Design And Characterisation of Poly Electrolyte Membrane's (PEM's) for Industrial Application

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Abstract

Poly electrolyte membrane's, PEM have a wide range of application over chemical, petrochemical industries, fuel cells, electrodialysis, ultrafiltration etc. This work is focusing on the design of polyelectrolyte membrane using Polyallylamine Hydrochloride, PAH and Polystyrene Sulphonate, PSS with Nylon 6,6 as supporting membrane by means of layer by layer,LBL method and characterisation of the multilayers with the assistance of analytical tools such as Scanning Electron Microscopy(SEM),Atomic Force Microscopy(AFM) , Fourier Transform Infrared spectroscopy (FTIR) and UV- Visible spectroscopy.

Keywords: PAH – polyallylamine hydrochloride, PSS – Polystyrene Sulphonate, LBL method - Layer by Layer method, PEM – Polyelectrolyte multilayer membrane

Chapter 1

1.1 Introduction

Polyelectrolyte multi layer membranes can be prepared from a wide range of applicable substrates using layer-by-layer deposition method. These PEM's are obtained by the self assembly method of cationic and anionic polyelectrolytes which undergo layer-by-layer deposition in the aqueous solution. PEM's have many applications in the fields like bio optics, water purification, petrochemical industries, bio sensors, electrodialysis and so on. We are going to construct the polyelectrolyte multilayer membrane from Poly Allylamine Hydrochloride (PAH) and Poly Styrene Sulfonate using Nylon 6,6 as supporting membrane.

1.1.1 Membranes A Brief History

Membranes are special type of barriers which allow certain substance to pass through and block other, simply they are selective . There are two types of membranes , biological and synthetic. The application of membranes were started from the period of 2nd world war for the filtration of drinking water but the cost and reliability was quite high so it was not widely used but now several companies had taken over the membrane techniques and ruling the market. Depending on the pore size of these membranes it is again classified into microfiltration(MF), ultrafiltration(UF), nanofiltration(NF), and reverse osmosis(RO) membranes. There is active and passive transport through membranes and which are charged or neutral. The main steps in the membrane process are [4]

1. Calculation of membrane permeability.
2. Calculation of operational driving force per unit membrane area which is known as trans membrane pressure (TMP)
3. Cleaning of the surface membrane.

The total permeate flow can be calculated using the equation

$Q_p = f_w \cdot A$

Where,

Q_p is the permeate stream flow rate and its unit is kg/ sec

f_w is the water flux rate and its unit is kg/m^2 s

A is the membrane area.

The permeability can be calculated by the equation

$K = f_w / P_{TMP}$

TMP can be calculated by the formula

$$P_{TMP} = \frac{Pf+Pc}{2} - P_p$$

TMP is calculated in kilo Pascal.

Pf is the inlet pressure,. Pc is the pressure of concentrate stream and Pp is the permeate stream pressure.

Flux may be defined as the hourly or daily flow of water through the membrane surface area and the water that passes through the permeate. The flux rate depends on the type of the membrane , physical property of the membrane and the environmental condition of operation.

The membrane process can be controlled by two modes

1. Constant TMP mode.
2. Constant flux mode.

The rejection of materials will be affected by these operation m0des

That is, the flux of water through the membrane decrease at a given TMP and the TMP will increase at a given flux which reduces the permeability. This is called the fouling phenomenon which is the major limitation of membrane process.

The two process modes is mainly used for

a) Dead end filtration where all the substrate passes through the membrane which result a permeate .

b) Cross flow filtration, here the feed water is pumped with a cross flow tangential to the membrane. Here only a fraction of feed water is converted to permeate.[5]

The recovery will be reduced if the permeate is further used. In dead end filtration, the flux and permeability decreases due to the increase in flow resistance. In cross flow process, there will be a continuous deposition of material up to a point where the binding force is balanced by fluid force, which is a steady state condition. So the flux will remain constant for a preferred period.

As we have already discussed, fouling is the main limitation for membrane process. This can be controlled by some pretreatment methods, cleaning requirements and operating conditions. At initial stage fouling can be expelled through physical or chemical cleaning. In physical cleaning the methods adopted are

1. Back washing, where we pump the permeate in the reverse direction through the membrane. Since this method requires energy to operate, the expenses are high.

2. Membrane relaxation, here the filtration is paused for a period. By this method the permeate can be maintained for a long time.

3. Back pulsing, it is a method mainly used for ceramic membranes where a high frequency back pulse effectively removes the dirt layer.

In chemical cleaning method we add certain cleaning chemicals to the back washing at a low concentration. The main cleaning reagent used is citric acid and sodium hypo chlorite.

The operating conditions can be optimized by reducing the flux, choosing cross flow filtration over dead end filtration and the pre treatment of the feed water. The recent studies are trying to alter the surface chemistry of these membrane materials to eliminate membrane fouling.[6]

1.1.2 Membrane Configuration

The geometry of the membrane is explained through membrane configuration which accounts based on the positions of the membrane , flow of the feed fluid and the permeate. Generally there are four types of membrane configurations;

1. Tubular configuration
2. Hollow fibre configuration
3. Plate and frame configuration
4. Spiral wound configuration

The tubular configuration resembles the shell tube heat exchanger. Even though the ratio of volume to surface area is not much high we can construct tubes of diameter within the range of 10 mm – 25 mm. A polymer or ceramic porous tube is used to synthesis these type of tubular configuration membranes. Usually the direction of flow is inside out but we can often carry out outside in flow too. On inside out flow, retentate flows through the tube and permeates are collected over the shell side. These configuration are mostly recommended for feeds containing highly concentrated suspended solids.

Hollow fibre configuration is also like a tubular configuration, the only difference is that the tube diameter is much thinner and have a range of 1mm.This is because the are called hollow fibers. This configuration not requires an external support as its tubes itself impart sufficient mechanical strength. The flow direction may inside out or outside in. The compactness these membranes are their greater advantage. The main challenge faced by the configuration is fouling and clogging. So their application is limited to low viscous liquids.

Plate and frame configuration is like a plate and frame press where the filter media is replaced by membranes. One can use circular and square shaped membranes which are arranged either vertically or horizontally. The main disadvantage is that it cannot withstand high pressure so their application is limited microfiltration and ultrafiltration.

In spiral wound configuration, two large sheets of membrane are heat sealed on three sides which forms like a bag. Into this, a flexible supporting layer is inserted which may be either a spacer mesh or a porous layer. This will produce a free space where the permeate can flow. Then it is wounded spirally. The open side of the spiral act as a collector for the permeate. The space between membrane sheets will provide a channel for retentate to flow. Spiral wound configuration poccess the highest surface area to volume ratio.

The main characteristics of a membrane configuration are

a. Compactness

b. Low resistance to tangential flow

c. Must poccess uniform velocity distribution

d. To minimise fouling and maximise mass transfer, high degree of turbulence is required at retentate side

e. Cleaning and maintenance of the modules must be easy

f. Cost of production must be less

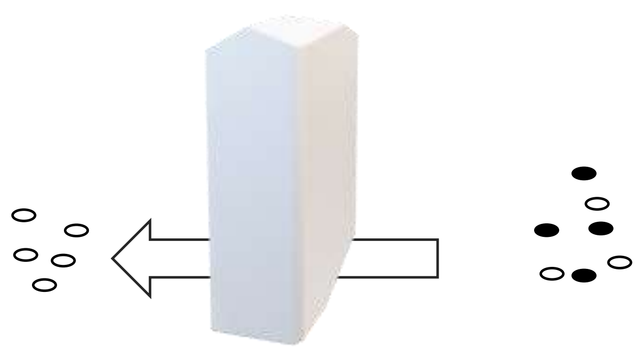


Figure 1.1 Schematic representation of transport of a particular species across a polymer membrane

1.1.3 Different Membrane Filtration Methods

The membrane filtration techniques have taken over other filtration methods because of their versetile features like low energy consumption, compactivity and green nature. Specially designed membranes are used to separate particle based on their shape and size. The main membrane filtration methods are;

1.1.3.1 Microfiltration(MF)

It is a conventional method of membrane filtration which is used to separate pollutants from fluids. The membranes used in this method poccess a pore size with in the range of 0.1- 10 micro meter and is operated at pressure of 2 bar. Mostly the polymeric microfiltration membranes are synthesised from isotropic network of polymer fibers and they poccess interconnected pore structures.[7] The main objective of this membrane filtration method is to provide a barrier for sediments, algae, protozoa, and large bacteria through the designed filter. Particles like water, sodium or chloride ions, dissolved and natural organic compounds are allowed to pass through the membranes. Cross flow mode is recently operated using MF membranes which intend to reduce the deposition process. MF found application in waste water treatment, separate pathogens like protozoans, cold sterilisation process, petroleum refining, dairy sector to terminates unwanted microorganisms, dextrose clarifying process, clarifying and purification of cell broth , paints and adhesive industries.

1.1.3.2 Ultrafiltration (UF)

Ultrafiltration is a pressure driven membrane filtration method mainly used to separate macromolecules and colloids from solutions. Particle size ranging from 0.002 – 0.1 micron is filtered off. During low pressure high flux rate can be achieved. UF membranes are synthesised by phase inversion process. Some Polymer materials used to synthesis UF membranes are polysulfones, polypropylene, cellulose acetate, poly acrylic acid. For high performance application ceramic membranes are used.[7] Both cross flow and dead end filtration methods are used in UF method. The major characteristics of these membrane technique is its pore size and the molecular weight cut-off. UF membranes are so versatile that they can filter even filter particles which are 5000 times smaller than human hair. UF membrane method found application in the fields like paper industry, dairy industry, acid recovery from enzymes, removal of bacteria from milk, fruit juice clarification and concentration, desalting ,solvent exchange of protein. The cleaning techniques will differ according to the membrane configuration. For tubular membrane generally cleaning is done using low foam alkaline detergents having a concentration range of 0.6-1% about 40 to 60 minutes. This method is employed for organic particulates. If it is inorganic then citric acid of concentration 3% is used for a time period of 1-3 hours. To clean these membranes we can also use hydrochloric acid, oxalic acid, sulphuric acid and nitric acid.

1.1.3.3 Nanofiltration

Nanofiltration which is a pressure driven membrane separation technique that is widely used to isolate sugars, specific salts, synthetic dyes and multivalent ions. These membranes have pore size larger than those of reverse osmosis membrane and smaller pore size than UF and MF membranes. A range of 1-10 nano meter is the pore size of nanofiltration membranes. The pressure applied will be in between 3.5 – 16 bar. The pore size of these membranes can be controlled on the development period by adjusting pH, temperature and time. So they are more compact than UF membranes and the membrane charge as well as the surface negative charge on these membranes plays a major role in the filtration process.[8] Low pressure operation, low cost of maintenance, better retention of multivalent ions are the merits of this filtration method. On the otherhand this method consumes more energy than UF and MF. And also the membranes are more expensive than the reverse osmosis membranes.

There are three layers which controls the membrane functionality. First one is the active layer which determines the selectivity and permeability of components. Second one is the porous supporting layer which regulates the mechanical properties of the membrane. And the final one ,macro porous layer. NF methods are applied in food and dairy industries, textiles , pulp and paper industries, waste water treatment, drinking water purification, edible oil processing industries.

1.1.3.4 Reverse Osmosis

Reverse osmosis is a widely used technique for production of demineralised water. The applied hydraulic pressure is the driven force for the transport of species. When the applied pressure is greater than the osmotic pressure Water molecules simply passes through the membrane while the salt ions get blocked. RO consumes lesser energy than other process and also it has no effect over pH or chemical composition of the substrate. The membranes used are thick polymer matrix which is either a skin layer of asymmetric membrane or an interfacially polymerised layer.[9] Reverse osmosis membranes are used in desalination, water purification and in the production hydrogen where it is used to prevent the mineral deposition at the electrodes.

1.1.4 Polymeric Membranes

Polymeric membranes are widely used for membrane separation because of their cost effective and versatile nature. The affinity towards a particular component is the important property required by a polymeric membrane. The pore sizes are regulated towards the producers requirement during the synthesis period. The commonly used polymeric membranes are cellulose acetate (AC), polyacrylonitrile (PAN), polyimide, polycarbonate (PC), polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE).[10] To improve the selectivity and permeability of membranes, the surface will be either hydrophilic or hydrophobic. The main classification of Polymeric membranes are glassy and rubbery. Where glassy membranes possess high selectivity and low permeability which results high purity during filtration on the other hand rubbery membranes have high permeabilty and lower selectivity. At low temperatures glassy membranes are brittle but they become ductile as the temperature approaches glass transition temperature. Polymeric membranes are widely used in gas separation due to their selectivity and permeability. And also they found applications over fuel cells, lithium batteries, optoelectronics and conductive polymeric films and coating.[11]

1.1.4.1 Nylon 6,6

Nylon 6,6 is a condensation polymer formed from the monomer hexamethylenediamine and adipic acid. Due its high mechanical strength, chemical resistance , rigidity and stability nylon 6 6 is used as fibers in textile and carpet industries. It is also used in the manufacture of various automobile parts , rocket covers, oil pans, parts of radiator end tanks, various machine parts and polymer framed weapons.[12] Nylon 6 6 is a more hydrophilic than PSu support but less swelling propensity than other hydrophilic polymers. These membranes can be used for Microfiltration. The SEM studies over the surface of nylon 6 6 support yields the result that there are rough and open pores which are of small pore region and large pore region.[13]

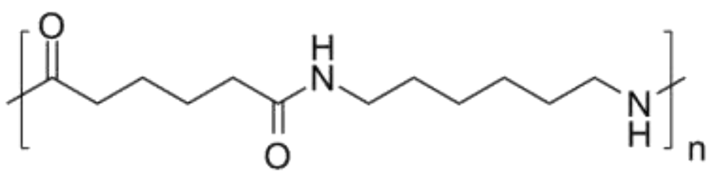


Figure 1.2 Nylon 66

1.1.4.2 Polyallylamine Hydrochloride(PAH)

PAH is a cationic pH depended weak polyelectrolyte which can be prepared by the polymerisation of allylamine.[1] By combining it with a anionic polyelectrolyte through layer by layer method we can construct a polymer film of negative and positive charge. Also PAH poccess many biomedical application such as cell encapsulation.

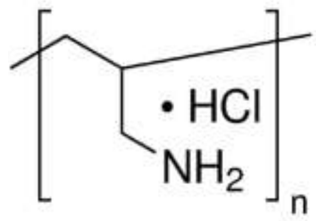


Figure 1.3 PAH

1.1.4.3 Polystyrene Sulphonate(PSS)

PSS is an anionic strong polyelectrolyte which can be combined with a cationic polyelectrolyte by means of layer by layer method to produce a charged polymeric membrane.[3] PSS can be also used for water softening, dye improvement agent for cotton, resin used as solid acid catalyst in organic synthesis.

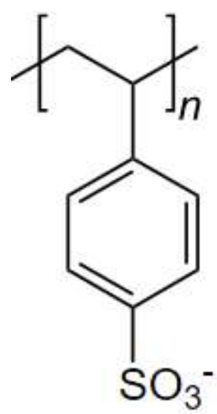


Figure1.4 PSS

1.1.5 Layer By Layer Method

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.[14]

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. Furthermore, the washing step has been eliminated from the multilayer build up process in favour of continual draining to remove the excess material sprayed on to the surface reducing deposition time by up to. 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.[15] 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.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. 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.[1]

1.1.6 Characterisation Techniques

Different types of analytical tools can be used to record information regarding the functional groups, chemical composition , surface morphology. UV Visible spectroscopy, FTIR spectroscopy, AFM and SEM can be used to characterise the polyelectrolyte membrane.

1.1.6.1 UV-Visible spectroscopy

UV-Visible spectroscopy is a widely used characterisation tool for nano particles. Energy absorbed in the UV Visible region changes the electronic excitation of the molecule and produce a change in its UV-Visible absorption in the electromagnetic spectrum. When the UV-Vis light fall on the PEMs the amount of light transmitted or absorbed are measured and is compared with the blank polyelectrolyte. Thus the properties of multilayers are found through UV-Vis spectroscopy. For example, if we take an aqueous buffered solution containing the sample is used for measurements, then the aqueous buffered solution without the substance of interest is used as the reference.[21]

1.1.6.2 Atomic Force Microscopy(AFM)

Atomic Force Microscopy is a surface characterisation tool used for nanostructured coating. The high resolution nanoscale images are the versatile feature of this technique. The surface topography of the polyelectrolyte membrane can be characterised. AFM generates 3 dimensional image by scanning the surface of sample. It is a versatile tool for the characterisation of structure and properties of polymer nanocomposites.[23] The main advantage of AFM is that it can make observations in both ambient and liquid environment.

1.1.6.3 Scanning Electron Microscopy(SEM)

By scanning the surface of the specimen through a focused electron beam will reveals the information about the surface topology and chemical composition. The SEM produces images by scanning the sample with a high energy beam of electrons. As the electrons interact with the sample, they produce secondary electrons, backscattered electrons, and characteristic X- rays. SEM analysis provides high resolution imaging useful for evaluating various materials for surface fractures, flaws, contaminants or corrosion.[22] SEM is a powerful tool that can be used to characterise the surface topology of the polyelectrolyte multilayer membrane.

1.1.6.4 Fourier Transformed Infrared Spectroscopy(FTIR)

The multilayer structure can be assessed by FTIR spectroscopy. It can reveal information about the presence and absence of specific functional group ,as well as chemical structure of the polymeric membrane. By measuring the absorbance of IR radiations between two bonds we get a spectral data. for each functional group, we get different set of peak which can be act like a figure print material. FTIR is widely used in research, early and late development, scale up and reaction optimization. This technology analyzes batch and floe reactions, reactions in polar and non-polar solvents, and reactions over broad pH, temperature and pressure ranges.[20] Data collection is automated, with qualitative or quantitative information typically generated every minute.

1.1.7 Application of PEM's

1.1.7.1 PEM's in Tissue Engineering

PEM**s** are used in Tissue Engineering due to their ability to interact with the biological molecules such as proteins or nucleic acid and also their sensitivity to external stimuli. HUMIC ACID, CS, Sodium Alginate etc are natural PEMs used for this purpose.[23] Khademhosseini et.al developed a bio compatible support based on PLL and HA. Multilayer consisting of two polyelectrolyte was deposited on a glass support and this was used to grow and differentiate two cell types like stem cells and fibroblasts. The result obtained showed that the cells were stable for about five days and also the viability of the support for the cell.[24]

1.1.7.2 Bio Sensing Applications

Bio sensing have wide range of application in the medical field. The selectivity of PEM surface is the key factor for the bio sensing property. The fabrication of electrochemical biosensors are based on the electrical properties of polyelectrolyte i.e. their ability to interact with oppositely charged functional group. Here a chemical response is converted to electrical response since enzyme incorporated biosensors have specificity and they mediate in chemical reaction between receptor and substrate.[25] Optical biosensors are based on the optical interaction with a bio-recognition material. The detected signal can be generated directly by the interaction of the probe with the transducer or by applying a colorimetric fluorescent or luminescent method.

1.1.7.3 Removal of Waste From Water

Water pollution is a major problem in our society. The various pollutants found in waste water by human activities causes serious health issues to both animals and humans and also for the ecosystem. Some of the pollutants updated by the Norman Network are dyes, pesticides, pharmaceuticals and household and personal care products such as perfume, disinfectants, insect repellent etc. These are called as emerging contaminants. These are resistant to degradation and have high persistence in aqueous media, which cause hazardous effect on ecosystem.[26] The hazardous risk involved are bioaccumulation, toxicity and carcinogenic potential. Layer by layer deposition is used for making characterized and porous multilayer. PEs used for the preparation of multilayer include PAA, PSS, PAH,PEI, CS etc. Membranes thus produced can be used for the removal of pollutants by UF, RO, NF etc. A large number of multilayer have been produced by different scientists. Ilyas et. al produced PEs of nanometer size based on PSS/PAH at pH=6 which was proven effective against retention of sulfamethoxazole and SO_4^{2-}. Rajesh et. al produced PEs based on PEI and PAA on PAN , which showed a high water flux and 98.7% retention of $MgSO_4$.[27]

1.2 Review Of Literature

Xin Li et. al published a journal based on the polyelectrolyte self assembly and its versatile membrane fabrication strategy in 2022. In this review the selection criteria, structure performance relation are detailed which is essential for the membrane making.

Transport of BSA, lysozyme and ovalbumin through chitosan/polystyrene sulfonate membrane at their isoelectric point(pl), pH below and above their isoelectric point is studied(Usha K. Aravind, Jissy Mathew, C.T Aravindakumar). 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.

An article of Monika Schonhoff published in the year 2003 gives the fundamental studies of self assembled polyelectrolyte multilayers on planar or colloidal supports. This was followed by new theorectical models or concepts in the assembly of multilayer. The development of coating procedures onto colloidal surfaces instead of planar substrates has had a large impact on this field. It lead to the formation of new types of nanostructures, such as hollow shells which carry high application potential or colloidal coating provides additional ways for the studies of multilayers using volume methods. Colloidal coating and core removal was a break through of the past few years.

Johannes Kamp, Mathias Wessling synthesized polyelectrolyte multilayer membranes ranging from dense nanoiltration to reverse osmosis deposited on tubular ceramic supports Over the lumen side, a dynamic coating of PAH/PSS on α-Al_2O_3 support membrane with pore diameters of 150nm(MF) and 50nm(UF) resulted in a dense separation layer with NaCl rejections exceeding 90%. Long term stability is improved by coating solution with higher ionic strength and subsequent covalent crosslinking of the amine group of the PAH.

The work of Frank N Crespilho, Valtencir Zucolotto and cowrokers the "Immobilization of Humic acid in Nanostructured LBL films for sensing application. studies published on year 2005, showed the globular morphology, that the very smooth films with roughness varying from 0.89 to 1.19nm for 5 to 15 bilayers of PAH/HA are found. The growth of bilayers are monitored using UV spectroscopy. Raman spectra is also taken but in contrast to IR there was no difference observed. Cyclic voltammograms obtained from PAH/HA films on ITO revealed the presence of only one reduction. These films found application in highly sensitive pesticide sensors, with detection of pentachlorophenol in solutions at concentrations as low as 10^{-9} mol L^{-1}. Thus HAs were successfully immobilized in nanostructured films using PAH in the template layers.

In a review published in Materials in 21 November of 2014, the external editor Todd R. Hoare deals with the LBL assembly of Biopolyelectrolytes onto Thermo/pH responsive Micro/Nano Gels. Here the layers of polyeletrolyte of biopolymers, polypeptides and polysaacharides onto synthetic PNIPAM and PAA or Hyaluronic acid and DEX-HEMA. The mechanical properties, stability, surface charge density, bilayer thickness, morphology etc are discussed. Then the mechanisms of interaction between biopolymers and gels are presented. They found swelling and de-swelling are reversible for polysaacharide terminated gels, whereas templates coated with polypeptides show strong response to temperature induced conformational changes due to the adsorption onto the gels. Depending on the nature of furthest layer an odd-even effect has been detected.

The long term stability of polyelectrolyte multilayer modified membranes is investigated by Jons de Grooth, Brian Haakmeester, Carlos Wever, Jens potreck, Wiebe M.de Vos, Kitty Nijmeijer. 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(ether sulfonate) shows no performance loss during successive backwash cycles.

In a study published online 17th April 2012, Maryam Jokar, Russly Abdul Rahman & Nor Azowa Ibrahim et. al a LBL self assembly approach was used to deposit multilayers of silver nanoparticles and chitosan on HDPE films. Chemical reduction was used to create silver nanoparticles with a size of around 5 nm, which were subsequently manufactured onto a polyelethylene substrate, resulting in a colourful films with thicknesses of 2,4,8,12,20 layers.

Ahmad M.Alghamdi et al. successfully fabricated a PEM by depositing alternating layers of branching polyethyleneimine(PEI) and polysodium4-styrenesulfonate(PSS) on an ultrafiltration on polysulfone(PSF) membrane using spin assisted layer by layer assembly. The divalent ion removal capability of the manufactured membrane was tested.

Science direct available Colloids and Surfaces published journal of Responsive Polyelectrolyte multilayers by Karine Glinel, Christopher Dejugnant and other coworkers represent developments of responsive multilayers formed by LBL techniques at particular temperature and at certain pH. The influence of the architecture and of the nature of the polyelectrolyte which is used to create responsive nature are discussed here. The knowledge accumulated of these system is important but they says that we still lacking a complete view of the dynamics of system. This journal was published in the year 2007 and all the copy rights are reserved by Elsevier.

The structure of PLL/HA (hyaluronan) poly electrolyte multilayer formed by electrostatic self-assembly is studied by using confocal laser scanning microscopy, quartz crystal microbalance, and optical waveguide lightmode spectroscopy. This is paper published in 2002 by C. Picart, J.Muttere , L.Richert and coworkers. As the number of depositing layer increases, the thickness of the films increases exponentially leading to micrometer thickness. They also used dye conjugated polyelectrolytes which leads to 3D visualization due to their fluorescence at different steps during the film build up.

These self assembled membranes have a wide range of applications and numerous research papers were published and publishing on the activity of poly electrolyte membranes. Through these reviews we will get an insight to navigate and explore the potential of self assembled polyelectrolyte membranes.

1.3 Scope Of The Present Study

The surface modified PEM's show a wide range of application in the field of tissue engineering, bio sensors, removal of water pollution, environmental remediation. The modern energy conservation and storage systems are relying on these PEM's. Due to their long term stability and high performance other commercially available membranes were ruled out from the market.

1.4 Objectives

- Selection of appropriate supporting polymeric membrane for PEM.
- Selection of the promising polyelectrolyte for designing and developing PEM's.
- Utilization of LBL method for the deposition of PEM's.
- Characterization of newly designed PEM using analytical instruments.
- Proposal of the applications of newly designed and developed PEM's.

Chapter 2

2.1 Materials And Methods

2.1.1 Materials

PAH, molecular weigt=65000 g/mol (0.5M), was purchased from Aldrich CO. and used without purification. PSS ,MW=70000 g/mol (0.5M), 30 weight percentage in water, purchased from Sigma Aldrich. 1M HCl to regulate pH, deionized water for rinsing and diluting the membrane, 250 mL beaker, spatula , Nylon-6,6 (no.4) as supporting membrane, 250 mL standard flask, glass rod, a pH meter.

2.1.2 Method

0.125g of PAH is weighed approximately then transferred to a 250 ml standard flask and made upto the mark. In another 250 mL standard flask 0.125g of PSS is made upto the mark. PAH being a weak electrolyte, it is pH dependent.1 M HCl is prepared to regulate the pH. 50 mL of each solution is transferred into 250mL beakers. A pH meter is immersed in PAH solution and its pH is adjusted to 6 by the addition of acid. The Nylon membrane is dipped in deionized water and keep it for 5 minutes. Then the membrane is dipped in the cationic electrolyte PAH for 15 minutes and then rinsed with deionized water. The washed membrane is then dipped into the anionic electrolyte PSS for 15 minutes and rinse it with deionized water. This procedure is repeated twice for 2 bilayers, 4 times for 4 bilayers, 6 times for 6 bilayers and 8 times for 8 bilayers.

2.1.3 Film Characterization

For the characterization of the bare membrane and the multilayer deposited membranes we use the analytical techniques IR ,UV-Visible, AFM and SEM.

Chapter 3

3.1 Result And Discussion

Successfully fabricated 2,4,6 and 8 bilayers of PAH/PSS polyelectrolyte membrane via LbL method. The membranes are characterized and the fabrication is confirmed by using microscopic analytical tools such as ATR-FTIR, UV-Visible Spectroscopy, AFM and SEM. The results of the bilayers are compared with the bare membrane results and between the membranes.

3.1.1 ATR-FTIR Analysis

IR is a simple and effective technique for characterization. The IR of sulphonate peak made on the Nylon 6 6 membrane is shown in the figure. The absorbance of bare membrane is shown in 0.00 cm^{-1}. The sulphonate group shows peaks at a range of 1020-1040cm^{-1} over pH range of 6. It is evident from the spectrum that the height of sulphonate peaks increases with increase in number of layers. The absorbance is exactly at 1034 cm^{-1} for the 8 bilayer membrane. The symmetric and antisymmetric deformation of NH^{3+} is usually shown in the region 1400-1700 cm^{-1}.

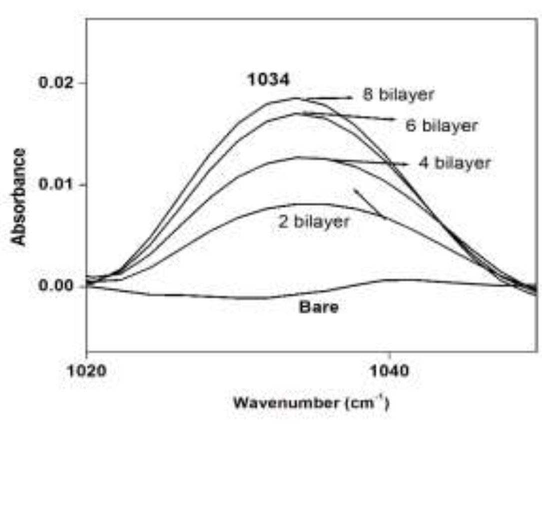


Figure 3.1 IR of sulphonate peak

3.1.2 UV-Visible Analysis

The growth of multilayers are analysed using uv-visible spectroscopy. The absorption of films increases linearly with the number of bilayers which means that the amount of material absorbed are same are same in each deposition step.

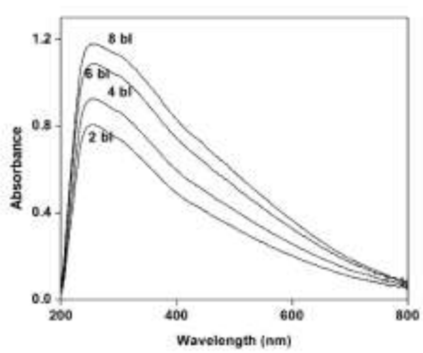


Figure 3.2 UV-Visible spectrum of synthesized bilayers

3.1.3 AFM Analysis

AFM gives globular morphological information and thickness of the bilayers on the surface of supporting membrane. All films present very smooth surface with root mean square roughness varying from 0.89 to 1.9 µm. The average thickness of PAH/PSS bilayers were found to be 2 µm. Usually is both are weak electrolyte, the bilayers are expected to be fully charged. But here PAH is weak and PSS is strong, so PAH is expected to be fully charged and pH dependent. AFM gives 3D image of the bilayers where the morphology turns to be more and more globular and crowded when the number of bilayers are increased.

Figure 3.3 AFM of bare layer

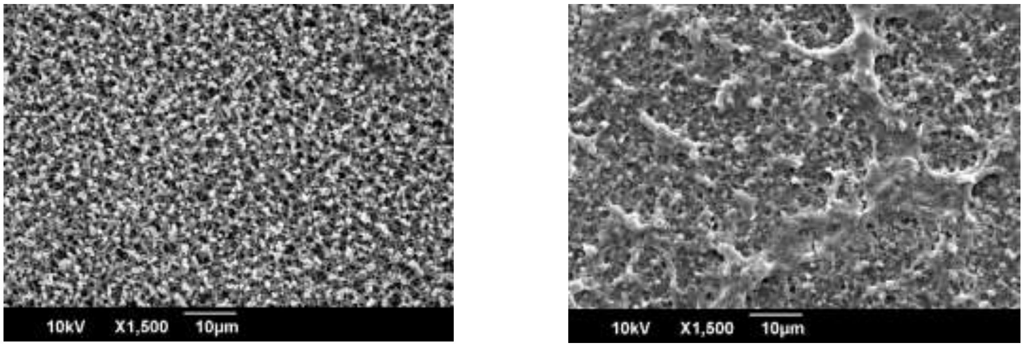
(a) **(b)**

(c) **(d)**

Figure 3.4 AFM of (a) 2 bilayer (b) 4 bilayer (c) 6 bilayer and (d) 8 bilayer membranes

3.1.4 SEM Analysis

The formation of multilayers on the surface of Nylon 6,6 supporting membrane has been investigated using SEM. Figure 3.4.1 is the bare membrane surface and figure 3.4.2 is the surface of 8 bilayer membrane. On examining the results we can see there is a slight decrease in the porous size of 8 bilayer membrane than the bare membrane. Which means as the number of bilayers increase , the sizes of the pores decreases proportionally.



(a) **(b)**

Figure 3.5 SEM of (a) bare membrane (b) 8 bilayer membrane

The fabricated PEM's were effectively characterized and the designing was confirmed using the above characterization tools. This work can be extend for industrial applications such as tissue engineering, waste removal from water, bio sensing application and so on.

Chapter 4

Conclusion

Successfully synthesized PEM membranes consisting various bilayers such as 2,4,6 and 8 using LBL method by the alternate deposition of PAH and PSS on Nylon 6,6. The developed bilayers were characterized by UV-Visible spectroscopy, ATR FTIR spectroscopy, AFM and SEM. The analysis result shows the surface modification has become more selective by the addition of bilayers and offers meaningful industrial applications like tissue engineering, bio sensing, waste disposal, chemical cleaning.

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