



HIGH PERFORMANCE OF POLYSULFONE ULTRAFILTRATION MEMBRANE: EFFECT OF POLYMER CONCENTRATION

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ABSTRACT

Utilization of synthetic polymeric membrane in the downstream processing of enzyme production is now well accepted due to its effectiveness and ability to generate high yield of product. This study aimed to investigate the effects of polymer concentrations and membrane surface modification on morphology and performance of ultrafiltration membranes for trypsin separation. Three membrane solutions with different polymer concentration of Polysulfone (15% [PSf 15], 17% [PSf 17] and 19% [PSf 19]) were used to prepare asymmetric flat sheets membranes via a simple dry/wet phase inversion technique. The data obtained shows that the permeability coefficient decreased with increasing polymer concentrations. PSf 15 membrane which showed the highest flux and trypsin transmission was subjected to membrane surface modification by chitosan solution.

Keywords: membrane, ultrafiltration, trypsin, trypsin separation, chitosan.

INTRODUCTION

Development of synthetic polymeric membrane as a powerful technique in the bioseparation of proteins and enzyme has become increasingly important in such widely diversified fields of biotechnology and food industry. Most polymeric membranes used for protein or enzyme applications were of the asymmetric ultrafiltration membrane types, which have high thermal stability, chemical resistivity, and thus lower usage of harsh cleaning chemicals (Reis and Zydney, 2007; Zydney and Kuriyel, 2000). They showed greater permeation rate than symmetric membranes of comparable thickness of the actual separation layer (Idris *et al.*, 2002). The asymmetric structure of UF membrane also gives the membranes its required mechanical strength together with its desired separation properties.

During dope preparation and membrane fabrication, the experimental conditions play a significant role in determining a good structure of asymmetric membrane and consequently the membrane performance. Dope composition is one of the important parameters which influenced the characteristics of membrane such as membrane morphology, pore size, thickness, and viscosity of membrane solution. These characteristics subsequently affect the membrane performance in term of selectivity and productivity (Mark and Chellam, 1999).

The morphology of asymmetric membrane normally shows a dense top layer and porous sub-layer. The sub-layer which consists of macrovoids, pores and micropores is governed by variation in the casting dope such as concentration, temperature and organic and inorganic additives (Bumsuk, 2004). The used of more concentrated polymer has led to the formation of higher concentration of dope at the binodal-phase separation point. Thus, a denser spongy structure will be formed as

well as a lesser possibility of solvent extraction occurs from the surrounding polymer solution to the polymer-lean phase during the formation of the macrovoids (Jean *et al.*, 2006). When the casting solution comes into contact with the non-solvent in the coagulation bath, a rapid outflow of the solvent from the casting solution to the coagulation bath causes higher-concentration polymer molecules to be aggregated at the top layer (Chakrabarty *et al.*, 2008). Therefore, due of the important role of polymeric membranes in separation technology, many studies of membrane formation mechanisms by wet phase separation of different ternary systems (polymer/solvent/nonsolvent) were carried out. Ahmad *et al.* (2005), (Ismail *et al.*, 2002), Ali and co-workers (2010), Ali *et al.* (2012). Those studies proved that the polymer concentration greatly affected the structural properties and membrane separation performance.

Polysulfone is an excellent polymer for membrane fabrication with high mechanical, electrical and chemical resistant properties. This polymer remained relatively constant over a broad temperature range from -150°F to 300°F. On top of that, preparation of ultrafiltration membranes from PSf solutions leads to a large variety of porous asymmetric structures, which can be controlled by changing the mixture composition of the membrane solution (Peinemann and Nunes, 2001). In spite of its good characteristics as membrane material, the hydrophobic surface of polysulfone also brings obstacles with severe fouling during ultrafiltration process, in particular during protein or enzyme separation. This fouling phenomenon contributes mainly from protein deposited onto membrane surface and also due to the surface properties (chemistry, morphology, etc.), hydrodynamic conditions, physic-chemical environment of feed solution, and solute concentration (Kim *et al.*, 1992).



The overarching goal of the present work is to study the effects of polymer concentration membrane surface modification on flat sheet asymmetric ultrafiltration membranes. The prepared membranes were characterized in term of membrane permeability, molecular weight cut-off, membrane surface charge, membrane morphology, flux recovery ratio and membrane porosity. To determine the optimum membrane able to transmit maximum amount of enzyme, commercial trypsin was used during permeation.

METHODS AND MATERIALS

Materials

All materials used are of analytical grades. The membranes were fabricated from ternary casting solution which consist of polysulfone (supplied by Merck) as polymer, N-methyl-2-pyrrolidone (NMP) (supplied by Merck) as a solvent and water (H₂O) as a non-solvent. Trypsin (*M_w* = 28 000 Dalton) purchased from Sigma Aldrich has been used for the evaluation of membrane performance.

Membrane preparation

Asymmetric PSf membranes were prepared using ternary dope with three different formulations which contain polymer, non-solvent and water. All polymeric membranes were fabricated via simple dry/wet phase inversion technique using an electrically casting machine at shear rate 200s⁻¹ and then immersed directly into a coagulation bath for 24 hours. The prepared membranes were stored in distilled water prior to usage.

Membrane characterization

The Scanning Microscopy Electron (SEM) (JSM P/N HP475 model) was used to inspect the cross section of in house fabricated membrane. For this purpose, the membrane samples were fractured in liquid nitrogen and sputtering with gold, before transferred under microscope. A series of protein and enzymes with different molecular weights (myoglobin [17kD], trypsin [28 kD], ovalbumin [45kD], pepsin [35kD] and bovine serum albumin [66 kD]) were used for rejection studied in order to determine the membrane molecular weight cut-off. 0.5 mg/ml protein solution was prepared using phosphate buffer. Permeate solution of corresponding membranes were analyzed for protein concentration using UV-vis spectrophotometer at wavelength 280nm. From the feed and permeate concentrations, the percentage of rejection was calculated using equation (3).

$$\text{Solute rejection (\%)} = \left[1 - \left(\frac{C_p}{C_f} \right) \right] \times 100 \quad (3)$$

where *C_p* is the concentration of permeate and *C_f* is the concentration of feed solution.

Pure water permeation and separation performance of native and hybrid membrane

All permeation experiments were carried out using dead end cell system with 300 ml processing volume and effective permeation membrane area of 14.6 cm². Distilled water was used for pure water permeation to obtain pure water permeability and to ensure the membrane stability. For trypsin permeation, 0.5 mg/ml trypsin solution was prepared in phosphate buffer (0.1M) at room temperature. Distilled water and trypsin enzyme were drawn through the membrane with compressed nitrogen; controlled in the range of 1 to 5 bars. The absorbance of feed and permeate were analyzed by UV-Vis spectrophotometer (Hitachi U-2000) at wavelength 280 nm. The average data of three replicates were reported.

Fouling quantification

Fouling can be quantified by the resistance appearing during the filtration and cleaning can be specified by the removal of this resistance. The resistance is due to the formation of cake or gel layer on the membrane surface. For fouling quantification, pure water permeation was conducted at constant pressure. Pure water flux was obtained from the volume of permeated water within 30 minutes and calculated as $J_0 = Q / (At)$ where *J₀* is pure water flux, *Q* is the permeate volume, *A* is membrane area and *t* is the time. After water flux measurement (*J₀*), the solution reservoir was refilled with 0.5 mg/ml trypsin solution. After 30 min filtration, the membrane was cleaned via shaking in pure water for 2 hours at 25°C and then pure water fluxes (*J₁*) were measured again. By comparing the value of *J₀* and *J₁*, water flux recovery ratio (FRR) and relative flux reduction (RFR) were determined.

$$\text{FRR (\%)} = (J_1 / J_0) \times 100$$

$$\text{RFR (\%)} = [1 - (J_1 / J_0)] \times 100$$

RESULT AND DISCUSSIONS

Permeability coefficient, membrane thickness and porosity

Pure water permeation was applied in all fabricated membranes in order to measure its permeability coefficient which can determine the porosity and identify the membranes stability. According to Mulder (1996), a membrane is characterized as a porous membrane if the permeability coefficient ranges from 20.8 to 208 L/m².h.bar (5.778×10^{-6} to 5.778×10^{-5} m³/m².s). The higher the permeability indicates that the membrane has high porosity.

Pure water flux measurements of all fabricated membranes were measured at five different pressures from 1 to 5 bars. The graph of filtrate flux versus pressure for different polymer concentrations of UF membranes is displayed in Figure-1. The fluxes were linear as a function of applied pressure

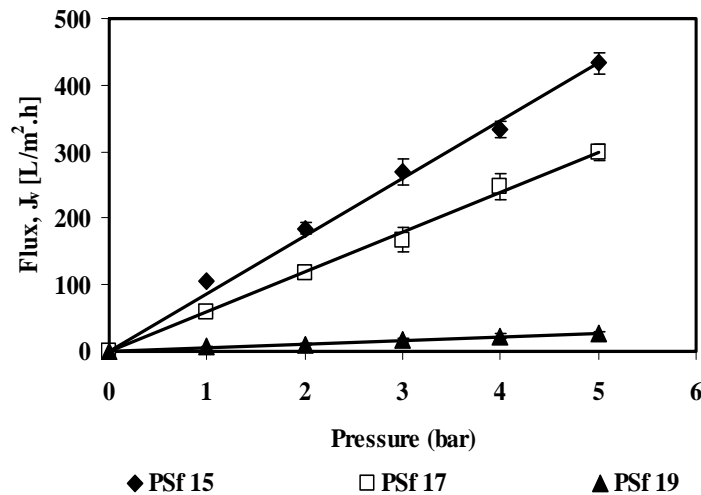


Figure-1. Pure water flux of (a) PSf15, (b) PSf17 and (c) PSf19.

Table-1 shows the permeability and regression coefficient of three in-house fabricated membranes together with their thickness and porosity. PSf 15 membrane showed the highest permeability coefficient of 86.995 L/m².h.bar. The permeability coefficient decreased

with increased polymer concentration in the membrane solution. This was clearly seen since the permeability coefficient for PSf 17 and PSf 19 reduced to 59.657 and 5.601 L/m².h.bar, respectively.

Table-1. Permeability coefficient, membrane thickness and porosity of PSf and modified PSf membranes.

Membrane ID	Permeability coefficient (L/m ² .h.bar)	Regression coefficient (R ²)	Thickness (mm)	Porosity (%)
PSf 15	86.995	0.9936	0.070	86.9
PSf 17	59.657	0.9966	0.081	75.4
PSf 19	5.601	0.9975	0.093	58.1
CH/PSf	71.017	0.9925	0.060	89.6
TiO ₂ /PSf	49.101	0.9980	0.087	69.4

Permeability coefficient also represents the porosity of UF membrane which greatly depends on the membrane thickness. According to the result obtained in Table-2, a lower polymer concentration produced a thinner and more porous membrane, consequently provided a higher hydraulic permeability as observed on PSf 15 and PSf 17. PSf 19 which is a thicker membrane has lower membrane porosity and permeability coefficient. These results were in agreement with the findings of previous research which mentioned that as the fluxes decreased, the permeability rates were also decreased with increasing polymer concentration (Ahmad *et al.*, 2005).

The results of pure water flux measurement also represent the hydraulic permeability of membranes which is a membrane property that depends on the membrane thickness and percentage of porosity. Increased in the polymer concentration has led to increase in the membrane thickness. As the thickness of membrane support increased, the membrane becomes denser and the presence

of sponge like structure has reduced the rate of water permeability through the membranes. In contrast, if a lower polymer concentration used a membrane with high porosity and hydraulic permeability could be produced which consequently improve the potential of productivity (Ghosh *et al.*, 2003).

Membrane morphology

In this study, all the prepared membranes show asymmetric structures which combined high permeate flow, provided by a very thin selective top layer and a reasonable mechanical stability, resulting from the underlying porous structure (Nunes and Peinemann, 2003). These asymmetric membranes pose heterogeneous morphology as clearly illustrated in Figure-2.

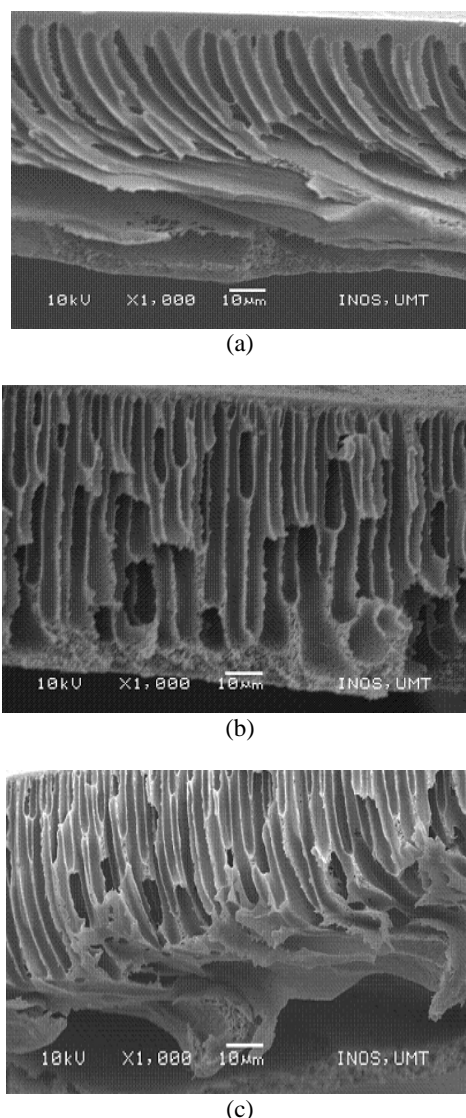


Figure-2. Cross section of membrane morphology of PSf membrane; (a) PSf 15; (b) PSf 17 and (C) PSf 19.

The membranes comprised of two layers; skin active layer and supporting layer in which both layers provided significant roles in membrane transport property. Skin active layer is a layer which controls the separation process and selectivity of membrane while the support layer below acts as a supporting structure. The porosity of the supporting structure is generally much greater than the top thin layer (Mulder, 1996). The structure of membrane is often described in terms of presence or absence of connecting voids. An asymmetric structure is usually formed across the membrane since the solvent-non-solvent exchange may lead to different starting conditions for phase separation at layers far from the surface. The cross sections of fabricated PSf membranes viewed from SEM displayed generally finger like structure for all types.

PSf 15 and PSf 17 comprise of skin layer which have well developed and supported by a porous supporting

layer with macrovoid structures, large finger like and sponge like cavities. Large macrovoids in the substructure typically result in increased permeability, and therefore may be desirable in moderate-pressure UF applications (Arthanareeswaran *et al.*, 2010). The formation of macrovoid is favored when the non-solvent diffusion rate into the polymer exceeds the rate of outward solvent diffusion.

Large finger-like structure and a thin supporting layer of both membranes have increased its porosity and permeability. The formation of these structures might be influenced by additional water content in the dope. Besides, the solvent exchange occurred immediately when a low polymer concentration membrane has immersed in the water, thus promoting the formation of larger finger-like pores from the processes of polymer-lean phase growth and coalescence. On top of that, PSf 15 and PSf 17 membranes with lower polymer concentration exhibited only few sponge structures due to the rapid solvent precipitation during phase inversion process (Young and Chen, 1995).

PSf 19 membrane exhibited the densest skin layer compared to the other fabricated membranes as shown in Figure-2(c). It displayed tiny and micropores finger like structure with fine tuned arrangement. The higher polymer concentration enhanced the viscosity of the dope solution, leading to the formation of smaller pore size in PSf membrane. This phenomenon occurred since high viscosity of dope solution can hinder the diffusional exchange rate of solvent (NMP) and non-solvent (water) in sub-layer, inducing fast phase separation at skin layer and slows the precipitation rate of the sub-layer. Hence, this phenomenon resulted in the formation of asymmetric membrane with dense and thick skin layer supported by a closed cell sub-layer (Kim and Lee, 1998). Moreover, the enhancement of dope viscosity consequently reduced the coagulation value due to a stronger interaction of solvent and polymer and a greater interaction of non-solvent and polymer that decreased dissolving power of solvent for polymer. Thus, this would further promote aggregation of polymer molecules through chain entanglement (Kimmerle and Strathmann, 1990) consequently reduced the permeability rate and transmission.

The higher the polymer concentration use, the more microporous and tinny liked structure formed. At lower polymer concentration, non-solvent concentration is higher during precipitation. The diffusion of non-solvent into the membrane will be increased and the phase separation velocity leads to the formation of big finger like pores in the membranes (Pinnau and Koros, 2005). Besides, lower polymer concentration will perform less dense and less thick skin layer which led to higher permeability as can be seen in the pure water flux measurement with PSf 15 and PSf 17.

Molecular weight Cut-Off (MWCO) and membrane zeta potential

Molecular weight cut off (MWCO) is customarily used to estimate the membrane pore size and its value can



be determined from the solute rejection of membranes against the stable molecules with various weights (Becht *et al*, 2008). In this part of study, the three fabricated membranes with different polymer concentration were subjected to permeation of different molecular weight protein molecules. The retention rate shown in Figure-3 increased with the increase of solute molecular weight and Table-2 shows the molecular weight cut off estimation of the three UF membranes.

The molecular weight cut-off of PSf15, PSf17 and PSf19 membranes were estimated to be 93.6 kD, 49.0 kD and 37.2 kD respectively. These values were determined at the point where the rejection is 80%; which the standard to determine the MWCO rejection is. Higher polymer concentration used has led to the formation of lower MWCO. This result might be explained in term of solvent and non-solvent composition in the dope solution. It influenced the rapidness of precipitation in the membrane during wet phase separation in coagulation bath.

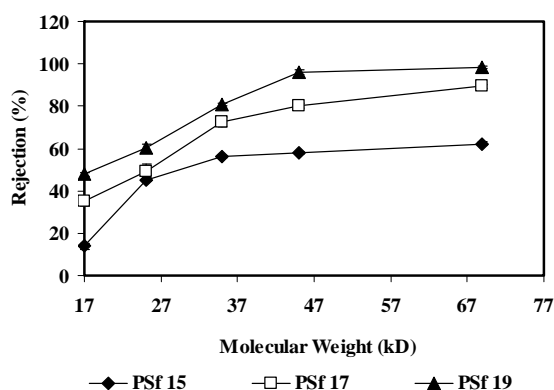


Figure-3. Protein rejections with different polymer concentration membranes.

Table-2. Molecular weight cut-off and zeta potential of PSf membrane with different polymer concentration.

Membrane ID	MWCO (kD)	Zeta potential (mV)
PSf 15	93.6	- 15.52
PSf 17	49.0	-17.98
PSf 19	37.2	-38.63

Zeta potential is an important indicator of the membrane surface charge which is essential for the design and operation of membrane processes. In house fabricated membranes were further characterized to determine their zeta potential and observed result was displayed in Table-2. All membranes were negatively charged and negativity increased with increased of polymer concentration. The result postulated that increased the polymer concentration has increased the sulfonate group (negatively charge) on the membrane surface. Negatively charge membranes are

widely used since it can selectively partition the ions or solutes in the salt mixture through the electrostatic interaction between ions and membrane (Wang and Chung, 2005). In this study, this negatively charge membrane would attract the positively charge trypsin onto the membrane surface and membrane pores. Operating pressure applied would desorb the trypsin molecule to pass through the membrane pores which tend to improve the filtrate flux and trypsin transmission.

Separation performance of trypsin single solution

In this experiment, the separation performances of fabricated membranes were evaluated using 0.5 mg/mL trypsin single solution in 100 mM phosphate buffer. Operating pressures in the range of 1 to 5 bars were applied in the permeation experiment. Figures 4 and 5 shows the flux and percentage of trypsin transmission through the three types of fabricated membranes at five applied pressures, respectively. For each membrane, the flux increased with increased of applied pressure.

The most promising results obtained by PSf 15 membranes when it reached the highest trypsin transmission around 89.4 % at a pressure of 3 bars. This high transmission was combined with high filtrate flux for about 21.9 L/m².h. It is evident that from this result, high porosity and large MWCO of PSf 15, in principle, would lead to the high permeate flux of this fabricated membrane. In this observation, both flux and transmission through membranes were increased with operating pressure up to 3 bars. Beyond this point, transmission was again decreased (as opposed to the flux which was continuously increased). The same findings occurred in the trypsin permeation using PSf17 when it reached the highest transmission around 85.6%, at a pressure of 3 bars and after this point, the transmission decreased.

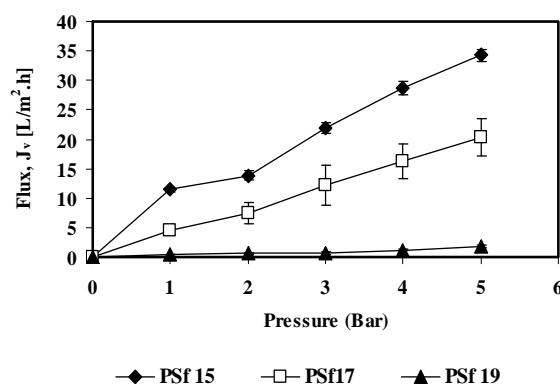


Figure-4. Filtrate flux of trypsin permeation.

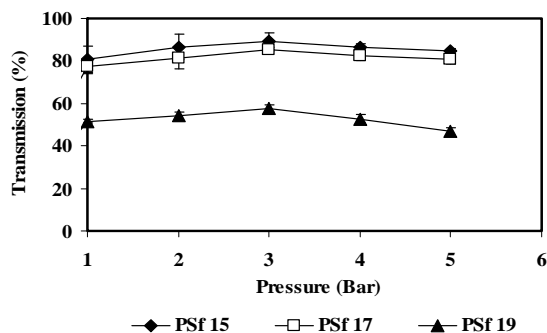


Figure-5. Trypsin transmission through PSf membranes.

For PSf 15 and PSf 17, the low operating pressure applied in this experiment (1-3 bars) would promote a lower flux and diffusion is a major transport mechanism at this condition. The isoelectric point of trypsin was around pH 10 and this enzyme was being positively charged when prepared in the phosphate buffer at pH 8. This positively charged trypsin was attracted by negatively charged membrane and let it easily pass through the membrane. Increased the pressures (4-5 bars) have increased the filtrate flux and the high flux characteristics of these membranes results in rapid convection of retained solutes to the membrane surface. This rejection and the low diffusion coefficient of trypsin that considerably reduce the rate of back transport leads to an increase of trypsin concentration on the membrane surface (Zaidi and Kumar, 2004). Further increase of trypsin concentration on the membrane surface consequently results to the well known phenomena of concentration polarization as shown in Figure-6.

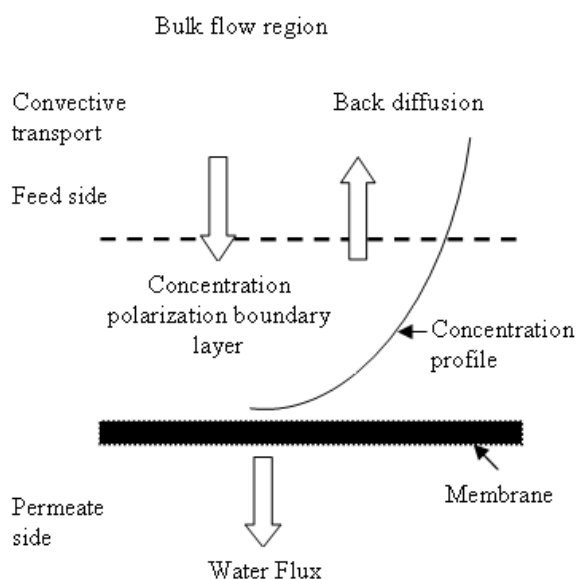


Figure-6. Concentration polarization boundary formed near the surface of the membrane.

In this case, the concentration at the membrane surface can rise to the point of incipient gel precipitation; build up a polarization layer on top of the membrane surface which offers the major resistance to flow. The thickness of this polarization layer has increased until the pressure-activated convective transport of solute with solvent toward the membrane surface just equals the concentration gradient-activated diffusive transport away from the surface. Thus, increased pressures would not help since the gel layer only grows thicker to offer more resistance to the increased driving force and a thicker protein layer build-up on the membrane surface consequently reduced the trypsin transmission (Narsaiah and Agarwal, 2007).

It is clear from Figure-4 that the permeate flux of PSf 19 is very low from the beginning until the end of filtration experiment; in which it ranged from 0.43 to 1.8 L/m².h. Only a slight increase of flux observed from 1 to 5 bars. This result can be explained due to its low porosity and MWCO which led to the increase of the membrane resistance (pore blockage) and the development of another resistance layer (cake formation) as shown in Figure-7.

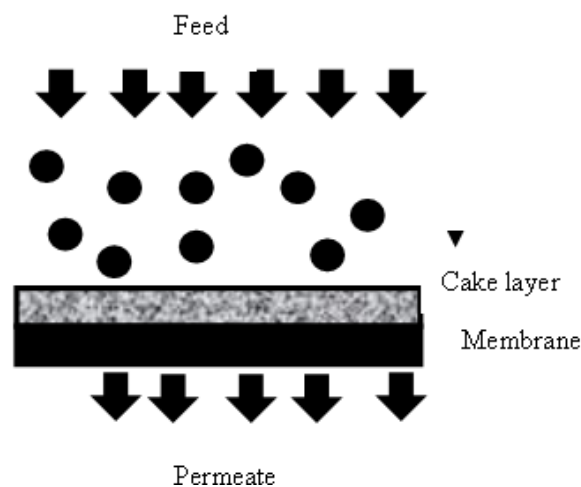


Figure-7. Formation of filter cake on the membrane surface.

The highest trypsin transmission achieved by PSf 19 was only 57.6% at a pressure of 3 bars. This low transmission was due to its low porosity and smallest MWCO which would retain the most of trypsin enzyme onto the membrane surface and membrane pores. After 3 bars, the reduction in enzyme transmission occurred since most of trypsin molecules can pass through the membrane during the initial stage of filtration process when the pore size of membrane is larger than the pore radius of trypsin. After it reached the saturating point, accumulation of trypsin drawn towards the filtering surface by dead end flow was occurred, led to the formation of highly resistant boundary layer and concentration polarization (Iritani *et al.*, 1995). On top of that, at high operating pressure, the concentration of solute accumulated in the polarization layer is increased due to the higher rejection and lower



back diffusion (Zaidi and Kumar, 2004) of trypsin molecules in bulk solutions.

Analysis of membrane fouling during ultrafiltration

The dominant barrier involving the application of UF membranes for enzyme separation is flux decline with operating time. This flux reduction may be attributed to the several factors such as concentration polarization, membrane fouling and changes in the properties of feed solution. According to Arthanareeswaran *et al.* (2009) concentration polarization and membrane fouling are the most common and major difficulty correlated with the flux decline.

Concentration polarization decreases the driving force of water flow across the membrane due to a local increase in foulant concentration. This effect is completely reversible, and can be reduced by modifying the flow over the membrane (Zeman and Zydney, 1996; Hilal *et al.*, 2005). The fouling of membranes may be due to the reversible fouling and irreversible fouling. Reversible fouling corresponds to the building up of protein solutes on the membrane surface which can be reduced with the increased stirring near the membrane surface. Irreversible fouling accounts for deposition or aggregation of protein molecules in the membrane which results in the decline of flux.

The flux changes due to the fouling and cleaning of trypsin were observed for all fabricated membranes are shown in Table-3. It is evident from the table that PSf 15 and PSf 17 have high flux recovery ratio of about 84.6% and 73.8%, respectively. These results might be attributed to the high porosity and large MWCO of both membranes, which can enhance the trypsin transmission and prevent a large amount of trypsin accumulated on the membrane surface and membranes pores. A slight reduction of flux (RFR) is still occurred for both membranes due to the irreversible fouling

Table-3. Fouling analysis.

Membrane ID	Flux recovery ratio (%)	Relative flux reduction (%)
PSf 15	84.6	15.4
PSf 17	73.8	26.2
PSf 19	42.4	57.6

It is clear from the Table-3 that a reduction in membrane flux occurred in PSf 19 and this result was due to the decrease of molecular weight cut-off and membrane porosity. Thus, the fast blocking of membrane pores occurred starting from the initial stage of filtration which led to the irreversible fouling since the membrane cleaning did not improve the membrane flux. After permeation with trypsin for 30 minutes, the membrane pores are being blocked by the retained particles. At this moment, the membrane pores are more likely to be blocked partially. The formation and growth of cake layer on the membrane surface led to reduce the pure water flux after trypsin

permeation (J_1) and consequently decreased the FRR value. This is due to the impact of membrane fouling that leads to an increase of hydraulic resistance and a reduction in filtration efficiency (Zularisam *et al.*, 2007).

On top of that, during the enzyme permeation, the separation of solute and solvent takes place at the membrane surface where the solvent passes through the membrane and the retained solute causes the concentration at the membrane surface to increase. Further increased of trypsin concentration near the membrane surface led to the effect of concentration polarization which accounts for both the gel layer and the solute rich layer at the membrane surface.

CONCLUSIONS

Asymmetric UF membranes with different polymer concentrations were successfully developed via a simple dry/wet phase-inversion technique. The findings of this study prove that the polymer concentration greatly influence the membrane performance and morphology. Increase in the polymer concentration produced a denser membrane which led to the reduction of flux and trypsin transmission.

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