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PAPER

Transport studies of ionic solutes through chitosan/chondroitin sulfate A (CHI/CS) polyelectrolyte multilayer membranes

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7 July 2020P Nikhil Chandra^{1,2}  and Mothi Krishna Mohan³¹ P.G. and Research Department of Chemistry, Sree Narayana College, Kollam, Kerala 691001, India² Advanced Centre of Environmental Studies and Sustainable Development, Mahatma Gandhi University, Kottayam 686560, India³ Kerala Department of Sciences and Humanities, Christ University Faculty of Engineering, Bangalore, Karnataka, 560074, IndiaE-mail: pnikhilchandra@gmail.com**Keywords:** nano scale assembly, polyions, layer by layer, polyelectrolytes, multilayers, chondroitin sulfate A, ion selectivity

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**Abstract**

Nano scale assembling has led to the capability to directly control and enhance the capabilities and properties of a material through change of its structural makeup at the nano scale. A novel class of functional layers in which various properties can be tunable via *in situ* modifications of nanostructure through stimuli such as pH, capping, and salt addition provides a promising strategy to develop polyion responsive polyelectrolyte multilayer membranes (PEM's). The concentration (diffusion dialysis) and pressure dependent (ultrafiltration) studies of solution containing polyvalent ions through the chitosan/chondroitin sulfate A (CHI/CS) multilayers fabricated on ultrapore membrane have been studied. The characterization of the bilayer pair was done with analytical instruments like ATR-FTIR, spectroscopic ellipsometry, SEM, AFM and finally TGA for water holding capacity. The characterization of bilayer pairs demonstrated the stability and integrity of bilayer pair. An important bilayer property such as water holding capacity and ion permeability across it was examined and a positive correlation was found with increase in number of bilayers. The possibility of capping a fabricated bilayer with another polyelectrolyte, polyethylene glycol (PEG) was used to examine the extend of efficiency. The permeation rate of ions across bilayers increased with makeup salt concentration was observed with capping. An increase in selectivity was observed with increase in the number of bilayers for $\text{Na}^+/\text{Cu}^{2+}$, Na^+/Ag^+ and $\text{Na}^+/\text{Mn}^{3+}$. 12.5 hybrid CHI/CS-PEG membranes shows a selectivity of 38.52 for $\text{Cl}^-/\text{PO}_4^{3-}$ with a permeation rate of $37.54 \times 10^{-5} \text{ cms}^{-1}$ and $4.23 \times 10^{-5} \text{ cms}^{-1}$ respectively for Cl^- and PO_4^{3-} . The transport profile of a model vitamin, ascorbic acid (AA) through CHI/CS multilayers showed the capability of bilayer membrane for selective solute transport.

1. Introduction

Ion separations are essential in modern times due to various important industrial applications such as water softening, desalination, selective ion separation, salt purification, concentration of industrial streams, waste water treatment, potable water production and precious ion recovery [1]. Membrane based pressure driven and non pressure driven methods are very attractive for such applications because of their low energy and capital costs. But, low pressure driven methods like ultrafiltration (UF) and microfiltration (MF) allows small materials, monovalent and polyvalent ions, dissolved organics and micro pollutants to pass through their membrane pores. High pressure filtration methods like reverse osmosis (RO) and nanofiltration (NF) are useful for the separation of ions and emerging contaminants having low molecular weight [2]. Due to low efficiency and further modification requirement of low pressure filtrations methods and due to high installation and operational cost required for high pressure filtration methods, both methods are considered expensive in ion separation processes [3]. Diffusion dialysis (DD) is an ion-exchange membrane separation process capable of selective ion transport mainly driven by concentration gradient [4]. Thus the concentration driven dialysis is also

known as a spontaneous separation process or concentration dialysis. DD is thermodynamically favorable as this spontaneous process tends to an increase in entropy and decrease in Gibbs free energy. The unique features of DD, especially the environmental benignity, low energy consumption, low installation and operating cost [5] combined with advantages of LbL membranes make it an effective competitor for selective ion transport.

Advanced surface coating techniques play an important role in confining an ordinary conventional ion permissible membrane surface to highly selective surface [6]. Surface coating methods like Langmuir–Blodgett (LB) and self-assembled monolayers (SAMs) can be very interesting; both have certain limitations with respect to substrates and do not have control at molecular level. Comparatively new method of layering or the layer by layer (LbL) coating is regarded high since they combine both the properties. The simplicity of application and ability to apply to various substrates with an economical and cleaner technology aspect makes it an excellent choice for a wide range of applications [7]. Thus, polyelectrolyte multilayers (PEM) fabricated over microfiltration membranes can be applied for separating polyvalent ions, thus membrane technique can be considered as a novel and emerging technique for selective ion transport. The multi-bipolar architecture obtained as a result of alternating layers of anionic and cationic polyelectrolytes enhance the ability for pure electrostatic interactions with charged ions. These nano skins of bilayer can attract opposite charges and reject similar charges by Donnan exclusion. T.R. Farhat *et al* (2001) showed the transport of ions through multilayers made from highly charged polyelectrolytes. M. L. Bruening *et al* (2002) showed the ability of multilayer polyelectrolyte membranes for enhanced ion-transport selectivity. A controlled ion transport through multilayer polyelectrolyte membranes by derivatization was demonstrated by J. Dai *et al* (2002). M. L. Bruening *et al* (2017) explored both gas and ion separations, and the latter included transport due to concentration, pressure and electrical potential gradients. W. Cheng *et al* (2018) proved the ability of multilayer PEM membranes using a layer-by-layer method for effective removal of different scale forming divalent cations from feed waters with different salinities. A PEM membrane with highly charged surface layer is obtained by incorporating various hydrophilic and hydrophobic groups which will further enhance its ion selectivity and flux [8].

The polyelectrolytes used for the present study are chitosan (CHI), chondroitin sulfate A (CS) and polyethylene glycol (PEG). Cationic CHI and anionic CS are naturally occurring polyelectrolytes which show excellent absorption properties due to the intra and intermolecular attraction with polymer charge sites [9, 10]. They are also low cost, environment friendly and can be tuned into excellent ion selective layer over membrane. Polyethylene glycols are synthetic, uncharged hydrophilic polymers made by joining units of ethylene glycol by an ether linkage [11]. The present work concerns with the transportation of small molecules like ascorbic acid (AA) and various polyions through CHI/CS multilayers under pressure driven and non-pressure driven conditions respectively. The effect of feed concentration, pH of polyelectrolyte and effect of outer layer on selectivity were analyzed. Capping of CHI/CS bilayers with PEG seems to be an effective method for enhancing the ion selectivity under non-pressure driven condition.

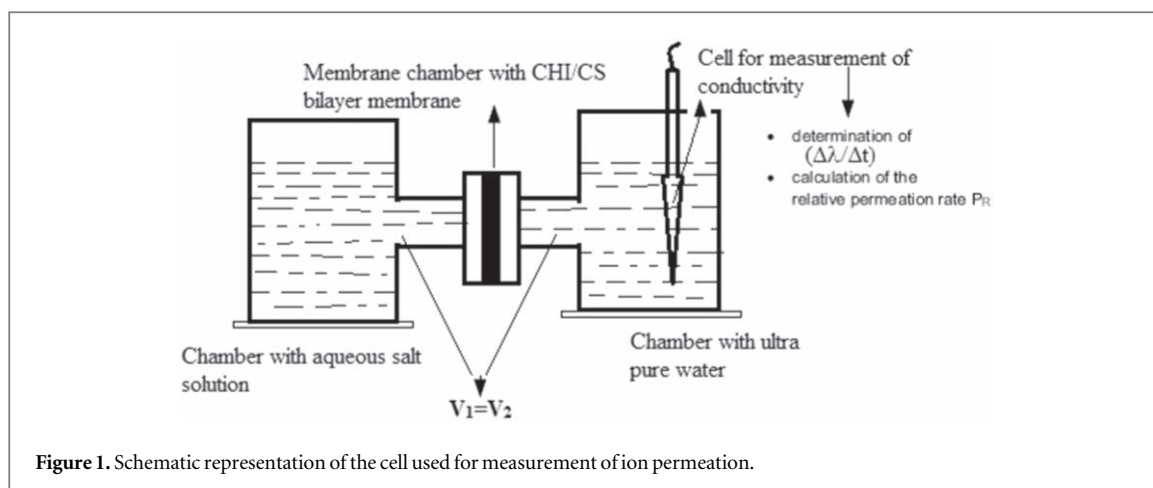
2. Experimental Methods

2.1. Materials

Ultipor N66 (nylon-6,6, 0.2 μm pore size, uncharged, Pall Life Sciences) MF membrane was used as support for multilayer formation. Chitosan (CHI, medium molecular weight, 75–85% deacetylated, Sigma-Aldrich), Chondroitin sulfate sodium salt (CS, MW $\sim 50,000 \text{ g mol}^{-1}$) from bovine trachea, Aldrich), Poly(ethylene glycol) (PEG, average Mn 400, Aldrich), HCl (Merck), and NaOH (Merck) were used without further purification. The salts used for the investigation of transport properties and selectivity, such as NaCl, KCl, AgCl, MnCl_3 , CuCl_2 , Na_2SO_4 and K_3PO_4 were purchased from Merck and were used without further purification. L-Ascorbic Acid (AA, extra pure AR, 99.7%) was purchased from SRL chemicals and were used as received. Ultrapure water (Milli-Q, 18.2 $\text{M}\Omega \text{ cm}$, Pall Corporation) was used for all preparations and experiments.

2.2. Preparation of polyelectrolyte multilayers

The Ultipor N66 MF membranes were kept in ultrapure water overnight for multilayer preparation. The polyelectrolytes used for the preparation of multilayers were chitosan (CHI, 0.01 M, at pH 1.7) and Chondroitin sulfate sodium salt (CS, 0.01 M, at pH 3) solutions (molarities of polyelectrolytes were taken with respect to repeating unit). The polyelectrolyte PEG was prepared with a concentration of 0.1 M at pH 2. The bare membrane was first dipped in positively charged CHI solution for 15 min followed by washing with 50 ml of distilled water to remove loosely bound polyelectrolytes. Then the membranes were again dipped in negatively charged CS solution for another 15 min. The membrane was again washed with 50 ml distilled water. Thus, one bilayer of oppositely charged polyelectrolyte was obtained by LbL method. By repeating the procedure desired number of CHI/CS layers is obtained. Different number of CHI/CS bilayers was prepared and AA was immobilization into it by simple absorption method. Hybrid membranes were synthesized to study the



improved selectivity without causing much fluctuation in the flux. The desired number of CHI/CS bilayers was used as the precursor layer for capping of PEG layer. After deposition of both precursor and capped layers, the membranes were dried at room temperature and used for selectivity studies of small molecules and ions.

2.3. Diffusion dialysis measurements

A membrane cell (figure 1) was used for the non pressure driven transport studies of ions. The membrane cell consists of two solution chambers with PEM membrane placed between these chambers with the aid of an O-ring. For determining the transport of ions, one chamber is filled with 0.1 mol l^{-1} salt solutions (NaCl, CuCl_2 , MnCl_3 for the determination of cation selectivity and NaCl, Na_2SO_4 , K_3PO_4 for the determination of anion selectivity) and the other with equal volume of ultrapure water. By diffusion, the ions will permeate into the ultrapure water causing an increase in its conductivity. It is possible to measure the change in conductivity of water in unit time using a conductivity meter (Equiptronics-EQ-667) with cell constant $K = 1$. From the change in conductivity of ultrapure water in unit time, permeation rate of the salt solution can be calculated using equation 1[12].

$$PR = (\Delta\lambda/\Delta t) \lambda_m^{-1} V (Ac)^{-1} \quad (1)$$

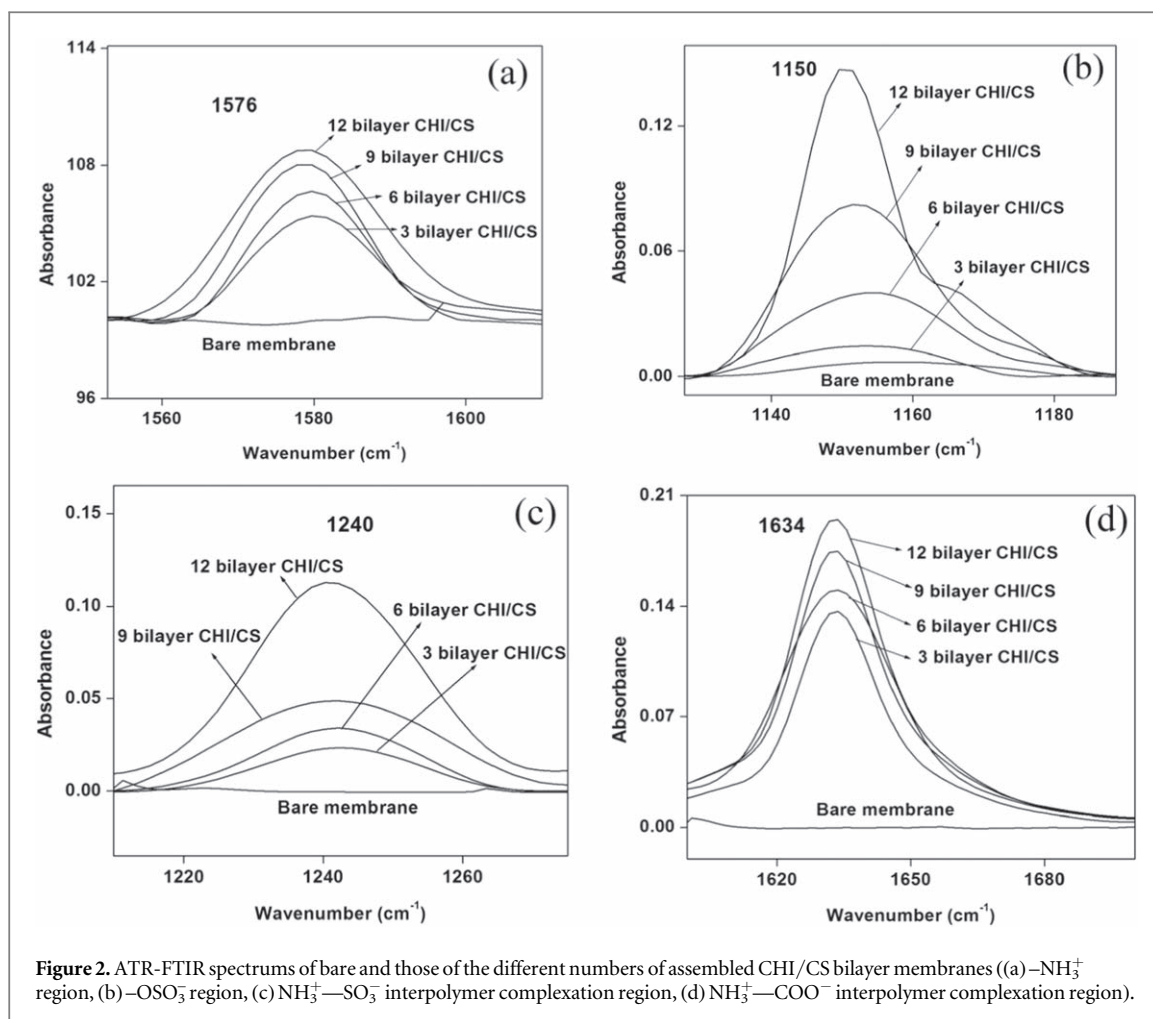
where P_R is the permeation rate of salt solution, $(\Delta\lambda/\Delta t)$ is the change in conductivity of salt solution per unit time, λ_m is the molar conductance of salt solution, V is the volume of salt solution taken in chambers, A is the effective area for permeation and c is the concentration of salt solution. However, the P_R values do not represent absolute values, because a possible contribution to $(\Delta\lambda/\Delta t)$ originating from the volume flow of water in the opposite direction (osmotic flow) has not been corrected. The ratio between the permeation rate of monovalent and divalent ions simply gives the selectivity of divalent ions over monovalent ions.

$$\text{i.e., selectivity}(\alpha) = P_R \text{ of monovalent ions} / P_R \text{ of divalent ions} \quad (2)$$

Ultrafiltration technique was used for the study of AA permeation and selectivity of CHI/CS multilayers under pressure driven condition. All the ultrafiltration experiments were carried out using Amicon—8050 Ultrafiltration cell.

2.4. Characterization methods

The CHI/CS multilayer membrane was monitored using ATR-Fourier Transform Infrared Spectroscopy (Shimadzu IR Prestige-21). The absorption spectra using FTIR were recorded from 650 to 4000 cm^{-1} using an ATR attachment with a ZnSe crystal with twenty scans were averaged per spectrum. The average thickness of CHI/CS multilayers and hybrid membranes were measured using spectroscopic ellipsometer (M-2000V, J. A. Woollam Co.) with incidence angles of 65° , 70° , and 75° . The wavelength of incident light was varied from 370.1 to 999.1 nm , each at five different locations on the bilayer sample under study. Data analysis and modeling were performed using Complete EASE software, version 4.81. The bilayer morphology studies were carried out using scanning electron microscopy, SEM (JSM-840) and atomic force microscopy, AFM (Witec alpha 300 RA). In SEM, the scanning was carried out with an accelerating voltage from 4 to 10 kV . The AFM was equipped with silicon nitride tip with $\sim 10 \text{ nm}$ radius of curvature, with a resonance frequency of 80 kHz and force constant of 2.8 N/m . Water holding capacity of CHI/CS multilayers were analyzed readily after the ultrafiltration of ultrapure water using TGA (SDT Q600) studies. After ultrafiltration experiments, hydrated samples were taken from cell and were cut in to small pieces weighing about $\sim 4 \text{ mg}$. In the case of bare membrane, ramping water loss method was carried out for TGA analysis. For multilayers, TGA experiment were carried out in two



successive steps viz isothermal water loss and ramping water loss method with the same specimen. The thermal studies were carried out at a ramp rate of $20^\circ\text{C}/\text{minute}$ up to 850°C with sample purge flow using nitrogen gas set at $100\text{ ml}/\text{minute}$.

3. Results and Discussion

3.1. Film characterization

The formation of functional layers on bare membrane by LbL method is confirmed from the ATR-FTIR spectra presented in figure 2. The bilayer membranes characterized were 6 months old in order to confirm the bilayer stability. It shows the ATR-FTIR spectra of bare and those of the assembled $(\text{CHI}/\text{CS})_n$ LbL membranes. The peaks at 1576 cm^{-1} and 1150 cm^{-1} in the IR spectrographs of CHI/CS bilayers (figure 2(a), (b)) is indicative of the presence of $-\text{NH}_3^+$ functional group (asymmetric stretching) of CHI and $-\text{OSO}_3^-$ functional group (symmetric stretching) of CS respectively [13–15]. The increased peak area with number of bilayers proved the sequential absorption of polyelectrolytes over bare membranes. The CHI/CS bilayer formation is a result of bonding between $-\text{NH}_3^+$ groups of CH and $-\text{COO}^-$ or $-\text{OSO}_3^-$ groups of CS. Thus strongly suggesting the existence of $\text{NH}_3^+-\text{COO}^-$ and $\text{NH}_3^+-\text{SO}_3^-$ electrostatic complexation which resulted in interpolymer complexation between CH and CS. Further, the characteristic peak of $\text{NH}_3^+-\text{COO}^-$ and $\text{NH}_3^+-\text{SO}_3^-$ occur in the range of 1400 cm^{-1} – 1550 cm^{-1} and 1150 cm^{-1} – 1300 cm^{-1} respectively [16]. Figure 2(c), (d) suggests the indicated uniform binding of carboxylate and sulfate linkages with number of bilayers.

The average film thickness of the self assembled bilayers produced by LbL method on silicon wafers was measured by spectroscopic ellipsometry and listed in table 1.

From table 1, the average thickness of CHI/CS from 3 bilayer to 12 bilayers was $\sim 72\text{ nm}$, 112 nm , 136 nm and 146 nm respectively. A linear relation can be obtained with the thickness of bilayers with an increase in number of bilayers. An increase of 30% in thickness of bilayer was observed for 12 bilayer CHI/CS from $\sim 146\text{ nm}$ to $\sim 182\text{ nm}$ with makeup salt. The poly-ionic solution facilitates the chance of repulsion between like charges within a single polyelectrolyte without the makeup salt, results a rod like configuration for polymer

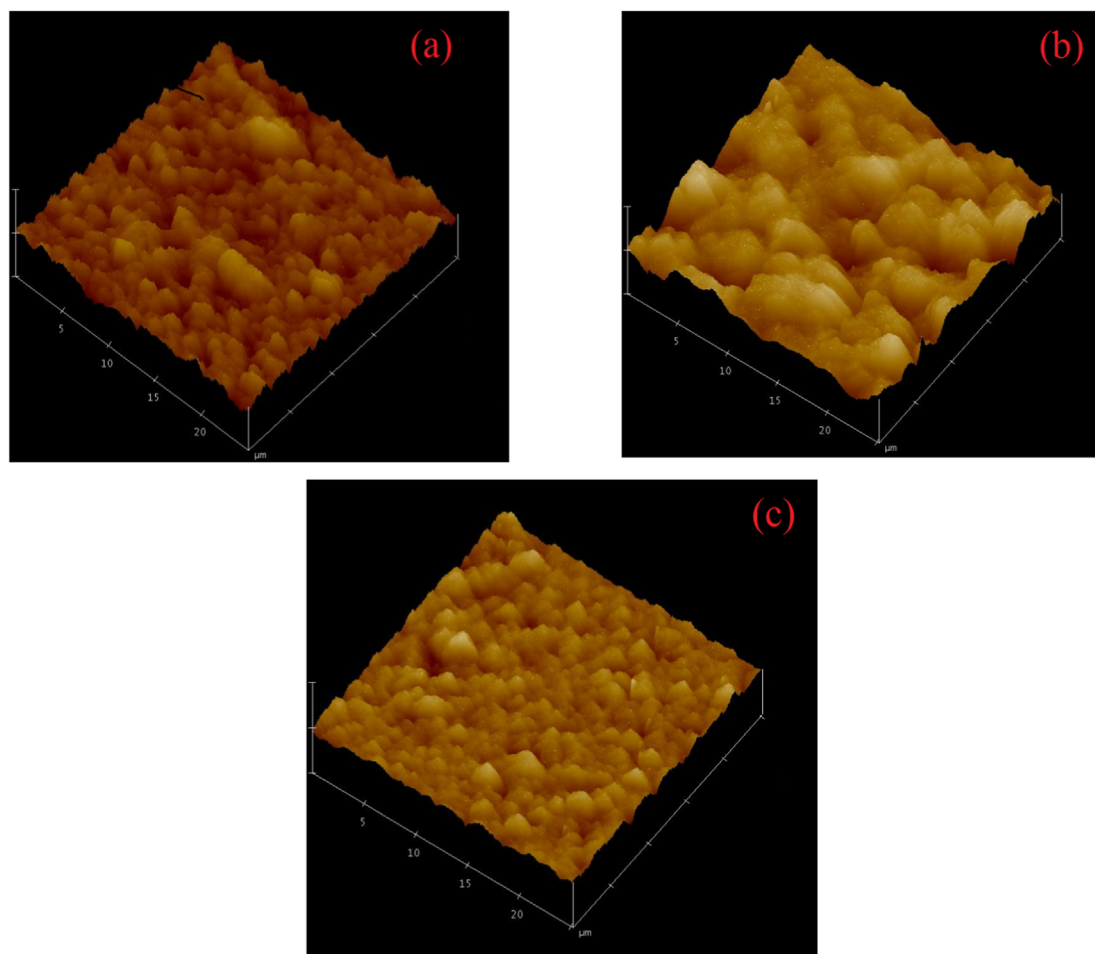


Figure 3. AFM images (3D) of 12 bilayer CHI/CS bilayer membranes (A) CHI/CS membrane (B) CHI/CS membranes with 0.1 M NaCl makeup salt (C) hybrid CHI/CS membrane with one layer PEG.

Table 1. Average thickness of CHI/CS bilayer (bl) membrane system.

| Number of Bilayers | Average thickness (nm) |
|--|------------------------|
| 3 | 72.34 ± 0.81 |
| 6 | 112.40 ± 8.89 |
| 9 | 136.54 ± 12.97 |
| 12 | 146.63 ± 5.90 |
| 12 bl with 0.1 M NaCl | 182.52 ± 13.72 |
| 12 bl CHI/CS with 1 layer PEG (hybrid CHI/CS-PEG membrane) | 173.27 ± 7.19 |

chains [17]. When salts were added in the poly-ionic solution, a random coiling of polymer chains occurs due to screening of like charges like counter ions. The increase in thickness of CHI/CS with 0.1 M salt in both poly-ionic solutions were related with the coiling and folding of polymeric chains resulting in mass gain and thickness [18]. The increase in thickness of hybrid layer was due to the addition of PEG layer to existing 12 bilayer CHI/CS membranes.

The surface morphologies of CHI/CS bilayer membranes were characterized by atomic force microscopy. The AFM images (figure 3) of coated, salted and hybrid membranes showed significant morphological differences. From table 2, different parameters were obtained from AFM images. The RMS roughness values of the bilayer membranes were calculated from AFM images using Gwyddion software. The values obtained for 12 bilayer, 0.1 M NaCl 12 bilayer and hybrid membranes were 83, 123 and 97 nm, respectively. The roughness of the 12 bilayer CHI/CS membrane increased with addition of salt in deposition solution and capping. The pore size was calculated from AFM images using the Image J software. The capping and presence of salt decreased the pore size of the membrane, suggesting that more number of pores is found to be closed. The pore size value of

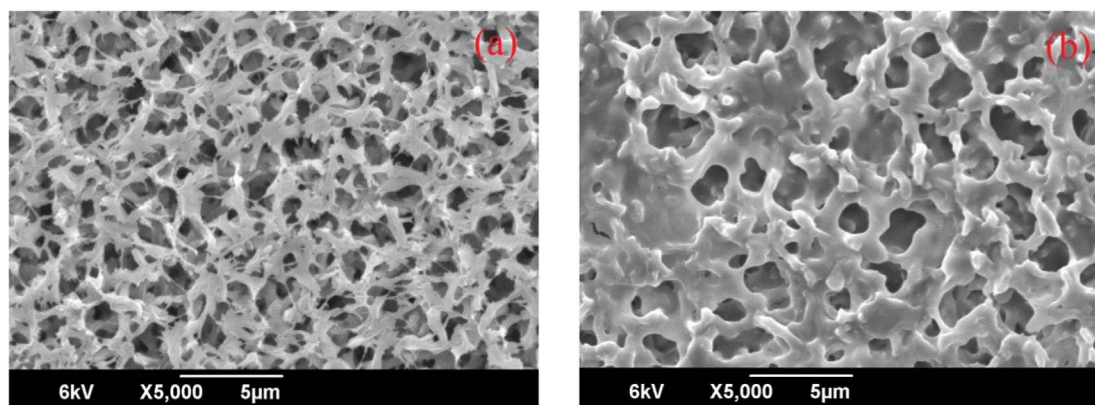


Figure 4. SEM images of ultrapore membrane (a) and 12 bilayer CHI/CS membrane (b).

Table 2. CHI/CS 12 bilayer membrane parameters from AFM images.

| Membrane type | Roughness(nm) | Pore size(μm) | Total area (μm^2) | Solidity | Perimeter(μm) |
|---------------|---------------|----------------------------|--------------------------------|----------|----------------------------|
| 12 bilayer | 83 | 0.189 | 0.239 | 0.761 | 1.797 |
| 0.1 M NaCl | 123 | 0.138 | 0.195 | 0.801 | 1.870 |
| hybrid | 97 | 0.152 | 0.167 | 0.913 | 1.524 |

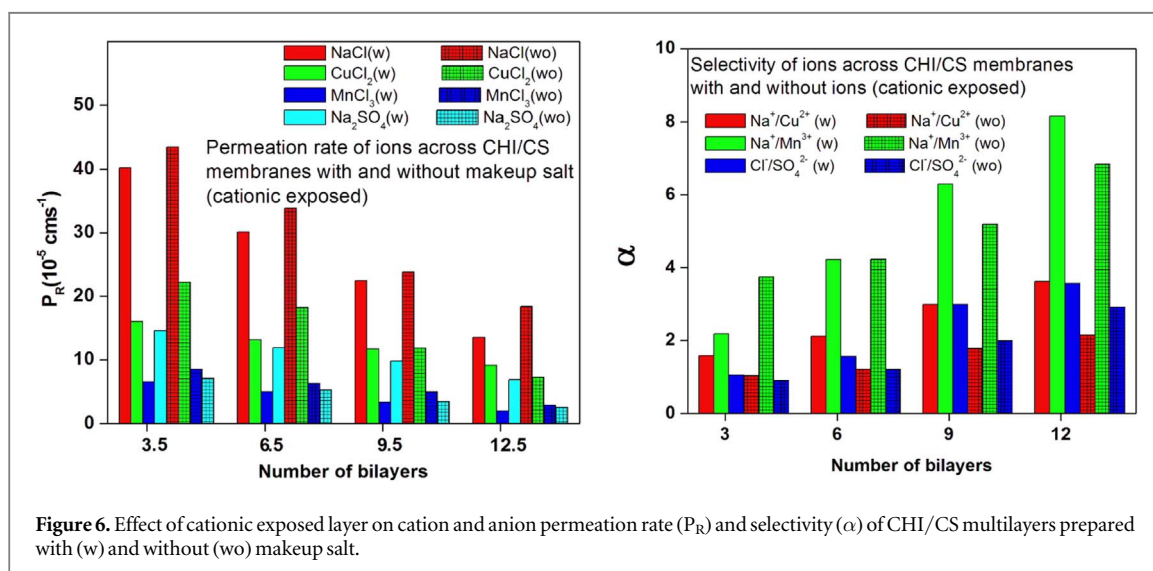
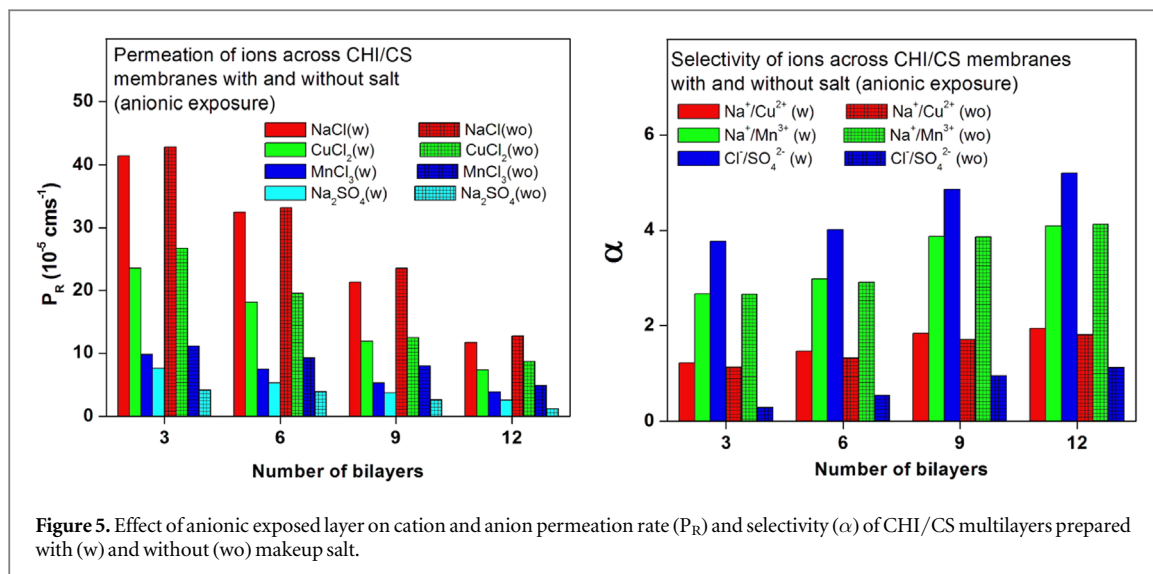
12 bilayer, 0.1 M NaCl 12 bilayer and hybrid membranes were found to be 0.189, 0.138 and 0.152 μm , respectively. The difference in the properties of bilayer surface can be attributed to the change obtained by the addition of salt and capping. With 0.1 M salt concentration, the LbL thickness and mass increase by surface and bulk uptake of polyelectrolytes mainly at/near the PEM surface resulting to a decreased pore size.

The 12 bilayer CHI/CS membrane surface from SEM analysis (figure 4(b)) showed some shaped aggregates of different shape over it making the pore closed at most positions. The addition of nano layers resulted in surface pore filling. The changes in the morphology of ultrapore membrane surface with CHI/CS absorbed can be correlated with interpolymer complexation between CH and CS.

3.2. Effect of exposed layer on ion selectivity using diffusion dialysis method

CHI/CS multilayers were placed between two chambers of membrane chamber (figure 1) for investigating the ion permeation and selectivity. One of the chambers is filled with pure water and the other with 0.1 mol l^{-1} salt solutions. The effect of outermost layer on cation selectivity was studied and the results are presented in figure 5. Experiments were carried out with multilayers ranging from 3 to 12 bilayers prepared with (w) and without (wo) makeup salt (0.1 M NaCl) in CS. The multilayers prepared from salt solution shows better cation selectivity. The CHI/CS bilayers show low permeation rate and considerable increase in $\text{Na}^+/\text{Mn}^{3+}$ selectivity compared with multilayers prepared from salt free conditions. Here the $\text{Na}^+/\text{Mn}^{3+}$ selectivity increases from 2.67 to 4.09. But such a variation is not observed in the case of multilayers with outermost anionic layer. This is due to the effect of outermost layer on permeation rate and ion selectivity. Multilayers with chitosan (CHI) as the outermost layer shows much better cation selectivity compared with outermost anionic layer (CS). This is due to the Donnan exclusion taking place in the multi bipolar bilayers. Thus, for better rejection of anions, multilayer with outermost anionic layer can be used. The high selectivity of $\text{Cl}^-/\text{SO}_4^{2-}$ for anionic exposure is due to high rejection when the charge of the outer layer membrane had the same sign as the divalent ion being rejected. Thus this high selectivity is largely due to ion rejection at membrane bilayer surface.

From figures 5 and 6, it is clear that, monovalent ions shows better permeation rate through the CHI/CS multilayers compared with divalent and trivalent ions. The permeation rate is in the order mono > di > tri. In the presence of salt, the multilayer shows better selectivity for both divalent and trivalent ions. The selective ion transport across membranes depends mainly on the charge and size of ions passing through the membrane [19]. The makeup salt creates some spacing between layers through coiling of polymer strands and is found to be effective in selective ion transport across it. The size of ions decreases with increase in charge (Fajan's Rule). Thus an easy passage of small ions can be expected through bilayer membranes. But here the smallest Mn^{3+} shows low permeation rate. This clearly indicates that, in this case the ionic charge outdates ionic size. The permeation rate in the present study is in the order of $10^{-5} \text{ cm s}^{-1}$, which is comparatively higher rate than usual permeation of



10^{-3} cms^{-1} [20]. The dependence of number of bilayers of CHI/CS multilayers on the selectivity and permeation rate of ions, prepared from salt free and salt added conditions are also evident from above figures. The various results suggest that as the number of bilayers increases, the permeation rate decreases and the selectivity increases.

The permeation rate of divalent and trivalent ions show considerable decrease through multilayer fabricated from salt solution. The selectivity showed an increase in the presence of salt for most cases. The thick layer formed with increased bilayer on the surface of membranes could effectively cover the underlying pores. This is one of the main reasons for the large decrease in permeation rate of ions as the number of bilayer increases.

From figure 6, it is clear that, the dependence of anion selectivity to the number of bilayers are comparable with the results obtained for cations. 12 bl CHI/CS membranes showed 3.62 and 8.15 as the mono/divalent and mono/trivalent selectivity (cationic exposure) respectively. It is clear from the results that trivalent and divalent anions experience much more repulsion and therefore better rejection is observed than monovalent ions. The difference in ionic size and charge can be suggested for the difference in the selectivity. Similar behavior was observed for both anions and cations with a transport rate in the order mono > di > tri. Thus it is clear that, besides ionic charge density, ionic size also plays an important role in its transport. The figure 7 gives the change in topography of bilayer with addition of makeup salts in polyelectrolytes with closure of pores.

The effect of concentration polarization is limited in this case due to lack of current densities. The selective uptake of preferred ions evidently leads to much lower counterion mobility in the bilayer as a result of the binding effect. The transport numbers of preferred counterions increase less rapidly than their

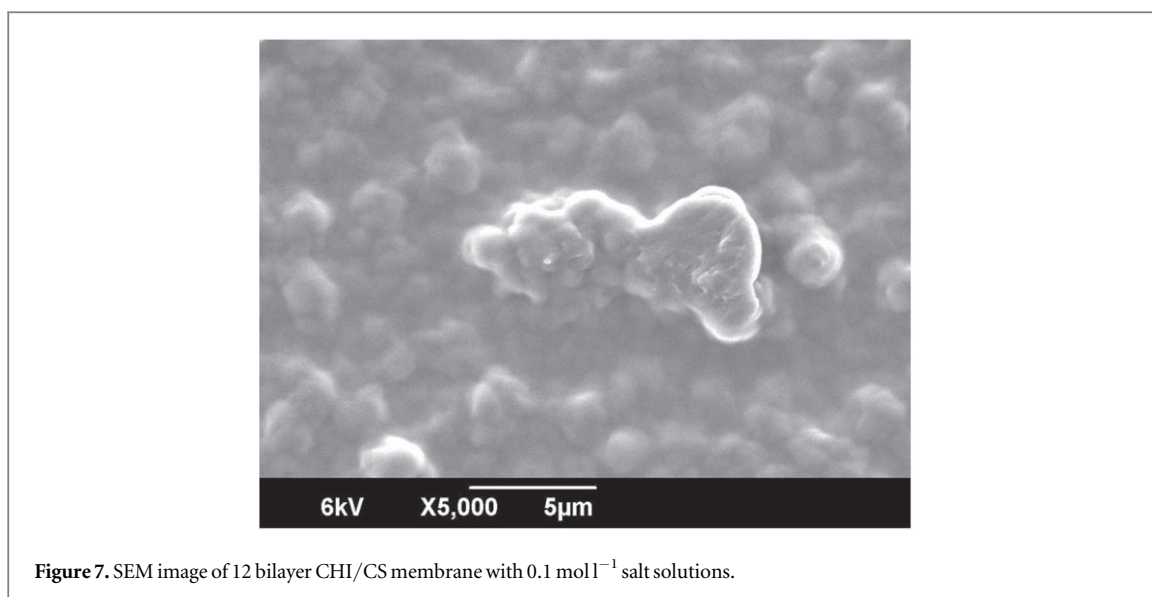


Figure 7. SEM image of 12 bilayer CHI/CS membrane with 0.1 mol l^{-1} salt solutions.

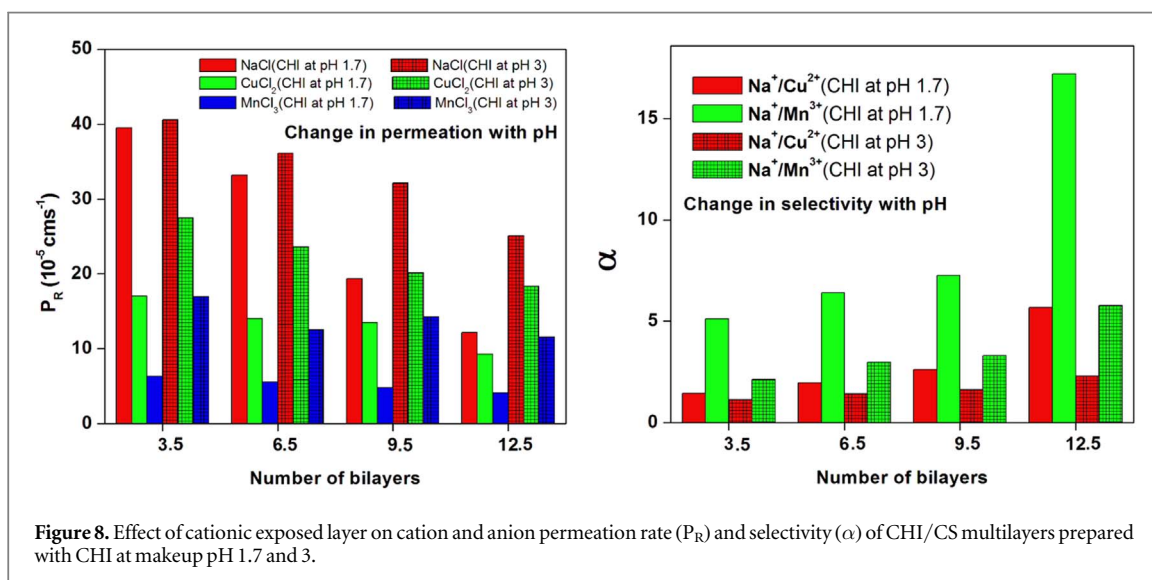


Figure 8. Effect of cationic exposed layer on cation and anion permeation rate (P_R) and selectivity (α) of CHI/CS multilayers prepared with CHI at makeup pH 1.7 and 3.

equivalent fractions in the hetero ionic state. The higher selective uptake of the trivalent ion than lower ones by the bilayer membrane would be on the basis of the electrostatic interaction rather than concentration polarization effect.

3.3. Effect of makeup pH on permeation rate and selectivity

The exposed layer of membrane has a greater role in ion transport studies than the inner layers. The ions in solution are directly interacting with the outer layer of multilayer. Thus, the properties of multilayers formed from oppositely charged polyelectrolytes greatly influence the ion permeation. The weak polyelectrolytes have different fabrication capacity due to change in their charge intensity at different pH [21]. So makeup pH of selected polyelectrolytes is very important during its preparation. Multilayers were prepared from CHI solution with pH 1.7 and 3 for studying the effect of pH of CHI on cation selectivity. CS is deposited from salt solution (0.1 mol l^{-1}) at pH 3. The results of pH dependent transport studies are given in figure 8. The divalent and trivalent selectivity is better at pH 1.7 with 12.5 bilayers. At pH 1.7, the CHI/CS membranes showed a monovalent/trivalent ion selectivity of 17.21 while a lower mono/divalent selectivity of 5.66 was observed for the same bilayer system.

All the ionic transport across the bilayer membrane can be explained on the basis of difference in interaction between transport ions and bilayers at different pH. The degrees of ionization of functional groups of weaker polyelectrolytes responsible for nano bilayer formation (PEM) are highly affected by change in pH. The

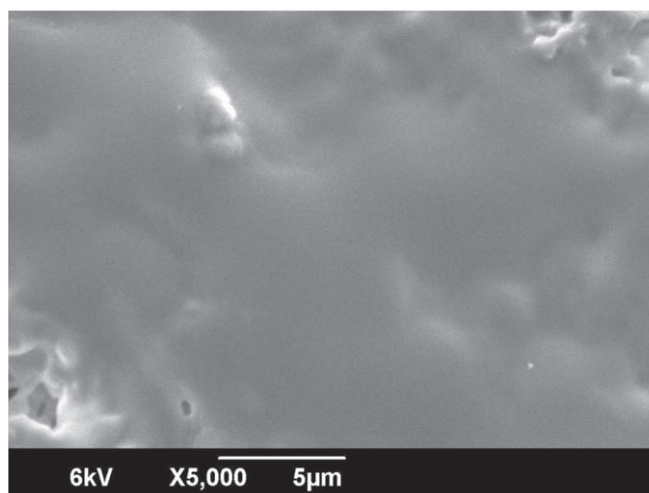


Figure 9. SEM image of 12 bilayer hybrid CHI/CS-PEG membrane.

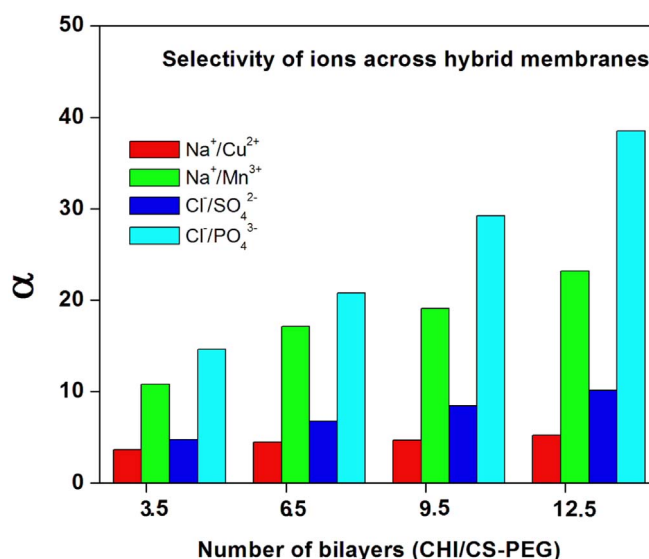


Figure 10. Selectivity of cations and anions through hybrid multilayers as a function of number of layer.

polyelectrolyte bilayer assembly attains serious change due to change in surface charge density, texture and other properties. In the case of CHI/CS bilayers, the pKa value of weak polyelectrolyte CHI is 6.2. Thus, CHI is positively charged below this pH range and the degree of protonation increases at pH 1.7. A highly ionized CHI at this pH and CS with makeup salt forms thicker bilayers which could hold charged molecules and ions inside its bilayer structure.

The thick multilayer formed in the presence of salt was found to enhance the ion selectivity [22]. As the transport ions travel more to permeate through thicker bilayers, the chance of interaction of ions with active binding sites of bilayer matrix also increases. Moreover, the surface charge densities of exposed CHI layer also get influenced by CS salt concentration. The change in inter-penetration properties due to increase in the Debye length which intern control the short ranged forces in the multilayer [23]. Thus, makeup pH's along with presence of salt are important parameters through which transport of ions across bilayers can be varied.

3.4. Effect of capping on selectivity of cations and anions

Capping of multilayers is a method employed to improve the ion selectivity without affecting the flux or permeation rate through the membrane. It can influence the nature of the CHI/CS multilayers as PEG got incorporated into it. The change in nature and charge density with new charge sites can enhance the possibility

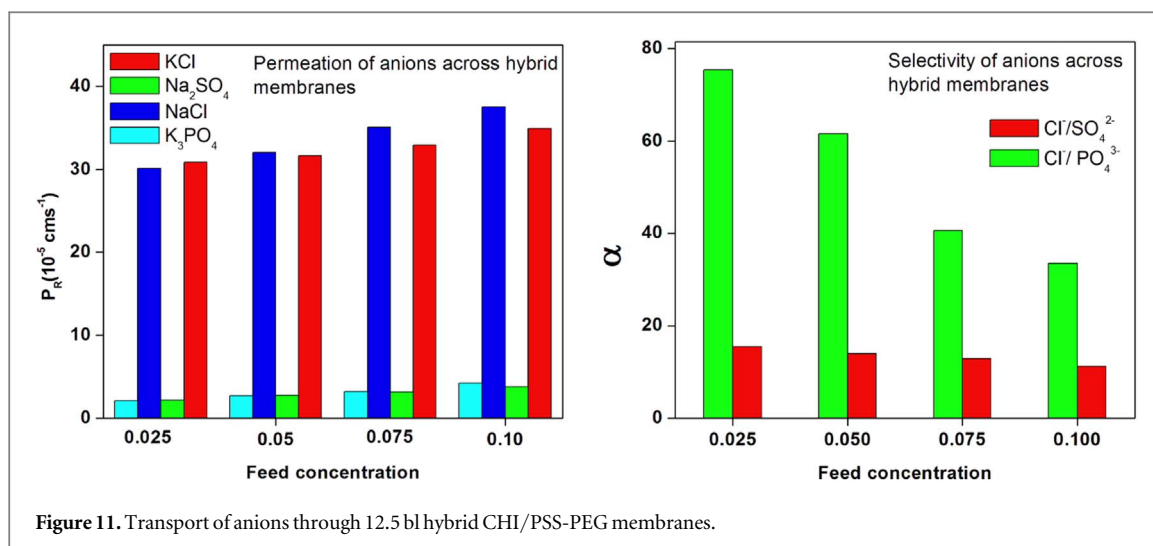


Figure 11. Transport of anions through 12.5 bl hybrid CHI/PSS-PEG membranes.

of better ion selectivity. The change in surface morphology for hybrid layers can be obtained from SEM image (figure 9). The surface coverage is more intense in the hybrid membrane and it can influence the overall performance of multilayer in ion selectivity.

From figure 10, results show the effect of capping on selectivity of both cations and anions. When compared with uncapped bilayer membranes, both cations and anions show enhanced selectivity through hybrid multilayers. The $\text{Na}^+/\text{Cu}^{2+}$ selectivity increases from 1.86 to 5.26 and $\text{Na}^+/\text{Mn}^{3+}$ selectivity increases from 4.09 to 23.17. This is almost 6 fold increase in selectivity compared with uncapped films (figures 5 and 6). The selectivity of anions show a large increase in the presence of capped layers. It increases from 1.81 to 10.14 in the case of monovalent/divalent ion selectivity, $\text{Cl}^-/\text{PO}_4^{3-}$ selectivity increases from 4.13 to 38.52. These values showed that hybrid membranes had increased the ionic selectivity to many folds. The change in surface morphology for hybrid layers can be viewed from SEM images (figure 9). Surface coverage is more in hybrid layers and it may improve the overall performance of multilayer during transport studies. The negatively charged electron clouds from electronegative oxygen strongly repel similar charges. Hence the permeation rate of anions shows a large decrease after capping. The enhanced selectivity and reduction in permeation rate in the case of anions is thus due to the change in surface morphology together with charge interactions. Also, the denser layer formed due to capping attains better surface ion rejection as the chance of swelling is not possible. Greater ionic interaction can be expected with capping and is thus a novel idea which is to be implemented in a wide range of membrane ion transport applications.

3.5. Effect of feed concentration on selectivity

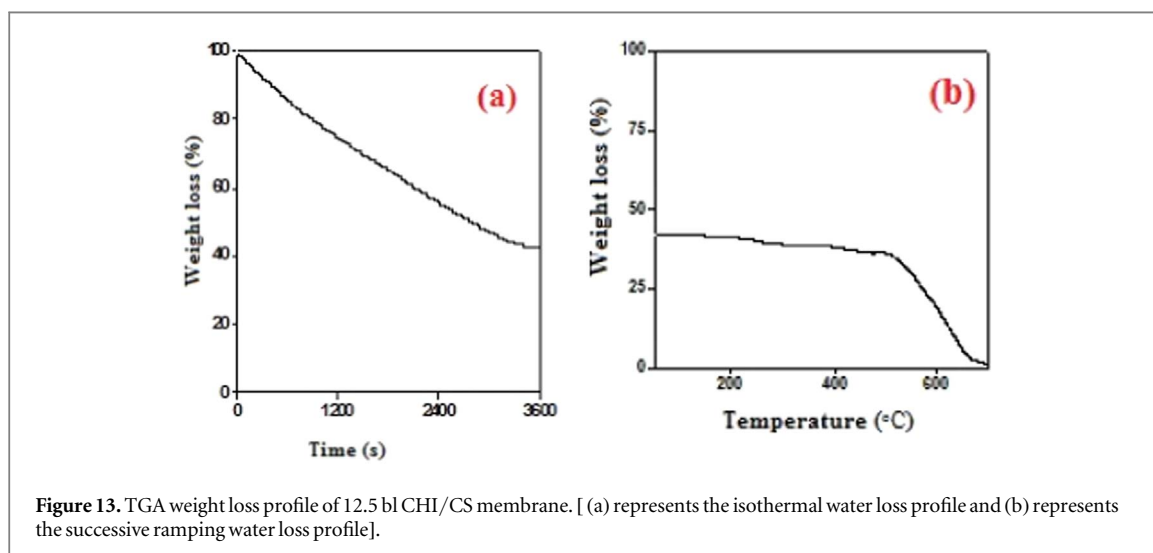
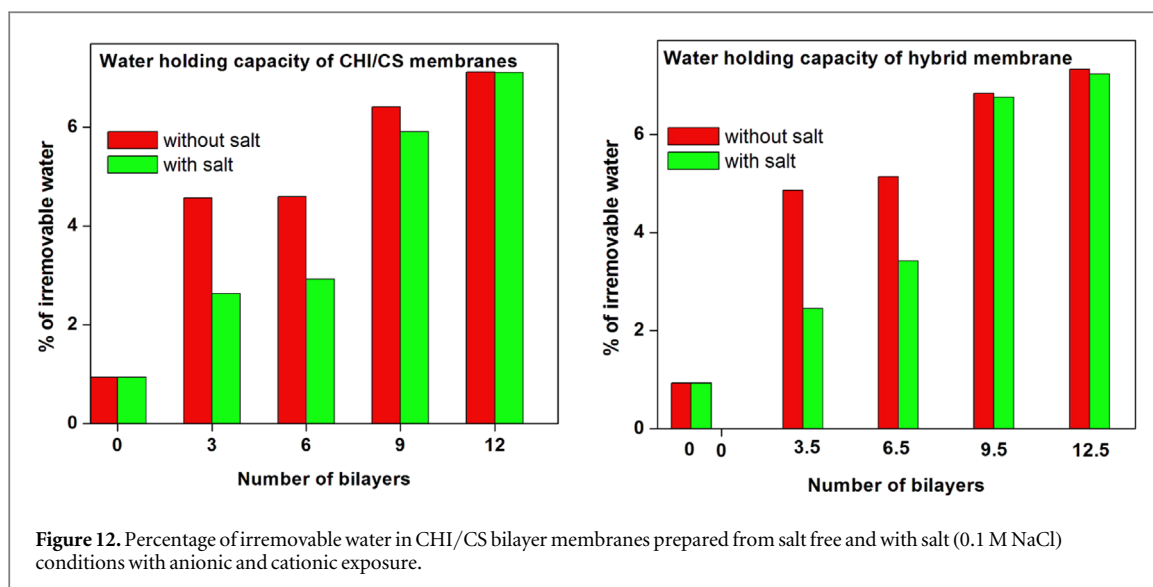
Effect of feed concentration on anion selectivity through PEG capped layer is presented in figure 11. Results show that the feed concentration slightly affects the permeation rate and selectivity. The permeation rate of anions decreased with decrease in the feed concentration of salt solution, but the selectivity found to increase. The $\text{Cl}^-/\text{SO}_4^{2-}$ selectivity increases from 11.14 to 15.47 during a change in feed concentration from 0.1 to 0.025 mol l^{-1} . Similar trends are obtained for $\text{Cl}^-/\text{PO}_4^{3-}$. Here the initial selectivity of 33.52 increases to 75.42 as we changed the feed concentration from 0.1 to 0.025 mol l^{-1} . The reason for this high selectivity under low feed concentration is the effective interaction of charged sites with ions.

As the anions start moving through the capped bilayers, they have first to overcome the boundary-layer resistance on the tube side. A concentration gradient usually exists in this region, whose thickness depends on the hydrodynamic conditions. A higher selectivity or lower permeation rate means a higher resistance is created for anions due to capping. Again, the electron cloud due to capping creates an electrical potential known as the Donnan potential at the boundary between the capped bilayer membrane and the solution. The Donnan potential attracts cations to the membrane while repelling anions away, thus increasing anion selectivity.

In the above case, the possibility of concentration polarization and fouling is negligible. From the integrity test of capped CHI/PSS-PEG hybrid layers, it is evident that there is no fouling or concentration polarization near the surface of multilayers.

3.6. Water holding capacity of CHI/PSS multilayers and ion transport

The water content in the CHI/CS multilayer membranes were determined using thermo gravimetric analysis. Thermal analyses of both bare and multilayer membranes were carried out in two successive steps i.e., isothermal water loss and ramping water loss. In the first step, the bilayer membrane was kept at room

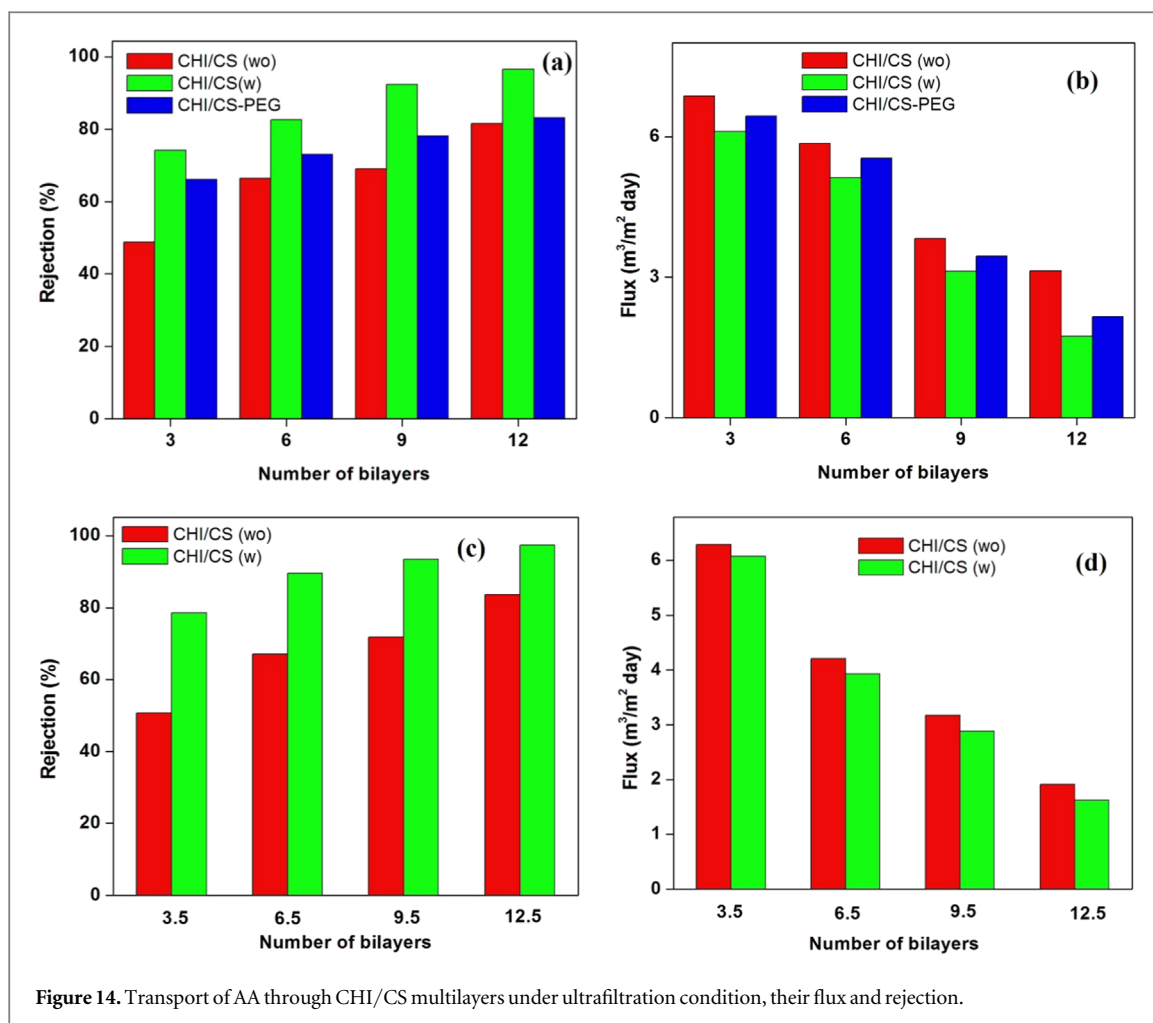


temperature for two hours under dry N_2 atmosphere and in the successive ramping loss process, the bilayer membrane was heated up to $800\text{ }^\circ\text{C}$ at a rate of $20\text{ }^\circ\text{C}/\text{min}$. Figure 12 represents the percentage of water content the bilayers at a temperature range of $100\text{ }^\circ\text{C}$ – $500\text{ }^\circ\text{C}$.

From TGA results, as the number of bilayer increases, the percentage of irremovable water in the multilayer also increases. Polyelectrolyte like CS is hydrophilic enough to attract water molecules and shows swelling as per its concentration [24]. This phenomenon is due to the affinity of charged polyelectrolyte sites to make bonds with water molecules. So deposition of polyelectrolytes increases the surface roughness, and rough surface swells more in the presence of water than a comparatively smooth unmodified membrane surface. Membrane prepared from aqueous solution shows slightly higher values of percentage water content compared with membrane fabricated from salt solution.

Figure 13 represents the TGA weight loss profile of 12.5 bilayer CHI/CS membranes. Figure 13(a) represents the isothermal water loss profile while figure 13(b) represents the successive ramping water loss profile. The absolute water content hold by bilayer membranes is obtained by analyzing the weight loss at different temperatures. The percentage weight loss of 12.5 bilayer CHI/CS membrane between $100\text{ }^\circ\text{C}$ and $500\text{ }^\circ\text{C}$ is 8.241 and that of the bare ultipore is 0.931 only. This is indicative of the better ability of polyelectrolyte multilayers to hold water.

The fast isothermal water loss (figure 13(a)) is due to the release of adsorbed water from the hydrated multilayer membrane matrix. The adsorbed water molecules within the bilayers are bonded with each other and to the ionic moieties by weak bonds. The interconnecting channel formed due to percolation structures inside



bilayers determine the transport of ions and water through it [25]. The high ion exchange and water diffusion capacity results the fast dehydration process of multilayers in the isothermal water loss profile.

In figure 13(b), the weight loss after 120 °C up to 140 °C is due to drying of water tetrahedrally coordinated with the ionic groups in the polymer matrix. This type of two stage water loss profile is not observed with fewer numbers of bilayers. Between 470 °C–550 °C temperature range, there exist only one major decomposition stage, is due to the decomposition of hard polymer segment and the polyionic segments of bilayers. The ultipore membranes completely decomposed to about 99.39% while the coated membranes (12 bilayered) showed more thermal stability of about 97.23%.

3.7. Permeation study of ascorbic acid (AA) through CHI/CS multilayers

The selective transport of small molecules from solution is as important as ion transport. Both have wide range of applications in medical field and industry [26]. Ascorbic acid or vitamin C is a vital nutrient and having significant role in many human physiological processes with pKa values of 4.17 and 11.6 [27]. Here, the transport of AA through CHI/CS multilayers prepared in the presence and in the absence of salt under pressure driven method is examined. This study also investigates the effect of salt in the selective transport of AA through CHI/CS-PEG hybrid membranes.

The rejection of AA through CHI/CS bilayers and hybrid membranes (figure 14(a)) increased with increase in the number of bilayers. The bilayer membrane showed extra rejection efficiency with makeup salt (0.1 M NaCl) solution, also found better than hybrid membranes. In the presence of salt the bilayers attain more thickness with an increased surface charge density due to conformational changes. The enhanced coiling and folding of polymer chains takes place causing thickness helped in better rejection. This also provides more sites in bilayers for the effective interactions between AA and multilayers. About ~98% of rejection is achieved by the present system in the presence of salt. Thus, it is clear that the rejection of AA is mainly depends on hydrophilic interaction and steric hindrance, which outcasts the dip in electrostatic interaction due to screening effect. Lower, but comparable rejection efficiency was achieved by the same system without salt and by hybrid membranes. The increased thickness in presence of salt lowered the flux of CHI/CS bilayer membrane system.

4. Conclusion

CHI/CS multilayer membranes are capable of effective diffusion dialysis for rejecting ions from aqueous electrolyte solutions. In the case of diffusion dialysis experiment, the divalent ions are rejected by Donnan exclusion as there is increase in the valency. Transmembrane conductivity show that CHI/CS films are more selectively permeable to anions than cations in more cases, but this selectivity increases with increasing bilayers. Capping with PEG for hybrid bilayer membranes further increased the ion selectivity. Ion selectivity also decreases with increase in feed concentration. Water holding capacity of CHI/CS multilayer increases with increase in number of bilayers. Better rejection of folic acid (AA) using CHI/CS under ultrafiltration condition indicates that this system can be a potential methodology for its purification and expected to be extended for some pollutants. As the magnitude of negative rejection decreases with the trace ion mobility and the method might prove useful in selective removal of various cations from electrolyte mixtures containing multiply charged cations.

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