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Ultrafiltration for hemicelluloses recovery and purification from thermomechanical pulp mill process waters

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ABSTRACT

Process waters of thermomechanical pulp (TMP) mills contain a large quantity of lignocellulosic materials that end up in the wastewater for biological treatment. The recovery of hemicellulose and lignin from these process water as value-added chemicals is beneficial for TMP mills because it reduces the organic loading to the wastewater treatment facility. The performance of three hydrophilic ultrafiltration (UF) membranes made of regenerated cellulose with different molecular weight cut-offs (5, 10, and 30 kDa) for hemicelluloses recovery and purification was evaluated in a laboratory-scale dead-end stirred cell filtration unit. The results of this study showed that 5 and 10 kDa membranes gave much better recovery and purity for hemicelluloses than 30 kDa membranes. The recovery of the hemicelluloses was above 95% for 5 kDa and around 89% for 10 kDa, with hemicellulose purity of approximately 75% and 80%, respectively. Cut-offs of 5 and 10 kDa seem to be operationally feasible for the separation of hemicelluloses, while 30 kDa cut-off membrane was unsuitable for hemicellulose recovery. An optimal cut-off of 10 kDa membrane gave the highest purity of hemicelluloses (80%).

Keywords: Hemicelluloses; Lignin; Ultrafiltration (UF); Bioproducts; Biorefinery; TMP wastewater

1. Introduction

Decreasing competitiveness of the forest products industries and the rising environmental concerns have motivated the research to focus on exploitation of the various wood components efficiently. This situation led to the study and development of integrated forest biorefinery (IFBR) which uses forest-based biomass and wastes rather than fossil fuels to generate value-added chemicals and bioenergy [1]. This new business paradigm offers a broad spectrum of potentially attractive bioproducts. These compounds can be economically recovered from IFBR either after hydrolysis of carbohydrates or from pretreatment process if effective separation technologies are developed.

In thermomechanical pulping (TMP), wood chips are treated with pressurized steam. During this process, approximately 5%–10% of woody materials, which include hemicelluloses, lignin, and extractives, are dispersed as colloidal particles into process waters [2,3]. These compounds can be recovered for better applications. Recently, isolation of hemicelluloses and lignin from wood has gained increasing interest, and several applications have emerged. Hemicelluloses have been found to be an excellent candidate for the production of hydrogels, oxygen barrier film in packaging materials, emulsion stabilizer in food, and surfactants, as well as a source of sugars that can be fermented to ethanol [4–6]. Lignin has been used in carbon fibers, adhesive materials, activated carbon (AC), asphalt, and lead storage batteries [7–9]. Thus, the recovery and separation of hemicelluloses and lignin from TMP process streams as value-added chemicals increase the profitability and competitiveness, reduce the organic loading to the wastewater treatment plant, and minimize overloading to bottleneck recovery boilers.

Although plenty of applications for lignocellulosic materials have been proposed, the lack of effective separation methods of hemicellulose and lignin with high purity [10] is

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a major challenge with the utilization of hemicellulose and lignins in certain industrial applications. Usually, the process water of forest industry is a complex mixture of wood components: hemicelluloses, lignin, wood extractives, and organic acids. In order to obtain a purified fraction of hemicelluloses and lignin, highly developed separation technologies that are cost-effective and environmentally responsible are needed [10]. Also, since each molecular weight of hemicelluloses has a specific application field, fractional separation and structural characterization of the hemicelluloses are required for the effective use of these materials.

Membrane technology has been proposed as a possible separation technique for IFBR because of its capacities to offer fractionation and separation. Also, it has short processing steps, less chemical utilization, and considerable energy saving, as well as can be integrated easily with the existing operating units [4,11]. Recent advances in membrane technology and system design have created a new opportunity for effective ultrafiltration (UF) of several organic polymers and inorganic chemicals. In IFBR, UF membrane is found to be an effective method for the treatment of pulp and paper effluent not only to purify the process water for reuse but also to recover and fractionate dissolved lignocellulosic materials [12–17].

The use of membrane filtration in IFBR has some challenges that need be addressed before commercially feasible membrane process can be used for process water concentration due to the complexity of wood hydrolysates. The major challenge for membrane separation of hemicelluloses and lignin recovery is membrane fouling [2]. So far, there is a lack of deep understanding of the interactions between the foulants and membrane structure as well as the operating conditions. Also, it has been found that pretreatment methods such as pH adjustment, or using ion-exchange resin, pulsed corona discharge, and AC adsorption significantly improve membranes filterability [2,18]. Koivula et al. [2] indicated that pretreatment processes have to be tailored separately for different hydrolysates due to their different characteristics. Persson and Jonsson [3] reported that a hydrophobic membrane has high fouling tendency than a hydrophilic membrane. Gonder et al. [19] stated that membrane fouling could be reduced by optimizing membrane operating conditions.

Usually, the successful application of a UF, for performing separation and purification processes, is associated with the selection of appropriate membrane molecular weight cut-offs (MWCOs), average permeate flux, and volume reduction (VR) factor. Although several UF studies have been reported in the literature, the optimal membrane cut-off for hemicelluloses recovery is not clearly specified [20]. The optimal conditions that give the maximum recovery and purity of hemicellulose are not identified yet. It is therefore worthy of conducting further research in UF for hemicellulose and lignin separation to identify the optimal membrane structure and operating conditions. Also, the membrane geometry can play a major role in the hemicelluloses retention and membrane flux because it impacts the membrane fouling and concentration polarization. To find the optimal membrane cut-off and operating conditions for hemicelluloses recovery and purification, in this study, a laboratory-scale dead-end stirred cell filtration unit was used for hemicelluloses and lignins separation and purification from a TMP process water. The performance (membrane flux, recovery, and purity of hemicelluloses) of UF membranes with different MWCO (5, 10, and 30 kDa of a hydrophilic regenerated cellulose (RC) membrane) for hemicelluloses recovery and purification from TMP process waters was systematically evaluated. New insight on the role of optimal membrane structure in hemicellulose recovery and purification was obtained.

2. Materials and methods

2.1. Process water

The raw material used in this study was process water from a Canadian TMP mill. The wastewater was stored in a cold room at 4°C to prevent hemicelluloses degradation. Table 1 summarizes characteristics of the tested process water. The content of total solids (TSs), TDSs (total dissolved solids), lignin (UV absorbance at 205 nm), hemicelluloses, ash content, chemical oxygen demand (COD), turbidity, and total organic carbon (TOC) of the samples was analyzed. The content of TSs was determined by drying and weighing method. The dry sample was further burned to 575°C in a furnace to determine ash content. The TDSs were measured by filtering the samples through a filter paper and then drying the sample which passes through in the oven at 105°C using the standard method. The turbidity was determined at room temperature using a turbidity meter (2100AN Turbidimeter, HACH Co., USA). Total carbon and total inorganic carbon were measured by TOC analyzer (Vario TOC select, Elementar Analysensysteme GmbH, Germany). In addition, pH was measured by Oakton pH/Ion 700 (Cole-Parmer, Canada). Total suspended solids were determined from the difference between TSs and dissolved solids. The composition of the process water is shown in Table 1. It was found that the concentration of the hemicellulose is around 0.72 ± 0.135 g/L. Accordingly, a high VR factor is needed for its recovery and concentration. All tests were made in triplicate, and results were presented as mean value ± standard deviation (SD).

Table 1
Composition and properties of TMP mill process water used in this study (average value ± SD)

Analyzed parameters	Average values
Ash content (g/L)	0.9 ± 0.2
Chemical oxygen demand (COD) (mg/L)	3,862 ± 99
Total solids concentration (g/L)	3.3 ± 0.14
The total dissolved solids (TDSs) (g/L)	2.3 ± 0.2
Suspended solids concentration (mg/L)	0.9 ± 0.2
pH	4.2 ± 0.15
Total organic carbon (TOC) (g/L)	1.4 ± 0.06
Turbidity	1,115 ± 5.29
Lignin concentration (g/L)	1.94 ± 0.21
Total hemicelluloses (g/L)	0.72 ± 0.135
• Arabinose (g/L)	0.075 ± 0.019
• Galactose (g/L)	0.516 ± 0.095
• Raminose (g/L)	0.001 ± 0.001
• Glucose (g/L)	0.046 ± 0.007
• Xylose (g/L)	0.013 ± 0.002
• Mannose (g/L)	0.070 ± 0.015

2.2. Membrane

The performance of three UF membranes with different MWCOs (5, 10 and 30 kDa) was investigated in this study. Table 2 displays characteristics of the tested membranes. Hydrophilic, RC UF flat sheet membranes from EMD Millipore Corporation, Billerica, MA 01821, USA with a filter diameter of 63.5 mm and active membrane area 0.00287 m^2 were used. Hydrophilic UF membrane has previously shown low fouling tendency during the filtration of pulp and paper effluent. Maartens et al. [21] reported that foulants present in the effluent of pulp and paper mills are of phenolic and hydrophobic nature and increasing the hydrophilic characteristics of the membranes have been found to reduce the amount of organic foulants that adsorbed onto the membranes. Weis et al. [22] stated that the hydrophilicity of the membranes has a significant role in reducing fouling of UF fouled with spent sulfite liquor when they studied fouling mechanisms of polysulfone, RC, and polyethersulfone (PES) UF membranes. Puro et al. [23] compared fouling of PES and RC membranes during the treatment of (softwood and hardwood) pulp mill process waters by UF. The results of this study showed that the fouling of PES was greater than that of RC with both types of process waters, regarding their flux recovery and membrane nature and morphology.

2.3. Equipment and filtration experiments

A laboratory-scale experimental setup, utilizing dead-end stirred cell filtration unit, purchased from EMD Millipore Corporation, was employed for measuring the performance of UF membranes with different MWCOs for hemicelluloses and lignin separation. A schematic diagram of the process used in this investigation is shown in Fig. 1. In each run, the filtration cell was fed with 150 mL of the process water. The experiments were conducted in concentration mode of filtration, where three samples were collected from each filtration: feed, permeate, and concentrate in separate containers. The feed quality continuously concentrated by reducing the feed solution gradually until the desired VR was achieved.

During the filtration experiments, a magnetic stirrer device was used to decrease the concentration polarization effect, which declines the permeate flux (J) during the filtration process. In contrast to membrane fouling, concentration polarization is a reversible phenomenon that occurs during filtration when the solutes concentrate on the membrane surface. Before the use, the membranes were pretreated by soaking in distilled water for 1 h. The water was changed three times during the soaking process. Membranes are soaked to prevent the membranes from absorbing any of the filtration water and removing any materials that may have been

Table 2
Characteristics of ultrafiltration membranes used in this study and their pure water fluxes (PWF) before and after filtration

Membrane (MWCO) (kDa)	Module type	Max. press. (bar)	Max. temp. (°C)	Membrane material[a]	PWF before (kg/(m^2 h))[b]	PWF after (kg/(m^2 h))[b]	Percentage change (%)
5[c]	Flat sheet	4.8	121	RC	10.45	9.22	11.77
10[c]	Flat sheet	4.8	121	RC	75.26	67.53	10.27
30[c]	Flat sheet	4.8	121	RC	491.29	468.29	4.68

[a]Regenerated cellulose.
[b]Test conditions: 1 bar, 22°C, stirred at 300 rpm (Thermo Scientific™).
[c]EMD Millipore Corporation, USA.

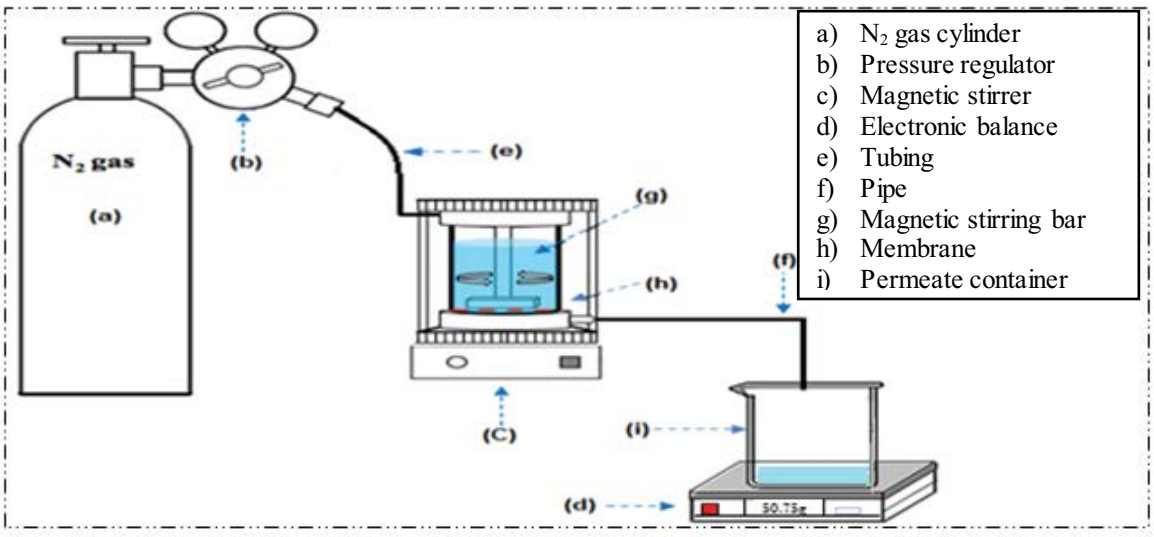

Fig. 1. Diagram illustrating ultrafiltration cell used in this study.

attached to the membranes during packaging and shipment such as glycerin which is used to prevent drying and sodium azide as a preservative.

2.4. Analytical methods

2.4.1. Hemicelluloses

Hemicelluloses quantification was measured by Dionex ICS-5000 ion chromatography system equipped with CarboPac™ PA1 column (Dionex-300, Dionex Corporation, Canada) and a pulsed amperometric detector (PAD) after diluting acid hydrolysis of the samples using a standardized method for acid hydrolysis. The settings of PAD were $E1$ = 0.1 V, $E2$ = 0.6 V, and $E3$ = −0.8 V. The deionized water (DI) was used as eluant with a flow rate of 1 mL/min, and a NaOH solution with the concentrations of 0.2 M was used as the supporting electrolyte with 1 mL/min flow rate [24]. Hemicelluloses were hydrolyzed by adding 5 mL of H_2SO_4 (4%w/w) at 121°C to the sample for converting the polysaccharide to monomeric sugars. The acid hydrolysate was oil bathed at 121°C for 1 h (Neslab Instruments Inc., Portsmouth, NH, USA) [25]. Then the monomeric sugars were analyzed via ion chromatography system, and the concentration of hemicellulose was obtained as the sum of the monomeric sugars as shown in Table 1. The concentration of hemicelluloses in the process water was determined before and after UF with different membrane cut-offs.

2.4.2. Lignin

For lignin content determination, photometric measurements were carried out using a GENESYS™ 10S UV-Vis Spectrophotometer at a wavelength of 205 nm according to TAPPI UM 250 [25,26]. Before the measurement of the light absorption, the samples were diluted with DI water, and the dilution factor included in the final calculations. Also, the pH of each sample (feed, concentrate, and permeate) was adjusted (between 7 and 8) from an original pH value of about 4.2, with 0.025 M sodium hydroxide as required before the measurements for stabilizing lignin network. Then lignin content of the concentrates and permeates was measured after each experimental run.

2.4.3. Molecular mass distribution of hemicelluloses and lignin

The molecular weight distribution of the hemicelluloses and lignin of concentrates and permeates samples were determined by a gel permeation chromatography (GPC) (Viscotek GPCmax, Malvern, UK) with multidetectors using a 0.1 mol/L sodium nitrate solution as the eluent and solvent with the flow rate of 0.7 mL/min. After preparation, the samples were filtered with a 0.2 μm nylon filter to prevent column blockage of GPC, and then the filtrate solutions were used for molecular weight analysis. The columns of polyanalytic PAA206 and PAA203 were used in the analysis, and the column temperature was 35°C. The UV detector at 280 nm wavelength was used for quantifying the lignin molecular weight, and refractive index (RI) detector was used for measuring the hemicellulose molecular weight, using polyethylene oxide as a standard sample. The lignin and hemicelluloses samples were determined as a weight-average (M_w) and a number-average molecular (M_n) weight. Also, the particle size distributions (PSDs) of concentrates were measured using Malvern Mastersizer 2000 instrument (Worcestershire, UK) which has a detection range of 0.02–2,000 μm. The instrument detects the scattered light using a detector that converts the signal to size distribution based on volume or number. Each sample was automatically measured three times with a SD of 0.1%–4.5%.

2.4.5. Calculation

In each run, the filtrations were interrupted at different VR. VR was defined as the ratio between the volume of the permeate and the initial volume of the feed and was calculated using Eq. (1) as follows:

$$\mathrm{VRF} = \frac{V_p}{V_f} \times 100\% \tag{1}$$

where V_p is the permeate volume and V_f is the initial volume of the feed.

Mass fluxes were measured for each separation process. Mass flux is the rate of permeate mass flow obtained during the process per area of membrane (m^2) as a function of time (h). In this study, it was calculated as mass flux at a specific VRF (kg/m^2 h) by Eq. (2) as follows:

$$J_m = \frac{m_f}{A_m} \tag{2}$$

where J_m is the mass flux (kg/(m^2 h)), m_f is the mass flow rate (kg/h), and A_m is the membrane surface area (m^2).

Membrane fouling was calculated by comparing the difference between the pure water flux (PWF) before and after the filtration as follows:

$$\mathrm{Fouling}(\%) = \frac{\mathrm{PWF}_b - \mathrm{PWF}_a}{\mathrm{PWF}_b} \times 100\% \tag{3}$$

where PWF_a is the pure water flux after filtration (kg/(m^2 h)) and PWF_b is the pure water flux prior filtration (kg/(m^2 h)).

The recovery of hemicelluloses during filtration was calculated as follows:

$$\mathrm{Recovery}(\%) = \frac{m_{\mathrm{hemi}(c)}}{m_{\mathrm{hemi}(f)}} \times 100\% \tag{4}$$

where $m_{\mathrm{hemi}(c)}$ is the mass of hemicelluloses in the concentrate and $m_{\mathrm{hemi}(f)}$ is the mass of hemicelluloses in the feed.

The separation performance of the different membranes was assessed by using the percent rejection (R) or retention of feed components. This measurement is calculated based on the following equation:

$$\mathrm{Rentention}(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{5}$$

where C_p represents the concentration of hemicelluloses in the permeate at the end of the separation and C_f is its initial feed concentration.

The following equation measures the purity of hemicelluloses recovered by different membranes. The purity of

hemicelluloses is defined as the ratio between the carbon content in the hemicelluloses, which accounts for about 40% of the hemicellulose molecular mass, and the TOC concentration in the final concentrate [12].

$$\text{Purity}(\%) = \frac{C_{\text{hemi}(c)} \times 0.4}{\text{TOC}_{(c)}} \times 100\% \quad (6)$$

where $C_{\text{hemi}(c)}$ is the concentration of the hemicelluloses and $\text{TOC}_{(c)}$ is the total organic carbon in the final concentrate.

3. Results and discussion

3.1. Permeate flux and fouling

Before each run, a new membrane was first stabilized with distilled water under the conditions of 1 and 2 bar, room temperature, and 0 rpm until its PWF remained stable. The endpoint of every filtration experiment was determined by the VRF, which is the ratio between the permeate volume and the initial feed volume as indicated in Eq. (1). Permeate flux decreased with increasing VR for all experiments. However, an initial rapid decline in flux was more seen at 30 kDa membrane compared with 10 kDa membranes, while the permeate flux of 5 kDa was to some extent stable as shown in Fig. 2.

The time evolution of the permeate flux for the different MWCOs is characterized by an initial decline of the permeate flux due to the deposition and growth of a polarized layer, as can be seen in Fig. 2. The filtration processes were conducted under a pressure of 100 kPa. Average permeate fluxes data for all the three membranes used in our study are shown in Figs. 3 and 4. The average fluxes of the 30 kDa membranes were 46.38, 50.43, 54.80, and 56.29 kg/m² h for 95%, 90%, 80%, and 75% VR, respectively. Whereas, the average fluxes of the 10 kDa membranes were 45.26, 46.39, 47.57, and 49.12 kg/m² h for 95%, 90%, 80%, and 75% VR, respectively. For 5 kDa membranes, average fluxes were 6.8, 7.5, 8.5, and 9.22 kg/m² h for 95%, 90%, 80%, and 75% VR, respectively.

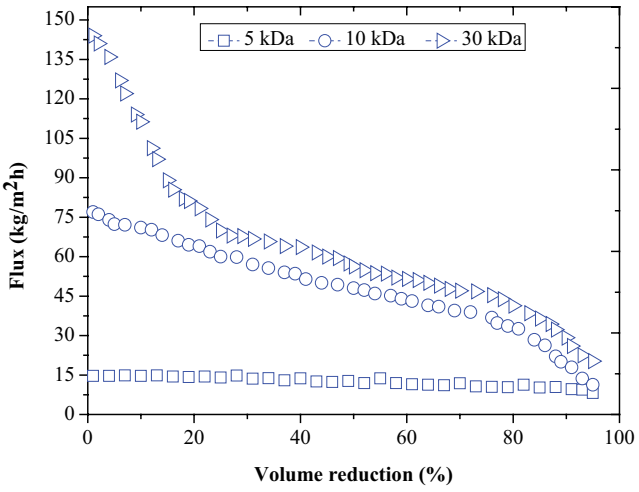

Fig. 2. Permeate fluxes of 5, 10, and 30 kDa membranes versus volume reduction values. Ultrafiltration was carried out at 1 bar, 22°C, and magnetic stirring plate 300 rpm for 10 and 30 kDa, while at 1.5 bar for 5 kDa.

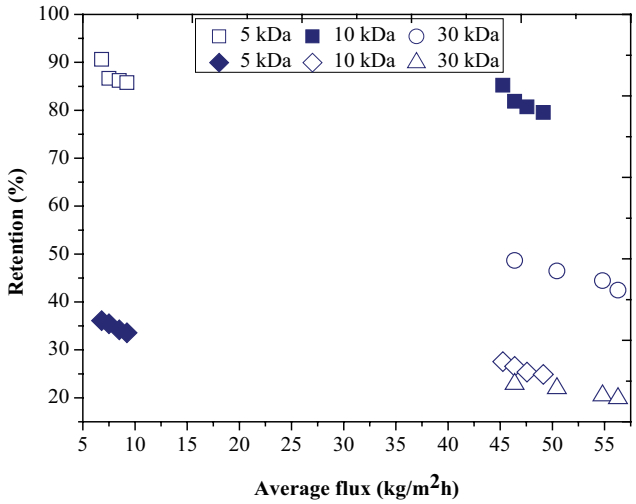

Fig. 3. Evaluation of membranes (5, 10, and 30 kDa) retention of hemicelluloses (□, ■, and ○) and lignin (◆, ◇, and Δ) and average permeate flux data. Ultrafiltration was carried out at 1 bar, 22°C, and magnetic stirring plate 300 rpm.

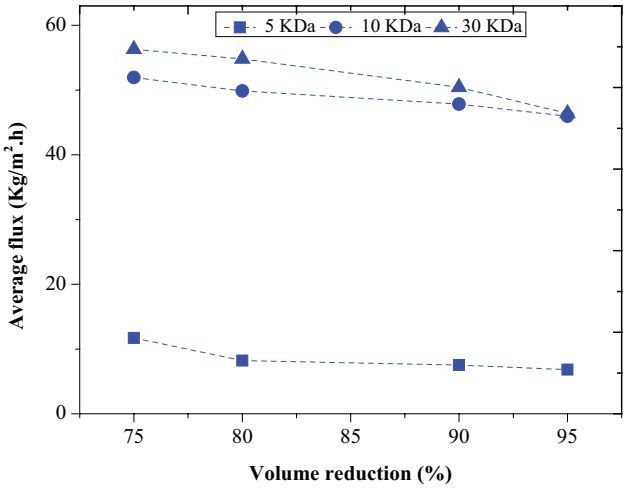

Fig. 4. Average fluxes of 5, 10, and 30 kDa membranes versus volume reduction values. Ultrafiltration was carried out at 1 bar, 22°C, and magnetic stirring plate 300 rpm for 10 and 30 kDa, while at 1.5 bar for 5 kDa.

The ratio of the PWF of the membrane prior to concentration to the flux after process water concentration is used as an indicator of flux decline. The PWF before and after the filtration measurements showed that slight fouling during the filtration has occurred as specified in Table 2, which may be partly explained by the most hydrophilic character of the RC membranes [2]. However, the concentration polarization layer effect at the surface of the membrane was observed more, which resulted in a decline of the membranes fluxes.

3.2. Hemicelluloses recovery

The three tested membranes have shown different ability to recover hemicellulose from the feed water, as can be seen in Fig. 5. 5 kDa membranes achieved the highest recovery

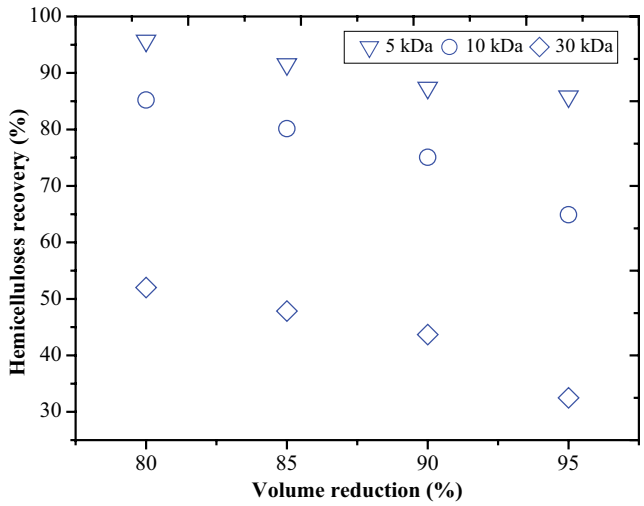

Fig. 5. Recovery (%) of hemicelluloses during ultrafiltration process using different membranes cut-offs and VR%. Ultrafiltration was carried out at 1 bar, 22°C, and magnetic stirring plate 300 rpm.

percent of hemicellulose 96, 92 and 86, followed by 10 kDa membranes 85%, 80% and 65% for VR value of 95%, 90%, and 80%, respectively. Whereas, 30 kDa membranes had the lowest recovery percent 52, 44 and 33 for VR value of 95%, 90%, and 80%, respectively. Fig. 6 shows the concentration of hemicelluloses in permeates for the different membrane cut-offs. Hemicelluloses concentration after UF varied between 3 and 12 g/L depending on VR factors and the membrane cut-off. The concentrations of hemicelluloses in retentates increased steeply from VR value of 80%–95%, as can be seen in Fig. 11. Due to the low concentration of hemicelluloses in the feed, a high VR (95%) is required for obtaining high concentrated retentate.

3.3. Retention of hemicelluloses and lignin

VR has a significant influence on the amount of hemicelluloses and lignin recovered by the membrane. In order to predict the purity and yield of these compounds, the correlations between the concentrations in the retentate, permeate, and VR are required. In this experiment, it was found that both 5 and 10 kDa membranes exhibited excellent overall hemicellulose retention, while retention of hemicellulose was noticeably lower for 30 kDa membrane. Figs. 7–9 show the retention of hemicelluloses and lignin, during concentration using 5, 10, and 30 kDa membranes. The retention of hemicelluloses was found to increase with increasing VR.

Retentions of lignin were markedly low with the tested 10 kDa membranes, compared with hemicelluloses retention. Hemicelluloses retention was in the range of 79%–85%, whereas lignin retention was between 24 and 28. For 5 kDa membrane, hemicellulose retention was between 85% and 91%, while lignin retention was between 34% and 36%. Consequently, hemicelluloses concentrated from 0.75 to 12 g/L, for the highest VR factor 95%. Hemicellulose retention of the 30 kDa membrane was markedly lower (between 42% and 48%) compared with that of the other membranes,

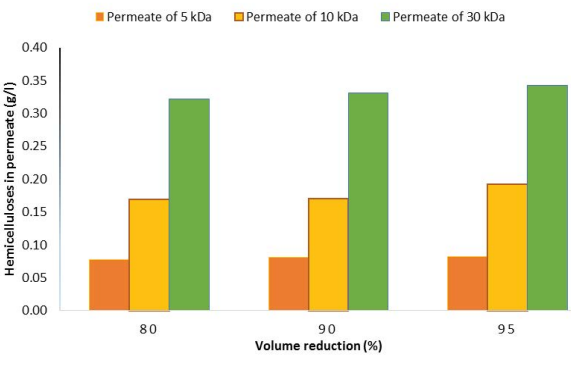

Fig. 6. The concentration of hemicelluloses in permeates during the ultrafiltration experiment with different MWCO, as a function of volume reduction.

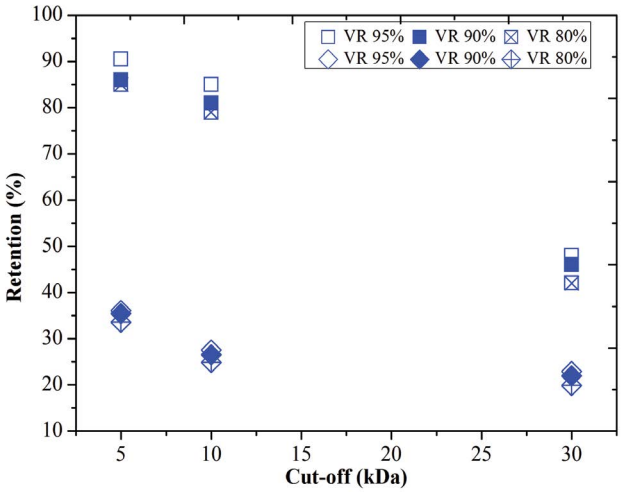

Fig. 7. Retention of hemicelluloses (□, ■, ⊠) and lignin (◇, ◆,⊕) during ultrafiltration of TMP process waters at 22°C, 100 kPa.

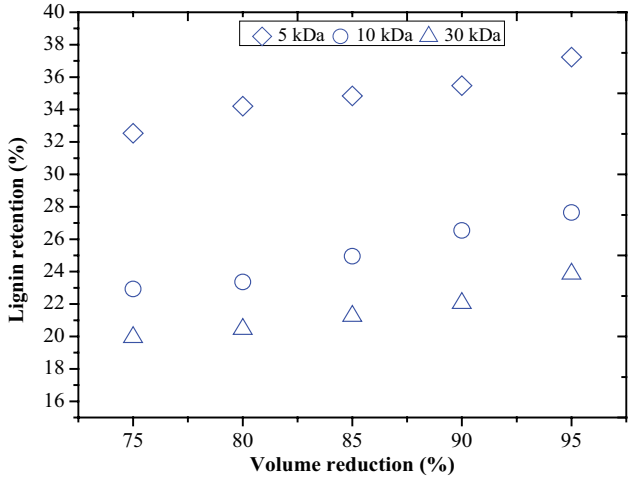

Fig. 8. The percent rejection rate of lignin for the different membrane cut-offs, as a function of volume reduction.

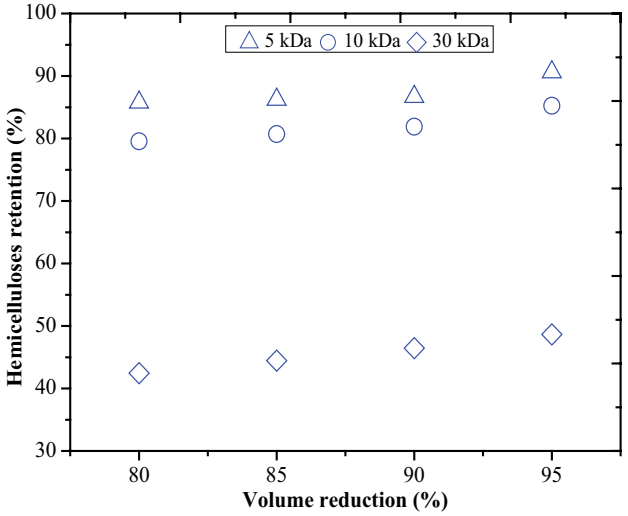

Fig. 9. The rejection rate of hemicellulose for the various membrane cut-offs and corresponding VR factor.

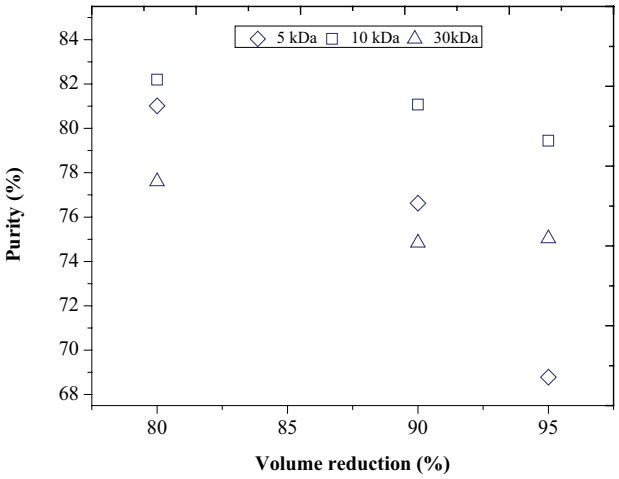

Fig. 10. Hemicelluloses purity of the different MWCOs, as a function of volume reduction.

but lignin also passed through the membrane, and the retention of lignin was only 15%.

The lignin retention can be attributed to lignin–hemicellulose complexes (covalent linkages) and molar masses overlapping [14,27]. Also, the hydrogen bonding between the individual polysaccharide and other components (lignin and pectin) may hinder the complete separation of hemicelluloses from lignin [28]. Likewise, the radical reactions during lignification process could lead to carbon–carbon linkage, and phenolic acids may play a role in this, thus resulting in reduced separation rate [29]. Other possible lignin–hemicellulosic linkages can be due to α-ether bonds between lignin and hemicelluloses [30,31], or ferulic acid bridges between hemicelluloses and lignin [32]. Furthermore, the formation of a concentration polarization layer on the membrane surface reduces the transmission of lignin through the membrane to the permeate side [20]. For overall effectiveness, a membrane with a nominal MWCO of 5 kDa was the best choice for a high hemicellulose yield from TMP process water. While for higher hemicellulose purity and lower lignin rejection 10 kDa membrane is more appropriate. Both 5 and 10 kDa membranes retained hemicelluloses better than they retained lignin and that can be used for effective removal of hemicellulose from process waters.

3.4. Hemicellulose purity

In order to make hemicellulose as a suitable raw material for the manufacturing of high-value-added products, a higher hemicellulose purity is required. The yield of hemicellulose and lignin/hemicellulose ratio relies on the VR applied during UF process. Thus, to predict hemicellulose purity and yield, correlations between the concentration in the retentate and permeate and VR are needed [20]. Fig. 10 shows the purity of hemicellulose for the three tested membranes and corresponding VR%. Based on the results of this study, it was found that a hydrophilic membrane with a cut-off of 10 kDa had better hemicellulose purity than a hydrophilic membrane with a cut-off of 5 and 30 kDa. The purities of hemicellulose after UF were between 75% and 80%. The optimal membrane cut-off of 10 kDa for the highest hemicellulose purity might be explained by the fact that a 5 kDa membrane could retain more lignin in the retentate, due to the membrane smaller pore sizes, while the 30 kDa membrane lost more hemicellulose in the permeate side, due to the larger pore sizes. In both cases (5 and 30 kDa), the purity of hemicelluloses in the retentate was decreased. To further increase hemicellulose purity, it is recommended subsequent purification steps such as diafiltration or size exclusion chromatography (SEC) be used. Diafiltration probably provides a less expensive alternative in this application [33]. Hartman et al. [34] obtained a purity of galactoglucomannan (GGM) of about 90% after diafiltration of the 1 kDa UF retentate. Willför et al. [35] achieved purity of 95 mole% when they recovered acetyl-GGM from the mechanical pulp using ethanol precipitation and polymeric adsorbents techniques. For a separation process to be successful, not only a high concentration and a high yield, but also a high purity is required. These results suggest that UF can be used as an effective separation method for preconcentration of hemicelluloses before further purification.

3.5. Concentrate and permeate composition

The characteristics of retentate and permeate of UF membrane with different cut-offs are given in Table 3. For 95% VR, samples of the permeate and retentate were analyzed to obtain the values of TSs, ash content, COD, pH, turbidity, lignin, and hemicelluloses. The pH of 5 kDa permeate was higher than 10 and 30 kDa, respectively. This can be attributed to most of the materials were recovered on the retentate side (Table 3). The turbidity of the permeate of 5 and 10 kDa membranes was much lower than that of 30 kDa membranes (Table 3).

It is also seen that the concentration of lignin in the permeates increased with increasing membrane cut-offs and VR. They were 1.2 ± 0.02, 1.5 ± 0.22, and 1.7 ± 0.06 g/L for 5, 10, and 30 kDa, respectively, while the concentration of hemicelluloses in the permeates followed the same trend, but

Table 3
Physicochemical analyses of permeate and concentrate of UF membrane with different cut-offs (average value ± SD) at VR 95%

Analyzed parameters	5 kDa		10 kDa		30 kDa	
	Perm.[a]	Conc.[b]	Perm.	Conc.	Perm.	Conc.
Total solids (g/L)	0.34 ± 0.01	18.3 ± 0.03	0.5 ± 0.04	17.6 ± 0.15	0.87 ± 0.01	14.7 ± 0.7
Total organic carbon (g/L)	–	6.9 ± 0.69	–[c]	5.1 ± 0.39	–	1.9 ± 0.02
Ash content (g/L)	–	2.2 ± 0.07	–	1.5 ± 0.2	–	0.61 ± 0.03
Total volatile solids (g/L)	–	16.4 ± 0.05	–	16.2 ± 0.13	–	14.1 ± 0.4
Chemical oxygen demand (mg/L)	908 ± 52	–	1,418 ± 32	–	1,521 ± 91	–
pH	5.2 ± 0.03	–	4.8 ± 0.01	–	4.4 ± 0.04	–
Turbidity	1.9 ± 0.2	–	3.2 ± 0.33	–	6.2 ± 0.32	–
Lignin concentration (g/L)	1.2 ± 0.02	12.5 ± 0.04	1.5 ± 0.22	6.9 ± 1.5	1.7 ± 0.06	6.4 ± 0.55
Total hemicelluloses (g/L)	0.10	12.14	0.15	8.82	0.34	4.61
Arabinose (g/L)	0.01	1.24	0.02	1.03	0.04	0.53
Galactose (g/L)	0.04	9.13	0.05	7.11	0.22	3.72
Raminose (g/L)	0.00	0.04	0.00	0.00	0.00	0.00
Glucose (g/L)	0.02	0.67	0.03	0.28	0.03	0.17
Xylose (g/L)	0.00	0.25	0.01	0.12	0.01	0.05
Mannose (g/L)	0.03	0.82	0.05	0.28	0.05	0.14

[a]Perm. = permeate; [b]Conc. = concentrate; [c]Indicates value not measured.

it was much lower compared with lignin concentration. The average concentration of hemicelluloses in 5, 10, and 30 kDa permeates was about 0.07, 0.15, and 0.30 g/L, respectively, as can be seen from the Fig. 6. The concentration of hemicellulose in the retentate was about 13 g/L (5 kDa), 10 g/L (10 kDa), and 4 g/L (30 kDa) for 95% VR, as shown in Fig. 11. According to Thuvander and Jönsson [16], hemicellulose could be further concentrated with a higher purity if the UF concentration is followed by ethanol precipitation or film model. Fig. 12 shows the lignin concentration in the retentates of the different membrane cut-offs. On the other hand, the concentration of TSs, TOC, and ash content increased with decreasing membrane cut-offs. TS was 18.3 ± 0.03, 17.6 ± 0.15, and 14.7 ± 0.7 g/L in 5, 10, and 30 kDa retentates, respectively. Whereas, TOC was 6.9 ± 0.69, 5.1 ± 0.39, and 1.9 ± 0.02 /L as shown in Table 3.

3.6. Molecular mass and distribution of concentrate and permeates

Each molecular weight of hemicelluloses has a specific industrial application. In some applications, high-molecular-mass hemicelluloses are favorable [36]. According to Kisonen et al. [37], high molecular mass of GGM is desirable because it improves the properties of GGM films. In the case of

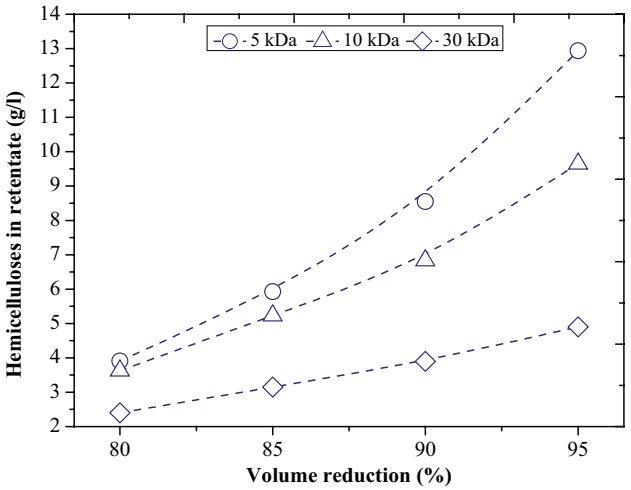

Fig. 11. The concentration of hemicelluloses in retentate during the ultrafiltration experiment with different MWCOs, as a function of volume reduction.

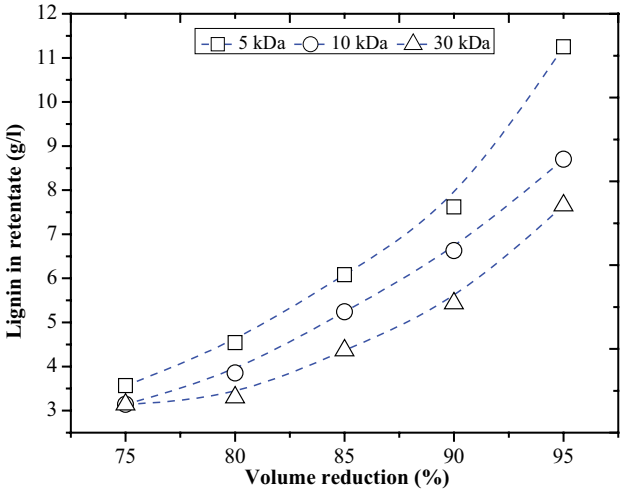

Fig. 12. The concentration of lignin in retentate during the ultrafiltration experiment with different MWCOs, as a function of volume reduction.

biofuel production, hemicelluloses need to be hydrolyzed into sugar monomers and then fermented, and for this purpose, low molecular mass extracts are required [36]. Therefore, determination of hemicelluloses molecular weight is useful for directing the properties of concentrated hemicelluloses stream toward proper processing step. Fig. 13 illustrates the PSD of all components in the concentrate. This result indicated that the molecular weight of all the elements in the concentrate fell in the range of lower than 1,000 μm. Table 4 shows the molar mass obtained by SEC; M_n, and M_w. The GPC results showed two main peaks corresponding to two different molecular weights of hemicelluloses in the retentate. From Table 4, it can be concluded that the molecular weight of hemicellulose appears in the 5 kDa concentrate have an M_w about 22,000 Da, whereas the average molecular weight of the hemicelluloses for both 10 and 30 kDa concentrate was about 33,000 and 54,000 Da, respectively. All three permeates of 5, 10, and 30 kDa had RI peaks at about 741 and 776 Da, this corresponded well with molecular weight distributions in TMP mill process water reported by Thuvander and Jönsson [16].

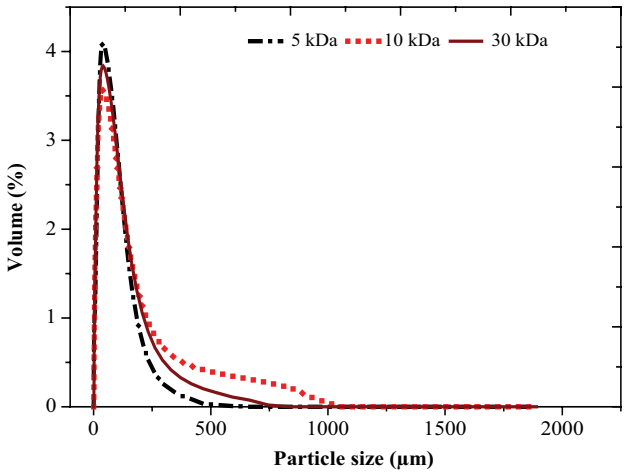

Fig. 13. Particle size distribution of the retentate components of 5, 10, and 30 kDa membranes.

From Table 4, it is clear that hemicellulose present in the 5 kDa permeate have an M_w of about 1,100, while the average M_w of hemicellulose of the 10 and 30 kDa permeates was about 2,800 and 6,800 Da, respectively. In contrary, the average M_w of lignin of the 5, 10, and 30 kDa permeates was about 2,000, 2,300, and 2,200 Da, respectively. However, the M_n of molecules in these permeates were varying from 740 to 770. Based on these results, the molecular mass of the hemicelluloses and the lignin (Table 4) suggests that an UF membrane with a cut-off between 1 and 15 kDa should be used to retain the hemicelluloses and allow at least part of the lignin to pass through. Since each molecular mass and purity of hemicelluloses has a specific industrial application, it is important to select the most compatible membrane (type, cut-off, area, and materials) for overall effectiveness.

4. Conclusions

Hemicelluloses and lignin recovery and purification from TMP mills process waters were studied using three hydrophilic UF membranes made of RC with different MWCOs (5, 10, and 30 kDa). After UF of the process waters, 5 and 10 kDa membranes showed high hemicellulose recovery compared with 30 kDa membranes. The recovery of the hemicelluloses was above 95% for 5 kDa membranes and around 89% for 10 kDa membranes, and the purity was approximately 75% for 5 kDa and 80% for 10 kDa membranes. Hemicellulose recovery of 30 kDa was only around 52%. Compared with 5 kDa membranes, a cut-off of 10 kDa seems to be the optimal MWCO for the separation of lignin from hemicelluloses; it retained hemicelluloses better (highest purity) than it retained lignin, while a cut-off of 30 kDa membrane was found to be unsuitable for this application since both the recovery and the retention of hemicelluloses were too low.

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Table 4
Analysis of GPC results of the average molecular mass distribution of (a) sugars (measured as refractive index) and (b) lignin (measured as UV absorbance) in the retentate of UF

	Hemicellulose						Lignin					
	Concentrate			Permeate			Concentrate			Permeate		
MWCO (kDa)	M_n (Da)[a]	M_w (Da)[b]	IP[c]	M_n (Da)	M_w (Da)	IP	M_n (Da)	M_w (Da)	IP	M_n (Da)	M_w (Da)	IP
5	12,018 1,192	22,310 1,474	1.858 1.237	747	1,108	1.483	1,405	3,669	2.611	776	2,096	2.701
10	13,742 1,167	33,002 1,467	2.402 1.257	1,018	2,827	2.777	2,348	4,429	1.886	741	2,365	3.192
30	14,798 1,261	54,052 1,623	3.653 1.287	1,427	6,805	4.769	990	2,676	2.704	755	2,281	3.021

[a]M_n, number-average molecular weight. [b]M_w, weight-average molecular weight from two measurements. [c]IP, polydispersity. Samples were diluted 13 and 9 times of 5 and 10 kDa retentate before the analysis.

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