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Article

Development of inorganic polymers to improve water treatment technologies: A review

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Abstract : Research and technologies pertaining to inorganic membranes constitutes a critical domain throughout membrane separating technology, that was formerly centered around polymeric membranes. In recent years, in-organic membranes have undergone rapid improvement and invention. Inorganic membranes offer distinct advantages. resistance to aggressive chemicals cleaning, elevated temperatures resilience, resistance to abrasion and enhanced stability of chemicals. Prolonged lifespan and compatible with autoclaving. Every one of this remarkable characteristics made inorganic membrane beneficial. appropriate for water purification as well as desalting purposes. These publication provides a status report on the evaluation of the synthesizing, development, as well as utilization of various inorganic membrane technologies for water and wastewater management. This study reviews inorganic membranes, including liquid types, membrane, dynamical membrane, various ceramics membrane, carbon-derived membrane, silica membrane and zeolite membrane. A concise overview of various synthetic methods utilized in the production of in-organic membranes designed to utilization by the water sector has been provided. Reports indicate that in-organic membranes, although having elevated synthetic costs, demonstrated highly positive outcomes with enhanced flow, complete salt rejection, as well as minimal or negligible contamination.

Keywords: Contamination water, Membranes, Inorganic membranes.

1. Introduction

Even though water is essential to human life, particularly for drinking, household chores and agricultural and industrial reasons, water quality has deteriorated due to the release of various contaminants into the water system [1]. Some of these contaminants are released into the environment either by garbage from households, waste from factories or both. Some of these pollutants from homes and factories are highly hazardous to the health of living things and the environment in which we live. Due to their actions, different colors, excessive turbidity, unpleasant odors, suspended solid materials, heavy metals, inorganic and organic microorganisms and other contaminants have been introduced into our water systems[2]. Resulting in water contamination. In 2019, the United Nations estimated that water pollution has resulted in more fatalities than any other form of violence, attributable to various diseases, including waterborne diseases (e.g., diarrhea), Both hepatitis HBs and HCV , as well as the HIV virus, among others. Waterborne infections represent a substantial health burden for numerous populations, particularly in poor nations. In Nigeria, the incidence of diarrhea among children under five years old is 1:25[3]. Consequently, inadequate management of solid and liquid waste has led to the proliferation of numerous diseases [4]. The WHO calculated that roughly 829,000 yearly deaths, translating to 54–65%, caused by diarrhea in countries with middle to low incomes, are attributable to the intake of unconventional water. According to research [5], inadequate access to safe drinking water was linked to around 13% of acute illnesses, which in turn led to approximately 370,000 fatalities. There is a possibility that disease transmission could occur if sewage effluent is used for irrigation purposes in agricultural settings [6]. In light of the problems of water pollution and shortage, it is of the utmost importance to recover, reuse, and recycle wastewater that is produced through a variety of treatment methods.

1. Technical to water Treatments

Currently, membrane-based separation techniques are widely utilized in several daily applications across the petrochemicals, nutrition, life sciences and pharmaceuticals industries, as well as in various environmental applications including treatment of water and desalting. Their straightforwardness and economic efficiency relative to alternatives Conventional separation techniques, such as adsorption and distilling, have proven to be highly effective. omnipresent along with widespread in its applications [1]. Minimal energy use, scalability, capacity for hybridization with alternative processes, and continuous operation. The primary advantages of membranes include high intensity and autonomous operation. Procedures. Conversely, their constraints encompass membrane fouling and restricted chemical steadiness and brief duration. Comprehensive study and improvement has been undertaken to improve the properties of the membranes. This efficient membranes must provide reliable performance, produce higher flow at lower pressure, minimize spatial footprints, enhance the purity of water, and decrease processing needs.

2. Membrane technology

Membrane technology is a successful strategy for treating water because it is easy to run, eliminates the need for added chemicals, is cost-effective, does not necessitate phase changes, has high efficiency, is easily scalable, and possesses a substantial removing capability[7]. Membrane technology is responsible for up to 53 percent of the total world processes that are used to produce clean water. Due to the characteristics described above, The technology of membranes is crucial in the treating of saltwater as well as wastewater, the desalting of seawater for potable reusing, and in dairy processing for milk skim and effluent management, and other vital applications [8]. It is possible to describe a membrane as a physical barrier that selectively permits materials that are desired to pass through while preventing things that are not desired to remain on the surface of the membrane [9].

Membranes can be categorized as polymeric and inorganic. Inorganic membranes such as metals or ceramics are used to construct inorganic membranes, which are characterized by strong structural, mechanical and thermal strength. In spite of the fact that they possess an exceptionally high selectivity, the fact that they have a restricted permeability makes them less appealing for a variety of applications. Micro porous silica membranes, categorized as inorganic membrane, are commonly utilized in applications involving molecular sieving[10]. Numerous sizing-dependent molecular filtering methods require pores widths in the range of a nanometer, this remains a challenge for inorganic silica micromembranes. Inorganic zeolite membranes exhibit their effectiveness in this particular scenario[11].

Because to their high thermal stabile and hydrophilic properties, Zeolite membranes function to be excellent molecular -scale filters compared to other inorganic alternatives. Despite the extensive utilization of zeolite membranes in diverse filtration procedures, Their characteristics like exchange of ions capacity, solids acidity levels, adsorption and release capacity, as well as catalysis properties—limit their application in situations requiring neutral filtering. Membranes are classified into four specific categories according to pore size and filtration mechanism: Microfiltration (MF), Ultrafiltration (UF), Nanofiltration

(NF), and Reverse Osmosis (RO). Microfiltration (MF) utilizes porous membranes with pore dimensions between 1 and 0.1 µm to separate particles within this spectrum, comprising larger things such as ions, macro molecule, bacteria, and different particles[12]. UF membranes have a pores size ranging from 0.1 to 0.01 µm, effectively separating viruses and macromolecules, as well as high molecular weight solutes, which are retained, while allowing water and lower molecular weights solutes to traverse as permeates. Nanofiltration (NF) membranes possess a dense structural with smaller pore than ultrafiltration (UF) as well as microfiltration (MF), efficiently eliminating divalent particles while allowing the passage of monovalent ions, having a pores size ranging from 0.1 to 0.001 µm [13]. The membranes used in reverse osmosis (RO) are more dense than those used in nanofiltration (NF). RO membranes are a high pressure driven filtration method that has a small pore size range (< 0.001 µm), which allows them to nearly completely separate out monovalent ions or contaminants, resulting in the recovery of pure water[14] **(Figure 1**).

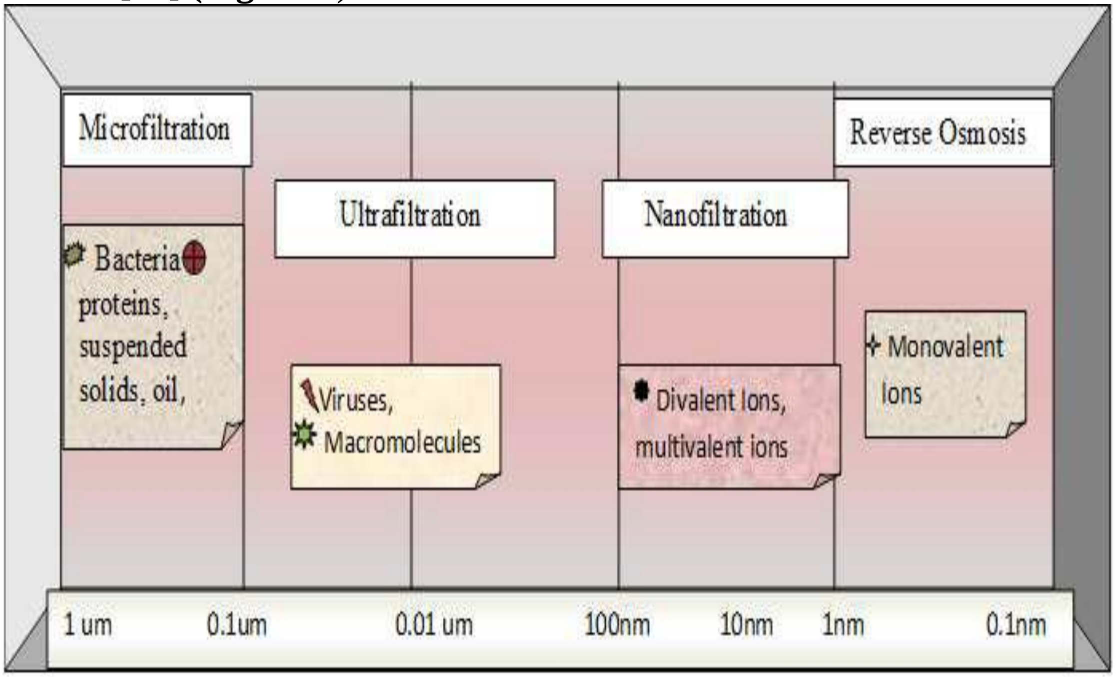


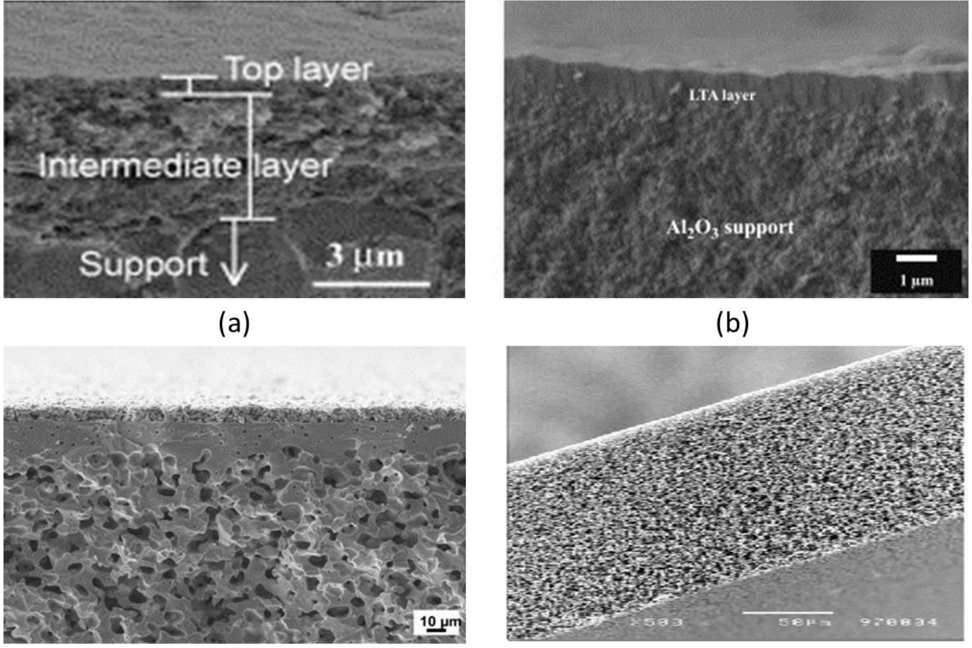
Figure 1: Filtration Spectrum for pressure driven membrane separation processes [15].

Membranes types

Membranes are typically categorized based on their synthesis material, differentiating between organic (polymeric) and inorganic types[16]. Organic membranes include poly-sulfone and polyphenylene oxides, whereas in-organic membranes comprise ceramic, carbons molecules sieves, nano-porous carbon, mixed-conducting perovskites, zeolite ,and amorphous silica [17]. Currently, polymeric membranes were employed, especially in the treatment of water and desalting, notwithstanding their constraints, involving stability at high temperatures and susceptibility to fouling[18]. Consequently, substantial research and development initiatives are currently concentrated upon the progression of inorganic membrane. Inorganic membranes, despite their higher cost relative to polymeric membranes, provide a number of benefits, such as resistance to aggressive chemical cleaners as well as regular rewashing, the capability of sterilization and autoclaving, the ability to endure higher temperatures (over 500 degrees Celsius)[19], durability, a distinct and consistent structure of pores, excellent stability of chemicals, as well as extended longevity. Nonetheless, their elevated expense and rigidity are their primary disadvantages[20] .

Structural of Inorganic Membranes

Structures with geometry of inorganic membranes substantially affect their efficacy. In-organic membranes may be categorized into porous membrane and non-porous (dense) membrane according to their structure and morphology[21] (as shown in Figure 2).



(a) (b)

(c) (d)

Figure 2. SEM image of (**a**) porous (**b**) dense ; (**c**) asymmetric and (**d**) symmetric inorganic membrane [15].

Porous inorganic membranes may feature porous supports composed of metals or ceramics, together with an additional porous layer that possesses a unique shape and structures. Membranes from this type display various pores geometries, particularly flat pores with uniform diameters traversing the membrane, conical pore with diameter at the membrane surface smaller than those at the base, pore with regular configurations and pores characterized by an a sponge architecture [22]. Some types of porous inorganic membranes include materials such as metals, glasses, alumina, zeolites, silica carbides, tin oxides and mica [23]. Dense and non-porous in-organic membranes comprise from solids layers of metallic substances, such as platinum, silver, or their alloys, or solid electrolyte. Hydrogen and oxygen can diffuse through the electrolyte layer, and ions can transport oxides through the pore formed by the membrane[24]. Dense membranes may also incorporate an extra layer of frozen liquid, specifically molten salts confined within porous steel or ceramics substrates, that are responsible for filling the pores of the membrane and producing a layer that is semipermeable [25].

The primary function of dense inorganic membranes is to enable the separating molecules of oxygen and hydrogen by particle charge. The efficiency of dense membranes is significantly influenced by various material types, characteristics for species requiring separation, as well as both the physicals and chemicals reactions occurring among the species with the membranes. The methodology used for the manufacture of the dense membranes determines the pore structure of the samples[26].

Both porous and non-porous membranes may exhibit symmetrical or asymmetrical configurations. If a separation from one layer of membrane is not discernible along the direction for its thickness, this membranes can be described as symmetrical or isotropical in properties The supporting layer of the symmetrical membranes is designed to impart the necessary mechanical strength for optimal functionality. In contrast, composite or asymmetric membranes, also known as anisotropic membranes, are membranes in which the upper layer and the underlying support layer may be differentiated from another [27]. In these kinds of membranes, The thin separating layer is the primary site of resistance to flow, sometimes referred to pressure drop. The supporting layer generally slightly porous than the thin layer and so doesn't impact the transportation resistant of the permeates. Furthermore, thin layer is generally more stiff adjacent to the membranes [28, 29]. A capacity of asymmetrical membranes to employ diverse materials based on the properties of the species intended for separation, is one of the advantages of these membranes[30].

Categories of Inorganic Membranes

The predominant categories of inorganic membranes comprise dynamical membranes, liquids membranes, ceramics membranes, silica membranes, zeolites membranes, carbon membranes, and hybrids inorganic-organic membranes[31]. The synthesis of inorganic membranes can be achieved using many ways, such as pyrolysis, chemical vapor deposition (CVD), slip casting and the sol-gel method, among others. These approaches have been mentioned as being commonly employed. There are numerous varieties of inorganic membranes that are currently utilized in the process of desalination and water treatment. Alumina (Al_2O_3), titania (TiO_2), zirconia (ZrO_2), silica (SiO_2), and carbons membranes are the membranes that are utilized the most Commonly utilized for purposes related to treating of water and desalting[32].

A. Ceramics Membranes

Alumina, titania, zirconia, silica and silicon carbide are some examples of the materials that more frequently utilized in the production of ceramic membranes. Furthermore, combining these metal oxides is also one of the most common materials[33]. Carbides, borides, nitrides, and other non-oxides are appropriate materials, Silicide with composites comprising both oxides and non-oxides. Membrane made of ceramic typically have an asymmetrical structure that is made up of at least two separate porosity layers and most of the time by three distinct layers[34]: A macro-porous supporting measuring several millimeters in thickness and has a pores size that falls somewhere between one and ten millimeters, to minimize the resistance to mass transfer while yet providing the membrane with its mechanical strength; the presence of a mesoporous intermediate layer, which has a thickness that falls somewhere between 10 and 100 micrometers with a pore diameter of as well as (iii) the top layer having a thickness from one millimeter and a pores diameters ranging from two to fifty nanometers, which demonstrates[35]. Both the selection and separating effectiveness of the membranes, as illustrated in Figure 3.

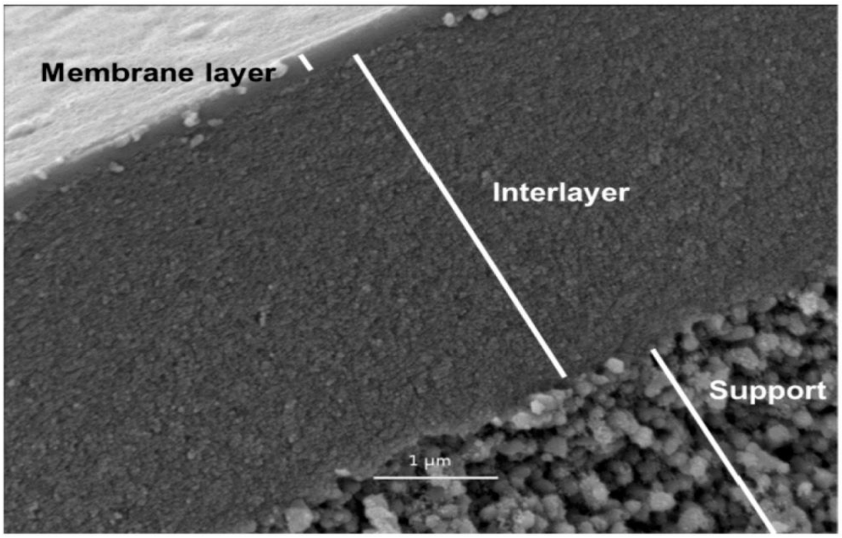


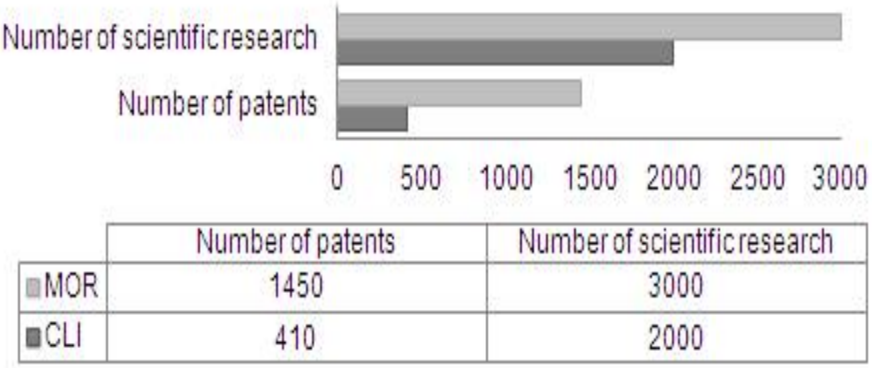
Figure 3: Scanning electron microscopic micrograph showing the cross-section of a ceramics asymmetric membranes [36].

B. Silica Membranes

This membrane are utilized within a broad variety of industrial applications, including the separation of hydrogen at high temperatures as well as simultaneous reactions and separation processes. High yields have also been reported to be achieved through utilizing silica membrane in membranes reactors, which has demonstrated considerable efficacy [37]. In addition to their high selectivity, thermal tolerance and chemical resistance, silica membranes are well-known for their outstanding properties. Additionally, in comparison to alternative inorganic or polymeric membranes, they represent a more affordable option [38]. In most cases, Amorphous silica is typically manufactured with pores diameters between 3 and 5 Å, making it suitable for water desalination applications. The production of membranes produced from silica has been accomplished through the use of a number of various methodologies, like the sol-gel method [39] as well as the chemicals vapor deposition (CVD) method [136,142,143]. On the other hand, extensive research into separating gases utilizing silica membrane made by both the chemical vapor deposition (CVD) method and the sol-gel approach has been conducted, but exclusively for water-based applications. Silica membranes produced by sol-gel technique are being extensively studied [40]. The sol-gel method is preffered mainly for its easy to use and economic efficiency, enabling enhanced adaptability in customizing the desired porosity. Moreover, due to the controllability and uniformity of the sol-gel method, its commonly employed within formation of membranes or the alteration of membranes pores[41, 42].

C. Zeolite Membrane

Natural and manmade zeolites are crystalline, hydrated aluminosilicates containing cations from groups I and II, including potassium, sodium, magnesium, calcium, Strontium, and Barium . Natural zeolites are sustainable and cost-effective hydrated minerals distinguished by exceptional the exchange of ions and adsorption properties. Their effectiveness in many technological processes depends on their physicochemical properties, which are intricately associated with their geologic formations[43]. The unique three-dimensional porous structure of natural zeolites offers various application possibilities. The excess negativity charged on the zeolites surface results from the isomorphic substitution of silicon with aluminum at the fundamental structure unit, categorizes natural zeolites as cation exchange agents. Numerous studies have confirmed their enhanced effectiveness in removing metal cations from wastewater[44]. Zeolites can be chemically modified by the application of the inorganic salt or organic surfactant, that adsorb onto their surface, leading to the creation of positive- charge oxi-hydroxides or surfactants micelles[45]. This alteration enables zeolites to bind anions, including arsenates or chromates, in both stable and less stable complexes. Natural zeolites offer advantages through alternative cation exchanging substances, such as commonly used organic resins, owing to their cost-effectiveness and enhanced selection for diverse ions under lower temperatures, compact size, and ease of maintenance in large-scale applications[46], as shown in **Figure 4.**



	Number of patents	Number of scientific research
▨ MOR	1450	3000
■ CLI	410	2000

Figure 4. Number of patents for clinoptilolite (CLI) and mordenite (MOR), (The last ten years) [15]

The architecture in natural zeolite is remarkably complex and intriguing. The primary structural elements of zeolite include the SiO_4 and AlO_4 tetrahedra. They unite via oxygen ions to create secondary building units (SBU), which are then linked into a three-dimensional crystalline structure of zeolite. The substitution of Si with Al creates a negative charge in the zeolite structure, which is balanced by alkaline and alkaline earth metal cations. Thus, natural zeolite operate as cations exchanger owing to their negatively charged surface. In the zeolite framework, substitution encompasses more than only Si-Al replacement. Atoms of Fe, B, Cr, Ge and Ti may substitute for silicon. The molecules of water can be present in the gaps of large holes and are connected to frameworks ions as well as available for exchange ions via liquid bridges[47].

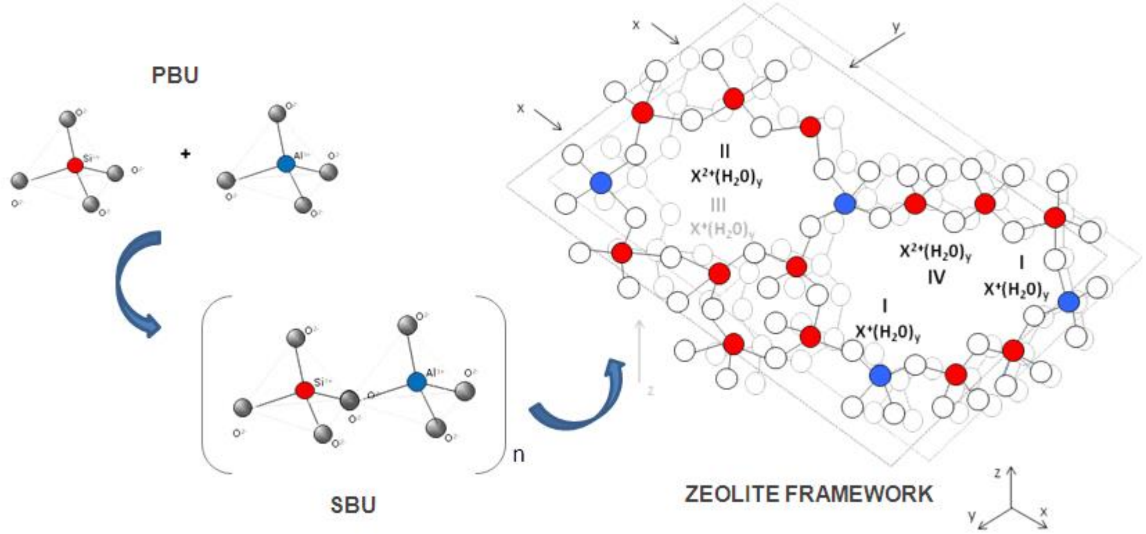


Figure 5. Binding of building units (PBU and SBU) in three-dimensional zeolite- clinoptilolite structure.

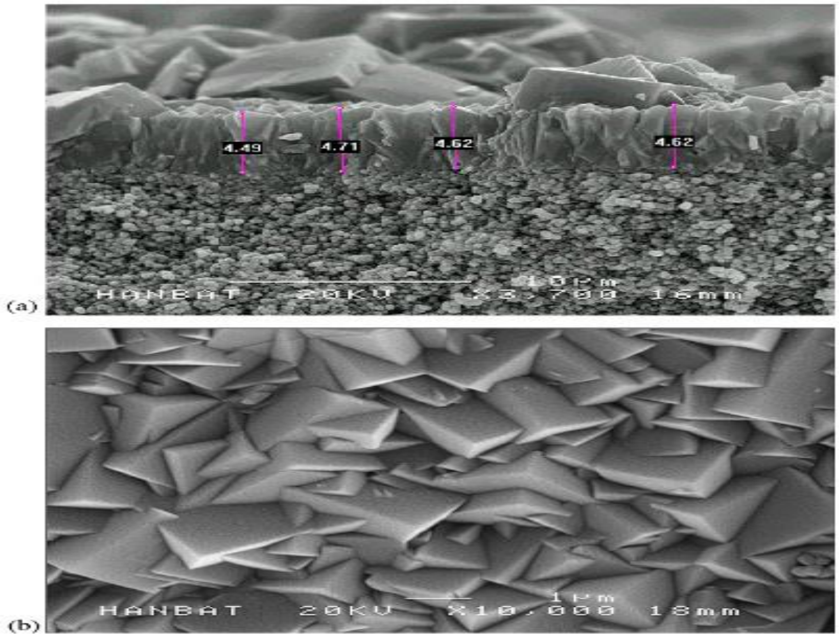


Figure 6: SEM photos of the NaA zeolites membranes: (a) a cross-section perspective; (b) a plan view [48].

3. Polymer-polymer composite

Polymers are organic substances possessing numerous advantageous properties, including elevated mechanical strength, exceptional flexibility, chemical stability, and extensive surface area. These features enable polymers to function as hosts for various organic and inorganic compounds. We acquired the capability to synthesis various composites with desired qualities. Consequently, polymer composites have garnered significant interest for water treatment and desalination. Polymer-polymer composites provide the opportunity to modify adsorptive characteristics by mixing, crosslinking, and surface functionalization. The primary advantages of this type of composites include ease of preparation and application, exceptional chemical stability under extreme operational settings, effectiveness in removing a broad spectrum of contaminants, and commendable recyclability coupled with high adsorption capabilities. Conversely, the primary disadvantage is the elevated production costs.

Dynamic Membrane

The dynamic membrane (DM) is an additional type of inorganic membrane that was investigated during the 1960s and 1970s due to its dynamic properties. During the process of filtering a dispersion that contains a suspended inorganic or polymeric colloid, This specific membrane type forms a colloidal support surface on the microporous supporting layer. [49]. This layer serves as active dividing layer that will ultimately erode and disappear over time. Self-forming dynamic membranes (SF-DM) and pre-coated dynamic membranes are the two primary categories that are used to classify dynamic membranes[50]. The SF-DM is composed of components found in the separating medium, including suspend particles within water. Conversely, a pre-coated DM is produced by traversing a colloidal solution of one or more components over the outer layer of a porous membrane **(Figure 7)** [51]. The difference between a conventional ceramic membrane. Self-forming dynamic membranes (SF-DM) and pre-coated dynamic membranes are two primary categories that are used to classify dynamic membranes. Substances that are Found inside the separating medium, like solids that are suspended in water, are responsible for the formation of the SF-DM, while a pre-coate[52].

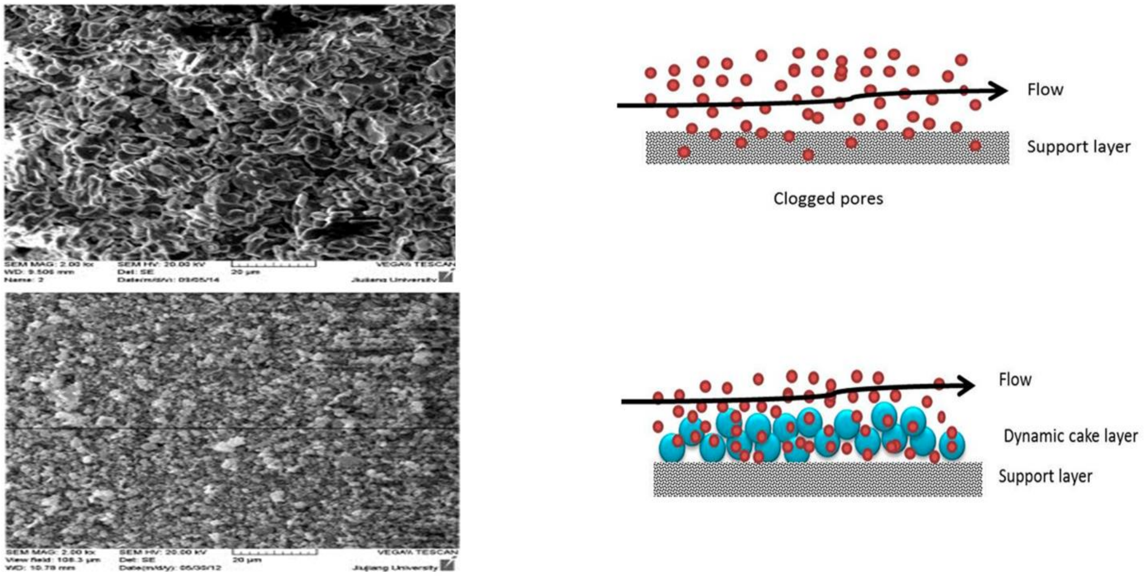


Figure 7: SEM pictures depicting the surface of (a) a ceramic inorganic membrane and (b) a Kaolin dynamic membrane **[53].**

This method was often utilized to reinforce substances like porous stainless steel, carbon, or ceramic. which can function as substitutes for microfiltration (MF) or ultrafiltration (UF) membranes [53].

Liquid Membrane

Other category of dense organic membranes is referred to as liquid membranes, as illustrated in Figure 8. These membranes utilize a liquid complexing or carrier agent that is either strengthened or immobilized within a rigid solid porous framework to function as the transport medium[54]. When the support is saturated with the liquid carrier agent, the pores become filled. medium, and reacts to the permeate present on the feed side. Upon production of the complex, it will diffuse through the support structure, subsequently releasing the permeate on the product side while concurrently Throughout time, the carrier agent is retrieved and subsequently reintroduced to the meal. Separation transpires in membranes of this nature achieved through the interplay of complexing processes and diffusion[55]. The following are the primary applications of such membranes: When it comes to gas separation or coupled transport, which involves the separation of metal compounds across ion liquid membranes. These membranes exhibit great selectivity; nonetheless, they lose psychological stability[56]. When the pores of the supporting medium are saturated, the liquid carrier agent is present. It interacts with the existing permeate on the feed side. The established structure extends through the membrane's or supporting framework, thereby discharging the permeate on the product side while concurrently initiating the discharge of the permeate. facilitates the recovery of the carrier agent, and then spreads returned to the feeding. One can achieve separating using membranes of this type. through dispersion and reactions that involve complexing[57]. These membranes are most commonly used in gas transmission applications. Ion transport is used in the process of separation or linked transport, which involves the separation of metal complexes. Furthermore, despite the fact that liquid membranes are very selective, they are not physically stable, which is what caused them to in the absence of commercial viability[58].

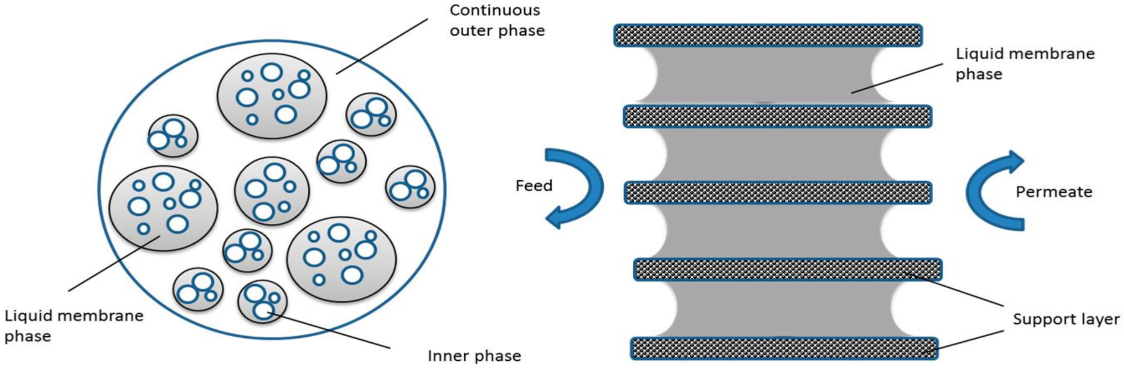


Figure 8: Schematic representation of a liquid membrane featuring an emulsion (left) and immobilized lamellae (right) [15].

Conclusion

Membrane technology is a method extensively employed in separating industry for diverse uses, especially in water processing and treatment applications. The use of such technology is both straightforward and economical. This review paper primarily focused on the developmental stages of inorganic membranes. This current review concentrated on the developmental phases of inorganic membranes in separating industry, particularly emphasizing treatment of water application. Comprehensive comparative analysis A comprehensive examination, analysis, and critical debate of the distinctions among inorganic and organic membranes have been conducted. Various types of inorganic membranes have been demonstrated from the synthesis perspective. Because of their application in the businesses that deal with water treatment. As a result of their superior features, including mechanical and electrical qualities, inorganic membranes are frequently used. Polymeric membranes do not possess temperature stability, which is a significant absence. Currently, most of the studies are focused on the planning and preparation of a wide variety of inorganic membranes. Only a tiny amount of focus has been placed on understanding the mechanisms responsible for water separation in deep water and how water molecules move through its membrane pores. If we pay greater attention to these features and areas, we might be able to develop a more accurate theoretical comprehension to create higher-efficiency inorganic membranes for utilization in treatment of water.

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