Recovery of lignin and lignans enriched fractions from thermomechanical pulp mill process water through membrane separation technology: Pilot-plant study and techno-economic assessment

M. Villain-Gambier, M. Courbalay, A. Klem, S. Dumarçay, D. Trebouet

HAL Id: hal-02474260

https://hal.science/hal-02474260

Submitted on 11 Sep 2020

Recovery of lignin and lignans enriched fractions from thermomechanical pulp mill process water through membrane separation technology: pilot-plant study and techno-economic assessment.

M. Villain-Gambier[a], M. Courbalay[a,b], A. Klem[c], S. Dumarcay[b] and D. Trebouet[a].

[a]*Université de Strasbourg, CNRS, UMR 7178, F-67000 Strasbourg, France*

[b]*Université de Lorraine, Faculté des Sciences et Techniques, Laboratoire d'Etude et de Recherche sur le Matériau Bois (LERMAB), Bld des Aiguillettes, F-54500,Vandoeuvre-les-Nancy, France*

[c]*Norske Skog Golbey, Route Jean-Charles Pellerin, BP 109, 88194 Golbey, France*

Corresponding author:
Maud Villain-Gambier
Email: maud.villain@unistra.fr

Wordcount : 8477 words (with list of references, list of captions and nomenclature)

Abstract

Membrane process is a viable option for valuable compounds such as lignin and lignans recovery in aqueous discharges of thermomechanical pulp industries. Recovery of lignin and lignans with continuous mode ultrafiltration/nanofiltration installation has not been studied in detail previously. After flotation used to remove lipophilic matter of pulp mill effluent, the three steps membrane process was composed of a clarification step by a 150 kDa ultrafiltration used to remove suspended matter, followed by two nanofiltrations of 1 kDa and 300 Da to respectively retain lignin and lignans. A techno-economic evaluation of this process has been performed. The process with a plant capacity of 60 $m^3.h^{-1}$ was able to produce 12 tons of lignin and 825 kg of lignans per month. The influence of plant capacity between 0.1 and 60 $m^3.h^{-1}$ on extracts production cost allows determining a production cost equal or below 10 €kg^{-1} as plant capacity reached 10 $m^3.h^{-1}$. Valorization of lignin and lignans as parts of the formulas of high added value products could allow thermomechanical plants to head towards

biorefinery and cleaner production concepts. Furthemore, the 300 Da permeate possessed the required characteristics to be re used and save fresh water utilization.

Keywords: biorefinery, lignans, lignin, membrane process, techno-economic assessment, thermomechanical pulp mill.

1. Introduction

The pulp and paper manufacturing industry is one of the world's biggest water consumers. The industry suffers from poor water recycling rates and there is a need for clean technologies able reducing fresh water use (Leithe, 2018). In the main time, effluent discharge of such industries is composed of unexploited valuable organic content. Wood based polymers and chemical could potentially be produced on a large scale in parallel with pulp production, generating additional revenue streams for the industry. Paper pulp can be produced with thermomechanical process (TMP) which is a high yield process retaining more than 90 % of the wood biomass in the end product (Sundholm, 1999). The organic loss mainly composed of hemicelluloses, lignin, lignin carbohydrate complexes (LCC), lipophilic and phenolic extractives (*i.e.* lignans) is dissolved in the process water representing the main side stream of TMP installations. Whereas lignin from chemical pulp process has found industrial applications as filler, additive in agriculture or as compounds of biobased materials (Laurichesse and Averous, 2014), lignin from TMP water is not yet considered as a valuable compound. Nevertheless, its native structure due to the soft conditions of TMP could make it as a suitable candidate for depolymerisation into a wide variety of bulk and fine aromatic and phenolic chemicals (Kuznetsov et al., 2018). Lignans can also be considered as molecules of

interest due to their applications in pharmaceutical and nutraceutical fields with their biological properties (Willför et al., 2006).

Contrary to chemical pulp process waters containing high amounts of lignin and hemicelluloses (Humpert et al., 2016; Kevlich et al., 2017), in TMP waters the concentration of wood components do not exceed 1-3 g.L^{-1} (Zasadowski et al., 2014; Thuvander and Jönsson, 2016; Persson and Jönsson, 2017). Therefore, TMP waters are highly diluted side stream and they are currently not valorized and rejected to wastewater plants. However, their potential for valorization is significant as the flow rate of TMP water is of several hundred cubic meters per hour.

For the majority of mature chemical processes, separation step usually accounts for 60 to 80 % of the global process cost (Ragauskas et al., 2006). Dubreuil et al. (2017) have recently reported the need of cost-effective separation processes to fractionate biomass components at industrial scale.

Due to their low energy consumption and low impact on the biological molecules, their suitability as a separation technique for the recovery of substances at really low concentration, membrane techniques have recently received increased attention in the context of future biorefineries and cleaner production (*i.e.* for example reduction of water consumption and resources recovery) (Weinwurm et al., 2016; Dubreuil et al., 2017 ; Dilaver et al., 2018 ; Wang et al, 2019).

Membrane technology is a sustainable, soft and clean process where the separation does not have extensive heat or chemicals requirements. This latter advantage leads to end products of high quality, and makes it easier to comply with the many stringent requirements from both consumers and public authorities (Steinmetz et al., 2019). Many studies report the use of membrane technology for TMP waters fractionation for galactoglucomannans (GGM)

valorisation as biopolymer for example (Persson and Jönsson, 2010a; Thuvander and Jönsson, 2016) whereas only two studies had the objective of lignin and extractives valorisation (Persson et al., 2010b; Courbalay et al., 2018b). They are usually performed with discontinuous mode (*i.e.* batch and semi batch mode) with increasing volume reduction (VR) allows determining information on recovery rate of valuable solutes and permeate flow rate. In literature, only one article was found about hemicelluloses recovery in continuous pilot testing with TMP waters (Thuvander et al., 2019) whereas these continuous tests are essential to accurately evaluate techno-economic characteristics of large scale membrane installation. 30% of investment can be saved with optimal pilot testing (Suarez et al., 2015).

Therefore, as this type of study does not exist for joint recovery of lignin and lignans from TMP waters, the objectives of this study were to perform continuous pilot tests to (i) identify long-term performance parameters (the lifetime of membranes, their cleaning frequency as well as the type and impact of fouling), (ii) use these parameters to scale up the membrane process and (iii) perform a process economic evaluation and a cost estimation of produced extracts. Thanks to the model of Sethi and Wiesner (2000), this latter point (iii) aims at supplying information about investment and maintenance, which is usually dispersed, and setting out the relevant hypotheses, data and calculations to assess a complete membrane process cost.

The economic assessment of a membrane process and the production cost of generated lignin and lignans enriched fractions require the evaluation of both capital and operating expenditures named respectively CAPEX and OPEX.

The main CAPEX components include designing, constructing and installing membrane plant. OPEX is composed of amortization, energy, labor, membrane replacement and chemicals (cleaning and disposal) (Sethi and Wiesner, 2000).

Typically, these continuous experiments are performed at a representative scale (between pilot and semi-industrial scale) and they also allow producing larger quantities of valuable extracts. Therefore, companies from targeted markets could assess their interest for the fractions and membrane process could be adapted to reach quality requirements of specific markets. A feed capacity of 0.1 $m^3.h^{-1}$ was considered as an adequate scale as it would allow to supply partner companies in various fields of prospecting (food, nutraceutical, cosmetic, agriculture, chemistry, material). In order to assess the scale from which the economy of scale was noticeable, the influence of plant capacity from 0.1 to 60 $m^3.h^{-1}$ was assessed on CAPEX, OPEX and related production cost of extracts.

2. Materials and Methods

2.1 TMP water

Process water came from a TMP mill with a mix of spruces and pines used as raw material (Norske Skog, Golbey, France). Main characteristics of process water, called clear filtrates are presented in table 1.

Mean values and corresponding standard deviation of table 1 came from the analyses in triplicates of 26 sampling events of process water spread during the four seasons of three successive years (Courbalay, 2018a). Before utilization in membrane process, process water was floated to remove lipophilic extractives as terpenes, fatty and resin acids prior to filtration step 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.

Table 1

Parameter	Mean value of each parameter ± sd
pH	6.2 ± 0.2
Turbidity (NTU)	430 ± 110
Conductivity (μS.cm^{-1})	1180 ± 150
Concentration (mmol$_{eq\ NaCl}$.L^{-1})	10 ± 1
Dry matter (mg.L^{-1})	3780 ± 690
Ash (mg.L^{-1})	650 ± 5
Suspended matter (mg.L^{-1})	220 ± 80
Polyphenols (mg$_{GAeq}$.L^{-1})[a]	710 ± 60
Lignin (mg.L^{-1})	690 ± 70
Hemicelluloses (mg$_{Geq}$.L^{-1})[b]	1170 ± 180
Lignans (mg$_{CAeq}$.L^{-1})[c]	18 ± 14
Terpens and fatty acids (mg$_{HAeq}$.L^{-1})[d]	7 ± 11
Phenolic acids (mg$_{SA\ eq}$.L^{-1})[e]	0.5 ± 0.7

[a] mg$_{GAeq}$.L^{-1}: in gallic acid equivalent ; [b] mg$_{Geq}$.L^{-1}: in glucose equivalent ;

[c] mg$_{CAeq}$.L^{-1}: in 4-hydroxy-3,5-dimethoxycinnamic acid equivalent ;

[d] mg$_{HAeq}$.L^{-1}: in heneicosanoic acid equivalent ; [e] mg$_{SAeq}$.L^{-1}: in syringic acid equivalent

2.2 Membrane filtration

A combined ultrafiltration/nanofiltration (UF/NF) stainless steel made set up was used (Firmus, France). The internal feed tank capacity of the set up was of 70 L.

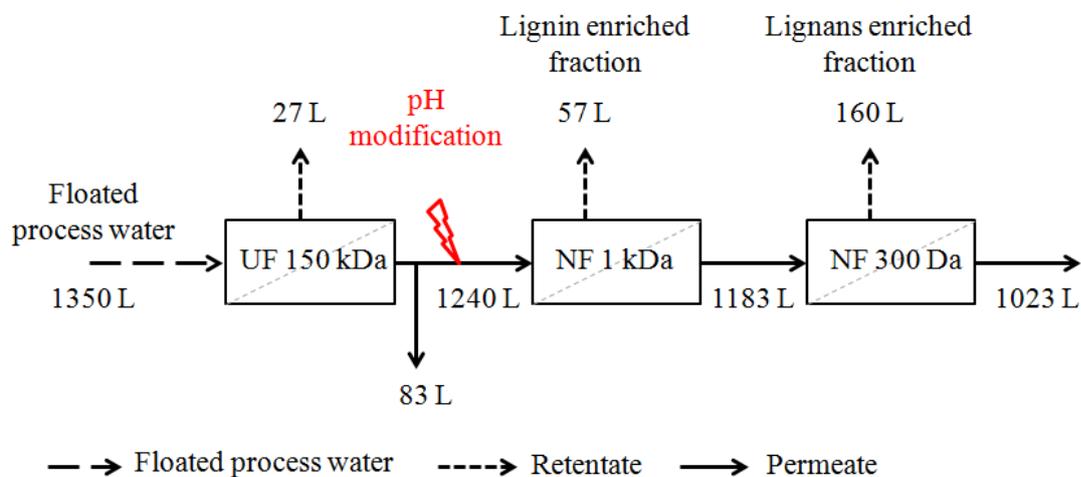The three successive filtration steps are presented in Figure 1.

Figure 1

150 kDa permeate pH was adjusted to 4 (acetic acid 13 mM). This pH was chosen thanks to a previous optimization study about the influence of 150 kDa permeate pH on 1 kDa and 300 Da membranes productivity (i.e. permeate flux), membrane fouling propensity and selectivity of 1 kDa membrane for high lignin retention and limitation of lignans retention. The different filtrations were realized in semi batch mode which means that retentate was recycled to the feed tank and permeate was withdrawn continuously. An additional pumping system was used to bring in feed tank a feed flow equal to the permeate flow in order to maintain a constant retentate volume. This method allows filtration of large volumes of process water and obtention of high VR. VR was calculated as the ratio between permeate and feed volumes.

The characteristics of the membranes used in these experiments are presented in Table 2.

Table 2

Membrane type	UF 150 kDa	NF 1 kDa	NF 300 Da
Module type	Ceramic tubular		Organic Spiral wound
Membrane material	TiO_2-ZrO_2		Polyamide
Number of channels	19	61	-
Dimensions (mm)			
Lenght	1,178		
External diameter	25		
Hydraulic diameter (d_h)	3.5		
Membrane Area (A_m) (m^2)	0,245	0,45	2,6
Supplier	Orelis environnement/Kleansep[TM]		GE Power & Water
Reference	KLMBWU3	KLMBWN1	DL2540F30
Transmembrane pressure (bars)[a]	2.5	6.4	6.0
Temperature (°C)	60		48
Cross flow velocity (u) ($m.s^{-1}$)[a]	5		1

[a]Optimized transmembrane pressure and cross flow velocity were determined at pH 6.2 for 150 kDa membrane and pH 4 for 1 kDa and 300 Da.

The filtrations were realized at optimized operating conditions (Table 2) (*i.e.* transmembrane pressure and cross flow velocity) obtained for each membrane in total recirculation mode (retentate and permeate were totally recycled to the feed tank). Pressures, temperature, permeate and retentate flows were recorded on a data acquisition device (Ecograph T, Endress+hauser). The different filtration steps were running at constant transmembrane pressure. This way of operation implied that permeate flux decreased with time due to membrane fouling.

Transmembrane pressure was calculated as the difference between the average pressure between the inlet and outlet pressures on membrane module and permeate pressure.

Retention rate (RR) of targeted compounds, expressed as a percentage, was calculated with the following equation (1):

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

Where C_{feed} and $C_{permeate}$ represent respectively the concentration in the feed and permeate of targeted compounds.

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. Total phenolic content was analyzed with the Folin-Ciocalteu colorimetric method (760 nm) (Singleton et al., 1999). To obtain hemicelluloses content of samples expressed in glucose equivalent, the colorimetric anthrone method was used (625 nm) (Dubois et al, 1956). For phenolic (lignans and phenolic acids) and hydrophobic extractives (terpenes and fatty acids) identification, Gas Chromatography (GC)-Mass Spectrometry (MS) method was adapted from Kebbi-Benkeder et al. (2014). 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):

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

Concentration of lignin was then obtained with the ratio between the mass of lignin on initial volume of process water sampled.

2.4 Techno-economic evaluation

2.4.1 Dimension calculations of membrane set-up with capacity of 0.1 $m^3.h^{-1}$

Membrane set up was developed to treat 0.1 $m^3.h^{-1}$ of floated process water. Calculations of required membrane area for each filtration stage (A_{m150}, A_{m1}, A_{m300}) were performed with equation (3) (expressed for A_{m150} assessment).

$$A_{m150} = \frac{Q_{150}}{J_{150}}$$ (3)

Q_{150} corresponds to the total feed flow entering 150 kDa UF in $L.h^{-1}$. J_{150} is the mean 150 kDa permeate flux in $L.m^{-2}.h^{-1}$ obtained in part 3.1.1.

Recirculation rate for filtration with ceramic membranes (150 and 1 kDa membranes) was calculated by multiplying the cross flow velocity (u in $m.s^{-1}$) by the membrane total section (S in m²). S was obtained with the equation (4):

$$S = \frac{d_h \times p_e}{4}$$ (4)

where d_h corresponds to the hydraulic diameter of the membrane and p_e is the total perimeter of membrane channels. Both parameters are expressed in m.

Recirculation rates in 300 Da spiral wound membrane modules are data obtained from the membrane supplier. A flowchart with techno-economic procedure is presented in figure 2.

9
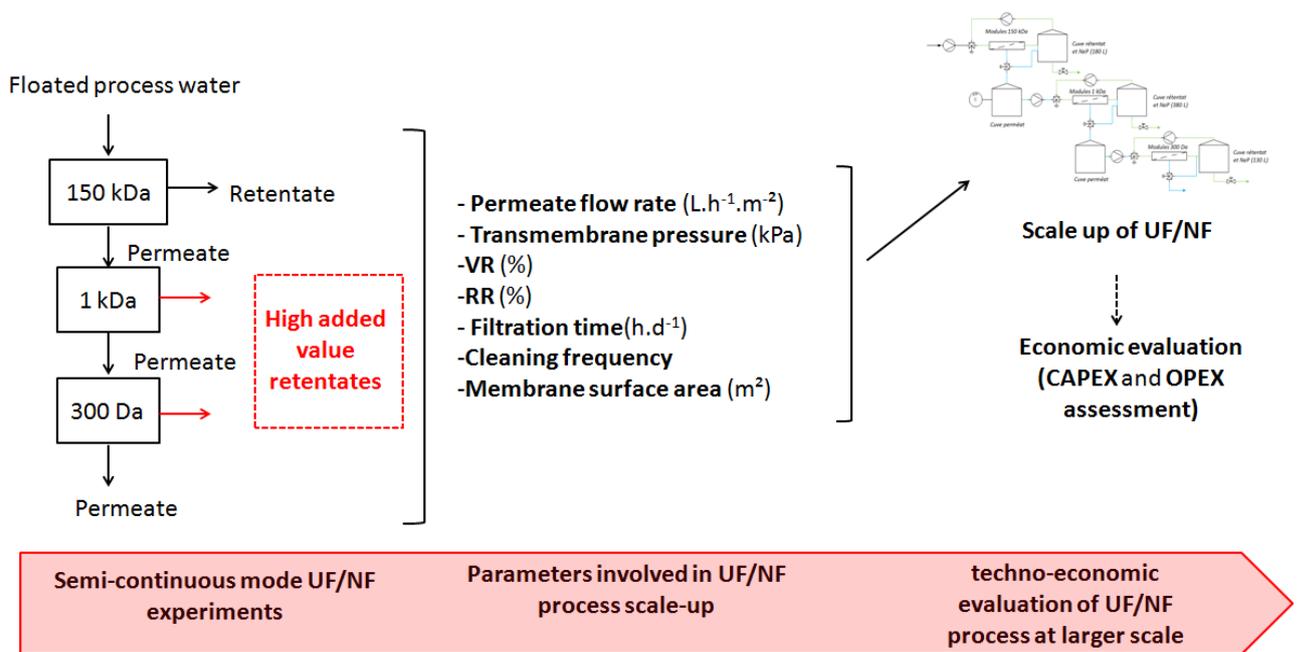
Figure 2

2.4.2. Economic evaluation

The model developed by Sethi and Wiesner (2000) and adapted by Suarez et al. (2015) was used to assess the CAPEX and OPEX of membrane process with a treatment capacity of 0.1 $m^3.h^{-1}$.

Calculation template of the economic model for production of enriched fractions in lignin and lignans is presented in figure 3 and a complete description of the model used and associated equations were provided in appendix. Table 3 presents the general data used for economic assessment of membrane set up.

Figure 3

Abbreviations: Ac: amortization constituent, $C_{aceticacid}$: Cost of acetic acid, Cc: cost of chemicals (alkaline or acid cleaning), CI: cost of installation, CIC: instruments and controls capital cost, Cm: membranes capital cost, CP: pumps capital cost, CPV: pipes and valves capital cost, CTF: tanks and frames capital cost, Cv: pressure vessels capital cost, CAPEX: capital expenditure or investment, CRDc: disposal costs of the cleaning and rinsing solutions, Ec: total cost of energy, Mc: membrane replacement costs, MA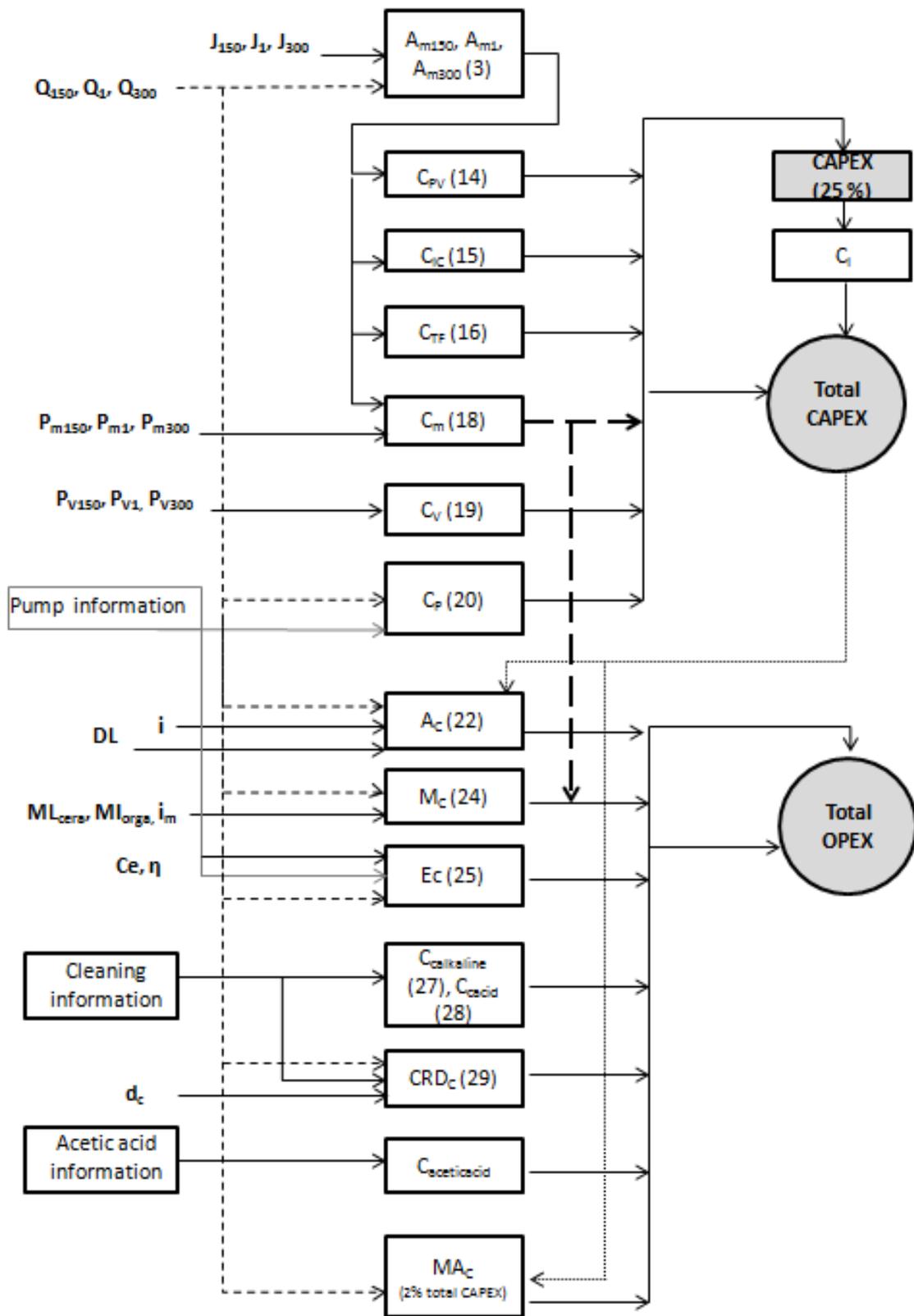c: maintenance costs, OPEX: operating and maintenance costs, Symbols: Am: membrane area, ce: energy cost, DL: design life of the plant, dc: factory demineralized water cost, i: interest rate, im: interest rate for membrane replacement, J: permeate flow rate, ML: membrane life time, η: pump efficiency, Pm: membrane price per unit area, Pv: pressure vessel price per membrane module, Q: flow entering membrane step in $m^3.h^{-1}$

With the obtained values of total CAPEX and OPEX, the production cost due to filtration process ($C_{production}$) in €kg^{-1} of the extracts could be calculated with the following formula (5) proposed by Roda (2017):

$$C_{production} = \frac{1}{M_{annual}} \cdot \left(Total\ OPEX \cdot V_{annual} + \frac{Total\ CAPEX}{IRR} \right) \tag{5}$$

Where M_{annual} and V_{annual} represent respectively the mass of extracts produced in kg (dry matter) and the volume of process water used in m^3 yearly. IRR corresponds to the internal rate of return in year.

Table 3:

Parameters	value	abbreviations
150 kDa membrane cost (€m^{-2})[a]	938	P_{m150}
1 kDa membrane cost (€m^{-2}) [a]	1471	P_{m1}
300 Da membrane cost (€m^{-2}) [a]	385	P_{m300}
ceramic module cost (€)[a]		
150 kDa (one module of 0.75 m² with 3 membranes) [a]	2,000	P_{V150}
1 kDa (one module of 1.75 m² with 7 membranes) [a]	3,600	P_{V1}
Organic 300 Da module cost (€)[a] (one module of 9 m²)	400	P_{V300}
Interest rate (%)[b]	7	i, i_m
Design life of the plant (year) [b]	15	DL
Ceramic membrane lifetime (year) [a]	5	ML_{cera}
Organic membrane lifetime (year) [a]	3	ML_{orga}
Acetic acid concentration (L.m^{-3})	2	concentration$_{aceticacid}$
Acetic acid cost (€L^{-1})[d]	3.06	cost$_{aceticacid}$
Energy cost (€Wh^{-1})[c]	5.10^{-5}	Ce
Pump efficiency (%)[b]	70	η
Cleaning volume for 150 kDa membrane (m^3)	5.1.10^{-3}	V_{C150}
Cleaning volume for 1 kDa membrane (m^3)	1.6.10^{-2}	V_{C1}
Cleaning volume for 300 Da membrane (m^3)	6.1.10^{-2}	V_{C300}
Rinsing volume for 150 kDa membrane (m^3)	1.01.10^{-3}	V_{R150}
Rinsing volume for 1 kDa membrane (m^3)	3.2.10^{-3}	V_{R1}
Rinsing volume for 300 Da membrane (m^3)	1.22.10^{-2}	V_{R300}
Alkaline detergent concentration for ceramic membranes (kg.m^{-3})	15	concentration$_{b150,1}$
Alkaline detergent cost for ceramic membranes (€kg^{-1})[d]	2.3	cost$_{b150,1}$
Surfactant concentration (kg.m^{-3})	0.75	concentration$_{S150,1}$
Surfactant cost (€kg^{-1})[d]	35.2	Cost$_{S150,1}$
Alkaline detergent concentration for organic membrane (L.m^{-3})	20	concentration$_{b300}$
Alkaline detergent cost for organic membranes (€L^{-1})[d]	4.5	cost$_{b300}$
Acid detergent concentration (L.m^{-3})	20	concentration$_a$
Acid detergent cost (€L^{-1})[d]	4.5	cost$_a$
Demineralized water cost (€m^{-3}) [a]	0.12	dc

[a] Data from membrane supplier

[b] Data from Suarez et al., 2015

[c] Data from paper producer NorskeSkog

[d] Data from chemical supplier

3. Results and discussion

3.1 Pilot plant study for the production of lignin and lignans enriched fractions in semi batch mode: assessment of parameters for the scale-up

3.1.1 Mean flux and cleaning frequencies assessment

The initial permeate flux of floated process water with the 150 kDa UF was 440 $L.m^{-2}.h^{-1}$ (Figure 4, (A)).

This value decreased by 69 % to reach a VR of 98 % with a permeate flux of 138 $L.m^{-2}.h^{-1}$ after 22 h of filtration. The evolution of 150 kDa permeate flux with time could be divided into three distinct zones. Loss of permeate flux was rapid initially as after one hour of filtration a value of 300 $L.m^{-2}.h^{-1}$ was measured. This loss of 150 kDa permeate flux was due to first fouling establishment by cake formation with suspended matter which took place as 150 kDa membrane was in contact with floated process water. After the initial rapid flux decline the flux stabilized somewhat and decreased steadily with 10 $L.m^{-2}.h^{-1}$ per hour during the 15 hours it took to reach VR 74%. A progressive pore blocking occurred. The last part showed the establishment of an almost steady state permeate flux with a diminution of 3 $L.m^{-2}.h^{-1}$ per hour of filtration. Membrane cleaning was performed as soon as permeate flux reached 10 % of its initial value. It allows defining the cleaning frequency of the membrane. Mean permeate flux of 150 kDa UF step was assessed at 135 $L.m^{-2}.h^{-1}$. With the assumption of a constant permeate flux loss of 3 $L.m^{-2}.h^{-1}$ per hour of filtration and considering final VR reached of 98 %, filtration with 150 kDa UF could have been proceeded 32 h before reaching the permeate flux limit of 44 $L.m^{-2}.h^{-1}$. Therefore alkaline cleanings have to be done every 54 h.

(A)

(B)

(C)

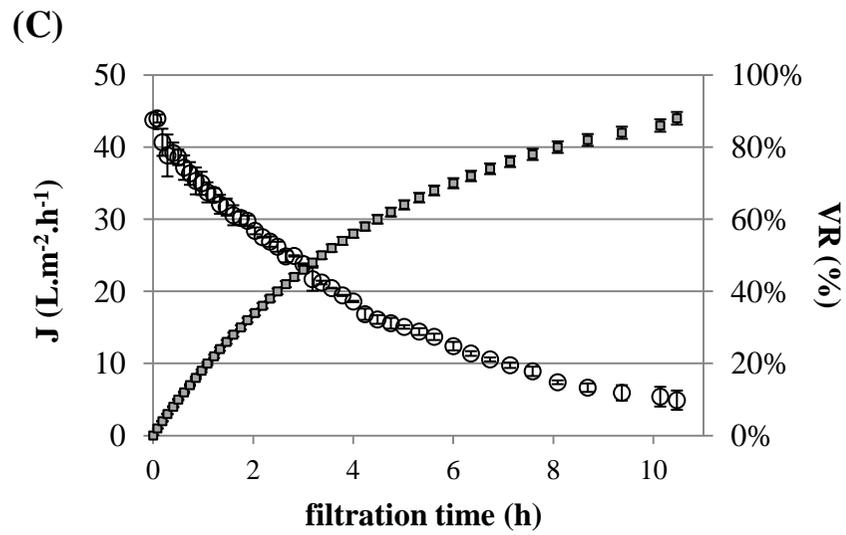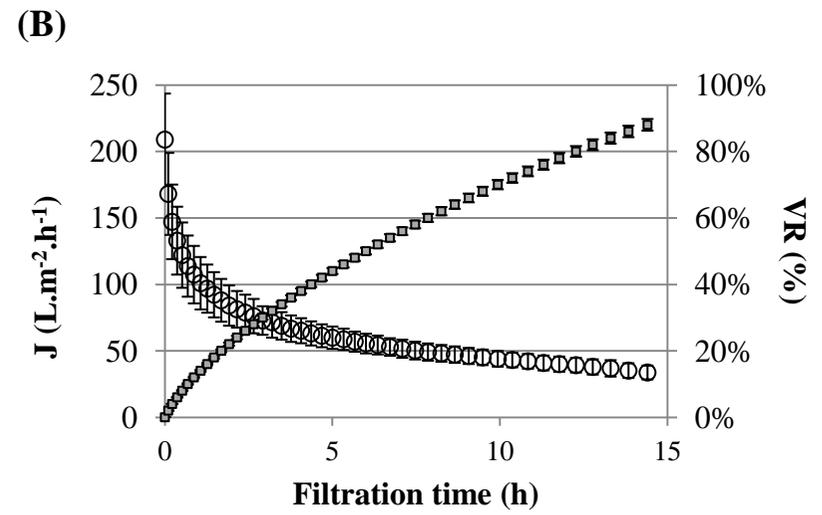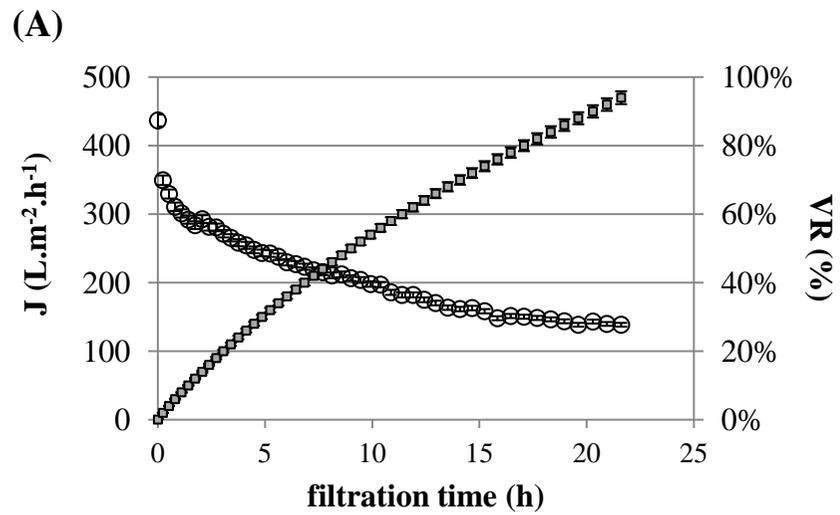Figure 4

NF 1 kDa filtration was performed during 14 h (Figure 4, (B)). The initial permeate flux was 210 $L.m^{-2}.h^{-1}$ and reached a final value of 30 $L.m^{-2}.h^{-1}$ with a VR of 95 %. During the first hour of filtration, permeate flux decreased to 48 % of its initial value due to external fouling establishment related to the residual part of suspended matter (14 $mg.L^{-1}$) initially present in TMP waters which remained at that stage. Then a slight permeate flux loss of 3 $L.m^{-2}.h^{-1}$ per hour of filtration was measured until the filtration end. To reach 10 % of initial 1 kDa permeate flux value at a constant VR of 95 %, NF 1 kDa could have run 5 h more. Therefore a cleaning frequency of 19 h can be defined. Mean permeate flux of 1 kDa NF was around 50 $L.m^{-2}.h^{-1}$.

With an initial permeate flux of 44 $L.m^{-2}.h^{-1}$, filtration 300 Da was running during 11 h and has reached a VR of 86 % with a low final flux of 5 $L.m^{-2}.h^{-1}$ (Figure 4, (C)). 300 Da membrane fouling was mainly external (99 %) and associated with progressive pore blocking and concentration polarization phenomena (data not shown). A CIP will be performed every 11 h on NF 300 Da. Mean 300 Da permeate flux was 10 $L.m^{-2}.h^{-1}$.

3.1.2   Fractions characterization and retention

The different characteristics of fractions obtained at final VR of semi-batch experiments are presented in Table 4. The main objective of 150 kDa UF was to clarify floated process water. This goal was clearly reached as only 2 % of polyphenols (*i.e.* lignin and lignans compounds) was retained (Figure 5). Clarification was efficient due to the retention of 28 % of dry matter mainly corresponding to suspended matter and hemicelluloses specifically stopped at 25 %. Hemicelluloses were mostly composed of GGM with identified sizes comprised between 0.2 and 20 kDa and some additional molecular weights higher than 100 kDa (Thuvander and Jonsson, 2016). Stack et al., (2014) mentioned that those hemicelluloses with high molecular

Table 4:

VR (%)	Fraction	Hemicelluloses ($g_{Geq}.L^{-1}$)	Polyphenols ($g_{GAeq}.L^{-1}$)	Dry matter ($g.L^{-1}$)	Lignans ($mg_{CAeq}.L^{-1}$)	Lignin ($mg.L^{-1}$)
-	**Floated water**	1.2 ± 0.2	0.65 ± 0.01	3.67 ± 0.10	30 ± 5	690 ± 70
98	**Retentate150 kDa**	14 ± 2	0.93 ± 0.03	24.3 ± 4.0	-	1400 ± 200
	Permeate150 kDa	0.9 ± 0.2	0.64 ± 0.02	2.65 ± 0.20	30 ± 3	620 ± 100
95	**Retentate 1 kDa**	15 ± 3	4.35 ± 0.20	27.4 ± 3.0	170 ± 20	6400 ± 500
	Permeate 1 kDa	0.20 ± 0.06	0.43 ± 0.01	1.40 ± 0.02	25 ± 5	290 ± 50
86	**Retentate 300 Da**	1.5 ± 0.3	2.90 ± 0.20	7.40 ± 1.0	175 ± 70	1700 ± 300
	Permeate 300 Da	0.010 ± 0.002	0.045± 0.005	0.40 ± 0.01	2.0 ± 0.6	40 ± 5
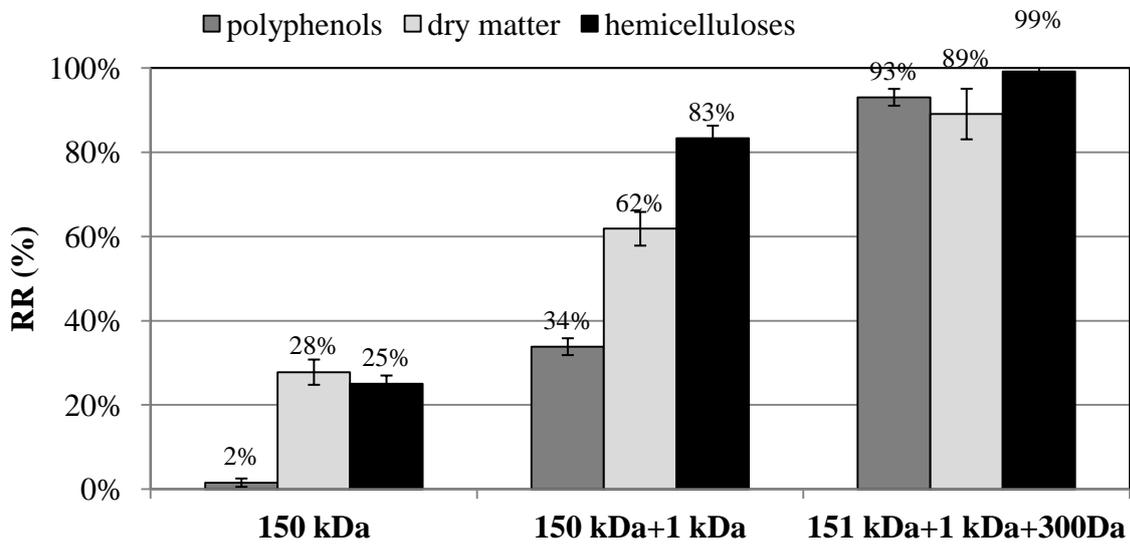
Figure 5

weights could be formed by adsorption on process water colloidal matter content. This
phenomenon could explain hemicelluloses retention observed with 150 kDa UF.

At final VR of 95 % and 86 %, polyphenols concentrations of retentates of NF 1 kDa and 300
Da membranes were respectively of 4.35 and 2.90 $g_{GAeq}.L^{-1}$. 39 % of lignin was retained at
this stage. 29 % of lignin and 70 % of lignans were retained with the 300 Da membrane. Both
fractions still contained hemicelluloses with concentration of 15 $g.L^{-1}$ in 1 kDa retentate and
1.5 $g.L^{-1}$ in 300 Da retentate. This result was also obtained by Oinonen et al. (2015) in their 1
kDa retentate of thermomechanical process water of spruce wood. They affirmed that in 1

kDa retentate, part of hemicelluloses were free GGM as another part was linked to a part of lignin content to form LCC. Steinmetz et al. (2019) have proposed the following composition in 1 kDa retentate of thermomechanical process water: 40 % of LCC, 35 % of GGM, 7 % of free lignin, 8 % of ash and 10 % of others (included lignans content). LCC are now considered as valuable compounds because they possess unique applications (bio materials, cosmetics, pharmaceutic) resulting from the combination of lignin and hemicelluloses properties (Oinonen et al, 2016 ; Sakagami et al, 2016). Therefore, depending on the targeted activity of the fractions by the companies, fractions 1 kDa and 300 Da could be used just after membrane filtration or further isolation and concentration processes could be required if high purity of lignin, LCC, GGM or lignans are wanted.

Due to its chemical characteristics, 300 Da permeate could be directly reintroduced in TMP process as industrial water. The implementation of such membrane process could lead to a reduction on the environmental impact of pulp and paper factories as it was proved in other sectors as wineries (Giacobbo et al, 2017).

3.2 Technical evaluation of membrane set up

For the treatment of 0.1 $m^3.h^{-1}$ of floated process water, the following membrane set up is proposed in Figure 6.

It was assumed that membrane installation was directly constructed on the thermomechanical pulp mill site as the company already has the flotation system for process water pretreatment and also to avoid transport costs. The membrane plant capacity was considered to run in continuous mode *i.e.* 333 days.year^{-1} and 8000 h.year^{-1} with a global factory stop for maintenance purpose of 32 days.year^{-1}. Each stage of membrane installation worked at constant transmembrane pressure therefore permeate flow rates decreased with time. The cleaning steps were carried out when permeate flux reached 10% of its initial value.

floated process water

flow rate (L/h)	100
DM (g/l)	3.67
DM flow rate (kg/h)	0.37
Polyphenols concentration (g/l)	0.65
Density	1
Polyphenols (% of DM)	18%

UF-150 kDa

150 kDa retentate

flow rate (L/h)	2
DM (g/l)	24.3
DM flow rate (kg/h)	0.0486
Polyphenols concentration (g/l)	0.93
Density	1
Polyphenols (% of DM)	4%

VR	98%
flow rate (L/h)	98
DM (g/l)	2.65
DM flow rate (kg/h)	0.26
Permeate flux (L/h.m²)	135
Theoretical A_{m150} (m²)	0.73

150 kDa permeate

NF-1 kDa

1 kDa retentate

flow rate (L/h)	5
DM (g/l)	27.4
DM flow rate (kg/h)	0.134
Lignin concentration (g/l)	6.4
Density	1
lignin (% of DM)	23%
Lignin flow rate (kg/h)	**0.031**

VR	95%
flow rate (L/h)	93
DM (g/l)	1.4
DM flow rate (kg/h)	0.13
Permeate flux (L/h.m²)	50
Theoretical A_{m1} (m²)	1.86

1 kDa permeate

NF-300 Da

300 Da retentate

flow rate (L/h)	13
DM (g/l)	7.4
DM flow rate (kg/h)	0.096
Lignans concentration (g/l)	0.175
Density	1
lignans (% of DM)	2%
Lignans flow rate (kg/h)	**0.002**

VR	86%
flow rate (L/h)	80
DM (g/l)	0.4
DM flow rate (kg/h)	0.032
Permeate flux (L/h.m²)	10
Theoretical A_{m300} (m²)	8.01

300 Da permeate

– – → Floated process water

- - - - → Retentate

——→ Permeate

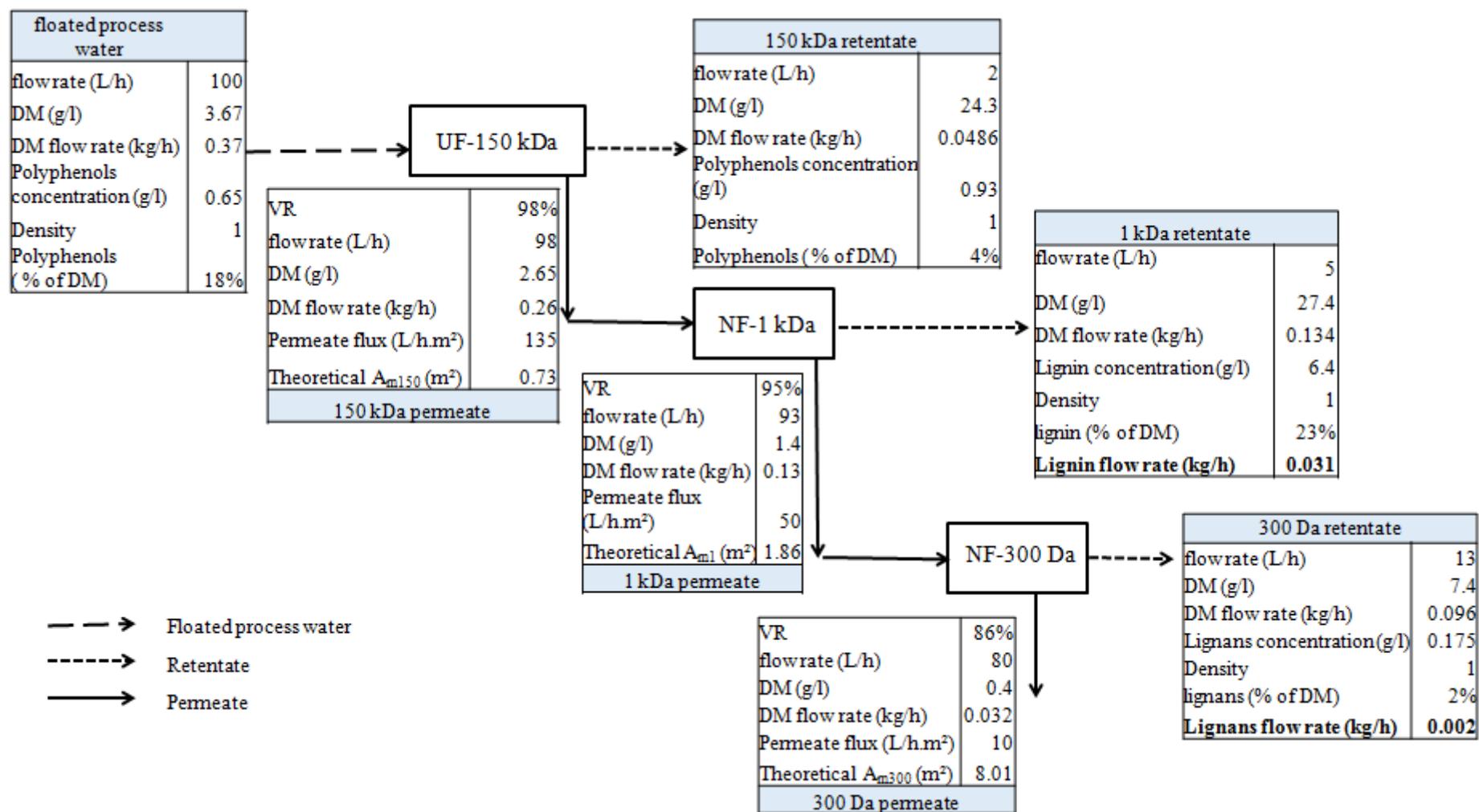Figure 6

Based on a continuous mode of operation (8000 h.year^{-1}) and duration of each filtration between cleaning step found in part 3.1.1, the alkaline and acid cleaning frequencies can be estimated. This implies that 150 kDa filtration was done during 7668 h.year^{-1} and with respective alkaline and acid frequencies of 142 ($Freq_{b150}$) and 36 times per year ($Freq_{a150}$).

NF 1 kDa can have a yearly filtration time of 7106 h. Alkaline and acid frequencies were of 374 ($Freq_{b1}$) and 94 times per year ($Freq_{a1}$) respectively.

NF 300 Da has a total filtration time of 6578 h.year^{-1}and with alkaline and acid cleaning frequencies of 598 ($Freq_{b300}$) and 150 ($Freq_{a300}$) times per year respectively.

Figure 6 gives the theoretical membrane areas obtained to treat floated process water at VR of 98 % for UF 150 kDa, 95 % for NF 1 kDa and 86 % for NF 300 Da. These theoretical membrane areas were of 0.73, 1.86 and 8.01 m² for UF, NF 1 kDa and NF 300 Da respectively. For economic evaluation (*i.e.* CAPEX and OPEX determination) real membrane areas available from membrane suppliers substituted for theoretical areas. Therefore for UF and NF of 1 kDa and 300 Da used membrane areas were 0.75, 1.75 and 9 m² respectively (Table 3).

With this configuration and according to the results of table 4 , membrane set up allows to produce 0.134 and 0.096 kg.h^{-1} of DM which respectively contained 23 % of lignin (1 kDa retentate) and 2 % of lignans (300 Da retentate). Therefore monthly 87.4 kg with 20.4 kg of lignin (1 kDa retentate) and 58.1 kg with 1.4 kg of lignans (300 Da retentate) could be produced. These masses are adequate to supply partner companies in various fields of prospecting (food, nutraceutical, cosmetic, agriculture, chemistry, material).

3.3 Economic evaluation of membrane set up of 0.1 $m^3.h^{-1}$ capacity

Economic assessment of membrane set up with a treatment capacity of 0.1 $m^3.h^{-1}$ developed to obtain extracts enriched in lignin and lignans are presented in tables 5 and 6. All the parameters mentioned in both tables came from performed experiments and data collected in table 3. Tables 5 and 6 exhibit a complete description of the calculations. In figure 4, a calculation template is presented to clearly show the method used to obtain results of both tables. With this information, CAPEX and OPEX of membrane installation with a plant capacity of 0.1 $m^3.h^{-1}$ were of 149,500 €and 35.4 €m^{-3} respectively. The calculated CAPEX present a deviation of 18.7 % with a commercial offer proposed by a membrane equipment supplier for a membrane set up with the same global characteristics and objectives. This difference could come from the CIP disposal cost which was not taken into account in the present study due to the lack of information whereas it was the case in the commercial offer. Suarez et al., (2015) used also the economic model developed by Sethi and Wiesner (2000) in their economic assessment of a reverse osmosis (RO) plant with a feed capacity of 20 $m^3.h^{-1}$ of condensate from a dairy factory. They obtained a deviation of 13.7 % between their capital cost estimations and an economic offer. This deviation was the lowest obtained as compared with the ones assessed with the six-tenths power rule model (33.9 and 29.1 % with data from Jönsson et al., (2008) and Shen et al., (2014) respectively)

Table 5

Costs	Parameters	Equations	Results (€)
C_{PV150}	conv : 1996 : \$1 = €0.81	$C_{PV150} = 5962.13 \cdot A_{m150}^{0,42} \cdot conv \cdot CEPCI$	6,8
C_{PV1}	CEPCI = 603.1/381.7 A_{m150} = 0.75 m²	$C_{PV1} = 5962.13 \cdot A_{m1}^{0,42} \cdot conv \cdot CEPCI$	11,0
C_{PV300}	A_{m1} = 2.38 m² A_{m300} = 9 m²	$C_{PV300} = 5962.13 \cdot A_{m300}^{0,42} \cdot conv \cdot CEPCI$	19,2
C_{PV}		$C_{PV} = \sum C_{PV150} + C_{PV1} + C_{PV300}$	36,9
C_{IC150}		$C_{IC150} = 1445.5 \cdot A_{m150}^{0,66} \cdot conv \cdot CEPCI$	1,5
C_{IC1}		$C_{IC1} = 1445.5 \cdot A_{m1}^{0,66} \cdot conv \cdot CEPCI$	3,3
C_{IC300}		$C_{IC300} = 1445.5 \cdot A_{m300}^{0,66} \cdot conv \cdot CEPCI$	7,9
C_{IC}		$C_{IC} = \sum C_{IC150} + C_{IC1} + C_{IC300}$	12,7
C_{TF150}		$C_{TF150} = 3047.21 \cdot A_{m150}^{0,53} \cdot conv \cdot CEPCI$	3,3
C_{TF1}		$C_{TF1} = 3047.21 \cdot A_{m1}^{0,53} \cdot conv \cdot CEPCI$	6,2
C_{TF300}		$C_{TF300} = 3047.21 \cdot A_{m300}^{0,53} \cdot conv \cdot CEPCI$	12,5
C_{TF}		$C_{TF} = \sum C_{TF150} + C_{TF1} + C_{TF300}$	22,0
C_{m150}	P_{m150} = 938 €m⁻²	$C_{m150} = A_{m150} \cdot P_{m150}$	0,7
C_{m1}	P_{m1} = 1471 €m⁻²	$C_{m1} = A_{m1} \cdot P_{m1}$	3,5
C_{m300}	P_{m300} = 385 €m⁻²	$C_{m300} = A_{m300} \cdot P_{m300}$	3,5
C_m		$C_m = \sum C_{m150} + C_{m1} + C_{m300}$	7,7
C_V	$N_{150, 1, 300}$ = 1 P_{V150}= 2,000 €module⁻¹ P_{V1} = 3,600 €module⁻¹ P_{V300}= 400 € module⁻¹	$C_V = \sum N_{150} \cdot P_{V150} + N_1 \cdot P_{V1} + N_{300} \cdot P_{V300}$	6,0
C_{P150}	Q_{150} = 0.1 m³.h⁻¹ P_{150} = 325 kPa Q_{R150} = 10 m³.h⁻¹ P_{R150} = 160 kPa	$C_{P150} = 389.12 \cdot ((Q_{150} \cdot P_{150})^{0.39} + (Q_{R150} \cdot P_{R150})^{0.39}) \cdot conv \cdot CEPCI$	10,8
C_{P1}	Q_1 = 0.098 m³.h⁻¹ P_1 = 715 kPa Q_{R1} = 31.8 m³.h⁻¹ P_{R1} = 210 kPa	$C_{P1} = 389.12 \cdot ((Q_1 \cdot P_1)^{0.39} + (Q_{R1} \cdot P_{R1})^{0.39}) \cdot conv \cdot CEPCI$	17,9
C_{P300}	Q_{300} = 0.093 m³.h⁻¹ P_{300} = 620 kPa Q_{R300} = 1.4 m³.h⁻¹ P_{R300} = 100 kPa	$C_{P300} = 389.12 \cdot ((Q_{300} \cdot P_{300})^{0.39} + (Q_{R300} \cdot P_{R300})^{0.39}) \cdot conv \cdot CEPCI$	5,6
C_P		$C_P = \sum C_{P150} + C_{P1} + C_{P300}$	34,3
C_I		$C_I = 0,25 \cdot (C_{PV} + C_{IC} + C_{TF} + C_m + C_V + C_P)$	29,9
Total CAPEX			**149,5**

Table 6

costs	Parameters	Equations	Results ($€m^{-3}$)
A_c	i = 7% DL = 15 years CAPEX = 149,520 € DF_{150} = 7668 h.year^{-1} Q_{150} = 0.1 m^3.h^{-1}	$$A_C = \frac{\frac{i \cdot (1-i)^{DL}}{(1+i)^{DL}-1} \cdot CAPEX}{DF_{150} \cdot Q_{150}}$$	21.410
M_{c150}	i_m = 7% ML_{cera}= 5 years C_{m150} = 703 €	$$M_{C150} = \frac{\frac{i_m}{(1+i_m)^{MLcera}-1} \cdot C_{m150}}{DF_{150} \cdot Q_{150}}$$	0.159
M_{c1}	C_{m1} = 2,574 € Q_1 = 0.098 m^3.h^{-1} DF_1 = 7106 h.year^{-1}	$$M_{C1} = \frac{\frac{i_m}{(1+i_m)^{MLcera}-1} \cdot C_{m1}}{DF_1 \cdot Q_1}$$	0.857
M_{c300}	C_{m300} = 3,462 € Q_{300} = 0.093 m^3.h^{-1} DF_{300} = 6578 h.year^{-1}	$$M_{C300} = \frac{\frac{i_m}{(1+i_m)^{MLorga}-1} \cdot C_{m300}}{DF_{300} \cdot Q_{300}}$$	1.637
M_c		$$M_C = \sum M_{C150} + M_{C1} + M_{C300}$$	2.653
E_{c150}	P_{150}= 325 kPa Ce = 5.10^{-5} €Wh^{-1} η = 70% P_{R150}= 160 kPa Q_{R150}= 10 m^3.h^{-1}	$$E_{C150} = \frac{\frac{Q_{150}}{3600} \cdot P_{150} \cdot 1000 \cdot Ce}{\eta \cdot Q_{150}} + \frac{\frac{Q_{R150}}{3600} \cdot P_{R150} \cdot 1000 \cdot Ce}{\eta \cdot Q_{R150}}$$	0.010
E_{c1}	P_1= 715 kPa P_{R1}= 210 kPa Q_{R1}= 31.8 m^3.h^{-1}	$$E_{C1} = \frac{\frac{Q_1}{3600} \cdot P_1 \cdot 1000 \cdot Ce}{\eta \cdot Q_1} + \frac{\frac{Q_{R1}}{3600} \cdot P_{R1} \cdot 1000 \cdot Ce}{\eta \cdot Q_{R1}}$$	0.018
E_{c300}	P_{300} = 620 kPa P_{R300} = 100 kPa Q_{R300} = 1.4 m^3.h^{-1}	$$E_{C300} = \frac{\frac{Q_{300}}{3600} \cdot P_{300} \cdot 1000 \cdot Ce}{\eta \cdot Q_{300}} + \frac{\frac{Q_{R300}}{3600} \cdot P_{R300} \cdot 1000 \cdot Ce}{\eta \cdot Q_{R300}}$$	0.014
E_c		$$E_C = \sum E_{C150} + E_{C1} + E_{C300}$$	0.042
$C_{aceticacid}$		$$C_{aceticacid} = \frac{1}{DF_1 \cdot Q_1} \cdot V_{aceticacid} \cdot (cost_{aceticacid} \cdot concentration_{aceticacid})$$	2.10^{-6}
$Cc_{alkaline}$	V_{C150} = 5.1.10^{-3}m^3 V_{C1} = 1.6.10^{-2}m^3 V_{C300} = 6.1.10^{-2}m^3 $Freq_{b150}$ = 142 year^{-1} $Freq_{b1}$ = 374. year^{-1} $Freq_{b300}$ =598. year^{-1}	$$Ccalkaline = \sum \frac{1}{DF_{150,1,300} \cdot Q_{150,1,300}} \cdot (V_{C_{150,1,300}} \cdot Freq_{b_{150,1,300}}) \cdot (cost_{b_{150,1,300}} \cdot concentration_{b_{150,1,300}}) \cdot (cost_{S_{150,1}} \cdot concentration_{S_{150,1}})$$	5.875
Cc_{acid}	$Freq_{a150}$ = 36. year^{-1} $Freq_{a1}$ = 94. year^{-1} $Freq_{a300}$ = 150. year^{-1}	$$Ccacid = \sum \frac{1}{DF_{150,1,300} \cdot Q_{150,1,300}} \cdot (V_{C_{150,1,300}} \cdot Freq_{a_{150,1,300}}) \cdot (cost_a \cdot concentration_a)$$	1.544
CRD_c	dc = 0.12 €m^{-3} V_{R150}=1.01.10^{-3}m^3 V_{R1}=3.2.10^{-3}m^3 V_{R300}=1.22.10^{-2}m^3	$$CRD_C = dc \cdot \sum \frac{1}{DF_{150,1,300} \cdot Q_{150,1,300}} \cdot \left((V_{R_{150,1,300}} \cdot Freq_{b_{150,1,300}}) + (V_{R_{150,1,300}} \cdot Freq_{a_{150,1,300}}) \right)$$	0.002
MA_c		$$MA_C = \frac{0,02 \cdot CAPEX}{DF_{150} \cdot Q_{150}}$$	3.900
	OPEX total		**35.4**

3.4 Influence of membrane installation capacity on CAPEX, OPEX and extracts production cost

In table 7, for the presented case study, different OPEX values for the filtration of 0.1, 1, 10, 30 and 60 $m^3.h^{-1}$ were assessed. For a plant capacity of 10 $m^3.h^{-1}$ the total OPEX was equal to 12.6 €m^{-3}.

Table 7

Plant	$(m^3.h^{-1})$	0.1	1	10	30	60
capacity	$(m^3.year^{-1})$	767	7,670	76,700	230,100	460,200
Total membrane area (m²)		12.1	105.9	1047	3290	6405
CAPEX (k€)		149.5	502.6	2,266	5,481	9,637
OPEX (€m^{-3})		35.4	17.4	12.6	12.2	11.6
Annual 1 kDa extract production ($ton_{DM}.year^{-1}$)		0.96	9.6	96.1	288.4	576.8
Annual 300 Da extract production ($ton_{DM}.year^{-1}$)		0.64	6.4	64	191.9	383.9

This OPEX value was lower the one presented by Arvaniti et al. (2012) for the same installation size (23 €m^{-3}) for the treatment of olive mill wastewater (OMWW) by a UF/RO system for nutrient and phenolic compounds recovery. The single operational cost with the higher contribution to the total OPEX value was the labor cost at 28.8 %. The authors specified that OMWW were collected from 50 different sites around the establishment area of UF/RO system. This labor cost includes transportation costs (evaluated at 0.25 €km^{-1}) and work with loading equipment. This labor cost is not included in the present study as membrane system would be directly connected to the TMP process water network. Arkell et al. (2014) have concentrated lignin from softwood black liquor with UF/NF process. They found OPEX value around 5 €m^{-3}. This reported OPEX cost is in the same range than the OPEX value obtained in Servaes et al. (2017) which concentrate and purify lignin from the spent liquor of the alkaline oxidation of woody biomass with UF/RO system. They obtained an OPEX value of 3 €m^{-3} for the treatment of 10,000 $m^3.year^{-1}$ when for equivalent plant

capacity the presented case study obtained a value around 17 €m^{-3} (value for 1 m3.h^{-1} which is equivalent to 7670 m^3.year^{-1}). One of the significative difference which can be pointed out is the membrane price. Servaes et al. (2017) used ESP04 polymeric tubes in modified PES as UF step and 8040 spiral-wound module for RO treatment. They announced prices of 142 €m^{-2} for UF membrane and 31 €m^{-2} for RO membrane whereas the price of membranes varies from 385 to 1471 €m^{-2} in this study (Table 3).

The distribution of specific costs to the CAPEX and OPEX for plant capacities of 0.1 and 60 m^3.h^{-1} are presented in figure 7.
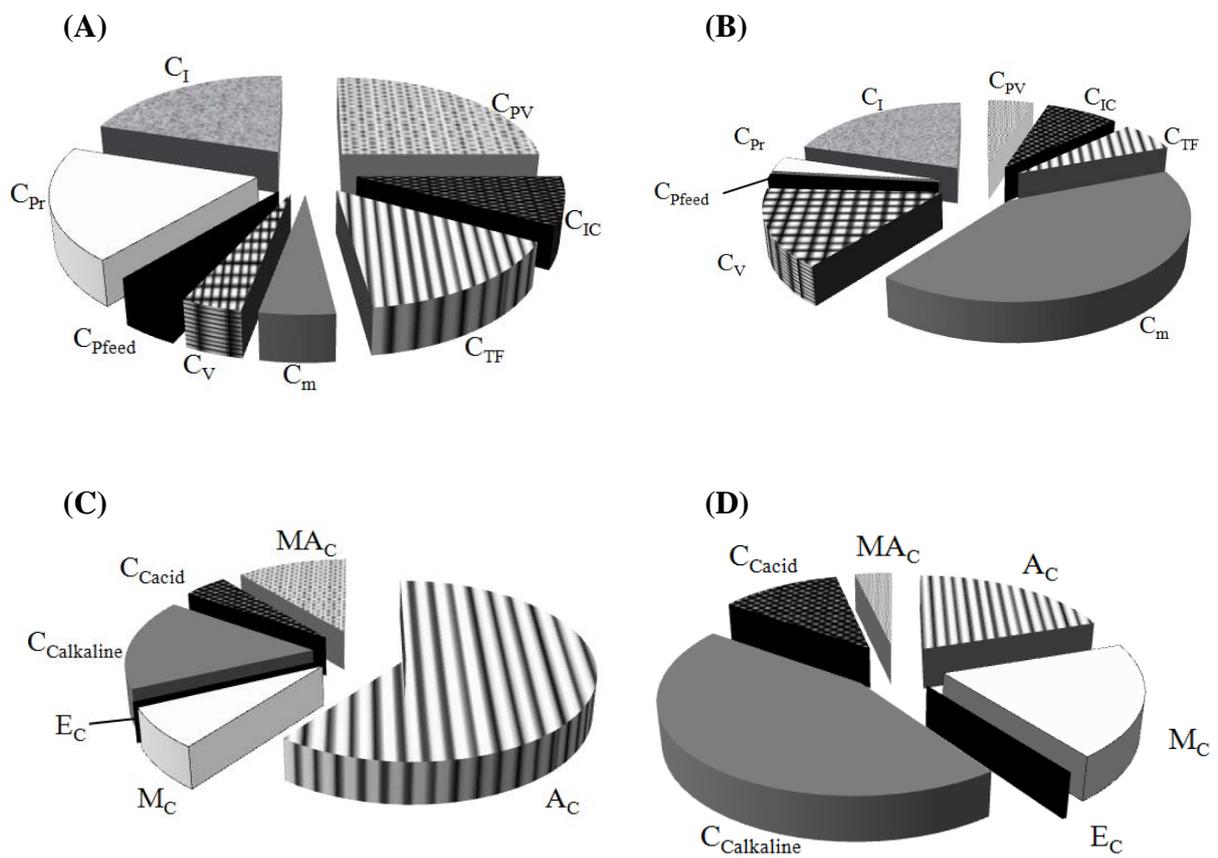
Figure

It can be noticed the small relevance of membrane investment (C_m) (5 %) in the capital cost of filtration plant of 0.1 $m^3.h^{-1}$ whereas this value increases until 40 % for a capacity of 60 $m^3.h^{-1}$. It is also the case for membrane module cost (C_v) contribution which is low (4 %) for the plant of 0.1 $m^3.h^{-1}$ capacity. This value was multiplied by 4 when capacity of plant was elevated to 60 $m^3.h^{-1}$. Membrane cost (NF) fluctuate in the range of 20-30% in the case of plants treated between 200 and 400 $m^3.h^{-1}$ and this value increases to near 50 % for installation of larger sizes (Liikanen et al., 2006). Suarez et al. (2015) obtained a contribution of less than 5 % for their membrane cost of RO plant designed to treat 20 $m^3.h^{-1}$ and Servaes et al. (2017) announced a contribution between 10 and 20 % for UF/RO installation with capacity between 1.4 and 140 $m^3.h^{-1}$. All the mentioned values from literature use only polymeric membranes whereas in the present study, two membrane steps are performed with ceramic ones. This difference of membrane material could explain the relative high contribution of membrane cost for installation treating 60 $m^3.h^{-1}$. This factor is highly dependent on the membrane material chosen, the total membrane area installed and its associated cost (Ahmad et al., 2009). As installation cost (C_I) presents a stable contribution to the total CAPEX (25 % of all the others CAPEX components), the contribution of all the others costs has decreased with the scale up of installation which is the benefits of the economy of scale. In contrast the cost of membranes during scale up is relatively linear. Therefore this phenomenon can also explain the more significant contribution of membranes cost in the cost repartition. The biggest part of OPEX for plant treating 0.1 $m^3.h^{-1}$ was the amortization constituent (A_C) with a value of 60.4 %. This value drops until 19.8 % for plant capacity of 60 $m^3.h^{-1}$. This last value well corresponds with value of Suarez et al. (2015) at 29.3 %. The membrane replacement costs (19.8 %) and the alkaline membrane cleaning (44.6 %) would also represent high cost of the global OPEX value for the treatment of 60 $m^3.h^{-1}$. The production cost of extracts (*i.e.* sum of 1 kDa and 300 Da extracts) (€kg^{-1}) calculated

with equation (13) was assessed depending on plant capacity and for IRR of 3 and 5 years (Figure 8).
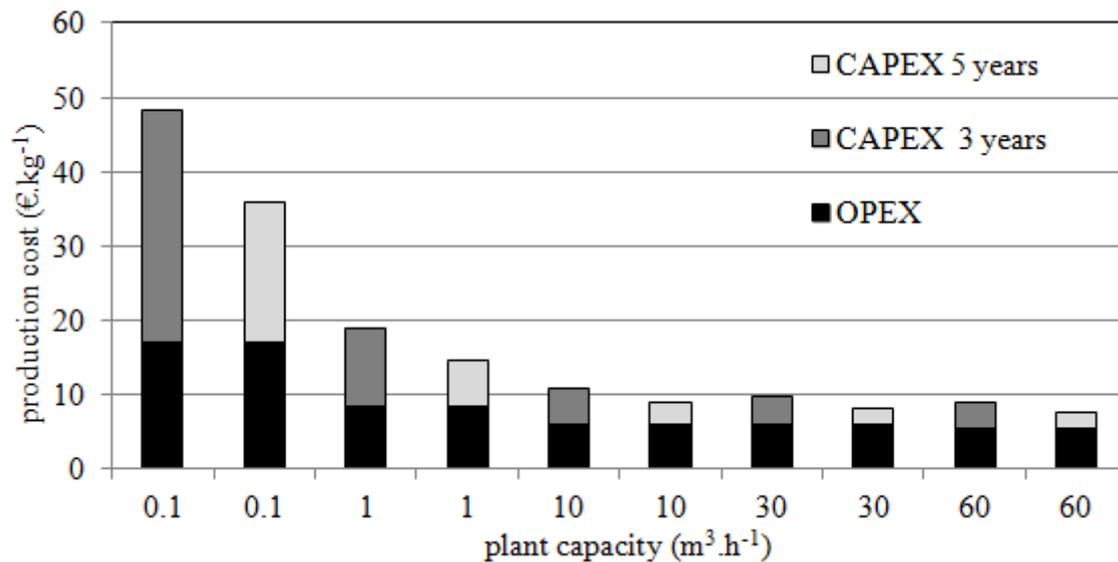

Figure 8

As confirmed by literature (Garcia et al., 2013; Servaes et al., (2017), total production cost decreases with the augmentation of plant capacity. For plant capacities equal or higher than 10 $m^3.h^{-1}$, OPEX contribution to the production cost of extracts was around 6 €kg^{-1} and represents around 55 and 75 % of production cost for IRR of 3 and 5 years respectively. From installation able to treat 10 $m^3.h^{-1}$ production cost of extracts was equal or below 10 €kg^{-1}. Production costs of 46 €ton^{-1} and 68 €ton^{-1} were proposed by Arkell et al. (2014) for the NF filtration of lignin from softwood black liquor with respectively organic or ceramic NF. This price increased until 120 €ton^{-1} (organic NF) and 430 €ton^{-1} (ceramic NF) when softwood black liquor was pretreated with UF. With an UF process used to concentrate and purify by diafiltration lignin from the spent liquor of the alkaline oxidation of woody biomass, Servaes et al. (2017) obtained a production cost of 616 €ton^{-1} for the treatment of 10,000 m^3 per year. This value increased until 1,175 €ton^{-1} with an added RO system for the recovery of 80 % of UF permeate. The significant difference of production costs between cited literature and this study comes from the initial concentration of valuable compounds (*i.e.* lignin, lignans, LCC)

present in liquors from paper industries and their final concentration reached in produced extracts. Liquors from chemical pulp processes such as kraft or sulfite processes usually have higher contents of lignin as 30-190 g.L^{-1} (Kevlich et al., 2017) and 30 g.L^{-1} (Al-Rudainy et al., 2017) respectively. In comparison lignin content of process water from thermomechanical pulp system was in the range 700-1300 mg.L^{-1} (Persson et al., 2010b; Zasadowski et al., 2014). As in this study dry matter concentrations were of 27.4 g.L^{-1} in 1 kDa extract (23 % of lignin) and 7.4 g.L^{-1} in 300 Da extract (2 % of lignan), 230 g.L^{-1} of only lignin were measured in the final NF retentate of Arkell et al. (2014) and 17 g.L^{-1} of lignin assessed in UF retentate of Servaes et al. (2017). Those high final concentrations of lignin after filtration processes lead to higher produced quantities and therefore lower productions costs. As fractions 1 kDa (enriched in native lignin and LCC) and 300 Da (enriched in lignan) could be reserved for high added value markets , a selling price including production cost (10 €kg^{-1}) could be acceptable for targeted industrial sectors. This price could increase if higher purity of fractions is necessary and downstream processes such as evaporation or spray-drying could be used. The objective would be to adapt the purity of the fractions to obtain the planned specificity by companies and in the same time to limit cost production of the extracts. This would ensure the economic viability of the process.

4. Conclusions

Chemical pulp mill turned to a sustainable development many years ago and valorize as chemical or energy their main side streams. It is not yet the case for thermomechanical pulp mill, as their main aqueous discharge is considered as highly diluted and too expensive for organic content recovery. Therefore its valuable content composed of hemicelluloses, lignin, LCC and lignans directly goes to wastewater treatment plant which has a huge impact on

water disposal total cost for the factories. The present study developed a process containing three membrane steps: 150 kDa UF for suspended matter removal and 1 kDa and 300 Da NF for respectively retaining lignin and lignans. The fraction obtained in the 1 kDa retentate, contains 23 % of lignin and the one obtained in the 300 Da retentate 2 % of lignans. The process with a plant capacity of 60 $m^3.h^{-1}$ was able to produce 12 tons of lignin and 825 kg of lignans per month. It can be considered that both extracts are pre concentrated in lignin and lignans. The high added value of 1 kDa extract came from the native structure of the lignin preserved during thermomechanical process due to its soft conditions compared to classic chemical process. This characteristic is currently highly researched for a better production of aromatics molecules coming from lignin. The content of lignans can also be considered as highly valuable as many companies are searching for alternative sourcing of lignans less expensive than the current one sold at 1 €mg^{-1} for hydroxymatairesinol in nutritional supplement.

It is true that further concentration would be necessary if higher purity has been required. In order to obtain the best production cost of those extracts, it is important to adapt purity to the required demand of industries using the extracts. It can be considered that the produced extracts are reserved for markets at high added value. An economy of scale was noticeable as soon as plant capacity reached 10 $m^3 \cdot h^{-1}$ where the production cost of extracts dropped down below 10 €kg^{-1}. To conclude, valorization of TMP water with the proposed membrane installation could improve the profitability of TMP plants and in the same time efficiently saving fresh water and reducing the amount of generated wastes as 300 Da permeate had the required characteristics to be re used.

References

Ahmad, A.L., Chong, M.F., Bhatia, S., 2009. A comparative study on the membrane based palm oil mill effluent (POME) treatment plant; J.Hazard.Mater. 171, 166–174. http://dx.doi.org/10.1016/j.jhazmat.2009.05.114

Al-Rudainy, B., Galbe, M., Wallberg, O., 2017. Influence of prefiltration on membrane performance during isolation of lignin carbohydrate complexes from spent sulfite liquor. Sep. Sci. Technol. 187, 380-388. http://dx.doi.org/10.1016/j.seppur.2017.06.031

Arkell, A., Olsson, J., Wallberg, O., 2014. Process performance in lignin separation from softwood black liquor by membrane filtration. Chem. Eng.Res.Des. 92, 1792–1800. https://doi.org/10.1016/j.cherd.2013.12.018

Arvaniti, E.C., Zagklis, D.P., Papadakis, V.G., Paraskeva1, C.A., 2012. High-Added Value Materials Production from OMW: A Technical and Economical Optimization. Int. J. Chem. Eng. https://doi.org/10.1155/2012/607219

Courbalay, M., 2018a. Recovery and valorisation of biomolecules from pulp and paper industries by membrane processes discharges. Ph.D. thesis. Strasbourg University.

Courbalay, M., Villain-Gambier, M., Klem, A., Dumarcay, S., Trebouet, D., 2018b. Fractionation of polyphenols from thermomechanical pulp mill process water by flotation and membrane integrated process, environ. technol. https://doi.org/10.1080/09593330.2018.1468826

Dilaver, M., Hocaoglu, S.M., Soydemir, G., Dursun, M., Keskinler, B., Koyuncu, I., Agtas, M., 2018. Hot wastewater recovery by using ceramic membrane ultrafiltration and its reusability in textile industry. J. Clean. Prod. 171, 220-233. https://doi.org/10.1016/j.jclepro.2017.10.015

Dubois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A., Smith, F., 1956. Colorimetric Method for Determination of Sugars and Related Substances. Anal. Chem. *28*, 350–356. http://dx.doi.org/10.1021/ac60111a017

Dubreuil, M.F.S., Servaes, K., Ormerod, D., Van Houtven, D., Porto-Carrero, W., Vandezande, P., Vanermen, G., Buekenhoudt, A., 2017. Selective membrane separation technology for biomass valorization towards bio-aromatics. Sep. Sci. Technol. 178, 56-65. https://doi.org/10.1016/j.seppur.2016.12.033

Garcia, N., Moreno, J., Cartmell, E., Rodriguez-Roda, I., Judd, S., 2013. The cost and performance of an MF-RO/NF plant for trace metal removal. Desalination. 309, 181–186. http://dx.doi.org/10.1016/j.desal.2012.10.017

Giacobbo, A., Meneguzzi, A., Bernardes, A.M., de Pinho, M.N., 2017. Pressure-driven membrane processes for the recovery of antioxidant compounds from winery effluents. J. Clean. Prod. 155, 172-178. http://dx.doi.org/10.1016/j.jclepro.2016.07.033

Humpert, D., Ebrahimi, M., Czermak, P., 2016. Membrane Technology for the Recovery of Lignin: A Review. Membranes. 6, 42. https://doi.org/10.3390/membranes6030042

Jönsson, A.S., Nordin, A.K., Wallberg, O., 2008. Concentration and purification of lignin in hard wood kraft pulping liquor by ultrafiltration and nanofiltration. Chem. Eng.Res.Des. 86, 1271–1280. https://doi.org/10.1016/j.cherd.2008.06.003

Kebbi-Benkeder, Z., Colin, F., Dumarçay, S., Gérardin, P., 2014. Quantification and characterization of knotwood extractives of 12 European softwood and hardwood species. Ann. For. Sci. *72*, 277–284. http://dx.doi.org/10.1007/s13595-014-0428-7

Kevlich, N.S., Shofner, M.L., Nair, S., 2017. Membranes for Kraft black liquor concentration and chemical recovery: Current progress, challenges, and opportunities. Sep. Sci. Technol. 52, 1070–1094. https://doi.org/10.1080/01496395.2017.1279180

Kuznetsov, B.N., Chesnokov, N.V., Sudakova, I.G., Garyntseva, N.V., Kuznetsova, S.A., Malyar, Yu.N., Yakovlev, V.A., Djakovitch, L., 2018.Green catalytic processing of native and organosolv lignins. Catal. Today. 309, 18–30. https://doi.org/10.1016/j.cattod.2017.11.036

Laurichesse, S., Averous, L., 2014. Chemical modification of lignins: Towards biobased polymers. Prog. Polym. Sci. 39, 1266–

1290. https://doi.org/10.1016/j.progpolymsci.2013.11.004

Leithe, R., 2018. Cleaner production, in: Martin, J., Haggith, M. (Eds.), The state of the global paper industry. Environmental Paper Network, pp 57-64.

Liikanen, R., Yli-Kuivila, J., Tenhunen, J., Laukkanen, R., 2006.Cost and environmental impact of nanofiltration intreating chemically pre-treated surface water. Desalination. 201, 58–70.https://doi.org/10.1016/j.desal.2006.03.520

Oinonen, P.; Krawczyk, H.; Ek, M.; Henriksson, G.; Moriana, R., 2016. Bioinspired Composites from Cross-Linked Galactoglucomannan and Microfibrillated Cellulose: Thermal, Mechanical and Oxygen Barrier Properties. Carbohydr. Polym. 136, 146−153. http://dx.doi.org/10.1016/j.carbpol.2015.09.038

Oinonen, P., Zhang, L., Lawoko, M., Henriksson, G., 2015. On the formation of lignin polysaccharide networks in Norway spruce. *Phytochemistry.* 111, 177–184. https://doi.org/10.1016/j.phytochem.2014.10.027

Persson, T., Jönsson, A.S., 2010a. Isolation of hemicelluloses by ultrafiltration of thermomechanical pulp mill process water—Influence ofoperating conditions. Chem. Eng.Res.Des. 88, 1548–1554. https://doi.org/10.1016/j.cherd.2010.04.002

Persson, T., Jönsson, A.S., 2017. Characterization of hemicelluloses in process streams in thermomechanical and chemi-thermomechanical pulp mills. J. Wood Chem. Technol. 37, 184–190. https://doi.org/10.1080/02773813.2016.1271433

Persson, T., Krawczyk, H., Nordin, A.K., Jönsson, A.S., 2010b. Fractionation of process water in thermomechanical pulp mills. Biores. Technol. 101, 3884–3892. https://doi.org/10.1016/j.biortech.2009.12.142

Ragauskas, A.J., Williams, C.K., Davison, B.H., Britovsek, G., Cairney, J., Eckert, C.A., Frederick Jr., W.J., Hallett, J.P., Leak, D.J., Liotta, C.L., Mielenz, J.L., Murphy, R. Templer, R., Tschaplinski, T., 2006. The path forward for biofuels and biomaterials, Science. 311, 484–489. https://doi.org/10.1126/science.1114736

Roda, J.M., 2017. The biorefinery in the circular economy of areas. In : Pluribois thematic school, Mont de Marsan, France.

Sakagami, H.; Sheng, H.; Okudaira, N.; Yasui, T.; Wakabayashi, H.; Jia, J.; Natori, T.; Suguro-Kitajima, M.; Oizumi, H.; Oizumi, T., 2016. Prominent Anti-UV Activity and Possible Cosmetic Potential of Lignin-Carbohydrate Complex. In Vivo. 30 (4), 331−339.

Servaes, K., Varhimo, A. , Dubreuil, M. , Bulut, M. , Vandezande, P., Siika-aho, M., Sirviö, J. , Kruus, K., Porto-Carrero, W., Bongers, B., 2017.Purification and concentration of lignin from the spent liquor of the alkaline oxidation of woody biomass through membrane

separation technology. Ind. Crop. Prod. 106, 86–96.
http://dx.doi.org/10.1016/j.indcrop.2016.10.005

Sethi, S., Wiesner, M.R., 2000. Cost modeling and estimation of crossflow membrane filtration processes. Environ. Eng. Sci. 17, 61-79. https://doi.org/10.1089/ees.2000.17.61

Shen, J. , Huang, J., Ruan, H., Wang, J., VanderBruggen, B., 2014. Techno-economic analysis of resource recovery of glyphosate liquor by membrane technology. Desalination. 342, 118–125. https://doi.org/10.1016/j.desal.2013.11.041Get

Singleton, V.L., Orthofer, R., Lamuela-Raventos, R.M., 1999. Analysis of total phenols and other oxidation substrates and antioxidants by means of folin-ciocalteu reagent. Oxid. Antioxid. Pt A. *299*, 152–178. http://dx.doi.org/10.1016/S0076-6879(99)99017-1

Stack, K., Lee, R., Richardson, D., Lewis, T., Garnier, G., 2014. Complex formation and stability of colloidal wood resin pitch suspensions with hemicellulose polymers. Colloids Surf. Physicochem. Eng. Asp. *441*, 101–108. https://doi.org/10.1016/j.colsurfa.2013.08.057

Steinmetz, V.,Villain-Gambier, M., Klem, A., Gambier, F., Dumarcay, S., Trebouet, D., 2019. Unveiling TMP Process Water Potential As an Industrial Sourcing of Valuable Lignin−Carbohydrate Complexes toward Zero-Waste Biorefineries. ACS Sustain. Chem. Eng. 7, 6390–6400. https://doi.org/10.1021/acssuschemeng.9b00181

Suárez, A., Fernández, P., Ramón Iglesias, J., Iglesias, E., Riera, F.A., 2015. Cost assessment of membrane processes: A practical example in the dairy wastewater reclamation by reverse osmosis. J. Membr. Sci. *493*, 389–402. https://doi.org/10.1016/j.memsci.2015.04.065

Sundholm, J., 1999. Mechanical Pulping, Gummers Printing.; Papermaking Science and Technology Series; Finnish Paper Engineers' Association and TAPPI. Jyväskylä, Finland.

Thuvander, J., Jonsson, A.S., 2016. Extraction of galactoglucomannan from thermomechanical pulp mill process water by microfiltration and ultrafiltration-Influence of microfiltration membrane pore size on ultrafiltration performance. Chem. Eng. Res. Des. 105, 171–176. https://doi.org/10.1016/j.cherd.2015.12.003

Thuvander, J., Lipnizki, F., Jonsson, A.S., 2019. On-Site Recovery of Hemicelluloses from Thermomechanical Pulp Mill Process Water by Microfiltration and Ultrafiltration. J. Wood Chem. Technol. 39, 214-223. https://doi.org/10.1080/02773813.2019.1565865

Van der Bruggen, B., Everaert, K., Wilms, D., Vandecasteele, C., 2001. Application of nanofiltration for removal of pesticides, nitrate and hardness from ground water: rejection properties and economic evaluation. J. Membr. Sci. 193, 239–248. https://doi.org/10.1016/S0376-7388(01)00517-8

Wang, Z.B., Ni, D., Shang, Y.L., Guan, Y.J., 2019. Recycling of dye from wastewater using a ceramic membrane modified with bismuth/stibium co-doped tin dioxide. J. Clean. Prod. 213, 192-198. https://doi.org/10.1016/j.jclepro.2018.12.159

Weinwurm, F., Drljo, A., Waldmüller, W., Fiala, B., Niedermayer, J., Friedl, A., 2016. Lignin concentration and fractionation from ethanol organosolv liquors by ultra- and nanofiltration. J. Clean. Prod. 136, 62-71. http://dx.doi.org/10.1016/j.jclepro.2016.04.048

Willför, S.M., Smeds, A.I., Holmbom, B.R., 2006. Chromatographic analysis of lignans. J Chromatogr A. 1112, 64–77. https://doi.org/10.1016/j.chroma.2005.11.054

Zasadowski, D., Yang, J., Edlund, H., Norgren, M., 2014. Antisolvent precipitation of water-soluble hemicelluloses from TMP process water. Carbohydr. Polym. 113, 411–419. https://doi.org/10.1016/j.carbpol.2014.07.033.

List of figures and tables captions

Figure 1: Process water flows in the overall process

Figure 2: Flowchart of the techno-economic procedure.

Figure 3: Calculation template of the economic model for the lignin and lignans fractionation from thermomechanical process water (adapted from Suarez et al., 2015)

Figure 4: Evolution of J (O) and VR (◾) versus filtration time for (A) 150 kDa membrane at transmembrane pressure of 2.5 bars (n = 2), (B) 1 kDa membrane at TMP of 6.4 bars (n = 3), (C) for 300 Da membrane at transmembrane pressure of 6.0 bars (n = 2). n: number of filtrations

Figure 5: retention rates (RR) of dry matter, hemicelluloses and polyphenols obtained with a VR of 98 % for UF, 95 % for NF 1 kDa and 86 % for both NF 300 Da in semi batch mode

Figure 6: flows and surfaces calculations of membrane set-up (VR: Volume Reduction, DM: Dry Matter)

Figure 7: Proportion of contribution of the different costs to the CAPEX for plant capacities of 0.1 (A) and 60 m^3/h (B) and to the OPEX for plant capacities of 0.1 (C) and 60 m^3/h (D)

Figure 8: Evolution of extracts cost production as a function of plant capacity

Table 1: Main characteristics of TMP water

Table 2: Characteristics of the different membranes used

Table 3: Membrane installation general data

Table 4: Characterization of the different fractions obtained with the semi-batch experiments

Table 5: calculations for CAPEX determination of membrane set up with plant capacity of 0.1 $m^3.h^{-1}$

Table 6: calculations for OPEX determination of membrane set up with plant capacity of 0.1 $m^3.h^{-1}$

Table 7: Evolution of total membrane area, CAPEX and annual production of 1 kDa and 300 Da extracts as a function of plant capacity

Nomenclature: abbreviations and notations

A_C	amortization constituent
AF	amortization factor
AF_m	specific amortization factor of membrane replacement
A_m	membrane area, m²
$C_{aceticacid}$	cost of acetic acid addition
CAPEX	capital expenditures
C_C	cost of chemicals
C_{Cacid}	cost of acid cleaning
$C_{Calkaline}$	cost of alkaline cleaning
C_e	energy cost, €Wh⁻¹
CEPCI	chemical engineer plant cost index
C_{feed}	concentration in the feed
C_I	installation cost
C_{IC}	instruments and control capital cost
CIP	cleaning in place
C_m	membrane capital cost
C_P	pumps capital cost
$C_{permeate}$	concentration in the permeate
$C_{production}$	production cost, €kg⁻¹
C_{PV}	pipes and valves capital cost
CRD_C	costs due to rinsing disposal
C_{TF}	tanks and frames capital cost
C_v	pressure vessels capital cost
dc	factory demineralized water cost
DF	Duration of filtration, h.y⁻¹
d_h	hydraulic diameter, m
DL	design life of the plant, years
DM	Dry matter
E_C	cost of energy
E_f	energy cost for pumping system of the feed
E_R	energy cost for pumping system of the recirculation
$Freq_a$	frequency of acid cleaning, times.y⁻¹
$Freq_b$	frequency of basic cleaning, times.y⁻¹
GC	gas chromatography
GGM	galactoglucomannans
i	interest rate, decimal %
i_m	interest rate for membrane replacement, decimal %
IRR	internal rate of return, year
J	Permeate flow rate, L.m⁻².h⁻¹
LCC	lignin carbohydrate complexes
MA_C	maintenance costs
M_{annual}	annual mass of extracts produced, kg.y⁻¹
M_C	membrane replacement costs
ML	membrane lifetime, years

m_{lignan}	mass of lignin
m_{lignin}	mass of lignans
$m_{phenolic\ acids}$	mass of phenolic acids
$m_{polyphenols}$	mass of polyphenols
MS	mass spectrometry
N	membrane module number
NF	nanofiltration
OMWW	olive mill wastewater
OPEX	operating expenditures
P	inlet pressure of membrane, kPa
p_e	total perimeter of membrane channels, m
P_R	pressure to compensate head-loss, Pa
P_V	membrane module cost
Q	feed flow entering each membrane step, $m^3.h^{-1}$
Q'	feed flow rate, $m^3.s^{-1}$
Q_R	recirculation flow rate, $m^3.h^{-1}$
Q'_R	recirculation flow rate, $m^3.s^{-1}$
RO	reverse osmosis
RR	retention rate
S	membrane total section, m²
TMP	thermomechanical process
u	cross flow velocity, $m.s^{-1}$
UF	ultrafiltration
V_{annual}	annual volume of process water, $m^3.y^{-1}$
V_C	volume of cleaning solution, m^3
VR	volume reduction,
V_R	demineralized water volume, m^3
η	energy efficiency of pumping systems, decimal %