CHEMICAL ENGINEERING TRANSACTIONS
VOL. 56, 2017
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Jiří Jaromír Klemeš, Peng Yen Liew, Wai Shin Ho, Jeng Shiun Lim

ISBN 978-88-95608-47-1; **ISSN** 2283-9216
DOI: 10.3303/CET1756252

Synthesis of Nanofiltration Membrane Developed from Triethanolamine (TEOA) and Trimesoyl Chloride (TMC) for Separation of Xylose from Glucose

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Synthesis of thin film composite (TFC) nanofiltration (NF) membrane has experienced tremendous development since the concept of interfacial polymerisation (IP) was first introduced. One of its new application is on the separation of xylose from glucose in biomass hydrolysate. In this present study, NF TFC membrane has been produced through interfacial polymerisation by manipulation the concentration of triethanolamine (TEOA) at 35 min reaction time with 0.15 % w/v of trimesoyl chloride (TMC). The membrane was then characterised 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 TEOA as the monomer and reaction time. As concentration of TEOA and reaction time increased, the layer of the TFC becomes thicker thus decreases the permeability of the membrane. Contradicted to this study, 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-min in TMC. The TFC membrane prepared with 4 % w/v TEOA has high in permeate flux, resultant in high xylose separation of 1.3. Low permeate flux but moderate xylose separation factor of 0.93 was obtained for the TFC membrane prepared with 8 % w/v TEOA.

1. Introduction

Xylose is a plentiful raw material and also as intermediate product in production of 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 mostly 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 (Mah et al., 2014) . Separation of these two different groups of sugar that is pentose (xylose) from hexose (glucose) by using thin film NF 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, NF offers cost-effective and easy-maintenance for the separation of xylose from glucose (Sjoman et al, 2007).
Nanofiltration (NF) around the world mainly applies the use of TFC membranes by interfacial polymerisation. A TFC membrane consists of three layers. The ultra-thin top layer around 0.1 to 3 µm is the actual selective barrier in the composite, and is responsible for the molecular selectivity. This top layer is supported by a porous sub layer; usually an asymmetric ultrafiltration or microfiltration membrane. The second layer consists of porous ultrafiltration support around 20 to 50 µm thick. The third layer is a non-woven reinforcing fabric that provides for the main part of the mechanical strength of the composite structure. TFC membranes have

Please cite this article as: Roli F.M., Yussof H.W., Saufi S.M., Seman M.N.A., Mohammad A.W., 2017, Synthesis of nanofiltration membrane developed from triethanolamine (teoa) and trimesoyl chloride (tmc) for separation of xylose from glucose, Chemical Engineering Transactions, 56, 1507-1512 DOI:10.3303/CET1756252

dominated most of the nanofiltration/reverse osmosis market since their commercial recognition in the 1980's (Dalwani, 2011).
The development of thin film composite membrane with high flux through the optimisation of formation conditions by interfacial crosslinking of reactive monomers and trimesoyl chloride has been discovered. The technique was acknowledged as interfacial polymerisation (IP) (Lau et al., 2012). IP is deposition of a thin selective layer on top of a porous membrane by interfacial in-situ polycondensation of diamine and diacid chloride. A preparation of the TFC membrane with interfacial polymerisation 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 (Tang et al., 2008) was used in this study. The membrane used in this study was prepared according to Tang et al. with slight modification base on the work by Jalanni et al. (2013) .
This paper aims to investigate the performance of TFC membrane in term of water permeability and xylose separation factor, after it was modified through IP by manipulating the concentration of TEOA at 0.15 % TMC.

2. Materials and Methods

2.1 Material

The asymmetric commercial polyethersulfone (PES) membrane was purchased from AMFOR Inc. (China) with the commercial name of UF PES50. The membrane has a nominal molecular cut-off of 50 kPa and water flux (at 25 °C) of 260 LMH. The chemicals used in this study were triethanolamine (R & M Marketing, Essex, UK), trimesoyl chloride (Alfa Aesar, UK), sodium hydroxide (Merck, Germany), n-hexane (Merck, Germany), xylose (Sigma Aldrich, USA), glucose (Sigma Aldrich, USA), and acetonenitrile (J.T. Baker, USA). All chemicals were analytical grade with high purity (> 99 %) and acetonitrile with High Performance Liquid Chromatography (HPLC) grade.

2.2 Preparation of TFC membrane

The base medium for aqueous phase monomer solution was prepared by dissolving 1 % (w/v) sodium hydroxide in ultrapure water. The aqueous phase monomer solution was prepared by dissolving 4, and 8 % (w/v) of TEOA with the base medium. The organic monomer phase solution was prepared by dissolving 0.15 % (w/v) of TMC in pure hexane. The commercial PES support membrane was soaked in the aqueous phase solution for a period of 35 min. The membrane was then drained and rolled with a glass rod to remove excess liquid. The membrane was immersed in the organic phase solution for a period of 35 min. The TFC membrane was dried in an oven at 60 °C for 30 min (UF 55, Memmert, USA).

2.3 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 Amicon stirred cell 8200 (Milipore, USA). Other parts were then assembled together and place on top of magnetic stirrer shown in Figure 1. The de-ionised water was filled into the stirred cell. Freshly prepared membranes were first flushed with de-ionised water at ambient temperature and pressure of 4 bar for 10 min. The water flux was measured at 2 bar, 3 bar, and 4 bar with de-ionised water at ambient temperature. An amount of 20 mL permeates was 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) (Road, 2007).

$$J_w = \frac{V}{A \times t} \tag{1}$$

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

2.4 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.

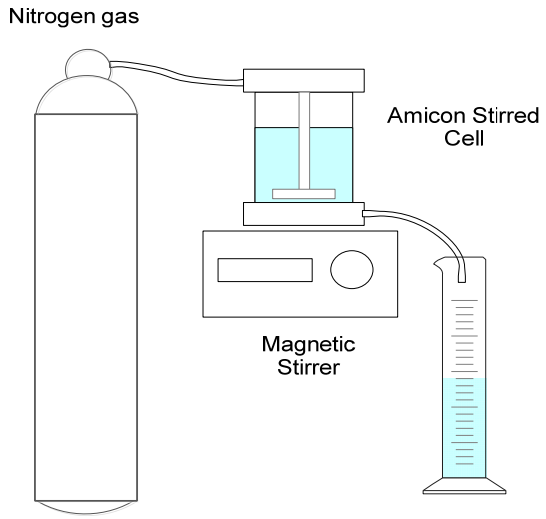


Figure 1: Experimental set up (Amicon stirred cell, model 8200)

2.5 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 were calculated using The Donnan steric pore model (DSPM) based on the extended Nernst-Planck equation (ENP) that proposed by Schlogl and Dresner according to Ahmad and Ooi (2005).

3. Results and discussions

3.1 Characterisation of top skin layer

Figure 2 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 0.15 % w/v TMC in n-hexane as organic phase produces polyester polymer layer on membrane surface (Jalanni et al., 2012) as shown in Figure 2. The presences of two bands on the membrane surface of 8 % w/v TEOA, which are 1,715.02 cm^{-1} and 1,241.41 cm^{-1}, indicate to the interfacial polymerisation. Based on Tang et al. (2008) work, interfacial polymerisation occurred on the TFC membrane when two strong bands at 1,723 cm^{-1} and 1,239 cm^{-1} present which are characteristic of vC=O and vC-O-C of ester compound. It can be seen from Figure 2 that both of the TFC membranes surface produced in this study were in range of the ester functional group, which verified the formation of thin-film on top of the PES membrane.

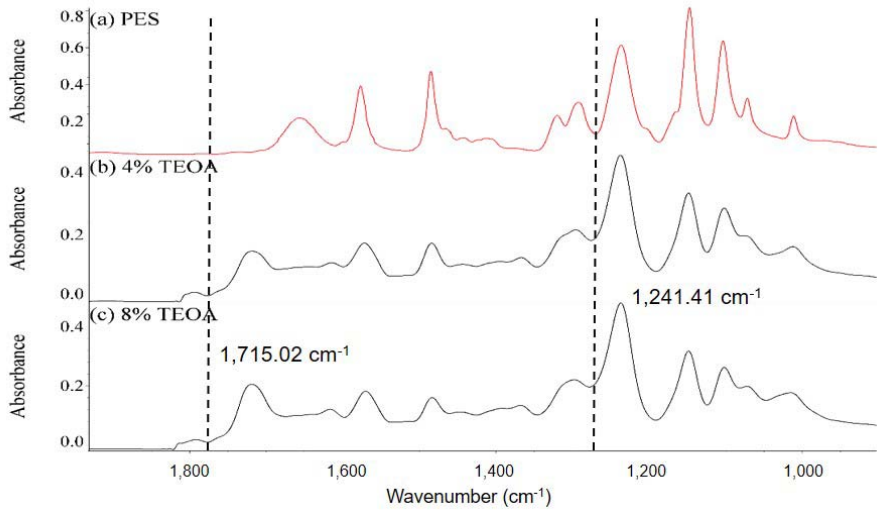
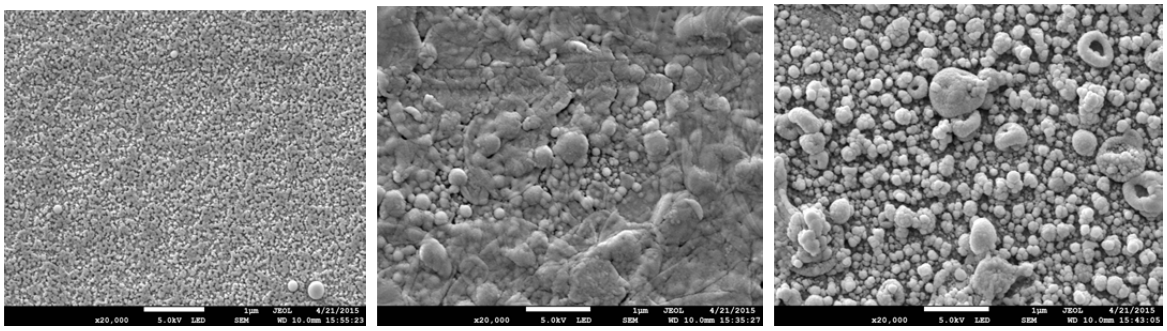


Figure 2: ATR-FTIR spectra of TFC membrane

Small pieces of TFC membrane samples were used for FESEM measurements. The analysis included the surface 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 for PES and TFC are compared between Figure 3(a), 3(b) and 3(c). The support PES membrane in Figure 3(a) has a smooth surface with porous structure. FESEM images in Figure 3(b) and 3(c) show that the polyamide-thin film was formed with a rough surface, nonporous structure and dense as compared to surface of PES in Figure 3(a). It can be seen that the membrane surface also becomes more uneven and or irregular at higher concentration of 8 % w/v of TEOA as in Figure 3(c) than the 4 % w/v of TEOA in Figure 3(b). This distinct different of surface roughness and porosity proved that there was the formation of TFC layer on top of the support PES membrane by IP. It has been reported by Mah et al. (2014) that this condition may resulted in higher ability to separate xylose from glucose.



(a) (b) (c)

Figure 3: FESEM images of surface of (a) UF PES (20,000× magnification), (b) 4 % TEOA (20,000× magnification) and (c) 8 % TEOA (20,000× magnification)

3.2 Effect of different concentration of triethanolamine

It has been reported from previous study by Tang et al. (2008), where the concentration of monomer is vital part in the synthesis of TFC membrane, by interfacial polymerisation. The flux and also the separation behaviour of the membrane are being affected by chemically changes during interfacial polymerisation process. Other membrane characterisation method was used to determine the effective pore radius (r_p) and the ratio of effective membrane thickness over porosity ($\Delta x/A_k$). Pure water permeability (PWP) was determined to estimate the effective pore radius (r_p) using mathematical model based on previous study. 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 Eq(2) (Mah et al., 2014).

$$J_w = \frac{r^2{}_p \Delta p}{8\mu(\frac{\Delta x}{A_k})} \tag{2}$$

Table 1 shows the result for PWP, predicted r_p and $\Delta x/A_k$ for each TFC membrane. The mean pore radius for commercial nanofiltration membrane is the range of 0.4-1.5 nm (Fellow and Mohammad, 1998). 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 1.

Result from Table 1 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. Differences in PWP for both TFC membranes might be due to the differences in r_p. Based on previous finding by Tang et al. (2008) shows that excessive TEOA higher than 6 % do not allow more cross-linking to occur hence resultant in incomplete polymerisation. This can be seen in Table 1 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.

Table 1 Result for Pure Water Permeability, Predicted Effective Pore Radius (r_p) and The Ratio of Effective Membrane Thickness Over Porosity (Δx/Ak)

Membrane	PWP (L h^{-1} m^{-2} bar^{-1})	r_p (nm)	Δx/Δk (μm)
4 % TEOA	1.96	0.41 ± 0.29	4.43 ± 3.13
8 % TEOA	4.98	0.67 ± 0.48	4.91 ± 3.47

3.3 Separation performance

The xylose separation factor, X_{xyl} is used to measure the xylose purification from glucose. It can be seen in Table 2 that the concentration of the monomer TEOA has effected the surface and pore size of the TFC membrane. The TFC membrane prepared with 4 % w/v TEOA has high in permeate flux, resultant in high xylose separation of 1.302. Low permeate flux but moderate xylose separation factor of 0.934 was obtained for the TFC membrane prepared with 8 % w/v TEOA. These xylose separation factor values were small when compared to work by Sjoman et al. in 2007, which is around 1.5 – 3.0 obtained using commercial nanofiltration membrane. This could be due the mass ratio of xylose to glucose used in this study which only at 1: 1 rather than 1:9 and 9:1.

Table 2 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	1.30
8 % TEOA	1.42	0.93

4. Conclusion

A TFC membrane for nanofiltration was synthesised by interfacial polymerisation of triethaolamine (TEOA) and trimesoyl chloride (TMC) on polyethersulfone (PES) supporting membrane. The concentration of TEOA was varied between 4 % w/v and 8 % w/v at 0.15 % w/v TMC. The TFC membranes were characterised using ATR-FTIR and FESEM showed the roughness, nonporous structure and dense polyamide-thin film obtained on top of the TFC membranes surface. The performances of the TFC membranes were evaluated using pure water permeability test and xylose separation performance. It can be concluded from this study that as the concentration of TEOA increased, the top layer of the TFC membrane becomes thicker. It also has created bigger effective pore radius (r_p) due to incomplete interfacial polymerisation when using high amounts of TEOA in aqueous phase react with insufficient TMC in organic solution. Excess amount of TEOA will also increase the hydrophilicity behaviour of the TFC membrane. All of these factors contributed to higher permeability for the TFC membrane prepared with 8 % w/v TEOA. Although the TFC membrane prepared with 4 % w/v TEOA has much smaller effective pore radius (r_p) of 0.41 ± 0.29 nm, it still gave high permeate flux of 8.32 $LM^{-2}h^{-1}$and high xylose separation factor of 1.30 due to the top layer of the TFC membrane was thinner at 4.43 ± 3.13 μm. Further study on membrane fouling would be required in future to see the interaction between membrane fouling with surface roughness, concentration polarisation, pressure effect and membrane compaction. It can be concluded that this thin composite nanofiltration membrane has high potential to be used in separation of xylose from glucose.

Acknowledgments

This research was financially supported by long grant RDU 140901. Appreciation is also expressed to the Ministry of Higher Education of Malaysia for supporting this study (MyBrain15). The authors are thankful to all technical staffs, Chemical Engineering Research Laboratory, Central Laboratory UMP and also Industrial Science and Technology Laboratory for providing the necessary facilities, constant guidance and encouragement.

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