SYNTHESIS OF NANOFILTRATION MEMBRANE DEVELOPED FROM DIFFERENT CONCENTRATION OF TRIETHANOLAMINE (TEOA) FOR SEPARATION OF XYLOSE FROM GLUCOSE

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ABSTRACT

Synthesis of thin film composite (TFC) nanofiltration membrane has experienced tremendous development since the concept of interfacial polymerization (IP) was first introduced. One of it new application is on the separation of xylose from glucose in biomass hydrolysate. In this present study, thin film composite (TFC) nanofiltration (NF) membrane has been produced through interfacial polymerization by manipulation the concentration of triethanolamine (TEOA) at different reaction time with 0.15 % w/v. of trimesoyl chloride (TMC). The membrane was then characterized in term of their chemical and physical properties, and separation performance between xylose and glucose. The growth of thin layer film depends on concentration of the monomer (TEOA) and reaction time. It was found that as concentration of TEOA and reaction time increased, the layer of the TFC become thicker thus decreases the permeability of the membrane. In contrast, the lowest and the highest permeability were recorded at 4% w/v of TEOA and 8% w/v of TEOA at reaction time of 35-minute in TMC, respectively. Moreover, higher sugar rejection of 0.896 % was obtained at 4% w/v TEOA after 35-minute reaction in TMC.

Keywords: Nanofiltration; Thin film composite; Interfacial polymerization; separation

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 yeasts, bacteria, and mycelial 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 cellulose covering around 25% of the total sugar [1]. Separation of these two different groups of sugar that is pentose (xylose) from hexose (glucose) by using thin film nanofiltration composite membrane was introduced in order to get the high productivity of desired products fermented, which is xylose. Among various

method of separation as an alternative to chromatography, nanofiltration offers cost-effective and easy-maintenance for the separation of xylose from glucose [2][3].

Nanofiltration around the world mainly applies the use of thin-film composite membranes by interfacial polymerization. Interfacial polymerization is deposition of a thin selective layer on top of a porous membrane by interfacial in-situ polycondensation of diamine and diacid chloride. Recent years saw that preparation of thin-film membrane with interfacial polymerization technique using monomers with special functional groups has been highly focused. Membrane surface charge developed with these monomers can be adjusted according to the amino groups and tertiary amino groups. A particular tertiary amino, triethanolamine (TEOA), which is environmental-friendly and economical [4] was used in this study. The membrane used in this study was prepared according to Tang et al. (2008) with slight modification base on the work by [5][6]. Membrane fouling is one of the critical issues in nanofiltration and need to be reduced in order to have xylose-glucose separation. Several types of commonly used polymers and their fabrication technique are shown in Table 1.

Table 1 Summary of Commonly Used Polymers and Fabrication Techniques for the Preparation of Polymeric Membranes for Separation Processes[7]

Type of membrane	Polymers used for membrane fabrication	Fabrication techniques	Averages pore size of membrane
RO	Cellulose acetate/triacetate Aromatic polyamide Polypiperzine Polybenzimidazoline	Phase inversion Solution casting	3-5 Å
NF	Polyamides	Interfacial polymerization	0.001 - 0.01 μm
	Polysulfones	Layer-by-layer deposition	
	Polyols Polyphenols	Phase inversion	
UF	Polyacrylonitrile (PAN)	Phase inversion	0.001 - 0.1 μm
	Polyethersulfone (PES) Polysulfone (PS) Poly (phthazine ether sulfone ketone) (PPESK) Poly (vinyl butyral) Polyvinylidene fluoride (PVDF)	Solution wet-spinning	

This paper aims to investigate the TFC membrane performance (water permeability and xylose separation factor) and evaluate their fouling behaviour.

MATERIALS AND METHODS

Interfacial Polymerization. Ultrafiltration (UF) polyethersulfone (PES) membrane was modified by interfacial polymerization technique using reaction of aqueous and organic solution to form thin film composite (TFC) nanofiltration (NF) membrane. UF PES membrane was cut into a disk forms shown in Figure 1. Sodium Hydroxide (NaOH) solution with concentration 1% w/v was prepared by dissolving 1g NaOH in 1000 ml de-ionized water and used as base medium for TEOA solution. The aqueous TEOA solution with different concentration 4% w/v and 8% w/v was prepared by dissolved 4g and 8g of TEOA respectively in different 100 ml beaker contained 100 ml NaOH aqeous solution. The PES membrane was immersed in aqueous TEOA solution (4% w/v) for 30 minutes. Then the excess TEOA solution on the surface of the membrane was drained at room temperature for 5 minutes. Upon completion of interfacial polymerization process, the membrane was then dried in oven at 60 °C until constant weight.

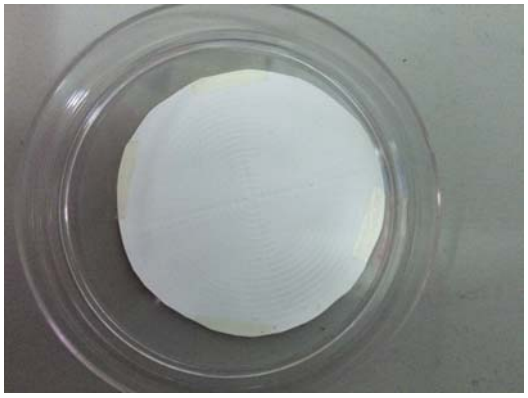


Figure 1 Membrane Cut into Disk Form

Water Permeability Test. The membrane was tested for pure water permeability (PWP) where the prepared membrane was fitted into the membrane holder and secured with O-ring and body of Millipore Amicon stirred cell (Model 8200). Other parts were then assembled together and place on top of magnetic stirrer shown in **Error! Reference source not found.**. The de-ionized water was filled into the stirred cell. Freshly prepared membranes were first flushed with de-ionized water at ambient temperature and pressure of 4 bar for 10 minutes. Next, the water flux was measured at 2, 3, and 4 bar with de-ionized water at ambient temperature. An amount of 20 mL permeates were collected and the total time taken was also noted. Pure water flux, Pm (L h^{-1} $m^{-2)}$ was tested for both coated and uncoated membrane at different operating pressures, ΔP. Water flux (J_w) is calculated by using following Eq. (1) [8].

$$J_w = \frac{V}{A \times t} \quad (1)$$

Eq. (1) showed the calculation for water flux where V is permeate volume as a function of time, t in hour and A is the area of membrane which 0.00287 m^2

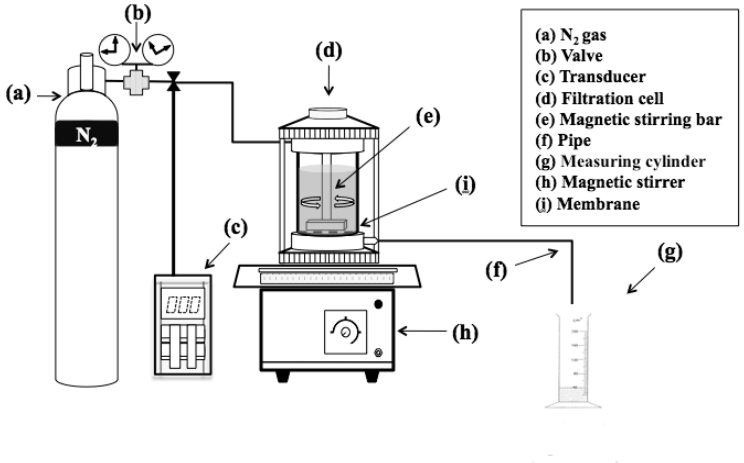


Figure 2 Experimental Set Up (Amicon Stirred Cell,Model 8200)

Xylose Separation. The solution of binary sugar, xylose-glucose were prepared in ultrapure water at total feed concentration of 20 g/L. Filtration were performed at fixed ratio of xylose to glucose (1:1), ambient room temperature and at 4 bar of pressure. Time was recorded when 20 mL volume of permeate was collected in order to calculate the flux for each membrane samples. The average time was 2 hour and half for the xylose separation.

Xylose-Glucose Concentration Analysis Method. After filtration using the two different membrane samples, 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 is at ambient temperature.

Determination of Pore Size and Effective Thickness/Porosity of the Membranes. In order to determine the pore size and effective thickness/porosity, the flux and rejection data of the solution was calculated using The Donnan steric pore model (DSPM) based on the extended Nernst-Planck equation (ENP) that proposed by Schlogl and Dresner according to [9].

Membrane Fouling Test. Next, fouling test on the membrane was done once the separation of sugar was completed. The membrane was flushed with ultrapure water in Amicon stirred cell about 10 minutes at 300 rpm. Initial water flux F_i, was measured at operating pressure of 4 bar with water permeation experiment. Then, filtration was done with xylose-glucose solution (1:1) at 4 bar and 300 rpm stirring rate. Time was taken until reached 20 ml of permeate. After sugar filtration was completed, the membrane was then flushed again with ultrapure water for 15 minutes at 350 rpm stirring rate in order to remove the weakly adsorbed sugar on the membrane surface. No pressure was applied during cleaning process. After that, the membrane was tested again with de-ionized water at pressure 4 bar and final water flux, F_f is measured. The fouling index which in term of irreversible fouling, IF was measured by using following Eq. (2) [5].

$$IF = (1 - \frac{F_f}{F_i}) \times 100\% \quad (2)$$

Eq. (2) showed the calculation of fouling index (IF) of the membrane where F_i is initial water flux and F_f is final water flux.

RESULTS AND DISCUSSION

Characterization of Top Skin Layer. Error! Reference source not found. shows the ATR-FTIR spectra comparison between TEOA, TMC, PES and TFC membrane, which have been modified at different concentration of TEOA: 8% w/v and 4 % w/v. The reaction between the monomer TEOA in NAOH (1% w/v) and TMC in n-hexane as organic phase produces polyester polymer layer on membrane surface [6] as shown in **Error! Reference source not found.**. The presences of two bands on the membrane surface of 8% w/v TEOA, which are 1719.01 cm^{-1} and 1236.56 cm^{-1}, indicate to the interfacial polymerization. Based on [4] work, interfacial polymerization occurred on the TFC membrane when two strong bands at 1723 and 1239 cm^{-1} present which are characteristic of νC=O and νC-O-C of ester compound, respectively. In this work, the TFC membranes surface is in the wavenumber range of the ester functional group.

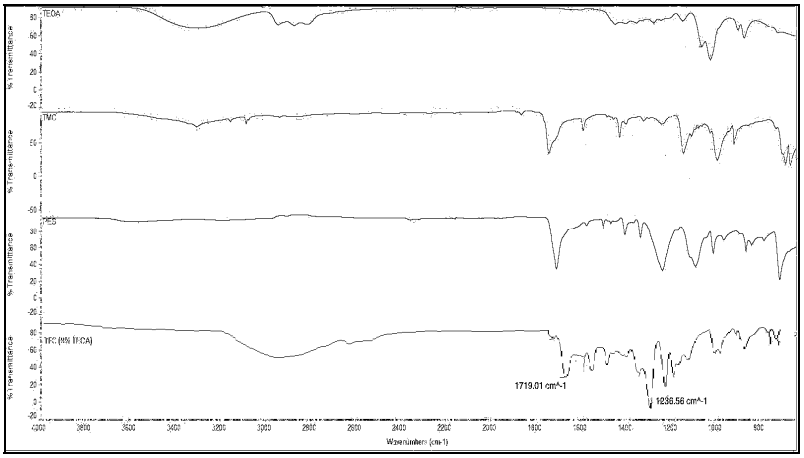
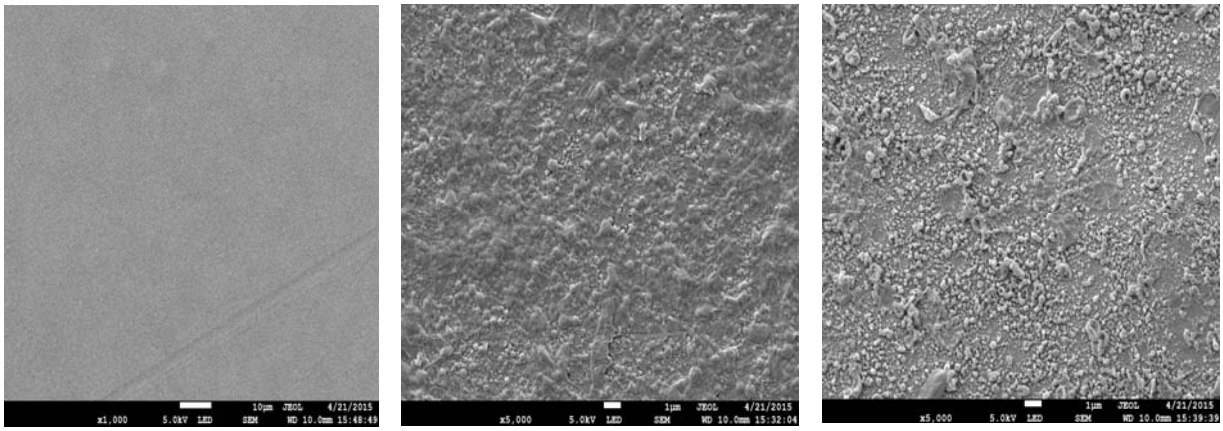


Figure 3 ATR-FTIR Spectra of TFC Membrane

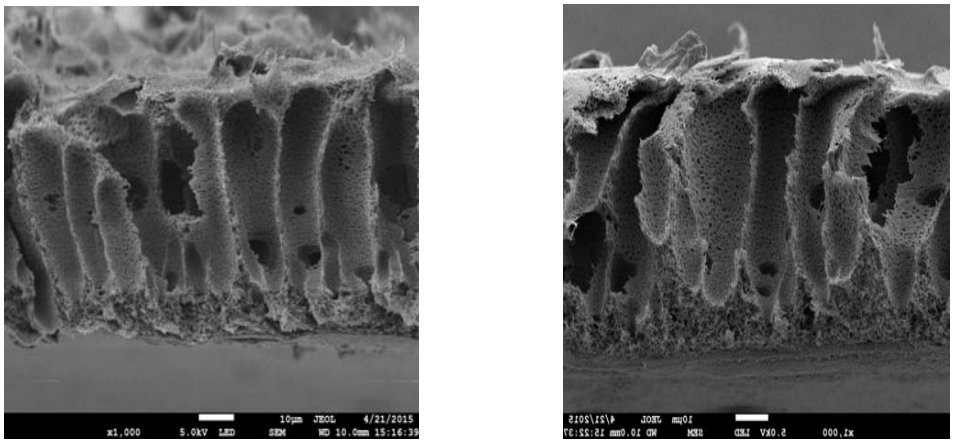
Small pieces of TFC membrane samples were used for FESEM measurements. The analysis included the surface and the cross-sectional of the membrane samples and the samples were fractured in liquid nitrogen before examined by FESEM. The scanning electron micrographs for the morphologies of the surface and the cross-section of the TFC membrane samples are shown in **Error! Reference source not found.** and **Error! Reference source not found.**, respectively. FESEM images as in **Error! Reference source not found.**a and Fig. 4b show that the polyamide-thin film was formed as compared to surface of PES and TFC membranes. It can be seen that the membrane surface also become more wrinkled at higher concentration of 8% w/v of TEOA than the 4% w/v of TEOA, respectively. The cross-sectional image from **Error! Reference source not found.**b shows that the number of pores with the size below 100 nm for nanofiltration membrane are more dense in TFC membrane prepared with 8% w/v of TEOA. It

has been reported by [10] that this condition may resulted in higher ability to separate xylose from glucose.



(a) (b) (c)

Figure 4 FESEM Images of Surface of UF PES and TFC Membrane (a) UF PES Membrane (1000x Magnification) (b) 4% w/v of TEOA Membrane (5000x Magnification) (c) 8% w/v of TEOA Membrane (5000x Magnification)



(a) (b)

Figure 5 FESEM Images of Cross Section of TFC Membrane (a) 4% w/v of TEOA Membrane (1000x Magnification) (b) 8% w/v of TEOA Membrane (1000x Magnification)

Contact angle is a measurement of hydrophilicity of the membrane surface. It can be seen **i**n **Error! Reference source not found.** that the contact angle of TFC membrane was lower than PES membrane. According to **Error! Reference source not found.** the PWP of the uncoated membrane (PES) and TFC membrane has huge significant different which the PWP is drop form 87.088 to 1.959 L h^{-1} m^{-2} bar^{-1} and 4.979 L h^{-1} m^{-2} bar^{-1} respectively. As referred

to previous study by [11], the PWP values obtained were in range for commercial nanofiltration membrane, which has the lowest of 1.331 L h^{-1} m^{-2} bar^{-1} to the highest of 50.50 L h^{-1} m^{-2} bar^{-1} .This indicated that there is a change to the surface properties deducing that interfacial polymerization is successful done.

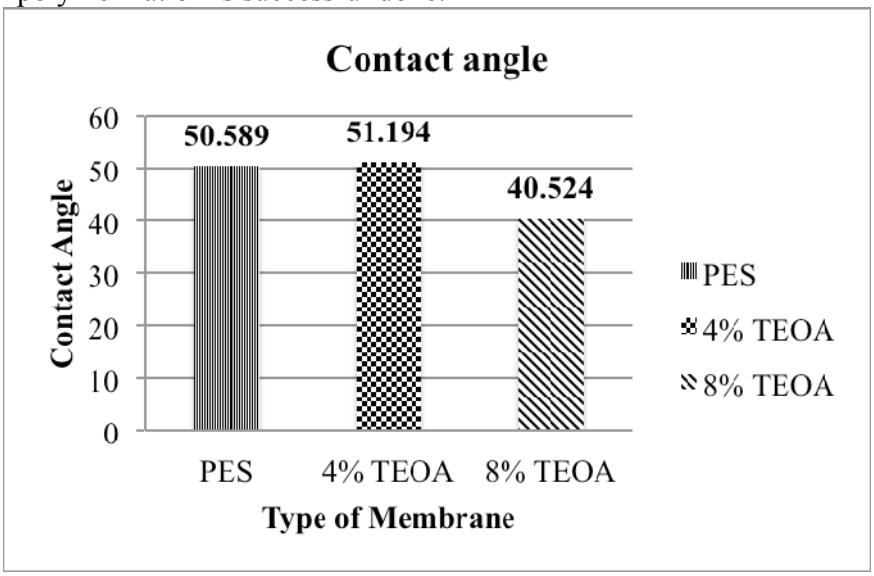


Figure 6 Contact Angle of PES Membrane and TFC Membranes at Reaction Time 35-min

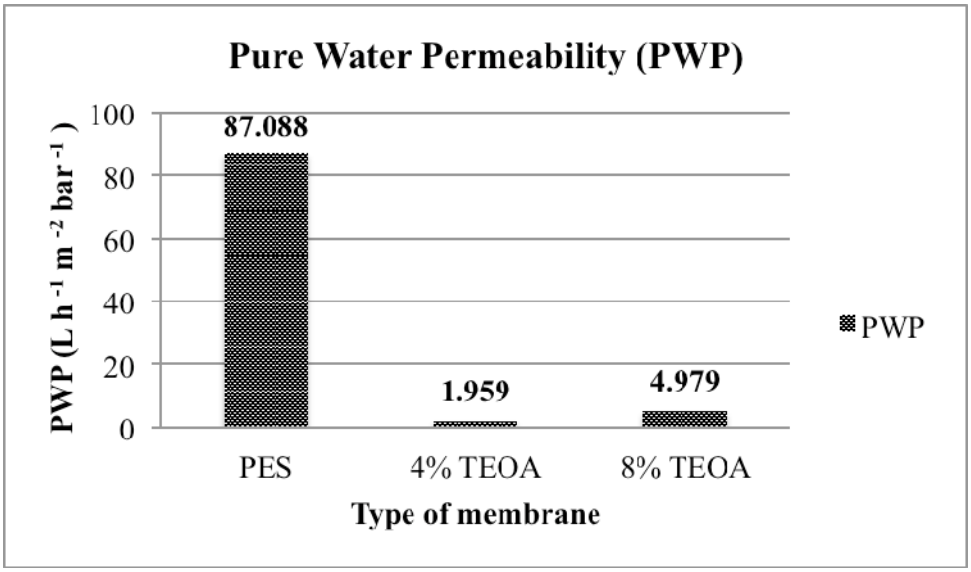


Figure 7 Pure Water Permeability (PWP) of PES and TFC Membranes with Different TEOA Concentration

Effect of Different Concentration of Triethanolamine. It has been reported from previous study, which the concentration of monomer is vital part in the synthesis of TFC membrane, by interfacial polymerization. The flux and also the separation behavior of the membrane is being

affected by chemically changes during interfacial polymerization process [4]. Other membrane characterization method was used to determine the effective pore radius (r_p) and the ratio of effective membrane thickness over porosity ($\Delta x/A_k$).

(3)

Error! Reference source not found. shows the result for PWP, predicted r_p and $\Delta x/A_k$ for each TFC membrane.

Table 2 Result for Pure Water Permeability, Predicted Effective Pore Radius (r_p) and The Ratio of Effective Membrane Thickness Over Porosity ($\Delta x/A_k$)

Membrane	PWP (L h^{-1} m^{-2} bar^{-1})	rp (nm)	$\Delta x/\Delta k$ (μmeter)
4% TEOA	1.96	0.41±0.29	4.43±3.13
8% TEOA	4.98	0.67±0.48	4.91±3.47

Table 3 Physical Properties of Xylose and Glucose[10]

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

The mean pore radius for commercial nanofiltration membrane is the range of 0.4-1.5 nm [11]. The pore size obtained for both prepared TFC membranes were within the range of commercial membrane, which is 0.41 and 0.67 nm as in Table 2. Result from TABLE 2 shows similar $\Delta x/\Delta k$ was obtained for both TFC membrane, indicated that the relative thickness of top skin layer was almost the same. However, different in PWP for both TFC membrane might be due to the differences in r_p. Based on previous finding by [4] shows that excessive TEOA higher than 6% do not allow more cross-linking to occur hence resultant in incomplete polymerization. This can been seen in TABLE 2 where the TFC membrane prepared with 8% TEOA produced skin layer with large r_p, but moderate in $\Delta x/\Delta k$ when compared to 4% TEOA. An increase in TEOA concentration increases the hydrophilicity of TFC membrane, which supported by the higher flux at 8% w/v TEOA.

Separation Performance. The xylose separation factor, X_{xyl} is used to measure the xylose purification from glucose. In Table 4, the TFC membrane prepared with 4 % w/v TEOA has high in permeate flux resultant in high of xylose separation which is 0.276 whereas TFC membrane prepared by 8% w/v TEOA with low permeate flux has 0.260-xylose separation factor. The concentration of the monomer TEOA has effected the surface and pore size of the membrane. It can be seen when lower concentration of TEOA (4% w/v) caused high permeate flux and high xylose separation factor. Those values were too little when reported in previous study which is 1.5 – 3.0 of xylose separation factor for commercial nanofiltration membrane [12]. This is due mass ratio of xylose to glucose in feed used in this study only 1: 1 rather than greater ratio mass xylose to glucose that is 1:9 and 9:1 used in previous study [10] [12].

Table 4 Permeate Flux (LM $^{-2}$h^{-1}) and Xylose Separation Factor

Types of membrane	Permeate Flux, Jw ($LM^{-2}h^{-1}$)	Xylose Separation factor
4% TEOA	8.32	0.276
8% TEOA	1.42	0.260

CONCLUSIONS

A TFC membrane for nanofiltration was synthesized by interfacial polymerization of triethaolamine (TEOA) and trimesoyl chloride (TMC) on polyethersulfone (PES) supporting membrane. The concentration of TEOA was varied to 4% w/v and 8% w/v. The membranes characterization using ATR-FTIR and FESEM showed the roughness and densed layer of polyester on top of the surface of the membranes. The performances of the TFC membranes were conducted by pure water permeability test, separation performance and fouling test. In this study, as the concentration of TEOA increased, the layer of TFC membrane become thicker and increased the permeability of membrane due to hydrophilicity behavior of the membrane and excess of TEOA in aqueous phase to react with TMC. As a result, 4% w/v TEOA membrane has small pore size, which is 0.41±0.29 nm with high permeate flux (8.32 $LM^{-2}h^{-1}$) and high xylose separation factor compared to 8% w/v TEOA membrane which has high pore size which is 0.67±0.48 nm with low permeate flux (1.42 $LM^{-2}h^{-1}$) and xylose separation factor. However, further study on membrane fouling would be required in order to have complete understanding on surface roughness, concentration polarization, pressure effect and membrane compaction so that fouling case related to xylose-glucose during membrane nanofiltration can be full clarified. Overall, it can be concluded that this composite nanofiltration membrane has high potential to be used in separation of xylose from glucose.

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