Ultrafiltration and Nanofiltration of E-stage bleaching plant effluent of a sulphite pulp mill

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ABSTRACT

With the continuous increase of the environmental constraints in the pulp and paper industry, efforts have been made to find possible ways that minimize water consumption by reusing treated process streams and improving the quality of the final effluent. In addition, the use of by-products from this industry increase its economic sustainability. The treatment of sectorial streams in the pulp mills can be an attractive alternative due to its lower volumes and more specific characterizations in comparison to the final effluents. Thus, the aim of this work was to evaluate the use of a membrane separation process in the treatment of a bleaching plant effluent, specifically, the alkaline extraction stage filtrate of a pulp mill that use the bleaching sequence, E-O-P. The process that concentrates the effluent was optimized, taken into account the use of the lignin and hemicelluloses of the final retentate, as well as the possibility of reusing the treated permeate obtained. Nanofiltration membrane ALFA-LAVAL-NF99HF was found to be the most suitable when operating at 70°C, with a cross-flow velocity of 0,8 m/s and a transmembrane pressure of 13 bar. An average permeate flux of 24,2 $Lh^{-1}m^{-2}$, lignin and hemicelluloses rejections between 94 and 97%, and an increase in total solids content from 3% to 7%(w/w) for a volumetric concentration factor of 3,1 were obtained. A total cost of 2,14€ per m^3 of permeate for a new plant that processes 70 m^3/h of the studied effluent was determined.

Keywords: Bleach plant effluent, Ultrafiltration/Nanofiltration, Concentration, Lignin, Hemicelluloses, Sulphite pulp

1. Introduction

1.1 Background

Pulp and paper industry is one of the major sources of industrial water pollution, thus waste water reuse is a globally imperative component of sustainable water management. The volume and characteristics of waste water differ according to the type of raw material, the process technologies, whether or not there is internal recirculation of the effluent, and the type of pulp and paper produced. (1)

The production of sulphite pulp is much smaller than the production of kraft pulp, the main reason is that sulphite pulps generally do not have good strength properties as those of kraft pulp. However for some specialty pulp applications sulphite pulp provides other advantageous properties. Sulphite pulps produced by different processes have different properties, which make them suitable for particular products. Most pulp is produced for the purpose of subsequent manufacture of paper, but some is destined for other uses such as thick fibreboard or textile products manufactured from dissolving pulp. For now, producers of dissolving pulp are producing low kappa (an indication of the residual lignin content) products that are predominantly sold to the viscose textile industry. (2)

One example on this framework is *Caima - Indústria de Celulose, S.A.*, a Portuguese pulp mill with a capacity to produce 125 000 tons per year of bleached hardwood (eucalyptus globulus) sulphite Tdissolving pulp. The bleaching process is Totally Chlorine Free (TCF) and the bleaching sequence E-O-P starts with an alkaline extraction (E) followed by an oxygen delignification (O) and a final bleaching with hydrogen peroxide (P) to enhance the removal of lignin, hemicelluloses and color to achieve the low kappa aforementioned. The 'E' stage is an alkaline extraction with sodium hydroxide and the effluent from the 'E' stage cannot be recycled to the recovery boilers.

Usually each bleaching stage is composed of a reactor followed by a pulp washer. The bleaching plant filtrates from the washers constitute the major source of effluent sent to the effluent treatment plant, particularly the alkaline filtrate from 'E' stage contributes significantly to the final effluent's high organic load. Furthermore, process streams in pulp mills are commonly dilute and the treatment of specific in-plant streams seems to be an attractive technical and economical approach because it allows for the use of advanced technologies such as membrane filtration. (3) (4)

In the case of pulp and paper industry, membrane filtration has been studied and applied in recent years for various purposes, including treatment of end-of-pipe effluents and particularly for processing of in-plant streams for water, energy and sub-products recovery. Lignin and hemicelluloses valorization constitutes a major subject of research and development in the biorefinery framework. (5)

1.2 Aim

The main aim of the present work is to propose an alternative way to treat an alkaline extraction stage ('E'-stage) BPE from a sulphite pulp mill with a TCF bleaching process that works on an E-O-P sequence to produce dissolving pulp. This treatment by UF/NF focused not only on the concentration of the stream for possible water reuse and energy-efficiency, as also evaluates the fractionated streams for sub-products valorization in the perspective of future works in the biorefinery point of view.

2. Materials and methods

2.1 Bleaching plant effluent

Table 1 - Some characteristics of the BPE used in this investigation

pH	9,87
ρ (g/L)	1042
TSS (mg/g)	0,44
TS (mg/g)	28,83
Ash (mg/g)	14,23
Total lignin (g/L)	2,88
Acid soluble lignin (mg/g)	1,31
Klason lignin (mg/g)	1,05
Hemicelluloses (mg/g)	0,19
Arabinose (mg/g)	0,00
Galactose (mg/g)	0,00
Glucose (mg/g)	0,03
Mannose (mg/g)	0,03
Xylose (mg/g)	0,13
Others (mg/g)	11,52

The bleaching plant effluent (BPE) used in this investigation was supplied by the *Caima - Indústria de Celulose, S.A.* pulp mill based in Constância, Portugal. *Caima - Indústria de Celulose, S.A.* has an annual capacity around 125,000 tonnes of bleached TCF hardwood (*eucalyptus globulus*) dissolving sulphite pulp. This mill operates the bleaching sequence E-O-P, where the first step 'E' is an extraction stage using sodium hydroxide (NaOH) to continue delignification and to extract hemicelluloses remaining after the cooking. Between the bleaching steps, wash presses are inserted that remove the consumed chemicals and the dissolved reaction products. The first physicochemical of the 'E' stage BPE filtrate characterization is presented in **Table 1**.

2.2 Membranes

Molecular mass distribution of hemicelluloses and lignin from the BPE supplied by Caima - Indústria de Celulose, S.A. was determined by size exclusion chromatography (SEC), in order to evaluate the order of magnitude of the size of these macromolecules so that it was possible to choose some membranes, based on their manufacturer molecular weight cut-off (MWCO) that were potentially suitable to retain these compounds.

The performance of six alkali resistant membranes was investigated in a parametric study. Two tight UF flat-sheet polymeric membranes and four NF flat-sheet polymeric membranes. The characteristics of the membranes are given in ***Table 2***.

Table 2 - Data for the polymeric membranes tested in the experiments

Membrane	Process	Material	MWCO (kDa)	Operating conditions		
				pH_{max}	TMP_{max} (bar)	T_{max} (°C)
ALFA-LAVAL - ETNA01PP	UF	Composite fluoro polymer	1	11	10	60
ALFA-LAVAL - GR95PP		Polyethersulfone	2	13	10	75
ALFA-LAVAL - NF99HF	NF	Polyamide type thin film composite on polyester	$MgSO_4$ rejection ≥ 98%	10	55	50
KOCH - MPF36		Composite	1	13	35	70
NADIR - NP010		Polyethersulfone	1 – 1,4	14	40	95
NADIR - NP030		Polyethersulfone	0,5 – 0,7	14	40	95

Sources: (6), (7), (8), (9)

2.3 Equipment

Two types of experiments were performed in different modules configurations. However, most of the used equipment was the same in both studies.

The transmembrane pressure (TMP) in both studies, was calculated in the same way, following the ***equation [1]***.

$$TMP = \frac{P_{in} + P_{out}}{2} - P_p \qquad [1]$$

Where P_{in} and P_{out} are the pressures at the inlet of the feed and the outlet of the retentate. Since there was no valve on the permeate side of the membranes, it was assumed that it is atmospheric pressure at the permeate side (P_p). The frictional pressure drop (ΔP) was calculated as the difference between the inlet (P_{in}) and outlet pressure (P_{out}).

The main components of the laboratory equipment used in the experiments were two heat controlled tanks, the feed tank with a capacity of 15 liters and the water tank with a capacity of 5 liters. Two Pt-100 temperature sensors (Pentronic, Gunnebo, Sweden) were immersed in the feed and in the water tank, both connected to temperature regulators (Shinko MCM, Shinko Europe BV, Haarsteeg, the Netherlands) controlling the temperature in the tanks by electrical heaters. A displacement pump (Hydra-cell D25XL, Wanner, Minneapolis, MN, USA) connected to a frequency converter (ELEX 4000, Bergkvist & Co., AB, Gothenburg, Sweden) controlling the cross-flow velocity (CFV). The pressure was regulated by a manual valve on the retentate line, with two pressure transmitters (Trafag DCS40.0AR, Regal Components AB, Uppsala, Sweden) placed at the inlet and the outlet. The permeate flows were measured with electronic balances (PL6001-S, Mettler-Toledo Inc., Columbus, OH, USA). Three stainless steel test sieves in series with 250μm, 180μm and 45μm pores respectively (Endecotts, London, England) were used to pre-filtrate the feed solution.

In this parametric studies four flat-sheet membrane modules were connected in parallel, as shown in ***Figure 1***.

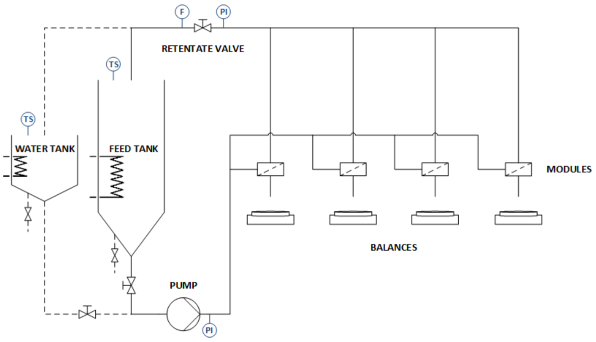

Figure 1 - Flow sheet of the equipment used in the flat-sheet membrane for parametric studies experiments. F = flowmeter, PI = pressure indicator, TS = temperature sensor

Only three of four modules connected in parallel were used simultaneously with different flat-sheet membranes. Each module was equipped with a circular flat membrane with an area of 0,00196 m^2.

During concentration studies all the equipment aforementioned was used, with the change of the four flat-sheet membrane modules in parallel for one DDS LabStak® M20. This module was equipped with two double-sided membrane discs with a total membrane area of 0,072 m^2. Instead of one feed thank with 15 liters capacity, one feed tank with 200 liters was used and the temperature was controlled by a steam coil. The 15 liters capacity tank was used as water tank, and the 5 liters water tank was removed.

In both studies, parametric and concentration, all balances, pressure indicators, temperature sensors and flowmeters were connected to a computer and all the data were recorded using the *LabVIEW® 2009* software (National Instruments Co, Austin, TX, USA).

2.4 Operating procedure

The membranes were cleaned with the alkaline cleaning agent Ultrasil 10 (Ecolab AB, Älvsjö, Sweden) for 1 hour at the concentration of 0,5 wt%, the temperature of 50°C, a TMP of 3 bar and a CFV of 0,5 ms^{-1} before the experiments were performed. After this was the system rinsed several times with deionized water. Then the pure water flux (PWF) for the new membranes (J_{wi}) was measured at 30°C and a CFV of 0,3 ms^{-1}, with the TMP range from 2 to 10 bar with a step size of 2. Flux was measured for 5 minutes at each pressure.

In order to investigate the influence of operating parameters on flux and retention levels, parametric studies were performed in which the CFV and TMP were varied. During the parametric studies, both the retentate and permeate were recycled to the feed tank in order to keep the concentration constant.

Only three membranes could be used simultaneously and there were six membranes to test, then were split in two series. So the first three membranes selected were the MPF36, NP010 and GR95PP. Experiments were performed at maximum temperature of the polymeric membranes, which means that the temperature was 70°C for these first three membranes, where the MPF36 had the lowest value of T$_{max}$ between the first three choices, see ***Table 2.*** For the other three membranes, NP030, NF99HF and ETNA01PP the parametric studies were performed at 50°C, which was the limiting temperature for the NF99HF, see ***Table 2.***

The tested CFVs were 0,4 and 0,8 ms^{-1} during the experiments. To minimize the risk of cake formation at the membrane surface, each experimental series was begun at the highest CFV and lowest TMP. The TMP was increased step-wise to the highest value and permeate samples were taken for each TMP. The TMP was then decreased to the lowest possible value and waited up to half an hour to remove the formed filter cake. After this, the CFV was reduced and then the TMP was increased step-wise again at the new velocity. Measurements were carried out for 15 minutes at each set of experimental conditions.

The MPF36 and NF99HF membranes were found to be the most suitable in the parametric studies, but only NF99HF was used in the concentration studies.

During the concentration studies, two double-sided membrane discs from DDS LabStak® M20 module were stacked by four NF99HF flat-sheet membranes and support paper. Both retentate and permeate were initially recycled to the feed tank, initially charged with approximately 67 liters of sieving BPE. The CFV was set to 0,8 ms^{-1}, and the temperature used was 50°C, that was the maximum operation temperature recommended by the manufacturer and the temperature used on the parametric studies for the selected membrane. Then the TMP was gradually increased to the final operating pressure of 13 bar. The concentration was then increased by withdrawal of permeate while recirculating the retentate. The experiment was interrupted at a volume reduction (VR) of 0,68, corresponding to a volume reduction factor (VRF) of 3,125. VR is defined as the ratio between the volume of the permeate (V_p) and the initial volume of the feed (V_0). VRF is the ratio between the initial feed volume and the volume of the resulting retentate. VRF and VR are correlated by ***equation [3]***.

$$VR = \frac{V_p}{V_0} \qquad [2]$$

$$VRF = \frac{1}{1 - VR} \qquad [3]$$

Samples were taken for the retentate and permeate side with a VR step-size of 0,1 for further analysis.

After each experimental series, in both parametric and concentration experiments, the PWF of fouled membranes (J_{w^*}) was measured, to evaluate the membrane fouling after the experiments. After that the membranes were chemical cleaned and the PWF of the regenerated membranes (J_w) was measured again. Both PWFs, for fouled and regenerated membranes, were conducted at 30°C and a CFV of 0,3 ms^{-1} with the TMP range from 2 to 10 bar with a step size of 2. Flux was measured for 5 minutes at each pressure.

2.5 Analysis

Total solids (TS) content was determined by taking 10 ml (5 ml in some cases) of each sample to dry in weighed porcelain crucibles in an oven at 105 °C for 24 h. After this were the porcelain crucibles putted in a desiccator for 30 min before weighed once again.

The dried samples were then put in an oven where they were first heated up to 250°C and maintained this temperature for 30 min and then to 575 °C for 180 min. After this, the samples were cooled down to 200°C in the oven with the door ajar before being placed in a desiccator to cool for another 30 min and then weighed. The weigh difference was the ash content.

For the measurements of Total suspended solids (TSS), 10 ml samples were filtrated through a pre-weighed glass microfiber filter Whatman Grade GF/B with 1,0 µm pores size. Filters with matter were dried in an oven at 105 °C for 24 h. After this were the filters putted in a desiccator for 30 min before weighed once again.

The concentration of lignin was determined by measuring the UV absorbance at a wavelength of 280 nm in a spectrophotometer (UV-160, Shimadzu Corp., Kyoto, Japan). To measure the total lignin content of the samples were they first diluted with deionized water. The extinction coefficient of 24,3 l/g cm was used. (10) It should be noted that besides lignin, pectin degradation products have strong UV absorbance at 280 nm. (9) Thus, the presence of these substances could lead to an overestimation of the lignin concentration.

In order to measure the content of sugar in the samples and the share of acid-insoluble and acid-soluble lignin, the samples were subjected to acid hydrolysis. The acid hydrolysis was performed by adding 1,5 ml (0,75 ml in some feed samples) of 72% sulphuric acid to 10 ml of the permeates samples (20 ml in the feed samples). The hydrolysis was then performed in an autoclave for around two hours.

Filter crucibles were taken from the oven at 105 °C and put in a desiccator for 30 min before it was weighed. Then is the fluid from acid hydrolysis vacuum filtered through the filter crucible. The filtrate is put in a container before some deionized water is used to rinse the hydrolysis bottle to get the lignin stock in it. This fluid is then vacuum filtered through the filter crucible. Next is the filter crucibles dried in an oven at 105 °C for 24 h and after being in a desiccator for 30 min is they weighed. The weigh difference was the content of Klason lignin.

The fluid from the vacuum filtration is used for the analysis for acid-soluble lignin. The content of acid-soluble lignin is measured by the UV absorbance at a wavelength of 320 nm of the fluid in a spectrophotometer (UV-160, Shimadzu Corp., Kyoto, Japan). The extinction coefficient of 15,0 l/g cm was used. (11)

The filtrate from the acid hydrolysis was also used to determine the sugar content in the samples. Before the analysis, the samples were filtrated through a 0,20 µm syringe filter. The samples were analyzed by high-performance liquid chromatography (HPLC) in order to find the concentration of monomeric sugars in the samples. The chromatography system (ICS-3000, Dionex Corp., Sunnyvale, CA) was equipped with a Carbo Pac PA1 analytical column (Dionex Corp.). The used eluent was deionized water at a flow rate of 1 ml/min and a solution of 200 mM NaOH dissolved in 170 mM sodium acetate was used to clean the column. The volume of the sample injection was 10 µl. The sum of the monomeric sugars after anhydro corrections of 0,88 and 0,90 for pentoses and hexoses, respectively, was used to define the concentration of hemicelluloses.

For determination of the total organic carbon (TOC) content of the samples, a TOC-5050A analyzer (Shimadzu Corp., Kyoto, Japan), consisting of an ASI-5000A autosampler (Shimadzu), a combustion tube, a reaction vessel and a non-dispersive infrared gas (NDIR) detector was used. The total carbon (TC) content and the inorganic carbon (IC) content were measured in the system and the TOC content determined by subtracting the IC content from the TC content.

The temperature in the combustion tube during TC measurement was 680°C and high-purity air was used as carrier gas, passing through the system at a constant flow of 150 ml/min. The sample volume injected into the combustion tube was 32 µl. Standard solutions of potassium hydrogen phthalate in deionized water at concentrations of 500, 250, 125, and 50 mg C/l were used for calibration. During IC measurement, the carrier gas was flowing in form of tiny bubbles through the reaction vessel, filled with water acidified with IC reagent (phosphoric acid). A sample volume of 40 µl was injected into the reaction vessel. Standard solutions of sodium hydrogen carbonate and sodium carbonate in deionized water at concentrations of 500, 250, 125, and 50 mg C/l were used for calibration.

The molecular mass distribution of hemicelluloses and lignin was determined by size exclusion chromatography (SEC) using a Waters 600E chromatography system (Waters, Milford, MA, USA) equipped with a refractive index detector (model 2414, Waters) and an ultraviolet detector operating at 280 nm (486, Waters). The analytical column was packed with 30 cm Superdex 30 and 30 cm Superdex 200 (GE Healthcare, Uppsala, Sweden). A 125 mM NaOH solution was used as eluent at a flow rate of 1 ml/ min. The system was calibrated with polyethylene glycol (PEG) standards with peak molecular masses of 0,4, 4, 10 and 35 kDa (Merck Schuchardt OHG, Hohenbrunn, Germany). Both the feed and the permeate samples were filtrated through a 0,20 µm syringe filter before the analysis.

3. Results and discussion

3.1 SEC of the BPE

Molecular mass distribution of hemicelluloses and lignin was measured by size exclusion chromatography (SEC). The SEC diagram of the untreated BPE, is shown in ***Figure 2***.

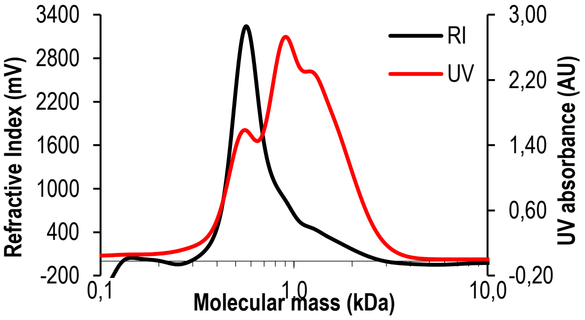

Figure 2 - Molecular mass distribution of lignin (measured as UV absorbance at 280 nm) and hemicelluloses (measured as refractive index) of untreated BPE.

It shows that lignin and hemicelluloses in the BPE have low and similar molecular masses, which makes the separation between these two components almost impossible.

Since it seems impossible to separate the hemicelluloses and the lignin presents in the BPE, the aim changes to concentrate the BPE by membrane filtration. Thus, mass average molecular masses ($\bar{M}_w$) were calculated, by ***equation [4]*** in order to facilitate the choice of the membranes that would be tested.

$$\bar{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \qquad [4]$$

Where N_i is the value of refractive index or UV absorbance for hemicelluloses and lignin respectively of molecular mass M_i. Mass average molecular masses of 0,88 kDa and 1,32 kDa were obtained for hemicelluloses and lignin, respectively. Based on it, was chosen to test some tight UF membranes (MWCO ≤ 2 kDa) and NF membranes (MWCO ≤ 1 kDa), already mentioned in the ***Table 2***.

3.2 Hydraulic permeability of the membranes

After being cleaned and rinsed several times, it was determined the hydraulic permeability with deionized water for all membranes. This determination is important because it serves as a reference to evaluate the fouling and cleaning performance after the experiments.

Hydraulic permeability (L_p) is the line slope of pure water flux (J_{wi}) as a function of transmembrane pressure (TMP) applied.

$$J_{wi} = L_p \times TMP \qquad [5]$$

Since different temperatures were used along this work, to be able to discuss the results, all the permeability values were adjusted to a standard temperature of 25°C. The correlation [6 used takes into account the pure water viscosity changes with temperature, which influences the flux and consequently the hydraulic permeability.

$$L_{p\,25°C} = \left(\frac{L_p}{0,901}\right) e^{\left(-6,96+\frac{2044}{273,15+T}\right)} \qquad [6]$$

Where L_p is the hydraulic permeability at the temperature T in °C. Values for the hydraulic permeability for each tested membrane at corrected temperature are shown in ***Table 3***.

Table 3 - Hydraulic permeability (Lp) of the membranes tested (1st usage).

Membrane	Linear regression	L_p (Lh^{-1}m^{-2}bar^{-1})	$L_{p\,25°C}$ (Lh^{-1}m^{-2}bar^{-1})
ETNA01P	$J_{wi} = 26{,}80 \times \text{TMP}$	26,8	23,9
GR95PP	$J_{wi} = 32{,}07 \times \text{TMP}$	32,1	28,6
NF99HF	$J_{wi} = 24{,}07 \times \text{TMP}$	24,1	21,5
NP010	$J_{wi} = 70{,}77 \times \text{TMP}$	70,8	63,2
NP030	$J_{wi} = 13{,}13 \times \text{TMP}$	13,1	11,7
MPF36	$J_{wi} = 23{,}57 \times \text{TMP}$	23,6	21,1

3.3 Parametric studies

Parametric tests are performed in a closed loop and are aimed to determine the crossflow velocity (CFV) and the transmembrane pressure (TMP) which provides greater flux and selectivity.

The influence of the TMP applied in the permeate flux (J_v) at different cross flow velocities for each membrane tested are shown in ***Figure 3*** and ***Figure 4***.

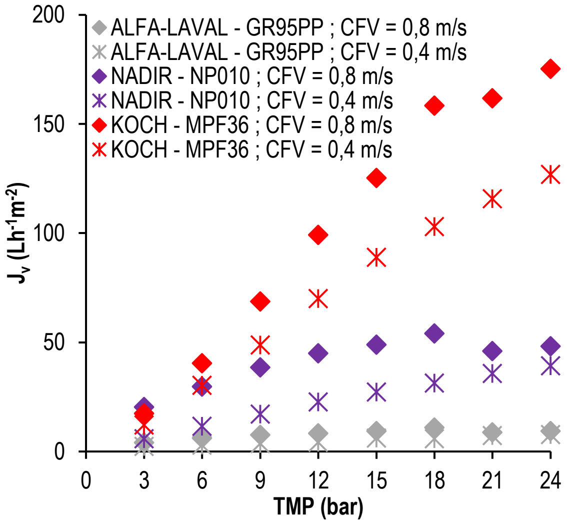

Figure 3 - Influence of the TMP and CFV on the permeate fluxes (Jv) for the first membrane series. T = 70°C

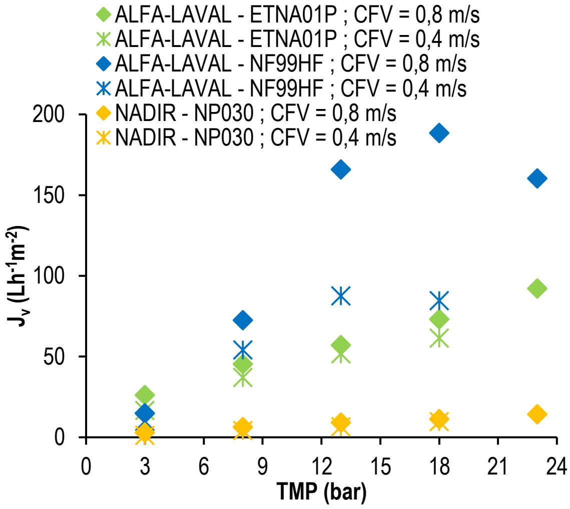

Figure 4 - Influence of the TMP and CFV on the permeate fluxes (Jv) for the second membrane series. T = 50°C

For some membranes, at higher pressures the permeate flux (J_v) is no longer significantly affected by the TMP, it levels off to almost constant values. This constant flux is called "limiting flux" and is independent of membrane resistance. For other membranes, we had more than one linear region till we got the "limiting flux", but we will only consider the first one.

The figures above allows us to conclude that at the higher CFV tested, 0,8 ms^{-1}, lead consistently a higher permeate flux. Thus, all the values presented hereafter are related to this CFV.

The performance of a membrane filtration process is usually assessed in terms of the magnitude of the permeate flux and the separation performance of the membrane. The ability of the process to separate components from each other can be assessed by comparing the retention of the individual components. In membrane processes the apparent retention (R_{obs}) was given by ***equation [7].***

$$R_{obs} = 1 - \frac{C_p}{C_b} \qquad [7]$$

Where C_p and C_b , denotes the concentration of the component in the permeate and in the bulk solution respectively.

Assuming as main goal the retention of total lignin ($R_{total\ lignin}$), ***Figure 5*** and ***Figure 6*** presents the different retentions for all the membranes tested at different conditions.

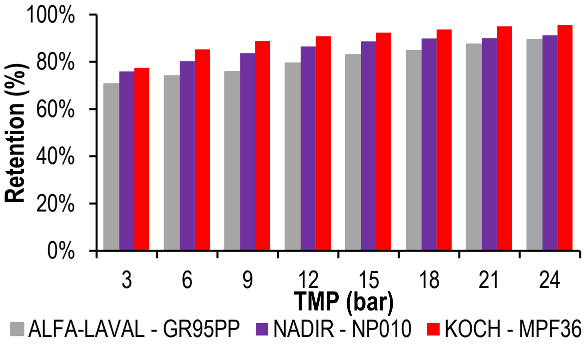

Figure 5 - Influence of the TMP on total lignin retention for the 1st membrane series tested in the parametric studies. T = 70°C, CFV = 0,8 ms^{-1}

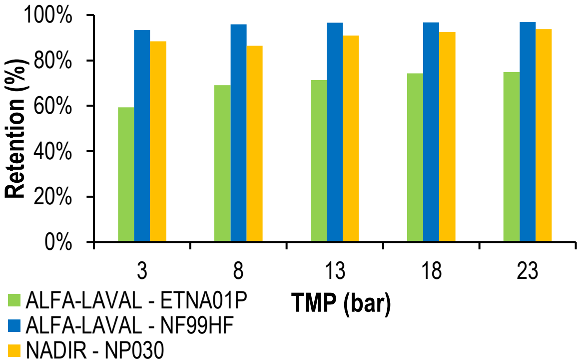

Figure 6 - Influence of the TMP on total lignin retention for the 2nd membrane series tested in the parametric studies. T = 50°C, CFV = 0,8 ms^{-1}

To conclude,

Table 4 has been added with values for the chosen optimal conditions, within their linear regions, for each membrane tested. Where the MPF36 and NF99HF membranes were found to be the most suitable in these parametric studies, due to their higher permeate fluxes and total lignin retentions.

Table 4 - Permeate flux (J_v) and total lignin retention ($R_{total\ lignin}$) at the maximum TMP within the linear region, for the membranes at CFV = 0,8 ms^{-1}.

Membrane	**GR95PP**	**NP10**	**MPF36**
Temperature		70°C	
TMP_{max}	9	9	15
J_v (L h^{-1}m^{-2})	8	39	125
$R_{total\ lignin}$	76%	84%	92%
Membrane	**ETNA01PP**	**NF99HF**	**NP030**
Temperature		50°C	
TMP_{max}	8	13	23
J_v (L h^{-1}m^{-2})	45	166	14
$R_{total\ lignin}$	69%	97%	94%

In addition to lignin retention, focused on the most suitable membranes, hemicelluloses (based on total sugars), total solids and ash retentions were calculated.

As the objective of NF was to concentrate the BPE and retain most of lignin and hemicelluloses, ***Figure 7*** and ***Figure 8*** presents the influence of the TMP on hemicelluloses, total solids and ash retentions.

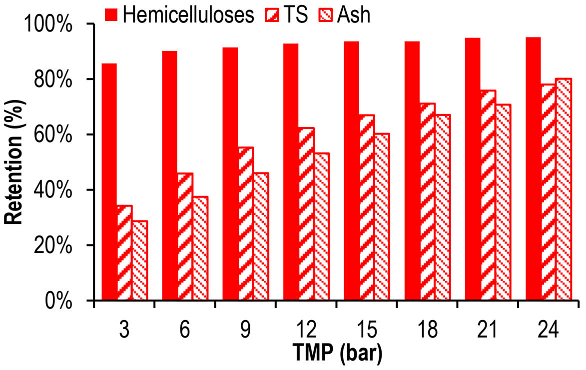

Figure 7 - Influence of the TMP on hemicelluloses, total solids (TS) and ash retention for the MPF36 membrane. T = 70°C, CFV = 0,8 ms^{-1}

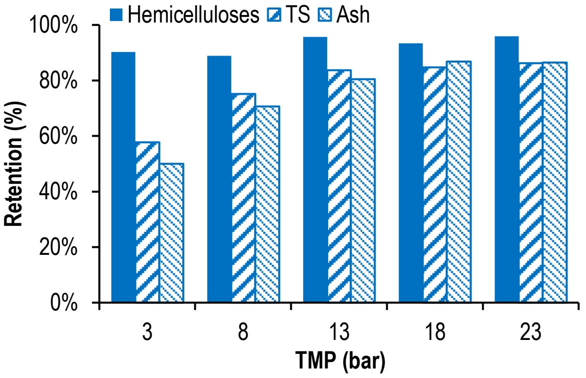

Figure 8 - Influence of the TMP on hemicelluloses, total solids (TS) and ash retention for the NF99HF membrane. T = 50°C, CFV = 0,8 ms^{-1}

It was possible to achieve high retentions of hemicelluloses (based on total sugars retentions) in both membranes. However, ash rejections and consequently total solids rejections were higher at lower TMP on the NF99HF membrane according to their manufacturer rejection of $MgSO4 \geq 98\%$, which is an indication that this membrane has better characteristics to retain inorganic salts.

Permeates from nanofiltration experiments conducted at the optimal conditions for the two most suitable membranes were analyzed by size exclusion chromatography (SEC). Once we have higher retentions for total lignin and hemicelluloses (based on total sugars) for NF99HF membrane in comparison with MPF36 it was expected that the SEC diagrams could support that. In ***Figure 9***, the SEC diagram for permeate of NF99HF membrane, shows really low peaks for total lignin and hemicelluloses content, which agrees with the higher retentions, between 95 and 97%, of these compounds in this membrane in such operating conditions.

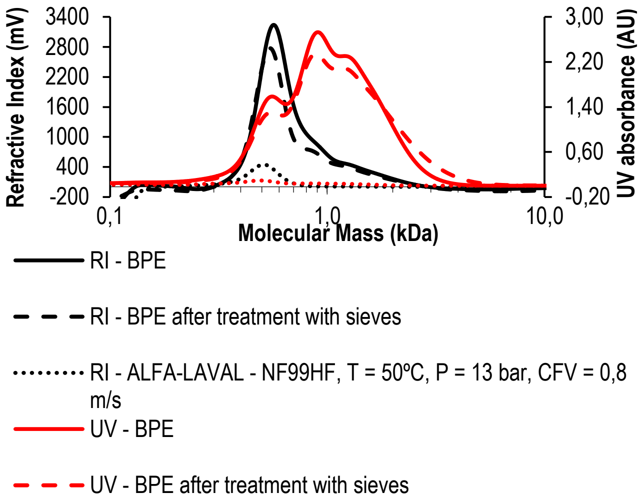

Figure 9 - Molecular mass distribution of lignin (measured as UV absorbance at 280 nm) and hemicelluloses (measured as refractive index) in the BPE, BPE after sieving and permeate of NF99HF membrane. T = 50°C, P = 13 bar, CFV = 0,8 ms^{-1}

In order to evaluate the molecular masses that permeate thru each membrane, mass average molecular mass of lignin and hemicelluloses for the feed after sieving and permeates for each membrane, values shown in ***Table 5***.

Mass average molecular mass for the hemicelluloses were the same in the two different membrane permeates, and lower than the feed. However, for the lignin, MPF36 membrane permeate present the same mass average molecular mass than the feed, but NF99HF have lower value. It could be to the fact that NF99HF have tightest pores in comparison with MPF36, which only smaller lignins were permeable.

Table 5 - Mass average molecular mass of lignin and hemicelluloses for feed BPE, MPF36 (T = 70°C, P = 15 bar, CFV = 0,8 ms^{-1}) and NF99HF (T = 50°C, P = 13 bar, CFV = 0,8 ms^{-1}) permeates.

	BPE	**MPF36 permeate**	**NF99HF permeate**
Hemicelluloses $\bar{M}_w$ (kDa)	0,88	0,52	0,52
Lignin $\bar{M}_w$ (kDa)	1,60	1,60	0,88

The study of resistance to mass transfer were analyzed by the resistance in series model.

It was considered that the total resistance results from a series of resistances, ***equation [8]***. Constituted by the membrane resistance (R_m) and the resistance caused by fouling divided into two contributions, the reversible resistance by fouling (R_{rev}) and irreversible resistance by adsorption (R_{irrev}).

$$R_t = R_m + R_{rev} + R_{irrev} \qquad [8]$$

The membrane resistance (R_m) corresponds to the resistance that the membrane offers to the passage of pure water. The value of this parameter is derived from the hydraulic permeability (L_p) presented previously in ***Table 3***.

$$J_{wi} = \frac{TMP}{\mu_w \times R_m} \Leftrightarrow R_m = \frac{1}{\mu_w \times L_p} \qquad [9]$$

The total resistance (R_t) is obtained by the BPE permeability (L_v) from ***Figure 3*** and ***Figure 4***.

$$J_v = \frac{TMP}{\mu_p \times R_t} \Leftrightarrow R_t = \frac{1}{\mu_w \times L_v} \qquad [10]$$

The value of R_{t^*} is the sum of intrinsic resistance of the membrane (R_m) and its irreversible resistance (R_{irrev}) which was not removed by water circulation. Its value is calculated from the hydraulic permeability values after the parametric studies (fouled membranes) (L_{w^*}).

$$J_{w^*} = \frac{TMP}{\mu_w \times R_{t^*}} \Leftrightarrow R_{t^*} = \frac{1}{\mu_w \times L_{w^*}} \qquad [11]$$

$$R_{irrev} = R_{t^*} - R_m \qquad [12]$$

The irreversible resistance (R_{irrev}) corresponds to the fouling caused by compounds adsorbed on the surface or within the pores of the membrane. This resistance cannot be eliminated only by passage of water, as the compounds are chemically bound to the membrane material.

Reversible resistance by fouling (R_{rev}) is the resistance due to concentration polarization and accumulation of solutes on the surface of the membrane, but not chemically bound thereto. This resistance disappears when it ceases to apply pressure in the system and only water passes, removing material existing on the surface of the membrane. Their value is obtained by ***equation [13]***.

$$R_{rev} = R_t - (R_m + R_{irrev}) \qquad [13]$$

Table 6 presents the results of the different resistances to the permeation of BPE, for two most suitable membranes in the parametric studies.

Table 6 - Different resistance types to permeation of BPE.

Resistance type	**Membrane**	
	NF99HF	**MPF36**
$R_m \times 10^{13}(m^{-1})$	1,67	1,71
$R_{rev} \times 10^{13}(m^{-1})$	3,23	4,62
$R_{irrev} \times 10^{13}(m^{-1})$	0,42	4,64
$R_t \times 10^{13}(m^{-1})$	5,32	10,97

One of the most important concerns for the application of the membranes is fouling, and chemical cleaning is therefore an integral operation for membrane filtration systems during effluents treatment. The permeability recoveries after washing and cleaning each membrane are presented in ***Table 7***.

Table 7 - Permeability recovery after washing and after cleaning.

Membrane	$\frac{L_{v\,25°C}}{L_{p\,25°C}}$ (%)	$\frac{L_{w^*\,25°C}}{L_{p\,25°C}}$ (%)	$\frac{L_{w\,25°C}}{L_{p\,25°C}}$ (%)
NF99HF	31%	80%	95%
MPF36	16%	27%	81%

3.4 Concentration studies

The influence of the volume reduction (VR) on permeate fluxes was studied by conducting an experiment in concentration mode. This concentration study was realized only with NF99HF membrane at the optimal conditions (T = 50°C, P = 13 bar, CFV = 0,8 ms^{-1}) that was found to be the most suitable for the aim of the project, due to their lowest membrane resistances, highest lignin and sugars retentions, higher permeate fluxes, and good cleaning conditions. As demonstrated before with parametric studies. The evolution of permeate fluxes during concentration of the BPE is presented in ***Figure 10***.

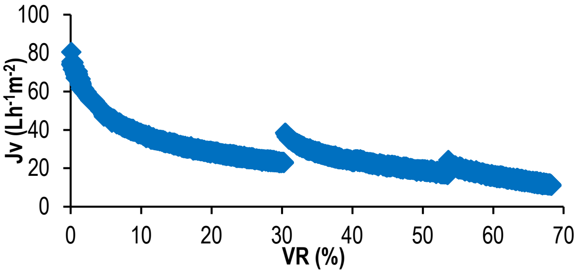

Figure 10 - Flux during concentration of process solution with NF99HF membrane. T = 50°C, TMP = 13 bar, CFV = 0,8 ms^{-1}

The initial flux of the NF99HF membrane was too much lower in the concentration study, 81 Lh^{-1}m^{-2}, compared with the parametric studies at the same operating conditions, 166 Lh^{-1}m^{-2}. This almost half initial permeate flux value could be justified for some reasons, a) very distinct modules configuration, parametric studies with a single circular flat membrane with 0,00196 m^2 against two double-sided membrane discs and support paper with a total membrane area of 0,072 m^2 in the concentration study. b) NF99HF membrane used in parametric studies was manufactured in 1997 and for the concentration study was manufactured in 2015. c) differences in CFV when changing the modules.

This concentration study was made in three consecutive days, for around 8h per day. During the nights, the system was left in total recirculation with the minimum TMP advised by manufacturer of the used module (around 3 bar) to keep the concentration levels until restart the work in the next day, at the same conditions. So, ***Figure 10*** shows two discontinuity points around 30% and 53,5% VR, which were the points that the system was left in total recirculation during the nights. At the first night the flux recovery was 19% and in the second night was 9%, this values shows that it was removed some of the accumulated solutes on the surface of the membrane, but not chemically bound thereto. This reversible resistances usually disappears when it ceases to apply pressure in the system and only water passes, however it was shown that it is possible to remove some of this cake layer by using total recirculation of the effluent and lower the TMP of the system.

During the days, the permeate fluxes decrease with the volume reduction factor, as a consequence of concentration polarization and membrane fouling, with a higher intensity of these phenomena when the concentration increases (higher volume reduction). Concentration study started with a flux of 81 Lh^{-1}m^{-2} and ended up with 11 Lh^{-1}m^{-2}, which represents a flux decline of 86,5%, till achieve 68% of volume reduction (VR), without any type of chemical cleaning.

During concentration studies, the increase of concentration leads with a slightly increase of a moving average of friction pressure drop (ΔP, the loss of pressure from the feed end to the concentrate end of a module) from 0,5 bar till around 0,7 bar.

Quantification of the concentration of BPE was analyzed by physicochemical characterization of concentrates and permeates. Experimental results for the feed (VR of 0%), concentrate and permeate at the end of the experiment (VR of 68%) are presented in ***Table 8***.

The main goal of this experiment was to promote the concentration of the effluent and retain valuable compounds such as lignin and hemicelluloses (measured in total sugars). Increasing Total Solids (TS) from 28,31 mg/g to 68,25 mg/g (from ≈3% to ≈7% (w/w)) it was achieved with a BPE volume reduction of 68%, this increase in TS concentration happened because permeable components were being removed and total lignin and hemicelluloses started to have a higher contribution in TS.

Table 8 - Physicochemical characterization of the feed (retentate at VR of 0%), concentrate and permeate for a VR of 68%

	Feed	Retentate	Permeate
pH	9,75	9,44	9,29
ρ (g/L)	1022	1031	1022
TS (mg/g)	28,31	68,25	26,96
Ash (mg/g)	14,35	32,53	14,58
Total lignin (g/L)	3,22	9,40	0,42
Acid soluble lignin (mg/g)	1,20	3,25	0,18
Klason lignin (mg/g)	1,51	6,09	0,06
Hemicelluloses (mg/g)	0,18	0,69	0,018
Arabinose (mg/g)	0,00	0,00	0,001
Galactose (mg/g)	0,00	0,00	0,000
Glucose (mg/g)	0,03	0,09	0,005
Mannose (mg/g)	0,02	0,09	0,004
Xylose (mg/g)	0,13	0,51	0,008
Others (mg/g)	10,56	25,62	11,95
Total carbon (g/L)	7,80	20,72	6,57
Inorganic carbon (g/L)	0,23	0,35	0,40
Total organic carbon (g/L)	7,57	20,36	6,17

Based on compositions for samples token for the retentate and permeate side with a VR step-size of 10% it was possible to evaluate the evolution of the apparent retention levels for each compound, as shown in ***Figure 11***.

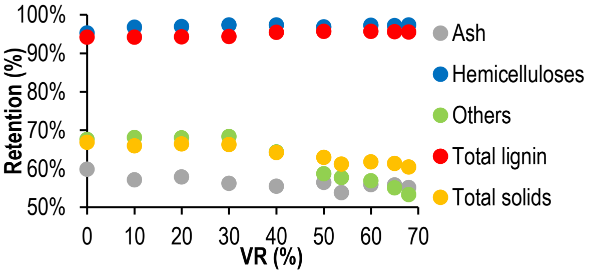

Figure 11 - Variation of apparent retentions with volume reduction (VR) for each component

Retention values for lignin and hemicelluloses remained almost constant between 94-97% with the increase of concentration. Which allows to say that NF99HF membrane, operating at 50°C a TMP of 13 bar and a CFV of 0,8 ms^{-1}, have a really impressive selectivity for these components, until a VR of 68%.

On the other hand, ash and consequently total solids rejections, in the beginning of experiments, were almost 20% lower than in the parametric studies. Furthermore, apparent retentions for these components were decreasing with the concentration. In the end of the experiment (VR = 68%) the retention for ash and total solids were 55,2% and 60,5% respectively.

Content of "Others", is the difference between total solids and ash, hemicelluloses and total lignin. As shown in ***Figure 11***, their retention decrease more than 15% between the beginning and the final of the study and it contributes to the decrease in total solids retention. So, it starts to have higher contribution in total solids content on the permeate side. In order to confirm that the "Others" could be organic matter, Total organic carbon (TOC) analysis were performed in the fractionated streams. Based on it, apparent retention evolution for TOC with VR is presented in ***Figure 12***.

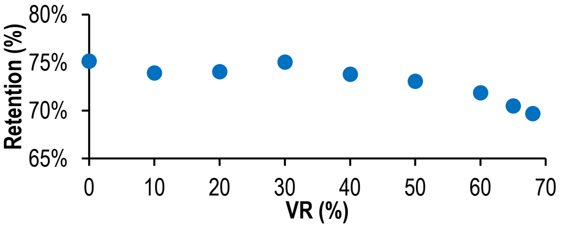

Figure 12 - Variation of TOC retention with volume reduction (VR)

The fall in TOC retention after the VR of 30% is in accordance with the fall in "Others" retention after the same VR. Besides the confirmation that "Others" is organic matter, it starts to have more contribution in the permeate streams with the increase of concentration, it arouses some curiosity in what type of compounds it could be. For that purpose, high performance liquid chromatography (HPLC) was employed with some standards, where acetic and formic acid had the higher contribution and credibility since the samples were complex, multicomponent mixture.

Permeates and retentate streams from concentration experiments were analyzed by size exclusion chromatography (SEC), SEC diagrams for molecular mass distribution of hemicelluloses, and lignin in the beginning and in the end of the experiments are presented in Figure 31 and Figure 32, respectively.

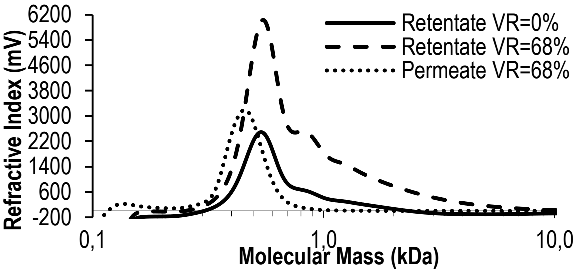

Figure 13 - Molecular mass distribution of hemicelluloses (measured as refractive index) for the feed (retentate at VR of 0%), concentrate and permeate for a VR of 68%

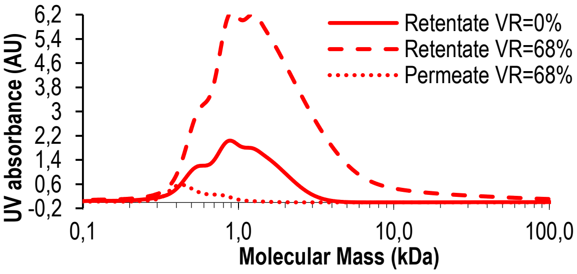

Figure 14 - Molecular mass distribution of lignin (measured as UV absorbance at 280 nm) for the feed (retentate at VR of 0%), concentrate and permeate for a VR of 68%

It was expected that the peaks in the final retentate stream would be higher than in the feed stream (Retentate at VR=0%), i.e. by ***Table 8*** the concentrations of hemicelluloses and lignin in the final retentate are around three and four times higher, respectively, in comparison with the feed stream due to the extremely high retentions of these compounds. Which are in accordance with the SEC diagrams presented above. However, for the final permeate stream it was not expected that the RI peak for hemicelluloses analysis would be higher than in the feed, i.e. by ***Table 8*** the concentration of hemicelluloses in the final permeate is around ten times lower than in the feed. Which is not in accordance with ***Figure 13***. So, it should be noted that, in the final permeate stream, some unknown compound is sensitive to the RI analysis beside hemicelluloses, which turns less credible the measurements of hemicelluloses by RI. In order to evaluate the molecular masses that permeates the membrane during concentration studies, the mass average molecular mass of lignin and hemicelluloses for the feed, final retentate and final permeate, values are shown in ***Table 9***.

Table 9 - Mass average molecular mass of lignin and hemicelluloses for the feed (retentate at VR of 0%), concentrate and permeate for a VR of 68%

	Feed	**Retentate**	**Permeate**
Hemicelluloses $\bar{M}_w$ (kDa)	0,79	1,77	0,48
Lignin $\bar{M}_w$ (kDa)	1,48	19,08	0,64

Since the rejection was not 100%, a very low quantity of some hemicelluloses and lignin are presented in the permeate side. However, their mass average molecular mass are lower than in feed, which proves that only the lowest molecular weight hemicelluloses and lignin are permeable. On the contrary, in the final retentate stream, high molecular weight components start to have higher contribution, which turns the mass average molecular mass of hemicelluloses and lignin higher.

After around 27 hours of concentrating the BPE in batch mode, membrane regeneration performance was evaluated. Linear regressions of each PWF against TMP are presented in ***Table 10***, as well as the permeability recoveries after washing and after chemical cleaning with the alkaline agent.

Table 10 - Hydraulic permeability values and permeability recovery, for new (L_p) after washing (L_{w^*}) and after cleaning (L_w)

L_p **(Lh⁻¹m⁻²bar⁻¹)**	$\frac{L_{w^*}}{L_p}$ (%)	$\frac{L_w}{L_p}$ (%)
26,7	38%	87%
L_{w^*} **(Lh⁻¹m⁻²bar⁻¹)**		
10,2		
L_w **(Lh⁻¹m⁻²bar⁻¹)**		
23,3		

The initial hydraulic permeability (L_p) of the NF99HF membrane is around 10% higher when compared with the measurements before the parametric studies, considering the big differences in modules configuration and membrane areas used, these values are not so misfits, which confirms the hydraulic permeability values for this membrane.

It was possible to recover 38% of their initial hydraulic permeability only with water washing after the concentration studies, this value is 42% lower than the value achieved after parametric studies. This value should be expected due to the higher operation time in concentration studies where the membrane get more fouled and leads with higher concentrations of compounds, in this case with more irreversible fouling, which is the one caused by compounds adsorbed on the surface or within the pores of the membrane and cannot be eliminated only by water circulation, as the compounds are chemically bound to the membrane material. Finally, after cleaning with an alkaline agent the hydraulic permeability recovery was 87%, which reveals again, as in parametric studies, that the chemical cleaning performed seems suitable for the process.

3.5 Cost estimates

The cost of a NF plant treating 70 m^3h^{-1} process solution was estimated based on the results of the concentration studies shown in ***Table 11***, and technico-economical data used in calculations are shown in ***Table 12***.

Table 11 - Experimental data used in the cost estimates

Feed flow, Q_{feed} (m^3h^{-1})	70
VR (%)	68%
CFV (ms^{-1})	0,8
TMP (bar)	13
Average flux, J_{av} ($Lh^{-1}m^{-2}$)	24,2
ΔP in each module (bar)	0,7

Table 12 - Technico-economical data

Investment cost (€.m^{-2})	2000[a]
Electricity price (€.kWh^{-1})	0,10[c]
Membrane replacement cost (€m^{-2})	95[a]
Membrane lifetime (year)	1,5[b]
Cleaning cost (€.m^{-2}year-^{1})	50[b]
Operating time (h.$year^{-1}$)	8000[b]
Pump efficiency (η)	0,8
Maintenance and labor (% of investment cost.$year^{-1}$)	5%[a]
Annuity factor (%)	10%[a]

[a] (12), [b] (9), [c] (13)

It was assumed that the plant will work in a single-stage feed and bleed process and will be equipped with a feed pump, a recirculation pump and Alfa Laval Flat Sheet Membrane Modules M38L/H (14) (Plate-and-frame configuration) equipped with NF99HF membranes.

The investment cost is composed of the cost of the plant and the cost of the membrane elements. For a first estimate of a large scale unit a 20% safety factor in the calculation of the membrane area was used.

Jönsson, et al., used an investment cost of 2000 € per m^2 of membrane area for an alkali resistant tubular polymeric nanofiltration membrane. (12) According to Table 2, tubular and plate-and-frame modules have both highly costs, so it should be reasonable use the same value to calculate the investment cost for this process. By this way, a total investment cost of 4,72M€ was predictable.

The operating costs consist on electricity, replacement of membranes, cleaning, maintenance and labour costs. Electricity is needed mostly for pumping. A feed pump will be needed to deliver the inlet pressure of the plant and a recirculation pump will be needed to compensate for the frictional pressure drop and to maintain the circulation flow in the membrane plant. The energy required per m^3 of permeate in the feed pump is given by ***equation [14]***, and in the recirculation pump by ***equation [14]***.

$$W_{feed} = \frac{TMP \times Q_{feed}}{\eta \times (VR \times Q_{feed})} = \frac{TMP}{\eta \times VR} \qquad [14]$$

$$W_{recirc} = \frac{\Delta P \times Q_{feed^*}}{\eta \times (J_{av} \times Membrane\ area)} \qquad [15]$$

The energy required by the feed pump is thus 0,66 kWh.m^{-3} of permeate and by the recirculation pump, 0,22 kWh.m^{-3}. Where, Q_{feed^*}, is the feed flow in the inlet of the modules. It was assumed that the $Q_{feed^*} = 7{,}5 \times Q_{feed}$. (15)

To summarize, both capital and operating costs are presented in ***Table 13***.

Table 13 - Cost estimates for NF installation with 8000h per year

Membrane area (m^2)	2360
Membrane modules	40
Investment cost (M€)	4,72
Capital cost (k€.$year^{-1}$)	**472**
Electricity required (kWh m^{-3} of permeate)	0,88
Electricity cost (k€ $year^{-1}$)	34
Membrane replacement cost (k€.$year^{-1}$)	150
Cleaning cost (k€.$year^{-1}$)	118
Maintenance and labor costs (k€.$year^{-1}$)	24
Operating costs (k€.$year^{-1}$)	**326**
Total cost (k€.$year^{-1}$)	**798**

Guiding principles for the energy requirement for evaporation is 30-40 kWh per m^3 water removed. (16) If it was considered an average of 35 kWh per m^3 of water removed with a price of 0,10 € per kWh, a cost of 3,5 € per m^3 of water removed in the case of evaporation was needed. However, in the NF process presented before 2,14 € per m^3 of permeate was achieved with capital costs included.

4. Conclusions

The use of UF/NF processes for the treatment of the E-stage BPE filtrate in a TCF sulphite pulp mill with an E-O-P bleaching sequence was evaluated.

Firstly, the BPE used in this investigation was submitted to a physicochemical analysis where it was found that is extremely diluted with around 3% (w/w) of TS, of which 50% was ash (inorganics) content due to the high quantity of caustic soda impregnated in the E-stage; the pH of the effluent is around 10.

The organic matter existing in the other half of the total solids composition, is of high interest. In the pulp and paper industries and biorefineries point of view, two compounds deserved our special attention: lignin and hemicelluloses. A concentration of 2,88 g/L for lignin and 0,19 mg/g for hemicelluloses was measured, in which xylans were the main polysaccharide (≈68%), with the raw material processed in the mill being hardwood (*eucalyptus globulus)*. By SEC analysis mass average molecular mass for both compounds was calculated being 1,32 kDa for lignins and 0,88 kDa for hemicelluloses. The fractionation of them looked hard due to the overlap and the very small difference between each one. With this being said, the aim of the project focused into concentrate both compounds.

For the pH and molecular masses of lignins and hemicelluloses presented before, two tight UF membranes (MWCO ≤ 2 kDa) and four NF membranes (MWCO ≤ 1 kDa), were chosen to test six alkali resistant membranes. Two of the NF membranes were found to be the most suitable for the process due to their high fluxes and high apparent retention levels for lignin and hemicelluloses, NF99HF and MPF36.

The best operating conditions tested for MPF36 were found to be at T=70°C, a CFV=0,8 ms^{-1} and a TMP=15 bar which gives a permeate flux (J_v) of 125 $L.h^{-1}m^{-2}$ with apparent retention levels of 92%, 94%, 67% and 60% for lignin, hemicelluloses, total solids and ash, respectively. For the NF99HF, the best operating conditions were found to be at T=50°C, a CFV=0,8 ms^{-1} and a TMP=13 bar, giving a permeate flux (J_v) of 166 $L.h^{-1}m^{-2}$ with apparent retention levels of 97%, 96%, 84% and 81% for lignin, hemicelluloses, total solids and ash, respectively.

By evaluation of the membrane resistances, it was found that MPF36 has more than twice of NF99HF due to its higher irreversible resistance (R_{irrev}), which corresponds to the fouling caused by compounds adsorbed on the surface or within the pores of the membrane. This resistance cannot be eliminated only by passage of water, as the compounds are chemically bound to the membrane material; indeed, the performance of membrane regeneration by a chemical cleaning with an alkaline agent was evaluated, in which 81% and 95% of PWF were recovered for the MPF36 and NF99HF membrane, respectively.

Due to its higher fluxes, retentions, less resistances and higher membrane regeneration performance, the NF99HF was found to be the most suitable for the process; using that membrane, concentration studies in a batch mode were also performed.

During almost 27 hours, 68% of volume reduction (VR) was achieved, in which the permeate flux decreased 87% from the beginning until the end of the experience, caused by a concentration polarization and fouling phenomena. An average flux (J_{av}) of 24,2 $L.h^{-1}m^{-2}$ was obtained and the frictional pressure drop (ΔP) had slightly increased from 0,5 to 0,7 bar.

With a VR of 68%, the TS concentration increased from 3% to 7% (w/w) in the retentate stream. The apparent retention levels for lignin and hemicelluloses remained almost constant between 94 and 97% which highlights the great selectivity of this membrane for these compounds. Lignin content increased from 3,2 g/L to 9,4 g/L and hemicelluloses content increased from 0,2 mg/g to 0,7 mg/g.

Total organic carbon (TOC) measurements were performed and for a VR of 68%, the permeate stream had a concentration of 6,2 g/L, having the feed stream started with 7,6 g/L. These results led to know which types of organic matter can be permeable; for that reason HPLC analysis was performed and it was detected the presence of acetic and formic acids.

Finally, cost estimation for an internal process modification of *Caima - Indústria de Celulose, S.A.*, which enables to concentrate their 70 m^3/h of the E-stage BPE until 68% of VR, leads to a necessary investment between 4,44M€ and 5,13M€. The NF plant would need a total membrane area of 2360 m^2, equipped with 40 Alfa Laval M38L/H modules (Plate-and-frame configuration).

The operating costs would be 326k€ per year which represents 0,87€ per m^3 of permeate or 2,14€ per m^3 of permeate if capital costs are included with an annuity factor of 10%.

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