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Graphical Abstract

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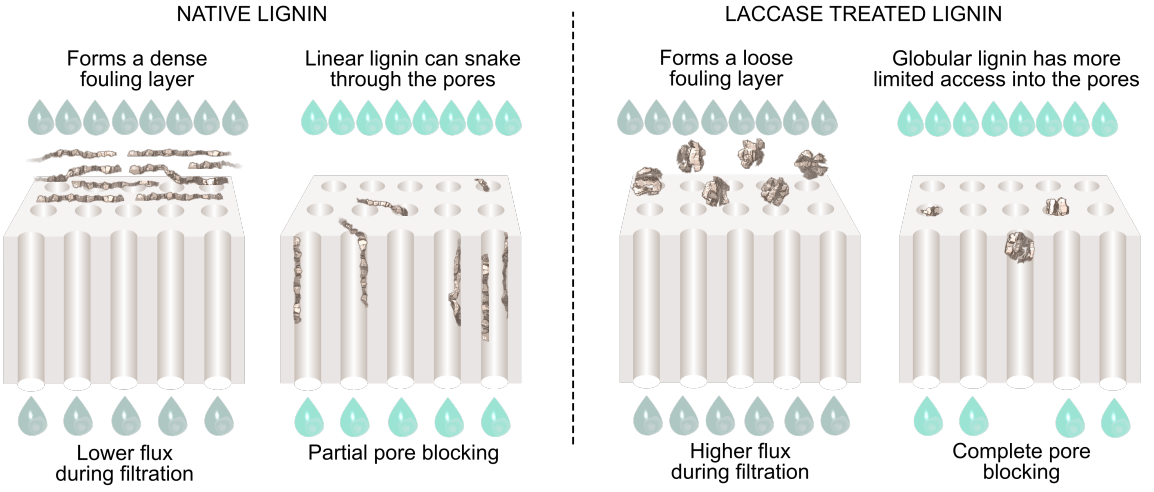

Influence of laccase treatment on fouling layer formation in ultrafiltration of birch hot-water extract

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ABSTRACT

Fouling problems caused by lignin have been limiting the use of membranes in the recovery of value-added materials from biorefinery streams. Fortunately, laccase-based catalytic pretreatments enable modification of lignin to the less fouling form. Because the mechanisms behind the fouling caused by ligneous compounds in wood-based streams are still not deeply understood, the aim of this study was to find out how laccase oxidation affects membrane fouling caused by pressurized hot-water extract. The effect of laccase on the fouling tendency of birch extract was explored both with adsorptive and pressure-driven experiments. The results suggested that laccase treatment increased the molar mass of lignin and improved significantly filtration capacity of commercial polyethersulphone membrane, possibly due to formation of less dense foulant layer during the filtration. Based on FTIR and BET results laccase oxidation decreased both adsorptive and pressure-driven fouling caused by lignin. However, decreases in pure water permeabilities were higher for the samples that were fouled with laccase treated extract. This may have originated from the transformation in the fouling mechanism from the pore narrowing to the pore blocking and could be prevented by the selection of a membrane with a different pore size.

1. Introduction

Modern biorefinery concepts target to exploit the full potential of lignocellulosic biomass via production of diverse high-value products such as platform chemicals, novel polymers and next generation biofuels from different components of biomass. Separation, purification and concentration of hemicelluloses, lignin and phenolics from process streams for further processing is essential in order to reach potential bio-based products. [1, 2] Ultrafiltration has proven to be a very promising separation technique for the fractionation and recovery of lignin and hemicelluloses from wood extracts. However, the commercial membranes available are typically fairly hydrophobic and thus prone to fouling by lignin and wood extractives. [2, 3, 4] The presence of lignin in the wood extract is detrimental also for value-added utilization of hemicelluloses. It may have negative effect e.g. on xylitol production or fermentation of xylose/xylan to ethanol due to its inhibitory effect on performance of microorganisms [5, 6]. The stucture of lignin dissolved in pressurized hot-water extracts is expected to have a similar linear structure than native lignin [7]. Presence of lignin-carbohydrate complexes is also probable [8].

Enzymatic laccase treatment provides an attractive approach for fragmentation and chemical modification of lignin to less sticky form [1, 9]. Laccases are copper containing biocatalysts that possess both polymerizing and depolymerizing activity depending on the size and chemical structure of the substrate [1, 10, 11]. Besides polymerization and depolymerisation of lignin laccases have been applied also to break linkages between lignin-hemicellulose complexes and to increase the molecular size of hemicelluloses by crosslinking them via lignin side groups bound to them. [12, 13] Laccase treatment removes also phenolic compounds [14, 15]. When combined to membrane filtration, this kind of pretreatment which breaks the molecules to smaller compounds and/or aggregates them to larger compounds, might influence the flux favourably [3, 16]. Laccase treatment can be done either prior to filtration or during the filtration via immobilization of the laccase on the surface of the membrane. Laccase treatment combined with mebrane filtration

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Table 1
Applications of combined laccase treatment and membrane filtration for removal and separation of phenolic compounds.

Origin of laccase	Laccase immobilization method	Membrane type	Material	Application	Reference
T. versicolor	Reverse filtration of laccase + dopamine coating	Commercial NF/UF	PES, RC	–	[17]
T. versicolor	TiO2 nanoparticles + APTES and GLU linkers	Lab-made	PES	–	[18]
T. versicolor	Electron beam grafting	Filter, 0.45 μm	PVDF	Removal of bisphenol A	[19]
T. versicolor	Reverse filtration of laccase + dopamine coating	Commercial NF/UF	PA, poly-piperazinamide	Removal of bisphenol A	[20]
R. vernificera	GLU crosslinker	Electrospun	HPEI/PES	Removal of bisphenol A	[21]
T. versicolor	Polydopamine/PEI coating + adsorption of laccase	Commercial NF	PA, PES, polypiperazine	Removal of bisphenol A	[22]
T. versicolor	Reverse filtration of laccase + dopamine, dopamine/PEI or dopamine/Cu^{2+} coating	Commercial NF	PA	Removal of bisphenol A	[23]
T. versicolor	Reverse filtration of GO and laccase + dopamine coating, adsorption of laccase + dopamine/GO coating	Commercial NF	PA	Removal of bisphenol A	[24]
T. versicolor	–	Filter, 0.45 μm	CA	Removal of bisphenol A and its derivatives	[25]
T. versicolor	Reverse filtration of PEI, MOFs and laccase + dopamine coating	Commercial NF/UF	PAN, RC, PA	Removal of bisphenol A, diclofenac and tetracycline	[26]
T. versicolor *P. sanguineus*	GLU crosslinker	Commercial MF	TiO_2	Degradation of bisphenol A	[27]
T. versicolor	Hydrazide linker	Commercial UF	PVDF	Removal of phenylurea pesticide in wastewater	[28]
T. versicolor	Crosslinked laccase aggregates in solution	Commercial MF	PS	Removal of pharmaceuticals	[29]
A. oryzae	Adsorption and filtration of laccase and CNTs	Commercial UF	PES	Removal of organic dye crystal violet	[30]
A. oryzae	Immobilization on Al pellets, APTES and GLU linkers	Lab-made	PS	Degradation of glucose-glycine Maillard products	[31]
F. fomentarius	–	Commercial UF	ZrO_2/TiO_2	Removal of phenolic compounds of pomegranate juice	[32]
A. oryzea	–	Commercial UF/MF	PES, PS	Removal of guaiacol, catechol and *m*-cresol	[33]
T. versicolor	–	Commercial NF	PA, PES, RC	Separation of vanillic, *p*-coumaric and ferulic acids from monosaccharides	[34]
A. oryzea	–	Commercial UF	PES, PS	Removal of phenolics and COD from pulp and paper wastewater	[35]
T. versicolor	–	Filter, 0.45 μm	Nylon	Removal of lignin from prehydrolysis liquor of kraft dissolving pulp	[5]
	–	Commercial NF	–	Removal of lignin from prehydrolysis liquor of kraft dissolving pulp	[16]
–	–	Commercial UF/MF	α-Al_2O_3, PS	Separation of high molecular mass hemicelluloses	[12]
–	–	Commercial UF	PS	Laccase combined with bentonite to remove lignin from birch extract	[3]

APTES = 3-aminopropyltriethoxysilane, CA = cellulose acetate, CNTs = carbon nanotubes, COD = chemical oxygen demand, GLU = glutaraldehyde, GO = graphene oxide, HPEI = hyperbranched, PEI = polyethyleneimine, PES = polyethersulfone, PS = polysulfone, PVDF = polyvinylidene fluoride, RC = regenerated cellulose

has been applied to removal and separation of various phenolic compounds including micropollutants, polyphenols and lignin (Table 1).

In addition to hemicelluloses and lignin, pressurized hot-water extracts contain wood extractives and organic acids that affect processing of the streams and decrease the purity and value of the hemicellulose fractions [36]. Dissolved and colloidal extractives such as lignans, triglycerides, steryl esters and free fatty and resin acids have been shown

Table 2
Characteristics of the pressurized hot-water extract. *Measured at 25 °C.

Raw material	Birch
pH*	3.3
Viscosity (mm^2/s)*	1.01
TOC (g/L)	15.7
Dry matter (g/L)	32.3
UV absorbance at 280 nm	126
Lignin (g/L)	3.5
Mn (Da)	421
Mw (Da)	684

to foul ultrafiltration membranes in filtration of pulp and paper mill process water [37, 38]. Removal of colloidal extractives prior to ultrafiltation of process water from thermomechanical pulping of spruce has been shown to increase the flux remarkably [39]. Laccase appears to be able to catalyze the oxidation of resin acids with conjugated double bonds and fatty acids with several double bonds, probably via secondary reactions that follow the initial oxidation of phenolic hydroxyl groups [40, 41, 42]. It has been shown in previous studies that the use of laccase-mediator systems enables indirect oxidation of non-phenolic, conjugated wood extractives to higher molecular mass reaction products. The oxidation removes efficiently most of the lipophilic extractives present in paper pulps from different origins. [43, 44, 45]

Membrane filtration combined with laccase catalyzed oxidation for lignin modification provides a possibility to contribute on lignin physicochemical properties, which may enhance the separation efficiency in membrane based processes. Laccase pretreament has been shown to enhance nanofiltration process of prehydrolysis liquor of hardwood kraft dissolving pulp [5, 16], and when combined to adsorption on bentonite, ultrafiltration efficiency of birch wood extract [3]. In both of the cases it was suggested that the filterability increased due to the removal of lignin, but the formed membrane fouling layers were not characterized. Since the general mechanisms behind the membrane fouling caused by ligneous compounds in wood extracts are still not know as the issue has not been deeply examined, this study aims to to achieve understanding on the influence of laccase oxidation on the lignin originated fouling phenomena occurring on the membrane surface. Based on our knowledge, this is the first study where the effect of laccase pretreatment on the membrane fouling layer composition and structure after the filtration of wood-originated streams has been characterized. In this study, the membrane fouling experiments were performed with and without pressure to study the changes both in pressure-driven and adsorptive fouling potentials birch wood extract. The effect of laccase pretreatment on the degree of fouling of the used PES UF membrane was evaluated by pure water permeability measurements, ATR-FTIR spectroscopy, contact angle measurements and Brunauer-Emmet-Teller nitrogen adsorption/desorption analysis. Changes in wood extracts were characterized by UV analysis, total organic carbon measurement and size exclusion chromatography.

2. Materials and Methods

2.1. Pressurized hot-water extract

Pressurized hot-water extract was obtained by cooking birch chips in a batch reactor setup at 160 °C for 90 min at pressure of 5–7 bar. The weight ratio of water to wood was 6 : 1. The extract was frozen for storing and melted for use. Prior to the experiments the extract was warmed up to 25 °C and centrifuged for 30 min at 9880 rpm (Sorvall RC-28S centrifuge, GSA rotor, RCF = 10 000) to separate the supernatant from insoluble sediment. Characterization of the birch extract (Table 2) showed that the extract contained lignin 3.5 g/L, most of the dry solids being xylan. Lignin concentration in the extract was measured by UV280 (in 0.1 M NaOH) and taking into account the contribution of furfurals, who also absorb UV-light at 280 nm. The dissolved lignin was oligomeric based on its molar mass measured by alkaline size exclusion chromatography. Description of the analytical methods hereinafter (2.4).

2.2. Ultrafiltration membrane

The commercial UH004 P polyethersulphone ultrafiltration membrane (Microdyn Nadir GmBH) with cut-off values of 4 kDa was used in all experiments.

2.3. Experimental procedure

The pure water permeability was measured before and after the filtration and adsorption experiments to evaluate degree of membrane fouling. ATR-FTIR spectroscopy was used as complementary method in fouling evaluation to characterize the changes caused by fouling and to compare the amount of ligneous foulants on different membranes. Brunauer-Emmett-Teller (BET) nitrogen adsorption was applied to study changes in porosity and surface area as the result of fouling. Retentate and permeate samples from pressure-driven fouling experiments were measured by UV spectroscopy and TOC analyzer to study the changes in retention.

2.3.1. Laccase treatment

Laccase catalyzed treatment of pressurized hot-water extract was used to modify the physicochemical properties of the lignin in extract. The enzymatic treatment was carried out at 60 °C in an open class container under efficient magnetic mixing to allow air (O_2) entrance to the extract for 15 min. Commercial M120 laccase (from *Trametes sp.*, Amano) with dosing of 500 nkat/g of lignin was used (protein 0.06 wt% of lignin). The alteration of lignin structure was characterized by size exclusion chromatography. Laccase activity was determined against guaiacol (at pH 3.5) as previously considered relevant in the case of lignin substrates [46, 47].

2.3.2. Pressure-driven filtration experiments

Pressure-driven filtration experiments were carried out by using a 300 mL nitrogen-pressurized and magnetically stirred dead-end Amicon cells (area 38 cm^2). Membranes were at first pressurized at 5.4 bar in order to stabilize them. Then, the pure water permeability was measured at 2 bar and 25 °C. Pressure-driven fouling step was done at 25 °C by filtrating reference extract and laccase treated extract at 5.4 bar until the yield of the permeate was 31 %. The cell was rinsed with pure water (2 × 100 mL) and finally, the pure water permeability was measured at 2 bar.

2.3.3. Adsorption experiments

Adsorption experiments were carried out by using a 4-cell cross-flow filter (area 40 cm^2) with two discrete flow lines for pure water permeability measurements and adsorption step. A schematic diagram of the experimental setup is shown in Fig. 1. Besides reference extract and laccase treated extract (cells B and C), pure water (cell A) and pH-adjusted water (pH 3.3, cell D) were circulated as references in the adsorption step. pH of the water was adjusted with hydrochloric acid (37 % Ph. Eur., VWR Chemicals) in order to see the affect of acidity on the performance of the membrane. The temperatures of feed tank and adsorption solutions were kept at 25 °C by using heat exchanger and water bath.

In the beginning of the experiment the transmembrane pressure was increased stepwise to 5 bar in order to pressurize and stabilize the membrane. Then the pure water permeability was measured at 3 bar with cross-flow velocity of 0.64–0.68 m/s. Adsorption step was carried out without applied pressure at 25 °C by using peristaltic pump. The pressure generated by the peristaltic pump was 0.1 bar and the cross-flow velocity was ∼0.004 m/s. The solutions were circulated for 2 hours and the adsorption step was followed by quick flushing of the setup at 3 bar and pure water permeability measurement at 3 bar. Both permeate and retentate were returned to the feed tank during pressurization and pure water permeability measurements.

2.4. Analytical methods

2.4.1. UV spectroscopy and liquid chromatography

In addition to lignin, furfural and 5-HMF (5-hydroxymethyl-2-furaldehyde) (degradation products of carbohydrates) have absorption maxima close to 280 nm. Thus, the accurate determination of aromatic lignin concentration in hot-water extract by UV spectroscopy (at 280 nm) requires the elimination of furfural contribution. Furfural and 5-HMF concentrations were quantified using a Flexar®HPLC-RI (PerkinElmer, Waltham, MA, USA) system equipped with an Aminex column (HPX-87H, 300 mm × 7.8 mm, Bio-Rad, CA, USA) under isocratic conditions (40 °C) at a flow rate of 0.5 mL/min of 2.5 mM H_2SO_4. The results were calculated by using corresponding standards: Furfural (Sigma-Aldrich) and 5-HMF (Sigma-Aldrich). The UV absorbance of the extract was measured at 280 in 0.1M NaOH. Based on the furfural concentration by HPCL (380 mg/L) and its specific absorptivity value, 146.9 L/(g·cm) [48], absorbance contribution of 56 for furfural at 280 nm was computed. The extract did not contain 5-HMFs. Aromatic lignin concentration was obtained by subtracting the computed absorbance of furfural (56) from the absorbance of the extract (126), and using the absorptivity value of 20.0 L/(g·cm).

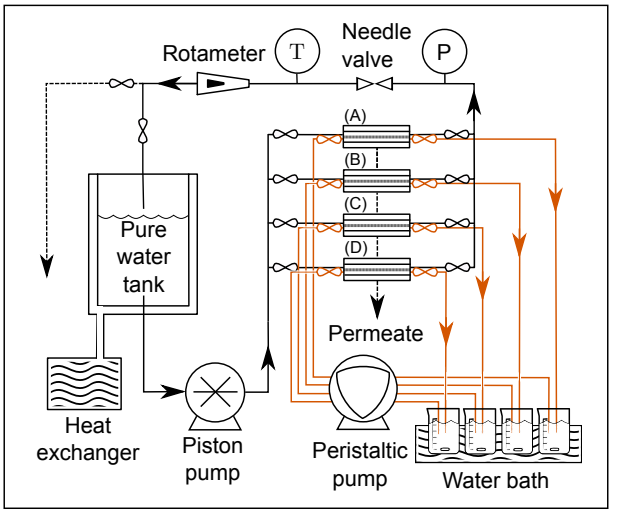

Figure 1: Schematic of the cross-flow filtration system used in the adsorptive fouling experiments.

2.4.2. Size exclusion chromatography

Alkaline size exclusion chromatography (SEC) was used to analyze the weight average molar mass (Mw), number average molar mass (Mn) and polydispersity (PD) of the wood extracts before and after the laccase treatment. The samples were dissolved in 0.1 M NaOH and prefiltered through 0.45 µm syringe filters. The molar mass measurements were performed with Waters HPLC system equipped with a UV detector at 280 nm. 0.1 M NaOH solution was used as eluent at a flow rate of 0.5 mL/min at 25 °C. PSS MCX 1000 and 100 000 Å columns were used. The molar mass results were calculated against polystyrene sulphonate standards (3420–148 500 g/mol).

2.4.3. Retention measurements

The changes in retention were determined by measuring total organic carbon (TOC) and UV absorbance from permeate and retentate samples taken during the pressure-driven fouling experiments. TOC was analyzed by using Shimadzu TOC-L total organic carbon analyzer. UV measurements were done in the range of 190–400 nm with a Jasco V-670 spectrophotometer. Absorbances were recorded at room temperature in quartz cells with 1 cm path lengths. The absorbances at 202 nm (unsaturated chains and carbohydrate monomers) and 280 nm (unconjugated phenolic hydroxyl groups and aromatic rings) were applied to calculate concentrations of different chemical species. The retentions were calculated from concentrations in the feed (c_F), retentate (c_R) and in the permeate (c_P) by using the relation:

$$Retention = (1 - \frac{\frac{c_P}{c_F + c_R}}{2}) \cdot 100$$

2.4.4. Infrared spectroscopy

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was carried out as an analytical method to measure the amount of lignin originated fouling. Membranes from both adsorption and pressure-driven fouling experiments were analyzed using Perkin-Elmer Frontier spectrometer equipped with a diamond crystal. 10 spectra were measured for each membrane from different points in the range of 400–4000 cm^{-1}. For each spectrum 4 scans were collected with the resolution of 4 cm^{-1} and data interval of 1 cm^{-1}. The scans were co-added and processed with ATR correction, baseline correction and normalization.

2.4.5. Contact angle

Contact angles were measured by KSV CAM 101 instrument connected to a CCD camera. Sessile drop method was applied and the captured images were treated by curve fitting analysis with CAM 2008 software in order to determine the contact angle. Samples were dried in a desiccator before the measurements.

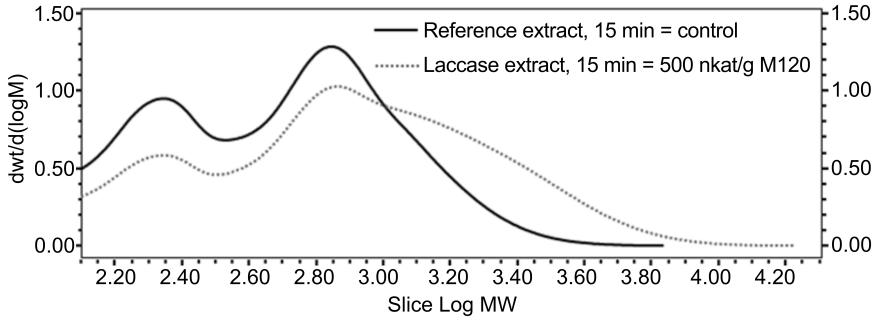

Figure 2: Impact of laccase treatment on lignin molar mass distribution of the birch hot-water extract.

2.4.6. Brunauer-Emmett-Teller (BET) nitrogen adsorption

BET analysis can be used for measuring surface area and pore size distribution of membrane. The method is based on physisorption and desorption of a gas on the surface and inside the pores of the sample. [49, 50] Pore size measurements were done by using 3Flex surface characterization analyzer (Micromeritics Instrument Corporation) and nitrogen gas. The membrane samples were prepared for analysis by cutting them into small pieces and degassing by the Smart VacPrep 067 unit under vacuum at 50 °C for 4 hours [51]. During the analysis samples were placed under vacuum and immersed in liquid nitrogen. BJH method and reference curve of Harkins-Jura method were applied to calculate the pore size distributions in the mesopore area from the measured desorption isotherms. t-plot method was applied to obtain micropore volumes of the samples.

3. Results and Discussion

3.1. Laccase-induced changes in the wood extract

The hypothesis was that laccase will modify lignin present in the wood extract, which can then decrease fouling caused by lignin. Molar mass distributions of reference extract and laccase treated extract are show in Fig. 2. It can be seen that the molecular mass distribution of laccase treated extract shifted to higher molecular weights. The laccase treatment caused clear change in colour from light to dark brown and increase in molar mass (Mw) of lignin (80 %, from 680 Da to 1230 Da). Polydispersity increased from 1.6 to 2.3. Laccase treatment caused also partial lignin agglomeration, which changed the extract from clear to turbid. The agglomerates were separated by centrifugation and dissolved in alkali for molar mass determination. The agglomerated lignin (Mw 1870 Da) showed higher molar mass than that measured from the treated extract.

3.2. Fouling experiments

The pressure-driven fouling experiments performed with the UH004 P membrane at 25 °C showed that the filterability of the laccase treated extract was better than the filterability of reference extract (Fig. 3). Flux of the laccase treated extract was higher in the beginning of the filtration and declined in all of the experiments. Filtrations were continued until VR value of 30 % where the flux of the reference extract was ∼5 kg/m^{2}h and the flux of the laccase treated extract was twice as high, ∼10 kg/m^{2}h. Increase in filtration capacity as the result of the laccase treatment may be partly explained by the removal of agglomerated high molecular mass lignin. Based on the UV absorption at 280 nm the retention of lignin increased about 10 % after the laccase treatment. The slight increase in retention of lignin found after the laccase treatment can be attributed to the polymerization of lignin. The increase in lignin retention was, however, not big enough to be seen also in TOC retention values because fraction of the lignin was small.

Minor differences in the reduction rate of the membrane capacity in the beginning of the filtration experiments as the result of the laccase treament (Fig. 3) may indicate that laccase oxidation has altered the cake layer formation or membrane fouling by pore-blocking slightly. Because the laccase oxidation changed the molecular weight distribution of lignin molecules, the resulting larger lignin molecules might have more limited access inside the membrane pores. But on the other hand, even though lignin molecules with certain size range may enter the membrane skin layer less frequently, they may block the pores of the membrane more severely. Thus in the development of laccase pretreatment processes, the matching of the membrane pore size and size of the resulting lignin molecules should be considered [3].

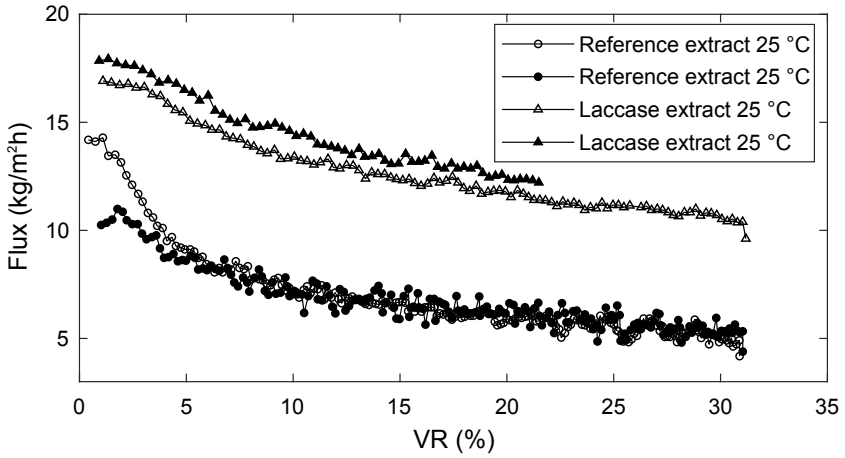

Figure 3: Filtration capacities in pressure-driven filtrations of reference extract (○ and ●) and laccase treated extract (△ and ▲) at 25 °C.

In addition, laccase treatment might have modified lignin molecules to a form that differs from the chemical structure of native lignin. Because the concentration of lignin was rather low in the studied extract, laccase oxidation has potentially lead to intramolecular cross-linking and compaction of linear lignin molecules [52]. As the lignin gets more globular the exposed surface area decreases and there are fewer interactions with membrane surface. The change in the shape of the molecules would also weaken the possibility of lignin accessing pores. Linear molecules can snake through the membrane pores whereas globular molecules of the same molecular weight are rejected cause they are not able to deform [53]. The changes in lignin structure might also alter beneficially the structure of the secondary layer, which is formed on the membrane surface during the filtration.

The pure water permeabilities (PWP) before and after pressure-driven and adsorption experiments are presented in Fig. 4. Pure water permeabilities decreased more in the pressure driven filtration experiments than in adsorption experiments of reference extract and laccase treated extract. Thus it seems that applied pressure results in more severe fouling. Interestingly, the decrease in pure water permeabilities was higher when the wood extract was treated with laccase both in pressure-driven and adsorption fouling experiments. This could be also explained by the changes in lignin molar mass distribution as the result of the laccase treatment because even small amount of lignin with certain size could block the pores and induce severe decline in the permeability of the membrane.

ATR-FTIR spectroscopy was applied as complementary technique to study degree of fouling. Through FTIR analysis it is possible to detect the peak at 1490 cm^{-1} that can be related to the amount of lignin. Infrared spectra of membranes from pressure-driven fouling experiments in Fig. 5 show that laccase treatment decreased membrane fouling caused by lignin both in pressure-driven and adsorption experiments. Based on intensities of the spectra the level of lignin originated fouling was the highest in the pressure-driven filtration of reference extract and about half lower in the pressure-driven filtration of laccase treated extract. Adsorption of reference extract lead to almost as high fouling degree as pressure-driven filtration of laccase treated extract. Adsorption of laccase treated extract caused about half less lignin originated fouling than adsorption of reference extract. Decrease in lignin originated fouling after the laccase treatment can be partly explained by the smaller amount of lignin present in the extract.

All in all, fouling decreased the contact angle of the membranes, i.e. surface of membranes turned into more hydrophilic compared to membranes which had seen only pure water (Tab. 3). Similar hydrophilization of the polysulphone and polyethersulfone membranes as the result of fouling has been observed when spruce hydrolysate [2], polyphenolic compounds [54] and dextran [55] have been filtered. Also modification of PES based membrane with birch DES-lignin (extracted from wood by a deep eutectic solvent) has been shown to increase hydrophilicity of the membrane surface [56].

The contact angle decreased to 47° after pressure-driven fouling and to 51° after adsorptive fouling caused by the reference extract. The contact angle results together with IR spectra indicate that the surface of the membrane turned into more hydrophilic due to the fouling. Fouling caused by the laccase treated extract decreased the contact angle

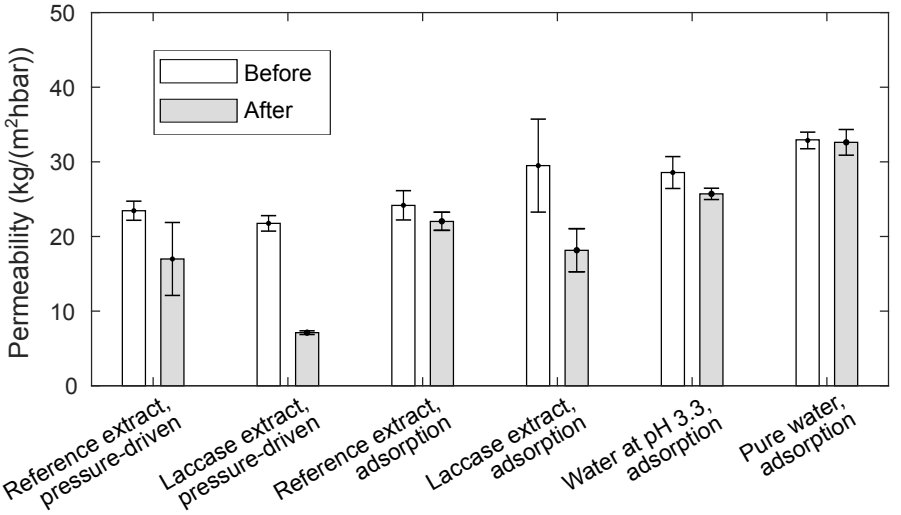

Figure 4: Average pure water permeabilities before and after fouling in pressure-driven and adsorption experiments at 25 °C. Results are average of two experiment, except in the case of pure water, where the results are average of four experiments. The error bars represent the standard deviation of the results.

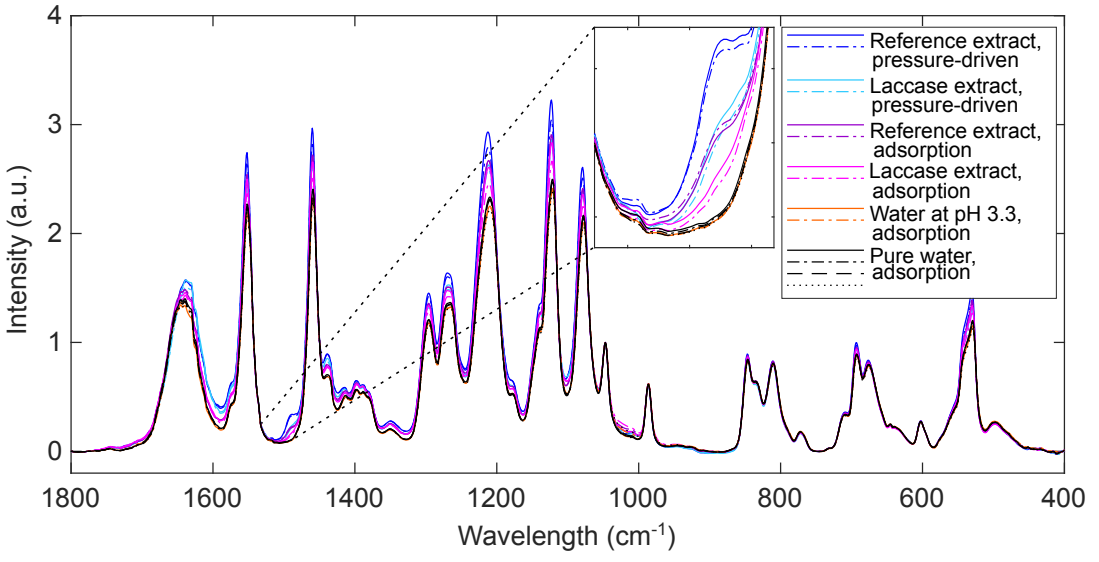

Figure 5: Infrared spectra of membrane from pressure-driven and adsorptive fouling experiments. Non-overlapping lignin originated foulant peak can be detected at 1490 cm^{-1}.

to 57° after the pressure-driven fouling and to 39° after the adsorptive fouling. This might indicate that also some other factors besides the fouling caused by lignin are affecting the hydrophilicity. Because laccase decreased the lignin originated fouling it is possible that the other foulants than lignin, such as extractives are more present on the surface.

Higher increase in hydrophilicity as the result of adsorptive fouling after the laccase treatment could stem from higher degree of organization of the fouling layer after adsorption, when compared to the formation of fouling layer under pressure. During adsorptive fouling process the foulants can self-organize more freely but in the pressure-driven fouling the deposition of the foulants may vary more. Based on the previous studies foulants which may either increase or decrease the contact angle depending on their orientation include wood extractives (e.g. fatty acids, resin

Table 3
Contact angle (CA) result with standard errors of the mean.

	Sample name	CA (°)
Pressure-driven experiments	Reference extract	47 ± 2
	Laccase extract	57 ± 5
Adsorption experiments	Reference extract	51 ± 5
	Laccase extract	39 ± 0
	Pure water	74 ± 4
	Water at pH 3.3	64 ± 3

acids and triglycerides) and phenolics possessing both hydrophobic and hydrophilic parts in their structures [57, 37]. For example, in the adsorption of amphiphilic foulants the hydrophobic heads of the molecules are adsorbed onto the relatively hydrophobic membrane and the hydrophilic parts are orientated towards the solution [57, 58]. In addition, surface roughness has effect on the apparent contact angle values [59].

Determination of wood extractives in prefiltered reference extract and in prefiltered laccase treated extract was tried by liquid-liquid extraction and gas chromatography analysis as described by Örså and Holmbom[60] but the analysis succeeded only partly due to the unexpected precipitation problems. Addition of silylation compounds BSTFA (bis-(trimethylsilyl)-trifluoroacetamide) and TMCS (trimethylchlorosilane) induced precipitation of laccase treated samples whereas reference extract samples remained dissolved. Based on the analysis of the dissolved fraction of the laccase treated sample (in which unexpected precipitation occured) there were at least some lignin residuals, lipophilics and fatty acids and trace amounts of other extractives. However, due to the problems in the analysis the total amount of wood extractives in the laccase treated sample is not known. Fully dissolved prefiltered reference extract samples contained significantly higher amounts of lignin residuals, lignans, syringaresinols and lipophilics than laccase treated samples. There were also minor amounts fatty acids, resin acids, sterols, medioresinols, syringaresinols and steryl esters. Thus, based on the literature and the clear change in the sample matrix due to the laccase treatment, it can be concluded that laccase treatment may have modified besides lignin also extractives present in the pressurized hot-water extract.

Results of the BET nitrogen desorption measurements are listed in Tab. 4. Changes in the specific surface area, specific pore volume and in the average pore diameter in the mesopore region show that fouling increased surface area, total pore volume and average pore size of the samples. These changes might originate from the formation of the porous fouling layer on the surface of the membrane. Fractions of the micropores were determined by t-plot method and the results are shown in Tab. 4. The disappearance of the small diameter pores as the result of fouling supports the observed changes in pure water permeabilities (Fig. 4). Micropore volume was the highest in the samples, which had seen only pure water and the lowest in the samples that were fouled by the wood extract in pressure-driven filtrations. Thus it seems that part of the fouling is caused by the pore blocking. Because the microporosity of the samples from the adsorption experiments was almost on the same level than in the pure samples (around 0.0006 cm^3/g), the results suggests that practically no pore blocking happened during the adsorptive fouling.

Pore size distribution of membrane samples based on the pore volume data from nitrogen desorption isotherms are presented in Fig. 6. Fouling of the membrane lead to increase in pore volumes of pores that had diameter larger than 10 nm. Order of the increase in pore volumes follows the same trend than degree of lignin originated fouling revealed by FTIR spectra (Fig. 5). Reference extracts caused slightly higher increase in pore volumes than laccase treated extracts both in pressure-driven and adsorption experiments and pressure-driven experiments caused significantly higher increase than adsorption experiments.

Altogether, the IR and BET results are in line with each other and support the finding that laccase oxidation decreased lignin originated fouling layer formation both in adsorptive and pressure-driven experiments. However, laccase treatment caused higher decrease in the pure water permeability. The changes in the micropore volumes revealed that the reference extract and laccase treated extract decreased the amount of micropores broadly as much. Thus the higher decrease in pure water permeability after the laccase treatment must originate from the changes in the structure and physicochemical properties of the deposited fouling layer and or from the changes in membrane pore blocking. Transformation in the fouling mechanism from the pore narrowing to the pore blocking is supported by the micropore volume results. Native, more linear lignin molecules could form densely packed layer on the surface of the membrane during

Table 4
Surface area, total pore volume and average pore sizes based on nitrogen adsorption–desorption isotherms. Estimated micropore volume and micropore area based on t-plot model.

	Sample name	Surface area (m^2/g)	Pore volume (cm^3/g)	Desorption pore size (nm)	Micropore volume (cm^3/g)	Micropore area (m^2/g)
Pressure-driven experiments	Reference extract	10.03	0.053	21.14	0.00041	1.17
	Laccase extract	9.65	0.051	20.97	0.00042	1.22
Adsorption experiments	Reference extract	9.31	0.041	17.73	0.00059	1.64
	Laccase extract	9.17	0.039	17.07	0.00059	1.63
	Pure water 1	8.20	0.033	16.31	0.00067	1.75
	Pure water 2	8.11	0.033	16.34	0.00060	1.61
	Water at pH 3.3	7.88	0.032	16.38	0.00053	1.45

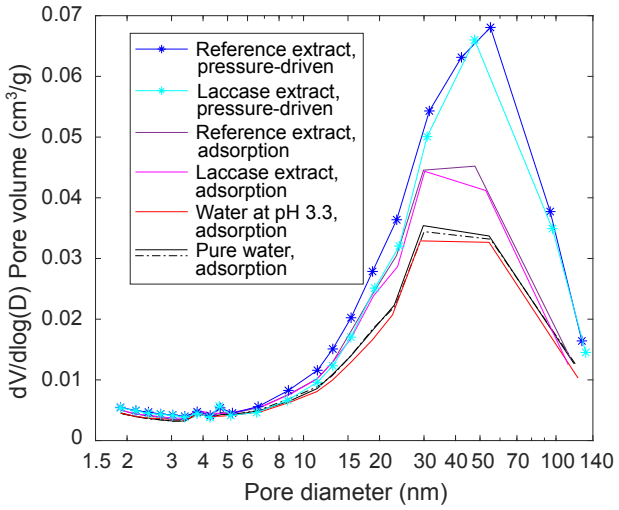

Figure 6: Logaritmic differential pore volume distributions from nitrogen desorption data.

the filtration, have easier access into to pores of the skin layer of the membrane, adsorb on the pore walls and narrow the pores but the permeability of the membrane would be maintained. Laccase treated lignin with increased size and globular shape could in turn form less densely packed layer on the surface of the membrane during the filtration and have more restricted access into the membrane pores. However, globular lignin foulants could block the pore openings completely if the size of the foulant and size of the pores would be matching and even small amount of foulants would be sufficient to decrease the permeability significantly. The decreases in the micropore volumes would be roughly the same if foulants were on the pore walls vs. on the pore openings.

Pure water permeability results may have been also affected by the hydrophilization resulting from the fouling. In general, the membrane fouling leads to decrease in permeability but an increase in hydrophilicity might counteract the effect of fouling by improving the pure water flux due to the improved wetting of the membrane. Increase in pure water flux as the result of adsorption has been observed after deposition of alkaline lignin on polyamide membrane [61], adsorption of humic acid on polyamide and polyethersulfone membrane in the neutral pH [58], adsorption of vanillin on polyethersulfone membranes [62] and after adsorption of nonionic Triton®X-100 surfactants on polyethersulfone membranes [63]. Due to this the higher decrease in pure water permeability after the laccase treatment may be partially explained by the lower amount of hydrophilic lignin in the fouling layer. Changes in the presence and orientation of amphiphilic foulants such as extractives after the laccase treatment may have also affected the permeability of the water through the fouling layer. It should be kept in mind that besides lignin and extractives also hemicelluloses and

lignin-hemicellulose complexes might play the role in the fouling. Thuvander *et al.* have shown that polysaccharides can cause significant irreversible fouling [64]. It is also possible that hemicelluloses linked to lignin are drawn to the surface of the membrane when the lignin part get adsorbed.

4. Conclusions

The goal of this study was to find out how the laccase catalyst prevents the membrane fouling caused by the lignin present in the wood extract. In this study, ultrafiltration was combined with laccase pretreatment of birch hot-water extract. The results showed that laccase treatment changed size and physiochemical properties of lignin and might have modified lignin molecules to less sticky form that differs from the structure, shape and/or size of native lignin. In filtration experiments, the catalytic pretreatment of the extract lead to significantly better filtration capacity. Laccase induced physiochemical changes and changes in molecular mass distribution can possibly explain the improved filterability of the birch extract. Based on the FTIR spectra and BET results the laccase treatment decreased both adsorptive and pressure-driven fouling caused by lignin. Larger lignin molecules have potentially less interactions with membrane surface, and cause less fouling than the more linear lignin. Contrary to the other findings, the decrease in pure water permeabilities was higher when the wood extract was treated with laccase both in pressure-driven and adsorptive fouling experiments. However, the changes in the micropore volumes revealed that the reference extract and laccase treated extract decreased the amount of micropores similarly. Adsorptive fouling decreased the amount of micropores only slightly and pressure-driven fouling caused the decrease of about 30 %. Thus, the higher decrease in pure water permeability after the laccase treatment could be explained by the transformation in the membrane fouling mechanism from pore narrowing to complete pore blocking as the result of the changes in the size and shape of the foulants. The selection of a membrane with a different pore size could possibly prevent the fouling problem faced in this study and the acquired improvement in the filterability could enhance the process stability and fulfill the demand for industrial applications. Thus, the gathered knowledge on studied pretreatment method and on mechanisms causing lignin originated fouling can be applied in the development of more efficient and economic filtration processes to fractionate and purify lignocellulosic streams.

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References

[1] S. Roth, A. C. Spiess, Laccases for biorefinery applications: a critical review on challenges and perspectives, Bioprocess Biosyst. Eng. 38 (2015) 2285–2313. doi:10.1007/s00449-015-1475-7.

[2] E. Koivula, M. Kallioinen, S. Preis, L. Testova, H. Sixta, M. Mänttäri, Evaluation of various pretreatment methods to manage fouling in ultrafiltration of wood hydrolysates, Sep. Purif. Technol. 83 (2011) 50–56. doi:10.1016/j.seppur.2011.09.006.

[3] E. Strand, M. Kallioinen, S.-P. Reinikainen, A. Arkell, M. Mänttäri, Multivariate data examination in evaluation of the effect of the molecular mass of lignin and hemicelluloses on ultrafiltration efficiency, Sep. Purif. Technol. 144 (2015) 146–152. doi:10.1016/j.seppur.2015.02.013.

[4] X. Chen, Q. Yang, C.-L. Si, Z. Wang, D. Huo, Y. Hong, Z. Li, Recovery of oligosaccharides from prehydrolysis liquors of poplar by microfiltration/ultrafiltration membranes and anion exchange resin, ACS Sustain. Chem. Eng. 4 (2016) 937–943. doi:10.1021/acssuschemeng.5b01029.

[5] Q. Wang, M. S. Jahan, S. Liu, Q. Miao, Y. Ni, Lignin removal enhancement from prehydrolysis liquor of kraft-based dissolving pulp production by laccase-induced polymerization, Bioresour. Technol. 164 (2014) 380–385. doi:10.1016/j.biortech.2014.05.005.

[6] H.-J. Lee, W.-S. Lim, J.-W. Lee, Improvement of ethanol fermentation from lignocellulosic hydrolysates by the removal of inhibitors, J. Ind. Eng. Chem. 19 (2013) 2010–2015. doi:10.1016/j.jiec.2013.03.014.

[7] G. Yang, M. S. Jahan, Y. Ni, Structural characterization of pre-hydrolysis liquor lignin and its comparison with other technical lignins, Curr. Org. Chem. 17 (2013) 1589–1595. doi:10.2174/13852728113179990068.

[8] J. Wojtasz-Mucha, M. Hasani, H. Theliander, Hydrothermal pretreatment of wood by mild steam explosion and hot water extraction, Bioresour. Technol. 241 (2017) 120–126. doi:10.1016/j.biortech.2017.05.061.

[9] V. Hämäläinen, T. Grönroos, A. Suonpää, M. W. Heikkilä, B. Romein, P. Ihalainen, S. Malandra, K. R. Birikh, Enzymatic processes to unlock the lignin value, Front. Bioeng. Biotechnol. 6 (2018) 1–10. doi:10.3389/fbioe.2018.00020.

[10] D. M. Mate, M. Alcalde, Laccase: a multi-purpose biocatalyst at the forefront of biotechnology, Microb. Biotechnol. 10 (2016) 1457–1467. doi:10.1111/1751-7915.12422.
[11] S. Riva, Laccases: blue enzymes for green chemistry, Trends Biotechnol. 24 (2006) 219–226. doi:10.1016/j.tibtech.2006.03.006.
[12] H. Krawczyk, P. Oinonen, A.-S. Jönsson, Combined membrane filtration and enzymatic treatment for recovery of high molecular mass hemicelluloses from chemithermomechanical pulp process water, Chem. Eng J. 225 (2013) 292–299. doi:10.1016/j.cej.2013.03.089.
[13] J. Thuvander, P. Oinonen, A.-S. Jönsson, Enzymatic treatment of hemicelluloses and lignin isolated from thermomechanical pulp mill process water, Chem. Eng J. 296 (2016) 141–145. doi:10.1016/j.cej.2016.03.087.
[14] A. Oliva-Taravilla, A. D. Moreno, M. Demuez, D. Ibarra, E. Tomás-Pejó, C. González-Fernández, M. Ballesteros, Unraveling the effects of laccase treatment on enzymatic hydrolysis of steam-exploded wheat straw, Bioresour. Technol. 175 (2015) 209–215. doi:10.1016/j.biortech.2014.10.086.
[15] M. Kolb, V. Sieber, M. Amann, M. Faulstich, D. Schieder, Removal of monomer delignification products by laccase from trametes versicolor, Bioresour. Technol. 104 (2012) 298–304. doi:10.1016/j.biortech.2011.11.080.
[16] Q. Wang, S. Liu, G. Yang, J. Chen, Improvement membrane filterability in nanofiltration of prehydrolysis liquor of kraft dissolving pulp by laccase treatment, Bioresour. Technol. 181 (2015) 124–127. doi:10.1016/j.biortech.2015.01.028.
[17] J. Luo, A. S. Meyer, R. Mateiu, D. Kalyani, M. Pinelo, Functionalization of a membrane sublayer using reverse filtration of enzymes and dopamine coating, ACS Appl. Mater. Interfaces. 6 (2014) 22894–22904. doi:10.1021/am507308k.
[18] J. Hou, G. Dong, Y. Ye, V. Chen, Laccase immobilization on titania nanoparticles and titania-functionalized membranes, J. Membrane Sci. 452 (2014) 229–240. doi:10.1016/j.memsci.2013.10.019.
[19] E. Jahangiri, S. Reichelt, I. Thomas, K. Hausmann, D. Schlosser, A. Schulze, Electron beam-induced immobilization of laccase on porous supports for waste water treatment applications, Molecules 19 (2014) 11860–11882. doi:10.3390/molecules190811860.
[20] X. Cao, J. Luo, J. M. Woodley, Y. Wan, Bioinspired multifunctional membrane for aquatic micropollutants removal, ACS Appl. Mater. Interfaces. 8 (2016) 30511–30522. doi:10.1021/acsami.6b10823.
[21] L. E. Koloti, N. P. Gule, O. A. Arotiba, S. P. Malinga, Laccase-immobilized dendritic nanofibrous membranes as a novel approach towards the removal of bisphenol A, Environ. Technol. 39 (2018) 392–404. doi:10.1080/09593330.2017.1301570.
[22] S. Li, J. Luo, Y. Wan, Regenerable biocatalytic nanofiltration membrane for aquatic micropollutants removal, J. Membrane Sci. 549 (2018) 120–128. doi:10.1016/j.memsci.2017.11.075.
[23] X. Cao, J. Luo, J. M. Woodley, Y. Wan, Mussel-inspired co-deposition to enhance bisphenol A removal in a bifacial enzymatic membrane reactor, Chem. Eng J. 336 (2018) 315–324. doi:10.1016/j.cej.2017.12.042.
[24] H. Zhang, J. Luo, S. Li, J. M. Woodley, Y. Wan, Can graphene oxide improve the performance of biocatalytic membrane?, Chem. Eng J. 359 (2019) 982–993. doi:10.1016/j.cej.2018.11.086.
[25] Y. Kimura, A. Takahashi, A. Kashiwada, K. Yamada, Removal of bisphenol A and its derivatives from aqueous medium through laccase-catalyzed treatment enhanced by addition of polyethylene glycol, Environ. Technol. 37 (2016) 1733–1744. doi:10.1080/09593330.2015.1130752.
[26] Z. Ren, J. Luo, Y. Wan, Highly permeable biocatalytic membrane prepared by 3D modification: Metal-organic frameworks ameliorate its stability for micropollutants removal, Chem. Eng J. 348 (2018) 389–398. doi:10.1016/j.cej.2018.04.203.
[27] C. Barrios-Estrada, M. de Jesús Rostro-Alanis, A. L. Parra, M.-P. Belleville, J. Sanchez-Marcano, H. M. Iqbal, R. Parra-Saldívar, Potentialities of active membranes with immobilized laccase for bisphenol A degradation, Int. J. Biol. Macromol. 108 (2018) 837–844. doi:10.1016/j.ijbiomac.2017.10.177.
[28] C. Jolivalt, S. Brenon, E. Caminade, C. Mougin, M. Pontié, Immobilization of laccase from Trametes versicolor on a modified PVDF microfiltration membrane: characterization of the grafted support and application in removing a phenylurea pesticide in wastewater, J. Membrane Sci. 180 (2000) 103–113. doi:10.1016/S0376-7388(00)00522-6.
[29] S. Ba, L. Haroune, L. Soumano, J.-P. Bellenger, J. P. Jones, H. Cabana, A hybrid bioreactor based on insolubilized tyrosinase and laccase catalysis and microfiltration membrane remove pharmaceuticals from wastewater, Chemosphere 201 (2018) 749–755. doi:10.1016/j.chemosphere.2018.03.022.
[30] W. Chen, J. Mo, X. Du, Z. Zhang, W. Zhang, Biomimetic dynamic membrane for aquatic dye removal, Water Res. 151 (2019) 243–251. doi:10.1016/j.watres.2018.11.078.
[31] N. Singh, S. Basu, I. F. J. Vankelecom, M. Balakrishnan, Covalently immobilized laccase for decolourization of glucose-glycine Maillard products as colourant of distillery wastewater, Appl. Biochem. Biotechnol. 177 (2015) 76–89. doi:10.1007/s12010-015-1729-5.
[32] M. Neifar, R. Ellouze-Ghorbel, A. Kamoun, S. Baklouti, A. Mokni, A. Jaouani, S. Ellouze-Chaabouni, Effective clarification of pomegranate juice using laccase treatment optimized by response surface methodology followed by ultrafiltration, J. Food Process Eng. 34 (2011) 1199–1219. doi:10.1111/j.1745-4530.2009.00523.x.
[33] C.-H. Ko, S.-S. Chen, Enhanced removal of three phenols by laccase polymerization with MF/UF membranes, Bioresour. Technol. 99 (2008) 2293–2298. doi:10.1016/j.biortech.2007.05.017.
[34] J. Luo, B. Zeuner, S. T. Morthensen, A. S. Meyer, M. Pinelo, Separation of phenolic acids from monosaccharides by low-pressure nanofiltration integrated with laccase pre-treatments, J. Membrane Sci. 482 (2015) 83–91. doi:10.1016/j.memsci.2015.02.022.
[35] C.-H. Ko, C. Fan, Enhanced chemical oxygen demand removal and flux reduction in pulp and paper wastewater treatment using laccase-polymerized membrane filtration, J. Hazard. Mater. 181 (2010) 763–770. doi:10.1016/j.jhazmat.2010.05.079.
[36] T. Sainio, M. Kallioinen, O. Nakari, M. Mänttäri, Production and recovery of monosaccharides from lignocellulose hot water extracts in a pulp mill biorefinery, Bioresour. Technol. 135 (2013) 730–737. doi:10.1016/j.biortech.2012.08.126.
[37] L. Puro, M. Kallioinen, M. Mänttäri, M. Nyström, Evaluation of behavior and fouling potential of wood extractives in ultrafiltration of pulp and paper mill process water, J. Membrane Sci. 368 (2011) 150–158. doi:10.1016/j.memsci.2010.11.032.
[38] L. Puro, J. Tanninen, M. Nyström, Analyses of organic foulants in membranes fouled by pulp and paper mill effluent using solid-liquid extraction, Desalination 143 (2002) 1–9. doi:10.1016/S0011-9164(02)00215-1.

[39] J. Thuvander, A.-S. Jönsson, Extraction of galactoglucomannan from thermomechanical pulp mill process water by microfiltration and ultrafiltration–influence of microfiltration membrane pore size on ultrafiltration performance, Chem. Eng. Res. Des. 105 (2016) 171–176. doi:10.1016/j.cherd.2015.12.003.

[40] A. Gutiérrez, J. Rencoret, S. Molina, D. Ibarra, J. del Río, A. T. Martinez, Recent advances in pitch control using laccase-mediator system, in: Proceedings of the 15th International Symposium on Wood, Fibre and Pulping Chemistry, 2009.

[41] R. Hilgers, J.-P. Vincken, H. Gruppen, M. A. Kabel, Laccase/mediator systems: Their reactivity toward phenolic lignin structures, ACS Sustain. Chem. Eng. 6 (2018) 2037–2046. doi:10.1021/acssuschemeng.7b03451.

[42] S. Grönqvist, Action of laccase on mechanical softwood pulps, PhD dissertation, VTT Science, Espoo, 2014.

[43] A. Gutiérrez, J. C. del Río, J. Rencoret, D. Ibarra, Á. T. Martínez, Main lipophilic extractives in different paper pulp types can be removed using the laccase–mediator system, Appl. Microbiol. Biotechnol. 72 (2006) 845–851. doi:10.1007/s00253-006-0346-1.

[44] A. Gutiérrez, J. Rencoret, D. Ibarra, S. Molina, S. Camarero, J. Romero, J. C. Del Río, Á. T. Martínez, Removal of lipophilic extractives from paper pulp by laccase and lignin-derived phenols as natural mediators, Environ. Sci. Technol. 41 (2007) 4124–4129. doi:10.1021/es062723+.

[45] S. Karlsson, B. Holmbom, P. Spetz, A. Mustranta, J. Buchert, Reactivity of trametes laccases with fatty and resin acids, Appl. Microbiol. Biotechnol. 55 (2001) 317–320. doi:10.1007/s002530000532.

[46] A. Kalliola, A. Savolainen, T. Ohra-aho, G. Faccio, T. Tamminen, Reducing the content of VOCs of softwood kraft lignins for material applications, BioResources 7 (2012) 2871–2882.

[47] A. Kalliola, M. Asikainen, R. Talja, T. Tamminen, Experiences of kraft lignin functionalization by enzymatic and chemical oxidation, BioResources 9 (2014) 7336–7351.

[48] G. J. Rocha, C. Martín, V. F. da Silva, E. O. Gómez, A. R. Gonçalves, Mass balance of pilot-scale pretreatment of sugarcane bagasse by steam explosion followed by alkaline delignification, Bioresour. Technol. 111 (2012) 447–452. doi:10.1016/j.biortech.2012.02.005.

[49] D. L. Oatley-Radcliffe, S. R. Williams, T. J. Ainscough, C. Lee, D. J. Johnson, P. M. Williams, Experimental determination of the hydrodynamic forces within nanofiltration membranes and evaluation of the current theoretical descriptions, Sep. Purif. Technol. 149 (2015) 339–348. doi:10.1016/j.seppur.2015.05.041.

[50] Y. Fang, L. Bian, Q. Bi, Q. Li, X. Wang, Evaluation of the pore size distribution of a forward osmosis membrane in three different ways, J. Membrane Sci. 454 (2014) 390–397. doi:10.1016/j.memsci.2013.12.046.

[51] T. Virtanen, G. Rudolph, A. Lopatina, B. Al-Rudainy, H. Schagerlöf, L. Puro, M. Kallioinen, F. Lipnizki, Analysis of membrane fouling by Brunauer-Emmet-Teller nitrogen adsorption/desorption technique (2019). Manuscript submitted for publication.

[52] R. Li, B. J. McCoy, Inter- and intramolecular crosslinking kinetics: Partitioning according to number of crosslinks, Macromol. Rapid Commun. 25 (2004) 1059–1063. doi:10.1002/marc.200400058.

[53] R. Baker, Membrane Technology and Applications, 3rd Ed., John Wiley & Sons Lts, Chichester, United Kingdom, 2012.

[54] H. Susanto, Y. Feng, M. Ulbricht, Fouling behavior of aqueous solutions of polyphenolic compounds during ultrafiltration, J. Food Eng. 91 (2009) 333–340. doi:10.1016/j.jfoodeng.2008.09.011.

[55] H. Susanto, M. Ulbricht, Influence of ultrafiltration membrane characteristics on adsorptive fouling with dextrans, J. Membrane Sci. 266 (2005) 132–142. doi:10.1016/j.memsci.2005.05.018.

[56] M. Esmaeili, I. Anugwom, M. Mänttäri, M. Kallioinen, Utilization of DES-lignin as a bio-based hydrophilicity promoter in the fabrication of antioxidant polyethersulfone membranes, Membranes 8 (2018). doi:10.3390/membranes8030080.

[57] L. Puro, M. Kallioinen, M. Mänttäri, G. Natarajan, D. C. Cameron, M. Nyström, Performance of RC and PES ultrafiltration membranes in filtration of pulp mill process waters, Desalination 264 (2010) 249–255. doi:10.1016/j.desal.2010.06.034.

[58] M. Mänttäri, L. Puro, J. Nuortila-Jokinen, M. Nyström, Fouling effects of polysaccharides and humic acid in nanofiltration, J. Membrane Sci. 165 (2000) 1–17. doi:10.1016/S0376-7388(99)00215-X.

[59] M. Esmaeili, T. Virtanen, J. Lahti, M. Mänttäri, M. Kallioinen, Vanillin as an antifouling and hydrophilicity promoter agent in surface modification of polyethersulfone membrane, Membranes 9 (2019). doi:10.3390/membranes9040056.

[60] F. Örså, B. Holmbom, A convenient method for determination of wood extractives in papermaking process waters and effluents, J. Pulp Pap. Sci. 20 (1994) 361–366.

[61] F. Zhang, Y. Wu, W. Li, W. Xing, Y. Wang, Depositing lignin on membrane surfaces for simultaneously upgraded reverse osmosis performances: An upscalable route, AIChE J. 63 (2017) 2221–2231. doi:10.1002/aic.15628.

[62] M. Nyström, L. Kaipia, S. Luque, Fouling and retention of nanofiltration membranes, J. Membrane Sci. 98 (1995) 249–262. doi:10.1016/0376-7388(94)00196-6.

[63] A. Maartens, E. Jacobs, P. Swart, UF of pulp and paper effluent: membrane fouling-prevention and cleaning, J. Membrane Sci. 209 (2002) 81–92. doi:10.1016/S0376-7388(02)00266-1.

[64] J. Thuvander, A. Zarebska, C. Hélix-Nielsen, A.-S. Jönsson, Characterization of irreversible fouling after ultrafiltration of thermomechanical pulp mill process water, J. Wood Chem. Technol. 38 (2018) 276–285. doi:10.1080/02773813.2018.1454962.