Simultaneous separation of impurities and exchange of surrounding media in Nanolignin suspensions

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November 2018

Abstract
The increase in the production of lignin creates a surplus of this raw material that can be used in a wide variety of applications to maximize its valorization. The production of solid nanolignin particles with a bigger surface area than standard lignin, enhance its the properties originating even more applications. The aim of this work was to evaluate the performance of ultrafiltration membranes with different Molecular Weight Cut-Off (MWCO) in the separation and purification of nanolignin particles from a suspension made of wheat straw extract, produced by an Organosolv Pre-treatment. No nanolignin particles were found on the permeates of each different membrane which means that all the nanolignin particles are retained by all the different cut-off ultrafiltration membranes. The Microdyn-Nadir 30 kDa membrane showed the most promising results for this separation process with a removal efficiency of dissolved components for the Dry Matter analysis of 47 %, showing this membrane retains less dissolved components. For the performance experiments using the 30 kDa membrane, the results show that at 4 bar and 0.7 L/min of flow-rate the fouling is less evident and so the removal efficiency of the dissolved components concerning the dry matter analysis is 61 %, which already shows an improvement when compared to the previous experiments.

Keywords: ultrafiltration, wheat straw, nanolignin, purification, diafiltration, Organosolv

1. Introduction

Lignin is the second most abundant biopolymer on earth, after cellulose. It confers rigidity, resistance and impermeability to plant cell walls. Normally, lignin is a by-product of paper and pulp industry. This lignin is mainly incinerated and used to produce energy [1].

Since technical lignin has a non-uniform structure, an uncertain reactivity and other organic impurities it is difficult to use it as a high added value material [2].

One of the ways to fractionate plant components is by using an Organosolv pre-treatment, which consists in using an organic solvent and water with the lignin plant source, at certain conditions, to break the plant structure into its different components (cellulose, hemicellulose and lignin). By using an Organosolv process to separate the plant components, the result is a less modified lignin, with more homogeneity than the lignin from lignosulphonates or alkali lignin. [3]

To maximize lignin valorization, it is possible is to produce nanolignin particles which have a different and wide variety of applications than standard lignin, mainly because these nanoparticles have a higher specific surface area [4]. As researchers find more and more applications for nanolignin particles [5], it becomes necessary to find a way of isolating and purifying this particles, to eventually produce them in an industrial scale.

1.1 Aim of the Thesis

The main purpose of this thesis is to contribute to the advancement of the state of the art on the separation and purification of wheat straw nanolignin particles from its impurities by using an ultrafiltration/diafiltration separation process. The following steps were based on previous experiments [6] and were used as the base of the production of nanolignin particles.

1. Production of an extract solution of wheat straw using an Organosolv pre-treatment with a mixture of pure ethanol and water as solvents.
2. Precipitation of the nanolignin particles using water as an anti-solvent.

The nanolignin particles suspension produced by precipitation were processed by Ultrafiltration/Diafiltration to separate and purify the nanolignin particles from the other impurities present in the suspension. The operating conditions of feed flow-rate and transmembrane pressure were also investigated to optimize the separation and purification process.

2. Materials and Methods

2.1 Procedure for nanolignin particles production

Wheat Straw Extract Production

40 g of wheat straw dry matter were weighted. A solution of 60 wt% ethanol and 40% of water was prepared. The final mixture had a 1:11 ratio of solute to solvent and was inserted in a 1L stirred autoclave (Zirbus, HAD 9/16, Bad Grund, Germany). The temperature of the jacket was 210 °C for 45 min and afterwards 190°C for 15 min, with the goal of reaching 180ºC inside the autoclave. In the end of the reaction, the reactor was cooled down using a cooling water system. The mixture was placed in a hydraulic press (Hapa, HPH 2.5, Achern, Germany) at 200 bar to separate the solid from the liquid. The remain liquid was centrifuged at 24000 g for 20 min to separate smaller particles that were still in the mixture.

Nanolignin particles precipitation

The following step was to obtain solid lignin nanoparticles. A precipitation was done using water as an anti-solvent. The choice of the anti-solvent was based on previous experiments. [6]. The production of suspension was made by using two Syringe Pumps (TSE Systems) to mix the solute and anti-solvent at precise flow-rates. The produced suspension is then used in the ultrafiltration separation, as soon as possible to avoid dissolution or agglomeration of nanoparticles.

2.2 Ultrafiltration cross-flow set-up

The set-up model is *Memcell* from *OSMO Membrane Systems* Figure 1 , shows a simplified diagram of the cross-flow system that was used. The active membrane area of the single flat module used is 80 cm^2 and the feed stream is connected to a *2-Series* gear pump, from *Liquiflo*, which allows changes in the feed flow-rate. The pressure can be altered by using the globe valve inserted near the retentate stream in the set-up. Later, a second similar pump was added in parallel to allow the increase of the feed flow-rate.

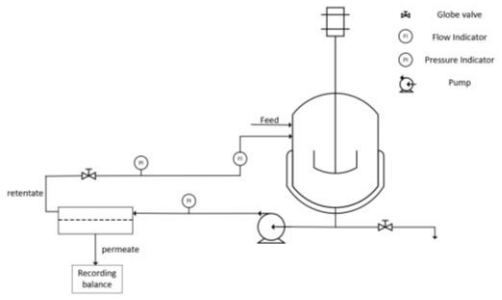

Figure 1. Cross-flow set-up simplified diagram.

2.3 Membrane Selection

Commercial ultrafiltration membranes from Microdyn were used. Two different PES membranes were used, the UP010 with 10 kDa MWCO, the UP020 with a MWCO of 20 kDa. Also, the UH030 membrane with a MWCO of 30 kDa and the UH050 with a MWCO of 50 kDa, both made of PESH.

2.4 Membrane Filtration

After choosing the membranes based on MWCO and membrane material, the membranes were all flushed with 15% ethanol solution prior to any experiments with the nanolignin particles suspension. A recording balance connected to a computer measured the mass of permeate over time. With this data it was possible to obtain a graphic of the mass of permeate (g) versus time (min). The initial transmembrane flux for each membrane is the slope of the linear regression obtained from the recorded mass of permeate per unit of membrane surface area versus time, according to equation (1):

$$\frac{\text{Mass of Permeate (g)}}{A_m} = \text{TF} \times \text{time (min)} \qquad (1)$$

TF is the transmembrane flux, $g/(cm^2.\text{min})$.

A_m = membrane active surface area, cm^2.

By evaluating the transmembrane fluxes for all the experiments for each membrane and the standard deviation of this value is possible to see no significant change in the fluxes and so conclude the membranes are stable in an aqueous solution of 15% ethanol.

UF/DF of nanolignin particles suspension

Each different membrane (with different MWCO) was used with the goal of separating the lignin nanoparticles from other impurities in the suspension. The other components include ethanol, acetic acid, carbohydrates and dissolved lignin that did not precipitate. After the initial experiments, the membrane with the best results was used in optimization of the operating conditions for increasing the efficiency of the separation and purification of the nanolignin particles. For that reason, several experiments using different transmembrane pressures (TMP) and feed flow-rates were performed.

Approximately 1.2 L of nanolignin suspension were produced for each experiment. The initial suspension was concentrated until a certain volume and afterwards two different diafiltration steps were completed with the goal of purifying the nanolignin particle concentrated solution and help with the membrane cleaning.

Assessment of Membrane Fouling

To understand the effect of the membrane fouling in the permeate flux of the chosen membranes, after the filtration with a suspension of nanolignin particles in a cross-flow system, each membrane was flushed with a 15 wt% ethanol solution in the end of all the experiments. The mass of permeate (g) over time (min) was again recorded and the final transmembrane flux calculated based on equation (1).

The obtained TF for the experiments after filtrating the suspension of nanolignin particles was then compared with the initial transmembrane flux, measured before the suspension filtration/diafiltration process to

evaluate the flux decline caused by the fouling in the membranes.

2.5 Analytical Methods

For all the analytical methods included in this work, samples of retentate and permeate were taken during the ultrafiltration process. For the experiments with membranes with different cut-offs 6 samples of retentate, two for each filtration step, and 3 samples of permeate, one for each filtration step, were taken and analyzed. Part of the sample was ultracentrifuged at 288000g and the resultant supernatant analyzed.

Particle Sizing

The particle size was measured using a Zeta Potential Analyzer from Brookhaven Instruments Corporation. This device uses Electrophoretic Light Scattering (ELS) technique to obtain the particle size of the nanoparticles. The permeate and retentate samples were diluted with deionized water in a ratio of 1:100 of sample to deionized water.

Ethanol Content

The nanolignin particles suspension over the experiments have, between other components, a large amount of ethanol. The ethanol content of the samples was measured using High Performance Liquid Chromatography (HPLC). The HPLC equipment used was the Nexera model from *Shimazdu Corporation* with the following components*:* Column: Sugar-SH1011 (Shodex), Guard Column: Sugar SH-G (Shodex), Detector: Refractive Index, Eluent 0.6 mL/min 0.005 molar H2SO4.

All the samples taken during the experiments were diluted with water in a volume ratio of 1:5, centrifuged once more at 14000 rpm for 20 min and the supernatant placed in the HPLC tray.

Total Organic Carbon Content

One of the ways to compare the membrane experiments, is to measure the total organic carbon (TOC) content of the samples over the experiments. During the experiments, the collected samples of retentate and permeate have a certain TOC concentration of nanolignin particles, dissolved lignin, ethanol and other dissolved components. Based on the assumption that there are no nanolignin particles in the supernatant of the samples collected after centrifugation for 1 hour at 288000g, it is expected that, for the retentate samples, the difference between the TOC of the samples before centrifugation and TOC of samples after centrifugation (supernatant) will give the TOC related with the nanolignin particles.

The (TOC) content was measured using a Total Organic Carbon Analyzer from Shimadzu Corporation. Finally, by knowing the TOC content related with the ethanol in the samples based on the HPLC results, it would be possible to subtract the TOC of ethanol from the TOC of the whole sample.

Dry matter Content

A dry matter (DM) analysis was performed by drying and weighting the samples. The difference, for the retentate samples between the DM content of the samples before centrifugation and DM content of the supernatant of samples after centrifugation will give the DM related with the nanolignin particles.

3. Results and Discussion

This chapter is divided in two main parts, the one that shows the results for the experiments using the different MWCO membranes (3.1) and the one that shows the results for the optimization experiments using a selected membrane (3.2)

3.1 UF/DF of nanolignin particles suspension using different MWCO membranes

Initially, membranes with different MWCO were analyzed and tested for the separation of a nanolignin particles from the other impurities in the suspension. For the experiments with different membrane cut-offs the operating pressure was set at 8 bar and the feed flow-rate at 0.7 L/min.

After, the initial flushing with an ethanol solution, the transmembrane flux for all the membranes was obtained considering the variation of permeate mass over time.

The initial amount of nanolignin particles was calculated based on the assumption that only 49% of the dissolved lignin in the extract precipitates. [7]. The amount of water added to each of the experiments after the filtration of the initial suspension was approximately the same amount of permeate collected in the previous step.

Assessment of membrane fouling

The final transmembrane flux was measured for the cross-flow system after all the filtration experiments using the nanolignin particles suspension were finished, with the goal of evaluating the effect of fouling in the permeate flux. For that reason, a 15 % ethanol solution was used to measure the permeate flux in each of the membranes used.

The difference between the initial and the final transmembrane flux for each of the membranes is represented in Figure 2. First, it is expected that the smaller the cut-off, the thickest the layer formed in the surface of the membrane (fouling), which means, the smallest the final transmembrane flux. On the other side, the 30 and 50 kDa membranes are made of hydrophilic PES, which means, that these membranes should be more resistant to fouling [8]. Having in account these two points, it makes sense that the final transmembrane flux increases from the smallest to the biggest cut-off.

For the 50 kDa membrane, the final transmembrane flux is lower than for the 30 kDa membrane. For the same operating conditions, the initial transmembrane flux is expected to be higher for membranes with bigger cut-offs, resulting in a bigger number of particles going

through the membrane. The concentration polarization effect increases as the total volume flow through the membrane increases. This effect will contribute to the membrane fouling which leads to a lower final transmembrane flux for the 50 kDa membrane when compared with the 30 kDa membrane. According to this evaluation, the best membrane should be the one where the difference between the initial and the final transmembrane flux is smaller because it means the filtration process will be less affected by fouling and other conditions over time. As seen in Figure 2, the 30 kDa membrane is the one in which the difference between the initial and the final transmembrane flux is lower, making this membrane the one that shows the best performance in this separation process. It is also possible to notice that all the membranes have a high decrease in the transmembrane flux after experiments, which might be explained by the thick layer of nanolignin particles that forms in the membrane surfaces.

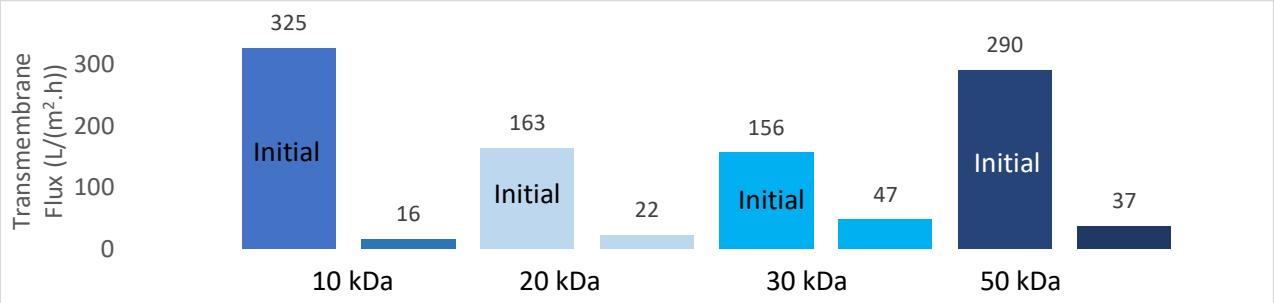

Figure 2. Initial and final Transmembrane Flux for membranes with different cut-offs

Analytics

For the following analysis, 10 and 12 samples, for the comparison of membranes with different MWCO experiments and for the optimization experiments with a selected membrane experiments, respectively, were taken. The experiments are divided into three different steps: suspension step, which corresponds to the filtration of the initial suspension; 1st diafiltration step, which corresponds to the filtration after the 1st addition of water; 2nd diafiltration step, which corresponds to the filtration after the addition of water for the second time. Those samples were used for further analytics and are labeled according to the code indicated in Table 1 to simplify the results analysis. The letter X corresponds to the membrane cut-off used in each experiment (10, 20, 30 and 50 kDa).

As a lapse, the first sample of retentate for the 30 kDa membrane experiments was not taken, so only the final retentate of the first filtration step was analyzed.

Table 1. Samples Labeling code.

Code name	Type of sample	Step of filtration when sample was taken
SX	Initial suspension	Before filtration starts
R1X	1st retentate	Middle of the suspension step
R2X	2nd retentate	End of the suspension step
W1R1X	3rd retentate	Middle of 1st diafiltration step
W1R2X	4th retentate	End of 1st diafiltration step
W2R1X	5th retentate	Middle of 2nd diafiltration step
W2R2X	6th retentate	End of 2nd diafiltration step
P1X	1st Permeate	Middle of the suspension step
P2X	2nd permeate	End of the suspension step
W1P1X	3rd permeate	Middle of 1st diafiltration step
W1P2X	4th permeate	End of 1st diafiltration step
W2P1X	5th permeate	Middle of 2nd diafiltration step
W2P2X	6th permeate	End of 2nd diafiltration step

Particle Sizing

As previously described, all the samples taken during the concentration and purification of the nanolignin particles suspension for each of the membrane experiments, before being ultra-centrifuged, were evaluated for their particle size using the ZetaPals from Brookhaven Instruments Corporation.

The next graphic (Figure 3) shows the obtained particle size for all initial nanolignin particle suspension and retentate samples taken before centrifugation, in their diluted form. Since the samples were diluted at a ratio of 1:100 of sample to deionized water, the viscosity and refractive index selected in the machine parameters were the ones from water, which means a viscosity of 0.890 cP and a refractive index of 1.330. Based on the results the particle size is constant between experiments and over time.

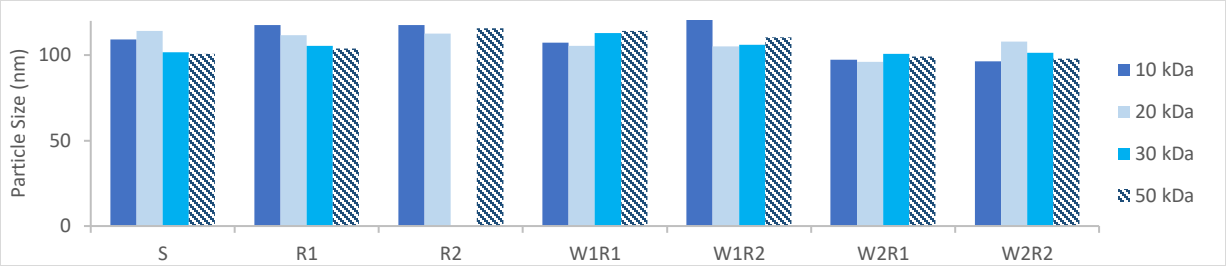

Figure 3. Particle size for each sample of all different membrane

Ethanol Content

HPLC was used to determine the ethanol content of the samples taken during the experiments with the nanolignin particle suspension. All the samples of retentate and permeate before and after centrifugation were analyzed. The initial assumption was that the total amount of ethanol in the solution over the filtration process would decrease in the same proportion as the total volume of solution. This would mean that the ethanol concentration should be approximately the same, for each filtration step of each different membrane experiment.

The ethanol content of the samples after centrifugation, is expected to be slightly higher, since the ultra-centrifugation at 288000g separates a small quantity of solids from the solution, decreasing the total volume of solution and consequently increasing the concentration of ethanol.

The next graphics (Figure 4 to Figure 7) show the ethanol content variation over the three steps of the filtration process, for both the samples before and after centrifugation, for all the four different membranes. In addition to that, it shows the expected ethanol concentration based on the amount of water added.

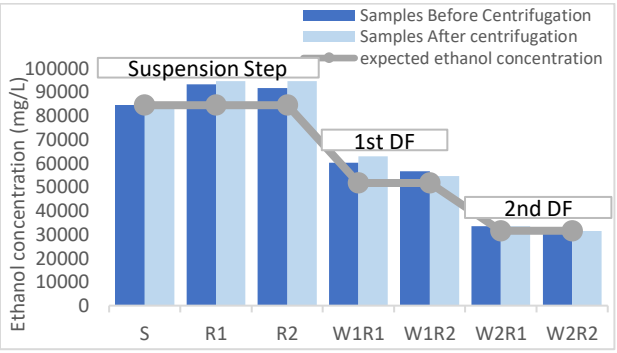

Figure 4. Ethanol Concentration (mg/L) for samples before and after centrifugation for 10 kDa membrane.

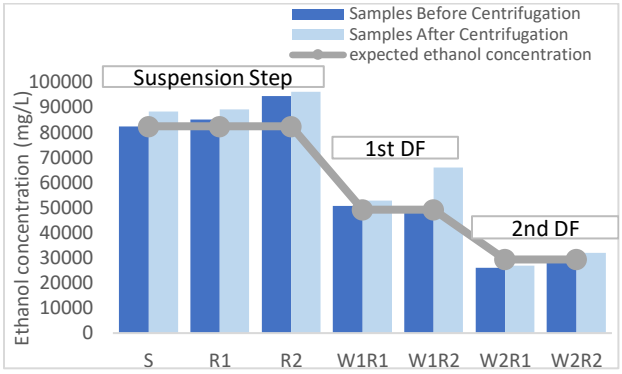

Figure 5. Ethanol Concentration (mg/L) for samples before and after centrifugation for 20 kDa membrane.

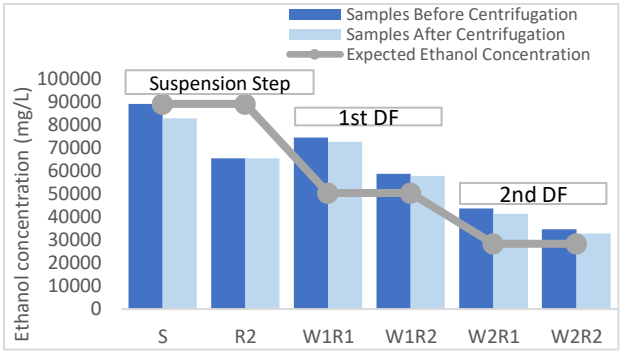

Figure 6. Ethanol Concentration (mg/L) for samples before and after centrifugation for 30 kDa membrane.

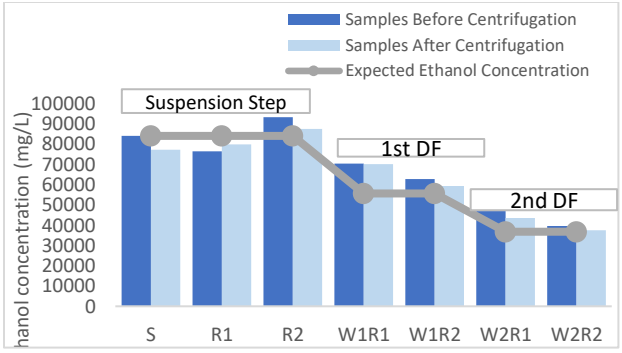

Figure 7.Ethanol Concentration (mg/L) for samples before and after centrifugation for 50 kDa membrane.

The best membrane should be the one that shows the highest concentration decrease between the initial and the final retentate (W2R2). All the membranes seem to have a

similar efficiency in separating ethanol from the nanolignin particles, since the difference between initial and final ethanol concentration is similar. The 50kDa membrane experiment as a lower difference in the initial and final ethanol concentration but there was a higher amount of initial suspension for the same collected permeate, which justifies that difference.

Total Organic Carbon content

The same analysis for each of the retentate samples of the TOC results was performed. Since the ethanol content is the most important contributor for the TOC content of the retentates, only the initial suspension samples and the TOC content of the permeates will be analyzed in detail. Figure 8 shows the TOC content of the initial suspensions of nanolignin particles used for each experiment with different MWCO membranes.

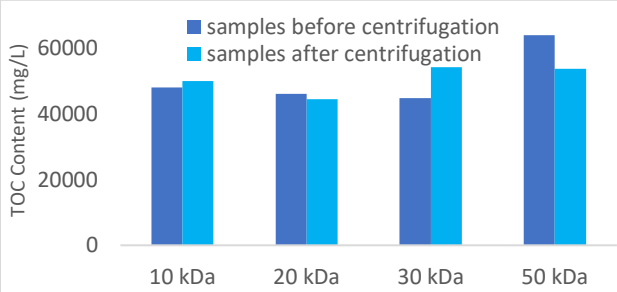

Figure 8. TOC content (mg/L) for the initial nanolignin suspension samples before and after centrifugation.

To compare the amount of TOC related with the dissolved components that is removed from the initial suspension the removal efficiency (RE) of dissolved components that were removed from the initial nanolignin suspension were calculated following equation (2). The TOC amount used for the initial suspension is the one from the supernatant of the suspension after centrifugation which only have TOC related with the dissolved components and not with the nanolignin particles.

$$RE = \frac{\sum_{i=1}^{3} TOC_{permeates}}{TOC_{initial}} \quad (2)$$

Where,

$TOC_{permeate}$ = total amount of organic carbon in each permeate, mg.

$TOC_{initial}$ = total amount of organic carbon of dissolved components in the initial suspension, mg.

The results obtained for this comparison method are shown in Table 2.

Table 2. Removal efficiency dissolved components based on TC results.

Membrane	RE of dissolved components (%)
10 kDa	67.7%
20 kDa	69.4%
30 kDa	97.3%
50 kDa	69.7%

Based on Table 2 the membrane which is more efficient in separating the dissolved components from the nanolignin particle suspension is the 30 kDa membrane, followed by the 50 kDa membrane. This conclusion was based on the TOC concentration of the permeates, shown in Figure 9, that compares the TOC concentration of the permeates for all the four experiments with different membrane cut-offs.

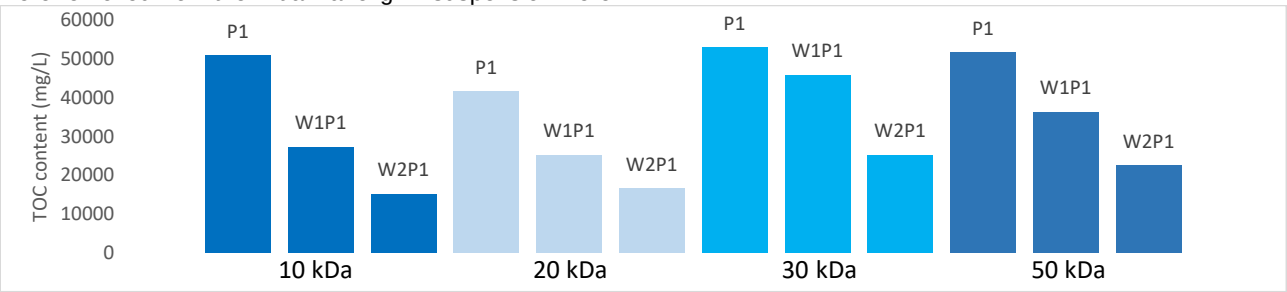

Figure 9. TOC concentration for all the permeates of all membranes used.

DM content

The dry matter content of the samples before and after centrifugation was obtained. For this case, only the DM of the initial suspension and the DM of the permeates will be analyzed in detail. The initial suspension DM concentrations for the samples before and after centrifugation is represented in Figure 10.

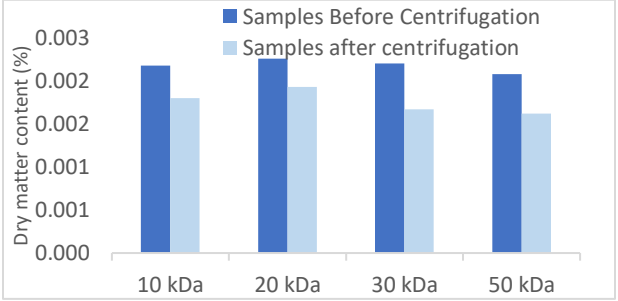

Figure 10. Initial nanolignin suspensions DM content.

The same comparison method used in the TOC analysis was used for the dry matter analysis. To compare the total dry matter related with the dissolved components that is removed from the initial suspension the removal efficiency of dissolved components was calculated following the equation (3). As for the TOC analysis, the amount of dry matter used for the initial suspension is the one from the suspension after centrifugation to use only the DM related with the dissolved components and not with the nanolignin particles.

$$RE = \frac{\sum_{i=1}^{3} DM_{permeates}}{DM_{initial}} \quad (3)$$

Where,

$DM_{permeate}$ = total dry matter in each permeate, mg.

$DM_{initial}$ = total dry matter of dissolved components in the initial suspension, mg.

The results obtained for this comparison method are shown in Table 3.

Table 3. Removal Efficiency of dissolved components based on DM results.

Membrane	RE of dissolved components (%)
10 kDa	30.3%
20 kDa	28.2%
30 kDa	47.0%
50 kDa	38.2%

Based on Table 3 the membrane which is more efficient in separating the dissolved components from the nanolignin particle suspension is the 30 kDa membrane, followed by the 50 kDa membrane. These calculations were based on DM permeates concentrations (Figure 11), that compares the dry matter concentration of the permeates for all the four experiments with different membrane cut-offs.

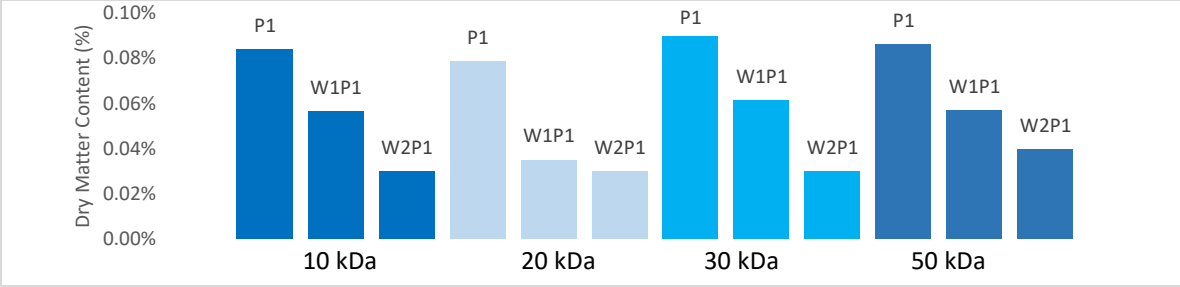

Figure 11. Dry Matter content for all the permeates of all different membranes.

3.2 Optimization of UF/DF process using 30 kDa membrane

As previously mentioned, after the experiments of separation and purification of nanolignin particles from the other impurities, the membrane with the best performance was used for optimization experiments by varying the transmembrane pressure and the feed flow-rate. The three different experiments were: 8 bar and 0.7 L/min, 4 bar and 0.7 L/min and 4 bar and 2 L/min.

Assessment of membrane fouling

As for the previous experiments the initial transmembrane flux (TF) was calculated. After all the UF/DF experiments with the nanolignin particles suspension the final transmembrane flux was obtained by measuring the mass of permeate over time when using a hydroalcoholic solution with 15% ethanol. The initial and final TF for all the different experiments is represented in Figure 12. Besides from the new experiments, the TF for the previous experiment using the 30 kDa membrane with 8 bar and 0.7 L/min was also included.

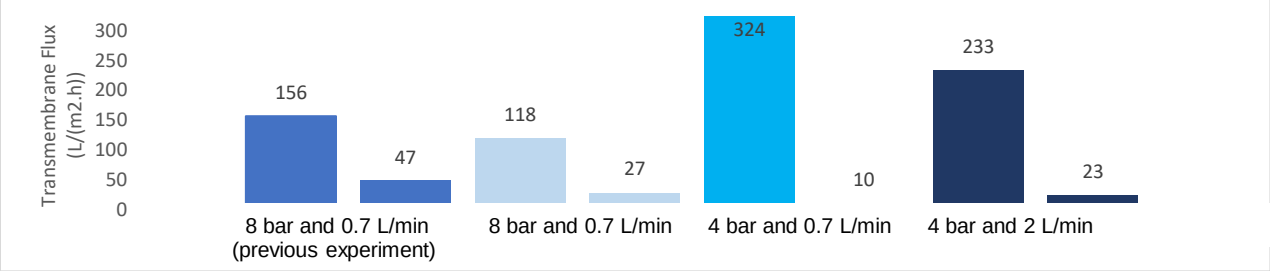

Figure 12. Initial and final transmembrane flux for the 30 kDa performance experiment.

On the previous graphic (Figure 12) is possible to see that the first experiment made in the new series of experiments with the 30 kDa membrane is very different from the previous experiment made in the same conditions. The initial transmembrane flux for the experiment repetition has a difference of approximately 24 % when compared with the first experiment. Further experiments with the same conditions needed to be done to conclude if this type of membrane is compressible and what is the effect of the pressure and the feed flow-rate in the passage of ethanol molecules through the membrane.

Comparing of all the experiments, it is possible to see in Figure 12 that even with decreasing the pressure and

increasing the flow-rate, the experiment that shows the smaller difference between the initial and the final transmembrane flux is the experiment at 8 bar and 0.7 L/min. Nevertheless, further experiments needed to be done to verify the reproducibility of the experiments.

Analytics

Particle Sizing

As it was made for the first membrane experiments, the particle size of all the samples (retentates and permeates) was measured. Once again it was proved that the particle size of the nanolignin particles over time and over experiments was kept approximately constant and in the expected range [6]. No particles were detected in the permeate samples which concludes no nanolignin particles exist in the permeate. The next graphic (Figure 13) show the particle size for all the optimization experiments.

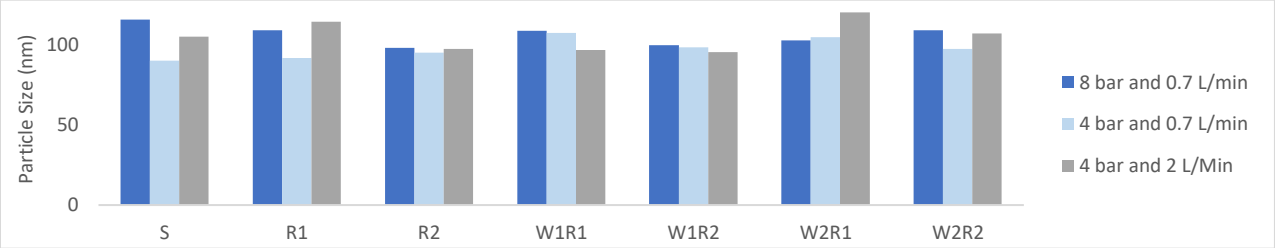

Figure 13. Particle Size measurement for performance experiments with 30 kDa membrane.

Ethanol Content

The same method used in the previous experiments to measure the ethanol concentration in the samples over the filtration process was used for the 30 kDa membrane performance experiments. The graphics below (Figure 14 to Figure 16), show the ethanol concentration variation for all the steps of the filtration process for the three experiments.

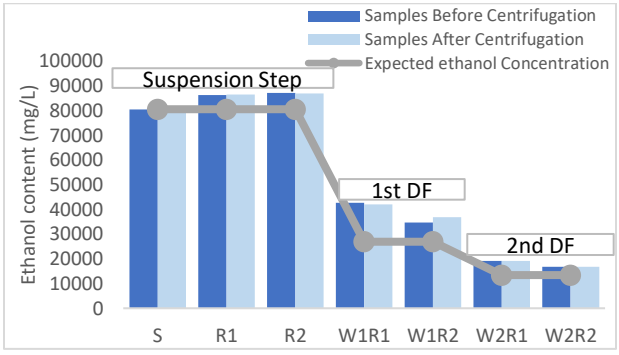

Figure 14. Ethanol concentration (mg/L) for the 8 bar and 0.7 L/min experiment.

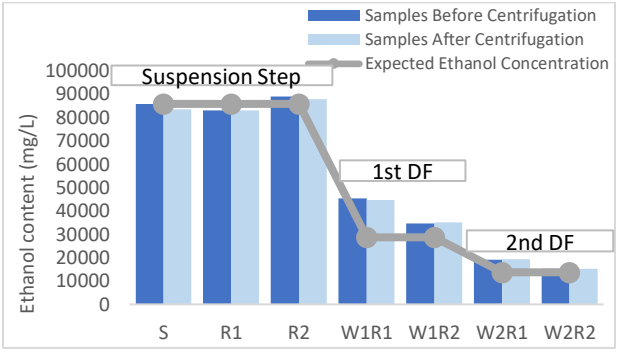

Figure 15. Ethanol concentration (mg/L) for the 4 bar and 0.7 L/min experiment.

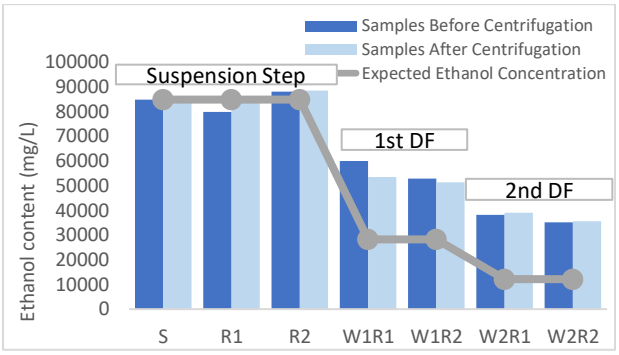

Figure 16. Ethanol concentration (mg/L) for the 4 bar and 2 L/min experiment.

For the optimization experiments, it is expected that the better conditions are the ones in which the ethanol concentration in the final retentate (W2R2) is lower for the same final volume of concentrated nanolignin suspension. Based on that, the operating conditions that seems to be more efficient are 4 bar and 0.7 L/min.

Total Organic Carbon Content

The TOC content analysis for each of the retentate samples was made. Since the ethanol content is the most important contributor for the TOC content, only the initial suspension samples and the TOC content of the permeate will be analyzed in detail. All the initial suspension TOC contents are represented in Figure 17.

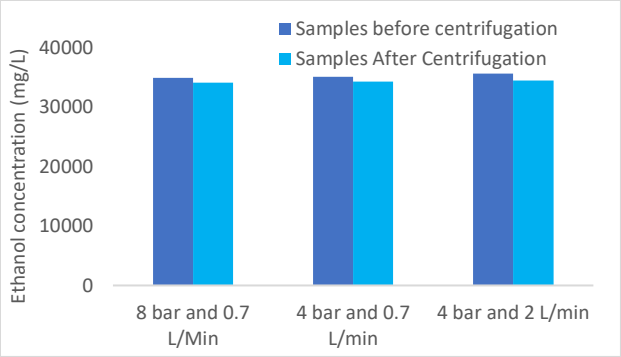

Figure 17. TOC content (mg/L) for the initial suspension of the different experiments.

As previously made, the best way to compare the efficiency of the UF/DF process for separating and purifying a nanolignin particle suspension is through the calculation of the removal efficiency of the dissolved components. This method compares the initial amount of TOC in the suspension before filtration with the amount of TOC in the permeates collected during the filtration process. The TOC concentration of all the permeates collected during the experiments is shown in Figure 18.

The results for the removal efficiency of the dissolved components for the TOC analysis gave above 100%, which demonstrates the unreliability of the results of the TOC. Nevertheless, the concentration trends are correct, but the exact values are not reliable. For that reason, the dry matter content was once again analyzed since it is a more reliable method of comparison.

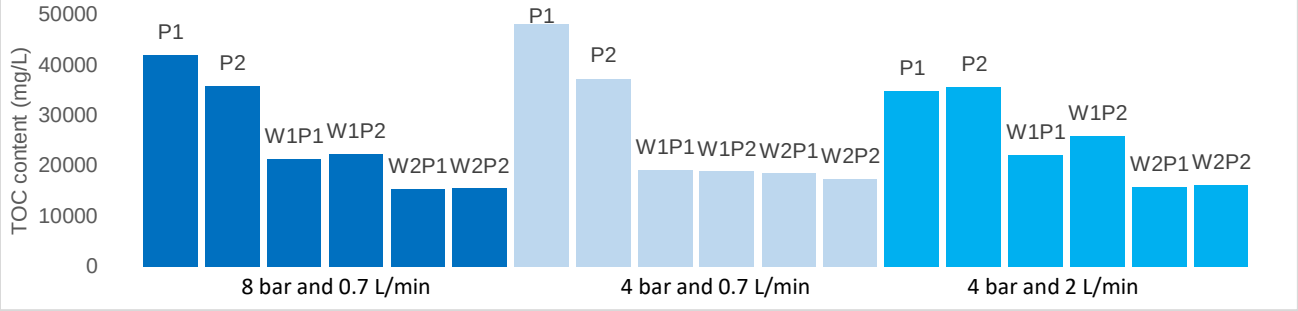

Figure 18. TOC concentration (mg/L) for all the permeates of all experiments.

Dry Matter Content

The dry matter content of the samples before and after centrifugation was obtained. For this case, only the DM of the initial suspension and the DM of the permeates will be analyzed in detail. The initial suspension DM concentrations for the samples before and after centrifugation for the optimization experiments is represented in Figure 19.

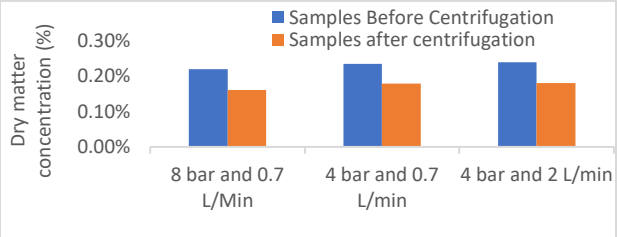

Figure 19. Inital nanolignin suspension samples DM content.

As previously mentioned, the calculation method used to compare the efficiency of the membrane under different conditions was the calculation of the removal efficiency of the dissolved components, shown in Table 4.

Table 4. Removal efficiency of dissolved components for the experiments at different conditions.

Membrane	RE of the dissolved components (%)
8 bar and 0.7 L/min	59.8%
4 bar and 0.7 L/min	61.1%
4 bar and 2 L/min	53.4%

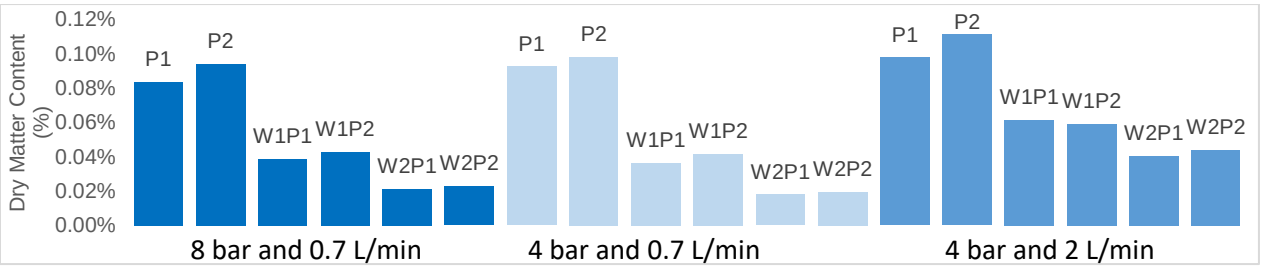

Figure 20. Dry matter concentration for all the permeates for all different conditions experiments

The results from the removal efficiency of the dissolved components show, that the lowest pressure and lowest flow-rate were the most efficient experiment conditions to separate the nanolignin particles from the dissolved components present in the suspension, as this experiment shows the highest removal efficiency of dissolved components from the initial nanolignin particle suspension.

Conclusion/Outlook

The conclusions related with this work are made only for wheat straw lignin that was pre-treated with and Organosolv technique using ethanol as an organic solvent. Also, the precipitation method using only water as anti-solvent at a specific ratio produces specific shapes and particle sizes than other precipitation methods.

The particle size analysis showed that all the membranes from 10 kDa to 50 kDa were able to retain the produced nanoparticles of lignin, since no nanolignin particles were found in the collected permeates. Also, the particle size was constant over the filtration process for all the membranes, which shows that during the ultrafiltration process there is no nanolignin particles agglomeration.

Regarding the ethanol content analysis, it was possible to conclude that the transmembrane flux through the membrane is not even during the experiments, which affects the ethanol concentration at different stages of the UF/DF experiments. It is influenced by the membrane MWCO and by the addition of water in the Diafiltration steps. Concerning the optimization experiments, when using the 30 kDa membrane, the least efficient operating conditions are 4 bar and 2 L/min, as these are the conditions in which the expected concentration differs more from the obtained results (for the diafiltration steps).

The (TOC) analysis showed, that the amount of nanolignin particles in the initial suspension was approximately the amount that was expected, since only 49 % of the dissolved lignin in the solution precipitates and forms nanolignin particles. Regarding the results of the retentate and permeate samples for the TOC analysis, it is not possible to take accurate conclusions, as this measurement method is subject to a lot of errors making it impossible to rely on the exact obtained values. In conclusion, both the ethanol and TOC content analysis results are subject to a lot of errors and were not considered a reliable method for comparing the removal efficiency of dissolved components of a nanolignin particles suspension when using membranes with different MWCO and different operating conditions.

A more simplistic and yet reliable method for the analysis of the removal efficiency dissolved components was the dry matter method which showed better results for the 30 kDa membrane with a value of approximately 47 %, showing that this membrane is the one that retains the least quantity of dissolved components.

To decrease the number of particles deposited on the membrane surface (fouling), several experiments were performed by changing the pressure and the feed flow-rate parameters. For the optimization experiments using the 30 kDa membrane the operating conditions that showed the most promising results was when using 4 bar and 0.7 L/min which had a removal efficiency of dissolved components of 61% but further experiments should be made to verify the reproducibility of this results.

For future work, it is necessary to repeat the experiments with the same conditions for several times, to verify the reproducibility of results. On the other hand, the fouling effect was to prominent in all the different membranes, decreasing the efficiency of the separation and purification of the nanolignin particles. For future experiments it is necessary to find a way of cleaning the membrane and decreasing the fouling during the experiments, since the used techniques to decrease the fouling phenomenon did not work as good as expected. As for the diafiltration steps, other experiments using more diafiltration steps could be performed to evaluate the improve of removal efficiency of the dissolved components.

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