# Impact of Salts in PEMs used in Various Environmental and Industrial Applications

**MSc. ANALYTICAL CHEMISTRY**

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2. PSS – Polystyrene sulfonate

3. PE – Polyelectrolyte

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5. PEM – Polyelectrolyte multilayer

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# Abstract

This paper is focused on the formation of polyelectrolyte multilayer (PEM) membrane fabricated from weak and strong polyelectrolytes. Layer by layer (LbL) alternating sequential adsorption of polyallylamine hydrochloride (PAH) and polystyrene sulfonate (PSS) electrolytes on a porous substrate is used to fabricate these membranes. The effect of salt on membranes performance is also investigated. The designed PEM membrane were characterized using spectroscopic as well as microscopic analytical instruments like attenuated total reflectance fourier transform infrared (ATR-FTIR) spectroscopy, UV-visible spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM).

# CHAPTER 1

## 1.1 Introduction

Membrane technology has becoming more popular as a result of its high efficiency, low energy consumption, low cost, and ease of use**.** Membranes are employed in wide range application including separation and purification of substance, environmental protection, energy conservation, and storage. In 1997, Decher demonstrated that the alternating exposure of a surface to positive and negative polyelectrolytes solutions, allows for layer by layer (LbL) deposition of thin films of polyelectrolytes, so called polyelectrolyte multilayers (PEMs)[1]. Among the methods developed to prepare thin films, the LbL deposition of polyelectrolytes has aroused considerable attention due to its simplicity and versatility. In addition this technique has the advantage of enabling nanoscale control of the thickness, the structure and composition of films. Beside the preparation of PEMs on flat surfaces, the LbL technology has been extended to produce well defined hollow capsules. These multilayers show specific response to change in the environmental conditions such as pH, temperature, ionic strength, magnetic field[2]. In this work, PEM are fabricated by dipping based LBL assembly of polyallylamine hydrochloride (PAH) and polystyrene sulfonate (PSS). The influence of salt in PEMs generated on membrane surface is investigated, followed by PEM membrane characterisation using ATR-FTIR, UV-visible, SEM, AFM. PEM membrane show great potential for application in field such as controlled release of bioactive compounds, tissue engineering, biosensors, and optics.

## 1.2 Membranes- History

Membrane is a thin layer of semipermeable material that allows just certain molecules or ions flow through while blocking the passage of others. The process that happens when a semipermeable membrane permits molecules to move through it is referred to as diffusion. The size and charge of membrane pores determine the degree of selectivity. Membranes are widely available in natural or synthetic materials. The synthetic materials could be organic such as polymers and macromolecules, and inorganic such as Ceramics and metals.

### 1.2.1 Inorganic membrane

The main types of inorganic membranes include the dynamic membrane, liquid membrane, ceramic, silica, zeolite, carbon and hybrid inorganic-organic membranes. For the production of inorganic membranes, many process such as slip casting, sol-gel method, chemical vapour deposition (CVD), and pyrolysis have been recommended as extensively utilized approaches[3].

#### 1.2.1.1 Ceramic membrane

The most widely utilised materials for the manufacture of ceramic membranes include alumina, titania, zirconia, glass, silicon carbide, or a combination of these metal oxides. Non oxides (carbides, borides, nitrides, and silicides) and composites of oxides and non oxides are also acceptable materials. Three primary steps are involved in the fabrication of tubular ceramic membranes: (a) making a paste or suspension from the ceramic powder; (b) moulding the paste or suspension in to the desired geometry (i.e., tubular or flat); and (c) heat treating using calcination and sintering[4]. In the first fabrication step, ceramic membranes are made from dispersion of fine particles called slip. The microstructure and quality of the membrane are affected by the additive added to the ceramic material at this stage[5]. For easy handling and to maintain the shape of the ceramic membrane precursor, Burggraaf and Cot additionally utilised a polymer binder and plasticizers[6]. In the second step, a slip casting process is utilised to deposit the slip on a porous membrane support and a porous mould is used to form the ceramic membrane in to the desired shape[7,8]. Extrusion is one more method to fabricate tubular and hollow fiber ceramic membranes[9]. After the ceramic membrane has achieved its appropriate shape, the ceramic membrane precursor are manufactured in the third and final stage. Pre sintering thermolysis, and sintering are the three basic stages in which ceramic membranes are dried and heat treated. To eliminate water from the membrane precursors pre sintering take place around $200^0$C. Thermolysis is the process of removing all organic components from the membrane precursor. The final sintering stage is necessary to make significant modifications to the membrane's porosity and pore size, creating the final membrane shape and mechanical strength[10].

### 1.2.1.2 Silica membrane

Silica membranes are commonly employed in industrial applications such as hydrogen separation at high temperatures and simultaneous reactions and separation process[11,12]. Silica membranes are well known for their high selectivity, temperature resistance, and chemical resistance[13]. Silica membrane made using the sol-gel technique have been studied, and the sol-gel approach is preferred due to its ease of use and low cost, as well as the ability to tune the needed porosity. Furthermore, because of its controllability and homogeneity, the sol-gel process is commonly used in membrane synthesis or membrane pore modification[14,15]. The sol-gel process involves coating of a porous substrate with an appropriate colloidal solution, which is then dried and heated[16,17]. In CVD, a gaseous interactions between a Silica precursor another reactive agent such as oxygen water or ozone, results in the formation of silica deposition. The oxidation of $SiH_4$ or tetraethylorthosilicate, hydrolysis of $SiCl_4$, and thermocracking are possible reactions of the silica precursor[18]. During the sol gel process, the substrate is coated using the dip coating, spin coating, and pendulum process[19]. Due to its high hydrogen sepearation selectivity and its lower utilisation in water applications, vycor glass has received more attention. Vycor glass is anticipated to be less susceptible to thermal cracking because its thermal expansion coefficient is comparable to that of $SiO_2$[20].

#### 1.2.1.3 Zeolite membranes

Natural and synthetic Zeolites are hydrated aluminosilicates that contain cations from group 1 and 2, such as Na, K, Ca, Mg, Sr and Ba. Most of the features such as membrane wettability and membrane surface charge are controlled by the ratio between Si and Al in zeolite structures. The surface hydrophilicity and water affinity of the membrane are controlled by the Al concentration of zeolite structure[21]. In comparison to polymeric membranes, zeolite membranes formed on porous inorganic substrates have several advantages, including homogeneity, molecular sized pores, and great chemical and thermal stability[22]. The method of hydrothermal crystallisation is commonly utilised to make zeolite membranes. A gel containing water, amorphous silica, a source of tetrahedron framework atoms other than Si, a structure directing organic template, and sometimes a mineralized agents, such as NaOH, is crystallized on porous support using an autoclave at a specific temperature and time in hydrothermal crystallization[23]. Furthermore, zeolite crystals generated via hydrothermal synthesis are not homogeneous in size due to low heating rate and non-uniform heating, as the zeolite nuclei do not form on the support surface at the same time[24].

### 1.2.2 Organic membrane

Polymeric materials are the most common materials used to make organic membranes. In terms of membrane morphology, polymeric membranes are typically classified as isotropic or anisotropic as shown in fig.1.1[25]. Isotropic membranes include nonporous dense membranes, microporous membranes, electrically charged membranes whereas anisotropic membranes include integrated asymmetric membranes, composite membranes, and supported liquid membranes.

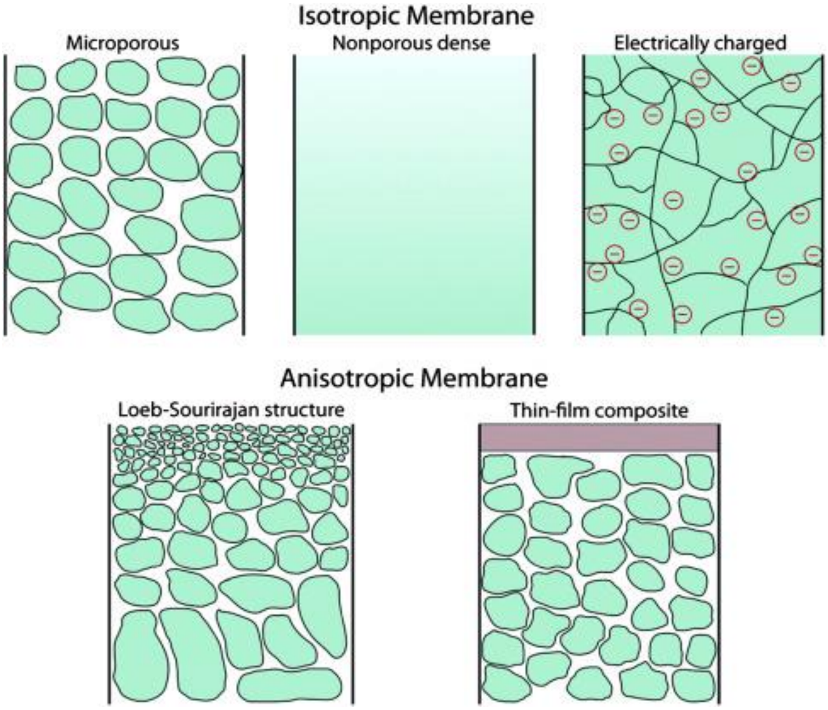


**Fig 1.1.** Schematic diagram of isotropic membrane and anisotropic membranes

#### 1.2.2.1 Isotropic membranes

Dense membranes have a dense film through which permeates are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. The separation of different mixture components is directly correlated to their respective transport rate within the membrane, which are dictated by their diffusivity and solubility in the membrane material, through process like pervaporation and reverse osmosis.

Isotropic microporous membranes have a rigid interconnected pore, and voided structure distributed randomly; its pore diameter is in the order of 0.01-10mm. According to the hydrodynamic and hindered transport hypothesis, particles bigger than the biggest pores are fully rejected, whereas particles smaller than the largest pores are partially rejected by deep filtration and screen filtration. The pore size distribution of micro porous membranes and the hydrodynamic circumstances govern the separation process.

Electrically charged membranes can be dense or microporous, although they are usually very finely micro porous with fixed positively or negatively charged ions in the pore walls. An anion exchange membrane is a membrane that binds anions in the surrounding fluid and has fixed positively charged ions. Similarly a cation exchange membrane is a membrane that contains fixed negatively charged ions. Separation using charged membranes is primarily accomplished by the exclusion of ions with the same charge as the fixed ions of the membrane structure, and to a lesser extent by pore size. The charge and concentration of the ions in solution have an impact on separation. For example, monovalent ions rejected less efficiently than divalent ions and selectivity falls in high ionic strength solutions.

#### 1.2.2.2 Anisotropic membranes

Anisotropic membranes have layers that change the porosity and pore size throughout the membrane wall. Anisotropic membranes typically have a thin surface layer that is supported by a thick microporous substrate. The thin skin layer serves as selective layer for separation, while the microporous substrate serves primarily as a mechanical support. Membrane fluxes are extremely high due to the very thin selective layer.

Loeb and Sourirajan produced integrally asymmetric membranes in the 1960s, which were made utilising the phase inversion approach and a single membrane material. Different layers of the membrane have different porosity and pore sizes. On the top surface, there is selective thin layer, which is followed by more and more loose layers. In the phase inversion process, the thin skin layer and porous substrate are formed simultaneously, and they are connected with one other.

Compared with integrally asymmetric membranes, composite membranes usually have two separated layers with different separation functions and different membrane materials. The porous substrate provides mechanical support, while the skin layer serves primarily as a selective layer. During the preparation procedure, they are not connected interface polymerization, plasma polymerization, solution coating, and other methods can be used to prepare skin layer independently. The benefits of higher fluxes provided by such membranes are so great that they are used in practically all commercial processes.

Supported liquid membrane have a microporous structure that is filled with the liquid membrane phase; the mechanical strength is provided by the microporous structure, and the selective separation barrier is created by the liquid filled pores. The liquid membrane phase should be supported under hydrostatic pressure by the microporous substructure, which should have a high porosity and small pore[26].

## 1.3 Polymeric membranes

Polymeric membranes are the industry's favourite choice for membrane separation, because they are both cost-effective and versatile. The most significant property required in polymeric membranes is affinity for a certain particular component. It is also simple to regulate the pore size of a polymeric membrane during its formation. Cellulose acetate (CA), polyacrylonitrile (PAN), polyimide, polycarbonate (PC), polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE) are the common examples of polymeric membranes[27].

Polymeric membranes can be classified based on the polymeric material, i.e. glassy and rubbery. Glassy polymers have high selectivity and low permeability, whereas rubbery polymers often have high permeability for gases but relatively low selectivity, making it possible to achieve high purity[28]. All glassy polymers are brittle at sufficiently low temperatures, but they become ductile when the temperature approaches the glass transition temperature. Glassy polymeric membranes have recently become the focus of research in the field of gas separation due to their mechanical strength, reproducibility, cost effectiveness, and processing capacity as well as their ease of use and versatility[29]. Polymeric membranes are used in fuel cell and lithium battery applications various optoelectronic applications, and conductive polymeric coatings and films[30].

### 1.4 Different filtration methods

Membrane filtration is a very effective and cost effective way of separating components that are suspended in liquid.  Pressure and specially engineered membranes with varied pore sizes are used to separate the particle based on their size and shape. Microfiltration, ultrafiltration, nanofiltration, and reverse osmosis are the different membrane filtration processes in order of increasing pore size. There are two operating modes for membrane filtration: dead end filtration and cross flow filtration. In dead end feed solution flow is perpendicular to the membrane surface. Some particles are caught in the membrane and form a filter cake in dead end filtering mode .In a cross flow system, the flow is parallel to the membrane surface. This operative modality is characterized by a lower tendency to fouling than dead end flow mode, and so cross flow operation is generally preferred for industrial applications.

#### 1.4.1 Microfiltration (MF)

Microfiltration is the most frequently used and economically valuable membrane technology. The MF membrane allows macromolecules and dissolved solids to flow through, while suspended particles and colloids are excluded. MF commonly used as a pre-treatment process of ultrafiltration as well as a post treatment for granular media filtration. MF removes particles in the range of approximately 0.1 to 10 micron[31]. Dead end mode of filtration is the most commonly used process for MF. The materials used for MF membranes also include nylons, poly(tetrafluoroethylene), polypropylene, polyethylene, and blends of CA and cellulose nitrate[32]. Water, monovalent species such as sodium or chloride ions, dissolved or natural organic materials, and tiny colloids and viruses will flow through the filter with ease.

Applications

- In the waste water treatment plant, it is used to separate pathogens such as protozoa, Cryptosporidium and Giardia lambia etc.
- It is also employed for petroleum refining. It filters flue gases for particulates. It is utilised in the dextrose clarifying process.
- The clarifying and purification of cell broths is also accompanied using microfiltration. It distinguishes macromolecules from proteins, large molecules, or cell waste.

  Microfiltration is also used in the paints and adhesives industries[33].

### 1.4.2 Ultra filtration (UF)

Ultrafiltration is a pressure driven membrane filtration technique for concentration, fabrication and purification of macromolecules in solution without the use of chemicals or solvents. The pore size of ultrafiltration membrane fall between nanofiltration and microfiltration with a pore size range of 0.001-0.05 micron. Many organic solvents, such as hexane, benzene, methanol, aceticacid, acetone, ethoxy ethanol and chlorinated hydrocarbons, are resistant to polyimide UF membranes, making them promising. UF operating pressure is low and in the range of 2-5bar[34]. Ultra filtration membranes are capable of separating larger materials such as colloids, particulates, fats, and proteins, where sugars, and other low molecular weight molecules pass through the membrane. UF membranes are manufactured by the phase inversion process. .Polysulphone (PSF) is an outstanding ultrafiltration membrane material due to its mechanical strength and outstanding thermal stability, and superior chemical resistance across the entire pH range[35].

Applications

- UF is used to clean raw water of particles and macromolecules. It separates the paper pulp mill's waste water.
- It is used in dairy industry to produce protein concentration. Whey protein concentrate (WPC) and lactose-rich permeate are obtained and it is also used in cheese making process.
- It aids in the bacterial elimination from the milk.
- Aids in the recovery of enzymes.
- Desalting and solvent- exchange of proteins are both done with this method[36].

### 1.4.3 Nanofiltration (NF)

NF membranes typically have pore size of 1nm, which corresponds to molecular weight cut-off(MWCO) values of 300-500Da. Due to the dissociation of surface functional groups or the adsorption of a charged solute, NF membranes in contact with aqueous solution are also mildly charged[37]. The main characteristics of NF membrane are their cost, surface chemistry, porosity, pore size distribution, and physical and chemical compatibility with process liquors. The membrane functionality depends on three layers, an active layer, a porous supporting layer, and macroporous structure underneath. The mechanical properties are modified with the aid of the supporting layer. And the final layer is a macroporous layer below the medium layer[38]. The micro hydrodynamics and interfacial events occurring at the membrane surface and within the membrane are necessary for the separation of solute in the NF range[39].

Applications

- It is employed in the natural essential oils industries for the gentle separations and Enrichment of natural constituents from crude extracts.

- Amino acids and lipids are extracted from blood and other cell culture for use in the medical field.
- It is used in oil and petroleum chemistry to purify gas condensates and eliminate tar components from feed[40].

### 1.4.4 Reverse Osmosis (RO)

Reverse osmosis is an effective and proven technology for producing water that is suited for wide range of applications that require demineralized water. The gradient of the chemical potential across the membrane, which includes the applied hydraulic pressure, provides the driving force for species transport through RO membrane. Water molecules travel through the membrane along such a gradient, while salt ion transport is largely hindered, resulting in water selectivity[41]. Because of the small size of the pores, it necessitates osmotic pressure. The elimination of the solvent does not necessitate a phase transition, hence RO saves energy. It has no effect on the pH or chemical composition of the product. As a result, RO has a negligible impact on quality characteristics and nutritional value of the finished product, especially when compared to evaporative concentration, which invariably results in heat deterioration as well flavour and nutritional loss.

Applications

- It is also used to make potable water from saline water in solar powered desalination units.
- Used in self-contained water treatment system called a reverse osmosis water purification unit (ROWPU).
- Used in manufacture of hydrogen in small scale. .It prevents mineral deposits from forming on the electrode surfaces[42].

## 1.5 Polyelectrolytes

Polyelectrolytes are polymers with ionisable repeating groups, such as polyanions and polycations. Polyelectrolytes can dissociate in solvent like water, leaving charges on polymer chains and releasing counter ions in to solution. Polyelectrolyte solutions exhibit a variety of behaviour due to electrostatic interactions between charges[43]. Based on their orgin, they are classified as natural, synthetic and chemically modified natural PEs. For eg: proteins are natural PEs, whereas PSS is synthetic and xanthum gum is chemically modified natural PE. According to their dissociation behaviour, PEs can be weak or strong. Strong polyelectrolytes receive full charge spontaneously such as poly sodiumstyrene sulfonate, polydiallyldimethyl ammonium chloride, while weak polyelectrolytes are only partially charged such as Polyvinylamine, poly L-lysine, polyacrylic acid, polyallylamine hydrochloride . The charge is determined by pH and ionic strength of the solution. Due to the repellent interactions between the molecules in solution, polyelectrolytes incline towards an extended form with lower ionic strength. However PE will thicken if the ionic strength of the solution increases. At low concentrations chain expansion polyelectrolytes are virtually rod-like in pure water, but when salt is added, the degree of expansion decreases because the polymer charges are somewhat protected from one another[44]. Although PEs are water soluble, when crosslinking occurs, they are not dissolved in water. Crosslinked PEs swell in water and act as water absorbers and are referred to as hydrogels or super absorbent polymers. Polyelectrolytes have a wide range of application in fields, such as in flocculation agents in water, dispersion agents in ceramic slurries as super plasticizers[45]. PE have been used in various fields, ranging from material science and colloids to biophysics due to their exceptional water stability and ability to interact with oppositely charged macromolecules and surfaces. The smaller counter ions balance the electrical neutrality by neutralising the repeated charged groups. The introduction of ionic moieties in to the PE environment can change the physical properties of PEs such as viscosity, diffusion coefficient, solubility, pH, ionisation constant, ionic strength. Optoelectronic devices, solar cells, rheology modifiers, adsorbents, coatings, biomedical implants, colloidal stabilisers and drug transport and medicinal uses are most common applications[46].

## 1.6 Layer by Layer method (LbL)

Layer by layer assembly method is one of the most frequent ways for fabricating thin films in the biomedical field. Various forms of interactions, including as electrostatic, hydrophobic, hydrogen bonding, charge transfer, and others, occur between the PEs throughout the LBL assembly process, resulting in film growth. To monitor the LBL process, many techniques like zeta potential, quartz crystal, microbalance, dynamic light scattering, fluorescence, correlation spectroscopy, and others have been applied[47].

The most common used LbL techniques are dipping, spaying and spin coating. Dipping LbL is time consuming process which allows them to cover surface of almost any size and shape by dipping a substrate alternately in to aqueous polycation and polyanion solutions with a washing step in between deposited layers. On the other hand, spray assisted LbL is a time saving technique and it was demonstrated by schlenoff et al.in 2000. It produces multilayer films in few seconds by sequentially spraying polycation and polyanion solutions, which makes it appealing for automatization and has the potential to scale up to the industrial level . The fundamental advantage of spray coating over dip coating is the reduction in multilayer creation time by up to 64 times. LbL assembly by spin coating was first demonstrated by Hong. The spin coating process produced a film thickness of 24A° per bilayer at spinning speed of 400 rpm, compared to roughly 4A° for the dip coating procedure under the same conditions. Spin LbL assembly is a time saving technique, and it is based on spinning a substrate to facilitate the deposition of polymers. Recently, a new LbL technique, named brush LbL was developed by Park et al., and it is based on the sequential brushing of polyelectrolye solutions over a substrate. The PE adsorption is determined by centrifugal forces, viscous forces, and electrostatic interactions during spin coating. They identified brushing LbL as a reliable and more effective multilayer film construction approach compared to traditional LbL methods for practical applications in dental and clinical situations[48].

In this method, initially charged membrane is first immersed in the positive dilute solution of cationic PE. The membrane is then taken out of the solution and washed with water to eliminate of unbound molecules. Then the obtained positively charged membrane is dipped in the negative dilute solution of anionic PE followed by water washing in each step, causing a small number of PEs to adsorb on the membrane surface, reversing the previous charge of the membrane. Multiple positive and negative layers on to the membrane surface cause the preparation of polyelectrolyte multilayers membranes[49]. LbL is best suited for the fabrication of drug delivery films because it imposes no constraints on the size or shape of substrate and does not require high temperature or pressure. PEs, micelles, graphene oxide (GO), nanoparticles and proteins can be employed as building blocks for the LbL assembled multilayer films[50].

### 1.7 Polyelectrolyte multilayer (PEM)

Polyelectrolyte multilayers (PEMs) are incredibly promising selective layers for membrane applications due to their versatility. The most widely used technique is dip coating that modifies a charged surface by Lbl deposition of polycations and polyanions[51].The PEMs overall electrical neutrality is explained by the charge compensation mechanism, as introduced by Schlenoff et al. Intrinsic and extrinsic charge compensation. The compensation of oppositely charged functional groups of the polycation and polyanion are known as intrinsically compensated and correspond to the ionic crosslinks in the PEM. While the compensation of charged functional group by mobile counter ions is referred to as extrinsic compensation. PEM with low ionic strengths stacks together to generate dense, thin layers with lots of intrinsically compensated charges. High ionic strength cause PEM build up, which leads in less dense, thick layers, with a higher amount of extrinsic charge compensation[52]. High selectivity and permeate flux are provided by these polyelectrolyte multilayer membranes. Electrostatic interactions, covalent bond, hydrogen bonds, van der waals forces or hydrophobic interactions are all contribute to the formation of multilayers as shown in the fig (1.2)[53].

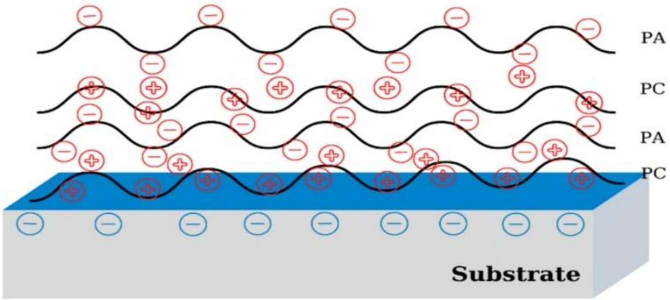


**Fig 1.2.** Schematic representation of polyelectrolyte multilayer

Numerous parameters were reported to affect the properties of PEMs including polyelectrolyte type, salt concentration, pH and even PE molecular weight. The ionic strength has an impact on the swelling and shrinkage properties of multilayers. When salt is added to the solution, the LbL film swells, and the ions in the solution adsorb some of the charges on the PE solution. Kharlampieva et al. investigated how ionic strength affected PEMs made possible by spin assisted deposition. The multilayers produced in salt free solutions had a well- defined structure, however when salt ions were present, the layers interdiffused[54]. Formation and properties of multilayers formed with weak PE are influenced by pH. According to Guzman et al. the pH largely affected the deposition of weak PEs, such as PAA, which diffused better in the surrounding layers at low pH, resulting to the adsorption of a thicker layer. The diffusion of PAA into the opposite charged layers is prohibited at high pH values[55].

Studying the LbL assembly of PSS and PAH on ethanol solution, Proptoshev et al. discovered that a higher concentration of ethanol in the solution results in the production of a thicker film due to the reduction in the solvation effect[56]. The number of bilayers in the multilayer film is a crucial element that influences the membrane permeability and selectivity. The number of bilayers determine the amount of polyelectrolytes deposited during each step. With more bilayers, selectivity improves as the pores of the support layer are better sealed, but the flux drops rapidly due to the increased thickness of the selective layer[57].The PE molecular weight can definitely influence the formation of PEMs on model surfaces by affecting the parameters like layer growth, thickness and mass. The difference in mobility and layer interpenetration between PEs of low and high molecular weight have been largely the influence of molecular weight. Low molecular weight PE are observed to form multilayers that grow exponentially, owing to their higher diffusion coefficient, which allows faster PE transport in to PEM bulk during layer formation. Layer interpenetration and the development of complexes at the PEM surface were both associated with low molecular weight. On the other hand, PEs with high molecular weight are said to grow layers in linear mode, resulting in films with limited interpenetration between layers. PEMs with a large molecular mass are more stable than those with a small molecular mass[58]. One of the most significant element in the LbL assembly process is the dipping time. Polyelectrolytes must diffuse from the bulk solution to the region of oppositely charged surface and deposit on it as dilute polyelectrolyte solutions. Counter-ions must also take time to form complexation on the charged surface. The optimal dipping time is determined by the combined effects of the diffusion speed of polyelectrolyte molecules in solutions, charge over compensation degree of polyelectrolyte on the substrate, and time spent forming cross linked structures among the charged groups[59].

The mechanical properties of multilayers are influenced by the macromolecular structure of PE employed in multilayer production, as well as self-assembly circumstances and the amount of water retained in the system .Depending on the water content multilayers may have a gel like or rigid behaviour depending on the amount of water in them, and their uses are directly tied to the material flexibility[60].PEM have the ability to respond to induced stimuli. The stimuli-responsiveness of these materials is a key characteristics for applications such as drug delivery or biosensing[61,62].

## 1.8 Characterisation methods

Characterisation is a crucial field in material science. Characterisation techniques are commonly employed in membrane research to confirm the quality and purity of the manufactured membranes. Characterisation techniques are also useful for understanding membrane performance and investigating membrane deterioration.

### 1.8.1 Fourier transformed infrared spectroscopy- Attenuated total reflectance

The infrared spectrum of absorption (or emissions) of a solid, liquid, or gas is obtained using fourier transform infrared (FTIR) technique. This method provide the information about polymer compounds, chemical bonds in a molecule, additives, or organic pollutants. It is regard as one of the most effective methods for studying and comprehending the chemical surface chemistry of diverse membranes. In terms of performance the FTIR approach can be used to assess the stability and durability of certain membranes. It is good for examining chemical changes at top layer. Attenuated total reflection (ATR) is another approach for generating FTIR spectrum without use of a reference material. A beam of infrared light is supplied to the sample in ATR through a diamond based ATR crystal. This will result in the formation of evanescence waves. The FTIR data is subsequently generated by detecting and analysing the reflected beam[63].

### 1.8.2 UV-visible spectroscopy

UV-Visible spectroscopy is a versatile, easy, low cost, non destructive analytical approach that can be used to analyse a wide range of organic and inorganic species. It measure the absorbance or transmittance of the light passing through a medium as a function of the wavelength[64].

### 1.8.3 Scanning electron microscopy

SEM analysis can be used to properly characterise ceramic, polymeric, and carbon membranes, taking in to account the membrane surface and cross sectional morphology. The signals of elasticity backscattered electrons and inelastically scattered secondary electrons are commonly combined in SEM images. SEM microscope may magnify objects up to 100,000 times, with a resolution limit of roughly 100nm or 2.5nm for high resolution instruments. Back scattered electrons penetrate deeper and are more sensitive to compositions, whereas secondary electrons are more sensitive to surface topography[65].

### 1.8.4 Atomic force microscopy

This technique is increasingly being utilised to investigate the surface morphology and physical properties of a wide range of surface at high resolution. AFM scans the surface of interest and generates a three dimensional map. Unlike many other high resolution imaging techniques, it can make observations in both ambient and liquid environment. The surface morphology of polyelectrolyte multilayer membrane can be evaluated by atomic force microscopy[66].

## 1.9 Applications

The advantages of LbL deposition process, such as facile deposition conditions, the ability to utilise a large number of materials, and the ability to generate systems with varying characteristics depending on the deposition conditions, have led to the use of multilayers in diverse applications.

### 1.9.1 Drug delivery

Nanomaterials as drug vehicles provides many advantages, such as controlled drug release, targeted delivery, and to bypass the cellular surface multi-drug-resistance mechanism[67]. Due to the increased permeability and retention effect, LbL assembled nanoparticles have a strong tendency to aggregate in tumor tissues, making it easier to targeted delivery of anticancer drug to specific locations with enhanced efficiency. These therapeutics encapsulated LbL assembled nanoparticles can circulate through the blood for a longer time. A chemotherapeutic agent like paclitaxel has been put in to PEGylated poly-l-lysine (PLL)/poly-L-glutamic acid (PGA) nanoparticles, with an average size of 100 nm. Paclitaxel is a chemotherapy drug used to treat a variety of cancers. In cell culture medium containing serum, the nanoparticles remained same. The PEGylated PEs adsorption increased antitumor efficacy against two cell lines: the mouse colon carcinoma cell line CT26-CEA and the mouse mammary carcinoma cell line 4T1, by extending the durability of nanoparticles in blood serum and improving their in vivo tumour targeting function. Similarly, PAH and PAA have been LBL coated on poly(3,4-ethylenedioxythiophene)/PSS, which has been changed with aminated PEG-derivative by esterification utilising ethyl-dimethylaminopropyl-carbodiimide(EDC) as a coupling agent. The resultant nanoparticles were employed to deliver anticancer drugs in a regulated manner shown high stability under physiological conditions. Furthermore, upon intravenous administration, they demonstrated stealth-like behaviour as well as lengthy blood durability, resulting in an exceptional tumor uptake[68]. Recently, a method for loading photosentizer drug onto the hollow $CaCO_3$ nanoparticles using LbL of PSS and PAH was developed. After being encapsulated, phthalocyanine derivatives loaded in microcapsules maintained their photophysical characteristics. The hollow multi-layered microcapsules were investigated using steady state and time resolved techniques. Cancer cells were used to evaluate their biological activity in vitro, and results showed 80% more cell death than control[69].

### 1.9.2 Protein delivery

Proteins have both positive and negative residues on the solvent-accessible surface, making them weak PEs. Proteins normally have a low charge density because only five residues (Asp, Glu, His, Lys, Arg) have a charge around physiological pH. Protein transport and construction of nanoassemblies in which proteins serve as real building blocks can both be accomplished using PE-protein electrostatic complexation[70]. To create a protein and peptide delivery system, the LBL method was employed to encapsulate proteins in nanoparticles made of natural polysaccharides, chitosan, and dextran sulphate. Bovine serum albumin (BSA), a model protein, and the PE were put together using the amino groups of the $SIO_2$ core. At pH values of 1.4 and 7.4, which simulate the blood and stomach conditions, the BSA controlled release from hollow nanocapsules was successfully carried out[71].

To increase the absorption of insulin given orally, pH sensitive methyl methacrylate (MMA)/itaconic acid (IA) nanogels have been utilised as carriers. In order to achieve this, insulin was added by LbL PE complexation to the nanogels. Several parameters were optimised, including the insulin: nanogel ratito, pH, incubation period, and stirring rate. In vitro, the nanogels released 28.71% of insulin in simulated gastric fluid and 96.53% of insulin in simulated intestinal fluid, respectively. The result of SDS-polyacrylamide gel electrophoresis test showed that the primary structure of insulin was unaltered. The injection of nanogels to diabetic rats decreased blood glucose level considerably. As a result, these LBL nanogels can be employed to deliver insulin in a different way[72]. Moreover, both alginate based and chitosan dextran sulphate nanoparticles may be employed to shield the protein in oral administration applications since they were stable at acidic pH and displayed pH-dependent insulin release. Biological activity of the released insulin was also retained for up to 24 hours at intestinal pH, and nanoparticles were stable for up to 4 weeks when kept in cold aqueous solutions. When administrated orally, the nanoparticles also increased the bioavailability of insulin[73]. Furthermore, for protein delivery, a unique method that induces nanoporosity within the LbL assembled films has been disclosed. Electrostatic interactions were used to generate multilayer films by sequentially adsorbing poly (ethylene imine) (BPEI) polycation, HA polyanion, and cationic gold particles. The nanoparticles incorporated in the assembly structure were simply dissolved in an aqueous cyanide solution to produce the nano-porous film, resulting in greater loading and release of protein like ovalbumin[74].

### 1.9.3 Tissue engineering

PEMs are also used in tissue engineering because of their ability to interact with biological components like proteins and nucleic acids, as well as their sensitivity to external stimuli. PEs employed in these applications are often natural PEs with biocompatibility, such as HA, CS, and sodium alginate[75]. A biocompatible support made on PLL and HA was developed by Khademhoseini et al. that promote cells to adhere and develop. The multilayer made up of two PEs were deposited on glass support and utilised to grow and separate two different types of cells (stem cells, hepatocytes, and fibroblast). The obtained results showed that the support was viable for cell culture and had a five-day stability[76]. In order to modify the surfaces of living cells and tissues for a variety of tissue engineering applications, nano-thin conformal coatings made of poly(L-lysin)-g-poly(ethylene glycol)(biotin)/streptavidin were fabricated. These coatings can be tuned without affecting the viability and function of the cells and tissues they are applied to[77]. LbL assembly was used to make PE films with alginates, chitosan-graft-phosphorylcholine, and poly-Lysine-graft-polyethylene glycol. The film ability to produce universal red blood cells was then tested. This is a successful technique for designing functional multilayers for encapsulating cells and tissue[78].

### 1.9.4 Thin films with antimicrobial activity

Many naturally occuring PEs have the ability to inhibit the growth of microorganisms, and their assembly in multilayers has application in the fabrication of non-adhesive or antibacterial films. These systems can be fabricated by LbL deposition of PEs, as well as by creating multilayers between PEs and inorganic substance that have antibacterial properties, including silver nanoparticles. Neto et al. developed LbL films with silver nanoparticles that completely inhibited Candida albicans and Staphylococus auureus[79]. Ivanoa et al. reported the fabrication of antimicrobial composite materials using a LbL assembly of HA and aminocellulose (AC) on a monobutyl ester of poly(methylvinylether/maleic) acid template. The antibiofilm forming ability of the multilayerd particles was tested, and it was found to be 94% effective against Escherichia coli and 40% effective against Streptococcus aureus[80]. Francesko et al. used LbL deposition of silver nanoparticles coated with CH or AC and HA to fabricate thin films. Streptococcus aureus and Escherichia coli both were inhibited by the developed composite material[81].

### 1.9.5 Environmental applications

Many authors have showed that layer deposited membranes may be used to separate contaminates from water, such as medicines, dyes, and metal ions, utilising ultrafiltration, reverse osmosis, or nanofiltration. Ilyas et al. developed the nanofiltraion membranes using LbL deposition of PEs. The dense structure of NF membranes based on PAH and PAA prepared at pH=6/6 improved the retention of organic pollutants tested (atenolol, sulfamethoxazole, atrazine, naproxen, and bezafibrate) whereas the membranes prepared at pH=3.5/3.5 and pH=6/3.5 had a better retention capacity for charged micropollutants[82].

Rajesh et al. developed a PEs based membrane on a polyacrylonitrile (PAN) nanofibrous material by LBL deposition of branching PEI/PAA. Baburaj et al.separated two dyes (methylene blue and Coomassie brilliant blue) from water using PEI/PAA and CS/PAA membranes. The dye removal efficiency of two membranes was good, with the amount of pollutants retained depending on the type of PE utilised, the number of deposited bilayers, and the pH of the dye solution[83]. Toutianoush et al. used a (PAN/poly(ethyleneterephtalate) support to deposit PVA and PVS. NaCl and sulphate ion were completely rejected by the membrane, while magnesium, calcium, and sodium ions were separated more effectively[84].

Fadhillah et al .showed the viability of using UF to purify water. On a polysulfone membrane, the researchers built a PAH/PAA multilayer and examined the ability to reject sodium ions. The membranes with 120PE bilayers had a 65% salt rejection, while the membrane with 60PE bilayers had a 58% salt rejection rate[85].

## 1.10. REVIEW OF LITERATURE

Ahmad M.Alghamdi (2021) successfully fabricated a PEM by depositing alternating layers of branching polyethyleneimine (PEI) and polysodium 4-styrene sulfonate (PSS) on an ultrafiltration polysulfone (PSF) membrane using spin assisted layer by layer assembly. The divalent ion removal capability of the manufactured membrane was tested. The fabricated membrane outperformed commercial membranes like NF 90 in test conducted under same conditions, exhibiting rejection rates of 89% and permeate permeability of 4.37L/h bar $m^2$. A rejection rate of 93.95% and a permeate permeability of 0.9L/h bar $m^2$.were achieved using $(PEI/PSS)_{10}$-0.05 respectively.

Bijay P Tripati et al (2013). developed a diverse set of multilayer assemblies with controllable surface charge by pressure driven permeation of poly(sodium-4-styrenesulfonate) (PSS) and poly(diallyldimethylammonium chloride) (PDDA) solution through track etched membranes. The developed membranes had good antifouling properties due to their high hydrophilicity and water uptake. After the formation of multilayer assemblies, pore size and water flux reduced, but dye rejection increased. The membranes were evaluated for their ability to reject a variety of water soluble dyes in order to determine their use in the removal of organic contaminates from water.  The developed membrane also shown good antibacterial properties which is capable of prevent the formation of biofilm. The dye rejection property showed by prepared membranes was high, and more than 99% for congo red was observed for LbL-15 membranes.

Ettora Virga et al (2021). investigated the influence of membrane surface chemistry on fouling in surface water treatment for PEM based nanofiltration membrane. They prepared nearly uncharged crosslinked PAH, strongly negatively charged PSS, and zwitterionic PMP-co-AA to make three membranes. They found that surface chemistry of PAH fouled more than the PSS. Because of the charge control, negative BSA adsorbed better on PSS than positive BSA. Filtration test using synthetic and actual surface water showed that bio inspired zwitterionic phosphatidylcholine surface chemistry has outstanding fouling resistance and stable filtration performance. These membranes are promising not just for surface water treatment but also for molecule separation and filtration of other feeds with high fouling potential due to their stable selectivity and exceptional fouling resistance.

Johs de Grooth et al (2015). studied the long term stability of polyelectrolyte multilayer modified membranes. They studied on both physical stability of multilayer as well as on the chemical deterioration of two different multilayers in the presence of hypochlorite. PEM modified membranes based on sulfonated poly(ethersulfonate) shows no performance loss during successive backwash cycles. After each backwash cycle, PEM modified membranes based on the non-ionic poly(ethersulfone) shows a gradual rise in permeability and loss in retention .UV-vis mesurements of polyelectrolyte solutions mixed with hypochlorite revealed that the polycation PAH is highly reactive with hypochlorite, while the polycation PDADMAC and polyanion PSS shows less reactivity. When PEM modified membranes were subjected to hypochlorite, the stability and retention was found to be 4-5 times higher for membranes coated with PDADMAC / PSS compared to PAH/PSS coated membranes. After 24,000ppm hours NaOCl (pH 8) membranes coated with multilayers based on PDADMAC are found to be stable for over 100,000ppm hours NaOCl (pH 8).

Usha k Aravind et al (2007). investigated the transport of BSA, lysozyme and ovalbumin through chitosan/polystyrene sulfonate membrane at their isoelectric point (pl), pH below and above their isoelectricpoint. They observed that the number of deposited layers and pH of the solution had a significant impact on the transport behaviour of proteins across these multilayers. Transport studies via composite membranes revealed that a bilayer CHI / PSS multilayer (permeate flux of $0.49m^3/m^2$ day) at 10 psi rejected BSA 95% of the time. At 10psi, a 5bilayer membrane at pH 8.8 showed permeate enrichment, with more than 100% of ovalbumin is permeated (permeate flux of $25.7m^3/m^2$ day) and 98% lysozyme rejected (permeate flux of $11.7m^3/m^2$ day).

Disha V J et al (2012). reported the potential use of PES/PSS assembled by layer by layer method on a nylon microfitration membrane for the recovery of phosphate from water in the presence of chloride under ultrafiltration condition. A total number of 9 bilayers constructed from polyelectrolyte solutions of varying ionic strength (0-1M of NaCl) were used for the selective recovery of phosphate. This particular bilayer combination resulted in high flux membranes that permitted selective $H_2PO_4$ removal in the presence of $Cl^-$ at low pressure (0.28 bar). The magnitude of negative solute rejection of chloride increased with the number of bilayers for a given salt concentration. The best observed $Cl/H_2PO_4$ selectivity (310.23, flux $2313.53m^3/m^2$ day) was obtained when the increase in magnitude with ionic strength was so large.

Danielle scheeper et al (2021). investigated the influence of charge density and ionic strength on poly(acrylamide-co-diallyldimethylammonium chloride) P(AM-co-DADMAC)/ polystyrene sulfonate (PSS) and polydiallyldimethylammonium chloride (PDADMAC/PSS, with a polycation charge density of 32 and 100%. The effect of charge density and ionic strength during layer formation had been investigated in terms of polyelectrolyte adsorbance, membrane surface charge, and filtration performance. Due to the limited uptake of two bilayers, they discovered that low charge density is a limited parameter for polyelectrolyte adsorption and retention. Results shows that NF membranes cannot be formed using solely p(AM-co-DADMAC/PSS layers. Increasing the ionic strength of high charge density polyelectrolytes was found to be increase PE adsorption and $MgSO_4$ retention. For p(AM-co-DADMAC) based membranes, increasing ionic strength causes a decrease in surface charge and an increase in permeability and viceversa for PDADMAC.

## 1.11 OBJECTIVES

- Selection of appropriate support polymeric membranes for PEM fabrication.
- Selection of apt polyelectrolytes for designing and development of PEMs.
- Utilization of LbL procedure for PEM fabrication.
- Characterisation of newly designed PEM membrane using various analytical instruments.
- Proposal of newly designed and developed PEMs for various applications.

## 1.12 SCOPE OF THE PRESENT WORK

PEM membranes has shown to be potent tool for surface modification, with numerous application in the field such as drug delivery, protein delivery, tissue engineering, cartilage regeneration, wound healing, medical implants, biosensors, optics, environmental remediation, and pollutant retention as well modern energy conservation and storage systems. In terms of long term stability and performance, these PEM membranes outperform the majority of commercially available membranes.

# CHAPTER 2

## 2. Materials and Methods

### 2.1 Materials

Nylon 6,6 (no.4) was used as support for multilayer formation. Polyallylamine hydrochloride (PAH, MW=65000 g/mol (0.5M) was purchased from Aldrich CO), Polystyrene sulfonate (PSS, MW=70000 g/mol (0.5M), 30% in water, purchased from Sigma Aldrich), 1M HCl, NaCl, distilled water was used for the membrane rinsing and for the preparation of polyelectrolyte solutions.

### 2.2 Multilayer buildup

The supporting membrane nylon 6, 6 was rinsed with distilled water and kept in water for 24hr. The supporting membrane was first dipped in PAH solution for 15 min. The pH of PAH were kept as 6. After dipping, membrane was rinsed with distilled water to remove loosely bounded polyelectrolytes for 5 min. Then the membrane was dipped in the solution of PSS for 15 min, followed by rinsing with water. Thus one bilayer PAH/PSS polyelectrolyte was obtained by LbL method. By repeating the procedure desired number of PAH/PSS layers can be obtained. For investigating the influence of salt on bilayer formation, supporting membrane was first dipped in the PAH solution, rinsed with distilled water, then immersed in the solution of PSS in 0.1M NaCl, followed by rinsing with water. The procedure was repeated until the required number of bilayers were formed.

### 2.3 Film characterization

ATR-FTIR, UV-Visible, SEM, AFM were used for the characterization of bare membrane and multilayer build up on the bare membrane.

# CHAPTER 3

## 3. Result and Discussions

We are fabricated 2, 4, 6 and 8 bilayers via LbL method. This has been confirmed and characterized using various analytical instruments like ATR-FTIR, UV-visible, SEM, AFM. The following results confirmed the fabrication of designed bilayers.

### 3.1 ATR-FTIR

A spectroscopic characterization of PAH/PSS multilayers (2bl, 4bl, 6bl, 8bl) was performed with ATR-FTIR. The formation of bilayers on the supporting membrane was confirmed using sulfonate peak as the indicator band. Fig.3.1. presents the characteristic infrared frequency region for the sulfonate group at 1034cm$^{-1}$. As seen in the figure, the sulfonate peak height increases with number of deposited layers. At this region, bare membrane has no peak. From fig.3.2. it is clear that , In the presence of salt peak height increases correspondingly.

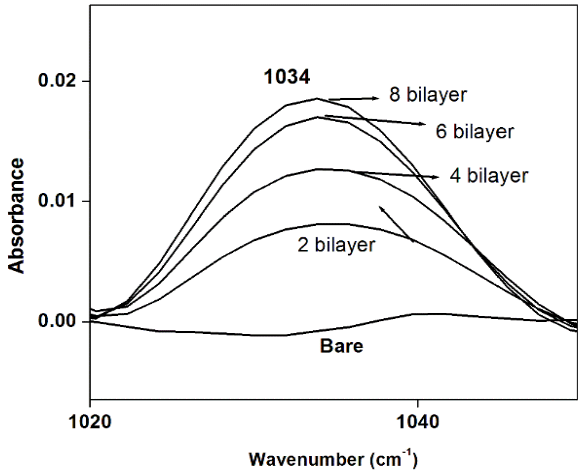


**Fig 3.1.** ATR-FTIR spectra of bare and PAH/PSS films consisting of different number of bilayers

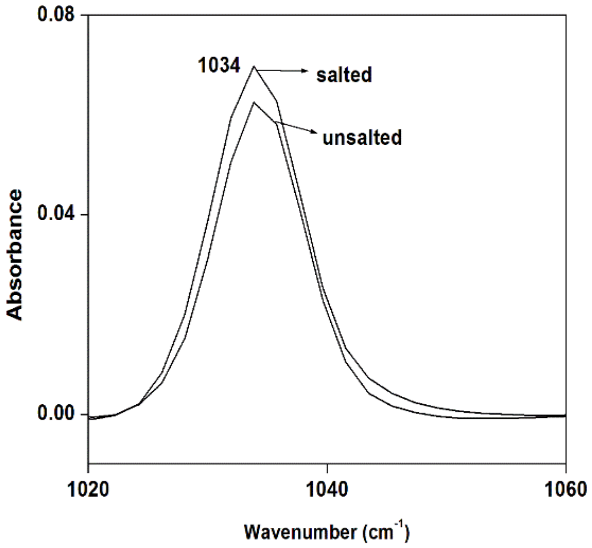


**Fig 3.2.** ATR-FTIR spectra of eight bilayered PAH/PSS (0.1M NaCl)

### 3.2 UV-visible spectroscopy

UV-visible spectroscopy was used to track the development of PAH/PSS multilayers and the result is shown the fig.3.3. The absorption spectra shows that the electronic absorbance of the films increased linearly with number of bilayers suggested that same quantity of material was adsorbed at each deposition step. This linear growth suggest an equal amount of polyelectrolyte is adsorbed at each step with exact charge compensation.

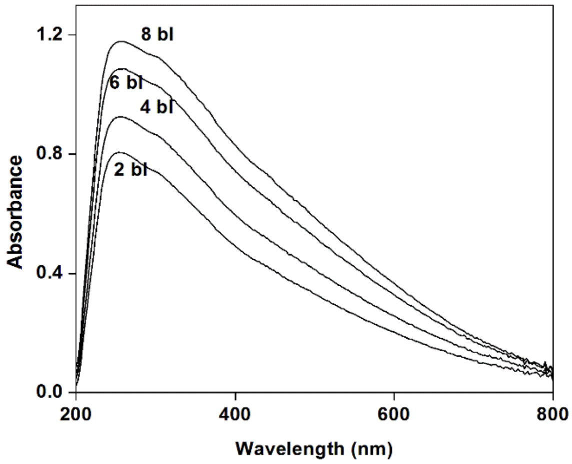
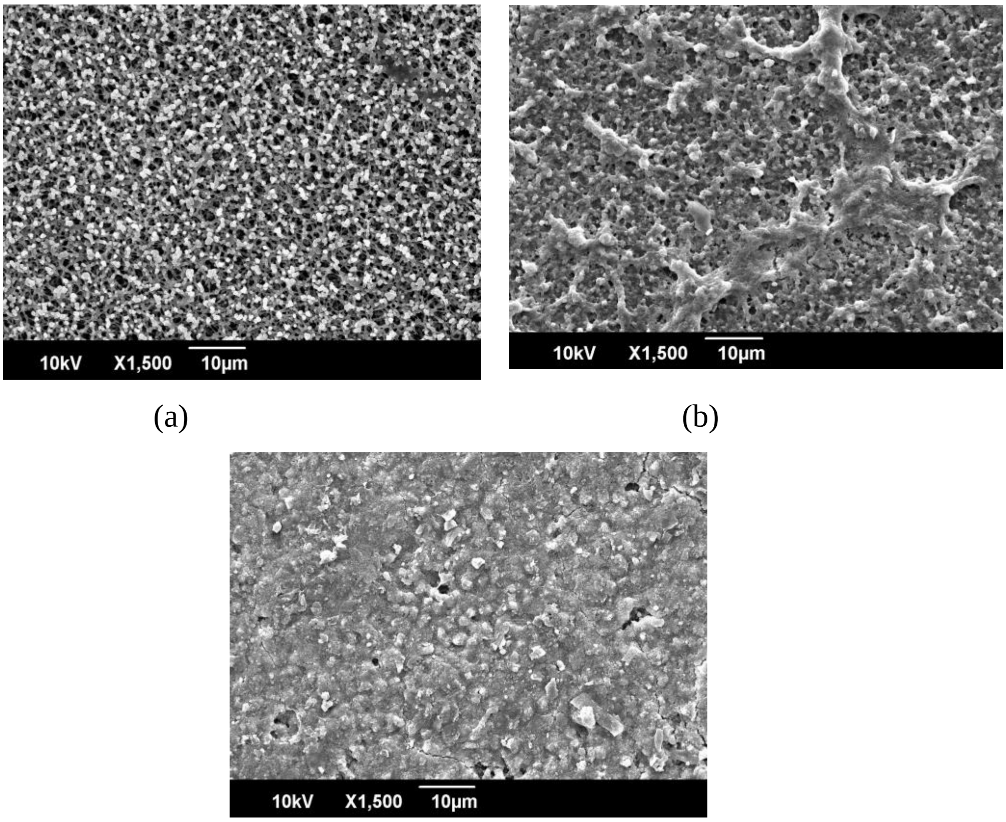


**Fig 3.3.** Absorption spectra of PAS/PSS films containing different number of bilayers

### 3.3 SEM

A cross sectional view of a bare membrane is presented in the fig.3.4(a). The development of multilayer on the surface of bare membrane has shown in the fig.3.4(b). The pore are visible even after coating 8 bilayers. The deposition of salt containing electrolyte results in uniform coating as seen in fig.3.4(c) A SEM image of 8 bilayers with salt evidenced the formation of the thick polyelectrolyte bilayers on the support. The bilayers appears more smooth and flat.



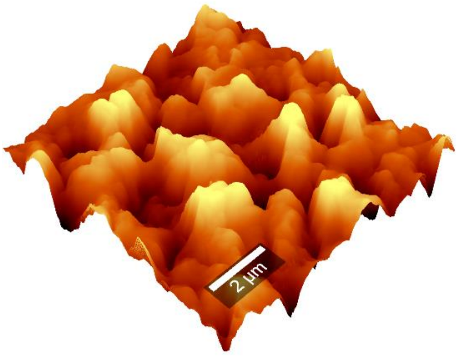
(a) (b)

(c)

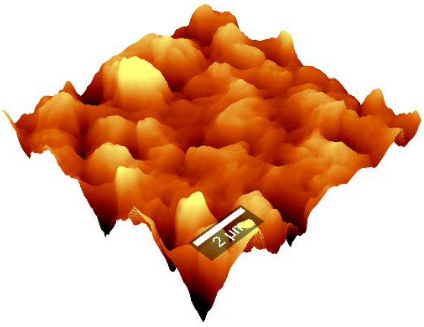
**Fig 3.4.** SEM images of membranes (a) Bare membrane (b) eight bilayered PAH/PSS on nylon6,6 (c) eight bilayered PAH/PSS (0.1 M NaCl)

### 3.4 AFM

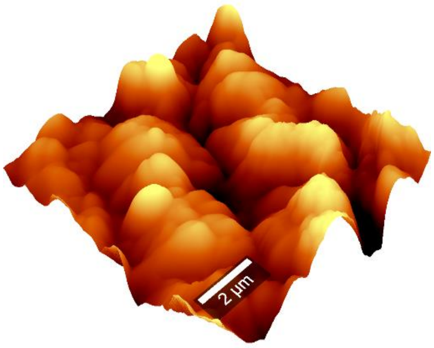
The surface topographic studies of bare and modified membrane is done using AFM images. Light region represent the highest point and dark region designating the depression and pores of the bilayer. The clearly visible dark regions on the images are represented as pores of bilayers. The average thickness of PAH/PSS were found to be 2μm. It is clear that the salted bilayers have smaller pores than bare ones which increased the smoothening of the surface for salted ones. This may be due to the increase in thickness by salt addition.



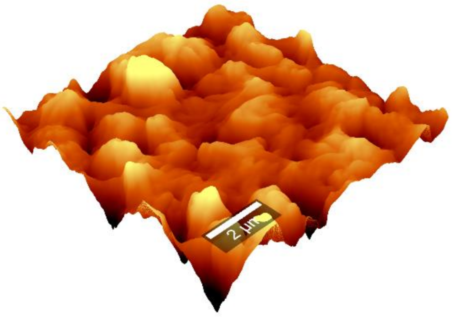
(a)



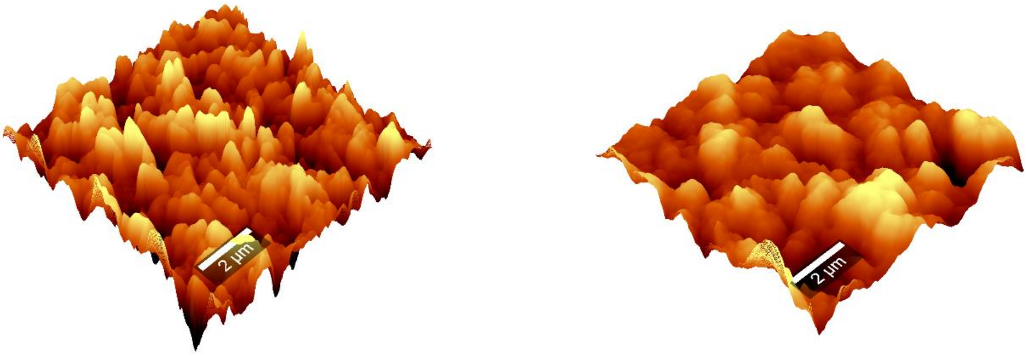
(b)



(c)



(d)



(e)

(f)

**Fig.3.5.** AFM images of membranes (a) Bare membrane, (b) 2 bilayer PAH/PSS, (c) 4 bilayer PAH/PSS, (d) 6 bilayer PAH/PSS, (e) 8 bilayer PAH/PSS, (f) 8 bilayer PAH/PSS (0.1 M NaCl).

# CHAPTER 4

## Conclusion

In this work, PEM membrane were successfully fabricated via LbL assembly by alternate deposition of PAH and PSS on nylon 6,6 substrate, The developed bilayers over the membrane were characterized and confirmed by different analytical techniques like UV-visible spectroscopy, attenuated total reflectance fourier transform infrared (ATR-FTIR) spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM). Impact of salt in bilayer formation has been studied. This study highlights that the salt addition caused an increase in thickness of bilayers compared to unsalted ones. This designed and developed membrane membranes offers meaningful applications such as drug delivery, protein delivery, tissue engineering, sensing applications and environmental applications like removal of micropollutants from water.

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