Modification of Cellulose Acetate Membranes with Graphene Oxide Nano-fillers for Water Treatment

By

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**List of Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>[Bmim]Cl</td>
<td>1-Butyl-3-Methylimidazolium Chloride</td>
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<tr>
<td>BSA</td>
<td>Bovine Serum Albumin</td>
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<tr>
<td>BSEs</td>
<td>Backscattered Electron</td>
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<tr>
<td>CA</td>
<td>Cellulose acetate</td>
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<tr>
<td>CB</td>
<td>Cellulose butyrate</td>
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<tr>
<td>CBT</td>
<td>Coagulation Bath Temperature</td>
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<tr>
<td>CP</td>
<td>Cellulose Propionate</td>
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<tr>
<td>CTE</td>
<td>Coefficient Thermal Expansion</td>
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<tr>
<td>DMAc</td>
<td>N-Dimethylacetamide</td>
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<tr>
<td>DMF</td>
<td>N,N-Dimethylformamide</td>
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<tr>
<td>DOC</td>
<td>Dissolved Organic Carbon</td>
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<tr>
<td>EA</td>
<td>Egg Albumin</td>
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<tr>
<td>ED</td>
<td>Electro-dialysis</td>
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<tr>
<td>EEMs</td>
<td>Florescence Excitation Emission Matrices</td>
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<tr>
<td>F-CTA</td>
<td>Free-Standing Cellulose Triacetate</td>
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<tr>
<td>FRR</td>
<td>Flux Recovery Ratio</td>
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<tr>
<td>GBL</td>
<td>γ-Butyrolactone</td>
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<tr>
<td>GO</td>
<td>Graphene Oxide</td>
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<tr>
<td>ICT</td>
<td>Initial Casting Thickness</td>
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<tr>
<td>IP</td>
<td>Interfacial Polymerization</td>
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<tr>
<td>LBL</td>
<td>Layer By Layer</td>
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<tr>
<td>LM</td>
<td>Liquid Membrane</td>
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<tr>
<td>MCC</td>
<td>Microcrystalline Cellulose</td>
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<td>MF</td>
<td>Microfiltration</td>
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<tr>
<td>MPD</td>
<td>M-Phenylenediamine</td>
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<tr>
<td>MWD</td>
<td>Weight Distribution</td>
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<tr>
<td>NCCA</td>
<td>Nano-Crystalline Cellulose Acetate</td>
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<tr>
<td>NF</td>
<td>Nano-filtration</td>
</tr>
<tr>
<td>NMP</td>
<td>N-Methyl-2-Pyrrolidone</td>
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<tr>
<td>NOM</td>
<td>Natural Organic Matter</td>
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<tr>
<td>OMWCTs</td>
<td>One-Dimensional Oxidized Carbon Nano-tubes</td>
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<tr>
<td>PA-TFC</td>
<td>Polyamide Thin Film Composite</td>
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<tr>
<td>PEG</td>
<td>Polyethylene Glycol</td>
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<tr>
<td>PES</td>
<td>Polyether Sulfone</td>
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<tr>
<td>pGO</td>
<td>Pristine Graphene Oxide</td>
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<tr>
<td>PI</td>
<td>Phase Inversion</td>
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<tr>
<td>PSf</td>
<td>Polysulfone</td>
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<tr>
<td>PVDF</td>
<td>Poly-vinylidene Fluoride</td>
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<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
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<tr>
<td>PWP</td>
<td>Pure Water Permeability</td>
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<tr>
<td>R</td>
<td>Retention</td>
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<tr>
<td>rGO</td>
<td>Reduced Graphene Oxide</td>
</tr>
<tr>
<td>RO</td>
<td>Reverse Osmosis</td>
</tr>
<tr>
<td>SA</td>
<td>Sodium Alginate</td>
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<tr>
<td>SE</td>
<td>Secondary Electron</td>
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<tr>
<td>TDS</td>
<td>Total Dissolved Solids</td>
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<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TFC</td>
<td>Thin Film Composite</td>
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<tr>
<td>TMC</td>
<td>Trimesoly Chloride</td>
</tr>
<tr>
<td>UF</td>
<td>Ultra-filtration</td>
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<tr>
<td>UVA</td>
<td>Ultraviolet Absorbance</td>
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Abstract
The aim of this study is to prepare membranes composed of CA and GO for water purification. Cellulose acetate (CA) (Mw = 52,000 Da) membranes containing different amounts of graphene oxide (GO) were prepared by phase inversion (PI). Acetone was used as a solvent and N, N-dimethylformamide (DMF) as a non-solvent, with a ratio of 4:1, and deionized water as the coagulation medium. The membranes were prepared using a mixture of 19 wt.% CA with 0.025 to 0.1 wt.% GO. The effect of GO on membrane characteristics was investigated by scanning electron microscopy (SEM), Brunauer-Emmett-Teller surface analysis (BET) and contact angle measurements. Salt rejection and permeation rates were tested using a 2000 ppm NaCl solution and 5000 ppm MgSO₄ solution at a pressure of 24 bars using a dead-end filtration cell.

SEM cross sectional images showed uniform dispersion of GO sheets in the polymeric matrix which implies the formation of strong hydrogen bonds between CA and GO sheets. An increase in the number and sizes of the pores of CA/GO membranes in comparison with blank CA membranes was also noticed. In addition, finger-like macropores were formed indicating the instantaneous solvent-non-solvent exchange as a result of the hydrophilic nature of GO added. This was supported by the gradual decrease in the contact angle measurements from 75° to 61° with increasing GO content from 0 to 0.1 wt.%. It was found that permeation rates increased with increasing GO content. The addition of 0.025 wt.% and 0.05 wt.% GO improved 2000 ppm NaCl permeation by 64% and 95% respectively when compared with CA membrane. An increase in permeation by 106%, as compared to the CA membrane when 0.1 wt.% GO was added, was observed. It is believed that this increase in GO content increased the number of hydrophilic sites in the membranes which attracted water molecules and facilitated their movement through the membrane. As for salt rejection, the membrane with 0.05 wt.% GO showed the highest salt rejection value of 74% and 81% for 2000 ppm NaCl and 5000 ppm MgSO₄ solutions respectively. This was explained by the increase in the total surface area of micropores with width less than 2 nm. However, on increasing GO content to 0.1 wt. %, blocking of the micropores occurred leading to a decrease in the salt rejection values to 23% and 11% for 2000 ppm NaCl and 5000 ppm MgSO₄ solutions respectively. This work demonstrates that CA/GO membranes outperform traditional CA membranes due to their improved permeation and salt rejection behavior and therefore have great potential in the field of water purification.
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I. Introduction

1.1. Historical development of water scarcity

It is no secret that the existence of humanity has always depended on the existence of fresh and clean sources of water. Historically, civilizations have existed and perished due to the availability or the scarcity of water. Ancient civilizations were created along water sources such as the Ancient Egyptians who built one of the earliest communities along the banks of the Nile. [1], [2]

Today, the water crisis is a global one. Although 70% of the world is covered by water, only 2.5% of it is fresh water. Fresh water contains less than 1000 mg/L of total dissolved solids (TDS). Even then about 1% of that fresh water is accessible. With the population explosion, competition for these water sources has increased. Due to political, economic and environmental inefficiencies there are about 1 billion people with no access to clean water that is pathogen or pollutant free. According to the United Nations, “4,500 children die every day from waterborne diseases”. [1], [2], [3]

The water crisis has begun to take its toll on Egypt. A robust and functioning economy depends on water as shown in Figure 1.1, and as the Egyptian economy depends significantly on agriculture it faces a huge dilemma.

![Figure 1.1 Total water withdrawal in Egypt (78000 million m³) in 2010 divided between agriculture, municipalities and industry. Adapted from [4]](image)

Figure 1.1 Total water withdrawal in Egypt (78000 million m³) in 2010 divided between agriculture, municipalities and industry. Adapted from [4]
The United Nations have already warned that Egypt will be facing a water crisis by 2025, but the crisis has already left villages in the Delta with low and sometimes no water supply. “The country’s annual water supply dropped to an average of 660 m$^3$ a person in 2013, down from over 2,500 m$^3$ in 1947, according to official records” [2]. Being the most downstream country of the Nile basin, Egypt depends heavily on its supply from the Nile as its rainfall is limited. With the threat of new dams in Ethiopia and Sudan, and inefficient usage of the water available, Egypt must address the water crisis and find new ways for the supply of fresh water. Figure 1.2 shows that in 2010, the total water withdrawal in Egypt was estimated at 78000 million m$^3$, including 0.3% of desalinated water, 1.9% of treated seawater, 3.5% of agriculture drainage water, 10% of primary and secondary water, and 84% of primary and secondary surface water. [1], [2], [4], [5], [6]

![Figure 1.2 Total water withdrawal in Egypt by source. Adapted from [4]](image)

1.2. **Historical development of membranes technology**

Membrane separation is a promising technology that is used in a broad range of applications. In separation applications, controlling the permeation rate of one component of a mixture through the membrane is the key property. The membrane allows the free permeation of a certain chemical species and hinders the permeation of others. The history of membranes dates back to the eighteenth century when Abbe Nolet, a philosopher scientist, described the diaphragm water permeation with the word “Osmosis”. Then in the early twentieth century, scientists used
membranes with the aim of developing chemical/physical theories rather than being used for industrial or commercial purposes. For example, in 1887, van’t Hoff used Traube and Pfeffer’s measurements of solution osmotic pressure made with membranes to develop his limiting law, which explains the ideal dilute solutions behavior. In addition, Maxwell used the idea of perfectly selective semipermeable membrane to develop the kinetic theory of gases. Bechhold, an early membrane investigator, prepared nitrocellulose membranes and determined the pore sizes using a bubble test. Other scientists, Elford, Zsigmondy, Bachmann, and Ferry, amended the technique of Bechhold. Thus, microporous collodion membranes became available by the early 1930s. Developments led to other polymers, especially CA, being used in early microfiltration technology. At the end of World War II, drinking water was tested using microfiltration membranes to test for water safety as the water supplies serving Germany and Europe had broken down. [6], [7], [8], [9], [10], [11]

1.3. Types of membranes

A membrane is a thin interface, when in contact with a mixture it moderates permeation of the chemical species in this mixture. In other words, a membrane controls the movement of chemical species passing through as it is a perm-selective barrier between two phases as shown in Figure 1.3. Phase 1 is the upstream side while phase 2 is downstream side. There are two parameters determining the membrane efficiency: the flow and selectivity of the membrane. The membrane selectivity is expressed by retention (R) for dilute aqueous mixtures consisting of a solvent and a solute. The solvent molecules pass freely through the membrane while solute molecules are retained.

Phase 1 Membrane Phase 2

Figure 1.3 Membrane separation of a two phase system. [7]
Membranes are divided in two categories: homogeneous/isotropic membranes and heterogeneous/anisotropic membranes. A homogeneous membrane is the type of interface that has a uniform structure and composition. On the other hand, an interface with a layered structure is a heterogeneous membrane. The different types of membranes are:

1.3.1. Homogeneous / Isotropic membranes

Homogenous membranes are membranes with a completely consistent composition and structure. It is divided into three categories: isotropic microporous membranes, dense membranes, and electrically charged membranes.

Microporous membranes

Microporous membranes are highly voided membranes with a rigid structure. Their pores are randomly distributed, interconnected, with a size range of 0.01 to 10 µm in diameter. In the use of these membranes for filtration applications, both pore size distribution and particle molecular size are the two factors determining the separation efficiency of the microporous membrane. In other words, the membrane completely rejects particles with a size larger than the largest pores. [7], [8]

Nonporous dense membranes

Nonporous dense membranes are thin films of dense material used for separation processes of small molecules to which a driving force must be applied to diffuse permeants through the membrane. Concentration, pressure, or electrical potential gradient are the main driving forces causing diffusion. The transport rate of different components of a mixture depends on the diffusivity and solubility of these components in the membrane material. Thus, separation between these components happens even if they have the same size with different concentrations in the mixture. Dense membranes are used in pervaporation, reverse osmosis, and gas separation membranes for separation purposes. [7], [8]

Electrically charged membranes

Both microporous and dense membranes can be electrically charged. However, microporous membranes are the ones commonly charged. There are two types of charged microporous membranes: anion-exchange membranes, with a positively charged pore walls binding with anions in the surrounding fluid, and cation-exchange membrane, with a fixed
negatively charged pore walls. Charged membranes separate according to the charge, as ions with the same charge as the ions existing in the pore walls repel, and concentration of the ions in the solution. For example, divalent ions separation is achieved more effectively than monovalent ions. [7], [8]

1.3.2. Heterogeneous / Anisotropic membranes

Membranes with an inconsistent structure, containing holes or pores of finite dimensions or consisting of a layered structure, are called heterogeneous. Thickness of the membrane is one of the factors affecting the permeation rate in membrane separation processes. Membrane thickness is inversely proportional to rate of species passing through the membrane. Anisotropic membranes consist of two layers: a thick porous layer supporting a very thin layer that can be prepared separately or in a single operation. The surface layer exclusively determines the permeation rates as well as the membrane separation properties. On the other hand, the porous substructure supports the surface layer mechanically. Anisotropic membranes are used widely in commercial processes because of their high fluxes compared to other types of membranes. Anisotropic membranes are classified into three types of membranes:

Loeb Sourirajan / phase separation membranes

The LoebSourirajan process for membranes fabrication is one of the remarkable discoveries in membrane technology. In the early1960s, Loeb and Sourirajan succeeded in fabricating an anisotropic porous membrane using CA as a polymer. The membranes consisted of a selective thin layer supported by a more permeable microporous layer that showed a high permeability and flux. Anisotropic membranes made by the Loeb Sourirajan technique consist of a single membrane material with a variation in the porosity and pore size in each layer of the membrane. The membranes are prepared using phase inversion in non-solvent (water) bath. [7], [8]

Thin film composite membranes

In composite membranes, different polymers can be used to manufacture each layer. This type of anisotropic membrane consists of an extremely thin layer, 0.1 mm or less, of a cross-linked polymer formed on a microporous support layer surface. As a result of using a highly cross-linked polymer, the membrane permeability is high in addition to its selectivity. This type of membranes is widely used in nano-filtration and reverse osmosis. [7], [8]
Supported liquid membranes

A liquid membrane (LM) is fabricated using a thin, dense polymer layers coated with a solution, which works as a selective barrier, on the surface of a microporous support. LMs are used in many industrial applications due to their high selectivity as the liquid phase contains dissolved carriers that have the ability to react with specific permeants to improve their rate of transportation through the membrane. The main disadvantage of using them is their low stability as pressure differentials may crack the pores and the liquid leaks out. In this case, the membrane won’t function as effective as it is supposed to be. [7], [8]

Figure 1.4 Types of membranes. [8]

1.3.3. Metal and ceramic membranes

Other types of membranes have emerged recently that are made from a less conventional materials such as metal and ceramic membranes. This type of membranes can be isotropic or anisotropic. Metal membranes, such as palladium, aluminum, and titanium membranes, have a thin porous layer containing straight channels allowing both liquid and gases to pass through the membrane. The thin layer of the membrane is supported by a metal plate to be used for water filtration and gas separation processes.[7], [8]

Ceramic membranes are described as permselective, ion exchanger, barriers. To prepare ceramic membranes, several layers of different ceramic materials are added to a support layer.
Ceramic membranes can only be prepared through multiple steps: a top dense separation layer, one or more intermediate mesoporous layers, and a macroporous support layer as shown in Figure 1.4. In addition, the advantages of the solvent resistance and thermal stability provided by ceramic membranes are so great that almost all ultrafiltration and microfiltration applications use such membranes.[7],[8],[9]

1.4. Membrane filtration processes

The membrane based desalination processes can be classified according to membrane pore size and rejection mechanism: electro-dialysis(ED), microfiltration (MF), ultra-filtration (UF), nano- filtration (NF) and reverse osmosis (RO) as shown in Figure 1.5.

![Figure 1.5 Separated species based on the membrane pore size. [10]](image)

1.4.1. Electro-dialysis membranes

Electro-dialysis is the process of using electrical potential difference as a driving force to separated ions from aqueous solutions using charged membranes. In this type of membranes, the membrane material has a fixed charged group attached to the backbone of the polymer to repel ions with the same charge as the charged membrane. There are two types of Electro-dialysis membranes depending on the charge of the polymer backbone: anionic membrane, with positively charged groups that permeates negatively charged ions while excludes positively charged ones,
and cationic membrane, with negatively charged groups that permeates positively charged ions while excludes negatively charged ones. This type of ion exchange membranes was originally developed by Ostwald in 1890. Few years later, Dannon succeeded to develop the concept of membrane potential. By 1939, Manegold and Kalauch introduced the idea of selective anionic and cationic exchange to be applied in the field of membrane followed by Meyer and Strauss who suggested the multi-cell arrangement between a single pair of electrodes to achieve better separation of ions. [7], [8]

1.4.2. Microfiltration membranes

Microfiltration is a process that aims to remove suspended particles with diameter of 0.1 to 10 µm using porous membranes. The origin of microfiltration dates back to 1926 when Membrane FilterGmbH was founded and the production of collodion microfiltration membranes started. Other companies started producing similar membranes in order to be used to culture microorganisms in drinking water. In 1990, the installation of the first microfiltration/ultrafiltration systems took place in order to treat municipal drinking water obtained from surface water. Forty years later, Millipore became the largest microfiltration company and the CA/cellulose nitrate blend membrane was and remains a widely used micro-filter. Despite the fact that micro-sized particles can be easily removed by non-membrane processes, using micro-filtration insures the quantitative retention of these particles more than any other processes. Microfiltration membranes are used for separation of suspended particles with diameters between 0.1 to 10 µm. They have an average pore diameter of 5 µm and as a result they fall between conventional filters and ultrafiltration membranes. Depth filters and screen filters are the main types of Microfiltration membrane filter in use. The top surface of screen filters has small pores to prevent large particles from passing in order to keep them on the surface of the membrane. On the other hand, the top surface of the depth filters has relatively large pores so particles pass to the membrane interior and get adsorbed onto the pore walls. [7], [8], [11]

1.4.3. Ultrafiltration membranes

Finely porous membranes reused in ultrafiltration in order to separate micro-molecules and water from colloids and macromolecules. The membranes have an average pore diameter of 10-1000 Å. Bechhold was the scientist to prepare an ultrafiltration membrane from nitro cellulose. After that, other important early workers such as Zsigmondy and Bachmann, Ferry, and Elford continued what Bechhold started. In mid 1920s, ultrafiltration and micro-filtration colloidal
membranes were available for laboratory use. In 1963, Loeb and Sourirajan succeeded in preparing anisotropic CA membrane followed by Michaels and his coworkers who used CA to produce ultrafiltration membranes. [7], [8], [11]

Ultrafiltration membranes have a surface layer with fine pores that perform the separation, and a microporous substrate that supports the surface layer. The solute rejection for these membranes is not only dependent on the molecular weight of the solute, but on the shape of the molecule to be retained and the pH of the feed solution. For example, linear molecules such as polydextran, poly (ethylene glycol) or poly (vinyl pyrrolidone) are less retained than proteins with the same molecular size. This is because most proteins have the shape of globular coils connected by hydrogen bonds that cannot pass through the pores. Concerning the pH of the feed solution, a clear example for this is the rejection of poly (acrylic acid) by Ultrafiltration membranes. At pH 5 and above, poly (acrylic acid) is negatively charged and the polymer coils repeal each other which make it difficult to permeate through the membrane pores. On the other hand, at pH lower than 3, the poly (acrylic acid) is in the neutral form and can easily pass through the pores. [7], [8], [11]

1.4.4. Nano-filtration membranes

Nano-filtration membranes are falling in the middle region between ultrafiltration membranes and RO membranes. Unlike RO membranes with NaCl rejections greater than 98% and ultra-filtration membranes with salt retention less than 5% at salt concentrations below 1000–2000 ppm, nano-filtration membranes are able to reject NaCl with a percentage 20 to 80% and with much higher water permeability values compared to RO membranes as shown in Figure 1.6. Nano-filtration membranes are commonly used for the filtration of relatively clean water to remove low levels of contaminants. [8], [12]
1.4.5. Reverse Osmosis membranes

RO membranes reject salts and solutes with low molecular weights. They exhibit salt rejection values higher than 95%. As mentioned earlier, desalination is the process of purifying saline water from salts in order to obtain fresh. RO has the advantages of low cost and low energy consumption compared to other separation processes that enabled it to have a leading role in desalination industry. [13], [14]

The natural process of flowing water from a low concentration solution to a solution with high concentration of solutes through a semi-permeable membrane is known as osmosis. At equilibrium, the solutes concentration will be the same in both solutions and the net flow between both compartments will be zero. The osmotic pressure created depends mainly on the concentration of the dissolved solute. The process at which a pressure greater than the osmotic pressure is exerted on the compartment with high solute concentration is called RO. [13], [14]

Reverse osmosis desalination is a process that is driven by external hydraulic pressure in order to exclude solutes using a semi-permeable membrane as shown in Figure 1.7. In 1959, Reid and Breton succeeded in performing RO using CA membranes. The membranes, with a thickness 5-20 µm, though with a low solution permeation values, achieved 98% salt rejection. The successful development of Loeb–Sourirajan CA asymmetric membranes, using phase inversion
was a breakthrough due to their high permeation rates as well as high salt rejection values. [8], [14]

![Figure 1.7 RO and FO processes. [14]](image)

1.5. **Operation of a filtration processes**

1.5.1. Dead end filtration

There are two basic ways for operating a filtration process: dead end filtration and cross flow filtration. In dead end filtration, the solids are left behind while the feed water is forced to pass through the membrane. Dead end filtration is considered a batch process, which means that an accumulation of separated solutes will occur on the membrane and as a result water will experience a higher resistance to pass through the membrane. In such a case, the membrane must be replaced or cleaned. This process is very useful for concentrating compounds. Figure 1.8 shows that for the dead-end filtration, the feed water is the raw water going through the membrane and the permeate is the water after the separation process, which is free of solids. [13], [14], [15]

1.5.2. Cross flow filtration

In cross flow filtration, the accumulation of separated solutes on the membrane surface is prevented through applying a constant flow. The driving force of the feed flow through the membrane is both an elevated pressure and a high flow speed that creates turbulent conditions. The difference between dead end filtration and cross flow filtration is that water pathway through the membrane is perpendicular to the membrane surface for the former and tangentially through the membrane for the latter. Hence, cross flow filtration minimizes the fouling of RO membranes as one influent stream is applied and two effluent steams are obtained. Cross flow filtration is a
continuous process that keeps the surface of the membrane free of solids. It is mainly used to filter liquids with a high concentration of filterable matter as shown in Figure 1.8. [13], [14], [15]

1.5.3. Hybrid flow filtration

Hybrid flow filtration is a combination of dead-end and crossflow processes. Tubes are used in this type of filtration with a membrane layer covering the tube inside wall. The process consists of two phases: the production phase and the flushing phase. In the production phase dead-end filtration is performed by closing the tubes on one side. In the flushing phase, the tubes are opened on both sides and the remaining untreated water that has not already passed through the membrane is removed and the membrane surface is cleaned. This filtration technique is commonly used for the treatment of water streams containing low concentrations of suspended solids as shown in Figure 1.8. [13], [14], [15]

![Diagram](image)

**Figure1.8** (a) Dead-end, (b) cross flow, (c) hybrid flow filtration. Adapted from [15]
II. Literature Background

2.1. Introduction

Polymeric membranes are commonly used for desalination through reverse osmosis. However, a number of challenges still need to be addressed. These entail the consumption of large amounts of energy as well as the need for improved water permeation, salt retention, and minimization of fouling. In this respect, scientists are continuously investigating novel approaches for fabricating membranes with the aim of optimizing their performance through tuning their physicochemical and structural properties such as porosity and hydrophilicity. With respect to desalination, a membrane must have pores with sizes less than 2 nm to be able to reject salt ions while allowing water molecules to pass through. Introducing carbon based nano-materials, especially graphene oxide (GO) for polymeric membranes synthesis has been reported recently. Owing to the functional groups present on the GO sheets surface, these are believed to have a high ability of adsorbing water molecules. This is due to the increase in membrane hydrophilicity which facilitates water molecules penetration through membranes which is advantageous for water desalination purposes. This chapter addresses the impact of CA amounts and solvent and non-solvent addition on membrane morphology and performance. Furthermore, the current state of incorporating GO sheets in polymeric membranes to be used for desalination and water treatment purposes is presented.

2.2. Effect of polymer concentration

Saljoughi et al. [16] studied the effect of CA concentration, among other factors, on the morphology and pure water flux of UF membranes which were prepared using phase inversion (PI). In this study, different concentrations of CA (13.5, 15.5, 17.5 wt. %) and polyethylene glycol (PEG) (0, 5, 10 wt. %) were added to a 1-methyl-2-pyrrolidone solution. After casting the membranes, they were immersed in coagulation baths with different temperatures (0, 11, 23 °C). Taguchi experimental design method was used to study the effect of various control parameters using the minimal number of experiments. These trials are summarized in Table 2.1.

Increasing CA concentration in the casting solution decreased both porosity and thickness of synthesized membranes based on SEM images of the membranes, which in turn caused a noticeable reduction in flux values. This was interpreted by the fact that increasing CA concentration increased the viscosity of the cast membranes. The mutual diffusivities between water and N-methyl-2-pyrrolidone (NMP) decreased during solidification and a slow demixing
occurred. Thus, using higher concentrations of CA resulted in the formation of a large number of small nuclei, which were distributed throughout the polymer film. In contrast, the effect of increasing PEG and coagulation bath temperature (CBT) resulted in intensifying thermodynamic instability of the casting solution and leading to the formation of greater macrovoids and more porous structures due to the instantaneous demixing.

Table 2.1 Preparation variables of CA membranes [16]

<table>
<thead>
<tr>
<th>Synthesized membrane</th>
<th>CBT (°C)</th>
<th>CA (wt.%)</th>
<th>PEG (wt.%)</th>
<th>Flux (L/m² h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M₁</td>
<td>0</td>
<td>13.5</td>
<td>0</td>
<td>9.85</td>
</tr>
<tr>
<td>M₂</td>
<td>0</td>
<td>15.5</td>
<td>5</td>
<td>35.05</td>
</tr>
<tr>
<td>M₃</td>
<td>0</td>
<td>17.5</td>
<td>10</td>
<td>6.60</td>
</tr>
<tr>
<td>M₄</td>
<td>11</td>
<td>13.5</td>
<td>5</td>
<td>72.70</td>
</tr>
<tr>
<td>M₅</td>
<td>11</td>
<td>15.5</td>
<td>10</td>
<td>80.10</td>
</tr>
<tr>
<td>M₆</td>
<td>11</td>
<td>17.5</td>
<td>0</td>
<td>0.75</td>
</tr>
<tr>
<td>M₇</td>
<td>23</td>
<td>13.5</td>
<td>10</td>
<td>216.70</td>
</tr>
<tr>
<td>M₈</td>
<td>23</td>
<td>15.5</td>
<td>0</td>
<td>7.75</td>
</tr>
<tr>
<td>M₀</td>
<td>23</td>
<td>17.5</td>
<td>5</td>
<td>1.70</td>
</tr>
</tbody>
</table>

Arthanareeswaran et al. [17] also used different concentrations of CA and PEG 600 in order to prepare membranes with improved properties to be used for ultrafiltration applications. The preparation method was PI and membranes were cast with initial casting thickness (ICT) of $0.22 \pm 0.02$ mm. Various combinations of CA and PEG 600 were dissolved in N,N-dimethylformamide (DMF) under constant stirring at 20 °C. The performance of the developed membranes was evaluated by on the efficiency of protein separation, such as pepsin, egg albumin (EA) and bovine serum albumin (BSA). Design of experiment was used to develop a series of membranes with different combinations of CA and PEG 600. These combinations are summarized in Table 2.2.
Table 2.2 Prepared combinations of CA, solvent and PEG 600 [17]

<table>
<thead>
<tr>
<th>Membrane no.</th>
<th>CA (%)</th>
<th>Solvent (%)</th>
<th>Additive (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15</td>
<td>82.5</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>77.5</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>72.5</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>21.25</td>
<td>72.5</td>
<td>6.25</td>
</tr>
<tr>
<td>5</td>
<td>15.5</td>
<td>78</td>
<td>6.5</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>82.5</td>
<td>7.5</td>
</tr>
<tr>
<td>7</td>
<td>17.5</td>
<td>72.5</td>
<td>10</td>
</tr>
</tbody>
</table>

Pure water flux of membrane 2 and 3 synthesized at constant values of PEG 600 concentration and varied CA content of 20 wt. % and 25 wt. % was investigated. Membrane 2 showed a flux of 42.6 Lm⁻²h⁻¹ while membrane 3 had a flux of 20 Lm⁻²h⁻¹, more than 20% decrease in the flux with increasing CA content indicating a decrease in the porosity of the synthesized membrane. This was further supported by protein rejection rates shown in Figure 2.1. As CA concentration increased from 20 to 25 wt. %, a significant increase in protein rejection was found.

2.3. **Effect of solvent and non-solvent addition**

Haddad et al. [18] prepared CA nano-filtration (NF) membranes using PI. Two polymer concentrations, 20-22 wt. % of CA, were added to a mixture of acetone/formamide with a ratio of 2:1. The solutions were cast at a 250 µm height and immersed in a coagulation bath of distilled water. Then, the membranes were annealed at 60-80°C for 10 minutes. The final membranes’
thicknesses were found to be 70-90 μm. Permeation and salt rejection rates were determined for all the membranes using a 2000 mgL⁻¹ NaCl solution. The membranes were tested for a range of pressures starting from 4 bars till 16 bars. The pure water flux increased with increasing pressure. On the other hand, pure water flux rates showed a drastic decrease with increasing the temperature of annealing, as shown in Table 2.3, for the two sets of polymer concentrations used. As for the salt rejection rates that were tested at trans-membrane pressure of 16 bars, an increase in salt rejection was detected with increasing the annealing temperature. This was attributed to the fact that annealing creates denser membranes as it reduces the pore sizes. Table 2.3 shows that the 22 wt. % CA membranes exhibited higher salt rejection compared to the membranes containing 20 wt. % CA. The membrane with the best performance was the one with a 22wt. % CA, annealed at 80° C for 10 minutes.

<table>
<thead>
<tr>
<th>Permeation rate L.m⁻².h⁻¹</th>
<th>Temperature</th>
<th>80 °C</th>
<th>75 °C</th>
<th>70 °C</th>
<th>65 °C</th>
<th>60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA 20wt.%</td>
<td>9.61</td>
<td>22.4</td>
<td>47.38</td>
<td>57.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CA 22 wt.%</td>
<td>7.18</td>
<td>16.48</td>
<td>16.02</td>
<td>23.45</td>
<td>42.72</td>
<td></td>
</tr>
</tbody>
</table>

| Salt rejection %          | CA 20wt.%   | 79.71 | 44.83 | 34.51 | 2.02  |       |
| CA 22wt.%                 | 86.12       | 79.64 | 42.7  | 24.91 | 17.65 |       |

Li et al. [19] investigated the effect of varying the ratio of two nonvolatile solvents, (NMP) and γ-butyrolactone (GBL), on the structure and performance of CA membrane. The membranes were prepared by PI according to the conditions summarized in Table 2.4. Different polymer solutions were cast with ICT 200 μm and then immersed, at room temperature, into a water bath. Membranes were kept in the water bath for a couple of days to ensure the removal of any residual solvents.
Table 2.4 Different compositions of CA solutions [19]

<table>
<thead>
<tr>
<th>CA (wt%)</th>
<th>GBL concentration in solvent mixture (wt%)</th>
<th>NMP concentration in solvent mixture (wt%)</th>
<th>Viscosity (mPa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>0</td>
<td>100</td>
<td>4335</td>
</tr>
<tr>
<td>11</td>
<td>50</td>
<td>50</td>
<td>5690</td>
</tr>
<tr>
<td>11</td>
<td>60</td>
<td>40</td>
<td>6028</td>
</tr>
<tr>
<td>11</td>
<td>67</td>
<td>33</td>
<td>6047</td>
</tr>
<tr>
<td>11</td>
<td>75</td>
<td>25</td>
<td>6285</td>
</tr>
<tr>
<td>11</td>
<td>80</td>
<td>20</td>
<td>6911</td>
</tr>
<tr>
<td>11</td>
<td>100</td>
<td>0</td>
<td>7875</td>
</tr>
</tbody>
</table>

The SEM images in Figure 2.2 showed that CA/NMP membrane exhibited large macrovoids structures due to the instantaneous demixing between NMP and water. On the other hand, using GBL as solvent resulted in a sponge-like membrane structure due to delayed demixing. Intermediate changes in the membranes structure were observed by changing the GBL content from 0% to 100% in the solvent mixture. Figure 2.2 shows that increasing GBL content in the solvent mixture from 0% to 75% caused a slight decrease in the size of macrovoids. However, increasing GBL content to 80% the membrane showed a dramatic change to a sponge like structure. Membrane performance was evaluated by measuring pure water permeability (PWP) rates and salt rejection rates of 100 Kdextran. By increasing GBL content from 0% to 75%, a decrease from 2803 to 178 L/m²h bar in the PWP was observed. In addition, the rejection rates of the membranes showed an increase from 0% to 90% for 100 K dextran at 10 bars indicating a tighter membrane structures due to the delayed demixing behavior with increasing GBL content.
Figure 2.2 Cross-sectional SEM images of CA membranes with various NMP/GBL ratios. [19]

Odena et al. [20] also prepared nano-filtration CA membranes by PI using acetone and dioxane as solvents, and methanol as a non-solvent. The CA polymer solution was deposited on a polypropylene/polyethylene non-woven support. Polymer concentration, solvent/non-solvent ratio, and annealing temperature and time were the parameters tested in this investigation. The polymer content ranged from 12 to 25 wt.%, methanol content ranged from 0 to 25 wt.%, acetone concentration was 20 wt.%, and dioxane was used to complete the composition up to 100 wt.%. A 250 µm thick polymeric solution was deposited on a polypropylene/polyethylene support. After casting, the membranes were left for evaporation time of 30, 60, 90 and 120s. Then, films were immersed in distilled water at 4 °C to induce the polymer precipitation. This was followed by thermal annealing for 2, 6, 10 or 14 minutes in a water bath at constant temperature of 65, 70, 75, 80 or 85 °C. The membranes were tested for ibuprofen retention, a known micro-pollutant, as shown in Table 2.5.
Table 2.5 Effect of CA wt. %, solvent/ non-solvent ratio, and annealing temperature on ibuprofen retention [20]

<table>
<thead>
<tr>
<th>Membrane</th>
<th>CA (wt%)</th>
<th>Methanol (wt%)</th>
<th>Dioxane (wt%)</th>
<th>Acetone (wt%)</th>
<th>Ev time</th>
<th>An time (min)</th>
<th>T</th>
<th>Retention (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M4-28</td>
<td>12</td>
<td>14</td>
<td>54</td>
<td>20</td>
<td>90</td>
<td>6</td>
<td>75</td>
<td>98.30</td>
</tr>
<tr>
<td>M4-8</td>
<td>21</td>
<td>12</td>
<td>47</td>
<td>20</td>
<td>60</td>
<td>6</td>
<td>75</td>
<td>97.43</td>
</tr>
<tr>
<td>M4-18</td>
<td>19</td>
<td>7.5</td>
<td>54</td>
<td>20</td>
<td>30</td>
<td>2</td>
<td>75</td>
<td>95.80</td>
</tr>
<tr>
<td>M2-29</td>
<td>22</td>
<td>17.8</td>
<td>40</td>
<td>20</td>
<td>60</td>
<td>14</td>
<td>85</td>
<td>95.80</td>
</tr>
<tr>
<td>M2-13</td>
<td>18</td>
<td>21</td>
<td>41</td>
<td>20</td>
<td>60</td>
<td>2</td>
<td>85</td>
<td>94.49</td>
</tr>
</tbody>
</table>

Five membranes were tested with 5000 ppm NaCl solution at an operational pressure of 40 bars. The membrane with the highest salt retention performance of 82.55% and permeation rate of 48 L/m²h at 40 bars had a CA content of 19 wt.%, methanol content of 7.5 wt.%, and was annealed at 75°C.

2.4. Effect of using Graphene Oxide

Wang et al. [21] managed to fabricate free-standing cellulose triacetate (F-CTA) GO membranes to be used for forward osmosis. GO was synthesized from graphite by Hummer’s method, used in different amounts of 0.3 wt.%, 0.6 wt.%, 1 wt.%, 3 wt.%, and 5 wt.% and dispersed in acetone using ultra-sonication. Afterwards, methanol, lactic acid, 1,4-dioxane and dried CTA granules were added and stirred at 70 °C. The membranes were prepared using PI at room temperature after evaporation of the solvent for 60s. The final membrane thickness was 50 ± 10 µm. The prepared GO-F-CTA membranes were characterized by SEM, contact angle measurements, permeation tests, and salt retention tests. The analysis showed an improvement in the membrane hydrophilicity as a result of GO incorporation. This was proved by the noticeable decrease in contact angle values. In addition, a significant enhancement in water flux up to 68% with the incorporation of 0.6 wt.% GO, using 0.5 M NaCl as a draw solution and deionized water as a feed solution, was found. The 0.6 wt.% GO membrane obtained a low salt flux (0.22 g/L) indicating an improved salt rejection. As for membrane biofouling, the anti-biofouling capability increased with increasing GO content. The presence of GO enabled excellent mechanical stability of the free-standing membranes.

Ganesh et al. [22] studied the effect of GO on polysulfone (PSf) mixed matrix membranes using PI. Graphite was oxidized, using KMnO₄, in order to introduce hydrophilic functional groups onto its surface. Small amounts (1000 ppm and 2000 ppm) of GO dispersed in NMP were added
to 25 wt. % PSf/NMP solution at 60 °C. Then, the membranes were immersed in water bath at room temperature. SEM was used to study the morphology of membranes while water swelling experiments and measuring surface wettability were used to detect the variation in the membranes hydrophilicity. Membrane performance in terms of the pure water flux and salt rejection was determined using a 1000 ppm Na₂SO₄ and NaCl solutions at different applied pressures.

The results indicated that doping the polymer matrix with GO resulted in enhanced hydrophilicity, water flux, and salt rejection properties of the membrane. The SEM images showed that significant changes occurred to the sub layer macro-voids as shown in Figure 2.3.

![Figure 2.3 SEM images showing effect of GO on PSf membranes. [22]](image)

The fast exchange of solvent and non-solvent during the PI process as a result of the hydrophilic nature of GO led to extended porosity as well as changes in the macrovoids structure. The top layer appeared darker than the rest of the membrane. This was explained by the fact that GO has higher affinity towards water. As a result, GO moved towards the top layer during PI. As for salt rejection, 2000 ppm GO-doped membranes exhibited salt rejection of 72% for 1000 ppm Na₂SO₄ solution at 4 bars which is higher than the 1000 ppm GO-doped membrane that showed a 65% salt rejection. The rejection decreased slightly with increasing pressure for both membranes. Rejection of 1000 ppm NaCl was 68% and 45% for 2000 ppm and 1000 ppm GO doped membranes, respectively. In addition, different pH solutions were used to study the effect of pH on the rejection rates. The
rejection increased slightly at basic pH as shown in Figure 2.4. The salt rejection of 1000 Na₂SO₄ increased by increasing the pH that means the membranes was negatively charged.

**Figure 2.4 Effect of pH on the rejection of 1000 ppm Na₂SO₄ solution. [22]**

The different dispersion states of GO in polymeric matrix as a function of GO loading was investigated by Wang et al. [23]. In this study, microcrystalline cellulose (MCC)/GO films were prepared by the tape template method. Different amounts of GO (0.0, 0.0251, 0.0505, 0.155, 0.263 and 0.376 wt. %) were dispersed in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), and then added to MCC (5 wt%)/[Bmim]Cl prepared solutions to have a total weight of 5 g. MCC/[Bmim]Cl GO solutions were spread on a glass plate which was then soaked in water for 6 hours to eliminate [Bmim]Cl. Finally, the films were kept for 12 hours in a 35 °C temperature oven to be dried. Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) spectra indicated a homogenous dispersion of GO in the MCC matrix. As the GO content increased to be higher than 0.155 wt. %, a network of GO nano-sheets started to form indicating good adhesion between MCC and GO as pointed out by rheological measurements. This was further proven by the cross-sectional SEM images of the composite films which showed the sheet structure of GO. In contrast, at higher GO contents (3 and 7 wt.%), aggregation of GO started to occur and poor interfacial adhesion between GO and MCC was observed. The 0.5 wt. % GO composite film exhibited enhanced mechanical properties such as tensile strength (+64.7%) and strain (+85.1%) when compared to pure MCC films. The relationship between the dispersion states according to GO loading and GO reinforcement effect was illustrated. Based on the structure of GO nano-sheets and MCC, hydrogen bonds between hydroxyl groups and oxygen atoms in MCC chain and the
oxygen containing groups in GO nano-sheets could form, which, according to the authors, was believed to be the reason behind the good dispersion of GO in MCC matrix. Figure 2.5 presents the varied dispersion states of GO in MCC as a function of GO content.

Kabiri et al. [24] fabricated nano-crystalline CA (NCCA)/GO films by combining NCCA and GO sheets in well-controlled manner. Both NCCA (200 mg/100 mL) and GO (10 mg/10 mL) were dispersed separately in deionized water under 6-kJ sonication for 2 hours. Then, the solutions mixed with mass ratios NCCA to GO: 99.9/0.1, 99.8/0.2, 99.5/0.5, 99.3/0.7, 99.2/0.8, 99.1/0.9, and 98.99/1. The solutions were filtered and freeze-dried to be used for nanocomposite films preparations. The NCCA/GO nanocomposites were prepared using simple solvent casting by being added to 5 mL of NMP, cast on a glass plate and heated at 50°C to obtain the films. The mechanical and thermal properties were investigated. GO nano-sheets were well-dispersed in the NCCA matrix based on SEM and XRD studies. With increasing GO loading, the films showed an enhanced tensile strength especially with 0.8 wt.% GO incorporation as shown in Figure 2.6 which resulted in 61.92 % increase in tensile strength compared with blank NCCA. In addition, the ability of the films to prevent the transmission of water vapor increased with increasing GO loading. This was attributed, as earlier explained, to the uniform dispersion of GO nano-sheets in the NCCA matrix.

![Figure 2.5](image_url)

**Figure 2.5 (a)** Molecular structure of GO and MCC chain, (b) different dispersion states of GO in MCC as a function of varied concentrations of GO. [23]
matrix. As a result, water molecules diffused through longer and more indirect pathways in the nanocomposites.

Figure 2.6 Water vapor permeability of NCCA-based films with increasing GO content. [24]

Xia et al. [25] focused on improving poly-vinylidene fluoride (PVDF) membranes by the direct incorporation of different amounts of GO as an additive to the casting solution. GO was dispersed in N-dimethylacetamide (DMAc). Then 25wt. % of PVDF was dissolved in the GO/DMAc solution. As for the GO contents, four amounts (0.0, 0.1, 0.5, and 1.0 wt. %) were tested. Membranes were prepared by PI with an initial thickness of 300 μm. The effect of GO addition on the membrane flux and natural organic matter (NOM) removal was investigated. Water permeated was examined for specific ultraviolet absorbance (SUVA), dissolved organic carbon (DOC), fluorescence excitation–emission matrices (EEMs), and molecular weight distribution (MWD).

The results showed that the hydrophilic character and permeability of the membranes improved significantly by adding GO as a result of the migration of oxygen functional group spontaneously to the membrane surface during PI. The effect of introducing GO on the micromorphology of the prepared membranes was observed using SEM. It was shown that the PVDF/GO membrane had a larger macrovoid layer compared to the blank membrane as shown in Figure 2.7. Consequently, pure water permeability results showed that adding GO as an additive promoted the flux significantly from 47L/m²h bar for the blank PVDF membrane to 94L/m²h for the 0.1wt.% GO membrane. Water contact angle results showed a reduction by approximately
6 degrees at the most. During the filtration process of NOM and DOM, modified membranes showed high fluxes demonstrating that GO incorporation enhanced the antifouling property of the membranes. The results revealed that the 0.5 wt. % GO membrane had optimal results regarding parameters such as pure water flux, hydrophilicity, and antifouling properties. Removal of NOM, and fluorescent DOM such as protein, humic acid, and fulvic acid, was increased slightly according to EEM spectra.

![SEM images of cross-section for (a) PVDF membrane and (b) PVDF with 0.5 wt. % GO membrane.](image)

Another functionalized GO membrane was fabricated by Ionita et al. [26] who prepared PSf/GO nanocomposites by PI using ethanol as non-solvent. The structural features, mechanical, and thermal performances of the prepared membranes were investigated using Raman spectroscopy, XRD and TEM. 0.25, 0.5, 1, and 2 wt. % GO were dispersed in DMF and added to a solution of 20 wt. % of PSf dissolved in DMF. Raman spectroscopy, XRD and TEM showed that the GO was dispersed well in the 0.25, 0.5, 1 wt. % solutions while the 2 wt. % had agglomerations of GO. 0.25, 0.5, 1 wt. % GO solutions showed higher mechanical properties (tensile modulus and tensile strength) compared to blank PSf which was attributed to more efficient load transfer from the PSf matrix to the GO due to the stronger interface. Increasing GO in the PSf matrix had a negative effect on the membranes as the agglomerations caused a decrease in the mechanical properties. The lowest amount of GO (0.25 and 0.5 wt. %) membranes showed the highest thermal stabilities compared to other membranes.
The effect of GO modification on PVDF membranes was explored by Zhao et al. [27]. PVDF/GO UF membranes were prepared by PI using DMAc as solvent, GO nano-sheets as the additive, and deionized water as the coagulation bath. 0, 0.5, 1, and 2 wt. % GO were dispersed in DMAc followed by the addition of 13 wt. % PVDF. The initial casting thicknesses of the membranes were 200 µm and the coagulation bath temperature was 20 °C.

Raman spectroscopy showed the existence of GO in the PVDF/GO UF membranes. In addition, FTIR spectra indicated the existence of large amounts of –OH groups as a result of incorporating GO nano-sheets. The SEM images showed an increase in porosity and mean pore size as shown in Table 2.6. A finger-like pore substructure was found to have developed. Pure water flux and BSA permeation flux increased with the incorporation of GO. The pure water flux and permeation flux of the 2% GO content membrane reached peak values of 26.49 L/m²hbar and 14.21 L/m²hbar, increasing 79% and 99% respectively. As for the BSA rejection, the membrane showed a rejection of 44.3%. The membranes showed better antifouling properties compared to pure PVDF as a result of high membrane hydrophilicity. The contact angle results agreed with the flux recovery ratio (FRR) and the fouling resistance results as the contact angle values decreased to 61 degree with increasing GO compared with 73 degrees for blank PVDF membrane.

Table 2.6 PVDF and PVDF/GO UF contact angles and pore structure parameters [27]

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Contact angle (deg)</th>
<th>Thickness (µm)</th>
<th>Porosity (%)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td>72.6 ± 1.5</td>
<td>95.2 ± 1.3</td>
<td>71.74 ± 0.20</td>
<td>7.99 ± 0.02</td>
</tr>
<tr>
<td>PVDF/GO-0.5</td>
<td>70.5 ± 1.1</td>
<td>131.4 ± 2.5</td>
<td>74.48 ± 1.20</td>
<td>10.61 ± 0.15</td>
</tr>
<tr>
<td>PVDF/GO-1</td>
<td>64.2 ± 0.8</td>
<td>143.5 ± 3.4</td>
<td>75.35 ± 0.67</td>
<td>12.34 ± 0.10</td>
</tr>
<tr>
<td>PVDF/GO-2</td>
<td>60.5 ± 1.8</td>
<td>149.7 ± 2.8</td>
<td>76.83 ± 0.50</td>
<td>12.61 ± 0.08</td>
</tr>
</tbody>
</table>

The same trend was reported by Zinadini et al. [28] who investigated the preparation of novel polyethersulfone (PES) mixed matrix nano-filtration membrane containing GO using PI. Pure water flux, dye removal and fouling parameters were measured to examine the effect of GO on the fabricated membranes. 20 wt. % of PES, 1 wt. % of polyvinylpyrrolidone (PVP), and GO (0.1, 0.5 1 wt. %) were dissolved in DMAc and casted with an initial thickness of 200 µm. The prepared GO-blended PVDF membranes were characterized by atomic force microscopy (AFM), SEM, porosity measurements, contact angle measurements and permeation tests.

As found in previous investigations, GO incorporation improved membrane hydrophilicity causing a significant improvement in water flux and noticeable reduction in contact angle as shown...
in Figure 2.8. Moreover, SEM images showed GO finger-like pores in comparison with the blank membranes. Membranes were tested for dye removal, direct Red 16 with concentration of 30 mg/L, in order to evaluate their nano-filtration performance. The rejection capacity of the unfilled PES membranes was lower than that of GO blended membranes. 1 wt. % GO/PES membrane showed 99% dye rejection. On the other hand, 0.5 wt. % GO/PES membranes showed the highest mean pore radius, antibiofouling property, porosity, and water flux (around 65.2 kg/m² h.).

![Figure 2.8 Fluxes and contact angles of PES after GO incorporation. [28]](image)

Using PI, Wang et al. [29] prepared organic–inorganic-blended ultrafiltration membranes using PVDF as a polymer, graphene oxide as an additive, and DMAC as a solvent. Different concentrations of GO (0 wt.%, 0.10 wt.%, 0.15 wt.%, 0.20 wt.%, 0.25 wt.% and 0.30 wt.%) were dispersed in 80 wt.% DMAC followed by the addition of 20 wt.% PVDF. The prepared membranes were characterized using FTIR, SEM, porosity measurements, permeation tests, and water contact angle.

Due to the hydrophilic nature of GO, increasing GO contents resulted in an increase in the hydrophilicity and pure water fluxes while the contact angles decreased as shown in Table 2.7. This implied that the anti-fouling ability of the membrane improved. The SEM images showed that larger pore channels formed due to the addition of GO. This was attributed to GO owning various types of hydrophilic groups that increased mass transfer between the solvent and non-solvent during PI. Thus, larger pore channels formed because the rate of membrane nucleation was accelerated due to the GO acting as a nucleating agent in PI. However, increasing GO content to 0.25 and 0.3 wt. % increased the viscosity of the casting solution, hindering the forming process,
causing lateral pore structures to appear in the membranes, and finally resulting in the formation of a dense structure with smaller pore sizes.

Table 2.7PVDF/GO membranes’ performances with different GO contents [29]

<table>
<thead>
<tr>
<th>GO content (wt.%)</th>
<th>Water flux (L/m²·h)</th>
<th>Porosity (%)</th>
<th>Mean pore size (nm)</th>
<th>Contact angle (°)</th>
<th>BSA retention ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>233.11</td>
<td>46.8</td>
<td>25.1</td>
<td>79.2</td>
<td>96.1</td>
</tr>
<tr>
<td>0.10</td>
<td>271.29</td>
<td>50.5</td>
<td>27.6</td>
<td>72.1</td>
<td>94.7</td>
</tr>
<tr>
<td>0.15</td>
<td>350.14</td>
<td>56.2</td>
<td>44.3</td>
<td>68.4</td>
<td>92.7</td>
</tr>
<tr>
<td>0.20</td>
<td>457.86</td>
<td>70.7</td>
<td>55.3</td>
<td>60.7</td>
<td>91.1</td>
</tr>
<tr>
<td>0.25</td>
<td>382.15</td>
<td>65.6</td>
<td>46.5</td>
<td>62.1</td>
<td>91.8</td>
</tr>
<tr>
<td>0.30</td>
<td>346.14</td>
<td>54.3</td>
<td>40.5</td>
<td>63.8</td>
<td>93.6</td>
</tr>
</tbody>
</table>

PI was also used by Ionita et al. [30] for the fabrication of CTA/GO porous membranes for albumin rejection applications. The effect of GO addition on the morphology, structure, water and ethanol flux, thermal properties, and bovine serum albumin rejection was investigated shown in Figure 2.9. The membranes had a concentration of 10 wt. % of CTA and three different amounts of GO, 0.25, 0.5, and 1 wt. %. SEM analysis indicated that the CTA morphology dramatically changed as GO was added to the CTA matrix. The formation of large macrovoids was detected within the highly porous area, with a vertical orientation towards the surfaces.

It was reported that when the weight fraction of GO reached 1 wt. %loading, both pure water and ethanol fluxes decreased. However, higher fluxes through the membranes were recorded for water at low concentrations of GO and were related to the increase in membranes hydrophilic character due to GO incorporation when compared to the blank CA membrane. Concerning the BSA rejection, the increase in the GO concentration caused a direct increase in the BSA rejection from 78% in the case of CA membrane to 99% in the case of CA/GO 1 wt%. This was explained by the decrease of the porosity at the active surface of the membranes as a result of the addition of the GO.
Lee et al. [31] embedded different wt. % of GO into PSf membranes prepared by PI. 15 wt. % PSf were dissolved in NMP followed by the addition of GO nano-plates dispersed in NMP. The prepared PSf/GO membranes had the following contents of GO with respect to PSf: 0.16, 0.32, 0.92, 1.30, and 2.60 wt. %. Increasing GO content in the membranes resulted in a noticeable increase in the membranes’ hydrophilicity and pore size. Thus, the pure water flux was significantly improved. The increase in water fluxes occurred up to 1.30 wt. % GO content then decreased. This was explained by the fact that the increase in GO wt. % increased the membrane hydrophilicity and pore sizes as mentioned previously until a point at which too much of the GO delayed the demixing process as a result of increasing the solution viscosity, resulting in smaller pore sizes that reduced permeation rate. In addition, the contact angle measurements decreased consistently with increasing GO content, showing more hydrophilic nature of the membrane with increasing GO content.
SEM images showed a noticeable decrease in the membrane pore size with 2.60 wt. % GO as shown in Figure 2.11. In general, the mechanical properties of the membranes were enhanced by adding GO to the polymer matrix. However, the 2.6 wt. % GO/PSf membranes showed a weaker mechanical strength due to aggregation of GO in the PSf matrix.

![Cross-sectional SEM images of GO/PSf membranes with different GO concentrations.](image)

**Figure 2.11 Cross-sectional SEM images of GO/PSf membranes with different GO concentrations. [31]**

Ionita et al. [32] studied the mechanical properties of PSf/GO membranes prepared by PI. Different amounts of GO (0.25, 0.5, 1, 2 wt. %) were dispersed in a homogeneous polymer solution of 20 wt. % PSf and DMF. Then, the solution was cast and immersed in an ethanol bath for complete phase inversion to take place. The effect of GO incorporation within the PSf matrix was investigated through the structural and surface features and the mechanical and thermal performances of the prepared membranes. Raman spectroscopy, TEM and XRD analysis indicated the excellent dispersion of GO within the PSf matrix which resulted in an increase in the porous and macro-voids dimension. However, upon increasing GO content to 2 wt. %, some GO bundles were observed in the membranes. Unlike films with high GO content (1 and 2 wt.%), higher thermal stability of the composite films was obtained when lower concentrations of GO (0.25 and 0.5 wt. %) were incorporated. In addition, the tensile strength and tensile modulus of the membranes with low content of GO were enhanced compared to blank PSf membranes as shown in Table 2.8. This improvement was attributed to the formation of a strong interfacial bond between the polymer matrix and the GO filler at low GO concentrations. When GO content exceeded 1 wt. % within
the polymer matrix, the tensile modulus and tensile strength values were even lower than the values obtained for the blank PSf. The formation of aggregates as a result of the incorporation of high contents of GO restricted the development of strong interface polymer/GO.

### Table 2.8 Mechanical properties for the prepared membranes [33]

<table>
<thead>
<tr>
<th>Sample</th>
<th>GO content (wt.%)</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSf</td>
<td>0</td>
<td>187 ± 11</td>
<td>3.33 ± 0.28</td>
</tr>
<tr>
<td>PSf/GO</td>
<td>0.25</td>
<td>201 ± 26</td>
<td>4.06 ± 0.53</td>
</tr>
<tr>
<td>PSf/GO</td>
<td>0.5</td>
<td>199 ± 14</td>
<td>3.67 ± 0.33</td>
</tr>
<tr>
<td>PSf/GO</td>
<td>1</td>
<td>218 ± 30</td>
<td>3.84 ± 0.39</td>
</tr>
<tr>
<td>PSf/GO</td>
<td>2</td>
<td>144 ± 9</td>
<td>2.36 ± 0.41</td>
</tr>
</tbody>
</table>

The same trend was observed by Chen et al. [34] who also studied the effect of GO addition on the mechanical properties of polyimide nanocomposites. 0.1, 0.5, 1, and 2 wt. % of GO were dispersed in DMAc and incorporated into polyimide by in-situ polymerization. The results showed that GO had a good dispersion and interaction with polyimide in the nanocomposites. This was attributed to the high hydrophilicity of the oxygen-containing groups of GO sheet which significantly enhanced the tensile strength by 40% for a 0.5 wt. % GO addition. The tensile elongation was three times greater than pure polyimide film. In addition, the thermal stability of the nanocomposites was also improved. Increasing GO to 1 and 2 wt. % showed a slight decrease in the mechanical properties due to aggregation of GO.

Zhao et al. [35] used PI to prepare PVDF/GO microfiltration membranes. In order to optimize the preparation conditions of the membranes, Taguchi experimental design was used. PVDF content, solution type, GO amount, and pore-former content were the parameters selected for this investigation. In addition, the effect of the varied amounts of GO incorporated in the membrane on the antifouling and mechanical properties were also investigated. PVDF was used as the polymer, GO nano-sheets as additive, PVP as the pore former agent and distilled water as the coagulation bath. Different concentrations of GO were dispersed in different solution: DMAc, NMP and DMF using sonication. Then, PVDF and PVP were dissolved at 70 °C in the GO dispersions. The membranes were cast with an initial thickness of 400 μm, exposed to air for 20 s and immersed into coagulation bath at 20 °C.

The results obtained showed that the combination of PVDF = 12 wt. %, GO = 3 wt. %, solution type = DMAc, and PVP =5 wt. % resulted in the membrane with the best antifouling and
mechanical properties. This improvement in the membrane antifouling was believed to be due to the introduction of 3 wt. % GO. The OH groups of the GO nano-sheets improved the hydrophilicity of the surface of the membrane causing a reduction in the interaction between the contaminants and the membrane surface. The SEM images of the membrane surface showed a decrease in the surface porosity with increasing GO content. As GO content increased, the viscosity of the casting solution increased causing a slower precipitation rate of the membrane, which formed a denser surface layer. In addition, SEM images of the membrane cross section showed the formation of finger-like macropores as a result of the addition of PVP.

Zhang et al. [36] investigated the synergistic effect of graphene oxide (GO) and oxidized carbon nanotubes (OMWCNTs) on the anti-fouling and permeation performance of PVDF composite membranes. Membranes were prepared by PI. Different relative amounts of GO and OMWCNTs (GO-OMWCNTs = 0:10, GO-OMWCNTs = 10:0, GO-OMWCNTs = 1:9, GO-OMWCNTs = 9:1, GO-OMWCNTs = 5:5) were added to DMAc solvent before the addition of PVP (1 g) and PVDF (15 g) powders. The membranes were characterized by Ultraviolet-visible absorption spectra to ensure the stabilization and dispersion of both GO and OMWCNTs. This showed that the hybrid material dispersion is much better compared to OMWCNTs or GO alone. The results demonstrated that OMWCNTs suspension inhibited GO agglomeration as they could bridge adjacent GO sheets to achieve the highest potential for improving the membranes antifouling performance. Contact angle measurements showed that the hydrophilicity of the modified membranes was reported to improve significantly compared to the blank PVDF. Pure water fluxes for membranes with the ratio of 0:10 (GO/OMWCNTs), 10:0, 1:9, 9:1 and 5:5 were increased by 103.54%, 85.68%, 224.94%, 207.09% and 251.73%, respectively. PVDF/OMWCNTs and PVDF/GO membranes were improved by 103.54% and 85.68% respectively. As indicated by SEM tests, the improved pore density of modified membranes is believed to have contributed to the enhancement of permeation performance.

Further analysis using AFM with a BSA-immobilized tip showed that the modified membranes exhibited low adhesion force while the blank PVDF membranes exhibited strong adhesion to the probe, consistent with the fouling properties of the membranes which indicated the formation of a fouling layer in case of the blank membrane. As a result, the optimum ratio of GO/OMWCNTs membranes in terms of highest permeability and lowest fouling for ultrafiltration membrane was 5:5.
Mokkapati et al. [37] used PI to prepare PSf–GO composite membranes. He reported a new facile method based on adding GO nano-sheets to the coagulation bath rather than using only distilled water. 6 wt.% PVP, used as a pore agent and hydrophilic additive, in addition to 16 wt.% PSf were dissolved in NMP till a homogenous solution was obtained. Then, the cast membrane was left for 10–20 s for the solvent to evaporate, followed by immersing in GO dispersion bath maintained under continuous stirring. Different GO dispersion amounts were used for PI: 0.009%, 0.012%, 0.024%, and 0.048%. Low contact angles were found for low GO content membranes (0.009% and 0.012%) indicating a more hydrophilic nature than pure PSf. High GO content membranes (0.024% and 0.048%) showed higher contact angles. This was explained by the fact that during PI, GO sheets migrate spontaneously to the membrane surface causing a reduction in the interface energy making the membrane surface more hydrophilic. However, with increasing GO content within the coagulation bath, more hydrophobic membrane surface was obtained. The SEM images showed that PVP addition resulted in asymmetric structure with finger-like pores for all the membranes. Increasing GO amounts in the coagulation bath resulted in the formation of a thicker skin layer with lower porous sub-layer when compared to pure PES. This was believed to be due to the delayed demixing taking place during PI. Thereby, high GO content membranes had lower permeability values compared to low GO content membranes. The paper concluded that addition of 0.012% GO to the coagulation bath was responsible for the formation of a good porous structure to have the highest water permeability value of ~180 L/m²h.bar.

![Figure 2.12 Effect of GO contents on contact angles and permeability of PSf membranes. [37]](image-url)
GO nano-sheets were introduced into PES polymer matrix by Jin et al. [38] to improve the membranes hydrophilicity and antifouling ability. UF PES-GO membranes were prepared using PI. In a typical preparation, PES was added to stable GO-DMF solutions with different amounts of GO (1, 3, 10 mg mL⁻¹) cast on a glass substrate and then put into water at 20 °C. The obtained PES-GO membranes showed improved hydrophilicity and antifouling capability. Cross sectional SEM images revealed that both pure PES membranes and PES–GO composite membranes with low GO concentrations (1 and 3 mg mL⁻¹) had a similar structure of ultrafine channels arrays. However, upon increasing GO amounts (10 mg mL⁻¹), larger disarranged channels were observed. Contact angle measurements showed a decrease from 78°, for the pure PES membrane, to 55° with increasing GO content to 10 mg mL⁻¹. Thus, fluxes of the membranes gradually increased with increasing GO. In addition, membranes with low GO content showed a 100% BSA rejection. Yet, the 10 mg mL⁻¹GO-containing membranes showed a decrease in BSA rejection (92.3%) as a result of destroying the membrane microstructure.

Figure 2.13 Cross-sectional SEM images of PES/GO membranes (b) Pure PES (c) PES/1 mg mL⁻¹GO (d) PES/3 mg mL⁻¹GO (e) PES/10 mg mL⁻¹GO. [38]

Feng et al. [39] used PI to prepare GO/polyimide mixed matrix membranes. In brief, 1.564 g polyimide was added to NMP/GO solution with different GO concentrations (0.5, 1, 2 wt. %). The membranes were cast with IT of 100 µm. SEM images showed that GO/ polyimide membranes contained a dense skin-top layer followed by finger like sub-layer, unlike the pure polyimide membrane with a sponge-like porous structure. Contact angle decreased from 92° to 59° for pure polyimide membrane and 1 wt. % GO/polyimide membrane respectively. However, contact angles increased to 75° when GO content surpassed 2 wt. %. Probably, an increase in viscosity of the 2 wt. % GO/polyimide
casting solution would reduce the exchange of solvent and non-solvent during PI. Hence, GO nanosheets would not migrate to the membrane surface resulting in an increase of contact angle. Membranes were tested for permeation and salt rejection using prepared sea water with concentrations of 2–10 wt%. GO/polyimide membranes showed high permeation and ion rejection rates for all concentrations of seawater. As shown in Figure 2.14, increasing the feed concentration from 2 to 10 wt. %, permeation decreased from 22.4 to 10.7 kg m⁻² h⁻¹ while rejection rates maintained high rates of 99.9 %.

![Figure 2.14 Water flux and salt rejection values of GO/polyimide membranes for the filtration of sea water with different salt concentrations.](image)

Chang et al. [40] prepared asymmetric GO/PVDF UF membrane by PI using NMP as a solvent and PVP as a pore former. 18 wt.% PVDF and different concentrations of PVP (0.10 wt.%, 0.20 wt.%, 0.25 wt.%, 0.35 wt.%, 0.50 wt.% and 0.75 wt.%) were added to a solution of 84 wt.% NMP with different amounts of GO (from 0 wt.% to 0.50 wt.%). The prepared casting solutions were cast on a glass plate and then immersed in the distilled water bath. SEM images of the obtained membranes showed more intensive finger-like pores of PVDF/GO membrane than those of pure PVDF membrane. The membranes with the largest pores were PVDF/PVP membranes without GO. The variation of the contact angle measurement of the membranes were as follows: PVDF > PVDF/PVP > PVDF/GO > PVDF/GO/PVP. The addition of GO and PVP improved hydrophilicity of the membranes. This behavior was suggested to be due to the presence of oxygen-containing groups on the sheets of GO in addition to water soluble PVP. As for water flux, it increased dramatically with the addition of PVP to pure PVDF membrane while BSA rejection decreased with increasing PVP. For PVDF/GO/PVP membranes, BSA rejection decreased initially
with increasing PVP, however it increased slightly at 0.25 wt.% PVP content due to the fact that some PVP were fixed in the PVDF/GO/PVP membrane by hydrogen bonds with GO which tuned the membrane porosity. 85% BSA rejection and 104.3 L m\(^{-2}\) h\(^{-1}\) water flux were achieved when the content of PVP is 0.25 wt.% and GO is 0.50 wt.%.

Polyamide thin film composite (PA-TFC) RO membranes were modified using GO in the surface layer, polyamide layer, or sub-layer. Surface modification is an effective method to prepare PA-TFC RO membrane with better surface characteristics such as hydrophilicity, roughness, and charge density in order to enhance their chlorine resistance and fouling [41]. In order to examine the effect of stacked GO nano-sheets on membranes surface modifications, Borges et al. [42] succeeded in fabricating a surface layer of GO on the PA-TFC RO membrane by the deposition of a GO layer. This was followed by an aminated GO layer, and an alternating using layer-by-layer (LBL) deposition, a method for ultrathin highly ordered multilayered membranes fabrication based on electrostatic or non-electrostatic interactions. The incorporation of stacked GO nano-sheets resulted in an increase in surface hydrophilicity, water flux, and salt rejection of the modified membranes while decreasing surface roughness. Permeation and rejection rates were conducted at an operational pressure of 15.5 bars. The GO PA-TFC modified membranes showed a water flux of 14.0 ± 0.3 L/m\(^2\)·h and salt rejection of 97.1 ± 1.1%. Membrane roughness was reduced from ~46.5 to ~21.5 nm while the contact angle decreased from 70.6 ± 2.4 degrees to 25.9±3.0 degrees. According to the results obtained, the modification of LBL assembled GO nano-sheets did not cause any reduction of the water flux like other surface modifications such as surface coating and surface grafting.

The incorporation of GO in the active polyamide layer of PA-TFC RO was also studied by Xia et al. [43] who dispersed GO nano-sheets into the polyamide active layer of a TFC membrane using interfacial polymerization (IP). Different contents of graphene oxide (0, 0.004, 0.008, and 0.012 wt%) were added to the organic phase of trimesoyl chloride (TMC). The surface morphology showed a significant change after GO incorporation from ridge-and-valley structure into leaf-like morphology. The membranes showed an increase in surface hydrophilicity and decrease in contact angle from 63.74° ± 0.69° to 55.04° ± 0.69° with increasing GO content from 0.000 wt% to 0.012 wt%. The highest water flux was obtained for a GO content of 0.004 wt% with a value of 23.30 ± 0.48 L/m\(^2\)·h compared with the blank 18.75 ± 0.09 L/m\(^2\)·h. Further increase of GO showed a lower water flux values which was attributed to GO agglomeration.
In another study Chae et al. [44] incorporated GO into the polyamide layer of PA-TFC membranes. GO was dispersed in aqueous solution of m-phenylenediamine (MPD) before being used in interfacial polymerization on the PSf UF membrane. 0, 15, 38, and 76 ppm of GO were dispersed in MPD and diffused on the surface during IP. GO was reported to have a significant effect on hydrophilicity, surface charge, surface roughness, and thickness of the PA layer. Membrane hydrophilicity showed an increase while the thickness of the polyamide layer was reduced. Moreover, GO enhanced the membrane permeability and anti-biofouling property by 80% and 90% respectively for 38-GO-TFC. When the GO content exceeded 38 ppm, the values of water flux declined. This was interpreted by three factors: (1) increased water permeability due to the increase of the membrane hydrophilicity generally, (2) decreased active layer thickness, and (3) decreased membrane surface roughness decreasing water permeability. The salt rejection showed a slight increase after the GO addition as shown in Figure 2.15.

![Figure 2.15 Water flux and salt rejection values of the 0, 15, 38, and 76-GO-TFC membranes for the filtration of 2000-ppm NaCl solution. [44]](image)

Ali et al. [45] prepared hybrid organic-inorganic TFC membranes from MPD and 1,3,5-benzenetricarbonyl chloride on the surface of PSf substrate using interfacial polymerization. GO nano-sheets were incorporated into the membrane during membrane preparation. Membranes were prepared by adding 10 mL of MPD solution (2 wt. %), containing different amounts of GO (0–300 ppm), to the top surface of the substrate membrane and allowing it to sit for 1 min. 10 mL of the TMC in hexane solution (0.1 wt. %) was deposited on the substrate surface for 5s. The resulting membranes were annealed at 65°C for 5min to complete interfacial polymerization. The effects of
GO addition on the desalination performance of the resulting membranes were investigated, in terms of flux and salt rejection, in comparison with a blank membrane. SEM cross sectional images showed that GO containing membranes obtained a rougher surface than the TFC blank membrane with different morphology. The water contact angle measurements decreased from 64°, for the blank TFC membrane, to 48°, for the TFC/GO membrane, with increasing GO content from 0 to 300 ppm indicating improvement in the membrane surface hydrophilicity. The addition of small amounts of GO in the membrane resulted in enhanced water permeability behavior whereas the salt rejection decreased. However, upon increasing GO concentration to exceed 150 ppm in the amine reactant, water permeability decreased due to GO agglomerations (Figure 2.16). Compared to Blank TFC membrane, 100 ppm GO/TFC membrane achieved a 39% increase in water flux and 97% salt rejection for 2000 ppm of NaCl at an operational pressure of 15 bars.

![Figure 2.16 Effect of GO incorporation on water flux and salt rejection values of TFC membranes. Pressure 15 bar, temperature 20 °C, feed NaCl concentration 2000 ppm, and pH 7.[45]](image)

Gao et al. [46] prepared two sets of hybrid membranes: pristine graphene oxide (pGO) and reduced graphene oxide (rGO) blended with a sodium alginate (SA) matrix. Different amounts of pGO and rGO (0.4, 0.8, 1.2, 1.6, and 2 wt. %) were dispersed in deionized water, added to SA and coated onto a polyacrylonitrile substrate. The SEM analysis showed a good dispersion of both pGP and rGO within the membranes at low concentrations (0.4, 0.8 wt. %). Hybrid membranes with rGO or pGO showed the same trend at high GO content (2 wt. %). Overlapping of GO sheets was observed, causing agglomerations which was further confirmed by cross-sectional and surface
morphologies images. Unlike other reported investigations, no change in the contact angle with increasing the concentration of GO was observed. This indicated that the membranes had the same hydrophilicity even with different contents and types of GO. It was justified that the polymer matrix masked the GO nano-sheets to the extent that hydrophilicity of membrane surface was mainly governed by SA. rGO-SA membranes showed better permeation flux and ethanol separation than pGO as a result of constructing water channels with high selectivity due to the smaller nano-sheet size. The optimum separation factor (1566) and permeation flux performance (1699 g/ (m²h)) was achieved with 1.6 wt% of rGO incorporated in SA membrane.

2.5. Summary

In this review, the application of GO nano-sheets for the fabrication and modification of polymeric membranes was presented. The incorporation of GO in polymeric matrices can lead to better hydrophilicity, higher porosity and lower fouling properties. Most of the publications reported that using GO in polymeric membranes led to higher solution flux, better solute rejection, and enhanced thermal and mechanical stability. When the smallest amount of GO was mixed with polymeric material, the hydrophilic functional groups on GO facilitated water adsorption onto the membrane surface and allowed better permeation of water molecules through the membranes. However, it was noted that when larger GO amounts were used in polymeric membrane preparation using PI, a reduction of the membrane porosity was observed, resulting from delayed demixing during the PI process due to increased solution viscosity. [47], [48], [49]

2.6. Research Aim

To the best of our knowledge, the preparation of CA/Acetone-DMF/GO membranes with improved hydrophilicity, water permeation, and salt retention based on the incorporation of GO has not been reported previously. It is proposed that GO represents one of the opportunities for enhanced RO desalination performance. In this respect, the work presented here prepares these membranes, investigating the effects of different preparative conditions, namely the CA content, solvent type and GO content on the morphology and performance of the prepared membranes. Prepared membranes were characterized using SEM and BET. In addition, their performance will be determined for the rejection of 2000 ppm NaCl and 5000 ppm MgSO₄ at an operational pressure of 24 bars.
III. Theoretical background

3.1. Cellulose acetate (CA)

Experts have lately paid a great attention to eco-friendly polymers from renewable resources due to the rapidly growing concerns of environmental pollution. One of the known biomass-based polymers is cellulose as shown in Figure 3.1. Cellulose is the most abundant organic polymer on earth and is extracted from the cell wall of plants. Because of its attractive physical properties such as biodegradability and mechanical strength, low cost, and renewability, 100-150 billion tons of cellulose is produced worldwide from natural sources each year to be used as an industrial, medical, and textile material in diverse areas. Concerning its chemical structure, cellulose is one of the simplest natural polymers. D-glucose is the single repeating unit linked by β linkage through carbons 1 and 4. Thus, it has a linear structure with a high degree of intra- and inter-molecular hydrogen bonding between hydroxyl groups of cellulose main chains. [49]

![Figure 3.1 Structure of cellulose.](image)

Many cellulose derivatives have been synthesized such as: cellulose esters, CA, cellulose propionate (CP), and cellulose butyrate (CB). Cellulose products were initially synthesized in 1865 by Schutzenberger who found out that the reaction of esterification of cellulose is hard to control. Instead, cellulose was treated with acetic acid and acetic anhydride to obtain cellulose triacetate. In the early 1900s, the preparation of cellulose diacetate was conducted in a two-step process. Acetic anhydride is added to cellulose to produce triacetate while using sulfuric acid as a catalyst; followed by the hydrolysis of triacetate obtaining diacetate or CA in the presence of dilute aqueous sulfuric acid. [8], [50], [51], [52]
3.2. **CA for RO membranes**

The first RO membrane prepared to show high salt rejection performance was made from CA. The reason for CA being used for membrane technology is that the membranes are easy to prepare, resistant to degradation by chlorine, and are mechanically strong. CA membranes have the ability to tolerate chlorine up to 1 ppm, so the feed water especially with high bacterial loading, can be sanitized using chlorination. The salt rejection of CA membranes is very sensitive to the degree of acetylation of the polymer used. [51], [52]

The acetyl content of CA used is considered one of the factors affecting membrane performance. Many investigations addressed the effect of substituting the three OH groups in C with acetate groups. It was found out that high acetyl content resulted in a high salt rejection with low water flux membranes. As illustrated in Figure 3.3, increasing the degree of acetylation causes a high water-to-salt permeability ratio, reflecting the membranes very high selectivity. In commercial CA membranes with 98-99% NaCl rejection, a polymer containing about 40 wt.%
acetate with a degree of acetylation of 2.7 is used. On the other hand, the membranes obtain a low water fluxes. [8], [53], [54], [55], [56]

**Figure 3.3 Salt rejection and water flux values for CA membranes as a function of acetyl content at 25 °C. [8]**

In order to improve the rejection of CA membranes, the membranes can be heated in a bath of hot water for a few minutes. This process is called annealing. The annealing process eliminates the micro-pores in the salt rejection layer of the membrane producing a denser, more salt-rejecting skin. The annealing temperature and time determines the final structure of the membrane. Thus, the NaCl rejection increases while the water flux decreases. Figure 3.4 shows the effect of annealing temperatures on the flux and rejection of CA membranes.
3.3. Phase Inversion (PI)

In the field of membranes, CA membranes were the first asymmetric membranes with high performance and widely used for microfiltration and reverse osmosis. This performance is improved by introducing nano-fillers in order to enhance mechanical and thermal properties. For water treatment, the design of membranes with higher permeability and better selectivity is an ongoing process. The preparation of porous polymeric films can be carried out in several ways such as: PI by water, water vapor absorption, thermal gelatin, and solvent evaporation. All PI processes have a liquid polymer solution that precipitates into two phases: a polymer-rich phase, a solid, that forms the membrane matrix and a polymer-poor phase, a liquid that forms the pores of the membrane. The pores of the membrane are affected mainly by the choice of the solution solvent. Some solvents such as DMF, NMP, and DMA gives anisotropic porous membranes as their casting solutions have a rapid precipitation when immersed in water. On the other hand, solutions such as acetone, dioxane and ethyl formate give nonporous membrane as their casting solutions precipitate slowly. [11], [57]

Both the precipitation medium and its temperature also have an effect on the formation of the membrane. Water is always used as a medium for the casting solution precipitation. Using methanol or isopropanol, an organic-based precipitation media, cause a slower precipitation of the
casting solution than water. As a result, a less anisotropic, denser, and lower flux membranes will form. In addition, the temperature of the water bath is an important factor: a low temperature water bath produces lower flux membrane as it slows down the precipitation process. In the case of RO CA membranes, chilled water is frequently used. The casting solution can also be tailored to affect the membrane properties. For example, in order to make the membrane denser, the polymer concentration can be increased in the casting solution. All these factors affect the rate of precipitation. In other words, the rate of precipitation controls the final structure of the membrane: slow precipitations result in an isotropic dense membrane while fast precipitation produces an anisotropic porous membrane. [57]

3.4. **Theoretical approach to the formation of CA membrane**

In order to rationalize the PI, polymer–solvent–precipitation medium phase diagrams interpreted by Strathmann, Michaels, and Smolders are used. In this approach, the membrane formation process is tracked through the phase diagram while changing the composition of the casting solution. The diagram has a start point and an end point: the start point represents the casting solution and the end point represents the final membrane. Through this process, the final membrane composition is reached by losing solvent and gaining water. As shown in Figure 3.5, each corner represents a pure component: polymer, solvent, and non-solvent. Any point inside the triangle is a mixture of the three components. There are two main regions: a one phase region and a two-phase region. The one phase region contains a mixture of the three components while the two-phase region contains a solid polymer rich phase and a liquid polymer poor phase. During the process of precipitation, in which water is gained and solvent is lost, the solution moves to a composition in the two-phase region from a composition in the one phase region. The one phase region is divided into sub-regions according to the polymer concentration. These sub-regions are: a liquid polymer solution region, at low polymer concentrations, a polymer gel region, with a polymer concentration range from 30% to 40%, and a glassy solid polymer region with a polymer concentration higher than 50%. [8], [58]

The precipitation process occurs according to the following steps:

1. Water replaces solvent, demixing process, causing a change in the composition of the solution from a viscous liquid, one-phase stable solution region, to a solid gel, one-phase gel region.
2. The new solid gel region is thermodynamically unstable, so the casting solution crosses the so-called binodal boundary to the two-phase region of the phase diagram.

3. Precipitation begins and the time for water-solvent exchange depends on the composition of the casting solution.

4. The polymer phase is converted to a relatively solid gel forming the final membrane structure while the liquid solvent–non-solvent phase forms the pores. [58]

Figure 3.5 Three component phase diagram for the formation of water-precipitation PI membranes. [8]

The precipitation path and the precipitation time change at different points in the same membrane. When the cast membrane is exposed to the non-solvent (water), water enters the surface of the membrane while solvent leaves the casting solution. The membrane top surface precipitates first and precipitation slows down gradually from the top to the bottom surface of the membrane. Further loss of solvent will be slowed down because the precipitated surface layer acts as a barrier. Thus, an increase in the average pore size of the bottom surface of the membrane happens. [8], [57], [58]

Although the membrane phase diagram is useful in explaining the relation between the composition of the casting solution and the precipitation process, it does not give any information about the final distribution of membrane pore size. In order to understand the porosity of the membrane, the demixing process must be examined. Demixing is responsible for the initiation of
macro-voids which are large extended pores with the different shapes, pin-like, drop-like or finger-like, and extend over the whole membrane. In other words, the transition from an instant demixing process on the membrane surface to a delayed demixing at a certain distance from the film interface creates macro-voids. The instant demixing happens on the top layer of the membrane forming a thin skin (0.2 um) which causes a delay in the demixing process in the following layers. [8], [57], [58]

3.5. Demixing

Demixing is the rate of the non-solvent replacing the solvent which happens during the precipitation process. Three main parameters can affect the formation of macrovoids: polymer concentration, type of solvent in the polymer solution and coagulation bath. These parameters determine if the liquid-liquid demixing will be instantaneous or slow. In instantaneous demixing, the exchange of solvent and non-solvent across the membrane occurs at the moment the membrane is placed in the coagulation bath resulting in the formation of macro-voids. On the other hand, in delayed demixing this exchange is delayed for a certain period of time resulting in the formation of symmetric structure. [59], [60]

In a polymer-solvent-non-solvent system, the formation of macrovoids occurs in two steps: initiation and growth. In the initiation step, the macrovoids formation occurs at the interfacial boundary between the coagulation bath and the immersed film. When the membrane is immersed in a non-solvent bath, the film loses more solvent than allowing the non-solvent to penetrate the top layer. The polymer concentration increases and a nascent skin layer forms. The nucleation of the following layer grows rapidly preventing the non-solvent droplets from escaping. As a result, diffusion of the non-solvent into the polymer rich phase will be delayed and the solvent diffuses inside the non-solvent droplets instead forming macrovoids. In other words, macrovoids form as a result of delayed demixing while the rest of the membrane goes through an instantaneous demixing process as shown in Figure 3.6. [59], [60]
3.6. **Graphene and Graphene Oxide**

Graphene has attracted much attention in the field of wastewater treatment. Graphene was first recognized theoretically in 1940. In 1962 Bohem and coworkers used heating and chemical reduction of graphite oxide to separate thin lamellae of carbon. In 2004, a group of researchers detected a single layer of graphene in an experiment at Manchester University. This was a revolutionary discovery as graphene showed a high specific surface area \((2630 \, \text{m}^2\text{g}^{-1})\) and excellent electrical conductivity, optical transmittance \((\sim 97.7\%)\), mechanical flexibility, thermal conductivity \((\sim 5000 \, \text{Wm}^{-1}\text{K}^{-1})\), and low coefficient of thermal expansion (CTE) behavior. The honeycomb lattice of graphene contains two equivalent sub-lattices of \(\text{Sp}^2\) bonded carbon atoms as shown in Figure 3.7. These atoms are bonded together with \(\sigma\) bonds. Each carbon atom in the matrix has a \(\pi\) orbital causing a network of delocalized electrons. [61], [62], [63]
Recently, graphene has drawn an interest as an alternative carbon based nano-fillers for polymers’ nanocomposites preparation. The carbon backbone of graphene can be functionalized providing infinite possibilities. One of these possibilities is GO. After oxidation, some distortions happen while the layered structure stays the same. GO has been used as filler in polymer nanocomposites in order to enhance their properties in the field of membranes. [64], [65], [66]

Brodie was the first to discover GO in 1859. GO has a hydrophilic nature as it has a good dispersion in water. Its ionizable edge with carboxyl (–COOH) groups, as shown in Figure 3.38, is the reason why it disperses well in water. GO’s basal plane is composed of unoxidized benzene rings with an epoxide (-O-) and phenol hydroxyl (-OH) groups mainly on the basal plane forming a hydrophobic polyaromatic islands. Thus, GO is an amphiphile that has a large hydrophobic basal plane with hydrophilic edges. Figure 3.8 shows that the hydroxyl groups are located away from each other reduce repulsion between them. [60], [67], [68]

![Figure 3.8 GO structure. [58]](image)

Although they are located randomly, two neighboring hydroxyl groups occupy opposite sites in order to decrease the force of repulsion between them. Moreover, epoxy groups and hydroxyl groups are far from each other to achieve electrical stability. Although GO thickness is measured as a single atomic layer, its lateral dimension extends up to tens of micrometers. [67], [68], [69]

3.6.1. GO as a nano-filler for water desalination

GO has been under the spotlight recently to be used as a nano-filler in polymeric materials. It is considered an ideal nano-filler due to its advantages: the physical characteristics of graphene are still possessed by GO although they both have partially different structure, moreover GO has an enhanced dispersion in polymeric matrices due to the function groups on its surface. GO can be easily exfoliated in water and organic solvents such as: DMF, NMP, and ethylene glycol using ultrasonication. The polar oxygen-containing functionalities, hydroxyl, carbonyl, and carboxyl, on
the surface of GO results in a high surface energy which increases its hydrophilicity and dispersion in water as well as in organic solvents as single layer sheets. Two main factors determine the dispersion behavior of GO in different solvents: the dipole moment of the solvent and GO surface area. Both water and the mentioned organic solvents show significant electrical dipole moment values and surface tension: 1.82 D, 78.2 Nm/m (water), 3.24 D, 37.1 Nm/m (DMF), 4.09 D, 40.1 Nm/m (NMP), and 2.31 D, 47.7 Nm/m (ethylene glycol). [70], [71], [72], [73]

For water desalination, GO is considered one of the most promising new membrane materials. GO enhances water permeation of the membranes as well as improves hardness and thermal stability. [74], [75], [76]

3.6.2. Transport mechanism of GO incorporated in polymeric matrix

The lack of understanding of the transport mechanism and molecular interactions of GO membranes is a key challenge for determining the potential of these membranes in selective separation applications. However, the layered structure of GO with the carboxyl, hydroxyl, and epoxide groups on the basal plane and edges enables GO to have a large specific surface area which leads to a good compatibility between the host materials (polymer) and GO. There are three crucial factors governing the molecular transport behavior in GO based membranes: inter-layer channels, selective holes/defects and functional groups of GO based membranes. [48], [77]

Buchster et al. suggested that the synthesis method of GO has an effect on the spaces between layers and water uptake. Hydrogen bonds forming between water molecules and oxygen of epoxide and hydroxyl groups on the surface of GO sheets result in slow movement of water through GO. On the other hand, Gao et al. studied the effect of incorporating GO nano-sheets in sodium alginate membranes. They claimed that the oxygen-containing groups, edge-to-edge slits, structural defects of GO sheets, and non-oxide regions work as selective channels with high transport rates for water molecules. Although the hydrogen bonds between water and oxygen containing functional groups around GO may slow down water movement, water molecules penetrate a non-oxidized area between GO layers and diffuse rapidly because of the “low friction contact with the hydrophobic central region”. A passage is formed by water molecules that facilitate their transport through GO sheets. As a result, smaller nano-sheets provide more water channels because fewer oxygen containing groups are present. [48], [77], [78], [79]
Introducing a polymer with various functional groups utilizes the formation of hydrogen bonds between the polymer and GO which brings a different GO nano-sheets stacking structure. The assembly of several-layered GO stacks which contains molecular interlayer spacing provides straight diffusion pathways to promote molecular transport through the membrane. The transport mechanism depends on the dispersion status of GO nano-sheets in addition to the chemical nature of the matrix. In the polymeric environment, GO nano-sheets are assembled into GO stacks dispersed in random directions. The alignment of these stacks is dependent on the concentration of GO in the polymeric matrix. At low concentrations of GO, the nano-sheets are randomly oriented in the GO-polymer composite membrane. As the GO concentration increases (<1 wt. %), the parallel alignment of GO stacks is preferred. [48], [77], [78], [79]

Path-parallel GO nano-sheets stacks

GO stacks which are parallel to the path of a permeate represent straight pathways with very short transport distance as shown in Figure 3.9 and equation (1).

Effective transport length of path-parallel GO stacks: \( L \times \frac{h}{d} \)  

\( L \) represents the length of the GO nano-sheets, \( h \) the membrane thickness, and \( d \) the \( d \)-spacing.

The path perpendicular GO stacks have longer transport distance which is 2-3 orders of magnitude longer than that of the parallel stacks. For example, if assumed \( h \) and \( d \) to be 500 nm and 0.7 nm respectively. The transport distance of the path parallel GO stacks has a very short transport distance which is 700 times shorter than the path perpendicular stacks distance. [48], [77]

![Figure 3.9 Inter-layer channels of inclined and vertical GO stacks incorporated in polymer matrix. [77]](image_url)
Path-perpendicular GO nano-sheets stacks

GO stacks which are parallel to the path of a permeate aren’t the only pathways available, stacks which are perpendicular to the path of a permeate are another pathway for water transport through the hybrid membranes. Assuming that water acts as a classical liquid while passing through the GO nano-sheets, Geim and co-workers employed Poiseuille’s law to describe the flow between GO sheets as presented in the following equation (2):

\[
J = \frac{d^4 \cdot \Delta P}{12L^2 \cdot \eta \cdot h}
\]  
(2)

where \(d\) is the vertical space between adjacent GO sheets, \(L\) the average lateral length of the GO sheets, \(\eta\) the viscosity of water, and \(h\) the thickness of the membrane.

As shown in Figure 3.10, there are two regions forming the inner part of layered GO nano-sheets: the oxidized regions and the pristine graphitic regions. The oxidized regions are characterized by epoxy and hydroxyl groups which not only interact with water molecules, but separates GO nano-sheets by acting as a spacer as well. The pristine graphitic regions form a network of capillaries that provides fast water transport. Water molecules are adsorbed by the hydrophilic O-rich edges of the GO nano-sheets. Then, a monolayer of H\(_2\)O molecules flows rapidly into hydrophobic C-rich central region that has a low-friction channel due to the capillary effect. According to capillary effect, water has the tendency to flow through narrow tubes, GO nano-channels, as a result of the hydrogen bonds between water molecules. This phenomenon is known as the cohesion of water. [48], [77], [80]

![Figure 3.10 Selective water permeation mechanism through the hybrid membrane with parallel stacked GO nano-sheets. [79]](image)

As for the salt rejection, the membranes allow water to flow freely through the nano-channels formed between GO layers while rejecting unwanted solutes by size exclusion as well as charge effects. Salt rejection is governed by the existence of negatively charged groups on GO
nano-sheets. Thus, electrostatic interactions between these groups and charged molecules or ions occur. The exclusion theory states that the interface between the solution and membrane has a potential which excludes ions with the same negative charge as the membrane surface. As the electro-neutrality of the solution must be kept on both sides of the membrane, the positively charged ions are rejected as well. [77], [81], [82]

3.7. Membrane Characterization

Membranes are used in a wide variety of applications. Thus, more fundamental knowledge of membranes properties could be obtained to enhance their performance. Several membranes characteristics with possible significant effects on the membrane performance are: surface charge, hydrophilicity, and chemical structure. This section will give an insight into fundamentals of several characterization techniques including brief history, theoretical backgrounds, and importance of each technique. Scanning electron microscopy (SEM), gas adsorption, and contact angle, are the techniques used for morphological analysis of the membranes.

3.7.1. Scanning Electron Microscopy (SEM)

Electron microscopy is a popular technique that allows the observation and characterization of a wide range of materials on micrometer and nanometer scale. It has the capacity to generate topographic images of the surface of heterogeneous organic and inorganic materials. The principle of SEM is that a finely beam of electrons is directed on the area to be examined, electrons react with the sample producing a signal that includes: secondary electrons (SEs), characteristic x-ray, backscattered electrons, and other photons of various energies. These electrons are then spotted with detectors to form an image. A typical SEM consists of: electron source, column with several electromagnetic lenses, electron detector, sample chamber, and the computer display.

Principles of SEM

The process of SEM image formation is associated with the detection of signals received as the electron signals interact with the scanned sample. Generally, elastic and inelastic interactions are two types of atomic interactions that may occur. Elastic interactions occur when the primer electron is deflected as a result of striking the atomic nucleus or the outer shell electrons of the specimen. The amount of energy lost in this process is negligible. If the scattered electrons deflected with angle more than 90°, the electrons become back scattered electrons (BSE). On the other hand, inelastic interaction is due to the bombardment of the sample by a primary beam of
electrons and a significant transfer of energy to a sample electron, known as secondary electron (SE), takes place. The secondary electron either leaves the sample or undergoes scattering. The atom will become an ion if this electron was ejected from an inner orbital and an outer-shell electron filled the resulting electron hole. In that case, an X-ray photon is released or an electron is ejected (Auger electron) to cover the de-excitation energy. [83], [84]

The interaction volume between the specimen and the electron beam determines the type of signals obtained. The focused beam of electrons hits the surface of the specimen and penetrates into the surface causing a collision between the energetic electrons and the atoms of the sample. The shape of the interaction region depends on the atomic number of the sample: low atomic number specimen has the shape of a teardrop while the high atomic number specimen has a hemisphere shape. In addition, the energy of the incident beam determines the depth of the interaction volume, increasing the beam energy increases both the volume and the depth of the interaction region. Also, using a low atomic number sample increases the depth of the interaction area as there will be lower number of particles on the path of the electron beam. Figure 3.11 represents the various mean-free paths for different elastic and inelastic particles, meaning that they have different signal emission zones. [83], [84], [85]

![Figure 3.11 Visualizing the interaction volumes for various interactions between electron beam and sample.](image)

There are two modes for SEM image processing: SE and BSE. SE mode is the most common as the sample can only be detected to few nanometers of the sample surface using low
energy electrons (below 50 eV). Thus, it is used for obtaining topographic information of the sample such as surface texture and roughness. By lowering the energy of the beam, the SE emission coefficient (SEEC), which is the ratio of the number of SEs emitted from the sample surface to the number of primary electrons, increases. In BSE scanning mode, the sample is scanned by the detection of high energy electrons (higher than 50eV) that have been scattered once or multiple of times and escaped from the sample surface with high energy. In general, when elastic collision takes place between an electron and the nucleus of the specimen, the electron bounces back with wide change in directions. The backscattered electrons represent 10-50% of the electrons in the beam. [84], [85], [86]

Figure 3.12 Schematic diagram of SEM. [87]

3.7.2. BET Method

Adsorption is a spontaneous surface phenomenon that occurs when gas/solutes/liquid molecules are attracted and concentrated on solid surfaces because of the strong affinity the solid surfaces have for these molecules. The driving force of adsorption is the solid natural tendency to decrease its surface energy. Gas adsorption by solids is the most common. Solids which have
porous structures, with macropores (≥ 50 nm), mesopores (2-50 nm), or micropores (≤ 2 nm), with exposed surfaces are considered good adsorbents because they obtain large specific surface area and thus large volumes of gases will be trapped on the surface. Various factors have an effect on the adsorption of gases by solid surfaces such as: temperature, surface area of the adsorbent and gas vapor pressure. The process of gas adsorption-desorption on the solid surfaces happens simultaneously and as a result a dynamic equilibrium is established. At constant temperature, increasing pressure increases gas adsorption. [88], [89]

**Adsorption isotherms**

An adsorption isotherm is the relationship between the adsorbed gas amount and equilibrium pressure (or concentration) at a constant temperature. By plotting the quantity of adsorbate against pressure of the gas, six types of adsorption isotherm are obtained, classified by their shape and discussed based on the conditions leading to their occurrence (Figure 3.13). [88], [89]

In the reversible type I isotherm as $p/p_0 \rightarrow 1$, the amount adsorbed reaches a limiting value indicating that type I isotherm is concave to the $p/p_0$ axis. Type I is observed in chemisorption as the adsorbate molecules are chemically bonded to the surface forming a monolayer that covers the surface. In the case of physical adsorption, type I is obtained for microporous materials, where the filling of micropores is rapid at low relative pressure $p/p_0$ because of the high adsorption potential and narrow pore width. The accessible micropore volume limits the adsorbate uptake rather than the internal surface area. [88], [89], [90]

Type II is obtained for non-porous or macroporous adsorbent, where the monolayer adsorption is followed by adsorption of multilayer at higher $p/p_0$. Point B, as shown in Figure 3.13, is the knee of the isotherm. This point indicates completion of monolayer coverage and the beginning of multilayer adsorption. [88], [89], [90]

Type III is a reversible isotherm that does not obtain a point B as it is convex to the $p/p_0$ axis over its entire range. This indicates relatively weak interactions between the adsorbate molecules and adsorbent surface. Thus, the coverage of the monolayer cannot be identified. The weak potential of the adsorbent surface to attract other molecules encourages the adsorbate molecules to attract one another forming multilayers. Generally, interactions between adsorbate
molecules play an important role in type of isotherm. An example of this type of isotherm is the adsorption of water vapor on graphite basal plane. [88], [89], [90], [91]

Type IV isotherm is obtained for typical mesoporous materials. The hysteresis loop is the most characteristic feature of this type and it is based on the shape of the pores. Hysteresis indicates the occurrence of capillary condensation, the process at which the adsorption of multilayers of vapor phase in porous solids reaches a point that the pores are filled with condensed liquid from the vapor, in mesopores. As in type II, type IV initial part represents the monolayer-multilayer adsorption. In addition, the plateau at the end of type IV can be associated with the limited adsorption of adsorbate molecules over a range of high p/p₀.

Type V isotherm is obtained for mesoporous materials, it shows the features of hysteresis and pore condensation. The initial part of type IV isotherm is similar to type III indicating relatively weak attractive interactions between adsorbent and adsorbate molecules. At low p/p₀, the amount of adsorbed gas is very small however as soon as a molecule is adsorbed, further adsorption is promoted through the attraction force between adsorbate molecules.

Type VI isotherm is very uncommon. It represents the shape of a stepwise multilayer adsorption isotherm indicating a highly uniform structure created by layer-by-layer adsorption on a uniform, non-porous surface (spherically symmetrical adsorbents). Temperatures, homogeneity of adsorbent surface and adsorptive are factors determining steps sharpness. Examples of such isotherm are the adsorption of argon and krypton on the surface of graphitized carbon when placed in liquid nitrogen temperature. [88], [89], [90]

Figure 3.13 Different types of adsorption isotherms. [89]
There are four major types of hysteresis loops: in type 1, the adsorption and desorption branches are almost parallel to each other creating a narrow loop as shown in Figure 3.14. This type of loop is obtained by materials having uniform pore distribution. On the other hand, type 2 has a much wider loop created by a curved adsorption branch and a steep desorption branch. Most inorganic oxide gels obtain a complex pore structure with various pore sizes and shapes creating interconnected networks which results in type 2 loops. In types 3 and 4, it is difficult to establish the boundary curve for desorption. This is because at high p/p₀, these two types do not terminate in a plateau. Particles obtaining slit shaped pores usually show type 3 or 4 loops.

![Figure 3.14 Different types of hysteresis loops. [89]](image)

**BET theory and multilayer adsorption**

One way to determine the surface area of porous materials is the measurement of amount of adsorbate. In 1922, Paneth used radioactive indicators and dye adsorption by an inorganic powder to determine the level of maximum adsorption, he noticed that this level corresponded to the formation of a uni-molecular layer. After that, dye adsorption was widely used for the study of fine powders. The possibility of using gas adsorption for determining the surface area was investigated using “Langmuir kinetic theory of monomolecular adsorption” comprehensive review by Langmuir. In 1938, Brunauer, Emmett and Teller proposed “(BET) theory of multilayer adsorption” that is considered an extension of the Langmuir model. By knowing the number of molecules of adsorbate in a monolayer, the specific surface area of a substrate can be obtained.
The Langmuir model of adsorption is based on the assumption that only a monolayer of gas is formed at maximum adsorption on the surface of a solid substrate. On the other hand, the BET theory is based on a monolayer-multilayer adsorption model with several assumptions:

- Physisorption causes the formation of multilayer adsorption
- There are equivalent adsorption sites in homogenous flat solid surfaces.
- In a multilayered adsorbate, only the uppermost molecules are in dynamic equilibrium with the vapor phase
- All layers, except the first, have adsorption heats that are equal to the condensation heat.
- A molecule cannot evaporate when it is covered by another molecule.
- The number of layers is infinite at saturation ($P/P^0 = 1$).
- When condensation rate is equal to evaporation rate, equilibrium is achieved.
- Adsorption at one site doesn’t have any effect on adsorption at the surrounding sites

Relying on these assumptions, the relation can be expressed by:

$$\frac{P}{v(P^0 - P)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} \left( \frac{P}{P^0} \right)$$  \hspace{1cm} (3)

where $v$ is the total volume adsorbed, $v_m$ is the volume adsorbed when a monolayer of gas molecules covers the surface of the solid, $P$ and $P^0$ are equilibrium and saturation pressures of the gas at temperature $T$, and $c$ is a constant that indicates the magnitude of interaction energy between the adsorbent and adsorbate and is given by equation (4):

$$c = \exp \left( \frac{E_1 - E_L}{RT} \right)$$  \hspace{1cm} (4)

where $E_1$ is the first layer adsorption energy and $E_L$ is the energy of the adsorption energy of the other layers which equals to the liquefaction energy of the gas. [88], [92], [93]

For an adsorbate-adsorbent system, both $v_m$ and $c$ are constant. A linear relationship is obtained when a graphical plot of $p/v$ ($p^0 - p$) against $p/p^0$ is carried out as shown in Figure 3.15. The line has a slope of $(c-1)/v_m c$ and an intercept of $1/v_m c$ that can be used to calculate $v_m$ and $c$. 
In addition, this graph is obtained only in the range of relative pressure \( \frac{p}{p_0} \) from 0.05 to 0.3. Capillary condensation occurs at higher \( \frac{p}{p_0} \) values and in that case the BET equation is no longer valid. [91], [93]

![Figure 3.15 BET equation verification. [90]](image)

3.7.3. Contact angle

Hydrophilicity of the membrane material has a significant influence on membrane properties and performances such as permeate flux, solute rejection, and fouling characteristics. The membrane surface chemistry governs the surface interaction with water molecules. This could be investigated by measuring the contact angle between the membrane surface and a pure water drop. Low contact angle values are an indication of the hydrophilic nature of the material, meaning that the membrane surface has high affinity towards water molecules. On the other hand, higher contact angles imply the hydrophobic nature of the material, meaning that the surface has little or no tendency to interact with water molecules. More specifically, if the contact angle has a value that is less than 90°, the water drop will extend over a large area. With a contact angle larger than 90°, the water drop will be more compact to minimize its contact with the surface. [86], [94]

*Young’s Equation*

Contact angle is the angle formed due to liquid-vapor and liquid-solid interface intersection as clarified in Figure 3.16. It can be calculated geometrically by drawing a tangent line from the point at which solid, liquid, and vapor are coexisting along with the interface of the liquid and vapor phase of the droplet. The magnitude of the contact angle relies on the balanced forces at the interface line between solid, liquid, and vapor. In an ideal situation, the liquid surface tension determines the shape of the liquid droplet. In a pure liquid bulk, the molecules pull each other in
the sense that each molecule is dragged equally by neighboring molecule in every direction. Yet, molecules at the surface don’t have a balanced net force because they are not surrounded by neighboring molecules in all directions. Thus, an internal pressure is created as the surface molecules are pulled inward by other molecules. In order to maintain the surface energy low, the liquid decreases its surface area. The intermolecular forces responsible for decreasing the liquid surface area is known as surface tension. In practice, gravity, for example, is an external force that causes deformation of the droplet. For contact angle to be measured, a combination of external forces and surface tension is considered.

![Figure 3.16 Schematic representation of the contact angle and surface tension. [95]](image)

In 1805, Thomas Young defined the contact angle of a liquid drop on an ideal surface by the drop mechanical equilibrium when exposed to three interfacial tensions as illustrated in Young’s equation:

\[
\cos \theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}
\]

\(\Theta\) is Young’s contact angle, \(\gamma_{LG}\), \(\gamma_{SG}\), and \(\gamma_{SL}\) refer to the liquid-gas, solid-gas, and solid-liquid interfacial tensions, respectively.

Young derived his equation by assuming that the surface is flat, rigid, inert, nonreactive, homogeneous, insoluble, nonporous, and smooth. In other words, the Young’s equation is based on the assumption that the surface is an ideal one which is not applicable in real surfaces. Thus, the value of the contact angle may be different from one point to another on the same surface as different interfacial tensions are applied. [86], [94], [95]
IV. Materials and Methods

4.1. Materials used

Materials used in the preparation of the GO/CA membranes included CA (avg. molecular weight 50,000 Da, 39.7 wt.% acetyl content) procured from Sigma-Aldrich USA; Acetone (Purity ~99.8%, density 0.791 g/mL at 25 °C) obtained from Sigma-Aldrich USA; \textit{N}, \textit{N}-Dimethylformamide (Purity ~99%, density 0.949 g/mL at 20 °C) obtained from Carlo Erba; and GOX (purity ~99%, single layer ratio ~ 80%, diameter 1-5 µm, thickness ~0.8 to 1.2 nm, prepared by Modified Hummer’s Method) obtained from ACS Material USA. NaCl (molecular weight 58.44 g/mol, purity ~99.5%, density 2.165 g/mL at 25 °C) and MgSO$_4$ (purity ~98%, molecular weight 120.37 g/mol) were purchased from Sigma-Aldrich and used for salt retention measurements.

4.2. Stock solution preparation

4.2.1. CA stock solution
- Various amounts of CA (17 and 19 wt.%) were dissolved in acetone. 16% of DMF, used as a non-solvent, was then added to the solution;
- The solution was stirred for 24 hours to ensure complete dissolution of the polymer;
- After all the ingredients were mixed completely, the solution was sonicated for 15 minutes and allowed to stand for 3 hours to remove air bubbles.

4.2.2. GO/CA stock solution
- CA powder was dissolved in acetone to prepare a 19 wt.% solution;
- The solution was stirred for 24 hours to ensure complete dissolution of the polymer;
- The desired amount of GO (0.025, 0.05, 0.1 wt.%) was soaked in 17 mL DMF and left overnight. Then, it was sonicated for 30 minutes;
- GO dispersed in DMF was added to the polymer solution and the mixture was stirred vigorously for another 24 hours to obtain a uniform GO dispersion in the casting solution;
- The solution was sonicated for 15 minutes and allowed to stand for 3 hours to remove air bubbles.

These steps are illustrated in Figure 4.1.
4.3. **Methods and instruments**

4.3.1. Membrane casting

An Elcometer 4040 Automatic Film Applicator was used for the casting of the CA and CA/GO membranes by introducing the casting solution into a feed container attached to a casting knife. A motor moved the knife at a specified speed to spread the membrane solution on a glass plate. The glass plate was then dipped into a coagulation bath containing distilled water for a few minutes at room temperature until complete PI was ensured. After that, the membrane was peeled and carefully washed with distilled water in order to remove any residual solvent. The membrane was kept in distilled water to be used for further analysis.

4.3.2. Sample surface area and porosity determination

A Micrometrics ASAP 2020 instrument was used for surface area and porosity analysis of the membranes. The samples were prepared as follows:

- Part of the membrane (5x5 cm²) was dried in a furnace at 80ºC for one hour;
- This membrane sample was then cut into very small pieces and weighed after it was left to cool down;
- The sample was put in a glass tube and placed in ASAP 2020 sample holder;
- The tube was degassed at 30ºC below 50 μmHg for 30 min to be ready for nitrogen adsorption.

4.3.3. Scanning Electron Microscope (SEM)
Leo Supra 55 (ZEISS) field emission scanning electron microscope was used for cross-sectional and surface imaging of the samples. The samples were prepared as follows:

- The membrane samples were fractured in liquid nitrogen;
- A double surface tape was used to mount the membrane samples on an aluminum disk;
- The sample holder was placed and evacuated in a sputter-coater;
- All the samples were gold sputtered for 3 minutes, at 20 mL amp using one gold target.

4.3.4. Contact angle measurement
Contact angle measurements were performed to investigate the hydrophilicity of the prepared membranes using the sessile drop method by drop shape analyzer-DSA25. The measurements were carried out as follows:

- Part of the membrane (0.5x0.5 cm²) was dried in a furnace at 80ºC for an hour and left to cool down to room temperature in air;
- The sample was placed on the sample table and the height of sample table was adjusted so that the lower part of the image contained the sample surface and the needle was just above the sample;
- A drop hanging from the needle, with a volume of 5μl, was put in contact with the sample surface and the contact angle measurement was obtained.

4.3.5. Liquid test cell
In order to evaluate CA and GO/CA membranes’ permeation and salt rejection performance, a dead-end Sterlitech HP4750 stirred cell filtration system with an effective area of 14.6 cm² connected to a nitrogen gas cylinder was used. The process of filtration was conducted using 2000 ppm NaCl solution and 5000 ppm MgSO₄ solution at room temperature [29] as follows:
Membranes were placed in the test cell. Both 2000 ppm NaCl [44], [45] and 5000 ppm MgSO₄ [20] solutions were used as feed solutions based on the literature to compare the membranes’ effectiveness on the removal of these salts based on size exclusion. As CA membranes have higher rejection rates for divalent ions than monovalent ions, these concentrations were chosen to test the suitability of GO/CA membranes to be used for 2000 ppm NaCl rejection as a model for brackish water containing a high concentration of (Cl⁻) ions. (Cl⁻) ion is a major component in brackish water that is present with an average concentration of 2200 ppm [96]. In addition, 5000 ppm MgSO₄ is also a model for seawater containing high concentration of (SO₄²⁻) ions that are present in seawater with an average concentration of 2701 ppm [97], [98].

A nitrogen cylinder was used to apply an external pressure up to 24 bars.

The concentrations of NaCl and MgSO₄ in both the feed and permeate solutions were determined using Jenway 4510 conductivity meter. This process was repeated at least 3 times using 3 different membrane sheets of each GO concentration to calculate an average value;

Permeation rates were calculated using the following equation (6):
$$J = \frac{V}{(A \cdot t)} \quad (6)$$
where \(J\) is the permeation rate in L/m²h, \(V\) is the permeate volume, \(A\) is the membrane area on which pressure is applied (m²), and \(t\) is the time (h)

The solutes rejection percentages were calculated using the following equation (7):
$$\text{Salt Rejection (\%)} = (1 - \frac{C_p}{C_f}) \times 100 \quad (7)$$
where \(C_p\) and \(C_f\) are concentration of permeate and feed solution respectively.

### 4.4. Samples preparation conditions

In order to synthesize a novel CA/GO nano-composite membrane with enhanced performance, different preparation parameters were varied in order to develop a blank membrane with high salt rejection and good permeation rate to which the GO was added. Adding GO to a blank CA membrane is expected to enhance the permeation performance while maintaining the high salt rejection rates of the blank membrane. In this regard, the effect of solvent non-solvent ratio and CA content were investigated. The following membranes were prepared:

- 17 wt.% CA in DMF with ICT 400 μm
- 17 wt.% CA in Acetone, 16 wt.% DMF as a non-solvent with ICT 450 μm
- 19 wt.% CA in Acetone, 16 wt.% DMF as a non-solvent with ICT 450 μm

Based on the findings of the prepared blank membranes, GO sheets were added to the blank membrane that showed the best performance regarding permeation and salt rejection. Thus, GO sheets were added to 19 wt. % CA dissolved in acetone with 16 wt% DMF, used as a non-solvent, the following GO contents were investigated, 0.025 wt.%, 0.05 wt.%, and 0.1 wt.% GO.

SEM was used for morphological characterization of the samples. In addition, contact angle measurements were carried out to measure membrane hydrophilicity. Membrane porosity and surface area were determined by nitrogen adsorption in addition to permeation and salt retention measurements.
V. Results and Discussion

This chapter describes the results of morphological analysis, surface analysis and membrane performance of GO/CA membranes. The chapter is divided into five sections. Section one addresses the approaches adopted to reach the optimal conditions for tailoring CA membranes. Section two presents the analysis of the structure and morphology of the prepared membranes using SEM in addition to the dispersion state of GO nano-sheets in the CA matrix. Section three presents the results of the pore size distribution and differential surface area and pore volume of the membranes. The contact angle measurements, permeation rates and salt rejection rates are presented in section four to investigate the surface hydrophilicity characteristics and performance. Section five discusses the interpretation of the obtained results in addition to the overall effect of GO on the CA membranes. A comparison between the blank membrane and GO incorporated membranes is included in all sections.

5.1. Optimal preparation conditions of GO/CA membranes

As a start, 17 wt. % CA membranes were fabricated using DMF as a solvent. PI was carried out at room temperature. The membranes’ morphology was investigated using SEM. Figure 5.1(a) shows the formation of excessively large macrovoids which extended to cover most of the membrane cross section while Figure 5.1 (b) shows the middle section of the obtained membranes. In addition, membranes demonstrated very high permeation rates (average permeation rate = 7 L/m²h.bar) with no rejection of a 2000 ppm NaCl at 10 bars operating pressure. This can be explained based on the type of demixing occurring during PI when using DMF which has been reported to be instant thus resulting in drop-like shaped voids. DMF has a high solubility parameter for polymers (which is a reflection of the degree of interaction of DMF with polymers). Casting solutions based on DMF precipitate in a very short time. As a consequence, further modifications were needed to obtain a membrane with high rejection values and good permeation rates. Different preparation conditions were tested in order to identify their effect on the membrane performance. Annealing effect on membrane performance using 17 wt. % CA membranes dissolved in DMF was studied. 17 wt. % CA membranes were immersed in hot water bath (70°C, 80°C) after PI for different periods of time (15, 30, 45, and 60 sec). The performance of the obtained membranes wasn’t affected much when tested for permeation and salt rejection of 2000 ppm NaCl and 5000 ppm MgSO₄. [7]
In order to decrease the average pore diameter of the blank membrane, acetone and DMF mixtures were both used for membrane preparation with a ratio of (4:1) based on numerous experimental trials conducted in this investigation. Unlike DMF, acetone has a much lower solubility parameter resulting in a slower demixing. 17 wt. % CA was dissolved in a mixture of acetone and DMF and then cast at room temperature. The obtained membrane showed a significant decrease in the macrovoids size, number and change in shape as shown in Figure 5.2. In addition, the prepared membrane exhibited enhanced salt rejection to reach a value of 21% for 2000 ppm NaCl and decreased permeation rate to 0.06 L/m²h.bar. Although the average pore diameter was successfully decreased, the membrane still exhibited considerably low salt rejection values.
Another strategy to improve the membrane salt rejection rates is increasing the polymer content to further decrease the pore diameter as suggested in the literature [16], [99]. The polymer concentration was increased from 17 to 19 wt.%. This value was chosen based on similar values reported in the literature [18], [20], [26]. The polymer was dissolved in acetone and DMF mixture with the ratio of (4:1) and cast at room temperature. The average salt rejection for 2000 ppm NaCl solution was improved significantly to reach a value of 55%. This was further supported by SEM cross sectional images in Figure 5.3. The increase in polymer concentration resulted in a significant decrease in the number of macrovoids as well as their sizes. However, upon increasing the polymer content to 19 wt. %, the average permeation rate declined to 0.01 L/m²h.bar which is very low for practical applications. Consequently, another strategy had to be sought to compensate for the decline in the permeation rate while maintaining the high salt rejection rate. Table 5.1 displays the permeation and salt rejection rates of CA membranes relative to polymer content and non-solvent addition.
Table 5.1 Effect of polymer content and non-solvent addition on permeation and salt rejection rates

<table>
<thead>
<tr>
<th>Polymer content</th>
<th>Solvent</th>
<th>Non-solvent</th>
<th>Ratio Solvent: non-solvent</th>
<th>Permeation rate (L/m² h.bar) 2000ppm NaCl</th>
<th>Salt Retention % 2000ppm NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>17 wt.%</td>
<td>DMF only</td>
<td>-----</td>
<td>-----</td>
<td>7</td>
<td>No rejection</td>
</tr>
<tr>
<td>17 wt.%</td>
<td>Acetone</td>
<td>DMF</td>
<td>4 acetone : 1 DMF</td>
<td>0.06</td>
<td>21</td>
</tr>
<tr>
<td>19 wt.%</td>
<td>Acetone</td>
<td>DMF</td>
<td>4 acetone : 1 DMF</td>
<td>0.01</td>
<td>55</td>
</tr>
</tbody>
</table>

Hydrophilic additives have a tendency to facilitate the passage of water molecules across the membrane by increasing the overall hydrophilic nature of the membrane [48]. GO is one of the hydrophilic additives that have been used recently in desalination applications due to the favorable water permeation properties it imparts to membranes it is incorporated within. Different concentrations of GO (0.025, 0.05, and 0.1 wt. %) were dispersed in DMF and added to 19 wt. % CA solutions. The obtained membranes were characterized for surface area and porosity, in addition to permeation and salt rejection performance. Further analysis using SEM was performed to investigate the effect of GO addition on membrane morphology and macrovoids shape and number.

5.2. **Morphological analysis of GO/CA membranes**

In order to study the effect of GO nano-sheets on the morphology of CA membranes, the cross-sectional SEM images of CA/GO membranes with different GO contents are presented in Figure 5.4. The blank CA membrane had a typical asymmetric structure that consists of a top dense layer with a thickness of 1.5±0.2μm followed by a layer incorporating macrovoids. After the addition of GO nano-sheets, membranes showed a structure of a skin layer and a layer incorporating much thicker finger-like pores. These finger-like pores extended to the center or even the bottom region of the membranes, especially in the 0.05 wt. % and 0.1 wt. % GO membranes. Some of these pores were even interconnected with each other to form large networks.
Figure 5.4 SEM images of pores and cross-sectional morphologies for CA/GO membranes:
(a) 0wt.%GO, (b) 0.025wt.% GO, (c) 0.05wt.%GO, (d) 0.1 wt.% GO.

A possible explanation for the emergence of finger-like macrovoids, which was observed in the cross-sectional SEM images of CA/GO membranes, is the hydrophilic nature of GO nanosheets. The function groups, carboxyl, hydroxyl, and epoxide, on the basal plane of GO nanosheets are responsible for the high hydrophilic nature. The additions of hydrophilic GO enhanced the thermodynamic instability of the medium causing fast exchange of solvent and non-solvent during the PI. To elaborate more, macrovoids formation occurs in three steps: instantaneous demixing which results in the formation of a skin layer with porous sub-layer, initiation and growth of a finger-like supporting structure, and finally a delayed demixing that is responsible for the formation of a sponge-like structure on the walls of the finger-like structures. When the cast membrane is immersed in the non-solvent bath, the hydrophilic GO in the polymer enhances the fast formation of a nascent skin followed by an unstable nascent porous structure with a polymer-
rich phase and polymer-poor phase. Then, the non-solvent diffuses into the polymer-poor phase
initiating the formation of macrovoids due to osmotic pressure. As the nascent porous structure is
still loose during macrovoids formation, more non-solvent diffuses into the polymer-poor phase to
replace the solvent inside the macrovoids. As a result, a delayed demixing inside macrovoids
occurs. The non-solvent displaces the casting solution surrounding the macrovoids and growth of
macrovoids to a finger-like structure occurs. Additionally, the main transport channels for non-
solvent to reach the casting solution surrounding the macrovoids and displace the casting solution
were the loose bases of macrovoids. Generally, the formation of finger-like structure of porous
membranes was due to hydro-dynamically unstable delayed demixing inside the macrovoids that
was enhanced when GO was incorporated in the casting solutions of the membranes. Increasing
GO content could enhance the thermodynamic instability of the medium during PI, increase the
demixing rate, and cause the formation of larger finger-like pores. This phenomenon is known as
“viscous fingering” and it is used to explain the formation of finger like macrovoids. [10]

SEM images in Figure 5.4 exhibit no GO aggregates in any of the samples, indicating the
good dispersion of GO in the membranes. This was most probably due to the interactions between
GO nano-sheets and CA in the casting solution during membrane preparation. These interactions
consist of hydrogen bonds between the numerous oxygen containing functional groups in the GO
plane and the hydroxyl groups exposed in CA chains as shown in Figure 5.5.
Zhang et al. [100] and his coworkers reported a similar behavior of a strong interaction between GO nano-sheets and CA in solution. They proposed that with the incorporation of only 0.1 wt. % GO, the gelation behavior of the solution was dramatically improved to form cellulose aerogel compared with the blank cellulose aerogels. They attributed this to the GO nano-sheets having strong interactions with CA which enhanced the dispersion and gelation rate. Similarly, in the current study, GO showed a good dispersion in CA solution with no agglomerations even with the highest concentration added (0.1 wt. % GO). This was also attributed to the intermolecular hydrogen bonds between CA and GO. Figure 5.6 shows the homogenous dispersion of different concentrations of GO in the CA solution. After 3 days of standing, all the samples were still homogeneous.
Figure 5.6 The dispersion of GO in CA solution:
(a) 0 wt. %GO, (b) 0.025 wt. %GO, (c) 0.05 wt. %GO, and (d) 0.1 wt. %GO
(e), (f), (g) were obtained after standing (b), (c), and (d) for 3 days at room temperature,
(h) GO agglomerations in CA casting solution.

5.3. Membrane surface properties
In this series of experiments, the pore size distribution was investigated for all the membranes including differential pore volumes vs. pore width, differential pore areas vs. pore width, adsorption isotherm and BET surface area.
5.3.1. Differential pore sizes

The pore structure resulting from the membrane formation process, which is affected by GO content in the prepared solutions, was examined. The pore size distribution of the GO/CA membranes was analyzed and compared with the blank membrane. All samples were prepared with the same final thickness 125 ±10 μm. Figure 5.7 shows the change of differential pore volume for membranes with different GO contents.

Figure 5.8 shows that all membranes had micropores with width less than 2 nm. Introducing GO to the membranes, these latter pores disappeared. As shown in Figure 5.7, the pores with width larger than 50 nm occupied the largest volumes. The membrane with 0.05 wt. % GO had the largest volume of pores which means that increasing GO content enhanced pore formation. However, with increasing GO content up to 0.1 wt. %, the curve shifted back to smaller pore sizes. The 0.05 wt. % GO incorporated membrane had the largest volume occupied by the 147 nm macrovoids.

![Differential Pore Volume vs. Pore Width](image_url)

**Figure 5.7 Plot of differential pore volume vs. pore width.**
Figure 5.8 Plot of differential pore volume vs. pore width for micropores and mesopores.

Figure 5.9 shows that all the membranes containing GO featured micropores at 1.7 nm with the highest value of total surface area of about 2.3 m²/g and 1.9 m²/g for membranes with 0.05 and 0.1 wt. % GO content, respectively. The blank membrane showed the lowest value of about 0.6 m²/g. However, the blank membrane had the highest total surface area of mesopores at 2.5 nm with maximum value 1.7 m²/g compared with GO membranes with a lower surface area of mesopores. The membranes with GO showed the lowest total surface area of mesopores from 3 to 7 nm. From 7 to 50 nm, the 0.005 GO wt. % membrane showed the highest mesopores surface area (Figure 5.10). Pores with sizes above 50 nm occupy significant volumes with maximum value of 0.013 cm³/g and surface area lower than 0.17 m²/g.
Figure 5.9 Plot of differential surface area vs. pore width.

Figure 5.10 Plot of differential surface area vs. pore width for micropores and mesopores.
The highest surface area value was obtained by micropores at 1.7 nm as indicated in Figure 5.10. Although they had the smallest volumes, they showed the highest surface area. These results indicate that they existed in large quantities unlike mesopores and macropores. As shown in Figure 5.9, both mesopores and macropores showed very small surface areas, meaning that their numbers per gram of the sample are small. The 0.05 wt. % GO incorporated membrane showed the highest surface area for micropores and macropores. On the other hand, the blank membrane showed the lowest surface area for micropores and macropores. As a result, GO additions not only increased the number of micropores, but the size of macropores as well resulting in high surface area values.

5.3.2. Adsorption isotherm

Figures 5.11, 5.12, 5.13, and 5.14 show the adsorption isotherms of the GO prepared membranes in comparison with the blank membrane. Based on the obtained graphs, the type of the samples was identified. It was found that all samples could be classified as type IV. The hysteresis loop of this type is based on the shape of the pores which is obtained for typical mesoporous materials. The obtained hysteresis loops are type H3 which indicates that the membranes obtained a complex structure of pores.

![Blank Isotherm](image)

**Figure 5.11 Adsorption isotherm of the blank membrane.**
Figure 5.12 Adsorption isotherm of the 0.025 wt. % GO/CA membrane.

Figure 5.13 Adsorption isotherm of the 0.05 wt. % GO/CA membrane.
5.4. Membrane performance

5.4.1. Contact angle measurements

Membranes with hydrophilic surface can easily draw water molecules and thus improve the membrane permeation property. Generally, when the contact angle decreases, the membrane hydrophilicity increases.

The images presented below (Figure 5.15) show a gradual decrease in the contact angle measurements with increasing GO content. The highest angle belongs to the blank membrane with a value of 75°. Upon adding 0.025 wt. % GO to the CA membrane, the angle decreased from 75° to 69°. When GO content increased from 0.025 to 0.05 wt. %, further decrease of the contact angle from 69° to 67° was measured. A sharp decrease in the contact angle from 67° to 61° was measured when GO content increased from 0.05 to 0.1 wt. %. The presence of GO in the membranes resulted in a consistent decrease in the contact angle reflecting the enhanced hydrophilic nature of the membranes.
Figure 5.15 Contact angles of CA membranes with various GO contents: (a) 0 wt. %GO, (b) 0.025 wt. %GO, (c) 0.05 wt. %GO, and (d) 0.1 wt. %GO.
5.4.2. Permeation rates

According to Figures 5.17 and 5.18, increasing GO content increased permeation rates of the GO/CA membranes. The addition of 0.025 wt. % and 0.05 wt. % GO improved permeation of 2000 ppm NaCl solution by 64% and 95% respectively compared with the blank CA membrane. With increasing GO content to 0.1 wt. %, permeation reached its peak value of 0.0219 L/m²hbar, corresponding to an improvement of 106% compared to the blank membrane. Using 5000 ppm MgSO₄ solution, the permeation rates also showed an increase with increasing GO content. Compared with the blank membrane, permeation rates of 0.025 and 0.05 wt. % GO/CA membranes increased by 21% and 25% respectively. Upon increasing GO content to 0.1 wt. %, the permeation rate increased by 87% (0.015 L/m²hbar). The results suggest that blending hydrophilic GO nanosheets could obviously improve the permeation rate of CA membrane significantly which is a trend reported by other researchers [29], [48], [79], [97], [98].

Figure 5.16 Contact angles of CA membranes with various GO contents.
Figure 5.17 Plot showing the effect of GO on the permeation rates of CA membrane using 2000 ppm NaCl solution.

Figure 5.18 Plot showing the effect of GO on the permeation rates of CA membranes using 5000 ppm MgSO₄ solution.
To analyze the membranes’ permeation rates further, the variations of the permeation rates with contact angle values are investigated and presented in Figures 5.19 and 5.20. It could be noticed that the blank membrane showed the highest contact angle value and the lowest permeation rate. As the GO content increased, the membranes’ contact angles decreased, and the permeation rates increased. With the addition of 0.1 wt. % GO, contact angle of the modified membrane decreased from 75 to 61 degrees and the permeation rates increased from 0.01 to 0.021 L/m²h.bar for the 2000 ppm NaCl solution and from 0.008 to 0.015 L/m²h.bar for the 5000 ppm MgSO₄ solution.

Figure 5.19 Plot showing the variations of the permeation rates of 2000 ppm NaCl solution with contact angle.
5.4.3. Salt rejection rates

Salt rejection of membranes with GO was enhanced as shown in Figures 5.21 and 5.22. The membrane with 0.025 wt. % GO showed a 5% and 20% increase in salt rejection rates for 2000 ppm NaCl and 5000 ppm MgSO₄ respectively relative to the blank membrane. Additionally, increasing GO content to 0.05 wt. % significantly improved rejection of 2000 ppm NaCl and 5000 ppm MgSO₄ by 34% and 33% respectively relative to the blank membrane. On the other hand, the addition of more GO, 0.1 wt. %, led to a noticeable decrease in the rejection rates to 23% and 11% for 2000 ppm NaCl and 5000 ppm MgSO₄ respectively. In general, the obtained results indicated that doping GO into the polymer matrix enhanced hydrophilicity as well as salt rejection properties of CA membrane.
Figure 5.21 Plot showing the effect of GO on the salt retention of CA membrane using 2000 ppm NaCl solution.

Figure 5.22 Plot showing the effect of GO on the salt retention of CA membrane using 5000 ppm MgSO₄ solution.
Figures 5.23 and 5.24 show a comparison between pure CA membrane and CA membranes incorporating different amounts of GO. This comparison shows that while a drastic change occurred in the permeation rates with GO content, salt rejection rates showed improvements to a lesser extent. Compared with pure CA membrane, the 0.05 wt.% GO membrane showed the highest salt rejection performance of 33% and 34% and permeation rates of 0.02 and 0.01 L/m²h.bar for 2000 ppm NaCl and 5000 ppm MgSO₄ at 24 bars, respectively. Thus, it can be concluded that the 0.05 wt. %GO containing membrane gives the best trade-off between permeation and salt rejection properties compared to the other membranes.

![Salt Retention vs. Permeation Rates 2000 ppm NaCl](image)

**Figure 5.23** Effect of different contents of GO on the membrane overall performance using 2000 ppm NaCl solution.
Figure 5.24 Effect of different contents of GO on the membrane overall performance using 5000 ppm MgSO$_4$ solution.

5.4.4. BET surface area

Figure 5.25 shows the change in CA membranes surface area at different GO contents. Compared with the blank membrane, the BET surface area decreased slightly from 1.2 m$^2$/g to 1.1 m$^2$/g as a result of adding 0.025 wt. % GO. However, on increasing GO content to 0.05 wt. %, a significant increase in the BET surface area of the membrane was observed, almost a doubling of the surface area, to reach a value of 2 m$^2$/g. Further increase in GO content to 0.1 wt.% caused a slight decrease in the BET surface area to reach a value of 1.7 m$^2$/g when compared to the 0.05 wt. % GO membrane.
To analyze the membrane BET surface area properties further, the effect of the surface area on the permeability of the membranes is presented in Figures 5.26 and 5.27. Generally, it could be seen that the slight decrease in the surface area of 0.025 wt. % GO containing membranes did not affect the increase in permeation rates of the membrane. However, the 0.05 and 0.1 wt. % GO membranes had the highest values of surface area and permeation rates when compared with the rest of the membranes. As for the 0.1 wt.% GO membrane, it had the highest permeation rates for 2000 ppm NaCl and 5000 ppm MgSO₄, although it showed a decrease in the surface area in comparison to the highest value of the 0.05 wt. % GO membrane.

**Figure 5.25 Plot showing the effect of GO on the surface area of CA membranes.**
Figure 5.26 Effect of surface area on the permeation rates of CA membranes using 2000 ppm NaCl solution.

Figure 5.27 Effect of surface area on the permeation rates of CA membranes using 5000 ppm MgSO$_4$ solution.
5.5. Membrane morphology and performance: general discussion

The previous results including data for permeation rates, salt rejection, and surface areas can be summarized in the following Table 5.2.

Table 5.2 Performances of the GO blended CA membranes, including permeation, salt retention, and BET surface area, with different GO contents

<table>
<thead>
<tr>
<th>CA wt.%</th>
<th>ICT*</th>
<th>FCT*</th>
<th>Additives</th>
<th>Additives %</th>
<th>Contact Angle (degree)</th>
<th>Avg. Contact Angle</th>
<th>Permeation rate (L/m² h.bar) 2000 ppm NaCl</th>
<th>Avg. Permeation rate (L/m² h.bar) 2000 ppm NaCl</th>
<th>Salt Rejection% 2000 ppm NaCl</th>
<th>Avg. Salt Rejection% 2000 ppm NaCl</th>
<th>Permeation rate (L/m² h.bar) 5000 ppm MgSO₄</th>
<th>Avg. Permeation rate (L/m² h.bar) 5000 ppm MgSO₄</th>
<th>Salt Rejection% 5000 ppm MgSO₄</th>
<th>Avg. Salt Rejection% 5000 ppm MgSO₄</th>
<th>BET Surface area (m²/g)</th>
<th>Name Displayed on Charts</th>
</tr>
</thead>
<tbody>
<tr>
<td>19%</td>
<td>DMF</td>
<td>16%</td>
<td></td>
<td></td>
<td>78.7</td>
<td>0.01</td>
<td>54.9%</td>
<td>0.01</td>
<td>62.4%</td>
<td>0.008</td>
<td>59.9%</td>
<td>0.008</td>
<td>60.7%</td>
<td>1.3</td>
<td>Blank</td>
<td></td>
</tr>
<tr>
<td>19%</td>
<td>DMF + GO</td>
<td>16% + 0.025%</td>
<td>67.6</td>
<td>60%</td>
<td>0.013</td>
<td>0.017</td>
<td>55.6%</td>
<td>0.011</td>
<td>74.8%</td>
<td>0.0099</td>
<td>73%</td>
<td>0.012</td>
<td>73.2%</td>
<td>1.02</td>
<td>0.025wt.% GO/CA composite</td>
<td></td>
</tr>
<tr>
<td>19%</td>
<td>DMF + GO</td>
<td>16% + 0.05%</td>
<td>67.9</td>
<td>60%</td>
<td>0.02</td>
<td>0.020</td>
<td>71.1%</td>
<td>0.011</td>
<td>86.8%</td>
<td>0.015</td>
<td>81%</td>
<td>0.012</td>
<td>81%</td>
<td>2.4</td>
<td>0.05wt.% GO/CA composite</td>
<td></td>
</tr>
<tr>
<td>19%</td>
<td>DMF + GO</td>
<td>16% + 0.1%</td>
<td>61.4</td>
<td>60%</td>
<td>0.02</td>
<td>0.021</td>
<td>69.1%</td>
<td>0.013</td>
<td>72%</td>
<td>0.013</td>
<td>68%</td>
<td>0.015</td>
<td>65.8%</td>
<td>1.4</td>
<td>0.1 wt.% GO/CA composite</td>
<td></td>
</tr>
</tbody>
</table>

ICT* = Initial Casting Thickness
FCT* = Final Casting Thickness
Based on the obtained permeation rates, GO-CA membranes always demonstrated higher permeation rates than blank CA membranes indicating that the performance of the membranes was significantly improved by the GO addition. The main reason to account for this is membrane hydrophilicity. The effect of GO on the membrane hydrophilicity was examined using contact angle measurement. The water contact angle decreased from 75° to 61° with increasing GO loading from 0 to 0.1 wt. %, meaning that GO addition increased the hydrophilic nature of the membranes which facilitates water transport across the membranes inducing an increase in the permeation rates. Figures 5.21 and 5.22 revealed a good match between increasing permeation rates and hydrophilicity improvement. [14], [31], [37], [38]

Another reason for enhanced permeation rates is the rapid mass transfer rate between solvent and non-solvent during PI. Once again, instantaneous demixing can be explained in terms of the decrease in water contact angles. The addition of GO altered the membrane structure to be a characteristic asymmetric porous structure that had a top skin-layer followed by a finger-like sub-layer. The instantaneous demixing resulted in an increase in the pore size with increasing GO content to 0.1 wt.%. This was supported by cross sectional SEM images that proved the formation of finger like macrovoids, large elongated pores that extended over the membrane thickness, which are much wider than the pores detected in the blank membrane. In addition, SEM top and bottom surface images (Figure 5.28) showed the base of macrovoids in the bottom layer of all membranes containing GO, unlike the blank membrane. [25], [31], [37], [38]
Figure 5.28 (a) blank bottom surface, (b) blank top surface, (c) 0.025wt.% GO bottom surface, (d) 0.025wt.% GO top surface, (e) 0.05wt.% GO bottom surface, (f) 0.05wt.% GO top surface, (g) 0.1 wt.% GO bottom surface, (h) 0.1 wt.% GO top surface.
These results indicate that GO addition had a major role in the membrane formation process to the extent of modifying the micro-structure of the membranes. Besides, the 0.1 wt. % GO-CA membrane appeared to have few lateral pore structures (encircled in Figure 5.29). This type of pores led to the formation of larger pore channels which improved the permeation rates significantly. Zinadini et.al [28] and Wang et. al [29] also observed the same lateral pores in their PVDF/GO blended membranes.

Figure 5.29 Lateral pore structures appeared within CA membranes with 0.1 wt. % GO.

Interestingly, the BET surface area presented in Figures 5.9 and 5.10 clarified that the 0.05 wt. % GO embedded membrane has a higher surface area than the membrane with 0.025 and 0.1 wt. % GO, despite the fact that the permeation rates of the 0.1 wt.% GO membranes is the highest. This could be understood by the differential pore area vs. pore width data. The figures show that the membrane containing 0.05 wt. % GO had the largest quantity of micro-pores at 1.7 nm. Although these micro-pores are very small in volume, their number must be significant as indicated
by the fact they had the highest value of pore area. In other words, the membrane with 0.05 wt.% GO showed higher BET surface area than the membrane with 0.025 and 0.1 wt. % GO because it contained the largest quantity of micro-pores. Relying on the SEM images, the membrane with the highest content of GO (0.1 wt. % GO) had the largest pores. These pores are large in volume (111 nm, 98 nm, 78 nm and 52 nm) but their number per gram sample was still small compared to the number of micro-pores.

A possible mechanism for the enhancement of the permeation rate with the addition of GO nano-sheets is shown in Figure 5.30. As stated earlier, the transport mechanism of water through GO/CA membranes is governed by the dispersion state of GO nano-sheets in the polymeric matrix [48], [77], [78], [79], [80]. CA chains would facilitate the formation of randomly distributed GO stacks in the membranes from GO nano-sheets as a result of the hydrogen bonds forming between different functional groups on GO nano-sheets and hydroxyl groups on CA chains. The vertical and inclined GO stacks will be favored by water molecules because they provide a straight pathway unlike parallel-stacked GO nano-sheets. In view of this, the high permeation rates were achieved through the transportation of water across vertical array of GO stacks. Nevertheless, the lack of direct proofs is the reason why the transport mechanism of GO sheets in polymeric matrix is still a controversial topic. [48]

![Figure 5.30 Schematic representation of the accelerated permeation rates mechanism of GO/CA membrane. Adapted from [45]](image)

The salt rejection performance of all membranes was examined using 2000 ppm NaCl and 5000 ppm MgSO₄. As stated earlier, increasing GO content caused a significant increase in the
total surface area of micropores with width less than 2 nm. This increase in the surface area of micropores could possibly be the reason for the increase of salt rejection rates by 5% and 19% for 2000 ppm NaCl and 5000 ppm MgSO$_4$ respectively for the 0.025 wt. % membranes, when compared to the blank. In addition, the 0.05 wt. % GO containing membrane showed a much higher differential surface area of micropores, indicating their higher numbers, and therefore leading to higher salt rejection values. However, at 0.1 wt. % loading of GO, the BET analysis showed a decrease in the number of micropores relative to the 0.05 wt.% GO membrane, as indicated by a decrease in differential surface area. This decrease could possibly be due to the blocking of these pores by adding high loading of GO nano-sheets [28]. Salt rejection was observed to decrease to reach a value of 23% and 11% for 2000 ppm NaCl and 5000 ppm MgSO$_4$ respectively relative to the blank membrane. Generally, salt retention is correlated with the abundance of pores of 2 nm in size as reflected by the differential pore area results. In addition, the membranes showed a dependence of rejection rates on GO loading which agreed with the pattern reported in the literature [22], [28], [29].

Another interesting approach to justify the increase in the salt rejection of GO containing CA membranes is the negatively charged functional groups on the surface of GO nano-sheets. With increasing GO content in the membranes, the negative charge induced on the surface of the membranes is expected to increase as well. Such an increase could enhance electrostatic repulsion between the negative charge of Cl$^-$ or SO$_4^{2-}$ ions and the membrane surface. This argument was supported by Zinadini et al. [28] who fabricated GO/PSf membranes with high dye rejection (99%). Based on Pauling’s principle of electro-neutrality, all the ionic species in an electrolytic solution have a net charge of almost zero, the Na$^+$ or Mg$^{2+}$ ions will be rejected as well to keep the solution neutral. This was further supported by the rejection behavior of GO/CA membranes to different salt solutions (2000 ppm NaCl and 5000 ppm MgSO$_4$) shown in Figures 5.21 and 5.22. The rejection of 5000 ppm MgSO$_4$ was higher than the rejection of 2000 ppm NaCl although higher concentration of MgSO$_4$ was used. Such a behavior indicates that the membrane is negatively charged because increasing anion valence caused a direct increase in the rejection values. In other words, the higher negative charge of the divalent anions (SO$_4^{2-}$) increased the membrane repulsive force to these anions and thereby they were rejected more than the monovalent anions (Cl$^-$). [101]
VI. Conclusion and future work

The aim of this study was to utilize GO for the modification of CA membranes for water desalination purposes. GO-blended CA membranes were easily prepared by PI at room temperature. The addition of different contents of GO greatly improved the membrane performance for solution permeation and solute rejection. The following experimental observations can shed some light on the reasons behind the observed enhancements:

- No agglomerations were detected for all the membranes which proved the good dispersion of GO in the matrix. This was further confirmed by SEM images. The hydrogen bonding between functional groups of GO and CA is believed to be the reason for this good dispersion.

- Contact angle measurements were used to study the effect of GO on membrane hydrophilicity. Contact angle showed a constant decrease with increasing GO amount in the membranes indicating enhanced hydrophilicity of the prepared membranes. The increased hydrophilicity is due to the polar oxygen-containing function groups on the surface of GO which increases the membrane hydrophilicity.

- The permeation rates improved significantly with the addition of GO. The 0.1 wt. % GO membrane had the highest permeation rate for both 2000 ppm NaCl and 5000 ppm MgSO₄. The improved permeation rates are believed to result from the increased hydrophilicity of the membranes in addition to the presence of finger-like macrovoids in the GO/CA membranes as a result of the instantaneous demixing taking place during PI.

- Morphological studies by SEM showed that increasing GO content altered the membranes’ structure to become more finger-like with increased porosity in comparison with those of pure CA membranes. This is due to the hydrophilicity effect of GO increasing the exchange of solvent and non-solvent during PI leading to the formation of larger pores.

- Membranes performance was evaluated based on the rejection of both 2000 ppm NaCl and 5000 ppm MgSO₄. Salt rejection increased with increasing GO content for 0.025 wt. % and 0.05 wt.% membranes, then decreased for 0.1 wt.% membranes. This is believed to be due to the change in the number of micropores of width less than 2 nm, as indicated by the change in the differential pore surface area. A possible additional effect is the expected increase of the induced negative charge on the surface of the membranes as a result of the
functional groups on GO, leading to a possible contribution to the salt rejection of the membranes. This is reflected by the higher salt rejection of MgSO₄ as compared with NaCl.

- The membrane with 0.05 wt.% GO not only showed a good permeation performance (0.02 L/m²h.bar) but it achieved the best rejection results as well (74% rejection for 2000 ppm NaCl), making it the membrane with the best performance compared to the blank and the other membranes with GO.

Looking to the future, approaches for better membrane performance could be further explored:

- Compatibility of GO with other polymers such as: poly-vinylidene fluoride, polysulfone, and polyethersulfone in comparison with CA.
- Adjustment of GO properties by incorporating different sizes of GO sheets functionalized with different functional groups.
- Modification of GO/polymer membrane surface properties by using different pH solutions for salt rejection.
- Addition of annealing in the membranes preparation steps to examine its effect on membranes permeation and rejection rates.
- Examination of the effect of adding both GO and CNTs with different concentration ratios on the performance of CA membrane.
- Exploring the separation performance of the membranes as a result of the membrane surface charges.
- Examination of the anti-biofouling activity of CA/GO membranes and its dependence on the GO content.
References


