DESIGN OF POLYELECTROLYTE MULTILAYER MEMBRANES FOR ION REJECTION
AND WASTEWATER EFFLUENT TREATMENT

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ABSTRACT

DESIGN OF POLYELECTROLYTE MULTILAYER MEMBRANES FOR ION REJECTION
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Polyelectrolyte multilayer (PEM) membranes present a special class of nanostructured membranes which have potential applications in a variety of water treatment operations. These membranes are fabricated by the layer-by-layer (LbL) assembly of alternately charged polyelectrolytes on commercial membrane surfaces. A large variety of polyelectrolytes and their varied deposition conditions (pH, number of bilayers etc.) allow very fine tuning of the membrane performance in terms of permeability and rejection. The first part of this thesis is about the application of PEM membranes to the removal of perchlorate ion from water. Being a monovalent ion, it is most effectively removed by a reverse osmosis (RO) membrane. However, these membranes inherently have very low fluxes which lead to high pressure requirements. In our work, we modified the surface of a nanofiltration (NF) membrane by the LbL assembly of oppositely charged polyelectrolytes. The appropriate tuning of the LbL conditions led to the development of a membrane with significantly higher flux than RO membranes but with equivalent perchlorate rejection. This was one of the best trade-offs offered by PEM membranes for monovalent ion rejection as has been reported in literature so far.

While PEM membranes have mostly shown great potential in ion-rejection studies, they have seldom been tested for real wastewater effluents. The second part of this thesis, therefore, deals with evaluating the applicability of PEM membranes to treating an electrocoagulation (EC)-treated high strength wastewater. Two types of very commonly used polyelectrolyte combinations were tried out – one of which was an ionically crosslinked system and the other one was covalently

crosslinked. Both the types of PEM membranes showed a high level of COD reduction from the feed stream with higher fluxes than commercial RO membranes. One major challenge in using membranes for wastewater treatment is their fouling propensity. Like many other wastewater samples, the EC treated solution also contained a fair amount of organic foulants. These PEM membranes, however, indicated better anti-fouling properties than commercial NF/RO membranes under normal flow conditions.

The last part of our work was focused on improving the anti-fouling properties of these membranes by the incorporation of clay nanoplatelets within polyelectrolyte multilayers. In this project, a commercial polyethersulfone (PES) membrane was modified by clay-polyelectrolyte composite thin films and tested against the EC effluent under tangential flow conditions. In comparison to the PEM membranes, these clay-PEM (c-PEM) hybrid membranes offered superior anti-fouling properties with higher fluxes and also required lesser number of layers. On crosslinking the polyelectrolytes, the c-PEM membranes yielded improved anti-fouling properties and high COD removal. Introduction of these inorganic nanoplatelets, however, led to a significant decline in the initial flux of the modified membranes as compared to bare PES membranes, which therefore necessitates further optimization. Some strategies which can potentially help in optimizing the performance of these c-PEM membranes have been discussed in this thesis.

Dedicated to my late father and the rest of my family

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My days of being a PhD student at Michigan State University have been memorable and I owe it to a number of people around me for making this journey eventful and helping me achieve my doctorate degree. First and foremost I am grateful to my advisor, Dr Ilsoon Lee for introducing me to the field of membrane separation and letting me work with full freedom. I could not have asked for a better research field to do my PhD and I hope to continue working in this area for many more years to come. I thank Dr Lee for always keeping me on my toes to make continuous progress in my work and submit journal manuscripts in a timely manner. He played a major role in shaping me as an independent researcher.

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only helped me in my research by providing ideas and helping me to do some characterizations, but was and will always be one of my closest friends. It was always a lot of fun having her around and she also happens to be one of the smartest students I came across while in MSU. Among the past members, I am very indebted to Dr Ankush Gokhale for helping me get started on my project and providing me innumerable suggestions/insights throughout my PhD. I also had a great time working with Anna Song and Dr Hong and among the past members, I am very much thankful to Dr Shaowen Ji and Dr Wei Wang. I hope and pray that all the people I mentioned above, achieve the success they truly deserve in their careers. A special thanks goes out to the undergraduate students, Anna Sommerfeld and Brooke Meharg who worked with me on my projects. I was blessed to have got the opportunity to mentor them and I hope the very best for both of them.

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Last but not the least, I would not have come this far without the constant guidance and encouragement from my family members. I deeply mourn the loss of my dear father while I was pursuing my PhD, but his words of optimism and encouragement continue to live with me. I am sure wherever he is now, he is still watching over me and I hope to live upto his expectations. My mother has been the greatest pillar of strength for me and I only wish that I can imbibe atleast a small fraction of her dedication and her ability to work relentlessly. My elder sister is my biggest role model and being the younger sibling, I will continue to emulate her throughout my life. My deepest thanks to my brother-in-law for his words of encouragement. My little niece has always been a great source of joy and during the course of my PhD she grew up to be a smart little girl.

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KEY TO ABBREVIATIONS

Chemicals

BPEI   Branched poly ethylene imine

DI water   Deionized water

EDC   N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride

HCL   Hydrochloric acid

KCl   Potassium chloride

LAP   Laponite

MES   2-(N-Morpholino) ethanesulfonic acid

MMT   Montmorillonite

$MnCl_2$ Manganese chloride

NaCl   Sodium chloride

NaOH   Sodium hydroxide

PAA   Poly acrylic acid

PAH   Poly allylamine hydrochloride

PDAC   Poly (diallyl dimethyl ammonium chloride)

PEG   Poly ethylene glycol

PEI   Poly ethylene imine

PES   Poly ether sulfone

PMMA   Poly methyl methacrylate

SPS	Sulfonated Polystyrene / Polystyrene sulfonate
VMT	Vermiculite

Symbols

C_f	Feed concentration
C_p	Permeate concentration
J_0	Initial flux
J_s	Solution flux
$J_w(0)$	Pure water flux
%R	Percentage rejection/removal

Terminologies

AD	Anaerobic digestion
BOD	Biological oxygen demand
BL	bilayer
COD	Chemical oxygen demand
c-PEM	clay-Polyelectrolyte Multilayer
EC	Electrocoagulation
IC	Inorganic Carbon
LbL	Layer-by-layer
MF	Microfiltration

MWCO	Molecular weight cut-off
NF	Nanofiltration
NOM	Natural Organic Matter
UF	Ultrafiltration
PE	Polyelectrolyte
PEM	Polyelectrolyte Multilayer
ppb	parts per billion
ppm	parts per million
QD	quadlayer
RO	Reverse Osmosis
TC	Total Carbon
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus
TS	Total Solids
X-linked	crosslinked

Instrumentation

AFM	Atomic force microscopy
LC-MS	Liquid chromatography- Mass spectrometry
MRM	Multiple reaction monitoring

QCM	Quartz crystal microbalance
SEM	Scanning electron microscopy
SPR	Surface plasmon resonance
XPS	X-ray photoelectron spectroscopy

1. INTRODUCTION

Some excerpts are directly reproduced from *Sanyal et al., J Nanosci. Nanotechnol.* **14**, *2178-(2014).*

1.1 Background

Water shortage is one of the most crucial problems that mankind has been facing. There is a pressing demand for drinkable water especially in the developing nations [1]. This demand for water is expected to further rise in the future owing to the increasing trend in the world's population. Although water is present in huge abundance throughout the planet the amount of fresh water available for consumption purposes (< 1%) is surprisingly low [2]. Factors like extended droughts and the exponential population growth are responsible for the reduction in the fresh water sources [1]. The problem is even more critical in case of the developing nations where rapid industrialization is taking place but proper wastewater management issues are overlooked [3]. As per the estimation presented by the World Water Council in 2030 almost 3.9 billion people will be surviving in "water scarce" regions[4]. According to the records of World Health Organization (WHO) more than a million people die of water-borne diseases like diarrhea every year [4] which is a direct result of improper sanitary management. Developing the technology for wastewater purification and proper water management is therefore the need of the hour.

1.2 Commercial membrane processes

1.2.1 Reverse Osmosis (RO)

Reverse osmosis (RO) is the leading desalination technology as of now[3] contributing to almost 44% of the world's total desalination capacity[5]. It exhibits more than 99% salt rejection .The membrane material however plays a key role in deciding the permeate flux and rejection across

the membrane[6]. The earliest of the RO membranes were of the asymmetric type, made from cellulose acetate[7]. These membranes have a reasonable flux and high salt rejection property but they have certain limitations. It cannot be applied over a wide pH range and is vulnerable to biological attack as well[8]. In comparison, the polyamide thin film composite (TFC) membranes which were developed later, typically give better performance than the cellulose acetate membranes in terms of permeate flux and rejection[6]. They are also applicable over a wide pH range and can resist biological attack although they exhibit comparatively lower chlorine tolerance[8]. The TFC membranes consist of a non-woven fabric support layer with a microporous polysulfone layer on it and the topmost layer is generally a few nanometers thin polyamide layer[9]. It is the topmost polyamide layer that plays the most vital role in salt rejection. Although RO is extremely efficient in salt rejection and the flux offered by the current desalination membranes is considerably higher than the previous generation of RO membranes, it still continues to be a high energy demanding process. The transmembrane pressure difference required for desalination purposes is even higher than 40 bar thus increasing the overall energy requirement of the process.

1.2.2 Nanofiltration (NF)

Nanofiltration (NF) has recently emerged as a potential alternative to reverse osmosis in many water treatment operations owing to its rapid development over the past few years. With the transmembrane pressure requirement being less than 30 bar, NF is a less energy intensive process as compared to reverse osmosis [10, 11]. NF is ideal for the rejection of multivalent ions both by virtue of size exclusion as well as charge based separation (Donnan mechanism) [12-14]. The monovalent ion rejection for NF is however lesser than RO membrane but it definitely offers higher selectivity of ions as compared to RO [13]. It is therefore applied in water treatment

processes like water softening and brackish water purification [13, 15-17]. The current commercial membranes are prepared from either cellulose acetate or polyamide thin film composite. There are however some piperazine based semi-aromatic polyamide NF membranes which are available commercially, the NF 270 membrane manufactured by Dow Filmtec being an example[9]. NF membranes are classified in between Ultrafiltration (UF) and RO membranes[18] and thereby cover a wide range of applications.

1.2.3 Ultrafiltration (UF) and Microfiltration (MF)

UF and MF are two pressure driven membrane processes involving the use of porous membranes with broad pore-size distributions. UF membranes usually have pore sizes in between 10-1000 Å and any membrane with bigger pore size can be classified as MF[19]. These membranes are mostly employed for rejecting macromolecules such as bacteria, proteins, colloids etc.[19, 20]. UF membranes, particularly, are often used during the pre-treatment stage before using a RO membrane in order to remove the bigger particulate matters which can potentially harm the delicate RO membranes. The UF/MF membranes are made from a number of different polymers like polysulfone, polycarbonate, polyesters, poly- vinylidene fluoride etc.

1.3 Polyelectrolyte multilayer (PEM) membranes

In recent years considerable amount of work has been going on in order to develop membranes with higher permeate flux and better rejection as compared to commercial NF/RO membranes. Nanotechnology has had a profound influence on developing new generation membranes for water purification[1, 21]. One major application of nanotechnology to membrane research is the use of the layer-by-layer (LbL) assembly technique to fabricate functional membranes. LbL was pioneered by Gero Decher [22, 23] and ever since then it has been used in a variety of engineering applications [24, 25]. This method involves the simple dipping of the substrate in alternate

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solutions of polycation and polyanion with deionized (DI) water rinsing steps in between in order to form nanothin films on the substrate. Figure 1.1 shows a schematic representation of the LbL process.
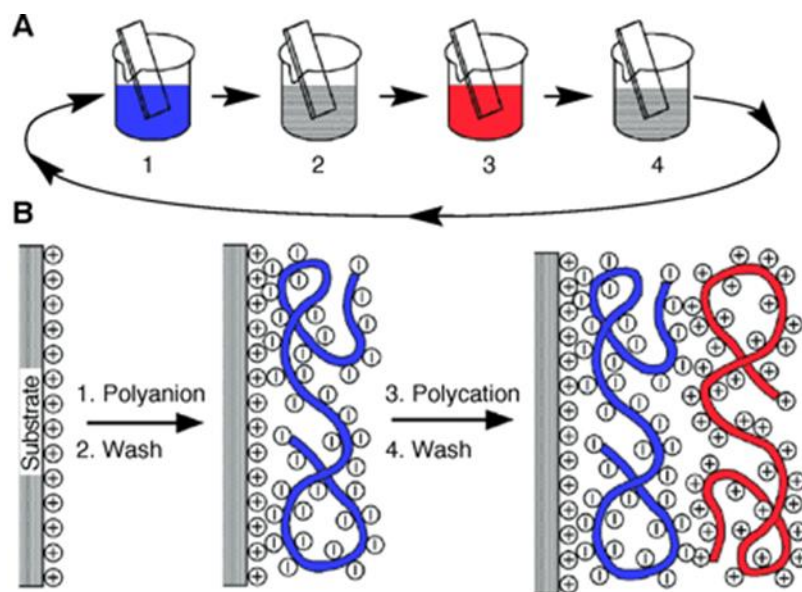
Figure 1.**1.** Schematic representation of layer-by-layer assembly. Reproduced with permission from[22].

Depending on the type of polyelectrolytes and the adsorption conditions used, the mode of multilayer deposition could be electrostatic[22, 26], hydrogen bonding[27, 28] or covalent bonding[29, 30]. LbL films have found applications in the varied fields of sensors[31-33] , fuel cells [32, 34, 35], oxygen barrier films [36]sensing and degradation of toxic environmental substances[37], biomedical applications such as drug delivery[38-43] and cell engineering[44]; however one of the most promising applications lies in the modification of membranes[45]. Polyelectrolyte multilayer films (PEMs) have been employed in gas separation and pervaporation membranes [46-49], ion exchange membranes [50, 51] as well as ion rejecting NF/RO membranes[52]. The versatility of the LbL process and some of its major applications can be seen in Figure 1.2.

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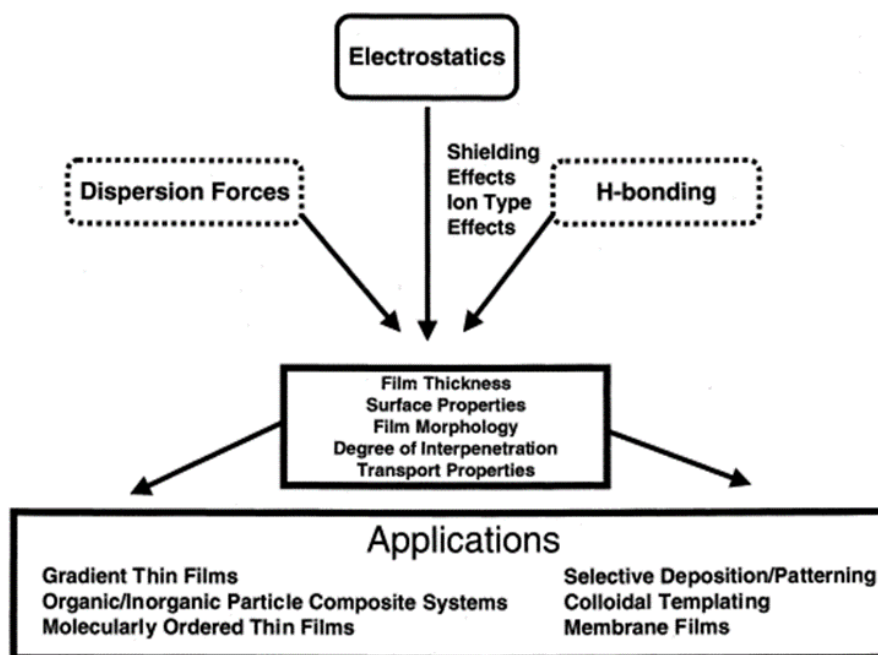
Figure 1.2. Schematic representation of how the different modes of layer-by-layer assembly affect the properties of the film and their applications. Reproduced with permission from[26].

The film properties are a strong function of the types of polyelectrolytes used and the deposition conditions like pH[53, 54] and the deposition time[15]. Based on their pH dependent ionization behavior polyelectrolytes are broadly classified into two types-strong and weak. Strong polyelectrolytes like poly (diallyl dimethyl ammonium chloride) (PDAC) and poly (sodium 4-styrenesulfonate) (SPS) remain charged over a wide range of pH[55, 56]. Weaker polyelectrolytes like poly allylamine hydrochloride (PAH), poly ethylenimine (PEI) and poly acrylic acid (PAA) exhibit strong pH dependent ionization behavior and the resulting film properties like morphology, thickness *etc.* are therefore a strong function of the pH of the deposition solutions[54, 57].

1.4 Deposition conditions influencing the thin film formation

As discussed above, the conditions in which the polyelectrolyte thin films are deposited have a significant influence on the film growth and morphology. A number of factors influence the film

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growth; the ones that we have mostly utilized to tune the PEM structure in our research have been listed below.

A. Type of polyelectrolytes: Very broadly, polyelectrolytes can be classified as strong and weak. Strong polyelectrolytes remain charged over a wide range of pH and can be deposited on any substrate by virtue of electrostatic interactions. PDAC and SPS are two typical examples of strong polyelectrolytes. The weak polyelectrolytes like PAH, PEI and PAA have pH-dependent ionization behavior and this property strongly affects the film fabrication[54].

B. Salt concentration: The use of salts like NaCl, $MnCl_2$ etc. as supporting electrolytes is fairly common in literature[58]**.** These are used especially with the strong polyelectrolytes like PDAC and SPS. The addition of salt leads to an increase in the film thickness and influences the nature of the multilayer growth (linear/exponential)[59]. The presence of salt also affects the net surface charge of the multilayers[58] by virtue of "extrinsic charge compensation"[60]. To our knowledge, salt has not been used for the weak polyelectrolyte combinations till date.

C. pH of the polyelectrolytes: pH has a major influence in case of weak polyelectrolytes. The pH that is used to deposit the polyelectrolytes influences their ionization, which in turn strongly affects the film thickness as well as the structure**.** Figure 1.3 shows the various configurations produced by tuning the pH conditions of PAH and PAA**.** When both the polyelectrolytes are at pH 6.5, they are fully charged and form very thin flat films by virtue of strong electrostatic linkages between them, as is shown in condition c) of Figure 1.3. When PAH remains partially charged at pH 8.5 and PAA remains virtually uncharged at pH = 3.5, these polyelectrolytes form thick interpenetrated films with a high degree of polymer interdiffusion. This can be seen in the condition marked as b) in Figure 1.3. When PAH is completely charged at pH 2.0 and PAA is uncharged at pH = 2.0, the

morphology shows an intermediate behavior between the above two described conditions, as is shown in condition a) of the following figure.
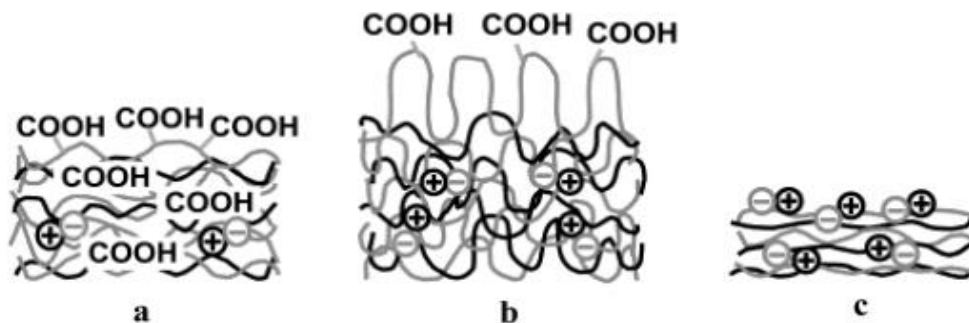
Figure 1.3. The effect of pH of the polyelectrolytes on the morphology and thickness of the films. Reproduced with permission from[61].

Depending on the pH, the polyelectrolytes may form thick interpenetrated films or very thin flat films[61]. Because of this tremendous flexibility, the PAH/PAA or PEI/PAA constitute the most widely used polyelectrolyte combinations for creating functional thin films.

D. Number of bilayers deposited: The relationship between film thickness and the number of bilayers maybe linear or exponential and in many cases a combination of both. As mentioned before, for strong polyelectrolytes like PDAC and SPS, there exists a strong dependence on the concentration of salt used. For combinations like PAH/PAA or PEI/PAA, the growth behavior is a strong function of the pH of the polyelectrolytes[54]. For certain polyelectrolytes, the multilayer growth also depends on their molecular weights [62-64] .

1.5 Thin film properties influencing membrane performance and characterizations

Thickness: The thickness of the deposited films can be directly correlated with the permeability of the resulting membrane. Higher thickness of the films provides higher resistance to the flow of water thereby reducing the flux. A number of techniques are available for determining the

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thickness of the PEMs. One of the most common techniques to measure the thickness of the multilayer films is ellipsometry. In order to determine the thickness, the multilayers need to be deposited on an optically transparent substrate like gold-coated silicon wafers with known optical constants[52, 58]. However with the deposition of a large number of multilayers the substrate might not be optically transparent and in that case other techniques can be used. For polyelectrolyte multilayers with thickness of 200A or more profilometry can also be employed[54]. Atomic force microscopy (AFM) can be used for thickness measurement as well[65]. Ahmadiannamini *et al.* have applied tapping mode AFM to determine the thickness of the films[66]. In many cases, scanning electron microscopy (SEM) has also been employed[67], a typical image of which is shown in Figure 1.4.
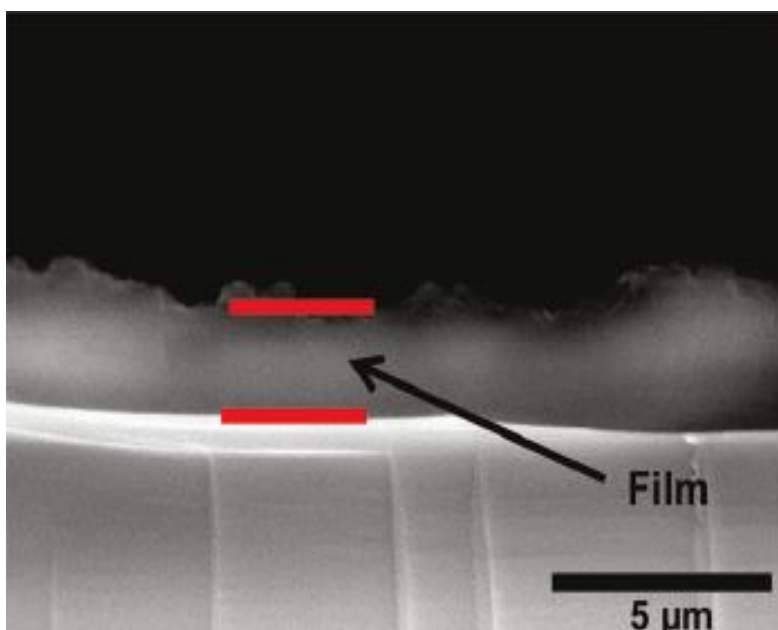
Figure 1.4. A typical cross sectional SEM image showing the deposited multilayer films on a support taken in order to determine the thickness of the multilayer films. Reproduced with permission from[68].

Scanning angle reflectometry[69] is another alternative technique discussed in the literature to determine the thickness of PEM films. Several other characterization tools described

in the literature include the usage of quartz crystal microbalance (QCM), reflection spectroscopy (RS), surface plasmon resonance (SPR), and X-ray photoelectron spectroscopy (XPS)[70].

Surface Charge: Surface charge is an important property for multilayers functioning as membrane surface modifiers. These LbL assembled membranes reject solutes by virtue of both size exclusion as well as charge exclusion also known as Donnan Exclusion[71, 72].The surface charge of the outermost layer plays a significant role in the rejection of ions[67] and hence its measurement is of utmost importance for membrane characterization. This is usually done by measuring the streaming potential across the membrane surface using a surface zeta potential analyzer and correlating it with the surface charge[73, 74]. A typical plot depicting the zeta potential variation with deposition of the multilayers is shown in Figure 1.5.
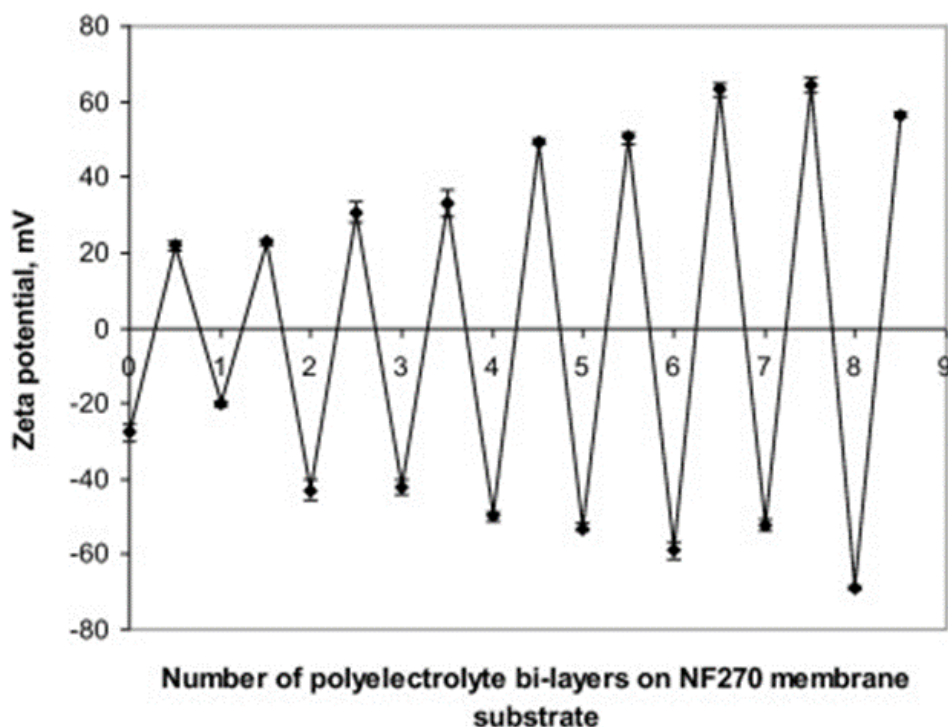
Figure 1.5. Variation of zeta potential with the deposition of polyelectrolytes by LbL technique. Reproduced with permission from [13].

1.6 Modes of LbL deposition

The traditional method of carrying out layer-by-layer technique is the dip-coating method. As the name suggests, it is carried out by dipping the substrate in alternate polyelectrolyte solutions with some rinsing steps in between. Usually around 10-15 minutes of dipping time is used. Although the method is really simple and inexpensive it is time consuming, thereby limiting its industrial application[78]. Very recently, a couple of studies have been reported where shorter dipping times (in the order of a few seconds / a minute) were used during LbL process[62, 79] .So far, however, none of these studies have been tested for membrane modification. Two other alternatives to dip-coating are spin coating and spray coating. A schematic representation of the three types of LbL processes has been shown in Figure 1.6.
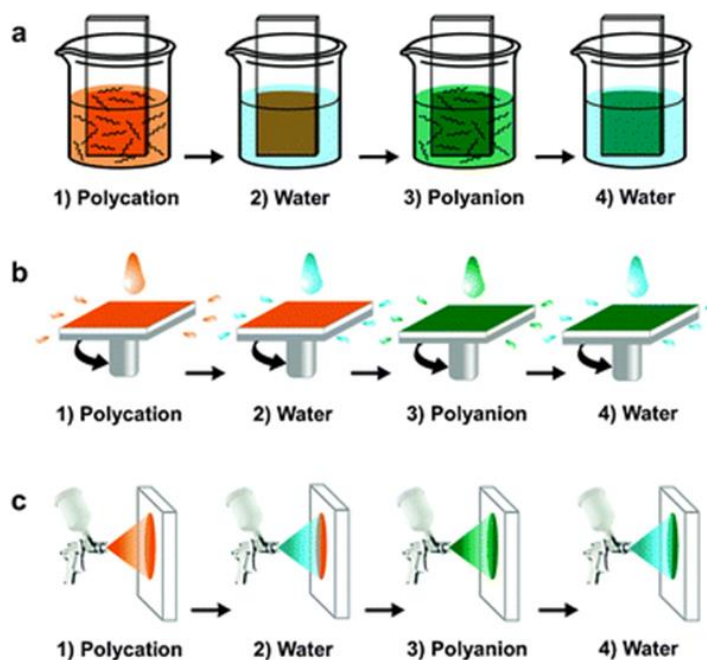
Figure 1.6. A schematic diagram showing (a) dip coating, (b) spin coating and (c) spray coating. Reproduced with permission from[80].

Spray coating developed by Schlenoff *et al.*[81] involves the spraying of the polyelectrolyte solutions onto the substrate with DI water rinsing steps in between. The time

involved in spraying is hardly a few seconds compared to the longer dipping times commonly involved in the dip-coating method and the resulting films are also thinner and more uniform surface coverage is obtained.[82] Unlike dip-coating method which involves only dipping time as a parameter, spray coating involves several other parameters like spraying distance, spraying pressure *etc.* and the surface of the resultant films are mostly rougher than in case of dip-coating methods[82]. Spray coating has been applied for membrane modification purposes. [83, 84] .Spin coating developed by Cho *et al.* [85] involves spinning/centrifugal force to deposit multilayers on the substrate within a few seconds[82, 86]. Spin coating has been applied to making desalination membranes using polyelectrolyte multilayers [82, 87, 88]. Higher the spinning rate thinner the films are formed, as the high centrifugal force removes the unabsorbed materials off the surface thereby preventing agglomeration [88]. Spin coating has also been reported to form lesser-interpenetrated layers compared to dip-coating but imparts a higher surface roughness to the membrane surface[87]. Apart from the duration of dipping in each solution, spin coating involves the parameter of spin speed in regulating the morphology and nature of the films produced and thereby offers more tuning flexibility. In the past decade significant research has been done in developing these two *LbL* techniques so that the processes can be industrially applied as well.

1.7 PEM membranes-current state of the art and scope of this thesis

1.7.1 PEM membranes as ion-rejecting membranes

PEM membranes have been widely applied as ion rejecting membranes. This is mainly because it is capable of rejecting both multivalent ions (by Donnan exclusion) as well as monovalent ions (size exclusion). These membranes are typically characterized by high water flux, high ion rejection and also high selectivity among different ions. PEM membranes pose an alternative to using many commercially available NF/RO membranes[89]. A porous membrane is usually

chosen as the substrate. The polyelectrolyte multilayers are then optimized based on their thickness, porosity etc. to provide nanothin barriers to the passage of ions. Several research groups have been working on designing PEM membranes with high ion selectivity and water permeability which can potentially replace the commercially available NF membranes for water softening applications. In most of these cases a UF/MF membrane is chosen as the substrate and the multilayers are deposited on it. The permeabilities of these modified membranes are found to be way higher than the commercial NF membranes. These membranes also have a high divalent/monovalent selectivity ratio by virtue of charge-based exclusion. Extensive research has been done on the removal of divalent/multivalent ions like sulfate[15, 17, 58, 90], magnesium[16, 91-94], phosphate[66, 95, 96], ferric/ferrous ion[97, 98] and copper ion[99, 100] by PEM membranes. It can very well be said that in the area of water softening and other NF related applications PEM membranes have shown very promising results both in terms of high perm-selectivity as well as ion-selectivity.

Efforts have also have been directed towards the optimization of PEM membranes to reject monovalent ions from water. Two types of approaches can be identified in literature for the fabrication of PEM-based RO membranes. In the first approach a MF/UF membrane is taken as the support and a significantly large number (20 or more) of bilayers are deposited on it [10, 11, 87, 101-103]. The second approach is based on choosing a NF membrane and depositing a smaller number (<10) of bilayers on it [13, 104]. In order for these membranes to actually replace the commercially available ones, attaining a good trade-off is the most important criteria. The first part of our research involves the application of PEM membranes to removing perchlorate ion, a monovalent ion. We focused on optimizing the membrane performance in terms of high

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permeability and rejection by tuning some of the properties of the polyelectrolyte-based thin films. The findings from this work have been described in details in Chapter 2 of this thesis.

1.7.2 PEM membranes for wastewater treatment

As described in the previous sections, PEM membranes have been extensively applied for ion-rejection applications. However, most of these studies have been carried out with lab-based synthetic solutions containing just the ion/ions under consideration. These modified membranes have been seldom used for treating an actual wastewater solution. A wastewater solution represents a very complex system consisting of solutes with varied size, charge etc. and the type of wastewater also plays a major influence on the performance of membranes. Typically these samples are characterized by parameters such as Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Nitrogen/Ammonia-Nitrogen and Total Phosphorus. While BOD is an indirect measure of the amount of biological organic matter present, COD measures the overall organic content of the sample. Total Nitrogen is an overall measure of all the N-containing compounds which includes Ammonia, nitrates/nitrites and reduced nitrogen. The phosphorus containing compounds can be categorized into orthophosphates, polyphosphates and organic phosphates. All of these can be collectively measured as Total Phosphorus. Other than these, there might be several types of ions present, the nature of which depends heavily on the source of wastewater. Commercial salt rejecting membranes like NF/RO membranes have been used to treat a wide variety of effluents which include textile effluent[105, 106], dairy effluent[107], landfill leachates[108] and effluent from pharmaceutical industries[109]. In some cases with NF membranes, the COD and Total N levels do not meet the regulatory standards. RO membranes can reduce these levels to very low values; however a pretreatment step with a NF membrane helps reducing the osmotic pressure of the RO membrane. PEM membranes pose an alternative solution

to these conventional membrane- based processes. By modifying an existing high permeability membrane we can potentially fabricate a membrane having similar rejection capabilities as that of RO membranes. However, the application of PEM membranes to treating actual wastewater samples has been reported so far by only one research group[110, 111]. In Chapter 3 of this dissertation we have thoroughly evaluated the applicability of PEM membranes to treating a high-strength wastewater effluent.

1.7.3 Membrane fouling

When it comes to dealing with wastewater, membrane fouling becomes a major concern for almost every type of membrane. In the exact words of Abdelrasoul *et al*., fouling is defined as the "blockage of membrane pores during filtration by the combination of sieving and adsorption of particulates and compounds onto the membrane surface or within the membrane pores"[112]. It is sometimes referred to as the "Achilles heel" of membrane technology. Over the past few decades, membrane technology has witnessed unprecedented development in terms of capacity, permeability and the current state-of-the-art desalination membranes are capable of more than 99% salt rejection. The issue of fouling is a major "bottleneck" in the application of membranes to wastewater/saline water treatment. Due to the physicochemical interactions between the foulants and the membrane surfaces, a drop in transmembrane pressure and therefore a drop in permeate flux occurs over a period of time. It is needless to mention that this affects the separation behavior of the membranes adversely and leads to increased operational/maintenance costs. The extent of fouling is determined by both the wastewater properties[113] as well as the membrane surface properties like charge, roughness and hydrophilicity[6].
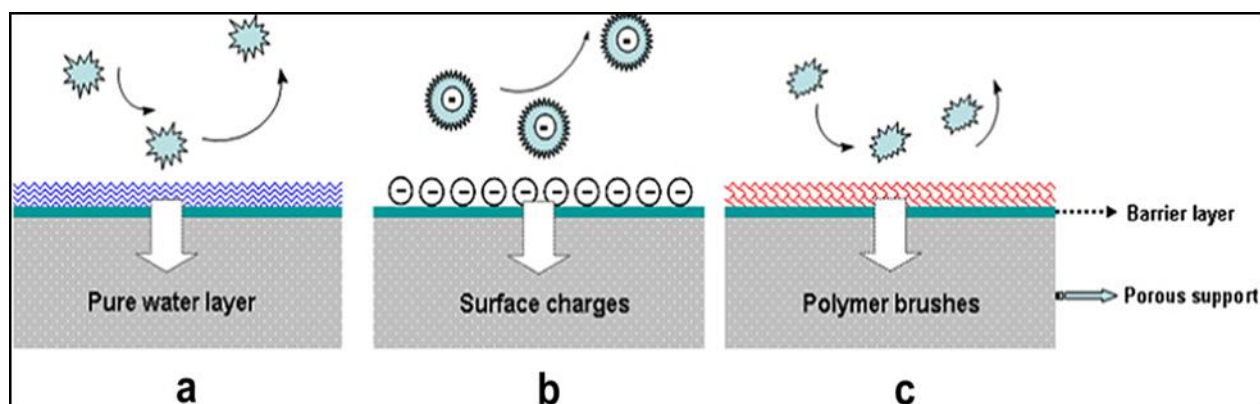
Figure 1.7. Schematic diagrams of antifouling mechanisms: (a) pure water layer; (b) electrostatic repulsion; (c) steric repulsion. Reproduced with permission from [6].

Since the properties of the wastewater cannot be controlled very well, membrane researchers have put considerable attention to surface modification of existing membranes in order to tackle the fouling issue. Several methods have been proposed in order to impart enhanced fouling resistance to commercial membranes. It is of general consensus that charged hydrophilic functional surfaces tend to foul less as compared to neutral hydrophobic surfaces[114]. This is also illustrated in Figure 1.7. Most surface modification methods therefore involve the functionalization of the membrane surface by the attachment of polymer thin films which involve one or more hydrophilic charged moieties. Some of the very common techniques reported in literature include grafting of Poly ethylene glycol (PEG)[115] or functionalized PEG[116, 117], deposition of polydopamine (PD)[118, 119], zwitterionic copolymers[120-122], nanomaterials[123] and also LbL assembly[124]. PEG, particularly has found extensive application in creating fouling resistant surfaces. It is a highly hydrophilic polymer with flexible long chains and due to its unique coordination with water molecules, it resists the adhesion of other biopolymers, macromolecules etc. It is an especially attractive candidate for developing protein resistant membrane surfaces[125]. A comparatively recent entry to this genre of hydrophilic fouling resistant polymers is polydopamine. Benny Freeman and his research group have reported some detailed studies on

the effects of PD / PD-g-PEG coatings on organic/biological fouling propensies of commercial

MF/UF/NF and RO membranes [119, 126, 127]. Among the polymeric materials, zwitterionic

polymers with both cationic and anionic functional groups have also gained significant

prominence. These materials have been claimed to have higher degree of hydration than PEG

chains and are also more stable from long term operation point of view[128, 129]. Besides

polymers, carbon-based nanomaterials like carbon nanotubes[123] and graphene oxide[124] have

also employed by some researchers for membrane surface modification purposes. In Chapter 4 of

this thesis we focused on developing fouling resistant membranes using both polymers as well as

inorganic nanomaterials as surface modifiers. The previously described LbL assembly technique

was used to co-deposit polyelectrolytes and clay nanoplatelets on a commercial polyethersulfone

membrane. Using LbL poses a clear advantage over other techniques, as it is enables the

underlying substrate to attain increased fouling resistance as well as improved rejection at the same

time. PES membranes modified with clay-PEM hybrid films have been earlier reported to have

shown high ion rejection, comparable to commercial RO membranes. However, these membranes

were never tested for their anti-fouling properties and more importantly, they were never tested

against a real wastewater effluent. Evaluation of these modified membranes against a wastewater

effluent formed the main theme of Chapter 4.

Summarizing, in this thesis, we first focused on attaining a good trade-off between high

flux and high rejection for a model ion (perchlorate) using PEM membranes. We then extended

the same concept to a high-strength wastewater effluent. While PEM membranes were shown to

be promising candidates for effluent treatment, their applicability needs further improvement in

their anti-fouling property. An attempt to solve this issue was made by incorporating clay

nanoplatelets within the PEM assembly and testing the nanocomposite membranes against the same effluent.

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2. DESIGN OF ULTRATHIN NANOSTRUCTURED POLYELECTROLYTE-BASED MEMBRANES WITH HIGH PERCHLORATE REJECTION AND HIGH PERMEABILITY

2.0 Abstract

The presence of perchlorate in drinking water sources is an issue of overwhelming concern in United States. Commercial reverse osmosis (RO) membranes show high rejection of perchlorate ions but with very low water permeability. We propose the modification of commercial nanofiltration (NF) membranes by layer-by-layer (LbL) assembly in order to enhance the ion rejection of these membranes to the same level as commercial RO membranes, but with much higher permeability. Poly allylamine hydrochloride (PAH) and poly acrylic acid (PAA) were the two polyelectrolytes used for surface modification. We found that, when both these polyelectrolytes were deposited on a NF 90 membrane at a pH of 6.5 and crosslinked with glutaraldehyde, we were able to achieve around 93% perchlorate rejection at a pressure of 5 bar with 10 ppm feed concentration. This was almost equal to the rejection offered by SW 30 membrane and higher than a BW 30 membrane under the same conditions of pressure and feed concentration. Most importantly, the modified membranes had 1.5 times the permeability of BW 30 membrane and 6 times that of SW 30. These membranes, therefore, had much superior permselectivity than the commercial membranes. In fact, this was one of the highest values of permselectivity reported so far for a PEM-based RO membrane targeting monovalent ion removal. Only 3 bilayers with an overall thickness of just 20 Å were sufficient to achieve such a high rejection. The mechanism of ion rejection by these modified membranes was more based on size-based exclusion rather than charge-based separation.

2.1 Introduction

In 1997 high levels of perchlorate were found in the drinking water supplies of the state of California. Ever since then, a number of other states within United States reported the presence of perchlorate in the groundwater as well as surface water supplies [1]. Recognizing the threats it poses to the environment and the health of millions of people, perchlorate has been added to the contaminants candidates list (CCL) as well as unregulated contaminant monitoring rule (UCMR) [2]. Perchlorate salts like Ammonium perchlorate are used as oxidizers for missiles and munitions [3] which makes perchlorate ion an ubiquitous groundwater contaminant in areas close to NASA or other military settlements [4]. When taken in at higher than recommended levels, it interferes with Iodide ion thereby impairing the hormone secreting abilities of the thyroid gland. Studies have shown that Iodine deficiency in case of pregnant women can lead to lower IQ levels in their babies [5]. Improved methods of perchlorate detection have shown the presence of perchlorate in at least 26 states all over United States [1]. The Colorado River which provides water for drinking as well as irrigation to almost 30 million people, has been known to be one of the most perchlorate-contaminated sites of the country [4]. Developing effective perchlorate removal strategies is therefore in urgent need.

As of now, the US EPA does not have any strict regulatory limits for perchlorate but according to recent reports they have initiated the process of regulating perchlorate to a uniform level throughout the nation under the Safe Drinking Water Act [3]. Various states like California, Massachusetts, Maryland etc. have set their own individual standards between 1-2 µg/l [6]. Reports have indicated that as many as 11 million people in United States have been consuming drinking water with perchlorate concentration higher than 4 µg/l [6].

So far, the clean-up of some of the perchlorate contaminated sites has involved several billions of dollars. In 2014, the Nevada division of EPA allocated 1.1 billion dollars to a trust for cleaning up the perchlorate contamination in Lake Mead. This contamination originated from the manufacture of jet fuels by Ker McGee Chemical Company (KMCC) and it eventually led to the creation of largest perchlorate plume in the nation [7]. Reports indicate that this perchlorate plume showed concentrations as high as 18000 ppm prior to the cleanup, especially in the areas closer to the industrial site [8]. In 2012, DOD and several other companies had to invest 50 million dollars for the cleanup of the perchlorate contaminated sites of Rialto, California [5]. Similar cleanup ventures were also taken up by NASA following the shutdown of several perchlorate-contaminated wells in Pasadena, California [9]. It is therefore quite clear that while developing the most viable treatment technique is essential, the latter also needs to be cost-effective in order to be actually implemented.

There are several wastewater treatment options available for the remediation of perchlorate, like fluidized bed biological reactor treatment, membrane-based processes like reverse osmosis (RO) and nanofiltration (NF), ion-exchange, ultraviolet laser reduction etc. [3]. In this paper, we mainly focus on the pressure-driven membrane–based processes for removing perchlorate. Different research groups have tried out ultrafiltration (UF), nanofiltration (NF) as well as reverse osmosis (RO) membranes to assess their efficiency in reducing perchlorate [10-16]. Being a monovalent ion, perchlorate can be most effectively removed by a RO membrane [17]. However due to the inherently dense structure of the membrane, the latter offers a very low water flux. This makes RO a highly energy-intensive process with a low energy recovery percentage. Nanofiltration (NF) membranes require a much lower transmembrane pressure compared to RO but their monovalent ion rejection is not sufficiently high [18]. Our research

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focusses on the surface modification of commercial NF membranes in order to enhance their monovalent ion rejection capabilities to the level of RO membranes without significantly lowering down their permeabilities. These highly perm-selective membranes have the potential to replace the existing RO membranes and thereby reduce the energy/electricity costs involved in the RO process. The surface modification technique used in our research is the Layer-by-layer (LbL) assembly which involves the alternate deposition of oppositely charged polyelectrolytes (PE) on a surface [19]. This aqueous based thin film deposition technique was pioneered by Iler [20] and much later, in 1992 Decher et al. [21, 22] brought to light the tremendous versatility of this technique. Over the last two decades this thin film deposition technique has found wide applications in the fields of sensors [23, 24], fuel cells [25, 26], gas barrier films [27, 28], drug delivery [29, 30] and membranes [18, 31, 32]. The wide choices of polyelectrolytes available, the deposition conditions used during the process and the number of bilayers are some of the tuning parameters that help in optimizing the performance of membranes [18]

PEM membranes have been widely employed to reject divalent/multivalent ions [33-38]. Comparatively fewer research groups have worked on the application of polyelectrolyte multilayer (PEM) membranes to typical RO applications involving the rejection of monovalent ions [39-44]. In order to fabricate PEM-based RO membranes, an approach commonly taken by a number of research groups is to modify a porous UF membrane using a considerably large number of PE bilayers. In most of these cases a high rejection value was reported but the permeabilities dropped down to values even lower than commercial RO membranes. A parallel approach was taken by Malaisamy et al., to make salt rejecting membranes by modifying a commercial NF 270 (Dow Filmtec, MI) membranes with just a few bilayers of polyelectrolytes [45]. A high value of permeability was attained; however the percentage removal of the target ion, i.e. fluoride ion was

not as high as a commercial membrane. Overall, a good balance between high permeability and high rejection has not been achieved so far. In our work we used the NF 90 membrane (Dow Filmtec, MI) as the base membrane and PAH and PAA as the surface modifiers. We worked on optimizing the LbL process in terms of number of bilayers and pH used for depositing the multilayers. The most optimized system was then compared with the commercial RO membranes in terms of permeability and perchlorate rejection. To our knowledge, this is the best combination of high permeability and high rejection of monovalent ions, as shown by a PEM based RO membrane, based on what has been reported in literature so far. Besides, the application of PEM based improved membranes for the removal of perchlorate ions has not been tried out before.

2.2 Experimental Section

2.2.1 Materials

The nanofiltration membranes (NF 270 and NF 90) as well as the reverse osmosis membranes (BW 30 and SW 30) were purchased from Dow Chemicals (Midland, MI). Potassium perchlorate salt, poly acrylic acid sodium salt (MW 15,000, 35 wt% solution in water) and poly allylamine hydrochloride (M_w 900,000) were purchased from Sigma Aldrich. Glutaraldehyde (50 wt% solution) was obtained from Electron Microscopy Sciences (Hatfield, PA). All aqueous solutions were prepared using deionized (DI) water (>18.2 MΩ) supplied by a Barnstead Nanopure Diamond-UV purification unit equipped with a UV source and a final 0.2 μm filter. Unless specified otherwise all procedures were carried out at room temperature.

2.2.2 CF 042 cross flow membrane system

A CF 042 cross flow unit (Sterlitech, Kent, WA) with an effective surface area of 42 cm^2 was employed as the membrane module. This type of cross flow cell has a rectangular geometry, the flow channel being 3.62" in length, 1.8" in width and 0.09" in depth. A positive displacement

pump (Hydra-cell M03, Wanner Engineering, Minneapolis, MN) was used to deliver the feed from a conical 5-gallon feed tank. A variable speed drive (Emerson, St Louis, MO) was attached to the pump which controlled its speed. A part of the feed stream was directed back to the feed tank via a bypass valve. A back-pressure regulator was used to control the transmembrane pressure across the membrane module. The retentate stream was recycled back to the feed tank and the retentate flow rate was measured by a Site Read Panel Mount Flowmeter (Blue-White, Huntington Beach, CA). The permeate stream was collected and weighed on a measuring balance and the flow rate was determined gravimetrically. The temperature of the solution inside the feed tank was maintained at room temperature by a digital chiller (Polysciences, Warrington, PA). All the components of the cross-flow setup were obtained from Sterlitech (Kent, Washington) and assembled in our lab. A detailed schematic diagram of the above cross flow system has been shown in Figure 2.1.
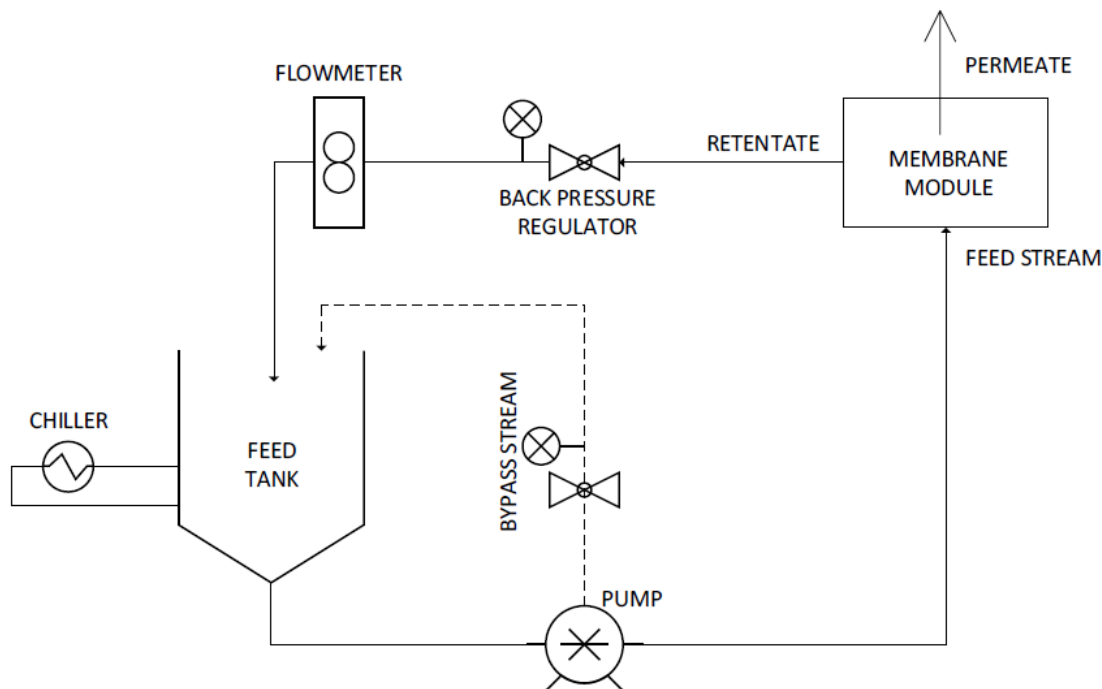
Figure 2.1. Schematic representation of Sterlitech CF 042 cross flow system.

2.2.3 Experimental protocols

2.2.3.1 Filtration protocol

All membranes were soaked in DI water overnight. Initially, the membranes were compacted for 24 hours by passing DI water across them at a pressure of 10 bar. The cross flow velocity was maintained at a value of 1 l/min. The flux was calculated by measuring the volume of water collected over a certain period of time. Following the DI water compaction stage, the perchlorate salt solution (10 ppm concentration) was made to flow across the membrane for another 24 hours at a pressure of 5 bar. At the end of this stage a steady value of solution flux was recorded. The permeate samples were collected for half an hour following this stage. The percentage rejection (% R) was calculated as $(1 - \frac{Cp}{Cf})$ where C_p and C_f are the concentrations of permeate and feed respectively. The concentrations were determined by a Q-Trap LC-MS/MS mass spectrometer in order to evaluate the membrane rejection. All experiments were validated using a minimum of three replicates for each type of membrane used.

2.2.3.2 Layer-by-layer (LbL) deposition process

Both PAH and PAA were prepared with a concentration of 10 mM. The pH of each of the solutions was adjusted to their desired values using 1 M HCl and 1 M NaOH. An Orion pH meter was used to read and adjust the pH of the solutions. The glutaraldehyde solution was prepared with a concentration of 1.5 wt% without any pH adjustment. The permeate side of the membrane was covered, in order to make sure that the deposition only takes place on the feed side. The LbL was carried out using Carl Zeiss Slide Stainer which employs a robotic arm to move the sample from solution bath to another. The dipping time in each polyelectrolyte solution was set to 10 mins. After each dipping step the substrates were rinsed with DI water three times consecutively for 2 minutes, 2 minutes and 1 minute respectively. Following the deposition of one bilayer, the sample

was sonicated for 2 minutes. The protocol was repeated for the desired number of bilayers. Following the deposition of the polyelectrolyte multilayers the membranes were dipped in glutaraldehyde solution for 90 mins. The sample was then washed with DI water three times for 15 minutes each and sonicated for 5 minutes to remove the excess glutaraldehyde. Following the LbL deposition, the membranes were soaked in DI water for atleast 12 hours prior to usage.

2.2.3.3 Quantification of perchlorate using LC-MS/MS

The perchlorate concentrations in the feed and permeate samples were quantified using Q-Trap 3200 LC-MS/MS. A prevail organic acid column (Grace Davison Discovery Sciences, Deerfield, IL) was used as the liquid chromatography column. Methanol and 10 mM ammonium acetate in a 9:1 methanol-water mixture were used as the solvents. A flow rate of 0.1 ml/min was used and the perchlorate retention time was 6 minutes. The temperature inside the oven was set to 50 $^{\circ}$C. Multiple reaction monitoring (MRM) was used as the method to detect and analyze perchlorate ions. ANALYST software was used for quantifying the results from the mass spectrometry tests. The calibration range was selected between 0.5 mg/l to 50 mg/l. The perchlorate concentrations used for preparing the calibration standards were 0.5,1,2,5,10,20 and 50 mg/l with three replicates of each. An R^2 value of around 0.98-0.99 was obtained in almost all cases. Before running any test the column was purged with the solvents and the instrument was equilibrated for at least 5 minutes.

2.2.4 Thin film characterization

The thickness of the deposited PE films was measured using a J.A Woollam M-44 Ellipsometer. For the purpose of this test, the polyelectrolyte films were deposited on gold coated glass slides (VWR International, Radnor, PA). These gold coated glass slides were treated with O_2 plasma for 20 minutes using a Harrick plasma cleaner (Harrick Scientific Corporation, Broading Ossining,

NY) with 30W RF power under 100 millitorr vacuum. Oxygen plasma treatment imparts hydrophilicity and leads to the formation of negatively charged gold-oxide on the surface [101]. Immediately after the plasma treatment, the gold-coated substrates were put in the slide stainer for the LbL surface modification, following the same protocol as described earlier (Section 2.3.2). For the PE films, the model for generic films (assuming refractive index as 1.5) was used. The surface zeta potential of the membranes was analyzed using an electrokinetic analyzer (BI-EKA, Brookhaven Instrument Corp., Holtsville, NY). A 1mM Potassium chloride (KCl) solution was used as the electrolyte. A poly methyl methacrylate (PMMA) substrate was used as the reference material. All membranes were soaked in DI water overnight prior to being used for the measurements.

2.3 Results and discussion

We based our research on the idea that if an existing NF membrane be modified by LbL we can essentially fabricate a RO membrane with high flux as well as high rejection of perchlorate ion. As the first step towards selection of the substrate we tried out two types of commercial NF membranes. Under the same experimental conditions, we also tried out two types of RO membranes which helped us determine the target performance that we expected the PEM membranes to achieve.

2.3.1 Performance of commercial membranes

NF 270 and NF 90 were the two types of NF membranes and BW 30 and SW 30 were the RO membranes that we tested in the CF 042 cross flow system. NF 270 is a "loose" NF 270 membrane with a poly piperazinamide based skin layer of 14-80 nm thickness while NF 90 is a "tight" NF membrane with a polyamide skin layer of around 134-214 nm [47]. Both of the RO membranes are fully aromatic in nature. The skin layer of the BW 30 membrane is around 0.2-0.5 μm and that

of SW 30 it is 0.6 μm [48]. All the tests were carried out at a transmembrane pressure of 5 bar under a cross flow velocity of 1 l/min with a perchlorate salt solution with a concentration of 10 ppm. Figure 2 shows the performance trend of all the commercial membranes.
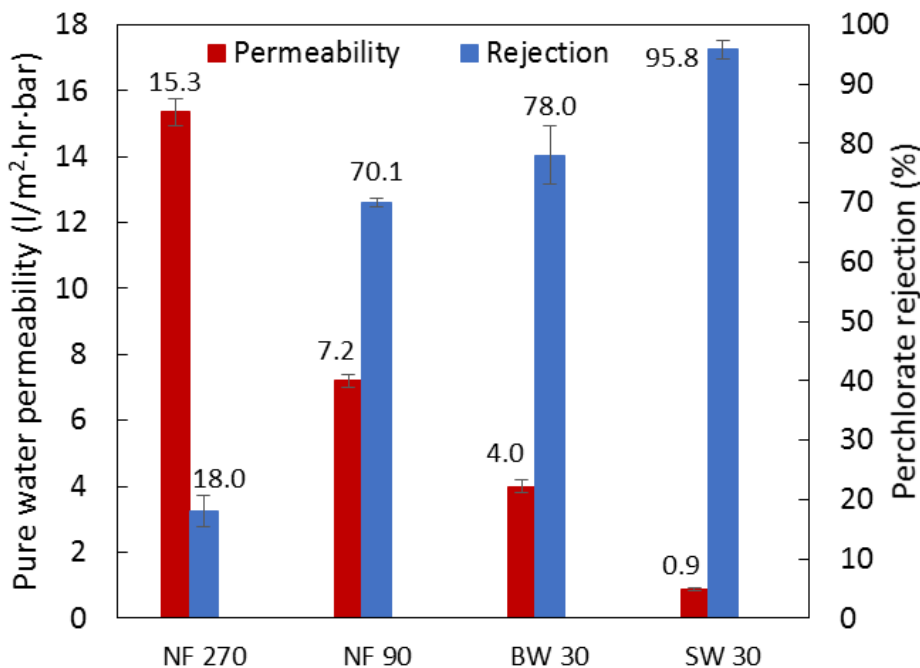
Figure 2.2. Performance of the commercial membranes with respect to pure water permeability and perchlorate rejection.

The results can be correlated very well with the structural properties of the respective membranes. As we move from NF 270 to SW 30 in the same order as shown in Figure 2 the skin layer progressively keeps getting thicker and denser with a higher degree of crosslinking. Consequently the NF 270 membrane has the highest water flux but the lowest perchlorate rejection. On the other hand the SW 30 membrane showed a very high rejection of around 95% at 5 bar but with a very low permeability of 0.88 $l/m^2 \cdot hr \cdot bar$. The NF 90 membrane showed an intermediate performance with a permeability of about 7.1 $l/m^2 \cdot hr \cdot bar$ and about 71% perchlorate rejection. We selected NF 90 as the substrate and fabricated the multilayers in a way that the rejection of the modified NF 90 could be equal to the perchlorate rejection of SW 30 but with higher permeability.

2.3.2 Performance of PEM membranes

The NF membranes, like NF 270 or NF 90 typically have pore sizes ranging between 1-5 nm [49] .The hydrated radius of perchlorate ion is around 1.37 Å, which explains the lower rejection offered by these membranes. The polyelectrolyte-based thin films layered on NF substrates can serve as nanothin barriers to the passage of ions. The challenge primarily lies in attaining a good perm-selectivity value which requires careful consideration of the choices of PEs used and their deposition conditions. Based on literature, it is quite an established fact that for weak PEs like PAH and PAA, the film properties like morphology, thickness *etc.* are a strong function of the pH of the deposition solutions [50, 51]. By tuning the pH conditions, we can build up thick loopy films wherein each layer measures upto 80 Å as well as very thin flat films with an average bilayer thickness of 3-5 Å [50]. The number of bilayers also plays a major role during the layer-by-layer buildup process. For the first few bilayers the film growth is linear, but beyond a certain critical number of bilayers, an exponential growth pattern creeps in [52], which can lead to lowering of the flux. These two polyelectrolytes were chosen as their properties can be varied to a large extent by changing some external parameters, adding considerable flexibility to the modification process. Polyelectrolytes swell in water. On swelling, the overall thickness of the film increases accompanied by an increase in the free volume between the polymer chains. This affects both the flux as well as ion rejection of the membrane. Crosslinking the polyelectrolytes limits their swelling to a great extent [53]. We therefore chemically crosslinked the polyelectrolyte system by using Glutaraldehyde to react with the amine groups of PAH thus limiting swelling to a certain extent [53-55].

2.3.2.1 Effect of pH of the polyelectrolytes

Depending on the pH of the polyelectrolytes, the type of interaction may be electrostatic or hydrogen bonding. According to literature, when both PAH and PAA are deposited at pH of 6.5, the film thickness is the lowest among all other pH conditions [50]. At this pH condition, both the polyelectrolytes are fully charged and are deposited on the surface as thin flat films via electrostatic interaction. On the other hand, when PAH is deposited at a pH of 8.5 and PAA at 3.5, both of them are partially charged and they are deposited as thick loopy films. We tried out 5 bilayers of each of the two polyelectrolyte systems to compare their performances. As shown in Figure 3, the modified NF 90 membrane with 5-bilayers of PAH (pH 8.5) and PAA (pH 3.5) showed an extremely low permeability value of 0.45 l/m^2·hr·bar which was even lower than a commercial SW 30 membrane. Compared to that, 5 bilayers of PAH (pH 6.5) and PAA (pH 6.5) had almost 6 times higher permeability than SW 30 membrane. The rejection offered by the 6.5/6.5 system was around 93% while for the 8.5/3.5 system it was around 81%.
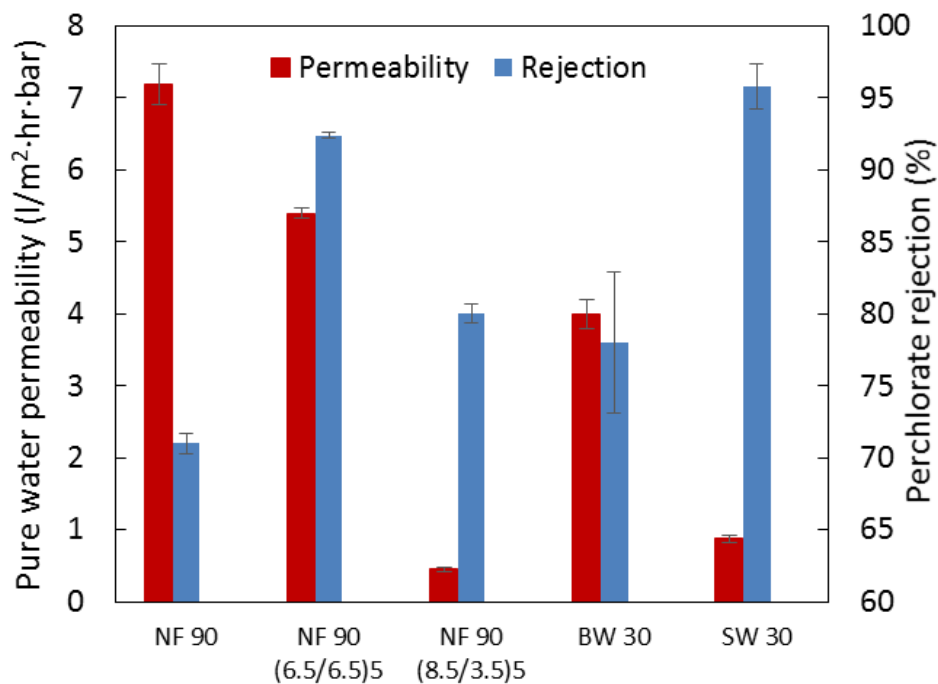
Figure 2.3. Effect of the pH conditions used during the deposition of polyelectrolytes and the comparison of the modified membranes' performance with the commercial membranes [NF 90(6.5/6.5)$_5$ represents NF 90 membrane modified with 5 bilayers of PAH (pH 6.5) and PAA (pH 6.5) and NF 90(8.5/3.5)$_5$ represents NF 90 membrane modified with 5 bilayers of PAH (pH 8.5) and PAA (pH 3.5)].

A schematic representation of the above phenomenon has been shown in Figure 4. The higher thickness of the 8.5/3.5 films results in lowering of the water flux. The swelling tendency of the 8.5/3.5 film is higher than the 6.5/6.5 film [56]. Cross-linking with glutaraldehyde reduces the swelling percentage to a certain degree in both the cases. However, glutaraldehyde only crosslinks the PAH layers leaving the PAA chains free to swell. An inherently higher degree of swelling for the PEMs under 8.5/3.5 condition as compared to the 6.5/6.5 condition, allows higher permeation of perchlorate ions across the film. In a previous study, a similar observation was made regarding the release of a certain cationic dye molecule from PEM films which were fabricated under different pH conditions [57]. According to the authors, the PAH /PAA films recorded a higher release rate when its degree of swelling was higher at the 2.0/2.0 pH condition as opposed

to the 6.5/6.5 condition. In conclusion it can be said that the flat film configuration worked better both in terms of higher permeability as well as higher rejection in comparison to its loopy counterpart.
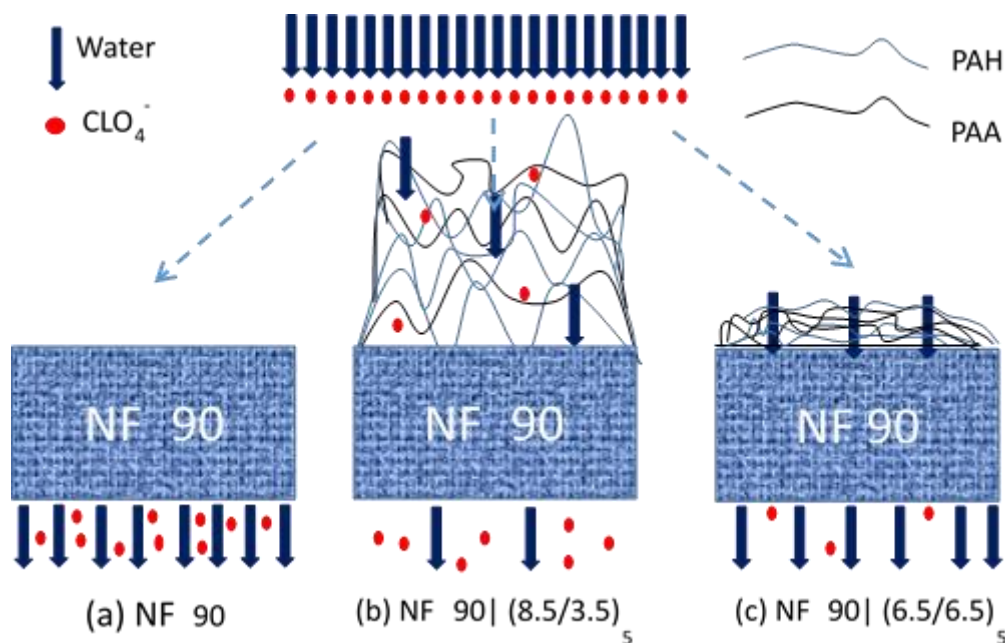
Figure 2.4. Schematic representation of the effect of pH on the performance of the modified membranes in terms of permeability and rejection.

2.3.2.2 Effect of the number of bilayers

The number of bilayers is another important parameter which helps us tune the performance of the membranes. Figure 2.5 shows the permeability and rejection of the modified membranes as a function of the number of bilayers.
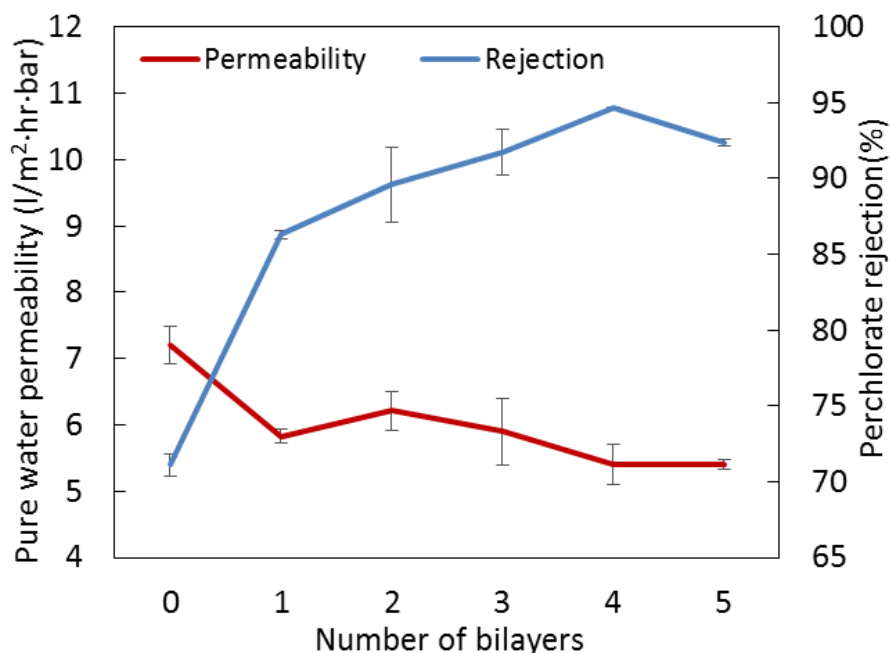
Figure 2.5. Variation in the permeability and rejection of the modified membranes as a function of the number of bilayers.

The rejection of the bare NF 90 membrane was around 71%. With just 1 bilayer of [PAH (pH 6.5)/PAA (pH 6.5)] the rejection of the modified membrane increased to 86%, with only a 20% decrease in water permeability from the underlying membrane. On increasing the number of bilayers, we found that 3 bilayers are sufficient to enhance the rejection of NF 90 to almost the same value as shown by SW 30. As far as the flux is concerned, no significant change was observed on increasing the number of bilayers from 1 to 5. The slight difference in the flux of the membranes, modified with different number of bilayers, can be attributed to the very low thickness of the films. The thickness data from 3 bilayer onwards is shown in Figure 2.6. The thickness values of one and two bilayers were too low to be detected, given the limited sensitivity of the ellipsometer. The layers grow linearly till 5 bilayers with an average bilayer thickness of 6 Å. This is in good agreement with previously reported data [50, 56, 58].
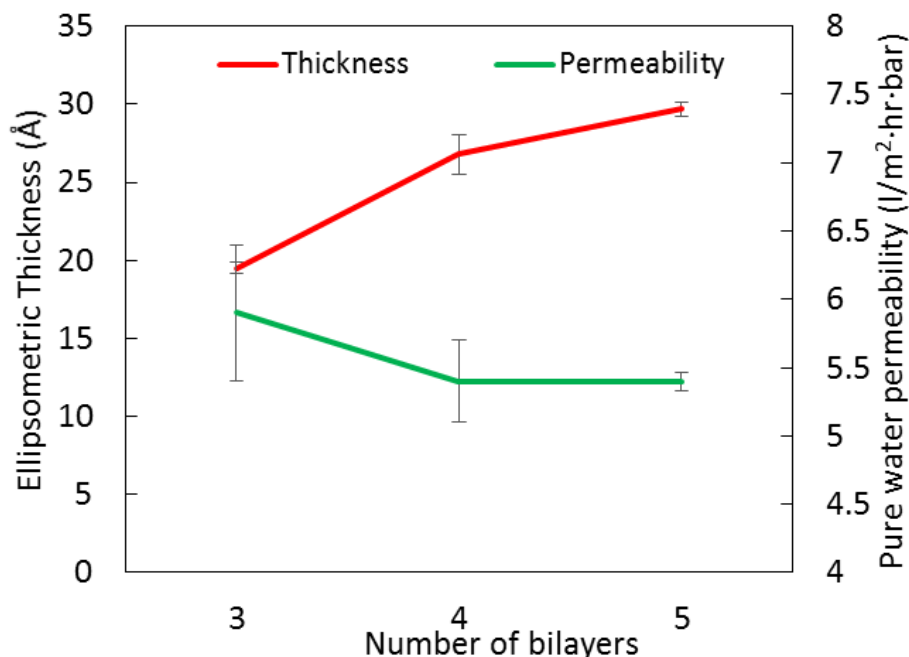
Figure 2.6. Variation in the film thickness and permeability with the number of bilayers. The thickness of the 1 and 2-bilayer systems could not be measured due to the lack of sensitivity of the ellipsometer used.

It can be assumed that with the deposition of the first bilayer, majority of the surface gets covered with the PEs which is the cause behind the increase in rejection. The 20% reduction in permeability that was observed can be attributed to the covering up of the very fine pores on the NF 90 membrane with the first bilayer. After the deposition of 4 additional bilayers, a negligible change in permeability was observed. The average value of permeability of the modified membranes was around 5.75 l/m^2·hr·bar. However in order to increase the rejection beyond 86%, we needed at least 3 bilayers. From 3 to 5 bilayers, no further improvement in rejection could be achieved as can be seen in Fig.2.4. The minor differences in the performance of the 3, 4 and 5-bilayer systems can be attributed to certain unavoidable experimental fluctuations. For all practical purposes, the rejection of these three systems can be averaged out to a value of 93%. In this context, it should be noted here that the difference in the skin layer thickness between a commercial NF 90

membrane and SW 30 membrane is around 400 nm. For the modified membranes, only 20 Å of PEMs deposited on a NF 90 membrane, is enough to achieve the same level of rejection as SW 30.

2.3.2.3 Optimized membrane performance

Taking the 3-bilayer system as the most optimized one, we compare its performance with some of the commercial membranes as shown in Figure 2.7. The permeability of the modified membrane is almost 6 times that of SW 30 membrane and 1.5 times that of BW 30. Its rejection is much higher than BW 30 and almost equivalent to SW 30. Therefore, we successfully designed a modified membrane system, having an excellent combination of high permeability as well as high rejection.
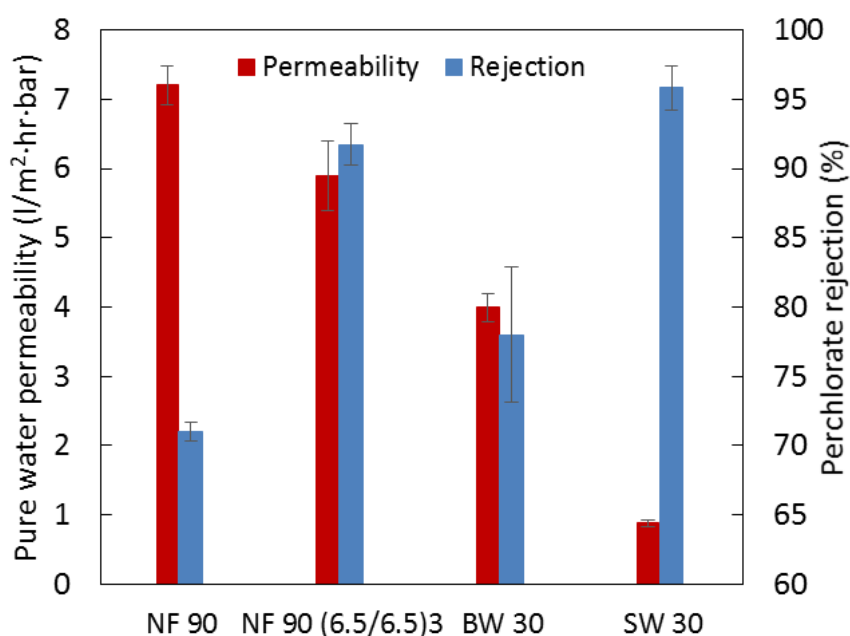
Figure 2.7. Comparison in the performance of the optimized membrane with respect to the bare membrane and commercial RO membranes [NF 90(6.5/6.5)$_3$ represents NF 90 membrane modified with 3 bilayers of PAH (pH 6.5) and PAA (pH 6.5)].

The level of perchlorate contamination varies significantly among different sites within the country. Consequently, the percentage rejection required to reduce the perchlorate concentration

to the regulatory standards, also varies from one site to another. The state of California, which is notorious for perchlorate contamination, is an example. Here the concentration varies within a wide range of less than 18 ppb to 280 ppb[4] and the maximum allowable concentration is around 1 ppb. This indicates that the same level of rejection is not required in all of the perchlorate contaminated sites. For the lower range of concentrations, just 1-bilayer of PAH (pH 6.5)/PAA (pH 6.5) is sufficient to effectively reduce the perchlorate concentration. For higher concentrations of perchlorate, however, the 3-bilayer system would be necessary to make sure the rejection is high enough to meet the standard requirements. Overall the LbL process presents a highly flexible modification technique, which can be tuned as per the application demands.

2.3.2.4 Mechanism of perchlorate rejection

The mechanism of ion rejection by PEM membranes can be either size-based [49] or charge-based [59] or most likely a combination of both. In order to find out the more dominant mechanism, we measured the streaming potentials of the modified membranes as a function of the number of bilayers. Figure 2.8 shows the variation of surface zeta potential with the number of bilayers along with their corresponding rejections.
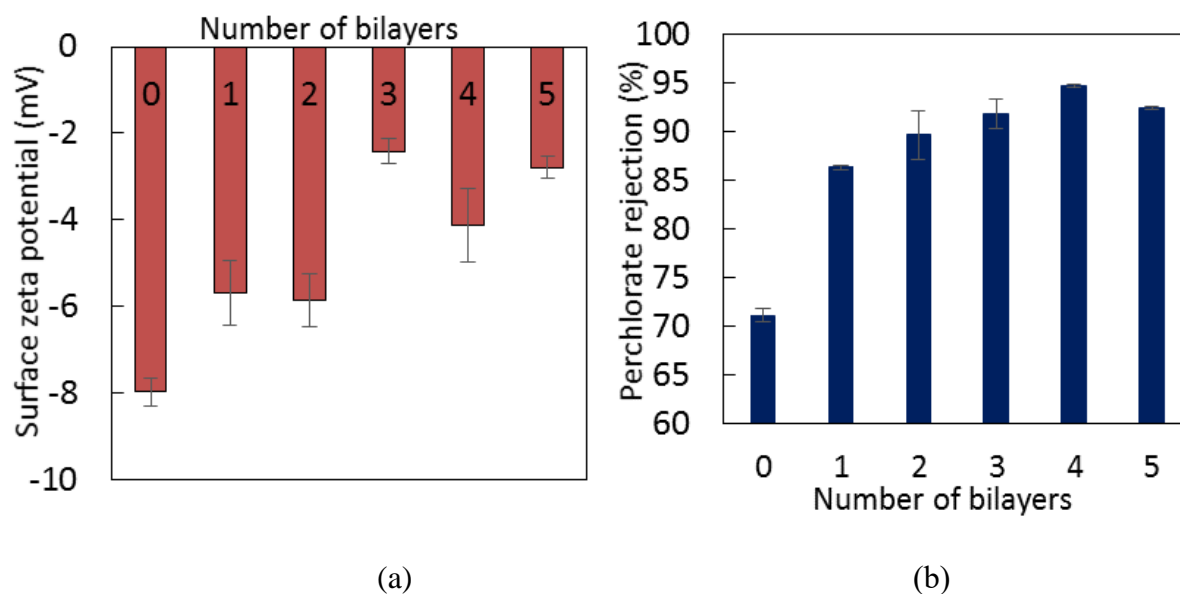
Figure 2.8. Variation of surface zeta potential (a) as a function of the number of bilayers along with the corresponding variation in perchlorate rejection (b).

As expected, the bare NF 90 membrane shows negative charge under the tested conditions. All the modified membranes had PAA as their outermost layer; hence they were negative as well. A screening of the surface charge was observed following the deposition of the first two bilayers and the magnitude decreased further after three or more bilayers are deposited. But overall, the deposition of PAH/PAA multilayers did not alter the magnitude of the surface charge of NF 90 to any significant degree. On the other hand, a careful look at the rejection profile of the modified membranes reveals an increase from 71% to 86% on deposition of only one bilayer and kept increasing till we reached 3 bilayers. Given that, the charge does not vary to a significant extent with the number of bilayers, the streaming potential data and the rejection data cannot be correlated very well. Our hypothesis of surface coverage being related with the rejection seems to fit better with this situation. With higher surface coverage on going from 1 bilayer to 3 bilayers, higher perchlorate rejection was obtained. Following the deposition of three bilayers, the surface coverage reaches a plateau and so does the rejection. The surface charge, therefore, does not play any major

role in determining the rejection behavior of these membranes. It is size-based exclusion that is the main perchlorate rejection mechanism for these modified membranes. This is in agreement with the findings of Bruening et al., regarding the rejection of Fluoride ion by PEM-based membranes [49].

2.4 Conclusion and Future Work

For the first time, PEM based membranes were applied for removing perchlorate ions from drinking water sources. A high flux and high rejection membrane was fabricated by the surface modification of NF 90 membrane by the LbL assembly of PAH and PAA. The pH used during the deposition of the polyelectrolytes played a pivotal role in determining the permselectivity of the membrane. When both the polyelectrolytes were deposited at a pH of 6.5, the modified membrane had higher permeability as well as higher rejection than the case where PAH was deposited at a pH of 8.5 and PAA at 3.5. The effect of the number of bilayers deposited was also investigated. There was only about 20% reduction in the permeability of the bare membrane after depositing one bilayer and after that the value practically remained the same till 5 bilayers. As for rejection, the highest increase was seen on going from the bare membrane to 1 bilayer and after that there was only a slight increase till 3 bilayers. Overall, modification of NF 90 with 3 bilayers of PAH and PAA, both being deposited at pH of 6.5 gave the most optimum results with a perchlorate rejection of around 93% and permeability of 5.75 l/m^2·hr·bar. The modified membrane had 6 times higher permeability than SW 30 and 1.5 times that of BW 30. The perchlorate rejection of around 93% was also very close to what is shown by SW 30 and higher than that of BW 30 under the same conditions of feed concentration and pressure. The streaming potential results showed that the ion rejection mechanism barely depends on the surface charge of the outermost layer. This

enabled us to conclude that size exclusion mechanism was more dominant than charge-based separation in this case.

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3. DEVELOPMENT OF POLYELECTROLYTE MULTILAYER MEMBRANES TO REDUCE THE COD LEVEL OF ELECTROCOAGULATION TREATED HIGH-STRENGTH WASTEWATER

3.0 Abstract

This study focused on developing a membrane-based purification process, coupled with electrocoagulation (EC) as the pretreatment step, to reduce the COD level of an anaerobic digestion effluent. Commercial brackish water reverse osmosis (RO) membranes offer high COD removal but very low water fluxes. In an effort to address this issue, polyelectrolyte multilayer (PEM) membranes were fabricated by the surface modification of loose nanofiltration membranes using layer-by-layer assembly technique. The application of PEM membranes to treat wastewater effluents has not been explored in details. Two polyelectrolyte combinations were tried – the first one consisted of poly (diallyl dimethyl ammonium chloride) and poly (styrene sulfonate) while the second one consisted of poly (allylamine hydrochloride) and poly (acrylic acid). In comparison to commercial RO membranes, these membranes offered significantly higher fluxes, albeit with equivalent COD reduction. The effect of effluent properties like pH and composition, on the performance of these membranes has been discussed. The PEM films were characterized based on properties like thickness and surface charge, which directly affected the separation behavior of the membranes. For the first time, the combination of EC and PEM membranes has been tried out as a simple, energy-efficient two-step process for treating high-strength wastewater.

3.1 Introduction

With rapid population increase and industrial growth, the fresh water resources are quickly being depleted. Improving the efficiency of water usage is critical to achieving global water sustainability. Recycle and reuse of municipal, industrial and agricultural wastewater are one of the key approaches to realize such efficiency improvement. Among different types of wastewater, high-strength wastewater with a significant amount of organic matter, solids, and nutrients requires more complicated processes to be treated and turned into clean water. In the present study, liquid effluent from an anaerobic digestion (AD) reactor was the target high-strength wastewater. Due to the chemical complexity of AD liquid effluent, Chemical Oxygen Demand (COD) was used as an indicator to evaluate the removal efficiency of different treatments [1, 2]. The combination of electrocoagulation (EC) and membrane technology has attracted attention as an effective approach to treat high strength wastewater [3-6]. Compared to other physical and chemical treatments such as sedimentation, flocculation and activated carbon, EC technology presents a superior method to remove solids and pollutants from various wastewater streams. It has advantages of shorter retention time, better removal of smaller particles, no need of additional coagulation-inducing reagents, and smaller footprint [7]. A previous study demonstrated that a two-stage EC process showed high COD removal from AD effluent [8]. However, the EC treatment was still not enough to meet the drinking water standards. Thereby, in order to turn AD effluent into clean water, membrane filtration was employed to purify the EC treated effluent. The overall wastewater treatment scheme is shown in Figure 3.1.
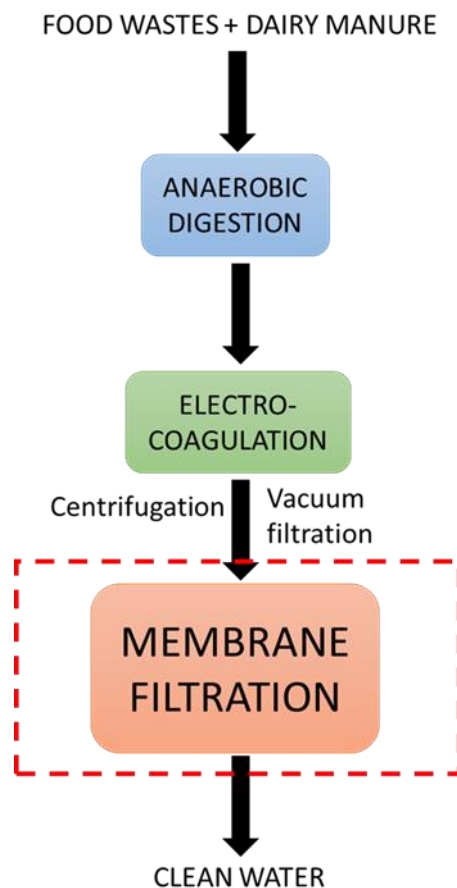
Figure 3.1. Flow diagram of the overall wastewater treatment process*
*: Membrane filtration was the focus of this study.

Various membrane technologies such as microfiltration (MF), ultrafiltration (UF), and reverse osmosis (RO) have been implemented on EC treated wastewater to produce clean water [4, 9, 10]. Dense nanofiltration (NF) and RO membranes exhibit high solute removal properties[11]. However, the permeability of the commercially available RO or dense NF membranes are extremely low, which leads to high operating costs. This study focused on the surface modification of NF 270 which is a "loose" NF membrane with high permeability. We used the layer-by-layer assembly (LbL), which is an aqueous based thin film deposition technique, to modify the membrane surface. It was hypothesized that these membranes, on modification, would offer equal COD reduction as commercial RO membranes, but with higher solution permeability.

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The LbL technique was pioneered by Iler [12], and Decher *et al.* did a significant amount of research in this area to make LbL one of the most versatile thin film deposition techniques [13, 14]. It involves the deposition of polyelectrolytes which can interact via secondary molecular interactions such as ionic bonding, hydrogen bonding, hydrophobic-hydrophobic interactions etc. [15].

Polyelectrolyte multilayer (PEM) membranes, which are fabricated by the LbL assembly of polyelectrolytes on different commercial membrane surfaces, have been widely employed for ion rejection applications such as water softening or desalination [16-22]. Most of these studies were performed using a lab-based synthetic solution, which fails to emulate the complexities involved in real wastewater samples. Only a few studies applied the PEM-based modified membranes on real effluents such as industrial effluents and tanning effluents [23, 24].In these studies, no detailed filtration performance and separation characteristics of the modified membranes have been reported. Besides, the combination of EC and PEM-based membrane filtration to treat high-strength agricultural wastewater also has not been studied. In order to elucidate the performance of PEM membranes two different sets of polyelectrolytes were selected and the resulting membranes were compared against a commercial RO membrane. The first set of polyelectrolytes comprised of the electrostatically crosslinked poly(diallyl dimethyl ammonium chloride) (PDAC) and poly(styrene sulfonate) (SPS), while the second set comprised of poly (allylamine hydrochloride) (PAH) and poly (acrylic acid) (PAA) that were covalently crosslinked by N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC). COD reduction and membrane permeability were used as the criteria to compare the performance of the PEM membranes with the commercial RO membranes.

3.2 Materials and Methods

3.2.1 Materials

PDAC (MW 100,000-200,000, 20 wt% in water), SPS (MW 70,000), PAH (MW 900,000) and PAA (MW 15,000, 35 wt% in water) were purchased from Sigma Aldrich. 2-(N-Morpholino) ethanesulfonic acid (MES) Buffer was also purchased from Sigma Aldrich. EDC was purchased from Fisher Scientific. Sodium chloride and potassium chloride crystals were procured from Avantor Performance Chemicals (Center Valley, PA). Three commercial membranes, NF 270, NF 90 and BW 30, from Dow Filmtec (Midland, MI), were used as the base membranes for this study. Among them, NF 270 and NF 90 are nanofiltration membranes, and BW 30 is a brackish water reverse osmosis membrane. All aqueous solutions were prepared using deionized (DI) water (>18.2 MΩ) supplied by a Barnstead Nanopure Diamond-UV purification unit equipped with a UV source and a final 0.2 μm filter. Unless specified all procedures were carried out at room temperature (25 °C).

3.2.2 The Dead End filtration set-up

The HP 4750 stirred dead end cell (Sterlitech, Kent, WA) was connected to a nitrogen cylinder which acted as the pressure reservoir. The net volumetric capacity of the setup was around 300 ml. The unit was placed on a magnetic stirring plate. The filtrate was collected in a measuring cylinder. The flux was calculated by measuring the volume of water collected over a certain period of time and normalizing it with respect to the membrane area. The effective membrane area for this setup was 14.6 cm^2.

3.2.3 Measurement of effluent properties

The total solids (TS) measurement was done using the dry weight method. COD, total nitrogen (TN) and total phosphorus (TP) measurements were done using HACH^{TM} standards methods

[130]. Total carbon (TC) and inorganic carbon (IC) were measured using Shimadzu TOC-VCPN total organic carbon analyzer (Columbia, MD, US). Total organic carbon (TOC) was measured by subtracting the IC value from TC.

3.2.4 Experimental methods

3.2.4.1 Electrocoagulation (EC) treatment

AD effluent was obtained from a 2500 m^3 completely stirred tank reactor (CSTR) in the Anaerobic Digestion Research and Education Center (ADREC) at Michigan State University. A two-stage EC treatment was then carried out as described in a previous study [8]. Current level of 2A was applied to two sets of electrodes with anodic surface area of 62 cm^2. The effective volume of the EC reactor was 0.5 L and retention time of 60 minutes was employed. The middle layer with relatively less turbidity was siphoned out as the feed for the second stage of EC, which applied same electricity conditions for another 40 minutes. Solutions were centrifuged at 236 *g* for 10 minutes before being used for the membrane filtration experiments.

3.2.4.2 Preparation of polyelectrolyte solutions and LbL assembly technique

The bare NF 270 membranes were stored in DI water prior to the LbL deposition. The permeate sides of the membranes were covered with four alternate sheets of parafilm and aluminum foil prior to the LbL process. The required portion of the membrane was then cut out and used for the filtration experiments. This way, we were able to prevent the deposition of polyelectrolytes on both sides of the membrane to a large extent.

The LbL deposition process was carried out using a Carl Zeiss Slide Stainer which employs a robotic arm to move the sample to different solution baths. For all polyelectrolytes, the concentration was maintained at 10 mM. PDAC and SPS were prepared in 0.5M NaCl solutions and no pH adjustments were made to these solutions (the unadjusted pH values of the PDAC and

SPS solutions were 6.6 and 6.0 respectively). For the PAH/PAA multilayer assembly, the pH of PAH and PAA were adjusted to 8.5 and 3.5, respectively, using 1M HCl/1M NaOH. The dipping time in each polyelectrolyte solution was set to 10 mins. After each polyelectrolyte dipping step, the substrates were rinsed with DI water for three consecutive times (2 mins, 2 mins and 1 min). Following the deposition of one complete bilayer, the sample was sonicated for 2 mins in an ultrasonicator bath. The procedure was repeated till the desired number of bilayers was deposited. After LbL deposition, the membranes were soaked overnight in DI water.

3.2.4.3 Crosslinking of PAH and PAA with EDC

The EDC solution was prepared in a 50 mM MES Buffer solution at a concentration of 50 mg/ml and pH of 5.5. Following the deposition of PAH/PAA multilayers on the membrane surface using the aforementioned LbL protocol, the modified membrane was dipped in the EDC solution using the slide stainer for 60 minutes with continuous agitation. The samples were then subject to three consecutive DI water rinsing steps, each of them being of 15 minutes duration, and then followed by 5 minutes of sonication.

3.2.4.4 Dead end filtration protocol

The membranes were stored in DI water at least for 12 hours prior to usage. All membranes were first compacted by running pure DI water across them at a pressure of 10 bar. After two hours of compaction, the steady state value of the flux was noted down as the pure water flux of the membrane under consideration. Prior to using the wastewater, the solution was pre-filtered using a 0.22 μm Millipore filter. This solution was then made to pass through the membranes at a transmembrane pressure (TMP) of 5 bar till the permeate volume reached 50 ml. The solution flux was calculated based on the time taken to filter 50 ml permeate across the given area of the membrane. The permeability and COD reduction values of various membranes which are

presented in the later sections of this paper, were calculated based on the average of three replicates of each membrane.

3.2.5 Thin film characterization

3.2.5.1 Measurement of streaming potential

The surface charge of the membranes were measured using the Brookhaven EKA Electro-kinetic analyzer (BI-EKA, Brookhaven Instrument Corp., Holtsville, NY) equipped with a rectangular cell and a clamp cell. A poly (methyl methacrylate) (PMMA) substrate was used as the reference. All streaming potential measurements were carried out using 1mM potassium chloride (KCl) as the electrolyte. The bypass lines and the cell were rinsed with KCl solution after being rinsed with DI water several times. At least three replicates were used for each of the membranes that were tested for streaming potential. In order to measure the membrane surface charge as a function of pH, the streaming potential tests were carried out with KCl solution at three different pH conditions (3, 7 and 9). The pH of these solutions was adjusted using 1M HCl/ 1M KOH.

3.2.5.2 Measurement of thickness

The thickness of the PEM films was measured using a Dektak surface Profiler. Both types of PEM films were deposited on plain glass slides for the measurement. In order to reconfirm the values obtained from the profilometry tests, we also used the J.A Woollam M-44 Ellipsometer. The PEM films were deposited on gold coated glass slides (VWR International, US) for the ellipsometry tests. Prior to the LbL deposition, the gold-coated glass slides as well as the plain glass slides were treated with O_2 plasma for 20 minutes using a Harrick plasma cleaner (Harrick Scientific Corporation, Broading Ossining, NY) at 30 W RF power under 100 millitorr vacuum pressure. Immediately after the plasma treatment, the substrates were put in the slide stainer for the LbL process, as per the protocol described earlier (Section 2.4.1). The model for generic films was used

for the ellipsometry measurements, assuming a refractive index of 1.5. The thickness was determined along several spots on the substrate and at least three replicates of each type of PEM film were used to get an average value.

3.3 Results and Discussion

3.3.1 EC treatment of diluted AD effluent

The characteristics of AD liquid effluent and EC treated AD effluent (post vacuum filtration) have been listed in Table 3.1. After a two-stage EC treatment [8] , a transparent solution was obtained and 97% of COD was removed, with the final COD level being 330 mg/L. Even though the EC treatment demonstrated excellent efficiency for solid and COD removal, the COD level in the effluent was still high, considering that the ultimate aim was to produce drinking water. Membrane-based filtration was therefore employed to reduce the COD of the EC treated AD effluent.

Table 3.1. Characteristics of the AD liquid effluent and filtered EC treated AD liquid effluent (post vacuum filtration)

Parameters	AD liquid effluent*	EC-treated AD liquid effluent (post vacuum filtration)
pH	7.5-8.0	9
TS (w/w %)	0.90	--
COD (mg L^{-1})	10017	330
TP (mg L^{-1})	340	1.18
TN (mg L^{-1})	1233	150
TOC (mg L^{-1})	2332	100

 *: The AD liquid effluent for EC pretreatment was made by diluting the raw AD liquid digestate five times.

3.3.2 Performance of commercial membranes on the EC treated AD effluent

The three commercial membranes, NF 270, NF 90 and BW 30 were tested with the EC treated AD effluent and their performances were compared in terms of their permeability and COD reduction.

The experimental data demonstrated that the NF 270 membrane had the highest pure water flux as well as solution flux among the three membranes, while BW 30 showed the highest COD removal (Figures 3.2 and 3.3). It has been reported that pH of the solution has significant influence on the separation behavior of the membranes [26]. The original pH of the EC treated AD effluent was around 9. The pH of the EC effluent was adjusted to 3 in order to evaluate the effect of pH on permeability and COD reduction. As shown in Figure 3.2, NF 270 membrane had higher COD reduction at acidic pH than alkaline pH, but the solution permeability was lower at acidic pH. (Figure 3.3a). In case of both NF 90 and BW 30 membranes, there was no significant difference in COD reduction under different pH conditions. The COD reduction of BW 30 membrane was higher than that of the NF 90 membrane. Both NF 90 and BW 30 had very similar solution permeability which was much lower than the solution permeability of NF 270 membrane. (Figure 3.3a).

The effect of pH on membranes, especially on NF 270 membrane, can be interpreted based on the membrane surface properties as well as the characteristics of the EC effluent. NF90 and BW30 are dense non-porous membranes as compared to NF 270 membrane, which is a "loose", relatively more porous membrane. Even though all three membranes have positive charge at acidic conditions and negative charge at alkaline conditions, the responses of the NF 90 and BW 30 membranes to changes in effluent properties are different than that of NF 270 membrane.

Natural organic matters (NOM) are present in almost all types of wastewater samples and the EC-treated AD effluent is no exception. TOC analysis confirmed the presence of a significant amount of organic matter in the EC effluent (100 mg/l). Among the various types of NOMs present in the solution, it has been reported that the humic compounds are largely responsible for the pH-dependent behavior of the effluent. [27-30]. As the humic compounds play critical roles as

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electron mediators in microbial electron transfer during anaerobic digestion [31], their concentration in the AD effluent was relatively high, and the EC treatment was not able to remove all of them. Consequently, a certain amount of them remained in the EC effluent. According to previous studies, humic compounds lose most of their charge under acidic conditions, resulting in their aggregation[29]. On the other hand, at alkaline pH these compounds exhibit negative charge. For dense membranes like NF 90 and BW 30, the aggregation of humic compounds has little influence on their performance. Therefore no significant difference in performance (both COD removal and solution permeability) was observed for the NF 90 and BW 30 membranes, when tested under two different pH conditions. The BW 30 membranes showed the highest COD removal (92-95%) with a COD level of around 21 ppm in the final filtrate, but extremely low solution permeability of around 0.6 $l/m^2 \cdot hr \cdot bar$.

For NF 270, the membrane surface properties as well as the EC effluent properties had significant influence on its performance. Under acidic conditions, the humic compounds were inclined to settle down on the membrane surface, resulting in lowering the permeability of NF 270 membrane at pH = 3 as compared to pH = 9 (Figure 3.3a). However, the deposition of humic compounds created an additional layer that prevented the passage of the remaining humic compounds and other fine particles in the effluent, which helped improve the COD reduction of the membrane (Figure 3.2). Under alkaline conditions, charge-based repulsion existed between the negatively charged humic compounds and the membrane surface. This repulsion was not enough to lower the COD level down to what was achieved under acidic conditions, but helped to maintain a higher solution permeability. Considering the fact, that a loose surface structure provides some flexibility for the LbL coating experiments, NF 270 was selected as the underlying substrate for fabricating the PEM membranes.
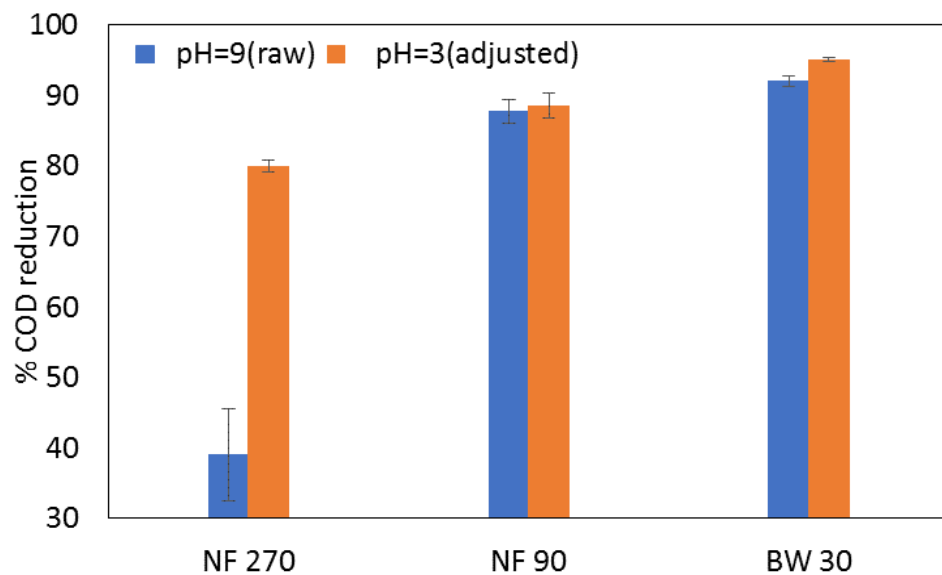
Figure 3.2. Comparison in COD reduction between the commercial membranes.
(TMP = 5 bar)
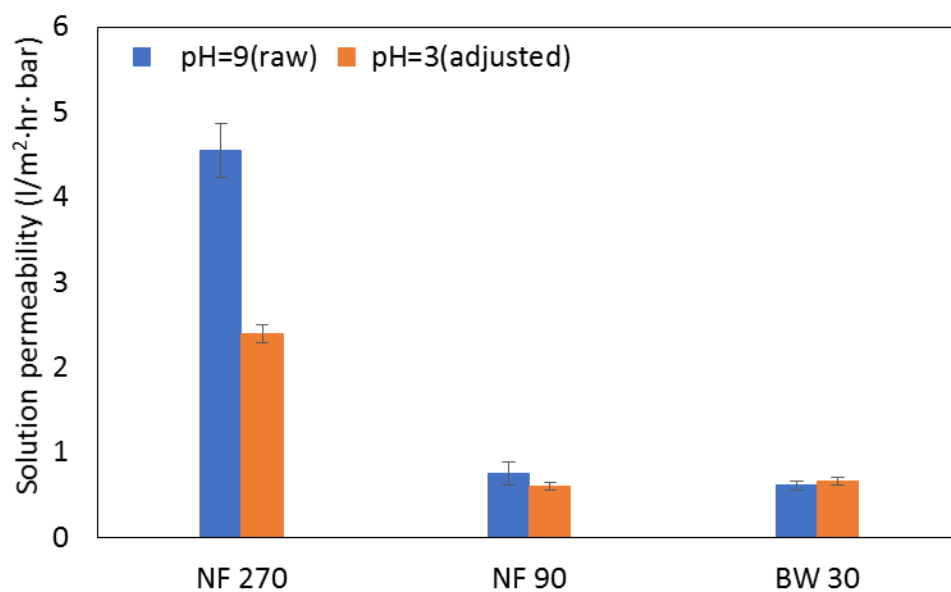
(a)

Figure 3.3. Permeability comparisons between the commercial membranes based on (a) solution tested under two different pH conditions and (b) pure water.

Figure 3.3 (cont'd)

(b)
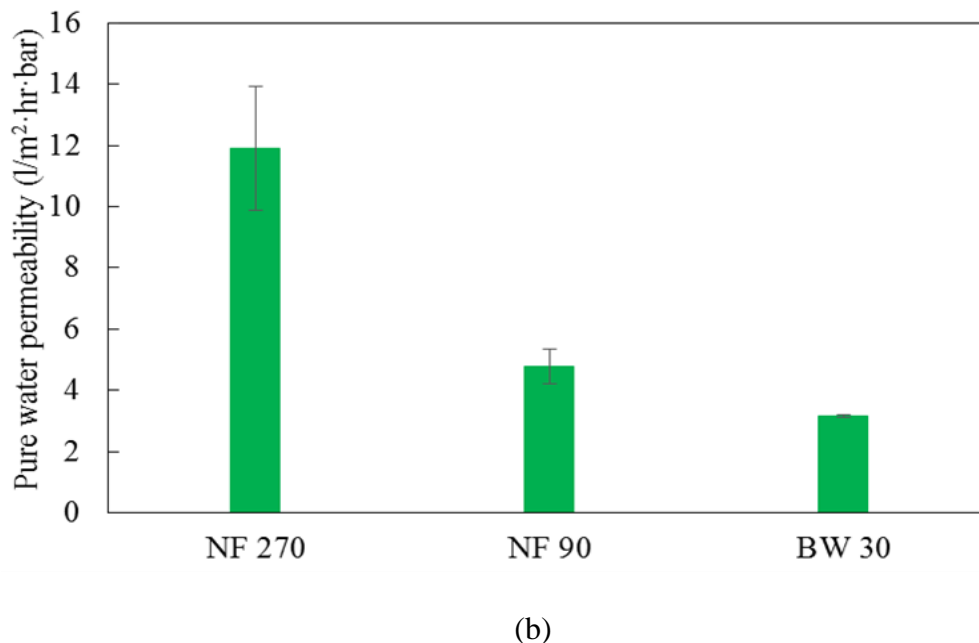
3.3.3 Performance of PEM-based membranes on the EC treated AD effluent

3.3.3.1 [PDAC (0.5 M NaCl)/SPS (0.5M NaCl)] $_{5.5}$ multilayer system

Both PDAC and SPS are strong polyelectrolytes, which remain charged over a wide range of pH.

0.5 M NaCl was used as the supporting electrolyte which helps to increase the surface charge

density [32]. The surface charge plays an important role in shaping the rejection behavior of these

polyelectrolyte-based membranes. Under acidic conditions, as the humic compounds lose most of

their charge, effect of the charge on the outermost layer is minimal. It was, however, important to

understand how the surface charge affects the rejection under alkaline conditions, when the humic

compounds are negatively charged. Two different systems were investigated to treat the EC

effluent at pH 9: the first one comprising of 5 bilayers of PDAC/SPS ending with SPS (negatively

charged), and the second one consisting of 5.5 bilayers of PDAC/SPS ending with PDAC

(positively charged). The experimental data demonstrated that the 5.5-bilayer system ending with

PDAC had higher COD reduction (~ 84 %) than the system ending with SPS (~70 %) (Figure 3.4).

Under alkaline conditions, the negatively charged humic compounds bind to the positively charged PDAC layer and form an additional barrier layer that helps enhance the rejection, while, the system ending with a SPS layer mainly uses charge-based repulsion to reject the negatively charged humic compounds. Therefore, under alkaline conditions, the barrier layer formation by humic compounds on a positively charged surface is more instrumental in reducing the COD level, than charge-based repulsion that occurs with a negatively charged outermost layer. Based on the performance results, the multilayer membrane ending with PDAC was chosen over the one ending with SPS, and used for the following experiments. The number of bilayers is also a tunable parameter for the LbL process. Following some preliminary experiments, 5.5 bilayers was found to be optimum in order to achieve both high flux as well as high rejection.
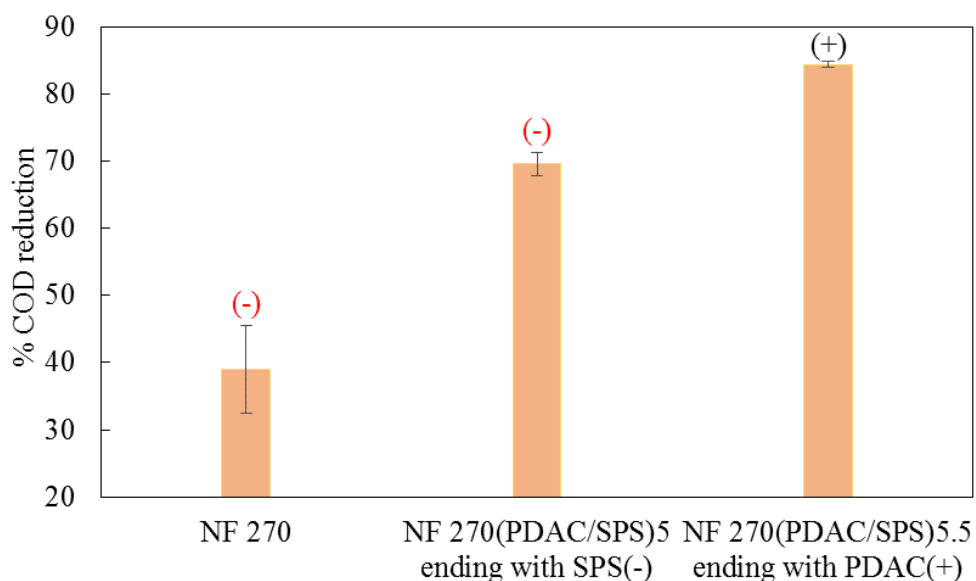
Figure 3.4. COD reduction of two PDAC/SPS based modified membranes. (TMP = 5 bar) (-) Bare NF270 or Multilayer assembly on NF270 ending with negatively charged SPS outer layer. (+) Multilayer assembly on NF270 ending with positively charged PDAC outer layer.

The performance of the PDAC/SPS–based membranes was further compared with the commercial membranes. These modified membranes showed around 84% COD reduction at pH = 9 and 90% at pH = 3 with corresponding COD values of 33 and 51.5 ppm in the filtered solution

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(Figure 3.5), which were significantly better than the original NF270. Permeability experiments demonstrated that the pure water permeability of the PDAC/SPS coated NF 270 membrane was much higher than NF 90 and BW 30 membrane (Figure 3.6b). The modified membrane also showed approximately 3 times higher solution permeability than BW 30/NF 90 at pH 3 and 5 times higher at pH 9 (Figure 3.6a). Similar to the underlying NF 270 membrane, the PDAC/SPS based membranes also had lower solution permeability at acidic pH as compared to alkaline pH (Figure 3.6a). As mentioned before, the formation of a barrier layer of humic compounds on the membrane surface was a key factor influencing the flux. However, the attachment mechanisms of the barrier layer under acidic and alkaline conditions are different. Under acidic conditions, the layer is formed due to the aggregation and settling of the humic compounds on the membrane surface. Under alkaline conditions, the negatively charged humic compounds adhere to the positively charged PDAC surface by electrostatic attraction. Given that the flux is lower under acidic condition, we presume that the barrier layer formed at pH 3 was thicker and denser than what was formed at pH 9. Owing to the thicker barrier layer, the rejection of the membrane was higher under acidic condition. The deposition of PDAC/SPS multilayers led to a considerable enhancement in the COD reduction compared to the bare NF 270 membrane. The percentage reduction was almost equal to that of BW 30 membrane under acidic conditions but lower than BW 30 under alkaline conditions. Covalently cross-linked multilayer structure was therefore studied in order to further improve the membrane performance.

3.3.3.2 [PAH (pH 8.5)/PAA (pH 3.5)]$_{5.5}$ multilayer system

Covalent cross-linking enables to create a tightly woven network, which is capable of blocking unwanted components of wastewater much more efficiently than ionic cross-linking. Therefore, a

covalently cross-linked multilayer structure was coated on the surface of the NF 270 membrane with PAH and PAA as the surface modifiers.

Both PAH and PAA are weak polyelectrolytes that exhibit pH-tunable behavior. When PAH is at pH 8.5 and PAA at pH 3.5, they form thick loopy films with inter-penetrated layers [33]. The amine groups of PAH and the carboxylic groups of PAA can be reacted to form covalent linkages between them. This can be simply done by heating the multilayers up to a high temperature (>180 °C) [34]. However, as the underlying NF 270 membrane cannot tolerate such high temperature, EDC induced chemical cross-linking was applied. [35]. A high EDC concentration of 50 mg/ml was used to ensure high cross-linking density [35]. In order to enable comparison with the PDAC/SPS –based membrane, the same number (5.5) of PAH/PAA bilayers were deposited. In order to enable comparison with the PDAC/SPS –based membrane, the same number (5.5) of PAH/PAA bilayers were deposited.

The performance of the PAH/PAA-based modified membrane has been presented in Figures 3.5 and 3.6. The COD reduction was between 91-95% under both acidic and alkaline conditions (Figure 3.5), and the final COD level in the permeate stream was almost equal to that of BW 30 membrane This could be attributed to a tight dense polymeric network that was formed by crosslinking PAH (pH 8.5) and PAA (pH 3.5), which was capable of completely blocking the passage of unwanted components. The pure water permeability of the PAH/PAA membrane was the lowest among all the membranes (Figure 3.6b), while the solution permeability under both pH conditions was higher than BW 30 and NF 90 membranes (Figure 3.6a). The thick layers of PAH/PAA coating contributed to the low pure water permeability of the modified membrane. In spite of having a lower pure water permeability, the PAH/PAA coated NF 270 membrane showed 1.7 times higher solution permeability than the BW 30 membranes. We believe this was due to

lower fouling propensity of the PAH/PAA coated membrane in comparison to the commercial RO membranes. This has been discussed in more details in a later section. In addition, because of the tight dense polymeric network and the thickness of the coated layers, the deposition of an additional layer of humic substances under acidic pH did not contribute much to the rejection. Therefore, there were no significant differences in COD reduction and solution permeability under acidic and alkaline conditions. The PAH/PAA multilayer membrane had the same COD reduction as the PDAC/SPS system at acidic pH, but higher reduction at alkaline pH The flux of this system was however, lower than the PDAC/SPS system. As the performance of the PAH/PAA coated NF 270 membrane was independent of the pH of the wastewater, it eliminates the need to acidify the solution prior to using it. This, in turn, helps to prevent the severe organic fouling that takes place under acidic conditions.
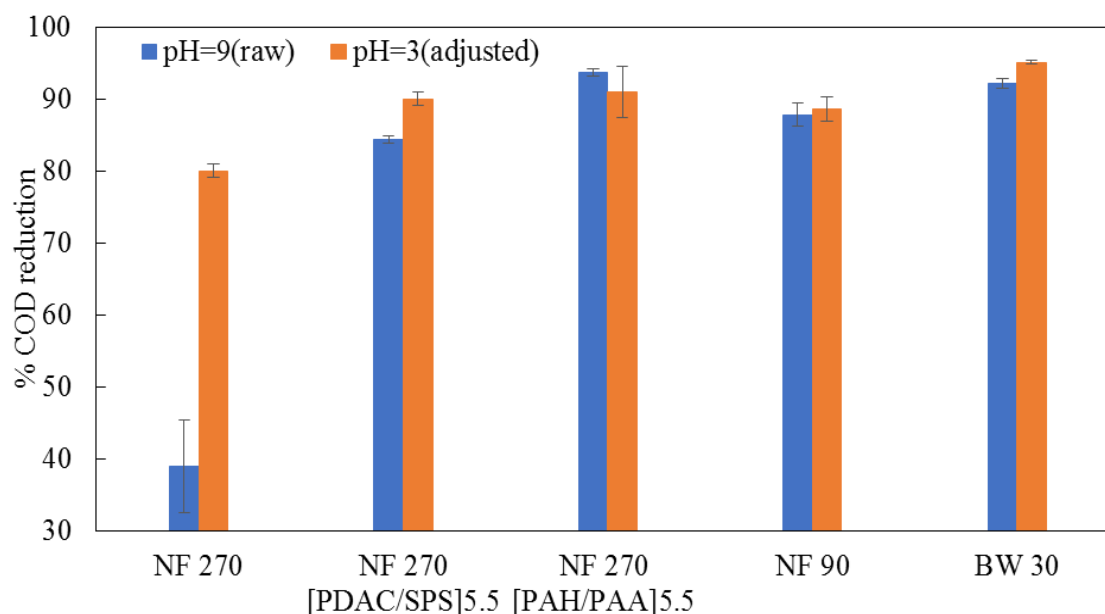
Figure 3.5. Comparison in COD reduction between the modified membranes and the commercial membranes at different pH conditions. (TMP = 5 bar)
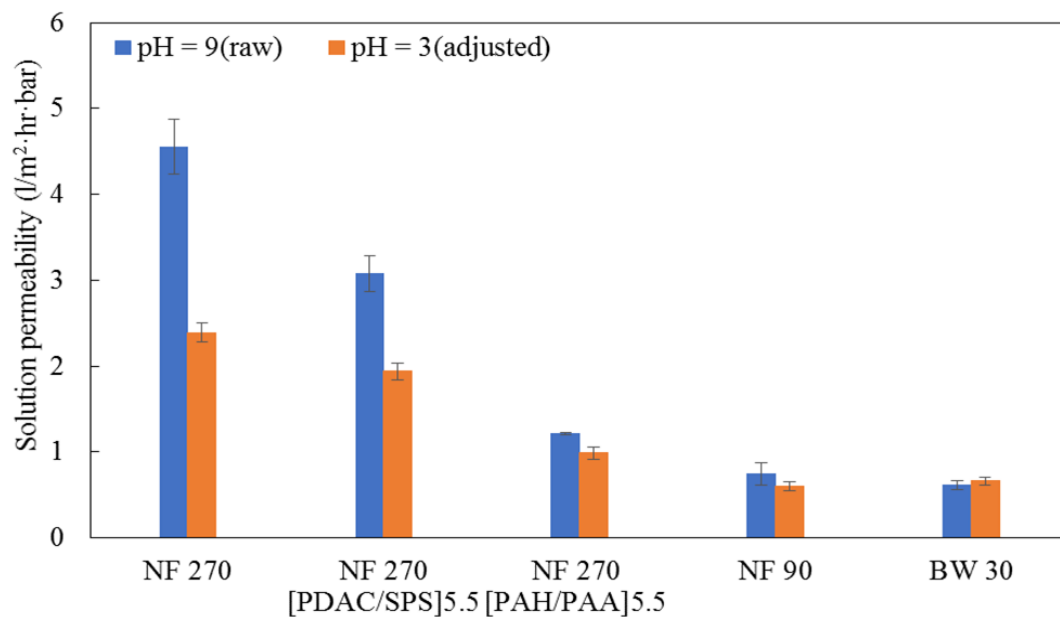
(a)
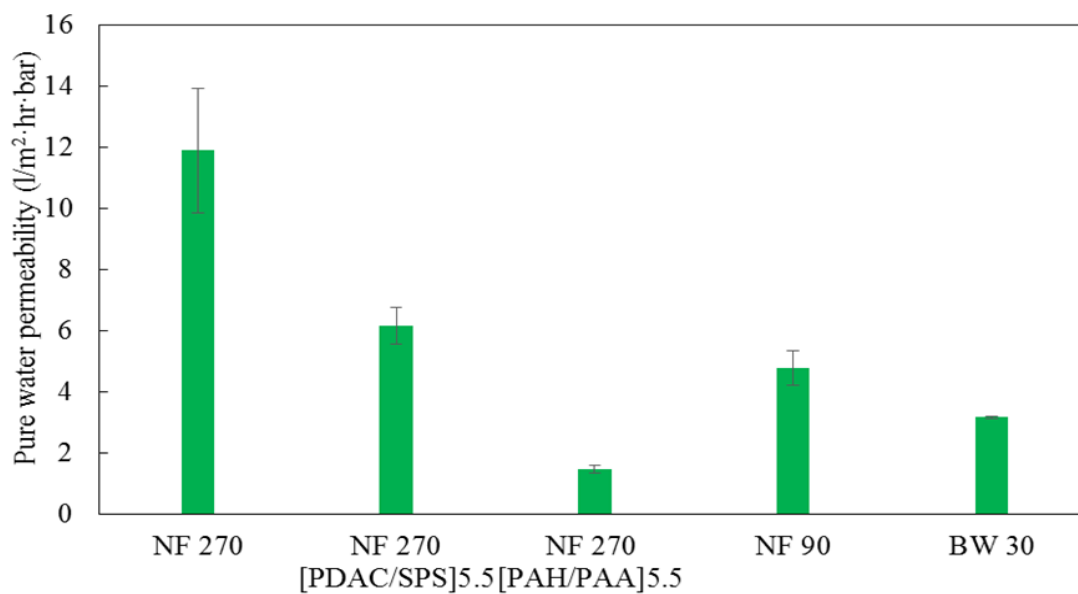
(b)

Figure 3.6. Permeability comparisons between the modified membranes and the commercial membranes based on (a) the solution at two different pH conditions and (b) pure water

The ratio of solution flux over pure water flux could be used as a criterion to evaluate the anti-fouling property of different membranes. A higher ratio indicates better fouling resistance

offered by the membrane surface[36]. The PEM membranes (PDAC/SPS and PAH/PAA) showed

better anti-fouling properties than their commercial counterparts (Table 2).The creation of anti-

fouling surfaces by the deposition of polyelectrolytes has been reported earlier as well [37-40].

Among all the membranes, the PAH/PAA-based membranes had the best anti-fouling performance

under both pH conditions.

Table 3.2. The ratio of the average solution flux to the average initial flux for commercial membranes and the PEM membranes

Membranes	$J_s(50)/J_w(0)$ at pH = 3	$J_s(50)/J_w(0)$ at pH = 9
NF 270	0.201	0.382
NF 270 modified with (PDAC/SPS)5.5	0.315	0.500
NF 270 modified with (PAH/PAA)5.5	0.678	0.829
NF 90	0.125	0.157
BW 30	0.209	0.193

$J_s(50)$: The solution flux of the membrane measured by calculating the time taken to filter 50 ml of the permeate solution
$J_w(0)$: The pure water flux or the initial flux of the membrane
Both the fluxes were normalized with respect to the pressure applied during the measurements.

With the combination of EC and membrane filtration, the color of the AD effluent was

completely removed (Figure 3.7). This is important from the point of view of producing potable

water. The EC process greatly removed the majority of the COD and TS in the AD effluent. The

following membrane filtration step, irrespective of the membrane used, further decolored and

cleaned the EC treated AD effluent. A relatively less energy-demanding method for treating high-

strength wastewater was therefore established.

Figure 3.7. Color change of the solution following different treatment stages
Left to right: AD effluent, EC effluent and membrane filtrate.

3.3.4 Effect of the coating properties on the membrane performance

3.3.4.1 Thickness of the PEM coatings

The thickness of the coatings plays an important role in determining the permeability of the modified membrane. The strong polyelectrolytes PDAC and SPS are fully charged irrespective of pH conditions. The strong ionic linkages between the positively charged PDAC backbones and negatively charged SPS lead to the formation of very thin flat coatings. The addition of NaCl increases the surface charge density and also increases the thickness of the films [20]. PAH and PAA exhibit pH dependent ionization behavior. PAH is around 50% ionized at a pH of 8.5, and PAA is only about 10% ionized at pH of 3.5 [41]. Since they are only partially charged, they arrange themselves in a coiled conformation, with a high level of interlayer diffusion [33], which leads to the formation of thick loopy films.. Crosslinking reduced the swelling tendency of the polyelectrolytes and in turn also led to a decrease in the film thickness.[42, 43]. The thickness values of the two types of polyelectrolyte systems have been shown in Table 3.3. It is apparent

that the thickness of the coatings directly affects the permeability. The thicker PAH/PAA coatings

had lower initial permeability than the PDAC/SPS-based coatings.

Table 3.3. The thickness values of the two types of polyelectrolyte coatings on NF 270 membrane

Type of coating	Thickness (nm)
[PDAC (0.5M NaCl) / SPS(0.5M NaCl)] $_{5.5}$	28.70 ± 4.66
[PAH (pH 8.5) / PAA (pH 3.5)]$_{5.5}$	134.15 ± 9.87

3.3.4.2 Surface charge of the PEM coatings

Surface streaming potential of membranes plays an important role in determining the membrane

rejection properties. The streaming potentials of all three commercial membranes as well as two

modified membranes under three different pH conditions (acidic, neutral and alkaline) are listed

in Table 3.4.

Table 3.4. The streaming potential data for the commercial membranes and the modified membranes as a function of pH

Membrane	Surface streaming potential (mV) @ pH 3	Surface streaming potential (mV) @ pH 7	Surface -streaming potential (mV) @ pH 9
NF 270	5.54 ± 0.13	$- 4.17 \pm 1.89$	-21.35 ± 0.36
NF 270 modified with (PDAC/SPS)$_{5.5}$	20.38 ± 1.66	29.24 ± 2.45	20.07 ± 5.86
NF 270 modified with (PAH/PAA)$_{5.5}$	20.50 ± 4.47	12.83 ± 2.30	10.26 ± 3.36
NF 90	20.91 ± 0.99	$- 15.74 \pm 0.09$	-15.33 ± 0.23
BW 30	12.70 ± 3.80	$- 4.70 \pm 1.45$	-3.66 ± 0.45

Data represent average of three replicates with standard deviation.

The PEM membranes remain positively charged throughout the entire pH range of 3-9, unlike the

commercial membranes. For the PDAC/SPS system, the outermost PDAC layer remained almost

fully ionized within a wide range of pH and therefore imparted positive charge to the membrane surface. This leads to a small variation in its performance under different pH conditions (Table 3.4). For the PAH/PAA system, the effect of pH is much more complicated since both polyelectrolytes have pH dependent ionization. When exposed to a pH of 3, the outermost PAH layer was fully ionized and therefore had the highest positive charge. With the decrease in percentage ionization, the surface streaming zeta potential also decreased as the pH was increased (Table 3.4). However, many other complicated phenomena are associated with this polyelectrolyte system, like the inter-diffusion of polyelectrolytes [44] and shifting of the pK_a value of the polyelectrolytes [41] when incorporated within the multilayers. Besides, the effect of cross-linking on the ionization of the weak polyelectrolytes not been studied till date. These factors can individually or collectively influence the surface streaming potentials under varying pH conditions.

3.4 Conclusion

With this study it can be concluded that integration of electrocoagulation and PEM-based membrane separation provides an efficient way to reclaim a high-strength wastewater. PEM-based membranes demonstrated excellent performance in treating an actual wastewater effluent. A comprehensive study of several key concepts involving the membrane surface properties as well as the effluent properties was performed to deal with the complexities involved in wastewater treatment. The pH of the wastewater solution played a pivotal role in determining the performance of the membranes mainly due to the NOMs present in the EC effluent. Both PDAC/SPS and PAH/PAA based membranes had higher solution permeability than the commercial reverse osmosis membrane (BW 30). The PDAC/SPS based membrane showed equivalent COD reduction as BW 30 under acidic conditions, while the PAH/PAA based membranes showed equal reduction

as BW 30, irrespective of the pH conditions used. Both the polyelectrolyte-based membranes had much lower fouling propensity than the commercial membranes, which expands the scope of applicability of PEM membranes beyond some simple ion-rejection studies.

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4. INCORPORATION OF CLAY NANOPLATELETS WITHIN POLYELECTROLYTE MULTILAYERS TO DESIGN MEMBRANES WITH ENHANCED ANTI-FOULING PROPERTIES

4.0. Abstract

This work is focused on the application of clay-polyelectrolyte hybrid thin films to develop fouling resistant membrane surfaces for wastewater treatment applications. Modifying the membrane surfaces by imparting more hydrophilicity and charged functional groups is one of the common approaches of reducing the fouling propensity. In our work, we used the layer-by-layer (LbL) assembly technique to modify the surface of a commercial ultrafiltration membrane to create polyelectrolyte multilayer (PEM) membranes. Other than the polyelectrolytes - poly allylamine hydrochloride (PAH) and poly acrylic acid (PAA), we also used clay nanoplatelets in the LbL assembly. The anti-fouling properties of these clay-PEM (c-PEM) hybrid membranes were evaluated against an electrocoagulation-treated high strength wastewater effluent. These hybrid nanostructured membranes showed enhanced fouling resistance as compared to the commercial membranes and the PEM membranes. Just 2.25 quadlayers were sufficient for designing the c-PEM membranes with good anti-fouling properties and on crosslinking the polyelectrolytes, these membranes showed enhanced fouling resistance. The crosslinked c-PEM hybrid membranes also showed much higher COD reduction compared to their uncrosslinked counterparts, the PEM membranes (both uncross linked and crosslinked) and the bare PES membrane. However, the improved fouling resistance was attained at the cost of compromising the high initial flux value of the bare UF membrane, which points out the need for further optimization. Several possible manipulations to the LbL assembly have also been suggested which could help improve the

performance of the modified membranes. This work, for the first time, demonstrated an attempt to evaluate the performance of c-PEM nanocomposite membranes against a real wastewater effluent.

4.1. Introduction

Water shortage is one of the most crucial problems that mankind is facing in this 21st century. The worldwide depletion in fresh water resources has created the need to purify other sources of water (like sea water) which are present in huge abundance. While desalination has grown to be a big area, the recycling and reuse of wastewater has also gained considerable attention. Various membrane based processes like ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) have been proposed and used for treating the many different types of water sources [1-3]. While membrane technology has witnessed tremendous development over the last few decades, its application in many cases is still challenged by the issue of membrane fouling. It accounts for a significant flux decline over a period of time that leads to higher pressure requirements as well as higher costs involved in membrane cleaning, replacement etc. Several research efforts have been directed towards mitigating membrane fouling like introducing changes in the process[4], bulk modification[5] and surface modification[6, 7] but so far, there is no one perfect solution to combat the issue of membrane fouling. Our current work is focused on layer-by-layer (LbL) assembly technique, which is one of the very cheap and economical methods of membrane surface modification. It is a thin film deposition technique involving the layering of polyelectrolytes or colloidal particles/nanomaterials which can be deposited via secondary molecular interactions like ionic attraction, hydrogen bonding, hydrophobic-hydrophobic interaction etc.[8]. It is of general consensus that changing the physicochemical properties of the membrane surface like increasing the hydrophilicity and surface charge help in reducing the fouling propensity of that membrane[9]. Polyelectrolyte multilayer (PEM) membranes which are fabricated by the LbL assembly of

polyelectrolytes on commercial membrane surfaces therefore can very well satisfy the criteria for being an effective modification process. Besides, LbL is a highly tunable thin film deposition process wherein a number of parameters can be manipulated in order to satisfy the application requirements[10].

PEM membranes have been widely applied as high flux alternatives to commercial salt rejection membranes and have shown their potential in removing many different types of ions [11-15]. However, most of these studies were confined to some simple ion-rejection tests. Very recently we published our work on extending the application of PEM membranes to electrocoagulation-treated high-strength wastewater effluent[16]. This work showed that PEM membranes are capable of reducing the COD value of the effluent to the same level as commercial RO membranes but with much higher flux values. These membranes also exhibited superior anti-fouling properties than commercial membranes, when tested under dead end conditions. In this work, we focus on evaluating the anti-fouling property of these membranes with a similar effluent under cross flow conditions.

In addition to the PEM membranes, we also studied the effect of introducing nanomaterials within the LbL films. The application of various nanomaterials like graphene[17, 18], carbon nanotubes[19, 20] and clay[21-24] to fabricate or modify membranes has been a widely researched topic. Among these, clay is easily dispersible in water and therefore can be incorporated within the LbL assembly without any additional functionalization. It is cheap, very easily available and imparts hydrophilicity to the surface. It therefore suits the requirement of a typical surface modifier which can be used for developing large scale anti-fouling membranes. The use of clay within PEM films has been studied in great details by Grunlan et al., to fabricate gas barrier films [25-27]. The introduction of clay increased the tortuosity of the gas under consideration[28, 29]. The application

of the clay-PEM hybrid films to water treatment membranes, has been comparatively rare. A couple of studies reported depositing such films on UF membrane surfaces to develop ion-rejecting membranes. Jungkyu et al., used these hybrid films for salt rejection and the incorporation of clay nanoplatelets rendered the membrane more chlorine resistant[21]. Very recently, Kovacs et al. also worked on the spray assembly of clay-polyelectrolyte quadlayers on PES membranes for fabricating desalination membranes with higher flux than commercial RO membranes, albeit with similar salt rejection[22, 23, 28]. In fact, their work encompassed the tuning of several factors to optimize the hybrid film structure as selective layers for ion rejection and provides an excellent methodology to identify the best suited system. However, the films developed by them were only tested with a certain ion and under dead end conditions which represent markedly different conditions than testing a real effluent under tangential flow conditions. So far, these clay-PEM modified membranes have not been used with any wastewater effluent and thereby not evaluated based on their anti-fouling property. However, Hang et al., developed a composite clay-PES membrane whereby they attained higher fouling resistance with the addition of clay[24]. With this background, we believed it would be interesting to co-deposit clay nanoplatelets with polyelectrolytes using LbL and evaluate the performance of the modified membranes against the EC effluent.

In this paper, the effluent from an Anaerobic Digestion (AD) reactor was fed to a 40 L electrocoagulation (EC) unit. The EC step served as a pretreatment step for the membrane separation process. Based on our knowledge about the nature of this effluent, as reported in our previous publication, it contains humic compounds which are responsible for the organic fouling. To counter the fouling propensity of commercially available membranes, a polyethersulfone membrane was chosen as the substrate for the deposition of PEM films and clay-PEM

nanocomposite films. For convenience, the PEM coated membranes will be henceforth referred to as PEM membranes and the clay-PEM hybrid film coated membranes will be simply referred to as c-PEM membranes. Poly allylamine hydrochloride (PAH) and poly acrylic acid (PAA) were chosen as the polyelectrolytes and montmorillonite (MMT) clay nanoplatelets were used to further modify the PEM membranes.

4.2. Experimental section

4.2.1 Materials

Poly (allylamine hydrochloride) (MW 900,000) and poly (acrylic acid sodium salt) (MW 15,000, 35 wt% in water) were procured from Sigma Aldrich. Sodium-Montmorillonite (MMT) clay (Cloisite-Na$^+$) was obtained from BYK Adhesives and Instruments. 2-(N-Morpholino) ethanesulfonic acid (MES) Buffer was also purchased from Sigma Aldrich. N-(3-Dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC) was purchased from Fisher Scientific. The commercial membranes NF 270 and BW 30 were purchased from Dow Filmtec (Midland, MI). The polyethersulfone membranes (MWCO 10,000 UE-10, Tri Sep) were provided by Sterlitech. All aqueous solutions were prepared using deionized (DI) water (>18.2 MΩ) supplied by a Barnstead Nanopure Diamond-UV purification unit equipped with a UV source and a final 0.2 μm filter. Unless specified otherwise all procedures were carried out at room temperature.

4.2.2 CF 042 Cross Flow system

A CF 042 cross flow unit (Sterlitech, Kent, WA) with an effective surface area of 42 cm^2 was employed as the membrane module. This type of cross flow cell has a rectangular geometry, the flow channel being 3.62" in length, 1.8" in width and 0.09" in depth. A positive displacement pump (Hydra-cell M03, Wanner Engineering, Minneapolis, MN) was used to deliver the feed from

a conical 5-gallon feed tank. A variable speed drive (Emerson, St Louis, MO) was attached to the pump which controlled its speed. A part of the feed stream was directed back to the feed tank via a bypass valve. A back-pressure regulator was used to control the transmembrane pressure across the membrane module. The retentate stream was recycled back to the feed tank and its flow rate was measured by a Site Read Panel Mount Flowmeter (Blue-White, Huntington Beach, CA). The permeate stream was also recycled back to the fed tank. The temperature of the solution inside the feed tank was maintained at room temperature by a digital chiller (Polysciences, Warrington, PA). All the components of the cross-flow setup were obtained from Sterlitech (Kent, Washington) and assembled in our lab. A detailed diagram of the setup can be found in our previous publication[15], the only exception in this case being the recycling of the permeate stream back to the feed tank.

4.2.3. Effluent characterization

The COD measurements are done following the standard procedure using COD kits purchased from HACH (Loveland, CO). All the three types of kits (ultra-low range, low range and high range) were employed based on the COD level of the sample. A HACH reactor was used to digest the samples and the values were read using a direct reading spectrophotometer.

4.2.4 Experimental protocols

4.2.4.1 Preparation of clay dispersion

MMT-Na$^+$ clay was added to DI water at a concentration of 1mg/ml. In order to properly exfoliate the clay nanoplatelets, the dispersion was stirred for about an hour and then sonicated. A 500 W Tip Sonicator (QSonica, Newtown, CT) with a standard 1″ horn along an additional booster, was used to sonicate the clay dispersion at 70% amplitude for 30 minutes. It was then left to being stirred overnight. Prior to using it in the LbL assembly, the MMT solution was sonicated once more for about 10 minutes under the same sonication conditions as mentioned above.

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4.2.4.2 LbL assembly technique

Prior to LbL deposition, the membrane substrates were soaked in DI water overnight. The permeate sides of the membranes were covered with four alternate sheets of parafilm and aluminum foil prior to the LbL process. The required portion of the membrane was then cut out and used for the filtration experiments. This way, we were able to prevent the deposition of polyelectrolytes on both sides of the membrane to a large extent. The LbL was carried out using Carl Zeiss Slide Stainer which employs a robotic arm to move the sample to different solution baths.

The pH of the PAH solution was adjusted to 8.5 while the pH of PAA was adjusted to 3.5. The MMT solution was used without any pH adjustment. Two types of coated membrane systems were considered for our experiments: 1. Polyelectrolyte-based membranes 2. Polyelectrolyte-clay hybrid membranes. For just the simple polyelectrolyte-based membranes, the usual bilayer type of assembly was used. While, for the c-PEM membranes, the polyelectrolyte and clay layers were deposited in the form of quad layer assembly.

Bilayer assembly: $[PAH/PAA]_m$; m = number of bilayers

Quadlayer assembly: $[PAH/PAA/PAH/MMT]_n$; n = number of quadlayers

The dipping time in each polyelectrolyte solution was 10 minutes followed by three consecutive DI water rinsing steps (2 minutes, 2 minutes and 1 minute). The dipping time in MMT solution was 20 minutes and it was followed by three rinsing steps. For the c-PEM membranes, the sample was sonicated in an ultrasonic bath sonicator after each quad layer. For the PEM samples, the sonication was done after every bilayer.

4.2.4.3 Chemical Cross-linking using EDC

The EDC solution was prepared in a 50 mM MES Buffer solution at a concentration of 50 mg/ml and pH of 5.5. Following the deposition of PAH/PAA multilayers on the membrane surface using the aforementioned LbL protocol, the modified membrane was dipped in the EDC solution using the slide stainer for 60 minutes with continuous agitation. The samples were then subject to three consecutive DI water rinsing steps, each of them being of 15 minutes duration, and then followed by 5 minutes of sonication.

4.2.4.4 Cross flow filtration protocol

All membranes to be tested were soaked in DI water overnight. They were then compacted in the cross flow system for atleast 12 hours by just passing DI water across the membranes. Following the compaction step, the membranes were tested against the EC effluent for 48 hours. The flow rate measurements were done at time t=0,0.5,1,2,3,5,8,12,24,30,36 and 48 hours for all membranes. For each type of membrane, atleast two replicates were tested. After every experiment, the setup was cleaned thoroughly with DI water for atleast three times. For each experiment, the feed samples and the permeate samples were analyzed for their COD level and the rejection was calculated based on these values.

4.2.4.5 Measurement of film thickness

The thickness of the different types of films was measured by Dektak Surface Profiler. For measurement purposes, the films were deposited on glass slides. Prior to LbL deposition, the bare glass slides were treated with O_2 plasma for 20 minutes using a Harrick plasma cleaner (Harrick Scientific Corporation, Broading Ossining, NY) at 30 W RF power under 100 millitorr vacuum pressure. Measurements were taken in atleast three different spots in each glass slide and for each type of film, atleast two replicates were tested.

4.3. Results and Discussion

4.3.1 Performance of commercial membranes

Three commercial membranes were first tested for their performance in terms of solution flux and COD removal- a) a polyethersulfone (PES) UF membrane, b) a NF membrane and c) a RO membrane. The PES membrane, with a MWCO of 10,000 had the highest flow rate, as would be expected. Its flux profile was that of a typical UF membrane wherein there was a drastic drop in the value in the initial few hours, followed by progressively lower flux declines for the rest of the time period. These membranes usually have slightly hydrophobic surfaces which is a major reason for their high fouling propensities[7, 30]. The NF 270 membrane is a polypiperazinamide-based semi-aromatic nanofiltration membrane primarily meant for removing small sugar molecules, divalent/multivalent ions etc. The BW 30 RO membrane is a polyamide thin-film composite membrane primarily aimed at removing salts from brackish water [15, 31, 32]. The flux trend of these membranes was in accordance with their MWCOs. The flux profiles of the commercial membranes are shown in Figure 4.1a. For the PES membranes, the COD reduction varied over a range of 5-50% because of the broad pore size distribution of such membranes. For the NF 270 and BW 30 membranes, the COD value of the permeate streams dropped below the detection limit of the COD Spectrophotometer, therefore indicating very low values. All three membranes, under consideration showed quite high fouling propensity. The PES membrane, being the least hydrophilic one suffered the maximum fouling, followed by NF 270 and BW 30. The fouling propensity was quantitatively estimated as the ratio of the flux at that particular time (J_s) to the initial flux (J_0). This profile can be seen in Figure 4.1b.
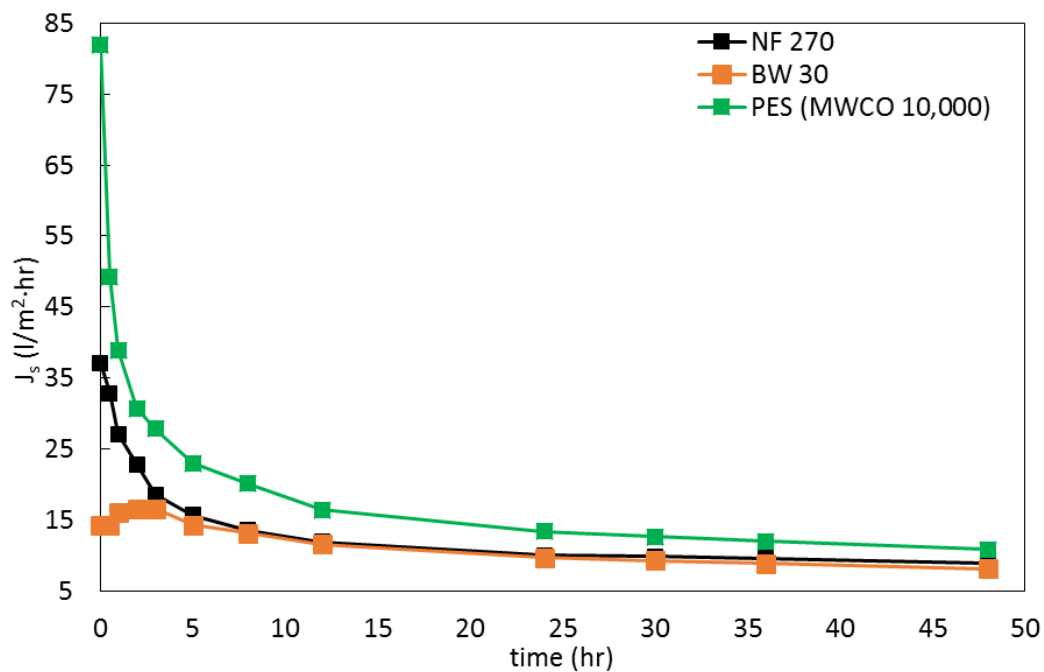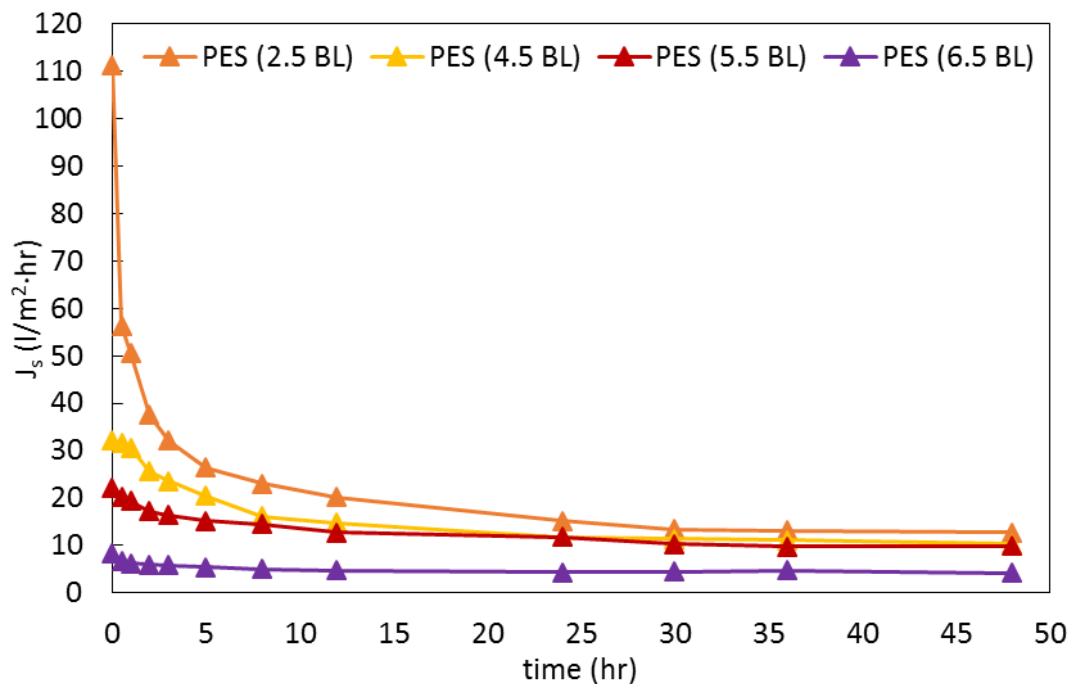
(a)
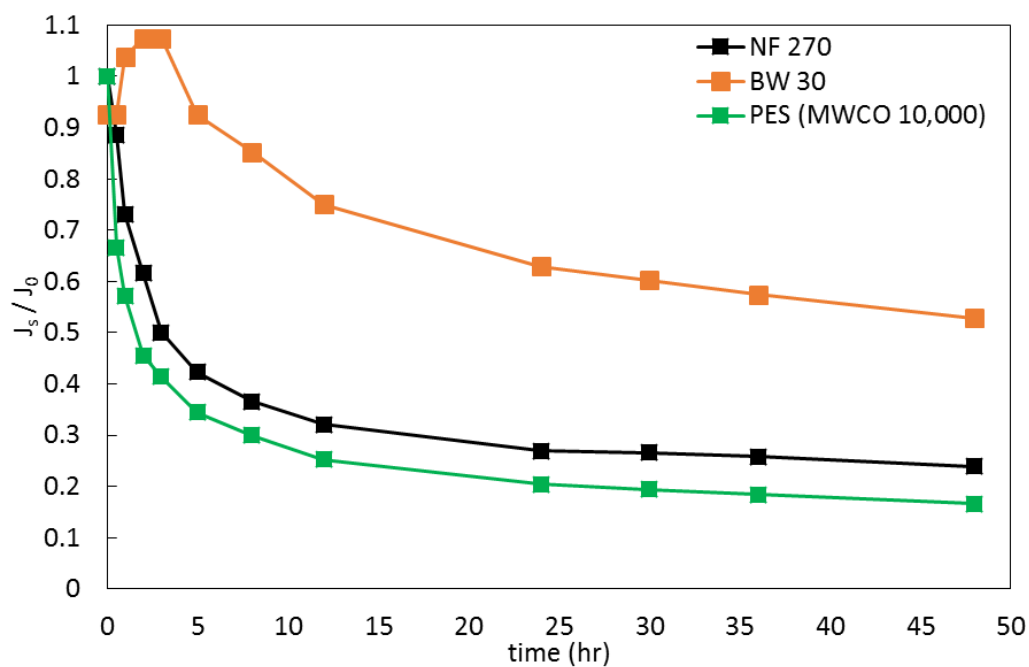
(b)

Figure 4.1. Performance of the three commercial membranes as a function of time in terms of (a)the solution flux and (b) the fouling propensity expressed as the ratio of solution flux at that particular time to the initial flux of the membrane.

The PES membrane was chosen as the substrate for further modification because of its high initial flux. Modifying the surfaces of NF 270 or BW 30 would lead to membranes with extremely low fluxes. In the following sections of this paper, the performance of the PES membrane, modified with PEM films and clay-PEM hybrid films have been discussed in great details.

4.3.2 Performance of polyelectrolyte-based membranes

Surface modification of commercial membranes using the LbL assembly of polyelectrolytes has been widely reported in literature. While most of these studies have focused on the aspects of ion rejection and ion selectivity, only a couple of studies were done on real wastewater effluents[33, 34]. In our previous publication, we showed the possibility of using PEM membranes in conjunction with electrocoagulation for the first time, to reduce the COD level of a high-strength effluent. These results were obtained using a dead-end filtration setup whereby these membranes also showed better anti-fouling properties than the commercial membranes[16]. In this study, we focused more on the anti-fouling property of such membranes under cross flow conditions. Based on the results from our previous publication, the PAH (pH 8.5) /PAA (pH 3.5) system with PAH as the outermost layer, was chosen. We tested this system with different number of bilayers (2.5, 4.5, 5.5, and 6.5). With increasing number of bilayers, we assumed, there was increased surface coverage. Given that the underlying PES substrate was highly porous, a uniform coverage necessitated a certain minimum number of bilayers. The results, as evident from Figure 4.2, are in agreement with our hypothesis. With the deposition of just 2.5 bilayers, the flux of the modified membrane remained practically unchanged from that of the underlying bare membrane. The change was more obvious from 4.5 bilayers onwards. The flux data of these membranes modified with different number of bilayers are shown in Figure 4.2a. The anti-fouling property of the modified membranes improved with increasing the number of bilayers. However, even after 6.5

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bilayers the membranes still showed significant fouling propensity as can be seen in Figure 4.2b. Besides, with the deposition of 6.5 bilayers, the flux of the modified membrane had already dropped to very low values (10% of that of bare PES membrane). Without continuing to deposit additional bilayers, we resorted to modify the PEM membranes by incorporating clay nanoplatelets within the layers.

(a)

Figure 4.2. Performance of PEM membranes as a function of time in terms of (a) the solution flux and (b) the fouling propensity expressed as the ratio of solution flux at that particular time to the initial flux of the membrane.

Figure 4.2 (cont'd)
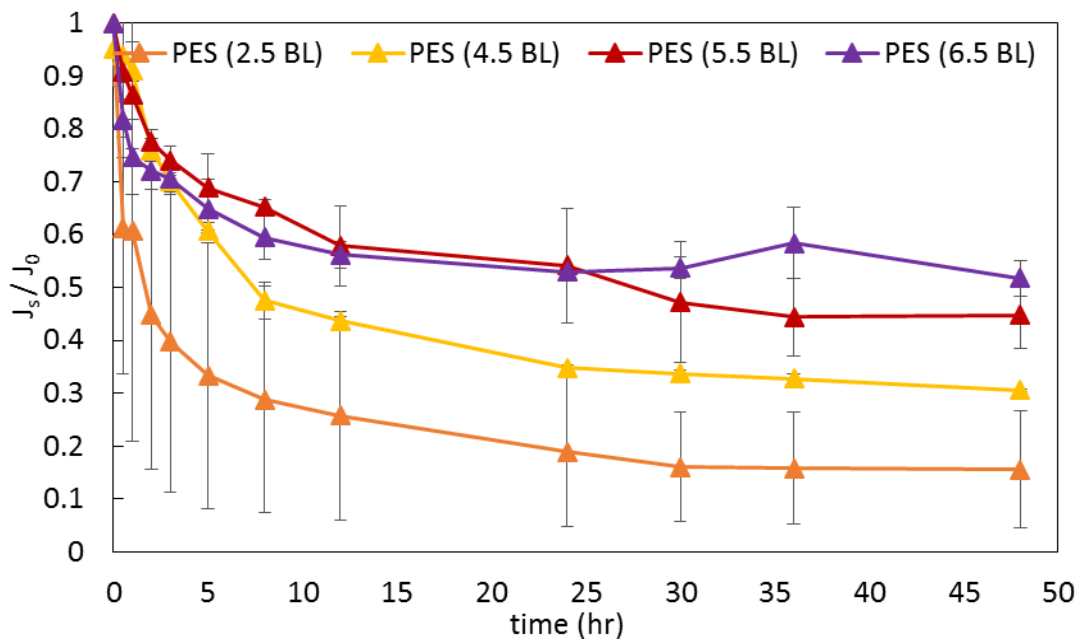
(b)

4.3.3 Performance of nanocomposite membranes

The c-PEM hybrid films were formed by incorporating MMT clay nanoplatelets within the PEMs in a quadlayer fashion, as described in the experimental section. Among the three types of clay (Laponite, Montmorillonite and Vermiculite) commonly used in literature[35], Montmorillonite (MMT) was chosen for our experiments as we speculated that, with its intermediate platelet size, it would provide the optimum balance between high flux and high removal. In the quadlayer assembly, the consecutive clay layers are separated from each other by three alternately charged polyelectrolyte layers. According to previous research findings, the distance between the clay layers plays a very important role in the performance of such films[36]. Several configurations have been reported in literature like the usual bilayer configuration[23, 28, 37] , tri-layer[38], quad-layer (sometimes also referred to as tetra-layer) , hexa-layer and even octa-layer configurations[35]. Based on the results reported by Kovacs et al., the quadlayer assembly was

chosen as it provides optimum inter-clay layer spacing and clay content[28]. PAH and PAA were used in the same pH conditions as in the case of pure PEM films and they were terminated with PAH as the outermost layer. As evident from the flux profile in Figure 4.3a, with the deposition of each quadlayer, the flux decreased considerably. However, the fouling propensity of the quadlayer-coated membranes is significantly better than the bare membrane or even the PEM membranes. This can be seen in Figure 4.3b. With the deposition of 1.25 quadlayer (the 0.25 signifies the outermost PAH layer) the fouling propensity of the membrane shows a marked improvement. Moving from 1.25 to 2.25 quadlayers, the anti-fouling property shows the most significant improvement and with another additional quadlayer, it attains perfection. However, with each quadlayer deposition there was a significant drop in the flux and with just 3.25 quadlayers, the flux of the PES membrane dropped to 2.14 $l/m^2 \cdot hr$ from 81.97 $l/m^2 \cdot hr$.

(a)

Figure 4.3. Performance of nanocomposite membranes as a function of time in terms of (a) the solution flux and (b) the fouling propensity expressed as the ratio of solution flux at that particular time to the initial flux of the membranes.
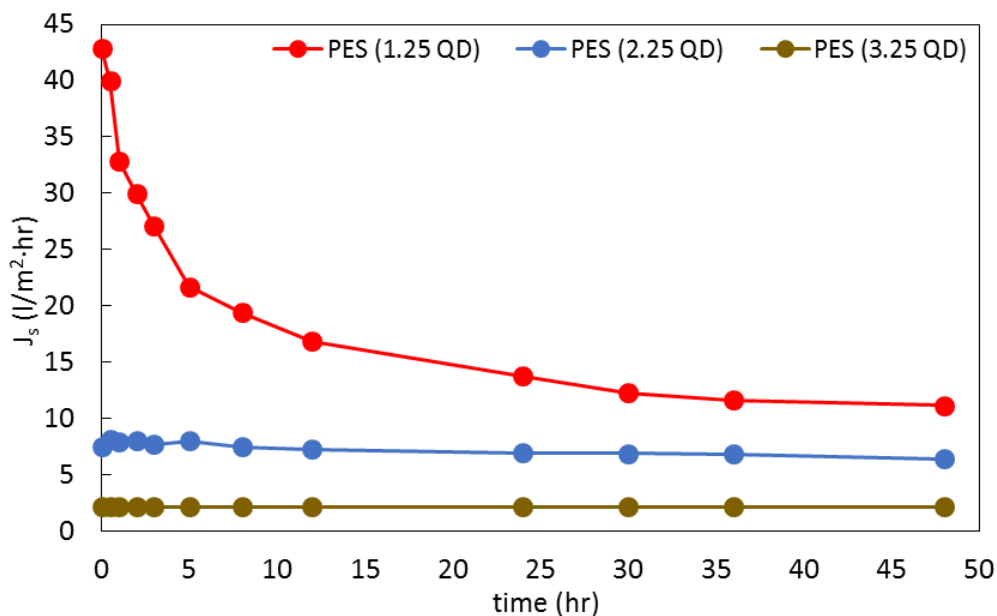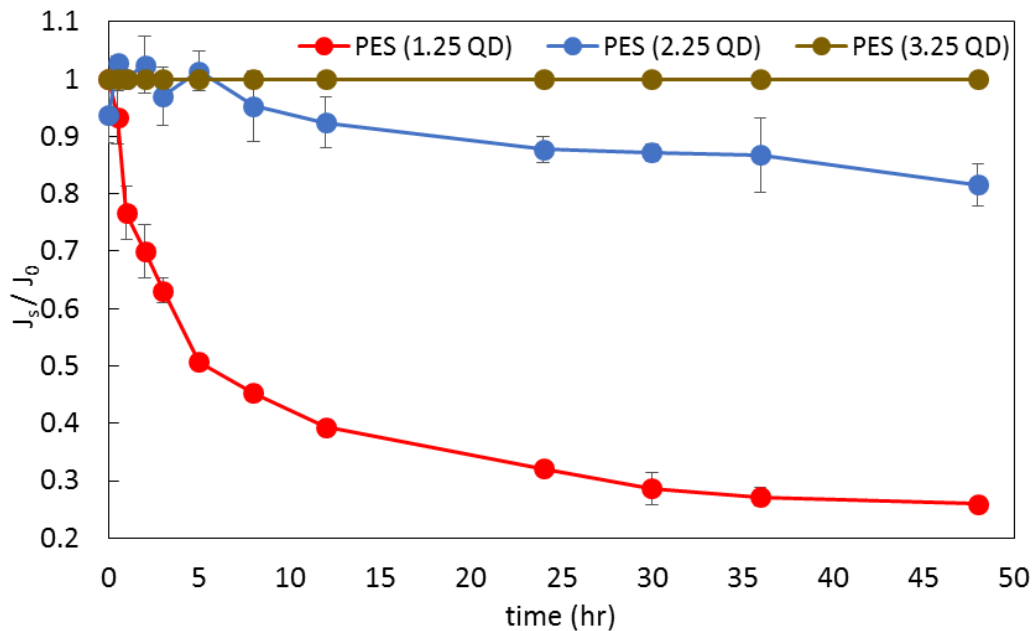
98

Figure 4.3 (cont'd)

(b)

4.3.4 Overall picture

In this section we compare the results from all the different membranes- the three commercial membranes, the PEM membranes and the c-PEM hybrid membranes, as can be seen in Figure 4.4. The modification of the bare PES membrane invariably brings about a decrease in its initial flux, irrespective of whether it was modified by PEMs or hybrid films as can be seen in Figure 4.4a. In terms of anti-fouling property, the nanocomposite membranes clearly show the best performance as evidenced in Figure 4.4b. All the c-PEM hybrid membranes, when compared against the corresponding PEM membranes with the same number of layers, show lower fouling propensity, albeit at the cost of lower initial flux. However, it must be noted here that the initial flux of the 6.5-bilayer (13 layers) coated PEM membrane had the same initial flux as 2.25 quadlayer (9 layers)-coated hybrid membrane but the fouling resistance of the latter membrane was higher than the former. This indicates that if we were to attain the same degree of fouling resistance as 3.25

quadlayers (13 layers), we would need way more than 6.5 bilayers of PEMs (exact number not determined). That would lead to an even lower initial flux value than what is currently offered by the 3.25 quadlayer system. Therefore inclusion of clay nanoplatelets definitely provides an edge over the PEM systems in terms of flux and number of layers required. The 2.25 quadlayer system has very similar initial flux value as the commercial RO membrane (BW 30) but its anti-fouling property is much better than the latter. Although the 3.25 quadlayer system showed excellent fouling resistance, it retained only 2.6% of the initial flux of the bare membrane which therefore doesn't make it suitable for practical purposes.
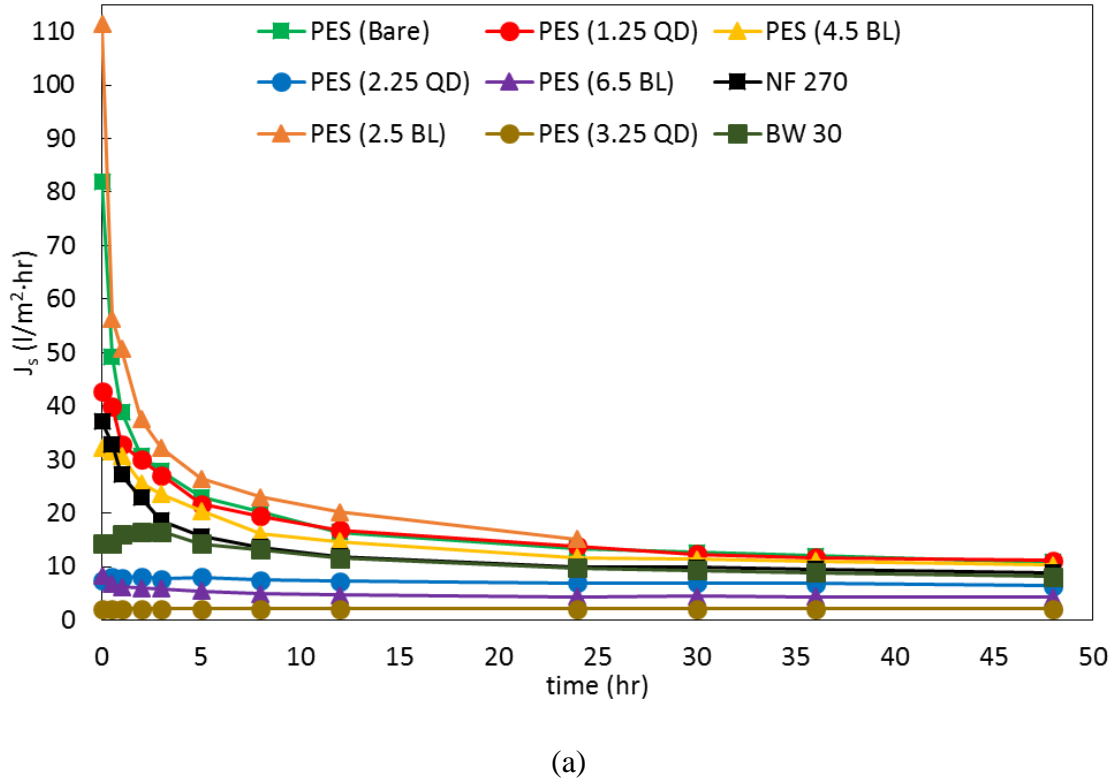

(a)

Figure 4.4. Comparison in the performance of commercial membranes, PEM membranes and nanocomposite membranes as a function of time in terms of (a)the solution flux and (b) the fouling propensity expressed as the ratio of solution flux at that particular time to the initial flux of the membranes.

Figure 4.4 (cont'd)
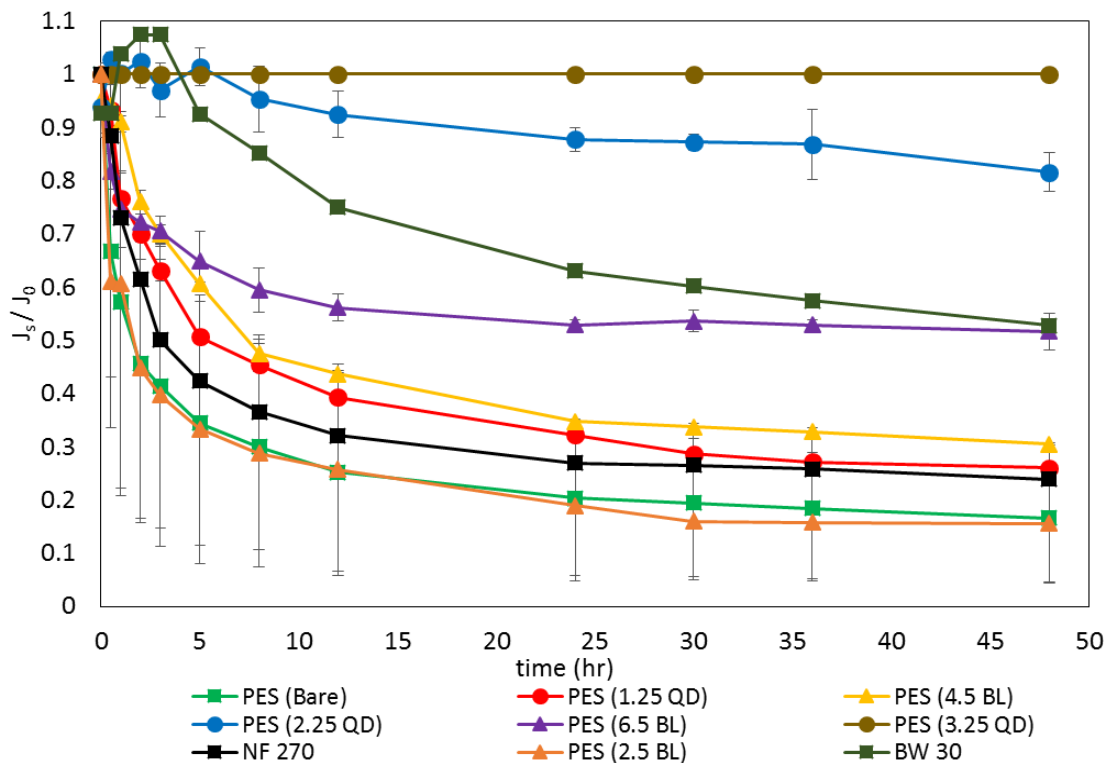
(b)

The thickness data of the PEM membrane system as well as the quadlayer-coated membranes are shown in Table 4.1. The trend of increase in thickness with the increase in bilayers/quadlayers deposited on the surface is quite expected and the flux profile can also be related quite well with the thickness date. However, the 6.5 bilayer system had a higher thickness value than the 2.25 and 3.25 quadlayer systems, but, as noted before, its flux was similar to that of the 2.25 quadlayer system and higher than the 3.25 quadlayer system. We believe, this might be due to suppression of the polymer interdiffusion by the clay nanoplatelets that leads to lower thickness values than the 6.5 bilayer PEM system. Then again, these nanoplatelets introduce a high degree of tortuosity which explains the low solution flux across these membranes.

Table 4.1. The thickness values of the PEM films and the clay-PEM composite films

| Type of coating	Thickness (nm)
[PAH(pH 8.5)/PAA(pH 3.5)]$_{2.5}$	46.67± 6.50
[PAH(pH 8.5)/PAA(pH 3.5)]$_{4.5}$	86.00 ± 14.14
[PAH(pH 8.5)/PAA(pH 3.5)]$_{6.5}$	182.67 ± 2.52
[PAH(pH 8.5)/PAA(pH 3.5)/PAH(pH 8.5)/MMT]$_{1.25}$	73.37 ± 6.18
[PAH(pH 8.5)/PAA(pH 3.5)/PAH(pH 8.5)/MMT]$_{2.25}$	108.47 ± 7.43
[PAH(pH 8.5)/PAA(pH 3.5)/PAH(pH 8.5)/MMT]$_{3.25}$	131.50 ± 4.95

4.3.5 Effect of EDC cross-linking

The PEM membranes and the c-PEM hybrid membranes showed a considerable reduction in the flux due to blocking of the pores of the underlying membrane. The COD reduction was however, not significantly improved as compared to the bare membrane. This necessitated the polyelectrolytes to be crosslinked in order to limit the passage of some very fine, dissolved contaminants. Chemical crosslinking with EDC was preferred over thermal treatment due to the very apparent deformation of the underling substrate under high temperature. The effect of crosslinking was studied for PEM membranes as well as c-PEM hybrid membranes. For the PEM membranes, a 5.5 BL system was chosen as it had almost similar anti-fouling property as the 6.5 BL system with a slightly higher initial flux. For the hybrid systems, 2.25 QD was chosen as the most optimum system as its flux was much higher than the 3.25 QD system and its fouling resistance was very good. As expected, there was a drop in the flux in both the cases as can be

seen from Figure 4.5. The drop in flux was more significant in case of the PEM membranes (~ 50%) compared to the PEM-clay hybrid membranes (~37%). This can be explained by the fact that the presence of clay nanoplatelets limits the interdiffusion of the polyelectrolytes to some extent and therefore limits the amine groups of PAH and acid groups of PAA from reacting with each other to the same extent as in the case of just PEM membranes. It was also interesting to note that for both the systems the flux decline was reduced due to crosslinking, a phenomenon which has not been studied till date. In fact, the anti-fouling property of the crosslinked 2.25 quadlayer membrane was at the same level as the uncrosslinked 3.25 quadlayer system but with higher initial flux. This, therefore opens up a new optimization strategy to improve the anti-fouling property of polyelectrolyte-based membranes.
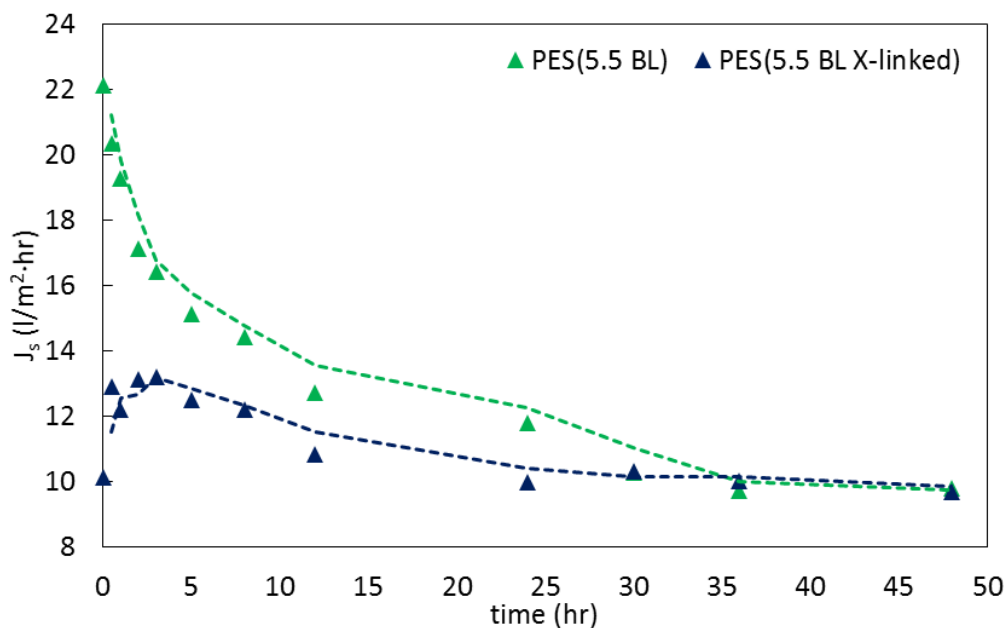
(a)

Figure 4.5. Effect of cross-linking on the solution flux of a) 5.5 bilayer PEM membrane and b) 2.25 quadlayer PEM-clay hybrid membranes.

Figure 4.5 (cont'd)
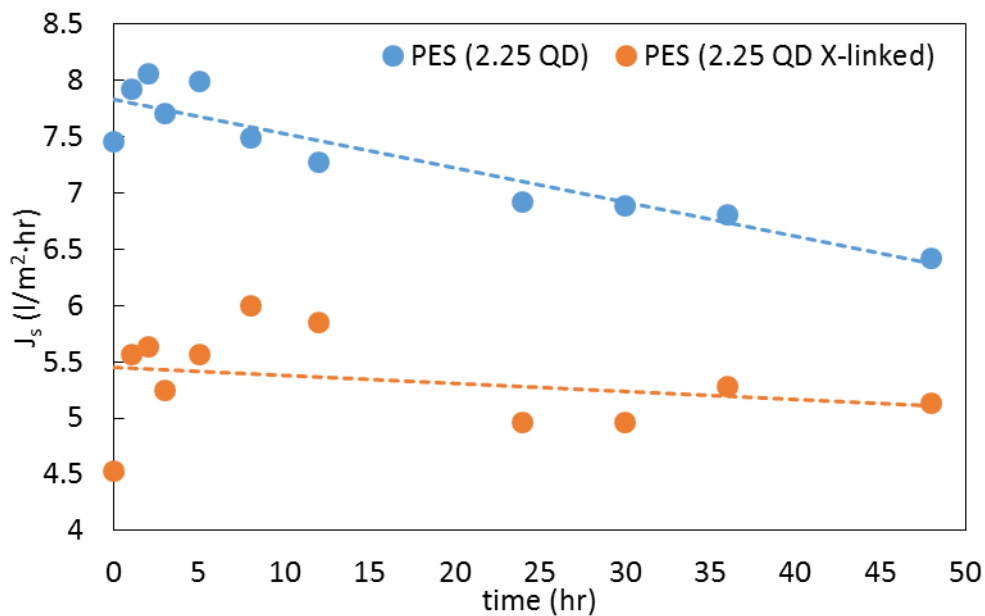
(b)

The most important reason to crosslink the multilayers was to improve the COD reduction

of the modified membrane. However, on crosslinking the 5.5 bilayer modified membrane, there

was no significant change in rejection compared to its uncrosslinked counterpart. On the other

hand, the PES membrane modified with 2.25 quadlayers of PEM-clay films showed a significant

improvement, as is evident in Figure 4.6. This fact therefore provides another justification to the

use of c-PEM membranes over PEM membranes. The clay nanoplatelets provided an additional

barrier to the passage of unwanted contaminants, as has been observed in the case of ion rejection

and gas barrier films. However, the reduction declined especially after 24 hours. This can be

attributed to the effect of concentration polarization. This issue can be solved pretty easily as the

concentration polarization effect can be minimized by increasing the crossflow rate and other

hydrodynamic conditions[39]. Also, if the experiment was done following a different protocol

which would involve collecting the permeate instead of recycling it back to the feed tank, the

decrease in rejection towards the end of the experiment could be compensated by the high rejection during the initial few hours. The same decreasing trend over time as not observed for the other membranes as the initial rejection itself was low for these systems. This meant there was lesser solute buildup and lower concentration polarization effect. This, however gave us a fair indication that it is possible to get high COD removal by crosslinking the 2.25 quadlayer system.
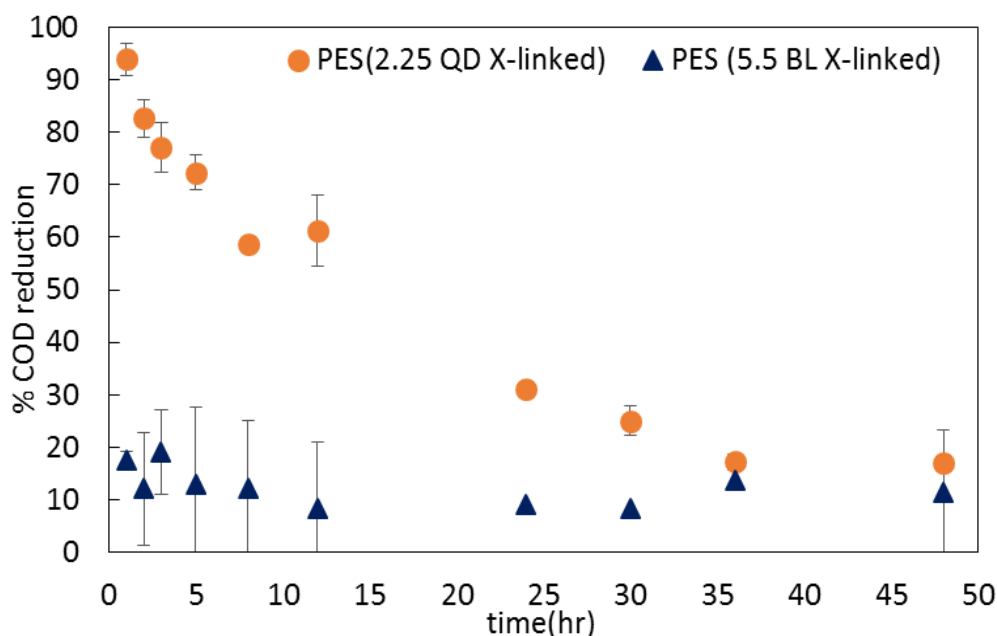
Figure 4.6. Comparison in the COD reduction of the cross-linked 5.5 bilayer PEM membrane and crosslinked 2.25 quadlayer PEM-clay hybrid membrane.

4.4 Conclusion

For the first time, c-PEM hybrid, nanostructured films were used to modify membranes for treating a real effluent. In comparison to PEM membranes, these membranes required lesser number of layers to acquire high fouling resistance and thereby provide an edge in terms of the initial flux. The membrane modified with 2.25 quadlayers was the most optimum system among the three c-PEM hybrid systems that were tried out. On crosslinking this system, the fouling resistance was further enhanced with a slight decrease in the initial flux. The COD reduction was also higher than

that of the underlying membrane and the crosslinked PEM membranes. The initial flux was severely compromised because of the deposition of the clay-PEM quadlayers. However, this was simply a proof-of-concept study and several manipulations to this type of assembly are possible. Previously the Grunlan research group and Hammond research group have performed some very detailed analysis to identify the factors which affect the performance of the hybrid membranes. However, since none of these films have been used for designing anti-fouling membranes and tested under tangential flow conditions, the steps for optimizing the performance should be performed all over again. A major factor which influences the filtration performance is the amount of clay incorporated, which can be varied by tweaking the parameters listed below. These parameters have already been discussed in previous literature and we have simply consolidated the ones which we believe would be essential to study in order to develop high flux and highly fouling resistant membranes.

1. **pH conditions of the polyelectrolytes**: The weak polyelectrolytes like PAH and PAA have pH-dependent ionization properties. Therefore the amount of clay incorporated within them can be varied, because at different pH conditions[22], the charge density of the polyelectrolytes and the number of functional groups available are very different.

2. **clay-PEM assembly configurations**: In our experiments, we followed the quadlayer assembly based on previous literature. However, some other configurations like bilayer assembly, trilayer assembly or hexa/octa-layer assembly might prove to be more beneficial for anti-fouling applications[35, 36]. By changing the clay-PEM configuration, the spacing between consecutive clay layers as well as the amount of clay within the composite film can be tuned.

3. **Type of polyelectrolytes:** There are a number of commercially available polyelectrolytes which can be used for LbL and therefore adds to the parameters that one can look into in order to improve

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the results. Among the weak polyelectrolytes, branched polyethylenimine (BPEI) /PAA also represent a pH-tunable system like PAH/PAA and has in fact shown high oxygen barrier properties[35]. It therefore seems to be the next obvious choice of polyelectrolyte combination for future experiments.

4. Type of clay: All our experiments were done with MMT clay. However, other types of clay like laponite (LAP) and vermiculite (VMT) can be tried out as has been done by other researchers for gas-barrier[35] and ion rejection[28]. Different clay types have varied properties like platelet dimensions, inter-platelet distance, zeta potential etc. and it is therefore needless to mention that the amount of clay incorporated within the PEM films will also be significantly different.

In conclusion, it can be said that clay-PEM hybrid films represent a class of films with good anti-fouling properties when tested against an EC effluent of real wastewater. Further optimizations with respect to the assembly conditions are required in order to achieve higher initial flux.

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5. THESIS SUMMARY AND FUTURE WORK

This thesis focused on two major applications of polyelectrolyte multilayer (PEM) membranes - ion rejection and wastewater effluent treatment. The primary aim of this work was to design these membranes with optimum flux as well as rejection with a broad purpose of developing an energy efficient membrane-based separation process. In the first part of our thesis, we worked on removing perchlorate ion which is waterborne contaminant and now a major cause of concern for several states across United States. In previously reported studies, PEM membranes have shown high removal of monovalent ions but in most cases the flux values of such membranes were even lower than commercial RO membranes [1-4]. Therefore the Chapter 2 of this thesis was dedicated to optimizing the membrane performance by choosing a commercial NF membrane (NF 90) as substrate and tuning some of the typical parameters of LbL process. Through this work, it was demonstrated that choosing the right conditions can enable us to fabricate a PEM membrane with almost 6 times the flux as a commercial sea water RO membrane with equivalent perchlorate rejection. This was one of the best trade-offs between high flux and high removal reported for PEM membranes targeted at removing perchlorate ion.

In the following chapter, i.e. Chapter 3 the PEM membranes were applied for treating an electrocoagulation-treated high strength effluent. It should be noted here that even though it has been more than a decade since these PEM membranes have been used for removing ions, there have been only a couple of instances in which their performances were evaluated against a real effluent system. Therefore we felt it was essential to test these membranes with a more realistic effluent in order for these membranes to be commercialized in future. We tested two very commonly used polyelectrolyte combinations and compared the performance of these membranes with commercial NF/RO membranes. These membranes demonstrated the same level of COD

reduction and higher flux as RO membranes. Not only that, these membranes showed higher fouling resistance than all the commercial membranes that were used for comparison. This is a major step forward for PEM membranes as it presents a low-cost energy efficient method of purifying water.

In Chapter 4, we tested the PEM membranes under tangential flow conditions instead of the dead end flow conditions used in Chapter 3. While it was already established that PEM membranes provide a high-flux alternative to commercial membranes, in this section we primarily focused on developing anti-fouling membranes. Membrane fouling is the most important concern in the field of water treatment membranes and till date, there has been no perfect solution to this problem. In this chapter we made an attempt to incorporate clay nanoplatelets within the PEM assembly in order to improve its fouling resistance. These hybrid membranes did show some advantage over PEM membranes in terms of flux and anti-fouling property, but the initial flux of these membranes was too low. This work, therefore needs further optimization in terms of the amount of clay contained within the PEM films. Once again, this was the first time clay-polyelectrolyte hybrid membranes were tested against a real wastewater effluent and their anti-fouling properties were explored.

In summary, our work showed the wide range of applications that PEM membranes can be used for. By manipulating the LbL process conditions, we can fabricate high-flux membranes with both high rejection as well as high fouling resistance. As LbL is such a versatile process and can involve any type of material which can be dissolved or even dispersed in water, it is possible to include a wide range of nanomaterials/nanoparticles which can add to the functionality of PEM membranes.

This area of membrane research holds significant promise in delivering an energy efficient separation medium to purify water. Beyond the limited scope of this thesis, there are several other opportunities that can be explored and based on our experience we hereby attempt to put down some recommendations for future research investigators. We believe, the issue which now requires the most attention is the ability to scale up the LbL process and make it more industry-friendly. So far, the LbL technique has been widely researched in lab-scale and demonstrated tremendous versatility in the field of thin-film deposition. It is indeed one of the best surface modification techniques for membrane applications as it offers precise control on the film properties which can be tailored as per the applications. But this process is time-consuming which makes it less lucrative in comparison to other thin film deposition processes. Recently, there have been a few attempts to shorten the conventional 10-15 minutes dipping time by our research group [5] as well as Grunlan research group at Texas A&M University [6]. This is a major step forward in the potential commercialization of these films. The effect of reduced dipping time has not been explored for membrane modification purposes yet but that is definitely an area that deserves the attention of membrane researchers. Spray LbL is another alternative to the dip-coating method as has been discussed in the Chapter 1 of this thesis. A careful literature survey reveals quite a few researches where spray coating was used, including some studies on membrane modification [7]. This technique is much faster than dip-coating as it takes only a few seconds to deposit each layer. It would definitely be worthwhile to try out our experiments with short time LbL or spray LbL [8]. It should also be noted here that most of the research works including ours have been focused on modifying flat sheet membranes. In most industrial applications, spiral wound or hollow fiber membranes are preferred. It is possible to LbL coat such membrane modules as well, as has been

demonstrated by Rong Wang and her research group [9, 10]. It is however, not as straightforward as coating flat sheets and needs more detailed investigation.

It is also worthwhile to mention here that the PEM membranes fabricated by LbL on commercial substrates need to be evaluated under more realistic conditions. A considerable portion of this thesis was dedicated to discussing the performance of these membranes with an EC effluent with respect to flux, COD removal and anti-fouling properties. However, more work remains to be done in this area. First of all, other than COD, there are several other parameters like Total N, Total P, BOD etc. and the performance of PEM membranes should be tested with respect to all of these parameters. Other than that, we had the scope of testing with only one type of wastewater. Different wastewater sources have very different compositions and most importantly widely different types of foulants. In terms of fouling, we were mainly concerned about organic fouling. Biofouling is a major area of concern and because in our work, the preceding EC step removed the majority of the "biofoulants", it was therefore not of any concern for us. However, this issue cannot be avoided for many other wastewater sources and therefore must be looked into.

In the last part of our thesis we focused on creating hybrid thin films by incorporating MMT clay nanoplatelets within PEM membranes. As we have mentioned in that discussion, there are several other manipulations possible for that system which can hopefully give us a more optimized result. Besides clay, some functional polymers like polydopamine [11, 12], PEG [13-15] etc. can be co-deposited with PEMs to create membranes with good anti-fouling properties. It has been found that a single layer of such polymers are instrumental in significantly reducing the fouling propensity of commercial membranes. However, these single layered coatings are too thin to prevent the passage of unwanted contaminants, which means they do not affect the rejection significantly. It is quite a feasible option to deposit an anti-fouling polymeric layer on PEM-coated

membranes by virtue of secondary molecular interactions using the same LbL protocol. This could open up the possibility of creating a surface modified membrane with all the desirable properties- high flux, high rejection as well as high fouling resistance. In conclusion, it can be said that a common approach taken by most surface modification techniques is to tackle one particular property at a time. However, when the membranes are used for an actual effluent, only a unified approach of tackling all the properties together can aid in their proper evaluation.

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