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Fabrication and Characterisation of Asymmetric Ultrafiltration Membrane for BSA Separation: Effect of Shear Rates

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Abstract: This study reported the influence of shear rates on the performance and morphology of asymmetric UF membranes for Bovine Serum Albumin (BSA) separation. Flat sheet UF membranes were fabricated from a dope solution with 17% polymer concentration and manipulation of shear rates was done at 176.2, 234.98, 352.47 and 704.9 sec^{-1}. Fabricated UF membranes have been characterised in term of pure water permeability, membrane morphology and membrane pore radius. The membrane performance was determined based on sodium chloride and BSA rejection profile. This study has proposed that a fabricated membrane with 704.9 sec^{-1} shear rate is the most appropriate membrane for BSA separation when it achieved the highest flux around 59.7 L m^{-2} h and BSA rejection of about 100% at an optimum pressure of 10 bars. Observation proved that higher shear rates applied during the membrane casting process would promote a significant effect on the performance and morphology of UF membranes and lead to an upgrade in membrane selectivity.

Key words: Asymmetric membrane, ultrafiltration, BSA and shear rate

INTRODUCTION

Development of new polymer membranes is one of the important elements in the quest for advances and improvements in membrane technology. The various membrane processes and range of particles diffusing through or retained are based on the membrane pore sizes. The success of using membranes is closely related to the intrinsic properties of the membrane where the interfacial interactions between membrane surface, surrounding environment and solutes have governed membrane performance to a great extent. These interactions have considerable impact on transport characteristics, selectivity, fouling propensity, bio-compatibility and hemo-compatibility of the membrane.

Since the development of ultrafiltration membranes in 1960s, membrane processes was being an important part of the rapidly growing biotechnology industry. There has been thousands of different ultrafiltration membranes sold commercially for variety of applications including concentration of therapeutics proteins, industrial enzymes and a variety of food and beverage products. Most polymeric membranes used for protein ultrafiltration are asymmetric membranes which generally consist of a very thin dense top layer supported by a porous sub-layer with thickness ranging from 50 to 150 μm (Mulder, 1996). They show a greater permeation rate than symmetric membranes of comparable thickness of the actual barrier layer (Idris *et al*., 2002a). The asymmetric structure of UF membrane gives the membranes its required mechanical strength (which is provided by the support layer) along with its desired separation properties (which are governed by the skin layer). It is recognised that the separation properties of porous membranes also depends on their physical properties including porosity and pore size distributions (Field *et al*., 2009).

In order to pull off the overreaching goal of membrane manufacturing which is to achieve high permeation rate and selectivity, the choice of membrane material with high intrinsic selectivity and permeability is necessary. On top of that, the preparation of membranes with defect-free ultrathin dense layer is to be aimed. Important progresses have been made in membrane materials, dope preparation, fabrication technology and fundamental understanding of membrane formation. Only during recent years, scientists gradually recognize that the rheological conditions in the membrane formation process are also provided significant impact in determining membrane performance (Kusworo *et al*., 2008).

Shear during casting and spinning has been shown to affect the flux rate of cellulose acetate membranes and this has been attributed to molecular orientation in the active layer (Ismail and Yean, 2002; Idris *et al*., 2002b).

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In recent years, scientists have gradually recognised that the effect of shear-induced molecular orientation has been observed in the separation of ultrafiltation, reverse osmosis and gas separation membranes (Chung *et al*., 2000). The study carried out by Kusworo *et al*. (2008) was focused on the effect of shear rates on molecular orientation and gas separation performance of polyimide/polyethersulfone (PI/PES)-zeolite 4A mixed matrix membrane. At low shear rates, the permeances of O_2 and N_2 decreased, while their selectivities increased with an increase in shear rates. This study was successfully came out with an optimum shear rate to yield optimal membrane morphology for gas separation.

For cellulose acetate flat sheet and hollow fibre membranes, increased shear was reported to evaluate membrane rejection beyond the intrinsic value of the polymer (Idris *et al*., 2002a). Ren *at al*. (2008) was study the effects of the thermodynamics and rheology of BTDA-TDI/MDI co-polyimide (P84) dope solutions on the performance and morphology of hollow fiber UF membranes. The performance of membranes was dominated by the shear rate of the dope solution within the spinneret according to shear induced molecular orientation. With an increase in shear rate, a low permeation flux and a small MWCO were achieved and the pore size distribution of the membrane exhibited a good selectivity.

In phase inversion, casting a shear-thinning and viscoelastic solution usually involves applying shear prior to a rapid coagulation. Shear-thinning properties of polymer solutions often suggest a progressive alignment of polymer molecules under shear in the flow direction. As a result, shear-induced molecular orientation induces favorable effects on the membrane properties (Ismail and Yean, 2002). Ali *et al*. (2010) was determined that manipulation of shear rate during membrane casting has significant effects on the morphology and structural details of the membranes. As shear rate increased, the pore radius was reduced while the membrane thickness increased, causing an increment in selectivity but tending to lower the selectivity.

Ultrafiltration membrane techniques seem to be quite plausible to be used to separate BSA protein in relation to its chemical and physical properties, especially its molecular weight (Ghosh and Cui, 2000). This protein has been given a great attention in respect to its role in pharmaceutical and biotechnology research. BSA has been applied as a carrier protein and as a stabilizing agent in enzymatic reactions. It can be used as a diluent or a blocking agent in numerous applications including ELISAs (Enzyme-Linked Immunosorbent Assay), blots and immunohistochemistry (Randon *et al*., 1995). On top of that, BSA is also used as a nutrient in cell and microbial culture. In restriction digests, it is used to stabilize some enzymes during digestion of DNA and to prevent adhesion of the enzyme to reaction tubes and other vessels. This protein does not affect other enzymes which do not need it for stabilization. BSA is recommended in buffers for nick translation, polymerase reactions and ligations. It is also a common additive for PCR amplifications, footprinting and gel-shift assays. In restriction digests, BSA has been shown to enhance enzyme activity (Millesime *et al*., 1994). Other positive characteristics include its stability and low cost of production since it is readily available in large quantities as it is purified from bovine blood, a byproduct of the beef industry (Randon *et al*., 1995).

This study attempted to investigate the effect of shear rates on the performance and morphology of asymmetric ultrafiltration membrane protein (BSA) separation. The fabricated membranes were characterised in term of permeability coefficient, salt rejection, membrane morphology, pore radius and membrane zeta potential. The membrane performance was finally evaluated based on the rejection of protein BSA.

MATERIALS AND METHODS

Materials: All materials used in this research were of analytical grades. The membranes were fabricated from a ternary casting solution which consisted of polyrsulfone (supplied by Merck) as polymer, N-methyl-2-pyrrolidone (NMP) (supplied by Merck) as a solvent and water (H_2O) as a non-solvent. BSA (Mw = 67 000 Dalton) purchased from Sigma Aldrich was used for the evaluation of membrane performance.

Membrane preparation: The membranes were prepared using a ternary dope solution which consisted of 17 wt.% PSF, 80 wt.% NMP and 3 wt.% water. Asymmetric UF membranes were fabricated via phase-inversion techniques using semi-automated electrically casting machine at various shear rates: 176.23, 234.98, 352.47 and 704.93 sec^{-1}. The shear rate was calculated from the following relationship:

$$\text{Shear rate } (\text{sec}^{-1}) = \frac{\text{Velocity of casting knife}}{\text{Membrane thickness}} \quad (1)$$

Distilled water was used as the first coagulation bath to induce the polymer precipitation for about 24 h. Subsequently, the membrane was immersed in methanol (supplied by Merck) for about 8 h to ensure the excess solvent was totally removed and to strengthen the molecules structure built in the membrane. Finally, the membranes ware dried at room temperature for 24 h before being used.

Membrane characterization: The membranes were characterised in terms of pure water permeability, membranes morphology, determination of pore radius, membrane zeta potential and BSA separation performance.

Permeation with pure water, sodium chloride solution and BSA: All permeation experiments were carried out using dead-end cell supplied by Sterlitech HP4750 with 300 mL processing volume and effective permeation membrane area of 14.6. Distilled water was used for pure water permeation to obtain pure water permeability and to ensure the membrane stability. Permeation of sodium chloride solution (0.01 M) was employed to determine the separation performance of charged solutes. Permeate and feed concentrations of sodium chloride were measured using a conductivity meter (Hanna Instruments, Padova, Italy, model HI8633). Based on the sodium chloride rejection measurement in conjunction with theoretical approaches, the membrane properties were estimated. The steric hindrance pore (SHP) model was employed to deduce the pore size (r_p) a and ratio of thickness to porosity ($\Delta x/A_k$) (Shilton *et al*., 1997).

For BSA permeation, a single solution of BSA was prepared at room temperature by dissolving a pre-weighed amount of BSA powder in phosphate buffer of 7.2 pH. Protein solution was prepared no longer than one hour before use and was stored at 4°C to ensure BSA molecules were active and had no bacterial contamination. It is desirable to avoid the formation of the precipitates in preparing the solution to obtain an overall high yield of BSA. Feed pressure was controlled in the range of 1 to 0 bars by using compressed nitrogen and 10 mL of permeate was collected. The absorbance of feed, permeate and retentate of lysozyme permeation were analysed by UV-Vis spectrophotometer (Hitachi U-2000) at wavelength 280 nm. The average data of three replicates were reported.

Determination of membrane morphology: The Scanning Electron Microscopy (SEM) (JSM P/N HP475 model) has been used to analyse the membrane morphology. The cross section of membrane was inspected by liquid nitrogen freeze-fracturing followed by an auuto-coating step with a thin gold layer using the automatic coater JFC 100 model.

RESULTS AND DISCUSSION

Pure water flux: Figure 1 represents the flux versus pressure for four membranes prepared with different shear rates; the results demonstrate that the plot for distilled water for each of the shear rates was a linear profile ($J_v \propto \Delta P$). The pure water fluxes of four membranes at different shear rates (176.23, 234.98, 352.47 and 704.93 sec^{-1}) were about 3.80, 5.45, 6.60 and 10.80 L m^{-2} h, respectively with a 2 bars applied pressure.

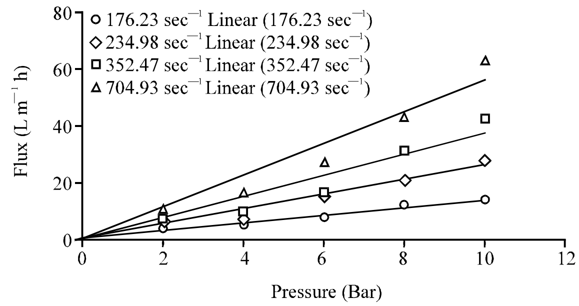

Fig. 1: Pure water flux for four membranes with Different shear rates

Table 1: Permeability of membrane at different shear rates

Shear rate (sec^{-1})	Permeability coefficient (L m^{-2} h Bar)
176.23	1.36
234.98	3.60
352.47	3.74
704.93	5.57

The results indicated that the pure water fluxes increased with increasing of shear rate until an optimum shear rate was achieved. As the flux increased, the permeability rates were also found to increase with increasing of shear rate as shown in Table 1.

Based on the pure water permeation results, it can be postulated that increasing the shear rate tends to improve the flux and membrane permeabilty. This result is in good agreement with the previous finding by Ismail *et al.* (2002) which reported that an increasing of shear rate will increase the pure water fluxes. It is supported by the SEM result where the membrane with a higher shear rate shows a porous substructure.

NaCl rejection measurement: Rejections of NaCl (0.01 M) solution for the prepared membranes were performed at operating pressures of 2, 4, 6, 8 and 10 bars. Filtrate flux and NaCl rejection of the fabricated membrane with different shear rates are depicted in Fig. 2. According to the experimental result, the percentage of NaCl rejection of four shear rates membranes: 176.23, 234.98, 352.47 and 704.93 sec^{-1}, were about 55.18, 57.11, 58.54 and 63.58% respectively with a 2 bar applied pressure. The fluxes were also found to increase as the pressure increased to 10 bars. The highest rejection was found to be 72.23% at the highest shear rate (704.93 sec^{-1}) with applied pressure of 10 bars. It appeared to show that the flux and

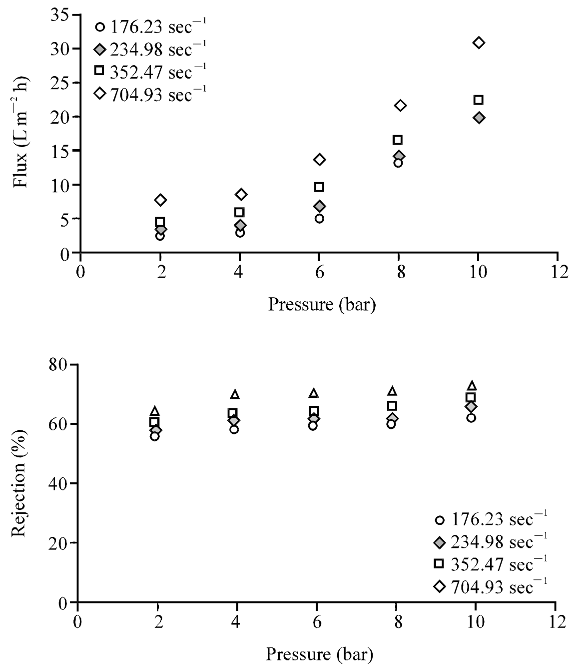

Fig. 2: Effect of shear rate on NaCl performance based on, (a) flux and (b) NaCl rejection

Table 2: Numerical results, membranes parameters obtained from SHP model and the convection and diffusion steric parameter at different shear rates

Shear rates (sec^{-1})	η	HF	SD	SF	σ
176.23	0.41	1.30	0.35	0.57	0.26
234.98	0.43	1.34	0.32	0.54	0.28
352.47	0.57	1.33	0.33	0.55	0.28
704.93	0.53	1.50	0.22	0.40	0.41

Table 3: The modeling results; values of PS, Δx, AK, rp and Δx/AK at different shear rate

Membrane (sec^{-1})	PS [x107] (m sec^{-1})	Δx [x10-5] (m)	AK	rp (nm)	Δx/AK [x10-5]
176.23	1.73	12.95	2.90	1.26	4.63
234.98	2.18	11.85	3.15	1.24	3.97
352.47	2.15	14.18	3.12	1.22	4.82
704.93	2.04	10.12	4.57	0.99	2.41

rejection ability towards Cl^- ions was in the following manners: R_{SR} = 704.93 sec^{-1} > R_{SR} = 352.47 sec^{-1} >R_{SR} = 234.98 sec^{-1} >R_{SR}= 176.23 sec^{-1}; meaning that the flux and the rejection of NaCl increased with increasing of shear rates.

This is due to the decreasing pore size of membrane skin, leading to a better rejection for a solute solution. It also promoted a higher resistance for water permeation, probably due to increased polymer molecules orientation in the membrane active layer (Ismail and Yean, 2002).

As shown in the result above, it was believed that the molecular chains of the dope solution experiencing high shear rate tends to align themselves much better than those experiencing the lower shear rate. Enhancing the orientation can cause the polymer molecules to become closely packed (Chung *et al*., 1998) and thus enhanced separation performance with better rejection.

As determined by Shilton *et al*. (1997) using polarised reflection infrared spectroscopy and gas permeation test, molecular orientation was found to be intensified in the high-shear membranes which has a favourable effect on membrane pressure-normalized flux and selectivity as well as raising the selectivity of the membrane. Some even surpassed the recognised intrinsic selectivity of the membrane polymer. This proved that the in-house fabricated membranes are ideal membranes since they not only pose a high permeability of water flux but are also high in selectivity. Based on the experimental result, the 30.82 L m^{-2} h with 10 bar applied pressure compared to other membrane at lower shear rate.

Modeling result: Membrane pore radius can be calculated membrane with 704.9 sec^{-1} shear rates was good potential in rejecting Cl^{-1} ions (72.05%) and at the assumed to be the optimum membrane since it showed a same time promoted the highest productivity with according to the SHP model. This model suggests that the pore radius is uniform but in reality, the pore radius distribution exists. By manipulation of the shear rates, the pore radius of membranes varied, thus affecting the membrane surface as discussed below. In order to determine the pore radius of this membrane, the solute/ion radius has to be determined first. The membrane is charged and the ions which have the same charge as the membrane will be excluded, while the positive ions will be attracted. Separation of electrolytes containing different charges having different sign and valences can be manipulated according to the rejection differences by the membrane. In this study, the developed membrane was considered as a negative barrier that will attract ions with an opposite charge that passes through.

Table 2 and 3 show the modelling results at different shear rates against the performance of the prepared UF membrane. The delicate nature of the membrane surface also results in susceptibility to imperfections. Thus, subtle alterations in process conditions, practical procedures or handling in casting, or salt-water test inevitably cause variations in the rejection rate performance of the membrane. Thus, the overall data trend reasonably represents the nature of the rheological effects on the rejection properties of the flat membrane.

From the modelling result, the highest porosity was found at the highest shear rate (704.93 sec^{-1}). This indicated that the membrane porosity increased with increasing shear rates and this trend was clearly viewed from the result, where the distinct membrane thickness and pore radius were reduced with an increase in shear rates. At this point, moderate flux and maximum rejection with dramatic reduction in membrane pore radius occurs with increasing of shear. Membranes cast at low shear tend to posses the larger pore radius, thus exhibiting low rejections. From the experimental and modelling result, it is shown that fabricated membrane at a shear rate of 704.93 sec^{-1} was the optimum UF membrane for NaCl separation process and has been assumed to be an appropriate membrane for BSA separation. This membrane possesses a good property among the membranes which has a small value of r_p. This condition is feasible to BSA protein separation where the solute radius of BSA (r_s =3.5 nm) is larger than membrane pore radius. It was clearly shown that membranes with high shear rate have a high potential of BSA separation whereby the membrane can separate 100% of BSA molecules. The increased in the flux and rejection rate suggest that the shear affects the phase inversion of the membrane active layer. The molecular orientation induced at the skin layer caused an increase in the free volume in the skin layer compared to the bulk polymer. The decrease in the pore radius with increasing shear may be a result of the way in which shear deformation interacts with the phase-inversion process. The influence of rheology on phase inversion in membrane fabrication and performance is an important aspect and shows that shear can either increase or decrease phase stability, depending on the relative ability of the components in the system to store energy.

Membrane morphology: The electron micrographs cross section of the membrane at different shear rates (polymer solution at 17% of Psf) is shown in Fig. 3 a-d. From the observation, increase of shear rate was greatly affected the morphology and membrane structure.

A relatively thick transition layer was observed in the membrane at the lowest shear rate (176.2 sec^{-1}) and the skin became thinner as the shear rate increased. At the highest shear rate (704.93 sec^{-1}), it can be seen that a significant effect on the amount of finger voids penetrating through the whole film and channels can be observed that lead from the top to the bottom of the membrane. Thus, for the membrane with these substructures, the separation capability (rejection) shows a greater impression of separation mechanism for BSA rejection.

The membranes with lower shear rate have more sponge-type substructure. From the electron micrographs cross section, it can be observed that the finger like sub-structure that exists in lower shear rate did not penetrate through the whole film. Thus, the water flux for this type of membrane was much lower compared to water flux membrane produced at high shear rate. These SEM results have supported the findings in pure water flux result where membranes at higher shear rate are more permeable due to porous substructure and therefore, produce higher water flux.

Separation performance of BSA single solution: A series of experiments ware conducted to investigate the

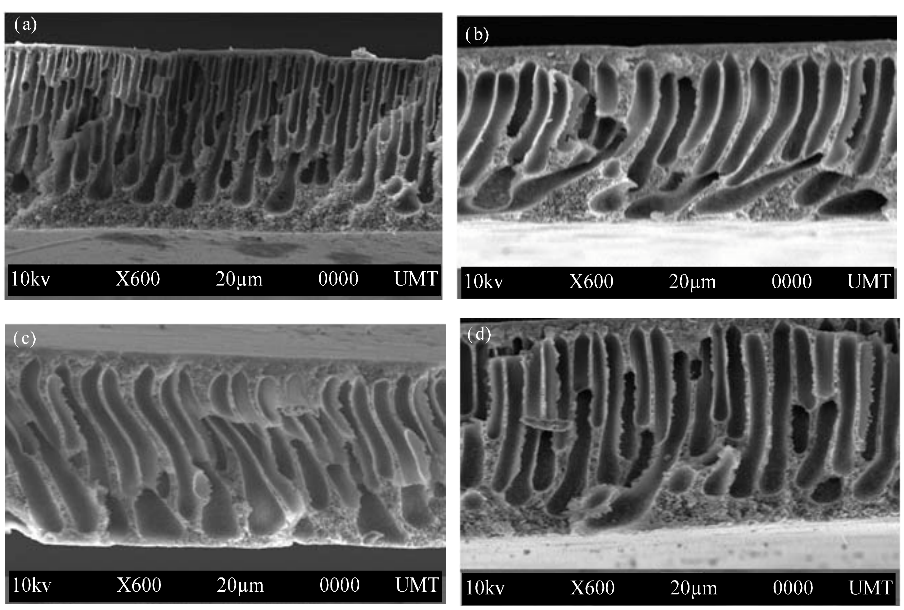

Fig. 3: Cross section of PSf membrane at different shear rate; (a) 176.23, (b) 234.98, (c) 352.471 and (d) 704.93 sec^{-1}

potential of different shear rates on separation performance which may influence the BSA rejection which has been discussed above. Apart from that, the effect of shear rate on controlling the cake layer formation was also scrutinised in this study. The results of BSA permeate flux and rejection for fabricated membranes with different shear rates are depicted in the Fig. 4 and 5.

From the Fig. 4, the fluxes for four membranes were 15.67 to 29.24 L m^{-2} h with a 2-bars applied pressure. As the pressure increased, there was an increasing of flux of membranes. At 6 bars, the highest flux was obtained by the highest shear rate (704.93 sec^{-1}). When the pressure increased to 8 and 10 bars, the flux for each shear rate seems to be increased. The rejection of BSA increases with the shear rate of UF membrane increases.

The rejection of BSA for four different shear rates membranes (176.23, 234.98, 352.47 and 704.93 sec^{-1}) were about 93.48, 98.11, 100 and 100%, respectively with a 2-bars applied pressure. As the pressure increase to 4 -bars, there was a slight increase in BSA rejection where the percentage was increased about 1.09 to 3.21% higher than before.

The increase in applied pressure has increased the rejection of BSA constantly but not by very much when the pressure was applied at 6 to 10 bars. However, the rejection was still around 90 to 100%. Great rejection

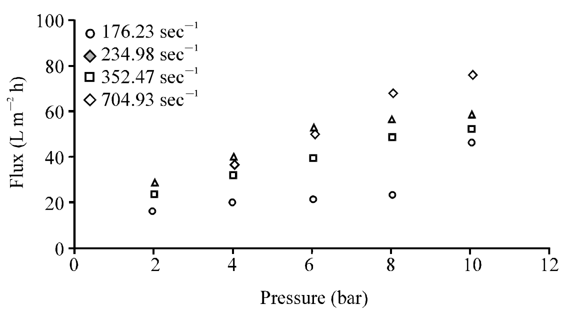

Fig. 4: Fluxes for BSA at different shear rate of membrane

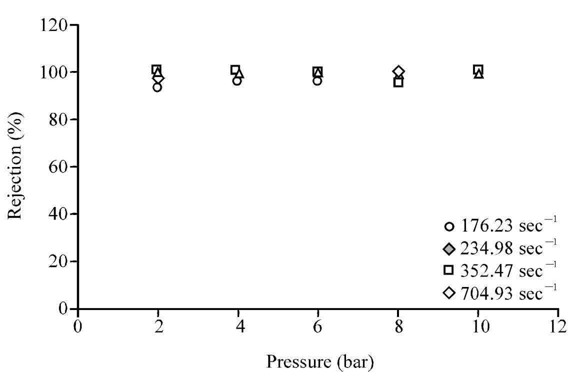

Fig. 5: BSA rejection at different shear rate of membranes

performance was shown by membrane with 704.93 sec^{-1} all applied pressures. The result shows that the membrane of shear rate where it totally rejects the BSA molecules at produced at this operating condition (at highest shear rate) gives the high performance of BSA rejection. From the observation, fabricated membrane with the highest shear rate (704.93 sec^{-1}) showed the best performance for BSA rejection where it shows 100% rejection of BSA at all operating pressure. In this case, the fabricated membranes are negatively-charged. The same trend as NaCl rejection was found for the rejection of BSA cases where the rejection ability was shown in the following manner: R_{SR}= 704.93 sec^{-1}> R_{SR}= 352.47 sec^{-1}> R_{SR} = 234.98 sec^{-1} > R_{SR}= 176.23 sec^{-1} where the percentage rejections of BSA were increased with increasing of shear rate.

BSA is negatively charged at pH 7.2 since its isoelectric point is 4.9. There was a repulsion effect at the membrane surface with this pH due to the intrinsic charge on the PSf membrane charge. The negative charges in membrane will repel the BSA molecules due to the same charge. As a result, the BSA molecules will be retained in retentate. Therefore, the PSf membrane reject better for BSA molecules with the pressure applied.

As mentioned by Ismail and Hassan (2005), an optimum shear rate (critical shear) is defined as a maximum point (shear rate) in which the resultant membrane exhibited an optimal performance, morphology and provides the best structure. This suggested that, in terms of BSA rejection, the membrane with shear rate 704.93 sec^{-1} have a decreased pore size of the skin. The smaller pore size of the final membranes resulted in better rejection for BSA, probably due to increase of polymer molecules orientation in the membrane active layer. Permeation rate (flux) and selectivity of membrane were found to increase with increasing shear.

Since the solution used in this study was shear-thinning, a severe increase in BSA rejection also occurred, presumably due to the larger molecular weight (MW) of BSA being easily rejected by the membrane. If only the sizes of the pores are used as the means of separation with membranes, mostly 10-fold differences in molar mass of the proteins are needed because of the dispersed membrane pore size and fouling of the membrane.

From this study, 704.93 sec^{-1} shear was the optimum shear rate since it was able to promote high performance of NaCl and BSA rejection. Thus, 704.93 sec^{-1} shear is the most suitable shear for applying the BSA rejection in ultrafiltration technology since it rejects 100% with fluxes 29.24 to 59.66 L m^{-2} h at 2 to 10 bars applied pressure. Compared to the other conventional process which has been considered as the most feasible approach in protein separation and purification, the use of PSf-UF membrane in this study also shows great potential in protein separation since ultrafiltration is gradually emerging as a powerful bioseparation process for purification of byproducts.

CONCLUSIONS

The influence of shear rates on the separation performance and morphology of asymmetric UF membranes were successfully investigated. By employing the theoretical models, the structure properties of fabricated membranes have been characterized. Based on the experimental result and modelling data, conclusions can be drawn as follows:

- Fabricated ultrafiltration membrane which prepared from 17 wt.% polymer concentration with optimum shear rate 704.93 sec^{-1} was exhibited pronounced BSA rejection (100%) at all operating pressure in this study. This indicated that the polymer molecular chains become more aligned at this shear rate
- Both sodium chloride and BSA permeation test suggested that there might have existed an optimum shear rate to yield membrane morphology with optimum separation performance. The optimum selectivity and permeability for in-house fabricated membrane in this study membrane occurs at a shear rate of 704.93 sec^{-1}
- The flux rate of membranes decrease with an increase in shear rate but the separation performance for a particular solute increases with increasing shear. This is due to the pore size of the skin decreasing with increasing shear rate and due to the smaller pore size of the final membranes resulting in better rejection for a protein BSA
- Shear rates greatly affected the membrane performance by providing, a certain extent, an oriented membrane skin structure which in turn promoted a higher separation ability

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