

Impact of Poly Vinyl Alcohol on Support Layer of Commercial Thin Film
Composite Membranes: Enabling use of Reverse Osmosis Membranes
in Forward Osmosis

by

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ABSTRACT

In today's world where sustainability is of prime importance, energy efficient method for sea water desalination and waste water treatment is gaining attention. State of art Reverse Osmosis (RO) method has high power consumption; hence people are diverting their attention towards Forward Osmosis (FO). It has been determined that the support membrane hydrophilicity plays an important role impacting the water flux through membranes in forward osmosis processes. The support layer of commercially available thin film composite RO membranes has been modified with a hydrophilic polymer Polyvinyl Alcohol (PVA). Previous research has demonstrated that PVA coating of the top selective layer of RO membranes has decreased selective layer roughness and increased selective layer hydrophilicity. The role of PVA with 2 different PVA cross-linkers: Maleic Acid (MA) and Glutaraldehyde (GA) at 2 different concentrations of 10% and 50% have been investigated. The hydrophilicity, water flux, salt flux and rejection of the neat and modified membranes in Reverse Osmosis and Forward Osmosis are measured. Maleic Acid when used with PVA at a lower degree of cross linking (10%) shows significant improvement in water flux in SW membranes in comparison to Glutaraldehyde crosslinked PVA coated membranes. This improvement is not so significantly observed in BW membranes due to its lower porosity. PVA when used with a small amount of crosslinker shows promising results in increasing the hydrophilicity of TFC membranes enabling RO membranes to be used efficiently in FO processes.

DEDICATION

To my parents

Aniruddha Saraf

Shubhada Saraf

And Sister Apoorva Saraf

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1. INTRODUCTION

1.1 Background

Over the years as the population is increasing it is becoming more difficult to fulfill our water needs. In many places most of the usable water flows into the sea with very little potable water remaining. Transportation of water from one place to another is also not a very economical option. Oceans account for 97% of water on earth which is unusable. The surface water and water melted from glaciers are the two main sources of drinking water, which account for less than 0.4% of total water.

Many techniques have been used to increase the clean water supply. Waste water treatment has been given a lot of importance because it will not only help us increase our water supply but also prevent further water pollution. Treated waste water can be used in irrigation, as a drinking water source and in semiconductor industries for manufacturing and other such purposes. Brackish water which is not as polluted as sea water can also be treated by this method.

It is thus imperative to recycle impaired water (e.g.: saline water and waste water) to meet its increasing demand. Currently the processes used to reclaim waste water are multistage flash distillation and reverse osmosis technique. The distillation technique is popular only in regions where energy production is not an issue [1].

Reverse Osmosis technique has been popular and continuous efforts have been taking place to optimize it to be very efficient in giving very clean water without

utilizing a lot of energy. To know reverse osmosis we need to understand the concept of Osmosis. Osmotic processes are capable of recovering water from these impaired resources. Osmosis is a natural phenomenon which when engineered depending on its pressure gradient character can be used in various areas. These areas include Water Treatment, desalination, power generation etc. The different types of Osmosis are Forward Osmosis, Reverse Osmosis and Pressure Retarded Osmosis [2].

Any osmosis requires a membrane. It is any material capable of separating one substance from another: organic or inorganic, natural or synthetic. In Osmosis various synthetic polymeric membranes have been studied to separate water from various aqueous solutions. The state of art membranes used for water treatment are efficient in Reverse Osmosis Processes [3].

1.2 Reverse Osmosis:

1.2.1 Definition:

Osmosis is a natural phenomenon in which a solvent passes through a semi permeable barrier i.e. through a membrane from the side with lower solute (generally salt) concentration to the higher solute concentration. Solvent (water) flows till there is equilibrium between the two sides. Equilibrium is a state when the chemical potential or the gravitational potential on both sides of the solution is the same. The pressure difference between the two sides of the membrane is equal to the natural osmotic pressure difference or osmotic gradient of the solution. Now for desalination we want to remove the salt concentration i.e. we want water

(solvent) to travel from a region of high salt concentration to a low salt concentration. To achieve this, pressure greater than the osmotic pressure difference between the two sides is applied to the salt water. Thus water from the solution flows from high concentration of solute (salt) to a low concentration. This phenomenon of applying external hydraulic pressure is called Reverse Osmosis and is used widely in Desalination, Water Treatment Purposes etc [4].

Unlike many conventional separation techniques like distillation or Ion Exchange, Reverse Osmosis set up is simple in design. RO can handle separation of organic as well as inorganic substances at the same time. Reverse osmosis is a pressure-driven process. Hence there is no chemical change or any heat exchange, phase change process [3] .

A reverse osmosis membrane acts as the semi-permeable barrier to flow of solute in the RO process. It allows selective passage of a particular species like the solvent water while partially or completely retaining other species (solutes). RO can separate solute particles as small as 0.1 to 1nanometer [3] .

1.2.2 RO Process Lab Scale System:

There are 2 types of RO systems: cross flow filtration system and a dead end filtration system. We use the dead end filtration type. In dead end filtration system pressure is applied to a salt solution in a closed container and the clean water coming out of the nozzle is collected as permeate. RO system used in our lab is the Sterlitech HP 4750 which consists of a high-pressure stirred cell that is both chemically resistant and features a low hold-up volume (1 Liter) to perform a

wide variety of membrane separations. It allows high-pressure operation up to 1000 PSI and a unique design that allows for fast membrane change-out. The water flow through the membrane is reported in terms of water flux (J_w)

$$J_w = \frac{V}{At}$$

Where; V: volume of permeate collected

A: Active membrane area for the system is 14.6 cm².

T: time in which the permeate is collected

Solute separation is measured in terms of rejection (R)

$$R = 1 - \frac{C_p}{C_f}$$

Where; C_p: conductivity of permeate

C_f: conductivity of feed

1.2.3 RO Membrane Materials and its properties:

Materials used to make RO membranes depends upon the nature of work for which it is going to be used. Chemical as well as the physical nature of the polymer determine the membrane production. A good RO membrane should be resistant against chemicals and microbes. It should be mechanically and structurally stable over a long period, and a very high selectivity for certain solutes. These membranes are generally hollow fiber or flat. They are incorporated in modules to give maximum surface area per unit volume of the membrane. These hollow membranes are generally grouped in bundles and then used in the RO process [5].

The most commonly used RO membrane materials are Cellulose Acetate, Polyamide, any heterocyclic polymer, crosslinked water soluble polymers and polymerizable monomer (formed by crosslinking), Polybenzimidazole, Polyacrylonitrile, Poly-piperazinamides etc.

But they are broadly classified into 2 groups: asymmetric membranes containing one polymer, and thin-film, composite membranes consisting of two or more polymer layers [3].

Cellulose Acetate Membrane is the most well known asymmetric or anisotropic membrane structure invented by Loeb and Sourirajan in 1960. It has a very thin solute rejecting layer on a coarse supporting layer [3]. The supporting layer is also generally made up of the same material as that of the selective layer but the thickness of the selective dense layer determines fluxes and rejection and the overall performance of the membrane. The supporting layer just offers mechanical strength to the membrane. These membranes are generally prepared by non solvent- induced phase inversion or polymer precipitation method. Loeb Sourirajan made the first asymmetric cellulose acetate membranes for RO. Problem with asymmetric membranes is that they are very thin of about 0.1 to 1 μm , hence they give extremely high fluxes without efficient rejection [3].

After cellulose acetate was the era of linear aromatic polyamide membrane. It eliminated some of the disadvantages of cellulose acetate membranes. Along with cellulose acetate membranes even linear aromatic polyamide membranes became popular. Polyamide is one of the most efficient selective layer known today. They

have a high rejection performance which can be used for single state sea water desalination. But still these membranes were as thin as cellulose acetate membranes (0.1 to 1 μ m) thick and high fluxes problem persisted [3].

The state of art membranes in Reverse Osmosis are the thin film composite membranes. They were discovered by Cadotte and his coworkers in 1970s. It consists of a dense active layer of about 200 nm upon a porous polymer support. A nonwoven fabric is attached for support. The porous support layer is generally 50 μ m in thickness. The support layer controls all the water flux, salt flux and hence the water and salt molecules transport phenomena. The non woven support fabric is approximately 120 μ m thick and is responsible for handling the high hydraulic pressures during Reverse Osmosis process. Hence the mechanical strength of the support fabric needs to be high. Polysulfone, polycarbonate and poly (phenylene oxide) are the three well known polymeric substrates available in RO industry. Polysulfone has the best performance and is highly used commercially [3].

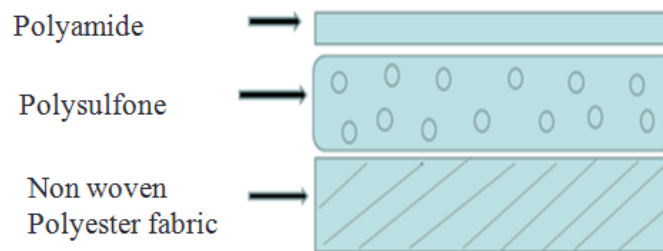


Figure 1: Structure of a Thin Film Composite Membrane

These membranes are prepared by interfacial polymerization i.e. polymerization at the interface of two immiscible liquids. The polymeric substrate is immersed in

an aqueous solution of amine monomer. Then it is immersed in acyl chloride monomer for the interfacial polymerization to take place. This leads the formation of very thin highly selective polyamide rejection layer on the polymeric substrate.

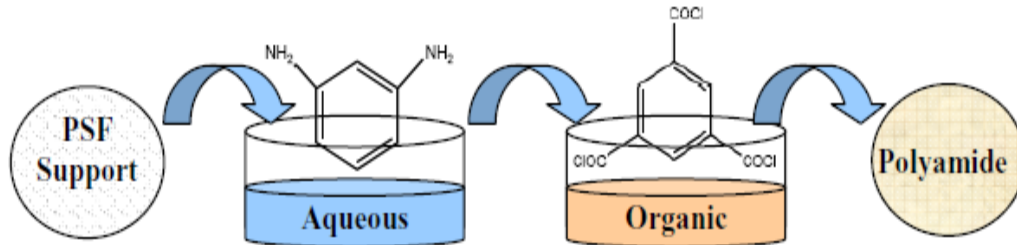


Figure 2: Formation of TFC Membrane [6]

The TFC membranes offer high water molecule transport rate, very good mechanical properties and stable over a wide pH range. They have very high rejection. However the fouling of TFC membranes is a very severe problem in the industry [7]. Various methods have been used to optimize the thin selective layer to reduce fouling [8]. Yet there are various other problems associated with RO applications currently.

To know the problems in RO plant one has to know the working of a typical Reverse Osmosis plant. First the saline feed water is sent to a pretreatment plant. In this stage all large particles are removed which could clog the membrane and reduce its functioning. The saline water is then pumped at a high pressure using hydraulics to the membrane assembly where salt and other minerals are removed by the process of reverse osmosis. After the membranes have done their work the water is released in 2 streams the feed water and the brine water which is generally discharged. A post treatment is done to stabilize the feed water [6].

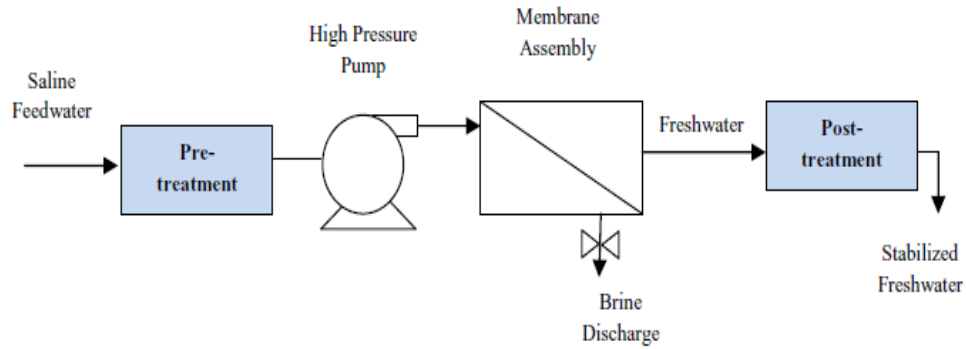


Figure 3: Working of Reverse Osmosis Plant [6]

1.2.4 Problems arising in RO processes:

Although the TFC membranes have set a new standard in RO processes they suffer from compaction effects under pressure. If the applied hydraulic or hence the water pressure increase the polymers get reorganized in a different orientation that results in a lower porosity and ultimately effecting the performance of the membrane [9] .

Surface or internal fouling of membranes is a very common problem. Fouling is the deposition of foulants on the membrane surface. Foulant is any specie (mainly solutes) which interacts physically or chemically with the membrane. They can be organic, inorganic bio compatible or colloidal. They strongly interfere with the passage of solvent (water) through the membrane. They deteriorate membrane performance and reduce its life span. Thus membranes need to be replaced frequently leading to high operating costs [7]. The main cause of fouling is the high pressures involved in reverse osmosis [10]. Reverse Osmosis is always opposite in direction to the natural water flow gradient. Naturally water flows from a region of low solute concentration to high solute concentration. In reverse

osmosis we force water out of a region of high solute concentration. For this a pressure significantly higher than the osmotic gradient of water is required. Considerable hydraulic power is required for the same. This further increases operating costs. Feed water recovery is also limited in RO which makes the brine discharge highly concentrated. This can have large environmental impacts on usage in coastal regions [11].

1.3 Forward Osmosis

1.3.1 Definition

Off late Forward Osmosis has been gaining popularity as an alternative method for desalination, water treatment and energy production [12]. Forward Osmosis is same as the natural phenomena of osmosis where water flows from solution of low concentration of solute to a high concentration of solute. A concentrated draw solution creates an osmotic pressure gradient across a membrane. The path of water is naturally from low solute concentration to high solute concentration. The draw solution can be recycled or discarded. The osmotic pressure gradients can be so high that there might not be a need of hydraulic pressures like in RO. This phenomenon occurs naturally when fresh water combines with sea water and it is termed as Pressure Retarded Osmosis (PRO) [11]. Thus it has proved to be quite advantageous to use FO or PRO operations for desalination and other purposes. Feed water recovery can be improved. For various contaminants the rejection capacity of these membranes is high in FO. They have lower membrane fouling tendency. This is because the only pressure involved in FO is by the flow

resistance of membrane module or the pressure gradient. The external hydraulic pressure which causes a lot of fouling can be eliminated in FO processes. The design is simple and the membrane support is not a big issue like RO. Hence fouling is reduced. Operating costs are low as the hydraulic pressures are not required as in RO. Energy consumption from an external power driven source can be neglected. Hence FO also finds applications in power generation processes. It can also be efficiently used in processes where we need to avoid high pressures and temperatures [10].

While all these advantages exist theoretically we need to concentrate on the membranes currently being used for FO processes. The current RO membranes when used in FO or specifically made FO membranes do not produce expected water fluxes in FO systems. As per the natural osmotic pressure gradients calculated very high water fluxes should have been achieved. The RO membranes designed so far have been made such that they work well under the conditions of pressure driven process, however their performance is not up to the mark when they are used for osmotically driven processes. Hence we need membranes specifically designed for FO purposes [12].

1.3.2 FO Process Lab Scale System:

The FO system used in the lab is a cross flow forward osmosis system.

The water flux in the system is calculated by:

$$J_w = \frac{M/\rho}{A \times T}$$

M refers to the change in mass of draw solution in time T

ρ is the density of water at that temperature

A: area of the membrane = 0.00194 m²

Salt flux is calculated depending upon change in conductivity of feed before and after the flux test [12].

1.3.3 Important factors affecting performance of membranes in RO/FO Processes:

1.3.3.1 Concentration Polarization

1) Concentration polarization in RO:

In RO concentration polarization effects are seen only on the feed side of the membrane. This is because we consider the mass transfer on the feed side of membrane which is pressurized. Convective forces cause the solute to flow from the bulk solution to the surface of the selective rejecting layer. Water permeates through but the solute remains on the surface at high concentrations. The water flux or the pressure with which water passes through the membrane has to be more than the pressure caused due to this salt layer concentration. This deposition of salt on the surface which affects the water flux through the membrane is termed as Concentration Polarization rather external concentration polarization. This is also one of the reasons why higher external pressures are required in RO [10, 11].

2) Concentration Polarization in FO:

In FO there are more complications. Unlike in RO we need to concentrate on mass transfer on both the sides of the membranes. Before knowing the problems let us know the membrane orientations in FO. There are 2 orientations 1) FO: The

active layer faces the feed solution while the support layer faces the draw solution. 2) PRO: (Pressure Retarded Osmosis Mode) The active layer faces the draw solution while the support layer faces the feed solution [13]. Based on this there are 2 kinds of concentration polarization: external and internal in FO.

External Concentration Polarization: When the feed solution flows along the active layer of the membrane (FO orientation) solutes built up at the active selective layer. This process is called concentrative external CP which is exactly same as CP we mentioned in RO pressure driven process. At the same time the draw solution is in contact with the support layer which is the permeate side. The salt molecules cannot pass through the support easily. Hence this permeate side is being diluted as water flows from the active layer to the support layer on draw side. This is referred to as dilutive external CP [10]. Here the convective force of water drags the dissolved salt away from the membrane. Thus the effective driving force of the draw solution is reduced [11].

Internal Concentration Polarization: When the porous support layer is facing the feed solution (PRO Orientation) water enters the support and diffuses across the active layer into draw side. But the salt cannot easily penetrate through the active layer and hence the concentration inside the porous layer increases. A polarized layer is formed along the inside of the dense active layer as water and salt travel through the porous support [10]. This is referred to as Concentrative internal CP.

Ideally a good FO membrane should have minimum internal concentration polarization, high water flux, minimum salt flux, chemical and mechanical stability and hydrophilic nature to reduce fouling and thus enhance performance.

Also it should be compatible with the type of draw solution used [10]. It is tough to measure Internal Concentration Polarization of a membrane but we can optimize to achieve a good water flux. A high water and salt flux is indicative of the fact that water and salt molecules are easily able to travel through the membrane meaning there is less internal concentration polarization.

Another problem associated with state of art Forward Osmosis membranes is lack of membranes with hydrophilic support layers.

1.3.3.2 Membranes with Hydrophilic Support Layers:

There are no membranes designed specifically for forward osmosis process which are osmotic gradient driven. The membranes available commercially have a highly selective polyamide layer supported by porous substrate. This porous substrate not only causes internal concentration polarization but also its hydrophobicity leads to lower water fluxes. The major challenge faced by FO membrane users today is the low water flux than anticipated. Hence we need to concentrate on increasing the hydrophilicity of the support [14]. In pressure driven RO processes the water need not wet the support completely to ensure high water fluxes. However in osmotic driven FO processes the support layer must be wet to ensure easy travel of water through it. For this hydrophilicity of the support layer is necessary as the water loving polymer allows the water molecules to pass through the membrane surface easily. If the support layer is not wet then the trapped air in the pores of the support can cause further internal concentration polarization. This will lead to further lowering of water flux and fouling of membranes. In the past work by Mc- Cutcheon et al has showed that improving

the wetting of the support layer i.e. the hydrophilicity results in a significant increase in water flux in FO processes [14].

One has to know that the entirely hydrophilic polymer cannot be used in TFC membranes as they cannot function as a very efficient support. Hydrophobic substances work better in imparting mechanical strength to the membrane. An entirely hydrophilic support would swell up in water and may even plasticize. The swelling property might differ from solution to solution say water or salt or alcohol etc. This may lead to post fabric perforation [12]. Thus we need a membrane which is hydrophobic to impart the required strength along with a polymer to impart hydrophilicity later to enhance its performance in the FO process. Also the hydrophilic substances interfere with the process of interfacial polymerization say for ex Polyamide on Polysulfone. Its interaction with the amine monomer changes polyamide properties. Hence a perfect balance needs to be struck between hydrophobicity and hydrophilicity of any membrane. It is advised that hydrophilicity is imparted after the polyamide has been formed on the hydrophobic support as then the hydrophilic polymer shall not interfere with the chemistry of polyamide selective layer [15].

2. LITREATURE REVIEW

2.1 A review of FO membranes

Before 1960's many materials like pig bladders, cattle fish, rubber porcelain etc have been tried as FO membrane. With time membrane sciences developed and Loeb-Sourirajan process gave us defect free, high flux anisotropic RO membranes. These were mainly the asymmetric aromatic polyamide membranes. Various studies have taken place to try to use these RO made membranes for FO (and PRO) processes. However they showed lower fluxes than expected. Then came in the time where in house cellulose acetate membranes were used to treat sea water by FO.

The state of art FO membranes are the ones produced by Hydration Technologies Inc. (HTC). In 1990 they were developed by this company. They are thought to be made up of cellulose triacetate (CTA). These membranes are about 50 μ m thick and consist of a polyester mesh embedded in the CTA polymer for mechanical support. These membranes have performed well in the FO systems and there structure is pretty different from the RO membranes used. These FO membranes are relatively very thin and unlike RO lack a fabric support layer [10].

Rather than to investigate the use of asymmetric RO membranes further in FO and enable them to perform better, research needs to be done on the use of thin film composite RO membranes in FO processes. The current TFC RO membranes (which are tried using for FO) they show considerable resistance to diffusion

through the membrane. This causes a very high internal concentration polarization and hence a low water flux [10] .

We learnt that a good FO membrane should be highly dense at the active layer and yet thin. The TFC FO membranes should be thin, extremely porous and should have low tortuosity. Thus the solute particles will have a short path from bulk draw solution to the active layer of the membrane. If the thickness of the unstirred boundary layer of the membrane is reduced the membrane performance can be improved. Or to optimize the membranes to achieve high water flux, various chemical changes would need to be made in the support structure of the TFC membranes [16].

The main aim of this thesis is to aid to the research been done in the TFC- FO membranes that try to reduce internal concentration polarization and fouling by imparting hydrophilicity.

Widjojo et al. developed a sulphonated polymer as the substrate for TFC-FO membranes. The sulphonated polymer imparted sponge like structure which induced hydrophilic properties to the support by allowing better absorption of water and resulting in imparting anti fouling characteristics [17] . Yip et al. worked on similar lines were a mixture of figure like and sponge like morphology was induced in the support layer by modifying the casting process to yield high performance forward osmosis membranes [18].

In 2010 Su et al. tried to develop Cellulose Acetate (CA) hollow fibrous membranes specifically for FO applications. Their water flux and rejection results

indicate that CA can be promising to make FO membrane support layer. CA is also hydrophilic in nature which makes it a good membrane for FO [19]. Cellulose acetate membranes have also been developed by Zhang et al [20]. Polybenzimidazole (PBI) has also been tried to be developed on FO membranes. It is known for its mechanical strength, chemical stability, hydrophilicity and non fouling nature. Hollow fiber membranes made from PBI have also shown promising results in FO applications [21]. Later on Poly-Ether-Sulphone and poly-vinyl-pyrrolidone (PVP) was incorporated with PBI to further improve its performance. PVP is necessary to enhance hydrophilicity [22]. A thin film composite membrane was made with a very thin polyamide layer, and a polyether- sulphone substrate layer was formed. These membranes had water fluxes comparable to commercial state of art FO membranes by HTI. Also their hydrophilicity was more than HTI FO membranes [23] .

2.2 Inspiration for this work

In 2011 Arena et al. coated the support layer of commercial thin film composite RO membranes with Polydopamine (PDA). Tests were performed in RO as well as PRO (FO) mode. This support layer modification improved the water and salt flux compared to the neat RO membranes. The research proved that the hydrophilic nature of PDA had improved the performance of RO membranes when used in FO applications [12]. This paper was our inspiration to study the effect of a hydrophilic polymer on support layer of TFC membranes.

Structure of Polydopamine: It is a bio-inspired polymer and can adhere to substrates under water very well. This trait is similar to the adhering properties of mussels. It is prepared by polymerization reaction using low concentration of dopamine in an aqueous solution. Recently it has been used to impart antifouling characteristics to water treatment membranes. Previous research indicates that Polydopamine was applied to selective layer and increase in hydrophilicity was observed. It is also known for its antifouling nature where it prevents the adhesion of proteins and other foulants on the membrane surface. It is well known to prevent oil / water foulants from contaminating the membrane [12, 24].

There is no one structure of Polydopamine which is proposed. Various research groups have been studying trying to know the exact structure of Polydopamine. It consists of various benzene monomer units attached together, with OH (hydroxyl) and NH (amine) groups attached to it. One can say that the attached OH group would be responsible for enhancing hydrophilicity [25].

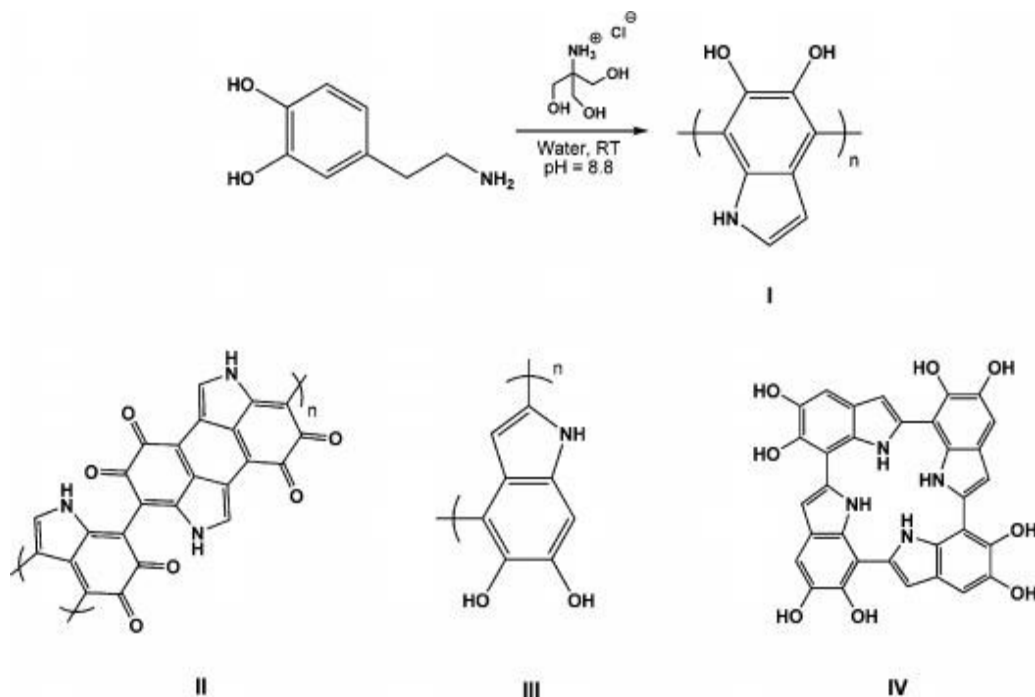


Figure 4: Structure of Polydopamine as proposed by Messer smith and others [25]

If we notice all the work done in improving membrane performance for FO, the support layer hydrophilicity has a high impact to reduce concentration polarization and fouling. Arena et al inspired us to try coating another hydrophilic polymer at the support layer of TFC-RO membranes to use in FO. Here we proposed the idea of experimenting with Polyvinyl Alcohol, an inexpensive and easily available hydrophilic polymer to coat on support layer.

2.3 A review on work in PVA in membranes

Let us have a survey on how PVA has been used in the membrane industry so far. Thin film composite membranes have been made by Gohil et al. with Polysulfone support and polyvinyl alcohol rejecting layer. With sufficient crosslinking with Maleic acid these membranes were efficient in removing sulfates from brackish

water when used for desalination [26]. Similar tests have been conducted by Lang using different crosslinkers where again PVA was used as the rejecting layer [27]. Li et al. used a dead end filtration system to coat PVA on internal as well as external surface of porous Polysulfone layer. These membranes were tested for ultra-filtration to see their resistance against fouling. The resulting membranes showed high antifouling characteristics as compared to non PVA coated ones [28]. Peng and group made very thin and defect free hydro-gels and casted them on Polysulfone layer. Transport properties of the membrane improved after doing so [29]. They used the same recipe to demonstrate that polymer free volume is necessary to make sure effective transport of solute molecules takes place through the membrane [30]. Yang et al. did electro spinning of PVA to form slightly soluble nanofiber membranes which showed success in water durability tests [31]. Zhang et al made ultra-filtration membranes only from hydrophilic polyvinyl alcohol. The resulting membranes showed high rate of permeation and good retention of BSA and reduce protein fouling [32]. Zhang and group also tried to immobilize PVA on a non woven fabric. Protein fouling tendency was decreased significantly [33]. In all these studies mentioned above PVA has been mainly used as a rejecting layer to improve antifouling properties of membrane in desalination or protein rejection studies. Here in our research we will try imparting PVA not on the selective rejecting layer but rather at the porous support, at the interface of polymeric support and PET nonwoven fabric.

3. MATERIALS AND METHODS

3.1 Polyvinyl Alcohol:

It is a water soluble biodegradable synthetic polymer which is mainly used to be coated on the hydrophobic support layer because of its hydrophilic nature. PVA, a 1, 3-diglycol polymer with a monomer molecular weight of 44, is an excellent hydrophilic membrane material [34]. Unlike other members of the vinyl group this polymer is not prepared by a polymerization reaction but rather it is prepared by hydrolysis of polyvinyl acetate in an alcohol solution. Due to this reaction a free radical mechanism takes place and the acetate ion is removed in the hydrolysis reaction. The product polyvinyl alcohol has same degree of polymerization as the reactant polyvinyl acetate. By varying the degree of acetate used we can have different grades of polyvinyl alcohol formed. The product alcohol is generally 87-99% hydrolyzed alcohol. Under these conditions a polyvinyl has 30-40% crystallinity. PVA is an atactic material which means its secondary alcohol group positioning is random. It shows crystallinity as the hydroxyl groups are small enough to fit into the lattice of any structure without causing any damage to it. Atactic also means that the positioning of side chains of secondary alcohol is random. This crystallinity is disrupted by crosslinking [35]. Degree of hydrolysis has a huge impact on crystallinity. The more hydrolyzed the PVA is more the crystallinity it exhibits. This also indicates that more the residual acetate groups less is the crystallinity. The existence of polar hydroxyl groups makes Polyvinyl Alcohol hydrophilic in nature.

It dissolves quickly in aqueous solutions. It has very good film forming properties. Its water loving nature makes it resistant to oils and greases, hydrocarbons or animal fat etc. It has good tensile strength along with flexibility. It is well known for its physical and chemical stability against organic solvents [27]. With more humidity polyvinyl alcohol can absorb more water.

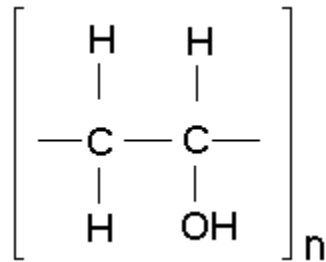


Figure 5: Structure of Polyvinyl Alcohol [35]

The PVA skin layer provides the membranes with high water permeation rate, good anti-fouling nature, excellent integrity in acidic and alkaline environments and significant resistance to abrasion. Thus to increase the hydrophilicity we use this water loving polymer and its coating at the porous Polysulfone support layer. We hope that it will aid free movement of water and salt molecules through the membrane. Our aim is to make PVA not only an agent to show increase in hydrophilicity but to reduce the internal concentration polarization of the support membrane [28]. Various techniques have been employed in the past to coat PVA on the selective polyamide layer using various crosslinking agents like aldehydes, dialdehydes and Maleic acid, Succinic, Suberic, Malic acid etc [29].

But why do we need crosslinker? The prepared coated membranes are stored in deionized water. But in the absence of a crosslinker PVA is an extremely water soluble polymer, hence it does not stay on the membrane. It dissolves in the water

and hence the coating becomes ineffective. PVA swells a lot in an aqueous medium and this may lead to a highly open pore structure. This has a lot of impact on the membrane performance. Because of this the membrane rejection quality decreases. A balance between hydrophobicity of PSF and hydrophilicity of PVA can be well established by the crosslinking. Crosslinkers react with the OH groups of the PVA individual units and helps maintain its stability on the membrane, a property useful especially while storage in aqueous systems [26]. There are 3 types of crosslinking which are assumed to take place on the PVA crosslinked membranes. (1) cross-linking of PVA between –OH groups of PVA polymer chains this can also be referred to as intra cross-linking, i.e., self cross-linking; (2) cross-linking between one carboxylic group of the crosslinker acid and an –OH group of the PVA polymer chain, i.e., partial cross-linking; (3) cross-linking between both carboxylic groups of the crosslinker used and –OH groups in PVA polymer chains, i.e., complete cross-linking. The formula mentioned above does not specify which among the 3 types of crosslinking is taking place [30].

3.2 Crosslinkers used for this experiment are Glutaraldehyde and Maleic acid.

3.2.1 Maleic acid as a crosslinker:

Maleic acid is also called as cis- butenedioic acid. They are unsaturated organic dibasic acid generally used in making fiber reinforced material. It is prepared by the catalytic oxidation of benzene. They show reactions typical of both olefins and carboxylic acids.

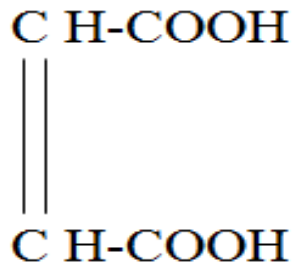


Figure 6: Structure of Maleic acid [36]

For crosslinking PVA reacts with Maleic acid. Reaction between acid and alcohol is called Esterification. Esterification of PVA leads to water-insoluble hydrophilic vinyl alcohol vinyl ester copolymers. For a long time Maleic acid has been established as a good crosslinker for PVA [26, 36, 37].

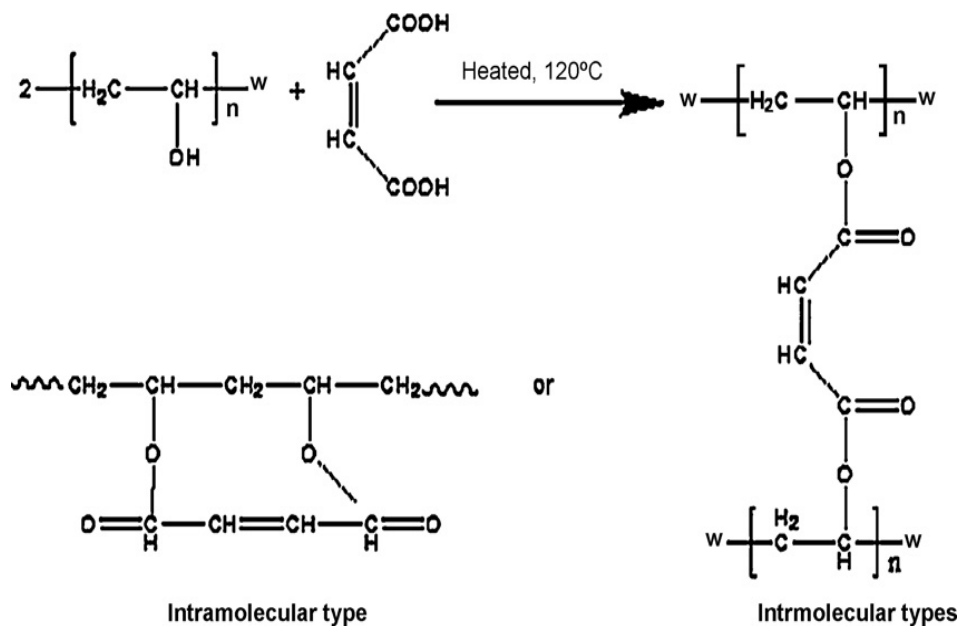


Figure 7: Probable reaction of PVA with Maleic acid [37]

PVA combines with the COOH-CH=CH-COOH getting rid of the water molecule and forming CHC=O-OR. The eliminated water molecule maintains hydrophilicity and the ester group formed is a stable molecule. Or we can also say that the Maleic acid crosslinked barrier layer (PVA layer) of these membranes

can be negatively charged because of the presence of un-reacted hydroxyl/carboxyl (OH of COOH of Maleic acid) groups and at the same time polar ester groups are also formed during the cross-linking reaction. In the PVA–Maleic acid system, a gel network is formed by the ester linkages of hydroxyl groups of all the PVA chains by the carboxyl group of Maleic acid. Various properties like the permeability or rejection depends upon the crosslinked density and the no of free hydroxyl groups of PVA present. Other than the ester linkages which are formed there are certain unesterified carboxyl groups of Maleic acid that can impart a charged character on the membrane surface [26, 37] .

3.2.2 Glutaraldehyde as a crosslinker:

Another crosslinker which we have tried for our experiments is the Glutaraldehyde commonly known as the GA. It is an organic compound actually an aldehyde by the formula $\text{CH}_2(\text{CH}_2\text{CHO})_2$. It is used in biological industry as a fixative. It can crosslink proteins and is generally used along with formaldehyde to stabilize biological specimens like bacteria, human cells etc. In the chemistry industry it is mainly used as a biochemical reagent. Its main function is that of an amine-reactive homo bi-functional crosslinker.

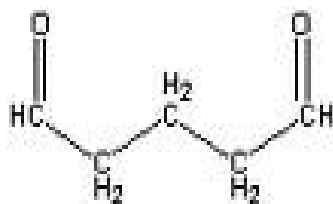


Figure 8: Structure of Glutaraldehyde [34]

When we treat PVA membrane with a specific amount of a dialdehyde in the presence of an acid solution (say HCl in our case) which acts as a catalyst, acetalization crosslinking takes place. Acetalization takes place of the 1, 3 diol units of PVA with GA. The reaction forms water insoluble polyacetals [38] . The acetal crosslinked structure formed is assumed to be by the following reaction:

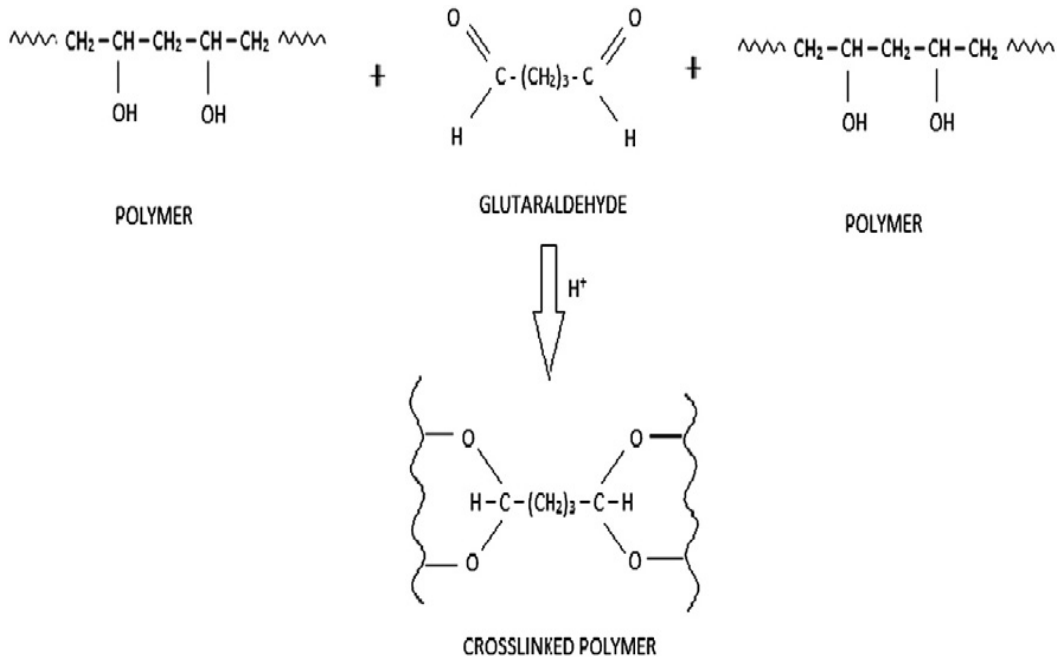


Figure 9: Probable reaction of PVA with Glutaraldehyde [34]

Acetalization is better controlled if we add GA directly to the PVA aqueous solution as in our case. After this curing takes place and storing the membranes in water is an essential step otherwise the HCL which is used as a catalyst can cause decomposition of the acetalized polymer.

Glutaraldehyde is considered as a very good crosslinker because it is readily available. It forms a homogeneous film with PVA. Its vapor pressure is also

considerably low; hence it remains well on the PVA coated membrane even after drying [34].

3.3 METHODOLOGY:

3.3.1 Preparation of Membranes for coating:

The membranes were taken as delivered from Dow and prepared for coating. Initially the polyester (PET) fabric was carefully peeled off using a razor blade from the Polysulfone support layer. This step is essential to expose the highly hydrophobic Polysulfone layer directly to the Poly vinyl alcohol coating. The membranes with PET removed were kept in deionized water for storage.

Before coating the membranes with PVA the membranes were soaked in isopropyl alcohol (IPA) at room temperature for about an hour. This alcohol wetting is essential to wet out the pore structure of the membranes. The wetting of the hydrophobic membrane layer facilitates the crosslinking reaction or the binding reaction of the PVA to the PSf support i.e. an aqueous environment is created to prepare for PVA coating. The hydroxide groups of PVA can adhere well to the membrane when it is wet. This is the main reason for imparting hydrophilicity. IPA is then rinsed out. This is done by soaking the membranes in 3 different baths of deionized water. In each water bath the membranes are kept for about 45 minutes. This step of rinsing is generally carried out in a refrigerator as we can avoid the nucleation of air bubbles on the surface of the membrane. The air bubbles can block the tiny pores of the thin film composite membranes.

The membranes are now ready for dip coating with PVA and are stored in deionized water in Nalgene containers [12].

3.3.2 Dip Coating

The dip coating method of PVA is inspired by the recipe of Peng et al. [30]. For dip coating with PVA first the PVA solution is made. DI water is kept for boiling at about 80 to 90° C. It is continuously stirred in a glass bottle kept on a magnetic stirrer. Once we see the water boiling add the PVA powder depending upon the concentration of PVA- water required. For our recipe 0.1% by weight PVA concentration is chosen. Once you see the PVA powder dissolve in the DI water, stop heating and stirring the solution. You should see a colorless boiling solution. If no traces of white powder are seen it means the PVA is dissolved properly in the DI water. Let the solution cool down. Now in the cooled solution add the desired amount of crosslinker along with few drops of 2 Molar HCl as catalyst. For our recipe we have chosen 2 different % of crosslinkers i.e. 10% and 50%, as well as 2 different types of crosslinkers i.e. Maleic acid and Glutaraldehyde. The crosslinker is added while continuously stirring the PVA solution for about 30 minutes. In the mean while the membranes are removed from DI water storage and kept on the glass plate in such a way that the Polysulfone support layer which needs to be coated is facing upwards. A rubber sheet of sufficient height is clamped on the membrane attached to the glass plate in such a way that when the PVA (with crosslinker) solution is poured on it, it would not seep in to the polyamide selective layer. Hence the surface modification shall be restricted only on the support layer. Pour the PVA solution with crosslinker on the membrane. Keep the PVA solution in contact with the support for 10 minutes. After 10 minutes, drain the PVA solution off the membrane. Keep the membrane overnight

for drying and then heat it at 100 °C for about 10 minutes. After heating store the membranes in DI water. The heating of membranes is generally termed as curing of membranes. The membranes are now ready to be tested.

While selecting the amount of crosslinker to be added in the PVA solution –it is measured in terms of what is known as the “crosslinking degree”

$$x_{CL} \% = \frac{W_{CL} \times MW_{pva\ unit} \times 2}{W_{pva} \times MW_{CL}} \times 100$$

Where x_{CL} represents the crosslinking degree (amount of crosslinker added), W_{CL} represents the weight of crosslinker to be added, $MW_{pva\ unit}$ refers to the molecular weight of one PVA chain. (CHOHCH₂) i.e. 44, W_{pva} refers to the weight of PVA used, MW_{CL} refers to the molecular weight of the crosslinker used.

Crosslinking degree is a term which refers to a molar ratio of crosslinker to a PVA unit. If PVA without crosslinker is coated on membranes and is stored in DI water, the PVA will dissolve in the water and the coating shall no longer exist. Hence a crosslinker is a substance that cross-links PVA monomer units to each other or with the crosslinker to enable efficient establishment or binding of the PVA on the PSf support layer.

3.3.3 Membrane used for the surface modification:

The PVA coating was performed on 2 commercial TFC RO membranes: SW30 XLE and BW-30 Dow Film Tec Membranes.

3.3.3.1 SW 30 XLE:

- Membrane Type Polyamide Thin-Film Composite

- Maximum Operating Temperature 113°F (45°C)
- Maximum Element Pressure Drop 15 psig (1.0 bar)
- pH Range, Continuous Operational 2 - 11
- pH Range, Short-Term Cleaning (30 min.) 1 - 13
- Maximum Feed Silt Density Index (SDI) SDI 5
- Free Chlorine Tolerance <0.1 ppm

This is the lowest energy sea water element available in the industry today. It is also ideal for two-pass seawater designs and high TDS brackish water applications. It enables systems to be designed to deliver the lowest cost of water by optimizing energy consumption, system productivity and operating flux. It can effectively be used in permeate staged seawater desalination systems without impairing the performance of the downstream stage. It delivers high performance over the operating lifetime without the use of oxidative post-treatments like many competitive products.

3.3.3.2 BW 30:

- Membrane Type Polyamide Thin-Film Composite
- Maximum Operating Temperature 113°F (45°C)
- Maximum Operating Pressure 600 psig (41 bar)
- Maximum Pressure Drop 15 psig (1.0 bar)
- pH Range, Continuous Operations 2 - 11
- pH Range, Short-Term Cleaning (30 min.) 1 - 13
- Maximum Feed Flow 85 gpm (19 m³/hr)
- Maximum Feed Silt Density Index SDI 5

- Free Chlorine Tolerance <0.1 ppm

It is a high-productivity element combining the highest active membrane area with the highest rejection of a brackish water membrane available in the industry today. It is designed to minimize capital expenses in high-purity industrial water applications without increasing operating flux.

3.4 Characterization Methods:

3.4.1 Determination of Contact Angles:

This is the main test conducted to check the hydrophilicity of membranes. The contact angles of the peeled and PVA modified membrane PSf support layers were measured using sessile drop method on a contact angle Goniometer. These values were taken as averages of at least six data points with a volume of 2 μ L of water.

3.4.2 Fourier Transform Infrared Spectroscopy (FTIR):

FTIR is a technique used to obtain an infrared spectrum of absorption, emission of a solid, liquid or gas. FTIR collects data over a wide spectral range. The spectrum can be analyzed to understand the nature of bonds present in the solid, liquid or gas. For our experiments Nicolet 4700 GATR FTIR Spectrometer obtained from Thermo-scientific was used.

3.4.3 Scanning Electron Microscope (SEM):

An SEM images a sample by scanning it with a beam of electrons in a raster scan pattern. The electrons interact with the atoms of sample producing signals containing information about sample's surface topography, composition, and

other properties. Our analysis was done using XL30 ESEM-FEG obtained from Philips. It has a resolution up to 2 nm and magnification of 12 to 500,000.

3.4.4 Testing hydraulically driven flux of the modified membranes:

The peeled and PVA modified membranes were subjected to RO tests to check if the surface modification had caused any changes in the permeability and flux. Study by Arena et al. indicates that the PET removal step does not cause any significant loss of selectivity [12]. Also we are assuming that the PVA modification of the support layer does not cause any chemical or physical damage to the polyamide selective layer at the top. To ensure these results pure water fluxes were measured ranging from 200 to 500 psi to get a permeability chart. Also salt rejection was tested at 300 and 500 psi pressures with a 2000 parts per million (ppm) sodium chloride solution (NaCl). For all these tests the removed PET fabric was inserted behind the membrane for additional mechanical strength. This addition is assumed not to cause any significant changes in the resistance to water flow and hence the flux values. The conductivity of the bulk permeate and feed were measured to calculate the rejection.

3.4.5 Testing osmotically driven flux of modified membranes:

The modified TFC SW and BW RO membranes were tested under different osmotic flux conditions. For these tests PRO orientation was selected where the polyamide selective layer faces the draw solution. Flux before and after the modification step was calculated. Also in both the cases, the fluxes of the neat membranes without PET were tested to see if this creates a significant difference

in flux. Thus the neat membranes, membranes lacking PET layer, membranes modified with PVA using GA and Maleic acid as crosslinker of different amounts were tested. NaCl solution was used as the draw solute at concentrations of 0.05M, 0.5M, 1M and 1.5 M. It was ensured that the temperature difference between the draw and the feed solution did not exceed $\pm 2^\circ \text{C}$. The osmotic pressures calculated by these draw solutions were calculated by Van't Hoff's Equation

$$\text{Osmotic Pressure} = i \times C \times R \times T$$

Temperature: it is assumed to be constant at 298K

R: universal gas constant= 0.082 L*atm/ (mole*K)

C: concentration of the salt (draw solution)

i: It is a Vant Hoff's constant which is 2 for NaCl as it contains 2 types of ions i.e. Na⁺ and Cl⁻. For each condition tests were run in triplicate using fresh membrane samples each modified independently.

4 RESULTS AND DISCUSSIONS:

4.1 Factors affecting membrane performance:

There are various factors on which the performance of PVA modified membranes depends:

- Concentration of PVA.
- Crosslinking degree or the amount of crosslinker added by wt.
- Temperature at which the membrane is heated.
- Time of curing (heating) of the membrane.
- Contact time of PVA solution with the support side of the membrane
- Stirring time of PVA solution with the crosslinker.
- Substance chosen as the crosslinker
- No of PVA coats

4.2 Preliminary Experiments:

To optimize and decide on the exact recipe of PVA to be used for surface modification some preliminary experiments were performed on the SW 30 XLE membrane using the dead end filtration system in Reverse Osmosis. All these initial tests were performed with Glutaraldehyde as the crosslinker.

4.2.1 To determine the effect of PVA concentration:

Before deciding on the concentration of PVA to be used, PVA solution concentration was varied from 0.1% by weight to 1% by weight. Crosslinking degree was fixed at 20% as per recipe used by Peng [30]. After surface modification it was observed that as the % of PVA concentration increased the

water flux decreased. Increase in the PVA layer concentration results in creating a dense barrier layer on the support [26]. As the flux increases were observed, simultaneously rejection dropped down slightly. Our aim is to increase the water flux of membranes hence a concentration of 0.1% by weight of PVA was fixed for optimization.

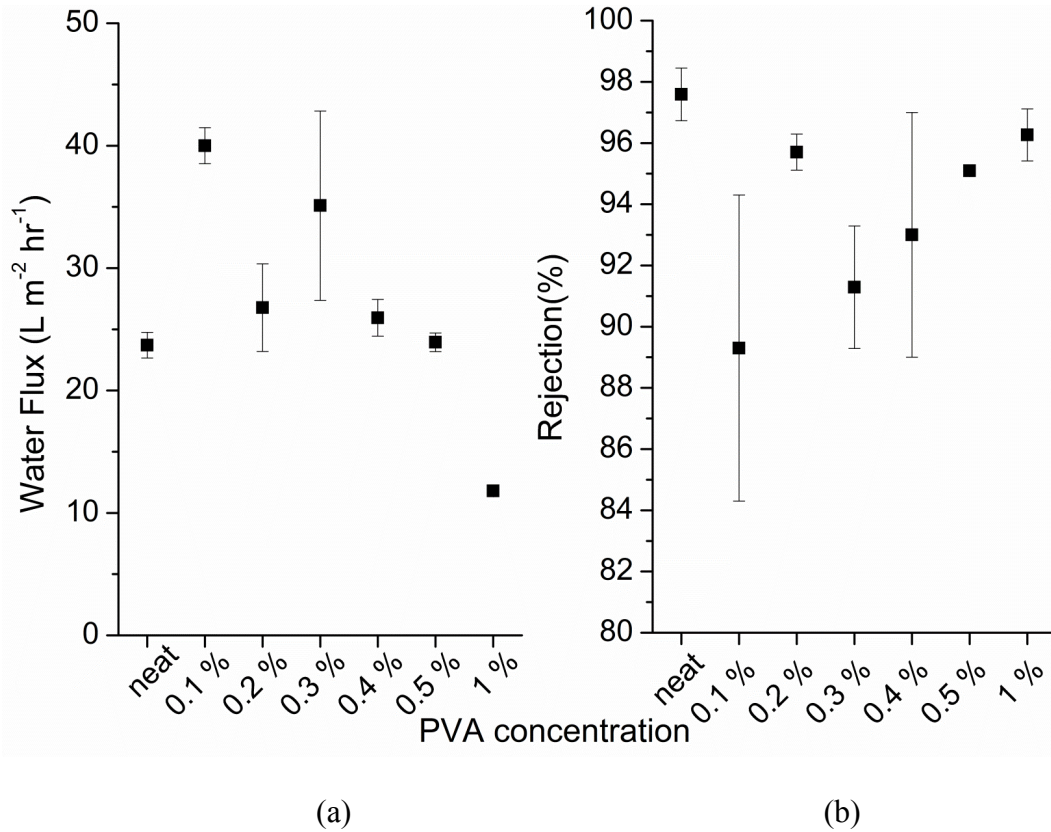


Figure 10: Effect of PVA concentration on a) water flux and b) Rejection on SW 30 XLE at 20% Glutaraldehyde crosslinking

4.2.2 No of PVA coats:

Some tests were conducted to see if another layer of PVA coat on the membrane improves performance. Hence the procedure by which PVA surface modification is done was repeated another day. The membrane was kept for drying overnight after coating with PVA solution for 2 consecutive days and then heat treatment

was done. This experiment was performed using Glutaraldehyde as a crosslinker at 50% crosslinking. The flux dropped drastically after the 2nd layer of PVA on the support side. Correspondingly the rejection increased. This would have been again due to formation of a dense barrier layer on the support. 2 layers of the hydrophilic polymer does not help in passage of water through it easily rather blocks the membrane pores. Hence after this test it was decided to keep 1 PVA coat on the support for further optimization.

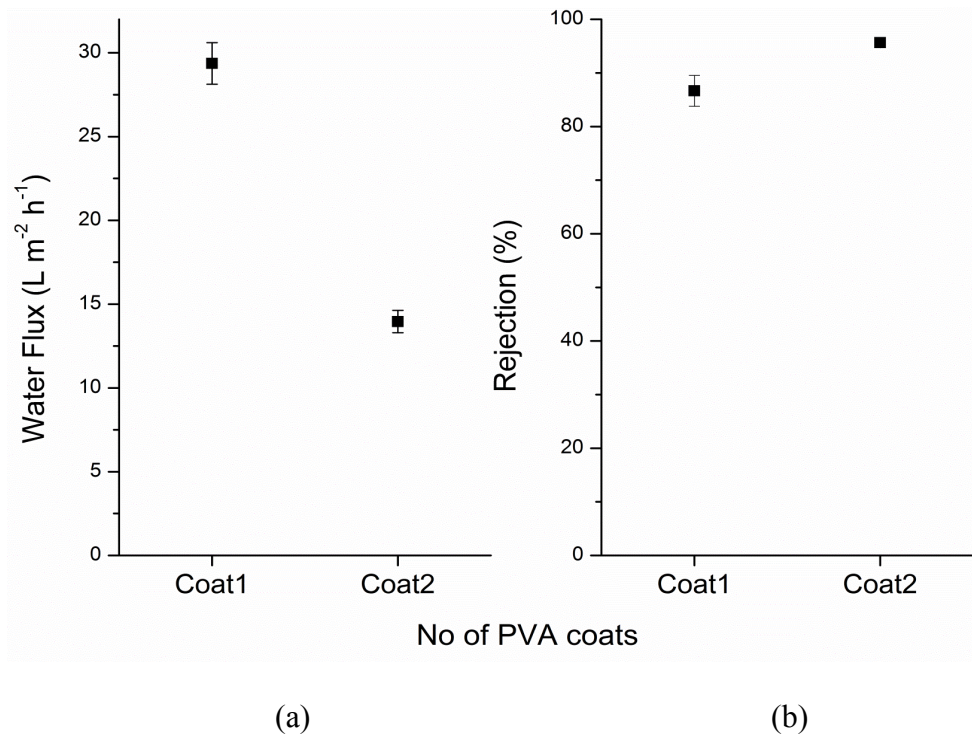


Figure 11: Effect of no of PVA coats on a) water flux b) Rejection of SW 30 XLE membranes at 50% Glutaraldehyde crosslinking

4.2.3 Effect of degree of crosslinking:

RO tests were done at 3 different crosslinking degrees of 20%, 50% and 80% to see its effect. These tests were performed at 0.2% PVA by weight concentration. As the amount of crosslinker increased the water flux decreased at the cost of

rejection. Increasing the crosslinking results in forming a tight network, hence a drop in flux [26] . At very high crosslinking of 80% the pores were almost blocked by the compact network formation and a significant drop in flux was seen.

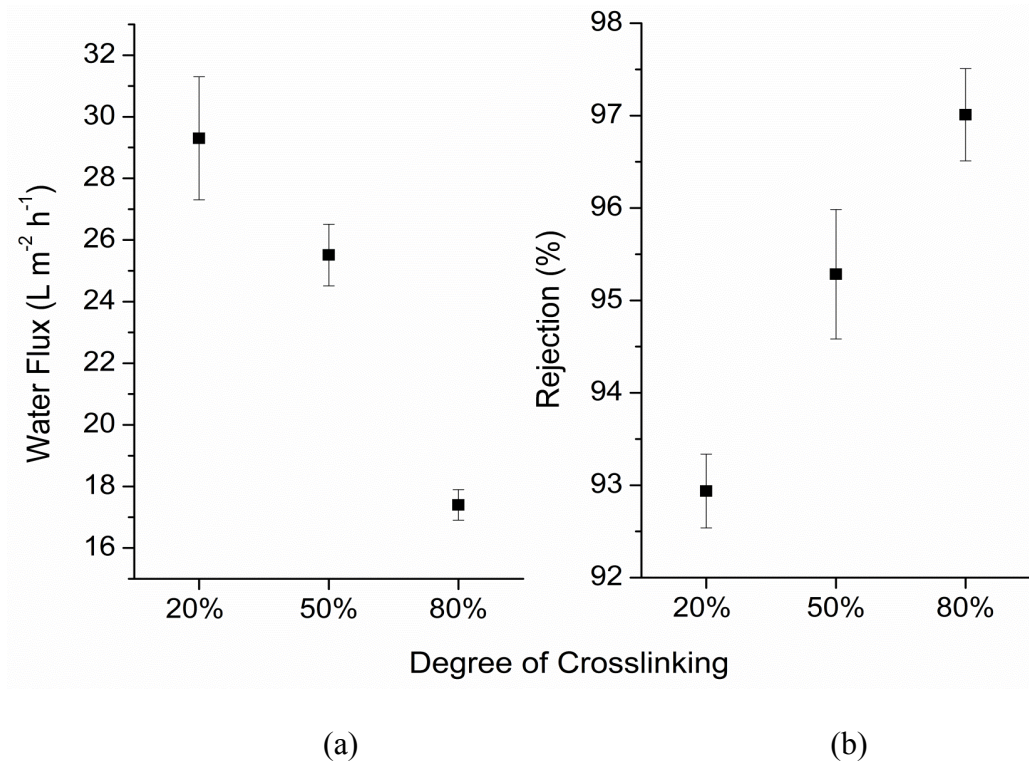


Figure 12: Effect of degree of crosslinking on a) Water Flux b) Rejection of SW 30 XLE membranes at 0.2% PVA

From these tests it was realized that degree of crosslinking affects membrane performance to a significant extent. Hence for further tests it was decided that 2 extreme crosslinking degrees would be varied i.e. 10% and 50%. 80% was not selected as it resulted in a significant drop in flux and our aim is to see if imparting a hydrophilic polymer causes an increase in water flux by easy transport of water molecules through it. It was decided to try a different crosslinker than an aldehyde to see its effect on the membrane performance, a

cross-linker which could promise more flux improvement than Glutaraldehyde. Maleic acid was chosen for this [30]. Hence all the further tests were performed at 10% and 50% crosslinking using Maleic Acid and Glutaraldehyde as the crosslinkers. All the other parameters were kept constant:

PVA concentration: 0.1% by weight

Time of contact of crosslinker with PVA : 30 mins [26]

Time of contact of PVA solution with the support : 10 mins [30]

Time of heating of membrane: 10 mins [30]

Temperature of heating the membrane: $100^{\circ}\text{C} \pm 1^{\circ}\text{C}$ [30]

4.3 Research Objective:

From our preliminary experiments we decided to see the impact of PVA on the support side of commercial thin film composite membranes using 2 different crosslinkers Maleic Acid and Glutaraldehyde. Also we aim at seeing the effect of amount of crosslinker on the PVA coating of the membranes in Reverse Osmosis dead end filtration system and Forward Osmosis cross flow system.

4.4 Contact Angle:

In SW-30 XLE there is around 15% increase in hydrophilicity from neat Polysulfone layer to PVA with 10% MA crosslinked PVA coated membranes. In BW the increase in hydrophilicity is very less, i.e. maximum 5% in case of 10% MA crosslinked PVA coated membranes. PVA when crosslinked with Maleic acid produces more hydrophilicity than that crosslinked with GA. Also as the degree of cross linking increases there is a decrease in hydrophilicity [30]. This

can be seen by the fact that 50% of MA crosslinked PVA as well as 50% of GA crosslinked with PVA have higher contact angles than 10% ones.

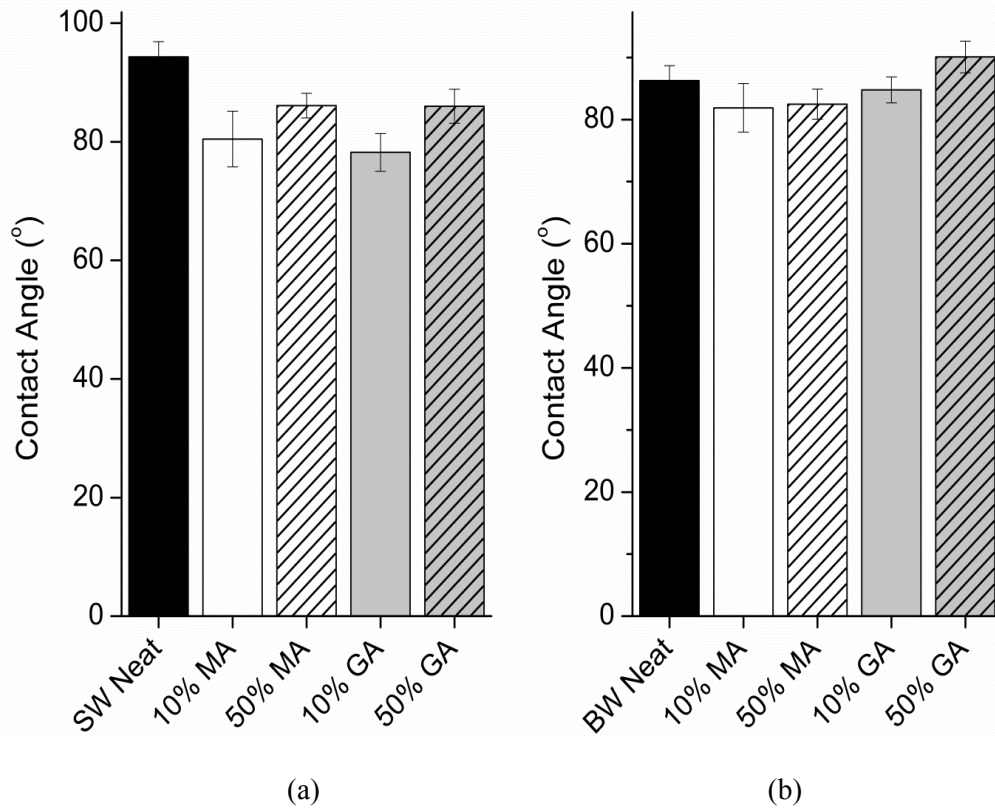


Figure 13: Contact angles for the porous support layers of neat and PVA modified TFC RO membranes. a) SW 30 XLE. b) BW 30- neat and modified

For BW membranes at a higher concentration of crosslinker GA with PVA, the hydrophobicity is more than the neat membrane. The plausible reasoning for this can be that the crosslinkers by themselves are not very hydrophilic in nature [27]. From the results we can also say that Maleic acid by itself can be little more hydrophilic than Glutaraldehyde.

4.5 Reverse Osmosis dead end filtration testing:

The pure water fluxes for the modified SW 30 XLE membranes were significantly higher than the neat membranes. This explains the hydrophilicity increase at the Polysulfone support layer. Water transport through the support layer is improved due to the polyvinyl alcohol coating. PVA improves the wetting of pores of the membrane and the water molecules which pass through it face less surface energy resistance. This can be termed as an increase in 'wetted porosity' [12]. The water fluxes are higher for MA crosslinked PVA than GA crosslinked PVA membranes, which explains more hydrophilicity imparted when PVA is crosslinked with MA. Also we can say that quantitatively as crosslinker amount increases, the hydrophilicity and so do the water fluxes decrease. As the amount of crosslinker increases it results in a tighter network on the support which prevents water to pass through it easily. Also both the cross-linkers by themselves are not very hydrophilic in nature yet from the results we can say that MA itself is slightly more hydrophilic than GA in nature. These results correspond to the contact angle test.

The effect in BW membranes is opposite; there is a drastic decrease in pure water flux compared to neat. There can be 2 reasons for this:

1. The hydrophilicity increase in membranes is not sufficient enough to let water molecules to pass through it easily and increase the water flux.
2. BW 30 has a tighter porosity and less number of macro voids as compared to the SW 30 XLE [12]. Hence PVA instead of increasing hydrophilicity tends to block the pores. Macro voids help in deeper penetration of PVA layer without

clogging the pores [12]. Although the PVA coated membrane flux is lesser than neat the trend of coated membrane flux is same as SW membranes. 10% crosslinked MA –PVA membrane shows higher flux than the GA crosslinked PVA membranes.

For SW membranes when the PET fabric is removed the flux goes slightly down. For BW membranes the flux is slightly higher for PET removed membranes than the neat membranes. This shows that its removal does not affect the hydraulic resistance offered by the membrane [12].

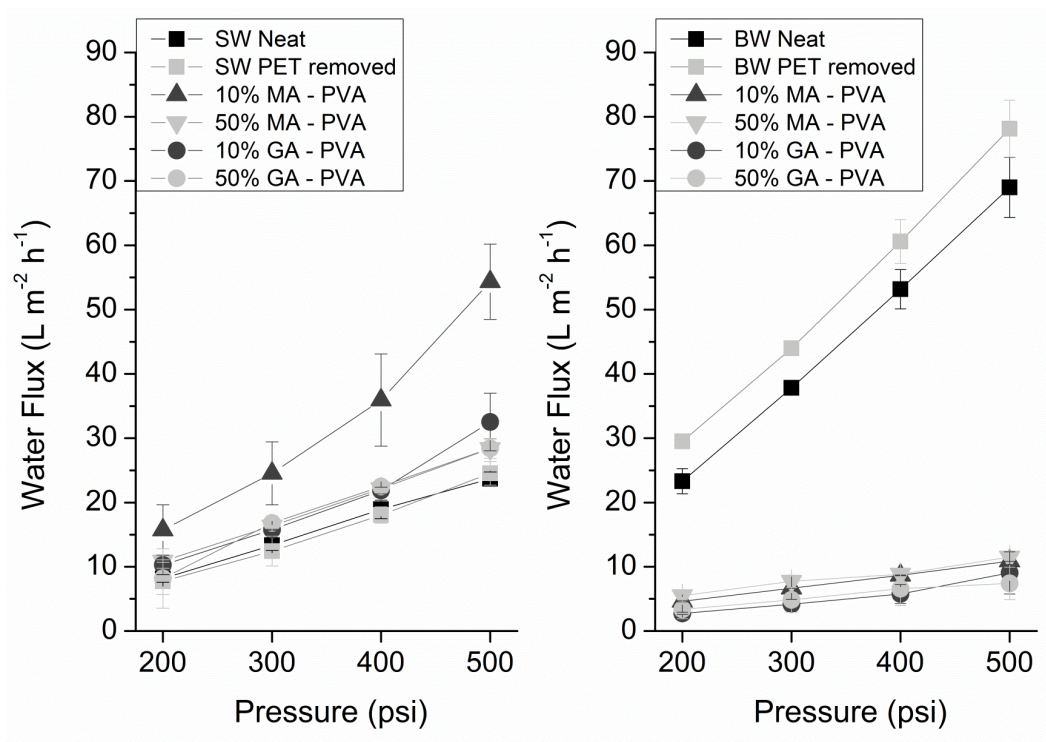


Figure 14: Pure water flux of the a) SW -30 XLE and b) BW 30 during RO from 200 to 500 psi. on 1) neat, 2) PET removed, PVA crosslinked with 3) 10% MA 4) 50% MA, 5) 10% GA 6) 50% GA

Permeability coefficient:

The permeability coefficient tells us about the permeability of the membrane. It is slope of water flux to the pressure applied. It directly correlates with the water flux. For SW membranes the permeability of 10% MA crosslinked is significantly higher than the neat membranes. Even for the 10% GA crosslinked PVA membrane it is higher. 50% crosslinked membranes do not show a very noticeable increase in permeability owing to comparatively low water flux result.

For BW membranes the permeability dropped very low as was indicated by the water flux in reverse osmosis. 50% GA crosslinked PVA membrane has further low permeability due the fact that the PVA and crosslinker have clogged the pores of these membranes as described in reverse osmosis water flux analysis.

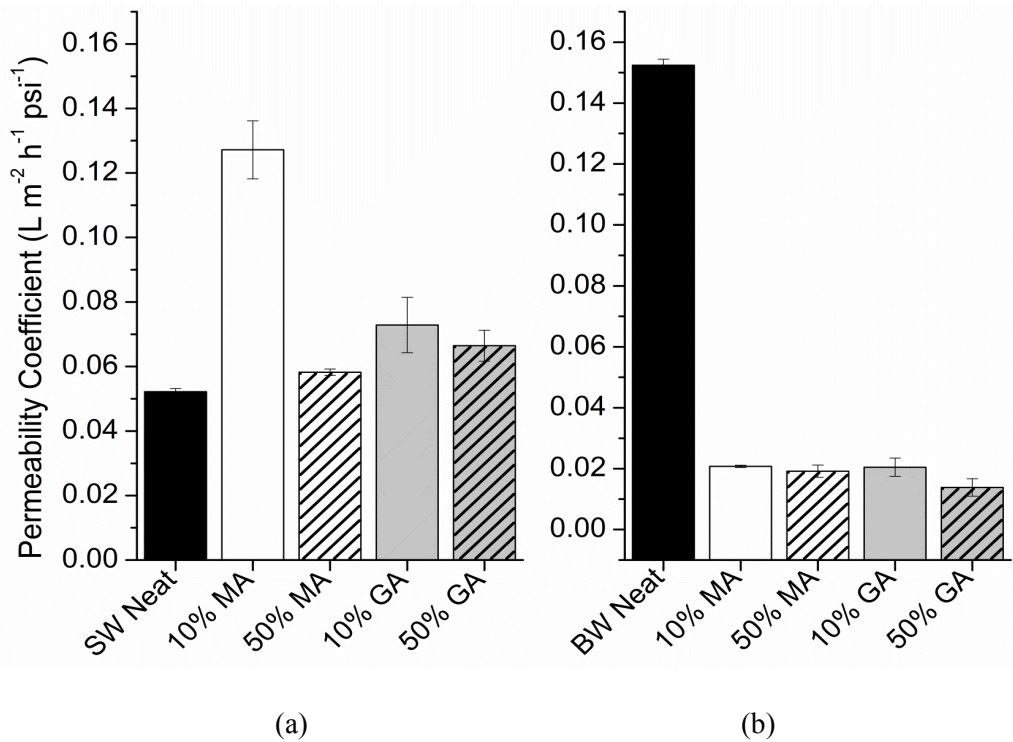


Figure 15: Permeability coefficient of neat and the different PVA coated membranes a) SW 30 XLE b) BW 30

4.6 Rejection:

PVA modified membranes have comparable rejection to the neat membranes. As the flux for any membranes increases correspondingly the rejection decreases. For SW membranes the 10% crosslinked MA and GA- PVA membranes have a lower rejection than 50% crosslinked ones owing to its higher flux. In BW membranes the PVA tends to clog the pores hence there is an actual increase in rejection in coated membranes compared to the neat membranes. When the PET is removed, for SW the rejection is same as neat ones. While for BW membranes the rejection goes down when fabric is peeled correspond to its higher flux.

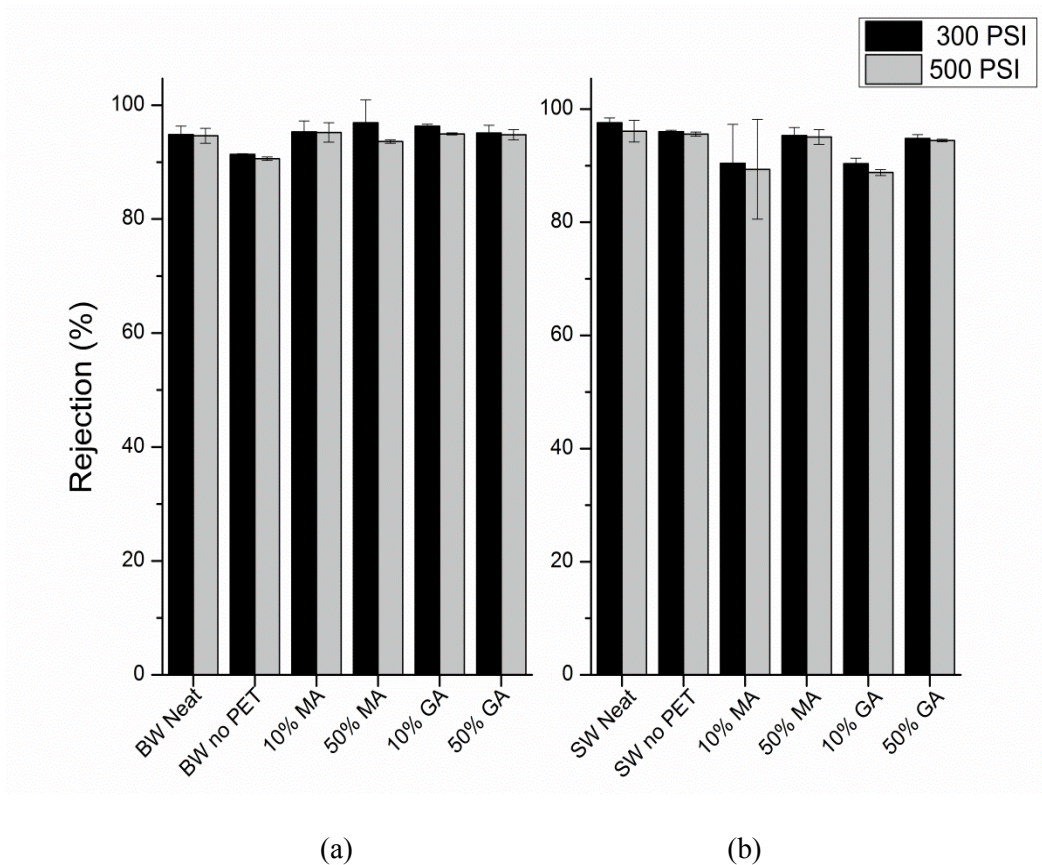


Figure 16: Salt rejection for the a) SW 30 XLE and b) BW30 during RO at 2 different pressures of 300 and 500 psi with 2000ppm NaCl solution on 1) neat 2) PET removed, PVA crosslinked with c) 10% MA d) 50% MA, e) 10% GA 6) 50% GA

4.7 Osmotic water flux testing:

To evaluate the impact of RO modified membranes in FO applications, the membranes were tested in PRO mode. The selective polyamide layer is facing the draw solution. For both the membranes pure water fluxes were low for the neat membranes and PET removed ones. At a higher osmotic gradient the fluxes for membranes without PET layer increased more compared to others. This may be due to no salt accumulation due to lack of thick support fabric as only the thin selective layer with the polymeric substrate is present. For SW coated membranes the 10% MA crosslinked PVA modified membranes showed a significant improvement compared to others. This proves that MA crosslinked PVA membrane at a low crosslinking degree can significantly increase the hydrophilicity of SW membranes. The increased water fluxes indicate that the SW membrane pores are wetted thoroughly and are effective in transporting water through it, which is a necessity in FO engineered methods. At a high degree of MA the flux goes down a little. The flux at 50% MA is almost same as 10% GA. Glutaraldehyde at a high % of crosslinking tends to block the pores leading to low water fluxes.

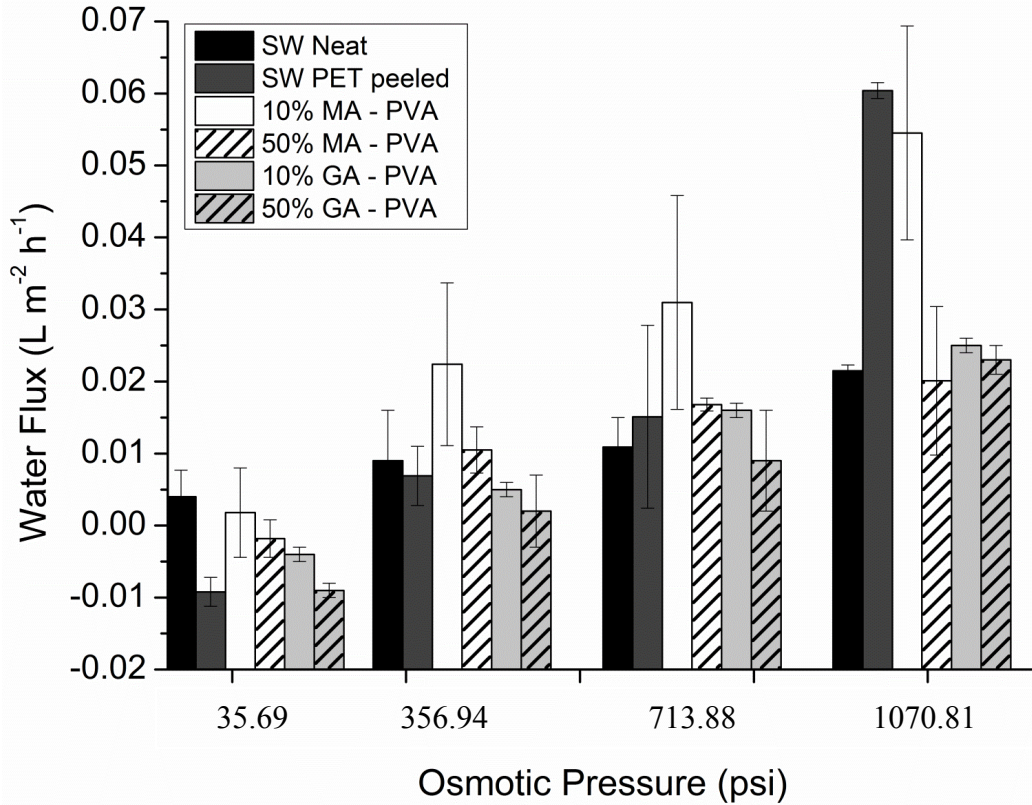


Figure 17: Osmotic water flux of SW 30 XLE neat and of PVA modified; at varying concentration of draw solution from 0.05 m, 0.5m, 1m and 1.5m. Flow rate 1 LPM. Temp: 25 C

BW modified membranes did not show a significant increase compared to neat membranes in FO mode, however they did not show a drastic drop in water flux like in RO mode as well. This indicates that there has been some hydrophilization of the support layer to wet the pores and reduce internal concentration polarization, but the extent of hydrophilization in BW needs to be improved more. The lower porosity of BW membranes makes its hydrophilization lesser than SW membranes. PVA and cross linker molecules are clogging the pores of these membranes. The trends of BW coated membranes are similar to SW coated membranes. 50% GA PVA membranes show very low fluxes. Correspondingly even its contact angle had been high. High % of GA must be blocking the small

size pores of the support. Relatively still 10% MA crosslinked PVA membranes showed higher fluxes.

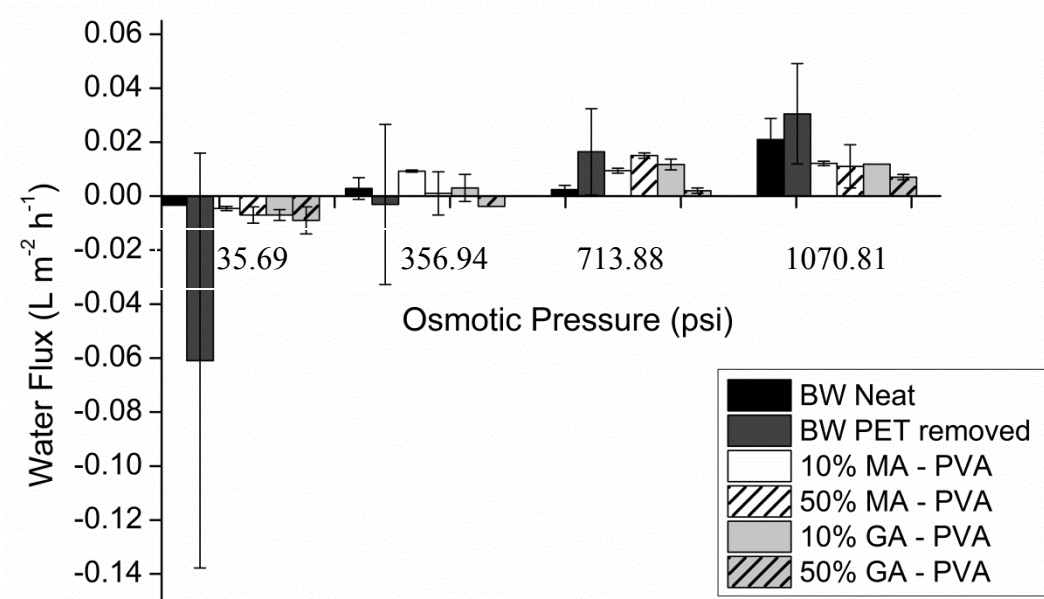


Figure 18: Osmotic water flux of BW 30 XLE neat and of PVA modified; at varying concentration of draw solution from 0.05 m, 0.5m, 1m and 1.5m. Flow rate 1 LPM. Temp: 25 C

4.8 Osmotic salt flux gradient:

At a low osmotic gradient at a salt concentration of 0.05molar the salt flux of PVA coated as well as uncoated membranes is approximately the same, there is no significant difference. The peeling of PET fabric increases the salt flux compared to neat membranes. The lack of backing PET layer allows large salt molecules to pass through it easily. In SW membranes as the osmotic gradient increases the salt flux of 10% Maleic acid crosslinked PVA membrane increases significantly compared to the others. Glutaraldehyde crosslinked membrane at a low concentration of crosslinker of 10% shows a slightly higher flux in

comparison to 50% Maleic acid crosslinked membrane. 50% Glutaraldehyde crosslinked PVA membrane does not have a significant rise compared to other coated ones. The trend of salt flux is in agreement with water fluxes and we can say that imparting hydrophilicity to the support by PVA not only improves movement of water molecules but also salt molecules through the membrane. As the water and salt molecules are travelling much easily through the membrane, it tells us about the concentration polarization also being diminished [12].

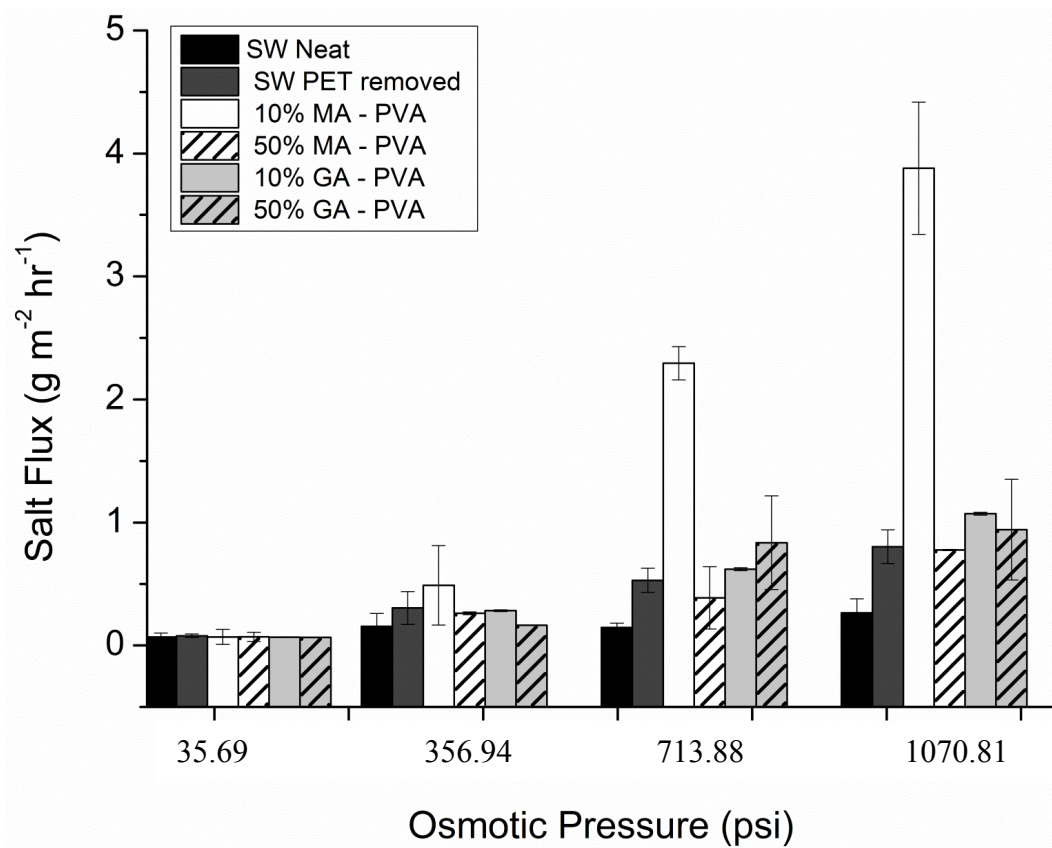


Figure 19: Osmotic salt flux of SW 30 XLE neat and of PVA modified; at varying concentration of draw solution from 0.05 m, 0.5m, 1m and 1.5m. Flow rate 1 LPM. Temp: 25 C

The salt flux of BW neat membranes is higher as compared to the PVA coated membranes. The PVA along with the crosslinker is blocking the pores of BW membranes. Instead of attempting to improve fluxes by coating PVA, the lower pore size of BW membranes prevents the salt molecules to pass through at a higher rate. But distinctly the salt flux of 10% Maleic acid crosslinked PVA membranes is higher than the other crosslinked membranes owing to the relatively higher hydrophilicity induced. It appears as if a high-50% of crosslinker Glutaraldehyde with PVA on BW has almost completely blocked the pores keeping the salt fluxes very low even at higher osmotic gradient. Maleic acid used at a higher concentration and Glutaraldehyde used at a lower concentration have approximately the same effects on salt flux.

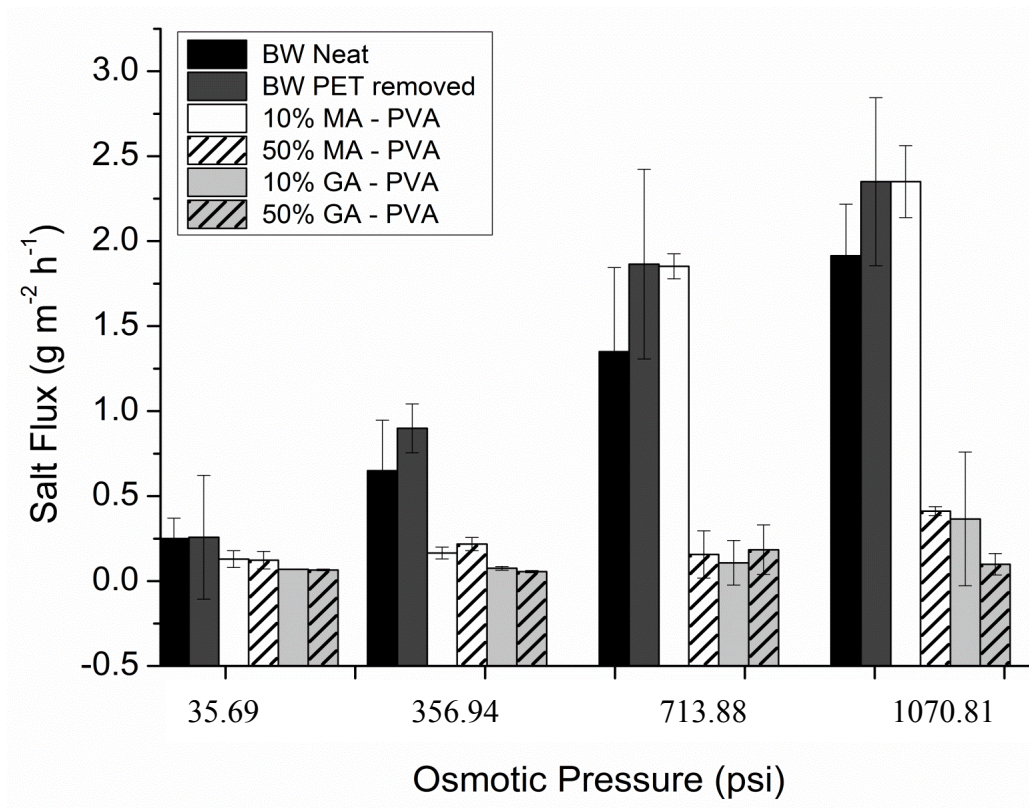


Figure 20: Osmotic salt flux of BW 30 XLE neat and of PVA modified; at varying concentration of draw solution from 0.05 m, 0.5m, 1m and 1.5m. Flow rate 1 LPM. Temp: 25 C

Hypothesis for effect of crosslinker: From the water and salt flux data we can say that Maleic acid crosslinked membranes show higher fluxes than Glutaraldehyde crosslinked ones. Maleic acid and polyvinyl alcohol combine to form an ester with the release of a water molecule. At the end of the reaction the products: water molecule, the remaining loose un-reacted- OH bonds of the PVA and the ester -OH bonds are responsible for increasing hydrophilicity. Glutaraldehyde and PVA reaction gives an acetal which has less no of free OH groups; unlike in ester formed from PVA and Maleic acid. The free OH groups are necessary to impart hydrophilicity. Thus more hydrophilicity is imparted when PVA is crosslinked with Maleic acid [34, 37].

4.9 Scanning Electron Microscopy Analysis:

We can see bigger pores in case of SW membranes than BW ones. Maleic acid or Glutaraldehyde both at a low concentration of 10% does not block the pores of SW. However 50% Glutaraldehyde top view tell us that many of the pores have been clogged, which explains the low fluxes compared to other PVA modified ones.

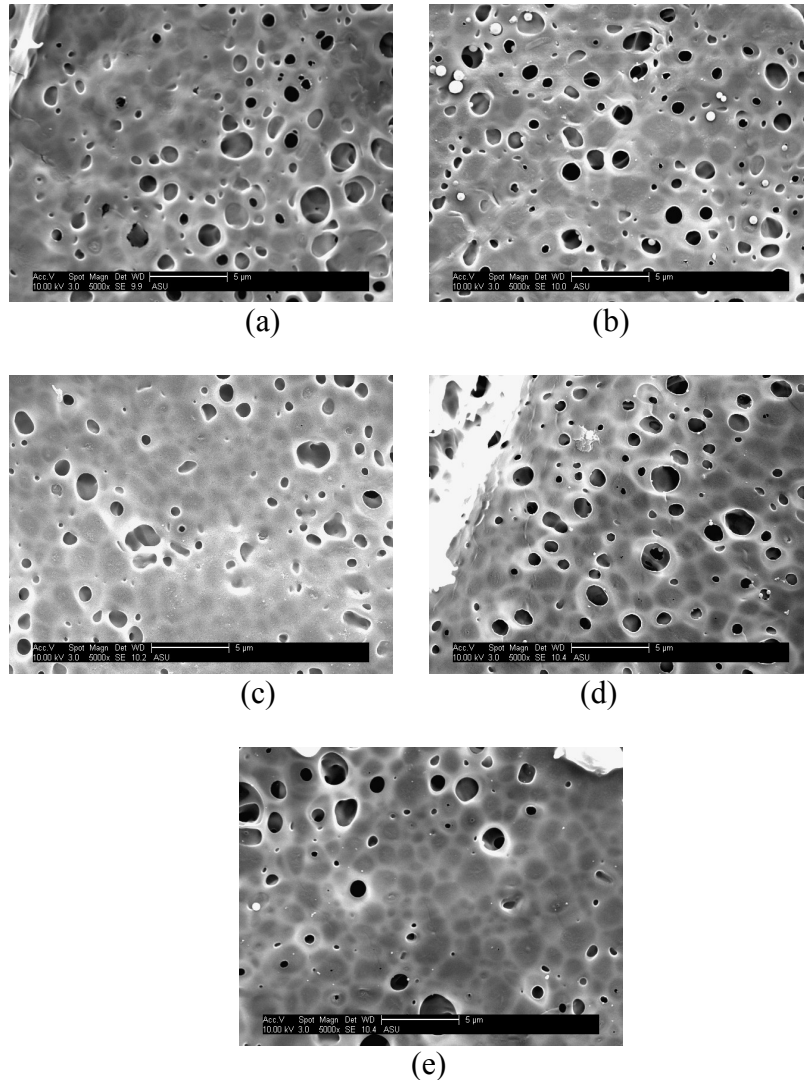


Figure 21: SEM images of SW 30 XLE membranes top view of the PSf support layer. All zoomed at 5 μm magnification; a) SW Neat, b) 10% MA, c) 50% MA, d) 10% GA, e) 50% GA

For BW membranes pore size appears to be lower than SW membranes. 50% Glutaraldehyde is completely blocking the pores. This observation is consistent with the fact that its fluxes dropped significantly in both RO and PRO modes. Its hydrophobicity is also more than the neat membranes. A lower degree of GA however does not block the pores. A lower degree of Maleic acid shows more open pore morphology than GA crosslinked PVA membranes.

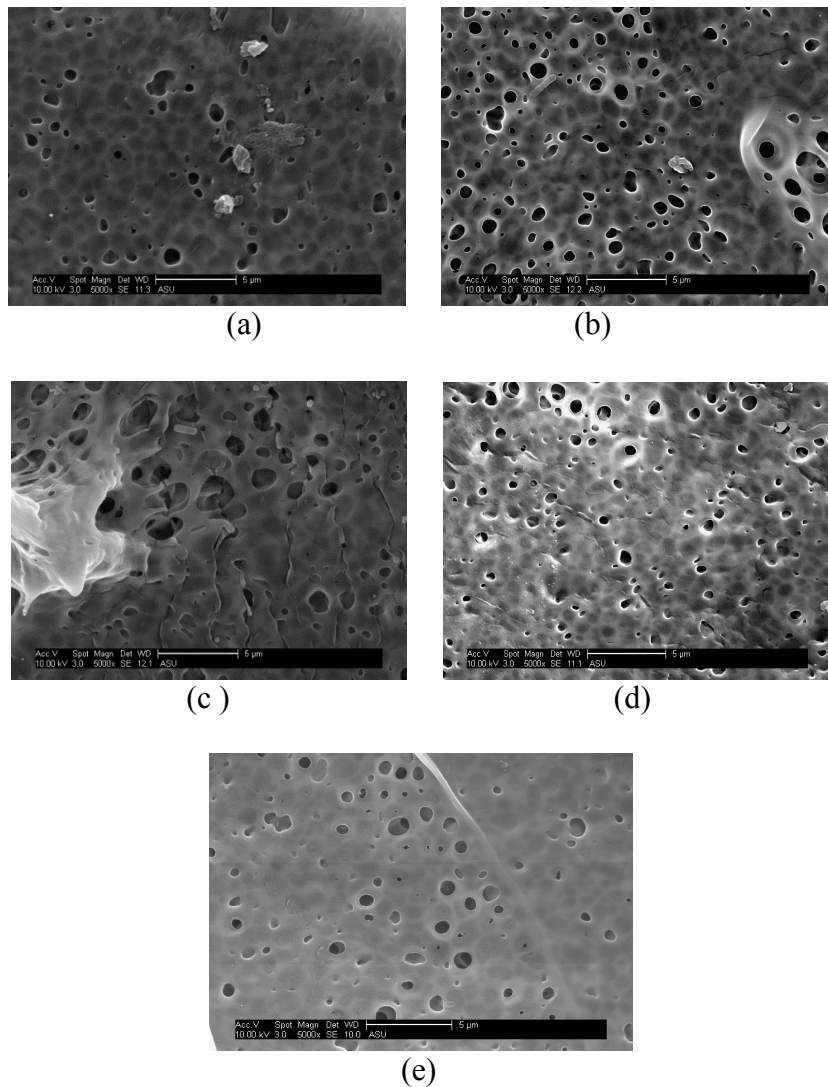


Figure 22: SEM images of BW 30 XLE membranes top view of the PSf support layer. All zoomed at 5 μ magnification; a) BW Neat, b) 10% MA, c) 50% MA, d) 10% GA, e) 50% GA

Comparison of pore morphology between SW and BW membrane:

A cross section view of BW v/s SW tells that the small pores of SW membranes are approximately 2 to 2.5 μ in diameter. For BW membrane they appear to be 0.6 to 1.6 μ in diameter. There are other noticeable bigger sized pores commonly known as the macrovoids. They are of order 11*25 μm in case of SW while of order 6.7*19 μm in case of BW.

Even the cross section images of the 2 neat membranes seen at 10 μ magnification tells us that there are more no of open spaces and macro voids in case of SW for a given area. The porosity of BW membranes appears to be lower than that of SW membranes.

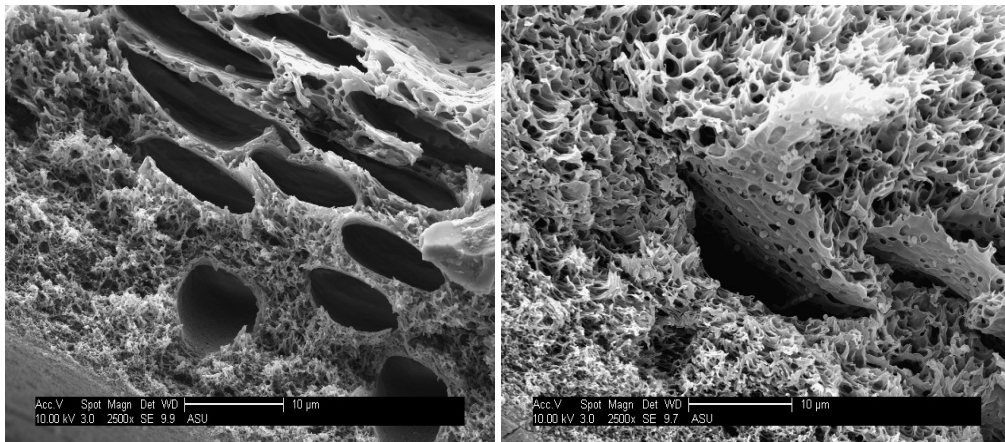


Figure 23: SEM of cross section of a) SW 30 XLE and b) BW 30 neat membranes at 10 μ magnification

4.10 FTIR Analysis:

Maleic acid crosslinked PVA membrane at 50% shows the characteristic peak of C=O ester bonding between Maleic acid and polyvinyl alcohol at stretching vibration of 1735 cm^{-1} [37]. This is one peak characteristically different from the neat membranes. The characteristic peaks are not visible at a lower degree of

crosslinking of 10% Maleic acid. Glutaraldehyde crosslinked PVA membranes also do not show any characteristic peaks. Even it is expected to show the C=O crosslinking peak. The Polysulfone support over powers the PVA coating and makes FTIR characterization insignificant. One can analyze that there is no coating on the membrane, however the hydrophilicity, water and salt flux tests in Reverse Osmosis and Forward Osmosis, and SEM images are indicative of the fact that there is a significant difference in performance between PVA coated membranes and neat membranes. The brackish water membranes are representative for sea water membranes as well since both have the same chemical structure.

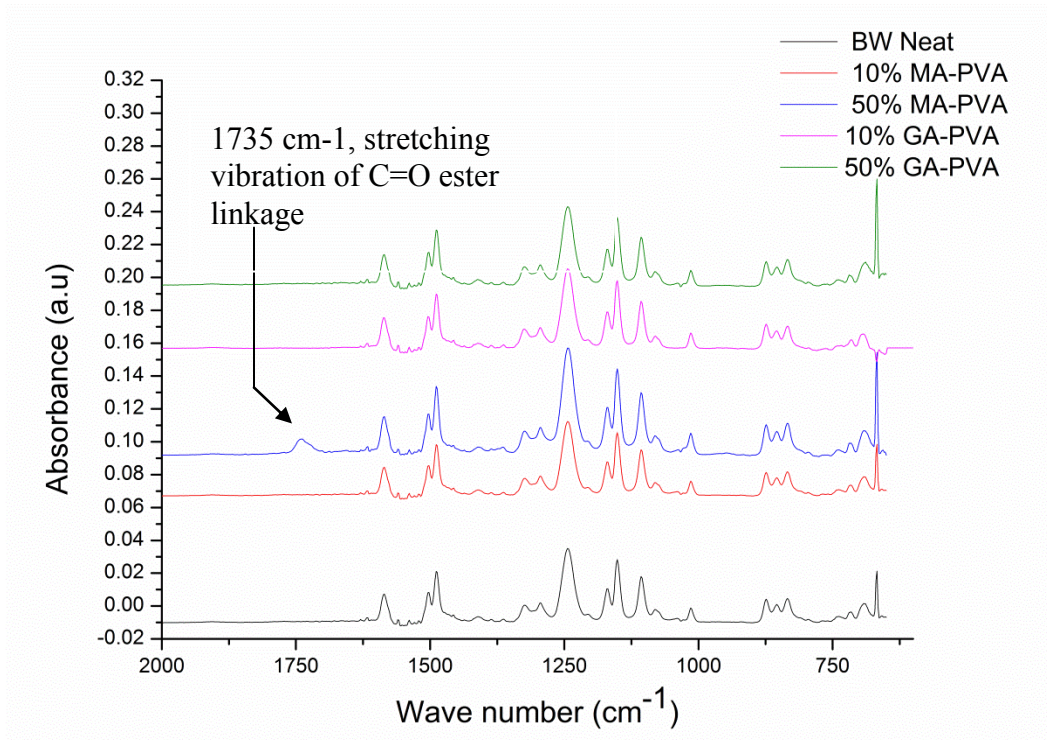


Figure 24: FTIR peaks for BW neat and different PVA coated membranes

5. CONCLUSION:

5.1 Comparison with Polydopamine used by Arena et al.

As previously described our work of PVA surface modification has been an inspiration from work done by Jason Arena et al. where they have done similar coating of SW 30 XLE and BW 30 membranes [12]. Hence we did a study to compare our Polyvinyl Alcohol coating results with their Polydopamine coating results. The table below shows a % increase or decrease in performance of neat v/s polymer coated membranes. The table shows comparison at 500 psi for Reverse Osmosis (RO) water flux test and rejection tests and at 1.5 molar salt concentration draw solution for Forward osmosis tests.

Table 1: Comparison of Polydopamine with Polyvinyl Alcohol coated membranes

	Polydopamine		PVA			
	PDA v/s neat	10% MA-PVA v/s neat	50% MA-PVA v/s neat	10%GA-PVA v/s neat	50% GA-PVA v/s neat	
% Contact Angle Decrease	50.00	14.67	8.70	17.07	8.80	
RO Water Flux % Increase	70.00	129.2	19.73	37.22	19.94	
FO Water Flux % Increase	1285.71	153.92	-6.30	16.11	4.99	SW
FO Salt Flux % Increase	3900.00	1020.14	124.25	209.36	171.94	
Rejection % Increase	0.36	-8.43	-2.56	-9.00	-3.21	
% Contact Angle Decrease	44.85	5.09	4.39	1.73	-4.40	
RO Water Flux % Increase	183.33	-84.24	-83.84	-86.89	-92.58	BW
FO Water Flux % Increase	857.14	-42.48	-46.22	-43.72	-25.35	
FO Salt Flux % Increase	900.00	52.30	-72.82	-74.67	-91.03	
Rejection % Increase	-0.41	1.91	-1.05	0.35	0.20	

From the above data we can see that the water flux increase in RO as well as FO system with Polydopamine is extremely high. The contact angle decrease is much higher in case of Polydopamine than in case of PVA coated ones. Our SW membranes shows similar trends of increase in flux for PVA coated membranes however the % increase is not as extreme as in case of Polydopamine. 10% MA and GA crosslinked membranes show higher flux compared to the 50% crosslinked membranes. In case of Polydopamine coated SW membranes the rejection increased slightly, however in case of PVA coated membrane as the flux increase slightly the fluxes dropped down slightly as well.

For BW membranes the contact angle decrease trends are similar like Polydopamine however not so significantly small. A high % of Glutaraldehyde crosslinker is inefficient in increasing hydrophilicity. RO water flux decreases for both Polydopamine and PVA coated membranes. The drop is more significantly observed in Polydopamine. FO water flux did not increase in case of PVA coated membranes. Salt flux did increase only for 10% MA crosslinked PVA membranes although not as high as Polydopamine coated ones. Polydopamine coating caused a slight drop in rejection for BW membranes however our membranes showed a slight increase owing to the reduced flux. Thus both Polydopamine and Polyvinyl Alcohol show similar trends however the increase in magnitude of Polydopamine is very large.

However one needs to know that although Polydopamine has shown a higher % increase in fluxes it is very expensive and commercially unavailable. While polyvinyl alcohol is cheap and very easily available commercially. It has been

more experimented with in the past on membranes due to its film forming properties. Hence optimizing PVA coated membranes further should not be a major challenge.

From the above comparison we can say that 10% MA crosslinked PVA membrane shows more promising results than other coated membranes.

5.2 Conclusion:

The data shows that there is a promising increase in the water fluxes in SW membranes in PRO mode as well as in permeability tests in RO mode. Maleic acid at a lower cross linking degree for PVA has shown substantial improvement in water fluxes. Contact angles decreased for these coated membrane. It tells us that by implementing hydrophilicity in the interface of support and selective layer we can enhance passage of water and salt molecules through it hence insuring 'wetter porosity' [12]. This will lead to non-fouling of FO membranes and drastic reduction in internal concentration polarization.

However no drastic drop in contact angle for BW membrane. Further work needs to be done in increasing the hydrophilicity of BW membranes. PVA modified BW membranes showed a drastic reduction in fluxes in RO mode while no improvement in PRO mode due to its pore structure. Smaller pore size and overall tight porosity seemed to be making PVA and the crosslinker clog the pores.

We can say that the pore morphology of the support as well as the hydrophilicity of support layer impact a membranes performance in FO processes to a great extent. State of art RO TFC membranes can be modified to improve their support

layer hydrophilicity and can be used efficiently in FO processes. By this we can definitely make a move towards energy consumption in water treatment processes.

5.3 Future Work:

There is still plenty of room for improvement in PVA modification process. A membranes performance is always determined by its preparation conditions. By tweaking every preparatory condition individually and optimizing it, more hydrophilicity can be imparted resulting in more increase in water and salt flux.

1. As seen earlier in preliminary experiments lowering PVA concentration results in increase in flux. We could further lower PVA concentration ex to 0.05% by weight and see the effects on membranes.
2. The lower the crosslinking the more the hydrophilicity imparted, hence we could fix the degree of crosslinking at 10% or further decrease it to see if it makes any significant improvement. However presence of crosslinker is necessary to stabilize PVA on the membrane.
3. Although Maleic acid turned out to be a better crosslinker than Glutaraldehyde in terms of increase in hydrophilicity , it itself is hydrophobic in nature [27]. A new crosslinker could be tried which does not tend to clog the pores by forming a very tight network and at the same time little more hydrophilic as compared to Maleic acid.
4. Various experiments could be conducted on the longevity of PVA solution in contact with the support layer of the membrane. We had restricted our contact

time to 10 mins, but effects could be seen if performances improve if this contact time is increased.

5. Crosslinking time i.e. time of stirring PVA and the crosslinker has a huge effect on the membrane flux. Beyond a time of 1 minute the flux increases drastically [26]. We kept the stirring time as 30 minutes sufficiently high as compared to results shown in [26]. However this could be further optimized to increase water flux further.

6. Heating time and temperature i.e. curing of membrane also has an effect on flux. More the curing is done the tighter is the network and crosslinking reaction between PVA and the crosslinker also is enhanced [26]. Hence the heating time and temperature could be optimized further.

By this we can improve the current PVA surface modification method further and significantly higher performance in Forward Osmosis process can be achieved.

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