Purification and Fractionation of Hemicellulose Concentrates Obtained by Ultrafiltration

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Abstract

The xylan rich filtrate obtained from alkaline extraction of bleached pulp was isolated by precipitation followed by washing and drying of the precipitate. This isolation/purification process was applied to filtrate as is (non-concentrated) and to a filtrate previously concentrated by ultrafiltration (UF). The advantages achieved by implementing the UF concentration process are significant when compared with results obtained with non-concentrated filtrate.

The membrane used in the concentration step, UFX5pHt, (MWCO 5 kDa), has an average flux of 30 L/h m^2 for previously optimized conditions of flow velocity (1 $m.s^{-1}$) and operating pressure (6 bar). Xylans were isolated from the concentrated filtrate using two different methods: neutralization with HNO_3 (7,5 N), and precipitation with methanol (20, 30, and 50 wt/wt %). For the concentrated filtrate a reduction of up to 61% in the consumption of nitric acid for the precipitation was achieved. On the other hand products of lower purity were obtained with methanol as precipitating agent. The molecular weights of the obtained xylans were determined by SEC leading to values between 24100 and 31000 Da.

Keywords: xylans; ultrafiltration; precipitation; diafiltration

1. Introduction

In the last decades the research effort to optimize processes aiming the obtainment of hemicelluloses has increased substantially as a result of the necessity to produce chemicals and fuels from sustainable resources in order to create an alternative for those derived from fossil oils.

In the wood pulp industry there is some uncertainty about future paper consumption. Thus the production of xylan (a hemicellulose largely found in nature) from the wood pulp might be a possible alternative to produce value-added products when there is not enough demand for the pulp in the paper industry. The range of applicability of xylans is enormous. Among many others it can be used to produce important products such as, furfural, xylose and xylitol (Peng et al., 2010). On the other hand, the use of xylan in packaging films, food coating, papermaking, and as an emulsifier and protein foam stabilizer are examples of applications which are still under research evaluation (Ebringerová and Heinze, 2000; Li, 2011; Peng et al., 2009).

The xylans in bleached kraft pulp can be recovered by alkaline extraction using sodium hydroxide (NaOH) followed by filtration. From

these steps, an alkaline filtrate (in what follows designated by FTQ) rich in xylans is obtained (Gabrielii et al., 2000; Jackson, M., 1977; Martínez et al., 2015; Peng et al., 2012). From this filtrate, xylans are isolated by antisolvent precipitation followed by the washing of the precipitate. This whole isolation procedure can be performed in two different ways namely, acting directly upon FTQ or acting upon an FTQ previously concentrated by ultrafiltration (UF). This UF concentration is an attractive alternative as it reduces the quantity of antisolvent used in the isolation step as well as it allows to recover a substantial amount of NaOH in the permeate which can then be recycled to the extraction process. Conditions for this recycling are discussed is some papers (Arkell et al., 2013b; Laine et al., 2015).

Despite the fact that several studies exist about the application of membrane processes in the concentration of the alkaline filtrate (Arkell et al., 2013a; González-Muñoz et al., 2013; Krawczyk et al., 2013; Laine et al., 2015) in none of them is reported what happens next to the xylans concentrate.

In this context the main goal of this work was the analysis of the advantages achieved by implementation of a FTQ concentration process prior to isolation and purification. The advantages, if any, are evaluated by comparison with results obtained by exactly the same isolation and purification procedures applied to a non-concentrated FTQ and taken as reference data.

2. Materials and Methods

2.1. Raw Material

The bleached kraft pulp from Eucalyptus Globulus used in this experiment, whose characteristics are shown in Table 1, was supplied by RAIZ (Paper and Forest Research Institute, Aveiro, Portugal).

Table 1. Characteristics of the kraft pulp.

Sample	Pulp 1	Pulp 2
Pentosans (%)	16,44	17,2
ºSR	66	66
Humidity (%)	70,6	69,09

2.2. Equipment

2.2.1. Membrane

The UF concentration tests were performed with the UFX5pHt flat sheet polysulphone membrane (Alfa Laval, Denmark, Nakskov) having a MWCO of 5 kDa.

2.2.2. Membrane filtration setup

One membrane pair with an effective membrane area of 0,036 m^2 was mounted in a plate-and-frame LabStak M20 unit (Alfa Laval, Denmark, Nakskov).

2.3. Experimental Procedure

2.3.1. Membrane Preparation

Preceding first use, the membrane was cleaned in order to remove chemical preservatives. The membrane was first submitted to a washing procedure with deionized water (30 min at 2 bar pressure and at 25ºC) followed by an alkaline cleaning with 0,5 wt.% Ultrasil 10 for 30 min at 25ºC and 2 bar. After that, the membrane was washed with deionized water until neutral pH.

After compaction (2 h at 20 bar) pure water flux (PWP) of the membrane was measured leading to a value of $L_P = 5 \times 10^{-11}$ $m.s^{-1}.Pa^{-1}$, at 25 ºC, for its hydraulic permeability.

The cross-flow velocity was kept at 1,1 $m.s^{-1}$ in every procedure.

2.3.2. Alkaline extraction of pulp xylans

Xylans were recovered from the kraft pulp by alkaline extraction at room temperature with 10% NaOH. The consistency of the cake (content of kraft pulp in the suspension) was kept at 5% and the extraction time was 1 h under agitation of 1100 rpm.

After this time the xylan rich filtrate was obtained by separation of the pulp with a vacuum filtration (G-3 filter 15 µm a 40 µm).

2.3.3. Concentration and Diafiltration Tests

The concentration (C) of the filtrate was carried out in the conditions optimized by parametric studies. The transmembrane pressure was kept at a constant pressure of 6 bar and a cross-flow velocity of 1 $m.s^{-1}$ was applied in all tests. The concentration factor (CF), which is defined as the ratio between the initial and the final volume at the membrane feed tank, varied between 3,6 and 4,6. For the tests with diafiltration (DF), after a first concentration, a given mass (equal to the mass of collected permeate during the concentration) of water was added. After this water addition a second concentration was performed until the same FC was reached.

2.3.4. Isolation of xylans in the UF concentrate

The xylans present in the alkaline UF concentrate were isolated by two independent methods:

- Precipitation by HNO_3 (7,5 N) until pH = 7 under constant agitation (300 rpm).
- Precipitation by methanol in different proportions (20, 30 and 50 wt. %) under constant agitation (300 rpm).

After addition of the antisolvents, the resulting solutions were centrifuged (B.Braun Sigma 4K10) at 8000 rpm for 20 min. The precipitates (pp), mostly xylans, salts or NaOH and humidity, were further purified while the supernatants were rejected.

2.3.5. Purification of xylan

In order to reduce/remove the inorganic matter of the precipitates, they were washed either with water or methanol.

The washing/purification using water, is controlled differently depending on the previous precipitation step. In the cases where precipitation was carried out with methanol, the addition of water was controlled by the pH (addition of water until pH = 7) of the resultant solution (water+pp). When the precipitation was made by HNO_3 the amount of water to be used in the washing operation was controlled by the conductivity (until $\approx$ 5 µS/cm) of the resultant solution.

Methanol washings were carried out using fixed volumes in 3 steps. At each step a centrifugation and separation of the supernatant were done.

2.3.6. Drying and grinding of the precipitates

After the purification step, every obtained precipitate was dried in a furnace at a constant temperature of 65ºC until constant weight was obtained. The dried precipitates were grinded with a mortar and pestle until a powder state.

2.4. Analytical Methods

2.4.1. Spectroscopic characterization (FTIR)

Powdered final samples of precipitates (isolated and purified) as well as UF permeates were analyzed by FTIR. The spectra of the hemicelluloses and the permeates were obtained on a FTIR spectrophotometer ABB, FTLA 2000 Analyzer in the range of 4000 to 500 cm^{-1} and 64 scans per sample.

2.4.2. Size-exclusion chromatograph (SEC)

Powdered samples were analyzed by Size Exclusion Chromatography (SEC) after being dissolved in dimethyl sulfoxide (DMSO) at a concentration of 0,2% for 24 h under agitation. SEC analyses were carried out in a WATERS-W717 plus auto sampler, W600 pump and a furnace: CHM. A PLgel 5 µm MiniMIX-D, 4.6 x 250 mm column, protected with a pre-column PLgel 5 µm MiniMIX-D Guard, 4.6 x 50 mm, both manufactured by Agilent Technologies, was used with DMSO as eluent (0,3 mL/ min, T = 80 ºC). Sample detection was made with a Gilson 133 refractive index (RI) detector. The molar mass distributions of xylans were calculated in relation to pullulan standards from 5900 to 212000 Da (Shodex Lab.) using Waters Empower software.

2.4.3. Total Organic Carbon (TOC)

UF rejections were calculated by total organic carbon (TOC) measurements of the UF feed and permeate samples.

The TOC analyses were carried out by ISQ (Instituto de Soldadura e Qualidade).

2.4.4. Ash Content

The ash content in the dry precipitate samples was measured according to the TAPPI T 211 om-2. A test specimen was ignited in a muffle furnace (Nabertherm Controller P320) at 525 °C. A separate test specimen was analyzed for the percentage moisture. The resulting weight of ash and moisture level in the sample were used to calculate the percentage of ash present at 525°C on a moisture-free sample basis.

2.4.5. Moisture

The humidity of the isolated precipitates was obtained according to TAPPI T 412 om-11.

3. Results and discussion

3.1. Reference Data for Direct Precipitation of FTQ (non-concentrated).

Results obtained for xylan isolation from non-concentrated FTQ are shown in Table 2.

These results are referred to a neutralization of the FTQ with HNO_3 followed by methanol washing. The purity of the precipitates was calculated as an approximate technique, and it is defined as the inverse of the ash content, i.e. the organic (org) matter.

Table 2. Reference data for a direct precipitation of xylans in FTQ without ultrafiltration

Test	FTQ (g) / pp org dry (g)	HNO_3 (mL) / dry org pp (g)	Precipitate (g)	MeOH (mL) / dry pp (g)	Humidity (%)	Purity (%)
5	1118.47	41.43	1.897	158.11	9.68	94.58
6	122.41	43.33	1.817	165.08	7.92	97.22
7	99.74	35.16	2.317	129.44	10.6	95.3
8a	122.21	43.17	1.943	46.31	9.85	89.19
8b	106.14	37.68	2.159	69.46	10.66	93.14

3.2. Concentration of FTQ by ultrafiltration

The nine concentration experiments were made for FC in the range of 3.6 to 4.6 and for different FTQ masses. Table 3 shows the details of each test. The permeate fluxes were similar in all experiments with an average of 30 L/h.m^2. Figure 1 (a, b, c) show the results of experiments 1 to 9 arranged according to the type of test (concentration, C or concentration plus diafiltration, C+DF) and to the FC reached.

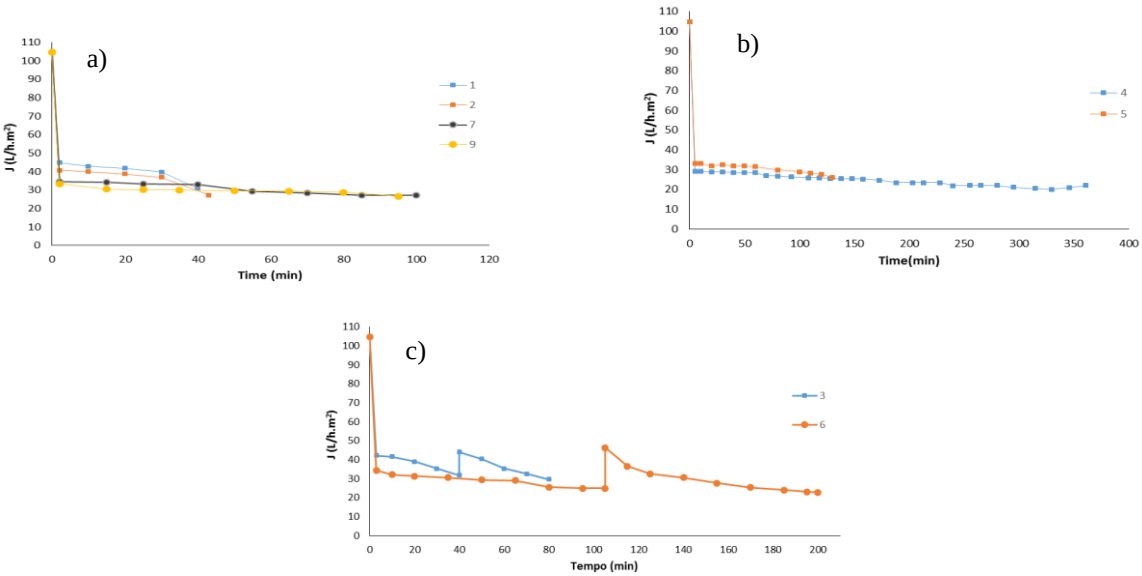

Figure 1. Permeate fluxes vs time of experiments 1 to 9.

Table 3. Data for the UF concentration of FTQ.

Experiment	1	2	3	4	5	6	7	9
Type	C	C	C+DF	C	C	C+DF	C	C
FTQ (g)	1600.0	1632.5	1741.1	7183.3	3384.2	3458.1	3350.0	3269.4
FC	3.6	3.6	3.6	4.6	4.6	3.6	3.6	3.6
Average flux, J, L/h.m^2	40.04	36.72	37.22	24.85	30.53	29.52	30.85	29.81
Concentrate collected (g)	324.0	324.0	324.0	1403.0	480.0	806.2	818.6	803.0
Precipitant Agent	HNO_3	HNO_3	HNO_3	-	HNO_3	MeOH	MeOH	HNO_3

After analyzing the results shown in Figure 1 along with the data in Table 3, it is possible to conclude that the permeate fluxes were stable during all the experiments. A correlation between the initial flux and amount of FTQ used was noticed. This influence, which is more relevant in tests 1, 2 and 3, is caused by the dead volume (water volume) of the membrane installation. This dilution decreases the viscosity of the FTQ. In order to avoid the interference caused by the dead volume, in the cases where comparisons were made, these 3 were rejected in 3.4.1 and 3.4.2.

In figure 1-b the difference between test 4 and 5 is related to the isolation procedure of the FTQ, after extraction. In the experiment number 4 the FTQ was obtained by centrifugation instead of filtration, and a more viscous solution was obtained. The flux is thus slightly lower than in all the other experiments.

3.2.1. TOC rejection

The rejections of the membrane to the total organic carbon, shown in Figure 2, were calculated as a ratio between the concentration of TOC present in the FTQ and the concentration of TOC in the UF permeates. The TOC rejection showed to be high in every test with an average value of 90%. These results are indicative of a good performance of the membrane for this separation.

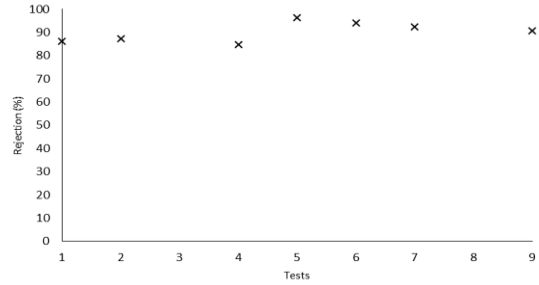

Figure 2. TOC rejection for the UFX5pHt membrane.

3.3. Precipitation and purification of the xylans in the UF concentrate

A summary of the methodology used in each experiment as well as the consumption of the HNO_3 used in the precipitation plus purification step is represented in Table 4.

Comparing both applied purification techniques, the water washing was shown, as expected, to give a final precipitate with a higher purity, independently of the used antisolvent.

On the other hand, as shown in Figure 3, when purification was carried out by methanol washing, it was noticed that the purity was lower in the cases of precipitation by methanol, as compared with nitric acid precipitation.

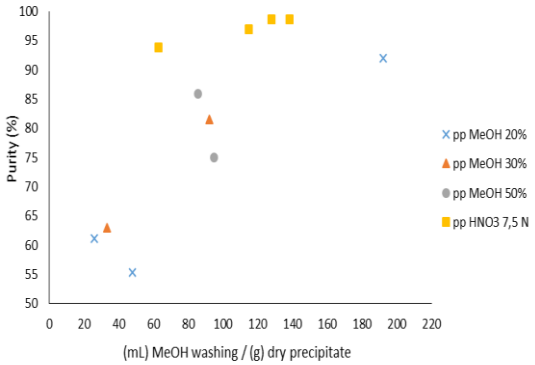

Figure 3. MeOH washing vs purity obtained.

In terms of yield (amount of organic precipitate (pp) per gram of concentrate), the precipitation with methanol 30% and HNO_3 seemed to be the best options. The quantity of the obtained precipitated was similar to those obtained from precipitation by 50% MeOH, while the consumption of MeOH was lower.

Table 4. Precipitation from the concentrate with HNO_3. Data used in the comparison with the direct xylans precipitation in FTQ.

Test	Concentrated / dry precipitate organic (g/g)	HNO_3 / dry precipitate organic (mL /g)	Water / dry precipitate (g/g)	Purity (%)	Methanol / dry precipitate (mL/g)	Purity (%)
1	149.8	36.5	829.0	99.0	-	-
2	95.8	26.0	-	-	114.7	97.0
3-(DF)	97.8	13.1	1237.2	97.1	138.2	75.7
5	51.9	15.7	1558.0	99.1	128.0	98.6
9	53.0	17.7	-	-	67.2	93.8

3.4. Benefits of concentration by ultrafiltration

3.4.1. Consumption of nitric acid in the precipitation

Reference data are referred to acidic precipitations followed by methanol washing purification. Thus, the comparison between precipitation of concentrated and non concentrated FTQ is made taking into account only the results that followed the same procedure.

To enable comparison, an average value of the acid consumption was calculated in both situations (concentrated and non-concentrated FTQ) (Tables 2 and 3).

Economies of 61 and 56% [HNO_3/ dry organic pp] for nitric acid consumption were reached for FC of 4,6 and 3,6, respectively.

3.4.2. Yield of xylans

The yield of precipitated xylans was expected to be higher for concentrated FTQ when compared with the results in Table 1 for non concentrated FTQ. The estimate of the yield varies with FC which is attained and cannot be done directly. In fact, it is known that the yield is higher due to the concentration step, which means that there are more xylans per unit of solution which are dissolved. The relation between the yield and the FC is not directly proportional because of the organic matter that is lost in the permeate. The reduction in the mass of solution necessary to produce one gram of xylan, is given in Figure 4 and was obtained by averaging the results from the experiments described in Table 3.

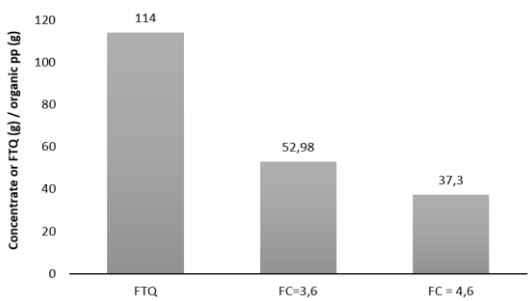

Figure 4. Differences in the consumption of nitric acid.

3.4.3. Purity of precipitates

For the washing step with methanol and when using the same quantity of this alcohol, it was observed that the purity of the precipitates increased as the precipitation was performed with a concentrated solution. This occurrence, shown in Figure 5, is related to the higher content of xylans in the solution, meaning that the content of salts after the neutralization is lower.

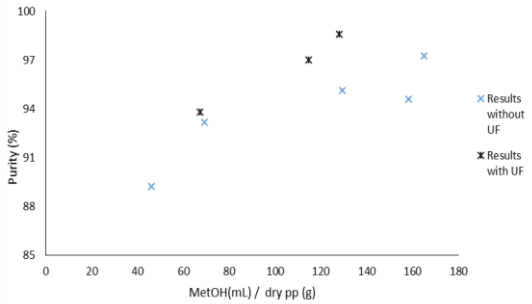

Figure 5. Purity with or without UF for the same conditions applied.

3.5. FTIR spectroscopy

The main goals of FTIR analysis were to be sure that the obtained precipitates were xylans; and to analyze the permeates of UF concentration searching for detectable xylans in those samples. The wavelengths related to the compounds under analysis and which are necessary for the interpretation of the spectrums are given in Table 4. The confirmation that the precipitates contained xylans was made by overlapping the spectrums of the products obtained with those of a commercial xylan sample (Sigma Aldrich).

Table 5. Characteristic wavenumbers present in FTIR spectrums.

Types of bounds	Characteristic wavenumber (cm^{-1})
O-H (water)	3450 and 1640
C-H (aliphatic carbons)	2933 and 2883
C-O-H; C-O; C-O-C (xylans / xylose chain)	1043
Na-NO3 (sodium nitrate)	1340

None of the analyzed UF permeates showed vibrations in the xylans correspondent areas (1043 cm^{-1}). However, there was a slight peak at 2833 cm^{-1} in every spectrum which is possibly related to the presence of carbons coming from degradation of xylans and remaining in the permeate after the concentration step.

For the precipitates, it was concluded that xylans were the main present product independently of the precipitation and purification method. However, according to these steps a few differences were found in the other areas

(1340cm^{-1}) which were related to the purity of the final product.

Figure 6-b shows an example of permeate spectrums. The biggest peaks are reference peaks for water and sodium nitrate (samples were neutralized with HNO_3 due to pH limitations of the equipment forming sodium nitrate). The permeate spectrums are all overlapping and it is not possible to identify each one separately.

Figure 6-a is showing three spectrums: the green is referring to the commercial xylan, the red and the black are xylans precipitated with HNO_3 and washed with methanol and water respectively. In this figure it is possible to see the influence of the washing method based on the intensity of the peak in the region 1340 cm^{-1}, which shows that the xylan washed with methanol contains more salt.

3.6. Molecular weight by SEC

The molecular weight of the xylans isolated in this work varies between 24100 and 31000 Da. Xylans isolated with 20% methanol are those with the higher values. This was expected taking into consideration that in the graded precipitation, the biggest molecules are those that precipitate first.

There was also found a difference when comparing the xylans obtained from the non-concentrated and concentrated FTQ. In certain cases, the chromatograms of the xylans from the non-concentrated FTQ showed two peaks: one with an average retention time and a second peak with a retention time lower than the lowest pullulan standard in the calibration curve (5900 Da), as shown in Figure 7-a. Meanwhile, for the xylans isolated from the concentrated FTQ only one peak was observed for all samples, as shown in Figure 7-b.

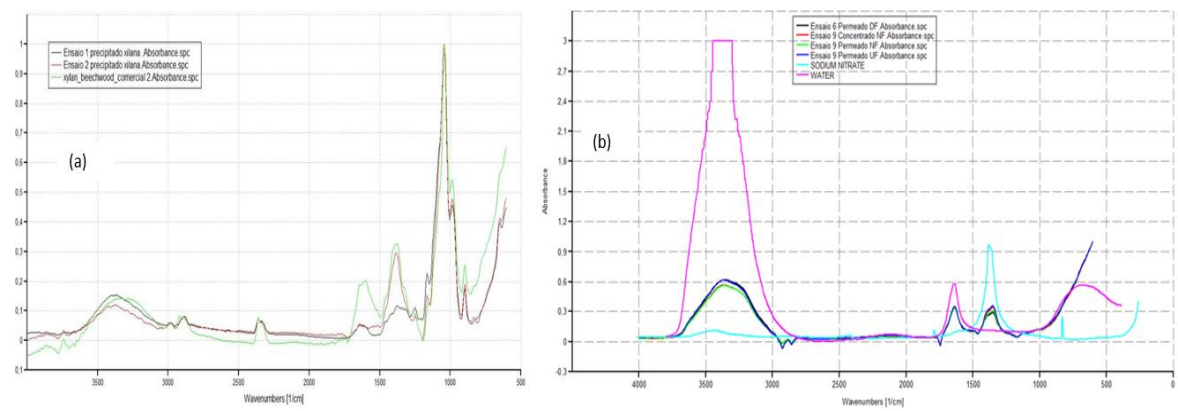

Figure 6-a Xylans precipitated in the present work and commercial xylan (Sigma Aldrich); 6-b Permeate spectrums with water and sodium nitrate (pink and light blue respectively) as reference.

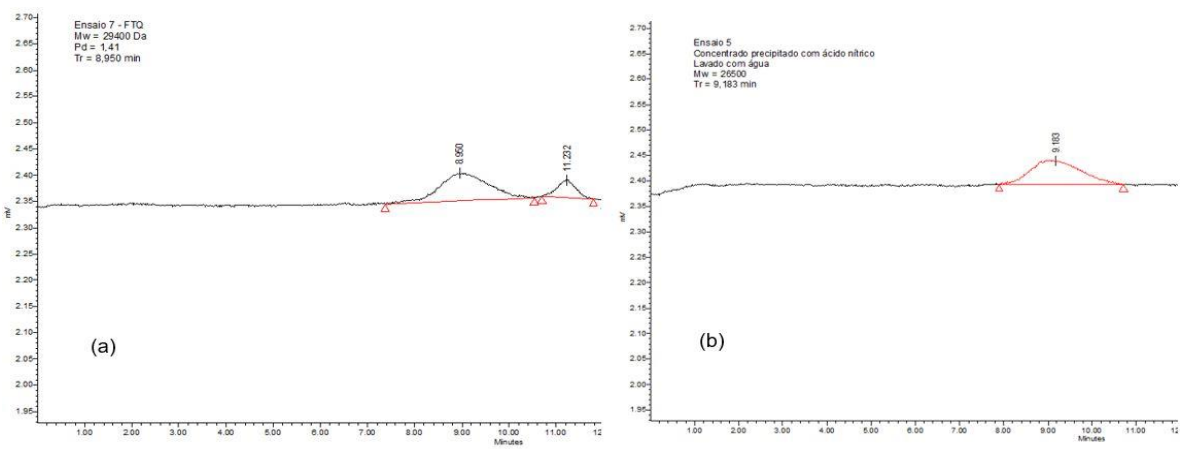

Figure 7-a Xylan isolated directly from the FTQ, presence of two peaks. 7-b Xylan isolated from the UF concentrate.

4. Conclusions

It was demonstrated that the use of membrane processes together with conventional techniques of isolation can bring significant advantages to the process of xylan isolation from kraft pulp. The obtained permeate fluxes were satisfactory with an average value of 30 $L/h.m^2$. The precipitates were xylans as confirmed in the FTIR spectrums. The purity was high for the xylans precipitated with HNO_3 in both purification methods.

A saving of 61% in the nitric acid consumption was estimated when a FC of 4,6 is reached in the UF process.

For the same purity, a lower amount of methanol was necessary in the washing of the precipitates isolated from the UF concentrate.

The isolated xylans had molecular weights between 24100 and 31000 Da.

5. References

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