Separation of furfural from monosaccharides by nanofiltration

Qi, Benkun; Luo, Jianquan; Chen, Xiangrong; Hang, Xiaofeng; Wan, Yinhua

Published in:
Bioresource Technology

Link to article, DOI:
10.1016/j.biortech.2011.04.041

Publication date:
2011

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Separation of furfural from monosaccharides by nanofiltration

Benkun Qi, Jianquan Luo, Xiangrong Chen, Xiaofeng Hang, Yinhua Wan*

National Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

ARTICLE INFO

Article history:
Received 13 February 2011
Received in revised form 13 April 2011
Accepted 16 April 2011
Available online 21 April 2011

Keywords:
Lignocellulosic prehydrolyzates
Detoxification
Furfural
Concentration
Nanofiltration

ABSTRACT

Furfural, found in the lignocellulosic prehydrolyzates at high concentration, is a strong inhibitor of growth and ethanol fermentation of Saccharomyces cerevisiae. Removal of furfural and concentration of monosaccharides were investigated by using two commercial nanofiltration (NF) membranes with synthetic glucose–xylose–furfural solution as model. The effects of main operating parameters such as feed pH, permeation flux, temperature and feed concentration on the rejections of the three solutes, were studied. Results showed that rejections of the three solutes decreased with increasing feed pH and temperature, and increased with increasing permeation flux for both membranes. The concentrations of the three solutes had interaction effect on the rejection of furfural by NF90 membrane and rejections of the three solutes by NF270 membrane. Furthermore, the effects of two filtration modes, concentration and diafiltration, on the separation of furfural from monosaccharides were also investigated. With the two commercial NF membranes, concentration and purification of monosaccharides in the model solution can be accomplished.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Bioconversion of lignocellulosic biomass to produce ethanol, a second generation biofuel, consists mainly of four steps, that is, pretreatment, enzymatic hydrolysis, microbial fermentation and separation (Hahn-Hägerdal et al., 2006). Of these four steps, pretreatment has been considered as the most expensive processing step (Wyman, 2007). Pretreatment is usually conducted under severe conditions to alter the structure and compositions of lignocellulosic substrate to make it more accessible to the cellulase, thereby improving the effectiveness of enzymatic hydrolysis (Hendriks and Zeeman, 2009). Among a lot of pretreatment methods employed to treat a variety of cellulosic materials, steam explosion and dilute acid pretreatment are the two most commonly used methods because of their effectiveness and inexpensiveness (Alvira et al., 2010).

Pretreatment of lignocellulosic biomass using steam explosion or dilute acid results in water-insoluble solids (a solid fraction) rich in cellulose and prehydrolyzates (a liquid phase) mainly containing hemicellulose-derived sugars at low concentrations and inhibitory compounds (Carrasco et al., 2010; Hsu et al., 2010; Qi et al., 2010). These inhibitors present in the prehydrolyzates are the degradation by-products of three main compositions of lignocellulosic materials, that is, cellulose, hemicellulose and lignin. Such inhibitory substances strongly affect enzymatic hydrolysis and reduce the productivity and yield of lignocellulosic ethanol fermentation (Palmqvist and Hahn-Hägerdal, 2000b; Panagiotou and Olsson, 2007). The type and amount of inhibitory compounds released during pretreatment depend on the ratio of solid to liquid, the pretreatment conditions (time, temperature, etc.) and the raw materials used (Klinke et al., 2004). On the other hand, fermentation of low-concentration fermentable sugars in the prehydrolyzates leads to low ethanol concentration, which in turn leads to high operation cost of ethanol distillation. Therefore, in order to enhance the effectiveness of prehydrolyzates fermentation, the prehydrolyzates should be detoxified to remove inhibitors and concentrated to increase sugar concentration prior to being used for ethanol fermentation. The detoxification of prehydrolyzates can be accomplished by means of physical (evaporation), chemical (solvent extraction, overliming, activated charcoal adsorption, ion exchange, etc.) and biological (microbiology, enzyme, adaption of fermenting microorganism, etc.) methods (Huang et al., 2008; Mussatto and Roberto, 2004; Palmqvist and Hahn-Hägerdal, 2000a). However, most of these detoxification methods have the disadvantage of adding high processing costs, and/or complicating the lignocellulose-to-ethanol production process, and/or generating additional waste products, and/or requiring long processing time, and/or losing sugars (Parawira and Tekere, 2010). Concentration of sugars in the prehydrolyzates can be accomplished by heating, vacuum evaporation and membrane separation, of which both heating and vacuum evaporation are energy-intensive, rendering them uneconomic for operation (Weng et al., 2010).

Nanofiltration (NF) is a promising and cost-competitive membrane separation technology. It has a molecular weight cut-off
ranging from 150 to 1000 g/mol, enabling high retention of compounds with molecular weight up to 150–250 g/mol as well as charged molecules. Thus, NF has a wide range of applications in fermentation broth separation, sugar fractionation, sugar concentration (Weng et al., 2009). To the best of our knowledge, only a few reports on treatment of lignocellulosic prehydrolyzates using NF are available. Liu et al. (2008) applied NF membrane with a molecular weight cut-off of 100 g/mol for concentration and purification of hydrolyzates from hot-water extraction of woody biomass and found that sugars in the hydrolyzates could be cleaned and concentrated using NF technology. Sjöman et al. (2008) reported purification of xylose in different hemicellulose hydrolyzates with three NF membranes, while recent work by Weng et al. (2010) on the concentration of rice straw hydrolyzates obtained from dilute acid pretreatment by NF also confirmed that NF technology can effectively concentrate sugars in the biomass hydrolyzates.

The objective of the present work was to investigate the feasibility of removing furfural and concentrating xylose and glucose simultaneously by NF, with focus on the effects of operating conditions and modes on the separation of furfural from monosaccharides with synthetic xylose–glucose–furfural solution as a model. Furfural was selected in the present study mainly due to its higher concentration and stronger toxicity on ethanol fermentation than other inhibitors found in the lignocellulosic prehydrolyzates according to previous studies (Guo et al., 2008; Palmqvist et al., 1999; Palmqvist and Hahn-Hägerdal, 2000b; Sanchez and Bautista, 1988).

2. Methods

2.1. Membranes, experimental set-up and chemicals

Two commercially available NF membranes obtained from Dow FilmTech, NF90 and NF270, were employed in the present study. Table 1 summarizes the typical characteristics of the two NF membranes. It is worth mentioning that although the active layers of both NF90 and NF270 were made of polyamide, they had singularly distinctive structures and compositions of the active layer. Thin semi aromatic piperazine-based polyamide constituted the active layer of NF270, whereas, the skin layer of NF90 was composed of a fully aromatic polyamide layer (Nghiem et al., 2005a).

A virgin membrane was first dipped in 50% (v/v) ethanol solution for 5 s and then washed with deionized water to loosen the shrunk membrane pores due to long-term storage. The membrane was subsequently soaked in deionized water for at least 24 h until used in the NF operation.

The experimental set-up, as described in detail elsewhere (Luo et al., 2008), mainly consisted of high performance liquid chromatographic (HPLC) pump (LC-20AT, Shimadazuy Corp., Kyoto, Japan), injection column (Superloop 50 ml, Pharmacia, Sweden), pressure sensor (MLH040BS09A, Honeywell, USA) monitoring the transmembrane pressure (TMP), self-made stirred-cell filter with a working volume of 12.8 ml, and a magnetic stirrer with a hot plate (Xuanwo 85-2, Shanghai Sile Equipment Co., Ltd., China). The membrane disk having an effective diameter of 24 mm was fitted in the stirred-cell filter with an effective membrane area of 4.52 × 10^{-4} m².

Both glucose and xylose were of analytical grade and purchased from Beijing Xiningke Biotechnology Co., Ltd., China and Beijing Aoboxing Biotechnology Co., Ltd., China, respectively. Furfural being of analytical grade was supplied by Tianjin Damao Chemical Factory, China. The physico-chemical properties of the above three compounds are presented in Table 2.

2.2. Model solution

Model solutions were prepared by dissolving pre-calculated amount of glucose, xylose and furfural into deionized water to obtain a mixture solution containing 25 g/l xylose, 10 g/l glucose and 4 g/l furfural. The pH of the mixture was adjusted by adding NaOH pellets or concentrated H₂SO₄ (72%, w/v). In the case of investigation on the effects of varied compound concentrations on the retention of each compound, the complete factorial design with three center points was performed and the concentration levels and corresponding coded values for the three compounds are shown in Table 3. The concentrations of xylose, glucose and furfural in model solutions were selected based on the real lignocellulosic prehydrolyzates obtained from dilute sulfuric acid pretreatment (Guo et al., 2008). The experimental matrix, designed using statistical software package Design-Expert 7.1.3 (Stat-Ease Inc., Minneapolis, USA), is shown in Table 4. Prior to NF operation, the model solutions were filtered through 0.45 μm filters.

2.3. Filtration procedure

A fresh membrane was used in each set of experiments. Prior to NF of model solution, the soaked NF membrane was compacted inside the cell by filtering deionized water at 3.0 MPa for 30 min to minimize pressure effect on the membrane performance in the subsequent tests. Approximately 20 ml model solution was injected into the injection column and then pumped into the filtration cell. Dead-end filtration experiment was performed at required constant permeate flux for 3–5 min until reaching steady-state and then the model solution was continuously nanofiltered to collect 1.4 ml permeate. The collected permeate and corresponding retentate in the cell filter was analyzed for the concentrations of xylose, glucose and furfural. The effects of feed pH, permeate flux, temperature and feed concentration on the performance of the NF process, in terms of retention and TMP, was studied in the experiments in which one of the variables was changed while the other ones were kept at a constant value. Before and after

<table>
<thead>
<tr>
<th>Table 1 Characteristics of NF membranes used in the study.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>NF90</strong></td>
</tr>
<tr>
<td>Manufacturer</td>
</tr>
<tr>
<td>Support material</td>
</tr>
<tr>
<td>Surface material</td>
</tr>
<tr>
<td>Average pore diameter (nm)</td>
</tr>
<tr>
<td>Maximum Temperature (°C)</td>
</tr>
<tr>
<td>Recommended pH range</td>
</tr>
<tr>
<td>Maximum pressure (MPa)</td>
</tr>
<tr>
<td>Isoelectric point (pI)</td>
</tr>
<tr>
<td>Molecular weight cut-off (g/mol)</td>
</tr>
</tbody>
</table>
the NF of model solution, pure water permeability was measured in order to determine the irreversible fouling of the membrane. During concentration operation mode using NF90 and NF270 membranes, model solution was continuously fed into the cell at constant permeate flux until the TMP reached 3.5 MPa. The pH of the model solution and the permeate flux were 10 and 26.5 l/m²h, respectively, for NF90. While for NF270, the pH of the model solution was continuously fed into the cell at constant permeate flux until the TMP reached 3.5 MPa. The pH of the model solution, pure water permeability was measured in order to determine the irreversible fouling of the membrane.

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>Xylose</th>
<th>Glucose</th>
<th>Furfural</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>C₅H₁₀O₅</td>
<td>C₆H₁₂O₆</td>
<td>C₅H₁₀O₅</td>
</tr>
<tr>
<td>Molecular structure</td>
<td><img src="image" alt="Xylose structure" /></td>
<td><img src="image" alt="Glucose structure" /></td>
<td><img src="image" alt="Furfural structure" /></td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>150.13</td>
<td>180.16</td>
<td>96.08</td>
</tr>
<tr>
<td>Diffusion coefficient at 25°C (×10⁻⁶ cm²/s)</td>
<td>7.5 (Lide, 2009)</td>
<td>6.7 (Lide, 2009)</td>
<td>11.2 (Yaws and Gabbula, 2003)</td>
</tr>
<tr>
<td>Stokes diameter (nm)</td>
<td>0.64</td>
<td>0.73</td>
<td>Not available</td>
</tr>
<tr>
<td>Dissociation constant (pKᵢ)</td>
<td>12.14 (18°C) (Lide, 2009)</td>
<td>12.46 (25°C) (Lide, 2009)</td>
<td>Not available</td>
</tr>
</tbody>
</table>

### Table 3

<table>
<thead>
<tr>
<th>Variables</th>
<th>Coded symbol</th>
<th>Actual values of coded levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylose concentration (g/l)</td>
<td>A</td>
<td>10.0 25 40</td>
</tr>
<tr>
<td>Glucose concentration (g/l)</td>
<td>B</td>
<td>2.0 10 18</td>
</tr>
<tr>
<td>Furfural concentration (g/l)</td>
<td>C</td>
<td>0.5 4 7.5</td>
</tr>
</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Variables</th>
<th>Responses</th>
<th>NF90</th>
<th>NF270</th>
<th>Rₑₑₑ (%)</th>
<th>Rₑₑ (%)</th>
<th>Rᵥᵥᵥ (%)</th>
<th>Rᵥᵥ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 1 1</td>
<td>–1 1 –1</td>
<td>22.4</td>
<td>71.3</td>
<td>86.1</td>
<td>7.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>–1 –1 1</td>
<td>31.2</td>
<td>80.9</td>
<td>90.0</td>
<td>–10.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>–1 –1 –1</td>
<td>12.4</td>
<td>69.8</td>
<td>85.1</td>
<td>13.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1 –1 1</td>
<td>28.6</td>
<td>76.8</td>
<td>80.6</td>
<td>1.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>–1 1 1</td>
<td>16.3</td>
<td>70.0</td>
<td>86.5</td>
<td>12.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0 0 0</td>
<td>22.6</td>
<td>78.3</td>
<td>89.1</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1 –1 –1</td>
<td>25.8</td>
<td>68.3</td>
<td>85.5</td>
<td>13.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1 1 1</td>
<td>31.6</td>
<td>76.8</td>
<td>89.2</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0 0 0</td>
<td>22.2</td>
<td>78.4</td>
<td>89.2</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>–1 1 1</td>
<td>39.1</td>
<td>79.1</td>
<td>89.8</td>
<td>3.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0 0 0</td>
<td>22.1</td>
<td>78.3</td>
<td>89.3</td>
<td>1.4</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 2.4. Analytical methods

#### 2.4.1. Determination of monosaccharides and furfural

The concentrations of xylose and glucose were quantified by HPLC (Shimadzu Corp., Kyoto, Japan) equipped with a refractive index (RI) detector (RID-10A, Shimadzu Corp., Kyoto, Japan) and Shimadzu Shimpack-SPR-H column (300 × 7.8 mm). Four millimolar perchloric acid was used as the mobile phase at a flow rate of 0.6 ml/min and the column temperature was 40°C. Furfural concentration was analyzed using the same HPLC analytic conditions as described above except that an UV/Vis-detector (SPD-20A, Shimadzu Corp., Kyoto, Japan) at 280 nm was used.

#### 2.4.2. Data processing

The observed retention, \( R_{obs} \), is used to evaluate the separation performance of a membrane for a specific solute, which is defined as follows:

\[
R_{obs} = \left(1 - \frac{C_F}{C_{R,av}}\right) \times 100
\]

where \( C_F \) is the solute concentration in the permeate; \( C_{R,av} \) the average solute concentration in the cell, which is calculated based on the mass balance as illustrated below (Luo et al., 2009):

\[
\begin{align*}
C_{R,av} &= \frac{C_R V_0 + C_F V_F}{C_R V_0 + C_F V_F} \\
&= \frac{C_R + C_F}{C_R + C_F} \\
&= \frac{C_R}{C_R + C_F}
\end{align*}
\]

where \( C_R \) is the solute concentration in the feed; \( C_{R0} \) and \( C_R \) are the solute concentrations in the retentate before and after NF operation, respectively; \( V_0 \) is the volume of the cell filter; \( V_F \) is the volume of the permeate.

In diafiltration operation, the solute concentration in the retentate (\( C_R \)) is calculated by measuring the solute concentration in the feed (\( C_F \)) and in the permeate (\( C_F \)) before and after the diafiltration operation, respectively. \( C_R \) can be represented as follows:

\[
C_R = \frac{C_R V_0 + C_F V_F}{V_0}
\]

The percentage recovery of monosaccharides and the percentage removal of furfural are represented as Eqs. (5) and (6), respectively

Percentage recovery (%) = \( \frac{C_R V_0}{C_F V_F} \times 100 \) (5)

Percentage removal (%) = \( \frac{C_F V_F}{C_R V_F} \times 100 \) (6)

All experiments were performed in duplicate and the average values were reported. Experimental data were statistically analyzed using OriginPro 8.1 (OriginLab, Northampton, MA, USA) at the 95% confidence level.

### 3. Results and discussion

#### 3.1. Effect of pH

Fig. 1 shows the retention of the three solutes and TMP profile as a function of feed pH for NF90 and NF270. The retention of both xylose and glucose by NF90 membrane was almost constant in the pH range examined, with the values higher than 96% (Fig. 1a). In contrast, the retention of both xylose and glucose by NF270 membrane gradually decreased with increasing feed pH (Fig. 1b). For example, the retention of xylose and glucose decreased from
75.6\% and 89.5\% at pH 3 to 70.0\% and 82.7\% at pH 10, respectively, that is, a decrease of 7.4\% and 7.6\% for retention of xylose and glucose, respectively, was obtained when NF270 membrane was used. Furfural retention with NF90 membrane gradually decreased from 46.0\% to 22.2\% as the feed pH changed from acidic pH 3 to alkaline pH 10 (Fig. 1a). While for NF270 membrane, variation of pH from 3 to 10 only slightly reduced the furfural retention (Fig. 1b). TMP profiles during the NF of model solution using NF90 and NF270 membranes shows that the TMP decreased with increasing pH.

The dissociation constant (pK_a) of xylose and glucose (shown in Table 2) was higher than 12 indicating that in the pH range tested, both molecules were in the neutral form. Although the pK_a of furfural was not available, by comparing its molecular structure with that of xylose and glucose, we could presume that its pK_a should also be greater than 12. The uncharged state of the three solutes in the feed solution excluded the retention mechanism of NF based on electrostatic repulsion. Therefore, size exclusion was the dominating factor for retention of the three uncharged molecules. The difference in the pore size of the membrane and the molecular size could lead to different retention. As can be seen in Table 1, NF90 had average pore diameter of 0.68 nm, smaller than that of NF270 (0.84 nm), therefore, towards the same solute, NF90 possessed higher retention than NF270. Furthermore, the Stokes diameter of the three molecules was in the following order: glucose (0.73 nm) > xylose (0.64 nm) > furfural (0.44 nm) (Table 2), which was in accordance with the retention difference using either NF90 or NF270. The very slight difference between the pore size of NF90 and molecular size of xylose and glucose could be responsible for the extremely high retention towards the two solutes. Similarly, the relatively low retention of xylose and glucose with NF 270 membrane could be attributed to the relatively larger pore diameter (0.84 nm) of the membrane compared with the molecular size of xylose and glucose.

The phenomenon that retention of uncharged solute decreased with increasing pH was also reported by Mänttäri et al. (2006) during the investigation on NF of glucose solution with different commercial NF membranes in the pH interval of 2–11, and by Weng et al. (2009) during the separation of acetic acid from xylose by NF. It was well-known that NF90 and NF270 showed a potential amphoteric behavior determined by the nature of functional groups (carboxylic and amine groups) of the active layer of the two membranes. Both NF90 and NF270 had an isoelectric point in the range of 3–6 (shown in Table 1). At pH values below the isoelectric point, membrane surface was positively charged, while for the pH values higher than the isoelectric point, membrane surface was negatively charged. The membrane surface charge would become more negative as the feed pH shifted towards more alkaline values, which resulted in greater intramembrane electrostatic repulsion and could make the pore size of the membrane become more open (Mänttäri et al., 2006). The increase of pore size of the membrane could explain the gradual decline of solute retention and TMP when pH values increased from 3 to 10.

### 3.2. Effect of permeate flux

Permeate flux is one of the most important operating parameters affecting the membrane separation performance. Variation in permeate flux can cause changes in concentration polarization and membrane fouling, thereby resulting in fluctuation of retention. Fig. 2 shows the effect of permeate flux on retention of the solutes and TMP profiles for both membranes. In the case of NF90, with increasing permeate flux from 11.9 to 26.5 l/m² h, retention of glucose and xylose increased from 90.1\% to 99.2\%, and then any further increase in permeate flux caused negligible effect on retention of glucose and xylose. Furfural retention...
gradually increased from 8.9% to 30.9% with increasing permeate flux from 11.9 to 53.1 l/m² h. As for NF270, the retentions of the three compounds gradually increased with increasing permeate flux. For both membranes, among the range of permeate flux examined, permeate flux increased almost linearly with increasing TMP, indicating that the membrane fouling and compaction effects were negligible in the applied pressure range. Increasing rejection of solutes as permeate flux (and TMP) increased could be explained by the solution-diffusion mechanism as explained by Murthy et al. (2005), who pointed out that increasing pressure caused more adsorption of water into the membrane pores than solutes (xylose, glucose and furfural) due to the stronger interaction of water with the hydrophilic active layer of the membrane and the stronger size exclusion of the solutes, therefore, water would pass faster through the membrane than solutes, resulting in the lower solute concentration in the permeate, and consequently higher solute retentions.

Comparison of pure water flux before and after filtration also confirmed that almost no membrane fouling occurred during NF process.

3.3. Effect of temperature

Fig. 3 depicts the solute retention and TMP profile for both membranes as a function of temperature. Retentions of xylose and glucose were independent of operation temperature within the tested temperature range and almost complete retentions for xylose and glucose were obtained for NF90 membrane. In contrast, NF270 retained more xylose (86.8%) and glucose (95.0%) at 25 °C than at 30 °C (77.2% for xylose and 89.8% for glucose) and further increasing temperature from 30 to 45 °C showed negligible effect on retentions of the two solutes. For NF90, a temperature dependent retention of furfural was found, which gradually decreased from 31.8% at 25 °C to 17.8% at 45 °C, whereas for NF270, furfural retention was negative meaning that more furfural passed through the membrane rather than being rejected, and independent of temperature. For both membranes, TMP gradually decreased at elevated temperatures.

Temperature had direct and indirect effects on retentions of the solutes. The direct effect was due to the fact that with increasing temperature, diffusions of both solvent (water) and solutes increased, while the viscosity of the solutions decreased, and both favored the transport of solutes and solvent through the membrane. Decrease of retentions of solutes in the tested temperature range could be attributed to the faster transport of neutral solutes across the membrane than water with increasing temperature, as pointed out by Nilsson et al. (2008). On the other hand, increasing temperature would cause significant changes in the structure and morphology of polymer comprising the active layer of these thin-film composite membranes, leading to increased mean pore size and the molecular weight cut-off (Sharma et al., 2003). Similar results were also reported by Amar et al. (2007) and Nilsson et al. (2008). Amar et al. (2009) investigated temperature effect on the rejection of neutral solutes by Desal-5 DK nanofiltration membrane and found that the effective pore radius increased from 0.58 to 0.67 nm as the temperature increased from 22 to 50 °C. This may explain why a significant decrease in retention of uncharged solute was accompanied with an increase in temperature and TMP also decreased with increasing temperature.

3.4. Effect of solute concentration

Available study with multi-component solution for NF treatment has demonstrated the possibility that the interactions between solutes might affect the performance of the NF membrane (Aydoğan et al., 1998). The model solution used for the present study contained three solutes, if the traditional one-variable-at-a-time approach, i.e. changing one variable while keeping the others constant, was adopted to investigate the effects of solute concentration on the rejection by NF, it would be time-consuming, tedious and more importantly, it would not provide information concerning interactions between variables. Factorial design is an effective mathematical method to investigate multifactor and multilevel process. Although it is more complex than one-variable-at-a-time approach, this approach can allow for evaluation of the statistical significance of individual variable, as well as the interactions between variables with fewer experimental runs (Montgomery, 2008).

A three-level complete factorial 2³ design with three center points (total 11 runs) was carried out to investigate the effect of solute concentration on the performance of NF operation in terms of rejection. The experimental matrix and results are shown in Table 4. Due to the fact that NF90 rejected almost all of the xylose and glucose in the concentration range evaluated, therefore, the rejections of xylose and glucose by NF90 were not listed in Table 4.

The results shown in Table 4 are used to estimate the main variable effects and their interactions for the chosen response (rejection of solutes by NF90 and NF270). Significance of the effects were checked by applying analysis of variance (ANOVA) and are shown as a pareto chart of the effects. The pareto chart visually demonstrate the relative size of effects by conferring a t-value limit. Effects above t-value limit are considered statistically significant at 95% confidence level, while effects below t-value limit are not likely to be significant. An effect is said to be positive when an increase in its level resulted in an increase in the response or negative when an increase in its level resulted in a decrease in the response.

Fig. 4(a) shows the pareto chart of standardized effects for rejection of furfural by NF90 within the concentration range of 25 to 45 °C.
solutes investigated. It can be seen from Fig. 4(a) that all the main effects (xylose concentration, glucose concentration and furfural concentration) and interaction effects (xylose concentration × glucose concentration, xylose concentration × furfural concentration and glucose concentration × furfural concentration) significantly influenced the rejection of furfural by NF90. The three main effects (xylose concentration, glucose concentration and furfural concentration) had a positive effect on the furfural rejection by NF90. Simultaneous increase of glucose and furfural concentration led to increase in the response, while simultaneous increase of xylose concentration and furfural concentration, or simultaneous increase of xylose concentration and glucose concentration, decreased the response.

Fig. 4(b) shows the pareto chart of standardized effects for rejection of xylose by NF270 within the concentration range of solutes investigated. As can be seen from Fig. 4(b), all the effects except glucose concentration significantly affected the xylose rejection by NF270. Increasing furfural concentration or decreasing xylose concentration caused an increase in the response. Increasing glucose concentration accompanied with decreasing xylose concentration also led to an increase in the response. When furfural concentration increased and xylose concentration decreased simultaneously, or both glucose concentration and furfural concentration increased simultaneously, xylose rejection by NF270 showed a decreasing trend.

Fig. 4(c) shows the pareto chart of standardized effects for rejection of glucose by NF270 within the concentration range of solutes investigated. The main conclusion obtained from Fig. 4(c) was that furfural concentration and interaction effects between glucose and furfural concentration were significant variables influencing glucose rejection by NF270. Decrease of furfural concentration or simultaneous increase of glucose and furfural concentration, caused a reduction in the response.

Fig. 4(d) shows the pareto chart of standardized effects for rejection of furfural by NF270 within the concentration range of solutes investigated. It can be observed from Fig. 4(d) that all the effects except glucose concentration significantly influenced furfural rejection by NF270. Xylose concentration showed a positive effect, while furfural concentration showed a negative effect on the response. An increase in xylose concentration associated with a decrease in furfural concentration or glucose concentration influenced negatively the response, leading to lower furfural rejection. Additionally, simultaneous increase of glucose and furfural concentration resulted in a decrease in furfural rejection by NF270.

3.5. Concentration experiments

Pretreatment of lignocellulosic materials was usually conducted at low solid/liquid ratio (Jørgensen et al., 2007; Lu et al., 2009; Qi et al., 2010), resulting in low sugars concentration in the prehydrolyzates, which was not economically feasible for microbial fermentation to produce useful products. In order to increase the sugars concentration in the prehydrolyzates, concentration experiments using NF was carried out at constant permeate flux until TMP reached 3.5 MPa (near the pressure limit of both membranes) and the results are tabulated in Table 5. When NF90 was used, concentrations of xylose, glucose and furfural in retentate increased from 25.5, 9.8 and 3.9 g/l to 87.6, 32.4 and 4.3 g/l, respectively, i.e. 243.5%, 230.6% and 10.2% increase in concentration was obtained for xylose, glucose and furfural, respectively. In addition, the concentrations of both xylose and glucose in the permeate stream were relatively very low, indicating negligible loss of sugars. When NF270 was used, at the end of concentration experiments, the concentrations of xylose and glucose in retentate increased by 193.5% and 267.3%, reaching 72.5 and 36.0 g/l, respectively. While at the same time, as indicated by the high sugars
Concentration in permeate, a substantial amount of sugars was lost. The furfural concentration in retentate decreased from 4.1 to 3.6 g/l, indicating the negative retention of furfural.

The results also suggest that NF90 could be more suitable for concentrating the prehydrolyzates in terms of the higher monosaccharide concentration obtained in the retentate and the low loss of monosaccharide in the permeate.

### 3.6. Diafiltration experiments with NF90

After concentration with NF90, the concentrations of xylose, glucose and furfural in the retentate reached 87.6, 32.4 and 4.3 g/l, respectively. The high furfural content in the retentate would exhibit strong inhibition on microbial growth and fermentation when the retentate solution was used as carbon source for microbial fermentation. Therefore, a diafiltration step to remove furfural was further investigated to obtain high sugar concentration solution with low furfural concentration.

Diafiltration operation is usually used to enhance the removal degree of an impurity component that is partially rejected by the membrane to obtain high-purity product. Diafiltration operation was performed to purify the retentate obtained from concentration operation with NF90 and the results are shown in Fig. 5. As can be seen from Fig. 5, with increasing diafiltration volume factor \( V/V_0 \), the percentage recovery of xylose and glucose slightly decreased, however, the percentage removal of furfural greatly increased. When the diafiltration volume factor was 2, the percentage recovery of both xylose and glucose in the retentate were higher than 98.5%. While at the same time, the percentage removal of furfural reached 66.2%.

Although diafiltration operation produced purified solution with small loss of xylose and glucose, it consumed a large amount of water, which should be strictly restricted in industrial application. In order to minimize the water consumption, it is necessary to optimize the diafiltration operation to obtain optimum dilution volume factor, at which furfural concentration in the retentate is just below the concentration exerting negative effect on microbial strain. On the other hand, water consumption can also be decreased by improving the strain and making it resistant to furfural concentration as higher as possible while still maintaining high product concentration and yield.

## 4. Conclusions

Concentration and purification of xylose and glucose in model solution containing furfural was studied by using two commercial NF membranes (NF90 and NF270). For both membranes, the rejections of the three solutes were significantly influenced by the operating conditions, such as feed pH and solutes concentration, permeation flux and temperature. Concentration experiments with NF90 greatly increased the concentrations of xylose and glucose, while furfural concentration increased to some extent. A NF process for concentration and purification of lignocellulosic prehydrolyzates was proposed. It included concentrating feed prehydrolyzate with NF90 followed by diafiltration of the retentate to remove furfural. The experimental results show that NF could be a promising approach for concentration and purification lignocellulosic prehydrolyzates.

### Acknowledgements

The authors would like to thank the Chinese Academy of Sciences’ Knowledge Innovation Program for the financial support (Grant No. KSCX1-YW-11D2) and FilmTech Corp., USA for providing NF90 and NF270 membranes.

### References


### Table 5

Concentration experiments of model solution until the TMP reached 3.5 MPa. Xylose, glucose and furfural concentrations were 25, 10 and 4 g/l, respectively; feed pH: pH 10 for NF90 and pH 3 for NF270; permeate flux: 26.5 l/m\(^2\) h for NF90 and 39.8 l/m\(^2\) h for NF270; stirring speed: 1200 rpm.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Xylose (g/l)</th>
<th>Glucose (g/l)</th>
<th>Furfural (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F</td>
<td>P</td>
<td>R</td>
</tr>
<tr>
<td>NF90</td>
<td>25.5</td>
<td>0.5</td>
<td>87.6</td>
</tr>
<tr>
<td>NF270</td>
<td>24.7</td>
<td>10.2</td>
<td>72.5</td>
</tr>
</tbody>
</table>

F: feed; P: permeate; R: retentate.

---

**Fig. 5.** Effect of \( V/V_0 \) on \( C/T_0 \) during diafiltration operation with NF90. Xylose, glucose and furfural concentrations were 87.6, 32.4 and 4.3 g/l, respectively; temperature: 30 °C; permeate flux: 26.5 l/m\(^2\) h; stirring speed: 1200 rpm.


