite membrane in bilayers geometry manufactured on a permeable substrate. Furthermore, due to the creation of an interlaced pore network in the contact zone, the COFCOF bilayers membrane has a higher selectivity for the separation of H_2 from other heavier gases than its separate covalent organic framework counterparts. Hence, on the basis of precise size exclusion, Fan and his collaborators propose a novel proposal comprising two dimensional covalent organic frameworks vertically providing a membrane for sufficient gas separation [62]. Using vertical CoLl LDH nano-layers as "templates" vertically aligned two-dimensional covalent organics framework layers are built as gas separation membranes inside them, which are described in this study for the first time. The slit-shaped pores have transport channels that established using the interlayer spacing of parallel 2D COF sheets as a result of the 2D COF sheets emerging in-plane on the vertical CoAl-LDH nanosheets surfaces.

In order to concurrently improve selectivity and permeability, three-dimensional (3D) COFs, a subset of the covalent organic framework family are directly supplied with ultrafine apparatus and remarkable pore connectivity. Therefore, due to their distinctive qualities, 3D COFs could provide considerable potential for the development of novel membranes that operate far more effectively and have precisely designed structures.

A three dimensional covalent organic framework with interconnected apparatus, or three-dimensional-OH-COF, was created by Shi et al. in [63]. In water and organic solvents, an increase and strong selectivity to tiny molecules is made available by the generated membrane's high crystallinity, significant porosity, and exceptional solvent resistance, which are all characteristics of the three dimensional-OH-COF that is the result. As demonstrated by the consistent performances during substantial bending and soaking in solvent at high temperatures, the membrane also remarkably demonstrates outstanding flexibility and robustness.

Under solvothermal circumstances, Lu and his collaborators created a three dimensional Covalent Organic Framework membrane on a porous α-Al_2O_3 substrate [37]. According to the results, the final product, a compact, uniform, and well-inter grown three dimensional Covalent Organic Framework-320 membrane with a thickness of around 4 mm, was determined, and it holds potential for use in membrane separation.

V Application of Covalent organic framework membranes

Owing to their intrinsic pore channels, high surface areas, and low transport resistance COF based membranes have been recognized as potential candidates for several energy and environment applications as well as transportation processes (Figure 4). The following sections highlight different reported applications.
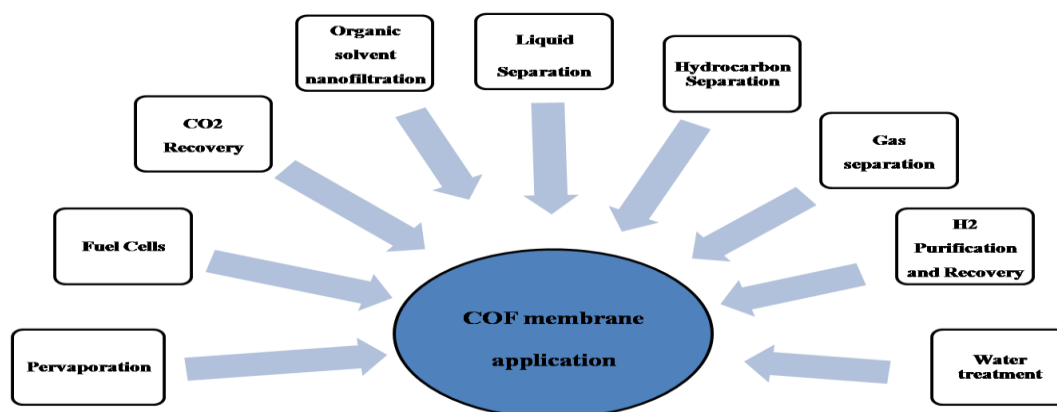
Figure 4: Application of Covalent organic framework membranes

Water treatment

COF based membranes are recognized as one of the potential membrane materials for resolving bottlenecks in   ion separation field. For instance, Wang et al used covalent COF membranes namely: TpPa–PO$_3$ H$_2$, TpPa–SO$_3$H, and TpPa-CO$_2$H to distinguish mixes of monovalent cations [64]. To appraise the separation phenomena, a confined cascade separation concept was suggested. In particular, the channels contained two different domains such as the acid area acting as confined stages and the acid-free domain. Their findings revealed that acid domains powerfully imposed with molecules of water and formed hydration shells, which in turn narrow the operative channel size. These acid domains led to high monovalent cations selectivity. However, the acid-free domains maintained the primary size and deliberated significant permeability performance. The obtained COF membrane conferred excellent ion separation efficiencies presented by an actual selectivity of 4.2-4.7 on behalf of K$^+$/Li$^+$ binary blends associated with an perfect selectivity of 13.7 K$^+$/Li$^+$. Taking the advantages of high mechanical property, stability together with the well-ordered pore, extraordinary performances of polyamide COF membrane for molecular sieving were previously achieved [55]. As mentioned, the dye separation was measured by the rejection rate of several dyes at room temperature. Outcomes revealed that the rejection rates of the COF-membranes reached much higher a value of 99.2% in comparing to that of the pure Nylon membrane that is about 45%. Moreover, this kind of membranes reached a solvent permeability of 482.3 Lm-2h^{-1}bar^{-1} to water and noteworthy separation selectivity. Zhang and coworkers, performed a series of filtration runs using dye solution and ions through-COF:Br membrane with the aim to identify its rejection capacity [36]. The rejection performance was investigated by nursing the ultraviolet absorbance intensity of filtrates. The membrane was able to reject 99.6%, of cationic dyes at different sizes caused by the presence of positive charge sites on the membrane channels. On the other side, anionic dyes occupied the internal surface of the membrane making their penetration through the membrane hard. However, during this work an excellent rejection rate of 99.6% was realized. Regarding the neutral dyes rejection rate of 74% was achieved (Table 3).

Tableau 3: Summary of COF membrane for water treatment

COF membrane	Rejection	References
EB-COF:Br	99.6%	[36]
Polyamide-COF	99.2%	[55]
TpPa–PO$_3$ H$_2$	Selectivity: 13.7 K$^+$/Li$^+$	[64]

Gas separation:

An ultrathin COF-based membrane was formerly developed to investigate its effect on gas separation [65]. The assessment of the fabricated membrane was conducted using a mixture of H$_2$ and CO$_2$ where gas permeation experiments were performed at 298 K and 3 bar. Results showed great gas permeance of H$_2$ which attained a value of 1.7 * 10^{-6} mol /(m^2 s Pa) and an H$_2$/CO$_2$ competitive selectivity of 17.4. Such values could only make the mentioned membrane a potential candidate for gas separation. More recently, Ying and colleagues made up another ultrathin COF membrane for gas separation [66]. They introduced COF as a gutter layer linking the support and the separation layer in order to avoid the top polymer solution penetration and to manage the kinetics of the precursor reaction. The COF-LZU membrane displayed large pores as well as great porosity, which in turn shrinks the resistance of gas transport and makes it an appropriate gutter layer material. This membrane exhibited higher performance in comparison to that fabricated by Ying and coworkers in 2016 [65] as the H$_2$ permeance reached a value of 2163 gas permeation units and H$_2$/CO$_2$ selectivity was 26. These observations provide the prepared membrane suitable candidate for H$_2$ separation. Furthermore, the COF-based membranes were used to CO$_2$ from CH$_4$ [67]. During this study, membrane selectivity and CO$_2$ permeability were calculated to investigate the COF-based membranes' performances. Results showed that CO$_2$ permeability surpasses 104 Barrer and separation efficacy was more than Robeson's upper bound (Table 4).

Tableau 4: Summary of COF membrane for gas separation application

COF membrane	H_2/CO_2	CH_4/CO_2	References
CTF-1	Selectivity:17.4 H_2 permeance: 1.7 10^{-6}mol/(m^2 s Pa)	-	[65]
COF-LZU	Selectivity:26 H_2 permeance: $2163 10^{-6}$mol/(m^2 s Pa)	-	[66]
Pebax/f-GO-0.9%	-	CO_2permeability:934.3 Barrer Selectivity: 71.1	[67]

Organic solvent nanofiltration (OSN)

Organic solvent nanofiltration has been viewed as an emerging approach in petrochemical and pharmaceutical industries requiring robust material membranes. The crystalline property of COFs could be competitive for organic liquid treatment by applying their high solvent resistance. In this view, Shi et al. designed 3D COF membranes for OSN application [63]. They estimated the membrane selectivity using a different filtrating solution containing methanol and numerous dyes with different molecular weights alternating from 287 to 961 Da. The elaborated membrane revealed extraordinary separation efficiencies to the studied little molecules together with significant refusal rates of 95 % to probes when using molecular weights more than 327 Da. To conclude these membranes received high solvent permeance and high molecular selectivity. As a representative of crystalline COF membranes for ONS, Shinde, and coworkers reported a TFP-DHF 2D COF membrane supported on anodic aluminum oxide (AAO) with a thickness of 61.2 nm [30]. According to their results, the membrane meaningfully amended the permeability for both polar and no polar organic solvents by 100 folders when compared to that elaborated by the same process. In particular, this membrane showed a molecular weight cut-off of 900 Dawhereas the permeation of different studied organic solvents was 140 Lm^{-2} h^{-1}bar^{-1}, 105 Lm^{-2} h^{-1}bar^{-1}, 30 Lm^{-2} h^{-1}bar^{-1}, for hexane, acetonitrile, and 2-propanol, respectively. These findings obviously stemmed from the well-defined porous structure of the TFP-DHF 2D COF membrane. Additionally, Li et al explored COF-incorporated thin film nanocomposite (TFN) membranes for OSN application [19]. The fabricated membranes not only improved the ethanol permeance up to 79.8 Lm^{-2} h^{-1}bar^{-1} but also increased Rhodamine B rejection up to 99.4 %. In fact, the several rewards exhibited by the membranes including enhanced surface hydrophobicity, and a rougher membrane surface structure contributed to the upgrading of the ethanol solvent permeance up to 46.7%. Meanwhile, robust covalent/graphene oxide (GO) composite membranes were elaborated for OSN application [68]. During this study, an increase in the long-term stability and the permeance of the membrane was observed subsequent to the GO incorporation. In fact, an increase in the GO 1 wt% to 2wt% content improved the permeance of acetone from 38 Lm^{-2} h^{-1}bar^{-1} to 45.2 Lm^{-2} h^{-1}bar^{-1}, while the further increase of the GO content to 3 wt% resulted in a fragile membrane with no suitable properties for nanofiltration. Moreover, it was revealed that the decline of membrane top layer thickness contributed to the intensification of the permeance that could be explained by the inhibition of the compaction of the polymer matrix by the GO. The highest flu reached during this study was 45.2 Lm^{-2} h^{-1}bar^{-1} which is 18 times greater than that of commercial OSN membranes with 2.5 Lm^{-2} h^{-1}bar^{-1}. The performance of the prepared membrane was also proved by its high rejection remaining over 93% for 420 g.mol^{-1} in polar and non-polar organic solvents (Table 5).

Tableau 5: Summary of COF membrane for organic solvent nanofiltration

COF membrane	Permeance	Rejection	References
TFPM-HZ/PAN membrane	Methanol: Lm^{-2} h^{-1}bar^{-1}	95 %	[63]
TFP-DHF 2D COF	Hexane: 140 Lm^{-2} h^{-1}bar^{-1}	90%	[30]
TEC TEN	Ethanol: 79.8 Lm^{-2} h^{-1}bar^{-1}	99.4 %.	[19]

Conclusion

Covalent Organic Frameworks are made of porous crystalline materials; in reason their periodic well-defined geometry, large surface area, and tunable pore design. Therefore, have received enormous interest in a large range of applications. Covalent organic frameworks make an excellent candidate material for the preparation of a membrane that may be employed in various domains due to its distinctive properties, including permanent porosity, changeable pore size, and extremely flexible molecular design. In this research, we give a view of important developments in COF conception and preparation as well as some of its numerous uses in photodynamic treatment, gas adsorption, sensing, energy storage, and catalysis. Various preparation methods for the COF membrane were outlined. In addition, the main techniques used for the characterization of COF membranes were discussed. Also, the drawbacks and the benefits of every chap of technique as well as the characterization techniques were also explained. In fact, a review of the most recent research on COF-based membrane applications throughout several domains was conducted. Lastly, experts indicate that the covalent organic framework membrane might be used in different applications that could have an impact on society's economy and ecology (environmental relevance). Covalent organic framework membrane research is a large topic that shows immense potential to be explored.

Statements and Declarations:

Conflicts of Interest: The author declare no competing interests.

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