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STUDY ON FACTORS AFFECTING SEPARATION OF XYLOSE FROM GLUCOSE BY NANOFILTRATION USING COMPOSITE MEMBRANE DEVELOPED FROM TRIETHANOLAMINE (TEOA) AND TRIMESOYL CHLORIDE (TMC)

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Abstract

Xylose is an abundant raw material coexists with other sugars that can be converted into xylitol. Separation of monosaccharides from each other is carried out commercially by chromatographic method. Nanofiltration may offer alternative to the current in use chromatographic method. This work aims to study the influence of pressure, total sugar concentration and xylose/glucose ratio on separation process using two-level factorial analysis. Membrane was prepared by conventional interfacial polymerization of triethanolamine (TEOA) and tri-mesoyl chloride (TMC) on polyethersulfone (PES) porous membrane. The experiment was performed using Amicon Milipore stirred cell with constant stirring speed at 300 rpm and at ambient temperature. The glucose and xylose concentration was quantified using high performance liquid chromatography (HPLC). In this study, it was found that the xylose/glucose ratio has affected the nanofiltration the most, at 63.56 %, followed by total sugar concentration at 19.52 %, and pressure contributed the least at 0.033 %. An interaction between factor total sugar concentration and composition of xylose to glucose were also found to contribute 16.10 % on nanofiltration. The coefficient of determination (R^2) from analysis of variance (ANOVA) study was 0.9921. Overall, in this present work it can be concluded that nanofiltration has high potential to replace chromatographic method in xylose separation.

Keywords: Nanofiltration, Interfacial polymerization, Separation.

1. Introduction

The strong demand of xylose is driven by the increasing commercial and scientific

Nomenclatures

$c_{f(glu)}$	Concentration of Glucose in Feed, g/L
$c_{f(xyl)}$	Concentration of Xylose in Feed, g/L
$c_{p(glu)}$	Concentration of Glucose in Permeate, g/L
$c_{p(xyl)}$	Concentration of Xylose in Permeate, g/L
J_w	Pure Water Flux, $L.m^{-2}.h^{-1}$
P_m	Pure Water Permeability, $L.m^{-2}.h^{-1}.bar^{-1}$
R^2	Coefficient of Determination
X_1	Coded Parameter of Pressure
X_2	Coded Parameter of Total Sugar Concentration
X_3	Coded Parameter of Xylose/Glucose ratio
X_{xyl}	Xylose Separation Factor
y_x	Coded Response of Xylose Separation Factor

Greek Symbols

ΔP	Pressure Differences, bar

Abbreviations

ANOVA	Analysis of Variance
HPLC	High Performance Liquid Chromatography
PES	Polyethersulfone
RI	Refractive Index
TEOA	Triethanolamine
TMC	Trimesoyl Chloride

interest in xylitol as substitute to sugar. Currently, commercial xylitol is produced by hydrogenating xylose with catalysis using from hydrolysates from birch trees in the United State and corncobs in China. Presently, the cost of hydrogenation is less than 20 % that of the total cost of xylitol production, and the cost of xylose crystal production is more than 80 % of the total cost of xylitol production. Most of the cost in producing xylose come from the purification steps of the hydrolysates [1].

The hydrolysates mostly contain a mixture of pentose and hexose sugar, typically glucose and xylose as shown in Table 1. The presence of sugar other than xylose during the hydrogenation process generates unwanted by-products, which are sugar alcohols corresponding to its sugar. Alcohol has higher solubility than their corresponding sugars making xylitol easier to be purified via crystallization in a mixture of sugars, compared to a mixture of sugar alcohols [1].

Presently, the separation between xylose from glucose depends solely on the chromatographic method, which is time-consuming and expensive. Separation of uncharged substance mostly based on the different in molecular sizes and diffusivities, and in this case the different between pentose and hexose is rather small falling in the scale of nanometres. Nanofiltration may offers cost-effective, and possible alternative to replace chromatographic method in separating sugars [2, 3].

2. Selection of Factors Affecting Nanofiltration

Past studies had identified four factors that have effect on the nanofiltration process [2-4]. The four factors are pressure, temperature, concentration of total sugars in solution, and composition of sugars. This work aims to study the influence of pressure, total sugar concentration and xylose/glucose ratio on separation process using two-level factorial analysis. Temperature was not studied because increases of temperature usually lead to the decrease in rejection. Higher rejection of neutral solutes was observed between temperature 20 °C to 30 °C [5, 6]. Thus, this study was carried out at ambient temperature.

Table 1. Monosaccharides from Hydrolysed Hemicelluloses of Agriculture [7].

Plant Residues	% of total sugar			
	Xylose	Glucose	Arabinose	Other
Corn residues				
Cobs	65.1	25.3	9.6	-
Leaves	59	29.7	9.4	2.5
Stalks	70.5	14.5	9.0	5.9
Husks	53.5	32.6	12.3	1.6
Pith	71.5	26.8	9.8	3
Fiber	63.8	26.8	6.6	2.8
Wheat straw	57.9	28.1	9.1	5
Soybean				
Stalks and leaves	59.9	6.1	6.6	27.4
Hulls	26.6	21	12.7	39.7
Sunflower				
Stalks	60.6	32.6	2.2	4.6
Pith	10.7	63.5	11.8	14
Flax straw	64.6	1.2	12.8	21.4
Sweet clover hays	49.3	8.9	21.9	9.9
Peanut hulls	46.3	46.6	5	2.1
Sugarcane bagasse	59.5	26	14.5	-

2.1. Influence of pressure

Pressure is one of the factor affecting nanofiltration because most nanofiltration is driven by pressure. Increase in pressure will led to increase in solvent flux and membrane compaction, hence increase the sugar rejection. The range of pressure studied were between 2 to 14 bar by Vegas et al. [4], 7 bar to 28 bar by Goulas et al. [3], and 2 bar to 30 bar by Sjoman et al. [2]. The study by Sjoman et. al [2] reported that concentrated monosaccharides at that high pressure favours the separation of xylose from glucose.

2.2. Influence of total sugar concentration

A patent example by Heikkilä et al. [8] presented partition separation of pentose from hexose by nanofiltration. The separation process by Heikkilä et al. [8] use 10 wt.% feed solution of arabinose and rhamnose diafiltered at 50 °C, resulting a rejection of 68-69%. Sjoman et al. [2] studies the separation process between pentose and hexose by using xylose and glucose at higher wt.% feed concentration, which are 2 wt.%, 10 wt.% and 30 wt%. Goulas et al. [3] on the other hand studied this factor between 1 wt.% to 8 wt.%.

2.3. Influence of xylose/glucose ratio

Mass ratio of xylose and glucose in feeds also affect the rejection of saccharides in nanofiltration. Studies by Sjoman et al. [2] discovered that higher glucose concentration in the feed enhances xylose permeation. The mass ratios of xylose to glucose studied by Sjoman et al. [2] are 1:9, 1:1 and 9:1.

3. Methodology

3.1. Material

The commercial PES membrane, UF PES50 was purchased from AMFOR INC (China). Chemical for surface modification are sodium hydroxide (Merck, Germany), TEOA (R&M Marketing, UK), 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 (Malaysia).

3.2. Membrane preparation

The membrane was prepared by conventional interfacial polymerization technology according to the procedure reported by Abu Seman et al. [9]. The aqueous solution was prepared by dissolving 6 % (w/v) TEOA in 1 % (w/v) sodium hydroxide (NaOH) solution. First, 10 g NaOH was dissolved in 1000 ml distilled water and used as base medium for TEOA solution. Aqueous TEOA solution with concentration 6% w/v was prepared by dissolved 6 g TEOA in 100 ml NaOH aqeous solution, (NaOH 1% w/v). The organic solution was made of 0.15 % (w/v) TMC dissolved in hexane by dissolving 0.15 g TMC in 100 ml n-hexane. PES membrane was cut into disc form with diameter of 63.5 mm 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.

3.3. Pure water permeability

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 step was done three times for each membrane. The obtained water fluxes were used in calculating the permeability using Eq. (1).

$$P_m = \frac{J_w}{\Delta P} \tag{1}$$

3.4. Experimental set-up

Prepared membrane was fitted into the membrane holder and secured with O-ring and body of Millipore Amicon stirred cell (Model 8200). 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 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.

3.5. Two-level factorial design

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 2. 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 Eq. (2).

$$X_{xyl} = \frac{c_p(xyl) \div c_p(glu)}{c_f(xyl) \div c_f(glu)} \tag{2}$$

Table 2. Factors Studied with Their Coded Levels and Actual Values.

Factors	Symbol	Real values of coded levels	
		- 1	+ 1
Pressure (bar)	X_1	2	4
Total Sugar Concentration	X_2	2	10
Xylose/glucose ratio	X_3	1:9	9:1

4. Results and Discussion

4.1. Pure Water Permeability, P_m

Pure water permeability was tested on all four membranes and the value is shown in Table 3 and Fig. 1. The range of values obtained was well within the range of values previously reported by Bowen and Mohammad [10], which is between 1 and 51 L/m^2.h.bar. The membrane developed can be categorized as tight nanofiltration membrane as previously reported by Abu Seman et al. [9] and Jalanni et at [11].

Table 3. Pure Water Permeability of the Membranes Developed.

Membrane	Pure Water Permeability, *Pm* (L.m^{-2}.h^{-1}.bar^{-1})
1	1.10
2	1.17
3	0.98
4	1.12
Mean	1.07(±0.09)

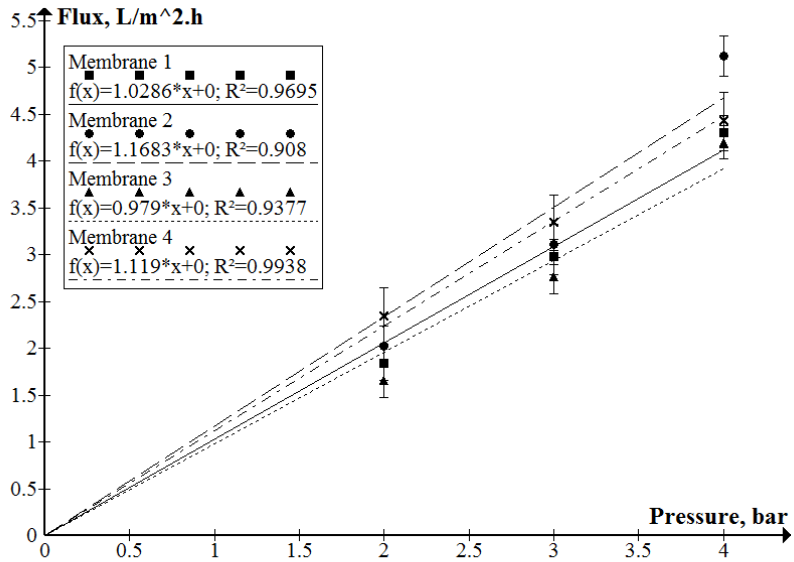

Fig. 1. Water Permeability Test on All Membranes Used in this Study.

4.2. Influence of pressure

Based on the analysis by Design Expert, pressure factor contribute the least to the response at 0.033 %. There is no significant interaction between pressure and total sugar concentration, or between pressure and xylose/glucose ratio. However, in this study the increase in pressure yield a slight decrease in response as shown in Figs. 2 and 3. The response obtained in this work was not in line with results obtained in past studies. However it should be noted that pressure differences in the past studies [2–4] were at least 6 times higher than the present work which lied at 2 bar.

4.3. Influence of total sugar concentration and xylose/glucose ratio

Based on the analysis by Design Expert, the xylose/glucose ratio factor has affected the nanofiltration the most, at 63.56 %, and by total sugar concentration at 19.52 %. An interaction between factor total sugar concentration and composition of xylose to glucose were also found to contribute 16.10 % on nanofiltration. The increase of xylose/glucose ratio and total sugar concentration generally led to increase of the xylose concentration in the feed solution.

An increase of xylose concentration in the solution did not led to better xylose separation factor as observed in Figs. 2 and 3, which contradicting with the work by Sjoman et al. [2]. In this study, decrease in xylose separation factor was observed at high xylose concentration in the feed. This probably caused by 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 due to the small different in size between xylose and glucose [12]. It can be concluded that the factors of total sugar concentration and xylose/glucose ratio have influence on the separation of sugars in this study.

4.4. Statistical modelling

The experimental data obtained were used to determine the regression coefficients for the model to describe the xylose separation factor in term of coded parameter and actual parameters. The coded parameter model is regressed linearly as in Eq. (3). The actual parameter model is regressed linearly as in Eq. (4). The coefficient 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.

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

$$\begin{aligned} &\textit{Xylose separation factor} = 1.0836 - 0.0093 \times \textit{Pressure} \\ &- 0.2223 \times \textit{Total sugar concentration} - 0.4011 \times \textit{Xylose / Glucose ratio} \\ &+ 0.2018 \times \textit{Total sugar concentration} \times \textit{Xylose / Glucose ratio} \end{aligned} \quad (4)$$

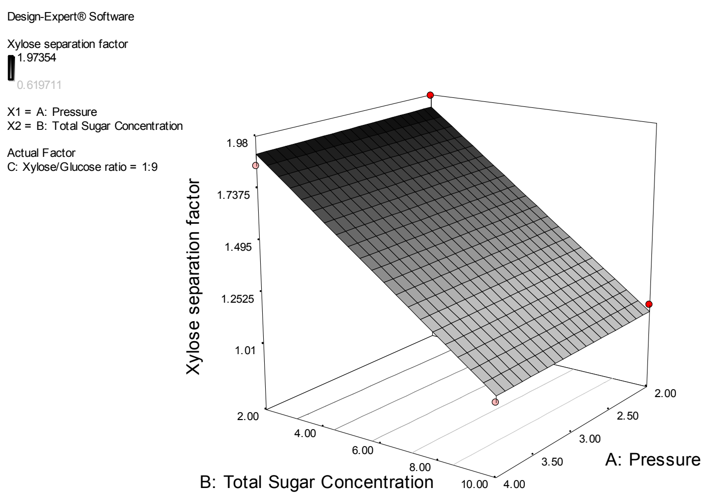

Fig. 2. Three-Dimensional Response Surface Plot for the Effects Pressure and Total Sugar Concentration at Respective Xylose/Glucose Ratio of 1:9.

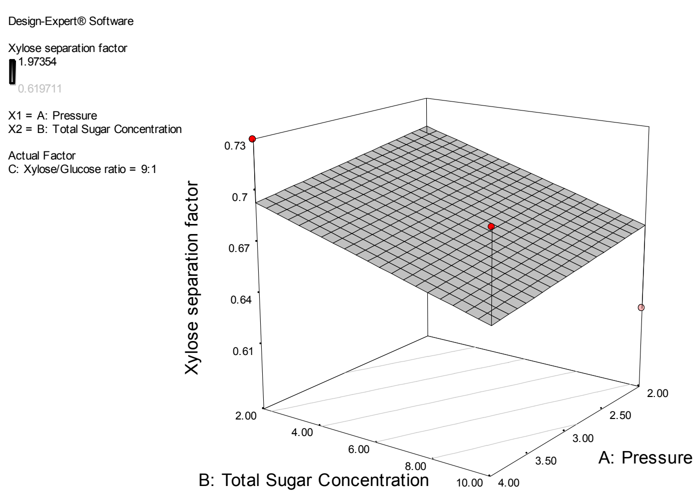

Fig. 3. Three-Dimensional Response Surface Plot for the Effects Pressure and Total Sugar Concentration at Xylose/Glucose Ratio of 9:1.

4.5. Analysis of variance (ANOVA)

The analysis of variance (ANOVA) was carried out using Design Expert software and presented in Table 4. It was found that the result from ANOVA proved the developed 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. In addition, it is also indicates that this model has a confidence level of 99.21 %.

Table 4. ANOVA of the Developed Model.

Source	Sum of Squares	df	Mean Square	F-Value	p-value (Prob>F)	
Model	2.008629	4	0.502157	93.85092	0.0018	**significant**
A	0.00066	1	0.00066	0.123345	0.7487	
B	0.395213	1	0.395213	73.86348	0.0033	
C	1.286883	1	1.286883	240.5127	0.0006	
BC	0.325873	1	0.325873	60.90415	0.0044	
Residual	0.016052	3	0.005351			
Corr. Total	2.024681	7				

Standard Deviation	0.073148
Mean	1.083639
R-Squared	0.992072
Adjusted R-Squared	0.981501

5. Conclusions

In conclusion, the factor that has the most influence was xylose/glucose ratio, followed by total sugar concentration, and the least was pressure. A significant interaction between factor total sugar concentration and xylose/glucose ratio was observed. However, pressure on the other hand has no significant interaction compared with total sugar concentration, or xylose/glucose ratio. The model developed was significant and has a confidence level of 99.32 %. The model indicated the existence of the design plateau with an optimum point. In this study, the three-dimensional response surface did not show a peak but planes inclining upward. This indicated that the optimum point lies outside the range studied in this work.

References

1. Da Silva, S.S.; and Chandel, A.K. (2012). *D-Xylitol: Fermentative Production, Application and Commercialization*. Springer, Heidelberg.
2. Sjoman, E.; Manttari, M.; Nystrom, M.; Koivikko, H.; and Heikkila, H. (2007). Separation of xylose from glucose by nanofiltration from concentrated monosaccharide solutions. *Journal of Membrane Science*, 292(1-2), 106-115.
3. Goulas, A.K.; Kapasakalidis, P.G.; Sinclair, H.R.; Rastall, R.A.; and Grandison, A.S. (2002). Purification of oligosaccharides by nanofiltration. *Journal of Membrane Science*, 209(1), 321-335.

4. Vegas, R.; Moure, A.; Domínguez, H.; Parajó, J.C.; Álvarez, J.R.; and Luque, S. (2006). Purification of oligosaccharides from rice husk autohydrolysis liquors by ultra-and nano-filtration. *Desalination*, 199(1), 541-543.
5. Ben Amar, N.; Saidani, H.; Deratani, A; and Palmeri, J. (2007). Effect of temperature on the transport of water and neutral solutes across nanofiltration membranes. *Langmuir* , 23(6), 2937-2952.
6. Nilsson, M.; Trägårdh, G.; and Östergren, K. (2008). The influence of pH, salt and temperature on nanofiltration performance. *Journal of Membrane Science*, 312(1-2), 97-106.
7. Flickinger, M.C.; and Drew, S.W. (1999). *Encyclopedia of bioprocess technology: Fermentation, biocatalysis, and bioseparation*. John Wiley & Sons, New York.
8. Heikkilä, H.; Koivikko, H.; Lindroos, M.; Maenttaeri, M.; Nyström, M.; Paananen, H.; and Puuppo, O. (2002). Separation process. *Google Patents*, US2807156 A.
9. Abu Seman, M.N.; Jalanni, N.A.; Faizal, C.K.M.; and Hilal, N. (2013). Polyester thin film composite nanofiltration membranes prepared by interfacial polymerization technique for removal of humic acid. In: Pogaku, R.; Bono, A.; and Chu, C. (Eds.) *Developments in Sustainable Chemical and Bioprocess Technology*. Springer, US, p.111.
10. Bowen, W.; and Mohammad, A.A.W. (1998). Characterization and prediction of nanofiltration membrane performance-a general assessment. *Chemical Engineering Research and Design*, 76(8), 885-893.
11. Jalanni, N.A.; Abu Seman, M.N.; and Faizal, C.K.M. (2013). Investigation of new polyester nanofiltration (NF) membrane fouling with humic acid solution. *Jurnal Teknologi*, 65(4), 69-72.
12. Mulder, M. (1996). *Basic principles of membrane technology*. *Zeitschrift für Physikalische Chemie* (2nd Ed.). AA Dordreht: Kluwer Academic Publishers.