

# SEPARATION OF HEMICELLULOSES FROM AN INDUSTRIAL STREAM BY NANOFILTRATION AND ULTRAFILTRATION PROCESSES

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The performance of nanofiltration (NF) and ultrafiltration (UF) membranes was studied for separating hemicelluloses from a highly alkaline industrial stream, containing 17-18 wt% sodium hydroxide, resulting from the viscose process. Initially, screening experiments were performed to select suitable membranes, which were then investigated on a pilot scale spiral module. Screening experiments showed that the UF membrane, with a nominal molecular weight cut-off (MWCO) value of 3 kDa, and the NF one, with a nominal MWCO value of 0.5 kDa, showed a similar range of filtration performance and a flux of 4.2 L/m<sup>2</sup>.h. Further, a retention efficiency of 50% was observed for the 5 kDa and the 10 kDa membranes, indicating absence of any significant proportion of hemicelluloses in this range of molecular weights. The effects of process conditions were studied to understand their correlation with membrane performance with respect to hemicelluloses retention and permeate flux. UF membranes were found to be more prone to performance deterioration over time and with the number of cycles of usage during the pilot scale study, whereas the NF membrane showed consistent performance. It was seen that feed dilution can improve the membrane performance with respect to sodium hydroxide recovery. Significant reduction in feed viscosity with dilution resulted in a 50% increase in flux after normalizing for concentration.

**Keywords:** ultrafiltration, nanofiltration, alkali resistant membrane, hemicelluloses, viscose

## INTRODUCTION

Hemicelluloses are the second most important and abundant, after cellulose, organic material on the earth. Actually, hemicelluloses are a mixture of various types of polysaccharides;<sup>1</sup> they are colourless and relatively stable carbohydrate polymers. They are heteroglycans containing various types of sugar units, comprising C<sub>5</sub> and C<sub>6</sub> sugars, and when extracted, they exist in monomeric and oligomeric forms arranged in different proportions and with distinct structures. Hemicelluloses can be made up of several types of sugar units, namely glucose, xylose, mannose, galactose, arabinose, fructose, glucuronic acid, and mannuronic acid.<sup>2</sup> The composition of sugar units in hemicelluloses varies in different plants, as well as in different parts of the plants. This heterogeneous branched group of polysaccharides has a degree of polymerization ranging between 50 and 300, including some acetyl and carboxylic groups.<sup>3</sup> Hemicelluloses occur in close association with cellulose, especially in lignified tissues, the term often being restricted to substances extracted with alkaline reagents, but not with water. In a broad classification, three main groups of polysaccharides are recognized – namely, those based on chains of D-xylose, D-mannose (either alone or in association with D-glucose), and D-galactose residues. In such a classification, for example, the term “xylan” is used to denote polysaccharides containing a backbone of D-xylose residues.<sup>4</sup> Hemicelluloses are less crystalline in nature and their chemical and thermal stability is lower than that of cellulose. Hemicelluloses represent 20-30% content of the dry weight of wood. Wood hemicelluloses exert a distinct biomechanical contribution to cellulose fibrillar networks.<sup>5</sup>

Viscose is a type of regenerated cellulosic fibre extensively used in textile and non-woven applications. Viscose fibres are produced from purified dissolving grade wood pulp by first treating it with strongly alkaline solutions to make alkcell (alkali cellulose), then reacting it with carbon disulphide to convert the alkcell to soluble xanthate ester. Xanthate ester is dissolved in dilute alkali to obtain a spinning solution (viscose) of honey-like colour and consistency. Viscose is reacted with acid solution for regenerating and precipitating cellulose while releasing carbon disulphide.

The main raw material used in viscose fibre production is dissolving grade wood pulp containing 92-94%  $\alpha$ -cellulose. Dissolving grade pulp also contains hemicelluloses as one of the impurities. Hemicelluloses can adversely affect the fibre production process and also the properties of the final fibre product. In the first step of the viscose process, the pulp is steeped (soaked) in a large excess of aqueous sodium hydroxide of about 17-18% concentration in order to achieve pulp swelling for greater reactant accessibility and to remove alkali soluble hemicelluloses. Recycling the excess alkali solution from the first step results in build-up of hemicelluloses in the circulating caustic stream and this can cause several limitations in the process, such as inefficient press operation because of increased viscosity, inadequate removal of water and alkali from alkcell during the dewatering press operation and deterioration of alkcell reactivity.<sup>6</sup> Hemicelluloses being more reactive than cellulose also impact subsequent reaction steps and this results in the deterioration of viscose quality. Being smaller molecules, hemicelluloses can also modify regeneration kinetics, thus impacting fibre properties, such as surface texture, friction and cross-sectional shape.<sup>7</sup> Theoretically, it is possible to completely remove hemicelluloses from the caustic stream of the process, but this will also result in loss of caustic soda along with hemicelluloses, thus resulting in higher process cost and material wastage.

Semi-permeable dialysis membranes were introduced in the early days to recover caustic from the used hemicelluloses containing alkali solution, but were then abandoned because of operational issues arising from dilution and costs. However, membrane-based separation is an effective way for removing solutes and thus to reduce costs and make the system more sustainable. Besides the nature of the raw material from which they are produced, viz. organic (polymeric) or inorganic (ceramic), membranes can be classified based on their pore size into microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) membranes.<sup>8</sup> As pore size reduces from MF to NF, the operating pressure for separation also increases. Depending on the nature of the solute, different membranes have been considered for a variety of applications, including water purification,<sup>9</sup> water treatment,<sup>10</sup> removal of heavy metals from water,<sup>11</sup> recovery of bioactive compounds,<sup>12</sup> separation and recovery of food ingredients<sup>13,14</sup> and recovery of metabolites from fermentation systems.<sup>15</sup>

Spiral winding of polymeric membranes helps reduce the footprint area. Normal spiral wound polymeric UF and NF membranes are made up of materials that cannot tolerate aggressive and harsh operating conditions, such as highly alkaline process streams, but in recent times, there have been several reports of investigations on membrane usage for separation of hemicelluloses. The performance of different commercially available alkali resistant polymeric nanofiltration and tight ultrafiltration membranes has been studied for hemicelluloses separation from the alkaline stream of the viscose process.<sup>16</sup> Higher flux decline and fouling was observed when hydrophobic UF membranes were used to treat process water from thermo-mechanical pulping.<sup>17</sup> An economical combination of UF and NF membranes was proposed for the recovery of the alkaline solvent from a hemicelluloses containing wheat bran residual stream.<sup>18</sup> In another process, hemicelluloses were first recovered from chemithermomechanical pulp process water and enzymatic treatment was used to increase the molecular mass of hemicelluloses markedly. Large hemicelluloses molecules were separated from small hemicelluloses molecules by ultrafiltration.<sup>19</sup> Recovered hemicelluloses can be valorised through several products, such as organic acids, including acetic acid, methane, monosaccharides, fuel ethanol, xylose, xylitol, solvent alternatives to petroleum-derived chemicals, plasticizers, hydrogels, and dyes.<sup>20-24</sup> More applications of hemicelluloses are being studied in the field of advanced materials, such as food packaging materials<sup>25</sup> and oxygen barrier films.<sup>26</sup>

In our previous work,<sup>27</sup> we studied the performance of polymeric ultrafiltration (UF) membranes for hemicelluloses separation from a highly alkaline process stream. We demonstrated the separation of hemicelluloses using UF membranes, but the membranes were found to be prone to performance deterioration owing to progressive clogging and deformation. In the present work, the performance of UF and NF alkali-resistant membranes was studied and compared for hemicelluloses separation from an alkaline process stream. The aim of this study has been to identify the most suitable membrane and the optimum process conditions for separating hemicelluloses from caustic solution.

## **EXPERIMENTAL**

### **Feed stream**

The process solution used in the experiments of this work was withdrawn from the dissolving grade pulp steeping process. In this process, pulp is first reacted with an excess of 17-18% NaOH solution and then the slurry is pressed in a twin roll press arrangement to remove and eventually recycle extra alkali and water containing dissolved hemicelluloses. This process stream was taken from a unit of Grasim Industries in Bharuch (India). The initial stream was diluted or concentrated using demineralised water, as per the specific experiment requirement.

### Membranes

Initially, the performance of four alkali-resistant membranes was investigated and compared. Four flat-sheet polymeric membranes with MWCO of 0.5, 3, 5 and 10 kDa were used in the screening experiment. The membrane sheets were of 8 cm diameter, and thus had an approximate used area of 50 cm<sup>2</sup>. Spiral wound membrane modules of 0.5 kDa and 3.0 kDa were selected based on the initial screening tests and were used in the following step for an extensive comparative study of performance and to investigate the effects of process parameters. Each spiral module was 40 inch in length, 4 inch in diameter and a filtration area of 5 m<sup>2</sup>. All membrane modules were purchased from M/S Permionics, Vadodara, India. All the membranes were of ARG grade, made of hydrophilized polyether sulphone on non-woven alkali-resistant polymer support.

### Equipment

Two experimental setups were used in the investigation: one in the experiments with flat sheet membranes, and the other in the experiment with the spiral wound membrane module. The components of the laboratory equipment used in the flat sheet membrane experiments were the following: a feed reservoir type high pressure module, with an arrangement to fix a circular flat sheet membrane, which could provide a continuous discharge of permeate. The module was pressurized using nitrogen. Polymeric spiral wound membrane modules were tested on a bigger experimental setup, having a feed tank, a pre-filtration system, a feed pump, membrane housing, along with feed pressure and temperature measurement devices. The experimental setup used is the same as that illustrated in our previous work.<sup>27</sup>

### Experimental procedure

All the membranes were cleaned for 1 h before and after each experiment, using 2.0 wt% NaOH solution. After cleaning, the membranes were rinsed with deionised water. Initially, 200 L of feed was taken for the experiments. The retentate and the permeate were recycled to the feed tank in order to keep the concentration constant. The cross-flow was kept constant at 2.5 m<sup>3</sup>/h. The feed temperature during the experiments was kept constant as per the requirement. The membrane feed pressure was increased in steps to avoid cake layer formation on the membrane. Initially, the membrane was kept under constant cross-flow for 15 minutes, then the permeate was drawn for 60 minutes to arrive at the average value of flux and retention. The permeate flux was measured at constant feed pressure of 3.0 bar for UF membranes and of 20 bar for the NF membrane, which was well below the critical trans-membrane pressure. The flow was continuously recorded to monitor the membrane performance. The permeate flux and retention were calculated using the following relations:

$$\text{Flux (L/m}^2\cdot\text{h)} = \frac{\text{permeate flow (l)}}{\text{membrane filtration area (m}^2\text{)} \times \text{time (h)}} \quad (1)$$

$$\text{Retention (\%)} = \frac{[\text{feed hemicelluloses (g/L)} - \text{permeate hemicelluloses (g/L)}] \times 100}{\text{feed hemicelluloses (g/L)}} \quad (2)$$

### Analytical method to determination hemicelluloses

Hemicelluloses were determined as total carbohydrate content in the alkali solution. In the given method, 5 mL of 1.0 N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> was introduced into an iodine flask. Then, 0.5 mL of filtered hemicelluloses containing caustic sample was added, followed by slow addition of 10 mL of conc. H<sub>2</sub>SO<sub>4</sub>. A G-2 sintered glass crucible was used for lye filtration. The sample was placed in the oven at the temperature of 125 °C for 5 min, keeping the funnel over the flask. 200 mL of distilled water was added after the sample cooled down. Also, when the sample cooled to 20 °C, 10 mL of 10% potassium iodide (KI) solution was added. The flask was corked and placed in the dark for 5 minutes. This content was titrated with 0.1 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution using starch as an indicator. Titre reading (TR) was noted. A blank was prepared in a similar manner, using 0.5 mL of pure caustic lye (without any hemicelluloses in it). Hemicelluloses concentration was calculated using the following relation:

$$\text{Hemicelluloses } \left(\frac{\text{g}}{\text{L}}\right) = \frac{(\text{Blank} - \text{TR}) \times 0.1 \times 0.00675 \times 1000}{0.5} \quad (3)$$

where TR = titre reading.

## RESULTS AND DISCUSSION

In an earlier study found in the literature, the performance of different commercially available membranes was compared for separation of hemicelluloses from an alkaline process stream of the viscose process.<sup>8</sup> The major focus of that study was to understand the effect of temperature and

pressure with respect to maximizing flux and the objective was limited to identifying the best available membrane. In our previous work,<sup>27</sup> we focused on understanding the behaviour of polymeric UF membranes and identifying possible issues in their use for hemicelluloses separation from a highly alkaline process stream. We concluded that the separation of hemicelluloses is possible using UF membranes, but their reliability was found to be a challenge, as we observed steady deterioration of membrane performance during the study. In the current work, we have tried to understand and address the issue of membrane robustness and reliability. This study has two major objectives: the first is to identify a suitable polymeric membrane cut-off size that can be used for reasonable hemicelluloses separation from a highly alkaline viscose process stream, and the second – to perform a comprehensive comparative study on ultrafiltration and nanofiltration membranes to understand their fouling tendency, performance deterioration over time, and under the effect of temperature, pressure and feed composition.

### Selection of ultrafiltration and nanofiltration membranes

An alkaline stream sample containing hemicelluloses was taken from a viscose fibre producing plant. The typical characteristics of the process stream used for the filtration study are given in Table 1. An initial screening test was done on a simple membrane sheet testing apparatus using a membrane sheet of 50 cm<sup>2</sup>. Three ultrafiltration membranes used for the separation study were of 3 kDa, 5 kDa and 10 kDa MWCO, respectively. One nanofiltration membrane of 0.5 kDa was used for the initial test. Initially, the membrane was kept under constant cross-flow for 15 minutes, then the permeate was drawn for 60 minutes to arrive at the average value of flux and retention. Filtration using the UF membranes was performed under the feed pressure of 3.0 bar, whereas in the case of the NF membrane, it was operated under a feed pressure of 20 bar. NF membranes require higher operating pressure due to significantly lower MWCO. The comparative performance of the membranes is given in Figure 1.

Table 1  
Feed characteristics

| Sr. No. | Test parameters                             | Results | Method of testing                    |
|---------|---|---------|--------------------------------------|
| 1       | Caustic soda (wt%)                          | 17.60   | Titration                            |
| 2       | Conductivity at 25 °C (mS/cm) (1% solution) | 1.97    | Conductivity meter                   |
| 3       | Total dissolved solids (wt%)                | 21.60   | Evaporation based gravimetric method |
| 4       | pH at 25 °C (1% solution)                   | 13.50   | pH meter                             |
| 5       | Total suspended solids (wt%)                | 0.20    | Filtration based gravimetric method  |
| 6       | Initial hemicelluloses concentration (g/L)  | 35.00   | Titration of carbohydrates           |

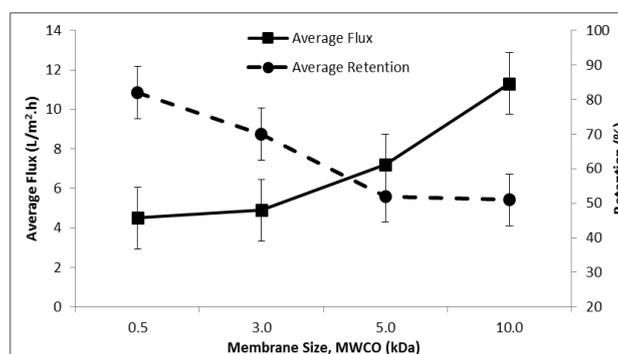


Figure 1: Average permeate flux and hemicelluloses retention by membrane sheets

Two interesting observations can be made based on Figure 1. Firstly, the average flux significantly rises while going up in the ultrafiltration range from 3 kDa to 10 kDa, but at the same time, when the tighter nanofiltration membrane of 0.5 kDa is used, the flux is in the same range as for the 3 kDa UF membranes. Secondly, hemicelluloses retention is similar for the 5 kDa and 10 kDa membranes. Both these observations indicate the non-symmetrical bimodal type of molecular weight distribution of hemicelluloses, thus the quantity of hemicelluloses with the molecular weight lying in the ranges from 5 to 10 kDa and from 0.5 to 3.0 kDa will be significantly lower than for the other fractions, which have a molecular size either less than 0.5 kDa or in the range of 3.0-5.0 kDa. A smaller fraction of hemicellulose molecules in the range of 5000-10000 Da would not greatly affect the retention for 5 and 10 kDa. However, a larger fraction of hemicellulose molecules between 500 Da and 3000 Da will impact significantly different retention rates for these two cases. This can be the reason for the similarity, in terms of retention, between the 5 kDa and 10 kDa membranes. The ultrafiltration membrane of 3 kDa MWCO and the nanofiltration membrane of 0.5 kDa were selected for the detailed performance study at a bigger scale of operations, as both membranes had a retention >70% and a similar flux. In addition to steric hindrance, electrostatic repulsion as well as the presence of carbohydrate complexes may play a role in filtration, but to rule that out, we ensured consistent feed characteristics for all the experiments.

### **Hemicelluloses separation study using the spiral UF membrane**

A 3 kDa ultrafiltration membrane was tested for performance with respect to retention and flux. The membrane used in the trials had the length of 40 inch and the diameter of 4 inch. Membranes of these dimensions correspond to an available membrane filtration area of 5 m<sup>2</sup>. Experiments were conducted at a fixed pressure of 4 bar.

### **Membrane performance with respect to time and usage cycle**

Five sets of separation experiments were conducted to understand membrane performance. Each experiment was continued for a minimum of 24 h, where membrane cleaning was performed every 8 hours. Each experiment was started with 200 L of feed solution, which was kept constant by performing the filtration run in a closed-loop, *i.e.*, the permeate as well as the retentate were recycled back continuously to the feed tank to ensure the same feed concentration. Experiments were performed at a constant temperature of 45 °C, unless otherwise specified. Results are given in Table 2. Detailed analysis of the data was done to assess membrane performance with respect to time and cycles of use. The average flux and retention trends are given in Figure 2.

The data (Fig. 2) indicate that the average flux values in the initial experiment were found to be ~4 L/m<sup>2</sup>.h, which steadily reduced and stabilized to 2.2-2.3 L/m<sup>2</sup>.h. In the case of retention minimum, it was found to be 54%, whereas highest hemicelluloses retention value was 64%. The flux indicates a steady deterioration in the performance of the membrane with an increase in operation cycles.

Table 2  
Permeate flux and hemicelluloses concentration for UF experiments with the 3 kDa membrane

| Experiment | Starting permeate flux (L/m <sup>2</sup> .h) | End permeate flux (L/m <sup>2</sup> .h) | Hemicelluloses in feed (g/L) | Hemicelluloses in permeate (g/L) |
|------------|--|---|------------------------------|----------------------------------|
| Exp. 1     | 5.0  | 3.0                                     | 50.0                         | 23.0                             |
| Exp. 2     | 4.4  | 3.0                                     | 50.0                         | 22.5                             |
| Exp. 3     | 3.5  | 2.3                                     | 60.0                         | 27.0                             |
| Exp. 4     | 2.6  | 2.1                                     | 65.0                         | 28.0                             |
| Exp. 5     | 2.4  | 2.0                                     | 65.0                         | 24.0                             |

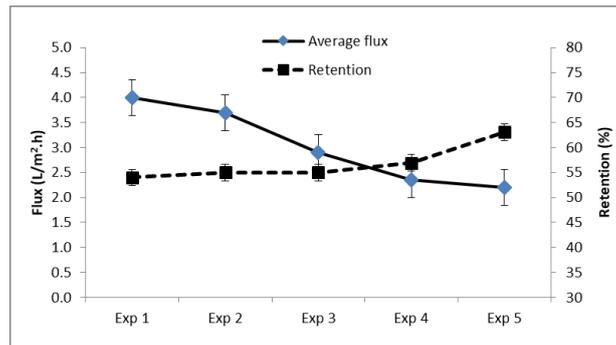


Figure 2: Permeate flux and hemicelluloses retention with the 3 kDa membrane

The relative membrane performance for an individual set of experiments can be understood from the flux data given in Table 2. In the first experiment, the starting flux was 5 L/m<sup>2</sup>.h, which is close to the values obtained in sheet filtration and offline trials. Just before cleaning, the flux dropped to a level of 3 L/m<sup>2</sup>.h and did not achieve previous flux values after cleaning. When taken for the next experimental run, the flux values kept on converging as the operation days increased. This indicated a non-reversible damage or clogging of the membrane with each operational cycle, leading to both reduced flux and increased retention.

The fouling of polymeric membranes by dissolved organic matter in alkaline solution, particularly at pH>10, is expected to be lower.<sup>8</sup> However, the polymeric membranes are also prone to structural damage when compressed under pressure and in the presence of harsh chemicals. The compression of polymer membranes and thus reduced porosity can also cause this reduction in flux. The highly alkaline nature of the feed can alter the swelling characteristics of the polymeric membrane material and thus increase the severity of the above-described membrane deformation. Further, the difference in retention of the spiral wound membrane and the flat sheet of the same MWCO is likely due to the different rates of choking of membranes. A membrane support sample, before and after cleaning, was subjected to scanning electron microscopy (SEM) to understand the extent of clogging, which can be responsible for deterioration in the membrane performance. SEM images are given in Figure 3.

Fibre elements of the non-woven membrane surface seemed to be fused in both cleaned and used membranes, though washed membranes appear free from deposits, which are visible on the uncleaned membrane surface in Figure 3. The feed for the filtration system was obtained from a pulp steeping process, the pulp being fibrous in nature results in the presence of these fibrous suspended impurities in the stream. The feed stream is normally subjected to multiple levels of pre-filtration, but still there is the possibility of a small quantity of smaller size suspended materials to escape through pre-filtration and clogging membranes.

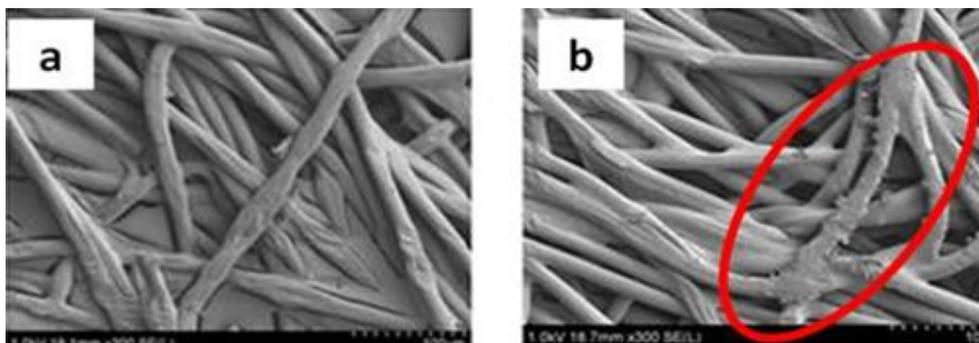


Figure 3: Surface SEM images of: a) cleaned membrane surface; b) membrane surface prior to cleaning

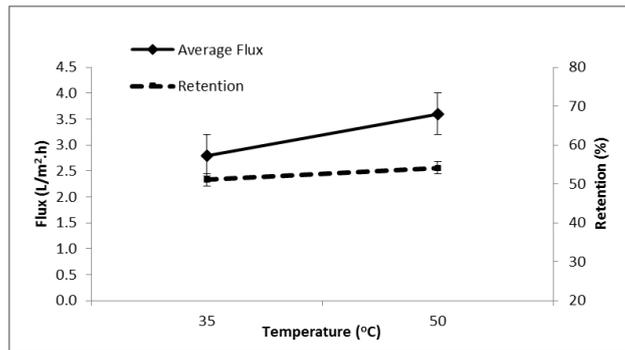


Figure 4: Effect of temperature on the performance of the 3 kDa UF membrane

Fused support fibres can be the result of fibre swelling in alkaline medium and simultaneous application of pressure. Membrane performance data and cross-section images of the non-woven membrane support indicate the presence of contaminants and a phenomenon of clogging, as well as structural deformation. This may have been aggravated by the membrane interaction with the highly alkaline feed at varying temperature conditions. Also, such variations in temperature are likely to affect critical TMP, besides feed viscosity and flow characteristics.<sup>8</sup>

#### ***Effect of temperature on membrane performance***

The effect of temperature was studied in the next set of experiments. The separation studies were conducted at the feed temperature of 35 °C and 50 °C. We selected only these 2 temperatures because these are the extreme ends of the available process window. We did several repeats using these temperatures to confirm the observed trend. Flux and retention values were compared for the two sets of experiments. Observations are given in Figure 4. Given data indicate that the flux at 50 °C was 3.6 L/m<sup>2</sup>.h, as opposed to 2.8 at 35 °C; that is a ~30% increase in the flux, whereas the retention of hemicelluloses remained around 52-54% in both cases. Thus, temperature has not been found to have an impact on hemicelluloses retention. An increase in flux with temperature indicates the beneficial effect of reduced feed viscosity and lower surface tension at higher temperature, which could have led to an increased permeation rate.

#### **Hemicelluloses separation study using the spiral NF membrane**

A performance study using the 0.5 kDa nanofiltration spiral wound membrane module was undertaken in the next set of experiments. The pilot unit used for the tests was the same as the one used with the ultrafiltration membranes. The membrane had an MWCO of 500 Da, module length of 40 inches and diameter of 4 inches. The effective filtration area was 5 m<sup>2</sup>. An average filtration pressure of 20 bar was used for the filtration experiments.

#### ***Membrane performance with respect to time and usage cycle***

Initially, five sets of separation experiments were conducted to understand membrane performance. The experimental design and procedure were kept similar to those in the case of the 3.0 kDa UF experiments. Each experiment was continued for a minimum of 1 day, where membrane cleaning was performed every 8 hours. Results are given in Table 3. Detailed analysis of the data was performed to assess membrane performance with respect to time and cycles of use. The average flux and retention trends are given in Figure 5. The average flux was found to be sustained ~4 L/m<sup>2</sup>.h. Unlike the UF membranes, where continuous deterioration of the flux was observed, the NF membrane showed sustained flux.

Hemicelluloses retention for all the experiments remained in the range of 72-73% and there was no increase or decrease in the retention with an increase in the number of experiment cycles. In the case of the 3 kDa UF membrane, we could see that retention values slowly increased along with experiment cycles. This indicates that the filter clogging tendency is lower in NF membranes. The relative membrane performance data for each individual set of experiments are given in Table 3. As shown in Table 3, in the first experiments, the starting flux was 5 L/m<sup>2</sup>.h, and it reduced to 3.8 L/m<sup>2</sup>.h in the final experiment. In the rest of the experiments, the starting flux was ~4.5 L/m<sup>2</sup>.h and reduced to 3.8-

3.9 L/m<sup>2</sup>.h by the end of the experiments. These data indicate good performance maintenance for the tested membranes. The nanofiltration membrane support was also subjected to SEM to observe the effect of cleaning on the membrane. SEM micrographs of the membrane are given in Figure 6. The observations regarding the scanning electron micrographs of the nanofiltration membrane are similar to those mentioned above for the ultrafiltration membrane. Non-woven support material fibres seemed fused both in cleaned and uncleaned membranes. The washed membrane support appears to be free from deposits, which are clearly visible on the uncleaned membrane. The amount of superficial material deposits seems to be higher on the nanofiltration membrane, as compared to the ultrafiltration one. These observations indicate that, in the case of the NF membranes, most of the impurities and contaminants get entrapped superficially, which are later removed during the membrane cleaning cycle.

Table 3  
Permeate flux and hemicelluloses concentration for NF experiments with 0.5 kDa membrane

| Experiment | Starting permeate flux (L/m <sup>2</sup> .h) | End permeate flux (L/m <sup>2</sup> .h) | Hemicelluloses in feed (g/L) | Hemicelluloses in permeate (g/L) |
|------------|--|---|------------------------------|----------------------------------|
| Exp. 1     | 5.0  | 3.8                                     | 60                           | 16.0                             |
| Exp. 2     | 4.3  | 3.8                                     | 58                           | 16.0                             |
| Exp. 3     | 4.5  | 3.8                                     | 60                           | 17.0                             |
| Exp. 4     | 4.3  | 3.9                                     | 59                           | 16.0                             |
| Exp .5     | 4.4  | 3.9                                     | 60                           | 17.0                             |

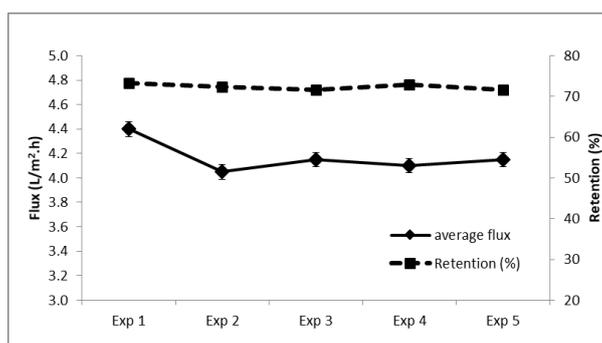


Figure 5: Permeate flux and hemicelluloses retention with 0.5 kDa membrane

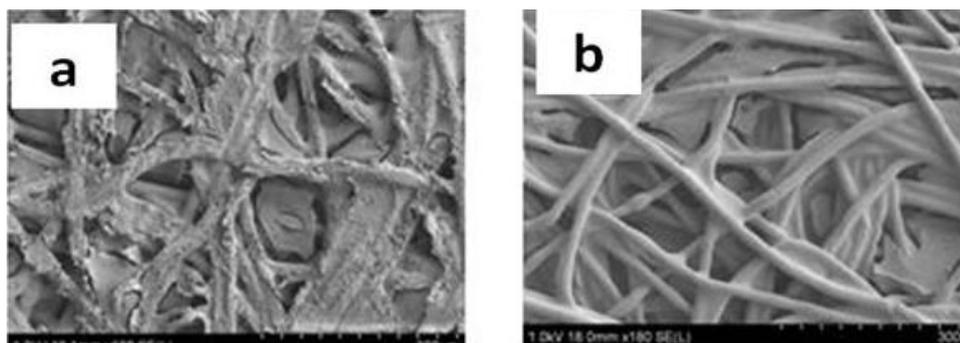


Figure 6: Surface SEM: a) before cleaning; b) after cleaning

### Comparative membrane performance of UF and NF membranes

Comparative performance data of NF and UF membranes are given in Table 4. We can observe a significant drop in the performance and a steady failure of UF membranes as the number of usage cycles increases. Also, the data show that the clogging tendency of the NF membrane is lower than that of the UF membranes; thus NF membranes are likely to offer comparatively better long-term performance. This can be explained by the smaller size of the pores in the NF membranes, which do not allow large-size molecules and impurities to get in and clog the membranes, whereas in the case of UF membranes, these large molecules can clog the membrane; while the low operating pressure doesn't allow these molecules to pass through the pores. In the case of the NF membranes, there is a

higher operating pressure, which also effectively cleans the membrane or opens the pores, in other words, prevents clogging. This mechanism is depicted in Figure 7. In this schematic, the five-pointed stars, circles and curves represent molecules of different sizes. The five-pointed stars represent the largest molecules, which result in blocking UF membranes, circular symbols represent the smallest molecules, which can pass through UF as well as NF membranes, and the curves represent molecules of intermediate size, which can pass through UF membranes, but not through NF membranes.

Table 4  
Permeate flux and hemi retention comparison for UF and NF membrane

| Membrane type | Final stabilized flux (L/m <sup>2</sup> .h) | Rejection at stabilized flux (wt%) | Drop in flux from first to last experiment (wt%) |
|---------------|---|------------------------------------|--|
| UF            | 2.5   | 62                                 | 37.5   |
| NF            | 4.2   | 72                                 | 4.5  |

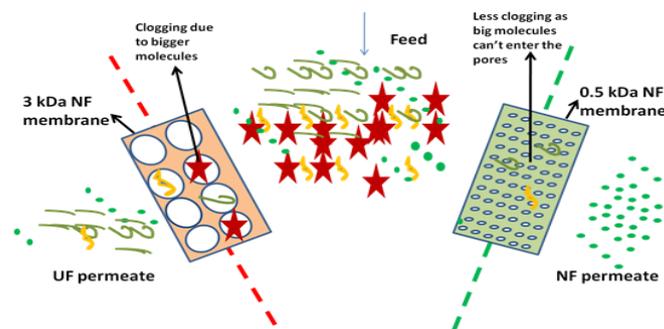


Figure 7: Relative clogging of UF and NF membranes

### ***Effect of feed pressure***

The NF membranes can be operated at a wide range of pressure; accordingly, the effect of feed pressure was studied. Data for flux and retention under different pressure conditions are provided in Figure 8 (a and b). Operating pressure was varied in the range from 22 to 30 bar to understand its impact on flux and retention values. We can observe an almost linear increase in flux from 4.0 to 5.6 L/m<sup>2</sup>.h, as the operating pressure went from 22 bar to 30 bar; this corresponds to a ~40% increase in the flux at an almost 36% increase in operating pressure. Retention remains similar (~75%) in all the cases, although we do see a small reduction at the pressure of 30 bar, which is possibly due to some increased passing of hemicelluloses through the membrane at higher operating pressure.

### ***Effect of feed concentration***

Nanofiltration membranes have very small pore size and their performance can depend on the hydrodynamic characteristics, which can cause a pressure drop. Fluid viscosity is one such factor, which can theoretically impact membrane performance. In order to understand the impact of viscosity, different sets of experiments were performed at different caustic soda and hemicelluloses concentration in the feed. This study also gains significance in the scenario where the recovery of caustic soda is of high importance and hemicelluloses are considered as impurities, as in the viscose process. In such a scenario, it is very important to understand if it is possible to optimize the performance by changing the concentration of caustic soda in the feed. Thus, experiments were done using 3 feed samples with concentrations of 9, 13 and 17% caustic soda. In all the cases, hemicelluloses in the feed were in the range of 45-47 g/L and in the permeate – in the range of 12-13 g/L. Average data on hemicelluloses retention and average flux are given in Figure 9.

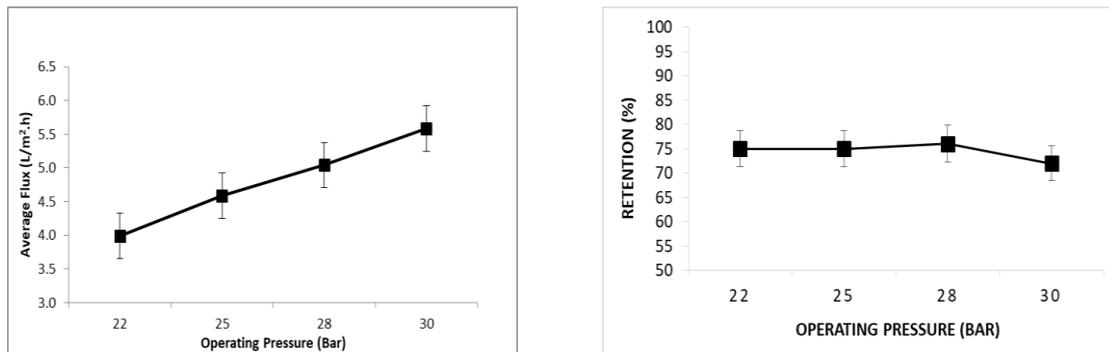


Figure 8: Effect of operating pressure on permeate flux (a) and retention (b)

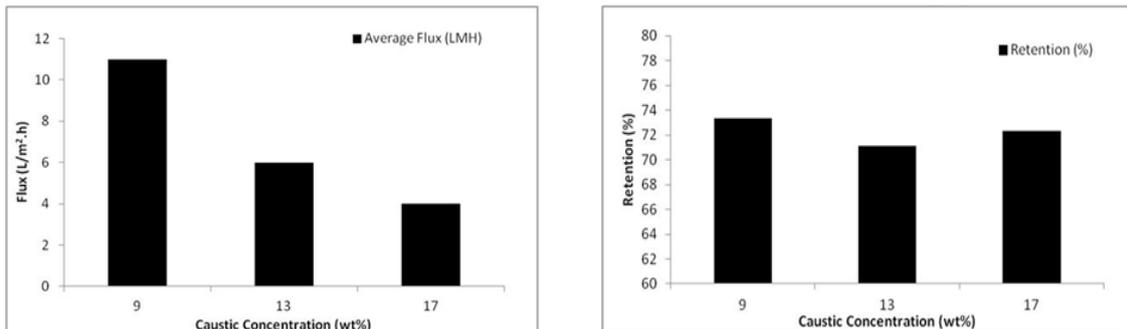


Figure 9: Retention of hemicelluloses and average flux by NF membrane as a function of caustic concentration of the feed

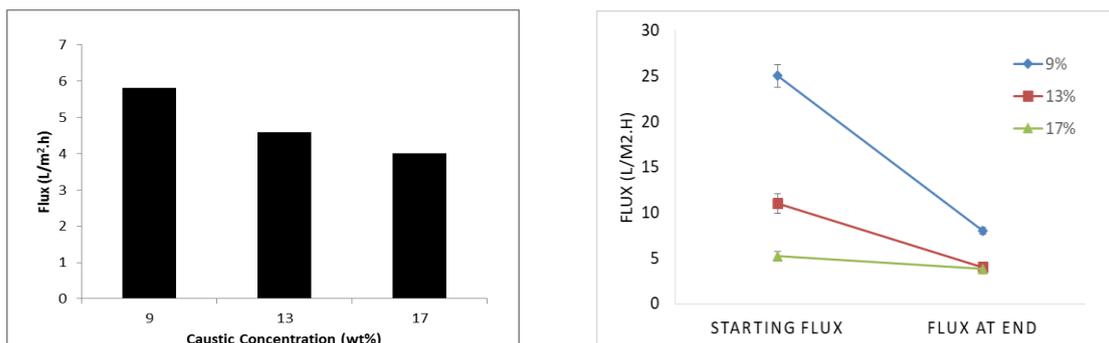


Figure 10: Average normalized permeate flux with change in caustic concentration

Figure 11: Change in the flux with different feed caustic concentrations

As it is clear from the above given data, the level of hemicelluloses retention is 71-73% in all the cases. The hemicellulose retention rate is independent of the hemicellulose concentration in the feed. A comparison of the flux for the three cases is also given in Figure 9. As we can see, there is a dramatic change in the flux as the caustic concentration is reduced. Flux reduces to almost 30% in the case of 17% caustic soda, when compared to the feed where the caustic concentration is 9%. In this case, the average flux value may not directly represent the true performance because the hydraulic load is increased on account of reduced caustic concentration; hence the flux is recalculated by normalizing the value for 17% caustic concentration. This also helps in comparing the actual caustic recovery for all the cases. A comparison of the normalized flux is given in Figure 10.

The data indicate that the average flux increases with a reduction in caustic concentration. The flux was found to be 11 LMH for 9% caustic feed, and 4 LMH for 17% caustic feed. Further, even when the flux is normalized with respect to caustic concentration, it is still higher by 30-40% for the 9% feed. Thus, diluting the feed can be advantageous with respect to recovering more caustic soda. The change in the flux during the experiments was studied by plotting the initial and the final flux. Plots are given in Figure 11. As we can see, the change in the flux during the run is higher in the case of lower caustic concentration, when compared to the runs where the caustic concentration is higher. One

probable reason can be that initial fouling is less during the run, but this is masked by the higher fluid viscosity when 13 or 17% caustic concentration is used.

## CONCLUSION

The experimental study has shown that hemicelluloses from the alkaline process stream can be separated both by UF and NF membranes. Initial screening experiments revealed that the hemicelluloses present in the alkaline process stream of the viscose process can have a bimodal type of distribution, where the quantity of hemicelluloses lying between the nominal cut-off of 0.5 kDa and 3 kDa can be very small and so is the quantity above 10 kDa. Incidentally, the flux is also found to be very close for both these membranes. The pilot scale studies indicated deterioration of performance for the 3.0 kDa membrane with the time of use. The performance in the case of the 0.5 kDa membranes was well sustained. This indicates that in the given application, UF membranes are more prone to failure, as compared to NF membranes, thus NF membranes are likely to give better long-term performance. Increased temperature resulted in an improvement in the flux, without compromising on the retention. Data on the effect of feed concentration on membrane performance suggest that the dilution of the feed stream by 50% can result in a relative performance improvement by 40% in terms of sodium hydroxide recovery. This indicates that, depending on the end utility, one can manipulate this synergistic effect on flux and find an optimum combination of membrane type and feed concentration. Thus, we can conclude that NF alkali-resistant membranes are more suitable for hemicelluloses removal from the alkaline process stream. There also exists an opportunity for optimization to find out the most suitable operational parameters as per the process requirements.

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