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Influence of Pluronic Addition on Polyethersulfone Membrane for Xylitol Purification

Khalefa A. Faneer[a,b], Rosiah Rohani*[,a,b], Abdul Wahab Mohammad[a,b]

[a]Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, UKM Bangi, 43600 Selangor, Malaysia
[b]Research Centre for Sustainable Process Technology (CESPRO), Universiti Kebangsaan Malaysia, UKM Bangi, 43600 Selangor, Malaysia
rosiah@ukm.edu.my

Xylitol is an important raw material in cosmetic, pharmaceutical and food industries due to its non-cariogenic sweetener properties. Xylitol in mixed sugars which obtained from fermentation media could be purified through adsorption or crystallisation. Xylitol may leach out during adsorption while the complexity of the fermentation broth in crystallisation has limits the utilisation of these techniques. The use of membrane filtration technique is foreseen could avoid these limitations as its separation is based on the solutes size, shape and/or molecular weight ranges. In this work, special blend polymer membranes were synthesised, characterised and tested in the xylitol recovery from synthetic solution. Pluronic F127 at 1 %, 3 %, and 5 % was blended with polyethersulfone (PES) to modify membranes. The effect of Pluronic ratio on the membrane selectivity for xylitol separation from sugars and also the fouling mitigation effect under Pluronic presence in the membranes were investigated. The results showed an improvement in the membrane hydrophilicity, where the contact angle of pure PES membrane has dropped from 80° to 65° in addition of Pluronic at different ratios. The water flux has also increased as the Pluronic ratio increased. The rejection of xylitol has found to decrease in Pluronic presence. Surprisingly, the membrane selectivity has enhanced greatly as desired. The PES blend Pluronic membranes have shown promising future in xylitol separation from sugars.

1. Introduction

Xylitol has become more attractive source of sugar due to its emerging use in food, cosmetic and medicine fields. It is also found naturally in fruits such as kiwifruits and strawberry in small amount, however, the extraction of xylitol is very hard and unbeneficial (Murthy et al., 2005). Xylitol is reportedly produced using xylose either by chemical route via acid hydrolysis or biotechnologically with yeast, bacteria or fungi (Martínez et al., 2015). The common purification methods of xylitol from sugars can be broken down at different performance percentage where adsorption (65 %) (Marton et al., 2006), crystallisation (75 %) (Canilha et al., 2008) or membrane filtration (80 %) (Affleck, 2000). Of all purified techniques, membrane technology is expected to give the best range of separation for xylitol because the molecular weight (MW) of sugars (normally consist of xylitol, xylose and arabinose) are within 152.25 – 150.15 g/mol. These MWs lie in the range of NF membranes, with known molecular weight cut off (MWCO) between 150 Da and 1,000 Da (Murthy et al. 2005). The membrane separation theory is based on a big difference in the components in the solution or the opposite charge between solution and membrane. Separation of xylitol from arabinose and xylose is a challenge because of its close MW values and neutrality of these organic materials. Affleck (2000) proposed 11 different membranes (from ultrafiltration (UF), NF, to RO) to purify fermentation broth containing xylitol, xylose and arabinose. The best separation performance has shown by the UF membrane but no remarkable selectivity between xylitol and other sugars was obtained. Polymer such as PES and Polyamide (PA) has been repeatedly used as the main polymer for synthesising membranes (Cui et al., 2010). PES has many merits such as widely used in microfiltration (MF), UF and NF processes (Ulbricht, 2006). It also possesses high mechanical and thermal properties (Lin et al., 2015). The major disadvantage of PES is its lack of hydrophilicity, which can cause fouling during filtration process. Addition of copolymer and/ or nanoparticles is necessary to increase the hydrophilicity of the membranes in order to reduce fouling. A number of research studies have been conducted to investigate on fouling effects in membrane filtration (Shi et al., 2014). Fouling either presence as a cake formation on the membrane surface (reversible fouling, Rr) or by adsorption of solute molecules, both on the membrane surface and in the membrane pores (irreversible fouling, Rir) (Richards et al., 2012). The reversible fouling happened because the solution particles size are bigger than membrane pores and therefore can be easily cleaned up by backwashing or water flushing. On the contrary, in the irreversible fouling, the solution particles are smaller or similar to the membrane pores and it will be hard to be removed by conventional methods, except by chemical cleaning (Hua et al., 2008). The membrane fouling usually can be minimised either by: (1) membrane incorporation with nanoparticles (Yang and Mi, 2013) or (2) blending with copolymers such as Pluronic which has a unique properties and differs from other additives, where it can work both as surfactant and pore former. Pluronic consists of the hydrophobic polypropylene oxide (PPO) segments that works as pore forming agent, while the hydrophilic polyethylene oxide (PEO) segments in Pluronic endows the membranes surface with higher hydrophilicity (surface modifier) (Lv et al., 2007). This work has investigated on the influence of Pluronic at 1 %, 3 %, 5 % blend with PES membrane on xylitol purification from sugar mixtures. The fabricated membranes were further characterised for their contact angle, water flux, permeate flux, rejection and type of fouling.

2. Experiments and methods

2.1 Materials

PES (MW = 37,000 Da) purchased from Good Fellow Co. was used as membrane main polymer. PES was dried at 60 °C for 72 h prior to use to remove moisture. N-methyl-2-pyrrolidone (NMP) was used as a solvent and purchased with analytical purity 99.7 % from Fluka, Germany. Pluronic F127 with a MW of 12,600 Da was purchased from Sigma as an additive. The synthetic sugar mixtures prepared from individual sugars of xylitol, xylose and arabinose were of analytical grade, purchased from Acros Organics and used without further purification.

2.2 Fabrication of PES/Pluronic F127 membranes

PES-Pluronic membranes were fabricated via phase inversion method (Mosqueda-Jimenez, Narbaitz et al. 2004). The formulation of dope solution used PES (18 wt% in the casting solution) as a membrane matrix; Pluronic as the membrane additive acted as a modifier and pore-forming agent. PES and different ratio of Pluronic (1 wt%, 3 wt%, 5 wt%) was dissolved in NMP and stirred at 60 °C for 8 h to ensure homogeneous mixing, and left for 24 h to allow complete removal of bubbles. Next, the solution was cast on glass plate with a steel knife, and then immersed for 2 h in deionised (DI) water for solvent exchange. To remove the residual solvent, the membrane was immersed again in DI water for 24 h.

2.3 PES-Pluronic membranes characterisation

The contact angle of all membranes were measured using Rame-Hart model 200 standard contact angle goniometer with DROPimage Standard software with an accuracy of 60.10°. The membranes were dried for 72 h before testing.

2.4 Separation performance measurement

Membrane water flux and solution separation performance were measured using a dead end filtration cell (Sterlitech HP4750, Sterlitech Corporation, USA). All filtration experiments were carried out at 25 °C with stirring speed at 500 rpm. Initially, membranes were pressurised with DI water at 14 bar for 2 h for compaction purposes. The compaction was done to ensure steady flow of water and solutes in the real filtration. The water flux1 is defined from Eq(1).

$$J_w = V/(A \times t) \qquad (1)$$

Where J_w indicates to water flux (L/m^2.h), V is permeate volume (L), A is an effective area of the membrane (0.00146 m^2), and t is the filtration time (h).

Rejection tests were conducted using synthetic solution of 19.1 g/L xylitol, 1.44 g/L xylose and 2.7 g/L arabinose, with MW ranging from 150.15 g/mol to 152.15 g/mol, similar to the solution produced in real fermentation broth (Mussatto et al., 2006). Firstly, the dead end cell was filled with xylitol mixture solution, where the experiments was run at 4 bar with 500 rpm. The rejection of xylitol was calculated from Eq(2) as shown below:

$$R = 1 - Cp/Cf \times 100 \qquad (2)$$

Where R is rejection (%), C_p and C_f (g/L) are permeate and feed concentration.

The permeate concentration, C_p is obtained from HPLC analysis (Ultimate 3,000, Thermo scientific, USA), under the following analytical conditions: RPM column (Rezex, dimension: 300 ņ 7.8 mm, USA), Refractive Index (RI)

Detector (Refractomax 520, ERC, USA), DI water as mobile phase, 60 °C temperature and 0.6 mL/min flow rate.

The separation of xylitol from sugars mixture is the key point for the membrane performance. Rejection test was performed to investigate the effect of blending PES membrane with Pluronic at 1 %, 3 %, and 5 % on the xylitol separation from the mixture. These results were then compared with the results from the pure PES 18 % membrane.

The antifouling ability/property of the pure and blend PES membranes was investigated using a model solution of xylitol. The fouling process was also analysed by determining several equations in order to describe the membrane antifouling property (R_t), which defined as the degree of total flux loss caused by total fouling as stated in Eq(3). High R_t value indicates to a large drop in flux.

$$R_t = 1 - (J_p/J_w) \tag{3}$$

Where R_t is the antifouling property, J_p and J_w are the permeate flux and water flux.

Reversible fouling (R_r) is the degree of the reversible flux loss caused by reversible fouling while irreversible fouling (R_{Ir}) is the degree of irreversible flux loss caused by irreversible fouling. R_r caused by xylitol mixture solution adsorption or desorption on the membrane surface can be washed by hydraulic cleaning but the R_{Ir} is the other way round and require extensive hydraulic cleaning. To distinguish between R_r and R_{Ir}, these two values were calculated using Eq(4) and Eq(5).

$$R_r = (J_{w2} - J_p)/J_{w1} \tag{4}$$

Where J_{w1}, J_p and J_{w2} are initial water flux, the permeate flux and the final water flux.

$$R_{Ir} = (J_{w1} - J_{w2})/J_{w1} \tag{5}$$

Next, the flux recovery ratio (FRR) was evaluated in order to evaluate the antifouling property (R_t) of the membranes and their efficiencies after refreshing by DI water. The water flux recovery was defined from Eq(6):

$$Flux\ recovery\ ratio\ = J_{w2}/J_{w1} \times\ 100 \tag{6}$$

The higher FRR value obtained, the better the antifouling ability and the higher washing efficiency are possessed by the membrane.

3. Results and discussion

3.1 PES/Pluronic membranes characterisation

Table 1 showed the contact angle values of the membranes at various Pluronic ratios from 0 % to 5 %. The results showed a significant improvement in the membrane hydrophilicity when different ratios of pluronic were blended with pure PES membranes. From Table 1, the contact angle improved significantly from 80 ± 4.95° to 61.7 ± 2.24° at the presence of higher Pluronic ratio. These results indicated that there is a substantial development of the surface hydrophilicity due to the presence of hydrophilic PEO segments in Pluronic. These results are corresponded with Liu et al. (2013) where the contact angle improved forward to be more hydrophilic when Pluronic ratio in the membrane was increased from 1 % to 9 % (Liu et al., 2013). To improve the membrane stability, the liking-water (amphiphilic) material such as Pluronic is recommended to be added into the membrane casting solution.

3.2 Separation performance measurement

3.2.1 Water and permeate flux filtration

The water and permeate flux of the pure and blend PES membranes was measured using Eq(1). It was found that the PES membrane blends with a range of Pluronic ratios has higher pure water flux as well as higher permeate flux than the pure PES as shown in Figure 1. The permeate flux here used a synthetic sugar solution of xylitol in sugar(s), which was prepared based on the real broth concentration as reported by Mussatto et al. (2006) with concentrations of xylitol (19.1 g/L), xylose (1.44 g/L) and arabinose (2.7 g/L).

The water and permeate flux raised gradually when Pluronic ratio increased in the membrane matrix. The water flux of pure PES 18 % improved from 13 L/m² to 33 L/m².h as 5 % pluronic was added to the cast solution. This enhancement in water flux was due to improvement in membrane hydrophilicity. Zhang et al. (2011) also reported that the water flux had increased when Pluronic ratio was increased from 20 % to 100 % (Zhang et al., 2011).

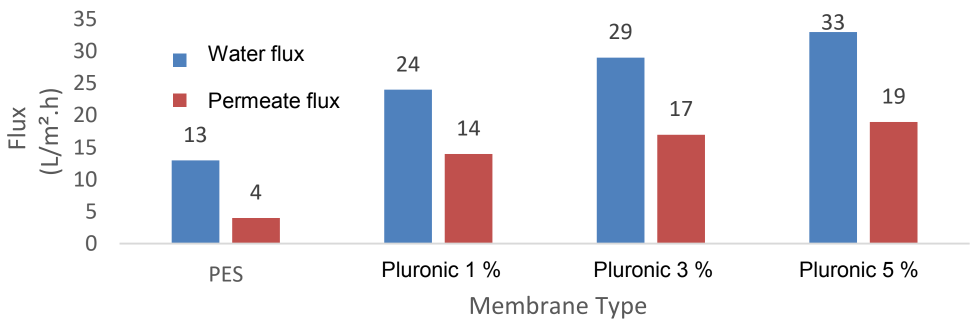

Figure 1: The water and permeate flux of the fabricated membranes at 0 %, 1 %, 3 %, and 5 % of Pluronic

Meanwhile the highest permeate flux of PES/Pluronic membranes at 5 % have higher solute flux of up to 19 $L/m^2.h$ as compared to pure PES membrane at only 4 $L/m^2.h$. The same reason was also applied when the PES blend membrane was tested for water flux. It is confirmed that the existing of Pluronic will increase the instability and viscosity of the membrane casting solution and may further lead to macrovoids formation in the membrane structure to create bigger pores after the phase inversion. Liu et al. (2013) have also concluded that addition of small amount of polymer additives (in their work using polyethylene glycol (PEG) or polyvinyl pyrrolidone (PVP)) can form macrovoids in the membrane matrix (Liu et al., 2013), while adding Pluronic copolymers to PES UF membrane will increase both permeation flux and antifouling properties of the membrane (Pagidi et al., 2014).

3.2.2 Membrane fouling properties

According to water and permeate flux filtration results presented in Figure 1, remarkable changes in water and solution flux under constant pressure at 4 bar were observed. Further investigations on the fouling properties of the membrane were determined by measuring the FRR, R_t, R_r, and R_{ir} of the membranes. These values were calculated following Eq(3) to Eq(5) and presented in Table 1.

Table 1: The fouling properties of PES/Pluronic membranes in xylitol nanofiltration

Membrane Type	Contact angle (theta)	R_t	R_r	R_{ir}	Flux recovery ratio (FRR) (%)
PES 18 %	80 ± 4.95	0.69	0.54	0.15	84.6
Pluronic 1 %	67.7 ± 4.95	0.41	0.33	0.08	91.7
Pluronic 3 %	66.6 ± 5.74	0.41	0.34	0.07	93.1
Pluronic 5 %	61.7 ± 2.24	0.42	0.39	0.03	96.9

The R_t decreased from 0.69 to 0.42 as Pluronic ratio reached to 5 %, which indicated the reduction in total flux loss. Further, it corresponds to less sugars adsorption or deposition on the membrane surface because of the Pluronic layer presence on the surface, which prevents sugars (neutral organics) from being adsorbed. The R_{Ir} value showed decreasing trend from 0.15 to 0.03 as the Pluronic ratio reached 5 %. The best method to mitigate membrane fouling especially R_{Ir} is by introducing a hydrophilic material to inhibit the adsorption of organic materials. Wang et al. (2005) obtained similar results where the R_t and R_{Ir} have both decreased as Pluronic ratios increased in their synthesised PES UF membrane. The R_t has decreased from 0.74 to 0.42 with increasing pluronic ratio from 0 % to 9 %. Also, R_{Ir} has decreased from 0.52 to 0.09 when 0 % to 9 % Pluronic was introduced in the PES membrane. As low amount of Pluronic was added, the PEO units cannot form a compact polymer layer; thus, the penetration of molecules were easy and therefore causing irreversible fouling. The PEO segments will form compact layer on the membrane surface in increasing Pluronic ratio. As a consequence, the dense PEO layer will prevent the molecules to touch the membrane surface directly. Most of the molecules will deposit on PEO layer and caused reversible fouling (Wang et al., 2005). The calculated FRR values for the synthesised membranes are presented in Table 1. These values are used to evaluate possible changes in the membrane's surface in term of hydrophilicity and antifouling properties after Pluronic addition. Higher FRR indicated a better membrane with reasonable hydrophilicity and excellent antifouling properties. From the results, the PES/Pluronic membranes have better FRR compared to the pure PES membrane. The FRR increased from 84.6 % to 96.9 % as Pluronic was blended in the PES membrane. Excellent FRR of the blend membranes was due to the introduction of highly hydrate and dense PEO polymer layer (in Pluronic) which prevented the solution molecules to be deposited on the membrane surface. This excellent FRR indicated that the PES/Pluronic membranes could be used for filtration several times without failed/fouled. Results also showed that all PES/Pluronic membranes possess lower Rt and Rir than the pure PES membrane. This remarkable improvement of the antifouling properties in PES/Pluronic membranes was achieved due to the surface modification of PES membranes by Pluronic.

3.2.3 Rejection test

The rejection results of xylitol, xylose and arabinose molecules obtained by utilising the prepared membranes are illustrated in Figure 2. The xylitol solution rejection ratio of the PES/Pluronic membranes have a notable variation with the increase of Pluronic ratio in the casting solution. The pure and blend PES membranes are showing a selective property towards different sugars. The membrane selectiveness is even clearer especially between the separations of xylitol from arabinose. This selectivity was qualitatively measured based on the difference in the rejection percentage of each components in one sugar mixture. The higher the percentage difference, the better selectivity that the membrane have for separating the mixed component. The rejection percentage has found to decrease gradually as the Pluronic ratio in the blend PES membranes increases. The PES/Pluronic 5 % membrane achieved lower xylitol rejection at 45 % compared to pure PES membrane at 66 %. The amount of Pluronic in the dope solution was one of the key factors that affecting the final membrane structure. PPO units in the Pluronic entrapped with the PES polymer chains and thus controlling the membrane pores structure at the membrane surface. The pore size of the fabricated membrane will be formed when water extracts the hydrophilic micelles. As a result of this, the Pluronic micelles size will affect the pore size of the membrane top layer. The increase of Pluronic concentration will lead to high aggregation number of Pluronic micelles (Kozlov et al., 2000). The same findings were observed by (Pacharasakoolchai and Chinpa, 2014) where pure PES membrane has higher rejection compared to the blend ones. The same conclusion can be drawn, as the membrane pore size enlarged, the membrane rejection dropped.

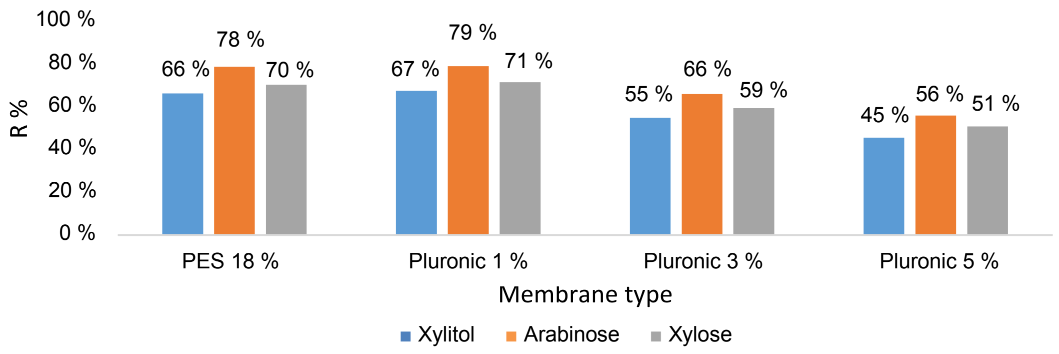

Figure 2: Rejection results of xylitol mixed solution at 19.1 g/L using pure PES and PES/Pluronic membranes at different Pluronic ratio

4. Conclusion

Pure PES and blend PES/Pluronic membranes of different ratios were successfully fabricated. The presence of Pluronic into PES membrane has positively affected the water and permeate flux. The contact angle has further enhanced as Pluronic ratio increased in the membrane matrix. Each membrane showed promising xylitol rejection, however, the rejection has dropped as the Pluronic ratio reached 5 % in the blend membrane. The FRR values of blend membranes proved the antifouling properties of the Pluronic. The membranes showed good separation factor between xylitol and arabinose, whilethe separation factor between xylitol and xylose became very low. The synthesised membranes possess promising separation performance and selectivity between sugar molecules despite their close MW of xylitol, xylose and arabinose.

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