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ON-SITE RECOVERY OF HEMICELLULOSES FROM THERMOMECHANICAL PULP MILL PROCESS WATER BY MICROFILTRATION AND ULTRAFILTRATION

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During mechanical defibration of wood, a minor fraction of the wood mass is dissolved in the process water. These dissolved substances represent an extra energy demand when they are treated in the mill's wastewater treatment plant. Galactoglucomannan, the main hemicellulose in spruce, can be recovered from thermomechanical pulp mill process water by a process based on microfiltration (MF) and ultrafiltration (UF). The purpose of this work was to study the scale-up of the process from laboratory scale to continuous industrial scale. MF was first studied in the laboratory, and then combined with UF in a continuous pilot process on-site at a pulp mill. The data obtained were used to estimate the cost of the membrane processes for galactoglucomannan recovery which was found to be about €1160 per ton hemicelluloses.

KEYWORDS. Microfiltration, ultrafiltration, hemicelluloses, galactoglucomannan, thermomechanical pulp

INTRODUCTION

Printed media such as newspapers and magazine are facing tough competition from digital media. This means that paper mills, in particular mechanical pulp mills, since they produce newsprint, are under pressure to reduce costs. The high pulp yield (90–97%) in the production of thermomechanical pulp (TMP) has meant that there has previously been no need to utilize the solids released during refining. The dissolved substances found in the wastewater from the mechanical pulping of spruce consist of soluble carbohydrates (hemicelluloses), lignin, and extractives. The hemicelluloses in the process water have previously been shown to mainly consist of high molecular mass galactoglucomannan (GGM)^[1] and smaller amounts of hemicelluloses of lower molecular mass like

arabinoglucuronoxylan and arabinogalactan.^[2] Today, there is considerably interest in utilizing these by-products. This is partly due to increased awareness that renewable raw materials must be used optimally in a sustainable society, and partly due to the desire to reduce the energy demand in biological wastewater treatment plants where these substances are degraded today.

Several GGM-based products have been developed on laboratory scale.^[3–8] The reason why development has not been scaled up is largely related to the fact that GGM is currently not available at the quantities required on the commercial scale. One of the challenges in recovering the solutes in process streams from mechanical pulping is their low concentration. The concentration of GGM is only about 2 g/L in process streams

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in TMP mills. Membrane processes are the only environmentally and energy-sustainable option for concentrating and purifying substances in such diluted solutions. Laboratory experiments on the extraction of GGM from TMP process water using membrane processes have yielded promising results,^[9,10] and on-site trials of GGM recovery on the kg-scale have been conducted to produce GGM for research purposes.^[3] However, to the best of our knowledge, no results have been published from pilot-scale filtration experiments conducted during on-site GGM recovery.

The aim of this work was to study the recovery of GGM in TMP process water. The recovery method is based on a three-step process proposed by Persson et al.^[11] In the first step, fibers and particles are separated by prefiltering, after which suspended and colloidal material (extractives) are removed by microfiltration (MF). Finally, the hemicellulose fraction is concentrated and purified to remove low-molecular-mass materials such as lignin, mono- and oligosaccharides, and salts through ultrafiltration (UF). The cost of the two membrane stages in the hemicellulose recovery process was estimated based on UF data from on-site experiments at a Swedish TMP mill, and MF data from lab experiments. Lab data were used to estimate the performance of the MF stage due to limitations of the prefilter and the MF plant used in the on-site trial.

MATERIALS AND METHODS

Process Water

Softwood (mainly spruce) is used as raw material at the TMP mill. The process water used in this work was withdrawn from the disc filter after the refiner. This stream is normally recirculated before being discharged into the wastewater system. The temperature and pH of the process water are about 80 °C and 4.2, respectively. Characteristic concentrations of solutes in the process water are given in Table 1. Apart from hemicelluloses, the process water contains residues of fibers, lignin, salt (ash in Table 1) and extractives. The extractives can be found dissolved in the

Table 1. Characteristic composition of TMP pulp mill process water

Total solids (g/L)	6.5 ± 0.7 ^a
Ash (g/L)	1.2 ± 0.4 ^a
Hemicelluloses (g/L)	2.3 ± 0.3 ^a
- Arabinan (g/L)	0.1 ± 0.0 ^a
- Galactan (g/L)	0.3 ± 0.0 ^a
- Glucan (g/L)	0.6 ± 0.1 ^a
- Mannan (g/L)	1.3 ± 0.1 ^a
Total lignin (g/L)	1.1 ± 0.1 ^a
Turbidity (NTU)	200 ± 64 ^b

^aBased on 12 samples withdrawn during 7 months.

^bBased on 22 samples withdrawn during 7 months.

process water, and as colloids stabilized by adsorbed polysaccharides.^[12]

Equipment

On-Site Pilot Plant. The pilot plant, containing three subunits, as shown in Figure 1, was stationed at the TMP mill. The subunits were an Auto-Line M (HiFlux Filtration, Denmark) prefilter, a MultiBrain CFU032 pilot unit (LiqTech, Denmark) MF unit and a MF/UF pilot plant 70236-6.3" (Alfa Laval, Denmark) UF unit.

The prefilter consisted of an 860 cm² filter basket with perforated round 100 μm holes, equipped with a scraper to cut fibers stuck in the filter. Process water withdrawn after the disc filter was first filtered in the prefilter in order to remove particles and fines.

The MF unit was supplied with prefiltered process water from a feed tank (Buffer tank 1 in Figure 1), whose level was controlled using a floater to regulate the withdrawal of prefiltered process water from the prefilter. The MF unit was equipped with 26 tubular LiqTech membrane elements (Liqtech, Denmark) made of SiC, with a total membrane area of 8.6 m². The membrane has properties in the boundary between MF and UF and is denoted "UF membrane" in the data sheet of LiqTech but is denoted MF membrane in this paper. The inner diameter of the flow channels of the MF membranes was 3 mm. The MF unit was operated at a crossflow velocity of 3 m/s, while the temperature was dictated by the temperature of the prefiltered process water, 74–77 °C. The MF retentate containing particles and extractives was discarded, while the clear MF

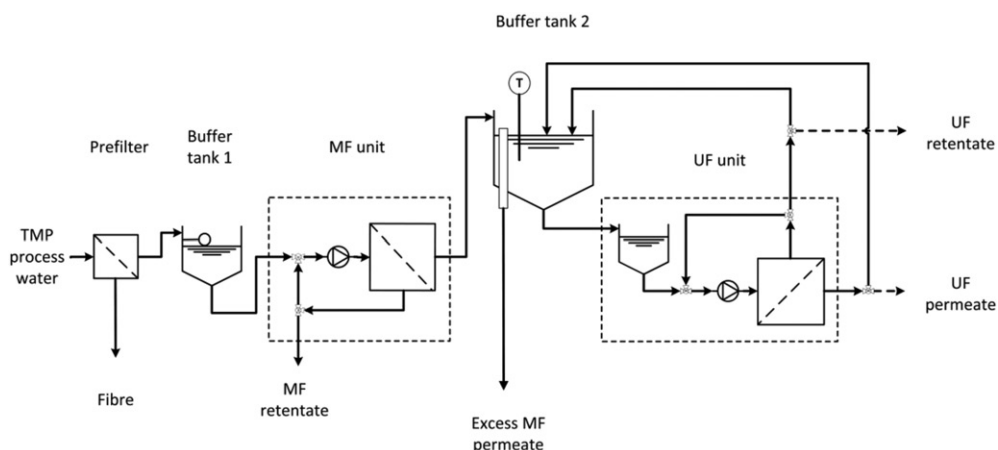


FIGURE 1. Schematic of the pilot plant used for the recovery of hemicelluloses.

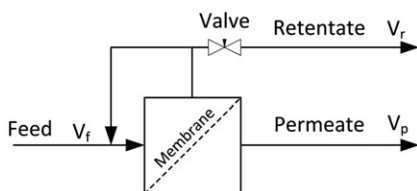


FIGURE 2. Schematic illustration of the process streams in a membrane unit.

permeate was collected in Buffer tank 2, which served as the feed tank to the UF unit.

The level in the feed tank for the UF unit was kept constant by allowing excess MF permeate to be withdrawn by an overflow. The UF unit has an additional internal feed tank whose level is regulated automatically by the UF unit. The UF unit was equipped with one 6.3" RC10PE spiral-wound element (Alfa Laval, Denmark) made of regenerated cellulose on a polyester support, with a nominal cutoff of 10 kDa and a membrane area of 15.75 m². The feed channel spacer was 48 mil.

The volume reduction (VR) is the ratio between the flow of permeate, V_p , and the flow of feed, V_f . In membrane plants, the VR is usually controlled by the ratio between V_p and the flow of retentate, V_r .

$$VR = \frac{V_p}{V_f} = \frac{1}{\left(1 + \frac{V_r}{V_p}\right)} \quad (1)$$

A schematic illustration of the feed, retentate, and permeate streams is shown in Figure 2. Constant VR was maintained in the

MF unit by automatic control of both the permeate and retentate flow in the unit. A constant permeate flux was maintained by successively increasing the pressure. The flux and VR of the MF unit were maintained at 90 L/m²h and 50%, respectively. These values were determined by the amount of prefiltered process water available from the prefilter, and the minimum MF retentate valve set point determining the lowest achievable retentate flow in the MF unit.

The volume reduction in the UF unit was automatically adjusted by regulation of the retentate valve when VR was <80%. When VR was >80% the VR was adjusted manually. During the UF studies at a VR of 98%, concentration was performed in two steps. First, the concentration in the UF loop was increased with the retentate valve closed while withdrawing permeate, thus operating the plant in dead-end batch mode. When the desired VR was reached, the retentate valve was opened slightly, until the ratio between the permeate and retentate corresponded to the desired VR, and the collection of retentate started.

The ceramic MF membrane was cleaned with the acidic cleaning agent Ultrasil 73 (Ecolab AB, Sweden), and periodically with oxidizing cleaning agents, either hydrogen peroxide or sodium hypochlorite, under alkaline conditions. The UF membrane was cleaned with Ultrasil 110 (Ecolab AB, Sweden). Steam condensate was used for rinsing and cleaning of the membrane units.

Lab MF Unit. The set-up used for the lab MF concentration study has been described previously.^[13] Briefly, the unit was equipped with a single ceramic MF membrane of the same type and dimensions as used in the on-site pilot plant. The TMP mill process water was preserved with about 1 wt% of the biocide Fennosan M9 (Kemira, Sweden) before being sent to our lab, where additional fiber was removed using a 75 μm mesh strainer. The MF batch concentration was conducted at a temperature of 80 °C, a crossflow velocity of 3 m/s and a transmembrane pressure of 0.6 bar. The concentration study started in semi-batch mode, new process water being added to the feed tank at the same rate as permeate was withdrawn until all the feed had been added, after which concentration continued as batch concentration. A total of 974 L of TMP process water was concentrated until a retentate volume of 20 L remained, corresponding to a VR of 98%.

Analytical Methods

The content of total solids, ash and lignin, as well as the turbidity of the MF feed, was determined using methods described elsewhere.^[14] The content of hemicelluloses was determined by acid hydrolysis and detection by high-performance anion exchange chromatography with pulsed amperometric detection, as described previously.^[14]

The on-site UF unit was equipped with a refractometer to measure the concentration of dissolved solids in the retentate continuously as degrees Brix (°Bx). This device was used for on-line observation of the changes in the content of dry substance in the UF retentate.

RESULTS AND DISCUSSION

Prefiltration

Severe problems were experienced with the prefiltration equipment at the beginning of the on-site experiments. The prefilter rapidly became blocked and was soon in constant cleaning mode. The studies could be

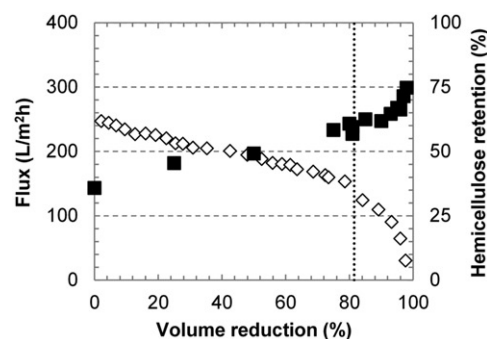


FIGURE 3. Flux (\diamond) and retention of hemicelluloses (\blacksquare) during lab MF concentration at 0.6 bar transmembrane pressure, a temperature of 80 °C and crossflow velocity of 3 m/s. The transition from semi-batch to batch mode is indicated by the dotted line.

resumed after the filter with 40 μm slots, was exchanged for one with round 100 μm perforated holes, and installing a new scraper capable of cutting fibers stuck in the filter. A sustainable filtration capacity of 1.5 m³/h was obtained.

Microfiltration

Laboratory-Scale MF. A MF batch concentration study was conducted to investigate the development of flux and hemicellulose retention with increasing VR. The batch of process water had a total dry solids content of 7.4 g/L, of which 2.0 g/L was hemicelluloses and 1.3 g/L lignin. The initial flux was 250 L/m²h, which decreased to 15 L/m²h at a VR of 98%, as shown in Figure 3. The concentration study transitioned from semi-batch to batch mode at a VR of 81.5%. The retention of hemicelluloses increased from 36% to 75% during the concentration study, yielding a MF permeate containing 1.7 g/L hemicelluloses, which corresponds to a recovery of 85%. The average flux during the entire concentration study was 145 L/m² h.

On-Site MF. The transmembrane pressure and retention of hemicelluloses in the MF unit during the period of the on-site UF experiments are shown in Figure 4. The transmembrane pressure increased gradually during filtration. The increase in transmembrane pressure was mainly due to the

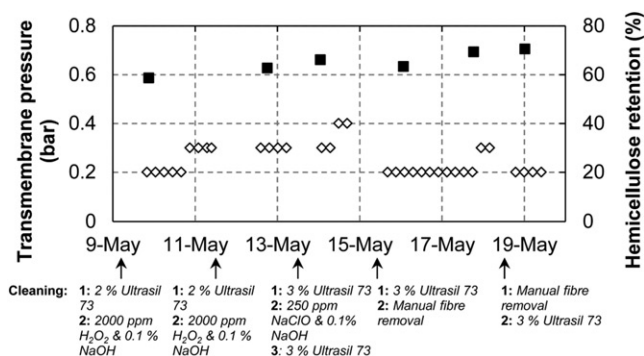


FIGURE 4. Transmembrane pressure (◇) and hemicellulose retention (■) during 10 days of operation of the MF unit during the on-site pilot trial. The MF unit was operated at a constant flux of 90 L/m²h.

accumulation of fibers in the membrane module inlet, and removal of these fibers decreased the transmembrane pressure to the initial 0.2 bar again. The retention of hemicelluloses was higher during MF at the continuous on-site trial (59–71%) than in the lab batch study (49% at VR 50%). This is to be expected as more fouling will accumulate in a continuously run plant with time compared to a batch study. The concentration of hemicelluloses in the MF permeate used as feed to the UF unit was 1.1–1.4 g/L.

It was noted that the turbidity of the MF permeate was low (≤ 2 NTU) when measured on-site, while the turbidity of the MF permeate increased somewhat in samples that had been frozen and analyzed on a later occasion (8–24 NTU). The action of freezing and thawing MF permeate thus causes dissolved material to aggregate. The ability of GGM to form aggregates has been previously demonstrated by Xu et al.^[15]

Ultrafiltration

Filtration studies were carried out to evaluate the UF flux and hemicellulose retention at various values of VR using the RC10PE membrane during continuous operation with fixed parameters. Figure 5 shows the flux and transmembrane pressure during the experiments at VRs of 50% and 80%. The transmembrane pressure was first increased stepwise up to 5.95 bar and then kept constant. The flux at a VR of 50% was reasonably stable, starting at 220 L/m²h and decreasing

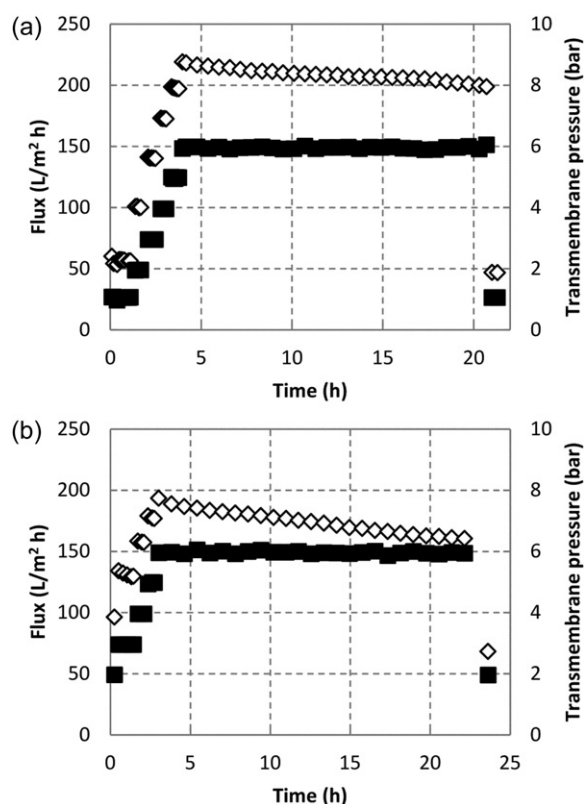


FIGURE 5. Flux (◇) and transmembrane pressure (■) during constant VR: (a) 50% and (b) 80%.

to 205 L/m²h after 13 h at constant pressure and VR (17 h from the start of the experiment), as can be seen in Figure 5a. After 17 h, the flux began to fall somewhat more rapidly, and was 200 L/m²h at 20.4 h. The flux decline starting at 17 h was due to interruption of the MF permeate supply, causing a 2 °C drop in temperature in the time interval from 17 to 20.4 h. The pressure at both the

start and end of the experiment was 1.05 bar. At the beginning of the experiment, the flux at 1.05 bar was $56 \text{ L/m}^2\text{h}$ and at the end $46 \text{ L/m}^2\text{h}$, indicating a moderate amount of membrane fouling, although the temperature was higher at the beginning of the experiment than at the end, 60°C and 56°C , respectively. The retention of hemicelluloses was 88%.

During the experiment at a VR of 80%, the flux was initially $195 \text{ L/m}^2\text{h}$ at 5.95 bar, and decreased to $160 \text{ L/m}^2\text{h}$ at 22 h (Figure 5b). The VR at the end of the experiment was reduced to 50%, and the pressure to 1.95 bar, resulting in a flux of $68 \text{ L/m}^2\text{h}$. This was lower than under the same conditions during the stepwise increase in pressure at the beginning of the experiment, $96 \text{ L/m}^2\text{h}$. The retention of hemicelluloses during the VR of 80% was 93%.

Two experiments were conducted at a VR of 98%. During startup of the first study, the transmembrane pressure was increased stepwise to 5.95 bar, resulting in a flux of $185 \text{ L/m}^2\text{h}$, as can be seen in Figure 6a. The retentate valve was then closed, to allow the UF plant to be run in dead-end batch mode until a concentration in the recirculation loop corresponding to VR 98% had been achieved. At the high flux at the beginning of the dead-end batch concentration, the UF permeate flow rate ($2.9 \text{ m}^3/\text{h}$) was higher than the MF permeate flow rate (i.e., the UF feed flow rate, $0.8 \text{ m}^3/\text{h}$), which meant that the volume in the UF feed tank (Buffer tank 2, about 2 m^3) was soon depleted. After 3 h, buffer tank 2 had been emptied and the permeate was recirculated to the internal feed tank for 1.5 h until enough MF permeate had been collected so that the UF permeate could be discarded again. This is reflected by a decrease in the rate of flux decline rate at about 3 h in Figure 6a, as the rate of concentration increase in the recirculation loop was slower during this period of time. The flux was $67 \text{ L/m}^2\text{h}$ when a VR of 98% was reached and the dry solids content in the recirculation loop had then increased to a

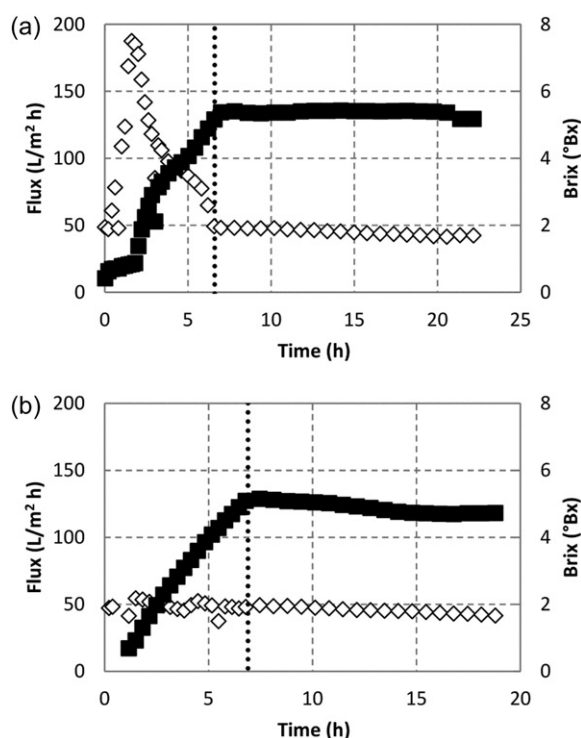


FIGURE 6. Flux (\diamond) and solids content (\blacksquare) of the retentate during UF, as degrees Brix, at a VR of 98%, where the pre-concentration was done at 5.95 bar (a) or at a constant flux of $50 \text{ L/m}^2\text{h}$ (b). The temperature was 60°C and the frictional pressure drop over the membrane element was 1.1 bar. The transmembrane pressure during the collection of UF retentate was 2.45 bar in both studies. The transition from dead-end batch concentration mode to continuous mode is indicated by the dotted line.

corresponding brix value of 5.3°Bx . The pressure was then reduced to 2.45 bar, reducing the flux to $50 \text{ L/m}^2\text{h}$, to match the production of MF permeate, and collection of UF retentate at a rate of 15 L/h began. The pressure was kept constant at 2.45 bar for 15.9 h, during which the flux decreased to $42 \text{ L/m}^2\text{h}$. The concentration of solutes was rather constant during the collection of UF retentate, as shown by the brix value.

During the second experiment at a VR of 98%, a constant flux of $50 \text{ L/m}^2\text{h}$ was maintained during dead-end batch concentration by gradually increasing the transmembrane pressure from 1 bar to 2.45 bar until the final VR was reached. When the collection of UF retentate started at 6.9 h, the pressure was kept constant at 2.45 bar for 11.4 h until the study was stopped at 18.3 h. During this

time, the flux decreased from 50 L/m² h to 43 L/m² h.

Samples were withdrawn about 1 h after collection of the retentate had started in both studies at a VR of 98%. The retention of hemicelluloses and lignin was 98% and 40%, respectively. Both retentates had a dry mass content of 43 g/L and a hemicellulose concentration of 30 g/L.

Cost Estimates

The cost of a membrane system indicates to possible plant users whether the project is economically feasible or not. Cost estimates for membrane plants in pulp and paper mills are however quite rare in scientific journals. The cost to produce lignosulphonates from spent sulfite liquor has been evaluated by Bansal and Wiley^[16] and Eriksson,^[17] and the cost of kraft lignin recovery by Kirkman et al.,^[18] Holmqvist et al.,^[19] Jönsson et al.^[20] and Jönsson and Wallberg.^[21] An economic evaluation of isolation of hemicelluloses from a process stream from a thermomechanical pulp mill, based entirely on laboratory experiments, has also been done.^[11]

The cost of a membrane plant is largely dependent on the flux as the membrane area required is directly proportional to the average flux. The determination of a representative average flux is therefore of great importance. The operating costs include electricity for pumps providing transmembrane pressure and crossflow velocity, costs for membrane replacement, chemicals and rinsing water for cleaning, and maintenance and labor costs. The cost of membrane filtration for hemicellulose recovery in this work was estimated based on the results of the lab MF batch study and the on-site pilot studies. The full-scale MF and UF plants were assumed to be continuous, multi-stage, feed-and-bleed systems.

The flux and retention data from the laboratory batch MF concentration study were used for the MF plant. However, a single batch concentration study is likely to overestimate the flux obtained in a continuous plant, due to the accumulation of

membrane fouling in the latter system.^[22] Experience from running MF continuously at a VR of 50% on-site revealed that it was difficult to maintain a flux higher than 150 L/m²h without membrane cleaning every second day, due to rapid membrane fouling (data not shown). Because of this, the MF flux curve was reduced to give a flux of 150 L/m²h at VR 50%, corresponding to a 21% reduction in the flux of the batch experiment. Using the same argument, the retention of hemicelluloses was increased by 30%, giving a retention of hemicelluloses of 69% at a VR of 50%, reflecting the average retention of hemicelluloses observed during on-site MF at this VR. Expressions for MF flux and hemicellulose retention as functions of VR were obtained from the adjusted MF flux and retention data by polynomial regression.

During the on-site continuous UF studies it was seen that the flux decreased with time. To obtain the average flux at a certain VR, it was assumed that the flux would continue to decrease linearly until the end of a 22-h filtration cycle before the membranes are cleaned. This would give average fluxes of 206 L/m²h and 178 L/m²h at VRs of 50% and 80%, respectively. Furthermore, it was assumed that at a VR of 98%, at least the same flux would be obtained at 5.95 bar transmembrane pressure as at 2.45 bar (44 L/m²h). It was also assumed that the flux at a VR <50% would be the same as at a VR of 50%. Polynomial regression was used to obtain expressions for UF flux and hemicellulose retention as functions of VR.

The full-scale plants were scaled to process 180 m³/h prefiltered process water containing 2.35 g/L hemicelluloses. The MF plant was assumed to contain 5 stages (plus one extra for cleaning), each containing 36 membrane housings with 8.6 m² membrane area per housing. The resulting VR would be 96.2% and the MF permeate would contain about 1.4 g/L of hemicelluloses. This is slightly higher than the MF permeate obtained during the on-site continuous MF which operated at a VR of 50%, a result of the higher final VR of

Table 2. Assumptions used in the cost estimates.

Microfiltration	
Investment cost (€/m ²)	3050
Membrane cost (€/m ²)	625
Membrane lifetime (years)	8
Cleaning chemical dosage (%)	3
Cleaning solution volume (L/m ²)	5.8
Rinsing water (multiples of cleaning solution volume)	5
Cleaning frequency of each stage (times per day)	0.5
Ultrafiltration	
Basic installation (€)	50 000
Installation cost (€/stage)	120 000
Membrane and housing (€/m ²)	150
Replacement membrane cost (€/m ²)	50
Membrane lifetime (years)	1
Cleaning chemical dosage (%)	2.5
Cleaning solution volume (L/m ²)	4.2
Rinsing water (multiples of cleaning solution volume)	5
Cleaning frequency of each stage (times per day)	1
Maintenance and labor (% of capital cost per year)	5
Clean water (€/m ³)	0.42
Cleaning chemicals (€/kg)	2.5
Electricity (€/MWh)	40
Pump efficiency (%)	80
Operating time (h/year)	8000
Annuity factor	0.1

the full-scale MF plant. The average flux of the entire MF plant was 112 L/m²h.

The full-size UF plant was set to contain three stages (plus one extra for cleaning), each with 9 parallel housings containing 3 spiral wound elements connected in series. The final VR of the UF plant would be 97.7% and 3.9 m³/h of UF retentate would be produced, containing 46 g/L of hemicelluloses (equivalent to 182 kg of dry hemicellulose/h). The concentration of hemicelluloses in the UF permeate would be 0.4 g/L. The average flux of the entire UF plant was 133 L/m²h.

The assumptions on which the cost estimate is based are presented in Table 2. These costs are based on a combination of in-house experience and communications with different membrane manufacturers.

The operational parameters for the MF and UF plants are presented in Table 3. The operational parameters for the MF plant are based on the lab concentration study, while the parameters for the UF plant are based on the conditions used during the on-site UF pilot trial.

The total cost was estimated to be €1159 per ton hemicellulose, as can be seen from Table 4. The cost is higher than previously

Table 3. Experimental data used in the cost estimates.

	Microfiltration	Ultrafiltration
Average transmembrane pressure (bar)	0.6	5.95
Pressure drop (bar per housing)	0.7	3.3
Crossflow	3 m/s	23 m ³ /h

Table 4. Cost of production of hemicelluloses.

	Microfiltration	Ultrafiltration
Capital cost (€/t _{hemi})	390	56
Operating cost (€/t _{hemi})	463	250
Electricity (€/t _{hemi})	61	26
Membrane exchange (€/t _{hemi})	100	59
Cleaning (€/t _{hemi})	108	138
Maintenance and labor (€/t _{hemi})	195	28
Total (€/t _{hemi})	853	306
Total cost (€/t _{hemi})		1159

reported, €630 per ton hemicellulose.^[11] However, this is due to the addition of the MF stage into the cost estimate. The largest cost is attributed to the MF plant, due to the high price of ceramic membranes compared to polymeric spiral wound membranes. The highest cost during UF arises from membrane cleaning, which constitutes 45% of the cost of UF.

Impact of Hemicellulose Recovery on the Mill

During the on-site trials, the concentration of organic material in the process water varied. The mean concentration of hemicelluloses in the process water was 2.35 g/L, which, with the full-size membrane filtration plants, would be reduced to 0.4 g/L after UF. Reducing the concentration of hemicelluloses by 1.95 g/L corresponds to a decrease in COD of 1740 mg/L. This can be compared to the polysaccharide xanthan, where 1 g/L of polysaccharide gives rise to 890 mg COD/g polysaccharide.^[23] Assuming an energy requirement of 674 kWh/t COD,^[24] the extraction of hemicelluloses results in an energy saving of 210 kW in a plant where the wastewater flux is 180 m³/h. This would cover

half of the power requirement of the membrane plants (total 400 kW). The savings would be even greater if the cost of waste water treatment chemicals and sludge disposal were included. Assuming a cost of waste water treatment of €0.28/kg organics removed,^[25] the removal of the hemicelluloses alone would save €280/ t_{hemi} . Additional savings could potentially be made, as other suspended materials and colloidal extractives are separated by this process in the MF retentate. The MF retentate could be further concentrated by evaporation and disposed of by combustion.

CONCLUSIONS

An on-site pilot trial with continuous recovery of hemicelluloses using MF and UF has been conducted. The average flux of full-scale MF and UF plants was estimated to be 112 L/m²h and 132 L/m²h, respectively, concentrating the hemicelluloses to 47 g/L. The cost of hemicellulose recovery using this method was estimated to be about €1160/ t_{hemi} , with the potential for further reductions of €280/ t_{hemi} or more when taking the reduced need for waste water purification into account.

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