Recovery of xylan by membrane separation processes

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Abstract

The economic sustainability of the pulp industry passes nowadays through the utilization of by-products that can provide added value added to the paper making process. One of this by-products is xylan and its recovery from bleached pulp may have a significant economic and environmental return that justifies their industrial application. This recovery can be made by an alkaline extraction, with NaOH, from which a strong alkaline xylan-rich liquor results. Membrane separation processes are very well suited to isolate xylan from this liquor.

In this work, several membranes were tested for this task, namely, the organic membranes GR95PP and SelRO-MPS 34 for UF and NF, respectively. Parametric tests were performed to assess the best operating conditions (pressure and velocity) aiming the obtention of the highest permeation flux as well as high concentrate and permeate purities.

In the case of organic membranes GR95PP and MPS 34, the optimum conditions were set at a velocity of 2.0 m/ s and a pressure of 6 bar and 1.0 m/ s and 14 bar, respectively. For these conditions permeate fluxes of 15.5 and 4 L / h.m\textsuperscript{2} were obtained for GR95PP and MPS 34, respectively. A deep decrease in the permeation flux was observed during concentration of xyans for all the membranes. At the end of all the concentration experiments NaOH remained equally distributed between concentrate and permeate.

The molecular weights were determined by GPC xylan with an average value of 18 kDa.

Keywords: xylan; ultrafiltration; diafiltration; HPLC, sugars, molecular weights
1. Introduction

Bleached pulp is mainly composed of cellulose (around 80%) and hemicellulose (around 20%), that are considered the first and second most abundant, cheap and renewable resources on planet earth. [1]. Its potential use as raw material for other processes than paper-making has been, in recent decades, the subject of intensive study.

Hemicelluloses, namely xylans, have been identified as highly promising materials for numerous applications including the production of films and coatings for packaging, production and application in foams and gels, hydrogels and products for the cosmetics, biomedical and pharmaceutical industries. The isolation of xylan present in bleached pulp is thus of great interest due to the economic potential that it represents.

The macromolecules of xylan have characteristics similar to cellulose but differing from it by their heterogeneity as they are composed of several sugars, including hexoses (glucose, mannose and galactose) and pentoses (xylose and arabinose).

To be isolated from bleached pulp xylans must be, in first place, extracted from it, the most common way being through an alkaline extraction [2]. From this operation a strongly alkaline liquor is obtained from which xylan must be isolated. For this task, membrane separation processes are very well suited [3].

Through a careful choice of the membranes these processes allow not only xylan concentration but also its purification as well as the recovery, in the permeate, of the sodium hydroxide used for the extraction. Usually, in a first ultrafiltration (UF) operation, xylan is concentrated and purified. Then, in a second membrane process, nanofiltration (NF), the UF permeate is purified leading to a concentrate of sugar monomers and low molecular weight xylans and to a permeate which is a high purity sodium hydroxide solution.

Membrane processes are, nowadays, very popular and the transport mechanisms ruling them very well known [3]. Pressure is the motive force for mass transport in ultrafiltration and nanofiltration. Usually, during both operations, there is a decline in permeate flux over time due to a number of different phenomena leading to the accumulation of mass material at the surface of the membrane which is designated by concentration polarization. Concentration polarization can degenerate in most limiting phenomena causing membrane fouling and also, in some cases, clogging of the membrane. To purify the concentrates upstream the membrane, a technique known as diafiltration (DF) [4] is used in some UF and NF processes. The main goal of diafiltration, which simply is a washing procedure is the purification of the concentrates. Through the addition of water low molecular weight components which otherwise would be kept on the concentrates are removed thus, purifying it.

The performance of UF and NF membranes are quoted by manufacturers in terms of the pure water flux and Molecular Weight Cut-Off (MWCO).

Pure water flux is given by

$$J_w = L_p \frac{\Delta P}{\mu_w}$$  \hspace{1cm} (1.1)

where $J_w$ represents the volumetric water flow (m$^3$/m$^2$.s), $\Delta P$ the pressure difference in the membrane (Pa), $\mu_w$ the water viscosity (Pa.s) and $L_p$ the hydraulic permeability of the membrane (m). $L_p$ is the inverse of $R_m$ (m$^{-1}$), the membrane intrinsic resistance which is due to its physical structure and is expressed by:
The other parameter, MWCO, defines the separation ability of the membrane and is defined as the molecular weight (in Da) of the molecule that is 90% rejected by the membrane.

So, MWCO is related to a parameter of the upmost importance in membrane processes, the rejection factor. This parameter measures the fraction of solute contained in the feed which is retained by the membrane and it is defined as:

\[ R = 1 - \frac{C_p}{C_f} \quad (1.3) \]

where \( C_f \) is the solute concentration in feed and \( C_p \) the solute concentration in the permeate.

Apart from more elaborate theories which lead to more complex equations, the basic equations describing mass transport (or permeation flux) across the membrane are

\[ J = \frac{\Delta P - \Delta \pi}{\mu(R_m + R_s)} \quad (1.4) \]

and

\[ J = k_s \ln \left( \frac{C_m - C_p}{C_b - C_p} \right) \quad (1.5) \]

The first one is a general equation containing all the factors which can be important for describing permeation across the membrane namely, \( \Delta P \) the pressure difference across the membrane (Pa), \( \Delta \pi \) the osmotic pressure (Pa), \( \mu \) , the viscosity of the solution which permeates the membrane (Pa.s), \( R_m \) and \( R_s \) the resistances to flow of the membrane and of the polarization layer (m\(^{-1}\)), respectively.

The second equation takes into account the effect of concentration polarization trough parameters such as the concentrations of the solute (kg.m\(^{-3}\)), \( C_b \), \( C_m \) and \( C_p \) respectively, in the feed, the membrane and the permeate (kg.m\(^{-3}\)).

In this work the possibility of isolation /concentration of xylans by UF and NF is evaluated. To accomplish this task ultrafiltration and nanofiltration experiments were performed using three membranes with MWCO of 10, 2 and 0.2-0.3 kDa. Permeation fluxes are evaluated and of xylans and monomeric sugars are quantified.

2. Materials and Methods

2.1 Extraction of xylans

In this work, Xylans in the bleached pulp were extracted with a solution of 10% (w / w) NaOH. To a given amount of bleached pulp (dry basis) is added, proportionally, a pre-determined volume of 10% NaOH solution. This suspension is then allowed to stir for about 1 h. The liquor resulting from this operation, which is the test solution, is designated by filtrate.

2.2 Membranes

Xylans are concentrated by UF using a 2 kDa organic membrane, GR95PP and by NF with a 200-300 Da organic membrane, SelRO-MPS 34.

2.3 Equipment

The experimental set-up includes a feed reservoir, a Wanner HydraCell pump and a Osmonics membrane module associated with an ENERPAC P-142 hydraulic pump and a scale.

Experiments with the M5 membrane were performed with the same feed reservoir and scale but with an AxFlow pump and a standard tubular housing.
2.4 Experimental procedure

To remove preservation chemicals, organic membranes were washed at 25 °C and at a pressure of 9 bar with 5 g/L NaOH solutions. Compaction of membranes was then accomplished by passing water for 30 minutes at a pressure of 9 bar and a temperature of 25 °C.

Regarding the ceramic membrane, washing was performed with a solution of 0.005 M NaOH circulating in the system for 30 minutes at 3 bar and a temperature of 25 °C.

To optimize operating conditions for UF and NF isolation/concentration processes parametric experiments were performed. The objective was to determine the optimum pressure and velocity leading to great permeation flux. For these, as the concentration should remain constant the concentrate and the permeate are both recirculated to the feed tank. Pressures of 2, 3, 4, 5 and 6 bar for GR95PP, 4 and 6 for M5 and of 10, 12, 14 and 16 bar for the NF membrane, SelRO-MPS 34 were tested. As to velocities values of 0.5; 1.0; 1.5 and 2.0 m/s were used for both GR95PP and for SelRO-MPS 34.

Concentration experiments were performed under the optimized conditions (velocity and pressure) set up in the parametric test for each membrane. In this case, the concentrate was recycled to the feed tank and the permeate was collected in a beaker placed on a balance. Permeate mass is thus recorded continuously.

DF tests were carried out in a batch mode. After a given concentration factor being reached a certain amount of water, the same as the collected mass of permeate, was added to the feed reservoir and the concentration process started again. Diafiltration was made under the same operating conditions (velocity and pressure) of the concentration experiment for each test membrane.

2.5 Analytical methods

Two types of analysis were made to quantify the samples taken during the experiments: chemical analysis and GPC. Sugars were determined using an alternative to the well known Dubois method [5]. For this new method [6], which has an advantage of not using phenol, samples are first hydrolyzed into monomeric sugars according to the technique of Saeman [7].

Quantitative analysis of xylan were made through pentosans determination using a standard technique based on the Tappi 223 cm.

As to the evaluation of molecular weight of xylans, using gel permeation chromatography (GPC), the procedure described elsewhere [8-9] was followed.

The GPC equipment, a PL-GPC 110 (Polymer Laboritories) was equipped with two PLgel Mixed-B 10 μm 300 x 7.5 mm columns protected with guard column Plgel 10 μm and a RI detector, PD2020. Analyses were done at 70 °C, a flow rate of 0.9 ml / min and injection volumes of 100 μL. The eluent was a mixture of DMAc with 0.1 M LiCl.

The calibration was made with pulullans molecular weights of 5800, 12200, 23700 and 48000 Da.

3. Results and Discussion

3.1 Determination of hydraulic permeability

After being washed and compacted (only organic membranes) hydraulic permeability, \( L_p \), was determined for all membranes. These values are shown in Table 1 for each membrane.

The NF membrane has a lower permeation flux which was expected due to its density.
### Table 1 - Hydraulic permeability of membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$L_p$ (L/h.m².bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GR95PP (UF)</td>
<td>6,7</td>
</tr>
<tr>
<td>SelRO-MPS 34 (NF)</td>
<td>0,5</td>
</tr>
</tbody>
</table>

### 3.2 Parametric study

From the parametric study the optimum operating conditions namely circulating velocity and applied pressure were set up for all the membranes, the values being shown in Table 2.

### Table 2 - Optimized operating conditions (velocity and pressure) applied to each membrane

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Pressure (bar)</th>
<th>Velocity (m/s)</th>
<th>$J_p$ (L/h.m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GR95PP</td>
<td>6</td>
<td>2,0</td>
<td>15,5</td>
</tr>
<tr>
<td>MPS 34</td>
<td>14</td>
<td>1,0</td>
<td>4,1</td>
</tr>
</tbody>
</table>

### 3.3 Concentration study

Within the concentration experiments several situations were studied namely the influence of feed load, circulating velocity, solution neutralization and successive diafiltrations.

#### 3.3.1 Feed load

In order to test the influence of the feed load, in the batch concentration process two tests were performed under the same operating conditions but with different loads: 764 g and 1294 g. The results are shown in Figure 1 where the effect of diafiltration on permeation flux can also be observed.

For both feed loads, the effect of diafiltration proved to be advantageous in terms of permeation fluxes. After adding water to the concentrate an increasing of the flux was observed and was maintained throughout all the second concentration until the final concentration factor (CF).

As to feed charges the most obvious conclusion is that for the test with the lower feed load, the flow is approximately half of the flow obtained for the larger load. However, the differences found in these two studies can be explained by the quality of pulp used in the higher load test which came from a different batch with a higher humidity.

#### 3.3.2 Circulation velocity

The velocity at which the fluid circulates can have a great influence on the concentration operation. The Figure 2, shows the result of experiments done for 1.3 and 2 m/s and the same initial charge. The membrane in use was GR95PP.

As expected, at a first glance, it can be seen that the higher the velocity the greater the permeate flow. For a higher flow the imposed CF is reached faster than for the lower velocity.
Following concentrations and diafiltration. \( \Delta P = 6 \) bar; mass = 764 g. Room temperature. \( \text{pH} = 12.5 \).

### 3.3.3 Neutralized solution

The average of pH values of the filtrates obtained for all the extractions is 12.5. This value is very close to the threshold value (pH 13), in operation, for GR95PP membrane. Therefore, a slight reduction of pH would be desirable as with this reduction there would be no risk of shortening the lifetime of the membrane. This is important bearing in mind the large operating periods found in industry where membrane faces aggressive conditions. To evaluate the feed-back of the system to pH variation a 43.7% sulfuric acid solution was used to decrease pH to 12. The fact is that, for this solution, as soon as pH started being reduced, the formation of a precipitate was immediately observed. This was attributed to the precipitation of xylans.

After the first diafiltration, the decrease of permeation flux for the second concentration step is much more pronounced than for the first concentration. On the other hand, the average flux during the third concentration is much lower than that of the 2nd and 1st concentrations. This important decrease of flux is related with precipitation which was induced by the addition of water which decreased pH. This is supported by the observation of some opacity of the solution immediately after the second addition of water. This opacity being a characteristic of the occurrence of precipitation.

Thus one has here the same effect which was observed previously when acid was added to the solution.

As would be expected, the permeation flux is very low evidencing a strong fouling of the membrane. On the other hand, in this case, diafiltration introduces no significant change in terms of permeation flux.

### 3.3.4 Successive diafiltrations (DF)

The beneficial effect of diafiltration (DF) on permeation fluxes is very well known and was observed for this solution as reported in Figures 1 and 2. So, an experiment with three diafiltrations was performed as shown in Figure 4.
3.3.5 Nanofiltration experiments

Besides isolate/concentrate the xylans of the extraction liquor the other goal of this work is, to investigate the possibility of recovering and recirculate to the process the NaOH which is consumed in the extraction. In the published [10-11] works that address this subject, this recovery is made upon the ultrafiltration permeate in order to obtain a purified NaOH solution. Besides NaOH, the ultrafiltration permeate may contain, as well, monosaccharide and low molecular weight xylans. When the monosaccharides would not be a problem regarding the purity of xylans upstream the membrane then with a single nanofiltration operation would obtain a concentrate of xylans and a purified NaOH permeate. To evaluate this possibility a MPS 34 nanofiltration membrane was used in an experiment under operating conditions previously determined in the parametric study. Results are displayed in Figure 5. The permeation flux was much lower compared to GR95PP membrane fluxes. However, it remained constant throughout the test which was very time consuming, about 9 hours. It indicates that the polarization layer that was formed adjacent to the membrane stabilized allowing a good control operation.

In table 3 operating conditions for each experiment are summarized where C means concentration and DF means diafiltration.

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Pressure (bar)</th>
<th>Velocity (m/s)</th>
<th>Type of experimente</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>1.3</td>
<td>C+1DF</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>1.3</td>
<td>C+1DF</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>2.0</td>
<td>C+1DF</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>2.0</td>
<td>C+1DF</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>2.0</td>
<td>C+2DF</td>
</tr>
<tr>
<td>6</td>
<td>14</td>
<td>1.0</td>
<td>C</td>
</tr>
</tbody>
</table>

3.4 Analysis

3.4.1 Molecular weight of xylans

Molecular weight of xylans was determined by GPC. The results, which are presented in Figure 6, clearly show that for all the analyzed samples of concentrates there is a unique population of xylans with an average molecular weight of 18000 Da.

Figure 6- Determination of molecular weights

Regarding the low MWCO of the membrane, 2 kDa, the existence of lower molecular weight xylans in the sample which would have passed to the permeate is not probable unless their molecular weight were less than 2 kDa.
3.4.2 Content of xylans

Content of xylans in the filtrates and concentrates are shown in the graph of Figure 7. Despite the fact that we do not have much filtrates analyzed, the tendency seems correct when we pass from the filtrate to the concentrates as the xylan content increases.

In fact, diafiltration force the low molecular solutes to permeate and, except for experiment 3, we can confirm that in all experiments. These removed low molecular weight solutes are ashes, monosaccharides and NaOH. Thus, we can obtain a larger amount of xylan by dry weight.

The low xylan content found for experiment 2 can be easily explained by the fact that this experiment was done with a much more wet batch of bleached pulp. This extra humidity was not taken into account in the calculations of the concentration of NaOH to be used for extraction. Thus a much less concentrated solution of NaOH was used and much less xylans were extracted from the bleached pulp.

3.4.3 Content of sugars

The determination of the monosaccharide content, (as xylose) was performed by the sulfuric method and can be observed in Figure 8.

The monosaccharide content should follow the trend of the results obtained from xylan, in other words, its content increased with increasing the content of xylan. However, we can only confirm that with the experiment 1 and 5.

A slight decrease of the monosaccharide content is observed for the first concentration of experiment 3 but, for experiments 4 and 5 this effect is not verified. Experiments 1 and 6 cannot be adequately evaluated as there are not sufficient information.

However, taking into consideration an average value for the monosaccharide content (about 55.9 %) in the filtrate based in its values for experiments 3 (69.8 %), 4 (48.3 %) and 5 (51.0 %) it is probable that for experiment 1 the content increased for the first concentration as well.

Despite a lack of results, it is not excluded that the discrepancies found in these results could be due to incomplete hydrolysis and / or bad sample preparation.

3.4.4 Comparison of content of xylan and xylose

Table 4 shows the results obtained for the determination of the content of xylan and xylose.
Table 4 - Comparison of content of xylan and xylose (%) (w/w)

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Concentration</th>
<th>Content of xylan (%) (w/w)</th>
<th>Content of xylose (%) (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1º Concentrate</td>
<td>72,5</td>
<td>51,4</td>
</tr>
<tr>
<td>1</td>
<td>2º Concentrate</td>
<td>95,7</td>
<td>72,9</td>
</tr>
<tr>
<td>3</td>
<td>Filtrate</td>
<td>69,8</td>
<td>56,4</td>
</tr>
<tr>
<td>3</td>
<td>1º Concentrate</td>
<td>50,9</td>
<td>53</td>
</tr>
<tr>
<td>5</td>
<td>1º Concentrate</td>
<td>52,4</td>
<td>56,7</td>
</tr>
<tr>
<td>5</td>
<td>2º Concentrate</td>
<td>91</td>
<td>77,9</td>
</tr>
</tbody>
</table>

Theoretically, we are analyzing results that should be very close. The relationship between xylan and xylose is: xylose = 1.14 x xylan so the xylose content should be slightly higher than xylan. This observation was confirmed by first concentrate of the experiment 3 and 5. Moreover, the values of the xylose contents, calculated by xylans vary randomly, that is, there are cases in which are higher and others that are smaller.

4. The recuperation of NaOH

The recovery of NaOH for possible reutilization in the extraction step is very important in costs structure due to its high consumption. The removal of NaOH from the concentrates through the action of DF purifies xylans and increases its content. Another beneficial effect is that the removal of sodium hydroxide probably allows a lower degradation of xylan. In this work a good recover of NaOH in the permeates was achieved with low rejections as can be observed in Table 5.

Table 5 - Rejection of NaOH (%)

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Membrane</th>
<th>Rejections (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GR95PP</td>
<td>1º Rejection = 25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2º Rejection &lt; 0</td>
</tr>
<tr>
<td>2</td>
<td>GR95PP</td>
<td>1º Rejection = 18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2º Rejection = 59</td>
</tr>
<tr>
<td>3</td>
<td>GR95PP</td>
<td>1º Rejection = 6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2º Rejection = 3</td>
</tr>
<tr>
<td>4</td>
<td>GR95PP</td>
<td>1º Rejection = 23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2º Rejection = 2</td>
</tr>
<tr>
<td>5</td>
<td>GR95PP</td>
<td>1º Rejection = 22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2º Rejection = 29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3º Rejection = 28</td>
</tr>
<tr>
<td>6</td>
<td>SelRO-MPS 34</td>
<td>1º Rejection = 27</td>
</tr>
</tbody>
</table>

5 Conclusions

Parametric tests were used to determine the best operating conditions for each tested membrane. In most cases, we obtain higher flow rates for higher velocities and pressures.

In concentration experiments, we concluded that the diafiltration helps to purify the xylan which is in the concentrate and, in some cases, increases the flow permeation.

The velocity has a significant influence on the permeation fluxes as it is possible to obtain higher permeation fluxes for high velocities as it was found to GR95PP membrane.

Since the membranes are subject to harsh conditions, a slight lowering of the pH of the filtrate was made. However, due to the immediate occurrence of precipitation this operation was not satisfactory as membrane was immediately fouled. Nanofiltration proved ineffective because it had very low flows of about 4 L/h.m². Moreover, this type of membrane is more suitable for treating the permeate in order to recover a purified NaOH.

Average molecular weight of xylans in the concentrates was as well determined and it was found to be approximately 18 kDa for all the samples analyzed. Regarding the xylan content, diafiltration shown to be very efficient for removing impurities and therefore purifying xylan.

6 References

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