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Influence of hemicellulose aggregate and gel layer formation on flux and retention during nanofiltration of alkaline solutions

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Abstract

Nanofiltration of process liquors from viscose-type textile fibre production was investigated using a laboratory-scale crossflow test apparatus. Feed solutions contained about 200 g/l sodium hydroxide and a high concentration of hemicellulose as a contaminant originating from the raw material wood. The effects of various pretreatments and the addition of reagents on flux, retention and irreversible fouling were studied. Reagent addition affected the solution state of hemicellulose thus purposely provoking aggregate formation. Dynamic light scattering and turbidity measurements were used to track the evolution of hemicellulose aggregates. Aggregation generally coincided with distinct flux decline during nanofiltration thus indicating that this phenomenon may result in the build-up of gel layers at the membrane surface. Partial neutralisation with sulfuric acid caused extremely severe fouling, whereas methanol addition had a minor effect. The impact of heat treatment and oxidative degradation of hemicellulose on nanofiltration performance was attributed to changes in molar mass distribution.

Keywords: Fouling; Hemicellulose; Aggregation; Gel layer; Dynamic light scattering

1. Introduction

The production of viscose-type cellulosic textile fibres from wood generates large amounts of

caustic soda waste liquors containing 200 g/l sodium hydroxide and dissolved hemicellulose as a contaminant. Hemicellulose is a collective term for polysaccharides originating from the raw material wood and their degradation products, e.g.

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sugar acids and hydroxycarboxylic acids. In the process liquors studied here, the high molar mass fraction mainly consists of 4-O-methylglucuronoxylan [1]. Hemicellulose is an undesired component in the viscose fibre production process because it deteriorates both processability and fibre quality. To maintain a certain hemicellulose concentration in the process liquors part of the hemicellulose has to be removed from the process with simultaneous minimisation of caustic soda losses. The purification of these process liquors by nanofiltration (NF) is a challenge not only because of the high corrosiveness of caustic soda but also due to the high concentration of organic solutes (chemical oxygen demand above 40,000 mg/l). Fouling is a critical issue of this process that reduces flux and leads to the need for rigorous cleaning procedures.

Carbohydrate chains in solution are able to interact with each other e.g. via hydrogen bonds thus forming different conformations and types of aggregates. The observation that xylans have a strong tendency to self-associate was first reported by Blake and Richards [2]. Several researchers investigated size exclusion chromatography (SEC) as a technique to detect xylan aggregates in dimethyl sulfoxide (DMSO)/water mixtures [3,4]. The mechanism of aggregation is not only influenced by the molar mass of the xylans but also by the nature and the occurrence of substituents such as acetyl groups and lignin residues. It was proposed that there is a relationship between xylan aggregation in aqueous solution and the formation of xylan structures on cellulose surfaces [4].

Massucco [5] modified the properties of ultrafiltration membranes by generating an irreversibly compressed hemicellulose gel layer under increased pressure. These gel layers adhered to the membrane surface even at high shear forces and reduced pressures and caused a permanent increase in retention at reduced flux. Aqueous suspensions of the acid-insoluble xylan fraction showed gelation at concentrations above 15–16 wt.% [6]. Gelation of the

bulk phase has also been observed in solutions of hemicellulose in DMSO/water mixtures [7]. It is therefore suggested that aggregation phenomena of hemicellulose in solution play an important role in the formation of gel layers during nano- and ultrafiltration.

Fouling phenomena during nanofiltration of polysaccharide solutions have been studied using both model substances [8–10] and real effluents from the pulp and paper industry [8,9]. It was observed that anionic substances were retained better and fouled less due to charge repulsion effects especially at high pH where most of the membranes are negatively charged as well. Flux decline was more distinct when using more open membranes particularly if they were permeable to the model substance [8]. In nanofiltration of real effluents a gel or cake layer formed that was controlled by crossflow velocity. The fouling layer disappeared upon rinsing the system, irreversible fouling was therefore found to be low [9].

The aim of the present study was to relate hemicellulose composition and supramolecular structure to nanofiltration performance parameters such as permeate flux, retention of hemicellulose and decrease in pure water permeability. A series of experiments was carried out using a laboratory-scale crossflow membrane test equipment. The evolution of hemicellulose aggregates was studied by dynamic light scattering (DLS) and turbidity measurements. The formation of aggregates and gel layers was purposely provoked by partial neutralisation and by addition of reagents that affect the solution state of hemicellulose such as copper cations or methanol. Hemicellulose composition and molecular structure were influenced by heat treatment and oxidative degradation.

2. Experimental

2.1. Test equipment, operating procedures and membranes used

Nanofiltration was carried out in laboratory scale with a flat-sheet crossflow membrane test

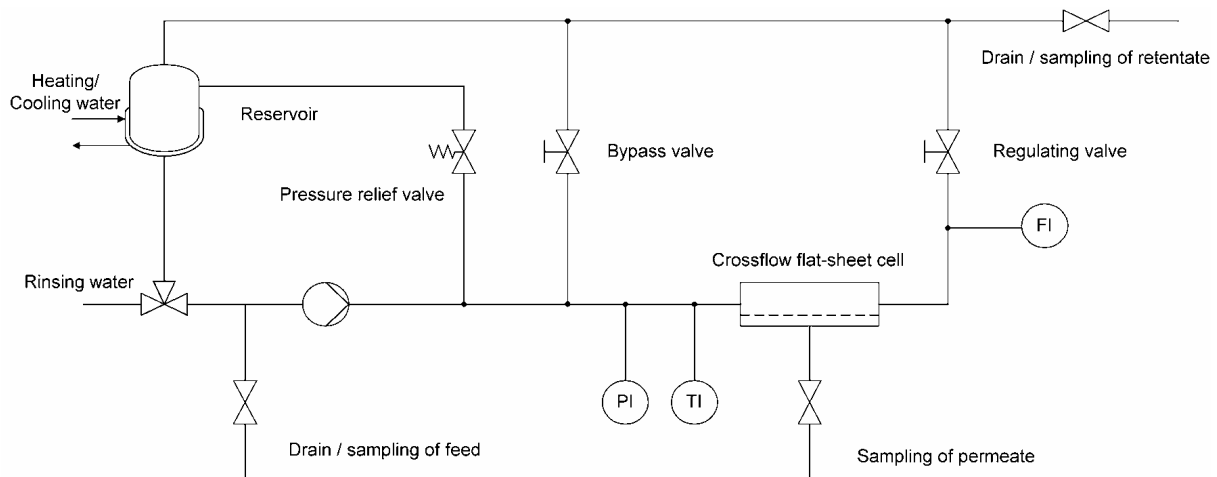


Fig. 1. Schematic drawing of the crossflow test apparatus.

equipment (Fig. 1) manufactured by KCS Osmota. The flow channel had a width of 40 mm, a length of 200 mm and a height of 1.1 mm, thus resulting in 80 cm² active membrane area. A 44 mil (1.1 mm) parallel spacer was inserted into the flow channel.

Alkaline resistant N30F membranes obtained from Microdyn-Nadir were used for all experiments (pH range 0–14). This polyethersulfone type of membrane is characterised by the manufacturer as follows. At the operating conditions of 40 bar, 20°C and 700 rpm in a stirred test cell, pure water permeability is between 40 and 70 l/(m²h), sodium chloride (0.5%) retention ranges from 25 to 35% and lactose (4%) retention is between 70 and 90%.

The operating procedure started with cleaning the membrane using a 1% Ultrasil 10 (Henkel-Ecolab) solution at 50°C for 60 min and thoroughly rinsing afterwards. This was followed by the determination of pure water flux at 20 bar, 20°C and a crossflow velocity of 0.75 m/s. After filling the apparatus with feed solution, all experiments were carried out at 25 bar, 30–40°C and 0.82 m/s. The retentate was always recycled back to the reservoir, whereas the permeate was either collected in a separate vessel (i.e. concentration mode) or

recycled to the reservoir as well (i.e. total recycle mode). Flux was calculated by measuring the time needed to collect a certain volume of permeate.

After each experiment, the equipment was rinsed again, and the pure water flux was measured at the operating conditions described above. The decline of pure water flux was calculated from the fluxes before and after the experiment. This reduction is regarded as a measure for the extent of irreversible fouling [9,10].

2.2. Properties and composition of process liquor

The process liquor studied here was taken from the pressing stage of the viscose production process, and it is accordingly designated as “press liquor”. It can be described as an orange-brown liquid containing about 200 g/l sodium hydroxide and a high concentration of organic solutes (Table 1). This causes appreciable viscosity and, in combination with high retention and low average molar mass, a high osmotic pressure difference between feed and permeate. The corrosiveness of this concentrated caustic soda solution is a challenge for materials selection, especially regarding the membrane material.

Table 1
Composition and physical properties of the process liquor

Property	Value
Chemical oxygen demand (COD), mg/l	44,200
Total organic carbon (TOC), mg/l	17,000
Sodium hydroxide, g/l	202.96
Total alkali ¹⁾ , g/l	207.18
Total inorganic carbon (TIC), mg/l	115
Fe ²⁾ , ppm	0.57
Mn ²⁾ , ppm	0.01
Mg ²⁾ , ppm	0.33
Si ²⁾ , ppm	1.26
Ca ²⁾ , ppm	3.73
Density ³⁾ , g/cm ³	1.19
Dynamic viscosity ³⁾ , mPas	3.33

¹⁾ expressed as sodium hydroxide equivalent

²⁾ analysed by ICP-OES

³⁾ at a temperature of 40°C

In the process liquors studied here, the high molar mass fraction which accounts for about one third of total hemicellulose mainly consists of 4-O-methylglucurono- β -1,4-D-xylan. Approximately 5% of the xylose units are substituted with 4-O-methylglucuronic acid residues [1]. The low molar mass fraction accounts for about two thirds of total hemicellulose. It predominantly consists of substances with a molar mass below 1,000 g/mol, but contains only 25% sugars in oligomeric form. Monomeric carbohydrates have not been detected in any of the fractions. The carboxylic acid groups of the hemicellulose molecules are deprotonated at the high pH leading to an anionic or polyanionic character of most organic molecules in the solution studied. Therefore it can be assumed that repulsive forces are acting between the solutes and the negatively charged membrane surface.

2.3. Methods of analysis

Sodium hydroxide concentration was measured by titration with 0.5N sulfuric acid to pH 8.2 using a Metrohm 716 DMS titroprocessor equipped with a pH electrode. Total alkali concentration (including sodium carbonate and sodium carbo-

xylates) was determined with the same method and titration to pH 3.7. Total organic carbon (TOC) and chemical oxygen demand (COD) measurements were used to calculate hemicellulose concentrations dividing by the ideal conversion factors for xylan of 1.212 and 0.454 for COD and TOC, respectively. COD was examined according to DIN 38409–H41-1 using potassium dichromate in sulfuric acid solution as an oxidant and silver sulfate as a catalyst. TOC was measured according to DIN 38409–H3-1 by catalytic oxidation of organic carbon and IR-spectrophotometric detection of the carbon dioxide generated.

The samples for SEC were diluted 1:20 with 0.5 N NaOH prior to analysis. SEC was performed using 2 MCX columns with a pore size of 1000 Å, 300 mm length and 8 mm diameter, obtained from Polymer Standards Service (PSS). The mobile phase was 0.5 N NaOH at a flow rate of 1 ml/min; refractive index (RI) detection was employed. Calibration was carried out with a set of cello-oligomers, pullulan and dextran standards. The plot of $\log(M)$ vs. retention volume was approximately linear. Dynamic light scattering detection showed that the amount of aggregates under these analytical conditions does not significantly influence the determination of molar mass distribution by SEC measurements [11].

The evolution of hemicellulose aggregates was studied by dynamic light scattering measurement of solutions that were stored in a cuvette at 60°C throughout the experiment. All measurements were performed on a laboratory-built goniometer (University of Graz) equipped with a 10 mW He-Ne laser ($\lambda = 632.8$ nm). The scattering cells (10 mm cylindrical cuvettes, Hellma, Germany) were tempered in a copper tower with small apertures for excitation beam and scattered light. For each experiment, the scattering angle was set at a fixed value (60° or 90°, depending on the initial intensity of scattered light). Detection was performed via a single mode fibre with GRIN lens coupled to a Thorn-Emi photomultiplier (type B2FBK/RFI), the output of which was analysed by an ALV-5000

digital multiple- τ correlator (ALV, Langen, Germany) with 256 quasi-exponentially spaced channels.

Measurement of turbidity was used instead of DLS for offline analysis of aggregation behaviour during the NF experiments. Samples were taken during NF, and the turbidity was measured using a cuvette before the samples were reintroduced to the NF test cell. However, this method does not provide information about average size or size distribution of aggregates. Turbidity was determined with a Lovibond LAB-IR turbidimeter at a wavelength of 860 nm and a scattering angle of 90° . This device conforms to specifications set forth in ISO 7027. Calibration was carried out with three formazin standards having turbidities of 0.02, 10 and 1000 NTU, respectively. Viscosity was measured by means of a rolling ball viscometer by Höppler (manufactured by Haake) according to DIN 53015.

3. Results and discussion

3.1. Dynamic light scattering experiments

The formation of hemicellulose aggregates was studied using dynamic light scattering measurements. Total intensity of scattered light as detected by the count rate of the photomultiplier increased during aggregate development and growth, while intensity distribution revealed relative changes in aggregate size. The quantity measured in DLS is the angular dependent auto-correlation function $g_2(q, t)$ of the coherently scattered light; $g_2(q, t)$ is related to the auto-correlation function of the electric field $g_1(q, t)$ in a homodyne experiment by Eq. (1):

$$g_2(q, t) = A \left(1 + B |g_1(q, t)|^2 \right) \quad (1)$$

A is the base line and B is the coherence factor. q is the scattering vector, defined by Eq. (2)

$$q = \frac{4 \cdot \pi \cdot n_0}{\lambda_0} \sin\left(\frac{\theta}{2}\right) \quad (2)$$

where n_0 is the refractive index of the solvent, λ_0 the excitation wavelength in vacuum, and θ the scattering angle. For a polydisperse system and at a constant scattering angle, $g_1(t)$ may be expressed as superposition of the contributions of all particle sizes present to the field correlation function:

$$g_1(t) = \int G(\Gamma_i) \exp(-\Gamma_i t) d\Gamma \quad (3)$$

Eq. (3) represents the Laplace transformation of the probability density function $G(\Gamma)$ of the translational diffusion coefficients D_i . With $\Gamma_i = q^2 D_i$, the diffusion coefficient D can be related to the hydrodynamic radius R_H with the Stokes-Einstein relation $D = k_B T / 6\pi\eta_0 R_H$, where η_0 is the dynamic viscosity of the solvent, T the temperature, and k_B Boltzmann's constant. By inverse Laplace transformation of Eq. (3), the intensity-weighted size distribution of the hydrodynamic radii of the particles present in the solution can be estimated [12]. This graphic representation accentuates larger particle populations by the intensity-radius relationship ($I \propto R_H^6$ for globular particles).

The DLS method is an appropriate tool to gain qualitative information about the distribution of the sizes of particles in diluted solutions on the basis of a measurement of only one sample solution. While absolute analysis of concentrated solutions is more complicated, solutions of equal concentrations (= equal viscosities) can be compared with each other. As a result, apparent hydrodynamic radii of the particles are obtained.

Aggregation of hemicellulose was observed in a retentate obtained from a NF pilot plant containing 145 g/l hemicellulose and 200 g/l sodium hydroxide (Fig. 2). There was an appreciable time lag (about two days) until aggregates were large enough to be detected. The growth of aggregates accelerated thereafter, and the average size of the aggregates increased markedly with time.

When retentate was diluted with pure NaOH solution or pure water in a cuvette, intensity of scattered light decreased again (Fig. 3a). This took

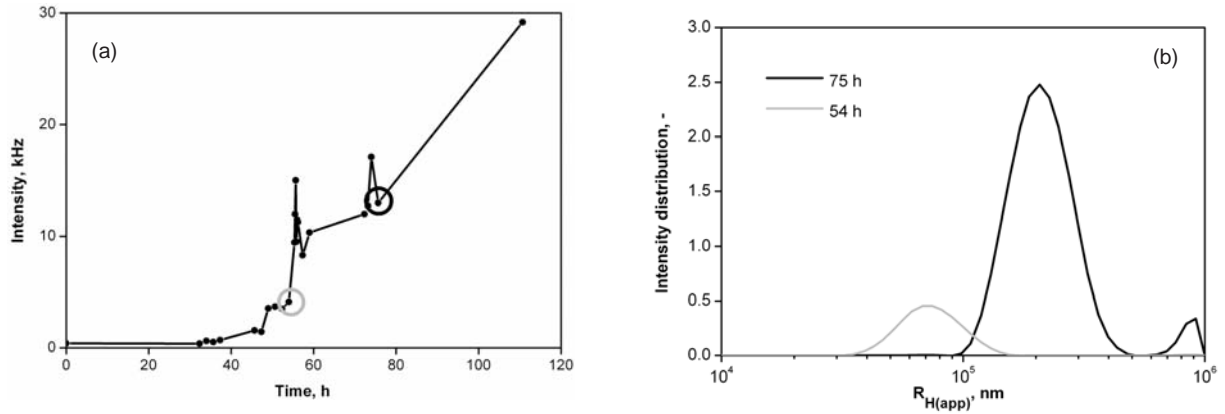


Fig. 2. (a) Intensity at a temperature of 60°C and 60° scattering angle as a function of time. Substrate: retentate with 145 g/l hemicellulose and 200 g/l NaOH concentration; (b) intensity distribution at selected time.

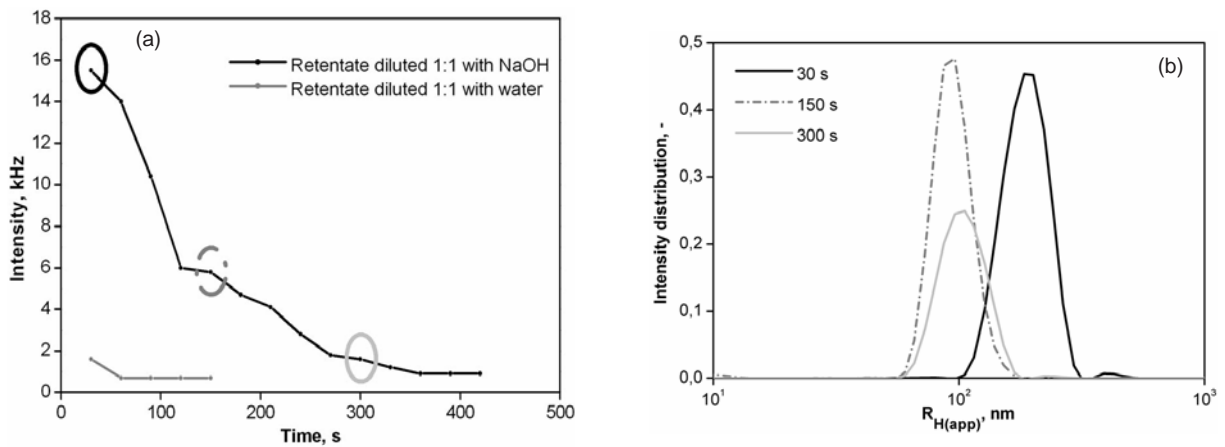


Fig. 3. (a) Decrease of scattering intensity upon dilution of retentate, measured at a temperature of 60°C and 90° scattering angle. Substrate: retentate with 175 g/l hemicellulose and 200 g/l NaOH concentration (undiluted). (b) Intensity distribution at selected time for dilution with NaOH. The pattern of each trace corresponds to that of its corresponding point on the intensity–time curve in Fig. 3a.

place much faster in the case of water dilution. Therefore, kinetic effects obviously played an important role in the redissolution of aggregates. When temperature was raised from room temperature to 60°C redissolution was accelerated by about three orders of magnitude. In a first step, aggregate size decreased, as indicated by a decrease in $R_{H,app}$ between 30 s and 150 s (Fig. 3b).

This was probably caused by a removal of molecules from the outer layers of the aggregates. The number of aggregates (represented by the height of the intensity distribution) was reduced in a second step either because small aggregates completely disappeared or due to a collapse of relatively large aggregates resulting in several small debris.

3.2. Heat treatment

Heat treatment is a means to change chemical composition and molecular structure of hemicellulose. Press liquor was heat treated in the darkness, without access of oxygen, at 60°C for 400 h, and permeate from a NF pilot plant was heat treated under the same conditions for 200 h. Press liquor showed enhanced flux at lower retention after heat treatment, whereas the opposite effect on the pilot plant permeate was observed (Fig. 4). These results were elucidated when the molar mass distributions before and after heat treatment (Fig. 5) were taken into account. Press liquor was degraded during heat treatment, and the relative amount of the high molar mass fraction decreased while the concentration of the low molar mass fraction increased distinctly. Total hemicellulose concentration remained constant, but the potential for the build-up of fouling layers was reduced as the fraction of high molar mass solutes diminished. Consequently, fouling was less severe after heat treatment of press liquor.

Heat treatment of pilot plant permeate showed quite a different effect. SEC revealed an increased area of the shoulder of the low molar mass peak

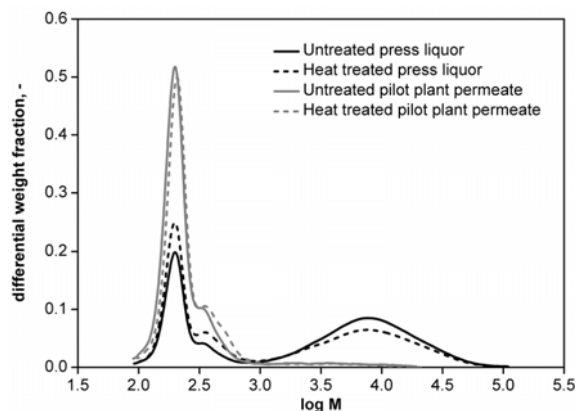


Fig. 5. Molar mass distribution of press liquor and permeate from a nanofiltration pilot plant before and after heat treatment.

(log (M) between 2.5 and 3.0) corresponding to the molar mass of oligosaccharidic components. This may be explained by re-condensation reactions during heat treatment of pilot plant permeate, possibly of the aldol condensation type. The result was a slightly increased average molar mass of hemicellulose after heat treatment. The change in molecular structure and chemical composition also increased the fouling propensity of pilot plant

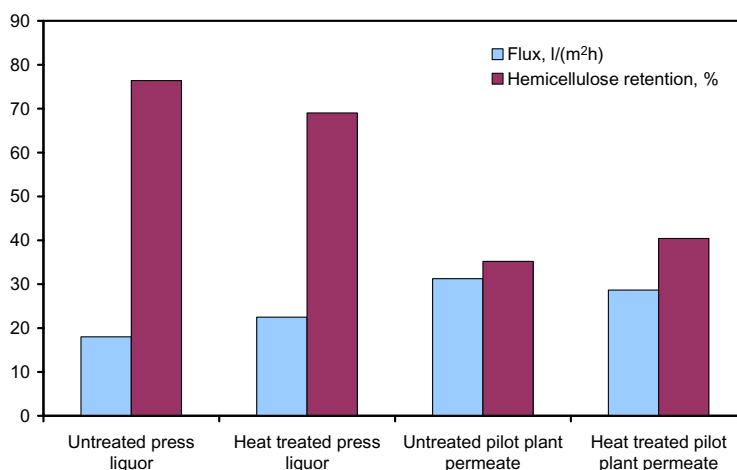


Fig. 4. Flux and hemicellulose retention of untreated and heat treated press liquor and permeate from a nanofiltration pilot plant (volumetric recovery: 37%, 25 bar, 36°C, 0.82 m/s).

permeate. The reduction of pure water flux after the experiment was noticeably higher for a treated pilot plant permeate than for untreated feed. The pure water fluxes during all experiments of this study were higher than specified by the manufacturer, probably due to the contact with strong caustic that increased membrane hydrophilicity.

The possible effect of changes in osmotic pressure difference between retentate and permeate ($\Delta\pi$) was estimated using the linear relationship by van't Hoff [13]. For the contribution of hemicellulose, the number averaged molar mass in retentate and permeate was obtained from the SEC results. Furthermore, the number of sodium ions that act as counterions for the carboxylate groups was calculated from the titration curve (difference of sulfuric acid volumes needed for titration to pH 8.2 and 3.7, respectively). Sodium carbonate concentrations were calculated from total inorganic carbon (TIC). Concentration polarisation was estimated from mass transfer correlations found in the literature [14]. In case of press liquor, the calculated $\Delta\pi$ was about 1.5 bar. After heat treatment, $\Delta\pi$ was about 0.9 bar due to variations in hemicellulose average molar mass and retention. The net driving force ($\Delta p - \Delta\pi$) was therefore approximately constant. Similar changes in $\Delta\pi$

were obtained for the pilot plant permeate. Accordingly, the variations in $\Delta\pi$ were not large enough to cause the flux changes observed.

3.3. Oxidative degradation

Press liquor was oxidatively degraded by successive addition of a 30% hydrogen peroxide solution (20 ml per litre of press liquor) when boiling under reflux at atmospheric pressure for 24 h. Nanofiltration was carried out in concentration mode until 51% of the feed solution had been recovered as permeate. The permeate obtained thereafter was recycled to the reservoir to keep hemicellulose concentration constant.

Oxidative degradation resulted in a significantly higher flux compared to the original process liquor (Fig. 6). However, whereas the original press liquor flux appeared to have stabilised, the oxidatively degraded press liquor flux was still declining at the end of the run.

SEC indicated a significant decrease of average molar mass as molecules were oxidatively degraded (Fig. 7). The relative amount of the acid-insoluble high molar mass fraction dropped from 37 to 12% of total hemicellulose, and a high quantity of UV-active low molar mass molecules was created.

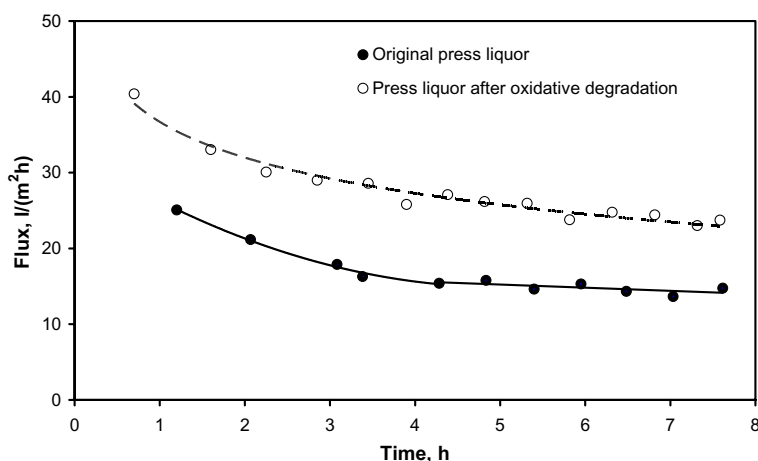


Fig. 6. Flux during nanofiltration of original and oxidatively degraded process liquor at 51% recovery, 25 bar, 41°C and 0.82 m/s.

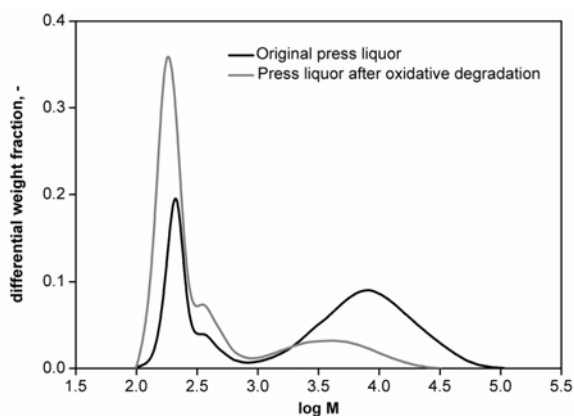


Fig. 7. Effect of oxidative degradation on molar mass distribution of hemicellulose in press liquor.

Press liquor after oxidative degradation showed a slightly lower COD/TOC ratio indicating a higher level of oxidation of the organic substances in the liquor.

Hemicellulose retention was reduced from 81 to 59% after oxidative degradation, which was attributed to the lower average molar mass of hemicellulose. The reductions of pure water flux after the experiment were 12 and 9% for original and degraded press liquor, respectively. Thus, irre-

versible fouling slightly decreased upon oxidative degradation.

Calculations of the osmotic pressure difference between retentate and permeate indicated that osmotic pressure effects were not responsible for the increase in flux after oxidative degradation. On the contrary, the net driving force was lower after oxidative degradation due to significantly reduced hemicellulose average molar mass and higher concentration of sodium carboxylates in the retentate.

3.4. Methanol addition

Lower alcohols are poor solvents for polysaccharides. For complete precipitation, alcohol has to be added in excess. In this study, comparatively low volumes of methanol were added to the press liquor in order to affect the solution state of hemicellulose and to provoke the formation of aggregates without generating significant amounts of precipitate.

When methanol was added incrementally during nanofiltration of press liquor, an insignificant increase of turbidity was observed after the first addition (Fig. 8). Appreciable amounts of aggregates were not formed, and flux remained

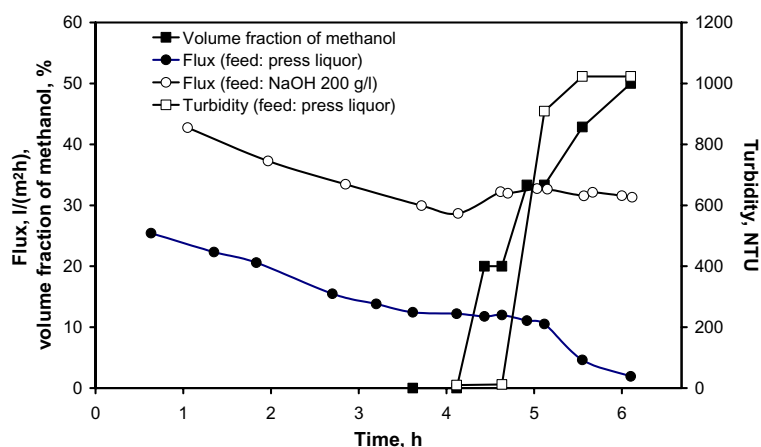


Fig. 8. Volume fraction of methanol added, flux and turbidity as a function of time during incremental addition of methanol to press liquor and NaOH 200 g/l (operating conditions: 48% recovery, 25 bar, 32°C, 0.82 m/s).

approximately constant. The addition of another volume of methanol lead to a marked increase in turbidity that can be attributed to the initiation of aggregate formation. Interestingly, flux did not yet fully respond to this observation and showed a minor decrease. A significant flux decline was encountered after the third addition of methanol. At that point turbidity exceeded the upper limit of detection. The fourth volume of methanol again decreased the flux significantly, but the instrument was not capable of measuring an additional increase of turbidity.

The corresponding blank experiment was conducted using an aqueous solution of 200 g/l sodium hydroxide (analytical grade) as feed and the same time and volume of methanol added as in the press liquor experiment. It was observed that the first addition of methanol caused an increase in flux. During further addition of methanol, flux remained constant at the level of the first addition. The observed flux behaviour was in contrast to the behaviour of press liquor/methanol mixtures.

Estimation of osmotic pressure effects during the addition of methanol is difficult due to the uncertainty in the activity coefficients. However, retention of methanol is close to zero under the experimental conditions employed. In addition,

hemicellulose retentate concentrations are reduced when the solution is diluted with methanol. Therefore methanol addition has a minor effect on the osmotic pressure difference.

For a detailed nanofiltration experiment, a solution containing 62.5 vol.% of press liquor and 37.5 vol.% of methanol was prepared as feed ('methanol diluted press liquor'), and a reference experiment was also done without methanol addition (Fig. 9). The same two experiments were conducted using an aqueous solution of 200 g/l sodium hydroxide (analytical grade). All runs were carried out in total recycle mode. Flux was distinctly lower when methanol was added to press liquor compared to the reference experiment with undiluted press liquor. In case of the NaOH feed solution, methanol addition had the effect of increasing flux.

The press liquor/methanol mixture was significantly turbid before the nanofiltration experiment indicating the formation of hemicellulose aggregates, but, surprisingly, the retentate became visually clear in the course of the experiment, and it got turbid again after discharge from the apparatus. Contrarily, a sample of retentate that was stored without stirring at the same temperature as the NF experiment remained highly turbid thus

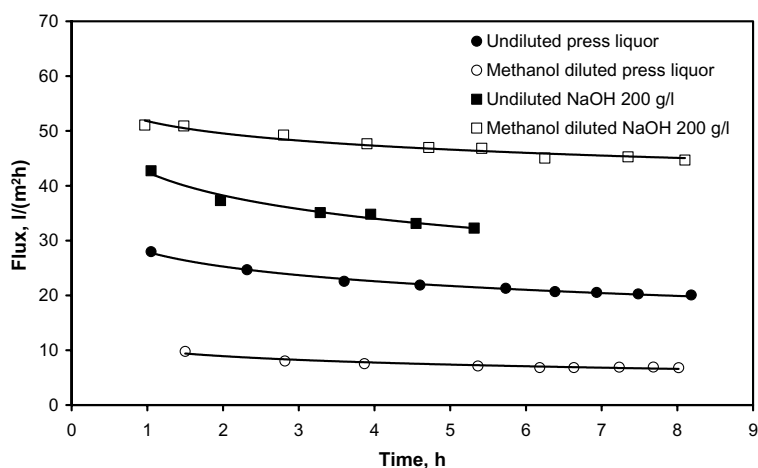


Fig. 9. Time dependence of flux during NF of press liquor and NaOH 200 g/l with and without methanol addition (total recycle mode, 25 bar, 41°C, 0.82 m/s).

indicating that no significant redissolution of hemicellulose aggregates occurred. It can therefore be concluded that the decrease in turbidity during nanofiltration was probably due to reduction of average aggregate size caused by shear forces during flow through the apparatus. This is in agreement with the behaviour of hemicellulose suspensions reported previously [6]. The hemicellulose aggregates may have formed a more compact gel or cake layer as compared to the reference experiment. Steady state flux at a low level was attained with methanol diluted press liquor after six hours, whereas the flux of pure press liquor continued to decline within eight hours.

3.5. Partial neutralisation by addition of sulfuric acid

Partial neutralisation by incremental addition of sulfuric acid was used to generate xylan aggregates and/or particles composed of high molar mass hemicellulose during nanofiltration of press liquor. Each step of addition was carried out dropwise over a period of about 8 min, then about 28 min of total recycle operation followed in which the system was allowed to equilibrate (Fig. 10).

The behaviour of flux during incremental addition of sulfuric acid to the feed tank was characterised by a gradual increase of flux followed by an extremely steep decline. Increasing flux during the first steps of sulfuric acid addition was attributed to a significant decrease in solution viscosity caused by the reduction of sodium hydroxide and hemicellulose concentrations. Interestingly, there was a point at 20% volume fraction of sulfuric acid where flux was higher than encountered without sulfuric acid addition although the solution already had noticeable turbidity. This point of operation corresponded to about 75 g/l of sodium hydroxide concentration remaining. In the region of the steep flux decline, formation of hemicellulose aggregates and particles as indicated by the evident increase in turbidity resulted in the build-up of a compact fouling layer.

The blank experiment using an aqueous solution of 200 g/l analytical grade sodium hydroxide revealed that osmotic pressure effects contribute to these flux changes, especially at high volumes of sulfuric acid added. Large amounts of sodium sulfate are generated during the neutralisation reaction. The high sulfate retention

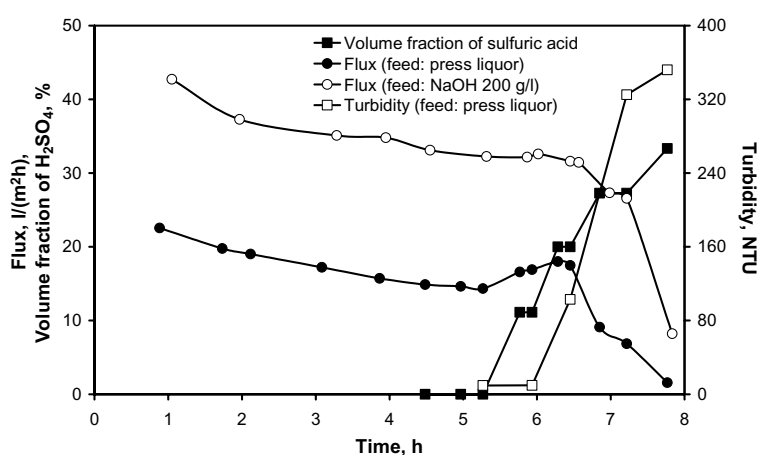


Fig. 10. Volume fraction of sulfuric acid added, flux and turbidity as a function of time during incremental addition of 9.5 N sulfuric acid to press liquor and NaOH 200 g/l (operating conditions: 52% recovery, 25 bar, 42°C, 0.82 m/s).

of the membrane causes a high osmotic pressure difference between retentate and permeate in NF of press liquor and also in NF of the NaOH solution. In contrast, aggregation results in a decrease of retentate osmotic pressure due to a reduced number of independently moving particles thus counteracting the effect of sodium sulfate. However, the effect of hemicellulose aggregation on the build-up of fouling layers is much higher than its effect on osmotic pressure. It was estimated that the contribution of the unaggregated high molar mass fraction of hemicellulose to retentate osmotic pressure is below 0.2 bar.

A significant reduction of apparent hemicellulose retention from 81 to 77% was observed when the volume fraction of sulfuric acid was increased from 0 to 20%. This is probably due to increased concentration polarisation in the fouling layer resulting in higher hemicellulose surface concentration. Irreversible fouling was extremely severe after partial neutralisation in contrast to the corresponding methanol addition experiment (Fig. 11).

3.6. Addition of a copper reagent

Xylan can be selectively isolated from polysaccharide mixtures by precipitation with copper

reagents, e.g. Fehling solution, forming an insoluble polysaccharide-copper complex [15]. Prior to the NF experiment, Fehling solution was prepared by mixing equal volumes of solution A (60 g/l $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and solution B (200 g/l potassium sodium tartrate tetrahydrate and 100 g/l sodium hydroxide). Press liquor was preconcentrated giving 700 ml of retentate, then 100 ml of Fehling solution were added stepwise (4×25 ml). During preconcentration, steady state flux was nearly attained after six hours of filtration time (Fig. 12). Subsequently, flux and turbidity were measured one hour after each addition of Fehling solution. Flux decreased steadily with increasing quantity of the copper reagent added.

Turbidity was high already after the first step confirming that Fehling solution exhibits high aggregation power for xylan. Flux continued to decrease thereafter, rapidly even after the last addition. The volume fraction of aggregates and the thickness of the fouling layer may have increased with the volume of copper reagent added though the turbidity reading did not increase further. Appreciable irreversible fouling occurred because the pure water flux decreased by 42% after the experiment. TOC and COD retention (comprising hemicellulose and the tartrate added) remained constant during the addition of Fehling

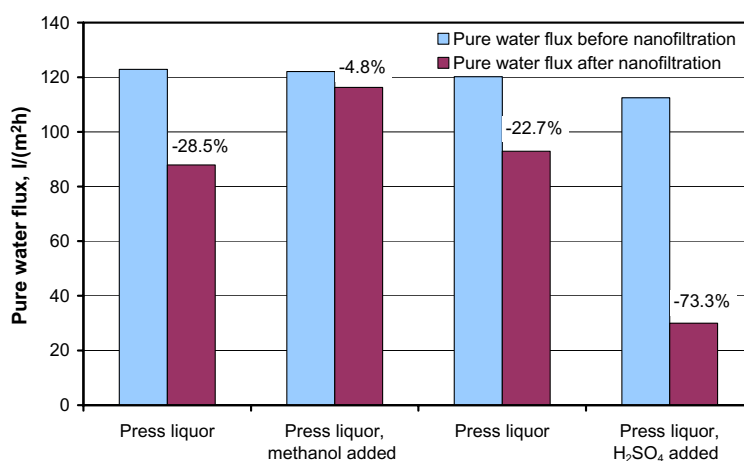


Fig. 11. Pure water flux before and after the addition of methanol and sulfuric acid to press liquor.

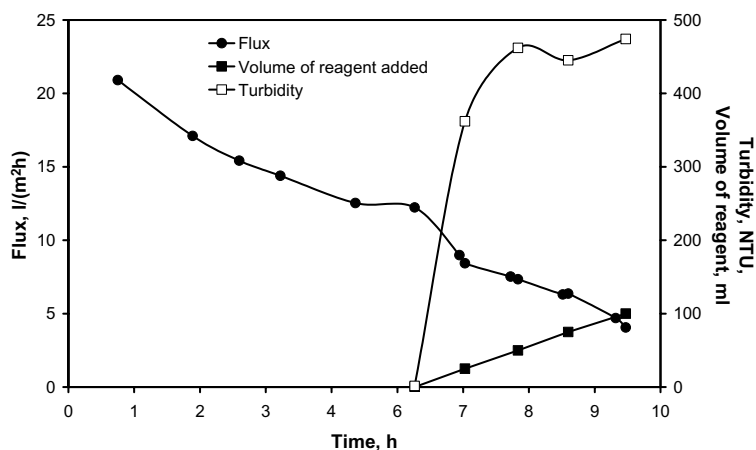


Fig. 12. Volume of copper reagent (Fehling solution) added, flux and turbidity as a function of time during incremental addition of reagent to press liquor (operating conditions: 52% recovery after six hours, 25 bar, 42°C, 0.82 m/s).

solution. The copper sulfate concentration in the mixture was too low to account for significant changes in osmotic pressure. Therefore, osmotic pressure effects were not responsible for the changes in flux observed.

4. Conclusions

Dynamic light scattering experiments revealed that hemicellulose forms aggregates in strongly alkaline solutions. This process took place more slowly than in DMSO/water mixtures [3,4] due to repulsive forces between deprotonated carboxylic acid groups. Heat treatment of press liquor caused a degradation of hemicellulose and a decrease in average molar mass thus enhancing flux and reducing hemicellulose retention. Degradation by addition of hydrogen peroxide revealed similar effects. A slight reduction of flux at increased retention was observed after heat treatment of pilot plant permeate which was attributed to an increase in average molar mass resulting from re-condensation reactions. A decrease in relative amount of the high molar mass fraction resulted in lower irreversible fouling, possibly due to a decreased ability of hemicellulose to generate gel layers at the membrane surface.

Precipitation agents in small to medium quantities were used to affect the solution state of hemicellulose thus purposely provoking aggregate formation and increasing the probability of gel or cake layer formation. The influence of several reagents having different effects on the mechanism of hemicellulose aggregation was studied. During nanofiltration of press liquor/methanol mixtures, a distinct flux decline was observed, however, irreversible membrane fouling was low. Sometimes shear forces were able to reduce average aggregate size during a nanofiltration experiment.

Flux was enhanced at the early stages of partial neutralisation by addition of sulfuric acid due to a decrease of solution viscosity that counteracted the build-up of a fouling layer. An extremely steep flux decline occurred when sulfuric acid volume fraction exceeded 20 vol.%, partly because of an increased osmotic pressure difference between retentate and permeate. Sulfuric acid addition also reduced apparent hemicellulose retention possibly because of increased concentration polarisation when particulate matter blocked the back diffusion of dissolved molecules from the boundary layer to the bulk phase. This suggested that the formation of a compact gel layer at the membrane surface was considerably enhanced, which would

explain the extremely severe irreversible fouling observed after the addition of sulfuric acid.

Addition of a copper reagent that forms insoluble complexes with xylan caused a gradual decline of flux at high turbidity of the resulting mixture and appreciable membrane fouling. Hemicellulose aggregation as measured by increasing solution turbidity usually coincided with distinct flux decline during nanofiltration. It was therefore suggested that the aggregation of hemicellulose results in the build-up of gel layers near the membrane surface.

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