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# **Influence of pH and fouling characterization during membrane process for lignin recovery from the process water of thermomechanical pulping**

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## **Abstract**

In thermo-mechanical process water, lignin presents an attractive potential for industrial applications due to the preservation of its native structure as free polymer or as part of ligno-carbohydrate complexes. In such effluent, lignin concentration is low, therefore its recovery with membrane process presents some advantages. As lignin tends to precipitate and forms lignin clusters with a pH decrease, assessing the influence of pH is relevant to understand membrane selectivity towards lignin and the related membrane productivity. It constitutes the main objective of the present study, as it was never done for thermo-mechanical process water. Two ceramic membranes with cutoff of 5 and 1 kDa were used alone or in a series and three pH were tested (4, 6.2 (native pH) and 10). For each condition, an in-depth fouling study was realized. pH 10 was not promising as a rapid flux drop was observed at low volume reduction of 40 % due to the compact deposit of lignin provoking 7 % of irreversible fouling and 83 % of fouling removed by cleaning with acid and base. The utilization of both membranes in a series was not pertinent as lignin was partly fractionated in both retentates. Process water filtration at pH 4 with a unique 1 kDa nanofiltration step gave encouraging results with 40 and 70 % of lignin and hemicelluloses respectively recovered. High flux of 33

$\text{L.h}^{-1}.\text{m}^{-2}$  was maintained at a volume reduction of 80%. Fouling was easily eliminated as it was composed at 70 % of fouling removed with water rinsing which was largely due to hemicelluloses which tend to agglomerate at pH 4 in the membrane surrounding.

**Keywords:** fouling, lignin, membrane filtration, pH, thermo-mechanical pulp mills.

## 1- Introduction

In their review of 2019, Wang et al. [1] announced that a good fractionation method of lignin from lignocellulosic biomass should preserve native structure of lignin (*i.e.* high content of  $\beta$ -O-4 bonds) which would be beneficial for subsequent bioconversions processes. In the pulp and paper manufacturing industry, an alternative way exists to chemical processes with drastic environment: the thermo-mechanical process which uses soft conditions (no chemicals addition, temperature and pressure below 100°C and 5 bars respectively). This high yield process recovers more than 90 % of the wood biomass in the final product [2]. The main side stream of thermo-mechanical process is an effluent containing hemicelluloses, lignin, ligno-carbohydrate complexes (LCC), lipophilic and phenolic extractives at low concentration (*i.e.* typical dry matter content below 4 g.L<sup>-1</sup> [3]). Due to the mild process conditions, native structure of lignin and LCC is preserved. Steinmetz et al. [4] reported comparable content of  $\beta$ -O-4 links for thermo-mechanical lignin and milled wood lignin at 36.6 and 37.9 number per aromatic rings (no./100ar) whereas this value does not exceed 6 in common technical lignins (kraft, soda and organosolv). Therefore the recovery of lignin as a free polymer or bonded to hemicelluloses (LCC) from thermo-mechanical process is an ecofriendly way towards the production of high added value compounds. The preservation of native lignin structure make it as a suitable candidate for depolymerisation into a wide variety of bulk and fine aromatic and phenolic chemicals [5]. In the context of biorefinery, cost-effective separation processes to fractionate biomass compounds are required [6]. Recently, an increased attention was given to membrane processes [7] for their ability to recover compounds without additives. This technology was proven to be energy efficient, easily scalable and offering a large range of operating conditions as materials, solvents, pH or temperature. Several studies have chosen ultrafiltration (UF) to recover galactoglucomannans (*i.e.* main hemicellulosic polymer found

in thermo-mechanical process water) with cutoff in the range 10-1 kDa [8,9] whereas lignin was retained with nanofiltration (NF) with cutoff between 1 kDa and 300 Da [10,11]. Due to their resistance at high temperatures, in the present study two ceramic membranes (an UF 5 kDa and a NF 1 kDa) were used in a series to preferentially retain hemicelluloses in UF retentate and lignin under its different forms in NF retentate. As 60 % of hemicelluloses were already retained during the 150 kDa clarification step, the selectivity of both membranes towards lignin was tested when these membranes stand alone. To obtain high productivity and selectivity of the tested membranes, the choice of physico-chemical conditions is of prime importance. Filtration of pulp and paper process water was reported in literature on a broad range of pH from 3.5 for pre-hydrolysate from kraft pulp mill [12] to 13.5 for kraft liquor [13]. Lignosulfonates liquors have typical pH around 8.5 [14] and thermo-mechanical between 4 and 7 [15]. Furthermore, depending on lignin sourcing, it can be present under different units (hydroxyphenyl, guaiacyl and/or syringyl) with various functional groups with specific pKa [16]. Lignin tends to precipitate and forms lignin cluster [17] with a pH decrease [18]. A review article that deals extensively with the issues of pH relative to lignin separation from spent alkaline pulping liquors, including membrane separation was recently published [19]. Therefore assessing the influence of pH is relevant to understand membrane selectivity towards lignin and its related productivity. As it was never done for thermo-mechanical process water, it constitutes the main objective of the present study and three pH were tested (4, 6.2 and 10). As fouling establishment constitutes the main drawback of membrane processes which can restrict industrial applications [20], the selection of operating parameter such as pH has to be done taking into account fouling aspect. For the studies filtrating thermo-mechanical process water, indirect interpretations of fouling deposit were developed (*i.e.* influence of transmembrane pressure, permeate flux) [8,9]. Therefore, the present study

proposes an in-depth fouling formation analysis in order to draw conclusions regarding the membrane life time and flux recovery for possible scale-up in a future industrial process.

## 2- Material and methods

### 2.1 Process water

Process water was collected from a thermo-mechanical pulp mill using a mix of spruces and pines used as raw material (Norske Skog, Golbey, France). Main characteristics of crude process water are presented in table 1. The untreated process water (pH 6.2) was clarified by flotation and then filtered with a 150 kDa microfiltration (MF) membrane. For the experiments realized at various pH, the pH of the clarified process water (*i.e.* the MF permeate) was adjusted with 13 mM acetic acid to pH 4 and with 2.5 mM sodium hydroxide to pH 10.

Mean values and corresponding standard deviations of crude process water came from the analyses in triplicates of 26 sampling events of process water spread during the four seasons of three successive years [21]. The different series of experiments done each at a specific pH and volume reduction were performed with a different process water sample. Their compositions were detailed in table 2.a.

Flotation with optimized conditions determined with preliminary experiments (air flow rate, turbidity kinetics) was directly done after sampling event at 80°C on thermo-mechanical pulp mill site (thermo-mechanical process is commonly realized around 90°C). Flotation was used to remove lipophilic extractives as terpenes, fatty and resin acids as these hydrophobic molecules cause severe membrane fouling. A Kadant Lamort column flotation cell was used. Flotation duration was function of turbidity decrease kinetics with the final turbidity decrease of 70 % in process water floated. A half-day was required to transport at ambient temperature the floated process water to the laboratory. Sample was directly filtered on 150 kDa membrane and the MF permeate was stored at 4°C before use for the other filtration steps.

Filtration with 150 kDa membrane was performed to remove suspended matter and a part of hemicelluloses (rejection around 60 %).

Table 1: Main characteristics of crude process water

<b>Parameter</b>	<b>Crude process water</b>
<b>Turbidity (NTU)</b>	430 ± 110
<b>Conductivity (<math>\mu\text{S.cm}^{-1}</math>)</b>	1180 ± 150
<b>Dry matter (<math>\text{mg.L}^{-1}</math>)</b>	3780 ± 690
<b>Ash (<math>\text{mg.L}^{-1}</math>)</b>	650 ± 5
<b>Suspended matter (<math>\text{mg.L}^{-1}</math>)</b>	220 ± 80
<b>Polyphenols (<math>\text{mg}_{\text{GAeq.L}^{-1}}</math>)<sup>a</sup></b>	710 ± 60
<b>Lignin (<math>\text{mg.L}^{-1}</math>)</b>	690 ± 70
<b>Hemicelluloses (<math>\text{mg}_{\text{Geq.L}^{-1}}</math>)<sup>b</sup></b>	1170 ± 180
<b>Terpenes and fatty acids (<math>\text{mg}_{\text{HAeq.L}^{-1}}</math>)<sup>c</sup></b>	7 ± 11
<b>Lignans (<math>\text{mg}_{\text{CAeq.L}^{-1}}</math>)<sup>d</sup></b>	18 ± 14

<sup>a</sup>  $\text{mg}_{\text{GAeq.L}^{-1}}$ : in gallic acid equivalent ; <sup>b</sup>  $\text{mg}_{\text{Geq.L}^{-1}}$ : in glucose equivalent ; <sup>c</sup>  $\text{mg}_{\text{HAeq.L}^{-1}}$ : in heneicosanoic acid equivalent ; <sup>d</sup>  $\text{mg}_{\text{CAeq.L}^{-1}}$ : in 4-hydroxy-3,5-dimethoxycinnamic acid equivalent.

## 2.2 Experimental filtration procedure

Tubular, ceramic ( $\text{TiO}_2\text{-ZrO}_2$ ) MF, UF and NF membranes from Kleansep<sup>TM</sup> supplied by Orelis, France, with cut-off 150 kDa, 5 kDa and 1 kDa were used in the experiments. The initial permeability of the MF at 20°C was  $277 \text{ L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$ . For the different experiments presented with 5 and 1 kDa, three membranes of each cutoff were used.

The initial water permeabilities of the 5 kDa UF were 26, 44 and  $59 \text{ L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$ . The permeabilities of the 1 kDa NF are 13, 15 and  $24 \text{ L.h}^{-1}.\text{m}^{-2}.\text{bar}^{-1}$ .

Each membrane element had 19 parallel channels with a hydraulic diameter of 3.5 mm. The length was 1,178 mm and the surface area  $0.24 \text{ m}^2$ .

A membrane equipment from Firmus, France, was used in the experiments. A frequency converter on the pump allowed the cross-flow velocity to be adjusted, the temperature was



measured with a Pt100 thermocouple element and controlled with a PID regulator and the volume of the feed tank was 70 L. Pressure, temperature, permeate and retentate flows were recorded on a data acquisition device (Ecograph T, Endress+hauser). Transmembrane pressure (TMP) was calculated as the difference between the average pressure between the inlet and outlet of the membrane module and the permeate pressure. TMP was regulated with a valve on the retentate line. The degree of concentration is given as volume reduction (VR) which is the ratio between the permeate and the feed volume.

The MF operation was first operated in semi-batch mode (*i.e.* the feed tank of 70 L was continuously topped up with floated process water as permeate was withdrawn). When the last of the process water had been added to the tank, the system was operated in batch mode. Batch concentration was used in all UF and NF experiments from the beginning. Optimized operating conditions (*i.e.* TMP and cross-flow velocity) previously developed during total recycle mode were used in the experiments. TMP was 2.5 bar and 5.5 bar in the experiments with the 150 kDa (clean water flux of 730 L.h<sup>-1</sup>.m<sup>-2</sup> at 2.5 bar) and 5 kDa membrane. The initial clean water fluxes of the 5 kDa UF at a TMP of 5.5 bar (as set for filtration of process water) were 150, 240 and 323 L.h<sup>-1</sup>.m<sup>-2</sup>. In the experiments with the 1 kDa membrane a TMP of 6.4 bar was used at pH 4 and 5.5 bar at pH 6.2. At this latter TMP, the initial clean water fluxes of 1 kDa were 73, 89 and 121 L.h<sup>-1</sup>.m<sup>-2</sup>. The cross flow velocity was 5 m s<sup>-1</sup> and the temperature was 60 °C in all experiments.

To assess selectivity of 5 kDa UF and 1 kDa NF on lignin recovery, two membrane lines were tested as described on figure 1. Rejection expressed as a percentage, was calculated with the following equation (1):

$$Rejection = \left( \frac{C_{feed} - C_{permeate}}{C_{feed}} \right) \times 100 \quad (1)$$

Where  $C_{\text{feed}}$  and  $C_{\text{permeate}}$  represent respectively the concentration in the feed and permeate of specific compound. To assess  $C_{\text{permeate}}$ , firstly the entire volume of permeate was collected in a tank allowing a mixing. At the final VR, sampling of permeate was realized from this tank.

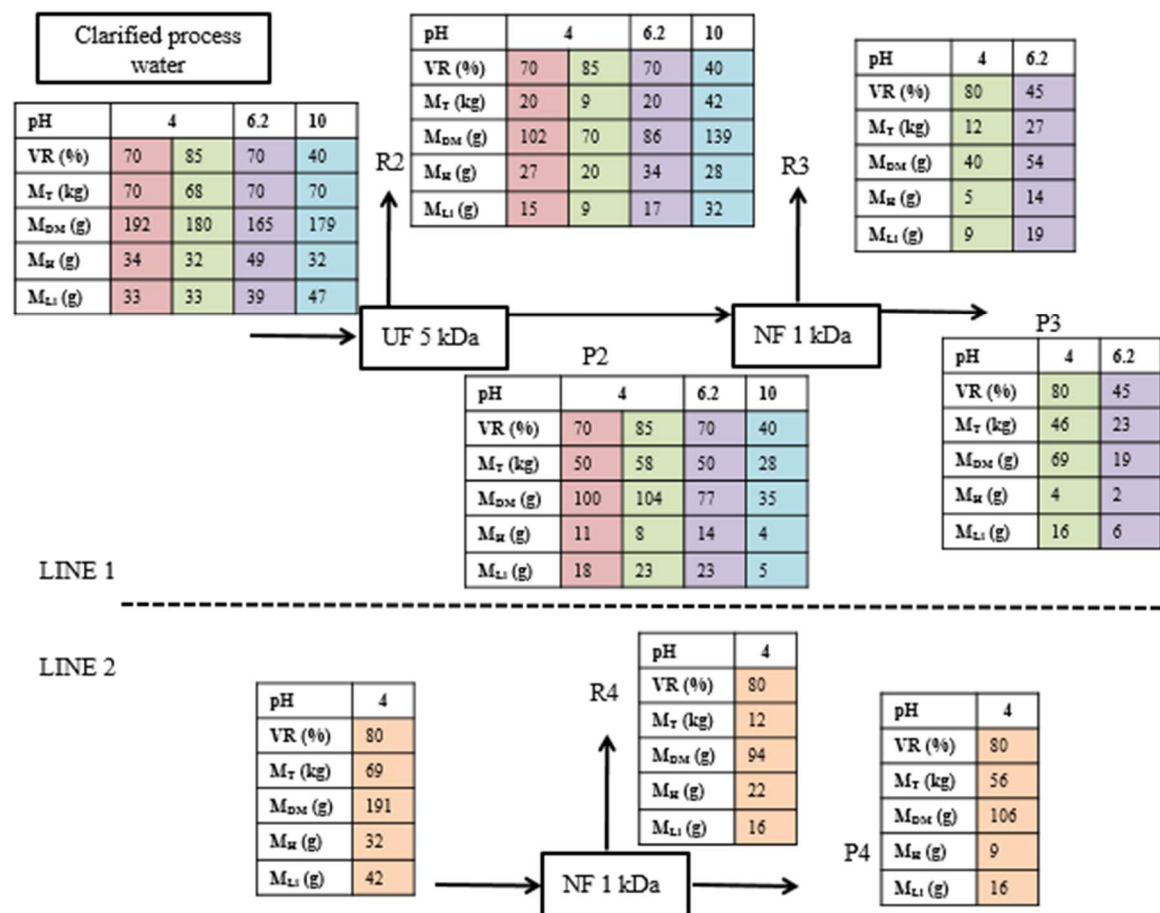


Figure 1: Schematic overall process with masses of fractions collected. M<sub>T</sub>: total mass of fraction ; M<sub>DM</sub>: Mass of dry matter ; M<sub>H</sub>: Mass of hemicelluloses ; M<sub>LI</sub>: Mass of lignin

### 2.3 Analytical methods

Samples were dried with a rotavapor (40°C ; 25 mbar) until constant weight. The residue was weighed and divided by the initial volume of the sample to obtain dry matter concentration. To calculate suspended matter, samples were filtered on 0.45 µm filter. The filter with the resulting filter cake was dried at 105°C until constant weight. As filter was initially weighted, suspended matter was obtained by difference between filter weight after filtration and before filtration. Total phenolic content including free lignin, lignin as a part of LCC complexes as well as phenolic extractives was analyzed with the Folin-Ciocalteu colorimetric method (760 nm) [22] and quantified in gallic acid equivalent. Hemicelluloses (expressed in glucose equivalent) were quantified at 625 nm with colorimetric method developed by [23]. For phenolic (lignans, phenolic acids) and hydrophobic extractives (terpenes and fatty acids) identification, Gas Chromatography (GC)-Mass Spectrometry (MS) method was adapted from [24]. GC-MS analysis was performed on a Clarus 680 gas chromatograph coupled to a Clarus SQ8 mass spectrometer (Perkin Elmer Inc., USA).

Lignin content was obtained thanks to the following mass balance equation (2) (m for mass):

$$m_{lignin} = m_{polyphenols} - (m_{lignans} + m_{phenolic\ acids}) \quad (2)$$

To obtain the lignin content of the sample (free or part of LCC), the quantities of phenolic extractives determined by GC-MS were subtracted from the total phenolic content measured by the Folin-Ciocalteu method. The concentration of lignin was then obtained with the ratio between the mass of lignin on volume of process water sampled.

The apparent molecular weight (aMW) distributions of lignin and hemicelluloses were determined using an aqueous SEC method on a Prominent Shimadzu HPLC equipped with a guard column Phenomenex Polysep GFC-P and three analytical columns Phenomenex Polysep P4000, P3000 and P2000. A solution of sodium hydroxide (NaOH) at 10 mM was

used as the mobile phase. Samples were pre filtered through 0.45  $\mu\text{m}$  PTFE membrane filters. Twenty  $\mu\text{L}$  of sample solutions were injected. The separation was performed at 30  $^{\circ}\text{C}$  and 0.5  $\text{mL}\cdot\text{min}^{-1}$  NaOH flowrate. An ultraviolet spectroscopy detector (UV) at 280 nm (Shimadzu SPD-20A) was used to detect lignin and a refractive index detector (RID, Shimadzu RID-20A) for detection of hemicelluloses and lignin. A calibration curve was obtained using a KIT of 10 pullulan standards (Agilent PL2090-0101) with molar mass ranging from 180 to 194 000 Da. Zeta potential measurements were carried out by Zetasizer Nano ZS (Malvern Instruments). All the analyses presented in part 2.3 were carried out in triplicate.

## 2.4 Fouling characterization

To characterize hydraulic resistance of fouling, the resistance-in-series model was used. It is based on Darcy's law and a succession of cleaning was applied to distinguish the different resistances due to membrane fouling. Initial membrane permeability was measured after membrane conditioning (with NaOH 10  $\text{g L}^{-1}$ ; 60 $^{\circ}\text{C}$  ; 1 h – followed by HNO<sub>3</sub> 3  $\text{g L}^{-1}$ ; 60 $^{\circ}\text{C}$ ; 1 h). It was obtained from the slope of the representation of water flux vs TMP. After membrane filtration of process water, first fouled membrane permeability was measured after a simple rinsing with distilled water. This water rinsing (distilled water ; 20 $^{\circ}\text{C}$  ; 15 min) was performed to take off fouling ( $R_{\text{rinse}}$ ) (*i.e.* the water reversible fouling) which was caused by concentration polarization, the loosely attached foulants and cake resistances simultaneously. After chemical cleanings (with NaOH 10  $\text{g L}^{-1}$ ; 60 $^{\circ}\text{C}$ ; 1 h – followed by HNO<sub>3</sub> 3  $\text{g L}^{-1}$ ; 60 $^{\circ}\text{C}$ ; 1 h), the fouling (*i.e.* the chemical cleaning reversible fouling) which is caused by strongly attached foulants can be removed, thereby assessing the resistance removed by cleaning named ( $R_{\text{clean}}$ ). Membrane was rinsed with distilled water between basic and acid cleanings. The residual difference between membrane resistance after filtration and chemical cleaning and initial membrane resistance ( $R_{\text{m}}$ ) was attributed to irreversible fouling ( $R_{\text{irreversible}}$ ). The irreversible fouling is a permanent fouling which cannot be removed by any approaches.

Between each cleaning step, the membrane permeability was assessed with distilled water.

With the use of equation (3), hydraulic resistances due to each fouling kinds previously defined can be calculated and contribution of each fouling type can be obtained.

$$L_p = \frac{1}{\mu \times (R_m + R_f)} \text{ with } R_f = R_{rinse} + R_{clean} + R_{irreversible} \quad (3)$$

With  $L_p$ : membrane permeability ( $\text{m}^3 \text{ m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ ),  $R_f$ : fouling hydraulic resistance ( $\text{m}^{-1}$ ),  $R_m$ : membrane hydraulic resistance ( $\text{m}^{-1}$ ),  $\mu$ : dynamic viscosity of the permeate at 20 °C ( $\text{Pa s}$ ).

The initial membrane resistances ( $R_m$ ) calculated with equation (3) with initial membrane permeability for the 5 and 1 kDa membranes were of  $1.4 \cdot 10^{13} \pm 5.3 \cdot 10^{12}$  and  $3.2 \cdot 10^{13} \pm 4.7 \cdot 10^{12} \text{ m}^{-1}$  respectively. Experimentally, the final value of permeate flux obtained during filtration of process water at each membrane processing stage and the corresponding TMP set were used to assess the final fouling hydraulic resistance corresponding to  $R_m + R_f$ . By subtracting  $R_m$  to  $R_f + R_m$ ,  $R_f$  can be obtained. After water rinsing,  $R_{rinse}$  is removed and total resistance due to fouling  $R_f$  become  $R_{clean} + R_{irreversible}$ . After chemical cleanings  $R_{clean}$  is removed and total resistance due to fouling  $R_f$  become equal to  $R_{irreversible}$ . With this method and by subtraction each component of  $R_f$  can be obtained.

To assess amounts of lignin and hemicelluloses partly responsible of fouling phenomena, their extracted amounts at the end of rinsing and basic cleaning steps were measured thanks to the analytical protocols presented in part 2.3.

Filtrated volumes were not the same for all the conditions tested (*i.e.* depending on membrane fouling phenomena). They were below or equal to 70 L. Therefore, in order to compare hydraulic resistances due to the different types of fouling for the tested conditions, they were expressed in figure 4 per unit of volume of permeate ( $\text{m}^{-1} \cdot \text{L}^{-1}$ ).

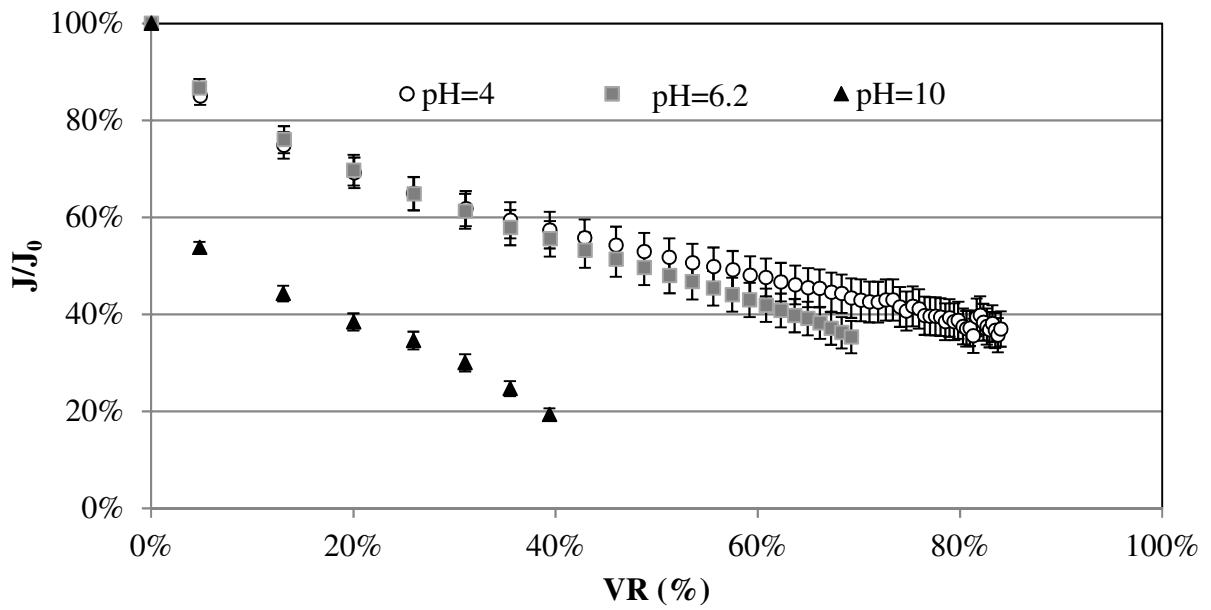
### 3- Results and discussion

#### 3.1 Hydraulic performances

The evolutions of normalized flux,  $J/J_0$ , of 5 kDa membrane as a function of VR at various pH of process water (4, 6.2 and 10) are presented in figure 2.A. The initial flux,  $J_0$ , at VR 0% was about  $220 \text{ L h}^{-2} \text{ m}^{-2}$  at pH 4 and 6.2 but only  $83 \text{ L h}^{-2} \text{ m}^{-2}$  at pH 10.  $J/J_0$  decreased with increasing VR for all process waters but while the flux for the process waters with pH 4 and 6.2 was approximately the same, the flux of the pH 10 process water was much lower.

At pH 10 with a VR comprised between 0 and 5 %, flux decreases at around 54 % of its initial value ( $45 \text{ L.h}^{-1}.\text{m}^{-2}$ ). Then, from VR around 10 %, flux declines were linear due to progressive accumulation of compounds at the membrane with higher slope at pH 10 (0.92) than at pH 6.2 (0.69) and pH 4 (0.48). At pH 10 final reached VR was 40 % with a flux around  $17 \text{ L.h}^{-1}.\text{m}^{-2}$  whereas flux of 81 and  $77 \text{ L.h}^{-1}.\text{m}^{-2}$  were measured at final VR of 84 and 70 % at pH 4 and 6.2 respectively. Persson et al. [11] obtained a flux of  $50 \text{ L.h}^{-1}.\text{m}^{-2}$  at a VR of 80 % in their semi-batch trial with a polyethersulfone 5 kDa UF during filtration of comparable process water from thermo-mechanical pulp mill at pH 4.3. During filtration of kraft liquor with high dry content matter ( $75 \text{ g.L}^{-1}$ ) at pH 10 with 5 kDa ceramic membrane, Mota et al. [25] measured low flux at  $10 \text{ L.h}^{-1}.\text{m}^{-2}$ .

(A)



(B)

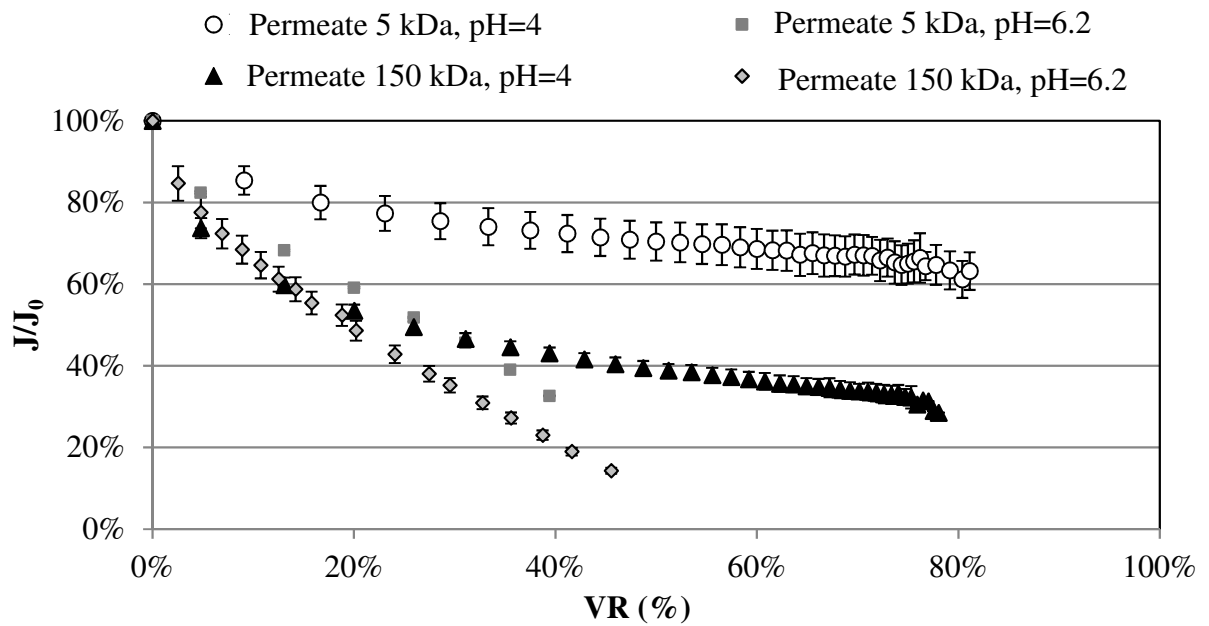


Figure 2: Relative permeate flux evolution with VR of (A) 5 kDa UF at different pH and of (B) 1 kDa NF at pH 4 or 6.2 alimented by 5 kDa permeate (line 1) or 150 kDa permeate (line 2).



As one objective of the present paper was to design a membrane process with high hydraulic performances, based on the previous results, pH 10 does not seem as a relevant pH of filtration. Therefore, results of 1 kDa filtration were only presented for pH 4 and 6.2.

In figure 2.B, permeates from 150 and 5 kDa (line 1) were filtered on 1 kDa membrane at native pH of process water (6.2) and at pH 4. Initial permeate flux of 1 kDa NF exhibited differences depending on pH and filtration with or without previous 5 kDa UF. Indeed, at pH 4,  $J_0$  was equal to  $210 \text{ L.h}^{-1}.\text{m}^{-2}$  when permeate 5 kDa was filtered whereas it was measured at  $110 \text{ L.h}^{-1}.\text{m}^{-2}$  when 150kDa permeate was filtered. Those latter fluxes dropped respectively at 117 and  $87 \text{ L.h}^{-1}.\text{m}^{-2}$  as pH was set at 6.2. At pH 6.2, both permeate fluxes rapidly decreased until respective  $J/J_0$  ratio of 33 ( $39 \text{ L.h}^{-1}.\text{m}^{-2}$ ) and 20 % ( $17 \text{ L.h}^{-1}.\text{m}^{-2}$ ) at the maximum VR reached around 40-45 % for permeates from 5 and 150 kDa. From VR of 10 %, at pH 6.2, flux declines were faster with slopes above 1.30 whereas at pH 4 slopes of  $J/J_0$  curves as a function of VR were lower than 0.50. The filtrations at pH 6.2 were not completed which underlines the establishment of significant fouling on 1 kDa membrane. On the contrary, at pH 4, VR of 80 % has been obtained, with permeate flux of 30 ( $33 \text{ L.h}^{-1}.\text{m}^{-2}$ ) and 63 % ( $132 \text{ L.h}^{-1}.\text{m}^{-2}$ ) of their initial values when 150 and 5 kDa permeates were respectively filtered. This flux difference was caused by a lower fouling propensity which took place during the filtration of 5 kDa permeate as larger molecules had already been removed from the liquor by UF 5 kDa. Large molecules still present in MF 150 kDa permeate form a cake layer at the 1 kDa membrane surface, causing a flux reduction. Mota et al. [25] found a flux at  $5 \text{ L.h}^{-1}.\text{m}^{-2}$  with a ceramic 1 kDa membrane during kraft liquor fractionation (pH 10 and dry matter concentration of  $64 \text{ g.L}^{-1}$ )

In order to obtain the best hydraulic performances in the present study, filtration of clarified process water on 5 and 1 kDa membranes has to be performed at pH 4.

### 3.2 Rejection and process selectivity

Compositions of feed process waters as well as collected fractions are presented in table 2.a and 2.b respectively. A dry matter concentration of only 3300 mg.L<sup>-1</sup> was measured in the 5 kDa retentate (R2) at pH 10. This low concentration was mainly explained by the premature filtration stop at a VR of 40 %. It was provoked by a rapid decline of flux until 20 % of its initial value. At this specific pH, a fouling structure detailed in part 3.3 was quickly deposited on and/or into membrane lowering membrane pore size. As a consequence, dry matter, hemicelluloses and lignin were highly retained at 50, 70 and 75 % respectively (figure 3.A). At this pH, membrane 5 kDa cannot fractionate selectively lignin and hemicelluloses. High rejection of lignin was also explained by the negative charge of lignin at high pH due to the dissociation of its phenolic and carboxyl groups. Lignin consists of various structures which have different pKa values. Lignin contained in process water was characterized by NMR spectroscopy in a previous study and revealed that thermo-mechanical process allowed only the extraction of a very specific fraction of softwood lignin exclusively composed of Guaiacyl (G) units [4]. The observed structures possessed pKa values between 8 and 10. These pKa values were assessed based on the study of Ragnar et al. [26]. Therefore at pH 10, the mentioned groups are almost completely deprotonated. Lignin molecules repel one another by means of electrostatic interactions. This result was also mentioned for kraft alkaline lignin which contains functional groups such as phenolic hydroxyl and carboxylic groups having pKa respectively around 10 and 4 [16]. As the membrane used is also negatively charged in alkaline conditions, those conditions improved the rejection of lignin [13]. The low selectivity and productivity can be considered as limiting points for process water filtration at pH 10.

Table 2a: Characteristics of process waters used for experiments

Stream	F2*				F4
pH	4		6.2	10	4
VR (%)	70	85	70	40	80
Dry matter (mg.L <sup>-1</sup> )	2740± 250	2640± 200	2360± 150	2560± 240	2770± 250
Hemicelluloses (mg <sub>Geq</sub> .L <sup>-1</sup> )	480±3 0	470± 30	700± 80	460± 30	460± 50
Lignin (mg.L <sup>-1</sup> )	470± 50	490± 60	550± 70	670± 80	610± 60

\*F: composition of Feed process waters

Table 2b: Characteristics of collected fractions

Stream	R2				P2				R3		P3		R4	P4
pH	4		6.2	10	4		6.2	10	4	6.2	4	6.2	4	4
VR (%)	70	85	70	40	70	85	70	40	80	45	80	45	80	80
Dry matter (mg.L <sup>-1</sup> )	5100± 440	7750± 650	4300± 280	3300± 340	2000± 130	1800± 100	1540± 30	1250± 240	3300± 400	2000± 200	1500± 250	840± 50	7800± 700	1900± 300
Hemicelluloses (mg <sub>Geq</sub> .L <sup>-1</sup> )	1330± 70	2180± 150	1720± 70	660± 30	210± 50	130± 30	280± 20	140± 30	380± 110	500± 10	80±5	90± 10	1850± 100	160± 60
Lignin (mg.L <sup>-1</sup> )	770± 50	950± 60	860± 10	760± 80	360± 40	390± 30	450± 10	170± 70	780± 10	710±1 0	350± 80	250± 20	1330± 20	290± 130

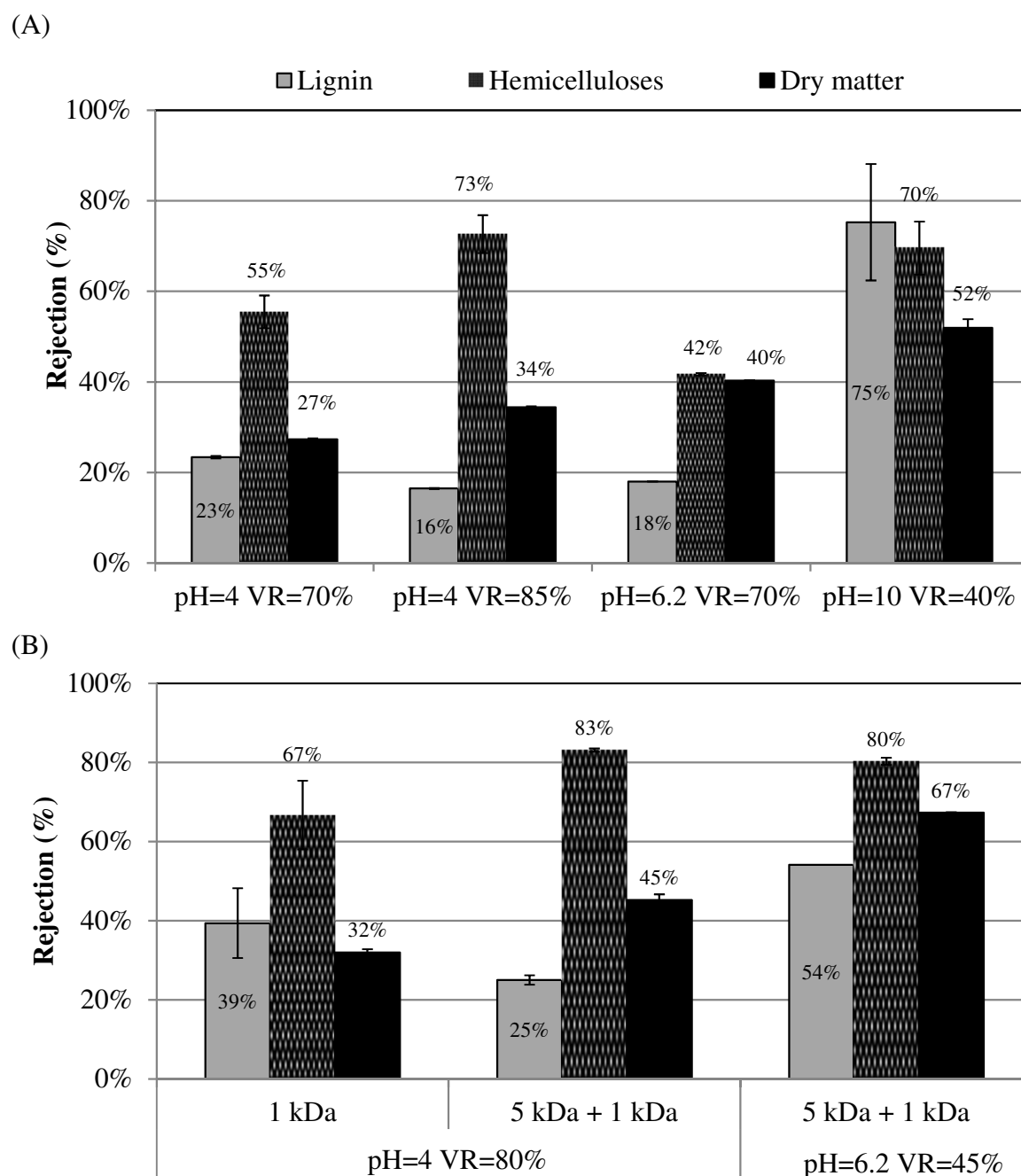


Figure 3: Rejections of lignin, hemicelluloses and dry matter for (A) 5 kDa UF at pH 4, 6.2 and 10 and for (B) 1 kDa NF with or without previous 5 kDa filtration at pH 4 or 6.2

Filtrations on 5 kDa membrane were performed until VR of 70 % at pH 6.2 and 85 % at pH 4. Results are compared at VR of 70 %. The dry matter concentrations in the 5 kDa retentate were of 5100 mg.L<sup>-1</sup> at pH 4 and 4300 mg.L<sup>-1</sup> at pH 6.2. Simultaneously, dry matter rejection

increased from 27 to 40 % when pH changed from 4 to 6.2. The accumulation of solutes at 5 kDa membrane surface has provoked a higher drop of mass transfer at pH 6.2 and intensified the rejection.

Hemicelluloses were retained at 55 % at pH 4 and 42 % at pH 6.2. Those rejections allowed reaching concentrations in retentate 5 kDa between 1330 and 1720 mg<sub>eq</sub> G.L<sup>-1</sup>. Persson et al. [11] (pH 4.3) and Thuvander and Jönsson [27] (pH not specified) mentioned hemicelluloses rejection between 61 and 92 % when a clarification step (filter with pore size at 0.1-0.2 µm) was combined with a 5 kDa organic membrane. In the present study, hemicelluloses rejection of membrane process coupling 150 kDa with 5 kDa were assessed at 88 and 76 % at respective pH of 4 and 6.2.

Lignin was poorly retained at pH 4 and 6.2 with values below 23 %. It is in agreement with data between 15 and 50 % found in the literature for the filtration of TMP process water with 5 kDa organic membranes for high VR (98-99%) at pH around 4 [8,11]. Therefore, pH 4 can be considered as a suitable pH to preferentially retain hemicelluloses with a 5 kDa UF.

As the main goal was to recover native lignin and LCC from thermo-mechanical process water, 1 kDa NF was used to filtrate 5 kDa UF permeate. However, as the multiplication of membrane steps will cause an increase of production cost of lignin enriched extracts, the filtration of permeate 150 kDa on 1 kDa NF was also considered.

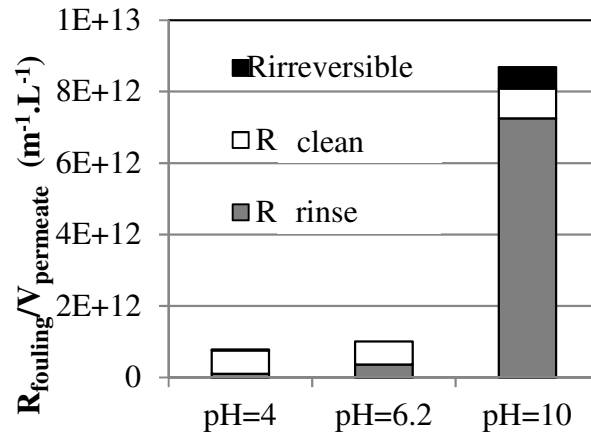
When the membranes 5 and 1 kDa were used in a series (Figure 1, line1), dry matter was retained at 45 and 67 % at pH 4 and 6.2 respectively (figure 3.B). In comparison, the 5 kDa UF allowed to retain 34 and 40 % of dry matter with the same pH. Therefore the rejection increase of dry matter due to the use of membranes in a series was limited. Furthermore, it can be highlighted that 1 kDa NF filtering permeate 150 kDa obtained the same rejection of dry matter than UF 5 kDa at pH 4. Indeed 32 % were recovered at VR of 80 % for 1 kDa NF and

34 % at a VR of 85 % for UF 5 kDa. Around 80 % of hemicelluloses were retained when both membranes were used in a series at pH 4 or 6.2. This rejection was higher of around 10 % compared to those obtained for 1 and 5 kDa membranes used independently. Lignin was retained at 39 % with the 1 kDa NF alone. This rejection was higher than the one assessed with membranes in a series (25 %) or for the 5 kDa (16 %). Therefore, based on these results of hemicelluloses and lignin selectivity, the coupling 5 and 1 kDa does not seem to be relevant. NF 1 kDa used to filtrate 150 kDa permeate allows to recover 39 % of lignin. This rejection could increase with the mode of filtration and VR used. Villain-Gambier et al. [28] obtained lignin rejection of 53 % during 1 kDa filtration of thermo-mechanical process water at a VR of 95 % in semi batch mode allowing filtration of 1240 L. In the present study, 1 kDa retentate still contained hemicelluloses ( $1850 \text{ mg}_{\text{eq G.L}^{-1}}$ ). This result was also obtained by Oinonen et al. [29] and Steinmetz et al. [4] in their 1 kDa retentate of thermo-mechanical process water of soft wood. The latter study proposed the following composition: 40 % of LCC, 35 % of hemicelluloses, 7 % of free lignin, 8 % of ash and 10 % of others such as phenolic acids. Hence, depending on the targeted compound (*i.e.* LCC or lignin) and the required purity, further isolation and concentration processes could be performed.

### 3.3 Fouling establishment

The global hydraulic resistance of fouling of UF 5 kDa observed in Figure 4.A at pH 10 ( $8.7 \cdot 10^{12} \text{ m}^{-1} \cdot \text{L}^{-1}$ ) was approximately ten times higher than resistances measured at pH 6.2 ( $1 \cdot 10^{12} \text{ m}^{-1} \cdot \text{L}^{-1}$ ) and 4 ( $7.9 \cdot 10^{11} \text{ m}^{-1} \cdot \text{L}^{-1}$ ). Therefore, fouling establishment was clearly promoted at basic pH. Figure 4.A showed that hydraulic resistance due to fouling removed by water rinsing represented 83 % of global hydraulic resistance of fouling at pH 10. This result implied that concentration polarization and cake layer formation were the predominant 5 kDa membrane fouling phenomena and were responsible for the permeate flux decrease observed (figure 2.A). Adsorption cannot be involved as flux decreases from only 1 to 3 % were assessed by static tests previously performed. The contribution of irreversible fouling resistance to the global hydraulic resistance was assessed to 7 % at pH 10. This latter result constitutes a limit for the utilization of basic pH at industrial scale as it would drastically decrease the membrane life time. During the filtration of kraft liquor at pH 10 with a 5 kDa ceramic membrane, Mota et al. [25] found a hydraulic resistance of fouling of  $2.9 \cdot 10^{13} \text{ m}^{-1}$  at 54 % due to fouling removed by chemical cleaning and 46 % to fouling removed by water rinsing. Compared to the present study, even if membrane and pH tested were close, a straightforward comparison is not possible as feed solution characteristics are different as well as operating conditions of filtration (*i.e.* TMP, cross flow velocity). Irreversible fouling was not observed at pH 4 and 6.2. The establishment of fouling removed with chemical cleaning was stable whatever the pH of process water.

(A)



(B)

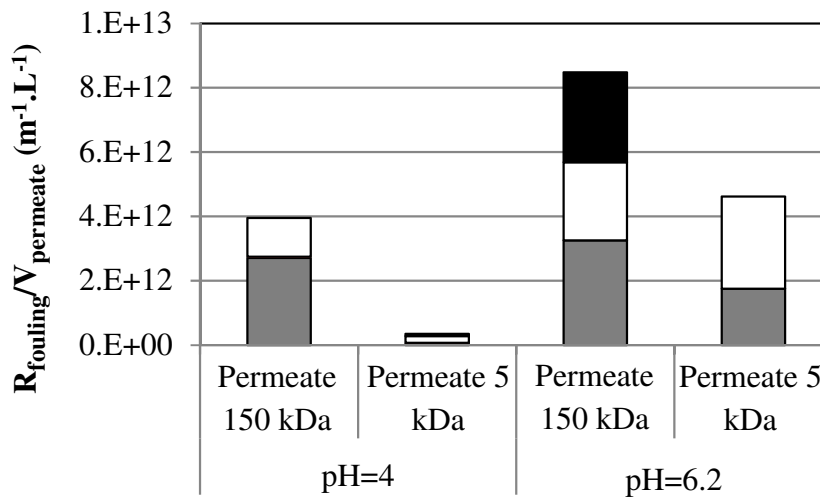


Figure 4: Hydraulic resistances of fouling for (A) 5 kDa UF at pH of 4, 6.2 or 10 and for (B) 1 kDa NF at pH 4 or 6.2 alimented by 5 permeate (line1) or 150 kDa permeate (line 2)

Figure 4.B presents the composition of fouling resistance of 1 kDa membrane at pH 4 and 6.2 alimented with either 150 or 5 kDa UF permeate. At pH 6.2, the global hydraulic resistance of fouling (values with or without previous 5 kDa UF were equal to 4.6 and 8 10<sup>12</sup> m<sup>-1</sup>.L<sup>-1</sup> respectively) were higher than values obtained at pH 4 (values with or without previous 5 kDa UF were of 5 10<sup>11</sup> and 4 10<sup>12</sup> m<sup>-1</sup>.L<sup>-1</sup> respectively). The high global hydraulic resistances

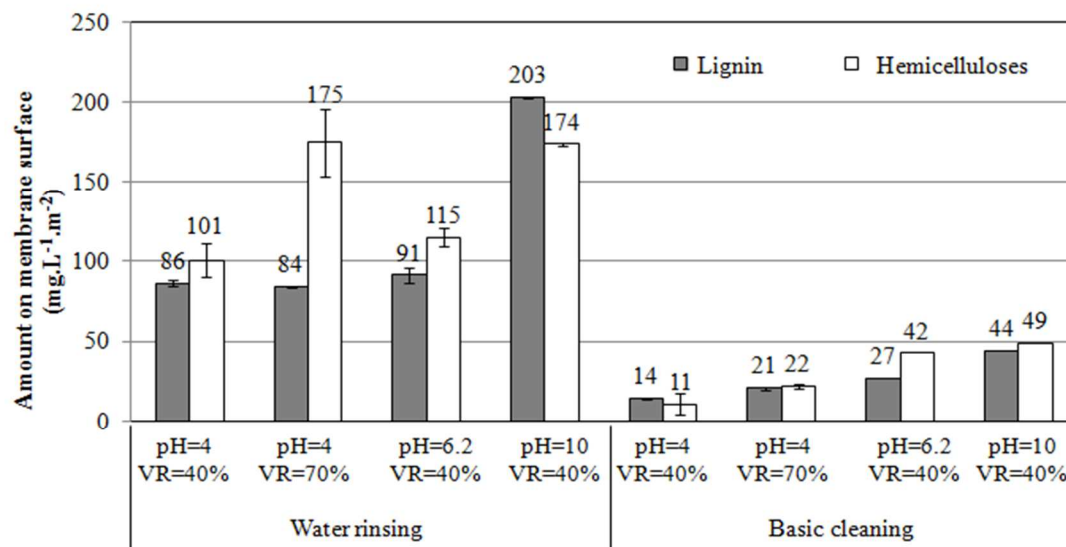


values were expected when 150 kDa permeate was directly filtrated as larger molecules were still present in this permeate. The main difference for hydraulic resistances of both experiments filtering 150 kDa permeate concerned the presence of an irreversible part of fouling resistance (33 % of total value) at pH 6.2. Fouling resistance of 1 kDa NF obtained at pH 4 without previous 5 kDa was 8 times higher the one obtained with previous 5 kDa. This latter resistance was composed at 68 % and 32 % of fouling respectively requiring water rinsing and chemical cleaning. At pH 4.5, after 15 trials (*i.e.* filtration and cleaning cycle), all performed with the same operating conditions with a 10 kDa regenerated cellulose UF filtering spent sulfite liquor, a stable fouling resistance around  $4 \cdot 10^{13} \text{ m}^{-1}$  was found with no mention of irreversible fouling [30].

Therefore, the 1 kDa NF with previous 150 kDa at pH 4 was supposed to be compatible with relevant process productivity. However, it is obvious that further processing stages must be carried out in the latter selected conditions to assess finely the evolution of membranes productivities after several cleaning cycles.

The quantities of hemicelluloses and lignin assessed on and into the 5 kDa membrane at a common VR of 40 % at the three tested pH of filtration and at a higher VR of 70 % at pH 4 were presented on figure 5.A.

(A)



(B)

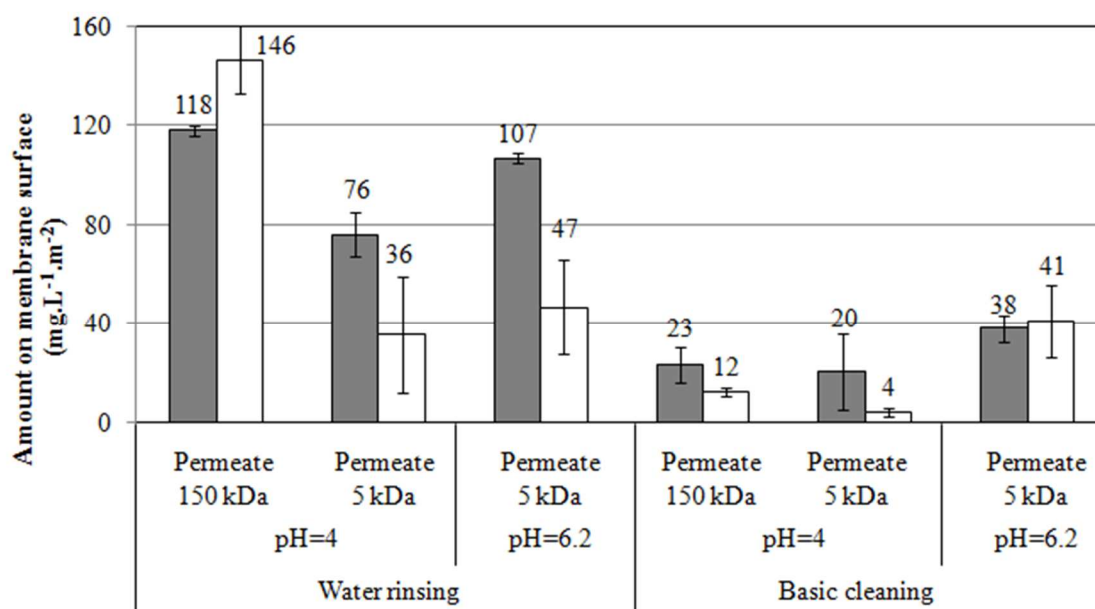


Figure 5: Extracted amounts of lignin and hemicelluloses measured after water rinsing or basic cleaning and removed from (A) 5 kDa UF at pH 4, 6.2 and 10 and from (B) 1 kDa NF at pH 4 or 6.2 alimented by 5 or 150 kDa permeate at a VR of 40-45 %

For the same VR of 40 %, the amounts of both compounds removed by a water rinsing were stable at pH 4 and 6.2 but increased at pH 10. The quantities of lignin and hemicelluloses extracted seem to be tightly related to membrane fouling (figure 4.A) and resulting permeate flux (figure 2.A). At pH 4, while VR rises from 40 to 70 %, a larger quantity of hemicelluloses was removed ( $175 \text{ mg.L}^{-1}.\text{m}^{-2}$ ) and stable measurement of lignin was assessed ( $84 \text{ mg.L}^{-1}.\text{m}^{-2}$ ). This could suggest that lignin interactions with 5 kDa membrane occurred at the early stage of filtration. Due to slow progressive 5 kDa permeate flux decrease between VR of 40 and 70 %, the impact of the hemicelluloses layer formation on membrane surface at pH 4 might be limited. At pH 10, large amounts of lignin ( $203 \text{ mg.L}^{-1}.\text{m}^{-2}$ ) and hemicelluloses ( $174 \text{ mg.L}^{-1}.\text{m}^{-2}$ ) were removed from membrane surface. This result was related to rapid permeate flux drop and high global hydraulic resistance of fouling measured at pH 10 due to fouling removed by water rinsing. Lignin and hemicelluloses might rapidly accumulate at the 5 kDa membrane surface and establish a cake layer. As negligible adsorption phenomenon was obtained, this cake layer might be compact to provoke fast permeate flux decrease and high rejection of matter (figure 3.A). The quantities of hemicelluloses and lignin extracted by a basic cleaning were noticeably lower than those obtained after the water rinsing. The amounts of both compounds caught into the 5 kDa membrane increased with pH. These compounds were responsible for fouling needing chemical cleaning which was the main contributor of global hydraulic fouling resistance detected at pH 4 and 6.2 and therefore of flux decline. At VR of 40 %, values from 11 and  $14 \text{ mg.L}^{-1}.\text{m}^{-2}$  at pH 4 to 49 and  $44 \text{ mg.L}^{-1}.\text{m}^{-2}$  at pH 10 were measured for hemicelluloses and lignin respectively. They were also responsible for fouling removed by chemical cleaning and irreversible one measured at pH 10.

On figure 5.B, it appears that amounts of lignin and hemicelluloses quantified in water rinsing effluent were the highest on the 1 kDa surface filtering 150 kDa permeate at pH 4 with 118

and  $146 \text{ mg.L}^{-1}.\text{m}^{-2}$  of lignin and hemicelluloses respectively. Those quantities were relatively more important than the ones measured on 5 kDa membrane at the same pH and VR of 40-45 %. The higher quantities assessed on 1 kDa surface were most likely due to the membrane cutoff decrease from 5 to 1 kDa. Regarding also the flux, selectivity and global hydraulic resistance of both membranes at pH 4, their behavior towards the filtration of thermo-mechanical process water are similar.

It is interesting to notice that the quantities of lignin found in water rinsing and basic cleaning of 1 kDa NF with previous 5 kDa were all equal or higher than hemicelluloses ones. This result was predictable as 5 kDa recovered an important part of hemicelluloses between 42 and 73 %. Quantities of lignin and hemicelluloses extracted by a basic cleaning were lower the one obtained by a simple water rinsing. The larger quantities were extracted from the 1 kDa at pH 6.2 with previous 5 kDa around  $40 \text{ mg.L}^{-1}.\text{m}^{-2}$  for both compounds.

### 3.4 Fouling formation analysis

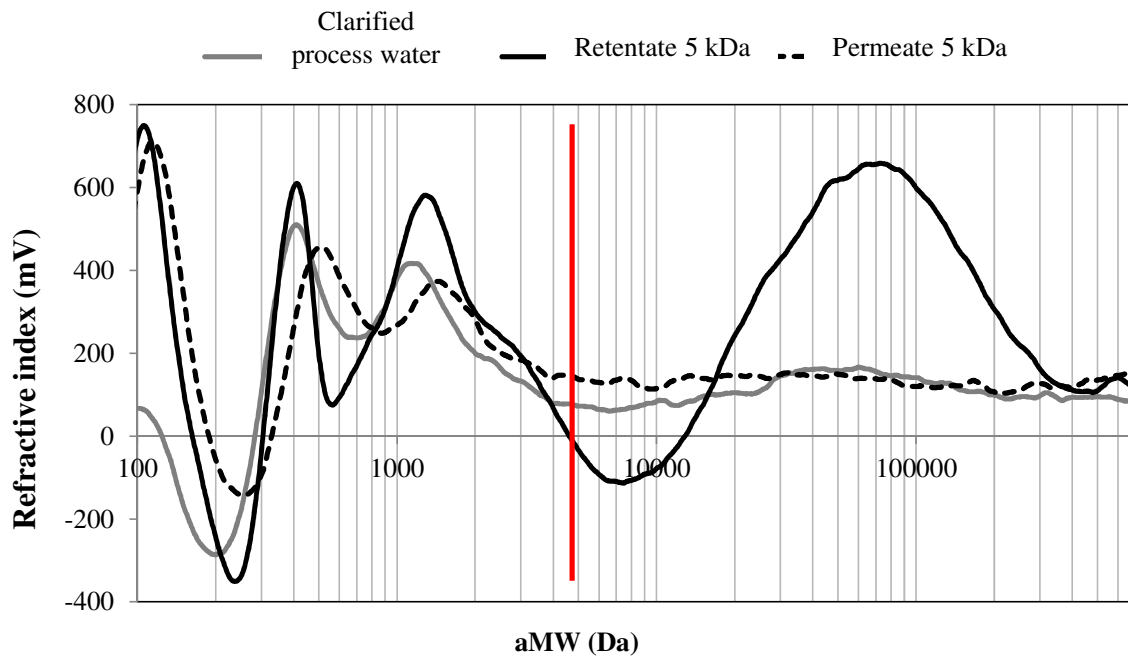
The hemicelluloses aMW distribution was studied for the fractions obtained after 5 kDa filtration at pH 4 (Figure 6.A). A bimodal profile with peaks at 400 Da and 1 kDa were visible on the hemicelluloses chromatogram from clarified process water. These MW are quite common in thermo-mechanical process water. Sizes of 700 Da and 3.9 kDa were found in a previous study [31].

A peak of high refractive index appeared on the 5 kDa retentate chromatogram with an aMW of 100 kDa. The specific conditions applied during this 5 kDa filtration at pH 4 tend to provoke the formation of larger structures. At pH 6.2 and 10, the chromatograms of hemicelluloses (*i.e.* clarified process water, retentate and permeate of the 5 kDa) were similar than chromatograms presented at pH 4 (data not shown). However the aggregates observed around 100 kDa were absent from the retentates. Hemicelluloses with larger sizes were observed in previous studies with similar process water [8,28].

A statistical study led by Carneiro-da-Cunha et al. [32] on polysaccharides size (some of them are bio sourced glucomannans) showed that their concentration was a factor influencing their size. A variation of polysaccharides between 2 and 6 g.L<sup>-1</sup> causes their agglomeration.

Authors announced that this phenomenon is provoked by the abundance of hydroxyl groups which create hydrogen bonds between those polymers. However, this agglomeration is reversible when dilution is operated. Persson and Jönsson [8] observed that size of hemicelluloses increases when they are concentrated from 0.9 to 5 g.L<sup>-1</sup> with UF.

(A)



(B)

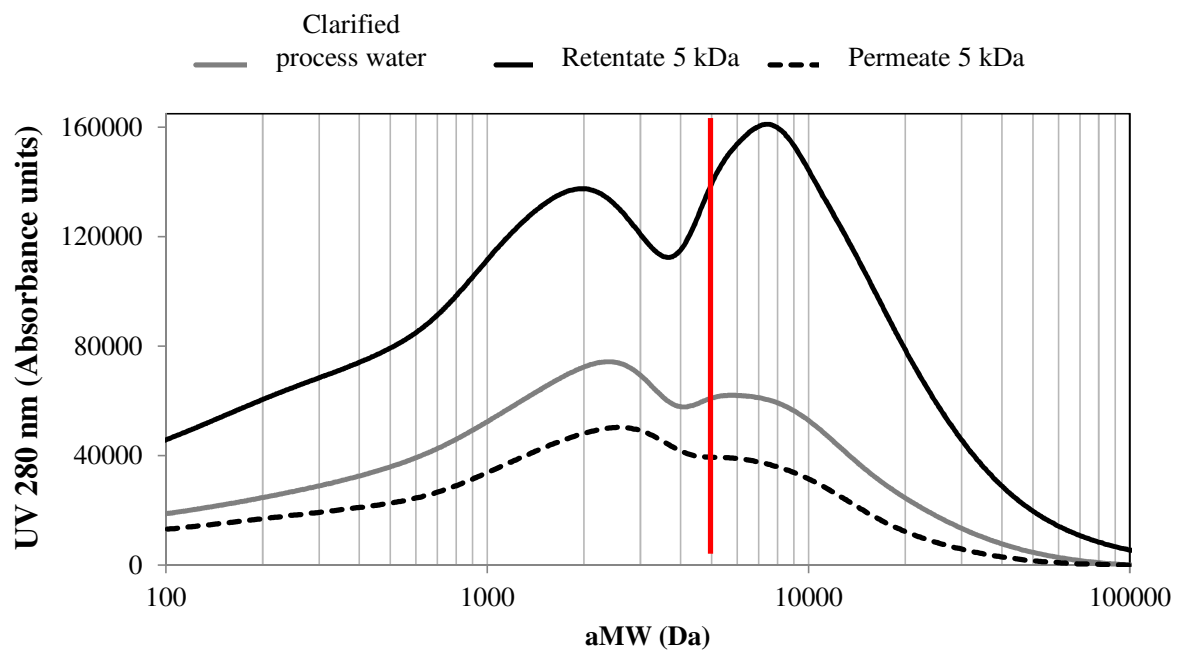


Figure 6: SEC chromatograms of clarified process water, 5 kDa retentate and permeate (pH 4 and VR=85 %) obtained with (A) RID detector and (B) UV detector at 280 nm. Red line corresponds to the UF cutoff of 5 kDa.

They proved that the molecular mass distribution of hemicelluloses will depend on the rejection characteristics. As a concentration around  $2200 \text{ mg}_{\text{eq}} \text{ G.L}^{-1}$  of hemicelluloses was measured in retentate 5 kDa at pH 4, the local concentration at membrane surface was certainly higher and the conditions of rejection could have promoted the aggregates formation. Those molecules of high aMW were retained by the 5 kDa membrane and they were not visible in 5 kDa permeate. This phenomenon could justify the relatively high rejection of hemicelluloses (73 %) obtained at pH 4 and a VR of 85 % (figure 3.A). The results obtained by SEC allow confirming the interpretations advanced in the previous parts. Those hemicelluloses agglomerates have aMW twenty times higher than the membrane cutoff. They could stay on the membrane surface with no possibility to go into membrane pores. They could form a thin and porous cake layer due to continuous tangential flux along the membrane. This cake layer could only provoke a superficial fouling easily removed by water rinsing (Figure 5.A).

The lignin chromatogram of clarified process water showed a bimodal aMW distribution with peaks at 2 and 7 kDa (figure 6.B). Those aMW are in agreement with MW between 0.1 and 6 kDa found for thermo-mechanical lignin of previous studies [15,28,32]. The comparison of the three chromatograms highlights the poor selectivity of the membrane 5 kDa for lignin rejection (rejection of 23 and 18 % at pH 4 and 6.2 respectively). As SEC can only give aMW, it might be considered that most part of the lignin as a smaller MW than membrane cutoff. Furthermore, MW are subjective and depend upon the shape and charge properties of the solutes used. Uncharged molecules larger than specified membrane cutoff are able to pass through pores while small charged molecules do not pass. Lignin as hemicelluloses were highly retained with 5 kDa UF at pH 10. The explanation could come from the variation of lignin stability with pH. According to the DLVO theory [33], the stability of lignin in aqueous solution is related to interactions of attractive and repulsive forces. In alkaline conditions, due

to deprotonation of main functional groups, lignin is negatively charged and repulsive electrostatic forces between the lignin molecules dominate and provide stability of lignin molecules with no aggregation behavior [17]. As membranes used are negatively charged at alkaline pH, the filtration through 5 kDa UF is complicated and due to TMP applied, a dense layer of lignin could accumulate on membrane surface and into it (Figure 5.A). With the decrease of pH, the hydrogen ions interact with the negatively-charged lignin and neutralize the charges on the lignin surface. Then, repulsive forces are reduced and lignin molecules can be closer. As at pH 4, functional groups present in lignin structure such as phenolic hydroxyl or carboxylic groups are almost completely protonated, lignin might in main part pass through 5 kDa UF. The evolution of zeta potential of clarified process water with pH can support this explanation (Figure 7).

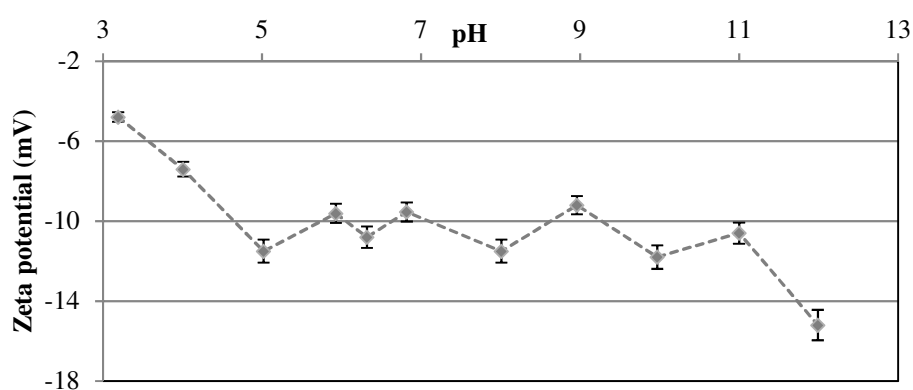


Figure 7: zeta potential of clarified process water as a function of pH

This figure indicates that zeta potential remained negative on all the pH range tested. At pH 4, as the zeta potential was still below the isoelectric point, the particles will have no tendency to aggregate.



The main phenomena implied in rejection and inherent fouling establishment during filtration of clarified process water with 5 kDa membrane at various pH are summarized in figure 8.

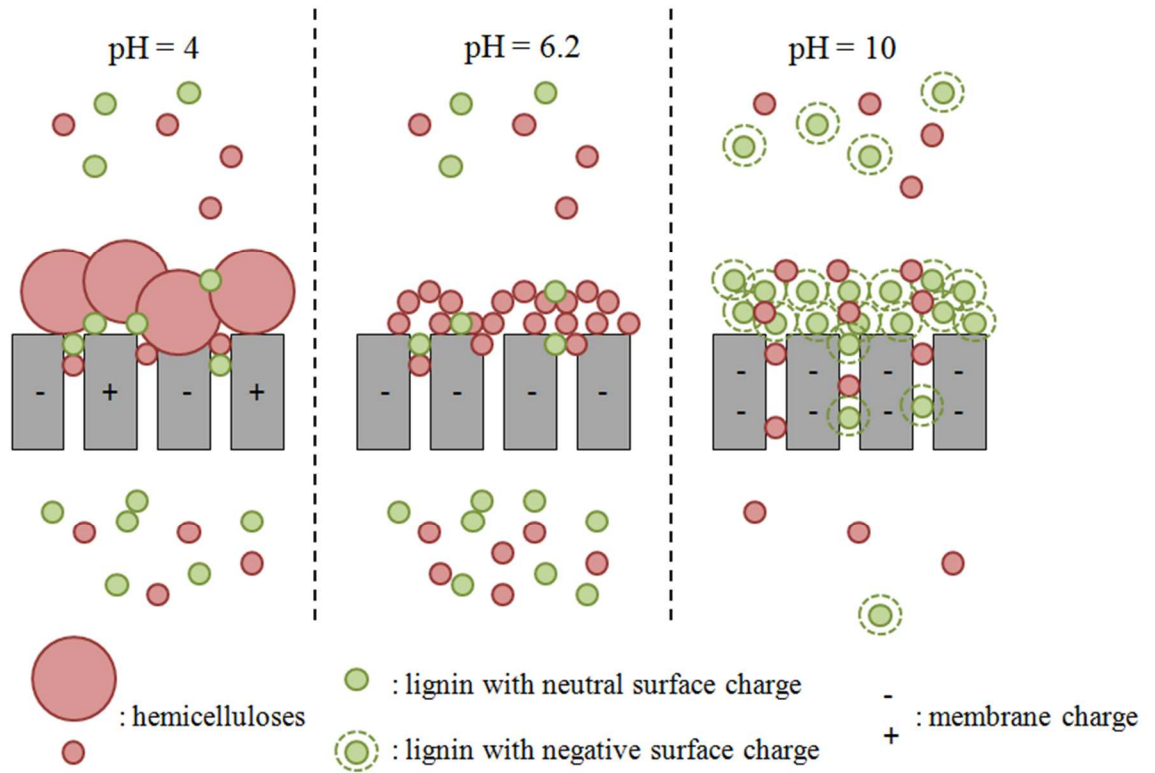
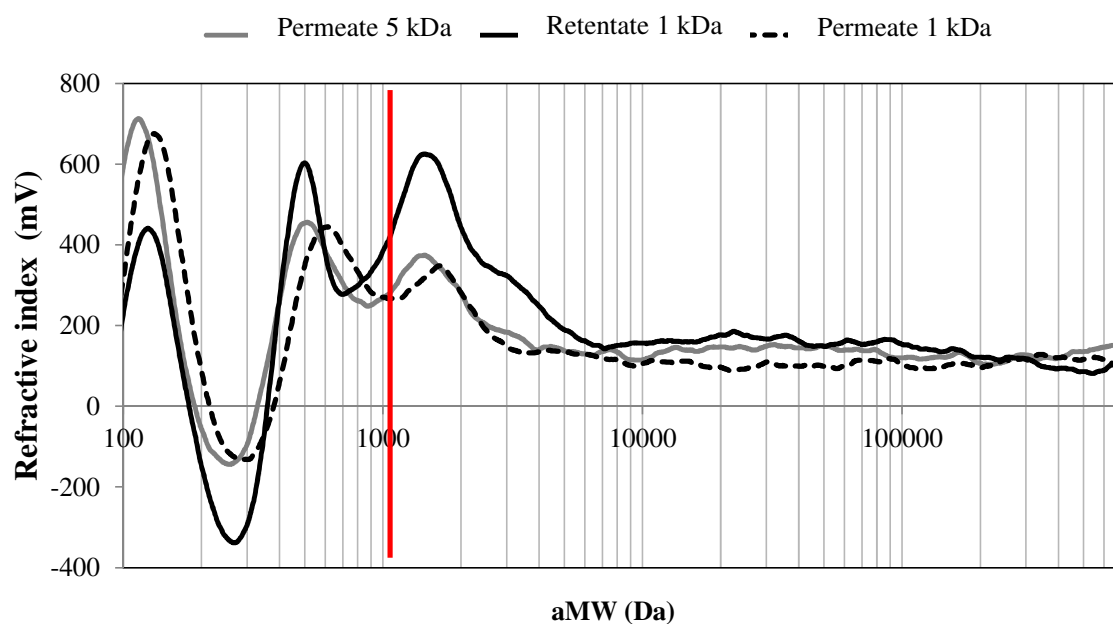


Figure 8: Proposition of fouling mechanisms involved during clarified process water filtration with 5 kDa UF at pH 4, 6.2 and 10.

Previous results have highlighted that fouling mechanisms of thermo-mechanical pulp process water were related to the pH of solution. The 5 kDa UF and 1 kDa NF membranes are charged materials. This charge comes from the active layer composition and/or is influenced by ions adsorption from the solution. Ceramic membranes in  $\text{TiO}_2\text{-ZrO}_2$  used in the present study possess an isoelectric point between 3-4 [34,35]. Therefore at pH 4, the global charge of membrane can be considered as neutral. At pH 6.2 and 10, the global charge is negative, generating repulsive interactions between membrane surface and charged species in solution. At acid pH, hemicelluloses were under aggregated structure and formed a porous cake layer easily removed by water rinsing and which did not stop lignin. As some of the main

functional groups of lignin are under protonated form, even with size in the range 2-7 kDa, lignin was able to pass through the 5 kDa membrane. Nevertheless some lignin fragments took parts in cake layer formed at membrane surface. At pH 6.2, hemicelluloses have not formed large structures. They were still implied in a cake layer formation with lignin easily removed by water rinsing. At pH 4 and 6.2, permeate flux decline was mainly provoked by fouling requiring chemical cleaning present into membrane pores. At pH 10, a rapid flux decline was certainly caused by concentration polarization and the formation of a compact cake layer which increased rejection of hemicelluloses and lignin. The chromatographic profile of hemicelluloses and lignin at pH 4 for 1 kDa NF filtering 150 kDa permeate are close to the ones showed in figure 6. Therefore the proposed fouling mechanisms implied for 1 kDa NF in those conditions was supposed to be similar at pH 4. Figure 9 exhibited the aMW distribution of hemicelluloses and lignin in 5 kDa permeate (feed solution of 1 kDa), 1 kDa retentate and permeate at pH 4. As in figure 6.A, chromatographic profile of hemicelluloses in 5 kDa permeate were mainly composed of 3 peaks at 150 Da, 500 Da and 1.5 kDa. This chromatogram highlights the poor rejection of those hemicelluloses. This result could complete the comprehension of low rejection increase of hemicelluloses when 5 and 1 kDa were used in a series at pH 4 (Figure 3(A) and 3(B)). As low hemicelluloses concentration was depicted in 1 kDa retentate ( $380 \text{ mg}_{\text{eq}} \text{ G.L}^{-1}$ ), agglomeration was not observed. Lignin aMW distributions presented in figure 9.B were really closed to the ones obtained in figure 6.B. The main visible difference came from the lower signal intensities observed. This latter figure showed that NF 1 kDa (in a series with UF 5 kDa) was not selective. The most part of lignin which passed through the 5 kDa UF could also goes through 1 kDa NF. This explained the low lignin recovery of membranes in a series (25 %). As a conclusion, those data confirmed that the use of both membranes selected for specific recovery of lignin was not relevant.

(A)



(B)

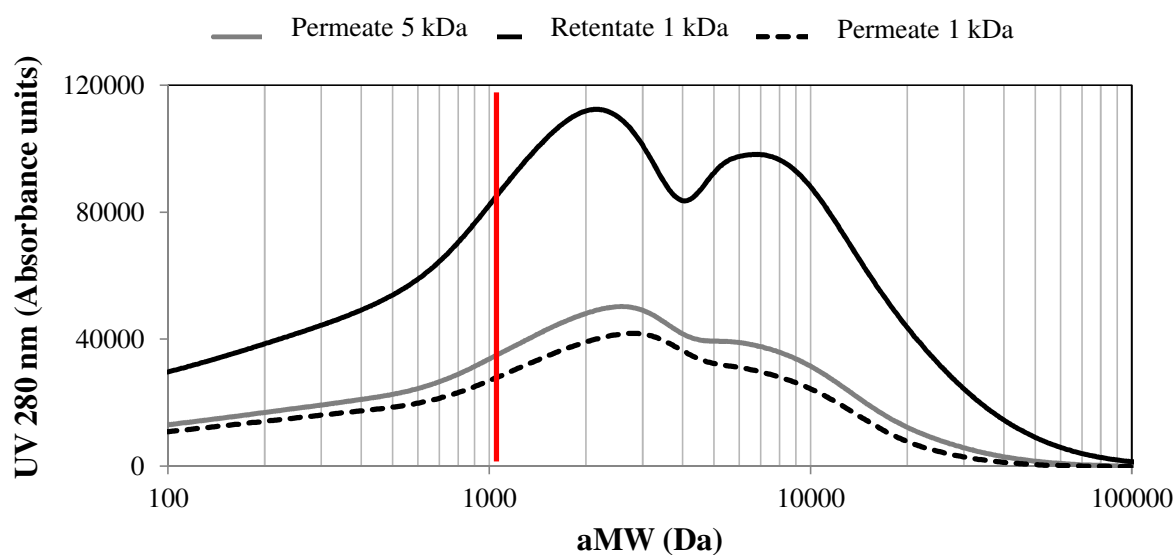


Figure 9: SEC chromatograms of 5 kDa permeate, 1kDa retentate and permeate (pH 4, VR = 80%) obtained with (A) RID detector and (B) UV detector at 280 nm. Red line corresponds to the NF cutoff of 1 kDa.

## **4- Conclusion**

The recovery of lignin from thermo-mechanical process water was evaluated. Three pH (4, 6.2 and 10) as well as two distinct membrane cutoff (5 and 1 kDa) used alone or in a series were tested. In order to determine the conditions offering a relevant compromise between high lignin selectivity and sustained productivity, those latter parameters were analyzed taking into account fouling characteristics. The coupling 5 kDa UF and 1 kDa NF was not suitable as lignin was fractionated between both steps. pH 10 was not appropriate for selective lignin recovery of thermo-mechanical process water as a rapid flux decline was noticed at low VR of 40 %. A compact fouling layer was deposited on and into the membrane mainly characterized by 83 % of fouling removed with chemical cleaning and 7 % of irreversible one. Lignin was clearly engaged in the fouling establishment at pH 10 as this polymer was under its stable form negatively charged implied in repulsive interactions with membrane surface. This type of membrane fouling is not pertinent for high membrane life time. pH 4 with a unique 1 kDa NF step gave promising results as high flux were maintained until VR of 80% and fouling could be easily managed as fouling was composed at 70 % of fouling removed by water rinsing. In these conditions around 40 % of lignin and 70 % of hemicelluloses were retained. Lowering membrane cutoff to maximize lignin recovery could be considered. However as both compounds possess aMW in the same range and could be engaged in LCC structure, the obtained extracts will always be a mixture of hemicelluloses and lignin. Therefore, to increase lignin purity, membrane process has to be combined with extraction process such as precipitation or liquid/liquid extraction.

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