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Stability and Performance Study of Polyethersulfone Membranes Modified Using Polyelectrolytes

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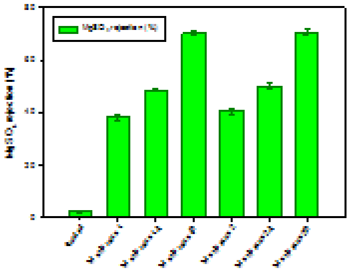
Graphical abstract



Abstract

In this research work, porous PES membranes were initially pre-heated for certain duration of time and then surface-modified to reject the $MgSO_4$ salt solutions through self-adsorption of polyelectrolytes. From the experimental work, higher membrane salt rejection capability can be obtained when the number of polyelectrolyte bilayers is increased. The images of the cross-sectional morphology of modified and non-modified membranes were obtained using field emission scanning electron microscopy (FESEM). All modified membranes showed relatively lower contact angle values.

Keywords: Polyelectrolytes; adsorption; salt rejection; membrane stability; heat treatment

■1.0 INTRODUCTION

Nanofiltration membranes differ from the reverse osmosis membranes mainly due to the fact that the nanofiltration membranes are specifically designed for the retention of multivalent ions or organic contaminants while allowing the permeation of others.[1, 2] Lower operating pressure of the nanofiltration membranes is another added advantage when compared to the reverse osmosis membranes due to the fact that the compounds that pass through the nanofiltration membranes will not elevate the osmotic pressure in the system.[1] Depending on the type of nanofiltration membrane and solute involved, several mechanisms are used to explain the solute rejection performances observed. The mechanisms employed in explaining the nanofiltration performances including physical sieving, electrostatic exclusion or adsorption and diffusion limitation. When neutrally charged solutes are present in the feed solution of filtration system, the main mechanism contributed to the rejection performance will be based on the steric hindrance. According to the work conducted previously by a group of researchers,[3] the membrane porosity has been confirmed to be the key factor during the rejection of solutes, especially neutrally charged solutes, where the solute molecular weights and the membrane pore size distributions can be well correlated to each other. Thus, controlling the membrane porosity using membrane heat treatment and polyelectrolyte self-assembly methods are believed to be able to modify the membrane final porous structure.

The production of NF membranes has benefited from the polyelectrolyte film coatings. It has been shown in the past research studies that the adsorption of neutrally, positively and negatively charged polyelectrolytes onto a material can contribute to the formation of extremely thin films and at the same time greatly alter the properties of the final material.[4, 5] When polyelectrolytes with opposite charges are alternatively adsorbed onto the substrate through the layer-by-layer (LbL) method, the thin film formed is sometimes designated as polyelectrolyte multilayer (PEM) film.[6] Layer-by-layer adsorption of polyelectrolytes onto the membrane surfaces had been successfully performed by several researchers.[7-10] This technique has been well-accepted in several research studies (especially regarding membrane modification) due to its simplicity and low production cost.[11] This technique also provides the desired performances in designated applications.

This work will present the possibility of combining this technique with membrane heat treatment to obtain the final membrane with improved hydrophilicity and rejection capability.

Formerly, polyethersulphone hollow-fiber membranes were reported to be sensitive towards the heat-treatment.[12] Researchers conducted several experimental works to determine the factors that can significantly affect the membrane performances during the heat treatment process. They concluded that the heating temperature and duration played the most important roles in determining the membrane characteristics. After the PES membranes were exposed to the heat-treatment, a significant decrease in flux and an increase in solute separation was observed. Similar heat treatment was also conducted on polyacrylonitrile membranes as reported.[13] Researchers found no significant changes for the surface pore size. In addition, some other works performed previously confirmed that the heat treatment can increase the membrane rejection property.[14] However, this improvement was accompanied by a significant flux reduction as well. It is hoped that by combining the heat-treatment and polyelectrolyte layers in the current work, membrane performance can be further improved in term of solute separation capability.

■2.0 EXPERIMENTAL

2.1 Materials

Polyethersulphone membrane was employed as the membrane support throughout this study. The commercial membrane PES20 was purchased from Amfor Inc., China. Polysodium-4-styrenesulfonate (PSS) solution with an average molecular weight of 1,000,000 and polydiallyldimethylammonium chloride (PDADMAC) solution with an average molecular weight of 400,000-500,000 were purchased from Sigma-Aldrich. In the current work, dry polyelectrolytes were avoided during the polyelectrolyte solution preparation as powdered sample would typically constitute 10 wt% or more water. $MgSO_4$ salt was purchased from Merck and used without further purification.

2.2 Membrane Surface Modification

During the membrane surface modification, a simple tool was used to assist the self-adsorption process. This device consists of a metal plate which was used as support at the bottom side of tool. It consist of an O-ring to position the membrane onto the metal plate and to prevent the polyelectrolyte solutions in direct contact with the PES membrane support side after these components are clamped tightly. This could be used to ensure a single-sided modification on the membrane active separation layer only. Single-sided modification is more preferable in this work as it can provide almost the same performances while maintaining the membrane pure water fluxes. Further discussion and comparison between the single-sided and double-sided modification methods were reported elsewhere.[15] Before the first layer of PDADMAC was deposited, the porous PES membrane was immersed in 0.5 M caustic solution for at least 2 hours. Immersion of the membrane in caustic solution was for cleaning purposes as reported by others.[16, 17] Besides, immersion of the membrane in caustic solution was also to improve the deposition efficiency.[18] The membranes were then intensively cleaned with RO water[18] for 30 minutes before the layer-by-layer modification of the membrane surfaces. Besides self-adsorption, this work also employed heat-treatment on the modified membranes for certain durations. In the current work, membranes were pre-heated for duration of either 0, 10 or 20 minutes, with or without the polyelectrolyte bilayer. The membrane label, heating duration and number of polyelectrolyte bilayer were tabulated in the Table 1.

Table 1 Membrane labels with their respective modification conditions

Membrane label	Heating duration at 50 ºC / min	Number of polyelectrolyte bilayer
Control	0	0
Membrane 1	10	0
Membrane 1A	10	1
Membrane 1B	10	2
Membrane 2	20	0
Membrane 2A	20	1
Membrane 2B	20	2

2.3 Characterizations

2.3.1 Membrane Permeability

Membrane permeabilities were determined from the pure water flux measurements using RO water at room temperature using Sterlitech HP4750 Stirred Cell. The dead-end filtration cell has an active membrane area (effective area) of 14.6 cm^2 and it has been extensively used in the previous works to produce reliable performances and results.[19-21] The membranes in the current work were also back-flushed after being tested with salt solution in order to investigate the stability of the thin films formed on top of the membrane supports. Each of the membrane permeability obtained after back-flushing was compared with the membrane initial permeability, it was then expressed in the form of permeability difference in percentage.

2.3.2 Salt Rejection Study

Although in certain study low solution stirring rate of as low as 400 rpm was employed,[22] this stirring rate was not employed in the current study. Besides, previous work[22] also observed that when the solution stirring rate was increased from 300 rpm to 900 rpm, it only increased the membrane rejection of about 1 %. They claimed that when the membrane permeability decreases, the effect of polarization layers increases significantly. Thus, in this case where various types of membranes having different permeability values, a fixed solution stirring rate was employed during the salt rejection tests. Salt rejection tests in this experiment were conducted at a stirring rate of about 600 rpm, which was aimed to reduce the concentration polarization effects and a solution concentration of 100 ppm was used. The permeate concentrations were determined using the measurements based on the electrical conductivity.[22] The salt concentration values were then determined based on the previously plotted standard curves. Thus, the membrane observed rejection capability (R_{obs}) could be calculated using the Equation (1) as shown:

$$R_{obs}\% = (1 - \frac{C_P}{C_f}) \times 100\% \qquad (1)$$

where C_p and C_f are the concentrations for permeate and feed solutions in unit ppm.[23]

2.3.3 Membrane Surface Hydrophilicity

One of the most effective methods used to measure the polymeric membrane surface hydrophilicity is through the contact angle measurement using sessile drop method. Sessile drop method can be divided into two, static and dynamic sessile drop method. The former method was used throughout this study as it is easier for operation[24] and it can produce higher consistency with less human operation error. RO water was used as polar liquid for contact angle measurements.[24] The contact angles for all the membrane samples were measured using goniometer Drop Shape Analysis System, DSA100, KrussGmbH, Germany. Syringe needle of 0.15 mm was used to produce a 3 µL drop of test liquid at ambient environment.

2.3.4 Membrane Cross-Sectional Morphology

The membrane cross-sectional morphologies were scanned using Gemini model SUPRA 55VP-ZEISS (Oberkochen, Germany). Similarly to the previous work,[25] the cross-sections of the membranes were prepared by fracturing the membranes at the temperature of liquid nitrogen before sputtered with gold for better resolution.

■3.0 RESULTS AND DISCUSSION

3.1 FESEM Analysis Result

Cross-sectional images of FESEM were displayed in the Figure 1. The objective of employing SEM in the current study is to capture the image of thin film formed after the self-adsorption of polyelectrolytes. Both of the membranes displayed typical asymmetric morphology with finger-like pores linked by spongy walls. The thin film formation can be clearly seen from the FESEM image obtained. Layer-by-layer construction of the polyelectrolyte separation thin film has been confirmed to be able to increase the thin film thickness as reported previously.[18, 26] Thus, measurement of the separation layer thickness is not concerned throughout this study. Besides, the reduction in the pore and macro-void sizes is not significant for membrane heated at 50 degree Celsius, which was reported previously.[27] Other researchers explained that the increase in the membrane separation layer thickness after deposited with polyelectrolyte molecules was the reason for increased trans-membrane resistance. This thus contributed to lower pure water permeability observed, which will be discussed later.

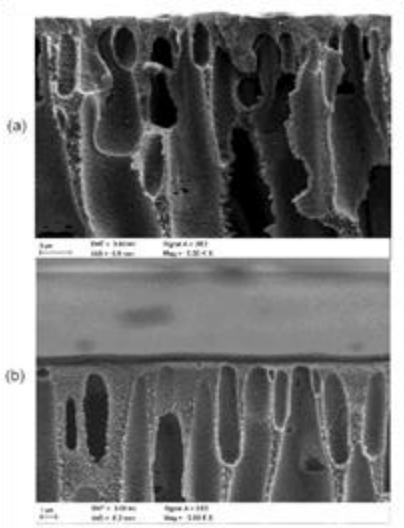


Figure 1 Membrane cross-sectional morphology for: (a) control membrane and (b) membrane 1B

3.2 Membrane Surface Contact Angle

Heat treatment employed to modify the polyethersulphone membrane has very little or negligible effect towards the membrane surface hydrophilicity. By referring to the Figure 2, the control membrane, Membrane 1 and Membrane 2, recorded similar surface hydrophilicity even though these membranes were exposed to various heat treatment durations. Previously, researchers also found similar findings when they heat-treated polyethersulphone and poly(vinylidene fluoride) membranes.14 They found that the membrane surface contact angle readings, for both polyethersulphone and poly(vinylidene fluoride) membranes, remained the same even they used high temperatures during the heat-treatment process. This observation is logical as the membrane surface chemistry, which has a significant effect towards the material hydrophilicity, is not changed. However, the observed membrane surface contact angles reduced when the polyelectrolyte bilayers were deposited onto the membrane surfaces. Membrane 1A, Membrane 1B, Membrane 2A and Membrane 2B showed higher surface hydrophilicity after the deposition of polyelectrolyte layers. However, the differences observed are relatively small and this observation was in good agreement with other researchers.28 They claimed that the membrane hydrophilicity was only greatly improved when more than five bilayers were adsorbed onto the membrane surface. For every single layer of polyelectrolyte adsorbed, the membrane contact angle was not constant due to fact that the PDADMAC surface is considered hydrophobic and the PSS surface is considered hydrophilic.29 Thus, it is highly suggested that the PSS (or any hydrophilic polyelectrolyte) should be used in the LbL method as the last surface coating to increase the overall membrane hydrophilicity and thus reduce the membrane fouling based on the findings in this study. However, the observed hydrophilicity property of PSS, and whether this is also true for other types of polyanions (with the same or different molecular weight), is worth further investigation.

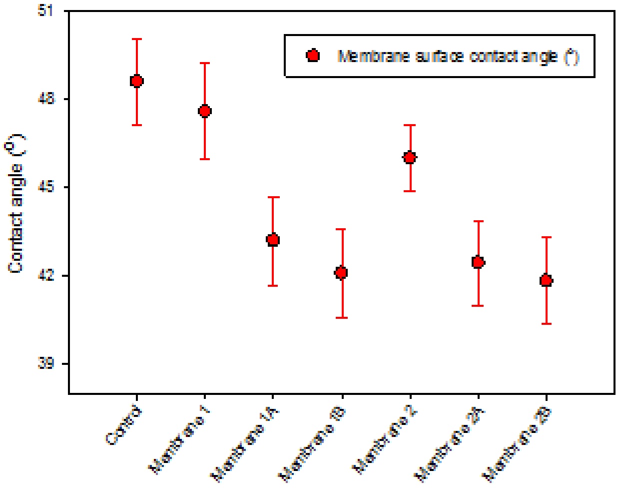


Figure 2 Membrane surface hydrophilicity changes due to different heat treatment duration and number of polyelectrolyte bilayer

3.3 The Effect of Membrane Heating Duration and Number of Polyelectrolyte Bilayer Towards the Membrane Permeability

Comparison between the control, Membrane 1 and Membrane 2 (by referring to Figure 3) confirmed that the membrane permeability could be significantly affected after the membranes were heat-treated. This observation has been reasoned with the morphological changes of membrane porous structures and the increased membrane separation thicknesses as reported.14 Besides, the membranes showed significant reduction in pure water permeability after the membranes were deposited with polyelectrolyte bilayers. In a previous study where researchers used the same deposition method,28 a loss in the pure water flux was recorded in comparison to the membrane before modification with polyelectrolyte multilayers. The authors claimed that the reduction in the pure water flux was due to the increased total membrane resistance as a result of polymer chains built on the membrane surface. In another work30 which employed PSS/PAH and PSS/PDADMAC multilayers, researchers suggested that in certain cases, the flux reduction observed can be contributed by the polyelectrolyte adsorption within the pores of porous support as well. However, they were unable to provide solid evidence through the FESEM imaging.

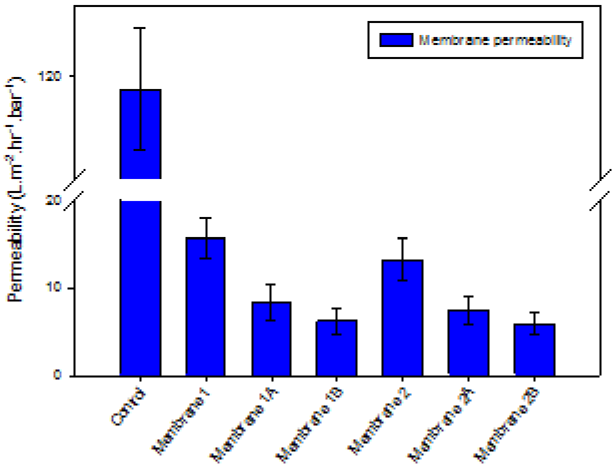


Figure 3 Membrane permeability results for non-modified, heat-treated and polyelectrolyte-modified membranes

3.4 Salt Solution Rejection Test

By referring to the Figure 4, heat-treated membranes displayed several times higher salt retention capability, when compared to the non-modified control membrane. By employing heat-treatment alone, the membrane retention can be increased significantly due to the shrinkage of membrane porous structures.14 This observation can be confirmed with the obtained permeability results which recorded a significant reduction after the heat treatment. Besides, it was observed that the salt rejection capability increased with increasing number of bilayers. Higher number of bilayers adsorbed which contributed to better size-exclusion mechanism can be explained using the three zones model.31 In the proposed three zones model, Zone I and Zone III will preserve their specific characteristics. Only in the zone III, the outermost layers, will display classic polyion-like behavior. As the number of bilayers increases, the only significant difference would be in the zone II. Since Zone II will grow in thickness with increasing number of bilayers, it contributed to better pore sealing effect and size exclusion effect. These combined effects thus contributed to higher rejection towards the solutes. At the current stage, it can be confirmed that by combining both of the heat-treatment and polyelectrolyte adsorption methods, membrane solute retention property can be further improved. However, heat-treatment and polyelectrolyte solution parameters still need further optimization in obtaining the membrane with the best performance.

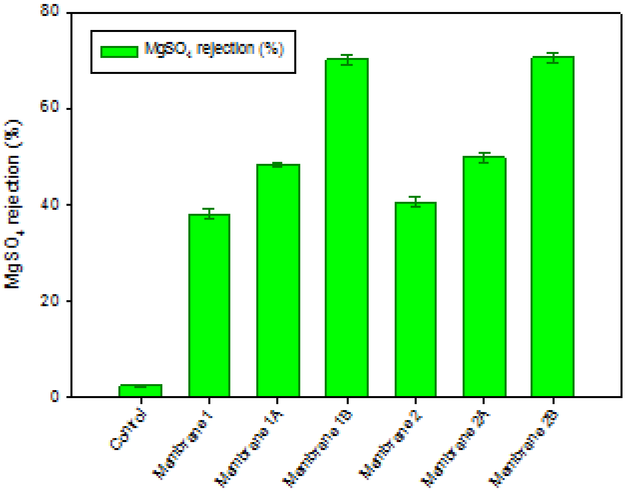


Figure 4 MgSO4 salt solution rejections at a concentration of 100 ppm

3.5 Membrane Permeability After Back-Flushing

Stability of the multilayer formation on the membrane substrates is seldom studied in many of the previous works. The reason for this observation can be due to the fact that there is no any well-organized or standardized method to evaluate the multilayer formation stability. However, the multilayer formation stability is important to evaluate the membrane performances in the long term applications. In the current work, the common membrane cleaning practice (back-flushing) was employed as a method to investigate the stability of the polyelectrolyte layers formed. For better evaluation, the membrane was back-flushed for at least 30 minutes and the membrane permeability was re-measured again. The results obtained are displayed in the Figure 5.

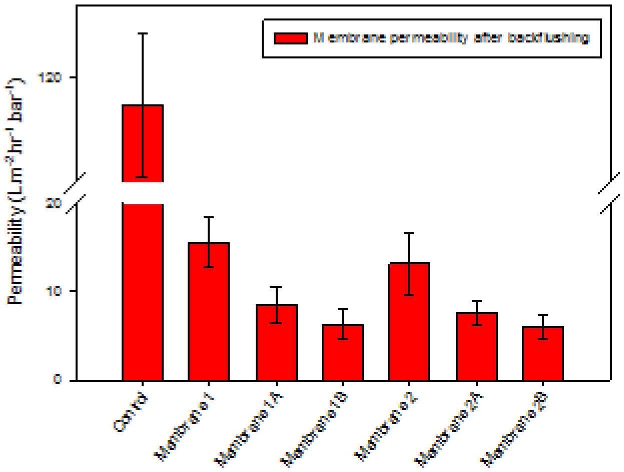


Figure 5 Membrane permeability results after back-flushing

As the membranes were tested with salt solution before the back-flushing process, some of the membrane permeability differences recorded negative values for irrecoverable fouling (refer to Figure 6). The membrane permeability (P) differences were calculated based on the Equation (2) as shown:

$$\Delta P\ (\%) = \frac{[P_{before} - P_{after}]}{[P_{before}]} \times 100\% \qquad (2)$$

However, the values of permeability differences recorded are relatively small and thus it can be postulated that the irrecoverable fouling can be neglected throughout this study. All of the polyelectrolyte-modified membranes displayed slightly increased permeability after the back-flushing process. However, all of the differences were less than 5 %, which indicated that the polyelectrolyte-modified membranes can withstand certain back-flushing conditions and thus provided good performance stability. By comparing with a previous work, cellulose acetate NF membranes were used as the support membranes during the static LbL deposition method in 2004.32 The investigators applied chitosan and sodium alginate polyelectrolyte layers with high molecular weights during the membrane modification. It was discovered that the permeation rates of salt solutions were higher than that of pure water after the membranes were modified with those weakly charged polyelectrolytes. Thus, they postulated that the increase in the solution fluxes could have been due to the detachment of the polyelectrolyte layers from the surfaces as the charge density for both the polyelectrolytes and cellulose acetate membranes were low. However, the employment of highly charged polyelectrolytes can avoid the layer detachment thus providing better membrane performance stability, as shown in this study.

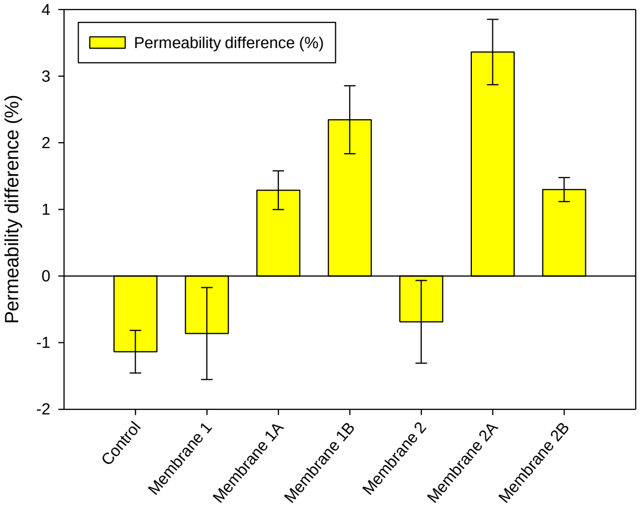


Figure 6 Membrane permeability difference in percentage

■4.0 CONCLUSION

The combination of heat treatment and polyelectrolyte self-adsorption membrane modification methods has been employed for the first time to produce nanofiltration membranes in sequential manner. Through the current study, both methods contributed to higher membrane salt rejection capability with reduced membrane pure water permeability. However, both of the methods produced reliable performances as they can withstand the back-flushing test conducted. Besides, self-adsorption method produced membranes with better surface hydrophilicity properties when poly(sodium-4-styrenesulfonate) is used as terminating layers. Lastly, the captured SEM cross-sectional images had verified the formation of the thin film on top of the membrane substrate. This work suggests the possible reduction of bilayer number using heat treatment method.

Acknowledgement

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