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Recent Progress in the Applications of Layer-By-Layer Assembly to the Preparation of Nanostructured Ion-Rejecting Water Purification Membranes

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Reverse osmosis (RO) and nanofiltration (NF) are the two dominant membrane separation processes responsible for ion rejection. While RO is highly efficient in removal of ions it needs a high operating pressure and offers very low selectivity between ions. Nanofiltration on the other hand has a comparatively low operating pressure and most commercial membranes offer selectivity in terms of ion rejection. However in many nanofiltration operations rejection of monovalent ions is not appreciable. Therefore a high flux high rejection membrane is needed that can be applied to water purification systems. One such alternative is the usage of polyelectrolyte multilayer membranes that are prepared by the deposition of alternately charged polyelectrolytes via layer-by-layer (LbL) assembly method. LbL is one of the most common self-assembly techniques and finds application in various areas. It has a number of tunable parameters like deposition conditions, number of bilayers deposited etc. which can be manipulated as per the type of application. This technique can be applied to make a nanothin membrane skin which gives high rejection and at the same time allow a high water flux across it. Several research groups have applied this highly versatile technique to prepare membranes that can be employed for water purification. Some of these membranes have shown better performance than the commercial nanofiltration and reverse osmosis membranes. These membranes have the potential to be applied to various different aspects of water treatment like water softening, desalination and recovery of certain ions. Besides the conventional method of LbL technique other alternative methods have also been suggested that can make the technique fast, more efficient and thereby make it more commercially acceptable.

Keywords: Membranes, Ion Rejection, Water Purification, Layer-By-Layer Assembly, Thin Films.

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1. INTRODUCTION

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

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consumption purposes is surprisingly low.[2] Less than one percent of fresh water is actually available for consumption purposes.[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 waterborne 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.

2. REVERSE OSMOSIS (RO)

Use of saline water to produce drinkable water by getting rid of the salt presents an alternative water source. In fact desalination is one of the most common technology to deliver clean drinkable water from salty sea water.[3] Among the desalination techniques pressure driven membrane processes are predominantly preferred over the conventional thermal processes like multi-effect distillation and vapor compression distillation.[5] Reverse osmosis (RO) is in fact the leading desalination technology as of now[3] contributing to almost 44% of the world's total desalination capacity.[5] Significant advances has been made in this membrane separation process which includes improved module design and pretreatment methods along with higher energy recovery.[3] Reverse osmosis has a capacity of 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. One of the first commercially applicable asymmetric membranes was prepared at UCLA by Loeb and Sourirajan in the early 1960s from cellulose acetate.[7] The cellulose acetate 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] The invention of the polyamide thin film composite (TFC) membranes was yet another breakthrough in the RO membrane development process. These membranes 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. In fact for a typical RO desalination plant the electricity (energy) requirement comprises the major share of the operating cost[3] while the energy recovery is only around 45%.[8]

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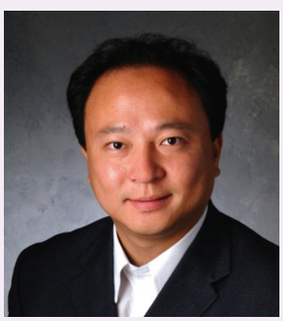

Ilsoon Lee joined the department of Chemical Engineering and Materials Science at Michigan State University in 2002. Previously, he studied at Seoul National University (Summa Cum Laude, South Korea), University of Delaware (USA), and MIT (USA) for his Bachelors' and Ph.D. degrees and also postdoctoral experience, respectively. His research interest includes molecular level control over self-assembled functional thin films and nanostructured materials and layer-by-layer assembly. His expertise also includes the nanofabrication and characterization of nanomechanical property of thin films, anisotropic functional nanoparticles, and high-surface and high-selectivity bioactive interfaces for sensors, biocatalytic reactors, and renewable energy.

3. 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. Membranes like NF 270 fall under the category of "loose" NF membranes[8] i.e., they have a pore-size distribution comparable to UF while the fully aromatic polyamide membranes like NF 90 are "tight" NF membranes and are closer to RO membranes. Most nanofiltration membranes offer selectivity of ions.[19] unlike RO membranes which indiscriminately reject all ions. It allows the passage of certain ions like Cl^- ions thereby reducing the osmotic pressure of the process[20] and hence the lower pressure requirement.

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4. POLYELECTROLYTE MULTILAYER (PEM) MEMBRANES

In recent years considerable amount of work has been going on in order to develop ion-rejecting 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 of the major applications of nanotechnology to membrane research is the use of the layer-by-layer (LbL) assembly technique in building functional membranes. Lbl was pioneered by Gero Decher[22,23] and ever then since it has been used in a variety of engineering applications.[24,25] This method involves the simple dipping of the substrate in alternate solutions of polycation and polyanion with deionized (DI) water rinsing steps in between in order to form nanothin films on the substrate. The deposition can be carried out manually by hand dipping method[13,15,17,20,26–28] or by using an automated slide stainer consisting of a robotic arm that moves the sample from one polyelectrolyte bath to another.[29–43] Figure 1 shows a schematic representation of the LbL process.

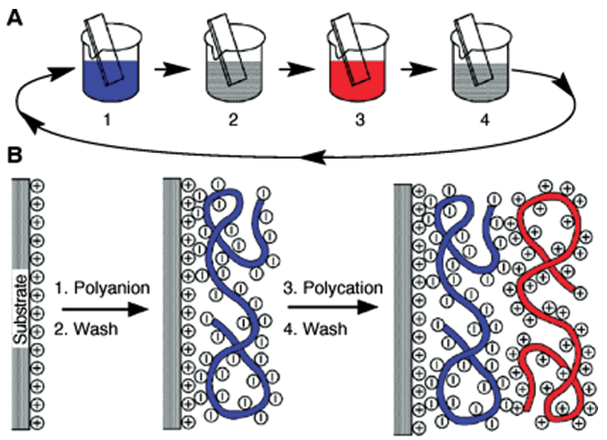

Figure 1. Schematic representation of layer-by-layer assembly. Reproduced with permission from [22], G. Decher, *Science* 277, 1232 (**1997**). © 1997, American Association for the Advancement of Science.

Depending on the type of polyelectrolytes and the adsorption conditions used the mode of multilayer deposition could be electrostatic,[22,44] hydrogen bonding[45,46] or covalent bonding.[47,48] LbL films have found applications in the varied fields of sensors,[49–51] fuel cells,[32,52,53] sensing and degradation of toxic environmental substances,[54] biomedical applications such as drug delivery[42,43,55–58] and cell engineering;[59] however one of the most promising applications lies in the modification of membranes.[60] Polyelectrolyte multilayer films (PEMs) have been employed in gas separation and pervaporation membranes,[61–64] ion exchange membranes[27,65] as well as ion rejecting NF/RO membranes.[66]

The film properties are a strong function of the types of polyelectrolytes used and the deposition conditions like pH[67,68] and the deposition time.[15] By varying these conditions different types of tunable film properties can be attributed to the PEM assembly leading to its varied scope of application as shown in Figure 2. 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.[69,70] 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.[68,71] The increase in film thickness may be linear or exponential depending on the type and concentration of polyelectrolytes used as well as deposition conditions. While the multilayer assembly with the minimal thickness produces a highly permeable membrane, high surface charge density enhances the membrane rejection property. The thickness and the surface charge of the polyelectrolyte multilayers can be modulated by using salt as a supporting

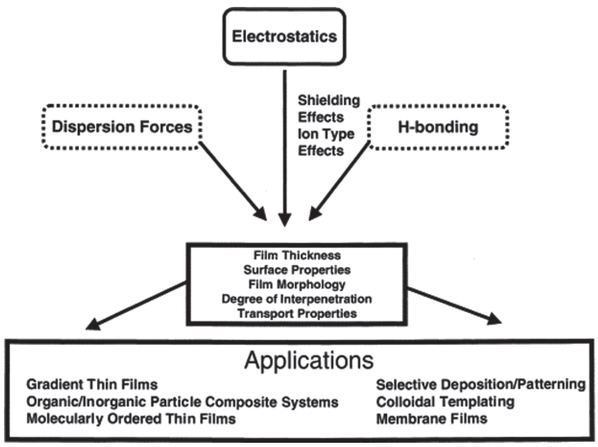

Figure 2. Schematic representation of how the different modes of layer-by-layer assembly affect the properties of the film and their applications. Reproduced with permission from [44], P. T. Hammond, *Curr. Opin. Colloid In.* 4, 430 **(1999)**. © 1999, Elsevier.

electrolyte.[77] It has been shown that the thickness of multilayers increases with increasing the concentration of NaCl till a certain point beyond which it reaches a plateau.[78, 79] Increase in thickness of the film leads to decline in the permeability of the membrane. On the other hand, increase in ion rejection of the membranes has been observed with higher concentration of NaCl due to the increased charge density.[80] In order to have a high rejection while maintaining a high water flow rate across the membrane as well it has been suggested that just the outermost layer of the assembly be deposited using a higher salt concentration.[80] The surface charge density can also be tuned by varying the type of salt used as the supporting electrolyte. For example using $MnCl_2$ instead of NaCl helps improving the charge density.[80] Besides manipulating the type and concentration of the salt used, another alternative to increase the surface charge density is to use a polyelectrolyte with higher ionic strenth as the capping layer.[81] Bruening et al. have also observed that by using PAA as the final capping layer to SPS/PDAC multilayers the anion rejection capability of the membrane increases.[80]

5. CHARACTERIZATION PARAMETERS AND THEIR CORRESPONDING TECHNIQUES

5.1. 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 thickness of the PEMs. One of the most common techniques to characterize 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.[66, 80] However with the deposition of a large

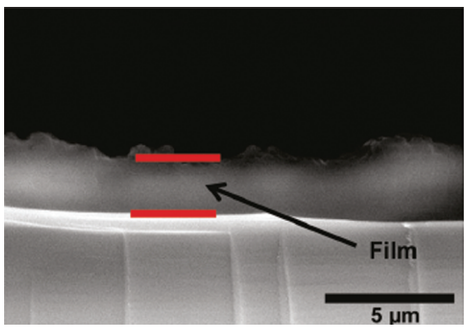

Figure 3. A typical cross sectional SEM image showing the deposited multilayer films on a support taken in order to determine the thickness of the multilayer films. Reproduced with permission from [26], M. Adusumilli and M. L. Bruening, *Langmuir* 25, 7478 **(2009)**. © 2009, American Chemical Society.

number of multilayers the substrate might not be optically transparent. In that case scanning electron microscopy (SEM) can be used to measure the thickness of the multilayer film,[82] a representative image of which is shown in Figure 3. For polyelectrolyte multilayers with thickness of 200A or more profilometry can also be employed.[68] Atomic force microscopy (AFM) can be used as a thickness measurement tool as well.[83] Ahmadiannamini et al. have applied tapping mode AFM to determine the thickness of the films.[84] Ahmadiannamini et al. have applied tapping mode AFM to determine the thickness of the films[84] as shown in Figure 4. Scanning angle reflectometry.[85] 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).[86]

5.2. Effective Porosity

In order that the polyelectrolyte multilayers be used as membrane skins, an important property to be quantified is the effective porosity. Bruening et al.[87] and Jin et al.[88] have developed a theoretical model for calculating the porosity of polyelectrolyte multilayer membranes as NF/RO membranes. Apart from the theoretical models, nuclear magnetic resonance (NMR) cryoporometry has been developed as a characterization technique to measure the effective porosity of polyelectrolyte thin films on porous supports. The results obtained from this technique and the theoretical models are pretty coherent.[85, 89] In this context it should be noted that the effective porosity values are a strong function of the polyelectrolytes used and their swelling behavior in presence of water.[20, 74, 90–92]

5.3. Surface Charge

Surface charge is another important property for multilayers functioning as membrane skins. These LbL assembled membranes reject ions both by virtue of size exclusion

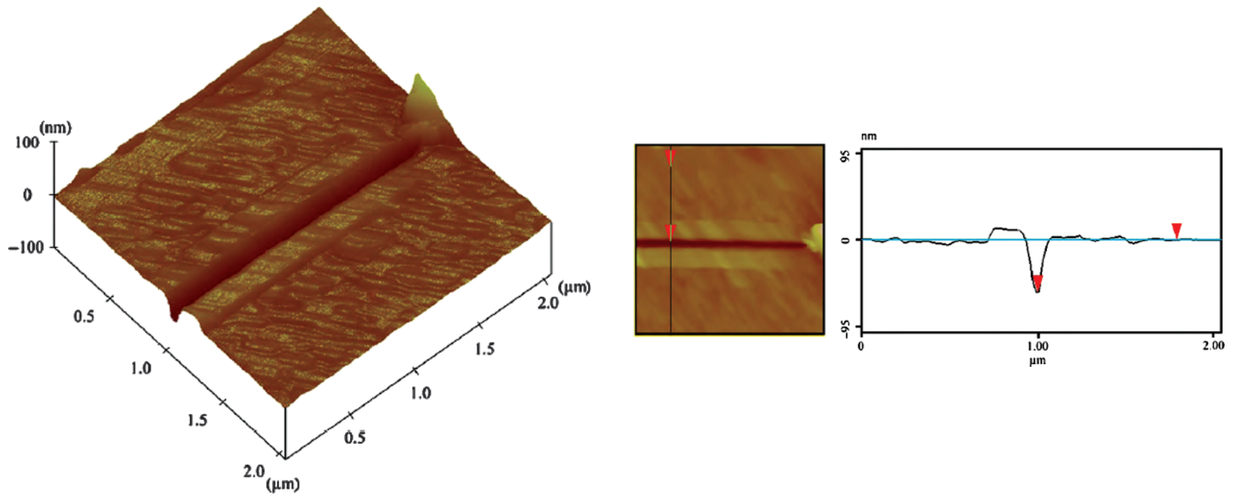

Figure 4. A typical AFM image showing the thickness of the multilayer film deposited by LbL technique. Reproduced with permission from [84], P. Ahmadiannamini, et al., *J. Membr. Sci.* 360, 250 (**2010**). © 2010, Elsevier.

as well as charge exclusion also known as donnan exclusion.[93,94] The surface charge of the outermost layer plays a significant role in the rejection of ions[82] and hence its measurement is of utmost importance for membrane characterization. This is usually done by measuring the zeta potential across the membrane surface using a streaming potential apparatus and correlating it with the surface charge.[95,96] A typical figure depicting the zeta potential variation with deposition of the multilayers is shown as follows.

As shown in Figure 5 the magnitude of the zeta potential typically alternates between positive and negative values corresponding to the deposition of alternately charged polyelectrolytes. However the zeta potential is a function of the number of bilayers and concentration of polyelectrolytes used, the pH used during the deposition of the multilayers, the type and concentration of the salt used as the supporting electrolyte.[97,98] Bruening et al. have observed an anomaly in the variation of deposition of zeta potential with the deposition of polyelectrolyte multilayers.[26] They have observed that with the deposition of more than 7 bilayers of PDAC/SPS bilayers using 1M NaCl as the supporting electrolyte the zeta potential continued to remain positive instead of alternating between positive and negative values.

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5.4. Hydrophilicity

Another important parameter that governs the permeability of any membrane is hydrophilicity. The more hydrophilic the membrane surface, the higher will be the water flux across the membrane. It is commonly quantified by a goniometer that measures the static air/water contact angle

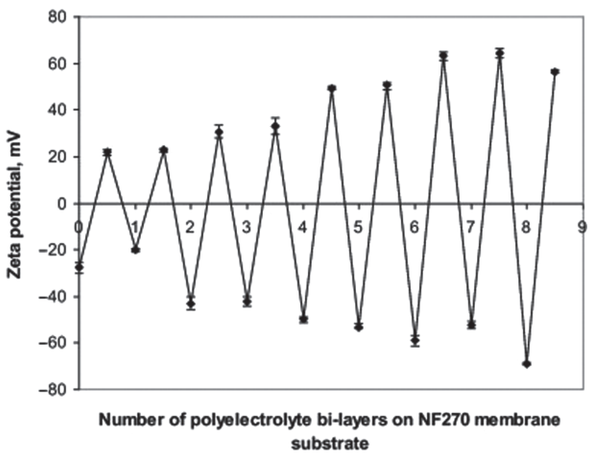

Figure 5. Variation of zeta potential with the deposition of polyelectrolytes by LbL technique. Reproduced with permission from [13], R. Malaisamy, et al., *Sep. Purif. Technol.* 77, 367 (**2011**). © 2011, Elsevier.

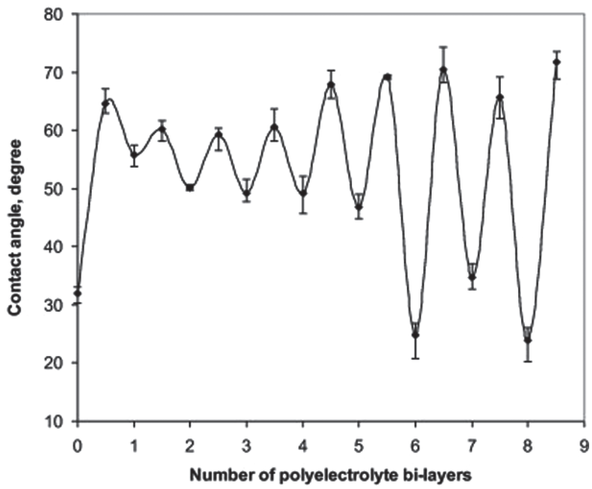

Figure 6. A typical plot showing the variation of contact angle with the deposition of polyelectrolytes by LbL technique. Reproduced with permission from [13], R. Malaisamy, et al., *Sep. Purif. Technol.* 77, 367 (**2011**). © 2011, Elsevier.

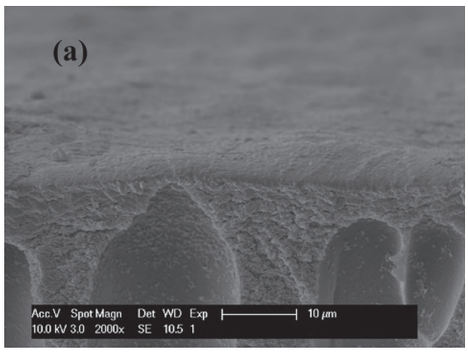

Figure 7. A typical cross sectional SEM image (at low magnification) showing the deposition of polyelectrolytes on a porous support. Reproduced with permission from [84], P. Ahmadiannamini, et al., *J. Membr. Sci.* 360, 250 (**2010**). © 2010, Elsevier.

at the surface of the sample. For PEMs the contact angle is measured after every step of depositing one particular polyelectrolyte layer.[13, 68, 99]

As evident from Figure 6 hydrophilicity of the modified membranes is higher than the original unmodified membrane[13] thereby creating a potentially high flux membrane.

5.5. Thin Film Morphology and Functionality

SEM can be used as very powerful tool to observe both the surface as well as the cross sectional view of the deposited films on the support.[84] Figure 7 shows a cross-sectional SEM image of a multilayer film assembly.

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Surface roughness of the polyelectrolyte multilayers can be quantified by the root mean square roughness value obtained from AFM measurements.[100] Following the deposition of the polyelectrolytes the surface functionality can be qualitatively determined using Fourier transform infrared reflection (FTIR) spectroscopy.[100]

6. ION REJECTION BY PEM MEMBRANES UNDER UF/NF CONDITIONS

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 and high ion-selectivity among individual ions. As discussed in the following sections these membranes can be potentially applied to water softening, fluoride ion separation and recovery of certain ions like phosphate or certain useful metal ions. The discussion has been divided into two major parts based on anion rejecting PEM membranes and cation rejecting PEM membranes.

6.1. Anion Rejection

Water softening is one of the principal areas where nanofiltration membrane is widely applied. It requires the removal of divalent anions like SO_4^{2-} by letting monovalent ions like Cl^- to pass through the membrane along with the permeate. Since this is a charge-based separation, PEM membranes can be easily applied to provide high flux and high selectivity, as shown by Bruening et al. and Tieke et al. Although by depositing 60 bilayers of PAH and SPS, a Cl^-/SO_4^{2-} selectivity as high as 45 was achieved by Tieke et al. the flux through such a system was obviously too low.[10, 101] Bruening et al. have done extensive research on this subject and have tried a number of different polyelectrolyte systems. The best results were however provided by $(PDAC/SPS)_{3.5}$ system deposited on a porous alumina membrane.[15, 17, 80, 102] They achieved around 96% SO_4^{2-} rejection with a Cl^-/SO_4^{2-} selectivity of around 2.7. While the sulfate rejection of commercial NF 270 membrane was still higher than this PEM membrane, higher permeability and high Cl^-/SO_4^{2-} selectivity make these membranes a better candidate to be applied to water softening.

The removal of F^- ion from drinking water is a major health concern as the presence of F^- in drinking water above a concentration of 2 mg/l can lead to adverse health effects. Commercial NF membranes do not show any Cl^-/F^- selectivity although they do show appreciable rejection of F^-. Bruening et al. developed a PEM membrane by depositing 4.5 bilayers of SPS and PDAC on alumina supports which offers high selectivity and can be potentially applied to water softening applications.[20] Such a system allows high water flux across it and the permeability was found to be higher than NF 270 and NF 90 as well. This was one of the few works reported on the separation of monovalent ions using PEM assembly. Such a type of separation is primarily based on size rather than charge (donnan exclusion) unlike multivalent ions. A similar work was shown Malaisamy et al.[13] to develop high flux PEM membranes with appreciable rejection of F^- along with high Cl^-/F^- selectivity. Instead of alumina membrane the authors deposited the multilayers on commercial NF 270 membrane in order to give a RO type rejection but having a higher flux and selectivity than typical RO membranes. Around 8 bilayers of PDAC/SPS could sufficiently reject F^- (around 70%) maintaining a high Cl^-/F^- selectivity (2.7) as well. Although the flux was 50% lower than the unmodified NF 270 membrane it was still higher than a typical RO membrane exhibiting the same type of rejection behavior.

Phosphate recovery is an important concern for many wastewater treatment applications. This can be achieved via membrane separation by virtue of selective removal of phosphate in presence of chloride ion. PEM membranes provide a good alternative for this type of selective separation as shown by some research groups recently. Selective removal of phosphate ion in presence of chloride was shown by Hong et al.[103] whereby they showed rejections as high as 98% for porous alumina membrane modified with PDAC/SPS multilayers along with a chloride/phosphate selectivity of 48. Phosphate ion rejection

is a function of the feed solution pH mainly because the valence charge carried by it varies with pH. When at pH 5.6 the phosphate ion exists as $H_2PO_4^-$ and the rejection attained by $(PDAC/SPS)_{4.5}$ bilayers is 84%. At around pH 7 half of the phosphate ions exist as $H_2PO_4^-$ while the other half exists as HPO_4^{2-} and the rejection went upto about 92%. At pH 8.4 when most of the phosphate ion exists as HPO_4^{2-} the rejection of 98% was attained. The commercial nanofiltration membranes like NF 270 or NF 90 show very high rejection of phosphate ions at alkaline pH but even the chloride rejection goes up thereby decreasing the selectivity. Besides the flux through the PEM modified alumina membrane is higher than either of the two commercial membranes. Ahmadiannamini et al. did a mixed salt NF study for a solution containing Cl^-, SO_4^{2-} and HPO_4^{2-} ions to study the rejection and selectivity of the ions involved.[84] Multilayers of PDAC and sulfonated poly(ether ether ketone) (SPEEK) were deposited alternately on hydrolyzed polyacrylonitrile support. When the mixed feed solution (pH 10.7) was tested for individual ion rejection, Cl^- had the lowest retention followed by SO_4^{2-} while HPO_4^{2-} had the highest retention. The different in retention between the divalent ions (SO_4^{2-} or HPO_4^{2-}) and Cl^- could be attributed to higher electrostatic repulsion experienced by the former type of ions. However SO_4^{2-} and HPO_4^{2-} were retained differently not due to the difference in their stokes radius, but also due to binding of HPO_4^{2-} ions with the topmost PDAC layer. The experiments were also performed with varying the pH conditions as phosphate ion H_3PO_4, $H_2PO_4^-$ and PO_4^{3-} at pH 1, 4.5 and 13 respectively. In the acidic pH range the retentions of all the ions reduced while at pH 13 the same performance was observed as in case of pH 10.7 which signifies the same binding effect between PO_4^{3-} and PDAC layer. Hence this PEM system was successful in exhibiting high Cl^-/SO_4^{2-} and Cl^-/HPO_4^{2-} selectivities but no SO_4^{2-}/HPO_4^{2-} selectivity could be achieved. A low pressure phosphate recovery process has also been demonstrated by Disha et al. by using a (PEI/SPS) multilayer system deposited on a porous polymeric support. This was probably one of the few low-pressure phosphate recovery processes whereby high chloride/phosphate selectivity was achieved.[104]

6.2. Cation Rejection

While a number of experiments have been done and reported about the removal of anions with the help of PEM membranes, several groups have also explored the subject of cationic rejection. As mentioned under anion rejection as well, water softening is one of the principal applications of nanofiltration membranes. In terms of cationic rejection it involves the removal of divalent ions like Mg^{2+} and Ca^{2+} by allowing the flow of monovalent Na^+ ion. Tieke et al. reported the use of PAH/SPS system for the selective removal of Mg^{2+} with more than 90% rejection; however they deposited as many as 60 bilayers.[10, 101, 105, 106] Bruening et al. have shown that it is possible to have rejections as high as 95% for Mg^{2+} with a Mg^{2+}/Na^+ selectivity of 20 just by depositing 4/5 bilayers of PAH/SPS multilayers on porous alumina/UF supports.[16] The fluxes of these nanostructured membranes were comparable to commercial NF membranes and the rejection was way better because mostly the commercially available membranes have a negatively charged surface. While PDAC/SPS system shows higher permeability the rejection is rather poor. Hence in order to develop a multifunctional membrane having both high flux as well as high rejection the authors had tried out a hybrid system of PDAC/SPS multilayers from with PAH/SPS as the capping layers. However even with such a system 90% rejection was only achieved when 2.5 M NaCl was used for the topmost layer. As it didn't show any marked improvement from PAH/SPS assembly the hybrid system was discarded. The PAH/SPS system was successfully applied for selective removal of Ca^{2+} ion as well.

A related research concerning the rejection of Mg^{2+} ion in presence of colloidal foulants was carried out by Shan et al.[81] In practical applications fouling is a very serious problem encountered in all membrane processes which reduces the membrane performance over a period of time. It is therefore necessary to design a membrane whose rejection is not adversely affected by the presence of foulants. This type of research has been previously done for commercial RO/NF membranes.[107, 108] but not for PEM membranes. The authors used SiO_2 as a colloidal foulant in their experiments to design PEM membranes by depositing polyelectrolytes on commercial polyethersulfone membrane. They deposited a variety of polyelectrolyte combinations with varying number of bilayers consisting of weak polyelectrolytes like PAH as well as strong polyelectrolytes like SPS and PDAC. While for one particular polyelectrolyte combination $(SPS/PAH)_4$ the performance (flux and Mg^{2+} rejection) after colloidal fouling was pretty much comparable to a commercial nanofiltration membrane (NF 270) it is interesting to note that for certain PEM conditions the deposition of the colloidal particles led to an improvement in Mg^{2+} rejection. As the authors postulate, this occurs due to the formation of PEM-colloid nanocomposites that have the ability to reject ions better than the original PEMs. As shown by the authors, an advantage of using PEM system is the possibility of regenerating the PEM layers. Weaker polyelectrolytes like PAH can be removed by dissolving them in a high pH solution and redeposited again using the same LbL technique. This definitely improves the chances of reusing the membranes after fouling, but the performance of the PEM membranes could not be fully restored post-regeneration. As per the authors the incomplete washing of the colloids off the membrane surface hinders the restoration of the membrane performance. This new direction provided by their research should definitely be explored further to produce reusable membranes.

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Besides water softening, removal and recovery of metal ions from wastewater is another very important membrane operation. PEM membranes can be used to selectively recover certain useful metal ions based on charge exclusion. One such work has been reported by Lakard et al. for the recovery of copper ions from the aqueous solution using PEM modified polyethersulfone membrane under UF operation conditions (< 3 bar operating pressure).[109, 110] Around 5.5 bilayers of PAH/SPS was deposited, PAH being the topmost layer in order to have the maximum rejection of copper ions by virtue of electrostatic repulsion. The effect of variation of pH conditions and concentration of polyelectrolyte solution used in the layer-by-layer technique on the rejection of copper ions has been described. It was shown that at pH = 5 and at a high polyelectrolyte concentration (10 g/l) the highest rejection of copper (nearly 88%) was obtained. On replacing the topmost PAH layer by a strong polycationic layer (PDAC) the rejection was not changed significantly which implies that the nature of the polycation used does not have a major role to play. Very recently Kobayashi et al. reported the deposition of multilayer assemblies of PAA and chitosan or PAA and chitosan microspheres on functionalized PAN supports for the removal of Cu^{2+} ion from sea water.[111] Such an assembly showed appreciable Cu^{2+} removal efficiency by the mechanism of adsorption and chelate formation.

Another major concern is the removal of Fe^{3+} ion and recover Fe^{2+} ion from a solution containing both the ions. Kobayashi et al. have shown the potential of PEMs deposited on functionalized polyacrylonitrile (PAN) membranes in the selective removal of Fe^{3+} ion under UF operating conditions.[111–113] Two types of PAN copolymer membranes were experimented with, one being poly(acrylonitrile-co-acrylic acid) [P(AN-co-AA)] and the other being poly(acrylonitrile-co-*N*,*N*-dimethylethyl ammonium bromide) [P(AN-co-EDAMA)]. While the former was a negatively charged support the latter one was positively charged and both were prepared from cast solutions of quaternized *N*,*N*-dimethylethyl ammonium bromide and acrylic acid respectively using the phase inversion method. Cetyl trimethyl ammonium chloride (CTAC) and tetramethyl ammonium chloride (TMAC) were used as polycations while PAA was used as polyanion. The permeability of the modified membrane using TMAC as the polycation was found to be lower than CTAC. Hence for their subsequent research the authors used CTAC/PAA polyelectrolyte system for the selective removal of Fe^{3+} ion. As known before, in order to achieve maximum rejection of Fe^{3+} ion the CTAC terminated system was more effective. But one of the important issues pointed out in their research was the effect of percentage functionalization of the charged membrane support. Their experiments showed that the positively charged membrane prepared from a higher weight percentage of the cast solution when terminated with CTAC exhibited 90% removal of Fe^{3+} with the highest selectivity as well. Although these experiments were performed under low pressure conditions using a simple solution containing just Fe^{3+} and Fe^{2+} ions, such a setup can potentially be applied to a more complex sea water desalination problem which involves various other types of ions.

7. PEM MEMBRANES AS DESALINATION MEMBRANES

PEMs have been widely discussed as water softening membranes for separating certain undesired ions and recovery of useful ions. There has been comparatively lesser amount of work put into applying PEMs in making desalination membranes. However desalination is a highly important industrial water purification process applied worldwide whereby it would be useful to develop membranes which have lower pressure requirement but comparable rejection as the commercially available ones. It is therefore worth reviewing the work done by certain groups in developing desalination membranes using the layer-by-layer technique. While water softening is mostly related to rejection of divalent ions desalination involves rejection of monovalent ions as well. Divalent ions are comparatively easier to reject than monovalent ions by virtue of higher electrostatic repulsion between them and the charged polyelectrolyte surface. Also reverse osmosis is a high pressure process; hence choosing a mechanically stable support but with sufficiently high permeability is of utmost importance to be applied industrially.[114]

Tieke et al. have done considerable research on both NF/RO membranes from polyelectrolyte multilayers.[10, 11] They deposited 60 bilayers of polyvinyl alcohol (PVA) and polyvinyl sulfate (PVS) multilayers on PAN/PET support and the resulting membrane was employed in high pressure ion rejecting membrane processes. They have experimented with a mixed feed solution consisting of both divalent and monovalent salts. As observed before, the divalent cations (Mg^{2+}) and anions (SO_4^{2-}) are rejected more efficiently as compared to the monovalent ions like Na^+ and Cl^-. By increasing the pressure higher rejection was obtained even for NaCl salt (93.5% at 40 Bar). However when the system was actually applied to a non-diluted sea water solution the rejections were found to be lower as compared to the diluted samples (56.6% for NaCl at 20 bar and 74.5% at 40 bar). The rejections for Mg^{2+} and Ca^{2+} ions were still higher than 95% at 40 bar. The decrease in salt rejection in case of pure sea water solution can be explained based on concentration polarization and the inability of the polyelectrolytes to reject high concentration salt solutions. The authors speculate that with pressure as high as 60 Bar the NaCl rejection might get close to 90% for non-diluted sea water. With the deposition of the large number of bilayers the permeability showed a dramatic decrease (2000 times lesser than the original substrate). Tieke et al. have also reported the

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use of nanoblended polyelectrolyte multilayer membranes where they used PAH as the polycation and a blend of PAA and SPS as polyanion in different blending ratios.[115] They found that at pH 1.7 using PAA and SPS in 1:1 ratio as the polyanion blend they observed rejections as high as 84% for NaCl and 97% for Na_2SO_4. The rejections were much higher in case of these nanoblended membranes as compared to pure PAH/SPS multilayer system under the same pH conditions. In all of these reported works appreciable salt rejection capability has been observed but at the cost of reducing the permeability of the resulting membrane. The absolute value of the permeability can be potentially improved by choosing a more permeable support. Also the authors used dead end filtration module for their preliminary studies, which is not as effective as a cross flow module to deal with concentration polarization. The results might improve when being tested under cross flow conditions.

Park et al. have reported a very detailed research on preparing desalination membranes using layer-by-layer technique.[114] In their study multilayers of PAA (pH 3.5) and PAH (pH 7.5) were used to form the nanothin films on a polysulfone support for the purpose of rejecting NaCl from a concentrated (2000 ppm) salt solution. These multilayers were thermally annealed by heating the membrane to 180 °C for 1 hour in order to form dense cross linked structures. With increasing the number of bilayers the flux reduced quite drastically but rejection of NaCl went on increasing. A rejection of 81% was obtained with 20 bilayers. The stronger polyelectrolytes like PDAC and SPS did not show significant NaCl rejection even with 20 bilayers and cross linking did not play a significant role with these polyelectrolytes simply because they don't have any cross linkable groups. The paper even reports the recycling of the dilute permeate solution across the membrane and with that the rejection became as high as 99%, which is at par with the commercial membranes. A limitation observed is the lower flux of the crosslinked membrane which can potentially be improved by choosing a different polyelectrolyte system.

Apart from the research works described above, Ishigami et al. have applied layer-by-layer deposition of PAH/SPS (adjusted to pH 7) multilayers on a commercial polyamide RO membrane (ES-20 from Nitto Denko, Japan).[116] The purpose of their study was to improve the fouling resistance of the membrane in order to be used for a prolonged duration without further increase in the operating pressure. While the modified membranes showed a significant decline in the initial permeability of the membrane the flux decline over a period of time was definitely lesser than the unmodified membrane. The rejection of NaCl was also improved due to the polyelectrolyte deposition. This means these modified membranes can at least function for a longer period of time than the commercially available membranes without a continual pressure increment to combat the flux decline caused by fouling. In order to improve the initial permeability the number of bilayers can be optimized without affecting the salt rejection property.

A common limitation observed in all the above research work is the low permeability obtained from the PEM membranes. In order to be applied for desalination purposes either a highly cross-linked polyelectrolyte system is required or an excessive number of bilayers need to be deposited. In both these cases a high operating pressure will be required to maintain a high flux, which again increases the operating cost of the process. However as observed by Ishigami et al.[116] and a couple of other researchers[81, 117, 118] deposition of these polyelectrolytes can lead to surface modification of the membranes making them more hydrophilic and thereby making them more resistant to fouling.[6] For that matter even though the initial operating pressure might be high for the modified membranes, a continual pressure increment to combat flux decline due to fouling may not be required. Therefore by using the polyelectrolyte multilayer membranes the overall cost efficiency of the process has the potential to improve.

8. LAYER-BY-LAYER TECHNIQUES OTHER THAN DIP COATING–SPRAY COATING, SPIN COATING AND DYNAMIC LAYER-BY-LAYER COATING

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The traditional method of carrying out layer-by-layer technique is the dip-coating method. Although the method is really simple and inexpensive it is time consuming thereby limiting its industrial application.[119] Spin coating and spray coating are two suggested alternative LbL techniques discussed in literature. Figure 8 provides an illustrative representation of the three types of coating techniques used for depositing polyelectrolyte multilayer films.

Spray coating developed by Schenoff et al.[121] 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 involved in the dip-coating method and the resulting films are also thinner and more uniform surface coverage is obtained.[122] 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.[122] Spray coating has been applied to making reactive membranes[123, 124] but its application to making ion rejecting membranes is not that widely available in literature. Although spray coating involves fixing several parameters to get the desired nature of coating it is definitely worth applying to preparing PEM membranes for ion rejection due to its extremely short preparation time.

Spin coating developed by Cho et al.[125] involves spinning/centrifugal force to deposit multilayers on the

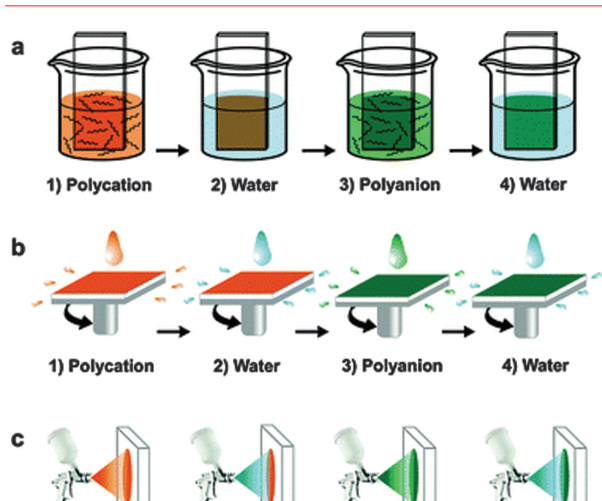

Figure 8. A schematic diagram showing (a) Dip coating, (b) Spin coating and (c) Spray coating. Reproduced with permission from [120], Y. Li, et al., *Chem. Soc. Rev.* 41, 5998 **(2012)**. © 2012, Royal Society of Chemistry.

substrate within a few seconds.[122, 126] Spin coating has been applied to making desalination membranes using polyelectrolyte multilayers.[122, 127, 128] Higher the spinning rate thinner the films are formed as the high centrifugal force removes the unadsorbed materials off the surface thereby preventing agglomeration.[128] Spin coating has also been reported to form lesser-interpenetrated layers as well compared to dip-coating but imparts a higher surface roughness to the membrane surface.[127] 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 going on in developing these two *LbL* techniques so that the processes can be industrially applied as well. Since they produce thinner and more uniform films they can be definitely considered as suitable for making NF/RO membranes with high permeability.

Dynamic *LbL* is another technique that hasn't been reported that often in literature but has the potential of making ion-rejecting membranes with higher rejection rate. Deng et al. have reported the making of PEM membranes for salt rejection using this method. Instead of dipping the UF support membranes in the polyelectrolyte solutions as in case of the conventional static *LbL* method, the polycation and polyanion solutions are alternately vacuum filtered across the membrane support for a specific duration thereby coating the membrane surface.[129] Dynamic *LbL* is reportedly faster than static dipping process and results show that it offers higher rejection of salts like $MgCl_2$, $MgSO_4$ and Na_2SO_4 than the conventional technique.[129] The dynamic process however does not significantly improve the rejection of NaCl. This is probably due to higher surface charge induced on the membrane surface by the dynamic process which leads to higher rejection of multivalent ions by virtue of donnan exclusion.[129] The flux across the resulting membrane is slightly lower than that obtained in static *LbL* process. The dipping times in each solution might be lower than the conventional method but one of the disadvantages encountered in this method is the need to take out the membrane from the filtration setup in order to have the DI water rinse steps in between. Ishigami et al. have tried a similar multilayer deposition technique using a cross flow membrane filtration setup.[116] This time the deposition was carried out under high-pressure conditions maintaining a certain flow rate of the solutions. The polycation and the polyanion solutions were passed alternately and DI water was made to flow across the membrane in between two polyelectrolyte deposition steps. Such a setup does not require the membrane to be taken out and washed with DI water but the duration of dipping does not seem to be lower than the conventional *LbL* technique. With further research in this area this technique might become more favorable to be applied to water purification membranes.

9. CONCLUSION AND FUTURE DIRECTIONS

We therefore see that layer-by-layer assembly is an extremely versatile technique in making ion-rejecting membranes. With a large variety of polyelectrolytes that can be used along with several other tunable factors like number of bilayers, concentration of the supporting electrolyte, conditions used for deposition of the multilayers etc., a PEM system can be a candidate for several applications requiring ion rejection. These membranes are typically high flux membranes thereby requiring lower operating pressure and rejection comparable to commercially available NF/RO membranes. Apart from the conventional dipping *LbL* technique, faster and more efficient methods like spray or spin coating are also available which can potentially aid in the application of such membranes in industrial scale. Many research groups have tried applying PEMs as desalination membranes as well which require high salt rejection. The results are promising but still require further optimization in terms of operating conditions so as to replace the existing commercial RO membranes. While most of the PEM membranes have been tested at laboratory scale with either a single salt or a solution containing a few particular ions it would be interesting to observe these membranes with actual wastewater systems which are definitely far more complex with a variety of ions present in them. A major problem encountered in membranes applied for waste water systems is fouling. This leads to a loss of membrane performance over a period of time and further increases the operating cost as well as maintenance cost. PEM membranes as discussed before can be good surface modifiers for commercial membranes thereby maintaining a higher flux than the

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latter over a longer time span. While Shan et al.[81] have tested the PEM membrane performance with silica colloids more research should be devoted to membrane performance in presence of actual waste water foulants. Also the concept of regeneration of the multilayer films by removing the fouled polyelectrolyte layers could be extremely helpful in dealing with membrane fouling. The membranes can be reused even after it gets fouled following the simple *LbL* procedure. It is however important to be able to restore the membrane performance with respect to both flux and rejection post membrane regeneration. In all, PEM membranes pose an excellent alternative solution to the highly expensive water treatment operations currently applied worldwide for ion rejection. In future it is important to have some research regarding the real life applications of such membranes in order to effectively solve the ongoing worldwide water shortage problems.

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