



Application of Membrane Separation for Cleaning and Concentration of Nanolignin Suspensions in a Biorefinery Environment

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Biorefining is a key technology for the sustainable production of chemicals, fuels and energy from abundant lignocellulosic resources. Within the concept, production of micro- and nanoscaled lignin particles recently gained increasing interest due to their excellent properties and potential application in high-value products. Fabricated via direct precipitation of Organosolv extracts, Nanolignin suspensions need to be increased in concentration and cleaned from impurities. Additionally, solvent background needs to be exchanged from hydroalcoholic solution to pure water for most applications. This work focuses on the application of ultrafiltration in diafiltration mode for this separation task. Experimental operation on lab-scale apparatuses demonstrate the reduction of Ethanol and impurities like sugars, dissolved lignin and sugar degradation products accessed by TOC analysis. Most important, the size of Nanolignin particles is not changed during 9 h of operation. Nevertheless, significant performance degradation due to compaction of polymeric membrane material as well as fouling resulting from deposited lignin particles has been monitored. Consequently, a rigorous optimisation of operating pressure and the development of an adequate membrane regeneration procedure is mandatory.

1. Introduction

Lignocellulosic biorefineries offer the potential for a transition of fossil-based production processes towards sustainable and bio-based products and production processes not only for fuel (Lozano-Moreno and Maréchal 2019) but also for base chemicals (Patsalou et al. 2017) and high-value specialities. The raw material is highly available on a global scale, either through fresh biomass (Corona et al. 2018) or through biogenous residues like agro-food waste and food waste (Dahiya et al. 2018). Numerous biorefinery processes are already commercially available like in the pulp and paper industry (Corcelli et al. 2018) but the broad market intrusion towards a bio-based economy is yet to come. The major reason behind that are the still higher production costs compared to conventional pathways. One solution might be the focus on the production of high-value special products in the first place in order to prepare the markets and lead technologies to maturity.

Lignin is the second most abundant terrestrial biopolymer after cellulose (Servaes et al. 2017) but its utilisation is currently limited to heat generation or low-value products (Toledano et al. 2010). Nevertheless, lignin is considered as valuable chemical (Servaes et al. 2017) and provides high potential in bio-based production of various compounds (Mabrouk et al. 2018). The complex structure of lignin, a highly branched polyphenolic polyether, and the dependency of structure on the chosen biomass resource and the applied pretreatment technology makes the molecule hard to handle (Beisl et al. 2018b). An approach to overcome these issues of complexity of lignin is the production and application of nanostructured lignin (Miltner et al. 2018). Characteristics and performance of such particles are extraordinary making them applicable as UV blocker, biocidal and antioxidative agent, emulsifier and mechanical strengthener in numerous applications (Beisl et al. 2017a).

One of the potential production methods for nanolignin particles which has been used in current work is the direct precipitation from untreated Organosolv extract of biomass through solvent shifting (Beisl et al. 2017b).

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The result of this process is a diluted nanolignin suspension with an alcohol content of around 15 %w/w and minor portions of impurities like dissolved lignin, monomeric and oligomeric sugars and sugar degradation products like organic acids, furfural and HMF. It is vital for the application in a product, that nanolignin concentration is significantly increased, impurities are separated and the alcoholic solvent of the suspension is exchanged to water. During this process, it is mandatory that particle characteristics like size and size distribution stay unchanged and agglomeration and aggregation are suppressed. One potential technique for this separation task is ultrafiltration in diafiltration mode (Baker 2012). The process is well established for inorganic nanoparticles (Choudhury et al. 2018) but publications on organic nanoparticles or even lignin nanoparticles are scarce. Ultrafiltration has been reported valuable during the separation of dissolved lignin from mild alkaline extracts (Oriez et al. 2019) and even for cleaning such extracts from impurities using diafiltration (Servaes et al. 2017). Additionally, the separation of components of lower molecular weights derived from lignin in Organosolv extracts has been reported (Moniz et al. 2018). Ultrafiltration and diafiltration of nanoscaled particulate lignin have not been covered in literature to date. Current work focusses on the concentration, cleaning and solvent exchange of Organosolv-derived nanolignin particles using commercial ultrafiltration membranes in diafiltration mode with a special focus on membrane performance degradation due to compaction and fouling.

2. Materials and methods

Nanolignin suspensions have been prepared by precipitation from untreated Ethanol-Organosolv extracts of wheat straw according to the method described in previous work (Beisl et al. 2018b). Multiple extractions have been performed separately and extracts have been unified to finally provide an amount of 3 L for subsequent precipitation. Lignin precipitation was performed by solvent shifting in a static mixer; the resulting aqueous suspension had an Ethanol content of around 15 %w/w and a nanolignin particle content of around 0.65 mg/g. In order to exchange the surrounding solvent and to clean the suspension from impurities, ultrafiltration membrane separation in diafiltration mode has been applied.

For the given task, a membrane has to be applied that allows permeation of all dissolved components (dissolved lignin, monomeric and oligomeric sugars and degradation products) but retention of precipitated Nanolignin particles. Previous work indicated that the mass-weighted molecular weight of lignin as the heaviest molecule dissolved in Organosolv extracts ranges between 1,000 and 1,700 Da depending on the extraction temperature (Beisl et al. 2018a). Solid Nanolignin particles show mean particle diameters of around 110 nm and significantly higher particle weight. Therefore, molecular weight cut-off MWCO of membranes was chosen in the range of 10,000 to 50,000 Da. For the calculation of equivalent membrane pore sizes from MWCO values a logarithmic relationship proposed in literature has been used which assumes spherical particles (Guo and Santschi, 2007). Membranes analysed for the given separation task are commercial products obtained from the company MICRODYN-NADIR. The individual specifications and membrane materials are summarized in Table 1. Material PES refers to Polyethersulfone whereas PESH represents Hydrophilic Polyethersulfone. Fresh membranes need to be conditioned by flushing with 15 %w/w hydroalcoholic solution for at least 30 min.

Table 1: Membranes analysed for the given separation task (Microdyn-NADIR 2018), equivalent membrane pore sizes determined according to Guo and Santschi, 2007

Membrane	Material	MWCO [Da]	Equivalent membrane	Permeance
			pore size [nm]	@ 4bar feed pressure [l/m ² ·h·bar]
NADIR® PM UP010	PES/PP	10,000	2.9	≥ 50.0
NADIR® PM UP020	PES/PP	20,000	3.7	≥ 70.0
NADIR® PM UH030	PESH/PP	30,000	4.2	≥ 35.0
NADIR® PM UH050	PESH/PP	50,000	5.0	≥ 85.0

Particle size of Nanolignin has been determined using a ZetaPALS from Brookhaven Instruments, Ethanol content has been analyzed using a Shimadzu LC-20A HPLC system equipped with a Shodex SH1011 column and TOC content has been measured using a Shimadzu TOC-VCSH instrument.

2.1 Ultrafiltration of Ethanol/Water mixtures in dead-end cell

The assessment of hydraulic permeance of single-phase Ethanol/Water mixtures for different polymeric membranes has been performed in a stirred dead-end membrane cell (Sterlitech HP4750). This cell has a processing volume of 300 mL and an active membrane area of 14.6 cm². The cell has been placed on top of a magnetic stirrer plate to create turbulent mixing on the membrane feed side. The feed has been prepared as a

pure hydroalcoholic solution with 15 %w/w Ethanol, filled batchwise into the cell and pressurized using nitrogen from gas cylinders up to a pressure of 10 bar(g). The permeate leaving the cell has been collected in a beaker placed on a precise balance and the cumulated mass has been constantly recorded. A scheme and a photograph of this experimental setup is provided in Figure 1 (a) and (b).

Experiments in this setup have been used to select suitable membranes for the subsequent Nanolignin suspension operations as well as to assess the compaction tendency of the membrane material under operating pressures applied. Compaction is an undesired effect resulting in a decrease of membrane hydraulic permeance caused by a compression of the polymeric membrane material at higher pressures. The definition of hydraulic permeance and the calculation of this factor from the collected permeate mass is given in Eq(1).

$$\pi = \frac{\dot{V}_P}{A \cdot (\Delta p)} = \frac{m_P}{t \cdot \rho_P \cdot (p_F - p_P)} \quad (1)$$

m_P ...permeate mass collected, p_P ...permeate pressure, p_F ...feed pressure, ρ_P ...permeate density, t ...time

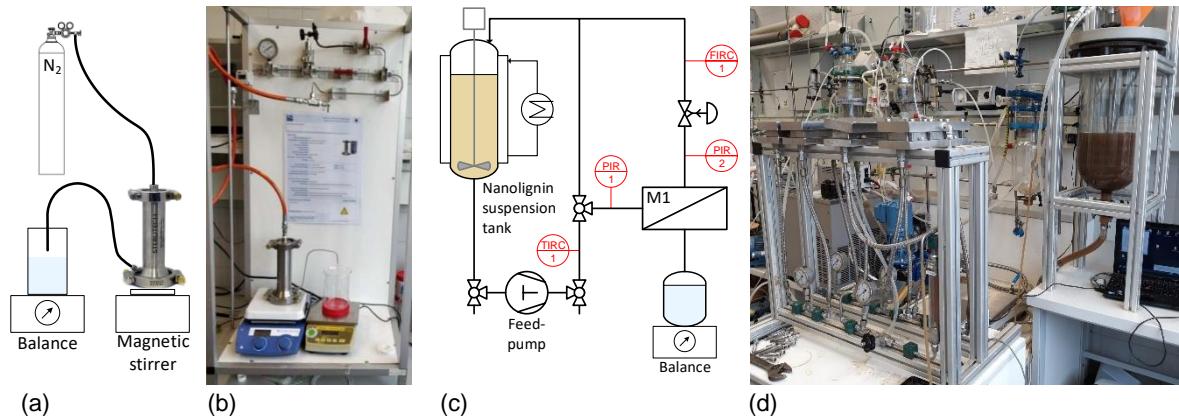


Figure 1: Experimental ultrafiltration setups: (a) dead-end cell schematic diagram, (b) dead-end cell photograph, (c) cross-flow cell schematic diagram, (d) cross-flow cell photograph

2.2 Ultrafiltration of Nanolignin suspensions in cross-flow cell

Preliminary ultrafiltration experiments with Nanolignin suspensions performed in the dead-end cell have resulted in almost immediate and complete flux decline due to the deposition of very dense layers of particles on the feed side membrane surface (fouling) irrespective of intense stirring in the feed side compartment. A membrane setup allowing for high cross-flow velocities on the feed/retentate side and significantly low stage cuts (<0.05) has been developed. In a cross-flow setup, the feed flows tangentially to the membrane surface, a small portion is cut off to the permeate and the remaining retentate is cycled back to the feed tank. Consequently, dissolved components and solvents are separated from the feed, which in turn is concentrated in solid Nanolignin particles. The high cross-flow velocity significantly reduces the build-up of fouling layers on the membrane surface. The used membrane module allowed for the application of flat sheet membranes with an active area of 80 cm². Permeate has been collected in a beaker and cumulated mass has been constantly recorded. A scheme and a photograph of this setup is given in Figure 1 (c) and (d). Feed pressures of 8 bar(g) and feed flow rates of 0.7 L/min have been chosen for the investigation.

3. Results and discussion

3.1 Membrane compaction behavior

Preliminary ultrafiltration tests with Nanolignin suspensions performed at different feed pressures indicated that the used polymeric membranes are prone to permeance degradation due to membrane compaction. This effect has also been reported in literature (Stade et al. 2013) for the membranes used in the present work. Pronounced compaction behaviour necessitates the application of relatively low feed pressures to keep the permeance high but on the other hand, the reduced driving force leads to increasing membrane area demand. The compaction behaviour of used membranes has been assessed in detail to provide sufficient data for later pressure optimization via minimization of total cost of ownership for the membrane separation step.

Membrane compaction behaviour has been assessed for the UH030 membrane by operation with pure hydroalcoholic solution with 15 %w/w Ethanol content at different feed pressures according to the method

described in Chapter 2.1. A given membrane sample has been exposed to different feed pressures, permeation of the total cell processing volume has been performed and mean transmembrane fluxes and permeances have been calculated. This procedure has been repeated for the given membrane sample until the calculated permeance was approx. constant. Feed pressures of 3, 5 and 7 bar(g) have been analysed with 3 different membrane samples for each pressure to check for reproducibility. Results of this analysis are given in Figure 2.

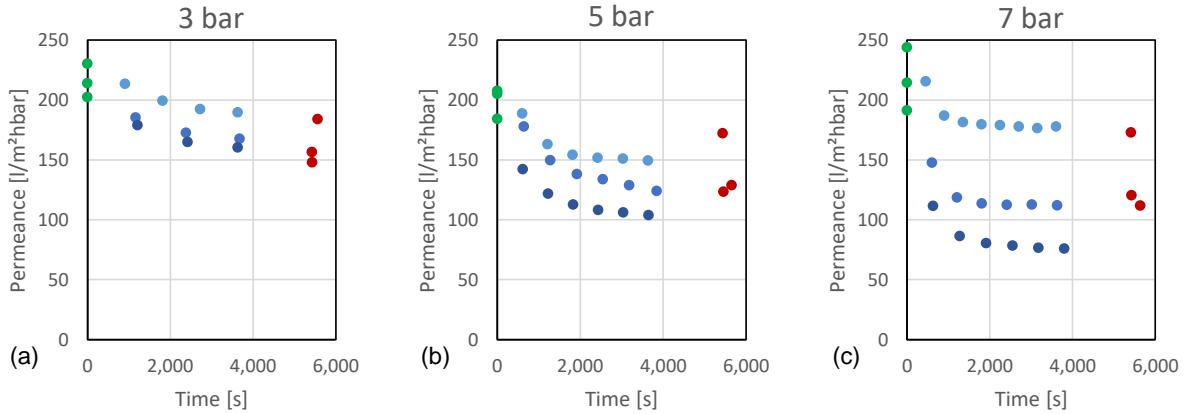


Figure 2: Permeance of UH030 membrane over time at different feed pressures (green dots at 1 bar before exposure, red dots at 1 bar after exposure, different blue dots correspond to different membrane samples): (a) 3 bar, (b) 5 bar, (c) 7 bar

Green dots in Figure 2 indicate permeances calculated from experiments performed at 1 bar(g) before exposure to the respective target pressure while red dots indicate those permeances at 1 bar(g) after the exposure. It becomes obvious that permeance deteriorates with time when the membrane is exposed to higher feed pressures. This deterioration is irreversible (plastic compression) in large parts as the permeance at 1 bar(g) after exposure is always significantly lower than the value before exposure. At 3 bar(g), 5 bar(g) and 7 bar(g), the permanent permeance reductions amount to 23.9 % ($\pm 13.7\%$), 29.0 % ($\pm 11.5\%$) and 38.2 % ($\pm 7.9\%$) respectively (difference of mean values of green and red dots for each operating pressure including single standard deviation). To a smaller degree, the permeance deterioration is reversible which corresponds to an elastic compression of the membrane material. A significant spreading of permeance values for different membrane samples of the same membrane material operated at the same operational conditions is obvious. Green dots represent exactly the same experiments only with different samples of the same membrane. Red and different blue dots represent similar experiments at individual pressures. This spreading of values increases drastically with increasing feed pressures leading to results with poor reproducibility. All measured values are well above the guaranteed performance parameters provided in the membrane specification data sheets (Table 1). Additional experiments performed with the four different membranes at a feed pressure of 8 bar(g) show that UP010 performed best with no significant permeance decline, while UP020, UH030 and UH050 exhibited declines of 28.0 %, 30.5 % and 55.3 % respectively.

3.2 Cleaning and concentration of Nanolignin suspensions

The four different commercial NADIR ultrafiltration membranes have been applied for cleaning, solvent exchange and increasing the concentration of Nanolignin particles using the method and apparatus described in Chapter 2.2 at a feed pressure of 8 bar(g). For this purpose, around 1.4 L of Nanolignin suspension have been diafiltrated until a volume reduction of around 40 % was reached corresponding to 500 mL of permeate collected (phase DF1). The remaining suspension has been refilled with pure water to the initial volume and diafiltrated again until a volume reduction of 40 % (phase DF2), followed by another repetition of refilling and diafiltration until a volume reduction of 40 % after which the experiment was ended (phase DF3). During these three phases, transmembrane fluxes and permeances have permanently been monitored and samples have been drawn from feed suspensions (2 samples during each of the phases DF1 through DF3) and permeate solutions (1 sample for each phase) for analysis of Nanolignin particle sizes, Ethanol contents and TOC. Figure 3 gives an insight to the characteristics of this triple-phase procedure of ultrafiltration/diafiltration. The left diagram (a) shows the total mass of feed/retentate as well as the actual content of Nanolignin particles in the feed/retentate over time. The values given are not experimentally retrieved but calculatory because the Nanolignin content currently is too low to allow for a periodical and precise measurement. The continuous withdrawal of permeate results in a constant reduction of feed/retentate mass while sampling for analytic

purposes is indicated by a sudden drop of around 40 g. The Nanolignin content increases gradually with the cutting-off of permeate as 100 % retention is postulated for particulate lignin. The addition of water at the beginning of each diafiltration phase is indicated by a sharp increase of the feed/retentate mass and a sharp drop of the Nanolignin content to the initial level. The right diagram (b) shows the gradual washing-out of Ethanol and impurities like dissolved lignin and sugars (represented by the sum-parameter TOC) by the diafiltration process. As a major result of the current work, the diagram also clearly shows that the Nanolignin particle size is not influenced by the ultrafiltration process over the investigated duration of 9 hours and stays constant at around 110 nm. This behaviour is true for all analysed membranes. Particulate lignin was not detectable in any permeate sample which indicates virtually complete retention of Nanolignin particles.

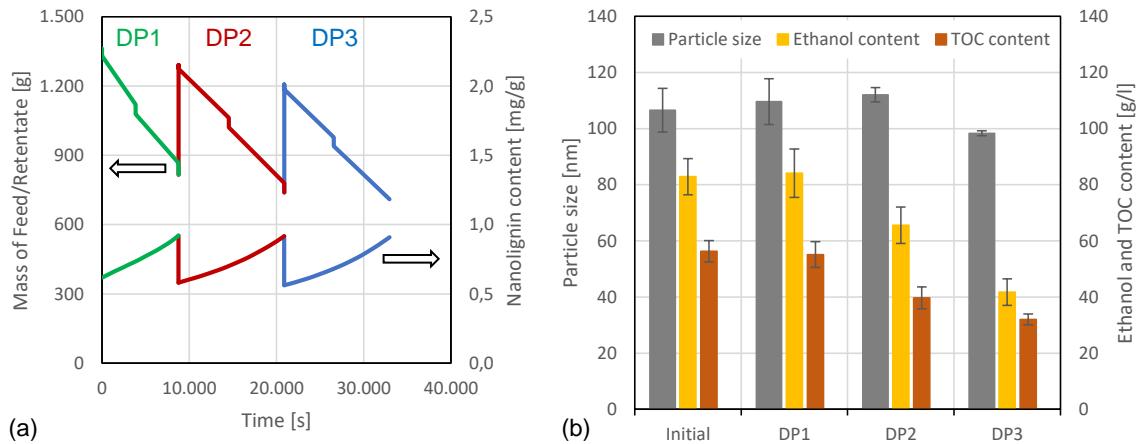


Figure 3: Decrease of feed mass and suspension characteristics during diafiltration with UH050 membrane: (a) feed mass and Nanolignin content in the feed/retentate, (b) Nanolignin particle size, Ethanol content and TOC

A major topic during ultrafiltration of particulate suspensions is the deposition and accumulation of solid particles on the membrane surface (fouling) resulting in a more or less pronounced performance decline. While this effect is partly reversible by flushing and backflushing the membrane, it is known that different membrane materials show different fouling behaviour, especially considering hydrophilicity of the membrane. Thus, a process like depicted in Figure 3 has been performed with all four considered membranes and a special examination focussing on fouling has been conducted. The fresh membrane has been conditioned and afterwards operated at a feed pressure of 8 bar(g) with single-phase 15 %w/w hydroalcoholic solution until stable transmembrane flux and permeance have been registered (waiting for compaction stabilization). The permeance determined after this stabilization is termed as initial permeance. Subsequently, the above-mentioned triple-phase ultrafiltration/diafiltration procedure with Nanolignin suspension and a duration of around 9 hours has been performed. After that, the suspension was drained and apparatus and piping rinsed with water. Finally, another experiment with single-phase 15 %w/w hydroalcoholic solution and a feed pressure of 8 bar(g) was performed until stable flux and permeance have been obtained. This permeance value is termed as final permeance. Results of this examination are given in Table 2.

Table 2: Membrane degradation due to deposition of particulate lignin on the surface (fouling)

Membrane	Initial permeance [l/m ² ·h·bar]	Final permeance [l/m ² ·h·bar]	Permeance deterioration [%]
NADIR® PM UP010	43.7 ± 0.4	1.96 ± 0.18	-95.5 ± 0.7
NADIR® PM UP020	17.9 ± 0.2	2.81 ± 0.15	-84.3 ± 1.5
NADIR® PM UH030	16.2 ± 0.2	3.61 ± 0.19	-77.7 ± 2.2
NADIR® PM UH050	23.9 ± 1.2	5.10 ± 0.10	-78.6 ± 1.3

Fouling provokes permeance declines in the range of 80 to 95 % within 9 hours of operation with Nanolignin suspensions. Membranes UH030 and UH050 seem to be more resistant to fouling which could be a result of the hydrophilic PES from which these membranes are fabricated. This correlation has already been suggested in literature (Nunes and Peinemann 2001).

4. Conclusions

The general applicability of ultrafiltration/diafiltration for cleaning, concentration and solvent exchange of Organosolv-derived Nanolignin suspensions using commercial polymeric membranes has been demonstrated. The method shows virtually complete retention of particulate lignin while contents of ethanol and dissolved impurities (sugars, degradation products) can be significantly decreased by washing out without altering Nanolignin particle size. Two major topics to be considered are performance declines due to membrane compaction and fouling. Compaction leads to significant permeance reductions in any case, but higher operating pressures lead to a higher spreading of values and lower predictability of membrane performance. Fouling due to deposition of solid lignin particles leads to performance degradation of 80 to 95 % and must be counteracted by membrane regeneration using flushing and backflushing with clean solutions. Future work will focus on these regeneration processes as well as increasing working volumes and improving analytic procedures.

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