SYNTHESIS OF CARBOXYMETHYL CELLULOSE (CMC) BASED COMPOSITE MEMBRANE AND TESTING ITS PERFORMANCE FOR SALINE WATER TREATMENT

By

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DEDICATED TO…….

MY BELOVED PARENTS

WITHOUT THEIR SUPPORT ALL THIS WOULD NOT HAVE BEEN POSSIBLE

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Ayesha Neelam

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LIST OF ABBREVIATIONS

SEM	Scanning Electron Microscopy
FT-IR	Fourier Transform Infrared Spectroscopy
TGA	Thermo-gravimetric Analysis
UTM	Universal Testing Machine
CWG	Cotton Gin Waste
CMC	Carboxymethyl Cellulose
PEG	Polyethylene glycol
PVA	Polyvinyl alcohol
PVP	Polyvinylpyrrolidone
WHO	World Health Organization
KPa	Kilo Pascal
PI	Phase Inversion
Psi	Pound force per square inch
EC	Electrical Conductivity

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ABSTRACT

Along with natural causes, anthropogenic activities have intensified the water scarcity issue. Apart from conservation techniques solution to water scarcity is recovery of clean water that could be done by desalination of inland brackish water or sea water by reverse osmosis membrane technology. When it comes to membrane technology polymer composite membranes are most efficient & inexpensive. The aim of the current study was to develop a composite membrane using carboxymethyl cellulose (CMC) as a basic component. For the purpose, carboxymethyl cellulose was prepared from already isolated cellulose by alkalization and etherification of cellulose. CMC along with polyvinylpyrrolidone (PVA) and polyvinyl alcohol (PVP) was then used to prepare composite membrane in order to treat (0.1, 0.3, 1, 3%) synthetic saline water. PEG was used as a pore forming agent. Furthermore characterization was done using Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy, Thermo-Gravimetric Analysis and Universal Testing Machine. SEM indicates that addition of PVP resulted in smoother surface as compared to the membrane fabricated without PVP and the membrane formed lies in microfiltration (0.1 - 10 micron) range. FT-IR spectroscope images gave the bands that are attributed to the dispersion of PVA and PVP in substrate matrix. Weight loss started at 270°C which was 210°C in the absence of PVP, hence TGA results showed that PVP effectively enhanced the thermal stability of membrane. The trend of increase in salt rejection in selected salts i.e. $NaCl < KCl < CaCl_2$ was due to the increase in molecular mass respectively and overall efficiency ranges from 27 to 37%. The removal was highest for $CaCl_2$ followed by KCl and NaCl (i.e. 37> 29 > 27%) respectively. It was concluded that PVP shows positive effect on thermal stability, surface morphology and

mechanical properties of membrane. The fabricated membrane can be used for pre-treatment to Reverse Osmosis (RO) in order to improve efficiency and the life of RO membranes.

Chapter 1

INTRODUCTION

1.1 Background

Water is vital for existence of every life form. More importantly this entity is significant for all features of human life, including food production, community health, ecosystem biodiversity and economic vitality. 80% of the human body is made up of water. Daily body functions, such as blood regulation, respiration detoxification and digestion require safe and clean water to perform activities. World population clock concluded that population surpasses 7 billion and by 2050 it will be 10 billion. For developing countries around world pure and clean drinking water will become an issue. It is assessed that 25% of world’s population has access to clean drinking water (Teixeira *et al.*, 2005).

According to U.S. Geological Survey, 96.5% of Earth's water is sited in oceans and seas while 1.8% of Earth's water is situated in glaciers. Almost 0.79% is estimated as freshwater. The remaining percentage consists of brackish water, marginally salty water that represents surface water and aquifers and estuaries represents ground water. The problem of fresh water scarcity effected most of the communities and human life for long has searched many ideas to resolve the issue of Earth's insufficient fresh water supply.

Basically converting salt water into fresh water is not that innovative idea. It is already in use for ages but the ways used to perform this function changed with the passage of time and in continuous development to cope with rising demand.

Now days it is becoming a universal concern to produce potable fresh water by filtration or any other mean because of rapid population growth that surpasses the conventional techniques used in various communities at different eras. According to the survey report more than 1 billion people have no access to safe drinking water and 42% of world's population is residing in the regions which is facing water shortage problem (Lauren *et al.,* 2009). Solution to the problem like water conservation techniques (rain water harvesting and sustainable use of resource) and water storage like dam construction, etc. are not enough to cope with the present demand. Already the present resources are getting polluted day by day and contamination levels are exceeding the threshold that shrinking the existing fresh water resources of ground water and rivers. This misuse of resources should be checked for sustainable development. With developing countries and cities fewer water resources can serve daily needs for fresh water. As an outcome, solutions like reuse of water and desalination of water have appeared as the answers to supporting future generations around world.

Desalination and reuse of water both have been developed effectively to deliver additional production of fresh water for societies consuming traditional water management and fresh water resources. Reuse of water provides options such as supplying water for industrial process water, groundwater recharge, power plant cooling water and irrigation and has been accepted as an approach for indirect production of drinking water resource. Thermal desalination methods evolving for 50 years and membrane methods emerging for the last 4 decades provide fresh water for drinking (Gleick, 2006). Enhancing the cost and efficiency of water treatment is an important challenge to eliminate potable water scarcity.

1.2 Scope of Study

Desalination is in general considered as the method of eradicating salts from saline water in order to produce fresh water. Fresh water is specified as water comprising less than 1000 mg/L of dissolved salts. Desalination provides one of the most significant answers to these problems. United States Environmental Protection Agency (US-EPA) has secondary criteria of fresh water which is 500 mg/L TDS and 250 mg/L chloride, while, World Health Organization has a fresh drinking water limits of 250 mg/L of dissolved salts. As compared to governmental criteria, maximum desalination plants are intended to attain TDS of 500 mg/L or even less than that (Sanz *et al.*, 2007).

Processes of desalination are divided in two main classes, membrane and thermal processes. Thermal desalination or distillation is being utilized for ages to yield fresh water, however desalination plants at large-scale were established during the 1950s for community drinking water (Gleick, 2006).

Middle East countries founded the strategy and implementation for thermal desalination of seawater, primary through process known as multi-effect distillation (MED) and secondly by means of a multi-stage flash distillation process (Saljoughi *et.al.*, 2009). Currently, Middle East cooperatively possess 49% of desalination capacity in total by principally using MSF technology. Although thermal desalination is a primary choice of technology for Middle East, other membrane practices have promptly established since the 1960s and at present exceed thermal procedures in novel plant installations (Winfield, 1979).

Other than Middle East, innovative RO installations for desalinations have been progressively developing. By 2002, 50% of established desalination capacity utilized RO desalination technology and by 2003 RO desalination facilities results in 75% of new production capabilities (Lauren, *et al.*, 2009). In Middle East still some countries are utilizing thermal desalination as fossil fuel resources are in access and due to poor quality of water for local feed water. Gulf of Oman and Persian Gulf have exceedingly high values for temperatures fouling abilities and salinities for membrane setups. At high retrievals as well as salinities (Above 35% recovery and 55,000 mg/L TDS), membrane desalination require pressure higher than the determined permissible limits in thermal desalination and membrane modules (Kim and Lee, 1998). High temperatures of feed water are also responsible for issues in membrane desalination which can be evaded through thermal desalination.

1.3 Treatment Technologies

Water treatment has been performed through multiple methods such as ultrafiltration (UF), reverse osmosis (RO), membrane distillation (MD), Nano filtration (NF) and microfiltration (MF), MF and UF are well-built practices utilized for treatment of water, while RO is broadly used for purification and desalination of water. A report from 1940 entitled "The Sea as a Source of Fresh Water" introduced research activities based on salt-rejecting membranes. At present, seawater RO membranes accomplished salt rejections higher than 99% (Brehant *et al.*, 2003). RO membranes have the capability to cast-off monovalent ions like chloride and sodium. If operated below standard test conditions some membranes (32,000 mg/L NaCl, 5.45 Mega Pascal, 25 °C, pH 8, 8% recovery), can attain salt rejection as high as 99.7–99.8%. Membrane technology for RO has been fabricated for both seawater and brackish water applications. RO membranes built for brackish water normally yield lower salt rejection, greater product water (permeate) flux and need minor pressures for operations (As saline waters have low osmotic pressure), comparatively RO membranes for seawater need concentrated salt rejection. Membranes established for greater salt rejection possess inferior permeate flux, for improved membrane permeability and selectivity. In addition, RO membranes designed for seawater should function at greater pressures for compensating greater osmotic pressure (Lalia *et al.*, 2013).

Membrane distillation is a novel emerging procedure and it has capability for desalinating of highly concentrated saline water. Role of membranes is vital in water treatment processes based on membranes. They regulate the economic and technological efficiency of the above-mentioned techniques; improvement of membrane can significantly affect the functioning of present technology.

NF membranes are an advanced technology that has been established on a variety of salt concentrations (Hilal *et al*., 2005). Research has revealed that as a regular process, NF, cannot decrease salinity of seawater to meet standards of drinking water, but it has been utilized effectively for treatment of slightly brackish feed water. Precisely, NF membranes have been designed to eliminate divalent ions, like magnesium and calcium that add to dissolved organic material and water hardness.

In case of desalination facilities the salinity of feed water varies from about 1000 mg/L TDS to 60,000 mg/L TDS, even though the synthetic solutions are usually categorized as one of two types: brackish water and seawater. Though maximum seawater sources encompass 30,000–45,000 mg/L TDS which can be made synthetically by using percentage solutions, reverse osmosis membranes designed for seawater are capable to treat waters with TDS values ranging between 10,000 – 60,000 mg/L. RO membranes established for brackish water are designed for treatment of water sources (normally groundwater sources) with TDS range values of 1000 to 10,000 mg/L (Mickley, 2006)

1.4 The Present Study

Hydrogels and membranes characterized with significant properties and structures can be simply prepared with Cellulose containing abundant OH groups. Byproducts of cellulose, comprising carboxymethyl cellulose (CMC) and methyl cellulose (MC) have been utilized for fabrication of hydrogels centered on cellulose by chemical as well as physical cross-linking (Deng *et al*., 2008).

Blending and unification of diverse polymers is an exceptionally inexpensive, attractive and beneficial method for achieving new and innovative structural materials (Bajpai *et al*., 2008) that can be utilized for desalination.

The following were the specific objectives of the study:

1. Development of a composite membrane using carboxymethyl cellulose (CMC) as a basic component
2. Efficiency evaluation of composite membrane in desalination process at lab scale.

Chapter 2

LITERATURE REVIEW

2.1 Background

2.1.1 History of Desalination

The beginning of desalination development started for commercial use in heavy ships, it was the modern era where distillation process was used to separate water and salts that were used for drinking purposes in ocean bound ships because it was nearly impossible to provide fresh water supplies (Sauvet *et al.*, 2007).

Thermal distillation was a key source that enables the heavy cruise ships to travel for much longer durations because fresh water supplies wasn't the hurdle anymore. Japanese sailors in 17th century used to boil water in large pots and bamboo sticks were subjected to collect water from evaporation. At a long run in late 18th century different countries started development in advanced distillation technology to provide water for boilers in steam cruise ships. More investigations were made in order to add chemicals as catalyst.

The commercial desalination plants were first introduced in 1881 at Tigne Malta, following with Jeddah Saudi Arabia in 1907. Jeddah's desalination plant was named "al Kindasah" that means condenser in local language, was unable to generate much fresh water (*Saudi Water and Power Forum, 2007)*, but the efforts resulted in improved and modified plant installed lately in 1970s at same place.

Today, Kindasa Water Services operate two seawater RO facilities in Jeddah, with a total production capacity of 40,500 m^3/day. Middle East countries were pioneer to install desalination facilities at such a larger scale for municipal drinking water purposes. The first developed sea water desalination plants were started in mid-19th century and in Kuwait industrial desalination plant was installed in 1960s.

That was the time when membrane technology was incorporated into the desalination market and in late 1960s the first Reverse Osmosis plant used brackish water to process (Marchese *et al.,* 2003). In 1970s materials used for membrane fabrication were improved to enhance permeability that shifted the feed water from brackish to sea water with high TDS values over these 50 past years RO membrane technology was enhanced and modified to such an extent that make this process a foremost choice for modern desalination facilities (Bruggen *et al.,* 2002). Figure 2.1 shows the worldwide capacity for desalination including distillation as well as membrane technology as a function of time for the last 60 years. Exponential growth was observed between 1960 and 1970 in desalination capacity due to the rapid development in both technologies offered for desalination.

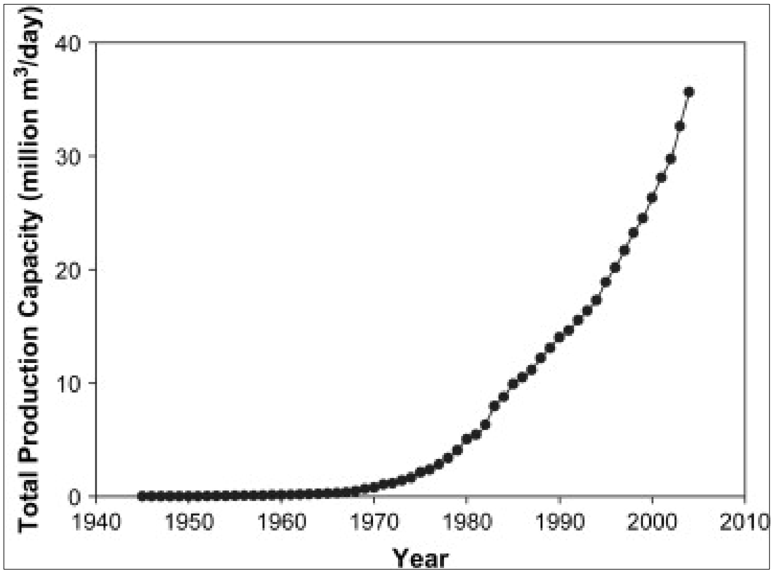


Figure 2.1: Worldwide Desalination Capacity as a Function of Time

It has been reported that about 15 to 20,000 desalination facilities are in operation worldwide, half of them are Reverse Osmosis. It was reported that Israel started the largest saline water treatment plant that produces about 331,000 cubic meter of fresh water daily (Sauvet, 2007). In 2005, Fujairah desalination facility was came into operation in United Arab Emirates that offers to produce 455,000 cubic meter of fresh water per day with combined technologies of Reverse Osmosis and membrane distillation (Sanz *et al.*, 2007).

Figure 2.2 illustrates the total production capacities of new desalination plant installed worldwide on yearly basis with membrane and distillation both process. The trend showed the significant jump in emerging capacities during recent years and the annual increase actually shows the technology advancement and modification of membrane materials.

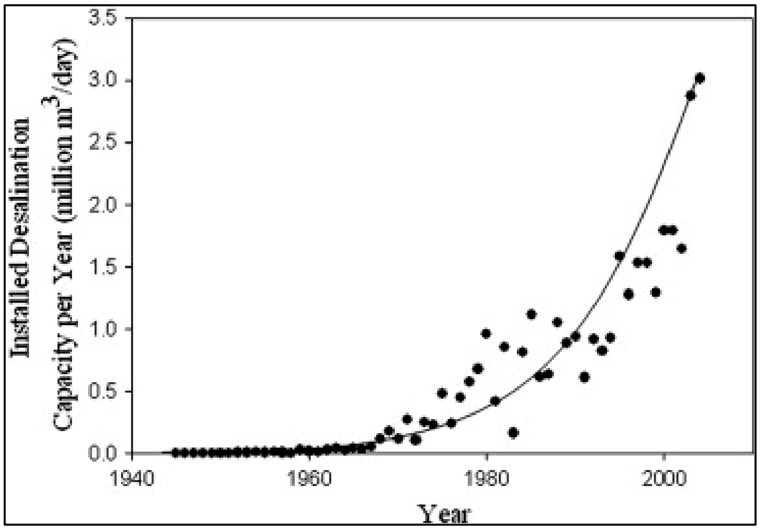


Figure 2.2: Yearly Worldwide New Desalination Production Capacity

Now Saudi Arabia is leading the world of desalination with 26% global production capacity and with 18% capacity United States ranks second on this chart (Gleick, 2006). However most of the counties with largest production capacity of fresh water are located in Middle East.

In addition 70% of United States desalination facilities use Reverse Osmosis with less than 10% uses saline water (Wolfe *et al.*, 2005). Statistics shows that U.S have 5% population of world whereas Saudi Arabia represents just 0.5%. Although 18% of the total desalination facilities are installed on thermal technology which depicts the wide application of this technology according to the requirement and resource difference of every country (Miller *et al.,* 1960).

2.2 Polymers

2.2.1 Cellulose

In renewable organic materials, cellulose is the most abundant material present on the surface of earth. About 33% of all plants is made of cellulose matter, in cotton it is over 94% and in wood it is above 50% as the major component (Klemm *et al.,* 2005). Most of the Cotton fiber is made up of cellulose as well as non-cellulosic material which surrounds the center of cellulose. These type non-cellulosic materials are commonly form in cuticle layer and primary wall. This layer surrounds cotton fiber (Wienk *et al*., 1996).

These types of fibers are made up of cellulose including hemicellulose as well as lignin, pectins and proteinaceus material including waxes and some other small soluble polysaccharides (Gumuskaya *et al.,* 2003). The arrangement of cellulose is ordered in to fibril which is surrounded by layers of lignin and hemicellulose Production of valuables like ethanol from solid organic waste and recovery of biomaterials is increased after the increase in tipping price as well as strict regulation implementation on particulate emissions (Kaushik *et al.*, 2011).

2.2.2 Derivatives of Cellulose

Observing the high demand for environment friendly and biocompatible products a comprehensive range of applications and number of new practicable materials from cellulose are rapidly developing (Eichhorn *et al.*, 2005).

Derivatives of cellulose which includes methyl cellulose written as (MC), hydroxypropyl cellulose written as (HPC), carboxymethyl cellulose written as (CMC) and hydroxypropylmethyl cellulose written as (HPMC) have been used to manufacture cellulosic hydrogels by the method of physical cross linkage and chemical cross linkage (Deng *et al.*, 2008).

2.2.3 Carboxymethyl Cellulose

CMC is produced when we react alkali cellulose and sodium monochloroacetate under strictly controlled regulations. The formation of the cellulose molecule is shown in Figure 2.3. It can be seen as a polymer chain which is made up of repeating cellobiose units. These are made up of two anhydroglucose units' known as ß-glucopyranose remains. In this type of composition, anhydroglucose units are denoted by n which can be linked through 1; 4 glucosidic linkages or can be called the degree of polymerization of cellulose.

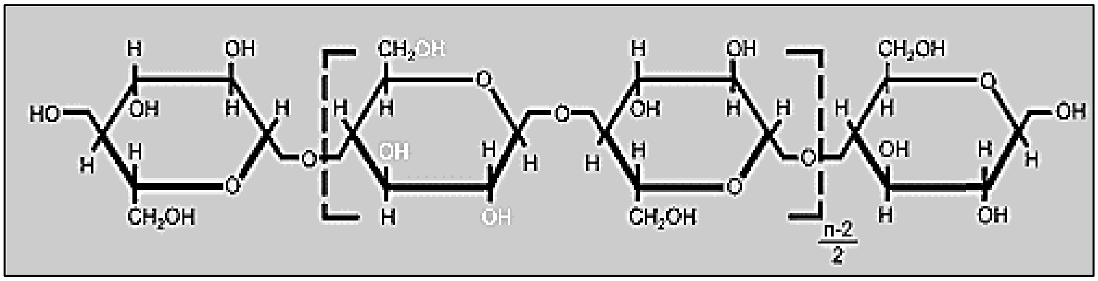


Figure 2.3: Structure of Cellulose

Every single anhydroglucose element comprises on mainly three groups hydroxyl which can be seen in white in above given fig. Sodium carboxymethyl cellulose is produced by replacing carboxy-methyl groups against some of the hydrogens of these hydroxyls which can be seen in Figure 2.3. By ''degree of substitution'' we mean 'the normal number of groups of hydroxyl are replaced per anhydroglucose. If all three hydroxyls are replaced than the extreme theoretical DS of 3.0 results which is not possible in daily practice.

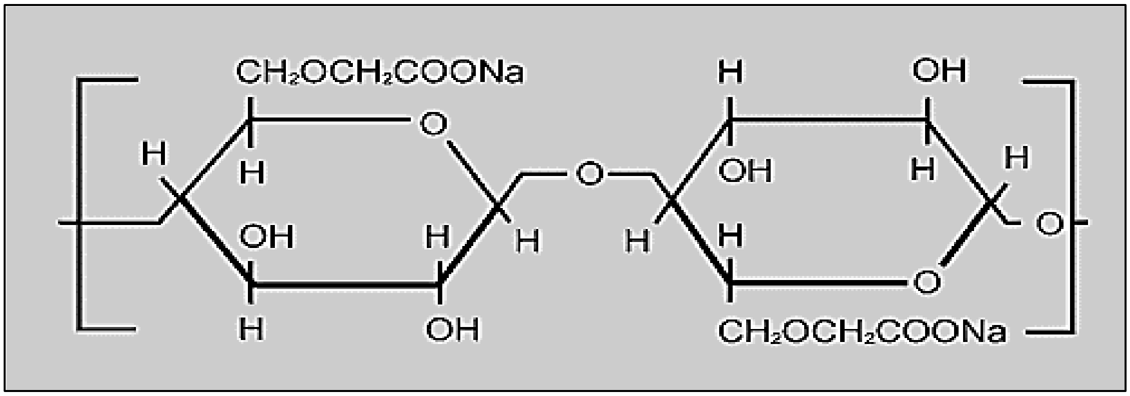


Figure 2.4: Idealized Unit Structure of CMC

Desirable physical properties of CMC and optimum water solubility can be found at a very low degree of substitution against 3. Most abundantly used types of Aqualon CMC have a DS of 0.7, or an average of 7 carboxymethyl groups per 10 anhydroglucose units. At higher degrees of substitution it gives that products which have an improved compatibility with other soluble components (Wienk *et al.*, 1996).

Cellulose such as CMC, are polymers which have long chains. Their solution features are highly dependent on the average chain length which can be called degree of polymerization denoted by DP as well as the degree of substitution. Whereas the average chain length as well as the degree of substitution regulates polymer's molecular weight. The viscosity of CMC solutions increases quickly as the weight increases. In Table 2.1, approximate weight averages for the degree of polymerization as well as molecular weight of different viscosity types of Aqualon CMC can be seen.

Table 2.1: Typical Molecular Weights for Different Viscosity Types of CMC

Viscosity Type	Degree of Polymerization	Molecular Weight
High	**3,200**	**700,000**
Medium	**1,100**	**250,000**
Low	**400**	**90,000**

Viscosity is effected by the rate of neutralization of carboxymethyl groups. In solutions the degree of neutralization is measured by the pH value. The mixture came from reaction have a minor quantity of sodium hydroxide at the end of process of carboxymethylation, which is neutralized usually. The neutral value of CMC have a pH of 8.25. Normally the pH value is adjusted between 7-7.5. If the pH value is 6.0 or less than 6 to which the CMC is neutralized the outcome dried product does not have good solubility in water as well as liquids become hazy and also they have insoluble gel elements, on the other hand if the pH is 4 or less than 4, the product is not soluble in water.

There are many uses of CMC in awl type of the food industry and detergents, cosmetics and pharmaceuticals also textiles, paper, adhesives as well as ceramics (Yang *et al.*, 2007). It is a form of cellulose which is water soluble with β-D-glucose and β-D-glucopyranose 2-O-(carboxymethyl)-monosodium salt and which are connected via β-1, 4-glycosidic bonds. This form of cellulose can also behave as a viscosity changer as well as thickener and emulsifier (Ninan *et al*., 2013).

Researchers and scientists have studied the production of CMC mostly from sugar beet pulp which is a cellulose source of agriculture waste. Another one is cashew tree gum and also sago waste (Pushpamalar *et al.*, 2013). Other sources are Cavendish banana pseudo stem as well as durian rind (Adinugraha *et al.,* 2005).

2.3 Treatment Technologies

A major challenge to overcome the shortage of portable water is the increase in the efficiency and price of water treatment. Membrane procedures offer many gains as compared to other separation methods such as low energy consumption or high removal efficiency as well as high flow rate and ease of scale up and small footprint (Thangawng *et al*., 2011).

2.3.1 Membrane Technology

In membrane-based water treatment processes and determining the technological and economic efficiency of the aforementioned technologies the membranes play a key role; it can also greatly affect the performance of current technology. Ultrafiltration (UF), Microfiltration (MF), Nano filtration (NF), Reverse osmosis (RO) and Membrane distillation (MD) are different filtration methods used for water treatment. Ultrafiltration and Microfiltration are strong techniques which can be used for water treatment as Reverse Osmosis is widely used for water desalination and purification. Membrane distillation is an emerging method and it has capacity for desalinating highly saline water also.

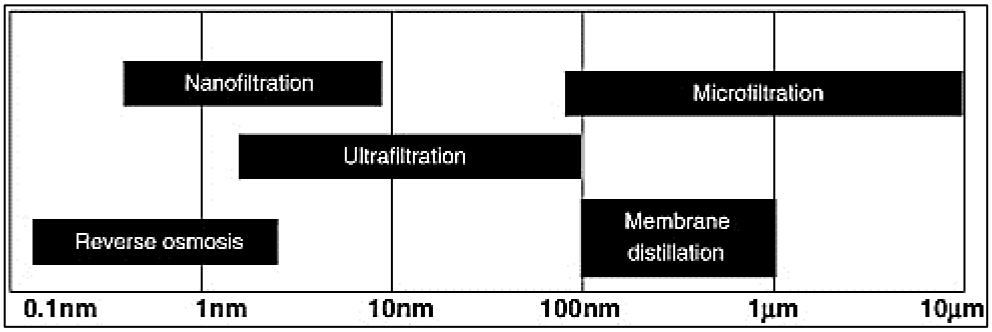


Figure 2.5: Different Membrane Technologies with Varying Pore Size

2.3.3. Membrane Fabrication Methods

Method selection for polymer membrane fabrication is highly depends upon firstly on a choice of polymer and secondly on desired structure of the membrane. Phase Inversion, Interfacial Polymerization, Stretching, Track-Etching and Electrospinning are the most used techniques for preparation of polymeric membranes (Lee *et al*., 2011).

2.3.3.1 Phase Inversion

It can be defined as de mixing method whereas the initially homogeneous polymer solution is turned into a restricted manner for conversion it from liquid to a solid state. This change can be completed in many different ways like;

1) **Immersion precipitation**. The polymer solution is immersed in a non-solvent jelling bath normally water. After that demixing and precipitation happens because of the turning of the solvent which is from polymer solution as well as non-solvent which is from coagulation bath, which means the solvent as well as non-solvent shall be miscible.

2) **Thermally induced phase separation**. It is based on this rule that the solvent quality usually decreases by lowering the temperature. After demixing is brought, the solvent can removed by extraction or evaporation otherwise freeze drying.

3) **Evaporation-induced phase separation**. In this method the polymer solution is made in a solvent or in a mixture of a volatile non-solvent, and on other hand solvent is allowed for vaporization, leading to precipitation or vice versa. Generally it is also known as a solution casting method.

4) **Vapor-induced phase separation.** In this technique the polymer solution is wide-open to an atmosphere having a non-solvent typically which is water; absorption of non-solvent creates demixing/precipitation.

However, the most commonly used method in the fabrication of polymeric membranes with different morphologies are immersion precipitation and thermally induced phase separation.

2.3.3.1.1. Immersion Precipitation

It is a process where a polymer solution is troupe on an appropriate support, then immersed in a coagulation bath which contains a non-solvent, where an exchange of solvent and non-solvent occurs and the membrane is shaped. After a limited time until the solution becomes thermodynamically unstable and the process of demixing takes place the exchange of solvent and non-solvent proceeds. At the end solid polymeric film obtained with an asymmetric structure.

On the other hand for membrane technologies, one of the most serious innovations in desalination was the development of the first high-flux anisotropic acetate cellulose (CA) RO membranes via immersion precipitation (Park *et al.*, 2006).

Now excessive knowledge exists on how to ‘tailor’ the membrane's pore structure including its cross-section morphology by the selection of polymer, solvents and non-solvents, additives, precipitation time, bath temperature and other parameters during immersion precipitation. Different casting conditions and post-treatments were planned to increase the water flux and salt rejection of the CA membranes.

Main polymers used in membrane formation and their advantages and disadvantages are presented in the following Table.

Table 2.2: Commonly Used Polymers in Membrane Fabrication

Polymer	**Advantages**	**Disadvantages**
CA	• Hydrophilicity • Flexibility in fabrication • Low cost	Low thermal resistance (< 25 °C) Low chemical resistance, pH range (2–7) Poor resistance to chlorine
PS /PES	• High thermal resistance (up to 70 °C) • Wide pH tolerances (1–12.5) • Good chlorine resistance • Flexibility in membrane fabrication (wide range of pore size) • High mechanical characteristics	Low operating pressure limits Hydrophobicity
PVDF	•High mechanical strength and chemical resistance •High thermal stability (up to 70 °C)	Hydrophobicity
PA	•Wide pH tolerance •High thermal stability •High mechanical properties	Poor chlorine resistance

Apart from the chemical nature of a casting polymer the absorption of the polymer is very important in membrane fabrication via immersion precipitation. Higher rate of polymer absorption in the casting solution gives membranes with lower porosity and lower pore sizes as a result. The macro void formation is repressed and their tendency to form structures like sponge is improved in this case. 12-20wt% is the polymer concentration in which the UF membranes can be found. On the other hand polymer concentrations ≥ 20 wt. % reacting with casting solutions, the RO membranes are normally formed.

Morphology and the properties of casted membranes also strongly affect by the selection of solvent as well as non-solvent. Fabrication of a nonporous membrane occurs when there is a low miscibility of polymer in the solvent, on the other hand when the miscibility is high more porous membranes are obtained. Aprotic solvents generally capable of contributing to hydrogen bonding where there are no hydrogen atoms are preferred for membrane casting. Some of the aprotic polar solvents which are preferable for rapid precipitation or instantaneous de-mixing are *N*-methyl-2-pyrrolidone, dimethyl formamide, dimethyl acetamide or dimethyl sulfoxide upon involvement in the non-solvent water as well as this produces anisotropic membranes with a high porosity (Wienk *et al.,* 1996).

To improve the membrane morphology and properties, various inorganic (such as LiCl) and high molecular weight organic (such as polyvinyl pyrrolidone (PVP) or poly(ethylene glycol (PEG) additives to casting solution are often used and an additive can function as a pore former, increase solution viscosity or accelerate the phase inversion process. For example, the effect of LiCl addition in the membrane formation was investigated in the studies and they found that LiCl addition in the PVDF/dimethylacetamide dope increases flux of the casted membranes at low LiCl concentration of 2.5 wt. %, but it suppressed macro void formation at a high concentration of 7.5% LiCl and resulted in a decrease of the membrane permeation flux.

Similar results were obtained for poly (amic acid) (PAA) casting solutions in *N*-methyl-2-pyrrolidone. They found that by increasing LiCl concentration in the PAA/*N*-methyl-2-pyrrolidone system, the solution viscosity can be raised to the point where macro void formation is hindered and development of a finely porous structure is favored (Marchese *et al.,* 2003).

The above observations were believed to be associated with the change of the thermodynamic and kinetic properties of the polymer dope system before and after LiCl addition. It was shown that LiCl addition increased the dope's thermodynamic instability in reaction with water, which facilitated a rapid phase demixing and resulted in macro void formation (thermodynamic effect). On the other hand, LiCl possesses strong interactions with the polymer and solvent, which was supported by the significant increase in viscosity of LiCl added casting solutions. The strong interactions among the components of the casting solution tended to delay the dope precipitation (the kinetic effect), which partially offset the thermodynamic impact of LiCl addition. As a result, the size of the macro voids in the fabricated membranes is reduced at high LiCl dosage in the casting solutions.

It was also reported that an increase of PVP concentration in the cast film from 0 to 1.5 wt. % resulted in the facilitation of macro void formation in the membrane sub-layer, which increased pure water flux. (Saljoughi *et al,* 2009). However, in the same study, it was observed that an increase in PVP concentration from 1.5 to 3, 6 and 9 wt. % resulted in a decrease in water flux, where the macro void had been suppressed gradually. (Wang *et al.*, *2009)* showed that the PVP-added PES membrane has a higher water flux and lower water contact angle than the neat PES membrane. The contact angle decreased by 16% when the PVP content in the casting solution was 10 wt. %. (Ochoa *et al.*, 2001) proved that the addition of PVP to the casting solution increases the UF PES membrane permeability without significant changes in selectivity.

Many researchers come to an end that the porosity or permeability of prepared membranes increased by the presence of low molecular weight PEG additive in the cast solution film. Different studies were under taken like Effects of PEG concentration (0 wt. %, 5 wt. % and 10 wt. %) on morphology as well as at different coagulation bath temperatures like 0 and 25 °C of pure water permeation flux of the prepared membranes.

Flux and rejection of human serum albumin Increases as a result of facilitation of macro void formation in the sub layer of membrane as PEG concentration in the cast film increases. Some researchers proposes that the reason for this phenomenon would be the PES-additive interaction is enhanced by the hydrophobic part. Ultrafiltration experiments also demonstrated that above 70% of the initial water flux can be recovered after Ultrafiltration of bovine serum albumin named as (BSA) solution only by water's external cleaning. Researchers also proposed that a highly hydrated and dense poly(ethylene oxide) polymer layer formed on the membrane surface prevented protein molecule from contacting membrane surface directly, as well as water washing is the easiest procedure of removing the protein molecules deposited on the poly(ethylene oxide) layer (Han *et al.*, 2013).

2.2.4 Membrane Materials

Different fabrication techniques are presented in Table 2.3 with commonly used polymers for the synthesis of composite membranes. Average pore size is also mentioned.

Table 2.3: Summary of Commonly used Polymers and Fabrication Techniques

Water treatment process	Polymers used for membrane fabrication	Fabrication techniques	Average pore size of the membrane
RO	Cellulose acetate/triacetate Aromatic polyamide Polypiperzine Polybenziimidazoline	Phase inversion Solution casting	3–5 Å
NF	Polyamides Polysulfones Polyols Polyphenols	Interfacial polymerization Layer-by-layer deposition Phase inversion	0.001–0.01 μm
UF	Polyacrylonitrile (PAN) Polyethersulfone (PES) Polysulfone (PS) Polyethersulfone (PES) Poly(phthazine ether sulfone ketone) (PPESK) Poly(vinyl butyral) Polyvinylidene fluoride (PVDF)	Phase inversion Solution wet-spinning	0.001 – 0.1 μm
MF	PVDF Poly(tetrafluorethylene) (PTFE) Polypropylene (PP) Polyethylene (PE) PES Polyetheretherketone (PEEK)	Phase inversion Stretching Track-etching	0.1–10 μm
MD	PTFE PVDF	Phase inversion Stretching	0.1–1 μm

Chapter 3

MATERIALS AND METHODS

In general, this chapter explains the methodological aspects of data collection and analysis to achieve the research objectives. The first section describes the experimental design and approach used to prepare Carboxymethyl Cellulose and then the blend membrane.

The second section provides detailed information on characterization and Physicochemical analysis of the prepared membrane. Furthermore, the statistical techniques employed for data analysis are also presented.

3.1 Materials and Reagent

Materials used in this research were of scientific standard. Isopropyl alcohol, acetone, glacial acetic acid, sodium hydroxide (analytical grade) methyl alcohol, ethyl alcohol, monchloroacetic Acid, polyvinyl alcohol, ammonium persulphate, polyvinylpyrrolidone were obtained from Sigma Aldrich. Distilled water was used throughout the experimental work.

3.2 Synthesis

3.2.1 Synthesis of Carboxymethyl Cellulose

Cellulose will be converted into CMC with in two steps under heterogeneous conditions

3.2.1.1 Alkalization of Cellulose

In the first step 5 grams of Cellulose was added to 300ml of water with an appropriate ratio (1:4) of isopropyl alcohol solvent. Then, 40 ml of sodium hydroxide with changing concentrations like 4, 8, 12, 16, 20 and 24% w/v was added drop-wise to the beaker. Assembly was assisted with continuous magnetic stirring for two hours on hot plate.

3.2.1.2 Etherification

Etherification was undergone by adding varying concentrations of sodium monochloroacetic acid (MCA) (1 to 5 g) to the reaction mixture in 250 mL beaker on magnetically stirred hot plate. The blend mixture was then heated up at different temperatures (40–60 °C) with continuous stirring for 3 h. The reaction mixture was then filtered and the filtrate was suspended in 100 ml of methyl alcohol for 45 min.

Dilute glacial acetic acid was used to neutralize suspended slurry. Procedure was then followed by filtration and then it was washed with absolute methyl alcohol. The residue from the filtration was then oven dried at 60 °C overnight and the powder obtained was CMC (Haleem *et al.,* 2014).

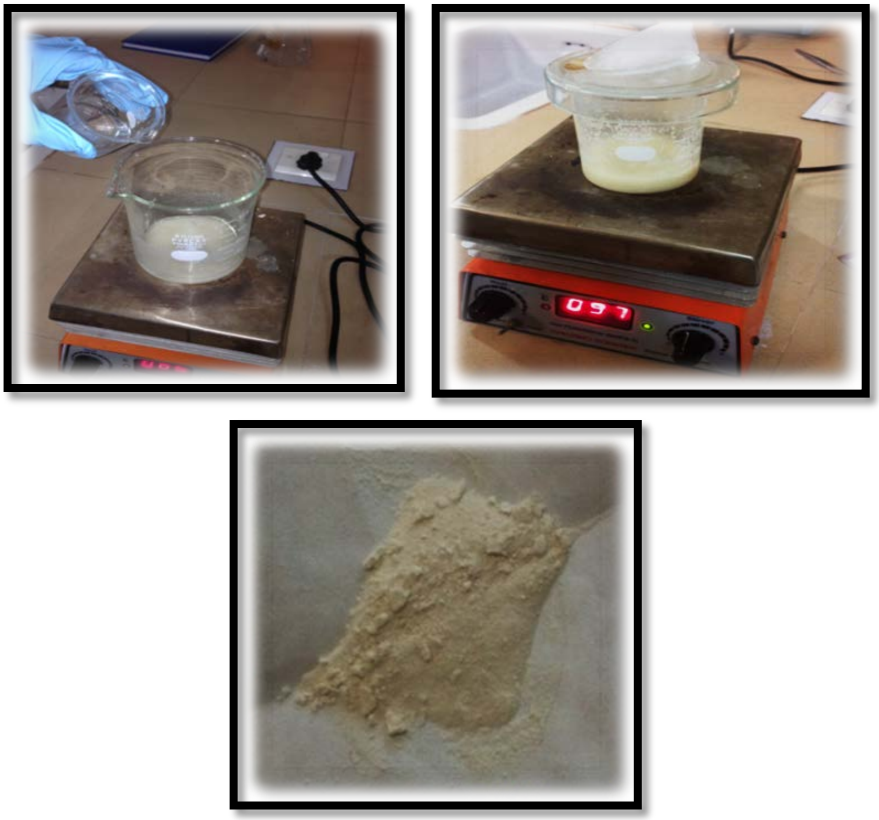


Figure 3.1: Synthesis of Carboxymethyl Cellulose

3.2.2 Synthesis of Composite Membrane

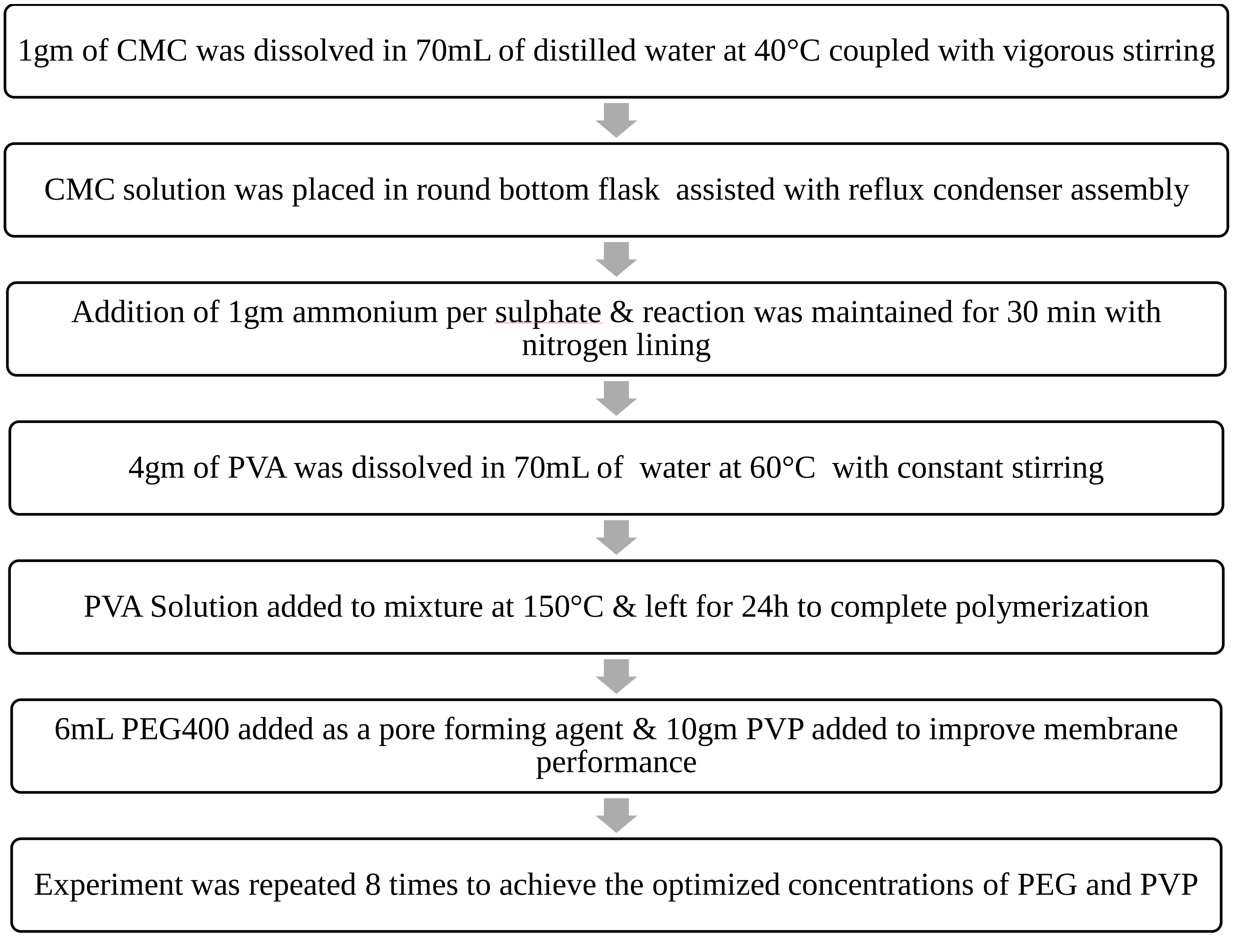
For membrane fabrication suitable amount 1 g of CMC, was dissolved in 70 ml aqueous solution in a 500 ml three-neck round bottom flask, manually equipped with reflux condenser. Flask was placed on magnetic hot plate for constant stirring. Assembly was attached with nitrogen line for inert environment. After being purged with nitrogen for 30 min, excess oxygen dissolved was removed from the system, little amount of ammonium persulphate as an initiator was added to the mixture to initiate CMC to produce radicals (Ibrahim *et al.*, 2013). Reaction was retained for about half an hour.

Meanwhile 4 g of PVA was left to get dissolve in 70ml distilled water at 60 °C. The solution prepared was then added to the reaction mixture at 150 °C for 2 h to complete polymerization. Varying concentrations (2, 4, 6 and 8 mL) of PEG were introduced to achieve optimization. The addition of additive in the casting solution is one of the significant characteristic that effects the membrane performance and structure. To enhance the hydrophilic properties of the membrane, the addition of polyethylene glycol (PEG) as a polymeric additive has been confirmed to achieve new requirements of present era (Liu and Yu, 2006).

For comparative studies two types of membranes were fabricated; one with polyvinylpyrrolidone as a filler on CMC/PVA substrate in comparison with simple PVA/CMC membrane. Varying concentrations of PVP were added at 150 °C to achieve optimization. In literature PVP is reported as a unique filler for high tensile strength. The casting solution was then maintained for 24 hours. The resultant homogenous polymer mixture was transferred into different petri dishes and washed with distilled water numerous times until it gets neutral. At the end membranes were achieved by drying in ambient air for

48 h at room temperature. Water bath was used to remove membranes from petri dishes at 60 °C. The acquired membranes were then heated in oven at 60 °C for 8 h.

- Membranes were prepared by using Phase Inversion method (Thürmer *et al.*, 2012). **Phase inversion** is a de-mixing process of initially homogeneous polymer solution which is transformed from a liquid to a solid state.
- Phase Inversion method has further sub categories, and the process used here is evaporation-induced phase separation. It is a method in which polymer solution is made in a solvent or in a mixture of a volatile non-solvent. The solvent was then allowed to evaporate, which leads to precipitation.
- This technique is also known as solution casting method. Solutions were prepared in a step by step procedure explained in figure 3.2.



1gm of CMC was dissolved in 70mL of distilled water at 40°C coupled with vigorous stirring

CMC solution was placed in round bottom flask assisted with reflux condenser assembly

Addition of 1gm ammonium per sulphate & reaction was maintained for 30 min with nitrogen lining

4gm of PVA was dissolved in 70mL of water at 60°C with constant stirring

PVA Solution added to mixture at 150°C & left for 24h to complete polymerization

6mL PEG400 added as a pore forming agent & 10gm PVP added to improve membrane performance

Experiment was repeated 8 times to achieve the optimized concentrations of PEG and PVP

Figure 3.2: Flow Sheet for Preparation of Casting Solution

Different composition of the casting solution is presented in Table 3.1.

Table 3.1: Optimization of Casting solutions (Values in wt. %)

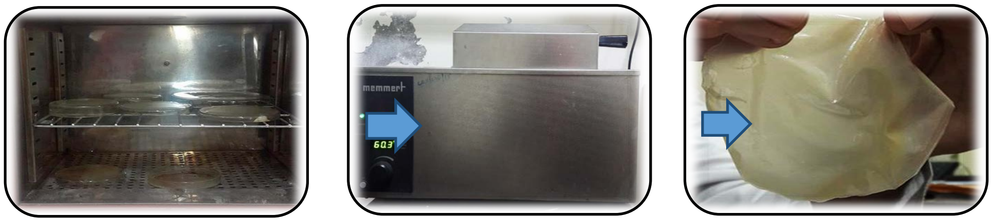
Sr. No.	**CMC** ***(gm)***	**PVA** ***(gm)***	**PEG** ***(mL)***	**PVP** ***(gm)***	**Results**
1)	1	2	-	-	CMC get soluble in water sorption test, Very fragile
2)	1	3	2	-	Poor porosity & Fragile
3)	1	4	4	-	Slightly porous & Less Fragile
4)	1	4	6	-	Hydrophilic & Flexible
5)	1	4	8	-	Visibly porous & Flexible
6)	1	4	6	8	Hydrophilic & good tensile strength
7)	1	4	6	10	Hydrophilic & Excellent tensile strength
8)	1	4	6	12	Hydrophilic & Excellent tensile strength

Solutions were prepared in reflux condenser assembly in heterogeneous conditions at optimized temperature of about 150 °C for continuous 24 hours. Obtained membrane can be seen in figure 3.3. PEG was optimized at 6 ml, where it gave good hydrophilcity but increasing the concentration of PEG results in more flexibility and lesser tensile strength. (Sajitha and Mohan, 2003). With the addition of PVP on CM/PVA substrate tensile strength was enhanced and optimized results with 10% PVP concentration gave a membrane with excellent tensile strength in addition to hydrophilic properties. By adding 12% PVP same results were achieved, so 10% PVP casting solution was selected for characterization and further experimental work.

Condenser Assembly

Homegenous polymer Solution

Solution Casting



Oven Drying

Water Bath

Obtained Membrane

Figure 3.3: Schematic Diagram for the Synthesis of the Membranes

3.3. Characterization of Membrane

The characterization of acquired membrane was performed using the techniques described below.

3.3.1. Scanning Electron Microscopy (SEM)

Scanning Electron Microscope (SEM) is a powerful technique which uses a focused beam of electrons to obtain largely magnified picture. The high-resolution, three-dimensional images produced by SEM provide information like;

- Topography
- Morphology
- Chemistry

- Crystallography

The topography and morphology of the membrane was carried out using scanning electron microscope (JEOL JSM-6490A) at different magnifications. Scanning Electron Microscopy was used for the direct estimation of pore size and examination of surface morphology. It is the type of electron microscope that uses focused beam of electrons to scan a sample for image production. It has the resolution of less than 1 nm. X-rays informed us about the elemental and chemical composition of the sample as shown in Fig. 3.4 (Bowen *et al.*, 2002).

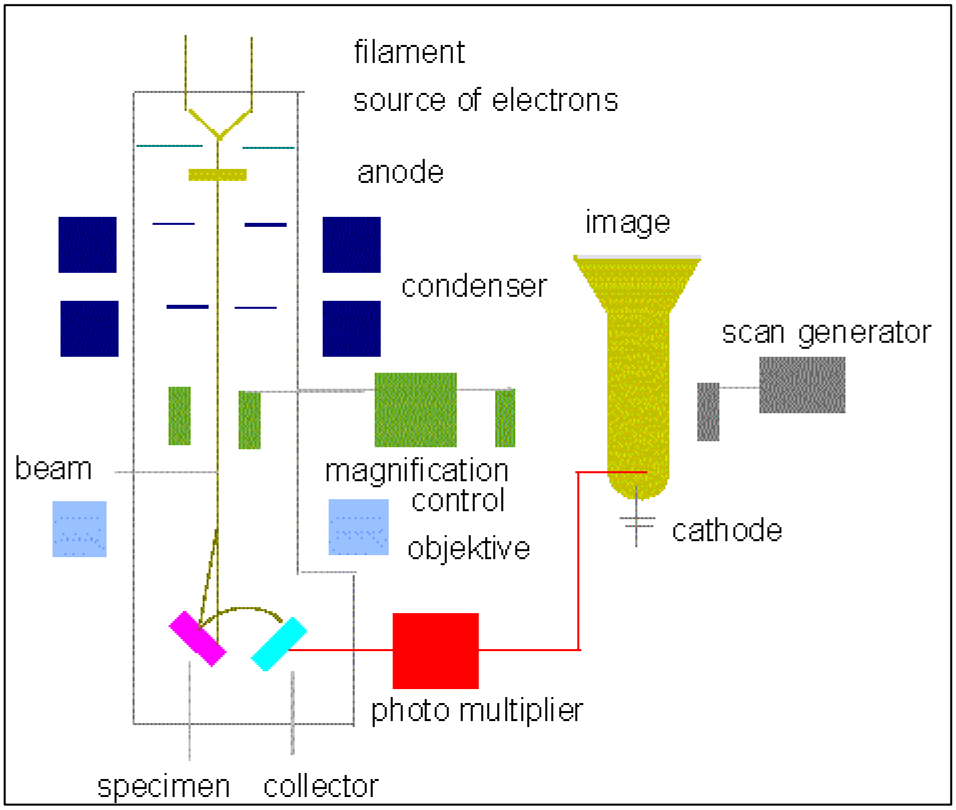


Figure 3.4: Block Diagram of a Typical SEM

The membranes were subjected to freeze under liquid nitrogen which is in extreme low temperature for 60 s, and then frozen membrane fragments were split and enclosed with gold by stammering to generate electric conductivity. SEM images of the membrane surface were captured in a low vacuum environment working at 10 to 25 kV.

3.3.2. Fourier Transform Infrared Spectroscopy (FT-IR)

Fourier Transform Infrared spectroscopy (FT-IR) is mainly used for the identification of certain functional groups in a sample. In this study, Fourier Transform Infrared spectrometer (Model-Perkin Elmer spectrum 100) was used to confirm the modification or functionalization of nanoparticles from APTMS by identifying the specific functional group peaks in the spectrum. The mixture of sample and potassium bromide (KBr) was used to prepare the sample disc by applying high pressure. This sample disc was then used to be tested by FT-IR.

FTIR works on the basic principle that IR radiation passes through the sample, some of the radiation is absorbed by the sample and other get transmitted and the resultant spectrum is obtained by plotting absorption or transmission against frequency of the sample which ranges from 500 cm^{-1} to 4000 cm^{-1} (Szabolcs *et al.*, 2002).

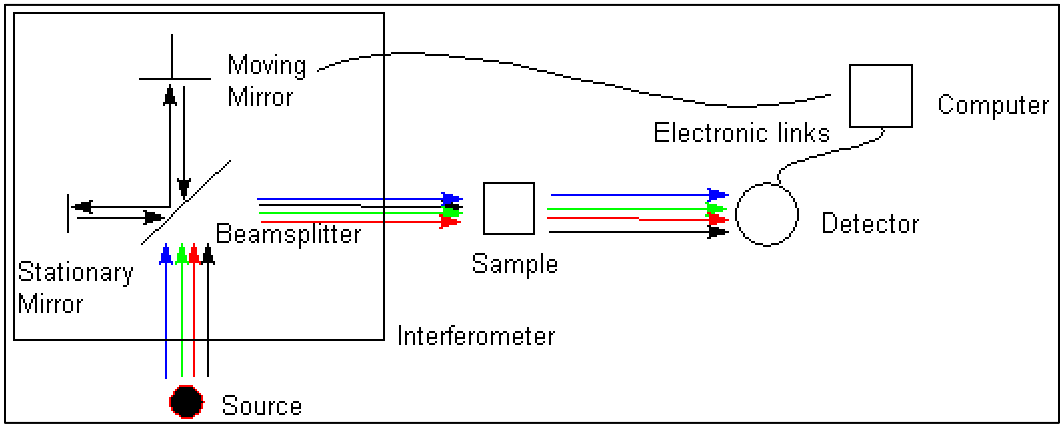


Figure 3.5: Working Principle of FT-IR

3.3.3. Thermo-Gravimetric Analysis (TGA)

Thermogravimetric analysis is a process in which variations in physical and chemical properties of given samples are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss) (Liu and Yu, 2006).

TGA can generate information about physical phenomena, such as second-order phase transitions, including vaporization, sublimation, adsorption, and desorption. Similarly, TGA can provide information about chemical phenomena including chemisorptions, decomposition, and solid-gas reactions (e.g., oxidation or reduction). Thermogravimetric analysis (TGA) was carried out with membrane samples of 15 mg to 20 mg at different temperature ranges from 30 °C to 450 °C at a heating rate of 10 °C/min provided with inert nitrogen gas atmosphere.

Selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation, or loss of volatiles (such as moisture) are usually determined using TGA. Materials characterization through analysis of characteristic decomposition patterns, studies of degradation mechanisms and reaction kinetics, determination of organic content in a sample, are common applications of TGA. These applications are very useful for corroborating predicted material structures or simple chemical analysis (Block *et al.,* 1983)

It is a very convenient technique for the study of polymeric materials, including thermoplastics, thermosets, composites, fibers and plastic films.

3.3.4. Universal Testing Machine (UTM)

A universal testing machine (UTM) is used to test the tensile strength and compressive strength of materials. It is named after the fact that it can perform many standard tensile and compression tests on materials, modules, and structures. Ultimate tensile strength (UTS), is the maximum pressure that a material can resist while being stretched or pulled before failing or breaking.

The UTS is usually found by carrying out a tensile test and by plotting a stress versus strain graphs. The highest point shown in the stress strain curve is UTS. Its value does not depend on the size of the testing material because it is an intensive characteristic. Though, it is dependent on different factors like presence of apparent defects, preparation of the sample and the temperature of the testing environment and prepared sample.

Tensile strength is usually taken in terms of a stress, which is basically measured as force per unit area. It could be reported as a force per unit width for non-homogenous samples.

The unit described in International System of Units is pascal or multiple of pascals often mega pascal MPa is used. Equivalently the unit used in this machine was N/mm^2 which is equal to 1 MPa (In-Chul *et al.*, 2003).

3.4. Physicochemical Analysis

Following tests were performed to evaluate physicochemical properties of the acquired membrane.

a) Water solubility

b) Salt rejection analysis with varying concentrations of three different salts

c) Flux rate

3.4.1. Water Solubility

Experiment described below was performed for water solubility analysis.

- Firstly the membranes were weighed and (W1) was obtained
- Then the membranes were immersed in distilled water for 2 hours
- After that the extra water was poured out and the surface was gently wiped off with tissue paper to obtain weight (W2)
- Then the membranes were dried in oven and (W3) was obtained
- The experiment was repeated thrice for average weight
- Water solubility for membrane was calculated using this formula (Kumar *et al.*, 2013).

Percentage water solubility = (W1-W3)/W1 x 100100

Where,

W1 = Actual weight

W2= Immersed in distilled water

W3= Oven Dried

3.4.2. Salt Rejection Analysis:

For salt rejection Analysis different concentrations of salt solution were prepared. As the maximum TDS of Saline Water is 35000 ppm, so the ratios were taken accordingly with the minimum concentration of inland brackish water of about 1000 ppm and mean values were taken to have best combination for analysis.

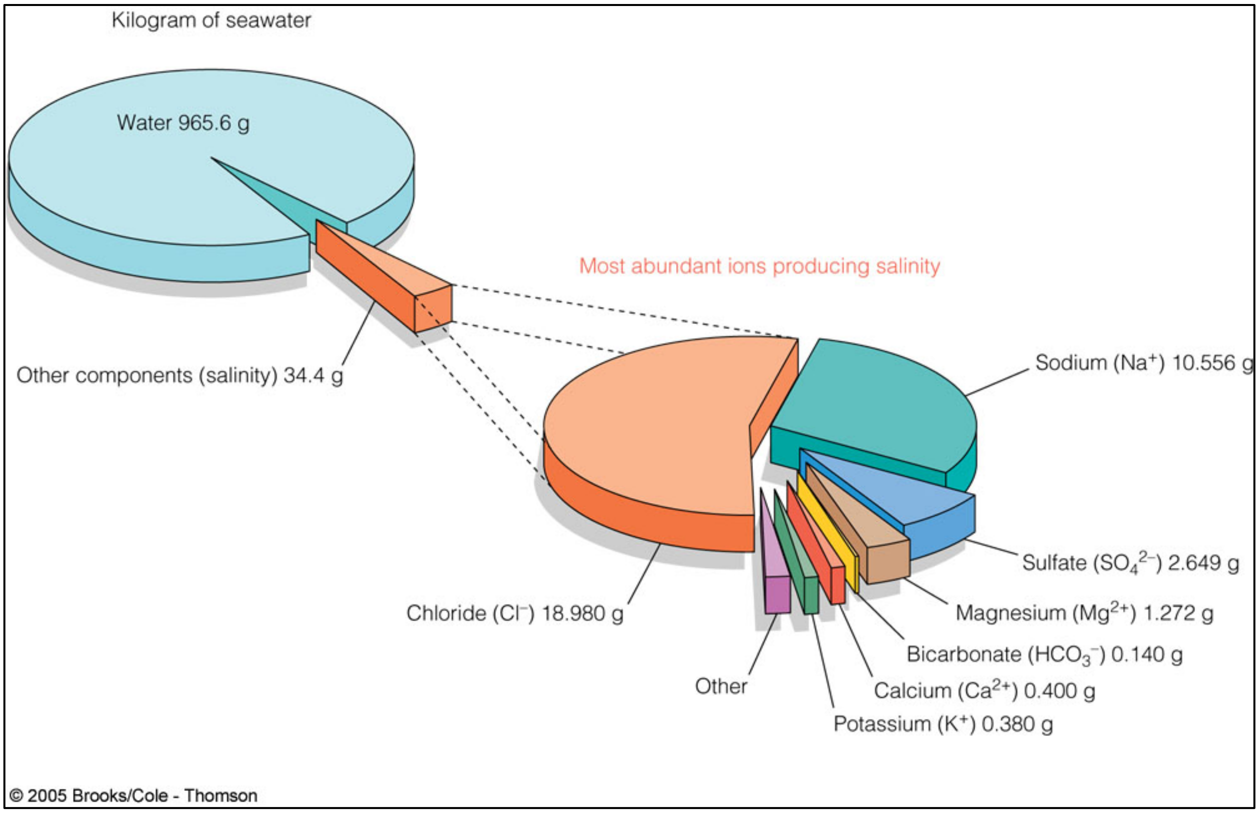


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Figure 3.6: Composition of Saline water

On the basis of Salinity composition these four percentage solutions were prepared for further experiments (Table 3.2).

Table 3.2: Salt Solutions Concentrations

Sr. No.	Conc. (mg/L)	Percentage (%)
1)	1000	0.1
2)	3000	0.3
3)	10,000	1
4)	30,000	3

Solutions were passed through obtained membrane via suction assembly with constant transmembrane pressure of 40 Kpa. Difference between the electrical conductivity (EC) readings of inlet & outlet gave salt rejection results.

Figure 3.7: Electrical Conductivity (EC) Analysis

3.4.3. Flux rate of Acquired Membrane

Water flux is defined as specific volume of water passed through the effective area of the membrane in time (h).

In present study, flux of all prepared membranes was measured at steady state condition and at constant pressure of 40 KPa. Flux rate was calculated using this formula:

Flux rate was calculated using this formula: **$J= Q_p/A_m$**

In case of 3% salt solution;

- Flow rate, Q_p = 0.05L/1h
- Area, A_m = 19.6 cm^2 or 0.00196 m^2
- Flux, J = 25.5 $L/m^2/h$

The data collected at different concentrations was then plotted on the graph and direct relationship was observed.

Flux unit of L/hr/m^2 is usually abbreviated as Lmh and gal/d/ft^2 as gfd.

3.4.4. Flow Rate

Flow rate is basically the volume of a fluid passed through a surface per unit time. It was identified by simple experiment performed on vacuum suction assembly for about 24 hours.

- First of all 3% salt solution was prepared
- Then 50 ml was separated in measuring cylinder
- Membrane was then fixed in the apparatus
- 50 ml salt solution was poured into the cup and time was noted
- Process was repeated at regular intervals to check the flow rate and fouling trend of membrane with the passage of time (t).

Figure 3.8: Flow Rate Analysis of 3% Solution

Chapter 4

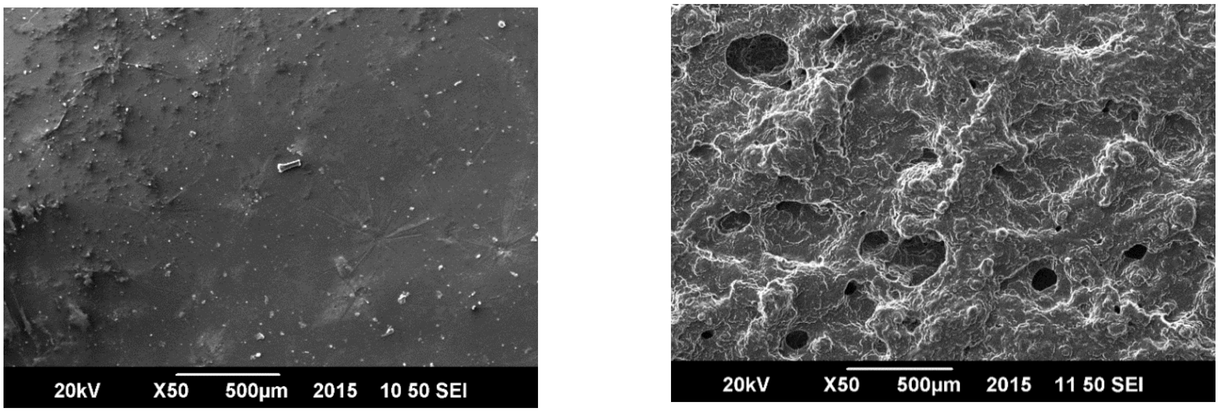
RESULTS AND DISCUSSION

4.1. Characterization of Membrane

4.1.1. Surface Morphology/Pore Size Analysis

Scanning electron microscopy was used to analyze surface morphology of the membranes particularly with reference to surface smoothness between two comparative membranes i.e. with and without addition of polyvinylpyrrolidone (PVP).

These SEM micrographs in figure 4.1 clearly shows the surface morphology of two comparative membranes.



a) PVA/CMC/PVP **b) CMC/PVA**

Figure 4.1: Surface Morphology of the Membrane through Scanning Electron Microscopy

In this figure 4.1(a) homogenous surface can easily observed at just 50% magnification. In other case simple CMC/PVA membrane shows rough surface compartively.

SEM indicates that the surface morphology of acquired membrane is dependent on the type of filler used. Phase inversion process starts when the cast film is immersed into distilled water bath due to low miscibility b/w the polymer and the non-solvent.

Morphology of membranes is effected by the rate of demixing process. Formation of macro voids in membrane structure is sometimes a result of instantaneous demixing. Whereas slow mixing is responsible for denser structure with no macro voids.

With the addition of PVP in the membrane matrix, it can be noticed that the smooth membrane surface was formed and smaller pores were found. On the other hand absence of filler in the casting solution resulted in a rough membrane surface. It can be perceived that the decrease in PVP concentration possibly caused the thermodynamic membrane-forming system to get unstable. That resultantly accelerated the rate of precipitation and the formation of porous membranes (Kim and Lee, 1998).

SEM images had also indicated the pore size at 15000 magnification. Figure 4.2(a) shows acquired Pore Size in the membrane with PVP ranges in nm and it has explicitly shown the range of application where the membrane can be used which is Microfiltration that ranges between 0.1 and 10 micron.

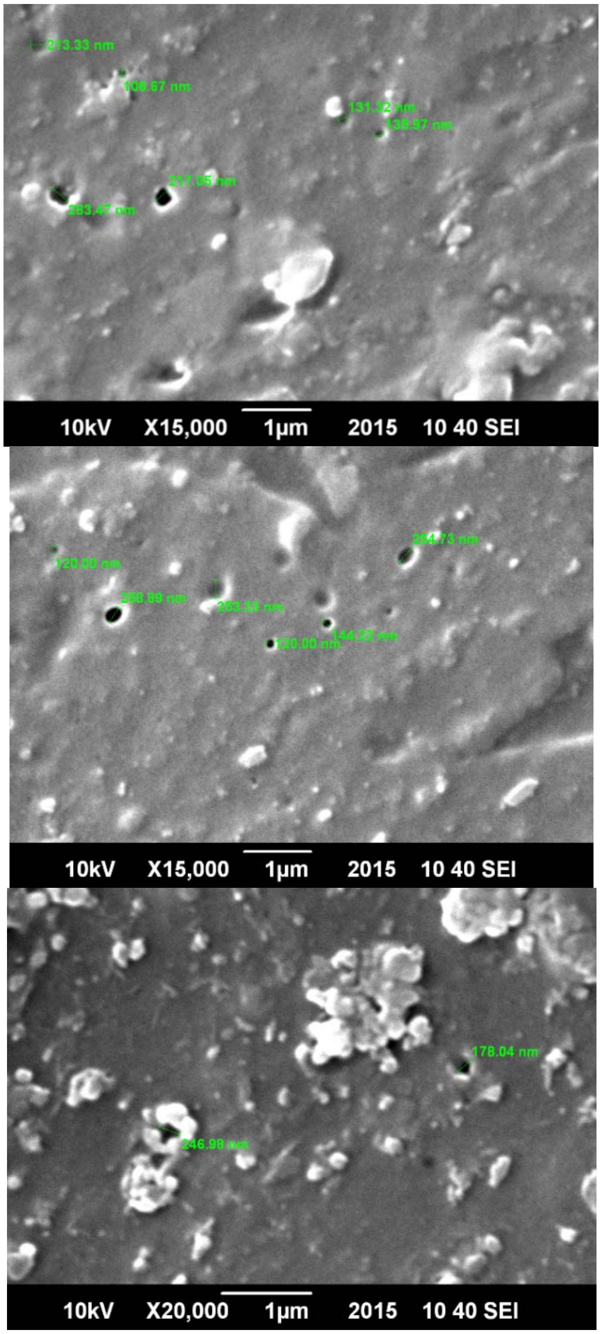


Figure 4.2: Pore Size of PVA/CMC/PVP Membrane at Different Magnifications

The changes in the morphologies can be attributed to the changes in the blend composition by the addition of PVP and different concentrations of PEG mentioned in Chapter 3. We can expect an increased membrane surface hydrophilicity by blending with PEG. I could be due to preferential orientation of carboxymethyl groups towards water during the formation of membrane process (Sajitha *et al.*, 2003). In the present study, the composite of CMC/PVA/PVP as a hydrophilic composition may have intensified the thermodynamic instability of the casted film. Increasing the PEG concentration results in accelerated rate of precipitation in the coagulation bath that ultimately started instantaneous demixing (Idris and Yet, 2006).This results in the development of macro voids at the surface of membrane.

From the other point of view, presence of PEG increases viscosity of the cast film due to higher molecular weight of PEG and intra-molecular aggregations or entanglements of the polymer chains in the presence of PEG (Kim and Lee, 1998). Diffusional exchange rate gets slow down with the increase in viscosity that results in the suppression of macro voids and consequently the development of relatively denser structures.

It can be perceived that the addition of hydrophilic additives in the casting solution, such as PEG, has numerous effect on surface morphology of the membrane. And it is believed that the characteristics of CMC membranes can be improved by adding PEG which will enhance the membrane performance of selectivity and permeability (Han *et al.,* 2013).

4.1.2. Functional Group Analysis

Fourier Transform Infrared Spectroscopy (FT-IR) gave the spectra of acquired membrane showed the presence of moiety functional groups that confirms the substitution occurred between PVA CMC and PVP. Peak at 648 cm^{-1} shows C-O bending vibration. Whereas the peaks at 677 and 618 cm^{-1} are due to out of plane bending vibrations of intermolecular H-bonded O-H group and out of plane Oxygen Hydrogen bending (Samal *et al.,* 2001). While peaks in the region of 1600 cm^{-1} to 1750 cm^{-1} shows C=O double bond stretching vibration which is attributed to the function of PVP (Kolboe and Ellefsen, 1962).

Peak at 858 cm^{-1} is due to N-H wagging which is again attributed to PVP. At 1365 cm^{-1} peak shows C-H rocking vibration which is associated to the deformation of plane in CH groups. At 2920 cm^{-1} peak is due to C-H stretching vibration which belongs to PVA. Peak at 952 cm^{-1} is due to O-H bending vibration which is a characteristic of CMC.

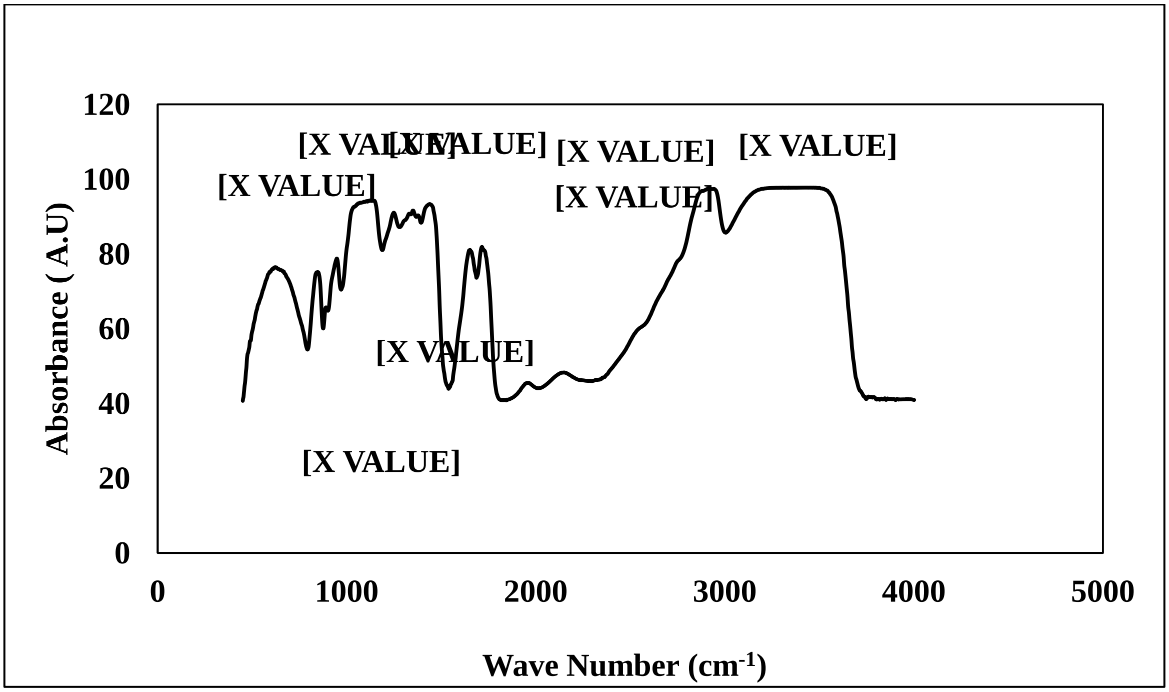


Figure 4.3: FT-IR Spectrum of PVA/CMC/PVP Membrane

The band in the area 1052 cm^{-1} involve the C=O stretching vibration of aliphatic primary and secondary alcohol group present mainly in cellulose, hemicellulose and lignin (Khan *et al.*, 1993). The peak in the region of 3460 cm^{-1} is also due to hydrogen bonded O-H stretching vibrations of CMC. These bands showed the partial dispersion of PVP in PVA/CMC matrix. The FT-IR spectra of PVA/CMC/PVP membrane is illustrated in Figure 4.3.

4.1.3. Thermal Stability Analysis

Figure 4.4 shows thermo-gravimetric curves of two comparative membranes i.e. PVA/CMC and PVA/CMC/PVP membrane. It was observed that the instant onset of weight loss (*T*s) for the membrane with PVP started at about 270 °C, and in simple PVA/CMC membrane weight loss started at 210 °C. These (*T*s) values indicated that PVP addition as an additive results in a membranes with higher thermal stability which is supportive in industrial application.

A working group also prepared simple PVA, PVA with Cellulose and PVA with CMC membranes and weight loss (*T*s) started at 275, 175 and 75 °C, respectively. The TGA presented that the (*T*s$_)$ started at lower temperature in PVA/CMC membranes as compared to other membranes, this could be associated to the fractional oxidation of the OH groups in the polymer chains present in substrate of matrix (Ibrahim *et al.*, 2013).

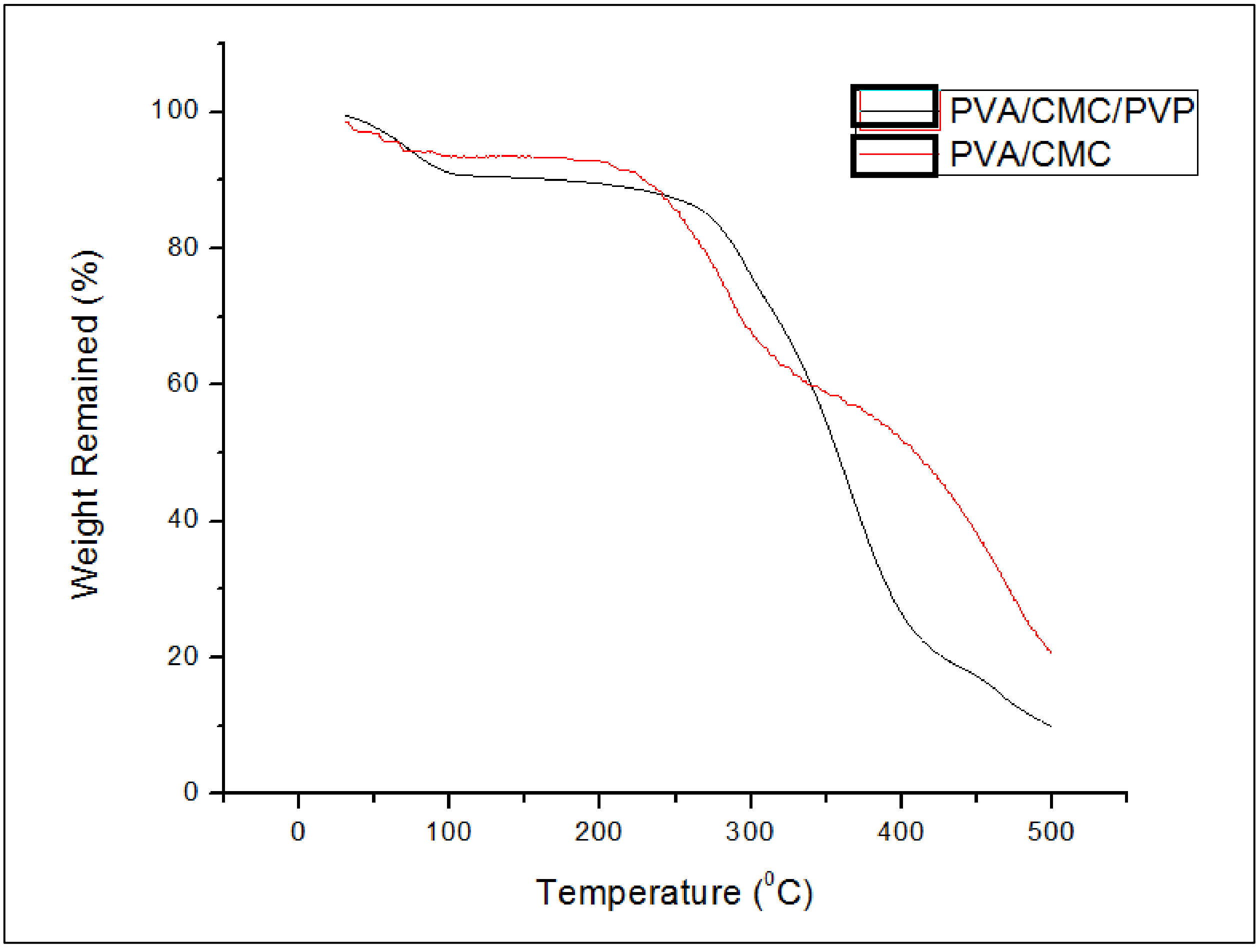


Figure 4.4: Thermo-Gravimetric Analysis (TGA)

4.1.4. Mechanical Strength

The mechanical property of the microfiltration membrane was another major concern for the practical application. This property was analyzed using Universal Material Testing Machine. The graph b/w stress and strain in figure 4.5 shows the maximum value where the membrane starts to fracture.

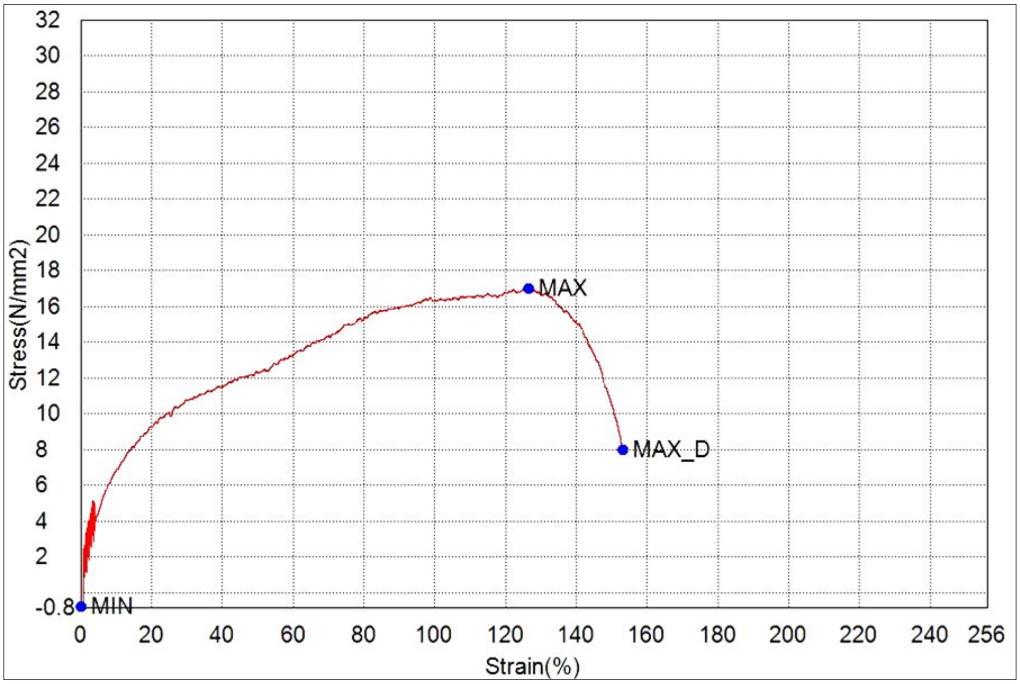


Figure 4.5: Mechanical Strength of PVA/CMC/PVP Membrane

Only the optimized PVA/CMC/PVP membrane was run under this test to find out the maximum stress that can be applied to it during practical application. Simple PVA/CMC membrane was so fragile and unable to undergo test. Maximum stress that membrane can bear was found to be 17 N/mm^2 or Mpa. After this point it started to fracture. MAX-D shows the point at which fracture is completed and it ends up with total breakage.

This result may be associated to the addition of PVP into the membranes that increased the degree of substitution in CMC/PVA. This incorporation ultimately enhanced the mechanical strength of resultant composite membrane. Nevertheless, it could be assessed that the acquired membrane could definitely meet the mechanical requirements for practical application of microfiltration at pilot scale. It was reported that Cellulose acetate/Carboxymethyl cellulose acetate blend membranes were prepared and results for tensile strength were about 4 Mpa under same conditions (Han *et al.*, 2013).

4.2. Physicochemical Analysis

4.2.1. Water Solubility

Soluble parts of the membranes calculated with & without PVP were 0.5% and 9% respectively. Results showed that the addition of PVP effectively reduced the amount of soluble parts present in the membranes that probably suggests that it was due to the decrease in unreacted molecules of PVP which could otherwise definitely leach down into the water. It was reported in literature that solubility in PVA/CMC membrane was 7% while for pure PVA membrane solubility was 68% (Ibrahim *et al.*, 2013). It can be justified that it was due to the absence of crosslinking matrix and substitution. On the other hand membrane with PVP modifier as a filler, high crosslink matrix is formed that reduces the solubility up to 0.5%.

4.2.3. Salt Rejection Analysis

Salt rejection Analysis was performed with three different salts at different concentrations.

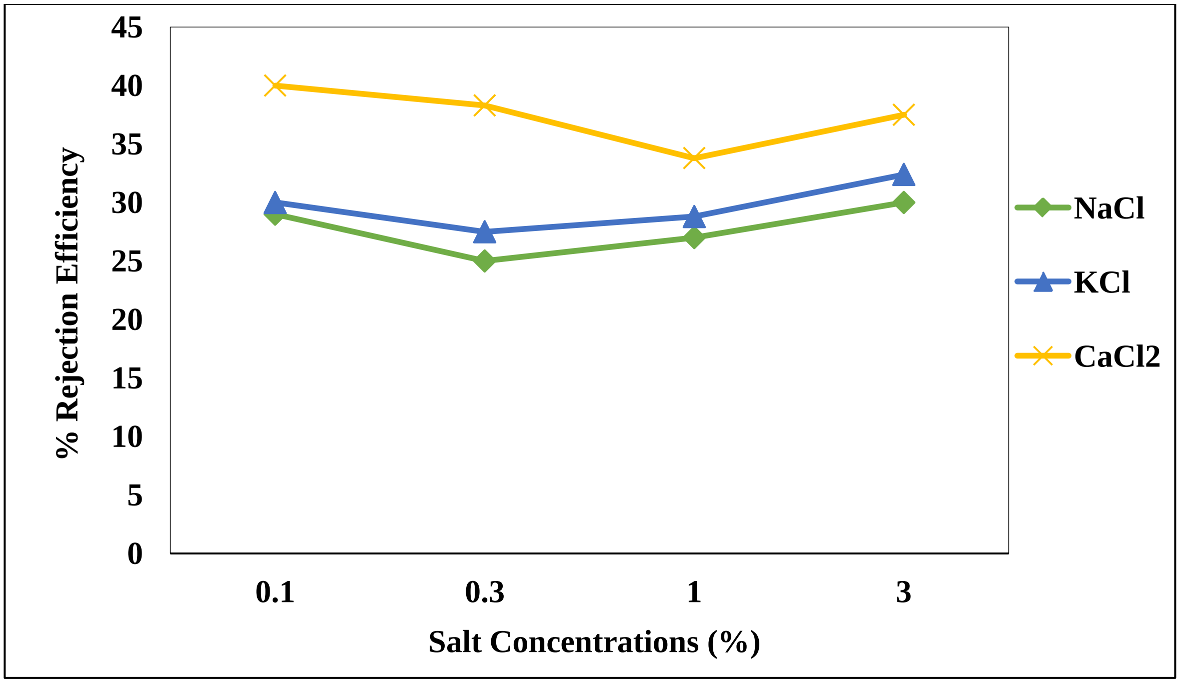


Figure 4.6: Rejection Rate at Different Salt Concentrations

Graphical representation has shown the percentage rejection efficiency at four selected concentrations. As every concentration is 3 times larger than the first one, the trend developed only depends on the efficiency percentage of each concentration.

In case of sodium chloride Average efficiency for all concentrations comes out to be 27.75%. For potassium chloride average efficiency for all concentrations is 29.67%. Which is comparatively greater than sodium chloride rejection efficiency. It is due to the reason that potassium chloride has more molecular mass i.e. 74.5 g/mol as compared to sodium chloride which is 58.4 g/mol. whereas calcium chloride shows average efficiency of 37.42%.

Partially permeable membrane allows selective particles to pass through it, as the size of molecule gets increase, more difficult it becomes to pass through the porous membrane structure.

The trend of increase in salt rejection rate in selected salts i.e. $NaCl < KCl < CaCl_2$ is due to the increase in molecular mass 58.4 < 74.55 < 110.98 g/ mole respectively. The Overall average efficiency for all the three salts comes out to be 30.84% which is considerably helpful in pretreatment for Reverse Osmosis RO. The combined effect of higher recovery and higher flux rate promises to significantly reduce the RO plant costs (Morrison *et al.,* 2002).

4.2.3 Flux Rate

To calculate long-term steady state flux, flow rate was extrapolated to the time axis to achieve time lag. It was observed that there was a long lead time before a steady state was achieved, this shows that first the permeate may started to dissolve or being absorbed which actually delays the time actually required for stable state to be achieved. For which one can mention that the addition of either PEG or PVP as an additive, plays an important role in the overall membrane properties (Ibrahim *et al.,* 2013).

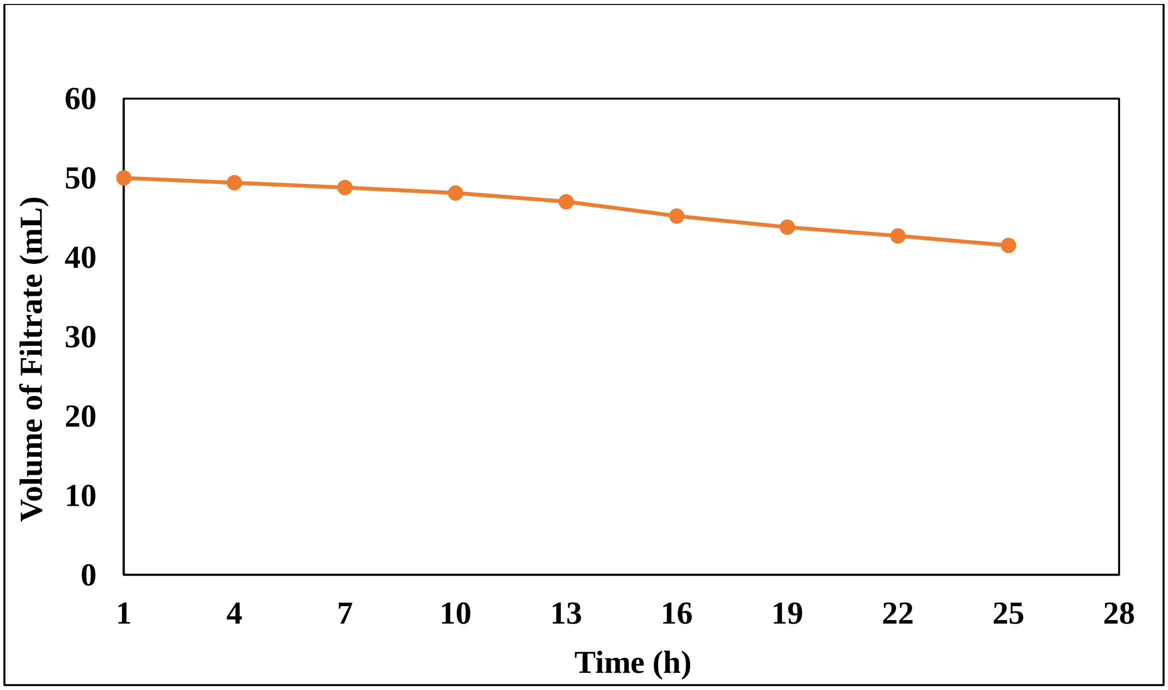


Figure 4.7: Change in Flow Rate as a Function of Time

Graphical illustrations showed that after 24 hours fouling occurred about 17 percent. Membrane fouling could reduce the permeation efficiency and restrict the wide application of microfiltration membrane.

Permeation efficiency is reduced to membrane fouling that restricts its wide application in microfiltration technology. Hydraulic cleaning is offered to improve membrane flux (Zhao *et al.*, 2011). Other anti-fouling agents are also in use to enhance membrane's function and to increase its life.

The flux decline behavior of the CMC/PVA/PVP blend membranes during filtration at 40 KPa were depicted in Figure 4.8. This result demonstrated that there is an inverse relationship b/w flux and concentration of feed solution i.e. higher the concentration of feed solution lower is the flux recovery. Minimum flux was 26 L/m^2/h which was observed at highest feed concentration that was 3% and maximum was 50 L/m^2/h.

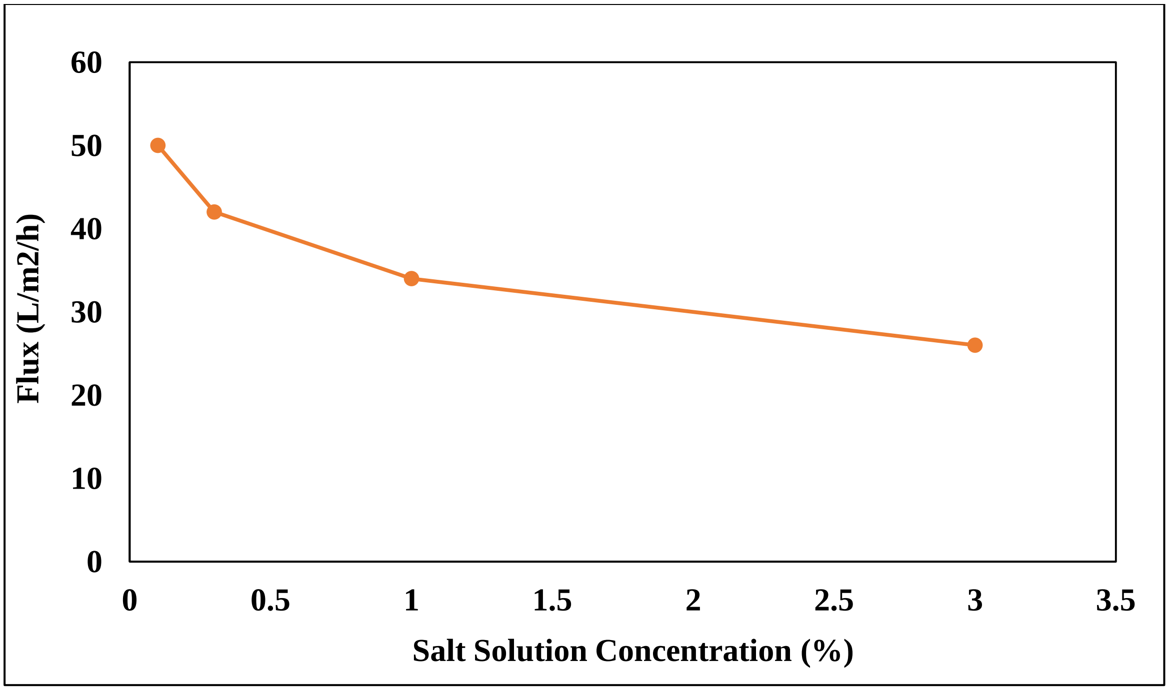


Figure 4.8: Change in Flux as a Function of Feed Concentration

It has been reported many times in literature that flux rate decreases with the increase in feed concentration in filtration membranes due to fouling. It was reported in literature that cellulose acetate and carboxymethyl acetate blend membranes gave pure water flux of 56 L/m^2/h.

It was reported that sea water clarification pre-treatment tests used membranes of instant fluxes lower than 100 L/m^2/h (Ibrahim *et al.*, 2013). With the addition of PVP modifier in the blend component, the flux recovery ratio (FRR) increased which is due to the increased hydrophilicity .It was also reported long-term seawater pilot testing and used 0.1 um filtration membrane for RO pretreatment desalination systems that confirms the application of membrane (Han *et. al.*, 2013).

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the research work described above, it is concluded that:

1. Fabricated Carboxymethyl Cellulose/ Polyvinyl alcohol/ Polyvinylpyrrolidone composite membrane is micro porous in nature.
2. PVP has positive effect on surface morphology, thermal stability and mechanical strength of the acquired membrane.
3. Pore size falls in the category of Microfiltration, hence the membrane can be used as a pre-treatment to Reverse Osmosis.
4. Salt rejection efficiency of the acquired membrane ranges from 27 to 37%.

5.2 Recommendations

Following are some of the suggestions for carrying forward the work reported in this thesis:

1. Anti-Fouling techniques can be studied to improve membrane performance
2. Effect of pH can be investigated to mitigate organic fouling
3. Membrane can be prepared with antiseptic properties that can perform dual function of salt rejection as well as disinfection of water

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