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MEMBRANE TECHNOLOGIES AND APPLICATION OF POLYMERIC MEMBRANE IN CO2 SEPARATION AND SEQUESTRATION

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Abstract: - Membrane technology is turning into the world's fundamental interest for enterprises because of its helpful and viable capacity for real life issues. It has numerous focal points, including selectivity, sensitivity, simplicity, easy fabrication, modest worth, high efficiency, economical and magnificent permeability. Membrane technology is being used in various disciplines for separation and identification processes. This study focuses on membrane types, functions and advantages especially on the application of polymeric membranes in CO2 separation and sequestration, Because, carbon emission in environment is the major contributor towards climate change and global warming. Polymeric membrane efficiently can separate the CO2 from flue gas streams of combustion system which make it easy for capturing, dumping storage or utilization.

Keywords: *Membrane Technology, Polymeric Membrane, CO2 Separation*

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INTRODUCTION

A membrane is a selective thin layer that acts as an obstruction between two phases. Membrane separation techniques are utilized to partition particles or solutes via electric charge, diffusion coefficient and difference of its solution. Their primary role is to enable the passage of certain elements and reinforce other particles of a mixture in the liquid.

At the present time, membrane technology getting to be the world's fundamental demand for industries due to its advantageous and successful work [1]. It has many advantages such as cheap value, greater efficiency, the comfort of processing, and excellent reliability. It is considered a growing technology as it does not require any dangerous chemicals, owing to its inherent features that may include environmental effect, permeability for transport of certain components, high selectivity and operational simplicity [2]. Polymeric membranes also have the advantages of low cost and easy fabrication [3]. One of the rapidly growing branch in modern technology is polymeric membrane which is being used for gas separation via selective transport [4]. The introduction of the thin film composite membrane has also earned great attention in research and industries [5].Membrane structure is one of the main factors determining the separation properties and carrier mechanisms across the membrane. Its morphology can be studied by taking both cross-sectional and surface images by using scanning electron microscopy (SEM) and Atomic Force Microscope (AFM). Symmetric structure and asymmetric structure are two types of membrane structures. Among these, symmetrical structure membranes will remain unchanged throughout the cross section whereas membranes with asymmetrical structures contain supportive layer and thin selective layer providing it with mechanical strength. Asymmetric membranes are comparatively more superior to symmetric membranes in terms of productivity and efficiency. Asymmetric membranes better work for industrial applications including microfiltration, reverse osmosis, ultra-filtration and gas separation etc. The asymmetric structure may be obtained in a simple film via phase inversion or in composite systems by forming a thin dense layer. Tsai et al. (2006) had stated that to achieve good separation of membranes, many polymer modification technologies have been used to improve it for industrial use.

Membrane and membrane technology

The membrane is a thin layer that acts as a separator between two phases. Membrane technology is among rapidly growing technology in this field of separation and purification. It covers a wide range of problems from particles to molecules. It usually explains the mechanical separation of gases and liquid streams and it is very important in the field of chemical engineering as it is able to control the permeation rate of a chemical species. Hence, it is widely known for its excellent separation, filtration with low consumption of energy, and cheap maintenance cost [6, 7].

History

The phenomenon of the membrane was first introduced in the 18th century. Through the 19th and early 20th centuries, there was no concept of using the membranes at the industrial and commercial levels, but it was used in the laboratory for development of chemical and physical theories. For instance, in 1887, Traube and Pfeffer developed membranes to measure the solution osmotic pressure, and their work was limited only to the ideal dilute solution. At the same time, Maxwell prepared selective semipermeable membranes and presented the kinetic theory of gases. Then, In 1907, Bechhold worked on nitrocellulose to develop the membrane of graded size to carried out the bubble test. Bechhlod's worked had modified later in 1930 by Bachmann, Elford, Ferry, and Zsigmondy, and they introduced colloidal microporous membranes in the market. From 1930 to 1950, this microfiltration membrane technology had extended to the polymeric membranes. Loeb–Sourirajan, in the 1960s, designed a high flux, flawless, anisotropic reverse osmosis membranes. Its flux was ten times greater than that of any other ordinary membranes in reverse osmosis, its availability had assured for the practical method of desalting water. Thus, the modern membrane separation industry introduced in the 1960s. This industry worked in the four phases in which the first phase had built on Loeb–Sourirajan techniques. Multilayer coating and casting include interfacial polymerization led to form highly efficient separation membrane. In the 1970s, ultrafiltration, microfiltration and reverse osmosis membranes were developed in the second phase and their supply for commercial purposes was made sure. In the 1980s, the emergence of industrial membrane gas separation methods led towards the third phase. The first separation carried out by these membranes was hydrogen gas. The final and last development in membranes phase occurred in the mid-1990s to yields consistent, reliable microfiltration-ultrafiltration systems for the treatment of municipal water sources. Since then, the treatment of municipal water has become fastest growing areas of membrane technology [8].

Types of membranes

A membrane is defined as a distinct, thin interface layer that regulates the permeation of chemical species in contact with other phases. This interface may have the same chemical composition or may have different. An ordinary filter meets the separation of particulate suspensions larger than 1–10 µm. The major kinds of membrane are as follows:

- **Isotropic membranes-** Nonporous, Microporous, Electrically charged and dense membranes
- **Anisotropic membranes-** Thin layer porous membranes,
- **Metal, Liquid and Ceramic Membranes-** Dense metal membranes, polymeric membranes.

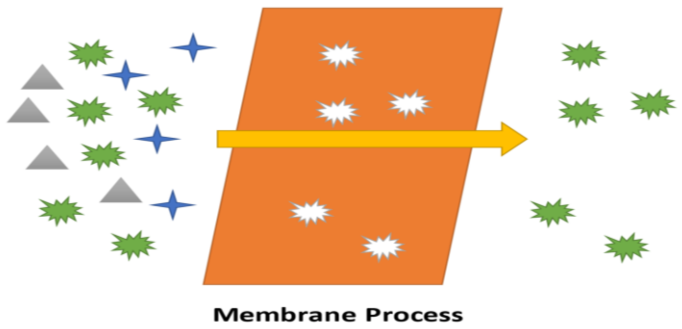
In an isotropic type of membrane, the microporous and non-porous membranes passed out the particle of size 0.01–10 µm in diameter. In these membranes, pore size distribution and particle size mainly decide the separation. Ultrafiltration and microfiltration separation are involved in it. Dense membranes carried out mostly the separation of gases. Electrically charged membranes are usually dense membranes which are employed in electrolyte solutions processing used in electrodialysis.

Anisotropic membranes involve thin layer and porous membranes. In these membranes, the transport rate of a species and thickness of the membrane are inversely proportional to each other. High and inflated transport rates are economically advantageous in membrane separation obtained by maximum thin layer membranes. Conventional film fabrication technology decreases the manufacturing of mechanically fault-less and strong films to thicknesses of about 20 µm. Thin surface layer braced on a much thicker, porous substrate is formed by anisotropic membranes. The high flux membranes formed using polymers made their use easy at the commercial level.

Metal, Liquid and Ceramic Membranes are mainly composed of organic polymers. For separation of ultrafiltration and microfiltration, microporous membranes are usually formed. Binary mixture of gases is separated by dense metal membranes and supported liquid films for the carrier facilitated transport processes [9].

Membrane processes

Energy consuming methods such as evaporation and distillation are being replaced by membrane processes, and are specifically appropriate for thermally sensitive products. The membranes are in the form of a frame and plate. Microfiltration, reverse osmosis, pervaporation and ultrafiltration are known as well-developed separation procedures. These methods are all well designed and assisted by numerous qualified companies. Ultrafiltration and microfiltration served as molecular sieving in the separation through fine pores. Colloidal particles and bacteria ranging from 0.1-10 µm are filtered out by microfiltration. Though the highest potential attributes to reverse osmosis and pervaporation. In reverse osmosis, the feed stream flows via a semipermeable membrane under pressure and the solvent flows through the membranes, leaving behind a residue solution of the solute. The small membrane pores ranging from 3-5 A in reverse osmosis that they lie in the range of thermal motion of the polymer chains forming the membrane. Pervaporation involves the combination of permeation and evaporation. Pervaporation is used mainly for dehydration of organic solvents like acetone and methanol from aqueous streams. Reverse osmosis and pervaporation membranes may be estimated to save approximately 40-55% primary energy in freeze concentration and melt crystallization. The developing industrial membrane separation processes include separation of gas with polymer membranes [10]. Gas separation is much advance among these. Membrane-based gas separation structures are being offered by nearly 20 companies globally for a variety of applications. In separation of gas, a gas mixture at high pressure passes across the surface of a selectively permeable membrane to one component of the feed mixture as shown in the figure:



Gas separation films carried out the separation of hydrogen from argon, methane and hydrogen in ammonia plants and the separation of carbon dioxide from methane in natural gas operations. It is an area of significant current research interest, and the number of applications is growing quickly [8-10].

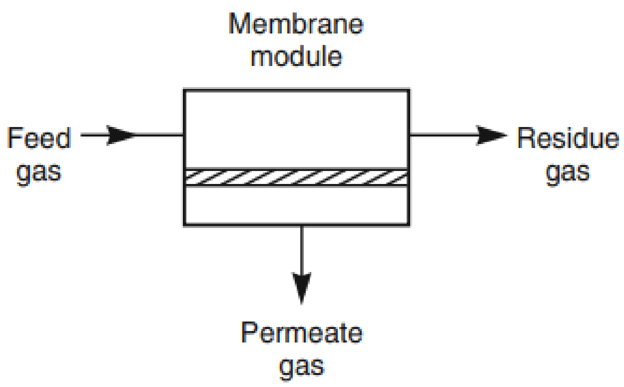


Figure 1: Membrane based gas separation

Polymeric Membranes:

Polymeric membranes, also called organic membranes, consists of liquid separation mechanism that is helpful in both efficiency and performance. There are four major categories of these membranes based on performance features and specific severance attributes[11]. Polymer membranes have been widely used for industrial purposes. These membranes are formed by phase inversion or solution casting techniques. In phase inversion, a homogeneous polymer solution is poured into a thin film or in form of thin-walled hollow fibre and then it is immersed into non solvent precipitation bath. Precipitation takes place by the exchange of the solvent and non-solvent. While in casting solution, the homogenized mixture of polymer is cast on a flat plate and an inverted funnel is placed on it. The solution is left for 24 hours for the removal of solvent. Thus, it yields a nonporous thin film. The polymer casting solution must have adequate viscosity so that its movement in the casting plate could be prevented. Polymeric membranes are formed by pure polymers as well as by blinding of two or more polymers [12][11]. The separation of coarser to the finest, they are: micro-filtration, ultra-filtration, nano-filtration and reverse osmosis.

1) **Microfiltration (MF)** may be defined as a type of membrane in which pore size is commonly considered to be in the range of 0.1 μm and greater and detachment range is exhibited in terms of micrometres. Detachment with microfiltration is established on molecular exclusion while certain conditions of the process can also be important parameters in separation efficiency. For countless process petitions, polyvinylidene fluoride (PVDF) polymers are used for manufacturing of organic microfiltration membranes. Generally, MF is employed as a pre-treatment step for further separation methods like ultrafiltration [13, 14].

2)**Ultrafiltration (UF)** refers to membrane family, UF separation range of 1,000 Da (1kd) to 100,000 Da (100kd). Separation with Ultrafiltration depends upon molecular exclusion. Organic UF membranes are manufactured by using poly ether sulfone (PES) or poly sulfone (PS) polymers. Ultrafiltration is primarily employed after Microfiltration or may be in as a bulk fractionation step in pre-filtration where the improvement of macromolecules is required[12, 13].

3)Nanofiltration (NF) refers to a class of membranes in which rejection features of solutes such as magnesium sulphate ($MgSO_4$) and sodium chloride (NaCl) determines the separation range (maybe ~90-99.5% and ~30-70%). NF separation depends upon diffusion of dissolved species over the membrane. Moreover, pH and chemical charge may influence it near or at membrane surface. Organic NF are produced by poly piperazine) to a poly ether sulfone (PES) or poly sulfone (PS) UF substrate. NF is employed with partial demineralization through the transmission of monovalent species simultaneously [12, 13].

4) Reverse Osmosis (RO) separation range (96-99.8%) depends upon solute's rejection characteristics mainly sodium chloride (NaCl). Reverse Osmosis is also impacted by overcoming osmotic pressure of the process liquid and on diffusion of dissolved particles via membrane. Polyamide to poly sulfone (PS) thin film application is applied for manufacturing of Organic Reverse Osmosis. Ultrafiltration or

Nanofiltration are employed prior to reverse osmosis generating its own permeate stream which is quite helpful for other processes and came out as an effective method for permeate concentration from UF or NF [12, 13].

Common deliberation of polymeric membranes

Glassy or rubbery polymers are being used to manufacture polymeric membranes. When the heating temperature of an amorphous polymer exceeds the transition temperature (T_g) of rubbery polymer, then there is a transfer of glass state to rubbery state. Glassy polymers have low permeability and higher selectivity, whereas rubbery polymers exhibit higher permeabilities for gases with relatively lower acuteness [15].

Physicochemical factors

- The potency of polymer chains.
- The penetrant-polymer interactions
- The intersegmental array, considered as the mean free volume of the polymer [15].

Application[14]

Dairy	De-fatting (production of protein isolates, casein and serum proteins separation from skim milk, cheese brines clarification
Sugar and sweetener	Clarification of saccharification liquors
Bioprocessing industries	Clarify bulk fermentation streams to improve performance, removal of undesirable minerals
Electrocoat paint	Retentate the paint pigment and resin for return to the coat tank

Polymeric Membranes for Water Filtration

Membrane technology due to its energy efficiency is anticipated to improve the water filtration and purification technologies. Membranes are actually mixture of certain materials destined to perform several functions during filtration procedure. For example, poly oxyethylene side chains (dark blue) provide selective fluid transport for nano-channels. They are characterized by low fouling propensity and higher wettability by water and organic species, that allows the water to pass thorough the filter but foulant molecules are pushed away. Their combination with poly(vinylidene fluoride) (PVDF) backbone chains provide them structural strength and are unsolvable in most organic liquids[16]. Typically, particulate removal and salt removal by other macromolecules following reverse osmosis are the two major membrane separation steps [17].

Carbon Dioxide Separation via Polymeric Membrane Systems for Flue Gas Applications

The capture and storage of carbon dioxide has been recognized as one of the conceivable answers to greenhouse gas navigating climate change. Though this solution can only be executed properly if effective and well-organized separation techniques are used for carbon dioxide removal from flue gas streams. Membrane gas separation is considered as a competent technology, which is energy efficient, compact and perhaps cheaper than other developed technologies like solvent absorption[18]. An average 600 MW_e coal-fired power plant effuse 500 m^3/s (1540 MMscfd) of flue gas exhibiting 13% CO_2, which total to about 11,000-ton CO_2/day. This flue gas flow rate is 5–10 times higher than other characteristic streams used for CO_2 removal with conventional absorption technology in the industries (natural gas and chemical). In inclusion, the flue gas is at atmospheric pressure, so the CO_2 partial pressure is only ~0.13 bar. This convey that there is a certain motivation available for separation[19].

Advantage of membrane processes

- Membrane procedures can be used to distinct the particles from molecular level to the scale where they can be seen, making membrane processes wide and expanded technology.
- Commonly, phase change is not required for separation (with the freak of pervaporation). Consequently, energy demands will be stubby except a higher energy distribute obligation to be dilated to rise the feed stream pressure in order to carry out the permeate constituents over the membrane.
- It represents a simple flowsheet that is easy to operate, with no moving parts (except for pumps or compressors), less maintenance, simple control schemes, and little auxiliary equipment related to many other methods.
- Membranes are produced with tremendously high selectivity for the constituents to be separated. Typically, selectivity values of these membranes are way greater than typical values for relative volatility for distillation processes.
- Separation selectivity can be controlled to a greater extent by utilizing huge numbers of inorganic media and polymers as membranes.
- Membrane processes are proficient to recover valuable and minor particles from a main stream without additional energy costs.
- Membrane systems are environment friendly since the membrane makes use of moderately simple and non-detrimental materials[20, 21].

Conclusion

Although the use of polymeric layers in enormous scope CO2 recuperation has been effective, there is still prospect to get better. These films are truly attractive and helpful, particularly with expanded profitability and selectivity, with improved protection from different mixtures. Cross-connecting polymers had the option to address certain issues. The polymeric layer adequacy in specific conditions can be improved through additional upgrade in film preparing and execution. Guiding examination to profoundly explicit usage empowers the films to be effectively utilized in the creating business sector of CO_2 partition. Certain specialized issues should be addressed before the execution of the most recent materials created. Nonetheless, polymeric layers for CO_2 partition have a promising future with an extraordinary development prospect.

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