

Elsi Strand

ENHANCEMENT OF ULTRAFILTRATION PROCESS BY PRETREATMENT IN RECOVERY OF HEMICELLULOSES FROM WOOD EXTRACTS

Thesis for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in the Auditorium 1383 at Lappeenranta University of Technology, Lappeenranta, Finland on the 14th of January, 2016, at noon.

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ABSTRACT

Elsi Strand

Enhancement of ultrafiltration process by pretreatment in recovery of hemicelluloses from wood extracts

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Hemicelluloses are potential raw material for several items produced in future wood-based biorefineries. One possible method for recovering hemicelluloses from wood extracts is ultrafiltration (UF). However, low filtration capacities and severe fouling restrict the use of tight UF membranes in the treatment of wood extracts. The lack of suitable commercial membranes creates a need for pretreatment which would decrease fouling and increase the filtration capacity. This thesis focuses on the evaluation of the possibility to improve the filtration capacity and decrease fouling with the pretreatment of wood extracts. Methods which remove harmful compounds and methods which degrade them are studied, as well as combinations of the methods.

The tested pretreatments have an influence on both the concentration of different compounds and the molecular mass distribution of the compounds in the extract. This study revealed that in addition to which kind of compounds were removed, also the change in molecular size distribution affected the filtration capacity significantly. It was shown that the most harmful compounds for the filtration capacity of the hydrophobic 5 kDa membrane were the ones capable of permeating the membrane and fouling also the inner membrane structure. Naturally, the size of the most harmful compounds depends on the used UF membrane and is thus case-specific. However, in the choice of the pretreatment method, the focus should be on the removal of harmful compound sizes rather than merely on the total amount of removed foulants.

The results proved that filtration capacity can be increased with both adsorptive and oxidative pretreatments even by hundreds of per cents. For instance, the use of XAD7 and XAD16 adsorbents increased the average flux in the UF of a birch extract from nearly zero to 107 kg/(m²h) and 175 kg/(m²h), respectively. In the treatment of a spruce extract, oxidation by pulsed corona discharge (PCD) increased the flux in UF from 46 kg/(m²h) to 158 kg/(m²h). Moreover, when a birch extract batch was treated with laccase enzyme, the flux in UF increased from 15 kg/(m²h) to 36 kg/(m²h). However, fouling was decreased only by adsorptive pretreatment while oxidative methods had a negligible or even negative impact on it. This demonstrates that filtration capacity and fouling are affected by different compounds and mechanisms.

The results of this thesis show that filtration capacity can be improved and fouling decreased through appropriate pretreatment. However, the choice of the best possible pretreatment is case-specific and depends on the wood extract and the membrane used. Finding the best option requires information on the extract content and membrane characteristics as well as on the filtration performance of the membrane in the prevailing conditions and a multivariate approach. On the basis of this study, it can be roughly concluded that adsorptive pretreatment improves the filtration capacity and decreases fouling rather reliably, but it may lead to significant hemicellulose losses. Oxidation reduces the loss of valuable hemicelluloses and could improve the filtration capacity, but fouling challenges may remain. Combining oxidation with adsorptive pretreatment was not a solution for avoiding hemicellulose losses in the tested cases.

Keywords: hemicelluloses, ultrafiltration, fouling, pretreatment

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November 17th 2015
Lappeenranta

Elsi Strand

LIST OF PUBLICATIONS

This thesis is based on the following papers, which are referred to in the text by the Roman numerals **I-V**

- I** Koivula, E., Kallioinen, M., Preis, S., Testova, L., Sixta H., Mänttari, M., Evaluation of various pretreatment methods to manage fouling in ultrafiltration of wood hydrolysates, *Separation and Purification Technology*, 83 (2011), 50–56.
- II** Koivula, E., Kallioinen, M., Sainio, T., Luque, S., Mänttari, M., Enhanced membrane filtration of wood hydrolysates for hemicelluloses recovery by pretreatment with polymeric adsorbents, *Bioresource Technology*, 143 (2013), 275–281.
- III** Strand, E., Kallioinen, M., Reinikainen, S.-P., Arkell, A., Mänttari, M., Multivariate data examination in evaluation of the effect of the molecular mass of lignin and hemicelluloses on ultrafiltration efficiency, *Separation and Purification Technology*, 144 (2015), 146–152.
- IV** Strand, E., Kallioinen, M., Kleen, M., Mänttari, M., Activated carbon treatment to improve ultrafiltration performance in recovery of hemicelluloses from wood extracts, *Nordic Pulp and Paper Research Journal*, 30 (2015), 207–214.
- V** Mänttari, M., Al Manasrah, M., Strand, E., Laasonen, H., Preis, S., Puro, L., Xu, C., Kisonen, V., Korpinen, R., Kallioinen, M., Improvement of ultrafiltration performance by oxidation treatment in the recovery of galactoglucomannan from wood autohydrolyzate, *Separation and Purification Technology*, 149 (2015), 428–436.

Contribution of the author

The author was responsible for the preparation of papers I–IV. The author performed most of the measurements for papers I, II and IV. In paper III, the author planned the experiments. In papers I–IV, the author interpreted the results together with the co-writers. In paper V, the author did part of the experimental work. The technicians of the Laboratory of Membrane Technology and Technical Polymer Chemistry did part of the analysis work.

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Symbols and abbreviations**Symbols**

A_{205}	absorbance at 205 nm, -
A_m	membrane surface area, m ²
ASL	acid-soluble lignin, g/l
a	absorptivity, l/(g cm)
c_f	concentration in feed, g/l
c_p	concentration in permeate, g/l
f	dilution factor, -
J	permeate flux, kg/(m ² h)
$J_{original}$	average flux of the original extract, kg/(m ² h)
$J_{pretreated}$	average flux of the pretreated extract, kg/(m ² h)
l	path length, cm
m_f	mass of feed solution, kg
m_p	mass of permeate, kg
t	time, h
P	permeability, kg/(m ² h bar)
p	pressure, bar
P_{rel}	relative permeability, -
PWF_a	pure water flux after filtration, kg/(m ² h)
PWF_b	pure water flux before filtration, kg/(m ² h)
PWF_r	pure water flux reduction, %
PWP	pure water permeability, kg/(m ² h bar)
R_{obs}	observed retention, %
V_c	volume of concentrate, l
V_f	volume of feed solution, l

V_p	volume of permeate, l
VRF	volume reduction factor, -

Abbreviations

AC	activated carbon
Ara	arabinose
ASL	acid-soluble lignin
AX	arabinoxylan
AXOS	arabinoxyloligosaccharides
CR	cross-rotational
Da	dalton
DEAE	diethyl aminoethyl
DP	degree of polymerisation
FTIR	Fourier transform infrared spectroscopy
Gal	galactose
GC	gas chromatography
GC-MS	gas chromatography - mass spectrometry
GGM	galactoglucomannan
Glc	glucose
HPSEC	high performance size-exclusion chromatography
HW	hardwood
LCC	lignin-carbohydrate complex
LHC	lignin-hemicellulose complex
MALLS	multi-angle laser light scattering
Man	mannose
MM	molecular mass
MTBE	methyl tert-butyl ether

MWCO	molecular weight cut-off
NMR	nuclear magnetic resonance
PAC	polyaluminium chloride
PCA	principal component analysis
PCD	pulsed corona discharge
PHWE	pressurised hot water extraction
p-DADMAC	polydiallyldimethylammonium chloride
PES	polyethersulphone
PESH	hydrophilic polyethersulphone
PET	polyethylene terephthalate
p.r.	phase ratio
PSu	polysulphone
RC	regenerated cellulose
RI	refractive index
SEC	size-exclusion chromatography
SW	softwood
TDS	total dry solids
TMP	thermomechanical pulp
UF	ultrafiltration
UV	ultraviolet
VR	volume reduction
VRF	volume reduction factor
VSEP	vibration enhanced module
Xyl	xylose
ZPC	zero point charge

1 INTRODUCTION

Increased environmental consciousness and dependence on a declining oil reserve have created a need for alternative and more environmentally friendly sources of raw material for a number of everyday products and fuels. Biomass as a renewable material has the potential to be raw material for a vast amount of products. Biorefineries produce chemicals, energy and other products from biomass, often from streams that are otherwise utilised less effectively. For example, lignocellulose feedstock, such as wood and straw, or crop can be used as a source of biomass [Carvalho et al. (2008), Huang et al. (2008), Kumar et al. (2009), Rafione et al. (2014), Moncada et al. (2014)].

Forest biorefineries respond especially to the need of the northern pulp and paper industry to produce other products from wood in addition to the traditional ones, in order to maintain their competitiveness. Naturally, also other regions, e.g. South America and Europe as a whole must develop their structure to produce also other than the traditional pulp and paper products. For instance, in the present pulping process, lignin and hemicelluloses are combusted for power generation, although the heating value of hemicelluloses is rather low, 14 MJ/kg, whereas the corresponding value for lignin is 25 MJ/kg [Leschinsky et al. (2009), Huang et al. (2008)]. Especially in the case of dissolving pulps, it would be convenient to extract hemicelluloses prior to pulping and use them in the production of e.g. fuels and high-value chemicals [Sixta (2006), Leschinsky et al. (2009)].

Recently studied potential products from hemicelluloses are biopolymers and bioplastics: coatings, barrier materials in packaging films, bioethanol, xylo-oligosaccharides e.g. in food and medical applications [Jansson et al. (2014), Deutschmann and Dekker (2012), Edlund et al. (2010), Mikkonen and Tenkanen (2012), Peng et al. (2012)], hydrogels [Söderqvist Lindblad et al. (2005)], furfural, and xylitol [Zhang et al. (2011), Kadla et al. (2002), Gellerstedt et al. (2010), Ghaffar and Fan (2014)].

Hemicelluloses can be dissolved from wood by extraction [Alén (2011), Sixta (2006)]. Also other pulp and paper industry process streams than the extract obtained prior to pulping can be used as raw-material for hemicellulose-based products. Such streams include e.g. process and waste waters and black liquor [Willför et al. (2003b), Arkell et al. (2014)]. Additionally, the extraction of hemicelluloses from wood can be done from different sources of woody material, such as forestry waste, and not merely in the pulping context. Other xylan sources than (hard)wood are e.g. agricultural crops, such as, straw, sorghum, sugar cane, corn stalks and cobs, hulls and husks from starch production [Ebringerová and Heinze (2000)]. In order to utilise hemicelluloses, they usually have to be separated from other components in the extract, concentrated, and depending on the wanted product, fractionated according to their size. Ultrafiltration (UF) can be used in the recovery, fractionation and purification of hemicelluloses from wood-derived solutions [Al Manasrah et al. (2012), Sainio et al. (2013), Krawczyk et al. (2013a)]. High-molecular mass hemicelluloses can be recovered, for example by hydrophilic

regenerated cellulose (RC) membranes without severe membrane fouling [Kallioinen et al. (2005), Al Manasrah et al. (2012), Persson and Jönsson (2005)].

UF is a separation process which can be used in fractionation, purification and concentration processes for dissolved macromolecular compounds. In the UF process, the mass transport is due to convective flux through pores caused by a pressure difference across the membrane. The membrane has a selective layer which rejects some compounds, while others can permeate the membrane. Many membranes are so called composite membranes, which means that they consist of more than one material in their structure, e.g. a porous supporting layer and a thin skin layer, which determines the selectivity. The rejected compounds are in the range of 10-200 Å, i.e. 1-20 nm, depending on the molecular weight cut-off (MWCO) of the membrane. In general, UF allows the separation of two macromolecules that differ 10 times in molecular mass (MM) or 3 times in the hydrodynamic radius. The separation is not completely based on the size of the solutes, as there are also other factors which affect the rejection (Fig. 1). [Cheryan (1998), Strathmann et al. (2006)]

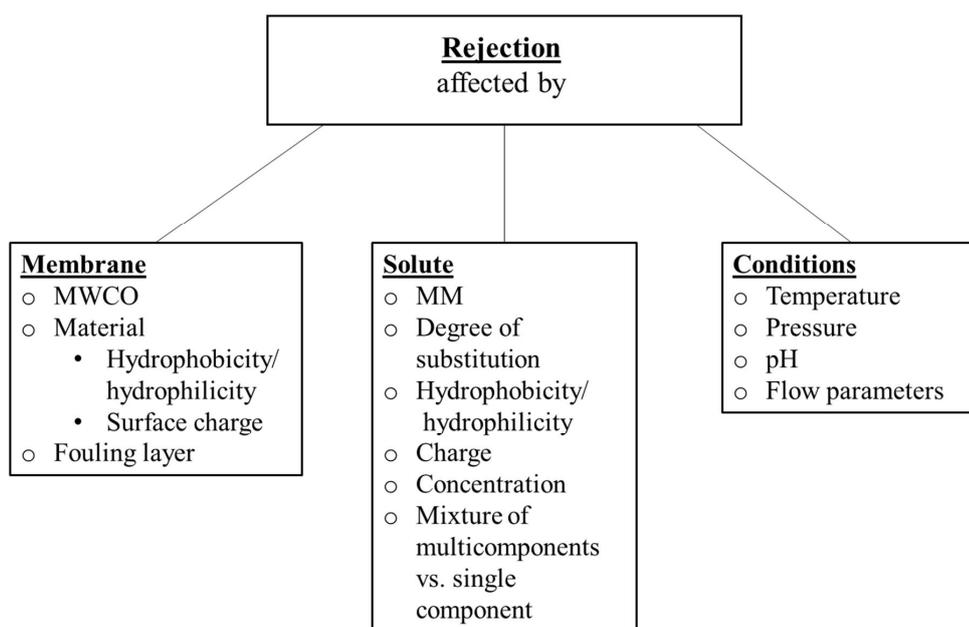


Figure 1. Factors affecting rejection in the UF process, according to contemporary knowledge.

The results of this study show that with tight hydrophobic ultrafiltration membranes, having cut-off values around 5 kDa or lower, fouling is a serious issue when wood extracts are filtered, because the flux decline during filtration is very rapid, making the process challenging (Fig. 2). Basically, in the recovery of 5–10 kDa hemicelluloses from wood extracts, the ways to reduce

fouling are 1) modifying the membrane material to be more hydrophilic, 2) adjusting hydrodynamic and other operational conditions e.g. with different module structures, and 3) pretreating the feed solution.

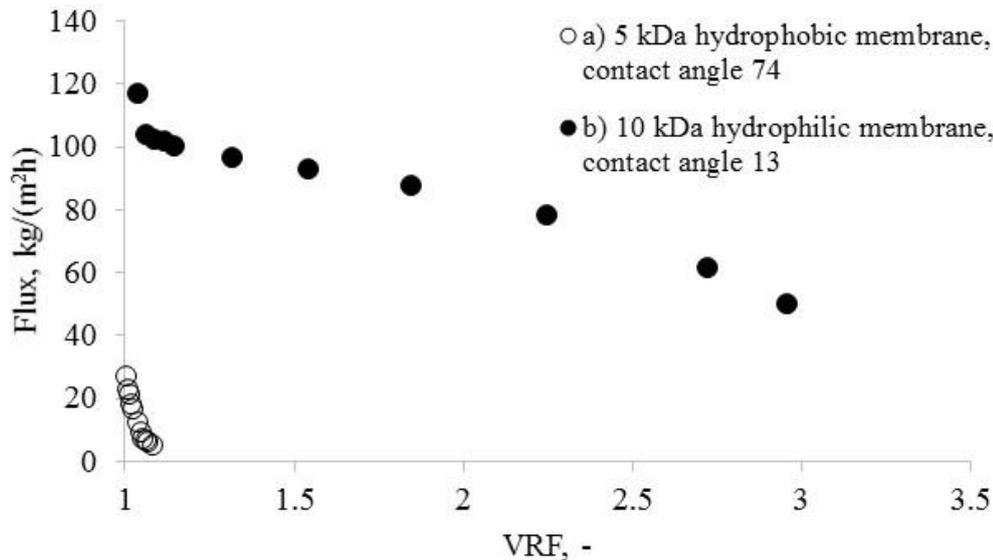


Figure 2. Filtration of a birch extract with a) a hydrophobic 5 kDa and b) a hydrophilic 10 kDa ultrafiltration membranes with an Amicon filter cell at 55°C, 5.5 bar and rotor tip velocity 1.6 m/s.

There are no tight extremely hydrophilic (contact angle below 20°) flatsheet ultrafiltration membranes suitable for industrial-scale high-turbulence filter modules available at the moment. Hydrophobic membranes are fouled more easily than hydrophilic ones in the treatment of wood-based solutions [Mänttari et al. (2002), Dal-Cin et al. (1995, 1996), Jönsson and Jönsson (1995)]. Even membranes having contact angles around 50–60° are more susceptible to fouling than membranes with higher hydrophilicity. Potential foulants, lignin, and more generally phenolic compounds and wood extractives, tend to foul hydrophobic membranes due to their hydrophobic nature [Maartens et al. (2002), Puro et al. (2011)]. Cross-rotational (CR) filter modules and tubular modules are commonly used in pulp and paper mill applications [Nuortila-Jokinen and Nyström (1996), Mänttari and Nyström (2009)]. Flatsheet membranes are used for example in CR filter modules. The current commercial tight hydrophilic ultrafiltration membranes are for plate and frame and spiral wound modules, which are susceptible to blockage e.g. by suspended solids often present in wood extracts. In CR filter modules, a rotor is used to increase the shear rates in the feed solution above the membrane surface. The increased shear rates lift particles away from the membrane surface, which decreases the

concentration polarisation. For decreased concentration polarisation and also for wide flow channels, the achieved fluxes are usually quite high with CR filter modules.

Ceramic membranes could be applicable for the ultrafiltration of wood-derived solutions due to their hydrophilicity and withstanding of aggressive cleaning conditions. They often have, however, higher capital costs than polymeric membranes. On the other hand, the operational costs consisting among others of cleaning and the frequency of the cleaning cycles may be lower than with polymeric membranes.

The increase of turbulence on the membrane surface is usually a sufficient action in the treatment of paper and pulp process waters. However, in a concentration of 5–10 kDa, hemicelluloses from wood extracts, it may be less efficient than with larger molecules and particles. The concentration polarisation in CR modules is reduced by lateral migration and shear-induced diffusion which lifts the particles from the membrane surface. However, the compounds susceptible to the effects of shear-induced diffusion are larger than 10 μm by size. When the molecular size is decreased from 10 μm to 10 nm, the transport of molecules by convection is influenced also by surface interactions and less by shear-induced diffusion. The convective transport of molecules smaller than 10 nm is influenced mostly by surface interactions [Bacchin et al. (2006)]. In native wood, hemicelluloses and lignin molecules are roughly smaller than or as big as 36 kDa and 20 kDa, respectively, which corresponds easily to less than 20 nm. In extracts, the compounds may be linked together or degraded to smaller ones, which expands the size distribution at both ends of the scale. Therefore, adsorptive fouling caused by small hydrophobic compounds is difficult to prevent merely by using a high shear-rate filter. Such small compounds can be e.g. wood extractives, unless they are in colloidal form, and small fragments of lignin molecules. For this reason, pretreatment is needed to remove or degrade these foulants from the wood extract prior to filtration.

The removal or degradation of foulants by a convenient pretreatment may, in addition to solving the fouling problem, increase the purity of the produced hemicellulose fraction. Foulants obviously act as impurities when hemicelluloses are the target compounds. Depending on the pretreatment method, lignin could be possibly recovered also after it has been separated from the wood extract. This would bring additional value to the pretreatment process, as there are several applications for lignin-based products.

2 AIM OF THE STUDY

This study focuses on finding suitable pretreatment methods to improve filtration performance, i.e. to increase the permeate flux and to reduce fouling in ultrafiltration of wood extracts. The pretreatment method should also be selective to foulants to avoid significant hemicellulose losses. The aim of this study is to learn what is required from the pretreatment to improve the filtration performance. In order to understand what makes a feasible pretreatment method, certain issues must be studied: (1) how the pretreatment affects the content of the extract, what is removed or degraded, (2) what connection there is between the removal or degradation of certain compounds and filtration capacity or fouling, and (3) whether hemicellulose losses and the degradation of hemicelluloses could be minimised, yet attaining the advantages of the pretreatment.

3 OUTLINE

This work consists of a literature part and an experimental part. The literature part discusses the origin and characteristics of the compounds in wood extracts, presents ultrafiltration as a method for hemicellulose recovery, discusses the problems in ultrafiltration, and what could be done to solve these issues.

The experimental part covers the first screening of potential pretreatment methods based on their ability to improve the ultrafiltration capacity and decrease fouling. Multivariate methods are used to provide information on the influence of the molecular masses of hemicelluloses and ligneous compounds on the ultrafiltration capacity. The purpose of this examination is to find out which sizes of compounds should be removed from wood extracts in the pretreatment process to increase the filtration capacity. Adsorptive and oxidative pretreatment methods are studied more intensively. Their ability to improve the filtration performance and to remove foulants and harmful-sized compounds from the wood extracts is discussed. To minimise hemicellulose losses during the adsorption, pretreatments combining oxidation and adsorption are studied. Also, optimisation of the amount of adsorbent in a selected adsorptive method is studied. The potential of regeneration of the used adsorbents is examined by adsorption, regeneration and filtration experiments.

4 WOOD EXTRACTS

The main structural components in wood are cellulose, hemicelluloses and lignin. Non-structural components in wood have a low molecular mass and their amount is lower than that of structural components. Nonstructural components include for example wood extractives and inorganic compounds [Alén (2011)]. The extract composition depends on the extraction conditions and the wood species used. The structure of lignin and hemicelluloses, and also the presence of each hemicellulose in native wood vary between different wood species, however, following the distribution to hardwoods (HW) and softwoods (SW).

Lignocellulosic biomass, such as wood, is a good resource of hemicelluloses. Dissolving hemicelluloses can be extracted from wood by different solvents and at different conditions depending on the required and the original characteristics of the hemicelluloses [Tunc and van Heiningen (2011)]. The extraction of hemicelluloses from wood can be done for example by acid, pressurised hot-water, alkali, steam explosion, or enzymes [Alén (2011), Sixta (2006)]. The idea is to open up the structure of wood, when part of the hemicelluloses, lignin, wood extractives, and minor amounts of other small components are dissolved into the water or the used solvent [Alén (2011), Huang et al. (2008)]. When water is used as the solvent, the method is called pressurised hot water extraction (PHWE), as water has to be pressurised to reach high temperatures (160-180 °C) in liquid form [Kilpeläinen et al. (2013)]. In this work, the extraction liquor obtained from wood by PHWE is called wood extract, or in short, extract.

In biorefinery, one alternative is to use extraction for wood chips before pulping in order to dissolve compounds that are wanted to be removed from the pulp and to be used elsewhere. If biorefinery is integrated with a pulp production unit, the used solvent in the extraction of wood is selected according to the purpose of the extraction. If the target is to recover hemicelluloses, the solvent should not degrade them to a great extent, but if the target is to remove hemicelluloses from the pulp as efficiently as possible the solvent should dissolve them from the wood by any means. The latter case is already applied in the production of high-purity pulps, where hemicelluloses are harmful in the pulp [Sixta (2006), Leschinsky et al. (2009)].

Generally, in kraft pulp, the presence of hemicelluloses has varying effects on the properties of the pulp [Hamaguchi et al. (2013)]. The significance of these effects depends on the intended use of the pulp. In normal kraft pulp, it is not reasonable to remove hemicelluloses from the pulp because the purity of the pulp is not the main factor – the carbohydrate yield is more important. If, however the pulp is used for high-purity cellulosic products, e.g. regenerated cellulose, the purity of the pulp and the molecular mass of the cellulose are important. For instance, short-chain carbohydrates cause precipitates on the pulp. In the production of high-purity dissolving pulps the amount of hemicelluloses has to be minimised. [Sixta (2006), Leschinsky et al. (2009)] Prehydrolysis kraft pulps are an example of dissolving pulps. In the production of prehydrolysis kraft pulps, a process called prehydrolysis is used to remove the

hemicelluloses prior to pulping. In prehydrolysis, a dilute or concentrated acid can be used as the solvent alternatively to hot water [Sixta (2006)].

In the extraction of HW, acetyl groups from a xylan backbone are dissolved forming acetic acid, which lowers the pH of the solution catalyzing the hydrolysis reaction [Testova et al. (2009)]. This phenomenon is called autohydrolysis. There are fewer acetyl groups in the hemicellulose structure of SW, which is why autohydrolysis is lesser with SW. Because of the formed acetic acid and cleaved uronic acids [Kilpeläinen et al. (2012)], both hardwood and softwood extracts are acidic, their pH being around 3-4. Deacetylation is a positive phenomenon for xylan extraction, as deacetylation accelerates the hydrolysis reaction. For glucomannan, the deacetylation is negative, as the cleavage of acetyl groups decreases the solubility of glucomannan in water, which affects the yield [Song et al. (2008)].

4.1 Main components in wood extracts

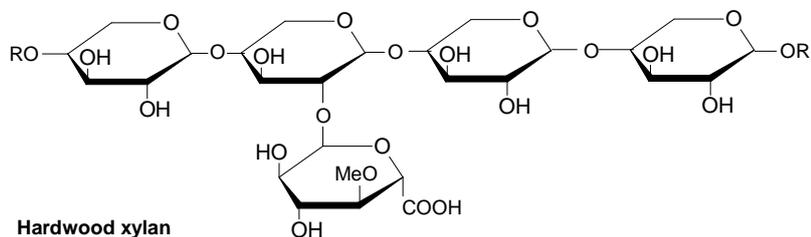
Not all the components in wood dissolve into water, and even those that do, dissolve only partly. Therefore, the composition of hemicelluloses, lignin and wood extractives is not identical to the one in wood. The amount of hemicelluloses is usually higher than that of lignin and especially wood extractives. The typical ratio between hemicellulose and lignin concentrations in the wood extracts used in this study was around 3–7, depending on the wood species and extraction conditions. The amount of wood extractives is a few per cents of the amount of hemicelluloses.

4.1.1 Hemicelluloses

Hemicelluloses are polysaccharides consisting of different sugar units. Monosaccharides consisting of five carbon atoms are pentoses, e.g. xylose and arabinose. Monosaccharides consisting of six carbon atoms are hexoses, e.g. glucose and mannose. Other sugar units are hexuronic acids, e.g. glucuronic acid, and deoxy-hexoses, e.g. rhamnose. Polysaccharides composed of only one type of monosaccharide are called homopolysaccharides and polysaccharides composed of two or more types of monosaccharides are called heteropolysaccharides. Xylan, for example, which consists only of xylose (Xyl) units is a homopolysaccharide. Galactoglucomannan (GGM) consisting of glucose (Glc) and mannose (Man) is a heteropolysaccharide. Hemicellulose chains are often branched, which increases their solubility in water. Their degree of polymerisation (DP) is around 50-200, corresponding approximately to molecular masses of 7.5–36 kDa. [Sixta (2006), Sjöström (1981)]

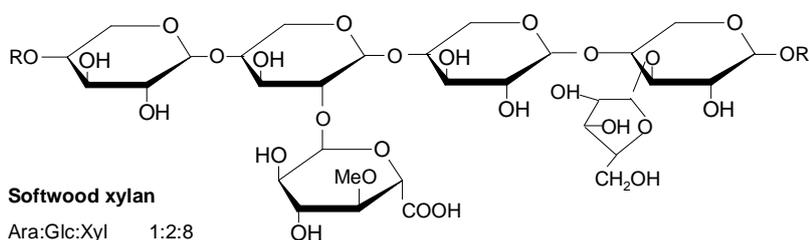
On average, there are 25-35% hemicelluloses of the dry solids in wood. The amount and type of hemicelluloses depends on the wood species. In hardwood, the most dominant constituent of

hemicelluloses is xylan (glucuronoxylan), and only a small amount of glucomannan is present. In softwood, the most dominant constituent is glucomannan (galactoglucomannan), and the amount of xylan (arabinoglucuronoxylan) is about a half of that of glucomannan (Fig. 3) [Alén (2011)]. In PHWE, the hemicellulose molecules are partly degraded, and these degraded hemicelluloses, consisting of oligosaccharides and monomers, are also dissolved into water as hydrophilic compounds.

**Hardwood xylan**

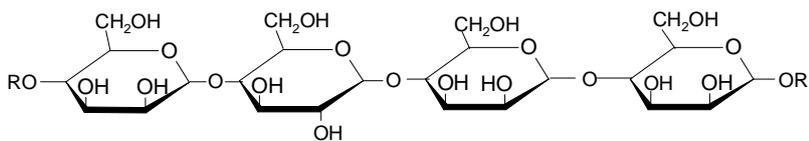
Glc:Xyl 0.1:1

Acetyl groups 8-17%

**Softwood xylan**

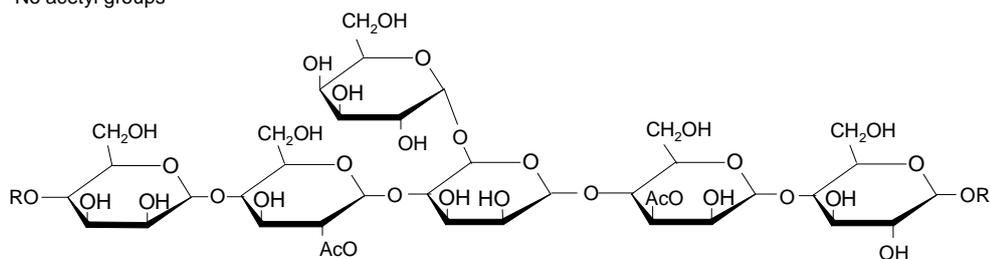
Ara:Glc:Xyl 1:2:8

No acetyl groups

**Hardwood glucomannan**

Glc:Man 1:1.5

No acetyl groups

**Softwood glucomannan**

Gal:Glc:Man 0.5:1:3.5

Acetyl groups 6%

Figure 3. Structure of the most dominant hemicelluloses in hardwood and softwood.

4.1.2 Lignin

Lignin is built up of phenylpropane units and has a complex phenolic structure consisting of three precursors (hydroxycinnamyl alcohols, or monolignols): a) p-coumaryl (4-hydroxycinnamyl), b) coniferyl (3-methoxy-4-hydroxycinnamyl), and c) sinapyl (3,5-dimethoxy-4-hydroxycinnamyl) alcohols (Fig. 4). A globular lignin molecule is formed originally from glucose through biosynthesis, in which the formed monolignol radicals are coupled together randomly to dilignols and eventually polyignols [Sixta (2006), Sjöström (1981)]. Structural units of lignin are bonded together mainly by ether linkages (most common) or carbon-carbon bonds [Alén (2011)].

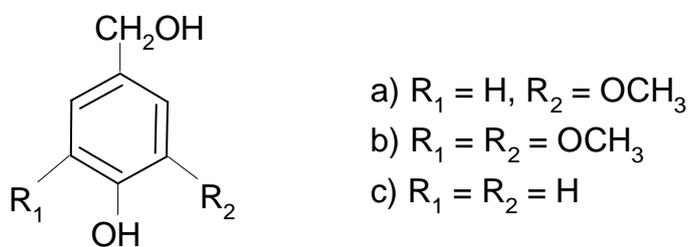


Figure 4. Precursors of a lignin molecule.

On average, there is 20-30% lignin of the dry solids in wood [Alén (2011)]. Native lignin has DP 75-100 which corresponds approximately to a molecular size of 15-20 kDa [Alén (2011)]. Hardwood lignin is often called guaiacyl-syringyl, which consists of varying amounts of coniferyl alcohol and sinapyl alcohol structural units. Softwood lignin is called guaiacyl lignin, and it consists of over 95% of coniferyl alcohol, the rest being p-coumaryl alcohol. [Lin and Dence (1992)]

Lignin can be divided into acid-insoluble lignin (Klason lignin) and acid-soluble lignin (ASL). The size of ASL is smaller than that of Klason lignin, and at least part of it is assumed to be degradation products of Klason lignin. In PHWE, the lignin molecule is partly degraded, i.e. depolymerised, and part of it is dissolved into the water. Aryl ether, e.g. β -O-4 bonds, are cleaved in the PHWE, leading to reactive components, which might repolymerise, forming also structures which are not present in native lignin. These condensed lignin molecules precipitate if their molecular mass is high enough, and the precipitates create scaling problems in downstream equipment [Leschinsky et al. (2009)]. From the point of view of membrane filtration, ASL is also, or in some cases particularly, the problematic lignin compound in PHWE solutions (pH 3-4) due to its hydrophobicity. The hydrophobic compounds present in pulp and paper effluents cause adsorptive fouling of hydrophobic membranes [Puro et al. (2002), Maartens et al. (2002)]. Even when dissolved in aqueous solutions, lignin is a hydrophobic compound, although the hydrophobicity is somewhat lower than that of larger lignin molecules.

4.1.3 Lignin-hemicellulose complexes

It was suggested already in 1866 that lignin and carbohydrates are chemically bonded together, forming “glycolignose” [Koshijima and Watanabe (2003)]. Currently, the idea of lignin-carbohydrate complexes (LCC) or lignin-hemicellulose complexes (LHC) has been considered by many researchers [Alén (2011), Lawoko (2005), Chen and Sarkanen (2010), Gübitz et al. (1998)]. Suggested bonds between lignin and hemicelluloses include benzyl ether, benzyl ester, glycoside and acetal linkages (Fig. 5a and 5b), of which the first two are the most probable ones [Koshijima and Watanabe (2003)].

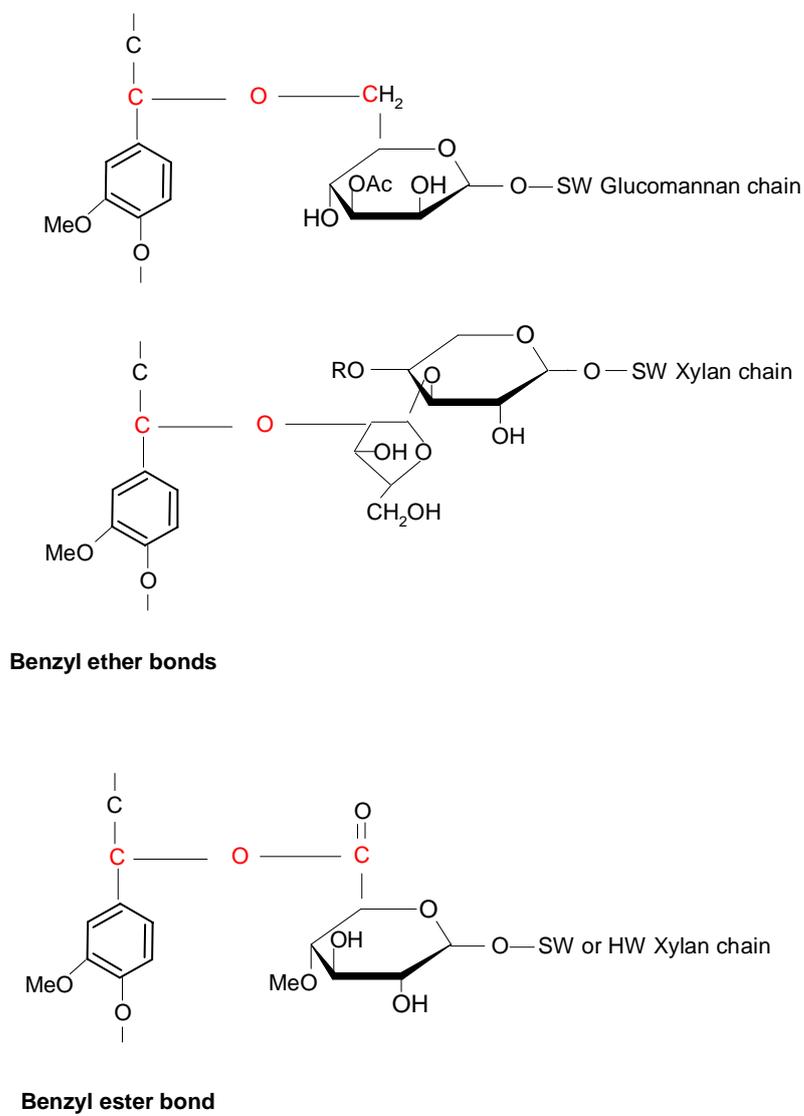
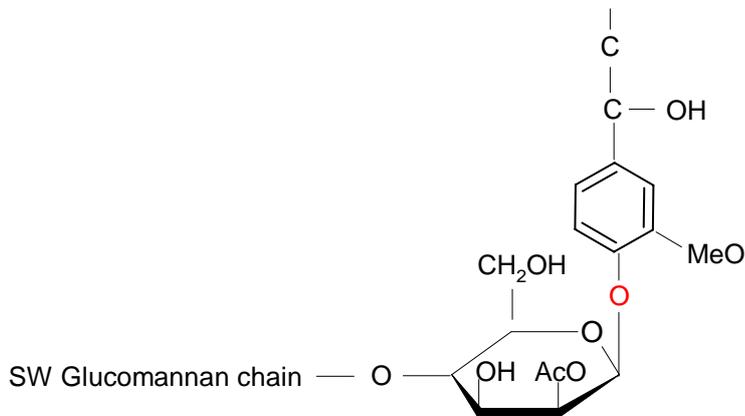
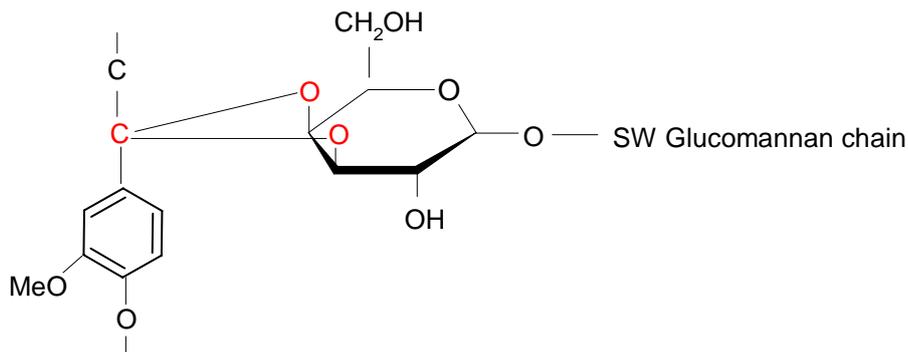


Figure 5a. The most probable of suggested bonds between lignin and hemicelluloses. Adapted from Alén (2011) and Koshijima and Watanabe (2003).



Glycoside bond



Acetal bond

Figure 5b. Possible bonds between lignin and hemicelluloses. Adapted from Alén (2011) and Koshijima and Watanabe (2003).

Lawoko (2005) found that lignin is covalently bonded with all the major polysaccharides in native softwood. These polysaccharides include arabinoglucuronoxylan, galactoglucomannan, glucomannan, pectin and cellulose. Hot water extraction of softwoods provides water-soluble, partly acetylated glucomannan and its complex with lignin. In the case of hardwood, fewer water-soluble components are released, mostly lignin-xylan complexes, which contain larger lignin moiety than SW LCCs. [Koshijima and Watanabe (2003)] There might also be larger complexes between lignin and more than just one polysaccharide, as lignin has the ability to cross-link e.g. glucuronoxylan and glucomannan together [Koshijima and Watanabe (2003), Lawoko (2005)]. For this reason, the separation of hemicelluloses and lignin by membrane

filtration, or by any means, is challenging. If all hemicelluloses are wanted to be recovered, additional actions to degrade LCCs may be required.

4.1.4 Wood extractives

On average, there are 3-4 % extractives of the dry solids in wood. The extractives cover several different compounds, usually of a small molecular size. It depends on the wood species which extractives are present in the wood or dissolved into extracts. The extractives are soluble in organic solvents or water, and they can be both lipophilic and hydrophilic by nature. Extractives can be used as a raw material for e.g. tar, turpentine, gum rosin, or tall oil. Bark extracts are used e.g. in traditional medicine, water-soluble polysaccharide gums in food additives, sap, natural rubber, and tall oil fatty acids as additives in paints, surfactants, lubricants, printing inks, fuel, oil field chemicals, corrosion protection, hot melt adhesives, and cosmetics. [Alén (2011)]

One way to classify wood extractives is based on their structure, giving aliphatic, phenolic and other extractives (Table I). In the experimental part of this study, the total wood extractives are a sum of measured 1) lignin residuals, 2) medioresionol and syringaresinol, which are lignans, and 3) fatty and resin acids, sterols, steryl esters and triglycerides, which are lipophilic extractives.

Table I Classification of wood extractives in wood [Alén (2011)].

Aliphatic	Phenolic	Other
Terpenes and terpenoids (e.g. resin acids and steroids)	Simple phenols	Sugars
Esters of fatty acids (fats and waxes)	Stilbenes	Cyclitols
Fatty acids	Lignans	Tropolones
Alkanes	Isoflavones	Amino acids
	Flavonoids	Alkaloids
	Condensed and hydrolysable tannins	Coumarins
		Quinones

5 METHODS TO RECOVER HEMICELLULOSES FROM WOOD EXTRACTS

Hemicelluloses have to be separated from other dissolved wood components before further use. Table II presents the most applicable methods and their advantages and disadvantages in hemicellulose recovery from biomass-based solutions. It depends on the further use of the hemicelluloses, and therefore the target characteristics, e.g. molecular mass and purity, which method meets the requirements best. On a large scale, UF could be the most suitable method since it provides a concentrated fraction. However, if very high purity is needed, chromatographic separation might offer the best solution. Precipitation consumes large amounts of solvents if the volumes of the hemicellulose solutions are large at the beginning. Therefore, the most feasible solution could possibly be a combination of UF and one of the other methods.

Table II The most applicable methods for the recovery of hemicelluloses from biomass-based solutions.

Method	Advantages	Disadvantages	Reference
Precipitation with ethanol	<ul style="list-style-type: none"> • Molecular mass of precipitated hemicelluloses can be controlled by adjusting the amount of ethanol 	<ul style="list-style-type: none"> • Ethanol consumption • Additional recovery system for ethanol • Ethanol loss in precipitate • Hemicelluloses have to be separated from a large amount of ethanol solution after precipitation • Precipitate also contains some lignin 	<p>Liu et al. (2011), Huang et al. (2008), Swennen et al. (2005), Song et al. (2013)</p>
Supercritical anti-solvent precipitation	<p>Supercritical carbon dioxide:</p> <ul style="list-style-type: none"> • Commonly used chemical • Non-toxic, inert, non-flammable • Particle size and morphology can be controlled to some extent 	<ul style="list-style-type: none"> • High pressures and accordant equipment required 	<p>Peng et al. (2012), Haimer et al. (2010)</p>
Chromatography (SEC, anion exchange, DEAE-cellulose)	<ul style="list-style-type: none"> • High recovery of hemicelluloses • High purity can be achieved 	<ul style="list-style-type: none"> • Product fraction dilute due to elution with additional solvent 	<p>Peng et al. (2012), Andersson et al. (2007)</p>
Membrane filtration	<ul style="list-style-type: none"> • No additional chemicals or solvents needed • Operates at moderate pressure • Applicable for concentration, purification and fractionation (from polymers to oligo- and monomers) 	<ul style="list-style-type: none"> • Membrane fouling • Limited operating temperature and pH (polymeric membranes) • More heterogeneous hemicellulose fractions obtained than e.g. by ethanol precipitation • Possible need for an additional purification step 	<p>Huang et al. (2008), Swennen et al. (2005), Song et al. (2013)</p>

5.1 Precipitation

The precipitation of hemicelluloses with ethanol enables the fractionation of hemicelluloses according to their molecular masses by adjusting the ethanol concentrations [Swennen et al. (2005)]. However, the ethanol consumption may become high if a high yield is required. For instance, Song et al. (2013) precipitated hemicelluloses from spruce extract with ethanol, noticing that the hemicellulose yield decreased and MW increased with decreasing ethanol to extract ratios (Fig. 6). Thus, the amount of ethanol can be adjusted according to the size requirements for hemicelluloses. Swennen et al. (2005) precipitated hemicelluloses from enzymically produced arabinoxylan (AX) hydrolysates with 60%, 60–90% and over 90% ethanol, and obtained precipitated hemicelluloses with an average DP of 53, 23 and 5, respectively. The precipitated material is mostly hemicelluloses, but it may contain some lignin, which must be removed if high purity of hemicelluloses is required. Due to the high ethanol consumption, equipment for the recovery of ethanol is necessary [Huang et al. (2008)]. The used ethanol could be recycled by e.g. evaporation or nanofiltration. Precipitation with ethanol from crude wood extracts might not be economic as such, due to dilute solutions. However, precipitation could be used to purify the UF concentrate which is rich with hemicelluloses but the volume is significantly lower than at the beginning. This combination would reduce the amount of ethanol in precipitation due to a smaller volume of solution to be treated. This process solution could be useful if dry hemicelluloses or higher purity than obtained by UF alone are required.

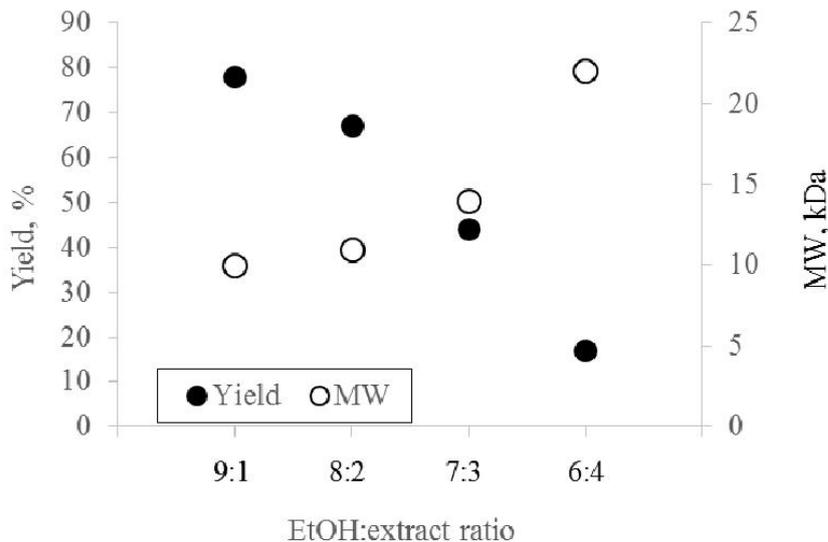


Figure 6. Yields and molecular weights of hemicelluloses obtained by ethanol precipitation from a spruce extract [Adapted from Song et al. (2013)].

Precipitation with supercritical antisolvents, e.g. carbon dioxide, would be more convenient even for large volumes of wood extracts than precipitation with ethanol, since it does not dilute the wood extract with a large volume of solvent. Also other gases can be used, but carbon dioxide is often used due to low expenses of both the gas itself and the process converting the gas into a supercritical state. The formed precipitates can be separated by using a steel frit and flushing and drying the supernatant from the precipitate with the same CO₂ as used in the precipitation step. The high-pressure equipment in supercritical carbon dioxide precipitation is, however, more demanding due to pressures as high as 60–110 bar [Haimer et al. (2010), Vega-González et al. (2008)]. According to Haimer et al. (2010), the size of the precipitating particles can be controlled by adjusting the precipitation conditions. This could be utilised in applications where size is an important factor. Similarly to ethanol precipitation, also supercritical antisolvent precipitation could be used to purify and dry already concentrated high-molecular mass hemicellulose fractions in applications where high purity is required.

5.2 Chromatographic separation

In chromatographic separation, great extract volumes may be problematic since the extract is not fed to the separation column as such, but an additional solvent is used for elution. This increases the total volume even more and dilutes the solution. For example, for efficient purification, the resolution should be above 1.5 in the chromatographic separation process [Poole (2003)]. Andersson et al. (2007) report of a resolution of 1.4 with the feed volume of 20% of the total column volume in SEC of UF concentrate of TMP process water, achieving a recovery of galactoglucomannan as high as >99%. Chromatographic separation could be used to purify UF concentrates similarly to precipitation. The feed volume to the chromatographic step would thus be smaller, which would decrease the amount of solvent needed. Also, the purity of the hemicelluloses could be increased compared to hemicelluloses from UF alone.

5.3 Ultrafiltration

The UF process can be adjusted to serve different needs in the field of separation technology. It can be used not only to isolate but also to fractionate, concentrate and purify hemicelluloses. UF has been studied and used successfully to recover hemicelluloses from solutions of different origins. Table III presents examples of UF in the treatment of wood-based solutions. The MM of dissolved hemicelluloses determines the cut-off to be no more than 30 kDa, most typically around 10 kDa or less, depending on the treatment which produced the hemicellulosic solution. In some of the cases presented in Table III, MF was used as a prefiltration to remove possible

solid material from the solution before UF [Andersson et al. (2007), Persson and Jönsson (2010), Krawczyk et al. (2013b)].

In many cases, the flux declines during the filtration to such an extent that it is not meaningful to continue the filtration, and the volume reduction (VR) or the volume reduction factor (VRF) remain low. In such a situation, the desired concentration or fractionation can be inadequate. Persson and Jönsson (2010) report of a reduction in flux of approximately 60% due to fouling of the membrane during three days' UF of TMP mill process water. They recirculated the retentate and permeate to the feed tank. Andersson et al. (2007) and Al Manasrah et al. (2012) obtained lower fluxes during diafiltration than the fluxes during preceding UF in the purification of produced hemicellulose fraction. Although membrane fouling is often an issue in the filtration of wood- or other plant-based solutions, it is not the only factor limiting the filtration capacity in UF [Hasan et al. (2011), Jorda et al. (2002), Mänttari et al. (2002)].

Flux decline can result from concentration polarisation or fouling. In concentration processes, as the filtration goes further, the MM increases in the concentrate, which can increase the viscosity of the solution and therefore reduce the flux. For example, Krawczyk et al. (2013b) report of an 85% reduction in flux and an increase in the MM of hemicelluloses approximately from 1 kDa to 4 kDa during UF of CTMP mill process water. Despite the low flux at the end of the process, they achieved high VR, which enabled the concentration of hemicelluloses from 0.6 g/l to 14 g/l. Also in diafiltration the MM increases as the filtration proceeds, although the increase in concentration can be hindered by adding water in the feed solution. The increase in concentration is another reason for the flux decline, in addition to the increased MM. When the concentration increases and the MM distribution is changed, the viscosity and viscoelastic properties of a polymeric solution may change significantly. When viscoelastic solution is exposed to shear forces, the polymers can become rearranged and therefore either increase or decrease the viscosity of the solution. The changes in these properties have unavoidably an impact on the filtration behaviour of the solution.

In the study of Al Manasrah et al. (2012), the 5 kDa RC membrane, which is currently off the market, performed with a stable flux both in a regular UF step and in a diafiltration step, which implies that at least no severe fouling occurred during the filtration. According to pure water flux reduction (PWF_r), the fouling of the 5 kDa RC membrane was 18%, which is not a very high value in this type of a process. For comparison, the PWF_r was 37% in the study of Andersson et al. (2007), who, however, managed to restore the PWF to its initial level by cleaning the membrane. Although a membrane would perform well as regards the permeate flux and resistance to fouling, it should also have adequate retention and selectivity for target compounds. Swennen et al. (2005) recovered arabinoxylooligosaccharides (AXOS) from wheat hydrolysates by UF membranes with different cut-offs and noticed that the higher the MM they produced, the smaller was the yield. This is reasonable, as generally, lower cut-off membranes reject more but also smaller compounds than higher cut-off membranes. Swennen et al. also report that the retentions for more substituted AXOS were higher than for less substituted

AXOS. This kind of fractionation could also be useful if the degree of substitution of hemicelluloses affects the final product quality.

Table III UF in treatment of wood-based solutions targeting at the concentration or fractionation of hemicelluloses.

Separation process	1) Preconcentration and 2) fractionation of hemicelluloses from a TMP'' mill process water	Fractionation of AXOS* from enzymically produced wheat hydrolysates	Concentration of hemicelluloses from CTMP'' mill process water	Concentration of GGM from PHWE of spruce-sawdust
Membrane	ETNA01PP (^A , 1 kDa, Alfa Laval)	1) P005F (PES, 5 kDa, Celgard) 2) PES-10 (PES, 10 kDa, Synder Filtration) 3) PES-030H (PES, 30 kDa, Celgard)	UFX5pHt (^B , 5 kDa, Alfa Laval)	UC005 (RC, 5 kDa, Microdyn Nadir GmbH)
Filtration conditions	UF and diafiltration (DF): 60°C, 10 bar	Room temperature, 4 bar	60°C, 5 bar	UF + DF: 65°C, 3.5 bar
Product fraction	UF: VR 80%, purity of hemicelluloses 57% DF: purity of hemicelluloses 77%, recovery 87%	VR ca. 67% 1) AX* yield 86%, DP 11 2) AX* yield 65%, DP 12 3) AX* yield 46%, DP 15	VR 97%, hemicellulose concentration increased from 0.6 g/l to 14 g/l, Av. hemicellulose MM increased from ~1 kDa to ~4 kDa	VR 86%, purity 63%, recovery 70%
Flux	UF: Av. 69 l/m ² h DF: Av. 55-63 l/m ² h	-	~170-25 l/m ² h	UF: At the end 107 kg/m ² h, DF: At the end 86 kg/m ² h
Reference	Andersson et al. (2007)	Swennen et al. (2005)	Krawczyk et al. (2013b)	Al Manasrah et al. (2012)

* GGM galactoglucomannan, AXOS arabinoxylooligosaccharides, AX arabinoxylan

'' TMP thermomechanical pulp, CTMP chemithermomechanical pulp

^A Composite fluoropolymer on polypropylene

^B Polysulphone permanently hydrophilic on polypropylene

5.3.1 Concentration polarisation and fouling

UF performance is hindered mostly by concentration polarisation and membrane fouling. Concentration polarisation is a reversible phenomenon that occurs during filtration when the concentration of solutes on the membrane surface, in UF mainly macromolecules or particles, is increased by the convection and rejection of the membrane. Accumulated solutes create a diffusive flow from the surface back to the feed solution, and after a certain time a steady-state condition is achieved (Fig. 7). Concentration polarisation decreases the permeate flux (J) during the filtration process because the resistance of transport across the membrane is increased. The increase in resistance can be partly due to increased viscosity and osmotic pressure as a result of higher concentration on the membrane surface. Increased osmotic pressure hinders the effect of the applied trans-membrane pressure.

In contrast to concentration polarisation which settles to a steady-state, fouling causes a continuous flux decline. Fouling is often irreversible, which can be observed as pure water flux reduction, PWF_r. Membrane fouling means the deposition and accumulation of particles or solutes, a.k.a. foulants, on the membrane surface or inside the membrane pores by different mechanisms, depending on the membrane and the solution. The foulant can be a compound that is rejected by a membrane or one that permeates the membrane. If the foulant permeates the membrane surface, it may foul the membrane structure layer. Membranes can be fouled by different fouling mechanisms, which are determined on the basis of the solute and membrane characteristics, as well as the operation conditions. General fouling mechanisms [Noble and Stern (1995), Strathmann et al. (2006)] are

- 1) Adsorption, which can make the membrane pores narrower or change the characteristics of the membrane surface. Adsorption may occur because of hydrophobic or polar interactions, or, electrostatic forces.
- 2) Pore plugging, which can in some cases also result from adsorption.
- 3) Gel/cake layer formation, which leads to the same kind of situation as in a precoat filter and may result from concentration polarisation.
- 4) Biofouling, caused by biological material attached to the membrane surface and forming biofilms.

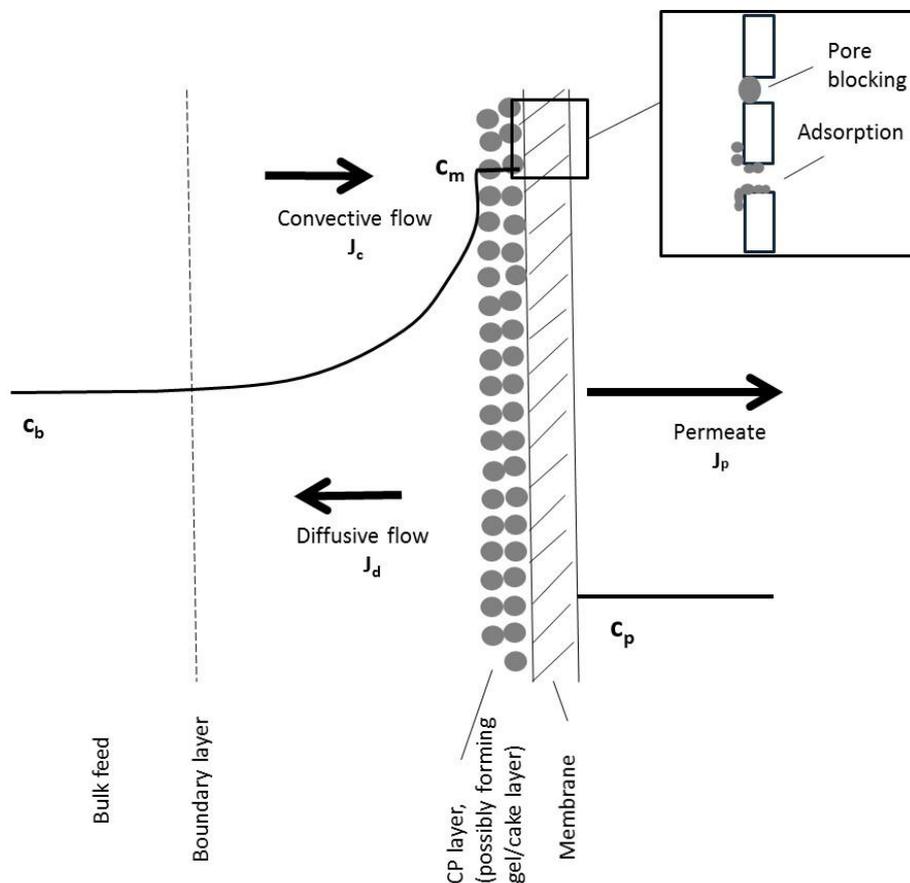


Figure 7. Concentration polarisation and different fouling phenomena in ultrafiltration. Adapted from Cheryan (1998) and Noble and Stern (1995).

Fouling depends strongly on the application, and it is thus difficult to describe theoretically or predict. The intensity and type of fouling depends on several interacting factors. Such factors are e.g. [Noble and Stern (1995), Strathmann et al. (2006), Cheryan (1998)]:

- Membrane characteristics:
hydrophilicity, surface topography, charge, MWCO and pore size distribution
- Solute characteristics:
conformation, charge, hydrophilicity and solute concentration
- Operating conditions:
temperature, pressure, shear rate

Fouling models for different solutions have been formed [Bolton et al. (2006), Cai et al. (2013), González-Muñoz and Parajó (2010)]. However, wood extracts are complex mixtures of many components, and the process is difficult to simulate with model compound solutions. There are

several solute-solute and solute-membrane interactions, and it is therefore difficult to create a model which would take all of them into account.

Due to the complexity of wood-based solutions, it is not obvious which components act as foulants, but it depends on the application. Different compounds have been reported to foul the membranes in the UF of wood-based solutions (Table IV). In many cases lignin, and more generally, phenolic compounds, including some wood extractives, have been found as potential foulants in the ultrafiltration of plant-derived solutions, e.g. pulp and paper process waters [Maartens et al. (2002), Puro et al. (2011)]. A potential fouling mechanism for phenolic compounds has been suggested to be adsorption in the UF of different solutions, such as the polyphenolic compound model solution and pulp and paper mill effluent [Maartens et al. (2002), Susanto et al. (2009)]. Susanto et al. (2009) studied the adsorptive fouling of two 10 and 100 kDa PES membranes and one 10 kDa cellulose membrane, caused by phenolic compounds. They noticed that adsorption was stronger with hydrophobic membranes and membranes with a smaller cut-off value.

A surface spectroscopic study of hydrophobic membranes by Carlsson et al. (1998) revealed that the membranes were coated with all the constituents of the effluent from the sulphite digestion of wood chips. Kallioinen (2008) studied the fouling of regenerated cellulose membranes in the treatment of GWM water by ATR-FTIR measurements. The IR spectra of the fouled membranes revealed that the fouling layer contained polysaccharides. Fouling linked to polysaccharides has been suggested to be pore blocking and consequent cake formation [Saha et al. (2007)], or adsorption [Mänttari et al. (2000)]. Polysaccharides as single solutes in the solution, however, do not seem to be as significant a fouling problem as phenolic compounds, according to the literature. For example, Goulas et al. (2002) did not observe irreversible fouling with several nanofiltration membranes in the purification of oligosaccharide mixtures.

Table IV Foulants in plant-based solutions and model solutions containing similar compounds.

Solution	Membrane	Detected foulant	Detection method	Reference
Pulp and paper effluent	PES (Weir Envig (Pty) Ltd)	Phenolic substances	Membranes: Colorimetric characterisation Solutions: UV-VIS	Maartens et al. (2002)
CTMP mill process water	UC030 (RC, 30 kDa), UH030P (PES, 30 kDa), UH050P (PES, 50 kDa) (Microdyn Nadir GmbH)	Wood extractives	Membranes: Extraction of the fouled membranes and GC analysis for extracted compounds, FTIR	Puro et al. (2011)
Aqueous polyphenolic compound solution	SG-10 (PES, 10 kDa), SG-100 (PES, 100 kDa), SC-10 (Cellulose, 10 kDa) (Sartorius AG)	Polyphenolic compounds	Filtration: PWF _r , Membranes: Contact angle, zeta potential, FTIR	Susanto et al. (2009)
Effluent from sulphite digestion	HFM-180 (PVDF, >100 kDa, Koch Membrane Systems), PCI PS20 (PSu, >100 kDa, Patterson Candy International)	Hydrated lignin sulfonates, cellulosic oligomers	Membranes: Infrared internal reflection spectroscopy	Carlsson et al. (1998)
Groundwood mill water	UC030T (RC, 30 kDa, Microdyn Nadir GmbH)	Polysaccharides	FTIR	Kallioinen (2008)

* SEM scanning electron microscope, NMR nuclear magnetic resonance

5.3.2 Control of fouling

Fouling increases the costs of the filtration process because it decreases the permeate flux. Because fouling depends on the process, the control and prevention of fouling should be considered for each case separately. Generally, the following methods can be used to manage fouling [Cheryan (1998), Strathmann et al. (2006)]:

- 1) Choosing an optimal membrane and filtration module
- 2) Tailoring the membrane (surface) properties
- 3) Adjusting operational conditions
- 4) Membrane cleaning
- 5) Pretreatment of the feed solution

As mentioned in the introduction section, the supply of commercial membranes is limited and there are no RC or other hydrophilic membranes commercially available below 10 kDa for industrial scale high shear rate filter modules. Thus, also other membrane materials have to be considered. The operational conditions could be adjusted to improve an already working process but not to solve fouling problems as significant as with wood extracts. Membrane modification could be one approach to solve the fouling problems. However, there are currently no modification methods for industrial scale membrane processes.

Membrane cleaning is more a matter of managing a situation where fouling occurs than preventing fouling. In an ideal case, membrane cleaning can be used in turns with filtration to remove the fouling and restore the level of the initial permeate flux. At its best, cleaning can modify the membrane in such a way that the fouling resistance of the membrane is increased, and fouling becomes slower. However, if the flux declines rapidly and the original problem is not removed, there is no point in cleaning the membrane, since the flux will decrease as rapidly after cleaning as it did before cleaning. It is also possible that the cleaning is insufficient and the membrane remains fouled. For example, Persson et al. (2010) noticed that alkaline cleaning was insufficient to recover the original PWF after the filtration of pulp mill process water with a 5 kDa PSu membrane. Membrane cleaning also increases chemical consumption and decreases the membrane life-time by ageing the membrane faster, and causes discontinuation to the process.

In the current situation, resulting in the circumstances discussed above, the feed solution needs pretreatment in the recovery of hemicelluloses from wood extracts with tight UF membranes. An additional advantage of pretreatment would be its ability to purify the produced hemicellulose fraction. It could, therefore, eliminate a possible purifying post-treatment for UF concentrates. The pretreatment should be selective to foulants to avoid hemicellulose losses. Pretreatment does not necessarily remove the fouling problem completely, it most likely only decreases it. Also, the removal of a specific foulant from the extract might not have the expected impact on the fouling, as the extract consists of also other compounds than the removed foulants. If the amount of the “main foulant” is reduced by pretreatment, the effect of other

“weaker” foulants might increase [Kallioinen (2008)]. Therefore, several factors have to be investigated to find out what measures are required to decrease fouling in the UF of wood extracts, and a thorough experimental study has to be performed to find out if pretreatment can be applied to solve the problem.

7 PRETREATMENT METHODS

Pretreatment of the feed solution in the UF of wood extracts aims at decreasing the amount of foulants in the feed solution in order to decrease fouling and thus increase the filtration capacity. Factors that have to be taken into account in the selection of the pretreatment method are e.g. the ability to decrease fouling, selectivity to foulants over hemicelluloses, pretreatment aid and equipment costs, chemical and energy consumption, the amount and nature of waste, and the time spent on the pretreatment. In addition to fouling, another issue concerning the UF of wood extracts is the purity of the produced hemicellulose fraction. UF does not necessarily purify the hemicellulose fraction from lignin efficiently enough. In such a case, purifying post- or pretreatment is required. Thus, fouling-reducing pretreatment could also increase the purity of the hemicellulose fraction, which would be additionally advantageous for the process.

There are different methods for decreasing the amount of foulants, i.e. lignin and/or wood extractives, based on e.g. adsorption, flocculation, oxidation, or extraction (Tables V, VI and VIII). The amount of foulants can be decreased by removal or degradation. Some of the methods presented in Tables V, VI and VIII have been widely studied [Willför et al. (2003), Schwartz and Lawoko (2010), Lehto and Alén (2012), Westerberg et al. (2012), Gütsch and Sixta (2011), Venkata Mohan and Karthikeyan (1997), Shen et al. (2013), Parajó et al. (1996), Miyafuji et al. (2003), Widsten et al. (2004), Jönsson et al. (1998)], but seldom combined with membrane filtration. Part of the lignin structure is built up of phenolic components, and thus, methods for the removal of phenolic compounds are also taken into consideration.

7.1 Removal of foulants

Pretreatment methods which remove foulants do not necessarily alter the foulant molecules, but remove them as they are in the solution. Such methods include e.g. adsorption, flocculation and extraction. The removal of foulants is based on interactions between foulants and either solid material, such as adsorbents, or another solvent, into which the foulants are more soluble than into the original solution (Fig. 8).

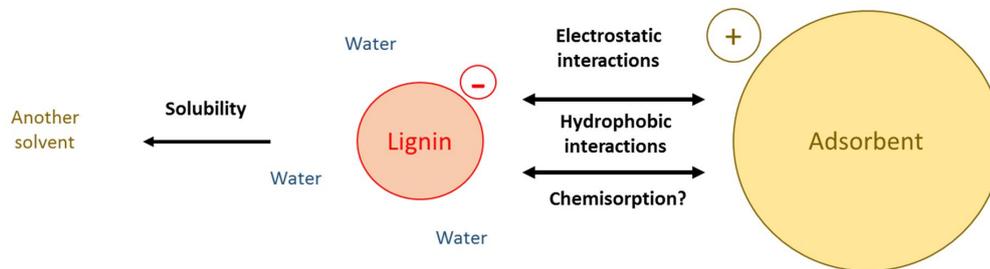


Figure 8. Removal of lignin based on different interactions.

Adsorbents are solid materials which bind compounds due to physical, chemical and electrical interactions. The adsorption on polymeric adsorbents is often based on physical interaction. Lignin is a hydrophobic molecule which can be adsorbed on nonpolar adsorbents, such as XAD adsorbents [Sigma (2014)]. Hemicelluloses are hydrophilic molecules, and therefore are not adsorbed as efficiently by XAD adsorbents as lignin.

The surface of activated carbon (AC) is also hydrophobic. Lignin molecules are negatively charged in water or in acidic conditions, whereas hemicelluloses are mostly neutral. Kraft lignin is negatively charged at pH values above 1.0, and for example at pH 4.5 the zeta potential of Kraft lignin is -40 mV [Maximova (2004)]. These values can differ from the values of lignin present in wood extracts, but they are still directional. The charge of the surface of AC depends on the pH of the surrounding solution and the material of the carbon. A zero point charge (ZPC) means a pH value at which the surface charge of the AC is zero [Al-Degs et al. (2000)]. At lower pH values, the surface has a positive charge, and at higher pH values, the surface charge is negative. Thus, at pH values lower than ZPC the charge of the AC is opposite to the charge of the lignin molecules, which increases the attraction between them. Al-Degs et al. (2000) have determined the ZPC value for F-400 activated carbon to be 7.2, which is close to other commercial activated carbon values [Martin et al. (2003), Kodama and Sekiguchi (2006)].

Bentonite consists of montmorillonite and other smectic group clay minerals which have a large surface area and high cation exchange capacity due to hydrated cations, such as Ca^{2+} , Na^+ , K^+ , in a silica layered structure [Vega et al. (2005)]. Bentonite contains also polar hydroxide groups, which can weaken the adsorption of organic molecules. Bentonite can be modified e.g. to increase its organophilic nature or surface area [Suzuki (1993), Amari et al. (2010)]. Electrostatic attraction can also be utilised in ion exchangers for the removal of phenolic compounds [Villarreal et al. (2006)], or in flocculation with cationic polymers to form easily removable flocs with lignin.

The extraction of lignin by organic solvents is based on the hydrophobic, i.e. nonpolar, nature of lignin molecules. The solubility of lignin, due to greater affinity, is thus higher in nonpolar solvents than in water. Extraction can remove also some wood extractives, mainly lipophilic ones, depending on their characteristics. Hemicelluloses are hydrophilic, and thereby more water-soluble than lignin.

Table V and VI present the removal of lignin, and in some cases wood extractives, by different methods. Adsorption seems to be capable of over 90% lignin removal [Schwartz and Lawoko (2010), Miyafuji et al. (2003), Gütsch and Sixta (2011), Parajó et al. (1996)]. Flocculation and extraction have been reported not to gain as high removal rates [Willför et al. (2003a), Duarte et al. (2010), Chen et al. (2004), Lehto and Alén (2012), Cruz et al. (1999)]. However, the experiments are not fully comparable since different solutions have been used and the conditions have not necessarily been optimised. The removal of extractives has been reported in the cases of adsorption on a XAD7 adsorbent and flocculation by a starch-based cationic polymer [Willför et al. (2003a)]. In these cases, the removal of extractives was at least as high as the removal of lignin. Since the information about the removal of hemicelluloses by these methods was limited, the selectivity and possible hemicellulose losses are not included in this discussion.

Table V Adsorption in the removal of lignin and wood extractives from different solutions.

Adsorption	Parameters	Lignin/ phenol removal	Extractives removal	Reference
XAD7 (Polyacrylate)	5 kg/140 l of TMP-water, 15 min	70%	70% (lignans)	Willför et al. (2003a)
XAD4 (Polystyrene- divinylbenzene)	1) Column: 4 g XAD and 5 ml wood extract, 10 min 2) Column: 3.5 g XAD and 25 ml hydrolysate, flow through	1) 92% 2) ~30%	-	1) Schwartz and Lawoko (2010) 2) Lehto and Alén (2012)
XAD16 (Polystyrene- divinylbenzene)	Column (7.8 x 300 mm): 300 ml wood extract (permeate from 1 kDa UF membrane) 3 ml/min	38%	-	Westerberg et al. (2012)
XBridge Phenyl 5 μ m (Analytical column)	Column (4.6 x 205 mm): wood extract (permeate from XAD16 column, above) 0.5 ml/min	22%	-	Westerberg et al. (2012)
Activated carbon	1) 48 g/l AC to autohydrolysate, 170 °C, 20 min 2) 200 mg AC + 50 ml aqueous lignin solution (50 mg/l), room temperature, 60 min 3) 1 g AC + 30 g wood prehydrolysis liquor 4) 1 g AC + 20 g wood hydrolysate, 3 days	1) 96% 2) 87% 3) 85% 4) 90%	-	1) Gütsch and Sixta (2011) 2) Venkata Mohan and Karthikeyan (1997) 3) Shen et al. (2013) 4) Parajó et al. (1996)
Wood charcoal	Charcoal:hydrolysate weight ratio 0.07, room temperature, 3 h	~ 90%	-	Miyafuji et al. (2003)

Table VI Flocculation and extraction in lignin and wood extractive removal from different solutions.

Method	Flocculation by PAC (Polyaluminium chloride)	Flocculation by p-DADMAC (Polydiallyldimethylammonium chloride)	Flocculation by starch-based cationic polymer	Extraction by ethyl acetate
Parameters	PAC 80 ppm to wood extract, 5 min + settling	1) p-DADMAC 60 ppm to wood extract, 5 min + settling 2) p-DADMAC 47.3 ppm + wood extract, 10 min + settling	Excess of polymer to TMP water, 15 min	1) 50 ml hydrolysate and 3 x 50 ml ethyl acetate 2) Wood hydrolysate to ethyl acetate ratio 1:5, 30°C, 30 min
Lignin/phenol removal	25%	1) 52% 2) 36%	20%	1) 50% 2) ~84%
Extractives removal	-	-	45% (lignans)	-
Reference	Chen et al. (2014)	1) Chen et al. (2014) 2) Duarte et al. (2010)	Willför et al. (2003a)	1) Lehto and Alén (2012) 2) Cruz et al. (1999)

The comparison of different methods based only on their ability to remove foulants is insufficient in order to select the best method for pretreatment purposes, as an increase in filtration capacity does not necessarily correlate with the removal of foulants. The pretreatment methods have to be studied in connection to UF. This has been done by Persson and Jönsson (2009), who used AC to reduce the fouling of a 10 kDa composite fluoropolymer membrane and 5 kDa regenerated cellulose membrane in the filtration of process streams from the forest industry. According to them, the AC treatment increased the fluxes during UF and improved the recovery of the pure water flux after the filtration.

The applicability of the listed methods (Tables V and VI) for pretreatment can, however, be evaluated (Table VII). Generally, based on the studies listed in Tables V and VI, adsorption, flocculation and extraction could be applied as relatively quick pretreatment methods. There are examples of each case where in less than 60 minutes the lignin or phenolic compound content has been decreased. In adsorptive pretreatment, no additional chemicals are usually needed, but the adsorbents themselves increase the costs and have to be separated from the solution at some point. In flocculation or extraction, the flocculant solution and extraction solvent obviously increase the chemical consumption. Also the formed flocs, as well as the extraction solvent have to be separated from the wood extract at some phase of the process. In theory, in any of these methods, the separated lignin could be possibly recovered and used in

the production of lignin-based products. Adsorbents and extraction solvents could be possibly regenerated, but the re-use of flocculants is more challenging.

Information about the regeneration of adsorbents is obtained mostly regarding the regeneration of AC, probably because it is a rather old and commonly used adsorbent, and also studied for the adsorption of lignocellulosic components by many researchers [Liu et al. (2012), Montané et al. (2006)]. AC is also a more expensive adsorbent than low-cost natural materials, such as clay or chitosan [Ahmaruzzaman (2008)]. Phenolic compounds might be irreversibly adsorbed on AC, especially at higher adsorption temperatures [Dąbrowski et al. (2005)]. Chemisorption has been suggested as an adsorption mechanism for lignin and AC at high temperatures [Gütsch and Sixta (2011)]. A high temperature is needed to fulfil the required activation energy in the formation of chemical bonds, which are stronger than physical bonds that are formed in adsorption at lower temperatures. This makes the regeneration of AC by solvents challenging. Regeneration at a high temperature, i.e. carbonisation of adsorbed material at temperatures exceeding 800°C, might be the most approachable alternative for the regeneration process. Thermal regeneration presumes that the adsorbent material can withstand high temperatures, which limits this method to be used mainly for AC rather than polymeric adsorbents. The adsorbed lignin could also be utilised in the thermal regeneration of AC as a new raw material for additional AC, as the thermal regeneration process is somewhat similar to the production process of AC [Gütsch and Sixta (2012)]. In the case of polymeric adsorbents, solvent regeneration could be practical, as the applicable adsorption temperatures are more limited than with AC, and thus the adsorption will more probably remain weaker and reversible.

Table VII Advantages and disadvantages of the presented pretreatment methods based on the removal of foulants.

Method	Advantages	Disadvantages
Adsorption	<ul style="list-style-type: none"> • Efficient in the removal of foulants, according to the literature • Quick method • Re-use of adsorbents possible? • Recovery of lignin possible? 	<ul style="list-style-type: none"> • Separation of used adsorbents • Regeneration
Flocculation	<ul style="list-style-type: none"> • Quick method • Recovery of lignin possible? 	<ul style="list-style-type: none"> • Less efficient in the removal of foulants than adsorption, according to the literature • Re-use of flocculants challenging if not impossible • Separation of formed flocs
Extraction	<ul style="list-style-type: none"> • Re-use of solvent possible? • Recovery of lignin possible? • Quick method 	<ul style="list-style-type: none"> • Less efficient in the removal of foulants than adsorption, according to the literature • Chemical consumption

One approach for decreasing fouling could also be prefiltration with a press filter or MF, or a higher cut-off UF membrane. This will not, however, solve the problem if the foulants are of a certain size so that they can permeate the prefiltration membrane, and therefore are present in the feed solution of the main UF step. Prefiltration may, however, have a positive impact on the filtration capacity even if it does not decrease the fouling. For example, Krawczyk et al. (2013a) found prefiltration with a filter press and a ceramic 0.2 μm MF membrane to be useful in the isolation of hemicelluloses from a wheat bran extract by filtration with a ceramic (TiO_2) 10 kDa UF membrane. They obtained fluxes as high as 225 $\text{l/m}^2\text{h}$ and 440 $\text{l/m}^2\text{h}$ in the UF after prefiltration with a filter press and MF membrane, respectively, whereas the flux of the UF membrane was 75 $\text{l/m}^2\text{h}$ without prefiltration. Prefiltration decreased the viscosity of the solution, which they assumed to be the reason for the remarkable increase in fluxes, and they did not discuss the effect of prefiltration on fouling. The MF membrane made of aluminium oxide might have adsorbed some of the hydrophobic foulants, which could possibly have had an impact on the flux obtained in the UF. However, the decrease in the viscosity of the feed solution might increase the filtration capacity remarkably, although fouling was not reduced (Paper V). On the other hand, a decrease in fouling alone might not be enough to increase the filtration capacity, and a decrease in viscosity is also required. In the study by Krawczyk et al. (2013a), the problem with MF was that it also decreased the amount of hemicelluloses considerably, but with the filter press, the decrease was only $< 5\%$. When hemicelluloses are the main product of the process, the selectivity of the used method to lignin over hemicelluloses is of great importance. Even a significant removal of foulants loses its profitability if also hemicelluloses are lost in the process.

7.2 Degradation of foulants

The degradation of foulants by oxidation decreases the size of the foulants and their total amount if the oxidation is complete. Lignin molecules can be oxidised in various ways. It would be convenient if the bonds binding LCCs were cleaved by oxidation in order to improve their separation from each other in UF. Often, when lignin is oxidised, β -O-4 bonds are cleaved. However, also e.g. $\text{C}\alpha$ - $\text{C}\beta$ cleavage between C1-C2 might occur, as well as alkyl-phenyl cleavage between C1 and the aryl group or $\text{C}\alpha$ oxidation. For example, the laccase enzyme can oxidise phenolic hydroxyl to phenoxy radicals. Without mediators, which are small auxiliary substances, laccase can oxidise only the phenolic structures of lignin, but with mediators also non-phenolic structures can be oxidised. Phenoxy radicals can then continue the degradation of lignin non-enzymatically, or the radicals can form larger molecules by coupling reactions. Lipophilic extractives can also be oxidised by laccase. [Higuchi (2004), Widsten and Kandelbauer (2008), Camarero et al. (2007)]

Another method to oxidise foulants is the pulsed corona discharge (PCD) treatment, which generates oxidative species, such as ozone, OH-radicals, atomic oxygen and peroxides, which

are able to oxidise organic material [Panorel et al. (2011)]. For example, aromatic compounds of phenolic pharmaceuticals can be oxidised by PCD [Panorel et al. (2012)]. PCD can also be utilised to enhance biodegradation e.g. in wastewater treatment because it increases the biodegradability of the wastewater [Pokryvailo et al. (2006), Grabowski et al. (2007)].

Table VIII presents the degradation of lignin by oxidation and wood extractives in the case of oxidation by laccase. PCD has been reported to remove phenols by as much as 99% [Grabowski et al. (2006)]. Enzymatic oxidation by laccase or cellulolytic enzyme have shown more moderate results than PCD in decreasing the amount of phenolic compounds [Widsten et al. (2004), Jönsson et al. (1998), Palmqvist et al. (1997)]. The removal of extractives has been shown to be higher than the removal of lignin by laccase [Widsten et al. (2004)].

Table VIII Oxidation and biodegradation in the degradation of lignin and wood extractives from different solutions.

Oxidation	Laccase enzyme by <i>Coriolus versicolor</i>	Laccase enzyme by <i>Trametes versicolor</i>	Cellulolytic enzyme by <i>Trichoderma reesei</i>	PCD
Parameters	Laccase dose 2.5 nkat/g biologically treated TMP whitewater, 45°C, 3 h, microfiltration	Laccase 1 µM in wood hydrolysate, 30°C, 12 h	Wood hydrolysate + inoculum (10% of the total volume), 30°C, 6 days	100 ml 1mM phenol solution, 40 kV, 10 Hz, 2 ml addition of H ₂ O ₂
Lignin/phenol removal	44% (MF alone 15%)	Phenolic monomers reduction 94%, but UV absorbance (280 nm) not decreased	>30%	99%
Extractives removal	82% (MF alone 24%)	-	-	-
Reference	Widsten et al. (2004)	Jönsson et al. (1998)	Palmqvist et al. (1997)	Grabowski et al. (2006)

Based on the oxidation of foulants, oxidation could be efficient as a pretreatment method. However, the oxidative methods seem to be more time-consuming than the removal methods, which is not desirable when the applicability of the method for pretreatment is considered. In complete oxidation, lignin cannot be recovered for further use. The partial oxidation of lignin can also create other compounds harmful to the filtration capacity, or some exploitable compounds such as vanillin [Panorel et al. (2013)]. On the other hand, oxidation does not involve separation of solids or liquids from the wood extract. PCD requires no chemicals.

Enzymatic oxidation requires an enzyme solution, which increases the costs, but the solution itself is not harmful to the environment.

7.3 Pretreatment as part of the recovery process

Among the discussed methods, oxidation and adsorption have shown the highest ability to decrease the amount of lignin or phenolic compounds in different solutions. They have, however, different impacts on the feasibility of the whole recovery process due to their different process steps and formation of waste, and on the other hand, the possibility to utilise lignin as a by-product. Oxidation would be a convenient pretreatment method because it does not require additional separation steps between pretreatment and UF. However, oxidative methods tend to be more time-consuming than removal methods. Extraction, flocculation and adsorption might presume separation of the solvent or adsorbent from the wood extract prior to UF. On the other hand, adsorption or flocculation could possibly be performed simultaneously with UF if adsorbents or flocculants were added to the feed tank and if the filtration were not disturbed by the presence of adsorbents or flocs in the feed solution. This type of set-up could be beneficial, as it would reduce the number of process steps. Nevertheless, the adsorbents or flocs should probably be separated from the UF concentrate before further processing, but the volume of the extract would be smaller than the volume of the feed solution. The oxidation step might be too slow to be performed simultaneously with UF. If the oxidation of foulants takes a long time, the foulants might have time to foul the membrane before they are degraded. The recovery of lignin after separation by pretreatment might be possible from the extraction solvent or adsorbent. In oxidation, it depends on how far the oxidation goes whether lignin is lost, or most conveniently, oxidised to a more valuable product than the original compound.

8 MATERIALS AND METHODS

The experimental setups are described in this chapter at a general level. More detailed information can be found in the corresponding papers I-V.

8.1 Wood extracts

Wood extracts obtained from different wood species at varying extraction conditions were used in the experiments (Table IX). The time of the extract outtake is mentioned if the total extract was not collected all at once but divided into e.g. pre-, main- and after -extracts.

Table IX Information on extraction conditions, raw material and characteristics of the wood extracts used in the experiments.

Used in paper #	Code	Wood species	Extraction conditions	Fraction	pH	TOC, g/l	Lignin, g/l	UV 280 nm,	Carbohydrates, g/l
I	B1	Birch	150°C, 130 min (90 min at target T)	Original extract	3.3	15.6	3.2	-	9.0 ^b
I	S1	Spruce	180°C, 50 min	Permeate of the RC70PP	3.8	2.3	0.8	-	1.9 ^b
II	EP	Eucalyptus and pine	185°C, 11 min	Original extract	4.0	9.0	2.0	88	12 ^a
II	B2	Birch	170°C, 120 min	Original extract	3.3	19.2	4.1	350	29 ^a
III	B3	Birch	160°C, 40 min	Original extract	3.2	20.2	7.9	-	22 ^a
III	S2	Spruce	160°C, 40 min	Original extract	4.0	10.5	4.0	-	12 ^a
IV	B4	Birch	Main extract, collected at 30–50 min, 145–170°C	Original extract	3.3	13.9	4.4	-	22 ^a
V	S4	Spruce	170°C, 52 min	Original extract	4.1	2.6	-	22	3.6 ^a
Unpublished 1) prefiltration and 2) PCD experiments	B5	Birch	Main extract, collected from two batches at 30–50 min, 149–155°C	1) Original extract 2) Permeate of the RC70PP	3.2	7.4	3.5	-	11 ^a
Unpublished PCD experiments	S3	Spruce	Main extract, collected at 25–50 min, 145–166°C	Permeate of the RC70PP membrane	3.9	4.5	1.3	-	7.3 ^a
Unpublished adsorption, filtration and regeneration experiments	B6	Birch	Main extract, collected at 26–55 min, 140–160°C	Original extract	3.2	12.1	4.6	-	19 ^a

* method a) GC analysis for total dissolved carbohydrates, or b) anthrone sulphuric acid method for total carbohydrates (section 8.5)

8.2 Filtration equipment and membranes

8.2.1 Amicon 8400 and 8050 laboratory-scale filters

Amicon laboratory-scale filters by Millipore [Millipore (2014)] are dead-end type filter cells with a magnetic stirrer, in which pressure is adjusted and maintained by nitrogen gas. Stirring increases turbulence on the membrane surface and diminishes the influence of concentration polarisation and fouling on UF performance. In Amicon 8400, the temperature can be controlled by a heating plate under the cell (Fig. 9), but in Amicon 8050, temperature control is not possible due to the plastic material of the cell. The volume of the cell and the membrane surface area in Amicon 8400 are 350 ml and 0.004 m², and the corresponding values for Amicon 8050 are 50 ml and 0.0015 m², respectively. The maximum operation pressure for Amicon 8400 is 6 bar and for Amicon 8050 3.5 bar.

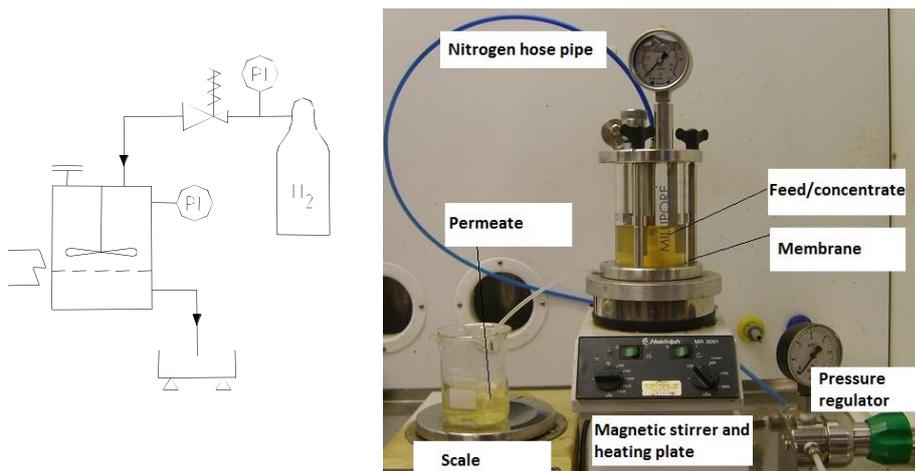


Figure 9. a) A simplified process diagram of the laboratory scale equipment (Amicon) and b) the filtration equipment: nitrogen for pressure adjustment, filter cell (Amicon 8400), magnetic stirrer and heating plate, and a scale for flux measurement.

8.2.2 CR filters

Cross-rotational (CR) filters CR200 and CR250 (Fig. 10) are plate and frame filter modules in which a blade is used to increase turbulence on the membrane surface to decrease concentration polarisation and fouling. The membrane surface areas of the filters are 0.06 m² and 0.09 m², respectively. The maximum operation pressures are 4 bar and 10 bar, respectively.

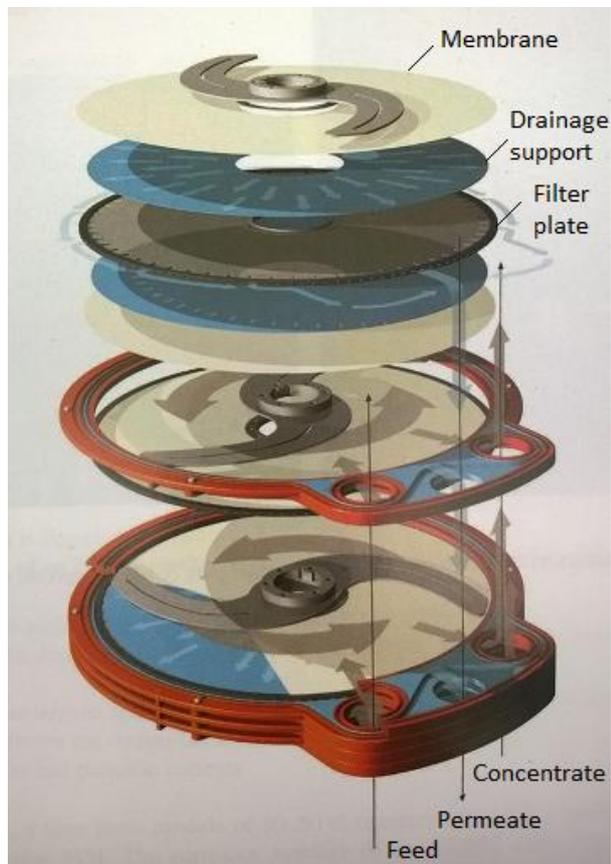


Figure 10. Structure of a CR filter. [From Metso Paper Inc. (2005)]

8.2.3 Membranes

The ultrafiltration membranes used in the experiments are presented in Table X. In the recovery of lower molecular mass hemicelluloses (< 10 kDa), UFX5pHt and UH004P were used. When the focus was on the recovery of high-molecular mass hemicelluloses, RC70PP, UC030 and UC100 were used. The material of the UFX5pHt membrane, according to the manufacturer, is polysulphone permanently hydrophilic on polypropylene. In this study this membrane is nevertheless sometimes referred to as a hydrophobic membrane due to its high contact angle (74 °) compared to the ideal hydrophilicity (contact angles below 20°) of membranes applied for wood-based solutions.

Table X Information on the ultrafiltration membranes used in the study [Alfa Laval (2014a, b), Microdyn Nadir (2014a, b)].

Membrane	Manufacturer	MWCO, kDa	pH range	Temperature range, °C	Material Skin/backing	Paper #
UFX5pHt	Alfa Laval	5	1-13	0-75	PSu/PP	I, II, IV, UP
RC70PP	Alfa Laval	10	1-10	0-60	RC/PP	I, III, V
UH004P	Microdyn Nadir GmbH	4	0-14	≤95	PESH/PP+PE	II, UP
UC030	Microdyn Nadir GmbH	30	1–11	55	RC/PET	V, UP
UC100	Microdyn Nadir GmbH	100	1–11	55	RC/PET	UP

PSu = polysulphone, PP = polypropylene, RC = regenerated cellulose, PESH = hydrophilic polyethersulphone, PE = polyethylene, PET = polyethylene terephthalate, UP = unpublished

8.3 Filtrations

The following filtration procedure was used in all experiments. Firstly, the membranes were cleaned to remove preservatives by submerging the membrane in either pure water (three times in 10 min) or a 0.01% NaOH solution (15 min). If water was used, the cleansing was enhanced by placing the decanter glass containing the membrane piece and water in an ultrasonic bath. Finally, the membrane piece was rinsed with pure water.

Pure water fluxes (PWF) were measured before and after each filtration. The temperature and pressure depended on the equipment and the membrane. The membrane piece was changed for a new one between every experiment.

In the filtration of the extracts, a target VRF was chosen depending on the equipment and the volume of the feed solution. The same target VRF was used for each set of experiments. The target VRF was not achieved in every filtration, for example with some of the original extracts, as in some cases it was impossible to carry on the filtration as far as wanted due to a rapidly decreased flux. Samples were collected from the feed, permeate and concentrate. The filtrations were carried out at 55–60°C.

8.4 Pretreatments

The pretreatment step in the recovery process of hemicellulose in the simplest case is located between PHWE and UF (Fig. 11). All pretreatment methods used in this study are presented in Tables XI and XII. In some cases, before these experiments, smaller-scale experiments were conducted to choose the conditions, e.g. phase ratios (p.r.) in the adsorption experiments. The pretreatment methods were chosen on the basis of their potential to decrease the amount of foulants, which was discussed for some of the methods in the literature part of this study.

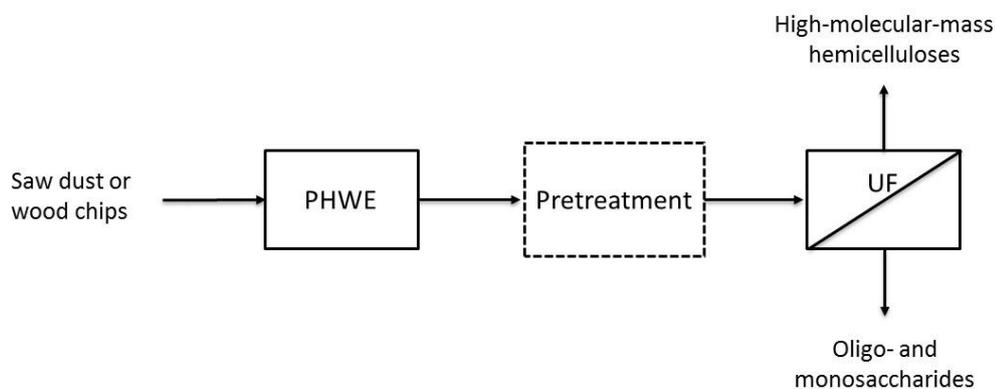


Figure 11. The recovery process of hemicelluloses including pressurised hot water extraction, pretreatment (for UF) and ultrafiltration.

Table XI Used pretreatment methods based on removal of foulants.

Pretreatment	Membrane prefiltration	Extraction	Adsorption	Adsorption	Adsorption	Adsorption
Pretreatment aid (manufacturer)	RC70PP, UC030, or, UC100 before UFX5pHt	Ethyl acetate	Activated carbon, granulated	Activated carbon, aldrich	Bentonite, powder (Hydrocol)	XAD16 and XAD7 (Rohm & Haas)
Phase ratio	-	3	1) 0.04 2) 0.2	0.018	0.05	0.15
t, min	60	30	1) 30 2) 180	20	60	60
T, °C	-	RT*	1) RT* 2) 60	160	60	60
Separation prior to membrane filtration	-	Centrifugation 5 minutes 2200 rpm	1) What-man Glass Microfibre filter (GF/F 70 Ø) 2) (S&S 604 Rund-filter)	Vacuum filtration (S&S 5893)	Centrifugation 15 minutes 20000 rpm	Vacuum filtration (S&S 604 Rundfilter)

RT*: Room temperature

Table XII Used pretreatment methods based on degradation, and, combination of degradation and removal of foulants.

Pretreatment	Enzymatic oxidation	Enzymatic oxidation + adsorption	Oxidation	Oxidation			
Pretreatment aid (manufacturer)	Laccase (Novozym 51003)	Laccase + activated carbon	Laccase + bentonite	Laccase + XAD16	PCD; electric pulse creating oxidative species	TiO ₂ + UV radiation with mercury lamp	
Phase ratio	0.01	0.01; 0.2	0.01; 0.1	0.01; 0.15	-	5 g/l	
t, min	180	60 (E) + 60 (AC)	60 (E) + 30 (Bento)	60 (E) + 60 (XAD16)	0-65 corresponding 0-4.68 kWh/m ³ (feed 100 kg), and 0-120 = 0-10 kWh/m ³ (feed 40 kg), and 45 = 4.7 kWh/m ³ (feed 100 kg)	6 h	
T, °C	60	60	60	60	RT	RT	RT
Separation prior to membrane filtration	Centrifugation 10 min 3500 rpm	Vacuum filtration (S&S 604 Rundfilter)	Centrifugation 15 minutes 20000 rpm	Vacuum filtration (S&S 604 Rundfilter)	-	Centrifugation 30 min 2200 rpm	

RT* Room temperature

8.4.1 Regeneration of adsorbents for reuse

Regeneration experiments were carried out for a commercial polymeric adsorbent (XAD16) with 0.2 and 1 M NaOH and a 1:1 water-ethanol solution. The regeneration test set (Fig. 12) included adsorption with a virgin adsorbent, regeneration, adsorption (regenerated adsorbent + original extract), and this was continued until four regenerations and five adsorptions were completed.

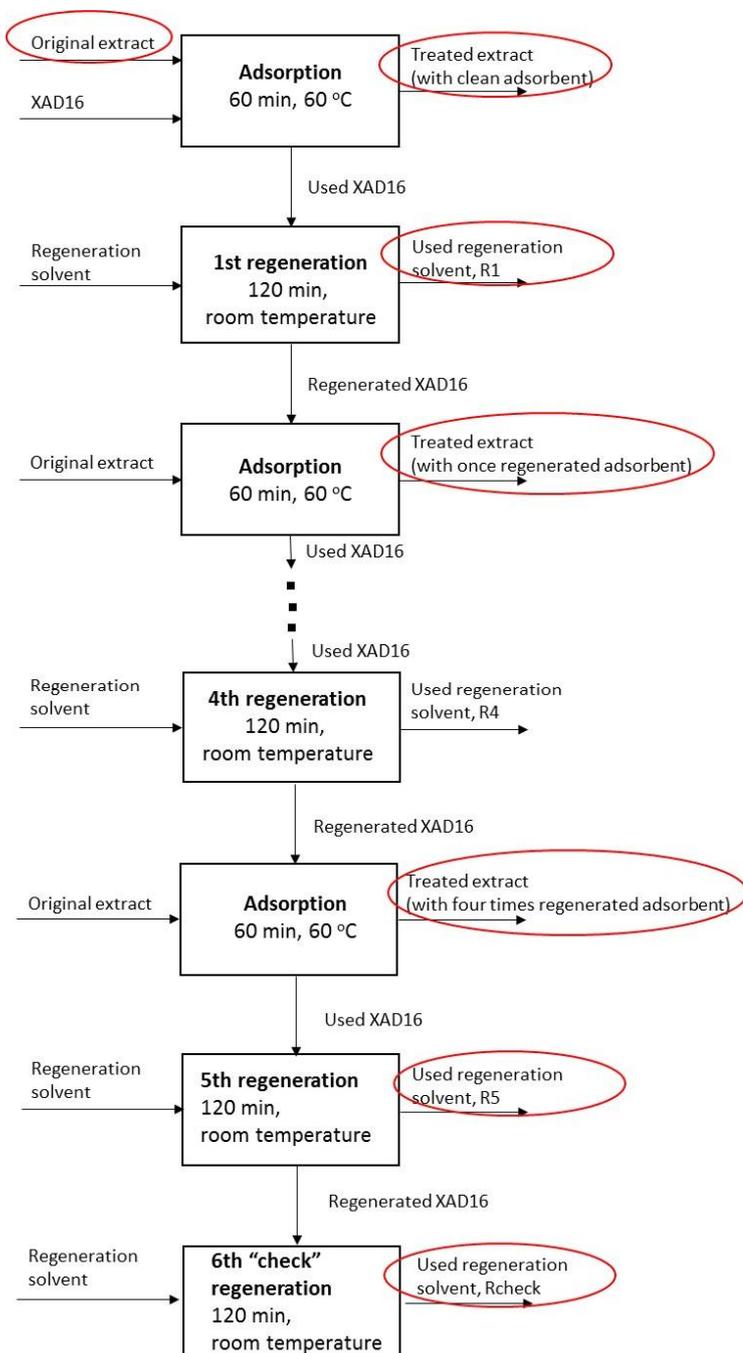


Figure 12. The adsorption-regeneration test set including a total of five adsorptions and five + one “check” regenerations. The fractions circled in red were further examined; extracts for filtration and analysis, solvents for analysis.

The same XAD16 adsorbent cycled through the whole test set, but the original, untreated extract was always used in the adsorption steps. The set was completed with a final adsorption. The effect of the regeneration was evaluated by the effect of the following adsorption, which was evaluated by UV absorbance measurements and ultrafiltration of the extract. After the actual regeneration test sets, the used adsorbents were regenerated a fifth and sixth time to observe whether the adsorbed solutes were accumulated on the adsorbents due to incomplete solvent desorption. Regeneration solvents from the first, fifth, and sixth check regeneration were analysed. In the UV analysis, the solvent samples were diluted with 0.2 M NaOH to avoid precipitations, and UV absorbance was measured at 280 nm.

The adsorbent-to-extract ratio was 0.05 (700g of extract and 35 g of adsorbent) and the adsorption time 60 min at 60°C with 500 rpm mixing. The adsorbent was separated from the extract by vacuum filtration (S&S 604 Rundfilter) and rinsed with 100 ml of pure water. A total of 500 ml of regeneration solution was added to the rinsed adsorbent and mixed at room temperature at 500 rpm for 120 min. After that, the adsorbent was separated as after the adsorption step and rinsed with 100 ml of pure water.

8.5 Analysis

The methods and equipment used in the analysis of the samples collected in the pretreatment and filtration experiments are presented in Tables XIII and XIV. The samples were stored in a freezer or for short times in a refrigerator if they were not analysed immediately after the experiments. In the experimental part, hemicelluloses are discussed as 'carbohydrates' due to the analysis, which degrades hemicellulose chains into monomers before quantitative measurement. It is, however, justified to categorise the hemicelluloses as carbohydrates in terms of content as there were not many free monomers in the extracts before the degradation in the analysis step. The amount of monomers in the extracts used in this study was approximately 10% of the total carbohydrates.

Table XIII Analysis methods and equipment.

Analysis	Method	Equipment
pH	-	Metrohm 744 pH meter, 25°C
Conductivity	-	Knick konduktometer 703, 25°C
Turbidity	ISO Method 7027	Hach 2100 AN IS Turbidimeter, 25°C
Total organic carbon (TOC)	-	Shimadzu TOC 5050A analyser and ASI 5000A autosampler, Shimadzu TOC-L analyser and ASI-L autosampler, 680°C, the carrier gas: high purity air 150 l/min, 2 parallel samplings, deviation < 2%
a) Total dissolved carbohydrates	a) Gas chromatography (GC) after acid methanolysis + silylation according to Sundberg et al. (1996)	a) Agilent HP6890 and injector HP7683
b) Total carbohydrates	b) Anthrone sulphuric acid method with glucose standard	b) Varian Cary 1C UV-Visible Spectrophotometer
Monosaccharides	GC after silylation	Agilent HP6890 and injector HP7683
Hydroxyl/ carboxyl acids	Analysis by capillary electrophoresis according to Rovio et al. (2010)	Beckmann-Coulter P/ACE MDQ CE equipment with a photodiode array UV/Vis detector (281 nm)
Acid soluble lignin	Tappi Useful Method 250 [TAPPI (1991)]	Varian Cary 1C UV-Visible and Jasco V-670 Spectrophotometers
UV 280 nm (lignin)	Part of the samples analysed after Methyl tert-butyl ether (MTBE) extraction (Paper V)	Varian Cary 1C UV-Visible Spectrophotometer, PG Instruments Ltd. T80 UV/VIS Spectrometer
Contact angle	Sessile drop method	KSV CAM 100 Contact Angle Meter and computer programme CAM 2008
Wood extractives	Analysis by GC from silylated samples according to Puro et al. (2011)	Agilent HP6890 and injector HP7683
Total dry solids (TDS)	Freeze-drying	Christ, Alpha 2-4 LD Plus

Table XIV Used molecular mass analysis methods and equipment.

Analysis	Method	Equipment
Molecular mass of lignin	a) High performance size-exclusion chromatography (HPSEC)	a) Agilent 1100 series (Hewlett-Packard), Agilent UV (280 nm) absorbance detector and the Superose 12 (10/300 GL) column (GE Healthcare)
	b) Size-exclusion chromatography (SEC)	b) Waters 600E, a Waters 486 UV (280 nm) absorbance detector and a column packed with 30 cm of Superdex 30 and 30 cm of Superdex 200 (GE Healthcare)
	c) HPSEC	c) Waters Ultrahydrogel 250 and 120, 7.8x300 mm, and Quard, 6x40mm columns, and Waters 2998 Photodiode Array detector (UV 280 nm)
Molecular mass of carbohydrates	a) SEC	a) A column packed with 30 cm of Superdex 30 and 30 cm of Superdex 200 (GE Healthcare) + Waters 600E, a Waters 2414 RI detector
	b) HPSEC	b) Waters Ultrahydrogel 250 and 120, 7.8 x 300 mm, and Quard, 6x40mm columns + Waters 2414 RI detector
	c) HPSEC	c) Waters UltrahydrogelTM linear 300 mm x 7.8 mm column (Waters, Milford, USA) + Multi-angle laser light scattering (MALLS) detector (miniDAWN, Wyatt Technology) and RI detector (Shimadzu Corporation)

8.6 Calculations

The permeate flux, J , during the filtration was calculated by using Eq. (1):

$$J = \frac{m_p}{A_m t}$$

where m_p is the mass of the permeate, kg

A_m is the membrane surface area, m²

t is time, h.

In some cases, the temperature of the feed solution was not completely stable, and the impact of temperature on viscosity Eq. (2), and therefore, on flux Eq. (3) was decreased by using a temperature correlation. [Coulson and Richardson (1992)]

$$\eta_T = \frac{100}{2.1482 \cdot \left[(\theta - 281.435) + \sqrt{8078.4 + (\theta - 281.435)^2} \right] - 120}$$

where η_T is the viscosity of water at temperature T, mPas

θ is the temperature, K

$$J_T = J_m \cdot \frac{\eta_m}{\eta_T}$$

where J_T is the corrected flux at temperature T, kg/(m²h)

J_m is the measured flux, kg/(m²h)

η_T is the viscosity of water at temperature T, mPas

η_m is the viscosity of water at measuring temperature, mPas.

The flux values of the pretreated extracts were compared to the value of the original, untreated extract. The flux increase, which was calculated with Eq. (4), describes how much the pretreatment increased the filtration capacity.

$$\text{Flux increase} = \frac{J_{\text{pretreated}} - J_{\text{original}}}{J_{\text{original}}} \cdot 100\%$$

where $J_{\text{pretreated}}$ is the average flux of the pretreated extract, kg/(m²h)

J_{original} is the average flux of the original extract, kg/(m²h).

Pure water flux reduction, PWF_r , which was used in the evaluation of fouling, was calculated with Eq. (4):

$$PWF_r = \frac{PWF_b - PWF_a}{PWF_b} \cdot 100\%$$

where PWF_b is the pure water flux before filtration, kg/(m²h)

PWF_a is the pure water flux after filtration, kg/(m²h).

Permeability, P , which takes operational pressure into account in the evaluation of the filtration capacity, was calculated with Eq. (5):

$$P = \frac{m_p}{A_m \cdot t \cdot p}$$

where p is the transmembrane pressure, bar.

Relative permeability, P_{rel} , was used to decrease the error originating from the heterogeneity of the membrane matrix when the effect of pretreatment on the filtration performance of the membrane was evaluated. P_{rel} was calculated using Eq. (6):

$$P_{Rel} = \frac{P}{PWP}$$

where PWP is pure water permeability, kg/(m²h bar).

Observed retention, R_{obs} , was calculated with Eq. (7):

$$R_{obs} = \left(1 - \frac{c_p}{c_f}\right) \cdot 100 \%$$

where c_p is concentration in permeate, g/l

c_f is concentration in feed, g/l.

The volume reduction factor, VRF , describes how much the feed volume is reduced by filtration. The densities of different fractions were approximately equal, and therefore the VRF could be calculated by using masses of the fractions instead of volumes. VRF was calculated with Eq. (8):

$$VRF = \frac{V_f}{V_c} = \frac{V_f}{V_f - V_p} \approx \frac{m_f}{m_f - m_p}$$

where V_f is the volume of the feed solution, m³

V_c is the volume of the concentrate, m³

V_p is the volume of the permeate, m³

m_f is the mass of the feed solution, kg.

The amount of acid-soluble lignin (ASL), was calculated from UV (205 nm) absorbance with Eq. (9):

$$ASL = \frac{A_{205} \cdot f}{a \cdot l}$$

where A_{205} is absorbance at 205 nm, -

f is the dilution factor, -

a is absorptivity (110 as an average for all wood species), l/(g cm)

l is the path length, cm.

Equations relating to the optimisation of the amount of adsorbent are presented in Paper II. Principal component analysis (PCA) was used to interpret the data and to find possible correlations between the variables, i.e. flux, PWF_r, the amount of lignin, carbohydrates and wood extractives, and the molecular masses of the ligneous compounds and hemicelluloses. The procedure and related equations are described in Paper IV.

9 RESULTS AND DISCUSSION

The results and discussion part of this thesis focuses on the pretreatment methods to improve filtration capacity and decrease fouling in the UF of wood extracts. In an ideal case, pure high-molecular mass hemicelluloses can be concentrated by UF, whereas lignin and wood extractives, which have not been removed by pretreatment, would be collected in the permeate fraction. The most potential methods among all the tested ones are chosen and studied more intensively. The ability of pretreatment to increase flux and decrease fouling, selectivity to foulants over hemicelluloses, and effects on molecular mass distribution in the wood extract are discussed. The selectivity of the pretreatment method directly influences the purity of the produced hemicellulose fraction, which, depending on the final product, could be a crucial factor together with the molecular mass of concentrated hemicelluloses.

The flux behaviour presented in Fig. 13 is typical for the concentration of wood extracts by ultrafiltration, as the flux declines when the filtration progresses, due to concentration polarisation and/or fouling. In some cases, however, the flux decline is remarkably rapid, and the initial flux may already be very low, making the filtration process impossible. This behaviour can be seen especially in the birch extract (batch B2) (Fig. 13). Generally, the flux decrease can result from several factors, such as CP, pore plugging and adsorptive fouling, but also increasing viscosity, molecular masses and osmotic pressure can decrease the flux [Dal-Cin et al. (1996), Song (1998), Wang and Tarabara (2008)]. Filtration capacity depends, therefore, also on other things than fouling, which in some cases have to be examined separately. The pure water flux reduction (PWF_r) provides information on fouling more directly, which is a more permanent change in the operability of the membrane.

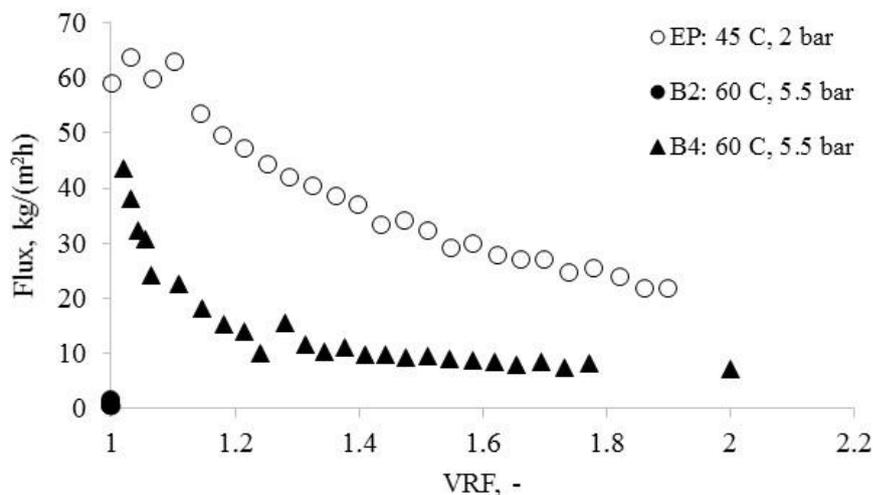


Figure 13. Eucalyptus-pine EP and birch extracts B2 and B4 (description in Table IX) filtered with the UFX5pHt membrane at varying conditions with Amicon filter cells.

The filtration performance depends on several factors including concentration, composition and molecular mass of the polymeric compounds in the extracts, the membrane used and filtration conditions. The composition of different wood extracts is presented in Table IX in section 8.1. The composition depends on the wood species and extraction conditions. For example, the flux of the eucalyptus-pine extract, which is a mixture of hardwood and softwood extracts, is higher than the flux of the birch extract, which is a pure hardwood extract, even though the pressure is lower in the filtration of the eucalyptus-pine extract. However, also the fluxes of the birch extracts made at different extraction conditions differ from each other. Although pulp and paper process waters differ from wood extracts, their composition also varies according to the original wood species. Softwood extracts and process waters have been reported to be less fouling than hardwood process waters in UF [Kallioinen et al. (2013), Puro et al. (2010)]. It is, however, difficult to explain the filtration capacity on basis of the extract analysis results alone.

Multivariate examination, and more specifically principal component analysis (PCA), was used to show the influence of the characteristics of birch extract B4 on the filtration performance of the UFX5pHt membrane (Paper IV). The results showed that in addition to the total concentration of lignin or carbohydrates in the treated wood extract, also their size had a significant effect on the filtration capacity. Compounds in certain size ranges had a clearly negative effect on the permeate flux (Table XV). Other compounds were classified to have a “less negative” effect on the flux. Both the ligneous and hemicellulosic compounds, having a negative impact on filtration capacity, seemed to be small enough to penetrate the 5 kDa

membrane skin layer. A pretreatment method should thus remove or degrade these especially harmful compound sizes rather than focus on the total removal of harmful compounds.

Table XV Effect of MM on the average flux in the filtration of birch extract B4 with the UFX5pHt membrane at 60°C, 5.5 bar and rotor tip velocity 1.6 m/s with an Amicon filter cell.

MM range		Effect on flux
RI detected compounds	UV detected compounds	
Mono- and disaccharides	< 0.05 kDa	Less negative
Oligo- and polysaccharides	0.2-0.8 kDa	Negative
Polysaccharides >7.4 kDa	>1 kDa	Less negative

The membrane material and cut-off have a significant impact on the filtration performance. The flux decline during the filtration of birch extract B1 was much more dramatic with the UFX5pHt membrane than with the RC70PP membrane (Fig. 14). In the case of birch extract B2, both the UFX5pHt and the UH004P membranes gave extremely low filtration capacities. The hydrophilic RC70PP membrane experienced less fouling than the hydrophobic UFX5pHt membrane based on PWF_f values: 14% and 84%, respectively, in the filtration of birch extract B1. Contact angles for the UFX5pHt, the UH004P and the RC70PP membranes were 74°, 68° and 13°, respectively, which emphasises the difference between the hydrophobicity of these membranes, hydrophobic membranes giving higher contact angle values than hydrophilic ones. The cut-off values of the UFX5pHt, the UH004P and the RC70PP membranes are 5, 4 and 10 kDa, which also affected the filtration performance. For instance, the size of harmful compounds for the 10 kDa RC70PP membrane is probably different than for the 5 kDa UFX5pHt membrane discussed above.

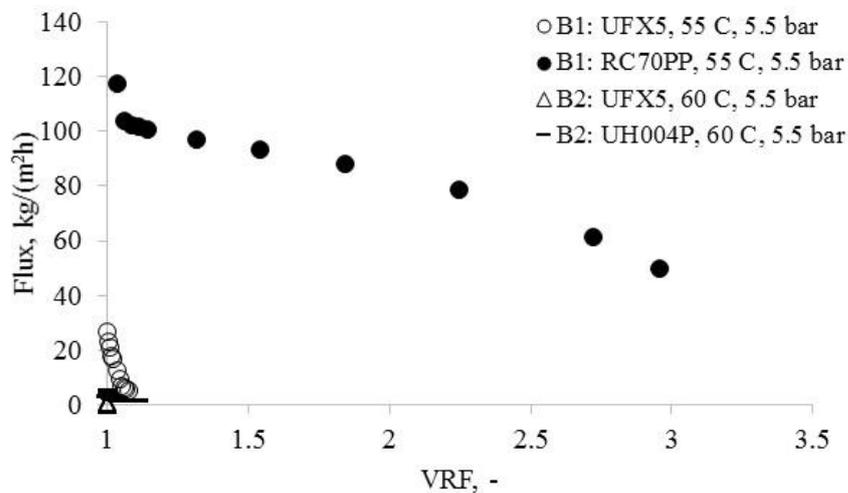


Figure 14. Birch extracts filtered with an Amicon filter cell and different membranes; B1 with the UFX5pHt and the RC70PP at 55°C and 5.5 bar, and, B2 with the UFX5pHt and the UH004P at 60°C and 5.5 bar and rotor tip velocity 1.6 m/s.

The UF of wood extracts depends strongly on the extract properties but also on the membrane used. With low cut-off hydrophobic membranes, the filtration capacities are low and fouling high. Thus, pretreatment is needed to improve the filtration performance.

9.1 Screening of potential pretreatment methods

Prefiltration

Membrane prefiltration would be a convenient pretreatment method, as it does not involve additional chemicals or high energy consumption, and it could be easily combined with the further filtration step with a tighter UF membrane. Thus, membrane prefiltration was tested with a set of UF membranes and cut-offs for the original birch extract (B5) (Fig. 15).

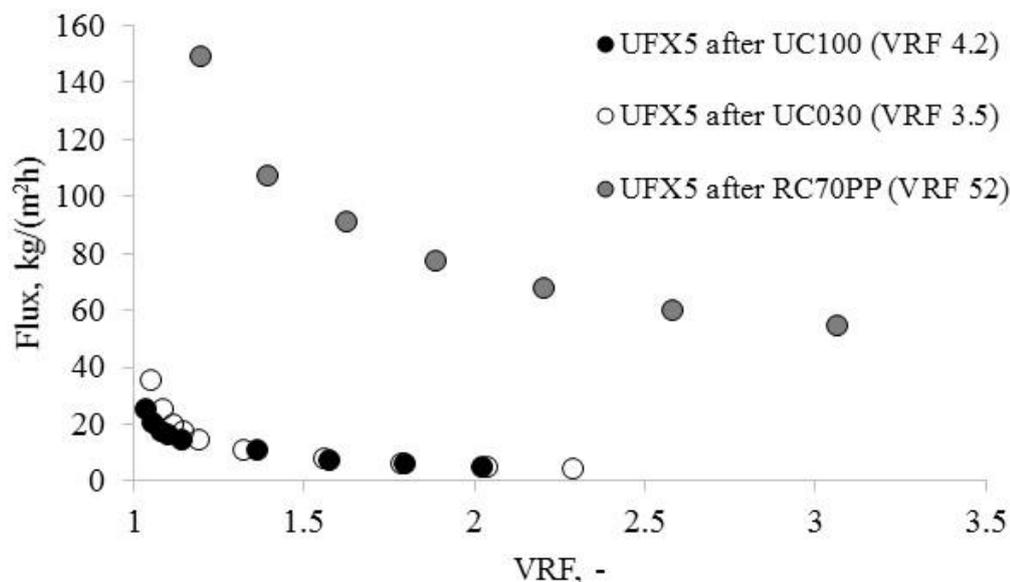


Figure 15. Permeate flux in the filtration of the original birch extract B5 with an Amicon filter cell and the UFX5pHt membrane at 60°C and 5 bar and rotor tip velocity 1.6 m/s after prefiltration with three different UF membranes: UC100, UC030 and RC70PP.

After filtration with the UC100 (100 kDa) and the UC030 (30 kDa) membranes, the flux of the UFX5pHt membrane was still remarkably low (Fig. 15), but after the RC70PP membrane (10 kDa), the flux of the UFX5pHt membrane was significantly higher. The cut-offs of the UC100 and the UC030 membranes were too high to reject enough harmful compounds from the extract. Lignin removal with both membranes was around 20%, which did not have a noticeable impact on the flux (Table XVI). Lignin removal with the RC70PP membrane was 62%. In addition to lignin, also the amount of carbohydrates was decreased by prefiltration. The carbohydrate removal was roughly the same, over 40%, with all the membranes despite the large differences in the cut-offs of the prefiltration membranes. This is possibly due to a certain part of carbohydrates that are rejected by all the membranes because of their size or their linkage to lignin.

Table XVI Fouling, average fluxes and VRF values in prefiltrations of birch extract B5 and following filtrations with the UFX5pHt membrane, and removal of lignin and carbohydrates in prefiltration.

Filtration	PWF_r, %	VRF, -	Flux, kg/(m²h)	Lignin removal, %	Carbohydrate removal, %
UC100	15	4.2	36	24	41
UFX5pHt after	91	2.0	13	-	-
UC030	12	3.5	35	19	46
UFX5pHt after	77	2.3	14	-	-
RC70PP	-	52	-	62	46
UFX5pHt after	58	3.0	86	-	-

The PWF_r was rather high (58%) with the UFX5pHt membrane after prefiltration with the RC70PP membrane, which implies that if the filtrations were continued further than in this case (VRF 3), fouling could have become an even greater issue. After the UC100 and the UC030 membranes, the PWF_r with the UFX5pHt membrane was 91 and 77%, respectively. Based on these results, fouling seems to be more dependent on the amount of lignin than on the amount of carbohydrates.

In contrast to this study, Sainio et al. (2013) found prefiltration with the UC030 membrane to be sufficient to enable the filtration of pine extract with the UFX5pHt membrane. However, they conducted the prefiltration at 25°C, which is, according to Kallioinen et al. (2011), more favourable than prefiltration at 70°C if the UFX5pHt membrane is used as the second membrane. At higher temperatures, the compounds that foul the UFX5pHt membrane are not rejected by the UC030 membrane, whereas at lower temperatures, the foulants are in such a form that the UC030 membrane rejects them more efficiently. In addition, the extract in the study of Sainio et al. was made from pine, which means that its characteristics may differ substantially from the birch extract used in this study. The lower temperature in the prefiltration step could have been more efficient also in this study. However, higher filtration temperatures were chosen to make the process more fluent. More energy and time is consumed if the extract has to be cooled down for prefiltration after extraction and then heated again for the second stage filtration.

Prefiltration with a higher cut-off membrane than the one in the actual concentration filtration removes large compounds from the solution. This probably decreases the concentration polarisation, which can be seen positively in the filtration capacity. However, prefiltration might not remove such smaller compounds which, in multivariate examination, were revealed to decrease the filtration capacity of the UFX5pHt membrane most (Table XV). In addition, prefiltration alone was not adequate to remove foulants from the extract in such amounts that they would not be a problem in the hemicellulose fraction as impurities. Therefore, also other pretreatment methods were studied.

Other pretreatment methods

Pretreatment methods based on adsorption, extraction and oxidation were studied and compared to prefiltration. The pretreatments were evaluated by their effect on the filtration capacity (Fig. 16) and fouling (Table XVII). The purpose of the screening was to find out whether the method had potential or not.

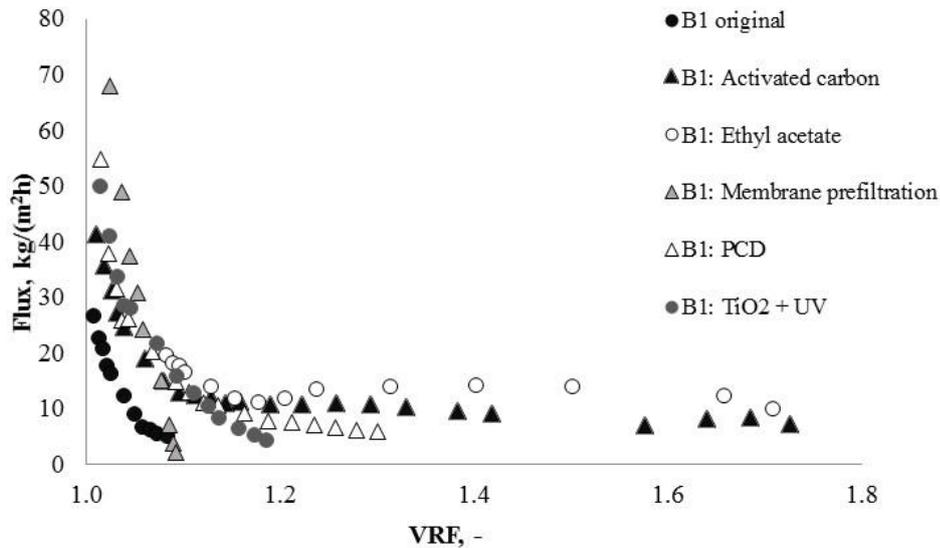


Figure 16. Birch extract B1 after pretreatment filtered with an Amicon filter cell and the UFX5pHt membrane at 55°C and 5.5 bar and rotor tip velocity 1.6 m/s.

Table XVII Pure water fluxes before and after filtration of the birch extract (B1), and calculated pure water flux retentions for each pretreatment case, average and initial fluxes and achieved VRF values.

Pretreatment	PWF _b , kg/(m ² h)	PWF _a , kg/(m ² h)	PWF _r , %	Initial flux*, kg/(m ² h)	VRF, -
Original	189	30	84	26	1.1
Activated carbon	152	121	20	41	1.7
Ethyl acetate	170	48	72	-	2.9
Membrane prefiltration	196	188	4	68	1.1
PCD	207	185	11	55	1.3
TiO ₂ + UV	151	156	~0	50	1.2

* Initial flux = flux at 1 min

All pretreatments increased the flux and decreased fouling according to PWF_r (Fig. 16, Table XVII). However, there were differences between the achieved VRF values due to differences in the flux decline during filtration. All the other pretreatments enabled a higher VRF value in

UF except membrane prefiltration. Although fouling was minimal after membrane prefiltration and the initial flux was remarkably high, the flux decreased fast. Therefore, low fouling does not guarantee a high flux and a high VRF. Extraction with ethyl acetate was the least efficient in decreasing fouling. However, the removal of ethyl acetate from the extract by centrifugation was not complete, and based on visual observations, the presence of ethyl acetate in the feed solution caused deterioration of the membrane surface, which probably had an impact on the PWF_a value.

The otherwise promising extraction with ethyl acetate was rejected due to the incomplete removal of ethyl acetate from the extract by simple methods in laboratory scale. In addition, extraction would increase chemical consumption, which is not intentional. Adsorption and oxidation were chosen for further studies, because they proved their potential in improving the filtration capacity, and they did not involve laborious process steps before filtration. The adsorption studies covered also other adsorbent materials than activated carbon. Oxidation was focused on methods which did not include any separation steps after the oxidation or expensive and un-ecological chemical consumption.

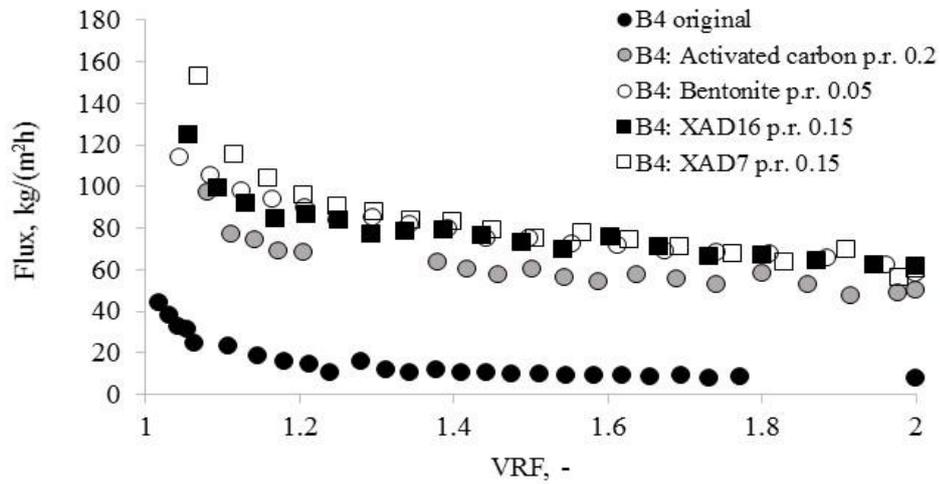
9.2 Adsorption

The possibility to improve the filtration capacity and decrease membrane fouling with adsorption was further studied by using activated carbon, polymeric XAD adsorbents and bentonite. These adsorbents were chosen on the basis of their reported capability to remove lignin and phenolic compounds [Westerberg et al. (2012), Willför et al. (2003a), Banat et al. (2000), Parajó et al. (1996)]. Bentonite was seen as an interesting adsorbent material also due to its natural origin.

Adsorptive pretreatment improved the filtration capacity and decreased fouling, according to PWF_f values, in the UF of the different wood extracts (Fig. 17, Table XVIII). The most remarkable improvement was achieved with XAD adsorbents in the case of birch extract B2 with membrane UH004P, where the average flux was increased from nearly zero to as high as 107 and 175 kg/(m²h) by pretreatment with XAD16 and XAD7 adsorbents, respectively. Also in the case of birch extract B4, the average flux was increased by over 400% by pretreatment with XAD adsorbents and bentonite. Fouling was also decreased the most, from 90% to 0–6 % by XAD adsorbents in the case of birch extract B2 with membrane UH004P. Although fouling was decreased by all the adsorbents, in birch extract B4, fouling remained a problem, especially when XAD adsorbents were used. AC and bentonite were clearly more efficient than XAD adsorbents in decreasing the fouling of the UFX5pHt membrane in the filtration of birch extract B4. When the XAD adsorbents were compared with each other, XAD7 decreased fouling more efficiently than XAD16 in all cases.

With the birch and spruce extracts (B3 and S2) which were filtered with the RC70PP membrane and pretreated by AC, an increase in flux and a decrease in fouling were achieved, although these values were at a good level already in the untreated extracts due to the low fouling tendency of the RC70PP membrane (Table XVIII). The focus of AC treatment in the cases of birch B3 and spruce extract S2 was to produce pure hemicellulose fractions by removing lignin at the extraction temperature before UF, and decreasing the already substantially low fouling was an additional advantage.

a)



b)

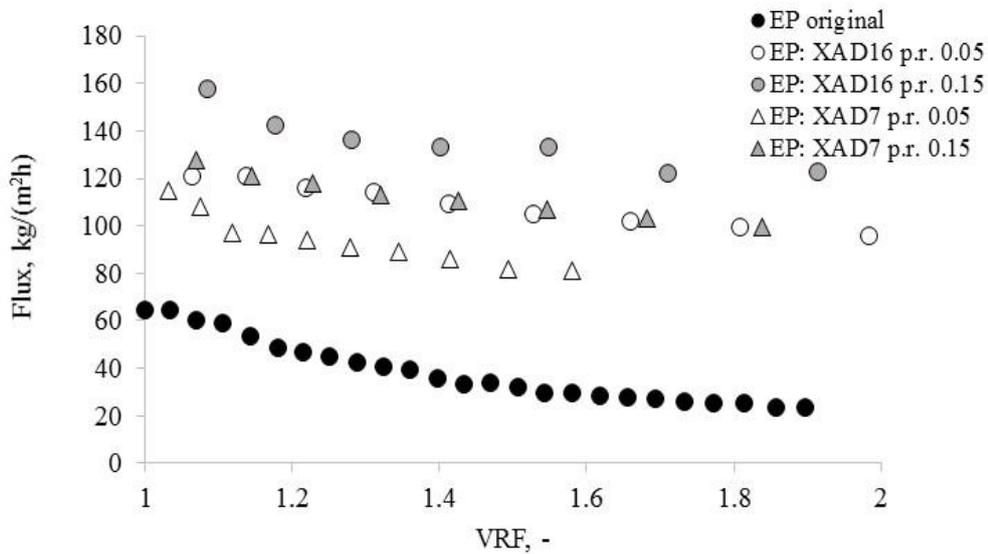


Figure 17. Permeate flux in the filtration of a) birch extract B4 at 60°C and 5.5 bar and b) the eucalyptus-pine extract (EP) at 45°C and 2 bar and rotor tip velocity 1.6 m/s with an Amicon filter cell and the UFX5pHt membrane after pretreatment with adsorbents. Original refers to the untreated extract, and p.r. means adsorbent to extract phase ratio in the adsorption.

Table XVIII Effect of adsorptive pretreatment methods on filtration capacity with different membranes and extracts.

Method	Related to Paper #	Extract	Flux (Original extract), kg/(m ² h)	Flux (Pretreated extract), kg/(m ² h)	PWF _r (Original extract), %	PWF _r (Pretreated extract), %	Membrane
XAD16 (p.r. 0.15)	II	EP	38	135	36	10	UFX5pHt
XAD7 (p.r. 0.15)	II	EP	38	112	36	1	UFX5pHt
XAD16 (p.r. 0.15)	II	B2	2	107*	90	6	UH004P
XAD7 (p.r. 0.15)	II	B2	2	175	90	~0	UH004P
XAD16 (p.r. 0.15)	IV	B4	15	78	83	63	UFX5pHt
XAD7 (p.r. 0.15)	IV	B4	15	79	83	53	UFX5pHt
AC (p.r. 0.2)	IV	B4	15	61	83	24	UFX5pHt
AC (25 g/l ≈ p.r. 0.025)	III	B3	79	126	17	8	RC70PP
AC (25 g/l ≈ p.r. 0.025)	III	S2	93	145	17	8	RC70PP
Bentonite (p.r. 0.05)	IV	B4	15	79	83	35	UFX5pHt

* PWF_r in the case of XAD16 treated birch extract (B2) was smaller than in the cases of the original birch extract (B2) and XAD7 treated birch extract (B2).

p.r. adsorbent to extract phase ratio

Adsorption affected the extract composition strongly, which could already be seen as a colour change in the extract (Fig. 18). This indicates that adsorption removed compounds which give the colour to the extract. E.g. lignin is such a compound. A more detailed analysis revealed that the amounts of lignin and wood extractives in the extracts decreased significantly (Fig. 19). However, the adsorbents also removed carbohydrates from the extracts. XAD adsorbents removed foulants most effectively, but they also caused the highest hemicellulose losses.

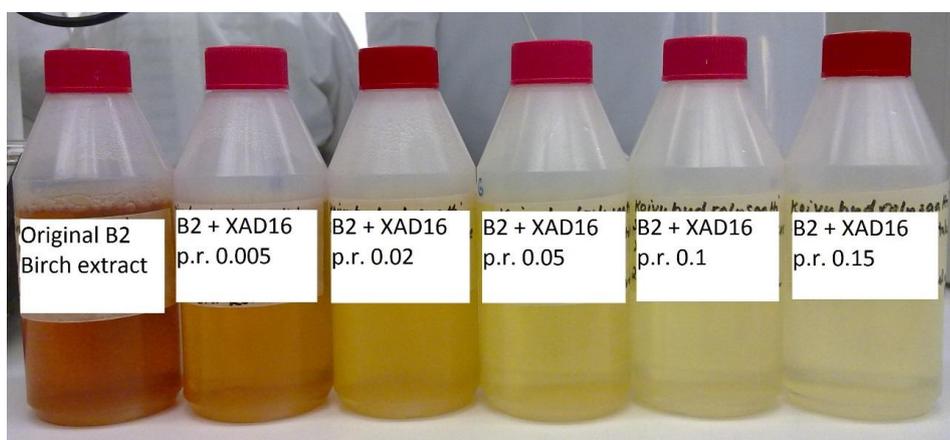


Figure 18. Visible change of birch extract B2 after adsorption with the XAD16 adsorbent at several phase ratios (p.r.).

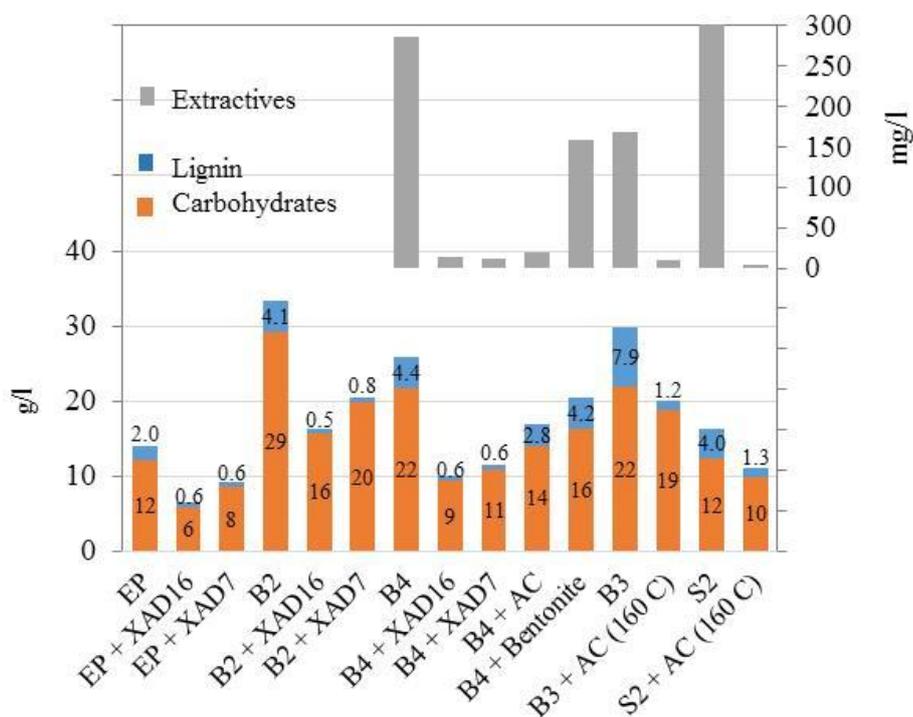


Figure 19. Compositions of eucalyptus-pine extract EP, birch extracts B2, B4 and B3, and spruce extract S2 before and after adsorption with different adsorbents.

The amount of lignin in the extracts was decreased most by adsorption on polymeric XAD adsorbents at 60°C and activated carbon at 160°C (Table XVIV). Adsorption on AC at 60°C led to lower removal of lignin. However, bentonite was clearly the least efficient in lignin removal. Polymeric adsorbents and AC also removed over 90% of the wood extractives in all the cases where they were measured, whereas bentonite removed 45% of the wood extractives (Fig. 19).

An adsorption isotherm for the XAD16 adsorbent and birch extract B2 presented in Paper II revealed that lignin was adsorbed on multilayers, which means that the adsorbent can still remove more lignin after its surface has been covered with lignin. This is certainly a great advantage because the adsorption capacity is not restricted by the surface area of the adsorbent but the capacity can be unlimited, in theory. This partly explains the high removal of lignin by the XAD adsorbents (Table XVIV). The adsorption isotherms were not determined for other adsorbents, and therefore it is not certain if the adsorption behaviour would be similar.

Adsorption removed also carbohydrates from the extracts, although it was not the purpose (Table XVIV). Against presumptions based on adsorbent materials, the removal of carbohydrates by the XAD adsorbents was significant, XAD16 causing regularly higher carbohydrate losses than XAD7. These XAD adsorbents should be, according to the

manufacturer, applicable to adsorbing e.g. non-polar (hydrophobic) compounds from polar solvents (e.g. aqueous solutions) (XAD16), and to decolourisation of kraft pulp mill effluents (XAD7) [Rohm and Haas (2011) a,b]. The decolourisation of wood-based solutions includes the removal of ligneous compounds.

The results of this study are, however, in line with results of other researchers who have reported on carbohydrate losses during the adsorption of lignin from wood-based solutions (Table XVIV). Thus, although polymeric adsorbents and AC seem to favour the adsorption of lignin more than that of carbohydrates, carbohydrate losses are difficult to avoid completely. In spite of the carbohydrate losses, the purity of the extract was improved in all the cases where the lignin removal was higher than the carbohydrate removal, i.e. with all the adsorbents except bentonite.

Bentonite differed from the other tested adsorbents because it did not remove lignin practically at all, but the carbohydrate removal was much greater. This means that bentonite treatment as such is not selective to lignin over hemicelluloses, but on the contrary selective to hemicelluloses, probably due to the weak organophilicity of unmodified bentonite. According to Suzuki (1993), there are polar hydroxyl groups in the bentonite structure. These groups which attract hydrophilic hemicelluloses might be sterically more approachable than cations inside the bentonite structure attracting negatively charged lignin.

Table XVIV Carbohydrate losses reported to occur, and obtained in this study, during removal of lignin from wood-based solutions by adsorption.

Adsorbent	XAD4	AC	AC	XAD16 and XAD7	AC	Bentonite
Feed solution	HW extract	Almond shell hydrolysate	Wood hydrolysate	Wood extracts	Wood extracts	Wood extract
Lignin removal, %	90	64	85	68–87	1) 36 2) 68–85	4
Carbohydrate loss, %	26–56	21	No significant carbohydrate losses	30–57	1) 35 2) 14–20	24
Noteworthy observations	Retained sugars were trapped inside the resin bed, or so weakly bonded with the adsorbent, that they were almost totally recovered by water wash.	-	Adsorption at high temperature (170°C) and straight after the extraction of the wood. With increased amount of AC and removal of lignin, also carbohydrates were lost.	-	Adsorption temperatures 1) 60°C 2) 160°C	
Reference	Schwartz and Lawoko (2010)	Montané et al. (2006)	Gütsch and Sixta (2011)	This study	This study	This study

A partial explanation for carbohydrate losses with adsorbents can be the removal of LHC when carbohydrate moieties are removed via adsorption of the lignin moiety. In contrast to this assumption, according to Westerberg et al. (2012), LHCs would not be adsorbed on XAD16 as much as pure lignin. Westerberg et al. fractionated the ultrafiltered hot-water extract of spruce by the XAD16 adsorbent, which removed hydrophobic lignin and lignans following the adsorption of less hydrophobic lignin-carbohydrate complexes (LCC) on a more efficient adsorbent XBridge Phenyl, leaving the target compound, galactoglucomannan, in the solution.

In the case of AC, the adsorption temperature affected the adsorption of lignin and carbohydrates differently, the high temperature increasing the adsorption of lignin and decreasing the adsorption of carbohydrate. Although the experiments at 60°C and at 160°C differed also by the wood extract, by the state and the amount of AC used and by the adsorption time, the effect could be observed (Table XVIV). In adsorption experiments at 60°C, the AC was granular and the amount was higher than in the experiments at 160°C, in which case the

AC was powdered. The powdered state gives a larger specific surface area for AC, which compensates for the difference in the amount. Generally, an increase in temperature increases the vibrational energy of the solute, which leads to increasing desorption. This inevitably decreases the adsorption. With carbohydrates, which are rather hydrophilic and in general less charged than lignin, the effect of temperature on the adsorption on AC seems to be more conventional than with lignin. Thus, at least when AC is used, a higher adsorption temperature is profitable because it increases the wanted lignin adsorption and decreases the unwanted carbohydrate adsorption.

According to Gütsch and Sixta (2011), the arrangement of hydrophobic and hydrophilic groups in the lignin structure can be different at 170°C than at room temperature. They also suggest that the arrangement of the lignin structure at 170°C can be favourable for adsorption on AC, possibly due to chemisorption. Generally, a high temperature enhances chemisorption because it requires high activation energy. Chemisorption has been suggested as an adsorption mechanism for the adsorption of lignin onto activated carbon also by other researchers [Venkata Mohan and Karthikeyan (1997)]. Therefore, it is possible that a high adsorption temperature would increase adsorption also with other adsorbent materials than AC. However, with polymeric adsorbents, the applicable temperature range is much narrower than with AC, restricting their use in high temperatures. It is also unclear if multilayer adsorption of lignin occurs also by chemisorption. Chemisorption involves usually strong bonds which may rebound if regeneration with solvents is applied. In thermal regeneration, chemisorption is not a problem, however.

On the basis of this study, carbohydrate losses can be reduced for instance by increasing the adsorption temperature or decreasing the amount of adsorbent. The relationship between the amount of lignin and the obtained permeate flux in the UF of birch extract was examined in Paper II. This information was used for the optimisation of the amount of the required XAD16 adsorbent to achieve a certain average flux in the filtration of birch extract B2 to the VRF value of 2 with the UH004P membrane. Now that an experimental procedure to calculate the optimal amount of adsorbent has been developed, the same procedure is ready to be applied in similar cases with experimental data available. UV (280 nm) absorbing material was generalised to cover the total amount of flux reducing foulants. To find out the correlation between the amount of adsorbent and an average flux in UF in this particular case, the following procedure was developed:

- 1) Different adsorbent-to-extract ratios were used to examine the relationship between the amount of removed foulants and the achieved flux systematically.
- 2) The average flux values were measured in the filtration of the XAD16 -treated birch extract (B2) as a function of the foulant concentration in the extract, represented by UV absorbance at 280 nm, after the adsorption pretreatment. A nonlinear correlation between the permeate flux and feed solution concentration was established. The related figures and equations are presented in Paper II.

- 3) The adsorption equilibrium data, i.e. the amount of foulants adsorbed on XAD16 at a given foulant concentration in the extract at equilibrium, was correlated by using the BET isotherm model that describes the formation of multilayers on the adsorbent surface.
- 4) With the obtained equations, the material balance between foulant concentration in the extract and adsorbent could be solved to calculate the amount of adsorbent at a given average flux value.

For example, to obtain a flux of 70 kg/(m²h) in UF with the UH004P membrane, 30 kg of adsorbent is required per 1 m³ of the birch extract (B2). It was calculated that the amount of adsorbent can be reduced by multistage adsorption. For instance, to obtain the same flux of 70 kg/(m²h) in UF, the two-staged cascade saves approximately 11% and the three-staged cascade almost 15% of adsorbent when compared to a single-stage adsorption process. With higher flux values, when a greater amount of adsorbent is needed, the saving is even higher. Hemicellulose losses occurring during the pretreatment increased rapidly with the increasing amount of adsorbent, which was needed to increase the average flux in the UF. In this example flux value of 70 kg/(m²h), however, the hemicellulose loss was around 10%, which is acceptable considering the relatively low amount of adsorbent required. The cost-efficiency of the adsorption process could be increased by feasible regeneration of the used adsorbent.

The results of this study showed that adsorption had a varying impact on molecular mass distribution in birch extract B4, depending on the used adsorbent (Fig. 20). The size distributions of carbohydrates (Fig. 20a) revealed that AC and XAD adsorbents decreased the amount of a wide range of detected carbohydrates. However, XAD adsorbents removed more carbohydrates than AC in the harmful size range, based on the results of a multivariate examination by PCA in the case of birch extract B4 and the UFX5pHt membrane (Paper IV). AC was nearly equal to XADs in removing small carbohydrates, or disaccharides, which were less harmful for the filtration capacity based on PCA. The removal of carbohydrates at all sizes was lesser by bentonite than by XADs or AC. Furthermore, the molecular mass distributions of ligneous compounds in the treated extracts (Fig. 20b) clearly showed differences between AC and XAD adsorbents. AC removed very small ligneous compounds more efficiently than XAD adsorbents, whereas XAD adsorbents decreased the amount of bigger ligneous compounds more efficiently than AC, including, according to the PCA results, the most harmful-sized compounds at the range of 0.2–0.8 kDa. Bentonite was the least efficient in all size ranges. The XAD16 and XAD7 adsorbents removed same-sized lignin and carbohydrates when they were used on birch extract B4, but XAD16, removed more carbohydrates than XAD7, which was noticed also with other extracts.

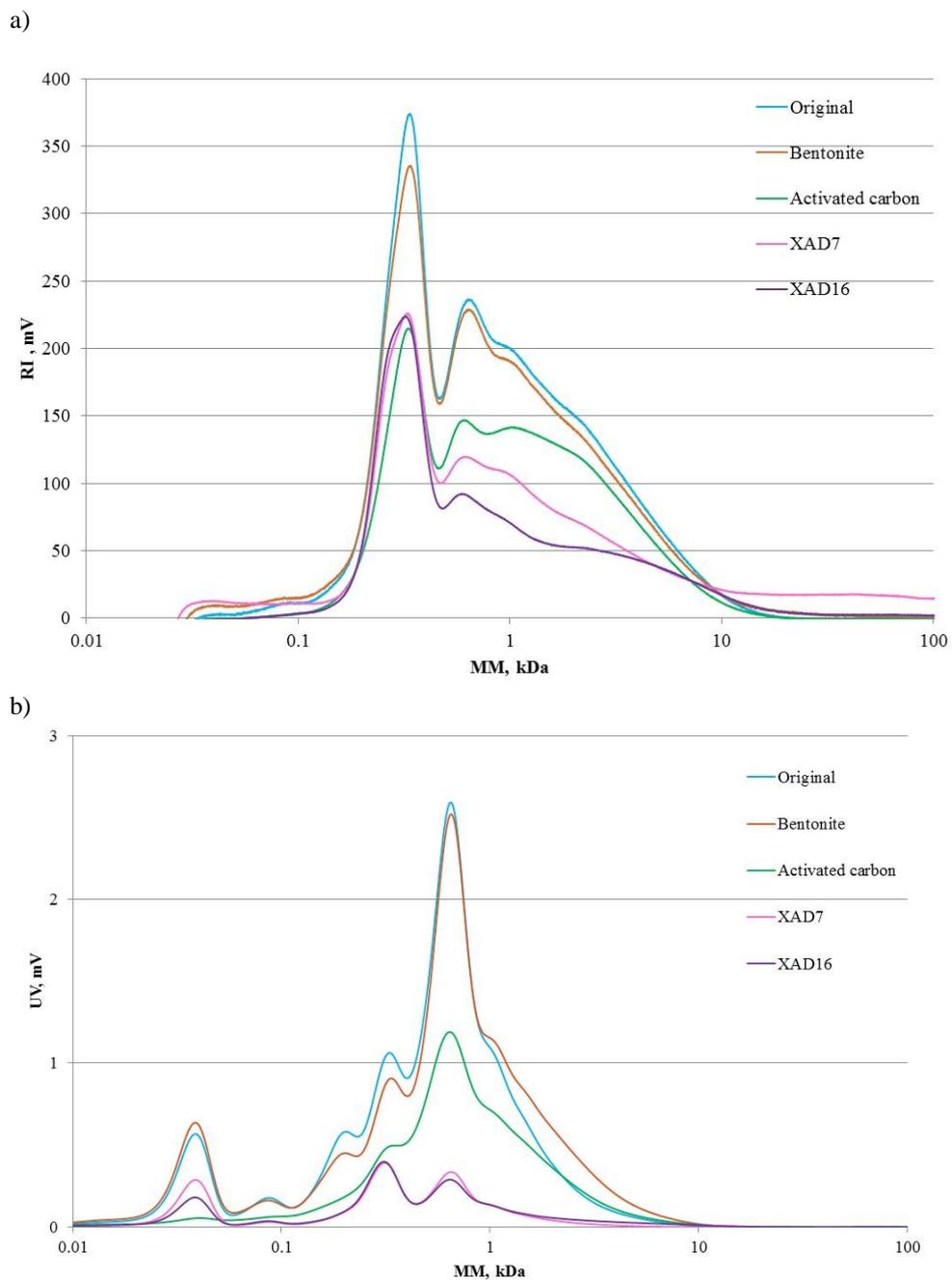


Figure 20. Molecular mass distributions in birch extract B4 originally, and after adsorption on activated carbon, bentonite and XAD adsorbents detected by a) RI detector (hemicelluloses) and b) UV (280 nm) detector (ligneous compounds). MM measured by methods a (carbohydrates) and b (lignin) from Table XIV.

Adsorption on AC at a higher temperature with birch extract B3 and spruce extract S2 seemed to remove especially high-molecular mass carbohydrates (Paper III). The average molecular masses of birch extract B3 and spruce extract S2 detected by the RI detector were decreased due to the AC treatment from 5.7 kDa to 3.3 kDa and from 10.2 kDa to 5.7 kDa, respectively. This result is in line with the result of Gütsch and Sixta (2011), who report that AC treatment at a high temperature removed high-molecular mass compounds prior to smaller-molecular mass compounds. Therefore, although adsorption at 160°C might be useful due to the higher lignin and lower carbohydrate adsorption than at 60°C, it could also mean a greater loss of high-MM hemicelluloses.

Multivariate examination by PCA in the case of birch extract B4 and the UFX5pHt membrane (Paper IV) revealed also a correlation between the amount of ligneous compounds and carbohydrates. Two separable peaks at 0.3 and 0.6 kDa were found both in RI and UV -detected molecular mass distributions (Fig. 20). These are possibly complexes between phenolic compounds and carbohydrates, even sugars in the case of the smaller compounds. Therefore, it would be misleading to call them lignin-hemicellulose complexes. The carbohydrates which disturb the filtration capacity, i.e. compounds at the range of 0.5-5.7 kDa, are partly in the same size range as these assumed complexes. This can partly explain the flux-decreasing effect of carbohydrates. Although it is reasonable to conclude that the size of any compound in the feed solution affects the filtration capacity, the phenolic moiety of the complex can increase the negative impact compared to a harmful-sized pure carbohydrate.

According to the results of this study, there were many possible reasons why pretreatment with XAD adsorbents increased the filtration capacity substantially with all the extracts. XAD adsorbents decreased the amount of lignin and wood extractives efficiently. They also decreased the amount of carbohydrates to such an extent that the flux was probably affected by the decrease of the overall concentration of the feed solution. For AC or bentonite, the removal of both lignin and carbohydrates was smaller than for XADs. XAD adsorbents were also the most efficient in the removal of harmful-sized compounds based on PCA. This partly explains the higher flux of the birch extract (B4) after XAD treatments than after AC treatment. The high flux value after bentonite treatment, however, remained inexplicable by this approach.

This study proved that fouling was decreased more by pretreatment with XAD7 than with XAD16, based on PWF_f (Table XVIII) in the case of all the studied extracts and membranes. This can be explained by the slightly higher removal of wood extractives by XAD7 than XAD16, which was observed in case of the birch extract B4 (Fig. 19). Although the difference was small, it can be significant for the fouling. According to Puro et al. (2011), the role of wood extractives as foulants in pulp mill process waters could be considerable even though their amount is rather small. However, fouling was decreased more by bentonite and AC than XAD adsorbents, although they removed less lignin and wood extractives. The compound size harmful for the filtration capacity is not necessarily the same as for fouling, and therefore, the same adsorbents may not be the most efficient ones in decreasing fouling and increasing the

filtration capacity. Pretreatment with bentonite also increased the filtration capacity notably. This implies that the total amount of foulants is not the main point, but some specific character of foulants, or any compounds in the solution, is an important factor as regards harmfulness for the filtration capacity and fouling. The foulants, i.e. lignin and wood extractives, are not homogeneous compounds by definition, but their characteristics vary for example due to molecular mass distribution and different functional groups in their structure.

9.2.1 Regeneration of polymeric adsorbents for reuse

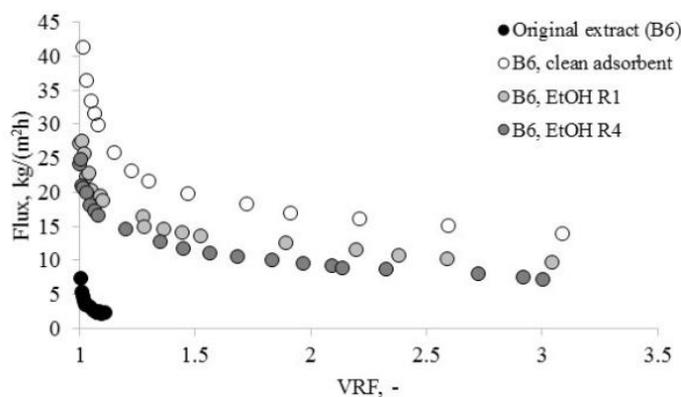
Regeneration could make the adsorbent reusable, and thus reduce the material costs. Another advantage would be the recovery of the adsorbed solutes, lost carbohydrates and on purpose adsorbed lignin, in case the regeneration is made by a solvent. The regeneration of AC by solvents is more complicated than the regeneration of polymeric adsorbents [Gütsch and Sixta (2012), Turku et al. (2009)]. Especially if the adsorption on AC is conducted at a high temperature, and if irreversible chemisorption therefore occurs, solvent regeneration is ineffective. Thermal regeneration for AC has been widely studied, and in the case of lignin as an adsorbed solute, thermal regeneration as itself can act as a process to make new AC from the adsorbed lignin [Chestnutt et al. (2007), Gütsch and Sixta (2012), Lindgren et al. (2011)]. Obviously, chemisorption is not a problem in the case of thermal regeneration. As there already exists a potential alternative for the regeneration of AC, it was not examined in this study. The focus was on solvent regeneration of polymeric adsorbents. The objective was to find out if there is potential in the regeneration and reuse of the XAD adsorbents used in the pretreatment in the UF of wood extracts.

The experiments were performed with the XAD16 adsorbent, birch extract B6, and the UH004P membrane according to the procedure shown in Fig. 12. The solvents, EtOH and NaOH, were chosen on basis of the adsorbent manufacturer's recommendations and on earlier studies by other researchers concerning the desorption of ligneous or similar compounds from adsorbents [Rohm and Haas (2011a,b), Gütsch and Sixta (2012), Weil et al. (2002), Schwartz and Lawoko (2010), Crook et al. (1975), Sandhya et al. (2013)]. Also the availability of the solvents and their easy use and safety during the experiments were among the selection criteria.

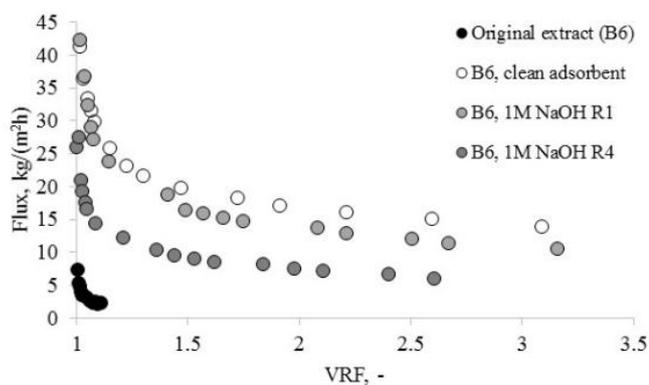
Regeneration restored most of the adsorption capacity with all the used regeneration solutions according to the obtained flux values in the UF of extracts pretreated with the used and regenerated adsorbents (Fig. 21). Although the adsorption capacity could be restored considerably by regeneration, it was not restored fully. Therefore, every adsorption period decreased the capacity compared to the previous adsorption. The adsorption isotherm obtained from the experiments with birch extract B2 and the XAD16 adsorbent revealed lignin forming multilayer adsorption on the XAD16 adsorbent (Paper II). This observation could lead to the conclusion that the adsorption capacity would not decrease with increasing adsorption times. Obviously, this was not the situation in this study. The interactions between the adsorbent and

lignin, and between the adsorbed lignin and lignin could be of a different magnitude. If the former interaction is stronger, the higher efficiency of the clean adsorbent would be logical in case the regeneration would not remove all the adsorbed material. However, even the flux values obtained with extracts treated with four times regenerated adsorbents were more than 50% of the flux value obtained with the extract treated with a clean adsorbent. This proves that even regenerated adsorbents have the ability to remove significant amounts of compounds from the extract.

a)



b)



c)

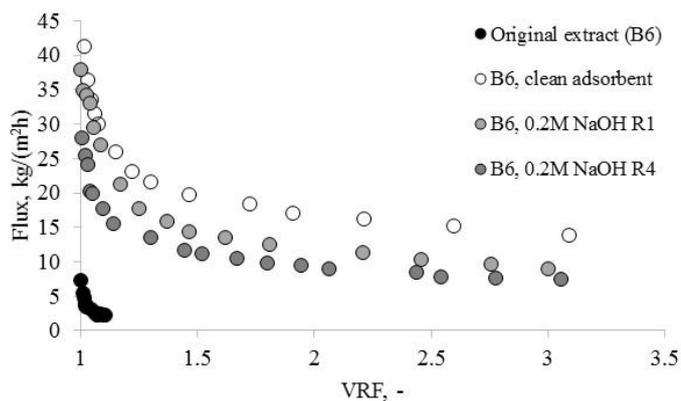


Figure 21. Permeate flux in the filtration of birch extract B6 with the UH004P membrane at 60°C, 5.5 bar and rotor tip velocity 1.6 m/s. The birch extract was treated with clean, once used and once regenerated (R1), and four times used and four times regenerated (R4) XAD16 adsorbent by a) 1:1 ethanol-water, b) 1 M NaOH and c) 0.2 M NaOH solutions.

The filtration capacity in the filtration of the extracts which were treated by once regenerated adsorbents (R1) was slightly higher after the regeneration with NaOH solutions than with the ethanol-water solution. However, the differences between the results obtained with NaOH and ethanol-water solutions were not great, and levelled off with increasing regeneration times. There are probably differences in the solubility of compounds in ethanol and in NaOH, and it is therefore possible that NaOH dissolved some compounds more efficiently from the adsorbents than EtOH. For example wood extractives have shown to have a significant role in the fouling of tight UF membranes, and although some of them absorb UV light at 205 nm, they were not analysed in detail in this study. Thus, their removal by the regenerated adsorbents could not be observed.

Fouling was severe in every case, based on PWF_r (Table XX). Even the clean adsorbent did not decrease fouling. Therefore, the effect of regeneration on the ability of the adsorbent to decrease fouling could not be detected in this study. Adsorption did probably not decrease fouling due to a lower adsorbent-to-extract phase ratio, 0.05, compared to the phase ratio 0.15 used in the adsorption experiments for eucalyptus-pine, and birch extracts B2 and B4 presented in section 9.2. Also the differences between birch extract B6 used in the regeneration experiments, and eucalyptus-pine EP, and birch extracts B2 and B4 may have affected the result.

The adsorbent was not fully restored by the solvents since the capacity to adsorb lignin and carbohydrates decreased with increasing adsorption times (Table XX). The ethanol-water solution was the most efficient one in restoring the adsorption capacity, based on the removal of lignin from the extract by the regenerated adsorbent. This was probably due to the most efficient removal of lignin from the used adsorbent by the ethanol-water solution. However, lignin is not the only compound affecting filtration capacity, and therefore, the NaOH solutions may have dissolved other compounds than lignin from the adsorbent more efficiently. For example, Prado et al. (2012) have studied the purification of lignin obtained from organosolv and soda pulping by using ethanol and NaOH as solvents, respectively, and found that the lignin fraction from soda pulping contained more impurities than the lignin fraction from organosolv pulping. This implies that more compounds were dissolved in NaOH than in ethanol in their study. The two studied NaOH concentrations gave similar results both in the lignin removal capacity and obtained flux values. Based on the data obtained in the present study, it is not justified to use the higher one of the tested concentrations as the same efficiency was obtained with both concentrations.

Table XX Flux values of the UH004P membrane and the amount of removed lignin and carbohydrates from birch extract B6 after adsorption with regenerated adsorbent.

Extract treated with	Flux, kg/(m ² h)	PWF _r , %	Lignin removal, %	Carbohydrate removal, %
Clean XAD16	24	94	77	26
EtOH R1	17	91	64	34
EtOH R4	14	95	53	13
1M NaOH R1	21	99	65	20
1M NaOH R4	13	94	31	14
0.2M NaOH R1	21	90	62	20
0.2M NaOH R4	14	89	44	14
Untreated extract	3	97	-	-

RN regeneration times

A greater solvent volume might have been necessary to remove the adsorbed compounds completely. Optimisation of the regeneration solvent volume, regeneration time etc. might also improve the efficiency. If also other regeneration solvents were studied, an environmental alternative to organic solvents could be a solution containing lignin-degrading fungi, or more precisely, an enzyme, e.g. laccase. For example, Silva et al. (2004) have studied bio-regeneration of the XAD4 adsorbent by bacterial mixed culture after molinate adsorption on XAD4. They succeeded in restoring part of the adsorption capacity, but the regeneration was not complete since the desorption discontinued every time when the amount of adsorbed molinate was decreased to about 60 mg/g of dry adsorbent.

The carbohydrate analysis and UV (280 nm) absorbance measurement of regeneration solvents indicated that UV absorbing compounds and carbohydrates behaved differently in adsorption and desorption (Table XXI). The UV absorbing compounds were not completely removed from the adsorbent by regeneration, as the solvent from the fifth regeneration contained more UV absorbing compounds than the solvent from the first regeneration, with all the studied solvents. Incomplete removal of adsorbed compounds from XAD adsorbents have been reported also by Sandhya et al. (2013), who report on around 72–78% desorption of furfural from XAD adsorbents by ethanol. In theory, if multilayer adsorption occurs, it should not be crucial if the adsorbed lignin could not be removed fully by regeneration because the adsorption does not require a clean adsorbent surface.

Table XXI UV absorbance and total carbohydrates measured from the regeneration solvents.

Solvent	UV 280, -	Carbohydrates, g/l
EtOH R1	57	4.4
EtOH R5	74	3.5
EtOH Rcheck	17	0.1
NaOH 0.2M R1	24	2.9
NaOH 0.2M R5	44	1.6
NaOH 0.2M Rcheck	6	0.0
NaOH 1M R1	31	2.2
NaOH 1M R5	49	1.3
NaOH 1M Rcheck	12	-

RN regeneration times

In the case of carbohydrates, the solvents from the first regeneration were more concentrated than the solvents from the fifth regeneration. This is in line with the carbohydrate analysis of the extracts, which showed that the more the adsorbent was used and regenerated, the fewer carbohydrates were removed during the adsorption. This also means that the adsorbed carbohydrates were more efficiently dissolved to the solvents than the UV absorbing material. The recovery of carbohydrates from the solvents by e.g. nanofiltration, chromatography, or distillation would be profitable. After the first adsorption, the amount of adsorbed carbohydrates, calculated from the mass balance of the adsorption, was 89 mg/g of dry adsorbent, corresponding to 26% of the carbohydrates in the original extract. After the first regeneration with EtOH, 0.2 M NaOH and 1 M NaOH, the amounts of carbohydrates remaining on the adsorbent were approximately 26, 48 and 58 mg/g of dry adsorbent, corresponding to 7, 14 and 17% of the carbohydrates in the original extract, respectively. The accuracy of the analysis from regeneration solvents is uncertain as the solvents were not water as normally, which reflects the uncertainty to the latter results. In the light of these results, it seems that the EtOH solution removed carbohydrates from the adsorbent best.

A check regeneration was carried out straight after the fifth regeneration (Fig. 12) to examine if the fifth regeneration had removed all the adsorbed compounds it is able to remove. The solvent from the check regeneration still had a small amount of UV absorbing compounds, implying that slightly higher amounts of regeneration solvents could be practical. The amount of carbohydrates in the check regeneration solvent was negligible, which supports the result that carbohydrates were more easily removed from the adsorbent than the UV absorbing compounds.

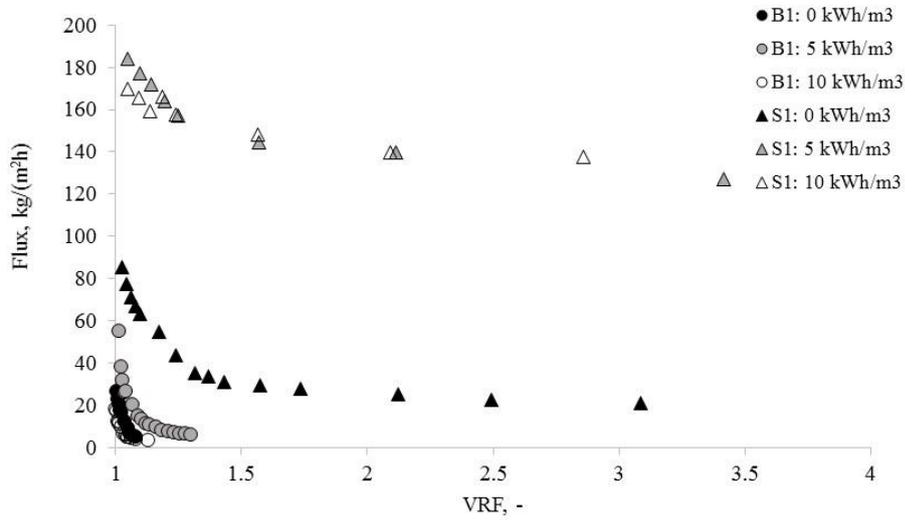
9.3 Oxidation

As an alternative to the removal of foulants, the degradation of foulants was studied. Oxidation by the laccase enzyme and by PCD was selected due to their reported ability to oxidise organic material, including lignin [Camarero et al. (2007), Higuchi (2004), Panorel (2013), Pokryvailo et al. (2006)]. In addition, they do not create problematic waste, and therefore do not harm the environment.

The impact of PCD oxidation on the filtration capacity varied among the studied extracts (Fig. 22, Paper V). The flux of the UFX5pHt membrane in the filtration of spruce extract S1 was increased even multifold by PCD. All the other extracts filtered with the UFX5pHt, i.e. birch extracts B1 and B5, and spruce extract S3, showed more moderate improvements due to the PCD treatment. The increases in average fluxes were at their best 8–53% (Fig. 22, Table XXII). Also, the enzymatic oxidation by laccase had a positive influence on the filtration capacity. The increase in the flux of the UFX5pHt membrane in the filtration of the laccase-treated birch extract B4 was about 130% (Table XXII). The effect of PCD was positive in most of the cases if the energy dosage was set to be suitable. The highest energy dosage in pretreatment did not necessarily bring the highest increase in flux, on the contrary, it led to a lower flux than a lower energy dosage. This could be seen in the flux values of the UFX5pHt membrane in the filtration of the pretreated birch extracts B1 and B5 and spruce extract S3 (Fig. 22, Table XXII). This implies that the most intense treatment changed the extract composition in such a way that it decreased the filtration capacity more than the extract composition after milder treatment. The revelation by PCA applied to birch extract B4 and the UFX5pHt membrane showed that a certain molecular size is more harmful for the filtration capacity than another size (Table XV, Paper IV). Thus, PCD oxidation might have increased the amount of harmful-sized compounds.

With the UC030 and RC70PP membranes, the PCD was conducted for concentrate fractions, which were filtered again with the same membrane (Paper V). The feed solution for the RC70PP membrane was the permeate solution of the UC030 membrane. In the case of the UC030 membrane, also an experiment in which the feed solution was pretreated, was carried out. With the UC030 and RC70PP membranes, only one energy dosage was used in the oxidation experiments. In this particular case, the PCD had a positive impact on the flux when it was used for the original extract and filtered with the UC030 membrane, and especially for the concentrate solution of the UC030 membrane (Paper V). For the feed of the RC70PP membrane, which was a permeate of the UC030 membrane, the impact of PCD was negligible, indicating that prefiltration had already removed such compounds that reduce the permeate flux of the hydrophilic RC70PP membrane. With the more hydrophobic membrane UFX5pHt, the impact of prefiltration was slighter, which implies that the reason for the decrease of flux was different for these membranes.

a)



b)

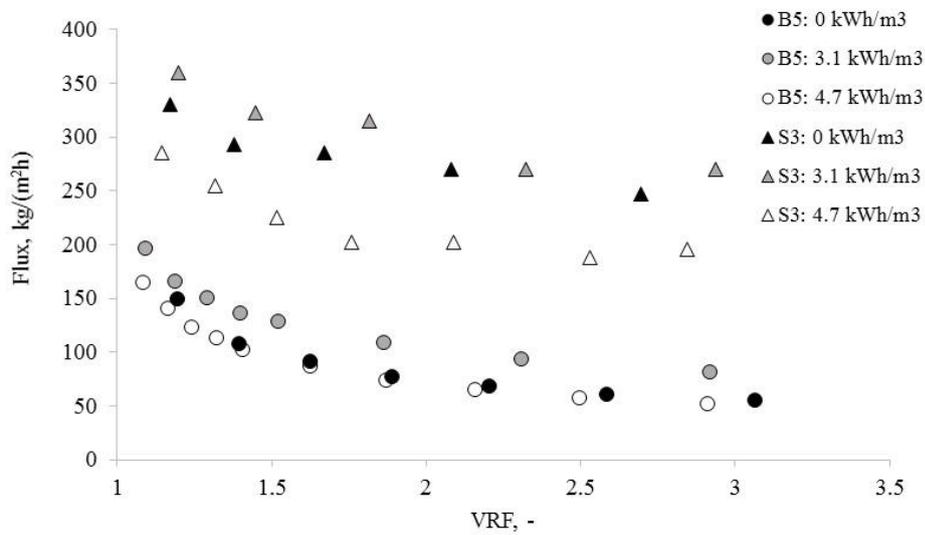


Figure 22. Permeate flux in the filtration of PCD-treated extracts with the Amicon filter cell and the UFX5pHt membrane at a) 55°C and 5.5 bar, and b) 60°C and 5 bar and rotor tip velocity 1.6 m/s.

Enzymatic oxidation by laccase had no effect on fouling according to the PWF_r values (Table XXII). The PCD treatment decreased the fouling of the UFX5pHt membrane only with spruce extract S1. With the other extracts, fouling remained at the same level or even increased. This indicates again that the PCD oxidation can have changed the size of the compounds to be more harmful, as the sizes of carbohydrates and lignin were noticed to have an impact on the filtration efficiency (Table XV, Paper IV). The results of both oxidation methods implied that the compounds causing flux decline and irreversible fouling were at least partially different, as was noticed also with the adsorption pretreatment. With the UC030 and RC70PP membranes, the effect of the PCD on fouling was minor, probably due to low fouling even with untreated extracts.

Table XXII The effect of oxidative pretreatment on the filtration performance of the UFX5pHt membrane with different extracts.

Method	Extract	Flux (original extract), kg/(m ² h)	Flux (pretreated extract), kg/(m ² h)	PWF_r (original extract), %	PWF_r (pretreated extract), %
PCD (5 kWh/m ³)	B1	13	17	65	78
PCD (10 kWh/m ³)	B1	13	9	65	89
PCD (5 kWh/m ³)	S1	46	158	18	11
PCD (10 kWh/m ³)	S1	46	156	18	-20
PCD (3.1 kWh/m ³)	B5	86	132	58	60
PCD (4.7 kWh/m ³)	B5	86	97	58	59
PCD (3.1 kWh/m ³)	S3	285	308	39	39
PCD (4.7 kWh/m ³)	S3	285	222	39	51
Laccase (p.r. 0.01)	B4	15	36	83	83

p.r. adsorbent to extract phase ratio

The amount of lignin in wood extracts was reduced more temperately by oxidation than by adsorption (Fig. 19 and 23). However, the amount of carbohydrates was in practice not affected at all. Therefore, both the tested oxidation methods were selective to lignin over carbohydrates in most of the cases, and the purity of the extracts was increased. The decrease in the amount of lignin by PCD oxidation was the highest, over 50%, in spruce extract S1. However, the lignin concentration in spruce extract S1 was low even before oxidation. The amount of lignin was decreased by 39–42% and 25–33% in birch extract B5 and in spruce extract S3, respectively. In birch extract B1, the amount of ligneous compounds was reduced only slightly.

The amount of total wood extractives was decreased by over 85% in spruce extract S1, and by 30–65% in birch extract B5 and spruce extract S3 by PCD oxidation. Especially lipophilic extractives have been reported to be one of the foulants in pulp and paper effluents [Puro et al.

(2011)]. The PCD treatment decreased the amount of lipophilic extractives in spruce extract S3 over 80% and in birch extract B5 by 50% at the energy dosage of 4.7 kWh/m³.

The laccase treatment decreased the amount of lignin and total wood extractives by 37% and 85%, respectively, in birch extract B4. The amount of lipophilic extractives was decreased only by 35%, but lignans and lignin residuals were removed more efficiently, by 92% and 89%, respectively. Laccase has been reported to be able to oxidise lipophilic extractives [Babot et al. (2011), Widsten and Kandelbauer (2008)].

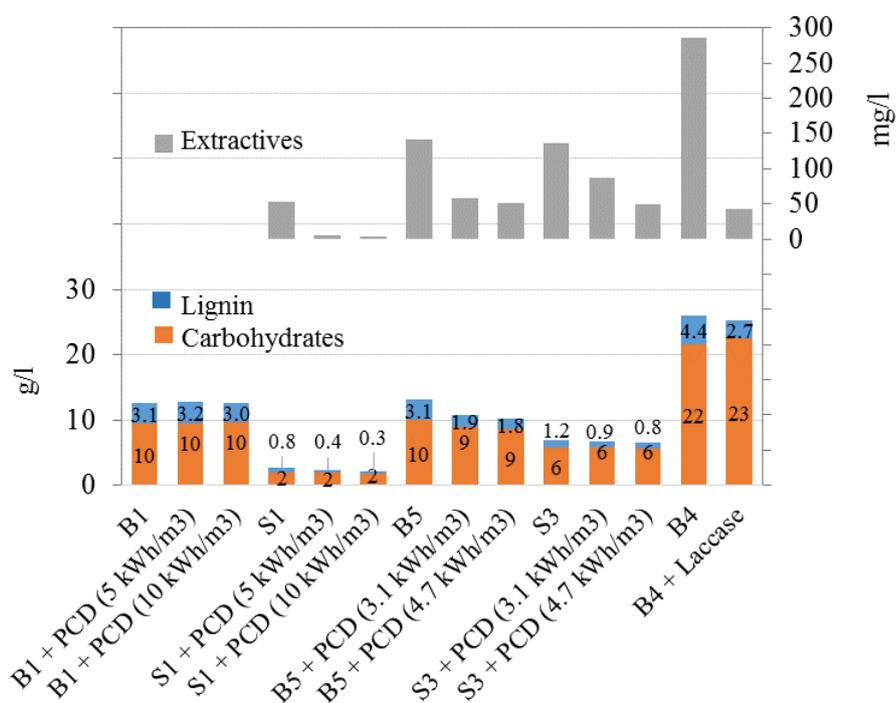


Figure 23. Wood extract composition before and after oxidation in birch extracts B1, B4 and B5 and in spruce extracts S1 and S3. Carbohydrates from birch extract B1 and spruce extract S1 were analysed by method b, from other extracts by method a (Table XIV).

In the case of spruce extract S4 (Paper V), the lignin was analysed from MTBE-extracted samples at 280 nm to eliminate the effect of other compounds that increase UV absorbance at the same wavelength, whereas with the other extracts the amount of ligneous compounds was analysed at 205 nm from unextracted samples. Disturbance in lignin measurements by UV absorbance may be caused by colloidal material [Holmbom and Örså (1993)], such as some

wood extractives, due to their similar functional groups and the molecular structures with lignin [Hase (1992)]. The amount of the other compounds participating in the UV absorbance is usually significantly lower than that of lignin, but their share of the total absorbance value is uncertain and is not necessarily determined by merely the amount of compounds. This means that the same concentration of two different compounds does not necessarily lead to the same UV absorbance. Although the amount of UV absorbing compounds was not reduced in spruce extract S4 according to UV absorbance, it is possible that the oxidation can have changed the molecular mass or other molecular characteristics of lignin.

The amount of carbohydrates was reduced by PCD only in the case of birch extract B5 and spruce extract S4, when 11–15% and about 7%, respectively, of the carbohydrates were lost (Fig. 23, Paper V). More detailed analysis of spruce extract S4 showed that the carbohydrate loss was at least partly due to the degradation of the carbohydrates to organic acids, the amount of which in the extract was slightly increased by the PCD.

The molecular mass distributions of UV-detected (lignin) (Fig. 24) and RI-detected (carbohydrates) (Fig. 25) compounds were measured in birch extract B5 and spruce extract S3 to detect changes in MM due to the PCD treatment. Also MM distributions in spruce extract S4 (Paper V) were measured. The MM distributions of ligneous compounds in spruce extract S3, and especially in birch extract B5 showed quite a systematic change in the retention times (Fig. 24). The change in the retention time may indicate either a slight increase in MM, or a change in the molecular properties. The MM distribution of carbohydrates in birch extract B5 and spruce extract S3 was not affected noticeably by the PCD treatment (Fig. 25).

With spruce extract S4, the molecular mass distribution of UV absorbing compounds was expanded by the PCD, but the average molecular mass remained about the same as in the original extract, based on the MALLS detector (Paper V). The formation of hemicellulose degradation products, a slight decrease in the MM of RI-detected compounds, and a small decrease in carbohydrate retention (Paper V) imply that some of the carbohydrates were degraded in spruce extract S4 by the PCD treatment.

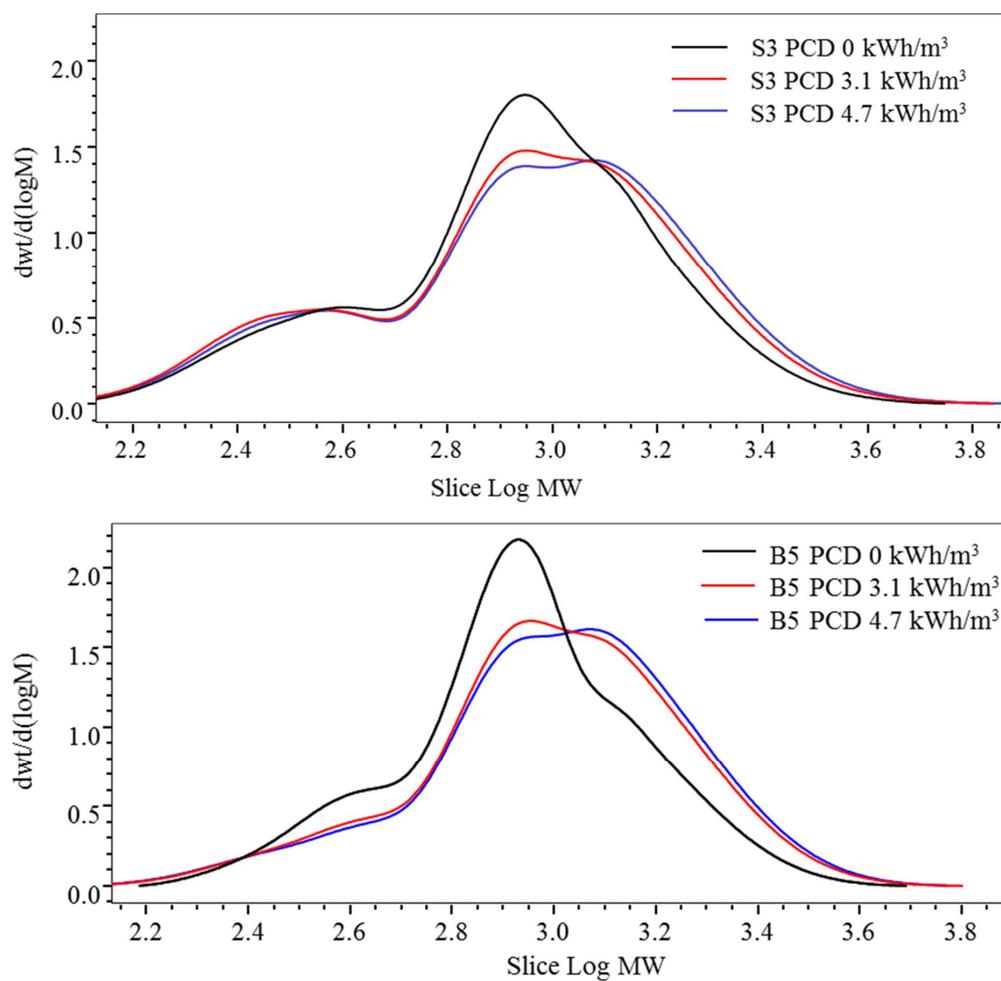


Figure 24. Molecular mass distributions of UV-detected compounds in birch extract B5 and spruce extract S3 before and after PCD treatment. MM measured by method c (lignin) from Table XIV.

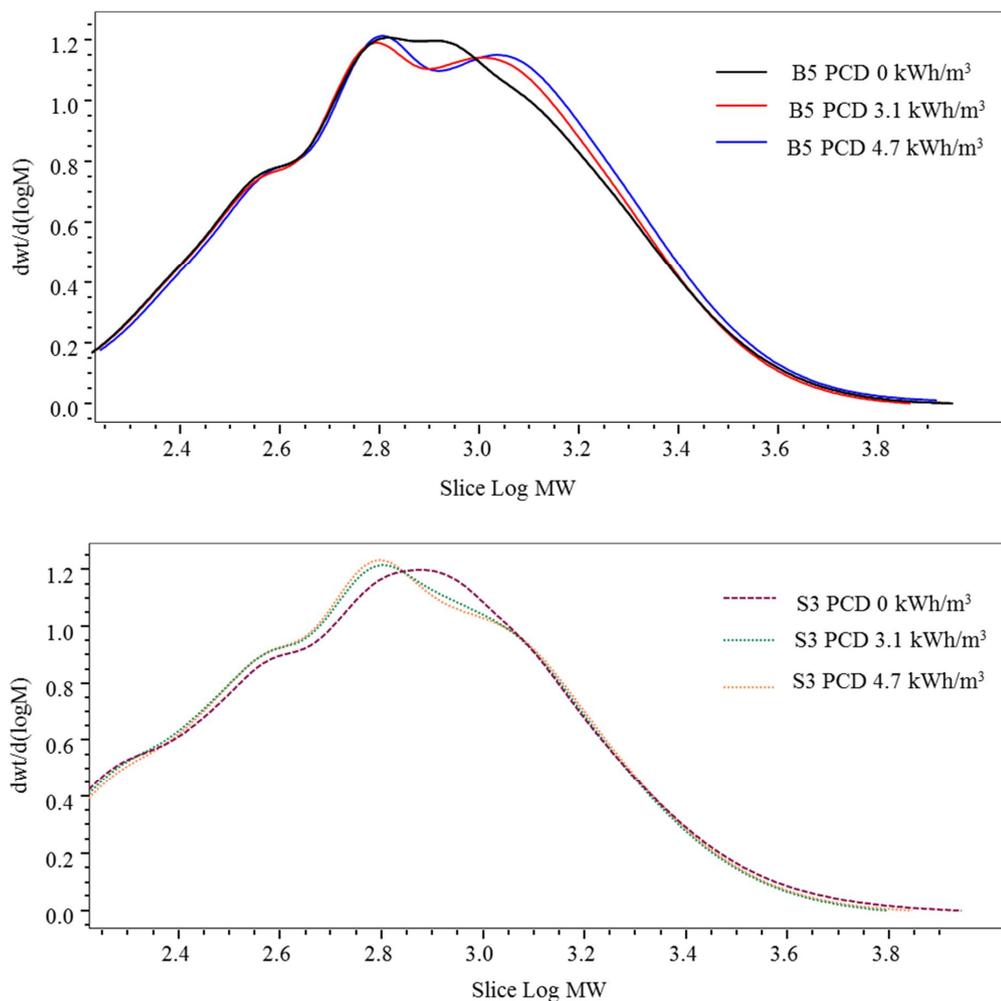


Figure 25. Molecular mass distributions of RI-detected compounds in birch extract B5 and spruce extract S3 before and after PCD treatment. MM measured by method b (carbohydrates) from Table XIV.

Molecular masses were not analysed from the laccase-treated birch extract (B4). However, lignin retentions of the UFX5pHt membrane in the filtration of the laccase-treated extract and original extract were 57% and 48%, respectively. The increased lignin retention was probably due to the higher average molecular mass of lignin as a result of the formation of larger lignin molecules from small lignin molecules by laccase. This explanation is in line with the results of Jönsson et al. (1998) who report that the UV 280 nm absorbance of willow hydrolysate did not decrease due to laccase treatment, but the absorbance for large-sized material increased and the absorbance for small-sized material decreased. The carbohydrate retention of the UFX5pHt membrane decreased slightly by laccase treatment from 78% to 70 %, which might be due to

degraded LHCs, thus increasing the permeation of liberated carbohydrate moiety. In contrast to this result, Krawczyk et al. (2013b) increased the molecular mass of hemicelluloses by cross-linking lignin moieties between hemicellulose chains. On the basis of the decreased carbohydrate retention, this phenomenon did not occur in this study.

The results imply that even though the average molecular mass of lignin did not change remarkably, the molecular properties, e.g. hydrophobicity, may have been altered. Li et al. (2007) observed the same kind of formation of a more heterogeneous lignin structure due to depolymerisation and repolymerisation during the steam explosion treatment of wood. The degradation products due to oxidation are e.g. reactive phenoxy radicals, which might participate in condensation reactions, yielding molecules with a different rearrangement and molecular size than the original one [Gierer (1980), Widsten and Kandelbauer (2008), Leschinsky et al. (2009), Higuchi (2004)]. Phenoxy radicals can form quinone-like structures if enzymatic oxidation proceeds, or they may participate in non-enzymatic reactions, such as hydration, disproportionation, or polymerisation [Rittstieg et al. (2002)]. The idea of altered molecular properties is supported by Almendros et al. (1992), who noticed that the degradation of wheat straw lignin by lignocellulose-degrading fungi did not merely degrade the molecule, but the amount of saturated alkyl structures was increased, whereas the amount of aryl carbons was decreased, changing the molecular properties of treated lignin. More accurate examination of the changes in the lignin structure by oxidation would be useful and could be done e.g. by NMR or FTIR. The same kind of phenomena may have occurred due to oxidation by PCD.

The flux-improving effect of the laccase pretreatment was probably due to the change in the MM or molecular characteristics of lignin to less harmful from the point of view of filtration. For instance, if larger compounds were formed, they could be too large to enter the membrane structure. Pretreatment with laccase did not decrease the fouling, which might be due to the low removal of lipophilic extractives even though the total amount of extractives decreased.

Based on the results, the amount of removed lignin by PCD oxidation was one factor affecting the flux increase in filtration with the UFX5pHt membrane. The achieved level for the flux, however, was determined, among others, by the amount of lignin still remaining in the solution. Generally, there were more lignin and carbohydrates in the birch extracts than in the spruce extract before oxidation by PCD. However, the amount of lignin is not the only factor which determines the flux value. For instance, the amount of ligneous compounds in birch extract B1 was affected only slightly by PCD, but the flux was still increased, possibly due to a decrease of the amount of wood extractives. Also, with the UC030 and RC70PP membranes the flux was increased substantially, although the amount of lignin in spruce extract S4 was not reduced by PCD. The flux increase was probably due to the reduced viscosity of the extract and almost totally removed lipophilic wood extractives and lignans (Paper V).

In theory, a higher starting concentration would require more intense PCD treatment than more dilute feed solutions. However, as it seemed that the too high increase in the energy dosage in the PCD created more harmful compounds for the filtration capacity and fouling, the energy

dosage cannot be increased unlimitedly. Therefore, the functionality and optimal conditions of the PCD treatment depends highly on the extract and the membrane in question, and the PCD seems to show its best potential with more dilute solutions when a hydrophobic tight UF membrane is used. The problematic compounds from the point of view of filtration capacity for the UC030 and the RC70PP membranes are probably somewhat different than for the UFX5pHt membrane, due to the difference in cut-off and hydrophobicity.

9.4 Oxidation and adsorption

The possibility to avoid hemicellulose losses occurring in adsorption pretreatment via the removal of LHCs was studied by combining oxidative pretreatment with the adsorption step. As discussed in section 9.3, laccase treatment did not affect the carbohydrate content. Therefore, laccase treatment was chosen for the oxidative method since the potentially observed changes in the carbohydrate content would be caused by adsorption. Activated carbon, XAD16 and bentonite were chosen for adsorbents due to their proven ability to increase filtration capacity.

When laccase treatment was conducted prior to adsorption, the type of adsorbent determined whether the combination increased the flux or decreased fouling compared to a solely laccase-treated extract (Fig. 26). The adsorption on bentonite and XAD16 after laccase treatment increased the flux compared to the flux of a solely laccase-treated extract. The increase in flux in the case of laccase + bentonite was as high as 230% compared to the flux of birch extract B4 after laccase treatment. In the case of laccase + XAD16, the corresponding increase was 67%. The adsorption on AC after laccase treatment did not bring any additional advantage in terms of filtration capacity.

When the fluxes are compared to the ones obtained by pretreatment with AC or XAD16 without preceding laccase treatment, bare adsorption led to higher fluxes than the combination treatment (Table XXIII). Only with bentonite did the preceding laccase treatment increase the filtration capacity compared to the situation obtained by bare adsorption. Laccase treatment probably changed the properties of the compounds that decrease filtration capacity in such a way that they were adsorbed more efficiently on bentonite. In the case of AC, the amount of the adsorbent was higher in the adsorption experiment than in the combination treatment experiment, which may have had an influence on the flux. Similarly, the amount of bentonite was lower in the adsorbent experiment than in the combination treatment experiment, and the resulting flux was higher after the latter. This was, however, probably not the only factor explaining these results.

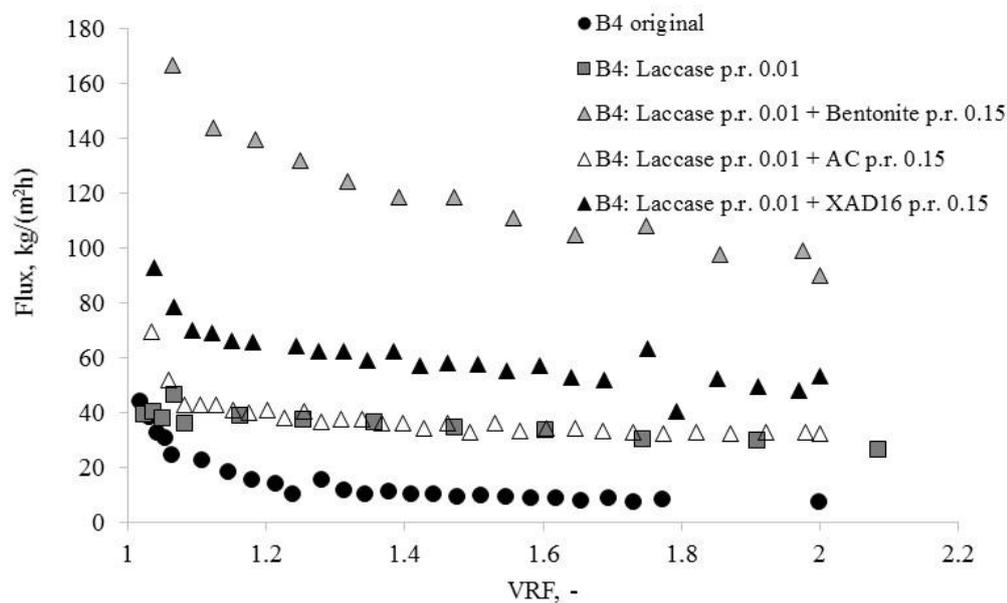


Figure 26. Permeate flux in the filtration of birch extract B4 with an Amicon filter cell and the UFX5pHt membrane at 60°C and 5.5 bar and rotor tip velocity 1.6 m/s, after treatment with laccase and laccase combined with bentonite, AC and XAD16.

Fouling was decreased in the cases of laccase combined with bentonite or AC, but it was not affected by laccase combined with XAD16 compared to the filtration after laccase alone or the original extract (Table XXIII). When the combination treatments are compared to the corresponding adsorption treatments, no additional decrease in fouling was obtained in any of the used adsorbents. On the contrary, laccase treatment seemed to change the characteristics of foulants in such a way that their adsorption on XAD16 was hindered. Laccase treatment had possibly decreased the hydrophobicity of the compounds that were originally adsorbed on XAD16. Therefore, when only filtration performance is considered, it is not reasonable to combine laccase treatment with AC or XAD16 adsorbents. However, the aim was to decrease carbohydrate losses during adsorption, and therefore the extract composition has to be taken into account in order to evaluate the performance of the combination treatments.

Table XXIII Filtration performance of the UFX5pHt membrane in the filtration of birch extract B4, and the amount of lignin, carbohydrates and wood extractives after pretreatment.

Method	Flux, kg/(m ² h)	PWF _r , %	Lignin, g/l	Carbohydrates, g/l	Extractives, mg/l
Original extract (B4)	15	83	4.4	22	286
Laccase (p.r. 0.01) + bentonite (p.r. 0.15)	120	34	2.2	12	6
Laccase (p.r. 0.01) + activated carbon (p.r.0.1)	38	38	2.3	17	23
Laccase (p.r. 0.01) + XAD16 (p.r. 0.15)	60	85	0.5	9	135
Laccase (p.r. 0.01)	36	83	2.7	23	42
Bentonite (p.r. 0.05)	79	35	4.2	16	158
AC (p.r. 0.2)	61	24	2.8	14	20
XAD16 (p.r. 0.15)	78	63	0.6	9	13

Laccase alone decreased the amount of lignin by 37% (Table XXIII). The adsorption on bentonite, AC and XAD16 alone decreased the amount of lignin by 4, 36 and 87%, respectively. The removal of lignin in the combination treatments of laccase + bentonite, laccase + AC and laccase + XAD16 were 50, 47 and 88%, respectively. Therefore, the combination of laccase + AC and especially laccase + bentonite improved the removal of lignin regardless of whether compared to bare laccase treatment or bare adsorption (Table XXIII). In the case of XAD16, laccase treatment prior to adsorption did not affect the lignin removal. This was probably because the removal of lignin by XAD16 was already so high that it would be difficult to increase it. As discussed in section 9.3, oxidation by laccase probably changed some molecular properties of the ligneous compounds. These modified properties, e.g. increased hydrophilicity, might be more favourable for adsorption on especially bentonite but also for AC.

Carbohydrate losses during adsorption were not avoided by combining laccase treatment with adsorption. Laccase alone did not cause any carbohydrate loss, but combined with bentonite, AC and XAD16, the removal rates of carbohydrates were 45, 21 and 57%, respectively (Table XXIII). The removal of carbohydrates by adsorption on bentonite, AC and XAD16 alone were 24, 35 and 57%, respectively. Thus in the case of bentonite, the preceding laccase treatment increased the removal of carbohydrates, whereas in the case of AC the preceding laccase treatment decreased the removal of carbohydrates. With XAD16, the removal of carbohydrates was exactly the same with or without laccase treatment. With AC and bentonite, the differences between adsorbent amounts in adsorption and combination treatments probably explain the differences in the removal of carbohydrates. The carbohydrate losses imply that either the laccase treatment was unable to cut the bond between the LHCs, or the carbohydrate losses were not completely due to the adsorption of LHCs. If the carbohydrate losses were completely due to the adsorption of pure carbohydrates, the degradation of LHCs would not decrease the

removal of carbohydrates. However, the degradation of the LHCs, which was deduced to happen, could improve the separation of carbohydrates from lignin by UF. However, when the cleaved lignin moieties reunite together, as assumed, their separation from carbohydrates suffer due to their increased size, as was noticed in Section 9.3. Even though laccase did not cleave the bond between lignin and carbohydrate moieties, it might have reduced the size of the lignin moiety by cleaving the inter-lignin β -O-4 bonds, making the complexes more hydrophilic.

Laccase alone decreased the amount of wood extractives by 85% (Table XXIII). Adsorption on bentonite, AC and XAD16 alone decreased the amount of extractives by 45, 93 and 95 %, respectively. The combination treatment of laccase + bentonite, laccase + AC and laccase + XAD16 decreased the amount of wood extractives by 98, 92 and 53%, respectively. The combination of laccase + bentonite treatment led to greater removal of extractives than adsorption or laccase treatment alone. The combination of laccase + AC decreased the amount of wood extractives slightly more than laccase alone, but almost equally to AC alone. In the case of laccase + XAD16, the decrease in the amount of wood extractives was smaller than with laccase alone or XAD16 alone. The result obtained with laccase + bentonite might be partly explained by the higher amount of bentonite in the combination treatment. However, laccase may have decreased the hydrophobicity of the wood extractives, which could possibly have increased their adsorption on bentonite and decreased their adsorption on XAD16. Laccase has been reported to be able to oxidise lipophilic extractives and to increase the molecular mass of lignans by the polymerisation of lignans to lignin-like material [Babot et al. (2011), Widsten and Kandelbauer (2008), Widsten et al. (2004)]. As discussed in section 9.3, laccase decreased the amount of lipophilic extractives by 35% and lignans by 92%. Therefore, changes in the structure of the wood extractives may have influenced their adsorption.

It can be clearly seen in Figure 27a that the molecular mass of UV-absorbing compounds was increased by the combination of laccase and bentonite. The increase in the molecular size can be explained by oxidation and the following polymerisation by laccase rather than the formation of flocs or aggregates by bentonite, because bentonite was separated from the extract before filtration or analysis. In addition, bentonite alone removed a very small amount of lignin. Thus, similar behaviour of laccase can be expected in other combination treatments.

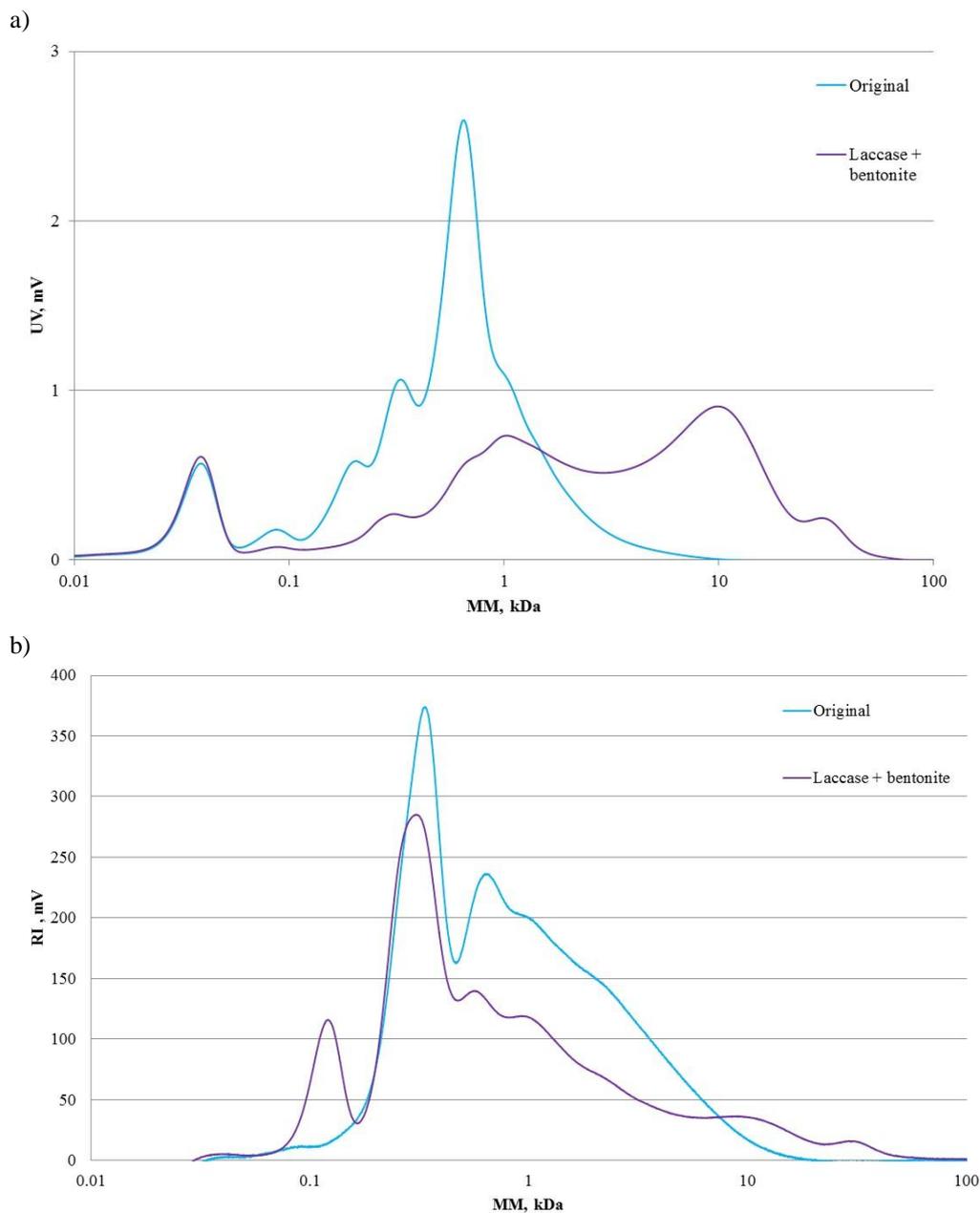


Figure 27. Molecular mass distributions of birch extract B4 originally and after treatment with laccase and bentonite by a) UV (280 nm) detector (ligneous compounds) and b) RI detector (hemicelluloses). MM measured by methods a (carbohydrates) and b (lignin) from Table XIV.

Based on the results, laccase decreased in this context the amount of middle-sized ligneous compounds and increased the amount of larger ligneous molecules (Fig. 27). The amount of small ligneous compounds, probably phenols from the degradation of lignin [Lobo et al. (2000)], was not affected by the laccase treatment (Fig. 27), possibly due to the absence of β -O-4 bonds in these structures. As mentioned above, based on a study of Rittstieg et al. (2002), some lignin model compounds were first oxidised to monomers by laccase, after which they polymerised to larger molecules. Not all oxidised compounds react again forming larger compounds. For example, phenolic aldehydes, ketones and acids are possible lignin oxidation products if repolymerisation does not occur [Lobo et al. (2000)]. In addition, the phenols in birch extract B4 were not formed due to oxidation by laccase since they existed also in the untreated extract, and therefore, they might be less reactive than the monomers formed in oxidation.

The MM distributions obtained in birch extract B4 after adsorption showed that AC removed especially very small ligneous compounds (Fig. 20), which were less harmful for the filtration capacity, according to PCA (Table XV, Paper IV). Thus, if laccase treatment increased the MM of lignin, additional advantages in adsorption by AC would not be obtained by laccase treatment prior to adsorption. Nonetheless, if adsorption is conducted at around 160°C, the increased molecular size of lignin might be advantageous, as AC was noticed to decrease the average MM of the compounds in birch extract B3 and spruce extract S2 at 160°C. This means that larger molecules were removed more than smaller ones (Paper III). However, as discussed in section 9.3, it is also possible that laccase changed the molecular properties of lignin, which may have increased lignin adsorption both on AC and bentonite (Table XXIII).

The MM distribution of RI-detected compounds in birch extract B4 showed that the amount of carbohydrates at molecular sizes 0.3 and 0.6 kDa, which possibly represent the complexes, was decreased by laccase treatment combined with bentonite (Fig. 27b). Also, the amount of very small carbohydrates, most likely monosaccharides, was increased. Both phenomena can be explained by the oxidation of the complexes. When laccase oxidizes lignin or LHC, carbohydrate moieties are liberated from the cleaved lignin, which can be observed in the increase in the amount of monosaccharides. The cleaved lignin moieties probably react together, forming larger molecules detected more strongly by the UV detector. Since the RI detector may detect also ligneous compounds, LHCs are likely detected by RI as well. Therefore, if laccase has the ability to break the complexes or at least part of them, and it is assumed to happen in these experiments, the reason for carbohydrate losses is not completely due to the complexes, as the carbohydrate losses could not be avoided by laccase treatment before adsorption.

There was a slight increase in the amount of RI-detected compounds larger than 10 kDa in the extract treated by laccase and bentonite (Fig. 27b). This may be due to either the fact that the RI detector shows also other compounds than carbohydrates, i.e. lignin in this case, or crosslinking of carbohydrates via lignin moieties. For instance, Krawczyk et al. (2013b) increased the average molecular mass of hemicelluloses through bound lignin moieties by

laccase treatment. In such cases, there will inevitably be some lignin in the produced carbohydrate fraction if laccase has been used as a pretreatment. It depends on the final product how high hemicellulose purity and MM is required. On the other hand, Oinonen et al. (2013) have shown that enzyme-catalysed crosslinking of spruce hemicelluloses improved the mechanical properties of the produced barrier films. Therefore, in such applications, a small amount of lignin in the hemicellulose fraction is not harmful but even necessary for the process.

The lignin and carbohydrate retentions were affected by treatments with laccase and laccase combined with adsorbents (Table XXIV). The increased lignin retention of the UFX5pHt membrane in the filtration of laccase and combination-treated birch extract (B4) supports the idea of formed larger ligneous compounds due to oxidation and polymerisation. The decreased carbohydrate retentions were probably due to liberated carbohydrates from the complexes, which are obviously smaller than the complex itself, and therefore more easily permeated. These actions affect the purity and yield of the carbohydrates negatively, as more carbohydrates and less lignin goes to the permeate fraction, although carbohydrates are meant to go to the concentrate, and as much lignin as possible to the permeate fraction. However, if the molecular size of lignin could be increased sufficiently, prefiltration could be used to remove lignin prior to the filtration step in which the carbohydrates are concentrated. The size of lignin molecules could be possibly increased enough for the mentioned purpose by ultrasonic treatment, as was done in the study of Wells Jr. et al. (2013) who created reactive lignin fragments from Kraft lignin by ultrasonic treatment, increasing the molecular mass to 450-fold compared to the original molecular mass. If this kind of increase in the MM of lignin in the extracts could be obtained, the separation of these large lignins from carbohydrates would be easier. However, the ultrasonic treatment might degrade the hemicelluloses, which would be disadvantageous.

Table XXIV Lignin and carbohydrate retentions from the filtration of the pretreated birch extract B4 with the UFX5pHt membrane at 60°C and 5.5 bar and rotor tip velocity 1.6 m/s. The VRF values in the filtrations were about 2.

Pretreatment	R(lignin), %	R(carbohydrates), %
None	48	78
Laccase	57	70
Laccase + activated carbon	69	53
Laccase + bentonite	68	22
Laccase + XAD16	65	55

When the flux values obtained from the filtrations of birch extract B4 after combination treatments are compared to the extract composition, the amount of lignin or carbohydrates do not seem to be the most important factor (Table XXIII). The highest flux was obtained with the extract treated with laccase and bentonite, in which case only wood extractives had been removed more than in the other combination treatments. Therefore, although the amount of

wood extractives was much lower than that of lignin or carbohydrates, their impact on filtration capacity could be significant. In addition, in the case of laccase and XAD16, the only difference between the extract compositions was a higher amount of extractives in the extract after the combination treatment than after bare adsorption. After the combination treatment of laccase and XAD16, the flux was lower than after bare adsorption. The amount of wood extractives of the total concentration was so small that changes in the filtration capacity, caused by changes in the amount of wood extractives, cannot be explained by the decrease of total concentration.

The higher flux value with AC was achieved without laccase treatment, which increased the lignin removal and decreased the carbohydrate removal. The removal of extractives remained at the same level. Therefore, although the difference in the removal of carbohydrates was probably due to a difference in the amount of AC, it was the only factor explaining the higher flux achieved with bare AC than with the combination treatment when only the amounts are considered. The changes in the lignin structure or MM resulting from the laccase treatment, may have also had an impact on the interactions of lignin molecules with the membrane, thus affecting the filtration capacity.

10 CONCLUSION

Hemicelluloses can be recovered from wood extracts with ultrafiltration. However, commercial tight ultrafiltration membranes feasible for use in industrial-scale modules with a high shear rate are mostly hydrophobic, and thus hydrophobic wood extract compounds, such as lignin and extractives, tend to cause significant fouling in them. Fouling and a low filtration capacity limit the applicability of ultrafiltration membranes seriously in wood-based biorefinery processes. Therefore, this thesis focused on the possibility to improve the filtration capacity and decrease the fouling of commercial tight ultrafiltration membranes by pretreating the wood extracts.

The screening of different pretreatment methods showed that prefiltration with higher cut-off ultrafiltration membranes was an insufficient solution for the fouling problem, but adsorptive and oxidative methods improved the filtration capacity significantly. The tested pretreatments had an influence on the extract composition and on the molecular mass distributions as well. Generally, research in this area reports which types of compounds have been removed from the extract. However, this study revealed that in addition to which compounds had been removed, also the change in molecular size distribution affected the filtration capacity significantly. It was shown that large compounds that are rejected by the membrane, as well as very small compounds are less harmful for the filtration capacity. Therefore, the most harmful compounds are between these two sizes. These compounds can permeate the membrane and foul also the inner membrane structure.

There was clear difference in how the different adsorption pretreatments affected the molecular mass distribution and filtration capacity of the UFX5pHt membrane. For instance, XAD adsorbents removed more carbohydrates in the harmful size range than AC. Moreover, AC removed very small ligneous compounds more efficiently than XAD adsorbents, whereas XAD adsorbents decreased the amount of larger ligneous compounds more efficiently than AC, including the most harmful-sized compounds. The removal of carbohydrates and ligneous compounds at all sizes was lesser by bentonite than by XADs or AC. The average molecular masses of the extracts were not affected to a great extent by PCD, but the molecular mass distributions were altered and more heterogeneous lignin was formed, on the basis of their changed retention times in the analysis. Laccase increased the molecular mass of ligneous compounds but possibly also affected other molecular properties.

The compounds decreasing the filtration capacity and increasing fouling were found to be at least partly different. Nevertheless, adsorptive pretreatment could both improve the filtration capacity and decrease fouling. The most remarkable improvement in this study was achieved with XAD adsorbents in the case of birch extract B2 with the membrane UH004P. In this case, the average flux was increased from nearly zero to as high as 107 and 175 kg/(m²h) by pretreatment with XAD16 and XAD7 adsorbents, respectively. Although AC and bentonite were more efficient than XAD adsorbents in decreasing fouling (birch extract B4) their effect

on the flux was at the same level as that of XAD adsorbents. AC and bentonite probably removed compounds of sizes which cause fouling more than XAD adsorbents. Comparing XAD adsorbents with each other, XAD7 decreased fouling more efficiently than XAD16 in all cases, most likely due to the greater removal of wood extractives by XAD7.

The amount of lignin and wood extractives in the extracts was decreased most by the adsorption on polymeric XAD adsorbents and activated carbon. An adsorption isotherm for the XAD16 adsorbent revealed that lignin was adsorbed on multilayers, which means that the adsorbent can still remove more lignin after its surface is covered with lignin. Carbohydrate losses existed with all of the used adsorbents. However, it was shown that optimisation of the amount of adsorbent and the number of adsorption stages to achieve a certain permeate flux enables the diminishing of carbohydrate losses. Moreover, at least in the case of the AC, the increase of temperature decreased the adsorption of carbohydrates and increased the adsorption of lignin. It was also shown that the carbohydrate losses which occurred during adsorption could not be avoided by combining oxidation with laccase and adsorption. This was most probably due to efficient removal of ligneous compounds and wood extractives in the combined process, and the formation of larger, less-harmful ligneous compounds by laccase oxidation.

In addition to the optimisation of the adsorption step, cost-efficient use of adsorbents also requires a successful regeneration step to enable the reuse of the adsorbents. This study showed that based on the filtration capacities of the extract samples treated with regenerated adsorbents, regeneration with NaOH and EtOH solutions restored most of the adsorption capacity of the XAD 16. However, the adsorbent was not fully restored and its capacity to adsorb lignin and carbohydrates decreased with increasing adsorption times. Both tested oxidation pretreatments, PCD and oxidation with laccase, had also a positive impact on the filtration capacity. However, the PCD treatment had only a minor or negative impact, and laccase treatment no impact on fouling. The flux of the UFX5pHt membrane was increased by PCD even multifold in the filtration of spruce extract S2, and laccase treatment increased the flux by 130% in the filtration of birch extract B4. The highest energy dosage used in PCD did not bring the highest increase in flux. The results indicate that with an excessively high energy dosage or oxidation time, PCD oxidation may have altered the size or other properties of the wood extract compounds to become more harmful foulants.

The PCD and laccase treatments decreased the amount of lignin less than adsorption, but also the carbohydrate losses were lower – in many cases merely negligible. Therefore, the purity of the extracts was increased by the oxidation. Both oxidative treatments were rather efficient in the removal of wood extractives, which proved to be one of the reasons for the improved filtration capacity.

The results presented in this thesis demonstrate the complexity of the fouling phenomena in the ultrafiltration of wood extracts. The choice of the best possible pretreatment is case-specific and depends on the wood extract and the membrane used. In conclusion, it can be said that adsorptive pretreatment improves the filtration capacity and decreases fouling rather reliably,

but it may lead to significant hemicellulose losses. Oxidation reduces the loss of valuable hemicelluloses. Combination treatment can also improve the filtration capacity remarkably, but the issue with hemicellulose removal remains. In the design of the pretreatment step, the focus should be strongly on the removal of harmful compound sizes rather than merely on the total amount of removed foulants.

11 SUGGESTIONS FOR FUTURE WORK

The phenomena occurring during oxidative pretreatment remained partly unrevealed, and therefore the methods should be studied in closer detail, especially concerning the oxidation products of ligneous compounds and their impact on the filtration capacity, in order to find out the optimal oxidation conditions for each case. The oxidation products of lignin could possibly be characterised by methods such as GC-MS, NMR or FTIR.

The adsorption temperature had a significant influence on the adsorption of ligneous compounds and carbohydrates; in the case of AC, high temperature increased the adsorption of ligneous compounds and decreased the adsorption of carbohydrates. Therefore, similar studies on the influence of the adsorption temperature with XAD adsorbents would be reasonable, at least with the XAD16 adsorbent, the maximum operating temperature of which is 150°C. With XAD7 the corresponding value is only 100°C, which is probably too low. It would be beneficial if the carbohydrate losses were reduced by performing the adsorption at a high temperature also with the XAD16 adsorbent. On the other hand, if the high temperature increases the possibility of chemisorption, regeneration could become impossible. In the case of AC, thermal regeneration and the applicability of the adsorbed lignin as raw material for new AC could be studied.

The regeneration procedure should be developed further and the amounts and concentrations of the solvents optimised. Separation methods such as nanofiltration, chromatography and distillation to recover carbohydrates and lignin from the regeneration solvents could be studied. Since carbohydrates seemed to desorb more easily from the adsorbent than lignin, they could possibly be rinsed out first with more dilute solvents, after which lignin could be removed by more concentrated solutions or by some degradation method, e.g. the laccase enzyme.

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Publication I

Koivula, E., Kallioinen, M., Preis, S., Testova, L., Sixta H., Mänttari, M.

**Evaluation of various pretreatment methods to manage fouling in ultrafiltration of wood
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Evaluation of various pretreatment methods to manage fouling in ultrafiltration of wood hydrolysates

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ABSTRACT

Process and waste waters of pulp and paper mills contain valuable and underexploited compounds. Interest in utilizing such compounds has increased, leading to the study and development of forest-based biorefineries. Efficient separation technology is vital for the economics of biorefineries. Recovery of valuable compounds, such as lignin or hemicelluloses, can be accomplished with membrane processes. In principle, ultrafiltration is suited for the recovery, fractionation and purification of hemicelluloses from wood hydrolysates. Unfortunately, wood hydrolysates have a high fouling tendency which might lead to inefficient process operations due to decreased filtration capacity and increased costs.

This study evaluates several pretreatment methods for hydrolysates prior to ultrafiltration. The pretreatment methods were selected based on the most probable foulants in wood hydrolysates, striving for their removal, degradation or inactivation. The efficiency of the pretreatment methods in fouling prevention was evaluated by filtering various wood-based hydrolysates with two commercial ultrafiltration membranes, a polysulphone (PSu) membrane and a regenerated cellulose (RC) membrane.

The hydrophobic PSu membrane was fouled more in the experiments than the hydrophilic RC membrane. In tests with the PSu membrane, the most significant improvement in filterability was achieved when pulsed corona discharge (PCD) treatment, an oxidation method, was used as pretreatment. The PCD treatment, which was tested only for the PSu membrane, increased the flux over sixfold compared to filtration of untreated spruce hydrolysate. Other pretreatment methods, such as activated carbon adsorption and pH adjustment, which were tested with both membranes, also had positive effects on the filtration capacity. The results of this study indicate that pretreatment processes have to be tailored separately for different hydrolysates due to their different characteristics.

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1. Introduction

Future forest-based biorefineries envision the extraction of several novel products from lignocellulosic biomasses, e.g. hemicelluloses, lignin, phenols and other monomeric compounds. These valuable chemicals will be separated from existing process streams (e.g. black liquor or thermomechanical pulp mill process water) or extracted prior to the pulping process by subjecting lignocellulose material to different pretreatment processes. In many cases, the

extracted compounds need to be separated, purified and concentrated to reach a marketable form.

Efficient separation technology in biorefineries is, therefore, vital, and membrane technology has proven to be a very promising separation technique in the field.

Hemicelluloses can be extracted from wood by water prehydrolysis (autohydrolysis) or alkaline pre-extraction [1]. This study considers autohydrolysates. Wood autohydrolysates contain hemicelluloses, lignin and wood extractives, such as fatty and resin acids. Hemicelluloses are compounds which can be used in the production of food additives (e.g. polymeric xylan, xylo-oligosaccharides, sugar alcohols etc.), furanic compounds (furfural and hydroxymethylfurfural), biofuels (ethanol, 2,3-butanediol etc.) and other products, such as, lactic and ferulic acids [2]. Xylooligosaccharides can be exploited in pharmaceuticals, feed formulations, agricultural products and food applications as prebiotics in functional food [3]. Hemicelluloses can also be used in the

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production of cationic polymers, hydrogels, ester derivatives and thermoplastic derivatives [4].

Hemicelluloses have to be separated from other products that have dissolved from wood before they can be converted into products. Ultrafiltration is a possible technique to recover, concentrate and fractionate hemicelluloses from wood hydrolysates. However, fouling seems to be a quite severe problem in the filtration of acidic wood hydrolysates, especially with hydrophobic membranes [5]. Degradation products of lignin and extractives released during autohydrolysis tend to form reactive insoluble particles which might cause fouling of the membranes [6,7]. It is difficult to obtain detailed information about the main foulants, because the composition of the wood hydrolysate is very complex, containing many challenging components, and studies focusing on fouling in biorefinery applications are thus far not widely available. Fouling of membranes leads to increasing costs because of a decrease in filtration capacity, an increase in the number of membrane cleanings required, and a decrease in membrane lifetime.

To be able to effectively separate hemicelluloses with ultrafiltration, fouling problems should be prevented or at least mitigated. This could be done by pretreating the wood hydrolysate to remove possible foulants before ultrafiltration. Persson et al. [5], for instance, noticed that activated carbon treatment of a feed solution prior to filtration reduced fouling and improved flux in ultrafiltration of masonite wastewater.

There are several possible methods to pretreat hydrolysates and a number of approaches for phenolic compounds removal or delignification of the hydrolysate can be found in the literature. Arslan and Eken-Saraçoğlu [8] reported that based on UV absorbance at 280 nm, charcoal treatment together with overliming with CaO reduced the amount of phenolic compounds in hazelnut shell hydrolysate. Phenolic compounds content was reduced to 2.1% of that of untreated hydrolysate. Parajó et al. [9] removed 75% of the phenolics present in *Eucalyptus globulus* wood hydrolysate using activated charcoal adsorption. Miyafuji et al. [10] also reported the removal of phenolic compounds from wood (spruce) hydrolysate with wood charcoals. In their study, the amount of phenolic compounds in charcoal treated hydrolysate was so low that it could not be detected with GC–MS and HPLC, while these compounds were clearly detected in the untreated hydrolysate. In addition to the above-mentioned approaches, other methods for ligneous material or phenolic compounds removal have been studied, e.g. extraction with organic solvent [11] or supercritical CO₂ [12], precipitation with acid [13], and ion exchange [14].

Removal of wood extractives is another approach for fouling prevention; although in practice, it might be reasonable to remove both phenolic compounds and wood extractives. Wood extractives can be removed from wood derived solutions using methods such as coagulation with cationic polyelectrolytes [15] or extraction with, e.g. ethyl acetate [16].

The complexity and high fouling tendency of wood hydrolysates make fouling management in membrane filtration of hydrolysates a challenging task. In this study several pretreatment methods were investigated in order to decrease fouling during ultrafiltration of wood hydrolysates. The aim was to find a pretreatment method able to improve filterability of wood hydrolysates and to establish if the same pretreatment process can be used for different hydrolysates.

2. Experimental

2.1. Hydrolysates

Two kinds of hydrolysates were used in this study; one from birch chips and one from spruce saw-dust. They were both

Table 1
Hydrolysis conditions for birch hydrolysate.

Type of sample	Hydrolysate
Temperature	150 °C
P-factor	200
Liquid-to-wood ratio	4:1 (four volume parts of deionized water and one weight part of dry chips, moisture in chips considered)
Total dwell time of chips	130 min
Dwell time of chips at target temperature	90 min

Table 2
Measured properties of solutions used in the experiments.

	Birch hydrolysate	Spruce hydrolysate
pH	3.3	3.8
TOC, g/l	15.6	2.3
^a Soluble lignin, g/l	3.2	0.8
Total carbohydrates, g/l	9.0	1.9
Turbidity, NTU	230–990	290
Conductivity, mS/cm	0.97	0.32

^a Calculated from UV₂₀₅ according to Tappi Useful Method 250 [18].

produced by autohydrolysis; wood chips were cooked in water at high temperature and pressure. During water autohydrolysis, short-chain polysaccharides, predominantly hemicelluloses, are degraded by the hydrolytic cleavage of glycosidic bonds catalyzed by acetic acid derived from the side-chains of the hemicelluloses. Lignin and extractives are also removed by degradation processes catalyzed by the weak acid and the high temperature. The hydrolysate composition depends on the treatment intensity and can be calculated by means of the prehydrolysis factor (*P*-factor), which expresses the change of temperature over time using an Arrhenius type Eq. (1) [17]. The higher the *P*-factor, the higher is the amount of released carbohydrates into the water. The two hydrolysates used in this study were manufactured in different laboratories in different operational conditions and with different equipment. Hydrolysis conditions for the birch hydrolysate are presented in Table 1 and Eq. (1) was used to calculate the *P*-factor for the birch hydrolysate process:

$$P = \int_{t_0}^t \frac{k_{H(T)}}{k_{100^\circ\text{C}}} dt = \text{Exp} \left(40.48 - \frac{15106}{T} \right) dt \quad (1)$$

in which *t* is time, *k_{H(T)}* is the rate constant of xylan hydrolysis at the temperature *T* and *k_{100°C}* is the reference reaction rate at 100 °C.

The spruce saw dust was extracted using a flow-through extraction apparatus. The extraction was performed at 180 °C for 50 min. The water flow rate was approximately 15–20 l/min and the accumulated hydrolysate volume was 820 l. The spruce hydrolysate was prefiltered with a RC70PP ultrafiltration membrane prior to the actual pretreatment tests. The properties of both hydrolysates are presented in Table 2.

2.2. Membranes

The hydrolysates were filtered using two commercial ultrafiltration membranes from Alfa Laval, a polysulphone membrane (PSu) and a regenerated cellulose membrane (RC). Information about the membranes is presented in Table 3.

2.3. Pretreatment methods

The pretreatment methods studied were chosen with the aim of degradation, removal or inactivation of foulants. The methods

Table 3
Information on the two ultrafiltration membranes used in filtration experiments given by the manufacturer.

Membrane	UFX5	RC70PP
Manufacturer	Alfa Laval	Alfa Laval
MWCO, g/mol	5000	10,000
pH range	1–13	2–10
Pressure range, bar	1–15	1–10
Temperature range, °C	0–75	0–75
Material	Polysulphone on polypropylene (PSu)	Regenerated cellulose on polypropylene (RC)

Table 4
Hydrolysate pretreatment methods.

Method	Purpose
No pretreatment at all pH adjustment	For comparison Unstabilizing of lignin network
Centrifugation at room temperature	Removal of insolubles (including insoluble lignin)
Centrifugation at 45 °C	Removal of insolubles (including insoluble lignin)
Ethyl acetate extraction	Removal of lignin
Activated carbon adsorption	Removal of lignin and extractives
Membrane filtration	Removal of any kind of foulants
Hemp adsorption	Removal of any kind of foulants, esp. lignin
Pulsed corona discharge (PCD) treatment	Oxidation of lignin

tested were: (1) pH adjustment, (2) centrifugation, (3) extraction with ethyl acetate, (4) treatment with activated carbon, (5) prefiltration with a looser ultrafiltration membrane, (6) adsorption with hemp and (7) oxidation by pulsed corona discharge (PCD) (Table 4).

2.3.1. pH adjustment

The pH of the hydrolysate was adjusted to 7–8, from an original pH value of about 3.3, with 5 M sodium hydroxide. When pH is increased, some carboxylic acids with pK_a 3–4 are converted to salts, which decreases their ability to form hydrogen bonds with the lignin stabilizing their network. At neutral, pH carboxylic acid groups are repelled by the negatively charged membrane, which might reduce fouling.

2.3.2. Centrifugation

Centrifugation was performed with a Sorvall RC-28S Supra-speed centrifuge and GSA rotor at room temperature and at 45 °C, to remove solids, including insoluble lignin, from the hydrolysate. Hydrolysate was centrifuged for 30 min at a rotation speed of 2200 rpm. Centrifugation at 45 °C was carried out such that the hydrolysate was first heated to the target temperature. The centrifuge was also preheated. The centrifugation (30 min, 2200 rpm) was then performed, and the temperature was again measured.

2.3.3. Extraction with ethyl acetate

Ethyl acetate extraction was carried out to extract lignin from the hydrolysate. The hydrolysate to ethyl acetate volume ratio was 1:3. Hydrolysate was centrifuged before extraction as described above. After mixing the hydrolysate with ethyl acetate in a 1 l bottle, the mixture was shaken for 30 min at a rotation speed of 500 rpm. After shaking, the contents of the bottle were transferred to six centrifugation jars and centrifuged for 5 min at 2200 rpm. The phases were then separated with a pipette such that the aqueous phase was reclaimed.

2.3.4. Adsorption onto activated carbon

Activated carbon (AC) treatment was carried out to adsorb lignin material and wood extractives from the hydrolysate. The hydrolysate was centrifuged before adsorption as described above. The hydrolysate was mixed with granulated (size about 3–5 mm) activated carbon (the hydrolysate to AC mass ratio was 24:1) with a magnetic stirrer for 30 min at about 1000 rpm. After stirring, the solution was vacuum filtered using Whatman Glass Microfibre filters (GF/F 70 Ø).

2.3.5. Membrane prefiltration

Membrane filtration pretreatment was performed with the RC membrane. Permeate from the RC membrane was collected and used as a feed solution for the PSu membrane. The first filtration was conducted with a CR (cross rotation) filter, which is large-scale equipment manufactured by Metso Paper; 45 kg of hydrolysate was filtered. The CR filter consists of plates, support layers, membranes and rotors. The active membrane area is 0.09 m² and operation pressure 0.5–10 bar. Membranes were pretreated for 30 min in 0.5% P3 Ultrasil 110 solution, and rinsed with tap water before use. Hydrolysate was filtered at 60 °C and 3 bar. Pure water fluxes were measured before and after filtration.

2.3.6. Adsorption onto hemp

Hemp was used to adsorb possible foulants, especially lignin, from the hydrolysate. Two kinds of hems were tested: reed canary grass (<1 mm) and fibre hemp (5 mm). The hemp was mixed with the hydrolysate and stirred (330 rpm) for about 19 h. In the case of reed canary grass, the hydrolysate was vacuum filtered (through Whatman Glass Microfibre filters (GF/F 70 Ø)). Vacuum filtering was unsuccessful with fibre hemp, so the hydrolysate was centrifuged as described earlier. After centrifugation it was filtered again through the same filter papers as used in the vacuum filtering, but using an Amicon filter cell and pressure of 1–1.5 bar.

2.3.7. Oxidation with pulsed corona discharge

Pulsed corona discharge (PCD) treatment was used for organic material degradation, based on the assumption that lignin might be selectively oxidized by oxidative species (ozone, OH-radicals, atomic oxygen and peroxides) generated in the electric discharge [19]. After the first PCD test with the birch hydrolysate, the spruce hydrolysate was also used in this treatment. The PCD treatment was the only pretreatment made for the spruce hydrolysate. Treatment was conducted in an 80–90% oxygen atmosphere. The discharge pulse repetition frequency was 840 pulses per second (pps) at a current amplitude of 400 A, voltage of 20 kV and pulse energy of 300 mJ. Oxygen consumed in oxidation was periodically replenished during the treatment. The duration of the treatment was two hours, during which five samples were collected at 0, 15, 30, 60 and 120 min. The corresponding energy doses consumed on the hydrolysate are 0, 1.25, 2.5, 5.0 and 10.0 kWh/m³, respectively. All samples were filtered with the PSu membrane.

2.4. Filtration experiments

The hydrolysate was filtered with a lab-scale filter cell (Amicon). The hydrolysate was heated to 55 °C and 300 g was weighed to the filter cell. The aim of the filtration was to continue the filtration until 100 g of the concentrate remained, that is, until 200 g of permeate was formed, a VRF (Volume Reduction Factor, ratio of the feed and concentrate volumes) value of 3, or until the flux value fell below 5 kg/(m² h). The temperature was maintained at 55 °C with a heating plate and a pressure of 5.5 bar was maintained with nitrogen gas. A magnetic stirrer with the tip linear velocity of 1.5 m s⁻¹ was used to decrease concentration polarization. Three

Table 5
Analyses for evaluation of pretreatments and filtrations.

Analysis	Method	Equipment
pH	–	Metrohm 744 pH meter
Conductivity	–	Knick konduktometer 703
Turbidity	ISO method 7027	Hach 2100AN IS Turbidimeter
Total organic carbon (TOC)	–	Shimadzu TOC 5050A total organic carbon analyzer
Total carbohydrates	Anthrone sulphuric acid method with glucose standard	Varian Cary 1C UV-Visible Spectrophotometer
UV _{205 nm} (lignin)	Tappi Useful Method 250 [18]	Varian Cary 1C UV-Visible Spectrophotometer
Contact angle	Sessile drop method	KSV CAM 100 Contact Angle Meter and computer program CAM 2008

samples were collected for each filtration: a feed sample, permeate and concentrate.

2.5. Analysis

The samples were analyzed to establish how the pretreatment had affected the hydrolysate composition, and whether hemicelluloses and lignin had been separated in the filtration step. Additionally, contact angles of the used membranes were measured and compared to the contact angle value of the virgin membrane to provide information about the influence of fouling substances on membrane characteristics. Analyses performed are presented in Table 5.

3. Results and discussion

The pure water flux (PWF) measurements showed that fouling with hydrolysate was a bigger problem for the PSu membrane than for the RC membrane (Table 6), which may be partly explained by the more hydrophilic character of the RC membrane (contact angle 13°) than the PSu membrane (contact angle 74°). In the filtration of process waters containing wood compounds, it has been found earlier that fouling is more severe with membranes having high contact angles than with membranes having lower contact angles [20,21]. As can be expected from the different cut-off values and materials of the membranes, the fluxes of the two studied membranes differed in the filtration of the birch hydrolysate; the RC membrane had higher flux values compared to the PSu membrane. Furthermore, the filtration capacity of the PSu membrane decreased to a greater extent and faster during the filtration than the filtration capacity of the RC membrane (Figs. 1 and 2).

Only some of the tested pretreatment methods influenced the filtration capacity of the tested membranes (Table 7). With the PSu membrane, the strongest effect on the filtration capacity was seen with the use of ethyl acetate extraction, activated carbon adsorption or PCD as pretreatment (Fig. 3). The results for pretreatment by activated carbon adsorption concur with those of Persson et al. [5], who presented that activated carbon treatment can reduce the fouling of ultrafiltration membranes in filtration of masonite wastewater. There are, however, practical disadvantages with both ethyl acetate extraction and activated carbon usage. Ethyl acetate, being slightly water soluble, could not be totally removed from the hydrolysate prior to filtration, which might have somewhat diluted the hydrolysate and thus increased the flux. Moreover, the membranes could not resist ethyl acetate and their surface was damaged. A major problem with activated carbon in

larger-scale and industrial applications is that a great amount of solid waste is generated. Therefore, PCD treatment seems to be the most practical pretreatment method in the filtration of the birch hydrolysate with the PSu membrane.

For the RC membrane improvement in filtration capacity was seen more clearly, especially with activated carbon (Fig. 2). pH adjustment and centrifugation also reduced fouling, based on increased fluxes compared to the filtration experiments with untreated birch hydrolysate.

The PSu membrane (5 kDa) showed higher hemicellulose retentions (evaluated based on the total carbohydrate retentions about

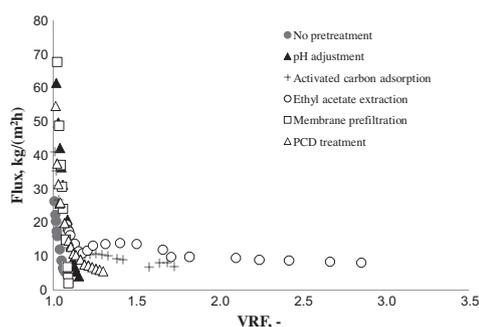


Fig. 1. Fluxes of the PSu membrane during filtration of pretreated birch hydrolysate at 55 °C and 5.5 bar.

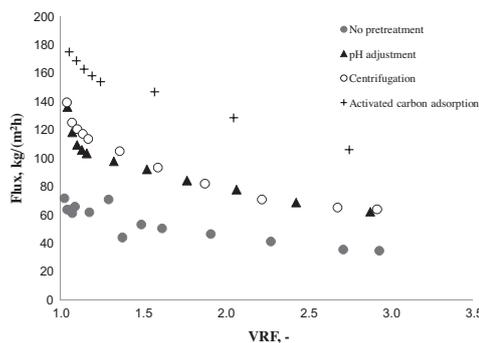


Fig. 2. Fluxes of the RC membrane during filtration of pretreated birch hydrolysate at 55 °C and 5.5 bar.

Table 6
Pure water fluxes for the PSu and the RC membranes before and after filtration of untreated birch hydrolysate.

Membrane	PWF before, kg/(m ² h)	PWF after, kg/(m ² h)	Decreased, %
PSu	190	30	84
RC	415	355	14

Table 7
Influence of tested pretreatment methods on filtration capacity of PSu and RC membranes.

Method	Influence on the filtration capacity detected
pH adjustment	No significant influence (minor influence with the RC membrane)
Centrifugation at room temperature	No significant influence (minor influence with the RC membrane)
Centrifugation at 45 °C	No significant influence
Ethyl acetate extraction	Improvement (but problems with completely separating ethyl acetate from hydrolysate; membranes did not withstand ethyl acetate)
Activated carbon adsorption	Improvement
Membrane filtration	Some improvement
Hemp adsorption	No significant influence
Pulsed corona discharge (PCD) treatment	Improvement (significant improvement for the spruce hydrolysate, presented later in the text)

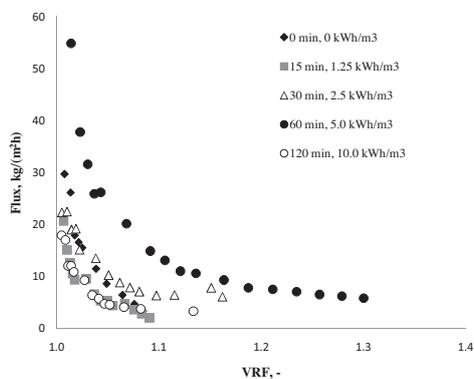


Fig. 3. Fluxes of the PSu membrane during filtration of PCD treated birch hydrolysate at 55 °C and 5.5 bar. (0–120 min refers to the duration of the treatment and the following value is the consumed energy dose.)

61–76%) than the RC membrane (10 kDa) (total carbohydrate retentions about 21–43%). Pretreatments other than membrane filtration (the hydrolysate was filtered first with the RC membrane, after which the permeate was filtered with the PSu membrane) had no effect on the retentions. Membrane filtration as pretreatment decreased all the measured retentions (TOC, UV absorbing matter, total carbohydrates and conductivity) except turbidity retention. This was a result of the RC membrane having already rejected most of the bigger particles.

Although the pretreatments resulted in some improvements in the filtration capacities, analysis of the hydrolysates showed only small changes in the birch hydrolysate composition caused by pretreatment. This finding suggests that even small changes in dissolved matter composition of hydrolysate can already improve filtration capacity; although in this study, the changes are so small that they were not detectable with the analysis methods used. The filterability of the hydrolysate increased in this study, even though analysis of sum parameters (e.g. total organic carbon) gave unchanged results.

The effect of PCD treatment was studied further because of its positive impact on filtration capacity and its practicality (Fig. 3). The highest flux with birch hydrolysate was achieved at a PCD treatment time of 60 min. Increased treatment time (120 min)

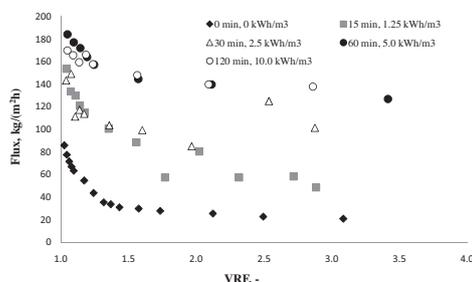


Fig. 4. Fluxes of the PSu membrane during filtration of PCD treated spruce hydrolysate at 55 °C and 5.5 bar. (0–120 min refers to the duration of the treatment and the following value is the consumed energy dose.)

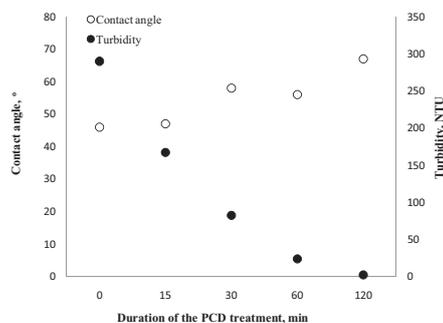


Fig. 5. Effect of PCD treatment on the turbidity of the spruce hydrolysate and contact angles of the used membranes. Contact angle of the virgin PSu membrane was 74°.

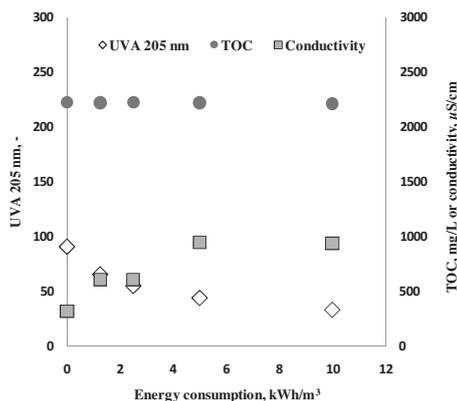


Fig. 6. Effect of PCD treatment on the UV (205 nm) absorbance, TOC and the conductivity of the spruce hydrolysate.

Table 8
Retention values (%) of PCD treated spruce hydrolysate filtered with the PSu membrane.

Treatment time, min	R_{TOC}	$R_{Carbohydrates}$	R_{UV}	$R_{Conductivity}$	$R_{Turbidity}$
0	38	49	34	14	96
15	36	42	23	5	99
30	28	43	23	9	100
60	13	13	17	–	98
120	9	13	28	3	88

did not improve the flux; on the contrary, the results were worse even than with untreated birch hydrolysate. A possible reason could be that some molecules might degrade only after treatment time greater than 60 min, and such degraded smaller compounds might cause more fouling than the original larger molecules. It can, therefore, be concluded that to avoid the formation of new foulants, optimization is vital in pretreatment based on disruptive oxidation.

Since the PCD treatment improved the fluxes of the PSu membrane when the birch hydrolysate was filtered (Fig. 3), the same treatment was also examined with spruce hydrolysate which had already been pretreated with the RC70PP membrane. In these experiments the fluxes of the PCD treated spruce hydrolysate increased significantly (Fig. 4). The flux of spruce hydrolysate treated for 120 min was found to reach values over six times higher than the flux of untreated spruce hydrolysate.

UV (205 nm) absorbance suggests that ligneous material is present [18] and turbidity of the solution indicates the presence of wood extractives. The experimental results showed that the amounts of wood extractives and UV absorbing materials (including lignin and also partly wood extractives) in the spruce hydrolysate decreased significantly as a result of the PCD treatment (Figs. 5 and 6). The longer the treatment continued, the greater was the decrease. Although the amounts of carbohydrates and TOC remained almost stable, both retentions (total carbohydrates and TOC) decreased with the hydrolysate treated for 60 and 120 min (Table 8). The degradation of compounds might have an influence on the decrease in retention values: the smaller degraded particles were not rejected as well as the bigger ones. Additionally, increase in flux might also have caused some deterioration in retention values.

The contact angle value of the virgin PSu membrane was 74° and, as can be seen in Fig. 5, the longer the PCD treatment, the closer the contact angle value of the used membrane was to the original value. This result implies that the treatment decreased the amount of foulants in the feed solution. These foulants which lower the contact angle might be wood extractives, as suggested by the decreasing turbidity values of the feed solutions with increased treatment time. Hydrophobic and hydrophilic parts in the structure of wood extractives [22] might also make the hydrophobic membrane more hydrophilic by sticking on the surface. The decrease in the contact angles of the fouled membranes may also be caused by adsorbed phenolic compounds on the membrane surface. According to Susanto et al. [23] the fraction of the hydrophilic component from the polyphenolic compound might hydrophilize the membrane when a solution containing polyphenolic compounds is filtered. Oxidation of lignin or removal of wood extractives might be the reason for the improvement in the filtration capacity, or both phenomena might have had an impact.

The PCD treatment increased the solution conductivity about 3-fold (Fig. 6), indicating that new ionic groups were formed. Simultaneously, solution pH decreased from 3.8 to 2.9, due to the formation of acidic compounds. Since the total carbon content remained the same, mineralization of organic compounds can be considered to be negligible.

4. Conclusions

This study was conducted to find possible pretreatment methods prior to ultrafiltration of wood hydrolysates with the aim of decreasing fouling by removing, degrading or inactivating foulants, especially lignin or wood extractives. Various pretreatment methods were tested and their effect was evaluated based on their influence on filtration capacity and fouling in hydrolysate filtration.

Ultrafiltration of wood hydrolysate with the PSu membrane proved to be very challenging due to rapid flux decrease. The flux decrease with the RC membrane was not as severe as with the PSu membrane. However, the PSu membrane retained hemicelluloses better than the RC membrane. With the PSu membrane, some methods, such as activated carbon adsorption, had some effect on the flux. However, significant improvement in the filterability of birch hydrolysate was achieved only with PCD treatment. PCD treatment of spruce hydrolysate was even more successful in improving the fluxes. It also progressively decreased turbidity and UV₂₀₅ absorbance with increasing treatment time. PCD treated hydrolysate was not filtered with the RC membrane. Of the methods tested, the most effective pretreatment method with the RC membrane was found to be activated carbon adsorption. pH adjustment and centrifugation also improved the flux to some extent.

This study showed that some pretreatment methods, especially PCD and activated carbon treatments, are effective methods to reduce fouling in the ultrafiltration of wood hydrolysates. However, the results also demonstrated that the pretreatment has to be optimized for different hydrolysates separately. Otherwise, membrane fouling might even increase with the use of methods based on disruptive oxidation, such as PCD treatment.

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Publication II

Koivula, E., Kallioinen, M., Sainio, T., Luque, S., Mänttari, M.

Enhanced membrane filtration of wood hydrolysates for hemicelluloses recovery by pretreatment with polymeric adsorbents

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Enhanced membrane filtration of wood hydrolysates for hemicelluloses recovery by pretreatment with polymeric adsorbents



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HIGHLIGHTS

- Ultrafiltration of lignin-containing wood hydrolysates is challenging.
- Adsorption pretreatment with XAD-7 and XAD-16 enhances ultrafiltration capacity.
- Ligneous compounds adsorbed on multiple layers on XAD-16.
- Disadvantage of the pretreatment is hemicellulose losses.

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ABSTRACT

In this study adsorption of foulants from birch and pine/eucalyptus wood hydrolysates on two polymeric adsorbents was studied aiming to reduce the membrane fouling. The effect of the pretreatment of hydrolysate on polyethersulphone membrane performance was studied in dead-end filtration experiments. Adsorption pretreatment improved significantly filtration capacity and decreased membrane fouling. Especially high-molecular weight lignin was efficiently removed. A multistep adsorption pretreatment was found to reduce the amount of adsorbent required. While large adsorbent amount was shown to increase flux in filtration, it was found also to cause significant hemicellulose losses.

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1. Introduction

Wood autohydrolysates are produced by thermal treatment in aqueous medium (typically from 150 to 180 °C). They contain hemicelluloses and other water soluble components from wood (Leschinsky et al., 2009). After separation from the hydrolysate hemicelluloses can be used, for example, for production of food additives, biofuels, organic acids, and various types of polymers (Vázquez et al., 2000, 2005). Traditional way to recover hemicelluloses is precipitation with organic solvents. The most commonly used solvent is ethanol. (Peng et al., 2012; Bian et al., 2012; Ma et al., 2012) The use of membrane filtration in recovery, purification and fractionation of hemicelluloses enables decrease in chemical consumption. Ultrafiltration has been used for instance in the recovery of hemicelluloses from spruce hydrolysate, pine hydrolysate and pulp mill process waters (Al Manasrah et al., 2012; Sainio

et al., 2013; Persson et al., 2010). Swennen et al. (2005) have compared ultrafiltration and fractionation by graded ethanol precipitation in the recovery of arabinoxylooligosaccharide (AXOS) fractions from wheat hydrolysates. They concluded that compared with the ultrafiltration, ethanol precipitation produces more homogeneous fractions. However, it is possible to achieve a similar degree of polymerization and degree of substitution with both of the tested methods.

The commercial membranes available for the recovery process are often hydrophobic and thus very susceptible to fouling by lignin and wood extractives (Koivula et al., 2011; Sainio et al., 2013; Maartens et al., 2002; Puro et al., 2002). For instance Koivula et al. (2011) reported over 90% permeate flux decrease within few minutes when birch hydrolysate was tried to fractionate by poly-sulphone UF membrane. To enable an effective hemicellulose recovery and high yield with the commercial tight (i.e. cut-off values less than 10 kDa) ultrafiltration membranes, pretreatment step reducing the fouling problem is needed. In an optimum pretreatment step the foulants are removed from the hydrolysate or they

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are degraded to a form in which they are less prone to foul. For lignin such degradation can be done, for example, by photocatalytic oxidation (Portjanskaja et al., 2006) or by treatment with oxidative enzymes (Durán and Esposito, 2000).

Lignin and its degradation products can be removed from the hydrolysate with adsorption (Louchouart et al., 2000; Gütsch and Sixta, 2012). Activated carbon has been tested as a pretreatment step prior to ultrafiltration in the treatment of wastewaters from Masonite process (Persson and Jönsson, 2009). The main target was to isolate hemicelluloses, while purified wastewater was considered as a by-product. The pretreatment made it possible to achieve a higher flux, which was explained by adsorption of phenolic compounds and various inorganic compounds onto the activated carbon. However, some hemicelluloses were lost.

There are also several different types of commercially available polymeric adsorbents, which can be used to lignin removal. For instance, Amberlite XAD adsorbents have been found useful in isolating of dissolved lignin phenols from aquatic environment (Spencer et al., 2010) and in removal of phenolic compounds from wood hydrolysates (Lehto and Alén, 2012). Schwartz and Lawoko (2010) reported that 90% of acid-soluble lignin present in the hardwood extract could be removed with the hydrophobic XAD-4 adsorbent (polystyrene-divinylbenzene). XAD-16, which is of the same type, has been used to adsorb lignin and lignans from a spruce based galactoglucomannan fraction (Westerberg et al., 2012). XAD-7, which is an uncharged polyacrylate adsorbent, has been used in removal of lignin and lignans from pulp mill process water (Willför et al., 2003).

This study aimed at enhancing filtration capacity and decreasing fouling in the recovery of hemicelluloses from different wood hydrolysates by introducing a XAD based adsorbent pretreatment step. Different solid to liquid phase ratios were used to systematically examine the relationship between the amount of removed foulants and achieved flux. XAD-16 and XAD-7 adsorbents were selected for this study because they are expected to be effective based on the above mentioned literature. In addition, optimization of the adsorbent amount giving a desired level of improvement in filtration capacity was investigated.

2. Methods

2.1. Hydrolysate and filtration

Hydrolysates prepared from a mixture of eucalyptus and pine as well as from birch were used. Hydrolysis conditions and compositions of the hydrolysates are given in Table 1.

Filtrations were conducted with two different dead-end filters using commercial ultrafiltration membranes (Table 1). The hydrolysate was filtrated until the volume reduction factor (VRF) value of 2 was achieved. Samples were collected for analysis from feed, permeate and concentrate. Pure water fluxes (PWF) were measured before and after the filtration of the hydrolysate in order to find out how severe the fouling was. The membranes were pretreated with 0.05% NaOH solution for 4.25 h (UF5 pHt) and in pure water in ultrasound bath three times for 10 min (UH004P).

The membranes used in this study were chosen based on their cut-off values enabling recovery of low molar mass hemicelluloses (i.e. molar mass around 5 kDa) from the hydrolysate. The potential commercial membranes at this molar mass cut-off range are usually made from polysulphone or polyethersulphone and they are rather hydrophobic. They have a high fouling tendency in the treatment of wood hydrolysates and are thus ideal for this kind of study, which focuses on the evaluation of influence of pretreatment on membrane fouling.

Table 1
Hydrolysis conditions, hydrolysate composition, and filtration conditions.

Raw material	Eucalyptus/pine	Birch
Hydrolysis temperature (°C)	185	170
Hydrolysis time (min)	11	120
UV absorbance at 280 nm (-)	88	350
Total hemicelluloses (g/l)	29	12
Viscosity (mm ² /s)	0.57	0.55
Dry matter content (%)	2.2	3.6
Density (g/cm ³)	1.005	1.009
Filter type	Amicon 8050, dead-end stirred cell	Amicon 8400, dead-end stirred cell
Membrane	UF5 pHt	UH004P
MWCO (kDa)	5	4
Membrane material	Polysulphone	Polyethersulfone
Membrane surface area (m ²)	0.0015 × 2	0.0040
Filtration temperature (°C)	45 (in the beginning)	60
Filtration pressure (bar)	2.0	5.5
PWF pressure (bar)	2.0	3.0
Target VRF (-)	2	2
Mass of the feed solution (g)	50 × 2	200

2.2. Adsorption

The XAD adsorbents in this study were Amberlite XAD16 and Amberlite XAD7HP (Rohm and Haas). XAD-16 is hydrophobic, styrene-divinylbenzene adsorbent, the surface of which is aromatic and uncharged. XAD-16 is applicable for adsorbing hydrophobic molecules from polar solvents, e.g. organic substances of relatively low to medium molecular weight. XAD-7 is an uncharged polyacrylate adsorbent, and its surface is aliphatic. XAD-7 can be used to adsorb non-polar compounds from aqueous systems, e.g. plant extracts and organic pollutants, and polar compounds from non-polar solvents. According to manufacturer, XAD-16 can be used to adsorb hydrophobic compounds with molecular weight less than or equal to 40,000 g/mol, and XAD-7 can be used to adsorb organic compounds with molecular weight less than or equal to 60,000 g/mol.

Adsorbents were first rinsed with distilled water to get rid of the preservatives. Preservatives are sodium chloride and sodium carbonate salts which increase the conductivity of the rinsing water when they are present. The rinsing was continued until the conductivity of rinsing water collected through the adsorbents no longer decreased (typically 10 rinsing times).

After rinsing, adsorbent was mixed with 200 g of eucalyptus/pine hydrolysate or 300 g of birch hydrolysate in decanter glass and agitated with a magnetic stirrer for 3 h (eucalyptus/pine), or 1 h (birch). Solid to liquid phase ratios between 0.005 and 0.167 were used. Experiments were conducted at 60 °C, which is a likely process temperature. In order to study the kinetics of the removal of ligneous material and wood extractives, samples of 1 mL were collected during the trial. After adsorption, the adsorbent was separated from the hydrolysate by vacuum filtering with Schleicher & Schüll 604 filter paper, which rejects particles over 8 µm (adsorbent harmonic mean size is 560–710 µm).

UV-absorbance was used to quantify the amount of ligneous material in the samples. In order to construct an adsorption isotherm from the batch adsorption, the absorbance was treated as a "pseudocomponent". In other words, it was assumed that absorbance is a direct measure of the sum of the mass concentrations of

all components that contribute to the absorbance. Therefore, conventional material balance approach was used to relate the concentration of this pseudocomponent on the adsorbent surface to its concentration in the liquid phase. The pseudocomponent is denoted with “A” in the following.

UV absorbance was measured from original and treated hydrolysate obtaining concentrations of A in the beginning and at the equilibrium; c_A^0 and c_A^{eq} , respectively. The concentration of A in the solid phase at equilibrium, q_A^{eq} , is obtained from the material balance:

$$V^L c_A^0 + m^S q_A^0 = V^L c_A^{eq} + m^S q_A^{eq} \quad (1)$$

from which:

$$q_A^{eq} = q_A^0 + \frac{V^L}{m^S} (c_A^0 - c_A^{eq}) \quad (2)$$

where V^L is the liquid phase volume, m^S is the adsorbed mass and q_A^0 is the concentration of A in the solid phase in the beginning. Here $q_A^0 = 0$ because the used adsorbent was initially clean. Adsorption isotherm was plotted as q_A^{eq} at corresponding c_A^{eq} values and correlated with a simple mathematical model as discussed in Section 3.4.

2.3. Chemical analyses

UV absorbance was measured at 280 nm with UV–VIS spectrophotometer (Varian Cary 1C) to detect phenolic components (lignin derived material). The amount of total carbohydrates was analyzed as monosaccharides using gas chromatograph (Varian 8200) and acid methanolysis as sample treatment (Sundberg et al., 1996).

Molecular weight distribution of ligneous material was determined by High Performance Size Exclusion Chromatography (HPSEC) using the chromatograph Agilent 1100 series (Hewlett-Packard). A volume of 5 μ L of sample were injected for its determination, using NaOH (0.5 M) as mobile phase (0.5 mL/min), the Superose 12 (10/300 GL) column (GE Healthcare) and a refractive index detector (RID) at 35 °C. Calibration of the method was done with solutions of sodium polystyrene sulfonates, fractions of sodium lignosulfonates and proteins with molecular weights from 0.058 to 990 kDa.

2.4. Treatment of filtration data

Pure water flux reduction (PWF_R) was calculated from pure water fluxes before and after the filtration:

$$PWF_R = \frac{PWF_b - PWF_a}{PWF_b} \cdot 100\% \quad (3)$$

where PWF_b is pure water flux before the hydrolysate filtration, and PWF_a after the hydrolysate filtration.

Volume reduction factor (VRF) was calculated from masses of feed and permeate because density differences can be assumed to be small:

$$VRF = \frac{m_f}{m_f - m_p} \quad (4)$$

where m_f is the mass of feed solution and m_p the mass of permeate.

Permeability, P , and relative permeability, P_{rel} , were calculated with Eqs. (5) and (6):

$$P = \frac{m_p}{A \cdot t \cdot p} \quad (5)$$

$$P_{rel} = \frac{P}{PWP} \quad (6)$$

where A is membrane surface area, t is time and p pressure and PWP is pure water permeability.

3. Results and discussion

3.1. Filtration capacity

Filtration of the birch hydrolysate was almost impossible without pretreatment. The average flux of the untreated birch hydrolysate with UH004P membrane was only 2 kg/m² h due to severe and rapid fouling. A similar result was obtained by Koivula et al. (2011). The average flux of the untreated eucalyptus/pine hydrolysate with UFX5 pHt was 38 kg/m² h. These values are clearly too low for an economical separation process.

The adsorbent pretreatment had a clear positive influence on filtration capacity of both hydrolysates (Fig. 1). When the original birch hydrolysate was filtered, fouling was so severe and flux low that a VRF of 1.1 was only reached. Adsorption treatment with XAD7 at the lowest phase ratio (0.005) increased the permeability at this VRF from 0.28 to 5.85 kg/(m² h bar). Treatment with XAD16 at the same phase ratio increased the permeability to 0.82 kg/(m² h bar). As observed in Fig. 1, the higher the phase ratio (i.e. the amount of adsorbent relative to the amount of hydrolysate), the larger the increase in permeability. With the birch hydrolysate, both of the tested adsorbents increased the filtration capacity to approximately 90% of the pure water permeability at the highest phase ration (0.15). However, at lower phase ratios the XAD-7 adsorbent treatment increased the relative permeability more than the treatment with the XAD-16.

In the experiments with the eucalyptus/pine hydrolysate, the XAD-16 adsorbent treatment was found to be slightly more efficient than the XAD-7 treatment. When the phase ratio was 0.15, the average relative permeability increased from 0.26 (original hydrolysate) to 0.94 by treatment with XAD-16. The corresponding value after the XAD-7 treatment was 0.79. When the smaller phase ratios were used, the difference in the capability of the adsorbents to increase filtration capacity was small.

3.2. Influence of adsorption pretreatment on hydrolysate composition

Influence of the adsorption treatment on lignin and hemicellulose content of the hydrolysate are displayed in Fig. 2. Adsorption pretreatment decreased the UV (280 nm) absorbance of both hydrolysates with both adsorbents. However, the amount of hemicelluloses was also decreased due to adsorption. This means that

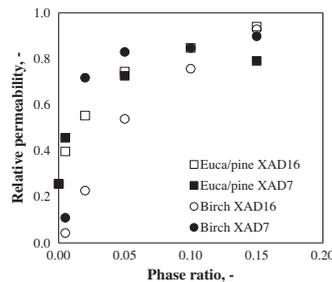


Fig. 1. Average relative permeabilities of the tested membranes with different phase ratios in the pretreatment, eucalyptus/pine hydrolysate with UFX5 membrane at 2 bar, 45 °C and 500 rpm, and birch hydrolysate at 5.5 bar, 60 °C and 500 rpm.

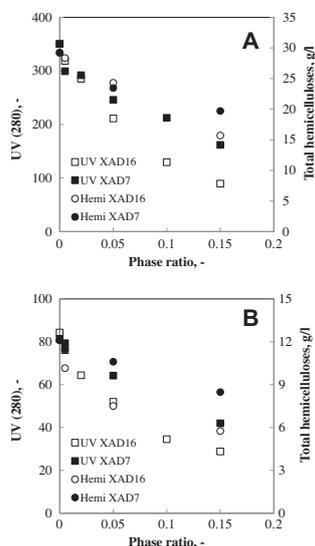


Fig. 2. UV absorbance (280 nm) and the amount of total carbohydrates in the adsorbent treated (A) birch hydrolysate and (B) eucalyptus/pine hydrolysate.

the pretreatment is not selective to lignin. In the treatment of the birch hydrolysate, more lignin was removed in proportion to hemicelluloses with all the used phase ratios. In the case of the pine/eucalyptus hydrolysate, however, more hemicelluloses were removed in proportion to lignin at low phase ratio whereas with large amounts of adsorbent the result was opposite. These results contradict with Lehto and Alén (2012), who reported no significant carbohydrate losses while about one third of lignin was adsorbed when 25 mL of birch hydrolysate was treated with 35 g of XAD-4 adsorbent in a column.

The carbohydrate losses can be at least partly explained by that part of hemicellulose is bonded to lignin (Lawoko et al., 2005, 2009), forming lignin–hemicellulose complexes (Alén, 2011), and when lignin was removed from the solution, probably also the part of the hemicelluloses, which is linked to lignin fragments, was also removed.

The molecular weight distribution of the untreated pine/eucalyptus hydrolysate is shown in Fig. 3. Most of the ligneous compounds (absorbing UV light at 280 nm) have molecular weight below 5000 g/mol. The influence of adsorption pretreatments on the molecular weight distributions are shown in the same figure as percentage decrease of UV absorbance. The adsorption treatment was capable of removing ligneous material over a wide range of molecular weights. The hydrophobic XAD-16 adsorbent eliminated almost all of the higher molecular weight material above 6000 g/mol. The less hydrophobic XAD-7 was somewhat less efficient in that region.

In absence of a direct method to analyze the adsorbed layer structure on the adsorbent surface, some conclusions can be made by inspecting the shape of the adsorption isotherm. Towards this end, an adsorption isotherm was plotted as solid phase concentration of UV 280 nm absorbing material (q_A^{UV}) at corresponding liquid phase concentrations in Fig. 4. Circles in Fig. 4 represent experimental data whereas lines are calculated results that will be discussed in Section 3.4. If adsorption was on a monolayer only,

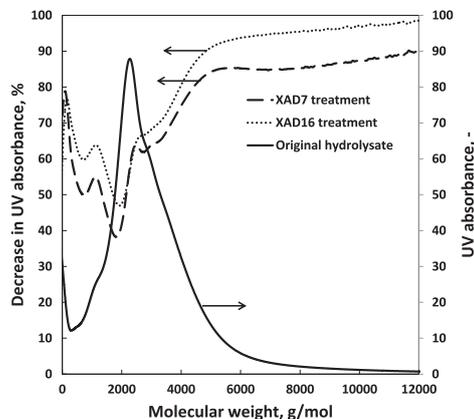


Fig. 3. Molecular weight distributions calculated from gel permeation chromatograms of the original eucalyptus/pine hydrolysate and adsorbent treated hydrolysate (phase ratio 0.15).

the adsorbed phase concentration would level off and remain constant at high liquid phase concentration region. The shape of the isotherm indicates that multilayer adsorption occurred when the liquid phase concentration at equilibrium was high (Sainio and Turku, 2010). In this case one of the adsorbates is lignin, which is known for its tendency to agglomerate. This supports the conclusion of multilayer adsorption; lignin molecules in the solution are more easily adsorbed on the lignin layer than on the clean adsorbent surface (polystyrene).

3.3. Fouling

Pure water flux reduction (PWF_R) was used here as a measure to evaluate fouling caused by hydrolysate during filtration. As shown in Tables 2 and 3, the adsorption pretreatment was found to decrease the PWF_R . This was at least partly due to removal of ligneous compounds from the hydrolysates, which have been shown to foul the UFX5 pHt membrane also in fractionation of pine hydrolysate. (Kalliainen et al., 2011) With both hydrolysates, the XAD-7 adsorbent treatment was found to be more efficient in reducing fouling than the XAD-16 adsorbent treatment.

PWF_R was higher with the untreated birch hydrolysate and UH004P membrane than with the untreated eucalyptus/pine hydrolysate and UFX5 pHt membrane (Tables 2 and 3). In other words, fouling was more severe in the former case. However, adsorbent pretreatment was more efficient with the birch hydrolysate and UH004P membrane than with eucalyptus/pine hydrolysate and UFX5 pHt membrane.

The negative values obtained for the birch hydrolysate may be due to experimental uncertainties but nevertheless indicate that fouling could be efficiently minimized by the adsorption treatment. On the other hand, some amphiphilic compounds in the hydrolysate, such as wood extractives, might be preferentially attached on the membrane surface in absence of lignin and thus improve flux by increasing membrane hydrophilicity. This is supported by Puro et al. (2011), who reported that wood extractives adsorbed on the membrane surface increase the hydrophilicity of the membrane. Some of the wood extractives have both hydrophobic and hydrophilic moieties and, when the hydrophobic

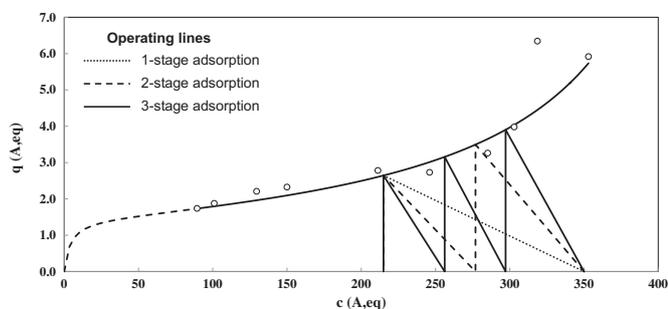


Fig. 4. Adsorption isotherm for UV (280 nm) absorbing material in birch hydrolysate on XAD-16 adsorbent. $T = 60^\circ\text{C}$, $t = 180$ min. Circles: experimental data. Curved lines: calculated BET isotherm (dashed part is extrapolation beyond experimental data range); straight lines: operating lines in design of adsorption pretreatment cascades. Target flux in ultrafiltration for the design problem: $70\text{ kg}/(\text{m}^2\text{ h})$.

Table 2

Pure water fluxes before each filtration of eucalyptus/pine hydrolysate with UFX5 membrane at 2 bar, 45°C and 500 rpm.

Phase ratio (-)	XAD-16		XAD-7	
	PWF $\text{kg}/(\text{m}^2\text{ h})$	PWF reduction(%)	PWF $\text{kg}/(\text{m}^2\text{ h})$	PWF reduction (%)
0	147	36	147	36
0.005	151	26	142	21
0.02	147	15		
0.05	146	9	130	2
0.1	140	6		
0.15	144	10	143	1

Table 3

Pure water fluxes before each filtration of birch hydrolysate with UH004P membrane at 5.5 bar, 60°C and 500 rpm.

Phase ratio (-)	XAD-16		XAD-7	
	PWF $\text{kg}/(\text{m}^2\text{ h})$	PWF reduction (%)	PWF $\text{kg}/(\text{m}^2\text{ h})$	PWF reduction (%)
0	126	90	126	90
0.005	102	69	127	42
0.02	109	62	134	<0
0.05	101	40	128	<0
0.1	105	22	132	<0

part is attached on the membrane, the hydrophilic part faces the aqueous phase making the membrane surface more hydrophilic.

3.4. Optimization of the adsorbent amount

The results of this study demonstrate that XAD adsorbents provide a feasible pretreatment method for enhancing filtration performance. An important aspect in evaluating the feasibility of the concept is the amount of adsorbent required to achieve a given average flux in filtration. Here we demonstrate how this can be assessed. XAD-16 adsorbent and birch hydrolysate are used as a model system.

The average flux values measured in the filtration of the XAD-16 treated birch hydrolysate samples are presented in Fig. 5 as a function of the liquid phase concentration c_A^{eq} (which is taken equal as the UV absorbance at 280 nm) remaining after the adsorption pretreatment. The flux obtained for the untreated hydrolysate was almost negligible whereas the average value measured for the pure water flux was approximately $119\text{ kg}/(\text{m}^2\text{ h})$. Between

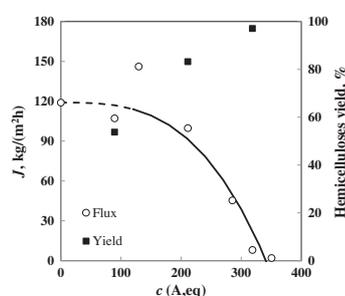


Fig. 5. Dependence of average fluxes during filtration of birch hydrolysate with UH004P membrane on the extent of adsorption treatment. $T = 60^\circ\text{C}$, $p = 5.5$ bar, rotation speed = 500 rpm. Circles = measured flux; line = calculated flux; squares = hemicellulose loss.

these two extremes, a nonlinear correlation between permeate flux, J , and feed solution concentration, c_A^{eq} , was established

$$J = J^0 - a_1 (c_A^{eq})^{a_2} \quad (7)$$

where J^0 is flux when all UV absorbing species are removed by adsorption and a_1 and a_2 are positive constants. The value of J^0 was set to the average of the experimentally determined pure water fluxes before filtration of the hydrolysate ($J^0 = 119\text{ kg}/(\text{m}^2\text{ h})$), whereas the two other parameters were estimated from the data in Fig. 4. Values of $a_1 = 2.22 \cdot 10^{-6}\text{ kg}/(\text{m}^2\text{ h})$ and $a_2 = 3.05$ were obtained.

The adsorption equilibrium data shown in Fig. 3 were correlated by using the BET isotherm model that describes formation of multilayers on adsorbent surface:

$$q_c = \frac{q_s b_s c_A^{eq}}{(1 - b_1 c_A^{eq})(1 - b_1 c_A^{eq} + b_s c_A^{eq})} \quad (8)$$

where q_c is calculated value for adsorbed phase concentration in unit of L/g , q_s is monolayer capacity and b_s and b_1 are interaction parameters. Values of $q_s = 1.457\text{ L}/\text{g}$, $b_s = 0.25$ and $b_1 = 0.002$ were obtained for the birch hydrolysate. As observed in Fig. 4, the model gives a reasonably good fit to the data. Extrapolation beyond the highest phase ratio (towards zero absorbance) is shown as a dashed line to emphasize that there is not enough data for reliable

estimation of the parameters. Nevertheless, the correlation is useful for the purpose of optimizing the adsorbent dosage for the pretreatment step.

If the adsorption treatment is carried out in a single stage, the amount of adsorbent, m^s , required to reach a given liquid phase concentration of UV absorbing material can be solved from the material balance, Eq. (1), after substituting q_c from Eq. (9) and c_A^{eq} that is obtained from Eq. (8). In practice, the calculation is most convenient to do numerically although the resulting expression for m^s is explicit.

To give an example, 51.07 kg of XAD-16 adsorbent is needed to purify a 1.0 m³ batch of the birch hydrolysate (UV absorbance c_A^0 equal to 350) to achieve a flux of 90 kg/(m² h) in the ultrafiltration. If a lower flux of 70 kg/(m² h) is sufficient, the required amount of adsorbent decreases to 30.14 kg per 1 m³ of hydrolysate. In other words, the phase ratio would be 0.03 in the latter example. A flux of 45 kg/(m² h) requires only 15.24 kg/m³ of XAD-16 adsorbent, which is only 30% of the amount required for the flux of 90 kg/(m² h). These examples demonstrate the trade-offs that need to be made between the desired flux and the adsorbent inventory.

Multistage adsorption cascades offer a means to reduce the adsorbent dosage and should be considered when evaluating the feasibility of the adsorption pretreatment process investigated here. Towards this end, the adsorbent amounts required in 1-staged, 2-staged, and 3-staged cascades were calculated. The distribution of adsorbent between the stages in each cascade was optimized such that the total amount of adsorbent was minimized. Typical operating lines are shown graphically in Fig. 4. The steeper the operating line is, the lower is the adsorbent dosage. Table 4 summarizes the optimization results for two values of the required flux.

As observed in Table 4, when a flux of 70 kg/(m² h) is required in the ultrafiltration, the 2-staged cascade saves approximately 11% and the 3-staged cascade almost 15% of adsorbent when compared to a single-stage adsorption process. For the higher flux requirement, 90 kg/(m² h), the savings are 13% and 17.5% in 2-staged and 3-staged cascades when compared to the single-staged adsorption.

Considering the aim of recovering hemicelluloses from a lignocellulose hydrolysate, the pretreatment should be able to remove lignin but leave hemicelluloses in the solution. Hemicelluloses yield in the (single-staged) adsorption pretreatment of the birch hydrolysate with XAD-16 are shown in Fig. 5. When only a small amount of ligneous compounds are removed, i.e. when the resulting liquid phase absorbance is around 300, the yield of hemicelluloses is high. On the other hand, for $c_A < 200$, the flux does not increase considerably with decreasing concentration of the ligneous compounds but the hemicellulose yield is as low as 50%. It is thus concluded that an ultrafiltration flux in the order of 70 kg/m²/h is readily achieved with a multistage adsorption pretreatment process without a large adsorbent inventory and high hemicelluloses losses.

Table 4
Optimized amount of XAD-16 adsorbent for multistage adsorption pretreatment of a birch hydrolysate with $c(A,0) = 350$.

Number of stages	Target flux (kg/m ² /h)	Adsorbent mass (kg/1000 L)			
		Stage I	Stage II	Stage III	Total
1	70	30.14	–	–	30.14
	90	51.07	–	–	51.07
2	70	15.04	11.79	–	26.83
	90	25.44	18.86	–	44.30
3	70	10.02	8.58	7.13	25.73
	90	16.94	14.03	11.08	42.05

4. Conclusion

Adsorption pretreatment on XAD-7 and XAD-16 was found effective for enhancing ultrafiltration performance of wood hydrolysates. Increased flux and decreased fouling were found to be mostly due to the removal of ligneous material from the hydrolysates. The pretreatment removed such material of all molecular weights from the pine/eucalyptus hydrolysate, but especially the larger molecules were removed. The adsorption on XAD-16 was found to occur on multiple layers. It was shown that a multistep adsorption pretreatment can be used to reduce the amount of adsorbent required. While large adsorbent amount increases flux in filtration, it also leads to significant hemicellulose losses.

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Publication III

Strand, E., Kallioinen, M., Reinikainen, S.-P., Arkell, A., Mänttari, M.

Multivariate data examination in evaluation of the effect of the molecular mass of lignin and hemicelluloses on ultrafiltration efficiency

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Multivariate data examination in evaluation of the effect of the molecular mass of lignin and hemicelluloses on ultrafiltration efficiency

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ABSTRACT

In this study, multivariate examination was used to show the influence of birch extract characteristics on filtration performance in the ultrafiltration based hemicellulose recovery process. Different pretreatments based on adsorption, flocculation or oxidative degradation by enzyme, and a combination of degradation and adsorption, were performed to change the extract characteristics. It was clearly demonstrated that in addition to the total concentration of lignin or carbohydrates in the treated wood extract, also their size has a significant effect on filtration efficiency. Both the ligneous and hemicellulosic compounds, having a negative impact on filtration capacity, seemed to be small enough to enter the membrane skin layer. Thus, in the development of pretreatment processes to enhance filtration efficiency in the recovery of hemicelluloses in biorefineries with ultrafiltration, the focus should not be strictly on maximal removal, but also the size of the lignin molecules has to be considered. From the tested pretreatment methods, the highest increase of flux was achieved with laccase treatment combined with adsorption on bentonite because it decreased the amount of harmful-sized compounds and increased the amount of large compounds, which were favourable to the higher flux.

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1. Introduction

Ultrafiltration is a potential technique for the recovery of hemicelluloses from wood extracts [1–3]. However, fouling challenges are often reported when wood-derived solutions, or solutions with similar content, have been ultrafiltered [4–7]. Based on the literature, potential foulants are lignin and wood extractives [5,8–10]. The removal of these compounds prior to ultrafiltration has been shown to improve filtration performance [11,12].

Lignin can be removed for instance by adsorption on activated carbon [13,14], polymeric adsorbents [15–17], or bentonite (phenol removal) [18]. However, the tested pretreatments have shown not to be specific to lignin but they remove also other compounds from the extracts. For instance, Koivula et al. [12] have reported that pretreatment with XAD adsorbents decreased the lignin amount in wood extract but also caused significant hemicellulose losses. Also Schwartz and Lawoko [16] noticed XAD4 adsorbent treatment to decrease the amount of monosaccharides in addition to the efficient removal of acid-soluble lignin from wood extract.

The monosaccharides were, however, mostly recovered from the adsorbent by water wash, whereas acid-soluble lignin remained attached to the adsorbent. In addition, Liu et al. [19] reported on hemicellulose losses during the removal of lignin from pre-hydrolysis liquor by activated carbon.

In order to decrease the adsorption of hemicelluloses, the amount of adsorbent should be optimised. Notable improvement in filtration capacity does not necessarily require the total removal of foulants. However, the hemicellulose losses during the adsorption process might not be controlled merely by optimising the adsorbent amount because part of the ligneous material present in the extracts is chemically bound with hemicelluloses [20–22]. For instance, Tunc and van Heiningen [23] have shown that in hardwood extract, lignin was bound especially to low molecular mass hemicelluloses. Thus, to minimise hemicellulose losses in the pretreatment, the linkages between lignin and hemicelluloses should be broken prior to adsorption.

In addition to the changes in extract composition, pretreatment also causes changes in the molecular mass distribution of the extract. For instance Koivula et al. [12] have shown that the XAD adsorbent removed most efficiently the highest molecular mass lignin when pine/eucalyptus extract was treated. Gütsch and Sixta [13] have also reported that high-molecular mass lignin was removed first, and low-molecular mass lignin after that, when

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activated carbon was used in lignin removal from wood autohydrolysate. Therefore, if the aim is to remove high-molecular mass lignin instead of low-molecular weight lignin, the amount of activated carbon should be fixed, enabling the adsorption capacity to be fulfilled after the high-molecular mass lignin has been adsorbed, leaving no “empty space” for the low-molecular mass lignin.

Earlier studies have shown that pretreatment removing lignin and wood extractives decreases membrane fouling and improves filtration capacity [11,12]. However, the overall changes in the treated wood extract derived from improvements in the filtration process have not been discussed in detail. Therefore, this study examines the influence of molecular mass distribution changes caused by pretreatment on filtration performance and evaluates the effect of the pretreatment on extract content. Multivariate examination was used to enable comprehensive examination of this complex phenomenon.

2. Materials and methods

2.1. Wood extract

Extraction was made with birch wood chips and water at 20 bar and 173 °C (maximum temperature during extraction) for 70 min, similarly to the efforts of Kilpeläinen et al. [24]. The original, untreated wood extract contained 35 g/l organic material. Of the total organic material, 22 g/l were carbohydrates and 4 g/l lignin. The other organic material present in the wood extracts consisted of, for instance, wood extractives, acetic acid and degradation products of carbohydrates, e.g. furfural and hydroxymethylfurfural [15].

2.2. Pretreatment

Different pretreatments based on adsorption, flocculation or oxidative degradation (by enzyme) were carried out for birch extract prior to filtration with a tight ultrafiltration membrane (Table 1). Also the combination of degradation and adsorption was studied. First, small scale experiments were performed to determine an adequate substance to extract phase ratio (p.r.). After small scale experiments, UV absorbance (at 205 nm) was measured to detect lignin, and the p.r. used in the actual pretreatment experiments was selected based on the decrease in the UV absorbance value. With XAD adsorbents, small scale experiments have been performed in earlier studies and are thus not included here [12].

2.3. Filtration

Filtrations were carried out with a dead-end laboratory-scale filter cell (Amicon 8400) and UFX5pHt membrane (Polysulphone, 5 kDa, Alfa Laval). The membranes were soaked in a 0.1% NaOH

solution for 15 min and rinsed with pure water before use. The pure water flux was measured before and after the filtration of the extract. The aim in the filtration was to continue until there was 100 g of the concentrate, that is, until 200 g of permeate was formed. The mass of feed solution was 300 g, and thus, a volume reduction factor (VRF, ratio of the feed and concentrate volumes) of 3 was achieved. If the VRF value of 3 could not be achieved, filtration was ended when the flux value fell below 5 kg/(m² h). Pure water flux (PWF) measurements and extract filtrations were carried out at 60 °C and 3 bar (PWF) and 5.5 bar (extract). PWF was measured until it remained stable, and PWF values presented in this study are average values of three stable PWF values. A magnetic stirrer with the tip linear velocity of 1.5 m/s was used to decrease the concentration polarisation. Three samples were collected from each filtration: feed, permeate and concentrate.

2.4. Analysis

The amount of lignin was determined by UV absorbance at 205 nm according to TAPPI UM 250 method [25]. The amount of total carbohydrates was analysed as monosaccharides using gas chromatography (Varian 8200) and acid methanolysis as sample treatment [26]. Wood extractives were analysed from silylated samples by gas chromatograph [9].

The molecular size distribution of hemicelluloses and lignin was determined by a size exclusion chromatography (SEC) system. The system was Waters 600E (Waters, Milford, MA) equipped with a Waters 2414 refractive index (RI) detector, a Waters 486 UV absorbance detector and a column packed with 30 cm of Superdex 30 and 30 cm of Superdex 200 (GE Healthcare, Uppsala, Sweden). The eluent was a 125 mM NaOH solution of a flow rate of 1 ml/min. To calibrate the system, standards of polyethylene glycol with molecular masses 0.4, 4, 10 and 35 kg/mole (Merck Schuchardt OHG, Hohenbrunn, Germany) were used. The samples were pretreated before injection into the SEC column; the samples were heated to 65 °C in a water bath and kept at that temperature for at least 15 min before the samples were filtered through a 0.2 µm filter, filled into vials and inserted into the autosampler. The RI detector detects both carbohydrates and lignin, but since the amount of lignin compared to the amount of carbohydrates is so small, the RI profile can be dealt with as a carbohydrate profile in later discussion. Also, the sensitivity of the UV detector is higher towards lignin than carbohydrates, which confirms the interpretation of the analysis results.

2.5. Mathematical tools

Due to the multivariate nature of the data sets, multivariate approaches were applied in their interpretation. Principal component analysis (PCA) formed the main core of the data-analyses, in

Table 1
Pretreatment methods to remove/degrade lignin in birch extract prior to ultrafiltration.

Pretreatment	x to extract p.r. ^a (small scale)	x to extract p.r. (actual experiment)	t (min)	T (°C)	Separation
Adsorption on activated carbon (granulated)	0.05, 0.1 and 0.2	0.2	180	60	Vacuum filtration with paper filter (S&S 604 Rundfilter)
Adsorption on bentonite (powder, Hydrocol)	0.01, 0.03, 0.05, 0.1 and 0.2	0.05	60	60	Centrifugation 15 min 20,000 rpm
Adsorption on XAD16 and XAD7 (Rohm & Haas)	0.005, 0.02, 0.05, 0.1 and 0.15	0.15	60	60	Vacuum filtration with paper filter (S&S 604 Rundfilter)
Enzymatic degradation by laccase (Novozym) combined with adsorption on bentonite	Laccase to extract: 0.01, 0.05; bentonite to extract: 0.1	0.01; 0.1	60 (Laccase) + 30 (Bentonite)	60	Centrifugation 15 min 20,000 rpm

x amount of adsorbent/enzyme.

^a p.r. phase ratio.

addition to univariate methods. PCA is a well-known method [27] and applied in a wide range of applications, when cross-correlated variables are of interest. Typically, the aim is also to compress information with principal components (PCs) into smaller dimensions easier to handle. For example, in the present case, the molecular size distribution of hemicelluloses and lignin determined with the SEC system contained 9000 original variables, i.e. 9000 molecular mass fractions. Approximately 5000 of them were utilised in the data analysis. This matrix X , containing 5000 variables, was compressed to four PCs, which contain the most important information to this study.

Also the low number of pretreatment samples compared to the number of variables creates a classic example of data where multivariate methods are required due to a lack of degrees of freedom and a low rank.

In PCA, the original data is in the X matrix having n samples and m variables. The X is decomposed into score (T) and loading (P) matrices, and residual matrix (E):

$$X = TP^T + E$$

where TP^T captures the systematic information with A principal components. In an ideal case, the residual matrix (E) contains noise, but in real cases it contains all variation which is not captured by the PCs.

In PCA, the data were pretreated with adequate procedures. When the diminished effect of dimensionality on the importance of original variables was required, autoscaling was applied. In this scaling, the mean value of each variable was set to zero and standard deviation to one (unit variance). Otherwise, the fact that the PCA solution always goes via the origin was taken account.

3. Results

This section presents the results, followed by the discussion.

In the present study, PCA has been applied in two ways: the first approach is the most classic procedure, where the matrix containing variables in columns and samples in rows is compressed to reveal a correlation structure, and the second procedure utilises scores from the first PCA as descriptor variables together with a new set of original variables. The first procedure therefore enables

the second procedure to include the molecular mass distributions among the other variables, i.e. extract composition and filtration data. Fig. 1 shows the modelling procedure.

The first procedure compresses the data from the molecular mass distributions presenting either ligneous compounds (UV) or hemicelluloses (RI) (Fig. 2) to score matrices, which are then exploited in the second procedure as additional variables in the pretreatment variable matrix (Table 2). As a result of the first procedure, variable loading vectors presenting general molecular distributions in samples were gained (Fig. 3). The samples on these loading vectors are described with score vectors. Thus, the score vectors $T1$ – $T4$ are independent and orthogonal, and contain the systematic variation of the original data. They can be treated as representatives of the original variation, i.e. of the original samples. In the second procedure, information on the correlation between all of the pretreatment variables and molecular mass distributions is obtained.

Table 3 consists of filtration data for the original and pretreated extracts. The characteristics of the original and pretreated extracts are presented in Table 4. Fig. 4 is a biplot from the PCA analysis with four principal components, where pretreatment methods, extract composition and filtration performance are variables.

In Fig. 4, the correlation between two factors can be interpreted as positive if the vectors are parallel and pointing in the same direction (from the origin). Correspondingly, the correlation is negative if the vectors are parallel but point in opposite directions. These are the extreme conditions in which the correlation is linear, but most of the cases fall somewhere between these two. When a profile ($T1$ – $T4$ UV or RI) correlates with other factors, more information can be observed from the loadings ($P1$ – $P4$ UV or RI) of these profiles (Fig. 3). Only $P1$ – $P2$ were found to be the most dominant ones, having coefficient of determination values of 75% and 20% (UV $P1$ and $P2$), and 79% and 17% (RI $P1$ and $P2$), and thus, only they are shown in Fig. 3.

If the correlation is positive, it means that when the loading is positive, the compounds in that size range increase the other factor in question, and when the loading is negative, the compounds in that size range decrease the other factor in question. The smaller the absolute value of the variable in Fig. 4 is, the less important it is for the present phenomenon.

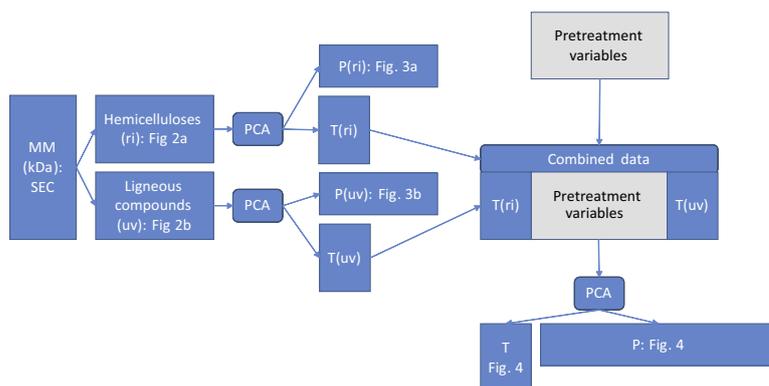


Fig. 1. Data sets used in PCA: PCA is applied separately for MM data sets analysed either with UV or RI to reveal the main molecular weight distributions (loadings $P(uv)$ and $P(ri)$, Fig. 3); Score vectors from both PCA models ($T(uv)$ and $T(ri)$) are combined with original variables to reveal the correlation structure between the pretreatment and MM distributions (and flux), Fig. 4.

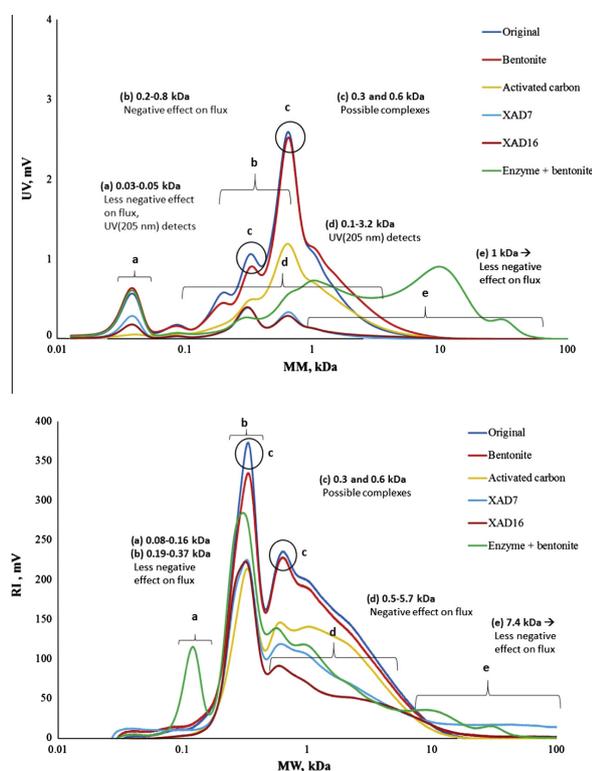


Fig. 2. SEC chromatograms of original and pretreated extracts analysed with (a) UV (280 nm) absorbance detector (for ligneous compounds) and (b) refractive index detector (for hemicelluloses).

Table 2

Data matrix observed from combination of pretreatment variable matrix and score matrices from PCA of molecular distributions of ligneous compounds (UV) or hemicelluloses (RI).

Pre-treatment	T1 (UV)	T2 (UV)	T3 (UV)	T4 (UV)	T1 (RI)	T2 (RI)	T3 (RI)	T4 (RI)	Flux, (kg/(m ² h))	PWF _r (%)	UV (205 nm) (-)	Lignin (g/l)	Carbohydr. (g/l)	Extractives (mg/l)
None	45.91	-6.52	1.76	-0.27	8310	-588.2	-67.55	-98.57	15	83	479	4.4	22	13
AC	24.44	-1.58	-3.58	2.81	5421	-892.9	183.36	-98.20	61	24	307	2.8	14	2
B	45.84	-3.03	-1.14	-1.60	7809	-535.3	94.24	83.20	79	35	460	4.2	16	12
XAD16	6.91	-0.43	3.26	1.74	4218	748.4	-667.71	-203.05	78	63	62	0.6	9	2
XAD7	7.36	-0.82	4.02	0.76	4834	352	-265.89	390.95	88	53	70	0.6	11	3
L + B	21.05	23.10	0.31	-0.03	5880	1539	498.87	-56.37	120	34	240	2.2	12	1

AC = activated carbon, B = bentonite, L + B = laccase + bentonite, PWF_r = pure water flux reduction.

4. Discussion

When modelling all pretreatment variables and molecular distributions together, the first two PCs in PCA capture 74% of the total variance of original data measured in this study. Thus, the PCA shows the dominant phenomena in this experimental case. However, there are also other factors impacting filtration capacity, but they are not covered by the measured variables or the first PCs and, thus, not discussed here. As expected, the PCA showed a negative correlation between the amounts of wood extractives, lignin and carbohydrates with the flux (Fig. 4). This means that the more

concentrated the extract is, the lower is the flux. Moreover, pure water flux reduction (PWF_r) had a negative correlation with the flux, meaning that when the PWF_r is small, and presumably no severe fouling occurs, the flux is high. This is not as straightforward if each pretreatment case is interpreted separately without PCA.

4.1. Molecular size of lignin and carbohydrates

The results of this study clearly demonstrate that the total concentration of lignin or carbohydrates in the treated wood extract is not the only factor that affects the filtration capacity of the

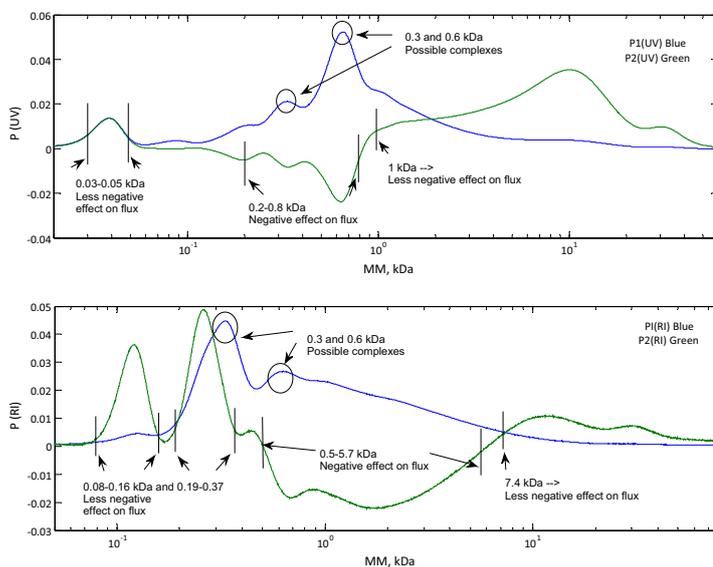


Fig. 3. First two loading vectors of the principal components (P) obtained from PCA for molecular size distribution of (a) ligneous components (T1(UV)–T2(UV)), and, (b) hemicelluloses (T1(RI)–T2(RI)).

Table 3

Average fluxes during filtration (60 °C, 5.5 bar, VRF 2, UFX5) of original and pretreated extract, and pure water flux reductions (60 °C, 3 bar) for each case.

Pretreatment	Flux (kg/(m ² h))	PWF _b (kg/(m ² h))	PWF _r (%)
None	15	317	83
Activated carbon	61	278	24
Bentonite	79	426	35
XAD16	78	377	63
XAD7	79	346	53
Laccase + bentonite	120	332	34

PWF = pure water flux, b = beginning, r = reduction.

Table 4

The amount of total wood extractives, lignin and carbohydrates in extracts.

Pretreatment	Total extractives (mg/l)	Lignin (g/l)	Carbohydrates (g/l)
None	286	4.4	22
Activated carbon	20	2.8	14
Bentonite	158	4.2	16
XAD16	13	0.6	9
XAD7	12	0.6	11
Laccase + bentonite	6	2.2	12

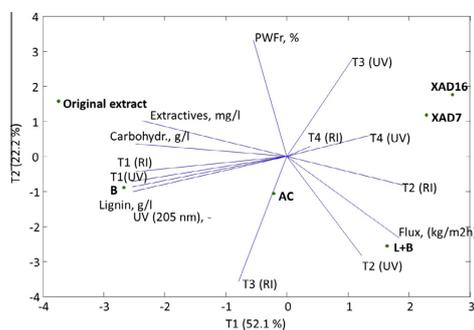


Fig. 4. Biplot from PCA analysis with all pretreatment methods applied, extract composition (UV, carbohydrates, extractives) and filtration performance (flux, PWF_r) as variables, T1–T4 are the score vectors of PCs, RI = refractive index detector (for hemicelluloses in SEC) and UV = UV (280 nm) absorbance detector (for lignin in SEC). Cumulative R² (coefficient of determination) values for molecular size distribution data with four PCs (T1–T4) are 99.8% (UV), and 99.9% (RI). AC = activated carbon, B = bentonite, L + B = laccase + bentonite.

membranes, but also their size matters. The PCA analysis revealed a correlation between filtration capacity and molecular size distributions (marked T1–T4 UV or RI in Fig. 4) and molecular mass areas negatively affecting the flux could be identified. The vectors P in Fig. 3 and T in Fig. 4 are related to each other, and should be interpreted at the same time. E.g. on the one hand a high linear correlation between flux, T2(UV) and T2(RI) was found from Fig. 4. On the other hand P2(UV) in Fig. 3a and P2(RI) in Fig. 3b describes the

molecular distribution related to T2s and flux. The ligneous profile loading P2 suggests that UV-absorbing compounds between 0.2 and 0.8 kDa decrease filtration capacity and the hemicelluloses profile loading P2(RI) indicates that carbohydrates at a molecular mass range of 0.5–5.7 kDa decrease capacity.

It has been found that retention of 5–6 kDa polyethylene glycol (PEG) with the UFX5 membrane is only around 30% (Laakso, Unpublished results). Thus, it can be concluded that the problematic compound size seems to be such that the compounds are small

enough to penetrate the membrane skin layer. This result is in line with the result of Retsja [28], who reported that ligneous molecules that were able to permeate 1 and 5 kDa membranes (ETNA01PP and UFX5) were the ones which caused fouling. Microscope pictures of membranes which were fouled by wood extract, and dyed to expose lignin, revealed lignin being located inside the membrane. With lignin, the possibility to foul the membrane is higher, because the attraction between hydrophobic lignin and the hydrophobic membrane is higher than in the case of hydrophilic carbohydrates.

The major MM profiles of ligneous compounds and hemicelluloses correlate with each other. In loading P1(UV) (Fig. 3a), there are two separable peaks between the range 0.1–3.2 kDa, located at 0.3 and 0.6 kDa. In loading P1(RI) (Fig. 3b), there are also two peaks at these same locations, 0.3 and 0.6 kDa. These are most likely complexes between phenolic compounds and carbohydrates. Due to their small size, it would be disinformative to call them lignin–hemicellulose complexes. The hemicellulosic compounds which disturb the filtration capacity (0.5–5.7 kDa) are partly in the same size range as these assumed complexes, which might partly explain the flux-decreasing effect of the hemicellulosic compounds. It might not be the hemicelluloses alone that decrease the flux but the complexes containing both the phenolic compounds and carbohydrates. Due to the hydrophobic nature of phenolic compounds, the complex might be more harmful to the flux than same-sized pure hemicellulose.

It has been reported that the bonds between hemicelluloses and lignin in native wood remain when they are dissolved in hot water extraction [29]. Hence, if these LHCs are not broken before or during the lignin removal, part of the hemicelluloses is removed with lignin in the pretreatment step. In the recovery of hemicelluloses, this causes unwanted hemicellulose loss.

The PCA analysis also revealed that UV-absorbing compounds having a molecular mass higher than 1 kDa, or very small UV-absorbing compounds, were less harmful for filtration capacity (Figs. 3a). Similarly, carbohydrates at a molecular mass range of 7.4–43 kDa and very small carbohydrates were less harmful for filtration capacity (Figs. 3b). Thus, it seems that a pretreatment, which either breaks the molecules to smaller compounds or aggregates molecules to larger compounds, influences the flux favourably. However, it has to be considered that when the filtration is continued to a high volume reduction factor and the concentration of the high molecular mass compounds increases significantly, the viscosity of the extract increases [30]. The high molecular mass compounds might also form a gel layer. These actions probably result in a decrease in filtration capacity.

The major profiles of ligneous compounds and hemicelluloses do not correlate directly with the filtration capacity, which suggests that a straight linear relation between the capacity and typical ligneous or hemicelluloses distribution do not exist. This means that there are also other factors than ligneous compounds and hemicelluloses, which represent the majority of these compounds in the extract, decreasing the filtration capacity. These other factors were not measured in this study, and therefore, not captured by PCA.

4.2. Impact of pretreatments on the birch extract composition

The SEC analysis (Fig. 2a) revealed that AC was namely good in removing very small phenolic compounds, which are not the most harmful ligneous compounds according to PCA. In contrast, XAD adsorbents removed more equally ligneous compounds within the entire detected range, including the possible complexes. This might be the reason why pretreatment with the XAD adsorbents led to a higher flux in the filtration (Table 3). Bentonite alone decreased the ligneous compounds only slightly, and therefore, it

is surprising that the flux after the bentonite treatment was quite high. This might mean that bentonite removed some harmful compound which was not analysed or included in the PCA. Laccase combined with bentonite decreased the amount of the complexes (bentonite alone did not remove them), especially at 0.6 kDa (Fig. 2b). Also, laccase combined with bentonite led to the formation of larger lignin compounds and hemicelluloses (roughly 10 and 30 kDa), which are connected to a higher flux according to PCA (Figs. 2 and 3). These two phenomena are probably the reason for the overwhelmingly high flux after pretreatment with laccase combined with bentonite.

There are two possibilities concerning the new compounds at 10 and 30 kDa created by laccase treatment (combined with bentonite). The profiles T2 (UV and RI) have a moderate correlation together, which implies that the compounds observed with both detectors at 10 and 30 kDa are the same ones. These compounds might be large lignin compounds which are also detected by RI, or, they might be large hemicelluloses with smaller lignin fragments, and therefore, are detected by both UV and RI. Laccase can act as a ligninolytic or polymerising (cross-linking) enzyme [31,32]. The formation of large ligneous compounds can be explained by the oxidation of lignin by laccase to phenoxy radicals [29,33] which can be rejoined by coupling reactions and form even larger molecules than the original ones [34,35]. On the other hand, large hemicelluloses might be formed by the cross-linking of lignin moieties between different hemicellulose chains after the original LHCs were oxidised by laccase. Krawczyk et al. [30] increased the molecular mass of hemicelluloses by enzymatic cross-linking with laccase.

Based on the results of this study, it is difficult to say surely which phenomenon occurred. However, some noteworthy observations support the idea of large ligneous compounds: (1) the signal of the RI detector at 10 and 30 kDa is rather weak compared to the signal of the UV detector, which suggests the large lignin compounds rather than large hemicelluloses with substantially smaller amounts of lignin moieties, (2) the amount of small carbohydrates, or sugars, was also increased by laccase combined with bentonite (Fig. 2b), which could have occurred due to released monosaccharides from the complexes. The increase of the amount of small carbohydrates might also mean that laccase oxidises and reduces the size of the phenolic moiety in the complex, and therefore, the whole complex becomes smaller and gives a signal later in RI (smaller compound). This means that the original molar mass value for hemicelluloses prior to the laccase treatment might be too high because RI detector measures also hemicellulose–lignin complexes and not only pure hemicelluloses. LHCs have been reported to give false peaks also in gel permeation chromatography (GPC) [29].

5. Conclusion

This study applied multivariate examination to expose the effects of birch extract characteristics on filtration performance. The results of the examination revealed that there are certain ranges in the molecular masses of both ligneous and hemicellulosic compounds that have a negative impact on filtration capacity. Therefore, if lignin is removed from wood extracts in order to decrease fouling in ultrafiltration, the focus should not be strictly on maximal removal, but also the size of lignin molecules has to be considered. In general, less harmful compounds for the filtration capacity are large compounds which cannot penetrate the membrane or sufficiently small compounds that can easily permeate the membrane without blocking it. The major profiles of ligneous compounds and hemicelluloses correlate with each other at 0.3 and 0.6 kDa, potentially indicating the size of complexes between

phenolic compounds and sugars. The most effective pretreatment method to increase flux was laccase treatment combined with the adsorption on bentonite because it decreased the amount of harmful-sized compounds, including complexes from the solution, and increased the amount large compounds which were favourable to the higher flux. Compressing and gaining information from molecular size distribution and experimental filtration data with PCA offered an effective tool enabling the handling of a large number of variables at the same time leading to improved understanding of the complex fouling phenomena.

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Publication IV

Strand, E., Kallioinen, M., Kleen, M., Mänttari, M.

Activated carbon treatment to improve ultrafiltration performance in recovery of hemicelluloses from wood extracts

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Activated carbon treatment to improve ultrafiltration performance in recovery of hemicelluloses from wood extracts

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KEYWORDS: Spruce, Birch, Adsorption, Lignin removal, Membrane filtration

SUMMARY: Adsorption of lignin and wood extractives on activated carbon (AC) at high temperature prior to ultrafiltration (UF) was shown to significantly improve filtration capacity about 1.5 fold in recovery of hemicelluloses from wood extracts. Furthermore, adsorption pretreatment enabled the production of purer concentrated high-molecular-mass hemicellulose fractions. For instance, purity of the produced concentrated spruce fraction was more than 20% units higher when the AC treatment was used prior to UF compared to the fraction produced without the pretreatment. AC adsorbed lignin and wood extractives. In addition, AC treatment caused some hemicellulose losses. The results indicated that at least part of the hemicelluloses was adsorbed onto the AC in lignin-hemicellulose complexes. It seemed that also xylans containing 4-O-Me-glucuronic acid might have been removed by adsorption. However, AC was nonetheless clearly selective to lignin over hemicelluloses. Adsorption on activated carbon removed from the wood extract more high-molecular-mass compounds than smaller ones. The decrease in molecular mass was compensated to some extent in UF, since concentration filtration increased molecular mass significantly.

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Ultrafiltration (UF) is a feasible technology to recover and concentrate hemicelluloses from wood-based solutions (Krawczyk et al. 2013; Willför et al. 2003; Al Manasrah et al. 2012; Kallioinen et al. 2012; 2013). The concentrated high-molecular-mass fraction, as well as other fractions; lower molecular mass hemicelluloses and monosaccharides, can be used as raw material for different products depending on the purity and size requirements. Such hemicellulose- or carbohydrate-based products are, e.g. biopolymers and -plastics (coatings, barrier materials in packaging films), bioethanol, xylo-oligosaccharides (in food and medical applications), and hydrogels (Deutschmann, Dekker 2012; Mikkonen, Tenkanen 2012; Saadatmand et al. 2012; Peng et al. 2012; Söderqvist Lindblad et al. 2005; Girio et al. 2010). Lignin and wood extractives present in the extracts tend

to cause fouling problems (Puro et al. 2002; Koivula et al. 2011; 2013). They are also impurities in the concentrated hemicellulose fractions, because they can be reactive in further processing and they cause an undesired, brownish colour.

Activated carbon (AC) is a commonly used adsorbent material for several adsorbates, including ligneous compounds (Montané et al. 2006). There are already some solutions for regeneration of the used AC, which increases its usability as a pretreatment aid (Gütsch, Sixta 2012). Earlier studies with AC (Koivula et al. 2012) have shown that AC pretreatment conducted at 60°C improved filtration capacity to 3-fold compared to UF of original birch extract but it also caused 36% carbohydrate loss. Gütsch and Sixta (2011) have purified wood autohydrolysate from lignin by activated carbon at 20-170°C straight after autohydrolysis without carbohydrate losses. They suggested that if the adsorption is conducted at the same temperature as the hydrolysis, and/or, straight after the hydrolysis, the AC dosage is small enough, and, the adsorption time short enough, the hemicellulose losses can be avoided. This idea was applied in this work.

This study aims to find out if an adsorption implemented with activated carbon both enhances UF performance and enables the production of very pure high-molecular-mass hemicellulose fractions. The wood extraction and AC treatment are conducted in a sequence at the same temperature to avoid hemicellulose losses. The effect of the AC treatment on filtration capacity and fouling, and, the influence of the AC treatment on the content of the produced high-molecular-mass hemicellulose fractions are evaluated and discussed.

Materials and Methods

The experimental process scheme is presented in Fig 1. Four extractions were done: two for spruce sawdust and two for birch sawdust. For each wood species the other extraction was followed by the activated carbon (AC) adsorption.

Extraction

Extraction was conducted at 160°C and 7 bar for 40 min. 4 kg D.S. (dry substance) of sawdust and 20 kg of water (including the water in the sawdust) was used in the extraction (Fig 1). When the AC treatment was not done,

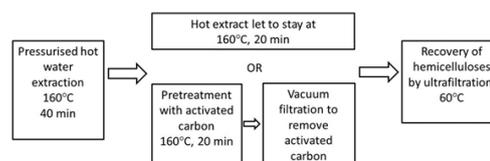


Fig 1 - The experimental process scheme used in this study.

the extract was allowed to stay at the extraction temperature for 20 min after extraction to have comparable temperature-time profile as in the AC treatment of the extract. After that time, the extract was led out through a cooling pipe.

Activated carbon treatment

After the extraction, the hot wood extract was led to another vessel containing AC (25 g/l) and kept there during the AC-treatment time for 20 min at 160°C. The type of the used AC and the treatment conditions were chosen according to Gütsch and Sixta (2011). The AC used was Sigma-Aldrich decolorizing activated carbon with BET 880 m²/g, pH 6.7, and ash 1.1%. After the AC treatment the liquid was allowed to cool down and then AC was separated by vacuum filtering with a Büchner funnel and paper filter (S&S 589^o, 2 µm retention).

Ultrafiltration

Ultrafiltration experiments were conducted with the cross-rotational (CR) 200 filter, in which a rotor is rotated on the membrane surface to diminish the influence of concentration polarization and fouling on filtration performance (Reinhard, Nurminen 2005). Membrane surface area of the filter is 0.06 m². The UF was performed with a regenerated cellulose membrane RC70PP (10 kDa, Alfa Laval), which has been found to be a feasible membrane for the recovery of high-molecular-mass hemicellulose fractions from wood extracts (Kallioinen et al. 2012; 2013).

Each experiment was done with a new membrane. The membranes were precleaned with an alkaline cleaning solution (0.5% Ultrasil 110, 15 min, 50°C, 1 bar, average circumferential velocity of the rotor 8.0 m/s) for removal of the preservatives and to wet the membrane. Pure water flux (PWF) was measured before and after the UF of the wood extracts at 50°C and 2 bar with average circumferential velocity of 8.0 m/s until the flux was stable. UF of the wood extracts was conducted at 60°C and 2 bar with average circumferential velocity of 8.0 m/s, and it was continued until VRF (volume reduction factor) between 3 and 5 was achieved depending on the feed volume.

Analysis

From the feed, permeate and concentrate samples lignin (UV 205 nm), total organic carbon content (TOC), turbidity, total dry solids (TDS), wood extractives, total dissolved carbohydrates and molecular mass of hemicelluloses were analysed. TOC was analysed with Shimadzu TOC-L analyser and ASI-L autosampler. Turbidity was measured with Hach 2100 AN IS turbidimeter. TDS was measured gravimetrically after freeze drying the samples. The proportional amounts of lignin, carbohydrates and other dry material was calculated from TDS. "Purity" of the extract means in this study the proportion of carbohydrates of the TDS. When the content of the total dry solids in the extract and the produced fractions is examined, "Others" includes among others wood extractives, acetic acid, and degradation products of carbohydrates; furfural and hydroxymethyl furfural, and secondary degradation products, such as, levulinic and formic acids (Borrega et al. 2011). The

amount of lignin was determined from UV absorbance at 205 nm according to TAPPI UM 250 method with Jasco V-670 spectrophotometer (TAPPI, 1991). Wood extractives were analyzed from silylated samples by gas chromatograph (Agilent HP6890 and injector HP7683) (Puro 2011). Also kinematic viscosity was measured from the feed and the concentrate samples with capillary viscometer, Comecta 4020, at 60°C. The kinematic viscosity for water at 60°C was measured to be 0.495 mm²/s.

The amount of total dissolved carbohydrates was analyzed using gas chromatograph (Agilent HP6890 and injector HP7683) after acid methanolysis and silylation (Sundberg et al. 1996). The polymeric and oligomeric hemicelluloses were transformed into monosaccharides by acid methanolysis. In the acid methanolysis, 2 ml of 2 M solution of HCl in anhydrous methanol was added to the sample. The sample was kept in an oven at 100°C for 3 h and agitated from time to time. After cooling to ambient temperature, about 320 µl of pyridine was added to neutralize the acidic solution. An internal standard, sorbitol in methanol (100 mg/l), was added to the sample. The sorbitol amount put into the sample was 100 µg. The sample was then dried in a nitrogen atmosphere. To ensure the complete removal of methanol, the sample was further freeze-dried for 1 h. The sample became dissolved by addition of 80 µl pyridine to facilitate silylation. For the silylation, 300 ml of BSTFA [bis-(trimethylsilyl)-trifluoroacetamide] containing 5% of TMCS (trimethylchlorosilane) was added to the sample. The sample was then shaken well and kept at 70°C for one hour to silylate it for the GC analysis. (Puro 2011) 4-O-methylglucuronic acid was not detected in the total dissolved carbohydrate analysis, since suitable standard was not used, and thus, it causes a minor error in the results giving smaller amount of carbohydrates and greater amount of other organic material. However, the amount of 4-O-methyl-D-glucuronic in xylan chain is so small that it does not affect the general view.

Average molecular masses of the dissolved hemicelluloses were determined by High Performance Size Exclusion Chromatography (HPSEC) in 0.1M NaNO₃ eluent (flow rate 0.5 ml/min, injection volume 50 µl) using Waters Ultra-hydrogel 120 and 250 columns with Waters 2414 RI (Refractive index) detector. The weight average molecular masses were calculated in relation to pullulan standards. All extract solutions were measured as such after filtration (0.45 µm), they were not dialyzed. Empower 3 software from Waters was used to calculate the average molecular masses.

Results and discussion

Influence of the AC-treatment on the extract content

Activated carbon treatment aimed to decrease the amount of lignin and wood extractives in the extracts. As can be seen from *Table 1*, the treatment reduced the amounts of lignin and wood extractives and, thus, decreased the proportional amount of lignin and increased the proportional amount of carbohydrates in the both extracts. In the treatment of the spruce extract 68% of the lignin present in the extract was removed. The

corresponding number in the treatment of the birch extract was 85%. Thus, the pretreatment, which includes adsorption on AC and vacuum filtration, removed more lignin from birch extract than from spruce extract (Fig 2). This happened in spite of that there was same amount of AC added to both extracts, if mass of AC and volume of extract is considered (25 g AC/l extract), but the amount of AC to TDS or AC to lignin was higher in the case of the spruce extract. The amounts were for spruce 1.2 g AC/g TDS and 6.2 g AC/g lignin, and, for birch 0.7 g AC/g TDS and 3.2 g AC/g lignin.

Therefore, it is obvious that AC adsorbs more effectively dissolved birch lignin than dissolved spruce lignin. The reason is probably the differences in the structure of lignin between different wood species. Hardwood lignin consists of both syringyl and guaiacyl lignin, whereas softwood lignin consists solely of guaiacyl lignin (Gierer 1980; Santos et al. 2011; Shimizu et al. 2012). Also, the molecular mass of lignin might have been different in birch and spruce extracts, which might have affected the adsorption behavior.

The pretreatment removed 93% and 96% of the lipophilic extractives from spruce and birch extracts, respectively (Table 1). In addition to wood extractives listed in Table 1, the birch extract contained also small amounts of medioresinol and syringaresinol. They were totally removed by the pretreatment.

When the extracts were treated with AC, 20% (spruce) and 14% (birch) of the total dissolved carbohydrates were removed. It is not sure if adsorption of carbohydrates occurred at high temperature, because extract was not separated from the AC at high temperature immediately after actual adsorption. Instead, the extract was cooled down before separation and therefore, the adsorption of carbohydrates on AC might have happened during the cooling. The pretreatment decreased the average molecular mass of the extracts. The decrease was 44% for spruce and 43% for birch (Table 1). This indicates that the pretreatment removed relatively more of the high-molecular-mass hemicelluloses. It is suggested that the observed decrease in molecular mass was not due to degradation of hemicelluloses at high temperature, since the time at 160°C was the same for all the extracts regardless of whether the adsorption was carried out or not.

In the spruce extract, the carbohydrates (analysed as monosaccharides after acid hydrolysis by methanolysis), which were percentually most removed, were glucuronic acid, glucose and galacturonic acid (Table 2). Only 22% of the mannose, which is the dominating monosaccharide

in the spruce extract, was removed. In the birch extract, xylose was clearly the dominating sugar monomer. From the birch extract, the AC treatment removed percentually most galacturonic acid, glucuronic acid, and xylose. It has been suggested that in softwoods, glucomannan and 4-O-Me-glucuronic acid takes part in lignin-hemicellulose complexes (LHC), whereas in hardwoods, xylan and 4-O-Me-glucuronic acid (as a substituent of xylan chain) are part of them (Koshijima, Watanabe 1988; 2003). Thus, it could be assumed that at least part of the carbohydrate loss is due to the adsorption of LHCs onto ACs. The possible decrease in the amount of 4-O-Me-glucuronic acid cannot be observed from the analysis result, since 4-O-Me-glucuronic acid was not detected in the dissolved carbohydrate analysis. Hence, its behavior in the adsorption can only be discussed speculatively.

4-O-Me-glucuronic acid, which was attached to the xylan chain, as well as glucuronic acid and galacturonic acids were probably removed by AC due to opposite charges of acids and AC. The pKa value of glucuronic acid and galacturonic acid are 3.28 and 3.51, respectively (Kohn, Kováč 1978). This means that in the pH range of the extracts these acids were partly dissociated, since the pH of the spruce extract was 3.98 and that of the birch extract 3.15. The pH of the AC was 6.7, which means that the surface of the AC was positively charged below this pH value (Al-Degs et al. 2000). Thus, xylan chains which contain greater amount of 4-O-Me-glucuronic acid, were probably removed via adsorption of 4-O-Me-glucuronic acid by AC. After adsorption the pH values of the extracts were increased, pH of the spruce extract was 4.66 and pH of the birch extract was 3.86, which also implies that acidic components were removed.

Unbranched xylan is degraded more easily than branched xylan (Mortimer et al. 2010; Sjöström 1981). Thus, xylan chains containing 4-O-Me-glucuronic acid are probably bigger than the unbranched ones. Therefore, when the xylans containing 4-O-Me-glucuronic acid are removed by adsorption of the acid moiety to AC, the molecular mass of the extracts is decreased (Table 1). Another explanation for the decrease of the molecular mass might be the removal of lignin-hemicelluloses complexes.

After the AC treatment of the birch extract, more carbohydrates, lignin, and other organic compounds (calculated from the amounts of TOC, lignin and total dissolved carbohydrates) were found in the AC than after the AC treatment of the spruce extract (Fig 2). The capacity of the AC should have been enough at least for the spruce extract, and, thus, there might be some other

Table 1 - Characteristics of extracts before and after activated carbon treatment.

Extract	TDS		Lignin		Carbohydrates		MM Da	Turbidity NTU	Extractives mg/l		
	g/l	mg/g wood	g/l	mg/g wood	g/l	mg/g wood			Lignin residuals	Lignans	Lipophilics
Spruce	20	57	4	11	12	35	10216	3516	39	233	30
Birch	36	121	7.9	26	22	73	5729	2575	107	44	17
Spruce AC	14	33	1.3	3	10	23	5747	160	2	0	2
Birch AC	28	83	1.2	4	19	57	3262	130	8	1	1

TDS = total dry solids, MM = molecular mass

Table 2 - Carbohydrate composition in the original and AC treated extracts obtained from the total dissolved carbohydrate analysis. Lignin amount and decrease as a reference value.

	Monosaccharide, mg/l			Monosaccharide, mg/l		
	Spruce	Spruce AC	Decrease	Birch	Birch AC	Decrease
Arabinose	1380	1420	~0%	640	620	3%
Rhamnose	310	310	2%	530	500	6%
Xylose	1910	1550	19%	16740	14280	15%
Glucuronic acid	110	60	46%	130	90	31%
Galacturonic acid	390	250	35%	830	430	48%
Mannose	5420	4230	22%	890	860	3%
Galactose	1350	1140	15%	870	870	0%
Glucose	1450	890	39%	1230	1190	3%
Lignin, g/l	4	1.3	68%	7.9	1.2	85%

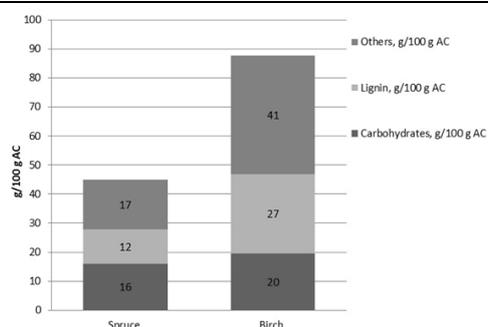


Fig 2 - Amount of organic material adsorbed in activated carbon from the spruce and the birch extracts. Adsorbed amount includes also material dissolved in the liquid that could not be separated from AC by vacuum filtering.

reason which restricts adsorption of the rest of the lignin in the spruce extract, or there might just be more reactive lignin compounds in the birch extracts. The capacity of the AC cannot be determined in our study, since the amount of adsorption data is limited. Also, the capacity of AC might vary between compounds dissolved from different wood species and lignins. The adsorption step should be optimized for each application (depending on wood species, required lignin removal, and flux during the UF) to obtain the best result. Gütsch and Sixta (2011) used AC for eucalyptus globulus extract at 170°C for 20 min with 24 g/l AC leading to lignin load 34 g lignin/100 g AC, this value being higher than values obtained for spruce and birch extracts in this study though the amount of AC was about the same, i.e. 25 g/l.

Influence of AC-treatment on ultrafiltration performance

The AC treatment increased significantly the filtration capacities in the ultrafiltration of the spruce and birch extracts (Fig 3). According to earlier studies (Koivula et al. 2011), prefiltration alone did not improve the flux, therefore, it is assumed that the improvement in the flux was due to adsorption on AC, not due to vacuum filtration, which was used to separate the AC from the solution. The average flux measured in the UF of the AC treated spruce extract was 56% higher than in the UF of the original spruce extract. The corresponding increase measured in the UF of the birch extracts was 59%. The

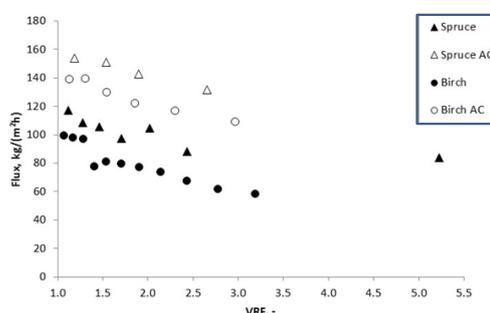


Fig 3 - UF of original and AC treated extracts with RC70PP membrane at 2 bar and 60°C with rotor speed of 8.0 m/s.

AC treatment decreased only slightly the viscosities of the wood extracts (Table 3). Since the decrease was small, it can be assumed that increase in the average flux was not only due to the decrease in viscosity. Higher viscosities in concentrate solutions than in feed solutions are probably partly due to greater amount and larger polymers in the solution. The viscosity of the produced spruce extract concentrate was higher than that of the produced birch extract concentrate because the VRF reached in the UF of the spruce extract was also higher. In addition, the average molecular mass of the original spruce extract was higher than that of the original birch extract (Table 1).

As it was expected, based on the earlier results (Kallioinen et al. 2012; 2013), the RC70PP membrane was only slightly fouled due to the UF of wood extracts. The pure water flux reductions were small in all the experiments (Table 3). In this case, and due to the short experimental time, the influence of the AC-treatment on fouling is difficult to notice. However, it has been seen in the treatment of pulp and paper mill process waters that wood extractives are significant foulants, although their total amount in the process streams is very low. They might accumulate on membranes in the long run, and cause deterioration of filtration performance (Puro et al. 2011). Thus, it is possible that in real scale applications the AC treatment would decrease fouling problems, because it decreases significantly the amount of wood extractives (Table 1). In these experiments, the decrease of fouling due to the AC treatment was seen only in the treatment of the spruce extract.

Table 3 - Pure water fluxes, average flux of the wood extracts and the VRF values reached in the ultrafiltration experiments and viscosities of the wood extracts before and after each UF.

Extract	VRF, -	PWF _b , kg/(m ² h)	PWF _a , kg/(m ² h)	PWF _r , %	J _{av.} , kg/(m ² h)	v _F , mm ² /s	v _C , mm ² /s
Spruce	5.2	127	106	17	93	0.622	1.737
Spruce AC	3.3	134	123	8	145	0.553	0.766
Birch	3.2	121	112	8	79	0.651	1.172
Birch AC	3.3	127	116	8	126	0.578	0.758

VRF = volume reduction factor, PWF = pure water flux (b before UF, a after UF, r reduction), J_{av.} = average flux during UF, v = viscosity (F feed, C concentrate)

Table 4 - Retentions of TOC, lignin and carbohydrates in each ultrafiltration experiments.

Filtration	R (TOC), %	R (Lignin), %	R (Carbohydrates), %
Spruce	51	22	61
Birch	56	37	60
Spruce AC	44	8	50
Birch AC	36	13	40

The AC treatment influenced clearly on UF retentions of lignin and carbohydrates, as shown in Table 4. Both retentions decreased due to the AC treatment. In recovery of high-molecular-mass hemicelluloses, the product is the concentrate fraction which should have high concentration of carbohydrates, but also low concentration of impurities, e.g. lignin. The decrease in retentions might originate from removal of high-molecular-mass compounds from the extract, and the compounds left in the extract were small enough to permeate the membrane. Moreover, when the high-molecular-mass compounds are present in the extract, they can form a secondary layer on the membrane surface during the filtration, which prevents the permeation of smaller compounds even though they were normally small enough to go through the membrane (Cheryan 1998; Strathmann et al. 2006). This suggestion is supported by the molecular mass analysis. It seems that the AC treatment has removed the high-molecular-mass compounds, because the average molecular mass of the extracts has decreased due to the treatment. The decrease in lignin retentions due to the AC-treatment indicates that the adsorption have removed also the high-molecular-

mass lignin compounds. The decrease in lignin retention is an effect, which was hoped-for, because it enables the production of more pure carbohydrate fraction.

Carbohydrate yield and purity of the produced high-molecular-mass fraction

The amount of extract obtained from the extraction varied between the wood species used, birch sawdust releasing higher amount of extract. Part of the extract was lost in the pretreatment step, probably because vacuum filtration did not remove all the extract from the AC, and, some of the extract might have evaporated during vacuum filtering. The average molecular mass of the spruce extract was higher than that of the birch extract, as, respectively, molecular masses of the corresponding concentrate fractions (Table 5). With the spruce extract, larger portion of the hemicelluloses present in the original extract were recovered to the concentrate fraction than with the birch extract, although UF was conducted further with spruce (VRF 5) than with birch (VRF 3), which would assumingly affect the other way.

However, because the molecular mass of the birch extract was lower, the hemicellulose loss in UF with the same membrane was higher although the VRF is lower. Also, the purity of the product fraction was higher in the case of the spruce extract than in the case of the birch extract. In the original sawdust, there was around 301 g hemicelluloses/kg D.S. (spruce) and 335 g hemicelluloses/kg D.S. (birch), based on average amounts of hemicelluloses in spruce and birch (Sjöström 1981). Thus, the hemicellulose yields over the whole process were for spruce 10% and for birch 17%. The AC-treatment decreased the hemicellulose yields giving 7% for spruce and 11% for birch.

Table 5 - The amount, molecular mass and purity of the high-molecular-mass hemicelluloses produced from 4 kg of dry wood, and the average filtration capacity (flux) for each case. VRF value for spruce was 5 and for spruce AC, birch and birch AC it was 3.

	Extraction	UF without AC-treatment	AC-treatment	UF after AC-treatment
Spruce				
Hemicellulose yield, g/kg wood	35	30	23	21
Purity, %	61	81	71	84
MM, kDa	10.2	15.1	5.7	9.3
Flux, kg/(m ² h)		93		145
Birch				
Hemicellulose yield, g/kg wood	73	56	57	37
Purity, %	60	68	68	75
MM, kDa	5.7	7.7	3.3	4.7
Flux, kg/(m ² h)		79		126

MM = molecular mass

Table 6 - Wood extract fractions used in the production of hemicellulose-based films.

Original solution	MM (hemicelluloses), Da	Lignin content, % of dry matter	Reference
Spruce hydrolysate	2400 and 4200	15 and 29	Saadatmand et al. 2012
Birch hydrolysate	950	16	Saadatmand et al. 2013
Xylan solution (commercial xylan from birch)	13000	-	Hesse et al. 2006
Spruce extract	15000	9	This study
Spruce extract with AC-treatment	9300	1	This study
Birch extract	7700	16	This study
Birch extract with AC-treatment	4700	4	This study

MM = molecular mass

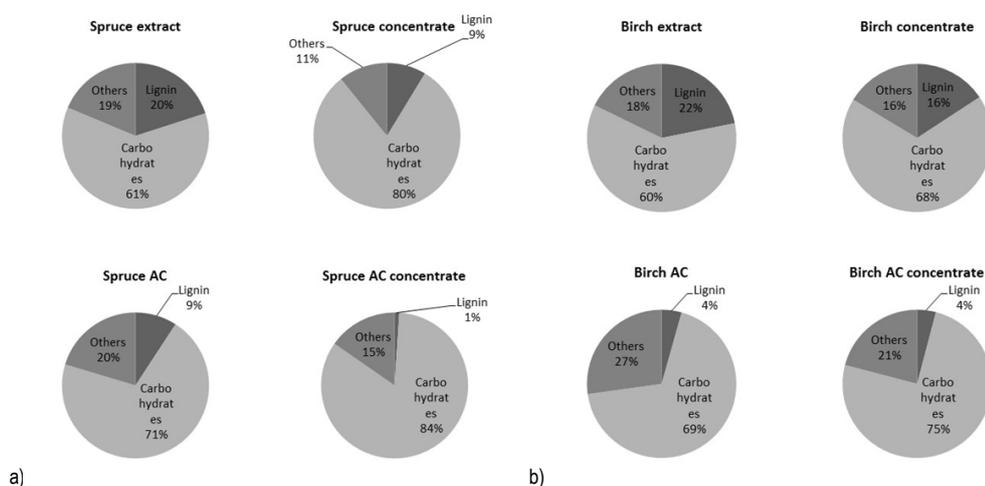


Fig 4 - The content of total dry solids in a) spruce extract, concentrate of spruce extract, AC treated spruce extract and concentrate of AC treated spruce extract, and, b) birch extract, concentrate of birch extract, AC treated birch extract and concentrate of AC treated birch extract.

The hemicellulose yields were lower than they would theoretically be, since it is impossible to extrude all the extract out from the sawdust after extraction.

Average molecular mass of the spruce extract increased 48% when original extract was ultrafiltered, and 62% when the AC treated extract was ultrafiltered. With the birch extract the corresponding values are 35% and 45%. Although AC treatment decreased the molecular mass of the extracts, the decrease was compensated to some extent by UF, since concentration filtration increased molecular mass significantly. That is reasonable because the membrane rejects compounds above certain size, and most of the small molecules permeate the membrane. Determining factors in hemicellulose-based film making are the molecular mass of hemicelluloses and the amount of lignin (i.e. the purity of the product fraction). Therefore, all product fractions obtained in this work can be considered suitable for film production, as they are even more pure and have higher molecular mass of hemicelluloses than those in comparable studies (Table 6). Although AC removed also some part of the carbohydrates, which can also be seen in the content of the produced concentrate fractions (Fig 4), the percentual part of carbohydrates in the concentrate fractions is

increased due to AC-treatment. In the concentrate fraction produced from the AC treated spruce extract 84% of total dissolved solids were carbohydrates and only 1% dissolved lignin while in the concentrate fraction produced from the original spruce extract the corresponding numbers were 81% and 9%, respectively. In the concentrate fraction produced from the AC treated birch extract 75% of total dissolved solids were carbohydrates and 4% lignin, while in the concentrate fraction produced from the original birch extract the corresponding numbers were 68% and 16%, respectively. Therefore, although the amount of carbohydrates was slightly decreased by AC, the products from both extracts were more pure.

Conclusions

Activated carbon (AC) treatment to remove lignin and wood extractives improved ultrafiltration capacity in the filtration of spruce and birch extracts about 1.5 fold and increased the purity of the produced high-molecular-mass hemicellulose fractions. Carbohydrate losses due to adsorption were substantially low (for spruce 20% and for birch 14%) proving that AC was more selective to lignin than carbohydrates. It seems that adsorption at the

extraction temperature is favourable in terms of lower hemicellulose losses. High-molecular-mass compounds were removed more than smaller ones from the wood extract by activated carbon, which was, however, compensated by ultrafiltration to some extent. The molecular mass of hemicelluloses was higher in the produced spruce extract fractions than in the produced birch extract fractions but the produced birch extract fractions contained more hemicelluloses. The produced hemicellulose fractions are suitable for film production, because they fulfil purity and molecular mass requirements.

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Improvement of ultrafiltration performance by oxidation treatment in the recovery of galactoglucomannan from wood autohydrolyzate

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ABSTRACT

The possibility to enhance ultrafiltration in the recovery of galactoglucomannan (GGM) from wood autohydrolyzate with the gas-phase pulsed corona discharge (PCD) oxidation was studied. The filtration capacity, membrane fouling, and purity of hemicelluloses in the membrane concentrates were used as criteria to evaluate the benefits of the hybrid separation process. The results showed that the PCD oxidation significantly improved the filterability of the wood autohydrolyzate, although its effect on the fouling of the very hydrophilic cellulose-based UF membranes was low. The positive influence on filterability can be at least partly explained by the decreased viscosity of the oxidized autohydrolyzates. Oxidation modified the structure of the lignin but its effect on the lignin molar mass was small. As a result of oxidation, the average molar mass of hemicelluloses was also slightly decreased. Therefore, the influence of oxidation on the purity of the concentrated hemicellulose fractions was not as high as expected. However, oxidation removed lignans and lipophilic wood extractives, which have some influence on the purity of the produced hemicellulose fractions.

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1. Introduction

Hemicelluloses are the second most common group of polysaccharides in nature. Globally, pulp mills treat approximately 70 Mt of hemicelluloses annually. Typically, hemicelluloses are not utilized in the most efficient way in the mill and they are usually incinerated in the recovery boiler although their heating value is relatively low. Therefore, hemicelluloses are a huge, existent raw material source for future oil-free economy.

Galactoglucomannans (GGMs) are the predominant hemicelluloses in the soft woods and their recovery and refining to value added products have recently attracted the attention of researchers [1–3]. One of the promising methods to extract GGMs from wood material is pressurized hot water extraction [4–8]. During the extraction other wood compounds are also dissolved into the wood autohydrolyzate and, therefore, further fractionation and purification is needed before the hemicelluloses can be further processed to compounds substituting oil-based compounds. Typically, wood autohydrolyzates contain phenolic compounds such as lignin and

its degradation products, and lignans. In addition, small amounts of organic acids and wood lipophilic extractives are present. Lipophilic extractives and lignans have low molar masses, which makes application of membrane technology, in particular ultrafiltration (UF), theoretically feasible in recovery and purification of dissolved high molar mass hemicelluloses [9–14]. The approach, however, often suffers from a noticeable decrease in filtration capacity making the process uneconomical [13,15]. In addition, UF is not selective as regards hemicelluloses, as other high molar mass compounds, such as lignin, are retained simultaneously.

The feasibility of the UF process may be improved by using a proper hydrophilic membrane [16,17], controlling filtration conditions (e.g. high shear rate on the membrane surface to reduce concentration polarization, and thus, usually also membrane fouling), and by applying suitable pre-treatment to the feed solution [13–15]. Lignin and wood extractives have shown to be potential foulants when wood originating solutions are treated. Various pre-treatment processes are able to degrade, inactivate, or remove these foulants prior to UF. Oxidation of the foulants is an attractive fouling management alternative, because it might lead to small molar mass lignin compounds permeating the membrane and offers the possibility to valorize lignin recovered from the

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permeate fraction. Moreover, the waste amount produced in the hybrid process combining oxidation and ultrafiltration is easier to minimize compared to a process combining adsorbents and ultrafiltration. Oxidation might also separate lignin from hemicellulose–lignin complexes and thus enable improvement of purity of the concentrated high molar mass hemicellulose fraction.

Different oxidation methods, for instance wet oxidation [18,19] and ozonation [20,21] have been studied in the degradation of lignin present in different biomass based solutions. Recently, oxidation with the pulsed corona discharge (PCD) method has also proven to decompose lignin in aqueous solutions [22] at an energy efficiency exceeding the one of traditional ozonation; this is due to utilizing short-living oxidants [23]. The degradation of lignin to vanillin and syringaldehyde as oxidation products has been presented as a possible perspective to valorize lignin using the PCD treatment [22]. In the PCD oxidation, only a small energy input is needed to generate ozone and hydroxyl radicals from oxygen and water and, therefore, less energy is needed compared to ozonation. Koivula et al. [13] showed earlier that pretreatment of spruce autohydrolyzates with PCD oxidation significantly improved the flux through a hydrophobic polysulphone membrane and reduced membrane fouling. However, the effect of PCD oxidation on the composition and properties of the wood autohydrolyzate was not examined in details. Furthermore, the effect of oxidation on the filtration performance of hydrophilic membranes, which generally have a lower fouling tendency in the treatment of wood originating solutions, was not studied.

Therefore, the aim of this study was to discover the influence of PCD oxidation pretreatment on the performance of a membrane-based recovery and purification process for hemicellulose (galactoglucomannan), when hydrophilic membranes are applied. The filtration capacity, membrane fouling, and purity of hemicelluloses in membrane concentrates were used as criteria to evaluate the benefits of the hybrid separation process. The effect of oxidative treatment on the autohydrolyzate composition and properties were analyzed and the filtration results explained based on the analysis results.

2. Materials and methods

2.1. Wood autohydrolyzate

Wood extract (autohydrolyzate) was prepared by the treatment of 29.4 kg of dry spruce saw dust with water in a 300 L flow-through extraction vessel at the volumetric flow rate of 14 L/min. The extraction temperature and time were 170 °C and 52 min. The total amount of wood autohydrolyzate was 728 kg, making the water/wood ratio approx. 25. The extraction equipment is described in detail by Kilpeläinen et al. [24].

The extracted liquor contained 2.6 g/L of organic carbon and about 3.8 g/L of carbohydrates. The proportion of monomeric sugars was less than 10% of the total carbohydrates. The average molar mass of hemicellulose was approximately 7 kDa. Due to autohydrolyses and cleavage of acetic acid during the extraction in hot water the pH of wood autohydrolyzate was 4.1. Lignin was expectedly the main impurity in the wood autohydrolyzate. Its content was evaluated by the UV absorbance at 280 nm comprising 0.6 g/L. The liquor also contained about 28 mg/L of lipophilic extractives, 44 mg/L of lignans, 440 mg/L of organic acids and less than 10 mg/L of furan compounds.

2.2. Membrane filter and membranes

In order to minimize membrane fouling, hydrophilic cellulose based UF membranes (water–air interface contact angles below

15°) in a high shear rate membrane filter were used in this study [16,17]. According to the manufacturers, the cut-off values of the membranes used were 30 and 10 kDa for the UC030 (Microdyn-Nadir) and the RC70PP (Alfa Laval) membranes, respectively. The membranes were selected based on earlier experience of the filterability of membranes with similar types of solutions [12,13,16]. A high shear rate cross-rotational (CR) filter was used, because it enables a high turbulence on the membrane surface, thus reducing the effect of concentration polarization [25].

2.3. Filtration experiments

All filtrations were made in the concentration mode to volume reduction factors (VRF) numerically presented in Fig. 1. During the filtration the permeate was collected in a separate vessel, and the concentrate was recirculated back into the feed tank. The pressure, temperature and rotor velocity were kept constant during filtrations. Filtrations were made at a pressure of 1 bar and 2 bar with the 30 kDa and the 10 kDa membrane, respectively. The rotor velocity in the CR-filter was approximately 9 m/s and the temperature 65 °C.

Sequential filtrations were carried out by filtering the previous stage concentrate or permeate using the same or a lower cut-off membrane as shown in Fig. 1. Based on the cut-off values 10 and 30 kDa, two kinds of hemicellulose fractions were recovered by the membranes used. Oxidation treatment was applied to three solutions (Fig. 1):

1. The original wood autohydrolyzate prior to the filtration with the 30 kDa membrane (UC030 III PCD).
2. The 30 kDa membrane concentrate prior to further concentration filtration with the 30 kDa membrane (filtration UC030 II PCD).
3. The 30 kDa membrane permeate (UC030 I) which was at first pre-concentrated by the 10 kDa membrane (RC70PP I) prior to further concentration filtration with the 10 kDa membrane (Filtration RC70PP II PCD).

Membrane performance was evaluated by measuring the permeate flux, pure water permeabilities before (PWP_0), and after (PWP_a) the filtration of wood autohydrolyzate and by analyzing the collected samples. Fouling was calculated from the pure water permeabilities and presented as a per cent difference in pure water fluxes before and after the wood autohydrolyzate filtration (Eq. (1)).

2.4. Oxidative treatment

Oxidative treatment was studied with the aim of improving the filtration efficiency and the hemicellulose fraction purity. A schematic diagram of the experimental set-up is shown in Fig. 2. The system consists of a pulse generator (power supply) and a simple reactor described earlier [23]. The power supply generates the discharge pulses of voltage pulse amplitude 20 kV, the current 380–400 A, and 100 ns in duration at pulse repetition frequency of 840 pulses per second (pps). The energy delivered to the reactor was calculated as an integral product of voltage and current peak areas. The maximum delivered energy was 250 W at the maximum pulse repetition frequency (840 pps). The energy consumption efficiency of the pulse generator was 67%.

An autohydrolyzate solution in the amount of 40 L was circulated from the reservoir tank through the reactor by a pump. The autohydrolyzate passed from the top of the reactor through a perforated plate and spread between the electrodes. The autohydrolyzate passed through the PCD zone where the target compounds reacted with hydroxyl radicals, ozone, and other

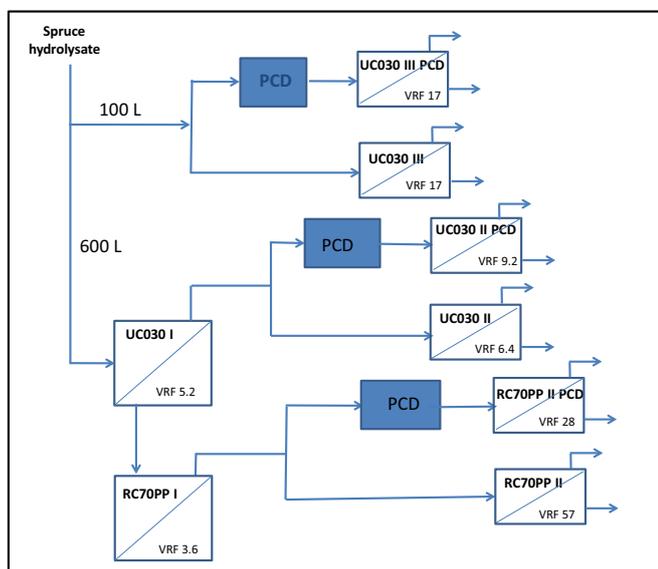


Fig. 1. Sequences of filtration and oxidation treatments.

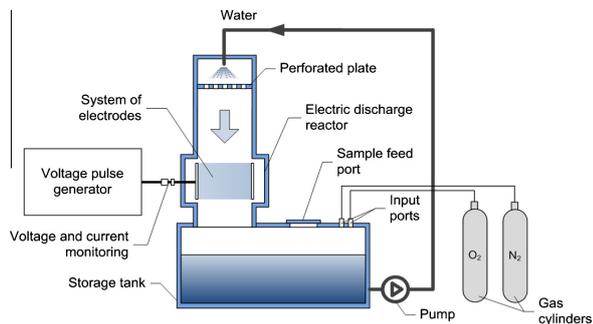


Fig. 2. Schematic illustration of the experimental setup.

short-living oxidants before returning back to the tank. To achieve an initial concentration of about 90% of oxygen in the reactor, pure oxygen gas was introduced to the reactor prior to the experiment.

The effect of the treatment intensity on the composition of the wood autohydrolyzate was studied by collecting samples from the reactor with a 15 min increment from 0 to 45 min and at 120 mins of treatment. The energy delivered to the reactor was calculated as a product of the pulsed power and treatment time relative to the treated autohydrolyzate sample, and comprised about 5400 kJ/m^3 for a 15 min of treatment. The samples of wood autohydrolyzates oxidized for 45 min were filtered as described in Fig. 1.

2.5. Analytical methods

Before analysis, feed and concentrate samples were centrifuged to remove suspended solids and fibers. Conductivity and pH were

measured at 25°C to determine the ionic content of the samples. Conductivity was measured with a digital conductivity meter (Knick Konduktometer 703) calibrated with 0.01 M KCl . The presence of suspended solids and possible extractives was detected by measuring turbidity using a Hach 2100AN IS turbidimeter.

Total organic carbon (TOC) was analyzed using a Shimadzu TOC-5000A analyzer (Shimadzu TOC-5050A analyzer with ASI 5000A autosampler, 680°C , high purity synthetic air 4.0 as the carrier gas at 150 mL/min , two parallel samplings, deviation $< 2\%$). The purity of hemicelluloses is related to the total organic carbon content of the samples.

Detailed sugar analysis was carried out to estimate the concentrations of hemicelluloses and monosaccharides. The carbohydrates were analyzed according to Sundberg et al. [26]. The carbohydrate content was analyzed by a gas chromatography (GC, HP6890 with injector HP7683, Agilent, USA). The column

was a 25 m/0.20 mm i.d. wide-bore capillary column with a nonpolar phase (HP-1, Agilent Technologies) having a film thickness of 0.11 μm . Carbohydrates were analyzed as monosaccharides derivatives, thus, before analysis hemicelluloses/polymeric carbohydrates were transformed to monosaccharides by acid methanolysis followed by silylation. Monomeric carbohydrates were analyzed in the same way but without acid methanolysis.

Wood lipophilic extractives and lignans were extracted from the samples by methyl *tert*-butyl ether (MTBE) extraction and, after silylation, analyzed by GC [27].

Lignin was determined by UV spectrophotometry (as UV absorbance at 280 nm) after removing lignans and other extractives by MTBE extraction of the samples [28]. The absorbance value was converted to a lignin concentration (g/L) by dividing the absorbance with the absorptive coefficient 17.8 L/(cm g). The UV absorbance was also measured in the original samples before the MTBE extraction. The UV absorbance after the MTBE extraction mostly measures polymeric lignin compounds.

Furfural and hydroxymethylfurfural (HMF) were analyzed by high performance liquid chromatography (HPLC) with an UV detector at 280 nm. The column Agilent Poroshell 2.7 μm , EC-C18 120 Å (4.6 \times 50 mm) was used, at an eluent flow rate of 1.2 mL/min. The injection volume was 3 μL and the used eluents were 95% water +0.5% acetic acid and 5% methanol +0.5% acetic acid. The total analysis time was 15 min.

The analysis of carboxylic/hydroxylic acids was made according to Rovio et al. [29]. Beckmann-Coulter P/ACE MDQ capillary electrophoresis (CE) equipment with a photodiode array UV/Vis detector was used in the analysis. Uncoated fused silica capillaries of 50 μm I.D. and with a length of 50/60 cm (effective length/total length) were employed in the experiments. Acids were monitored by indirect UV detection at 281 nm. The applied voltage was 30 kV. The used electrolyte solution consisted of 20 mM of 2,3-pyrazinedicarboxylic acid, 65 mM of tricine, 2 mM of BaCl_2 , 0.5 mM of cetyl trimethylammonium bromide and 2 mM of urea.

To evaluate changes in the structure of the polymeric compounds, molar mass distributions as well as the viscosity of the wood autohydrolyzates were analyzed. The average molar mass (M_w) was determined by size-exclusion chromatography (SEC) in on-line combination with a multi-angle-laser-light-scattering (MALLS) instrument (miniDAWN, Wyatt Technology, Santa Barbara, USA, $\lambda_0 = 690 \text{ nm}$) with three scattering angles of 41.5°, 90.0°, and 138.5° and a refractive index (RI) and UV detectors (Shimadzu Corporation, Japan). A two column system 2 \times Ultrahydrogel TM linear 7.8 mm \times 300 mm + guard column was used. An 0.1 M NaNO_3 solution, after being filtered through a 0.1 μm Anodisc 47 membrane filter, was used as the eluent at a flow rate of 0.5 mL/min. The samples were filtered through a 0.22 μm nylon syringe filter before injection. The dn/dc value 0.15 was used [30]. The injection volume was 200 μL . Astra software (Wyatt Technology, Santa Barbara, USA) was used to interpret the data. Kinematic viscosity was measured by viscometer (COMECTA I, no. 4020, size 1, constant 0.0091131).

2.6. Calculations

Membrane fouling was calculated by comparing the difference between the pure water permeability before and after the filtration, as the following Eq. (1) shows.

$$\text{Fouling (\%)} = \frac{\text{PWP}_b - \text{PWP}_a}{\text{PWP}_b} \cdot 100\% \quad (1)$$

where PWP_b is the pure water permeability before filtration and PWP_a is the pure water permeability after filtration ($\text{kg}/(\text{m}^2 \text{ h bar})$).

The yield of hemicelluloses in the membrane concentrate was calculated by:

$$\text{Yield (\%)} = \frac{m_{\text{hemi(C)}}}{m_{\text{hemi(F)}}} \cdot 100\% \quad (2)$$

where $m_{\text{hemi(C)}}$ is the mass of hemicelluloses in the concentrate and $m_{\text{hemi(F)}}$ is the mass of hemicelluloses in the feed.

The purity of the hemicelluloses was defined as the ratio between the carbon content in the hemicelluloses, comprising about 40% of hemicellulose molecular mass, and the total organic carbon (TOC) in the final concentrate and was calculated by:

$$\text{Purity (\%)} = \frac{0.4 \cdot C_{\text{hemi(C)}}}{\text{TOC}_{(C)}} \cdot 100 \quad (3)$$

where $C_{\text{hemi(C)}}$ is the concentration of the hemicelluloses (e.g. GGM) and $\text{TOC}_{(C)}$ is the total organic carbon concentration in the final concentrate.

3. Results and discussions

3.1. Effect of oxidative treatment on filtration capacity and fouling

The effect of oxidative treatment on the filtration capacity is illustrated in Fig. 3. The oxidative treatment had a significant effect on the flux when the original wood autohydrolyzate was concentrated (filtration UC030 III PCD, in Fig. 1). The increase of flux was even more remarkable when the concentrate of the 30 kDa membrane (filtration UC030 I) was concentrated further after the PCD treatment (filtration UC030 II PCD). When the permeate of the 30 kDa membrane was further filtered with the 10 kDa membrane, and the concentrate of this 10 kDa filtration was treated with oxidation, the filterability of oxidized concentrate did not differ from the non-oxidized concentrate (Fig. 3b). Therefore, it can be concluded that the 30 kDa membrane sufficiently removed foulants, causing a decrease of flux through the 10 kDa hydrophilic cellulose membrane. As a result, the effect of oxidation on the flux of the hydrophilic 10 kDa cellulose membrane was negligible (Fig. 3b) if the solution was pre-filtered prior to oxidation.

As Table 1 shows the measured fouling values were low which indicates that the decrease in flux was mostly caused by other phenomena such as concentration polarization, the increase of osmotic pressure, the increase of viscosity or the formation of a gel layer on the membrane surface when the polymeric compounds were concentrated. Removal of the high molar mass compounds by pre-filtration or their partial degradation by oxidation presumably decreases the solution viscosity and the potential of the compounds to form a gel layer during concentration filtration.

The viscosity measurements proved that the oxidation significantly reduced the viscosity of the UF concentrate. When the original wood autohydrolyzate and the pre-oxidized extract were concentrated by the 30 kDa membrane to VRF 17 the kinematic viscosity coefficient in the concentrates comprised 1.71 mm^2/s and 1.36 mm^2/s , respectively. The viscosity of oxidized liquor was about 20% lower, and the flux (Fig. 3a) was about 30% higher than that of the original liquor. Therefore, the change in viscosity explained a significant part of the flux increase observed after pre-oxidation of the autohydrolyzate.

3.2. Effect of oxidative treatment on the chemical composition of autohydrolyzate

Fig. 4(a) and (b) show the effect of PCD treatment time on the quantity of parameters of the wood autohydrolyzate. Since the largest changes in the parameters were observed at 45 min of oxidation with little progress after that, the detailed analysis of autohydrolyzate was performed in the samples collected at this treatment time.

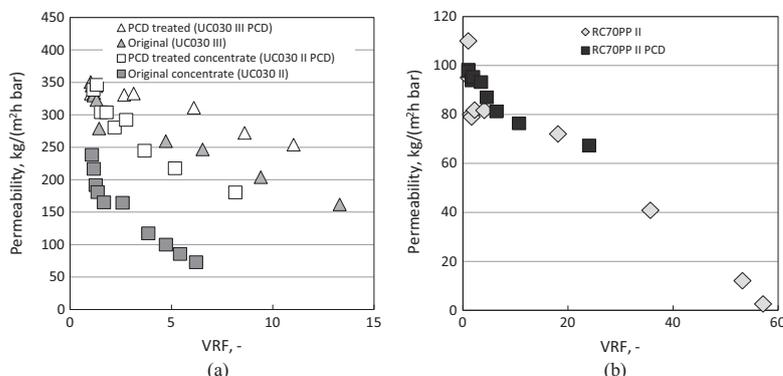


Fig. 3. Effect of PCD treatment on the permeability of (a) the UC030 (30 kDa) and (b) the RC70PP (10 kDa) membrane with the following feed solutions: UC030 membrane – original autohydrolyzate and pre-concentrated autohydrolyzate with and without the PCD treatment; RC70PP membrane – primary permeate of UC030 pre-concentrated at the RC70PP membrane with and without the PCD treatment (see Fig. 1).

Table 1
Pure water permeabilities and membrane fouling with and without oxidative pre-treatment of the autohydrolyzate.

Feed solution		Filtration code in Fig. 1	PWP _p , g/(m ² h bar)	PWP _a , kg/(m ² h bar)	Fouling, %
UC030	Original extract	UC030 I	305	270	11%
	Original extract	UC030 III	314	310	1%
	Oxidized original extract	UC030 III PCD	296	298	-1%
	Concentrate from filtration I	UC030 II	308	270	12%
	Oxidized concentrate from filtration I	UC030 II PCD	307	275	10%
	UC030 permeate	RC70PP I	104	102	2%
RC70 PP	Concentrate from the filtration RC70PP I	RC70PP II	102	107	-5%
	Oxidized concentrate from the filtration RC70PP I	RC70PP II PCD	108	104	4%

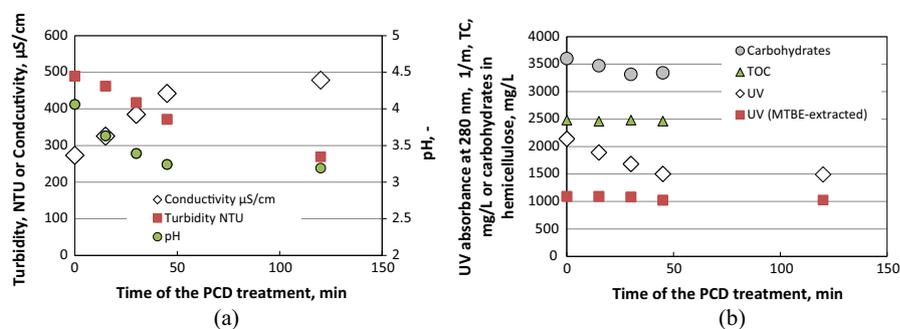


Fig. 4. Effect of the time of oxidation treatment on the composition of the wood autohydrolyzate.

The growth in electric conductivity and acidity of PCD-treated wood autohydrolyzate indicate the formation of acids common for oxidation processes [31]. The CE analysis showed the presence of acetic, formic, glycolic, oxalic and glucoisosaccharinic (GISA) acids. Table 2 shows the concentration of acids increasing with oxidation time except for the acetic acid. The GGM is partly acetylated and the acetyl groups are already liberated from hemicellulose during the hot water treatment and they form acetic acid, which decreases the pH and accelerate the hydrolysis. Therefore, the

amount of acetic acid no longer increased in the oxidation. The results showed that the main organic acid formed in oxidation was formic acid, the concentration of which more than doubled from 50 to 119 mg/L. Concentrations of other identified organic acids, i.e. lactic, succinic, malic, 2,5-dihydroxypentanoic, 2-hydroxybutanoic acid and xyloisosaccharinic (XISA) acids were around 10 mg/L. The total increase in acids concentration did not exceed 140 mg/L, making the total sum after oxidation 570 mg/L, which comprised about 10% of the total organic carbon.

Table 2
Concentration of organic acids (mg/L) in the original autohydrolyzate and after different periods of the oxidation treatment.

Treatment time, min	Concentration, mg/L					
	Acetic acid	Formic acid	Glycolic acid	Oxalic acid	Gisa	Other acids
0	270	50	27	12	24	49
15	293	87	43	23	23	48
30	293	105	45	29	33	54
45	284	119	46	33	31	63

The analysis of carbohydrate composition showed the predominant character of GGMs comprising over 75% of hemicelluloses in the autohydrolyzate. Pre-oxidation caused about a 7% loss of hemicellulosic carbohydrates (Table 3). The amount of monomeric hexoses slightly increased, although their total concentration did not exceed 2% of hexoses. About 28% of the pentoses existed in monomers and their concentration slightly decreased during oxidation. The main monomeric pentose was arabinose, comprising about 70% of all the monomeric pentoses' content.

The results indicate that oxidation did not increase the amount of furfural and 4-hydroxymethylfurfural, but their concentrations remained at a very low level being less than 10 mg/L also after the treatment. Thus, it can be assumed that the minor loss in carbohydrates is mostly due their degradation to organic acids.

An interesting observation was made concerning the UV absorbance behavior in autohydrolyzate solutions and those samples treated with the MTBE extraction (Fig. 4). The PCD oxidation reduced the UV absorbance of wood autohydrolyzate samples, e.g. from an initial 2200–1500 m⁻¹ in the 45 min of treatment (Fig. 4b). However, when the samples were compared after the MTBE extraction, only a minor effect of oxidation on the UV absorbance could be seen. Methyl *tert*-butyl ether is known as a solvent for lipophilic wood extractives and also for extracting phenolic compounds such as lignans, small molar mass phenols, and furan type compounds optically active at 280 nm but not polymeric lignin. Therefore, the degrading UV absorbance of the original samples, compared to the constant one of MTBE-extracted autohydrolyzate, indicate selective degradation of lignans and other small molar mass phenolic compounds in PCD-oxidation.

It seems that the oxidation intensity was not sufficient to degrade a significant amount of polymeric lignin from the autohydrolyzate. However, based on the SEC/MALLS analysis oxidation modified the lignin structure. The oxidation treatment had a noticeable influence on the signal of the UV detector by spreading the signal over time (i.e. lignin concentration at different retention times) although only a minor effect on the average molar mass was seen. The retention time of most of the UV absorbing compounds

in the original wood autohydrolyzate was from 40 to 42 min – spreading from 38 to 44 min as a result of oxidation. This indicates the formation of new UV absorbing compounds the molar masses of which remained predominantly unchanged being for instance 2910 g/mol for the UV absorbing compounds in the untreated, and 2760 g/mol for the UV absorbing compounds in the pre-oxidized autohydrolyzate.

The decreased turbidity (Fig. 4a) in the PCD treatment indicates the removal of lipophilic wood extractives, which is confirmed in their detailed analysis. For instance, the lipophilic extractives and lignans in the original feed solution in the filtration UC030 III (Fig. 1) were reduced as a result of 45-min PCD-treatment from 26 and 42 mg/L to 6 and 2 mg/L, respectively. The efficient removal of wood lipophilic extractives is shown in Fig. 5. Lipophilic wood extractives are reported to foul the membranes in many studies, this fouling mostly concerns hydrophobic membranes [32]. Fouling of hydrophilic membranes in this study was not significant.

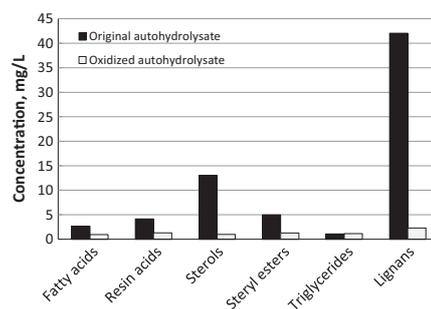


Fig. 5. Concentration of wood lipophilic extractives and lignans in the original wood autohydrolyzate and after 45 min of oxidation treatment.

Table 3
Polymeric and monomeric sugar compounds in the wood autohydrolyzate after the oxidation treatment.

Treatment time, min	Hemicelluloses, mg/L				Monomeric carbohydrates, mg/L				Sugars loss, %	
	0	15	30	45	0	15	30	45	Hemicellulose	Monomers
Arabinose	99	105	88	99	198	185	184	179	~0	10
Rhamnose	66	64	63	67	7	7	7	7	~0	~0
Xylose	559	540	519	520	73	68	67	66	7	9
∑Pentoses	724	709	670	687	277	260	258	252	5	9
Mannose	1820	1744	1672	1671	14	19	20	20	8	-39
Galactose	393	381	361	369	19	36	36	35	6	-80
Glucose	502	483	464	467	3	5	4	5	7	-87
∑Hexoses	2714	2608	2497	2507	36	59	60	60	8	-65
Glucuronic acid	15	18	17	20	1	0	0	0	-36	
Galacturonic acid	146	134	128	125	2	1	2	2	14	
Total, mg/L	3599	3470	3313	3340	316	321	320	314	7	1

Although evident changes in the composition of organic compounds were seen after oxidation, the amount of TOC remained constant (Fig. 3b). The energy delivered to oxidation was not high enough to cause the mineralization of organic compounds. This was most probably due to the high concentration of the organic compounds in the treated stream.

3.3. Purity of the high molecular mass galactoglucomannan

The possibility of degrading the impurities existing in the wood autohydrolyzate to the extent that they would not be retained together with hemicellulose in the downstream UF process and would not disturb filtration performance, made the oxidation step an attractive pretreatment option. The main impurity in the wood autohydrolyzate is lignin, which might disturb the film-forming process and cause unwanted odor and color in the hemicellulose

based products. Other impurity groups are the lipophilic wood extractives consisting of different resin and fatty acids, waxes, steryl esters, and triglycerides. Their molecular masses are low compared to the recovered hemicelluloses and to the cut-off value of the membranes used. However, they also exist in colloidal form and are, therefore, partly retained by the UF membrane. The lipophilic wood extractives can form sticky deposits on process equipment, or they may create spots e.g. in films formed from hemicellulose.

As presented above, under the experimental conditions used in this study, oxidation treatment for 45 min did not degrade lignin significantly; however the oxidation modified the lignin structure. This, together with the other changes originating from the oxidation of the autohydrolyzate, lead to a situation in which the concentrated fraction produced from the oxidized wood autohydrolyzate contained less lignin compared to the

Table 4
Filtration results for original (UC030 III) and pre-oxidized (UC030 III PCD) wood autohydrolyzates at VRF = 17.

	pH	Conductivity μS/cm	Turbidity NTU	TOC mg/L	Lignin mg/L	Lipophilic extractives, mg/L	Lignans mg/L	Pentoses mg/L	Hexoses mg/L	Sugar acids mg/L
Original feed	4.1	278	551	2555	624	26	42	623	2339	142
UC030 III permeate	4.1	277	40	1958	545	25		560	1364	116
UC030 III concentrate	4.0	325	8528	13,010	2404	38	52	1611	16,216	647
Yield at VRF 17, %		7%	93%	30%	23%	9%	7%	15%	42%	27%
Concentration factor at VRF 17		1.2	15.5	5.1	3.9	1.5	1.2	2.6	6.9	4.6
Pre-oxidized feed	3.2	478	269	2548	579	6	2	595	2060	121
UC030 III PCD permeate	3.2	460	11	1990	500	5		407	1084	78
UC030 III PCD concentrate	3.2	481	3226	10,084	1888	18	2	1228	12,470	441
Yield at VRF 17, %		6%	72%	24%	20%	19%	6%	12%	36%	22%
Concentration factor at VRF 17		1.0	12.0	4.0	3.3	3.2	1.1	2.1	6.1	3.7

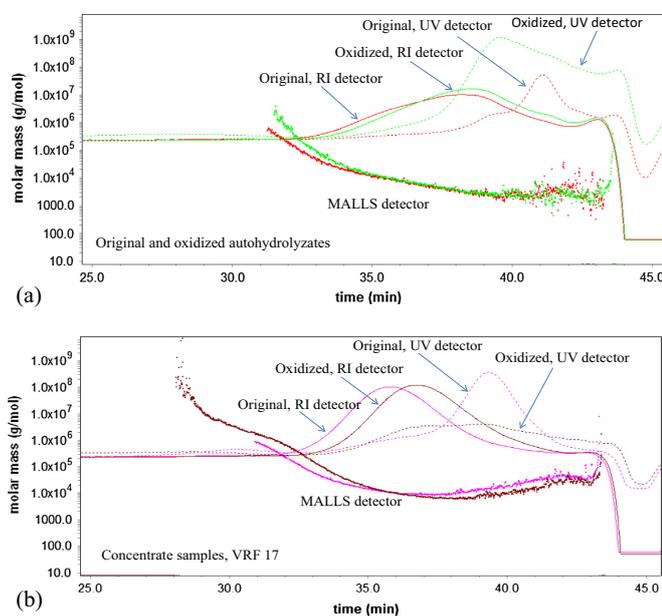


Fig. 6. SEC chromatograms (MALLS, UV and RI detectors) of (a) the original and oxidized wood autohydrolyzates and (b) their concentrates of 30 kDa membrane (number average molar mass).

concentrated fraction produced without pre-oxidation. For example, at VRF = 17 the lignin concentrations were 2.4 and 1.9 g/L in untreated and oxidized autohydrolyzates respectively. However, purity of GGM in the concentrated fractions was only slightly improved due to the pre-oxidation used. The reason for this were the minor changes the oxidation caused in the hemicellulose structures leading to a decrease in GGM retention. As Table 4 shows, the concentration of hemicelluloses (hexoses) increased 6-fold and lignin about 3-fold when a VRF of 17 was achieved. The ultrafiltration with the 30 kDa membrane (VRF 17) only slightly reduced the lignin proportion of the total carbon from 16%, in the original feed, to 11% in the final concentrate when the non-oxidized autohydrolyzate was treated. The results were rather similar to the pre-oxidized autohydrolyzate.

As already mentioned, oxidation caused a decrease in the average molecular mass of hemicelluloses and decreased the high molecular mass hemicellulose yield achieved in the ultrafiltration. For instance, the calculated weight average molar masses of hemicelluloses (RI detector in Fig. 6) were 7000 and 6300 g/mol for the original and pre-oxidized autohydrolyzates, and after the concentration to the VRF-value of 17 19,700 g/mol and 14,800 g/mol, respectively. The yield of hexose sugars in the UF was 42% and 36% with the original and pre-oxidized autohydrolyzates, respectively. UF naturally decreased the concentrate polydispersity by concentrating high molar mass compounds and permeating low molar mass compounds. The polydispersity (2.0) of the original autohydrolyzate decreased to about 1.6 in the UF concentrate. The oxidation also probably had minor effect on the polydispersity of polymeric compounds, although further experiments are needed to confirm the effect.

The oxidation significantly reduced the turbidity of the autohydrolyzate and almost completely removed the lipophilic wood extractives (Figs. 4 and 5 and Table 4). Turbidity was well retained by UF membrane (concentration factor 15 in Table 4) and, therefore, its removal by oxidation before UF significantly improved the concentrate purity.

Lignans, which are hydrophilic, low molecular mass compounds, were efficiently degraded in the oxidation. Moreover, their retention in the ultrafiltration was negligible. Thus, their degradation did not improve the purity of the produced hemicellulose fraction. The oxidation treatment also led to the formation of minor amounts of organic acids thus causing some loss of carbohydrates. The organic acids have low molar masses, and they permeate 30 and 10 kDa membranes completely. Therefore, they will not be accumulated in the membrane concentrate, and the diafiltration of concentrates can be applied if further purification is needed.

4. Conclusion

This study focused on the examination of the possibility of enhancing ultrafiltration efficiency in the recovery of GGM from spruce autohydrolyzate by applying a pre-oxidation step implemented with a pulsed corona discharge (PCD)-method. Moreover, the possibility to improve the purity of the produced high molecular mass GGM fraction with the PCD pre-oxidation was evaluated.

It was shown that although the mild oxidation used in the study was not seen to mineralize the organic compounds, oxidation still significantly improved the filtration capacity of the wood autohydrolyzate. This occurred despite the fouling of the hydrophilic cellulose membranes being very low, even without the pre-oxidation. The improvement of the capacity was partly due to the reduced viscosity of the oxidized wood autohydrolyzate. The PCD oxidation treatment removed the majority of wood lipophilic extractives and lignans from the wood autohydrolyzate, and low molar mass organic acids, mainly formic acid, were formed. The oxidation did

not significantly degrade the lignin but did modify the lignin structure. Applying pre-oxidation led to a slightly lower lignin content in the produced UF concentrate, and the oxidation also resulted in some decrease in the hemicellulose molar mass and lower retention. Approximately a 10% hemicellulose loss was also measured as occurring in the pre-oxidation step. Therefore, it can be concluded that the oxidation prior to the UF significantly improved the filtration capacity, but its effect on the hemicellulose–lignin ratio was small.

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