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Separation of Xylose From Glucose Using Thin Film Composite (TFC) Nanofiltration Membrane: Effect of Pressure, Total Sugar Concentration and Xylose/Glucose Ratio

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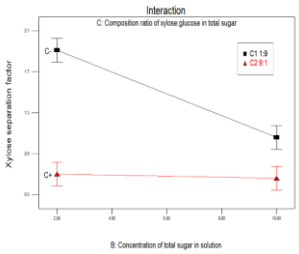
Graphical abstract



Abstract

Xylose is an abundant raw material coexists with other sugars that can be turned into useful products, such as ethanol, xylitol and 2, 3-butanediol by microorganism such as yeasts, bacteria, and mycelial fungi. However, more than 80 % of the production cost of these products comes solely from the production of xylose. Presently, the separation of xylose from hemicellulose hydrolysate relies on chromatographic separation alone. The use of nanofiltration membrane may offer alternative in recovering xylose due to the differences in size compared to other sugars. The aim of this study is to evaluate the ability of membrane developed by interfacial polymerization reaction between triethanolamine (TEOA) (6 % w/v) and tri-mesoyl chloride (TMC) (0.15 % w/v) as monomers on polyethersulfone (PES) microporous substrate to separate xylose from glucose. In this study, factors affecting the process, namely pressure, concentration of total sugars in solution, and composition of monosaccharides in total sugar, were investigated using two-level factorial analysis. The experiment was performed using Amicon Milipore stirred cell (Model 8200) with constant stirring speed at 300 rpm and temperature at ambient. The glucose and xylose concentration was quantified using high performance liquid chromatography (HPLC). It is found that the developed nanofiltration membrane has the ability to separate xylose from glucose.The analysis of the experimental response revealed that the total sugar concentration and composition ratio of xylose: glucose had significant interactive effect on xylose separation factor. Overall from the present study, it can be concluded that nanofiltration has high potential to replace currently in use chromatographic method in xylose separation.

Keywords: Nanofiltration, interfacial polymerization, separation, xylose, glucose

Abstrak

PLEASE PROVIDE

*Kata kunci:***PLEASE PROVIDE**

1.0 INTRODUCTION

Xylose is an abundant raw material coexists with other sugars that can be turned into useful products, such as ethanol, xylitol and 2, 3-butanediol by microorganism such as bacteria, yeasts and mycelia fungi. Xylose mainly comes from hydrolysis of hemicellulose of agriculture waste, which consists around 55% of total sugar. Another monosaccharide of interest, which is glucose, also results from the hydrolysis of hemicellulose covering around 25% of the total sugar.[1] Glucose is a primary source of energy for

microorganism. The presence of glucose inhibits the utilization of xylose by microorganism in producing the desired output. Microorganism tends to consume glucose for growth and metabolism and later on other monosaccharides, when supply of glucose come to an end.[2-3] This resulted in low productivity of desired products fermented from xylose.

Production of xylose crystal in a xylitol production plant was estimated to cost more than 80% of the total cost.[4] There are few reasons for the high cost of xylose crystal production.[4] First, the composition of the non-sugar components in the hemicellulose hydrolysates is very complicated, and the purification steps required to remove these component are rather tedious. Second, the physicochemical properties of the sugar impurities are fairly similar to those of xylose and can inhibit xylose crystallization. Currently, chromatographic separation is the only method available to the industry to recover xylose. The complexity of the purification procedures and low product yield further push the cost of producing xylose production to a high level.[4] Among various separation methods available, nanofiltration offers cost-effective and easy-maintenance alternative separation of xylose from glucose.[5-6]

Previous studies on the separation of monosaccharides using nanofiltration have identified four main factors that affect the nanofiltration process. These are pressure,[5-7] temperature,[6] concentration of total sugars in solution,[5-6] and composition of monosaccharides in total sugars.[5] However effect of temperature was not considered in this present study. The increases of temperature usually lead to the decrease in rejection. Higher rejection of neutral solutes was observed between temperature 20˚C to 30˚C.[6, 8-9] Thus, this study was carried out at ambient temperature.

The aim of this study is to evaluate the ability of membrane developed using interfacial polymerization reaction between triethanolamine (TEOA) (6% w/v) and tri-mesoyl chloride (TMC) (0.15% w/v) as monomers on polyethersulfone (PES) membrane microporous support to separate xylose from glucose. Two-level full factorial experimental design was used to simultaneously study the three selected factors, pressure, concentration of total sugars in solution, and ratio xylose: glucose. This experimental design varies the two levels of the factors simultaneously rather than one at a time, allowing the study of interactions between factors.[10]

■2.0 EXPERIMENTAL

2.1 Material

The commercial polyethersulfone membrane, UF PES50 was purchased from AMFOR INC (China) and nominal molecular weight cut-off (MWCO) of 50 kDa. Chemical for surface modification are sodium hydroxide (Merck, Germany), triethanolamine (TEOA) (R&M Marketing, UK), tri-mesoyl chloride (TMC) (Alfa Aesar, UK), and hexane (Merck, Germany) with purity of more than 99%. The monosaccharides of interest, glucose (≥ 99% purity) and xylose (≥ 99% purity), were purchased from Sigma-Aldrich Co.

2.2 Experimental Procedures

2.2.1 Membrane Preparation

The aqueous solution was prepared by dissolving 6% (w/v) TEOA in 10% (w/v) sodium hydroxide solution. The organic solution was made of 0.15% (w/v) TMC dissolved in hexane. PES membrane was cut into disc form and immersed in the aqueous solution for 30 minutes. Then, excess TEOA solution was drained and left dried at room temperature about 2 minutes. The TEOA-coated membrane was then immersed into the organic solution for 35 minutes. The resulting membrane was then dried overnight at room temperature. Four membranes were identically prepared for the purpose of this study.

2.2.2 Pure Water Permeability Test

Freshly prepared membranes were first flushed with de-ionized water at ambient temperature and pressure of 4 bar for 5 minutes. Next, the water flux was measured at 2, 3, and 4 bar with de-ionized water at ambient temperature. 5 mL of permeates were collected and the total time taken was also noted. This test was done to predict the characterization of the prepared membranes.

2.2.3 Experimental Set-up

Prepared membrane was fitted into the membrane holder and secured with O-ring and body of stirred cell. Other parts are then assembled together and place on top of magnetic stirrer. The monosaccharides mixture was filled into the stirred cell. Filtration was started immediately after the mixture was poured. Pressure of 2 and 4 bar was provided by the attached nitrogen cylinder and continuously monitored by the pressure gauge on the cylinder. 5 mL of permeates were collected and the total time taken was recorded. The concentration of xylose and glucose were quantified by HPLC equipped with refractive index (RI) detector and SUPERCOSIL LC-NH2 column (25 cm × 4.6 mm). Acetonitrile: water (75: 25) was used as the mobile phase at flow rate of 1 mL/min and the column temperature was at ambient temperature.

2.2.4 Design of Experiment

The design was done using Design-Expert version 7.0.0 (Statease Inc., USA). A total of 8 experiments were performed according to a full factorial design with three factors. The variable factors with the coded and actual value were presented in Table 1. The experiments were carried out in randomized run order to determine the response: xylose separation factor. Xylose separation factor is a measure of xylose purification from glucose calculated using the following equation [5]:

$$X_{xyl} = \frac{c_p(xyl) \,/\, c_p(glu)}{c_f(xyl)/c_f(glu)} = \frac{1 - R_{xyl}}{1 - R_{glu}} \qquad (1)$$

where $c_p(xyl)$ is the concentration of xylose in permeate (g/L), $c_f(xyl)$ is the concentration of xylose in feed (g/L), $c_p(glu)$ is the concentration of glucose in permeate (g/L), and $c_f(glu)$ is the concentration of glucose in feed (g/L). This equation measure the difference between composition ratio of xylose and glucose in permeate and feed. A value of 1 implies that no separation between xylose and glucose occurs. While, value greater than 1 implies ratio of xylose over glucose is higher in permeate than the original ratio (feed), thus xylose enriched in permeate. Value

lower than 1 implies the opposite, where glucose is enriched rather than xylose.[5,11]

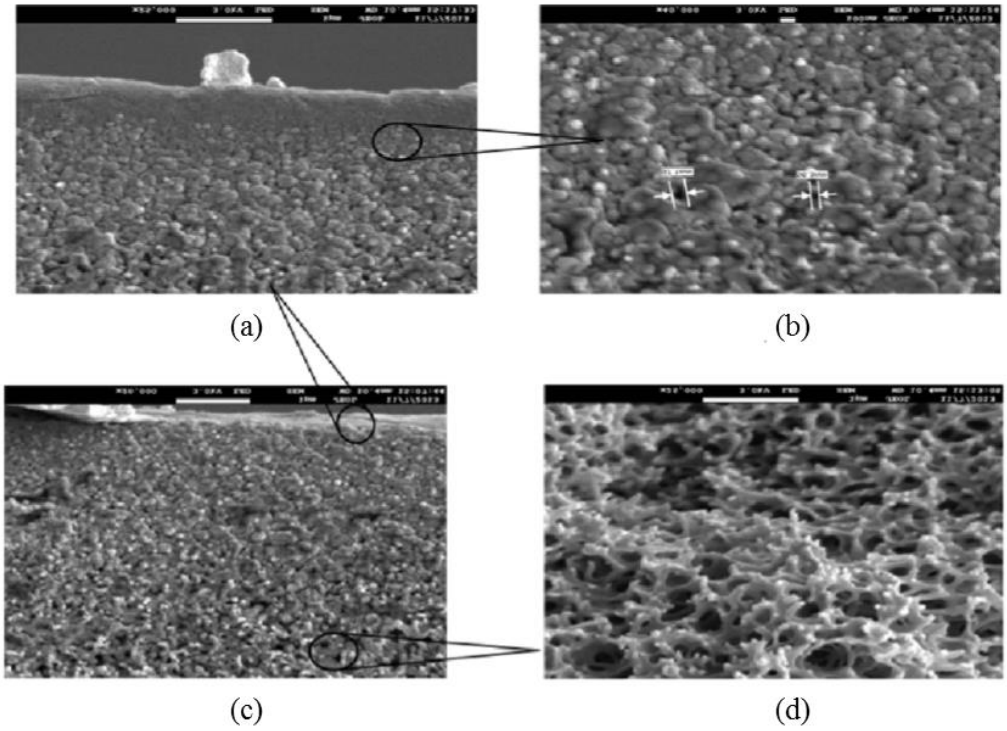


Figure 1 FESEM images of cross section of NF membrane (a) top layer (25,000x magnification) (b) top layer (40,000x magnification) (c) the whole membrane and (d) bottom layer

Table 1 Factors studied with their coded levels and actual values

Variable	Symbol	Real values of coded levels	
		-1	+1
Pressure (bar)	X_1	2	4
Concentration of total sugar in solution (% (w/v))	X_2	2	10
Ratio of xylose: glucose	X_3	1: 9	9: 1

■3.0 RESULTS AND DISCUSSION

3.1 FESEM Images

Figure 1a shows the FESEM image of the cross section of the NF thin film composite membrane. As can be seen in the Figure 1, the composite membrane has a porous structure on the bottom layer (Figure 1b) while a very dense on the top layer (Figure 1c) which determines the solute separation. From Figure 1d, one can see that just under the top dense layer, there are a few pores with size below 100 nm (i.e. 56.3 nm and 97.1 nm). So, it was postulated that the top dense layer may have pore size with a few nanometer and has an ability to separate sugar in our study. Figure 2 shows the FESEM image of the surface of NF top layer.

3.2 Pure Water Permeability

Pure water permeability (PWP) was carried out to estimate the effective pore radius (r_p) using mathematical model based on previous study.[12] Prediction of r_p for each membrane was carried out to make sure the membranes developed were in nanofiltration range. Prediction pore radius for each membrane was calculated using Hagen-Poiseuille equation:

$$J_w = \frac{r_p^2 \Delta P}{8\mu\left(\frac{\Delta x}{A_k}\right)} \quad (2)$$

The value $\Delta x/A_k$ was referred to past study[13] at 0.66 μm, 16.9 μm, and 4.75 μm, of minimum, maximum and average, respectively. Figure 3 present the test done on all the membranes used in this study. The slope for each membrane was the PWP for the respective membrane with unit $L.m^{-2}.h^{-1}.bar^{-1}$. Table 2 shows the obtained PWP and predicted r_p of each membranes.

Table 2 Obtained pure water permeability and predicted effective pore radius

Membrane	PWP ($L.m^{-2}.h^{-1}.bar^{-1}$)	r_p (nm)		
		Min.	Max.	Avg.
1	1.10	0.12	0.62	0.33
2	1.17	0.13	0.66	0.35
3	0.98	0.12	0.61	0.32
4	1.12	0.13	0.65	0.34
Mean	1.07(±0.09)	0.13(±0.01)	0.64(±0.03)	0.34(±0.01)

The PWP values obtained were well within the range reported previously[13] for nanofiltration membrane, which is between 1.331 $L.m^{-2}.h^{-1}.bar^{-1}$ to 50.50 $L.m^{-2}.h^{-1}.bar^{-1}$. The pore radius of the popular commercial nanofiltration membranes are from 0.3 to 1 nm, including the mean pore radius being approximately 0.4 – 0.45 nm.[13-15] The estimated pore radius in this study as shown in Table 2 is in agreement with previous studies. The reported radius of xylose and glucose is summarized in Table 3. Based on the mean for average r_p in Table 2,

theoretically in this present study, the glucose will retain on the membrane while xylose passes through.

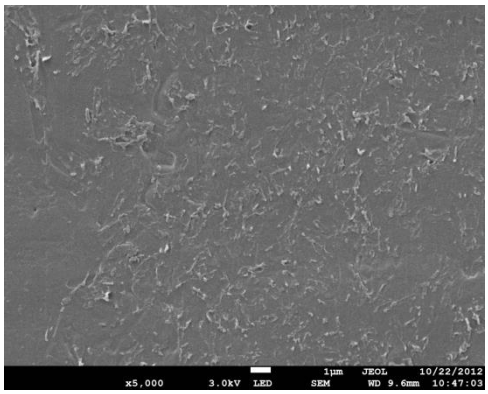


Figure 2 FESEM image of the surface of the top layer (5,000x magnification)

Table 3 Physical properties of xylose and glucose

Properties	Xylose	Glucose
Molar mass [5] (g/mol)	150.3	180.6
Stroke radius [16] (nm)	0.325	0.365
Equivalent molar radius [5] (nm)	0.34	0.36

3.3 Effect of Pressure

In this present study, nanofiltration was driven by pressure. Difference of pressure between retentate and permeate forces the solute from high pressure region (retentate) to low pressure region (permeate). An analysis done using Design Expert software showed that an increased in pressure, decreased the xylose separation slightly as in Figure 4. It was found that the relationship between pressure and separation performance was no in line with the result from other researchers. Past studies[5-7] reported an increase in pressure resulted in a higher permeation flux leading to a better rejection of desired component, which in this case, xylose. The pressure range used in their studies were from 2 to 14 bar,[7] 7 to 28 bar,[6] and 2 to 40 bar.[5] Pressure differences in the past studies were at least 6 times higher in this present study which lied at 2 bar. Thus, it is thought that the pressure difference applied was too low for significant effect of pressure on nanofiltration to be seen.

3.4 Effect of Total Sugar Concentration and Ratio of Xylose: Glucose

Total sugar concentration had been reported affecting nanofiltration with both positive and negative effects on separation performance. On the positive side, the larger molecule that were retained form a kind of second or dynamic membrane inducing high selectivity of small molecule.[17] On the negative side, higher total sugar concentration may increase larger molecule concentration at the membrane surface creating resistance for smaller molecule to pass through, also known as concentration polarization.[6,17]

An increase in concentration of total sugar from 2 to 10% (w/v) at both ratios saw a decrease in xylose separation factors as shown in Figure 5. Increase of total sugar concentration led to an increase of concentration polarization upon the membrane, where a decrease in flux was also observed as reported in the past studies[6,17] but contradicted with study by Sjoman *et al*.[5] However, Sjoman *et al*.[5] also reported a possible impact of membrane compression and concentration at more concentrated solution.

There was lack of information on the factor composition ratio of xylose: glucose. Most of the past studies[6-7] investigated the influence of xylose and glucose on separation independently. A change of xylose: glucose ratio from 1: 9 to 9:1 gave to a decrease in xylose separation factor at both concentration of 2% (w/v) and 10% (w/v), respectively as shown in Figure 4. At xylose: glucose ratio of 1:9, better xylose separation performance was observed. The higher concentration of larger molecule (glucose) pushes smaller molecule (xylose) through the membrane, enhancing xylose permeation but reducing the flux in return.[5]

There was an appreciable interaction between total sugar concentration and ratio of xylose: glucose as observed by the significant changes on xylose separation factor as shown in Figure 4. An increase of xylose concentration in the solution did not led to better xylose separation factor as observed in Figure 5 contradicting with study by Sjoman *et al*.[5] Sjoman *et al*.[5] concluded that higher xylose concentration in feed gave higher total permeate fluxes and xylose rejection than when the glucose concentration was high. High glucose concentration in feed do enhances xylose permeation and reduce total permeate flux.[5] In this study, decrease in xylose separation factor was observed at high xylose concentration in feed. This was mostly caused by the concentration polarization occurred hindering the permeation of xylose. The increase of concentration polarization may due to the small different in size between xylose and glucose. This cause the build-up of both xylose and glucose on the surface of the membrane creating a kind of second membrane blocking smaller molecule, which is xylose, from passing through.

3.5 Statistical Modeling and Analysis of Variance (ANOVA)

The analysis of variance (ANOVA) was carried out using Design Expert software. It was found that the result from ANOVA proved the model was significant with the p-value at 0.0018. In addition the F-value of 93.85 from ANOVA implied that there is only 0.18 % chance that the F-value could occur due to noise. This also indicates that this model has a confidence level of 99.21%. The coefficient of the model was calculated by Design Expert software and the following statistical model equation was established:

$$Xylose\ separation\ factor = 1.0836 - 0.0093X_1 - 0.2223X_2 - 0.4011X_3 + 0.2018X_2X_3 \quad (3)$$

The coefficients for the factors are lower than the interception, which indicated the existent of the design plateau. This plateau showed that the design had an optimum point.

3.6 Performance Comparison with Previous Study

The developed nanofiltration has shown potential in separating xylose from glucose in lab scale. Table 4 showed the result for all the experiment done and Table 5 compared membrane developed in this study with previous study. In this study, the xylose separation factor obtained are from 0.620 to 1.974.

Xylose separation factor of 1.5–3.0 was reported in previous study.[5] The highest xylose separation factor achieved in this study is 1.974 which is comparable to the previous study.[5] When comparing the permeate flux, it is notable that previous study employed cross-flow nanofiltration at pilot scale with high pressure. This resulted permeate fluxes in previous study[5] were much higher than the permeate flux obtained in this study.

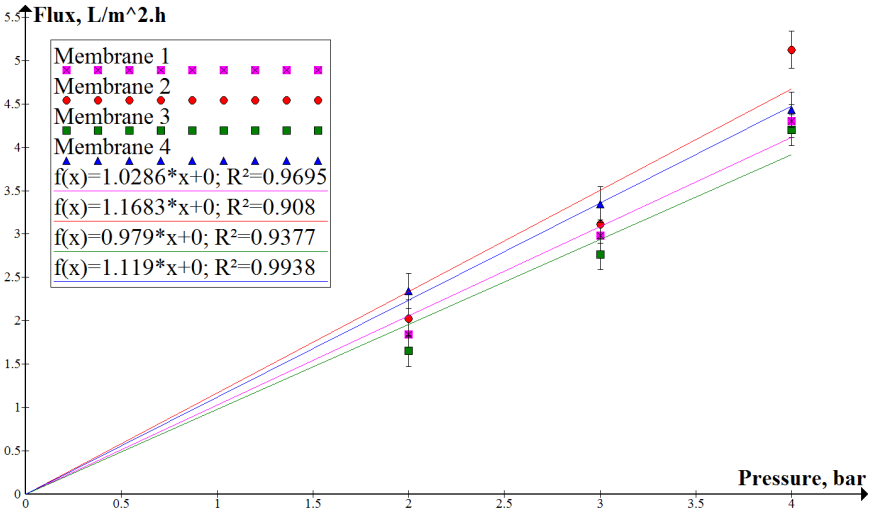


Figure 3 Water permeability test on all membranes used in this study

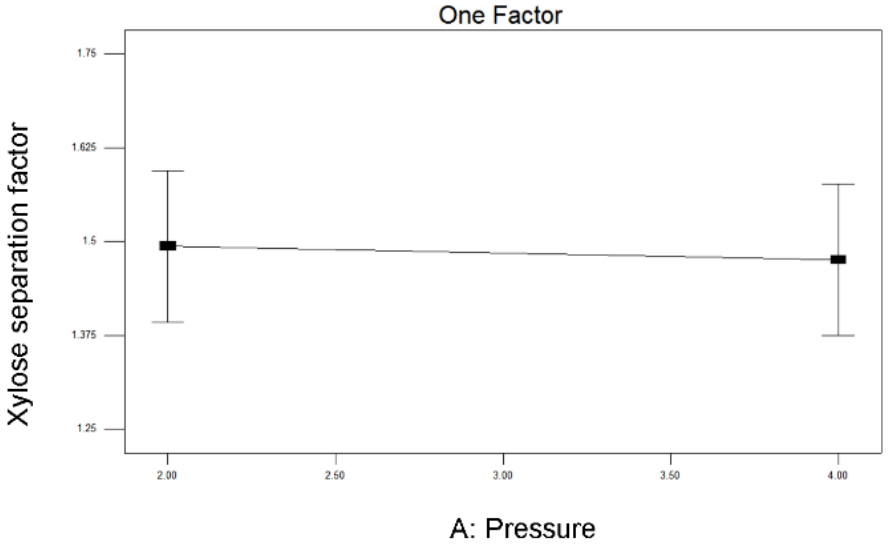


Figure 4 The graph between xylose separation factor and pressure

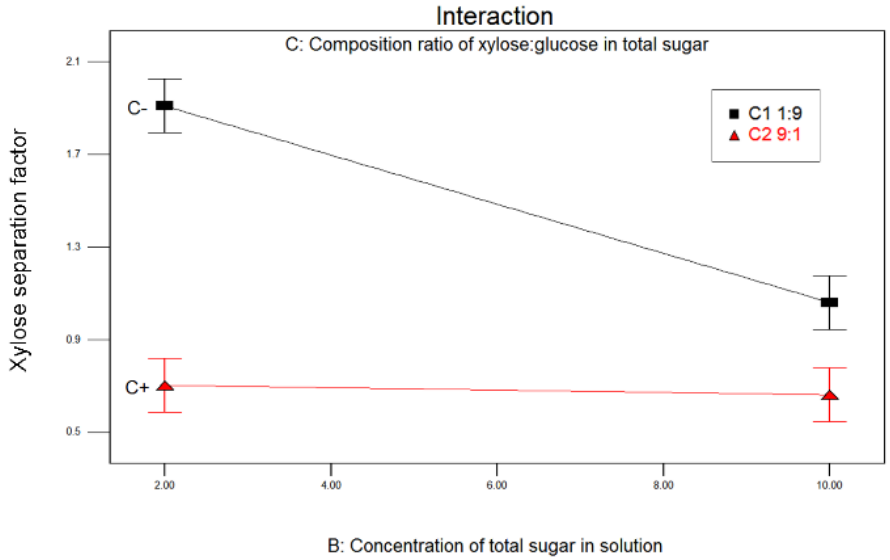


Figure 5 The interaction graph between total sugar concentration and ratio of xylose: glucose

Table 4 Experimental result

Std. Order	Pressure, X_1 (bar)	Total sugar concentration, X_2 (% (w/v))	Xylose/ Glucose ratio	Flux ($L.m^{-2}.h^{-1}.bar^{-1}$)	Xylose separation factor
1	2	2	1:9	0.5094	1.974
2	4	2	1:9	3.0298	1.844
3	2	10	1:9	0.0483	1.101
4	4	10	1:9	0.2774	1.020
5	2	2	9:1	0.4164	0.676
6	4	2	9:1	1.5149	0.730
7	2	10	9:1	0.2671	0.620
8	4	10	9:1	0.3154	0.705

Table 5 Comparison between developed membrane in this study and commercial membrane in previous study

	This study	Previous study [5]		
		Desal-5 DK	Desal-5 DL	NF270
Pressure (bar)	2 and 4		2 – 30	
Total sugar concentration (% (w/v))	2 and 10		2, 10 and 30	
Temperature (° C)	25		50	
Mean Pore Size, r_p (nm)	0.34	0.42 [14]	0.45 [14]	-
Average PWP ($L.m^{-2}.h^{-1}.bar^{-1}$)	1.07	8.1	9.1	15.9
Permeate Flux (kg. $m^{-2}.h^{-1}.bar^{-1}$)	0.3–3.0		5–30	
Maximum achieved, *Xyl*	1.974[a]	~3.3[b]	~2.3[b]	~2.4[b]

[a]Achieved at pressure 2 bar, total sugar concentration of 2 % (w/v) and xylose/ glucose ratio of 1:9
[b]Achieved at pressure 30 bar, total sugar concentration of 10 % (w/v) and xylose/ glucose ratio of 9:1 [5]

4.0 CONCLUSION

In the present study, membrane prepared by conventional interfacial polymerization of TEOA and TMC on PES porous membrane were first characterized. The characterization was performed using water permeability test with calculation using Hagen-Poiseuille equation. The average pore sizes radius of membrane used in this study was estimated at 0.34 nm. Theoretically, xylose (Stroke radius = 0.325 nm and equivalent molar radius = 0.34 nm) can pass through the membrane and glucose (Stroke radius = 0.34 nm and equivalent molar radius = 0.36 nm) will be retained.

In this study, the relationship between pressure and xylose separation factor demonstrated the increase of pressure led to decrease of separation performance. The finding from this study was not in agreement with past studies and theory. The pressure difference used in this study was most likely too low for significant effect of pressure on nanofiltration to be seen. There was an appreciable interaction between total sugar concentration and ratio of xylose: glucose as observed by the significant changes on xylose separation factor. In this study, decrease in xylose separation factor was observed at high xylose concentration in feed. This was mostly caused by the concentration polarization occurred hindering the permeation of xylose. The increase of concentration polarization may due to the small different in size between xylose and glucose. This cause the build-up of both xylose and glucose on the surface of the membrane creating a kind of second membrane blocking smaller molecule, xylose, from passing through. This indicates high possibility of concentration polarization strong enough to build a high resistance barrier restricting xylose from passing through.

The coefficient of determination R^2 from ANOVA study was 0.9921 proving the statistical model is significant. The coefficients for the factors were lower than the interception, which indicated the existent of the design plateau. This plateau showed that the design had an optimum point. In a nutshell, nanofiltration using membrane developed from TEOA and TMC as monomers on PES membrane has the ability to separate xylose from glucose. Overall in this present study it can be concluded that nanofiltration has high potential to replace currently in use chromatographic method in xylose separation.

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