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Fabrication and Characterization of Asymmetric Ultrafiltration Membrane for Lysozyme Separation: Effect of Post-Treatment Medium

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Abstract: In this study, we reported the effects of post-treatment medium on the morphology and performance of asymmetric ultrafiltration membrane. The membranes were prepared *via* simple dry/wet phase-inversion technique using ternary mixture of membrane solution consist of 15 wt.% polyethersulfone, 77 wt. % N-methypyrolidone and 8 wt.% water. The prepared membranes were characterized in terms of permeability coefficient and membrane morphology. Separation performance of proteinwas demonstrated using lysozyme as protein model. The optimum transmissionobtained when the lysozyme separationachieved 97.4% transmission using UF membrane with methanol post-treatment., the optimum flux for these four membranes decreased as the boiling point of the post treatment medium increased from methanol to glycerol. This study proved that the post-treatment mediumhighly influenced the performance and morphology of UF membranes which in turn exhibited an improvement in separation ability.

Key words: Membrane · Asymmetric · Post-Treatment · Ultrafiltration · Lysozyme

INTRODUCTION

Asymmetric membrane demonstrates a heterogeneous morphology which builds up from a thin skin with a thickness between 0.1-0.5 μm and a porous supporting sub-layer with a thickness between 50-150 μm [1]. The investigation on post-treatment parameter is restricting by a few researchers. Xu and Quay [2] studied the effect of ethanol and glycerol at different concentration in post-treatment medium. This research found that the membrane which post-treated with ethanol and glycerol were produced higher membrane porosity. Deshmukh and Li [3] studied the effect of coagulation medium, ethanol (10–50%) and water (90–50%), on the PVDF hollow fiber membranes. This study was determined that the presence of ethanol in the coagulation bath reduced the polymer precipitation rate in phase inversion process and the effective porosity of the resulting membranes decreased as ethanol concentration in the coagulation bath increased.

Shukla and Cheryan [4] reported the effect of membrane conditioning on the performance of UF membranes. Ethanol-water mixture at different concentration and ratio were used as a second coagulation bath. The method of conditioning has a strong effect on the solvent flux, membrane integrity and pressure rating of polymeric membranes. With cross-linked PAN-chitosan membranes, Musale and Kumar [5] observed the highest flux with methanol followed by ethanol and isopropanol. These differences in flux were explained on the basis of the combined effects of increase in molecular weight, viscosity, hydrophobicity and dielectric constant of the alcohol. On top of that, Reddy *et al* [6]. observed a lower flux of primary and secondary alcohols with increase in molecular weight and hydrophobicity of the solvent with a polyamide-polyphenylenesulfone membrane.

This study aimed to investigate the effect of post-treatment medium on the performance and morphology of asymmetric polysulfide ultra filtration membranes. The objective was further to validate the characteristics of the membranes by employing membrane morphology inspection, the pure-water permeation and molecular weight cut-off determination.

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MATERIALS AND METHODS

Materials: All materials used were of analytical grades. The membranes were fabricated from a ternary casting solution which consisted of polyethersulfone (supplied by Merck) as polymer, N-methyl-2-pyrrolidone (NMP) (supplied by Merck) as a solvent and water (H_2O) as a non-solvent. Lysozyme (*Mw* = 14 700 Dalton) purchased from Sigma Aldrich has been used for the evaluation of membrane performance.

Membrane Preparation: The membranes were prepared using a homogeneous dope which consisted of PES (15 wt. %), NMP (77 wt. %) and distilled water (8 wt. %). Asymmetric UF membranes were fabricated via phase-inversion techniques. Distilled water was used as the first coagulation bath for about 24 hours. Subsequently, the membranes were immersed in four types of post-treatment medium: methanol, ethanol, propanol and glycerol for about 8 hours. The membranes were dried at room temperature for 24 hours before being used.

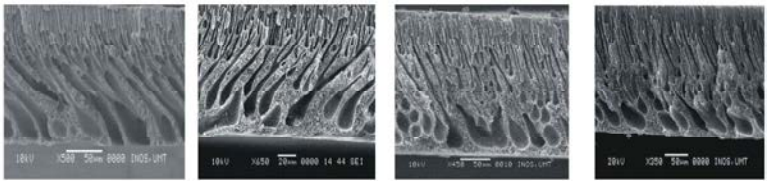
Membrane Characterization: The Scanning Microscopy Electron (SEM) (JSM P/N HP475 model) was used to inspect the cross section of the fabricated membranes. For this purpose, the membrane samples were fractured in liquid nitrogen and sputtered with gold, before transferring them under the microscope. To determine the molecular weight cut off, a series of protein (myoglobin [17kD], ovalbumin [40kD], Pepsin [35kD] and BSA [66 KD]) with different molecular weights were used for rejection study.

RESULT AND DISCUSSION

Membrane Morphology: Figure 1 represents the cross sections of membranes immersed in different post treatment medium. All of the membranes have typical asymmetric structure. Membranes comprise of skin layers that are well developed and supported by a porous support layer with large finger like and tear like structure.

Fig. 1(a) represents the micrograph structures of UF15-M. The top layer of this membrane was comprised with the finger-like structures and large tear drop structures were also existed near the bottom of supporting layer in UF15-M. Figure 1(b) represents the morphology of UF15-E. The top layer consists of finger like structure while a porous sponge like structure was existed at the cross section of the membrane. The low polymer concentration and strong interaction between water and PES results in the growth of thin polymer layer [7] since water is a strong non-solvent for PES polymer. Large finger-like structure is generally formed when the coagulation process is fast, whereas the slow coagulation rate results in a porous sponge-like [8]. The bottom part of UF15-E consists of macro void structures that increase the porosity of this membrane. Macro void formation is favored when the non-solvent diffusion rate into the polymer poor phase being formed exceeds the rate of outward solvent diffusion [9]. Thus, formation of macro voids in UF15-E membrane was due to the lower polymer concentration and low boiling point of ethanol used during post-treatment.

The cross-section of UF15-P was presented in the Figure 1(c) which performed a denser structure compared to UF15-M and UF15-E. This result postulated that, larger molecular size and structure of propanol would reduce the membrane pore size since it was filled up some part of that pores when the membrane was immersed in propanol. Furthermore, high boiling point of this alcohol has retarded the solvent exchange process, leading to the formation of a denser membrane. As can be seen in Figure 1(d), UF15-G consists of denser sponge structures compared to the other membranes. Very small finger like structures presented in UF15-G would promote more resistance to the membrane in allowing the solute to pass through. It is proven that low boiling point of primary alcohol (methanol and ethanol) have great ability to improve the porosity of the membrane. In contrast, the used of tri-old (glycerol) as post treatment medium would reduce the membrane porosity due to the larger molecular structure and high boiling point.



(a) (b) (c) (d)

Fig. 1: SEM images of (a)UF15-M, (b)UF15-E (c) UF15-P and (d) UF15-G

Table 1: Permeability Coefficient of UF membrane with different post-treatment mediums

Membrane ID	Post treatment medium	Permeability coefficient x10^{-6} (m^3/m^2.s.bar)	Regression Coefficient R^2
UF15-M	Methanol	22.87	0.997
UF15-E	Ethanol	20.16	0.996
UF15-P	Propanol	1.67	0.991
UF15-G	Glycerol	1.10	0.994

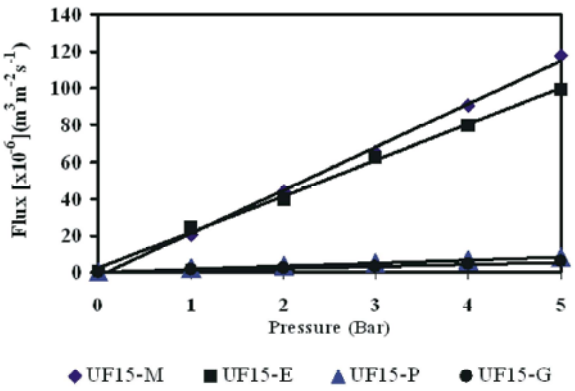


Fig. 2: Pure Water Flux of UF membrane with different post-treatment mediums

Permeability Coefficient: The permeability coefficient determined by the statistical linear regression of volume flux J_V versus applied pressure $J_V = Pm\Delta P$ as plotted in Figure 2. The pure water flux for all membranes with different post- treatment medium demonstrates a very good approximation with the Hagen–Poiseuille equation.

All membranes have shown linear profiles which demonstrate that the pure water flux were proportional to the applied pressure. At applied pressure of 1 bar, all membranes exhibit the lowest flux and increased of flux occurred linearly as the pressure increased up to 5 bar. The slopes of the graphs represent the permeability coefficient of the UF membranes [1] as depicted in Table 1.

From the observations, all membranes performed the permeability coefficient close to the range of ultrafiltration membrane. Permeability coefficient for UF15-M and UF15-E were slightly higher the range of UF membrane. In contrast, permeability coefficient for UF15-P and UF15-G were below the range of UF which were 1.67 x 10^{-6} and 1.10 x 10^{-6} m^3/m^2.s.bar; respectively and this may results in lower flux and protein transmission. UF15-M which presented the greatest permeability coefficient was predicted to be the most suitable membrane for lysozyme separation in this study.

Table 2: Filtrate flux and lysozyme transmission at optimum pressure

Membrane ID	Permeate Flux x10^{-6} (m^3/m^2.s)	Transmission (%)
UF15-M	10.4	97.4
UF15-E	10.2	95.7
UF15-P	4.5	58.7
UF15-G	2.2	84.1

Separation Performance of UF Membrane for Lysozyme Separation: The prepared membranes were further evaluated by applying the separation of lysozyme single solution. Table 2 represents the filtrate flux and lysozyme transmission through different UF membrane at an optimum pressure of 3 bars. The optimum filtrate fluxes were decreased in similar sequence; UF15-M> UF15-E > UF15-P > UF15-G. Reduction in the filtrate flux from UF15-M (10.4 x10^{-6} m^3/m^2.s) to UF15-G (2.2 x 10^{-6} m^3/m^2.s) was due to the porosity and membrane structure itself. UF membrane which has immersed in methanol would have a loose structure, bigger pore size and high porosity since methanol was the simplest alcohol which posses the smallest molecular size and molecular weight compared to ethanol, propanol and glycerol. Thus when the methanol molecules enter the membrane pores during the post treatment process, it is only fill up a small part of that pores compared to other alcohols. Furthermore, its low viscosity also improved the membrane structure since the solvent exchange will be faster in methanol post treatment which could produced a bigger pores and high permeable membrane. As the molecular weight and viscosity of alcohol increased from methanol to glycerol, the membranes become denser and consequently reduced its permeability and filtrate flux.

According to the transmission results, UF15-M also presents the highest lysozyme transmission at optimum pressure, for about 97%, followed by UF15-E (96%), UF15-G (84%) and UF15-P (58%). High transmission occurred for UF15-M and UF15-E was also due to its porosity and high permeability as previously mentioned. The UF15-P revealed a lower transmission compared to UF15-G even UF15-G was claimed to be the most porous membrane in this study. Glycerol is a triol which posses

larger molecular weight and viscosity rather than primary alcohol. However the presence of three hydroxyl group (OH^-) in glycerol molecule might increase the negative charge of membrane when it was immersed in glycerol during post treatment. More negative charge on the membrane surface was attracted more lysozyme molecules towards membrane pores and high operating pressure was desorbed the lysozyme to pass through the membranes. Thus, more lysozyme molecule would be transmitted through the UF15-G. Low transmission in UF15-P was due to the high density propanol which has slower the diffusion rate during the second coagulation bath, consequently reduced the membrane pore size. Its small pore size could retain the lysozyme molecule onto the membrane surface instead of transmitted it through the membrane. Based on the data, this study proposed that the UF15-M membrane is the most appropriate membrane for lysozyme separation and purification.

CONCLUSION

The findings of this study prove that the post-treatment medium greatly influence the membrane performance and morphology. Increase in the molecular size of medium produced a denser membrane which led to the reduction of flux and lysozyme transmission. Based on the experimental data, 15 wt% seems to be an optimum polymer concentration in preparing an ultrafiltration membrane with outstanding performance of lysozyme separation process.

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REFERENCES

1. Mulder, M., 1996. Basic Principles of Membrane Technology, 2nd Edition. The Netherlands: Kluwer Academic Publishers.
2. Xu, Z.L. and F.A. Qusay, 2004. Polyethersulfone (PES) hollow fiber ultrafiltration membranes prepared by PES/non-solvent/NMP solution. Journal of Membrane Science, 233: 101-111.
3. Deshmukh, S.P. and K. Li, 1998. Effect of ethanol composition in water coagulation bath on morphology of PVDF hollow fiber membrane. Journal of Membrane Science, 150: 75-85.
4. Shukla, R. and M. Cheryan, 2002. Performance of ultrafiltration membranes in ethanol-water solutions: effect of membrane conditioning. Journal of Membrane Science, 198: 75-85.
5. Musale, D.A. and A. Kumar, 2000. Solvent and pH resistance of surface cross-link chitosan-poly(acrylonitrile) composite nanofiltration membranes. Journal of Applied Polymer Science, 77: 1782-1793.
6. Reddy, K.K., T. Kawakatsu, J.B. Snape and M. Nakajima, 1996. Membrane concentration and separation of L-aspartic acid and phenylalanine derivatives in organic solvents. Journal of Separation Science and Technology, 31: 1161-1178.
7. Lenchki, R.W. and S. Williams, 1995. Effect of nonaqueous solventon the flux behavior of ultrafiltration membrane. Journal of Membrane Science, 101: 43-45.
8. Klein, E. and K. Smith, 1972. The use of solubility parameters for solvent selection in asymmetric membrane formation. In Reverse osmosis membrane research, ed. H. K Londasale, H.E. Podall. New York: Plenum Press.
9. Lukaszewicz, R.C. and T.H. Meltzer, 1980. On the structure compatibilities of membrane filters. Journal Parental Drug Assoc, 34: 463-472.