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Nanofiltration of Xylitol Mixed Solution Using Polyethersulfone Membrane in Presence of Silicon Dioxide Nanoparticles or Pluronic F127 Additives: A Comparative Study

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Abstract

Xylitol is a valuable product in medicine and food fields and can be produced mainly by two processes: (1) chemically with catalyst and (2) bio technologically with yeast, fungi or bacteria. This xylitol is commonly present in mixture form which consist of xylitol, xylose and arabinose. Thus purification is required to increase its value either by crystallization, adsorption or membrane technology. The aim of this work is to investigate the influence of using different nanofiltration (NF) membranes to achieve high purity of xylitol from model solution. In order to achieve a desirable purity of xylitol, in-house synthesized NF membranes from pure PES, PES/SiO_2 and PES/Pluronic f127 were used in this study. These NF membranes were fabricated via phase inversion method and further characterized to investigate their performances suitable for xylitol purification. To achieve that: a contact angle was used for hydrophilicity, pure water flux (PWF), xylitol permeation and rejection were investigated for the best membrane performances. The contact angle results for these three membranes showed that the SiO_2 nanoparticles (NPs) have the best effect on hydrophilicity, moreover, the PWF enhanced and the PES/ Pluronic showed the higher water flux. The highest rejection was accomplished with single PES membrane.

Key words: Xylitol, nanofiltration, PES, Pluronic, SiO_2 NPs.

1. Introduction

Xylitol is a five-carbon sugar alcohol, known as a sweetener for diabetics, which shows good outstanding preventing properties dental caries [1, 2]. The main source of xylitol is from hemicellulose which can be obtained from wheat straw, rice straw etc. [3, 4]. The production processes of xylitol from xylose are: 1- chemically or 2- biotechnologically [5]. Xylitol yield is in the range of 65 - 85 % when produced via biotechnological process, and the yield is lower than the biotechnological way, normally at 50 – 60 % when it is produced chemically [6]. Xylitol is either crystallized (> 75 %) or adsorbed (> 65 %) for purifying the component for a higher value product [7, 8]. Moreover, due to the fermentation broth complexity, the purity grade of xylitol obtained by direct crystallization is not acceptable (around 75 % only) [9]. For these reasons, purification of the fermented broth prior to crystallization is required in a way to produce high purity of xylitol [8]. Recently, membrane technology plays an important role in purification and separation of products for various applications [10-12]. It has high selectivity and absorptivity for specific components to be transported, requires low energy, stable under a spectrum of operating conditions and compatible with the environment. This membrane has also improved in its thermal and mechanical resistance to the environment and stable [13, 14].

Purification of xylitol using membrane technology is based on its molecular weight cut off (MWCO), where the NF membrane has MWCO between 200 - 2000 gmol-1. Therefore, NF is suitable for xylitol rejection since the main compounds after the pretreatment fermentation broth are monosaccharides [10]. This made the utilization of polymer based NF membrane for purifying xylitol become possible and have been repeatedly reported in an open literature [9, 15]. Polyethersulfone (PES) is one of the promising polymer reportedly used due to lots of merits such as easy to fabricate, high chemical resistance and vast pH tolerance [16, 17]. The task to improve PES hydrophilicity has involved great effort such as: mixing with a hydrophilic polymer, polymerized surface graft, coating and adding inorganic fillers [18]. The hydrophilic SiO_2 NPs were the main factor affecting the permeability of PSF membrane when up to 12 wt.% of NP were added to the membrane [19, 20]. Furthermore, fouling that caused by PES hydrophobicity might be avoided by blending hydrophilic copolymer to PES membrane matrix such as polyvinyl pyrrolidone (PVP), polyethylene glycol (PEG) and pluronic[21]. Among these copolymers, pluronic f127 was reported as a good surfactant and pore former, further Pluronic is chemically stable [21, 22]. Recently, Pluronic triblock copolymers of poly (ethylene

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oxide) and poly (propylene oxide) have worked as surface modifier and pore former in membrane fabrication [23]. The Pluronic additive (PEO–PPO–PEO) segregated during phase inversion process to the polymer/water interface due to the low interfacial energy between the hydrophilic segment and water, while the hydrophobic, water-insoluble segment of the copolymer firmly anchored in the polymer matrix [24]. The surface chemistry of Pluronic F127/PES blend membrane can be reconstructed to minimize the interfacial free energy [25]. The hydrophilic PEO chain introduced to the membrane matrix as adsorption resistant of the molecules. While hydrophobic PPO segments distributed closer to the center of membrane pores [26-28].

Overall, there are two main processes lead to formation of PES/ Pluronic f127: (1) aggregation of hydrophilic units which were responsible of surface modifier, and (2) Micellization of hydrophobic units that form the membrane pores.

Thus, this study is aimed for the fabrication of three different NF membranes: (1) pure PES membrane, (2) PES incorporated with 5 % of SiO_2 NPs, and (3) PES blended with 1.71% of Pluronic f127; via phase inversion immersion precipitation method. These membranes were subjected to specific characterization study such as contact angle, pure water flux and rejection in order to investigate their performances for xylitol purification from xylitol model solution.

2. Materials and Methods

2.1 Materials

Polyethersulfone (PES) granule (Goodfellow), was used as the membrane based polymer. Silicon dioxide (SiO_2) as the nanoparticle for membrane enhancement (99.5%, 20 nm) (Nanoamor). Pluronic f127 (Nanoamor) was used as the copolymer/additive. The solvent used for doped solution making is N-methyl-2-pyrrolidone (NMP) with analytical purity 99.7% (Fluka, Germany) and distilled water was used as non-solvent for phase inversion. Xylitol, xylose and arabinose powder of 99 % purity (Acros Organic) are the sugar alcohol and sugars used in the preparation of the fermentation broth model solution, which were used as received.

2.2 Membrane preparation

Initially, PES was mixed with NMP and phase inversion method was implemented for membrane fabrication. For the PES/ SiO_2 membrane, stirring of SiO_2 with 10 % of NMP was done for 4 h followed by sonication for 1 h in order to overcome SiO_2 aggregation in the doped solution. Each polymer doped solution then stirred for 4 h to get a homogenous solution (refer to Table 1 for composition and operation parameters). Next, the doped solution was left overnight for degassing. Elcometer 4340 Automatic Film Applicator with a speed at 76 mm/s was used to cast the membrane. A suitable amount of suspension was cast using a casting knife set at 200 µm onto a glass plate at ambient atmosphere (27 °C). The membranes were submerged in distilled water for 2 h and then immersed in distilled water for solvent exchange. The synthesized membranes were then stored in distilled water at room temperature prior to use.

Table 1 The dope solution compositions and operation parameters

Membrane type	PES (wt. %)	NMP (wt. %)	Additive (wt. %)	Temperature	Stirring speed
PES	18	82	----	60 °C	450 rpm
PES/SiO_2	18	82	5%	60 °C	450 rpm
PES/ Pluronic	18	82	1.71%	60 °C	450 rpm

2.3 Membrane characterization

2.3.1 Contact Angle

In order to figure out the hydrophilicity of PES, PES/SiO_2 NP, and PES/Pluronic f127 membranes, the contact angle was used to measure the hydrophilicity in presence of either the NP or additive. Initially all membranes were dried at room temperature for 48 h before testing them using a contact angle goniometer (Rame -Hart model 200 standard) with DROP image standard software with an accuracy of 60.10°. The measurement of the contact angle was done in the deionized water and air at 25 – 28 °C.

2.3.2 Pure Water Flux (PWF)

Dead-end cell filtration (Sterlitech HP4750, Sterlitech Corporation, USA) was used to evaluate the PWF of the membranes at three different pressures (4, 6 and 8 bar) in the deionized water. The PWF was calculated using equation (1):

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

where J is PWF (L/m^2.h), V is the permeate volume (L), A is the effective membrane area (14.6 cm^2) and t is sampling time (h).

In order to minimize the experimental errors, 3 to 5 samples were collected for each volume and then the average value of flux was recorded.

2.3.2 Permeate flux performance

Permeate flux measurement was performed at 4 bar using xylitol mixed solution (Table 2) in the dead-end cell. The concentration of the components in the xylitol mixture is tabulated in Table 2. This mixture was based on the work reported by Mussatto et al. who used sugarcane bagasse as a fermentation broth [8]. This mixture was used as the model solution for the NF using the synthesized membranes.

Table 2 The xylitol mixed solution composition and its concentration.

Component in xylitol mixture	Concentration (g/L)
Xylitol	2
Xylose	0.15
Arabinose	0.3

2.3.3 Rejection test

The rejection study of xylitol mixed solution was evaluated on the batch type filtration by using dead-end cell. 300 ml of xylitol mixed solution (refer Table 2 for the composition) was poured into this cell, then the experimental run was started at 4 bar. Equation 2 below was used to calculate the rejection:

$$R\ (\%) = \left(1 - \frac{Cp}{Cf}\right)*100 \qquad (2)$$

where R is the rejection (%), C_p is the permeate concentration and C_f is the feed concentration.

The standard calibration curve was plotted in order to calculate the C_p and rejection. The permeate xylitol, xylose and arabinose concentrations were quantified using High Performance Liquid Chromatography (HPLC) (ultimate 3000, Thermo scientific, USA) under these conditions:

Column type: RPM (Rezex, dimension: 300*7.8 mm, USA), Mobile phase: water, Detector: Refractive Index (RI) (Refractomax 520, ERC, USA), Flow rate: 0.6 min/ml and Temperature: 60 ºC.

3 Results and Discussion

3.1 Contact Angle

The hydrophilicity/hydrophobicity of the membranes is revealed by their contact angle value. Surfaces with contact angles greater than 90° are considered as hydrophobic [29]. As clearly seen in Table 3, SiO_2 NP presence in a membrane has a significance effect on PES hydrophilicity. The PES membrane's initial contact angle was at 80.1± 1.93 o and the value has decreased to 58.8 ± 0.75 o after SiO_2 NP was added in it. This is due to the fact that after SiO_2 was added into the polymer doped solution, SiO_2 NP have spread among PES chain segments. The typical result was reported where the 2 % of SiO_2 NP was added to increase PES/SiO_2 membrane hydrophilicity from 78.6 ± 1.0º to 58.1 ± 0.9º [30]. On the other side, the addition of 1.71 % pluronic to the doped solution has shown not much effect on the PES hydrophilicity. This slight improve in the hydrophilicity from 80.1± 1.93º to 72 ± 0.3º indicated that there was substantial membrane surface modification when pluronic was added. During the phase inversion process, the additive is migrated spontaneously to the membrane/ water interface to reduce the interface energy [31]. Therefore, the membrane hydrophilicity is improved as the hydrophilic units of the additive are migrated to attach with the membrane surface and thus the interface energy on the membrane surface will be reduced that will help to improve positively on the membrane hydrophilicity.

Table 3 The contact Angle of PES, PES/SiO_2 NP, and PES/Plu f127 membranes

Membrane type	Contact angle (º)
PES	80.1± 1.93
PES/SiO2	58.8 ± 0.75
PES/Plu f127	72 ± 0.3

3.2 Pure water flux (PWF)

Fig. 1 illustrated the pure water flux of PES, PES/SiO2 NP, and PES/ Plu f127 membranes measured at three different pressures (4, 6, 8 bar). In this study, the addition 5 % of SiO_2 NP or 1.71 % of Plu f127 to PES membrane have enhanced the water flux significantly. For PES/SiO_2 NP, the PWF become doubled from 24.56 to 59.14 L/m^2.h at 4 bar. This result is supported by Vatsha et al. [32] where the addition of SiO_2 NP to PES membrane have increased the water flux. The same goes to PES/Pluronic f127 membrane where the water flux have increased three times higher than the PES membrane only from 24.56 to 70.3 L/m^2.h. This happened due to the variation in the porosity when pluronic was added [27, 33].

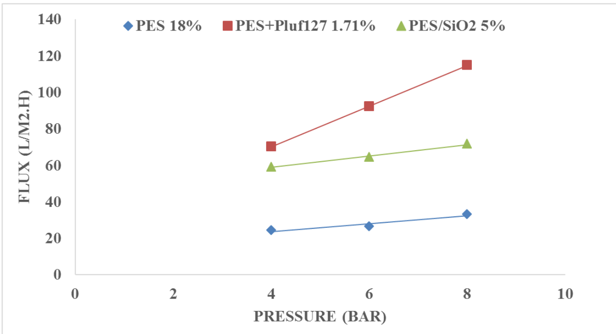

Figure 1 PWF of PES, PES/SiO_2, and PES/Pluf127 membranes measured at 25 °C

3.3 Permeate flux of xylitol mixture solution

Each membrane was pressurized at 12 bar for 30 minutes for compaction and the flux was measured for xylitol mixed solution (xylitol model solution refer to Table 2) at 4 bar for membrane permeability assessment. All membranes permeability was evaluated and their flux was monitored over the time for 50 minutes, the time dependent fluxes for all membranes are shown in Fig. 2. PES/Pluronic membrane showed a higher permeate flux compared to pure PES and PES/SiO_2 membranes. The flux dropped dramatically at initial operation due to xylitol solution droplets adsorption and/or deposition on the membrane surface especially in the first few minutes of operation by the permeate flow. Subsequently, PES/SiO_2 membrane achieved slightly higher than control PES membrane. The permeate flux enhancement was due to the presence of SiO_2 NP, where these nanoparticles improved the membrane hydrophilicity and altered the membrane structure.

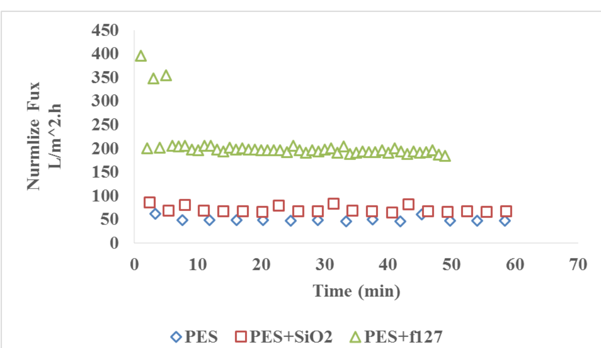

Figure 2 The permeate flux of xylitol mixed solution of PES, PES/Plu f127, and PES/SiO_2 membranes.

As seen in Fig. 3, the pure PES membrane has a lower permeate flux and the PES blended Plu f127 membrane has the highest permeate flux. As pluronic f127 works as a pore forming agent, the xylitol permeate flux increased and the fouling resistance was obtained. Moreover, membrane fouling caused by deposition of sugar molecules on the membrane surface or in the membrane pores may be considered as one of the reason that declining the permeate flux [18, 25].

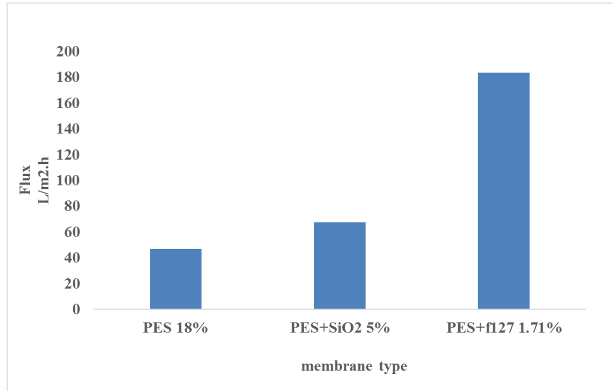

Figure 3 The flux performance of xylitol mixture solution of PES, PES/SiO_2, and PES/Pluronic f127.

3.4 Rejection test

The rejection test was performed to investigate the suitability of PES, PES/SiO_2 and PES/Pluronic membranes to reject the xylitol from its mixture. This test was performed under constant pressure at 4 bar using the xylitol mixed solution (Table 2). The permeate concentration was obtained from the calibration curve (Fig. 4) which represented the standard plots of xylitol, xylose, and arabinose. It is clearly seen that the R^2 values (the linearity) were ideal (0.98) for all plots.

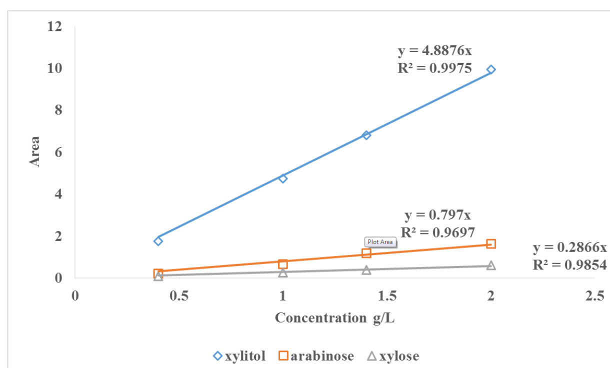

Figure 4 The calibration curve of xylitol, xylose, and arabinose.

Next, the rejection test of PES, PES/SiO2, and PES/Pluronic f127 membranes by using xylitol mixed solution is presented in Table 4. It is clearly seen that the rejection was 87.9%, 80.6% and 79.8% for the respective pure PES, PES/Pluronic f127 and PES/SiO_2 membranes. The main reasons for the decline in the rejection of PES/SiO2 and PES/Pluronic f127 membranes were probably the leaching out of NP during phase inversion method and the enlargement of the membrane pore diameter due to the addition of pluronic [33].

Table 4 The rejection test of PES, PES/SiO_2 NP, and PES/Plu f127 membranes

Membrane type	xylitol	arabinose	xylose
PES	87.9	82.3	76
PES/SiO2 5%	79.8	82.7	66.7
PES/Pluronic 1.71%	80.6	73.8	71.3

4 Conclusions

The fabrication of PES, PES incorporated with SiO_2 and PES blended with Pluronic f127 membranes have been successfully done via phase inversion method. All fabricated membranes were fairly characterized to investigate the hydrophilicity, water and permeate flux as well as the rejection. It is obviously found that the NP or the additive incorporated with pure PES membrane have enhanced the hydrophilicity as well as the water flux and the permeate flux. On the contrary, the rejection of xylitol has dropped due to (1) the enlargement of the pore diameter on the membrane surfaces and (2) the leaching out of the NP during phase inversion process.

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