

Liisa Puro

**IDENTIFICATION OF EXTRACTIVES AND
POLYSACCHARIDES AS FOULANTS IN
MEBRANE FILTRATION OF PULP AND PAPER
MILL EFFLUENTS**

Thesis for the degree of Doctor of Science (Technology) to be presented with due permission for public examination and criticism in the Auditorium 1382 at Lappeenranta University of Technology, Lappeenranta, Finland on the 18th of December, 2011, at noon.

Acta Universitatis
Lappeenrantaensis 466

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ISBN 978-952-265-198-3
ISBN 978-952-265-199-0 (PDF)
ISSN 1456-4491

Lappeenrannan teknillinen yliopisto
Digipaino 2011

ABSTRACT

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Identification of extractives and polysaccharides as foulants in membrane filtration of pulp and paper mill effluents

Lappeenranta 2011

106 p.

Acta Universitatis Lappeenrantaensis 466

Diss. Lappeenranta University of Technology

ISBN ISBN 978-952-265-198-3, ISBN 978-952-265-199-0 (PDF), ISSN 1456-4491

The search for new renewable materials has intensified in recent years. Pulp and paper mill process streams contain a number of potential compounds which could be used in biofuel production and as raw materials in the chemical, food and pharmaceutical industries. Prior to utilization, these compounds require separation from other compounds present in the process stream. One feasible separation technique is membrane filtration but to some extent, fouling still limits its implementation in pulp and paper mill applications. To mitigate fouling and its effects, foulants and their fouling mechanisms need to be well understood. This thesis evaluates fouling in filtration of pulp and paper mill process streams by means of polysaccharide model substance filtrations and by development of a procedure to analyze and identify potential foulants, i.e. wood extractives and carbohydrates, from fouled membranes.

The model solution filtration results demonstrate that each polysaccharide has its own fouling mechanism, which also depends on the membrane characteristics. Polysaccharides may foul the membranes by adsorption and/or by gel/cake layer formation on the membrane surface. Moreover, the polysaccharides interact, which makes fouling evaluation of certain compound groups very challenging.

Novel methods to identify wood extractive and polysaccharide foulants are developed in this thesis. The results show that it is possible to extract and identify wood extractives from membranes fouled in filtration of pulp and paper millstreams. The most effective solvent was found to be acetone:water (9:1 v/v) because it extracted both lipophilic extractives and lignans at high amounts from the fouled membranes and it was also non-destructive for the membrane materials. One hour of extraction was enough to extract wood extractives at high amounts for membrane samples with an area of 0.008 m². If only qualitative knowledge of wood extractives is needed a simplified extraction procedure can be used.

Adsorption was the main fouling mechanism in extractives-induced fouling and dissolved fatty and resin acids were mostly the reason for the fouling; colloidal fouling was negligible. Both process water and membrane characteristics affected extractives-induced fouling. In general, the more hydrophilic regenerated cellulose (RC) membrane fouled less than the more hydrophobic polyethersulfone (PES) and polyamide (PA) membranes independent of the process water used.

Monosaccharide and uronic acid units could also be identified from the fouled synthetic polymeric membranes. It was impossible to analyze all monosaccharide units from the RC membrane because the analysis result obtained contained degraded membrane material. One of the fouling mechanisms of carbohydrates was adsorption. Carbohydrates were not potential adsorptive foulants to the same extent as wood extractives because their amount in the fouled membranes was found to be significantly lower than the amount of wood extractives.

Keywords: membrane fouling, wood extractives, hemicelluloses, identification of foulants
UDC 66.081.63 : 676.04

ACKNOWLEDGEMENTS

This study has been carried out at Lappeenranta University of Technology in the Laboratory of Membrane Technology and Technical Polymer Chemistry.

I am indebted to my supervisors Professor Mika Mänttari and Emerita professor Marianne Nyström for their advices, help and encouragement during this work. I am also grateful to Docent D.Sc. (Tech.) Jutta Nuortila-Jokinen who introduced membrane technology to me and Professor Heli Sirén who opened the analytical world for me. The many fruitful discussions I had with all of them are greatly acknowledged.

I thank the reviewers, Professor Anja Drews and Professor Ann-Sofi Jönsson, for their valuable comments and corrections, which significantly helped me to improve the thesis. In addition, I want to thank B.Sc. Peter Jones for revising the language of the thesis.

I express my warm gratitude to all the people who have worked with me during this study. Especially I would like to thank D.Sc. (Tech.) Jukka Tanninen, Mr. Toni Väkiparta and M. Sc Elsi Koivula, for collaboration and worthy discussions. I am also greatly thankful to M.Sc. Eero Kaipainen, who helped me with my practical problems and Mrs. Helvi Turkia for collaboration and invaluable help with analysis.

I owe my warmest gratitude to my friends D.Sc. (Tech.) Mari Kallioinen and M.Sc. Elina Seppälä, whose support and encouragement have been enormous and precious during this work. Mari always told me that 'thesis never goes backwards'. Without her this thesis would never been finished. Elina, my personal trainer, has challenged me to reach new goals. They both have affected my life in many ways and they both have always been there for me during this long and rocky road. Our long and fruitful discussions have given me a lot of strength and faith during this work and have made many of my days. In addition, I am grateful to my friends outside the university for their support.

The Academy of Finland, Gust. Komppa Foundation, The Finnish Foundation for Economic and Technology Sciences, Lahja and Lauri Hotinen Fund and the Research Foundation of Lappeenranta University of Technology are acknowledged for funding and financial support. In addition, UPM Kymmene Kaukas Mills is acknowledged with warm thanks for their co-operation.

I express my deepest gratitude to my parents Terttu and Timo and my sister Helena for their encouragement and understanding throughout this study. Finally, I thank with all my heart my family; my Diamond Panu who is the bedrock of my life and my three wonderful children, Oskari, Viljami and Amanda who has given me a life beside this work. I am grateful for their support both in good and bad times throughout this work.

'Everything happens for a reason...'

Lemi, November, 2011

Liisa Puro

LIST OF PUBLICATIONS

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

- I** Mänttari M., Puro L., Nuortila-Jokinen J., Nyström M., Fouling effects of polysaccharides and humic acid in nanofiltration, *J. Membr. Sci.*, 165(2000), 1-17.
- II** Puro L., Tanninen J., Nyström M., Analyses of organic foulants in membranes fouled by pulp and paper mill effluents using solid-liquid extraction, *Desalination*, 143:1(2002), 1-9.
- III** Puro L., Kallioinen M., Mänttari M., Natarajan G., Cameron D. C., Nyström M., Performance of RC and PES ultrafiltration membranes in filtration of pulp mill process waters, *Desalination*, 264(2010) 249-255.
- IV** Puro L., Kallioinen M., Mänttari M., Nyström M., Evaluation of behavior and fouling potential of wood extractives in ultrafiltration of pulp and paper mill process water, *J. Membr. Sci.*, 368(2011) 150-158.

Contribution of the author

The author was responsible for the preparation of papers **II**, **III** and **IV**. The author performed most of the measurements in papers **I** and **II**. In papers **III** and **IV**, the author planned the experiments with co-writer Mari Kallioinen. The author interpreted the results in papers **III** and **IV** and performed part of the extractives analysis in paper **IV**. Mari Kallioinen was responsible for the sieving curve measurements in paper **III**. 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

c_f	concentration in feed	kg m^{-3}
c_p	concentration in permeate	kg m^{-3}
CF	calibration factor	-
CP	concentration polarization and reversible fouling	%
F	irreversible fouling	%
FR	flux reduction	%
J	model solution or process water flux	$\text{kg m}^{-2}\text{h}^{-1}$
J_{PWFa}	pure water flux after filtration	$\text{kg m}^{-2}\text{h}^{-1}$
J_{PWfb}	pure water flux before filtration	$\text{kg m}^{-2}\text{h}^{-1}$
J_{rel}	relative flux	-
$PWFR$	pure water flux reduction	%
R_{obs}	observed retention	-

Abbreviations

AcGGMs	O-acetyl-galactoglucomannans
AFM	Atomic Force Microscopy
ATR	Attenuated Total Reflection
BSTFA	bis-(trimethylsilyl)-trifluoroacetamide
CA	cellulose acetate
CF	calibration factor
Cl-DHA	chlorodehydroabiatic acid
CLSM	Confocal Laser Scanning Microscope
COD	chemical oxygen demand
CP	concentration polarization
CR	cross rotation
CTA	cellulose triacetate
CTMP	chemithermomechanical pulping
DHA	dehydroabiatic acid
DOC	dissolved organic carbon
EDS	Energy Dispersive X-ray Spectroscopy

FAs	fatty acids
FID	Flame Ionization Detector
FR	flux reduction.
FRAs	fatty and resin acids
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
GWM	groundwood mill
IC	inorganic carbon
LUT	Lappeenranta University of Technology
MF	microfiltration
MTBE	tert-butyl methyl ether
NA	not analyzed
NF	nanofiltration
NTU	nephelometric turbidity unit
PA	polyamide
PAI	polyamide-imide
PAN	polyacrylonitrile
PAR	polyaramide
PEG	polyethylene glycol
PEI	polyether-imide
PES	polyethersulfone
PGW	pressure ground wood
PS	polysulfone
PVDF	polyvinylidene fluoride
RAs	resin acids
PSFP	plug screw feeder pressate
RC	regenerated cellulose
RO	reverse osmosis
SCMP	semi-chemical mechanical pulp
SDA	simultaneous diffusion adsorption
SEM	Scanning Electron Microscope
SGW	stone ground wood
TC	total carbon

TFC	thin film composite
TMCS	trimethylchlorosilane
TMP	thermomechanical pulp
TOC	total organic carbon
ToF-SIMS	Time-of-Flight Secondary Ion Mass Spectrometry
UF	ultrafiltration

1 INTRODUCTION

Many parts of the world are experiencing a shortage of clean water and energy constraints, a situation that is likely to be exacerbated by population growth and changes in climate patterns. Membrane filtration is a separation technique which can be used for many purposes, for instance, in drinking-water production, cleaning of waste water fractions, and the production of raw materials for energy production. New renewable materials for energy production are nowadays the subject of intensive research and pulp and paper mill process streams, for example, contain compounds which could potentially be used in biofuel production. However, these compounds have to be separated from other compounds in the process streams before they can be utilized. One possible technique for such separation is membrane filtration.

Pulp and paper mill process streams are complex mixtures of different compounds originating from wood and chemical-additives used in the production process. In mechanical pulping, different kinds of dissolved and colloidal substances are transferred into the process streams. These substances are mainly lipophilic extractives, hemicelluloses and lignin-like substances [1-3]. Some of these compounds are substances which interfere in the process and, therefore, they limit reuse of the process streams, while others are value-adding chemicals, such as lignins and hemicelluloses.

The value-adding chemicals are valuable for many applications. Lignin can be used as a component in polymer composites [4, 5] and is a raw material for biofuels [6-8], carbon fibers [9], adhesives [10-12], binders [5] and surfactants [13, 14]. Hemicelluloses can be used as raw materials in the food, pharmaceutical and chemical industry, as well as in biofuel production. Monosaccharides can be used, for example, for ethanol production [15], while oligomeric hemicelluloses can be used in the food industry as functional-food ingredients [16, 17] and emulsion stabilizers for beverages [17]. Polymeric hemicelluloses can be used as hydrogels [18, 19] or barrier films in food packaging [20, 21]. Before utilization, lignin and hemicelluloses are separated from the process streams for instance by ultrafiltration (UF) [22]. However, to some extent, fouling still limits the adoption of UF in pulp and paper mill applications.

In the context of the pulp and paper industry, evaluation of membrane fouling resulting from by a specific compound is challenging due to the complexity of the process streams. Surface characterization methods such as Fourier transform infrared (FTIR), Raman and scanning electron microscope energy dispersive X-ray spectroscopy (SEM-EDS) give only information about major or representative functional groups of the foulants. Microscopical methods such as scanning electron microscopy and confocal laser scanning microscopy (CLSM) give additional information about the fouling layer and may also distinguish between surface fouling and pore fouling. However, these methods alone may not be entirely appropriate for identification of foulants in filtration of a complex solution; they give only hints of possible foulants, their ability to provide a definitive identification of foulants is limited.

It is generally assumed that colloidal substances, in particular, are potential foulants in filtration of pulp and paper mill streams [23-25] but only few studies have identified them as foulants. Thus, more information on colloidal fouling is needed to understand fouling in pulp and paper mill applications and to permit procedures to be adopted which will keep membrane capacity at a desired level for as long as possible.

2 AIM AND OUTLINE OF THE STUDY

The aim of this work is to characterize and identify fouling in membrane filtration of pulp and paper mill process streams. These streams are complex mixtures of different compounds originating from wood and chemical-additives, thus evaluation of the role of a specific compound in fouling is challenging. In the work, certain compounds, such as hemicelluloses and wood extractives, are assumed to be foulants in these streams.

The thesis is divided into a literature part and an experimental part. The literature part starts with a short introduction to fouling in membrane filtration. Fouling in filtration of pulp and paper mill effluents is then reviewed and its characterization discussed. The focus of the evaluation lies on the fouling behavior of wood extractives and carbohydrates and on their characterization as foulants.

The experimental part concentrates on studying fouling of carbohydrates and wood extractives. Carbohydrate fouling is studied using polysaccharide model solution filtrations. The influence of model substance concentration, pH and crossflow velocity on carbohydrate fouling is studied with two different nanofiltration (NF) membranes. Extractives-induced and carbohydrates fouling is studied by extracting these foulants from the membranes and analyzing them with gas chromatography (GC). The wood extractive and carbohydrate content and composition are studied from both hydrophilic and hydrophobic membranes. The overall aim of these experiments is to develop a procedure to identify wood extractives and carbohydrates as foulants and to enhance understanding of this form of fouling in the filtration of pulp and paper mill streams.

LITERATURE PART

3 REVERSIBLE AND IRREVERSIBLE FLUX DECLINE

Filtration capacity, i.e. flux, is an important factor in membrane applications. Flux should be as high as possible to maintain economically optimal processes. The lower the flux, the higher are the investment costs because a larger membrane area is needed. On the other hand, if membranes are fouled significantly in the process, the flux will decrease and the membranes require greater cleaning, which increases operational costs. Generally, there is always a flux reduction in membrane applications. Flux decline can be irreversible or reversible. Concentration polarization (CP), osmotic pressure and/or cake/gel layer formation on the membrane surface decrease the flux temporarily and thus, they are causes of a reversible flux decline. Fouling, on the other hand, causes an irreversible flux decline. Adsorption and pore blocking are fouling mechanisms which decrease the flux permanently, although cake/gel layer formation may also result in irreversible flux decline. It should be noted that concentration polarization and cake/gel layer formation may enhance membrane fouling.

3.1 Reversible flux decline

The hydrodynamics of a membrane module, flux, solute concentration and the molar mass of the solute compounds all affect concentration polarization and gel/cake layer formation. These layer formations are minimized if the mass transfer at the membrane

surface is maximized. Mass transfer can be increased by increasing the shear rate and the turbulence on the membrane surface. Compounds with larger molar mass have a greater influence on the formation of CP because they have a smaller mass transfer coefficient than compounds with smaller molar mass [26]. Furthermore, if high molar mass compounds have a high retention they may foul membranes more severely due to accumulation on the membrane surface [27, 28].

3.2 Irreversible flux decline - fouling

Fouling is the reason for irreversible flux decline, but membrane compaction may be a cause of irreversible flux decline also. Fouling is a major problem in membrane applications because it shortens membrane lifetime and thus increases costs. Fouling in this study is defined as pure water flux reduction after rinsing of the membrane with water. Thus, the fouling can be adsorption, pore blocking, and/or cake/gel layer type fouling. Three major factors contribute to membrane fouling: the properties of the membrane material, the characteristics of the feed solution, and the operating parameters. In order to understand fouling well, the membrane-solute and solute-solute interactions have to be fully understood. Membrane-solute interactions play a key role in adsorptive fouling, while solute-solute interactions affect pore blocking, cake/gel layer formation and multilayer adsorption. Moreover, adsorptive fouling can enhance other fouling mechanisms. A schematic diagram of the various fouling mechanisms is presented in Fig. 3.1.

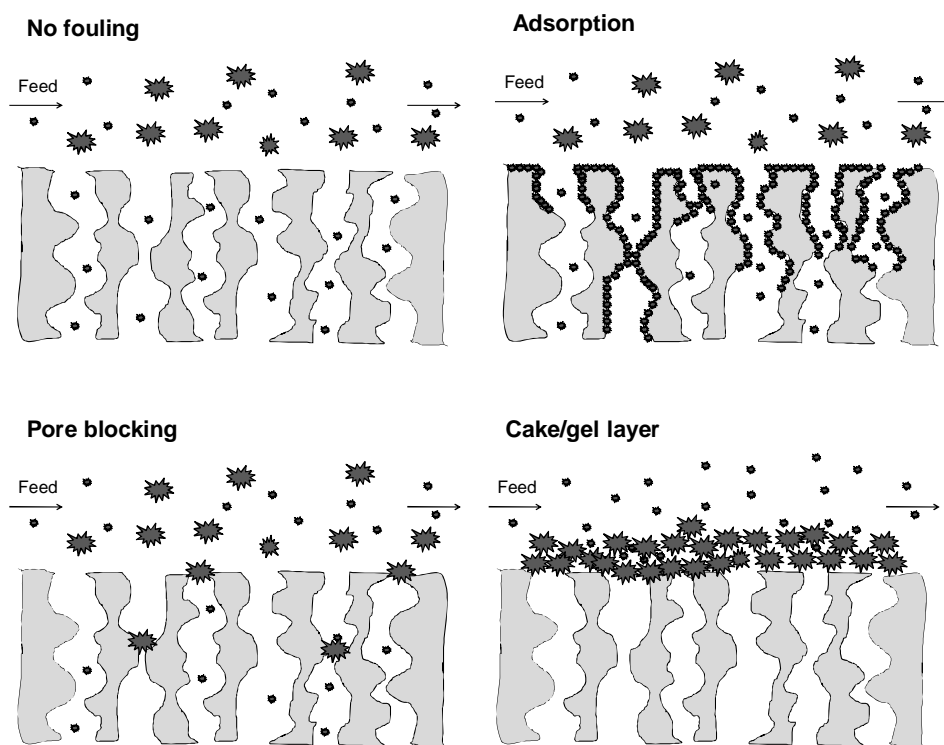


Fig. 3.1 Schematic diagram of fouling mechanisms in membrane filtration adapted from Eykamp [29] and Belfort [30].

4 COMPOUNDS IN PROCESS STREAMS OF PULP AND PAPER MILLS

Pulp and paper mill process streams are rather complex mixtures. Their chemical oxygen demand (COD), total organic carbon (TOC) amount and the amount of fatty and resin acids vary significantly depending on the origin of the streams. Based on the reviewed studies, COD can be in the range 740-6100 mg L⁻¹ [24, 28, 31-38], TOC 770-5700 mg L⁻¹ [38-41] and the amount of fatty and resin acids can be, 3-430 mg L⁻¹ [24, 31, 32, 39, 40, 42]. Pulp and paper mill streams also contain substances from a wide molar mass range. For example, plug screw feeder pressate (PSFP) from semi-chemical mechanical pulping was found to contain compounds in a molar mass range <0.1-4000 kg mol⁻¹ and their particle size was 0.1 to 20-60 μm [25].

Process streams contain added chemicals and compounds originating from wood. The process stream composition varies depending on the wood species, process and chemical

additives used. For instance, in mechanical pulping, about 2-5% of the wood material is transferred into the process streams [43]. The compounds originating from the wood are dissolved and colloidal substances. In mechanical pulping, the main dissolved and colloidal substances released from the wood are polysaccharides, wood resin, lignin material and lignans [3, 44]. A greater amount of dissolved and colloidal substances are transferred to the process water at high process temperature (105°C) and at high pH (pH 10.5-11) [45]. The work of Holmbom and Sundberg [46] found that the dominant compound group in dissolved and colloidal material of unbleached pulps is polysaccharides, i.e. dissolved hemicelluloses and pectins. After bleaching of Norway spruce TMP the composition of the process water changed; the amount of lignin and acetic acid increased, while the amount of hemicelluloses and pectins decreased. The amount of wood extractives was unchanged [46].

The amount of dissolved and colloidal substances depends on the process stream and the filter pore size used in the fractionation (Table 4.1). Thornton et al. [3, 44] used 0.1 µm filter media in characterization of the colloidal and dissolved fraction. They found that most of the wood extractives, over 95%, were in the colloidal fraction, while the hemicelluloses permeated through the filter, indicating that they were in dissolved form in unbleached Norway spruce TMP process stream [3, 44]. Rundlöf et al. [47], when they fractionated an unbleached Norway spruce TMP water sample using a membrane which had a cut-off value of 300 kg mol⁻¹, recorded similar results with wood extractives but found contrasting results with hemicelluloses. In their study, only about 5% of the wood extractives and 10% of the hemicelluloses were in dissolved form in the water. These dissolved hemicelluloses were mainly low-galactose content galactoglucomannans and most were in colloidal form in the TMP water [47]. In another study, Dunham et al. [41] filtered TMP model water through a 0.1 µm filter and reported that 87% of the TOC was in the dissolved fraction and 13% in the colloidal fraction. Similar results were obtained by Zhang [42], who fractionated white water of mixed softwood with a 0.22 µm membrane filter and found that the majority of the compounds had a size of 0.25-1 µm and only a few particles had sizes smaller than 0.22 µm. The most abundant compound group in the white water was carbohydrates and almost all of them were in the dissolved fraction. The colloidal fraction contained mostly lignin, but also smaller amounts of fatty and resin acids, steryl esters, triglycerides and galacturonic acids were detected. Over half of the

fatty and resin acids, lignin and galacturonic acids present in the process water were in the colloidal fraction, while most of the hydrophilic wood extractives (lignans and sterols) were in the dissolved fraction. The neutral carbohydrate fraction in the colloidal fraction was very small [42].

Based on the information presented in Table 4.1, it can be seen that the amount of wood extractives and carbohydrates in colloidal and dissolved fractions depends greatly on the filter pore size and/or the membrane material used in the fractionation. Fouling above the filter medium is totally neglected in all the fractionations given in Table 4.1. However, wood extractives may adsorb on the membrane, which means that they can change the pore size of the filter medium, which in turn may influence the fractionation results.

Table 4.1 Amount of colloidal and dissolved substances in different pulp and paper mill effluents.

Effluent	Filter material/ pore size	Colloidal	Dissolved	Reference
Unbleached Norway spruce TMP water	Aluminum oxide/ 0.1 μm	Extractives >95% Carbohydrates 20%	Extractives <5% Carbohydrates 80%	Thornton et al. [3, 44]
Unbleached Norway spruce TMP water	Not given/ 300 kg mol^{-1}	Extractives >80%* Polysaccharides ~85%	Extractives 5%* Polysaccharides 11%	Rundlöf et al. [47]
Bleached TMP model water	Polysulfone/ 0.1 μm	TOC 13%	TOC 87%	Dunham et al. [41]
White water of mixed softwood	Mixed cellulose esters/0.22 μm	Extractives 10% Neutral sugars 1%	Extractives 90% Neutral sugars 99%	Zhang [42]

* Amount of extractives is less than 100% because there was material lost in filtration.

4.1 Wood extractives

Wood extractives are hydrophobic, i.e. lipophilic, components in wood which can be extracted with neutral solvents [48]. These water-insoluble lipophilic extractives are generally called wood resin. Usually, dry wood contains less than 10% resin by weight

[48]. The amount of wood resin in the water phase of pulp suspensions depends on many factors, including pulp consistency and pH. At alkaline pH, fatty and resin acids can be dissolved as soaps and they are transferred into the process streams to a greater extent than neutral components. As much as 75% of the wood resin can be transferred into the process streams at different stages in pulp and paper production [49]. Wood resin is mostly present in colloidal form in pulp and paper mill process streams [47, 50]. Thus, they could be problematic in membrane filtration because colloidal particles [23, 24] and/or fatty and resin acid micelles [25] are claimed to be potential foulants for membranes in pulp and paper mill applications.

In this work, the analytical method used defines wood extractives as lignans and lipophilic extractives [51]. Lipophilic extractives are further divided into five different groups: fatty acids, resin acids, sterols, steryl esters, and triglycerides. Most of the lipophilic extractives in process streams are in the form of colloidal resin particles [47, 50]. In research by Rundlöf et al. [47] about 5% of the wood extractives in TMP process streams were in dissolved form, and these wood extractives were lignans, sterols and fatty and resin acids. Colloidal resin particles are composed mainly of steryl esters and triglycerides, which are the most hydrophobic components of the wood extractives [46]. They form the hydrophobic core, while smaller amounts of free fatty and resin acids and sterols form the thin surface layer of the particle [46, 52]. The carboxyl groups of fatty and resin acids are orientated toward the aqueous phase [50, 52], which enables hydrogen bond formation at the droplet surfaces. The particles are negatively charged in the studied pH range 2-11 [50].

Colloidal resin particles are stabilized both electrostatically and sterically [50]. Carboxyl and hydroxyl groups of fatty and resin acids and sterols on the surface of colloidal resin particles stabilize colloidal resin particles electrostatically [52], while hemicelluloses and other undefined water soluble compounds originating from wood in the process water stabilize the colloidal resin particles sterically [53]. Especially acidic hemicelluloses, such as glucomannans, contribute to the stability and charge of lipophilic extractives particles [46, 54-56]. These hemicelluloses are water soluble and loosely bound to the lipophilic extractives [55]. This sterical stabilization prevents the aggregation of colloidal resin particles with salts such as NaCl or CaCl₂ at acidic and neutral pH. However, in alkaline

conditions, fatty and resin acids are present as salts; that is, if there are calcium ions present in the process water, the fatty and resin acids are present as calcium salts. Salt neutralizes the charged colloidal particles, which destroys the electrostatic stabilization and the colloidal resin particles are more prone to aggregate and deposit [57]. A schematic diagram of a colloidal particle is presented in Fig. 4.1.

The particle size distribution of the colloidal resin in different pulp qualities; Kraft, sulphite and groundwood pulp, is similar, according to Allen [50]. Most of the colloidal resin particles have diameters in the range 0.1-2 μm [46, 47, 50] and only occasionally are the resin particles larger than 2 μm [50]. The average size of colloidal resin particles is about 0.6 μm [46, 50]. In process streams, these particles are spherical in shape [50].

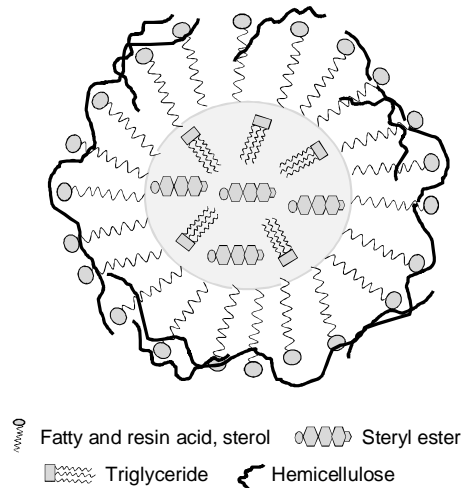


Fig. 4.1 Schematic diagram of a colloidal wood resin particle which is sterically stabilized by dissolved hemicelluloses.

The resin acids have, at 20°C, colloidal pK_a values between 6 and 7. At 50°C, the values are lower, around 6, according to research by McLean et al. [58]. Consequently, at around pH 6, the resin acids gradually dissolve into the water from the colloidal resin particles; the higher the pH, the less resin acids present in the colloidal resin particles. Furthermore, fatty acids have higher colloidal pK_a values than resin acids [58] and, therefore, they dissolve from the colloidal particles at higher pH.

The amount of wood extractives in the process streams varies depending on, for example, the wood species, the age of the wood raw material [59], the harvest time, and the length

and type of storage. In process streams of Norway spruce TMP, the major components of lipophilic extractives are triglycerides, steryl esters and resin acids [60]. The dominant fatty acids are oleic, linoleic and pinolenic acids [1]. The dominant resin acid is dehydroabietic acid although pimaric, isopimaric, sandaracopimaric, abietic, neoabietic, levopimaric and palustric acids are also found [61]. A typical compound from each wood extractive group is shown in Fig. 4.2.

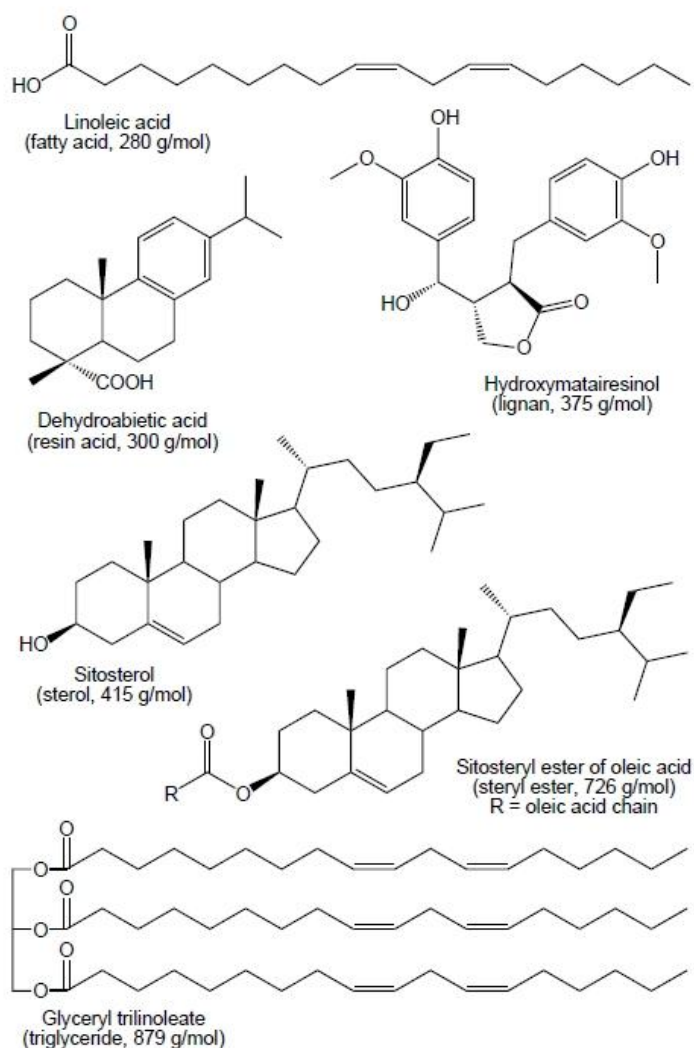


Fig. 4.2 Structures of typical compounds from each wood extractive group.

4.1.1 Retention of wood extractives in membrane filtration

In UF the retention of wood extractives is usually high, even though the molar masses of the wood extractives are rather small (less than 1000 g mol^{-1} , Fig 4.2). Retention of wood extractives in different filtrations is presented in Table 4.2. Dal-Cin et al. [25] found that in filtration of plug screw feed pressate (PSFP) from a semi-chemical mechanical pulp (SCMP) mill, with a membrane which had a cut-off value of 100 kg mol^{-1} , the retention of fatty and resin acids was 70-90%. Zaidi et al. [62] filtered different model substances such as dehydroabietic and chlorodehydroabietic acids, which are resin acids. The thirteen membranes used in the study had cut-off values in the range $1\text{-}30 \text{ kg mol}^{-1}$. Even though the model substances had lower molar masses than the cut-off values of the membranes, the retentions were 40-90%. Moreover, it was noticed that the retention of the model substances was generally lower for the more hydrophilic membranes. The lower retention of hydrophilic membranes could be because wood extractives foul hydrophilic membranes less, as hypothesized in this thesis (II, IV). Lipophilic extractives adsorb favorably on hydrophobic membranes compared to hydrophilic membranes [63] and this adsorption may decrease the pore size of the membrane, which may increase their retention.

In research by Elefsiniotis et al. [39] of polyethersulfone (PES) membranes having cut-off values of 10 and 100 kg mol^{-1} in UF of a model white water, the retention of fatty acids was over 90% while the resin acid retention was 25-45%. In their research, the pH was 6.9-7.6, and thus, the reason for the lower retention of resin acids could be that at this pH range the resin acids were more dissolved than the fatty acids due to their lower colloidal pK_a values [58]. Elefsiniotis et al. [39] also noticed that different resin acids behaved differently: retention of isopimaric and abietic acid was high (over 50%) while retention of dehydroabietic acid was low (about 10%). Furthermore, their study revealed that in the temperature range $20\text{-}60^\circ\text{C}$, the retention of fatty and resin acids varied with filtration temperature [39]. Table 4.2 shows that the different pH and temperatures were used in the filtrations and thus, these factors cannot explain the high retentions of lipophilic extractives. It seems that their colloidal character/nature may be the reason for their high retention and/or adsorption on the membrane material.

Table 4.2 Retention of wood extractives in different studies.

Retention,	Membrane material	Cut-off, kg mol ⁻¹	Solution	pH, -	Temperature, °C	Reference
70-90% extractives	PS	> 100	PSFP effluent FRAs 432 mg L ⁻¹	5.7	50	Dal-Cin et al. [25]
40-90% DHA	PS, cellulosic, modified PES	1-30	Water with 200 mg L ⁻¹ DHA Molar mass of DHA is 298 g mol ⁻¹	NA	25	Zaidi et al. [62]
60-80% Cl-DHA			Water with 200 mg L ⁻¹ Cl-DHA Molar mass of Cl-DHA is 333 g mol ⁻¹			
90% (FAs) 40% (RAs) 95% (FAs) 30% (RAs)	PES PES	10 100	Simulated white water with 28 mg L ⁻¹ FRAs	6.9- 7.6	20, 30, 40, 50 and 60	Elefsiniotis et al. [39]

DHA dehydroabietic acid

Cl-DHA chlorodehydroabietic acid

FAs fatty acids

RAs resin acids

FRAs fatty and resin acids

NA not analyzed

PS polysulfone, PES polyethersulfone

4.2 Wood polysaccharides

Wood and wood pulps consist mostly of polysaccharides: cellulose, hemicelluloses and pectins. Cellulose is a homopolysaccharide, while hemicelluloses are heteropolysaccharides. The polysaccharide content of wood is 60-80% for different softwood species, i.e. spruce and pine [64]. Wood contains approximately 40-45% cellulose and it is the dominant polysaccharide. The amount of hemicelluloses in wood is about 20-30% [48].

The amount and composition of dissolved carbohydrates in process streams depend on the treatment of the wood. The thermomechanical pulping (TMP) process dissolves more polysaccharides than the steamed groundwood process [42, 65]. In process stream from

unbleached Norway spruce, the dominant compound group in dissolved and colloidal materials was polysaccharide, mostly dissolved hemicelluloses and pectins [3, 46, 54, 60].

4.2.1 Softwood hemicelluloses in TMP process streams

O-acetyl-galactoglucomannans (AcGGMs) are the most abundant non-cellulosic polysaccharides in Norway spruce wood and softwood in general [3, 48, 66]. Softwood consists of about 10-20 % AcGGMs [48, 65, 67] and they are the major non-cellulosic polysaccharides dissolved from Norway spruce in mechanical pulping [3, 47, 60, 66], although small amounts of arabinogalactans, arabinoglucuronoxylans and pectins (galacturonic acids) are also dissolved [3, 60]. Hemicelluloses are mostly present as polymers or oligomers in the process waters of softwood [65, 68].

Hemicelluloses in unbleached TMP suspensions are mainly neutral wood polymers [3]. In research by Thornton et al. [3] the neutral polysaccharides (mostly AcGGMs) formed 88% of the polysaccharides and the anionic polysaccharides 12% (mostly arabinogalactans). In research by Mustaranta et al. [60] AcGGMs accounted for 80% of the hemicelluloses in TMP model water.

Under alkaline conditions, such as during peroxide bleaching, the dissolved AcGGMs are deacetylated and thus their solubility is decreased. In addition, they are adsorbed on TMP fibers. Consequently, there is a decrease in their amount in the process water [3, 45]. The reduction in solubility leads to the formation of aggregates [64]. The deacetylation of hemicelluloses releases acetic acid into the process streams [44]. Most of the dissolved organic carbon in the process streams after peroxide bleaching is therefore acetic acid. Furthermore, the amount of anionic polysaccharides in the bleached TMP increases. After peroxide bleaching, about half of the dissolved polysaccharides are neutral and half of them are anionic. The amount of anionic polysaccharides increases due to the release of anionic polygalacturonic acids, arabinoxylans and galacturonans from the pulp [3, 45, 49, 66].

Anionic hemicelluloses, such as, xylans, arabinogalactans and pectic acids, have a significant influence on the cationic demand of the process water. The cationic demand of

dissolved and colloidal substances is increased in peroxide bleaching even threefold. The increase can be explained by the release of polygalacturonic acids from TMP fibers. In research by Thornton et al. [66] polygalacturonic acids contributed to 50% of the cationic demand even though their amount in the water fraction of bleached TMP was only 5%. Formic and acetic acid, which are formed during peroxide bleaching, contribute very little to the cationic demand [44].

AcGGMs dissolved in mechanical pulping contain mannose, glucose and galactose sugar units in an approximate ratio of 4.5:1:0.5 [46]. AcGGMs in the process streams are present as low-galactose and galactose-rich fractions [48]. The degree of polymerization is 130-400 for these hemicelluloses, depending on the source from which they are analyzed [46, 48, 65]. Thus, the average molar mass of dissolved hemicelluloses is about 20-65 kg mol⁻¹ [48, 65]. AcGGMs are water-soluble because of the acetyl group at every second or third monosaccharide unit [46].

4.2.2 Hardwood hemicelluloses

Based on the studies of Willför et al. [69] dry hardwood, e.g. aspen and birch, contains 30-50% cellulosic and 20-40% non-cellulosic polysaccharides. The dominant polysaccharide in hardwood is cellulose and the dominant non-cellulosic polysaccharide is partly acetylated acidic xylan, O-acetyl-(4-O-methylglucurono)xylan [48, 69, 70]. Hardwood contains 10-35% O-acetyl-(4-O-methylglucurono)xylan and its number-average degree of polymerization is 200 [70]. The second most abundant non-cellulosic polysaccharides are glucomannans or pectins, i.e. polygalacturonic acids, depending on the wood species [69]. Hardwoods contain only 3-5% of galactoglucomannan, whose glucose and mannose ratio is 1:1 or 1:2. [54, 70]. Hardwood polysaccharides contain 15-23% acidic sugar units. In a study by Willför et al. [69] the amount of water-soluble polysaccharides for different hardwood species was 2.8-45 mg g⁻¹ wood. According to Willför et al. [69] galactose, containing easily soluble galactans or arabinogalactans and mannans, formed the most water-soluble polysaccharides in hardwood species; xylans were the most water-soluble polysaccharides only for a few species.

4.2.3 Ultrafiltration of TMP and Masonite process streams

Filtration experiments by Persson et al. [22, 71-73] of hemicellulose separation from pulp and paper mill process streams are presented in Table 4.3. Different membranes were used, both hydrophilic and hydrophobic membranes, made of different materials and having cut-off values of 1-10 kg mol⁻¹. It was concluded that hemicellulose isolation from dilute pulp and paper mill process streams (hemicellulose concentration 0.5 g L⁻¹) is economically feasible if the hemicellulose concentration in the concentrate is 30 g L⁻¹ [22] but hemicelluloses can be concentrated to at least 60 g L⁻¹ [71]. In all of the studies by Persson et al. [22, 71-73] hydrophobic membranes suffered severe fouling irrespective of the composition of the process water filtered. Moreover, the best membranes, based on filtration capacity and separation efficiency, proved to be the composite fluoro polymer membrane ETNA10 and regenerated cellulose (RC) membranes.

In UF of masonite wastewater, Persson and Jönsson [71] changed the pH of the process water by adjusting it with sodium hydroxide and hydrochloric acid. Their study revealed that there was significant adsorption of organic foulants on the ETNA10 membrane but not on the hydrophilic RC membrane UC005. The flux of the hydrophilic RC membrane UC005 decreased as pH increased, while the flux of the hydrophobic membrane (ETNA10) was less affected by the pH change. In another study [22] they concluded that when the hemicellulose concentration increased, the flux decreased. In UF of disc clear filtrate process stream, the retention of the ETNA10 membrane increased as the concentration of the hemicelluloses and the pressure increased [73]. According to Persson et al. [73] the retention improvement was due to the formation of a gel layer on the membrane surface.

In the studies of Persson et al. [22, 71-73], in which RC membranes were not used, the ETNA10 membrane showed the best performance. When its performance was compared with the performance of RC membranes, the RC membranes proved to be better for the concentration of hemicelluloses from different process streams.

Table 4.3 Isolation of hemicelluloses in TMP process water and Masonite wastewater by Persson et al. [22, 71-73].

Membrane (Cut off, kg mol ⁻¹)	Filtered water (hemicellulose amount)	Result	Reference
ETNA01 ^a (1) ETNA10 ^a (10) NP030 ^b (1) UP005 ^b (5) UC005 ^c (5) PLCC ^c (5)	Masonite wastewater (1-2 g L ⁻¹)	Hydrophilic RC membranes UC005 and PLCC performed well, possible to concentrate hemicelluloses to at least 60 g L ⁻¹	Persson and Jönsson [71]
ETNA01PP ^d (1) ETNA10PP ^d (10)	TMP mill process water (0.5 g L ⁻¹)	ETNA10 performed better, hemicelluloses concentrated to 30 g L ⁻¹ , purity of 80%	Persson et al. [22]
ETNA01PP ^d (1) GR95PP ^b (2) N30F ^b (1) NF-PES-10 ^b (3) P005F ^b (5) C005F ^c (5)	TMP mill process water (2.3 g L ⁻¹)	RC membrane C005F performed best, hydrophobic membranes suffered severe fouling, membranes separated oligo- and polysaccharides differently, hemicellulose concentration not told	Persson et al. [72]
UFX5 ^f (5) ETNA01 ^d (1) ETNA10 ^d (10)	Disc clear filtrate process water from TMP mill (1-1.5 g L ⁻¹)	PES membrane UFX5 suffered significant fouling, retention of ETNA10 membrane increased as the concentration of hemicelluloses and pressure increased, hemicelluloses concentrated to 25 g L ⁻¹	Persson and Jönsson [73]

^aComposite fluoropolymer, hydrophobic

^bPolyethersulfone, hydrophobic

^cRegenerated cellulose, hydrophilic

^dSurface modified polyvinylidene fluoride, hydrophilized

^fHydrophilized polyethersulfone

5 FOULING IN MEMBRANE FILTRATION OF PULP AND PAPER MILL PROCESS STREAMS

Fouling in filtration of pulp and paper mill process streams is influenced by process conditions [35, 36, 74], and membrane [40, 63, 74, 75] and process water characteristics [37, 38, 76-78]. Different fouling mechanisms have been reported, such as adsorption [25, 40, 63], pore plugging [23, 25, 35], and gel/cake layer formation [23-25, 33, 79, 80] as reasons for flux decline in filtration of pulp and paper mill process streams.

Process conditions, such as, crossflow velocity has a little influence on small molecules (particle size less than 10 nm), but it influences especially on larger molecules (particle size more than 10 μm) and thus on colloidal fouling. The particles with size of 0.01-10 μm are the most susceptible for fouling because the Brownian diffusion and lateral and shear induced diffusion is the lowest for them. Thus, for complex mixtures, often only low fouling i.e. sustainable flux is achievable but not no-fouling situation [81]. This means that colloids such as, wood extractives, hemicelluloses and lignins are susceptible foulants in pulp and paper mill applications.

5.1 Influence of membrane hydrophilicity/hydrophobicity

Based on flux measurements, Dal-Cin et al. [40] concluded that hydrophilic cellulosic membranes showed little or no adsorptive fouling in filtration of plug screw feeder pressate (PSFP) effluent from a semi-chemical mechanical pulp mill, but hydrophobic membranes showed severe adsorptive fouling. The adsorptive fouling of the cellulosic membrane decreased as hydrophilicity increased (cellulose triacetate < cellulose acetate < cellulose). Similar results were obtained by Carlsson et al. [63] for hydrophobic polyvinylidene fluoride (PVDF) and polysulfone (PS) membranes and hydrophilic thin-film composite polyamide (PA) and RC membranes in UF of PSFP. The hydrophilic PA and RC membranes performed well during filtration, while the hydrophobic PVDF and PS membranes suffered from significant flux decline. Moreover, there was more fouling of the hydrophobic membranes than of the hydrophilic ones [63]. Huuhilo et al. [74] also noticed that hydrophobic PA and PES membranes fouled more in UF of groundwood mill (GWM) process effluent than a hydrophilic RC membrane. Maartens et al. [75] used tubular PES membranes in the filtration of bleach plant effluent and concluded that

hydrophobic compounds in the effluent fouled hydrophobic membranes. The hydrophilicity of membranes reduced the adsorption of organic foulants. They concluded that the flux decline was due to adsorption, pore blocking and concentration polarization. In filtration of acidic and neutral filtrates with NF and tight UF membranes, Mänttari et al. [77] found that hydrophobic membranes were fouled more than hydrophilic ones. In all the above filtrations of pulp and paper mill effluents, hydrophobic membranes were fouled more than hydrophilic membranes. Membrane hydrophilicity/phobicity can clearly be seen to have an influence on fouling in filtration of pulp and paper mill effluents.

5.2 Influence of filtered process stream characteristics

It has been shown that the characteristics of the process stream affect fouling in filtration of pulp and paper mill streams. Fälth et al. [37] used two different tubular membranes, a PS membrane (ES404, 4 kg mol⁻¹) and a modified PS (EM0006, 6 kg mol⁻¹) in UF of bleach plant filtrates. In their research, process stream which contained more and larger hydrophobic compounds fouled the membranes more severely. Thus, the amount of hydrophobic compounds rather than the COD value of the streams affected the flux decline. The research suggested that in estimation of the fouling tendency of a filtered solution, its adsorption on a hydrophobic surface should be evaluated.

A study by Nuortila-Jokinen et al. [76] revealed that acidic filtrate fouled membranes more than neutral filtrates in UF of three different paper mill streams: acidic white water, and neutral clear and super clear filtrates. The fouling was more severe with membranes with cut-off values higher than 100 kg mol⁻¹. For membranes in the cut-off value range 30-100 kg mol⁻¹ the lower the cut-off value the less fouling occurred. Mänttari et al. [77] found similar results in filtration of acidic and neutral filtrates with NF and tight UF membranes; acidic filtrate fouled the tested membranes more than neutral filtrate.

Yao et al. [38] have claimed that high molar mass compounds are the reason for membrane fouling in tight UF of Kraft pulp bleach plant effluent because fouling was reduced if these high molar mass compounds were removed with more open membranes (130 kg mol⁻¹) before tight UF (5.5 kg mol⁻¹) [38]. Furthermore, Merry et al. [78] noted that hardwood process water fouled a PS membrane (ES404, 4 kg mol⁻¹) more severely

than softwood process water in UF (tubular membrane operating in crossflow mode) of bleach plant effluent. Similar results were obtained in a study forming part of this thesis (III) in which hardwood process water was found to foul the membranes more than softwood process water.

5.3 Fouling mechanisms

In a study by Dal-Cin et al. [25] PSFP effluent fouled a variety of membranes severely. The membranes used in the research were from different materials and they had a large range of cut-off values (0.2-500 kg mol⁻¹). The fouling was quantified by a modified series-resistance model using flux loss ratios and retention measurements. RC membranes showed low adsorptive fouling, while PS membranes showed severe adsorptive fouling in PSFP filtration. In addition, high cut-off value membranes (more than 30 kg mol⁻¹) were fouled significantly by pore blocking. A membrane with a cut-off value of 1 kg mol⁻¹ was also fouled by pore blocking because PSFP contains a wide variety of different sizes of compounds. The pore blocking was rapid for high cut-off value membranes, while lower cut-off membranes required high pressure and longer filtration times for pore blocking to occur., while for lower cut-off value membranes At high pressure, concentration polarization rather than pore blocking controlled the flux. According to Dal-Cin et al. [25], it is also possible that a gel or cake layer controlled the flux at higher pressures because PSFP contains lignin and fatty and resin acids which can promote the formation of a gel or cake layer. In their study, however, they did not consider hemicelluloses as potential foulants.

Pejot and Pelayo [79] concluded, based on retention measurements, that a gel layer was formed on the membrane surface in crossflow UF of paper mill effluent. Both ceramic and polymeric membranes were used in their study. Ragona and Hall [24] ultrafiltered mechanical newsprint mill white water and also concluded that the flux was most likely decreased because a gel layer of colloidal particles was formed on the surface of the ceramic membrane. Woerner and Mc Carthy [80] also concluded that the flux was decreased in UF of two different Kraft lignin samples and two different lignin sulfonate samples by the formation of a gel layer on the membrane surface. The study by Woerner and Mc Carthy [80] was the only study to evaluate the limiting concentration and thus was able to mathematically verify that gel layer formation occurred in UF of Kraft black

liquor. In the other studies, the formation of a gel layer was concluded only from flux and retention measurements, which, without data on limiting concentration, are non-conclusive methods for analysis of gel layer formation.

6 FOULING CHARACTERIZATION IN PULP AND PAPER MILL APPLICATIONS

Table 6.1 presents analysis methods used to characterize fouling and foulants in filtration studies of pulp and paper mill effluents. In these studies, fouling is mostly characterized only by flux and retention measurements and few studies research fouling at the mill-site. In the fouling studies by Kallioinen et al. [82] and Carlsson et al. [63], the membranes were used at a mill-site for 30 days and 32 hours, respectively. It should be further noted that only a few studies have used analytical methods in the characterization of fouling and/or foulants in the filtration of pulp and paper mill streams, and even fewer studies have analyzed fouling from membranes fouled in mill-site experiments.

The strength of the use of flux and retention measurements in fouling studies is that they are easy and quick to perform. Reduction in the pure water flux after circulation of effluent at 0 bar pressure indicates that there is adsorptive fouling on the membrane. With this method, it is possible to estimate the amount of adsorptive fouling in a particular filtration application. However, the weakness of using flux and retention measurements in fouling studies is that they are unable to give knowledge about the adsorptive foulants. Thus, if only flux and retention are measured, a large number of filtration experiments are needed to obtain the information needed to reduce fouling and to improve filtration capacity. If the chemistry of the fouling phenomena is known, the membranes and filtration conditions can be chosen more precisely. Therefore, since thorough understanding of the chemistry behind the fouling is important, the membrane foulants have to be analyzed and identified.

Table 6.1 Analysis methods used to characterize fouling and foulants in filtration of pulp and paper mill effluents or similar model substances.

Effluent	Membranes		Analysis method	Result/Conclusion	Reference
	Cut-off, kg mol ⁻¹	Material			
Mechanical newsprint mill white water		Ceramic	Flux	Probably a formation of a gel layer of colloidal particles	Ragona and Hall [24].
Tall oil, dextran	10*	Sulfonated PS	Flux	Tall oil and dextran possibly formed a gel layer	Ramamurthy et al. [23]
4,5-Dichlorocatechol, 4,5-Dichloroguaiacol, Dehydroabiatic acid, Chlorodehydroabiatic acid, Dichlorodimethylsulfone, Sulfonated lignin (Polyfon O)	2-60* 1.5- <150**	PS, RC, PES, modified PES, cellulosic/PVDF	Flux and retention	Influence on flux negligible, hydrophilic membranes had lower retentions	Zaidi et al. [62]
Plug screw feeder pressate (PSFP)	92% NaCl >500*	RC, PAI, PS, PVDF, TFC	Flux+retention/modeling	Significant pore blocking, adsorption, CP, gel/cake layer	Dal-Cin et al. [25]
Kraft lignin and lignin sulfonate	10-300*	PS	Flux/modeling	A gel layer	Woerner et al. [80]
PSFP	1-100*	Teflon, RC, PVDF, CA, PS, PAN, CTA, PEI, PES, PA, PS	Flux/pore size measurement with polyethylene glycol (PEG)	A decreased pore size – adsorbed fouling layer on the membrane surface, severe adsorption for hydrophobic membranes	Dal-Cin et al. [40]
Paper machine white water	0.4-1*	PES	Flux /contact angle/SEM	Pore blocking at low pressure, cake layer at high pressure, increased hydrophobicity	Kaya et al. [35]
Octanoic acid	20*	PES	Flux/ellipsometry, calculations	Adsorption on membrane matrix	Jönsson et al.[83]

Octanoic acid, sodium octanoate	6-30*	RC, PS, PES, PVDF, PAR	Flux/contact angle	Fouling in hydrophobic membranes, hydrophilic RC membrane was not fouled, adsorption (flux)	Jönsson and Jönsson [84]
Screw press filtrate from CTMP mill	10*	Sulfonated PS	EDS	Membrane deposits calcium, aluminium, silicon	Ramamurthy et al.[23]
Groundwood mill circulation water (GWM), Biologically treated GWM	30	RC	Multivariate analysis methods	Wood extractives influence on fouling was minor, fatty acids and lignans have negative influence on flux while sterols and steryl esters have positive	Kallioinen et al. [82]
Dehydroabietic acid	100*	PVDF	ToF-SIMS	RA inhomogeneously adsorbed on membrane surface, detection limit 10 mg mL ⁻¹	Spevack and Deslandes [85]
PSFP	0.2- >100**	PA/PS, RC, PVDF, PS	ATR-FTIR	Hydrophobic membranes were fouled, hydrophilic not, fatty rather than resin acids were found from the membranes	Carlsson et al. [63]
Spent sulfite liquor	30*	PS, PES	Extraction+GC, ATR-FTIR	PES membrane contained twofold more wood extractives than PS membrane	Weis et al. [86] based on the method developed in this thesis
Bleach plant effluent		PES	Staining of lignin in fouled membranes with toluidine blue solution	Membranes were fouled by lignin	Maartens et al. [75]

* Given by manufacturer

** Measured with polyethylene glycol (PEG) and/or dextrans

RC regenerated cellulose, PVDF polyvinylidene fluoride, CA cellulose acetate, PS, polysulfone, PAN polyacrylonitrile, CTA cellulose triacetate, PEI polyether-imide, PES polyethersulfone, PA polyamide, PAI polyamide-imide, TFC thin film composite, PAR polyaramide

6.1 Use of analytical methods

Energy dispersive X-ray spectroscopy (EDS) or scanning electron microscope energy-dispersive X-ray spectroscopy (SEM-EDS) have been used to characterize fouling in filtration of different pulp and paper mill effluents [23, 33, 87, 88]. Aluminium [23], calcium [23, 33, 88], carbonate ions [33], iron [87], potassium [88], magnesium [33, 87], phosphorous [88] and silicon [23, 87] have been found from the fouling layers in filtration of different pulp and paper mill effluents. Dorica et al. [33] conjectured that at alkaline conditions, fatty and resin acids are probably present in the form of calcium salts and a small fraction of them could coagulate and deposit on the membranes. Mänttari et al. [88] concluded that organic foulants were the main reason for irreversible fouling, although the fouling layer contained traces of inorganic foulants in NF of pulp and paper mill process effluent, which contained a paper machine and a pulp mill effluents. A weakness with the above SEM-EDS measurements is that characterization of organic foulants is challenging because the membrane polymers consist of the same elements as the organic foulants [89]. Moreover, their identification is close to impossible. For thorough understanding of fouling, organic foulants have to be characterized and identified from polymeric membranes.

Kaya et al. [35] used scanning electron microscopy (SEM) and a sessile drop contact angle measurements to characterize fouling on NF membranes after filtration of paper machine process water (white water). They claimed, based on SEM measurements, that deposition of particles reduced the pore size of the membrane. The fouled membranes also had higher contact angles than virgin membrane. The measured contact angles thus indicated that hydrophobic compounds were the reason for the measured fouling.

Maartens et al. [75] ultrafiltered bleach plant effluent with PES membranes. They studied phenolic foulants, such as lignin, by staining fouled membranes with Toluidine blue. They concluded that hydrophobic foulants fouled the hydrophobic membranes, and that process water flux decline was due to adsorption, pore blocking and concentration polarization. Staining of foulants is an easy and fast analysis method for fouling but its weakness is that it is usually a specific chemical bond, not a compound, which is reacted with the staining

color. Thus, foulant identification may be uncertain if there are many compounds which have this chemical bond.

6.1.1 Wood extractives

A few, rare studies have characterized extractives-induced fouling in the filtration of pulp and paper mill streams using analytical methods. Spevack and Deslandes [85] used Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) to analyze the adsorption of dehydroabietic acid on a PVDF membrane. They found that dehydroabietic acid adsorbs inhomogeneously on the membrane surface, which suggests that specific sites are present for the adsorption. The detection of dehydroabietic acid foulant was possible with ToF-SIMS if the dehydroabietic acid feed contained 10-1000 mg L⁻¹ foulant. This detection limit does not properly indicate the detection limit of ToF-SIMS because the membrane area used is not specified in their research. To estimate the detection limit of ToF-SIMS more precisely, the detection limit should be given in the unit, mg adsorbate per membrane area m², which would tell more about this detection limit than the unit mg L⁻¹.

Carlsson et al. [63] used ATR-FTIR to study membrane fouling in the filtration of PSFP pulp mill effluent with PVDF, PS, PA/PS thin-film composite and RC membranes. They derivatized carboxylic and carboxylate groups (-C(=O)-OH or -C(=O)-O⁻) with SF₄ to get adsorption at 1810-1850 cm⁻¹. Using this analysis method, they found that there were fatty rather than resin acids in the membranes. The detection limit seemed to be 100-200 mg L⁻¹ for adsorbed resin acid. As in the above study of Spevack and Deslandes [85] the information given in their research is insufficient to calculate the detection limit in mg adsorbate per membrane area m², which would estimate the detection limit of ATR-FTIR more precisely. The FTIR spectra indicated that there was no sign of contamination in the hydrophilic PA and RC membranes, whereas the hydrophobic PVDF and PS membranes were severely and identically contaminated.

Weis et al. [86] extracted organic foulants from PS and PES membranes using the method developed in this thesis (II). Besides this method they also characterized fouling with ATR-FTIR. Based on extraction of wood extractive foulants from the membranes, they found that there were more wood extractive foulants in PES membranes than in PS

membranes. ATR-FTIR was unable to identify fouling of a specific compound group. The measured zeta potential of the fouled membranes was more negative than the zeta potential of the virgin membranes. Thus, the analysis indicated that the foulants had negatively charged groups in their structure.

Spectroscopic analysis methods are good for foulant characterization because special sample pretreatment is not needed [89]. A weakness of these methods, however, is that they detect only chemical bonds, and if the filtered effluent is complex, the identification of foulants may be uncertain. Moreover, the membrane material may interfere with interpretation because its chemical bonds give significant absorbance. Thus, if the chemical bond of the foulant is at the same wave length as that of the membrane, it may be impossible to characterize and/or identify the foulants. More specific analysis methods are therefore needed to confirm the results of spectroscopic analyses.

6.1.2 Polysaccharides

Most studies in which polysaccharide fouling is characterized have been done with model substances. There is however a small number of studies in which polysaccharide fouling is characterized in filtration of real industrial effluents.

Susanto and Ulbricht [27] measured contact angle (static captive bubble and sessile drop), surface charge and sieving curves to verify dextran fouling. They studied dextran fouling with one cellulosic and two PES membranes. All the membranes used had a nominal cut-off value of 10 kg mol^{-1} . Their study revealed that dextran was adsorbed on the surface and pores of hydrophobic PES membranes but not on the hydrophilic cellulosic membrane. The pore blocking was more severe with larger dextran molecules ($15\text{-}17 \text{ kg mol}^{-1}$) than with smaller ones ($4\text{-}6 \text{ kg mol}^{-1}$). The adsorption was at its maximum at 8 g L^{-1} of dextran. The contact angles of the PES membranes reduced significantly after adsorption of dextran. The reduction in contact angle was more significant for the more hydrophobic PES membranes. Furthermore, the surface charge of the PES membranes changed after adsorption of dextran, while the surface charge of the cellulosic membrane remained unchanged. After the adsorption tests, the sieving curves of the PES membranes (but not the cellulosic membrane) shifted significantly toward the

lower pore radii, indicating that the membrane was severely fouled. Based on calculations using the Langmuir adsorption model, it was concluded that there was a monolayer of dextran on the membrane surface and adsorption in the deeper pores.

In another study, Susanto and Ulbricht [90] used contact angle, zeta potential, sieving curve and simultaneous diffusion adsorption (SDA) measurements, as well as ATR-IR spectroscopy and Atomic Force Microscopy (AFM), to study adsorptive fouling of dextrans. They studied two different PES membranes with cut-off values of 10 and 30 kg mol⁻¹ and two cellulosic membranes with a cut-off value of 10 kg mol⁻¹. Based on the SDA measurements, there was significant dextran binding to the PES membranes and diffusion through the pores; while dextran was only mechanically entrapped on cellulosic membranes. Other analysis methods used also indicated that the PES membranes were fouled by dextrans and the cellulosic membranes remained unfouled.

Saha et al. [91] used FTIR and SEM to analyze fouling of polysaccharides in filtration of sugarcane juice. Based on their results, the fouling layer thickness was not large enough to permit detection of polysaccharide fouling in PES and PS membranes by FTIR analysis, because deposition of polysaccharides could not be detected even though the color of the polysaccharide fouled membrane had changed. When the cellulose-based membrane was fouled for a longer time, polysaccharide fouling could be detected. Their SEM analysis revealed that the highest cut-off value PS membrane, 100 kg mol⁻¹ was fouled more by pore blocking than the PES membranes with cut-off values of 30 and 50 kg mol⁻¹.

Jermann et al. [92] characterized fouling of sodium alginate by surface charge measurements. They noticed that hydrophilic sodium alginate was adsorbed on hydrophobic PES membranes because the alginate fouled membranes had more negative surface charges than the virgin membrane.

Nataraj et al. [93] used ATR-FTIR to characterize polysaccharides of xanthan, actigum CS 11 and glucan from fouled RC membranes. The FTIR spectra showed polysaccharides on the membranes.

6.2 Flux and retention measurements

Wood extractives are often mentioned as potential foulants [23-25] in filtration of pulp and paper mill streams but their analysis and identification as foulants [63, 86] has been limited by the complexity of process streams. Fouling due to wood extractives is therefore often studied with filtration of model substances and is often evaluated only by flux and retention measurements.

6.2.1 Wood extractives

Octanoic acid [83, 84] has been used as a model substance in filtration tests because of its resemblance to fatty acids; it has a hydrophobic alkyl chain tail and a weak carboxylic acid head. Jönsson and Jönsson [84] used RC, PES and PS membranes in their study. They concluded from the flux measurements that octanoic acid fouled the membranes by adsorption, and that the fouling was more severe for hydrophobic PES and PS membranes. In another study it was found that octanoic acid adsorbed on the surface of the membrane and in the pores by blocking them even though it was much smaller than the cut-off value of the membrane used [83]. The study of Brinck et al. [94] showed that the adsorbed amount of octanoic acid on a PES membrane increased at lower pH. The reason for the increased adsorption was the lower amount of dissociated octanoic acid. There was multilayer adsorption at the saturation concentration of octanoic acid, otherwise a monolayer was adsorbed. Octanoic acid has also been used in the evaluation of membrane hydrophobicity in research by Persson and Jönsson [71]. They concluded that the more hydrophobic the membrane, the more severe the flux decline.

Ramamurthy et al. [23] used tall oil and dextran to characterize the fouling potential of pulp and paper mill process streams. The tall oil represented fatty and resin acids while dextran was a model substance for linear hemi-cellulosic material. The highest flux was obtained with tall oil while the lowest flux was achieved with a combination of these two model substances. They concluded from their flux measurements that fatty and resin acids promote gel layer formation on the membrane surface when high molar mass solutes are present [23]. In filtration of only dehydroabietic acid (200 mg L^{-1} , one resin acid) Zaidi et al. [62] found that the flux decline of PS, PES and cellulosic membranes was negligible.

The use of model solutions in fouling studies may give indications about the fouling mechanisms in a specific application. However, a weakness is that the model substances are usually filtered independently and thus, interdependent influences with other compounds in the effluent are absent. Moreover, they only partly resemble the compounds present in real effluents and the compounds in real process stream may show significantly different fouling behavior.

6.2.2 Polysaccharides

Polysaccharides can form a gel and/or cake layer on the membrane surface in membrane filtration [92, 93, 95-97]. If the concentration of polysaccharides is high, the solutes are next to each other, which leads to interconnections and the formation of a gel layer [81]. This gel and/or cake layer formation may be problematic in membrane filtration because it is believed to be resistant to removal by shear rate and has high resistance, which reduces the flux [97].

In the study of Wang and Waite [97] the gelling propensity of the colloids and the operational mode (constant pressure or constant flux) influenced membrane fouling in UF of Na- and Ca-alginates and yeast. They concluded that constant flux filtration is more sensitive to the sizes of particles than constant pressure filtration, suggesting that the operational mode has a significant influence on the fouling behavior of polysaccharides.

Broeckmann et al. [98] studied polysaccharide fouling with particulate or microcrystalline cellulose as a model substance in NF. They used a hydrophobic PA membrane in their research. Their results suggested cellulose fouling depended on the solution chemistry and it increased as the concentration of cellulose increased. Moreover, the fouling was more pronounced at a higher crossflow velocity, 2 m s^{-1} , than at 1 m s^{-1} ; fouling was reversible at the lower crossflow velocity, but it was irreversible at the higher crossflow velocity. In their research neutral to high pH and low ion concentration favored polysaccharide filtration because permeability was higher at these conditions.

In UF of sodium alginate with a hydrophobic PES membrane, Jermann et al. [92] concluded that the membranes were fouled by pore blocking at an early stage of sodium

alginate filtration, and that at a later stage cake layer formation was the dominant fouling mechanism. In the presence of calcium, the fouling layer was a gel layer rather than a cake layer. Katsoufidou et al. [95] obtained similar results when they studied fouling of sodium alginate in hollow fiber UF with backwashing using hydrophilic RC and hydrophobic PES membranes. They concluded that at an early stage of filtration the membrane was fouled by adsorption but at a later stage of filtration cake layer formation was the dominant fouling mechanism. Moreover, divalent ions affected the gelling properties of polysaccharides. In their study flux decline decreased as calcium concentration increased. It was found that without calcium present, the membrane fouled irreversibly more by adsorption but as calcium concentration increased, cake formation became the dominant fouling mechanism, and there was reversible fouling rather than irreversible fouling [95].

Nataraj et al. [93] used model solutions of xanthan, actigum CS 11 and glucan to study polysaccharide fouling of regenerated cellulose membranes (10 and 30 kg mol⁻¹). At low concentrations (20 mg L⁻¹) cake formation was the predominant fouling mechanism for xanthan and actigum suspensions. Moreover, each model polysaccharide had its own fouling behavior and the feed concentration affected the fouling mechanism. A study by de La Torre et al. [99] in which they characterized polysaccharide fouling of UF PES membranes using eight different model polysaccharides also showed that different polysaccharides had different fouling behaviors.

Mänttari and Nyström [96] nanofiltered karaya gum and locust bean gum. Their results showed that karaya gum was adsorbed instantaneously on the hydrophobic NTR-7450 membrane with hydrophobic interactions but not on the more hydrophilic membranes PVD-1 and Desal-5. Locust bean gum also fouled the hydrophobic membrane NTR-7450 severely, while fouling of the more hydrophilic membranes PVD-1 and Desal-5 was less significant. They concluded that locust bean formed a loose gel layer on the membrane surface and probably fouled the membranes by plugging. The studies above and the results presented in this thesis (**I**) indicate that correct choice of the model substance and concentration is critical for fouling studies using a model solution approach.

6.3 Multivariate data analysis

Kallioinen et al. [82] studied membrane fouling in UF of groundwood mill (GWM) process water with multivariate data analysis methods. They concluded that the relevant factors affecting the permeability were temperature, the operating life of the membranes, and the amount of dissolved lignin related compounds, sugar and starch, in the GWM water. Based on their multivariate analysis, wood extractives were considered not to be the reason for the flux decline in UF of GWM process water. Using multivariate data analysis for the filtration data is useful because it may reveal hidden knowledge about the fouling behavior of membranes which cannot be seen from the raw data.

6.4 Conclusion of fouling characterization in pulp and paper mill applications

Fouling characterization techniques currently used still have significant limitations and thus, further development is required. Fouling studies based on flux and retention measurements are easy and fast but they are unable to identify the foulants and the fouling mechanism. Microscopical methods give information about the shape of foulants and fouling layers on/in the membrane surface and pores but these methods alone are unable to identify foulants. If microscopical methods are combined with other approaches, e.g. with EDS analysis, more detailed information about the elements of the foulants is revealed, although challenges still remain, particularly in characterization of organic foulants from polymeric membranes [89]. Spectroscopical methods give information about chemical bonds or functional groups of foulants but if the filtered effluent is complex, it is possible that the identification of foulants is limited. In conclusion, it is clear that more precise analytical methods are needed for the characterization of fouling and the identification of foulants and to improve understanding of the chemistry of fouling phenomena. Greater knowledge of fouling phenomena would permit more precise selection of membranes and would enable accurate filtration and cleaning conditions to be specified. This thesis therefore presents an analysis procedure for the identification of wood extractives and carbohydrate foulants in pulp and paper mill applications which was developed to advance understanding of fouling phenomena in such applications.

EXPERIMENTAL PART

7 MATERIALS AND METHODS

The experimental procedures used in the thesis are summarized in the following chapters; more detailed descriptions of the experiments are presented in the corresponding papers (I-IV).

7.1 Membranes

In most cases, UF membranes were used and they were chosen such that they differed in material and cut-off values. The hydrophilic regenerated cellulose (RC) membrane was used because it is widely applied in the pulp and paper mill industry [100]. Membranes with better thermal resistance were considered of interest, and, thus, hydrophobic polyethersulfone (PES) and polyamide (PA) membranes were also chosen for the filtrations. Nanofiltration membranes were used only in the model substance filtrations to evaluate possible polysaccharide fouling potential in pulp and paper mill applications. Table 7.1 shows the characteristics of the membranes used in this study as given by the manufacturers.

Table 7.1 Characteristics of the membranes used, as given by the manufacturers. UC030 and UH030P membranes are former C030F and PES050H membranes, respectively.

Membrane	Manufacturer	Surface material	Cut-off, kg mol ⁻¹	pH	T _{max} °C
Desal-5 DK (NF)	GE Osmonics*	Proprietary	0.18**	2-11	50-70
NTR 7450 (NF)	Nitto Denko (Hydranautics)	Sulfonated PES	1**	1-13	80
C030F (UF)	Microdyn-Nadir GmbH***	RC	30	1-13	55
PA050F (UF)	Microdyn-Nadir GmbH***	PA	50	1-12	90
PES050H (UF)	Microdyn-Nadir GmbH***	PES	50	1-14	95
UC030 (UF)	Microdyn-Nadir GmbH	RC	30	1-11	55
UH030P (UF)	Microdyn-Nadir GmbH	PES	30	1-14	95
UH050P (UF)	Microdyn-Nadir GmbH	PES	50	1-14	95

* Former Osmonics/Desal

** Wang et al. [101]

*** Former Celgard GmbH

RC regenerated cellulose

PA aromatic polyamide

PES polyethersulfone

7.2 Model substances

In the nanofiltration experiments (I), two different polysaccharides from Sigma Chemicals Co, USA, locust bean gum and karaya gum, were used to investigate the fouling potential of polysaccharides. The concentrations used for the model substances were 5, 50 and 125 mg L⁻¹. The concentration for model substance experiments was chosen based on the concentration of hemicelluloses in paper machine circulation water. The characteristics of the polysaccharides are shown in Table 7.2.

Table 7.2 Characteristics of the polysaccharides used as model substances.

Model substance, (Lot)	Molar mass, kg mol ⁻¹	Structure	Charge in pH range 4-8
Locust bean gum (G-0753, Lot 75H0638)	310	Mannose polymer with galactose branches on every 4 th unit	Uncharged
Karaya gum (G-0503, Lot 84H0256)	9 500	Polymer of galactose, rhamnose and partially acetylated glucuronic acid	Negative

7.3 Process streams

The filtered stream in analysis of wood extractives from the fouled membranes (**II**) was ground wood mill (GWM) circulation water from an integrated pulp and paper mill. The GWM water contained acidic paper machine water, pressure ground wood (PGW) water and stone ground wood (SGW) water from mechanical pulping.

Two different process streams from a pulp mill were used in the fouling experiments for the evaluation of the performance of RC and PES membranes in filtration of pulp mill process water and the assessment of the fouling behavior of the wood extractives (**III**, **IV**). The process water samples for the filtration experiments were collected at a chemithermomechanical pulping (CTMP) mill. One water sample originated from a pulping process using softwood and the other was from a pulping process using hardwood. The collected process water samples were mixed as well as possible to minimize variation in the feed and after mixing divided into one liter bottles. These bottles were then stored in a freezer before the filtration experiments.

7.4 Filtration equipment

Four different filtration apparatuses were used. Laboratory-scale filters were used in model substance studies (**I**), in sieving curve measurements, in evaluation of the performance of RC and PES membranes in filtration of pulp mill process water, and in assessment of the fouling behavior and potential of wood extractives (**III**, **IV**). In the analysis of wood extractives from fouled membranes (**II**), the filtrations were done with a CR 1000/10 (cross rotation, CR-filterTM) pilot plant module [29]. The filtration equipment is described in more detail below.

7.4.1 Laboratory scale filtration equipment

Model substance filtrations (**I**) were carried out on laboratory-scale crossflow flat-sheet module apparatuses manufactured at Lappeenranta University of Technology. One apparatus contained one cell and the other apparatus had three cells in parallel. Simplified process diagrams of the equipment used are given in Figs. 7.1 and 7.2. The membrane area was 0.0053 m^2 , the height of the flow channel in the cell was 1 mm, and the cross-sectional area for flow was $17 \cdot 10^{-6} \text{ m}^2$ in the one-cell apparatus. In the three-cell apparatus, the membrane area of each cell was 0.0046 m^2 , the height of the flow channel in the cell was 1 mm, and the cross-sectional area for flow was $21 \cdot 10^{-6} \text{ m}^2$.

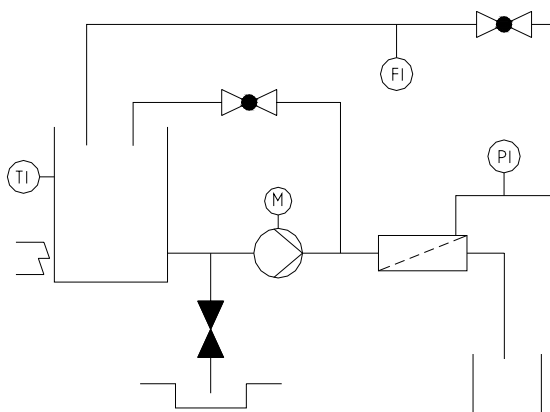


Fig. 7.1 Simplified process diagram of the one-cell laboratory-scale equipment used in model substance filtrations (**I**). The total filtration area was 0.0053 m^2 and the feed tank volume was 8 L. The concentrate stream was circulated back to the feed tank, which caused the mixing of the feed.

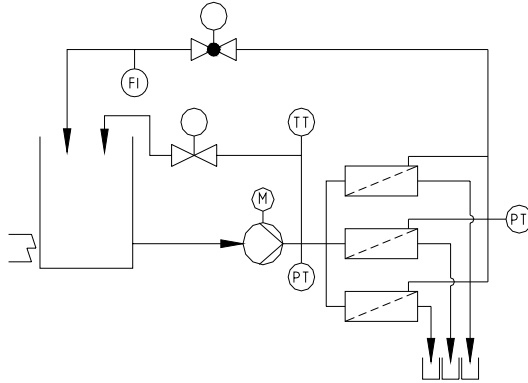


Fig. 7.2 Simplified process diagram of the three-cell laboratory-scale equipment used in model substance filtrations (I). The total filtration area was 0.0138 m^2 (in each cell 0.0046 m^2) and the feed tank volume was 20 L. The concentrate stream was circulated back to the feed tank, which caused the mixing of the feed.

Sieving curve measurements were made with a long cell filter, which was designed to give a fully developed flow across the membrane [102]. The membrane area of this filter was 0.0021 m^2 , the height of the flow channel in the cell was 4.1 mm, and the cross-sectional area of flow was $12 \cdot 10^{-5} \text{ m}^2$. A simplified process diagram of the apparatus is given in Fig. 7.3.

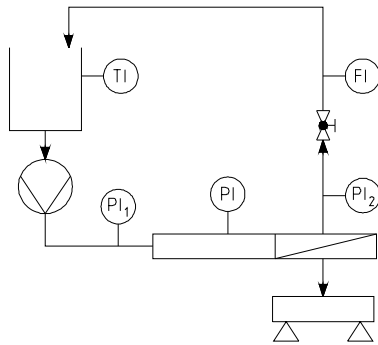


Fig. 7.3 Simplified process diagram of the laboratory-scale equipment used in sieving curve filtrations (III). The equipment is designed to give a fully-developed flow across the membrane [102]. The total filtration area was 0.0021 m^2 and the feed tank volume was 20 L. The concentrate stream was circulated back to the feed tank, which caused the mixing of the feed.

An Amicon filter, manufactured by Millipore USA, was used in the evaluation of the performance of RC and PES membranes in filtration of pulp mill process water and in the analysis of the fouling behavior and potential of the wood extractives (**III**, **IV**). The filter operates in a dead-end mode and the membrane area was 0.004 m². A simplified process diagram of the filter equipment is given in Fig 7.4.

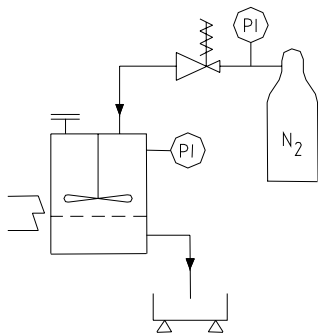


Fig. 7.4 Simplified process diagram of the Amicon filter, operating in dead-end mode, used in the evaluation of the performance of RC and PES membranes in filtration of pulp mill process water (**III**) and in analysis of the fouling behavior and potential of wood extractives (**IV**). The total filtration area was 0.004 m² and the feed tank volume was 300 mL.

7.4.2 Filter used in pilot plant studies at a pulp and paper mill site

For the analysis of wood extractives from fouled membranes (**II**) the filtrations were done with a CR 1000/10 (cross rotation, CR-filterTM) pilot plant module made by Metso Paper Inc. (formerly Valmet Raisio) [100]. There are 10 cells in a CR 1000/10 module, mounted one above the other. Each cell has two membranes and there are rotors between the cells to increase turbulence on the membrane surface. The maximum rotor speed used was 365 rpm, which is equivalent to a velocity of 19.1 m s⁻¹ at the outer shell and 5.7 m s⁻¹ at the inner shell of the rotor. Each cell has its own permeate outlet. Feed is introduced to the filter on the bottom and concentrate is collected from the top of the filter. The total membrane area of this filter was 13.5 m². The structure of a CR filter is presented in Fig. 7.5.

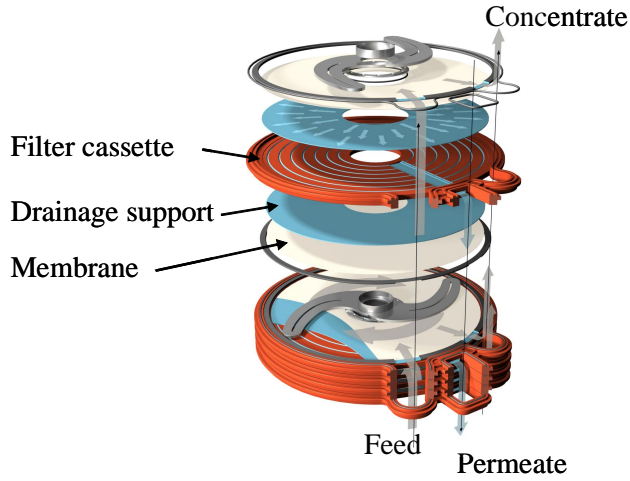


Fig. 7.5 Structure of a CR filter made by Metso Paper Inc used in the experiments in Paper II.

7.5 Filtration experiments

Filtration experiments were performed to characterize membrane fouling in filtration of pulp and paper mill process streams. The filtration experiments are listed in Table 7.3.

Table 7.3 Filtration experiments performed as part of the thesis.

Purpose of the experiment	Filter	Membrane	Experiment
Polysaccharide fouling in NF	One or three-module filters	Desal-5 DK NTR 7450	Paper I Chapter 8.1
Characterization and identification of wood extractives as foulants (UF)	CR 1000/10	C030F PA050F PES050H	Paper II Chapter 8.3
Fouling of RC and PES membranes in UF of pulp mill process water	Amicon filter	UC030 UH030P UH050P	Paper III Chapter 8.3 Chapter 8.4
Fouling behavior and potential of wood extractives (UF)	Amicon filter	UC030 UH030P UH050P	Paper IV Chapter 8.3

7.5.1 Model substance experiments (I)

The NF experiments were carried out on a laboratory scale using the crossflow flat-sheet modules described above at a transmembrane pressure of 8 bar. Generally, fresh pieces of membrane were used in the experiments. Flow velocities of 3 and 1.6 m s⁻¹ and pH ranges of 4-5 and 7-8 were used. The pH ranges were chosen based on typical pH values of pulp and paper mill process streams. The flow velocities were chosen based on previous experiments with paper mill effluents [36]. The filtration temperature was 40±1°C, which is a very common temperature for paper mill streams.

7.5.2 Membrane fouling by wood extractives (II)

The membranes for analysis of extractives-induced fouling were obtained from a 30 day filtration with a CR 1000/10 filter. The filter had been connected directly to the process water line, thus, the feed characteristics varied considerably. The temperature range during filtration was 46-78°C and the pH was 5. The rotor speeds used in the tests were 50%, 70% and 90% of the maximum of 19.1 m s⁻¹ at the outer shell and of 5.7 m s⁻¹ at the inner shell of the rotor. A more detailed description of the filtration procedure is presented by Huuhilo et al. [74].

7.5.3 Filtration procedure in UF of softwood and hardwood process waters (III, IV)

Filtration experiments were performed as described in paper **III** and are presented here only briefly. The fouling experiments were done with the Amicon filter (see chapter 7.4.1).

The membranes were pre-treated before the experiments by rinsing them three times in an ultrasonic bath with reverse osmosis (RO) purified water for ten minutes to remove preservatives. A new piece of membrane was used in each filtration. The filtered RO water and the process water samples were heated to 40°C before filtration. The pure water fluxes of the membranes were measured at a temperature of 40°C before and after the process water filtration for identification of irreversible fouling. The feed batch was 300 g in each filtration. 225 g permeate was collected during the filtration. Thus, 75 g was left in the concentrate. The experiments were performed at pressures of 1 and 2 bar. The feed was

mixed continuously at a peripheral velocity of 1.8 m s^{-1} . Each experiment was repeated three times to verify the results.

Adsorption tests were made for the membranes in order to test if adsorption is one reason for fouling. No pressure was used in the adsorption tests, and the adsorption time was the same as in the filtrations at 1 bar.

7.6 Membrane characterization

The equipment and methods applied in analysis of the membranes are presented in Table 7.4. The fouled membranes were kept in a frozen state before analysis.

Table 7.4 Equipment and methods used in analysis of membrane samples.

Analysis	Equipment/method/(manufacturer)
Roughness (III, IV)	Atomic force microscopy (AFM), CP-II Scanning Probe Microscope (Veeco Instruments, USA)
Contact angle (III, IV)	KSV CAM 101 instrument (KSV Instruments Ltd., Finland)
Zeta potential (III, IV)	Streaming potential equipment [103] (LUT, Finland)
Sieving curves (III, IV)	A long cell filter, see chapter 7.4.1, (LUT, Finland)
Foulants (I, IV)	Perkin-Elmer 2000 FT-IR spectrometer (Perkin Elmer Limited, USA)
Wood extractives (II)	fexIKA 200 (IKA Labortechnik, Germany) Varian 3400/3700 + autoinjector Varian 8200 (Varian Inc, Australia)
Wood extractives (IV) Carbohydrates	A Soxtec System HT6 1433 Extraction unit (Tecator, Höganäs, Sweden) HP6890 + injector HP7683 (Agilent, former Hewlett Packard, USA)

Topographic imaging for evaluation of membrane roughness was performed with a digital atomic force microscope (AFM) operating under atmospheric pressure at ambient

temperature. The imaging was done in non-contact mode with a doped-diamond coated Si tip. WSXM 4.0 software was used for the roughness analysis, according to Horcas et al. [104]. Root mean square surface roughness R_{RMS} was calculated over an area of $1 \mu\text{m} \times 1 \mu\text{m}$.

Membrane hydrophilicity was evaluated by contact angle measurements, which were performed using a sessile drop method using membrane samples dried at room temperature [105].

The membrane charges were evaluated by zeta potentials calculated from measured streaming potentials using the Helmholtz-Smoluchowski equation. The measurements were performed with 0.001 mol L^{-1} KCl solution at 25°C in a pH range from 3 to 8 with Ag/AgCl electrodes. The measurements were performed both along the membrane surface and through the membrane pores. When measuring the zeta potential along the surface, the electrodes were on the membrane surface. When the measurement was made through the membrane pores, one electrode was on the surface of the membrane, while the other was under the membrane in a permeate collector cell. The measurement procedure is introduced more precisely by Nyström et al. [103].

The sieving curves of the membranes for cut-off analysis were determined with polyethylene glycol (PEG, supplied by Fluka Chemie GmbH, Switzerland) solutions ($150\text{--}180 \text{ mg L}^{-1}$) using laboratory-scale crossflow filtration equipment. The filtration temperature was 40°C , the pressure 0.25 bar , and the crossflow velocity 0.85 m s^{-1} . PEG retention was analyzed as total carbon (TC) from samples taken in the filtration of PEG solutions at 10, 20 and 30 minutes.

For the sieving curve measurements, the pure water flux was first measured. Then the PEG retention was measured, the membrane was rinsed, and the pure water flux was measured again. The measurements were repeated twice for each PEG and the molar masses of the PEGs were $1.5, 6, 10, 20$ and 35 kg mol^{-1} . No fouling was detected between measurements.

7.7 Membrane foulant extraction and analysis

Study of the literature suggests that wood extractives have never been extracted from fouled membranes and analyzed. Thus, the extraction procedure had to be created and optimized before starting the systematic analysis. A schematic diagram of the extraction and analysis procedure for wood extractives and carbohydrates is given in Fig. 7.6. This procedure is explained in detail in the following chapters 7.7.1-7.7.3. The optimization procedure is explained in more detail in chapter 8.3.2.

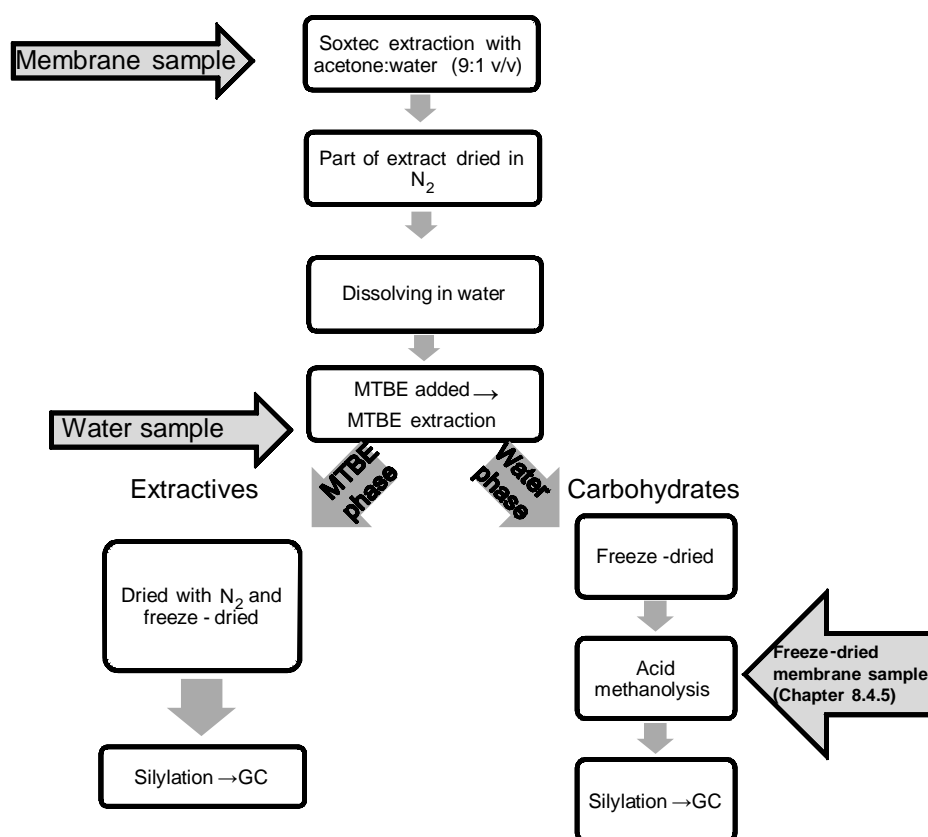


Fig. 7.6 Schematic diagram of the extraction and analysis procedure for wood extractives and carbohydrates. GC – gas chromatography, MTBE - tert-butylmethylether

7.7.1 Optimized extraction procedure for the membranes (II, IV)

In paper II the membrane samples were extracted in a series-extractor, fexIKA 200 made by IkaSoft, which resembles the Soxhlet extractor. A Soxtec System HT6 1433 Extraction unit (Tecator, Höganäs, Sweden) was used in the extractions in paper IV. Membrane samples of 0.0314 m² and 0.0034 m² were extracted in papers II and IV, respectively. They were extracted with 30 mL acetone-water solution (1:9, v/v) for 1-6 hours. After solid extraction, a 1 mL sample was taken to the liquid-liquid extraction (chapter 7.7.2) to remove the polymeric material. A more detailed description of the extraction procedures is found in papers II and IV. In these papers, only wood extractives were analyzed from the acetone:water extract of the fouled membrane. However, this acetone:water extract of the fouled membranes was also used for the analysis of carbohydrates as foulants, but the extraction procedure was not optimized for this analysis.

7.7.2 Liquid-liquid extraction

Liquid-liquid extraction for the process water samples and the samples from the membrane extraction was done as described by Holmbom and Örså [51]. First, some bromocresol green (indicator for pH level) and 0.05 M sulfuric acid were added to the sample to adjust the pH to 3-3.5. Then 2 mL of tert-butylmethylether (MTBE) and 200 µL of standard solution were added. The standard solution contained heneicosanoic acid, betulinol, cholesteryl heptadecanoate and 1,3-dipalmitoyl-2-oleoyl glycerol 35 mg L⁻¹ in MTBE each. The samples were vigorously shaken for 5-7 min and were then centrifuged at 500g for 5 min. Finally, the clear MTBE layer was carefully pipetted off. The extraction was repeated once with 2 mL of pure MTBE. The obtained MTBE solution (about 4 mL) was evaporated in a nitrogen stream and freeze-dried.

7.7.3 Acid methanolysis of hemicelluloses for the fouled membrane

Acid methanolysis was performed for the fouled membrane pieces according to Sundberg et al. [106] to analyze hemicelluloses directly from the fouled membranes. Membrane pieces of 0.00086 m² were first freeze-dried. Then 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 hours (water samples) or 5 hours

(membrane samples) 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^{-1}), 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 complete removal of methanol, the sample was further freeze-dried for 1 hour. The sample, which still could contain some pyridine, was dissolved by addition of 80 μL pyridine to facilitate silylation. For the silylation, 300 μL 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.

7.7.4 Membrane foulant analysis by GC for wood extractives

To analyze wood extractives from the freeze-dried samples of the liquid-liquid extraction, the samples were silylated with 100 μL BSTFA and 50 μL TMCS for GC analysis. The solution was kept in an oven at 70°C for 40-45 min prior to analysis with GC. A detailed description of the GC analysis is given in papers **II** and **IV**.

7.7.5 Membrane foulant analysis by GC for hemicelluloses

Hemicelluloses from the process water samples and the acetone:water extracts were analyzed according to Sundberg et al. [106]. The samples were first freeze-dried. Then the polymeric and oligomeric hemicelluloses were transformed into monosaccharides by acid methanolysis, as explained in chapter 7.7.3.

The hemicellulose samples were injected with an autoinjector directly in the column. The column was a 25 m/0.20 mm i.d. wide-bore capillary column with a nonpolar phase (HP-1, Agilent Technologies), film thickness 0.11 μm .

The injection temperature was 80°C . 1 min after injection the column was heated at $40^\circ\text{C min}^{-1}$ to 170°C and held at this temperature for 7 min. Finally the oven was heated at $50^\circ\text{C min}^{-1}$ to 280°C and held there for 2.5 min. The flame ionization detector (FID) temperature was 310°C . Hydrogen was used as the carrier gas. The total analysis time of each sample was about 20 minutes.

To calculate concentrations from peak areas, a calibration factor for different sugar units was determined. This was done by analyzing an acid methylated standard which contained arabinose, galactose, galacturonic acid, glucose, glucuronic acid, mannose, rhamnose and xylose, 0.1 mg each, in each analysis series. The calibration factor was determined by the ratio of the total area of each sugar unit peak to the area of the internal standard, sorbitol.

7.8 Analysis of solutions

The equipment and methods used in analysis of the model solution and process water samples are presented in Table 7.5. The analyses were done at room temperature. The samples were stored either in a cold room (6°C) or in a freezer before analysis. Solids disturbing the analysis were removed by centrifugation at 500g for 5 minutes.

Table 7.5 Equipment and methods used in analysis of the membrane and water samples.

Analysis	Equipment/method/(manufacturer)
pH	Metrohm 744 pH meter, 25°C (Metrohm, Switzerland)
Conductivity	Knick Konduktometer 703, 25°C (Knick, Germany)
Turbidity	Hach 2100 AN IS Turbidimeter, 25°C (Hach Company, USA)
Total carbon (TC)	Shimadzu TOC-5050A analyser + ASI 5000A autosampler, 680°C, the carrier gas: high purity air 150 mL min ⁻¹ , 2 parallel samplings, deviation < 2% (Shimadzu Corporation, Australia (TOC) and Japan (ASI))
Dissolved organic carbon (DOC)	
Inorganic carbon (IC)	
Anions	Dionex dx-120 chromatograph
Cations	GW AA 860 atomic absorption spectrophotometer
Suspended solids	SFS 3037 standard
Cationic demand	Mütek particle charge detector 02 (Mütek GmbH, Western Germany)
Carbohydrates	A) Anthrone colorimetric method
	B) HP6890 + injector HP7683 (Agilent, former Hewlett Packard, USA)
Wood extractives	A) Varian 3400/3700 + autoinjector Varian 8200 (Varian, Australia) (II)
	B) HP6890 + injector HP7683 (Agilent, former Hewlett Packard, USA) (IV)

7.9 Calculations

Relative flux at steady state was calculated using Eq. (1):

$$J_{rel} = \frac{J}{J_{PWFb}} \quad (1)$$

where J_{rel} is relative flux at steady state, J is sample flux, and J_{PWFb} pure water flux before filtration.

Observed retentions of the species were calculated using:

$$R_{obs} = \left(1 - \frac{c_p}{c_f} \right) \quad (2)$$

where R_{obs} is the observed retention, c_p the concentration in the permeate, and c_f the concentration in the feed.

The pure water flux reduction was calculated using Eq. (3):

$$PWFR = \left(1 - \frac{J_{PWFa}}{J_{PWfb}} \right) \cdot 100\% \quad (3)$$

where $PWFR$ is the pure water flux reduction and J_{PWFa} is the pure water flux after model solution or process water filtration. The pure water flux reduction indicates the amount of irreversible fouling (Fig. 7.7).

Flux decline, i.e. reduction, was calculated using Eq. (4):

$$FR = \left(1 - \frac{J}{J_{PWfb}} \right) \cdot 100\% \quad (4)$$

where FR is the flux reduction.

The amount of reversible fouling, i.e. concentration polarization and/or reversible secondary layer formation, was calculated using Eq. (5):

$$CP = FR - PWFR \quad (5)$$

where CP is the amount of reversible fouling.

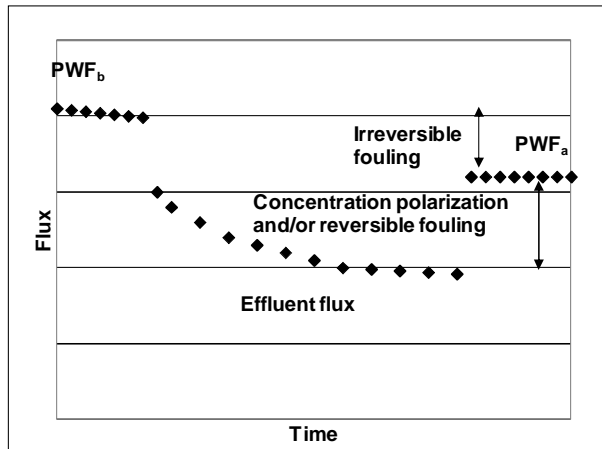


Fig. 7.7 Schematic illustration of concentration polarization and fouling calculation in membrane filtration.

The wood extractives amount in mg m^{-2} if internal standard was added before solid-liquid extraction was calculated using Eq. (6):

$$\frac{\text{Extractives, mg}}{\text{Area, m}^2} = \frac{(\text{Sample peak area})(\text{Standard amount, mg})}{(\text{Standard peak area})(\text{Extracted membrane area, m}^2)} \quad (6)$$

The wood extractives amount in mg m^{-2} if internal standard was added after solid-liquid extraction was calculated using Eq. (7):

$$\frac{\text{Extractives, mg}}{\text{Area, m}^2} = \frac{(\text{Sample peak area})(\text{Standard amount, mg})(\text{Total extract amount, mL})}{(\text{Standard peak area})(\text{Extracted membrane area, m}^2)(\text{Extract sample amount, mL})} \quad (7)$$

The wood extractives amount in liquid samples in mg L^{-1} was calculated from the following equation

$$\text{Extractives} \frac{\text{mg}}{\text{L}} = \frac{(\text{Sample peak area})(\text{Standard amount, mg})}{(\text{Standard peak area})(\text{Sample amount, L})} \quad (8)$$

The fatty and resin acids were determined relative to the peak area of the heneicosanoic acid standard, lignans and sterols relative to betulinol, steryl esters relative to cholesteryl hepradecanoate, and triglycerides relative to 1,3-dipalmitoyl-2-oleoyl glycerol.

The monosaccharide amount in mg m^{-2} was calculated using Eq. (9):

$$\frac{\text{Monosaccharide, mg}}{\text{Area, m}^2} = CF \frac{(\text{Sample peak area})(\text{Standard amount, mg})(\text{Total extract amount, mL})}{(\text{Standard peak area})(\text{Membrane area, m}^2)(\text{Sample amount, mL})} \quad (9)$$

where CF is the calibration factor.

The monosaccharide amount in mg L^{-1} was calculated using Eq. (10):

$$\text{Monosaccharide } \frac{\text{mg}}{\text{L}} = CF \frac{(\text{Sample peak area})(\text{Standard amount, mg})}{(\text{Standard peak area})(\text{Sample amount, mL})} \quad (10)$$

The calibration factor for monosaccharide calculation was calculated using Eq. (11):

$$CF = \frac{(\text{Standard peak area})(\text{Monosaccharide amount, mg})}{(\text{Sample peak area})(\text{Standard amount, mg})} \quad (11)$$

7.10 Validity of results

A problem in evaluation of membrane behavior in fouling is the heterogeneity of the membrane. Membrane coupons, even from the same membrane batch, may differ from each other, and there may be considerable differences between membrane batches. Therefore, the experiments which evaluated the fouling behavior of pulp and paper mill process streams (**III**, **IV**) were repeated three times to get more reliable results of the fouling behavior of the membranes used. Moreover, the experiments were done with the same batch of process water to minimize the variation effect. The batch was divided into one liter bottles, as carefully as possible. Consequently, the variation of feed was reduced to a minimum, but there was still some variation in the feeds between the experiments.

In analysis of wood extractives and polysaccharides, the possibility of analysis error exists when measuring the sample or the standard. An internal standard was used in both analyses to minimize the error.

8 RESULTS AND DISCUSSION

The results and discussion part of this thesis focuses on the identification of wood extractives and hemicelluloses as foulants in the membranes, and the evaluation of the fouling potential and behavior of wood extractives and carbohydrates in membrane filtration of pulp and paper mill process streams.

The results and discussion part begins by considering the model substance filtrations. First, the influence of model substance concentration and filtration conditions on polysaccharide fouling is discussed. Then, the fouling mechanisms for each model substance are evaluated. Finally, fouling in the binary mixture filtrations is compared to fouling in the individual model substance filtrations.

The next section presents the development of a procedure to extract organic foulants from fouled membranes. The optimum extraction time and solvent to extract the highest amount of wood extractives from the fouled membranes are discussed. The influence of membrane material and its characteristics as well as the influence of process water characteristics on fouling by wood extractives are also presented. The results and discussion part ends with a fouling study of carbohydrates.

8.1 Model solution filtrations

Pulp and paper mill process streams are complex mixtures of different compounds and thus it is difficult to estimate the fouling potential of different compound groups. Therefore, polysaccharide model substances that resemble hemicelluloses, polysaccharides found in pulp and paper mill streams, were used in this study to estimate the fouling potential and behavior of hemicelluloses. First, the effect of solute concentration and filtration conditions on flux is discussed. Then, the fouling mechanisms of the polysaccharides used are compared. The model solution section ends by considering binary solution filtrations, which reveal the interactions of the model substances.

8.1.1 Influence of model substance concentration (I)

The flux of the tested NTR-7450 membrane decreased with increased concentration of the polysaccharide model substances, karaya and locust bean gums (I). The Desal-5 DK membrane behaved similarly in NF of locust bean gum, i.e., the flux decreased as the concentration of locust bean was increased. Desal-5 DK behaved differently in NF of karaya gum; the flux was unchanged or it increased slightly as the concentration increased (Fig. 8.1). Nataraj et al. [93] found similar results using regenerated cellulose membranes. They concluded that each model polysaccharide had its own fouling behavior and the feed concentration affected the fouling mechanism. This result is consistent with the results presented here; karaya gum and locust bean gums had different fouling behaviors (Fig. 8.1). Nataraj et al. [93] also concluded that when the concentration of polysaccharide in a model solution increases, its deposition on the membrane surface increases.

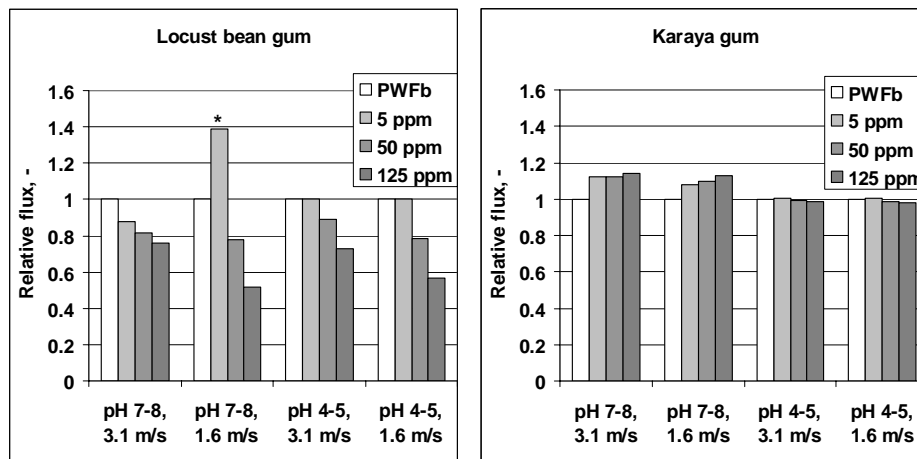


Fig 8.1 Effect of concentration on the relative flux in NF of karaya and locust bean gums with a Desal-5 DK membrane. Concentrations were 5, 50 and 125 mg L⁻¹, the temperature used was 40°C, the pressure was 8 bar, the pH ranges used were 7-8 and 4-5, and the flow velocities 1.6 and 3.1 m s⁻¹.
* There were difficulties in pH adjustment in NF of locust bean at 5 mg L⁻¹, pH 7-8 and 1.6 m s⁻¹.

8.1.2 Influence of filtration conditions

Figures 8.2 and 8.3 show the flux decreases with NTR-7450 and Desal-5 DK membranes due to fouling and concentration polarization in NF of karaya gum and locust bean gum, respectively. Concentration polarization and fouling were calculated according to Fig. 7.7. From Fig. 8.2, it is seen that karaya gum fouled the more hydrophobic membrane

(NTR-7450) irreversibly in both pH ranges and flow velocities used, while the more hydrophilic membrane (Desal-5 DK) was not fouled. On the contrary, its flux increased after karaya filtration at pH 7-8 (Fig. 8.2). The fouling of the NTR-7450 membrane was over two times greater in the lower pH range 4-5. The charge of the NTR-7450 membrane and karaya gum in this pH range is less negative than in the pH range 7-8 (Table 7.2, D). Thus, the higher amount of fouling in the lower pH range can be explained, at least partly, with the smaller repulsion of the NTR-7450 membrane and the karaya gum polysaccharide. The influence of the flow velocity was negligible in NF of karaya gum and there was negligible secondary layer formation on the membrane surface.

Broeckmann et al. [98] also noticed in NF of particulate or microcrystalline cellulose with a hydrophobic PA membrane that neutral to high pH was favorable for polysaccharide filtration.

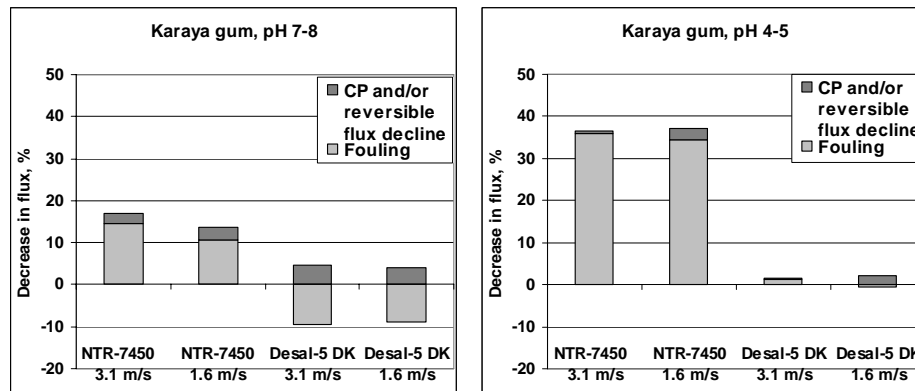


Fig. 8.2 Fouling and concentration polarization of NTR-7450 and Desal-5 DK membranes in NF of karaya gum (125 mg L^{-1}). The temperature used was 40°C , the pressure was 8 bar, the pH ranges used were 7-8 and 4-5, and the flow velocities 1.6 and 3.1 m s^{-1} .

In contrast to the karaya gum filtration, there was secondary layer formation in NF of locust bean gum with the NTR-7450 membrane and the influence of the secondary layer on the flux was greater at lower flow velocity (Fig. 8.3). Even though concentration polarization and/or secondary layer formation was at least two times higher at the lower flow velocity, the irreversible fouling of NTR-7450 membrane was more severe at the higher crossflow velocity used (3.1 m s^{-1}). This phenomenon may be due to the fact that based on the particle size analysis, locust bean gum was broken at higher crossflow

velocities. This lower molar mass locust bean gum may form a more dense gel layer on the membrane surface and, as a result, it is harder to rinse from the membrane surface and fouling of the membrane is more severe.

Broeckmann et al. [98] found similar results in NF of cellulose with a hydrophobic PA membrane. They found that the fouling was more pronounced at the higher crossflow velocity 2 m s^{-1} than at 1 m s^{-1} ; fouling was reversible at lower crossflow velocity but at higher crossflow velocity it was irreversible.

Irreversible fouling was minor for the more hydrophilic Desal-5 DK membrane, but there was significant secondary layer formation at lower crossflow velocity in NF of locust bean gum. Ramamurthy et al. [23] and Persson et al. [73] have claimed that polysaccharides form a gel layer on the membrane surface. It is possible that there was gel layer formation for both membranes at lower crossflow velocity in our study also, because locust bean is used as a gelling agent in the food industry. The influence of pH was negligible in NF of locust bean for both membranes used, which can be explained by the uncharged character of the locust bean gum in the pH ranges used.

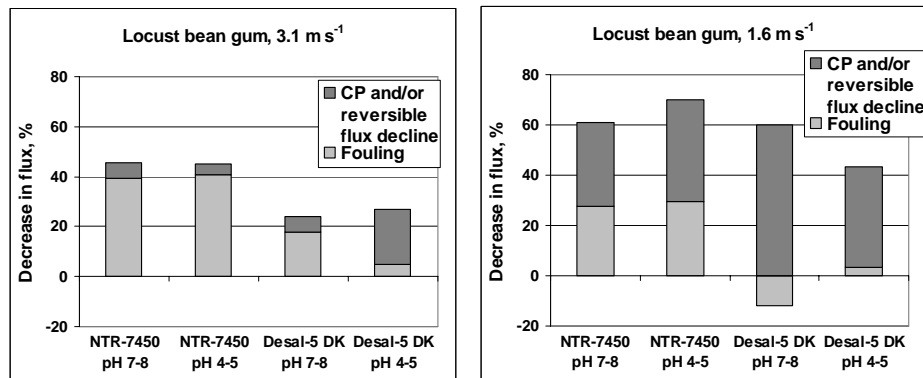


Fig. 8.3 Fouling and concentration polarization of NTR-7450 and Desal-5 DK membranes in NF of locust bean gum (125 mg L^{-1}). The temperature used was 40°C , the pressure was 8 bar, the pH ranges used were 7-8 and 4-5, and the flow velocities 1.6 and 3.1 m s^{-1} .

8.1.3 Adsorption of model substances

Both model substances adsorbed on the membrane surface (Fig. 8.4) but the uncharged locust bean gum was adsorbed more than the negative karaya gum in the adsorption tests. Adsorption was more pronounced for the more hydrophobic NTR-7450 membrane than for the more hydrophilic Desal-5 DK membrane. It is remarkable that the amount of adsorptive fouling (0 bar) in NF of locust bean gums with the NTR-7450 membrane is greater (about 50%, Fig. 8.4) than the fouling at 8 bar (about 30-40%, Fig. 8.3). Since the fouling is more severe in the adsorption test and at higher crossflow velocity (3.1 m s^{-1}), it seems that the formed secondary layer may protect the membrane from adsorptive fouling.

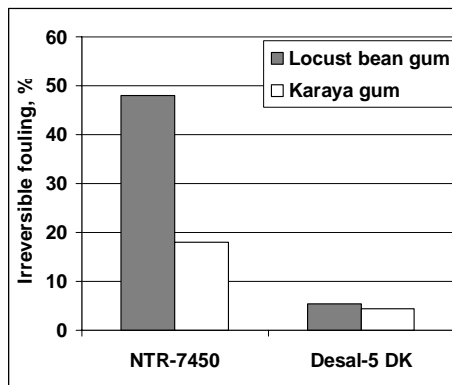


Fig. 8.4 Adsorptive fouling of NTR-7450 and Desal-5 DK membranes with karaya and locust bean gums. Concentration of the foulant 125 mg L^{-1} , pH range 4-5, flow velocity 0.2 m s^{-1} , no applied membrane pressure, 40°C , feed volume 18 L, and adsorption time 18 h.

Susanto and Ulbricht [27] obtained similar results in UF of dextran as a model substance when using one cellulosic and two PES membranes. Their results indicated that dextran was adsorbed on the surface and pores of the PES membranes but not on the cellulosic membrane. The cellulosic membrane was the most hydrophilic of the membranes used when measuring the sessile drop contact angle. The results of this study are consistent with this finding; both polysaccharides used adsorbed more on the more hydrophobic membrane. Jermann et al. [92] and Katsoufidou et al. [95] also noticed that sodium alginate, which was the model substance for polysaccharides in their study, was adsorbed on the hydrophobic PES membranes.

8.1.4 Binary mixture filtrations

Karaya and locust bean gums were filtered together as binary mixtures. Fouling of the NTR-7450 membrane was less severe in filtration of the binary mixtures than in filtration of the model substances separately (Fig. 8.5). Moreover, the influence of flow velocity and pH was insignificant in binary mixture filtrations for the NTR-7450 membrane. On the other hand, fouling of the Desal-5 DK membrane was more severe in binary mixture filtrations in the pH range 4-5. The addition sequence of the model substances was of importance with the Desal-5 DK membrane; there was more irreversible fouling if karaya gum was added first. All the results above suggest that the membranes used had different fouling mechanisms and the polysaccharides interact, affecting fouling.

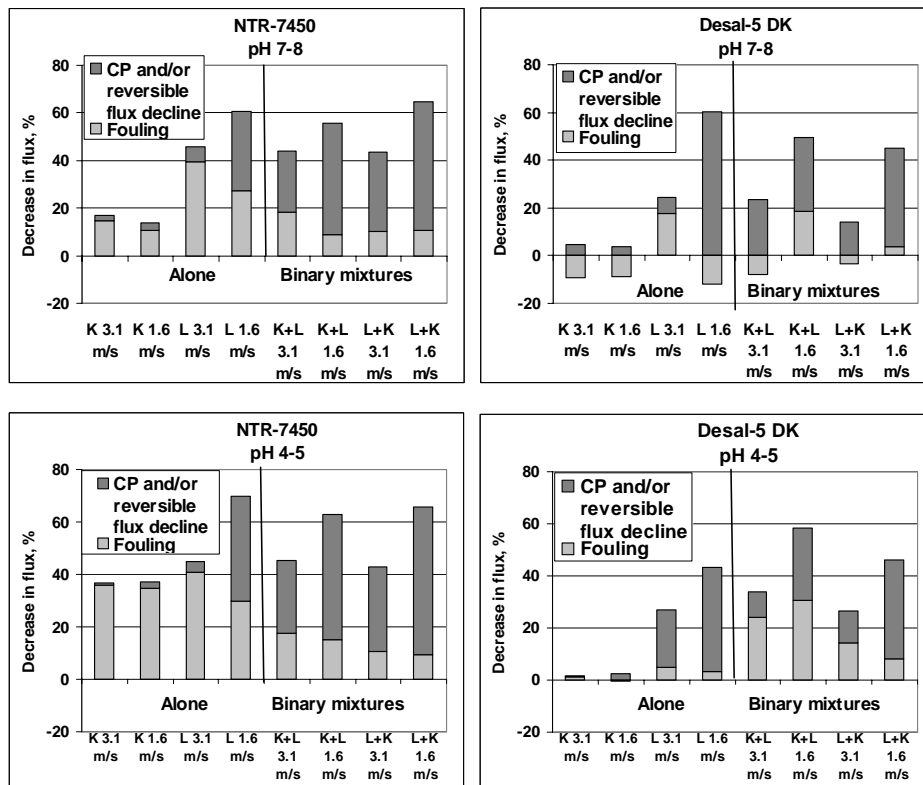


Fig. 8.5 Fouling and concentration polarization of NTR-7450 and Desal-5 DK membranes with karaya (K) and locust bean (L) gums and their binary mixtures. Concentration of the model substance was 50 mg L^{-1} , and the pH range used 4-5 and 7-8, feed volume 8 L, flow velocities 3.1 and 1.6 m s^{-1} , temperature 40°C , and pressure 8 bar.

8.1.5 Conclusions

The model solution filtrations performed in the thesis revealed that each polysaccharide has its own fouling mechanisms and the mechanism depends on the membrane used. The charge of the polysaccharide and the membrane used has influence on the fouling. Moreover, polysaccharides can foul the membranes by adsorption, and not only by gel and/or cake layer formation on the membrane surface. In binary mixture filtrations, polysaccharides interact, which makes fouling evaluation of certain compound groups extremely challenging.

8.2 Comparative analysis of the pulp and paper mill process streams filtered

Three different pulp and paper mill effluents were used in the filtration experiments. The characteristics of the process effluents used (Table 8.1) differ from each other remarkably, e.g. conductivity is 15-fold higher in the hardwood+softwood process water than in the GWM process water. The GWM process water is a mixture of acidic paper machine water, pressure ground wood (PGW) water and stone ground wood (SGW) water from mechanical pulping. Its characteristics, however, indicate that it contains mostly paper machine water and the amount of mechanical pulping water is negligible. When the chemithermomechanical (CTMP) process water samples were collected at the mill site, it was expected that one process water would originate from softwood (e.g. spruce, pine) and the other from hardwood (e.g. aspen, birch) pulping. However, analysis of the wood extractives composition of the CTMP process effluent revealed that also the hardwood process water contained resin acids. Therefore, the hardwood process water used must originate from a pulping process using a mixture of hardwood and softwood because hardwood should be free from resin acids. Thus, water analysis may reveal knowledge of the wood used in pulp and paper mill processes.

The pH of the process effluents is similar but the total carbon amount is tenfold and twentyfold and the turbidity is 30-fold and 45-fold greater in the hardwood+softwood and the softwood process effluents than in the GWM process water, respectively. The higher turbidity indicates that the hardwood+softwood and softwood process effluents contain more colloidal substances or fines than the GWM process water. The TOC content of the GWM process water (400 mg L^{-1}) was less than in reviewed pulp and paper mill streams (TOC $770\text{-}5670 \text{ mg L}^{-1}$ [38-41]) while the hardwood+softwood process water contained more TOC (8300 mg L^{-1}).

Table 8.1 Characteristics of the pulp and paper mill effluents used in the filtrations. The groundwater mill (GWM) circulation water contained mainly paper machine white water, the chemithermomechanical pulp (CTMP) process streams originated from softwood and hardwood+softwood pulping.

Parameter	GWM ^a (II)			Softwood ^b (III, IV)			Hardwood+softwood ^b (III, IV)		
	Average±sd	Range (min-max)	Average±sd	Range (min-max)	Average±sd	Range (min-max)	Average±sd	Range (min-max)	
pH, -	5.4±0.5	4.7-6.4	6.1	6.09-6.12	6.4	6.38-6.42			
Conductivity, mS cm ⁻¹	0.8±0.4	0.1-2.1	5.2±0.1	5.1-5.3	14±5	12-21			
Turbidity, NTU	200±140	65-560	5800±2100	4400-9700	9200±2000	6900-11500			
Total carbon (TC), mg L ⁻¹	400±90	200-560	4300±400	3800-4700	8300±400	8000-8900			
Carbohydrates ^c , mg L ⁻¹	260±72	94-390	970±130	820-1100	1200±200	1000-1400			
Cationic demand, µeq g ⁻¹	NA	NA	3.4±0.1	3.2-3.5	11±0.6	10-11			
Fatty acids, mg L ⁻¹	3.3±3.2	0.9-17	300±150	110-420	130±60	60-210			
Resin acids, mg L ⁻¹	3.3±1.2	1.3-6.1	560±180	330-770	410±140	270-570			
Lignans, mg L ⁻¹	38±7.7	20-53	61±19	45-90	60±30	28-110			
Sterols, mg L ⁻¹	1.6±0.7	0.3-3.1	17±8	11-28	20±7	11-30			
Steryl esters, mg L ⁻¹	4.5±0.8	2.2-5.8	270±35	230-320	620±130	460-770			
Triglycerides, mg L ⁻¹	2.7±1.7	0.6-7.4	500±47	450-540	500±100	410-630			
Lipophilic extractives, mg L ⁻¹	15±3.9	8.5-25	1600±400	1100-2100	1700±400	1300-2200			
Ca ²⁺ , mg L ⁻¹	17±4	14-24	NA	NA	NA	NA			
Cl ⁻ , mg L ⁻¹	6.2±2.0	4.3-9.1	NA	NA	NA	NA			
SO ₄ ²⁻ , mg L ⁻¹	210±90	150-360	NA	NA	NA	NA			

^a 30 samples, in Ca²⁺, Cl⁻, SO₄²⁻ analysis 5 samples

^b 6 samples, ^c Anthrone method

sd standard deviation NA not analyzed

The cationic demand of the hardwood+softwood process water is threefold that of the softwood process water. Fatty and resin acids are negatively charged but the difference in cationic demand between the process effluents cannot be explained by the amount of fatty and resin acids, because hardwood contains less fatty and resin acids and its cationic demand is higher. Therefore, the difference in cationic demand may be due to the hemicelluloses. Hemicelluloses in the unbleached TMP Norway spruce suspension (softwood) are mainly neutral wood polymers [3] while in the hardwood process water samples the dominant non-cellulosic polysaccharide is a partly acetylated acidic xylan called O-acetyl-(4-O-methylglucurono)xylan [48, 69, 70], which is anionic. Thus, the difference between the cationic demand of the process effluents may be due to their different hemicellulose content.

In this study, wood extractives were divided into six different groups: fatty acids, resin acids, lignans, sterols, steryl esters and triglycerides according to the analysis method used [33]. All but lignans are lipophilic extractives. The amount of fatty and resin acids was higher in the softwood process water than generally found in pulp and paper mill process streams (3-432 mg L⁻¹ [24, 31, 32, 39, 40, 42]). The total amount of lipophilic extractives was about 1650 mg L⁻¹ for the softwood and hardwood+softwood process effluents used, while the GWM process water contained 15 mg L⁻¹ lipophilic extractives. The composition of the wood extractives also varied; the softwood process water contained more fatty and resin acids, while the hardwood+softwood process water contained more steryl esters. In addition, the hardwood+softwood process water contained more fines, which was seen by the fact that the amount of wood extractives was the same but its turbidity was higher than the turbidity of the softwood process water.

The carbohydrate content of the softwood and hardwood+softwood process effluents were quite similar (Table 8.2). The only monosaccharide whose content differed remarkably in the process effluents is xylose; there was threefold more xylose in the hardwood+softwood process water than in the softwood process water. The result is expected because the principal hemicellulose in hardwood is O-acetyl-(4-O-methylglucurono)xylan [48, 69, 70]. Moreover, the variation of the process water content was significant, even though the effluents are from the same batch. This

process water variation simulates well the real situation at a pulp and paper mill site, but it makes a comparison of the filtration experiments challenging.

Table 8.2 shows that the carbohydrate content analyzed with the fast and easy anthrone method was quite similar to the carbohydrate content without galacturonic and glucuronic acids analyzed with the time-consuming GC. Thus, the anthrone method may be used to estimate roughly the total carbohydrate content in the samples, at least with the effluents used here.

Table 8.2 Carbohydrates of the the chemithermomechanical pulp (CTMP) process streams originated from softwood and hardwood+softwood pulping.

Parameter	Softwood ^a	Hardwood+softwood ^a		
	(III, IV)	Range (min-max)	Average±sd	Range (min-max)
Anthrone method:				
Carbohydrates, mg L ⁻¹	970±130	820-1100	1200±200	1000-1400
GC:				
Arabinose, mg L ⁻¹	70±10	70-100	110±13	99-120
Galactose mg L ⁻¹	180±40	110-210	180±20	160-210
Galacturonic acid, mg L ⁻¹	470±100	340-570	590±50	530-620
Glucose, mg L ⁻¹	290±40	230-320	330±17	320-350
Glucuronic acid, mg L ⁻¹	19±8	10-27	26±13	12-37
Mannose, mg L ⁻¹	510±80	390-570	260±260	110-570
Rhamnose, mg L ⁻¹	29±9	20-40	55±25	30-80
Xylose, mg L ⁻¹	37±18	23-63	110±70	37-150
TOTAL, mg L ⁻¹	1600±300	1200-1900	1700±110	1600-1800
TOTAL without uronic acids, mg L ⁻¹	1100±200	810-1300	1100±50	1060-1150

^a 6 samples
sd standard deviation

8.3 Wood extractives

Wood extractives are mentioned many times as potential foulants in the filtration of pulp and paper mill streams [23-25] but analysis and identification of wood

extractives as foulants [63, 86] (**II**) is limited due to the complexity of the process streams. Therefore, a procedure for the extraction of organic foulants from fouled membranes and the analysis of such foulants was developed in this study. In this section, a typical gas chromatogram of the wood extractives is first presented. Then optimization of the extraction procedure to extract the highest amount of wood extractives from the fouled membranes, i.e. the influence of extraction solvent and time, is discussed. The wood extractives section ends with a comparison of the amount of different wood extractives compound groups on the different membranes and analysis of how the process water and membrane characteristics affect the fouling potential of wood extractives.

8.3.1 Gas chromatogram of wood extractives

Figure 8.6 presents a typical gas chromatogram of the acetone:water extracts of a RC membrane C30F. These analyzed wood extractives account for most of the wood extractives present in the process streams [1]. There is an unknown peak at about 19 minutes, whose carbon number is about 40. This peak does not appear in typical chromatograms of wood extractives analyzed from process streams. It can thus be concluded that this peak originates from the membrane.

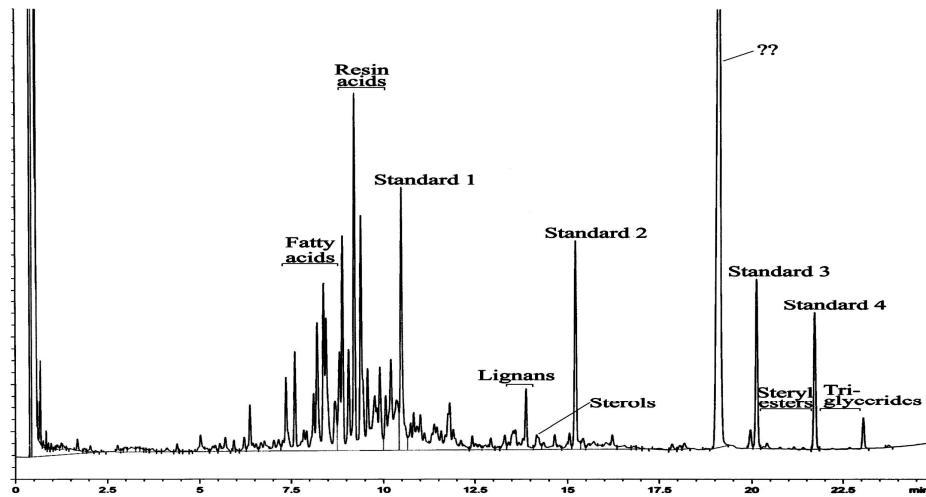


Fig.8.6 Typical gas chromatogram of the acetone or acetone-water extracts of RC membrane C30F. Standard 1, heneicosanoic acid; Standard 2, betulinol; Standard 3, cholesteryl heptadecanoate; Standard 4, 1,3-dipalmitoyl-2-oleyl glycerol. (From Paper **II**)

8.3.2 Optimization of membrane extraction (II)

First, Soxhlet type extraction was tried as such for the isolation of wood extractive foulants from the membranes. The aim was to specifically extract wood extractives and to obtain qualitative results. The preliminary results showed that it is possible to extract wood extractives from the membranes and thus, the extraction procedure for membrane analysis was developed further. To develop a viable procedure, the optimum extraction solvent and time for acquisition of the highest amount of wood extractives from the fouled membranes were first evaluated. The optimization was done with two different membranes, C 30F and PA 50H, to establish whether different extraction procedures are needed for different membrane materials. The samples were extracted at 160°C in a series-extractor for 1, 2, and 4 hours to evaluate the optimum extraction time for the membranes. The optimum extraction time was tested with four different solvents: acetone, acetone-water solution (9:1), hexane, and MTBE. An internal standard was added to all samples before extraction to avoid errors in sampling.

Membrane samples of 0.004-0.008 m² sizes were used. The solvent amount was 50 mL. After each extraction, 5 mL samples were withdrawn from each of the basic vessels. They were then dried, diluted with 4 mL of RO water and finally extracted a second time with liquid-liquid extraction as described in chapter 9.7.2. In the liquid-liquid extraction, no more standard solution was added.

After extraction in a series-extractor, the solvent was removed and the membrane samples were dried. To verify that no wood extractives were left in the membrane samples, the samples were re-extracted with 35 mL of the solvent and 1 mL of the standard solution. 5 mL samples were taken after 1 and 2 hours and treated as described earlier (chapter 7.7).

8.3.2.1 Optimum solvent and extraction time

Four different solvents, acetone, acetone:water (9:1), hexane and MTBE, were tested in the extraction of wood extractives from the membrane fouled in UF of GWM water. An acetone:water (9:1) solution is an effective and better solvent than acetone for wood resin components [107]. Acetone extracted more lipophilic extractives than

acetone:water solution, although acetone:water also extracted lipophilic extractives at high amounts (Fig. 8.7). Moreover, more lignans were extracted with acetone:water (Fig. 8.7). The tested solvents, hexane and MTBE, were unsuitable for the membrane extraction because of noise, possibly originating from the membrane material, especially in the GC chromatograms of the PA membranes, which interfered with the interpretation of the results. Fatty acids and resin acids were present in the samples but some other compounds were also present, which were not identified and which had the same retention time in silylated form as fatty and resin acids. Moreover, it is possible that the amount of lignans in the solid-liquid extractions with hexane is not fully correct and that part of the response comes from degraded membrane material; hexane should extract only lipophilic extractives not lignans. It can therefore be concluded that milder solvents such as acetone or acetone-water solution should be used.

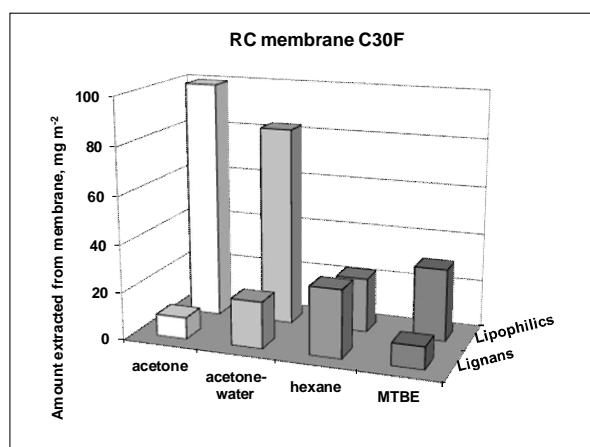


Fig. 8.7 Influence of the extraction solvent on the lipophilic extractives and the lignan -contents of the RC membrane C30F after a 30-day filtration of GWM circulation water in an integrated pulp and paper mill. Solid-liquid extraction is done with a Soxhlet type extraction and followed by liquid-liquid extraction.

It was found that if the extracted membrane area was 0.008 m², 1 hour was enough to extract most of the lipophilic extractives and lignans out of the membranes (Fig. 8.8). The extraction time was the same with both the acetone and the acetone-water solution (9:1). In Fig.8.8, the values are tenfold bigger than in Paper II, Fig. 5, due to a calculation error in Paper II, Fig. 5.

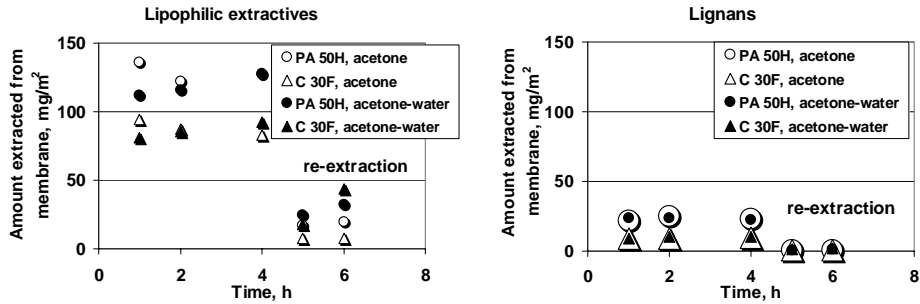


Fig. 8.8 Influence of the extraction time on lipophilic extractives and lignan - contents of the C 30F and PA 50H membranes after a 30-day filtration of GWM circulation water in an integrated pulp and paper mill. Solid-liquid extraction is done with Soxhlet type extraction followed by liquid-liquid extraction. (II)

8.3.2.2 Simplification of membrane extraction (II)

The membrane extraction procedure was simplified by extracting the fouled membranes in test tubes. In these experiments, the membrane samples were extracted in test tubes with acetone:water, MTBE and hexane, without heating. Membrane samples of 0.00086 m² size were cut into small pieces and put in the test tubes with 5 mL of solvent and 0.5 mL of standard solution. The test tubes were vigorously shaken by machine for 1 hour. The obtained samples were further handled as described in chapter 7.7.

The results (Fig. 8.9) showed that lipophilic extractives are extracted to a lesser degree in simple extraction than in Soxtec extraction. Thus, the simplification of the extraction procedure is not recommended if it is important to know the quantitative amount of wood extractives, but if knowledge of the wood extractives needs only to be qualitative in nature, then the simplified extraction procedure could be used.

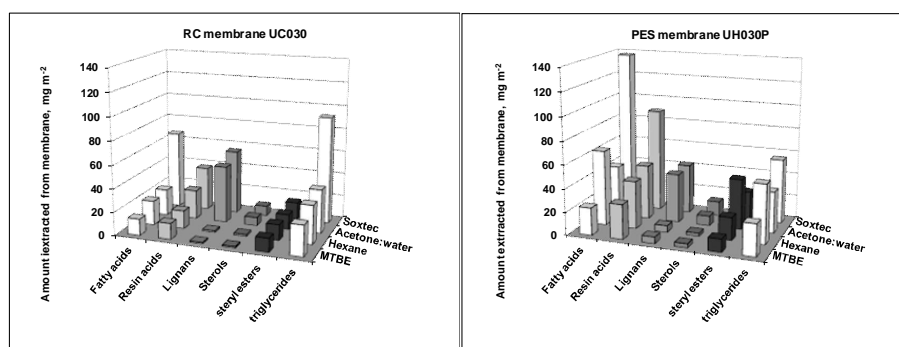


Fig. 8.9 Influence of the extraction procedure on lipophilic extractives and lignan -contents of the RC membrane UC030 and the PES membrane UH030P after filtration of softwood process water in an Amicon filter, 2 bar, 40°C, 1.3 m s⁻¹. The extraction procedure was Soxtec acetone:water (9:1 v/v) extraction or shaking with MTBE, hexane or acetone:water in test tubes for 1 hour, followed by liquid-liquid extraction.

8.3.3 Extractives-induced fouling and membrane material

Fig. 8.10 shows the wood extractives found in membranes after a 30-day test run in filtration of GWM circulation water in an integrated pulp and paper mill. Fig. 8.10 shows that especially resin and fatty acids were found in the membranes, but some lignans and traces of sterols were also found. Steryl esters and triglycerides were only found from the regenerated cellulose membrane C30F. The polymeric membranes PA 50H and PES 50H contained more wood extractives as foulants than the regenerated cellulose membrane C 30F. One reason for this could be the hydrophobic nature of the PA 50H and PES 50H membranes; the RC membrane C 30F is the most hydrophilic of these membranes [74]. As resin and fatty acids are fairly hydrophobic compounds, they prefer to adhere to the hydrophobic materials.

If fractionation of the colloidal and dissolved wood extractives is done with a filter which has a pore size of less than 0.1 μm (Table 4.1, [3, 44, 47]) about 5-10% of the wood extractives are dissolved in the TMP process streams. These dissolved wood extractives include only lignans, sterols and fatty and resin acids. As was explained in chapter 4.1 colloidal resin particles are composed mainly of steryl esters and triglycerides, which are the most hydrophobic components of the wood extractives [46]. Steryl esters and triglycerides form the hydrophobic core, while smaller amounts of sterols and free fatty and resin acids form the thin surface layer of the particle [46,

52]. It seems, thus, that the dissolved wood extractives mostly fouled RC, PA and PES membranes used, not the colloidal ones, because the fatty and resin acids were the major compounds in all the fouled membranes. However, the RC membrane C30F was fouled partly also by colloidal wood extractives, because traces of steryl esters and triglycerides were found. Furthermore, the pore size of these RC, PA and PES membranes was so small (cut-off value of 30-50 kg mol⁻¹) that the colloidal wood extractives (size 0.1-2 µm) cannot penetrate into the membranes, whereas dissolved wood extractives (size < 0.1 µm) can. A reason for the colloidal fouling of the RC membrane C30F could be its hydrophilicity. Colloidal particles are stabilized sterically by especially acidic hemicelluloses [46, 54-56] and the hydrophilic part of the fatty and resin acids are on the colloid surface. Thus, these hydrophilic parts of hemicelluloses and fatty and resin acids could prefer to adhere to the hydrophilic surfaces.

More fatty acids than resin acids were found from the membranes after filtration of the GWM process water (Fig. 8.11). The result is consistent with the study of Carlsson et al. [63]. Based on ATR-FTIR spectra, they presented that there were fatty rather than resin acids in membranes fouled in filtration of PSFP pulp mill effluent. Their analysis was, however, only qualitative. Their effluent had a similar pH to the GWM process water in this study. It contained 432 mg L⁻¹ of fatty and resin acids while our GWM process water contained less than 10 mg L⁻¹. As in this research, their membranes were fouled at a mill site.

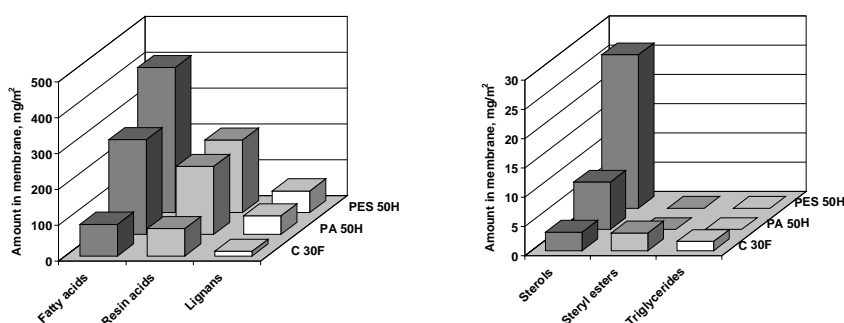


Fig. 8.10 Wood extractives found in C 30F (RC), PA 50H and PES 50H membranes after a 30-day test run in an integrated pulp and paper mill with GWM process water. Extraction was done with a series extractor and the solvent used was an acetone-water solution (9:1). The analyzed membrane area was 0.0314 m². (II)

8.3.4 Influence of membrane characteristics and process water

Softwood and hardwood+softwood process effluents contain the same amount of lipophilic extractives (Table 8.1) but have different extractives composition. Thus, if only the amount of wood extractives affects membrane fouling, the process effluents should perform similarly. The process effluents, however, performed differently, which indicates that the composition of the wood extractives and/or the composition of other compounds in the process effluents are meaningful in membrane fouling. As wood extractive particles are stabilized by hemicelluloses (Fig. 4.1) [53], it is possible that the amount of hemicelluloses and their composition also influence membrane performance. Fig. 8.11 presents the amount of extractives found from the fouled membranes at three different filtration pressures, 0, 1 and 2 bar.

Extractives-induced fouling is remarkable already at 0 bar pressure, which indicates that adsorption is the main fouling mechanism in extractives-induced fouling (IV). It seems that at least 50% of the fouling is due to adsorption of wood extractives on the membrane matrix (Fig. 8.11). Over 60% of this adsorptive fouling is due to fatty and resin acids, and moreover, resin acids fouled the membranes more than fatty acids. This result contradicts results from an earlier study (II, Fig. 3) and also deviates from the study of Carlsson et al. [63]; both study (II) and Carlsson et al. [63] found that there were fatty rather than resin acids in the fouled membranes. The effluent of Carlsson et al. [63] had a similar pH (above 5) to the GWM process water used in this

study. However, their effluent contained 430 mg L^{-1} of fatty and resin acids while the GWM process water contained less than 10 mg L^{-1} .

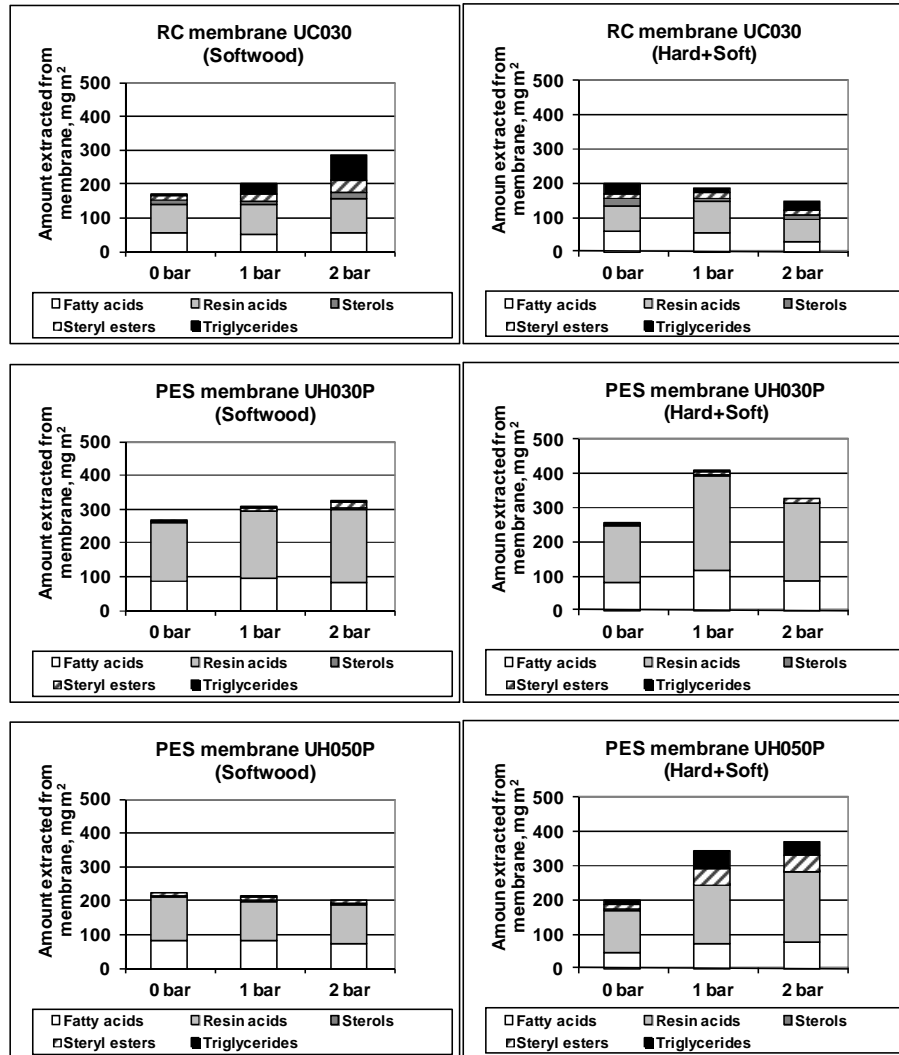


Fig. 8.11 Average amount of wood extractives found in UC030, UH030P and UH050P membranes after UF of softwood and hardwood+softwood process effluents. Filtrations were performed at 40°C at pressures 0, 1 and 2 bar. The membrane area was 0.004 m^2 . There are three replicates of each filtration. UC030 is RC membrane and UH030P and UH050P are PES membranes. (IV)

In both studies (II and Carlsson et al. [63]) the analyzed membranes were fouled at a mill site, and thus, the membranes were in contact with a significant amount of

foulants. However, in UF of softwood and hardwood+softwood, the UF was done in a batch mode (IV). The pH of the process effluents was a little higher (above 6) than in our earlier study (II) and study of Carlsson et al. [63] and the fatty and resin acid amount was 300 mg L^{-1} and 560 mg L^{-1} in softwood, and 130 mg L^{-1} and 410 mg L^{-1} in hardwood+softwood (Table 8.1), respectively. The amount of resin acids was higher than the amount of fatty acids in these effluents, which can explain the higher fouling potent of resin acids. Another reason for the difference in fouling potent of these wood extractives could be their degree of dissociation. Because resin acids have colloidal pK_a values of about 6, which are lower than the pK_a values for fatty acids, they are more dissociated in softwood and hardwood+softwood process effluents (pH over 6) than in GWM process water (pH 5.4) [58]. Thus, more of them are in dissolved form, which makes them potential foulants for the membranes according to study (II).

In UF of softwood process water, the membrane characteristics had an influence on fouling because the wood extractives composition in the two fouled PES membranes (UH030P and UH050P) was similar, but the composition was clearly different in the fouled RC membrane UC030 (Fig. 8.11). This indicates that the membrane hydrophilicity and/or the material were the reasons for the difference in fouling behavior and foulant composition. Moreover, the lower cut-off value PES membrane UH030P contained more resin acids than the higher cut-off value PES membrane UH050P.

The higher the pressure used the more steryl esters and triglycerides were found from the RC membrane (Fig. 8.11), which means that colloidal extractives-induced fouling was more pronounced at high pressure. The amount of fatty and resin acids was similar at all the pressures used. In UF of hardwood+softwood process water using the PES membrane UH050P there were also more steryl esters and triglycerides in the membranes at higher pressures.

The composition of wood extractives found in the membrane was unique for each membrane used in UF of hardwood+softwood process water (Fig. 8.11). This indicates that the membrane material and/or the hydrophilicity were not the only parameters which influenced fouling. Moreover, there was colloidal fouling in the RC

membrane and in the higher cut-off value PES membrane UH050P at all pressures used because steryl esters and triglycerides were found in these membranes. The colloidal fouling of the PES membrane UH050P was less pronounced if no pressure was used in the filtration. This indicates that colloidal fouling depended possibly on membrane roughness and charge, because the RC membrane UC030 and the PES membrane UH050P were the roughest membranes used and they had the least negative surface charges (III, Table 3). However, strong conclusions cannot be drawn because the differences in surface charges and roughness values are minor. The PES membrane UH030P was fouled similarly by wood extractives in UF of softwood and hardwood+softwood process effluents because the fouled membranes contained mostly fatty and resin acids.

Fig. 8.12 shows wood extractives found in the membranes after UF of three different process effluents. With the GWM process water, the amount of lipophilic extractives was 100 times lower than in softwood and hardwood+softwood process effluents. It should, however, be noted that it was filtered for 30 days in a pilot plant study while the other two process effluents were filtered on a laboratory-scale and in batch-mode. Thus, in the UF of GWM process water, the membranes have been in touch with a significant amount of wood extractives even though their content in the process water was low. In spite of the fact that the filtration procedure and the process effluents are different, a trend can be seen in Fig. 8.12 that the RC membrane was less fouled than the PES membrane and the major wood extractive groups found in the membranes were fatty and resin acids.

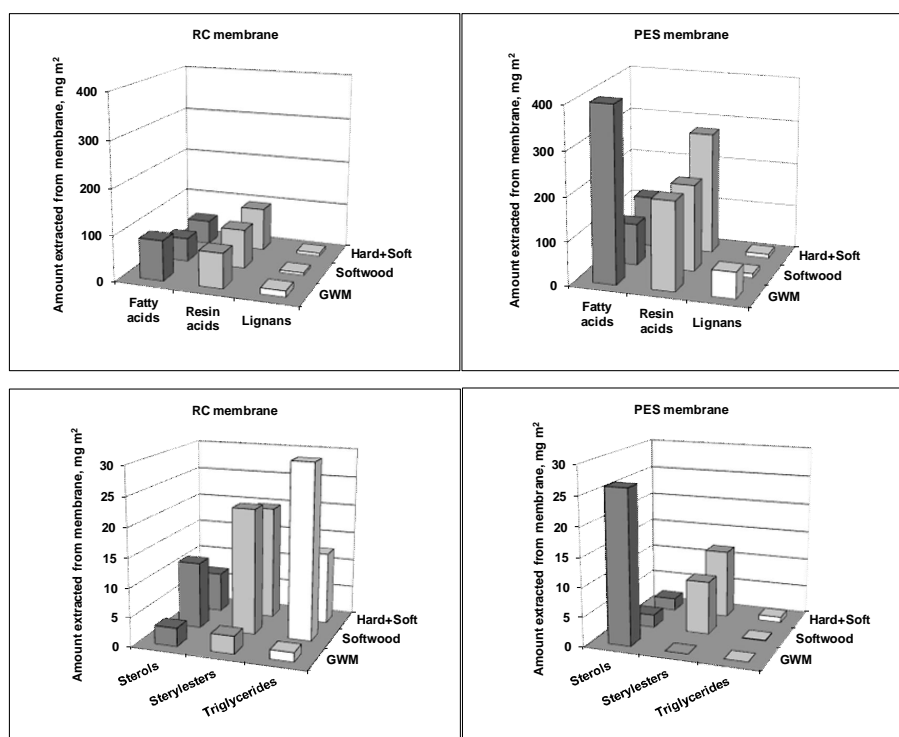


Fig. 8.12 Amount of fatty and resin acids, lignans, sterols, steryl esters and triglycerides found in the RC and PES membranes after UF of GWM, softwood and hardwood+softwood process effluents. GWM process water was used in pilot plant studies for 30 days (1 bar, 46-78°C) while softwood and hardwood+softwood process water filtrations were performed at a laboratory-scale in batch mode (1 bar, 40°C). (II, IV)

8.3.5 Correlation of extractives-induced fouling with other parameters

The correlation between the amount of wood extractives extracted from membrane and fouling was studied. The correlation between the amount of wood extractives extracted from membrane and pure water flux decline, pure water flux before filtration and the contact angle of the fouled membranes was investigated. A correlation was found between wood extractives and irreversible fouling, i.e. pure water flux decline, (Fig. 8.13) only for the RC membrane UC030 in UF of softwood process effluents and the PES membrane UH030P in UF of hardwood+softwood process water. For the UC030 membrane, an increasing amount of fatty and resin acids found in the fouled membrane decreased fouling, while for the UH030P membrane, the situation was the opposite; an increased amount of fatty and resin acids in the fouled membrane increased fouling. For the other membranes, it was

impossible to find any correlation between fouling (i.e. pure water flux reduction and contact angle) and the amount of wood extractives in the fouled membrane. This may be due to other foulants, such as hemicelluloses or lignins, in the fouled membranes.

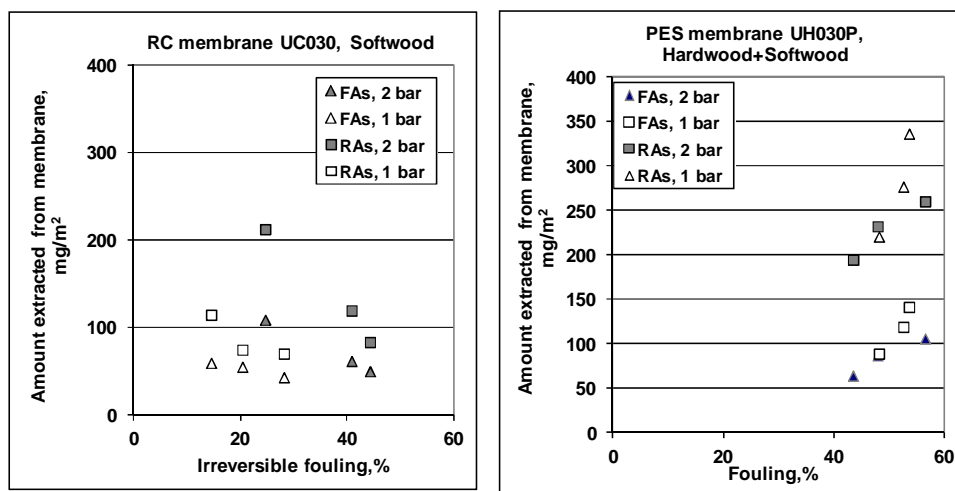


Fig. 8.13 Correlation between irreversible fouling and the amount of fatty (FAs) and resin acids (RAs) found in fouled membranes for the RC membrane UC030 in UF of softwood and for the PES membrane UH030P in UF of hardwood+softwood process effluents. (III, IV)

8.3.6 Conclusions

On the basis of the results presented above, the following conclusions can be drawn. Acetone:water (9:1 v/v) was the most effective solvent of the four solvents tested for the extraction of lipophilic extractives and lignans from membranes fouled in the filtration of pulp and paper mill streams. It extracted lignans well and extracted large amounts of lipophilic extractives. Moreover, one hour was enough to extract the wood extractives using Soxtec extraction for membrane samples with an area of 0.008 m². The hydrophilic RC membrane contained less wood extractives than the hydrophobic PES and PA membranes. Dissolved fatty and resin acids were mostly the reason for the fouling, and fouling by colloidal wood extractives was negligible. Furthermore, it was impossible to find any correlation between fouling, i.e. pure water flux reduction, contact angle and the amount of wood extractives in the fouled membrane.

8.4 Hemicelluloses

Since polysaccharides can adsorb on the membranes (I) [27, 90, 92, 93, 95, 96], hemicelluloses were characterized as monosaccharide and uronic acid units from the membranes fouled in UF of pulp and paper mill process effluents in this thesis. FTIR analysis of the fouled membranes in UF of softwood and hardwood+softwood process effluents indicated that the fouling layer contained hemicelluloses (the glycosidic bond C-O-C was seen in the spectra). Thus, qualitative analyses were made from acetone:water extracts of the fouled membranes to verify hemicelluloses as foulants in the membranes. Monosaccharide units of the hemicelluloses were also identified directly by performing acid methanolysis for the fouled membranes.

In the following section, a typical gas chromatogram of monosaccharide and uronic acid units is first presented. Monosaccharide and uronic acid unit analysis of the acetone:water extract and their adsorptive fouling are then discussed. The influence of process water and membrane characteristics on monosaccharide and uronic acid unit fouling is also discussed. The hemicellulose section ends with a comparison of two methods to isolate hemicelluloses from membranes for monosaccharide and uronic acid unit analysis; acetone:water extraction, and direct acid methanolysis of fouled membranes.

8.4.1 Gas chromatogram of monosaccharides

A typical gas chromatogram of the monosaccharide and uronic acid units is illustrated in Figure 8.14. In each sample series, a standard solution containing a known amount of monosaccharides and uronic acids was analyzed to calculate the calibration factor. Sorbitol was used in each sample as the internal standard.

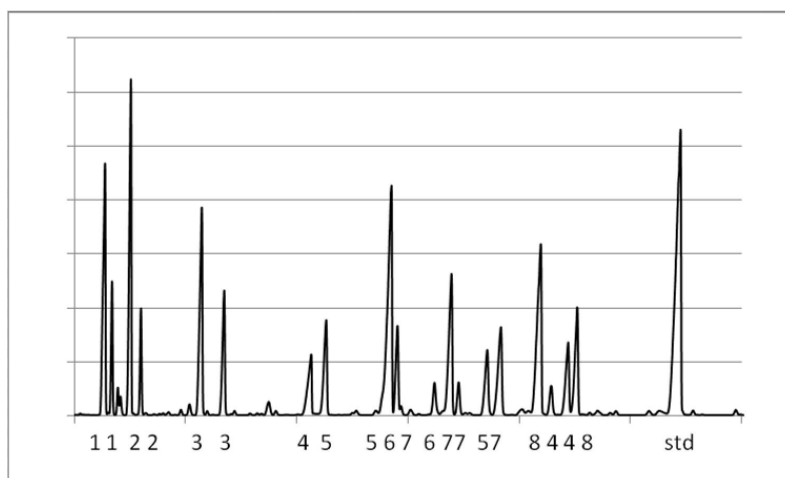


Fig.8.14 Typical gas chromatogram of monosaccharides and uronic acids. 1. arabinose, 2. rhamnose, 3. xylose, 4. glucuronic acid, 5. galacturonic acid, 6. mannose, 7. galactose, 8. glucose and std is sorbitol.

8.4.2 Monosaccharide and uronic acid analysis of acetone:water extract

The carbohydrate content of the acetone:water extract obtained from Soxtec extraction was analyzed by GC. The results showed that acetone:water (9:1 v/v) extracts contained carbohydrates from the membranes. The GC chromatograms of the acetone:water extracts of the RC membrane UC030 contained more glucose than expected, which indicates that membrane material, regenerated cellulose, was also broken down in the acid methanolysis (Fig. 8.15). As a result, it is impossible to analyze glucose quantitatively from RC membranes using this method. It is also not possible to analyze the amount of glucuronic acid because the glucose peaks overlap with the glucuronic acid peaks and, thus, the amount of glucuronic acid presented by the chromatogram is skewed by the glucose. However, all the other monosaccharide and galacturonic acid units can be analyzed quantitatively from the fouled RC membranes (Fig 8.16). The amount of xylose units in the membrane fouled with softwood process water is surprisingly high compared to the membrane fouled with hardwood+softwood process water because softwood water contains one third of the xylose units of hardwood+softwood process water. The analysis procedure of hemicelluloses in this thesis was not optimized, thus, the results can only be considered to provide an estimation of the amount of xylose in the membranes.

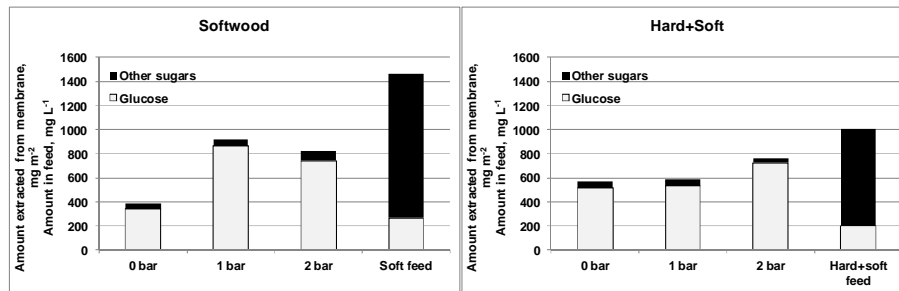


Fig.8.15 Average glucose, analyzed monosaccharide and uronic acid content in the RC membrane UC030 and in the feed in UF of softwood and hardwood+softwood process effluents. Filtrations were performed at 40°C at pressures of 0, 1 and 2 bar. The membrane area was 0.004 m². There are three replicates of each filtration.

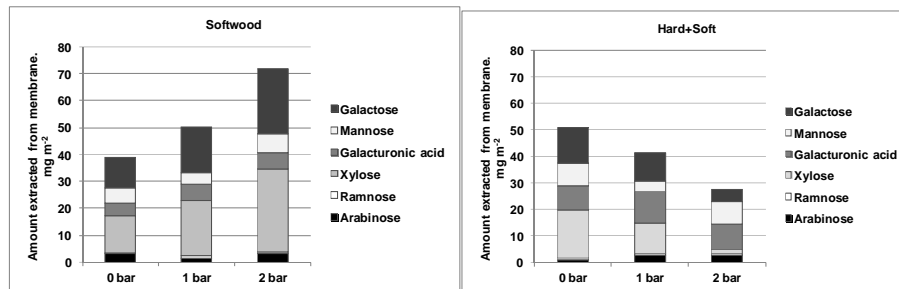


Fig.8.16 Average monosaccharide and galacturonic acid units content in the RC membrane UC030, excluding glucose and glucuronic acid units. Filtrations were performed at 40°C at pressures of 0, 1 and 2 bar. The membrane area was 0.004 m². There are three replicates of each filtration.

8.4.3 Adsorptive fouling caused by hemicelluloses

There was adsorptive fouling of carbohydrates in all the membranes used in filtration of softwood and hardwood+softwood process effluents (Fig. 8.17). However, the amount of monosaccharide and uronic acid units in the fouled membranes was significantly lower (softwood about 45 mg m⁻², hardwood+softwood 20-50 mg m⁻²) than the amount of wood extractives (softwood 180-280 mg m⁻², hardwood+softwood 150-380 mg m⁻²) (IV, Fig. 2). Thus, carbohydrates do not have the same potential as foulants as wood extractives. Fig. 8.17 also shows that the process water characteristics had an influence on the fouling because the membranes used fouled differently in UF of the softwood and the hardwood+softwood process water. In UF of the softwood process water, xylose and galactose units were found from all the membranes used, while in UF of hardwood+softwood process water they were found

remarkably only from the RC membrane. Moreover, the RC membrane UC030 contained more mannose and galacturonic and glucuronic acid units than the PES membranes.

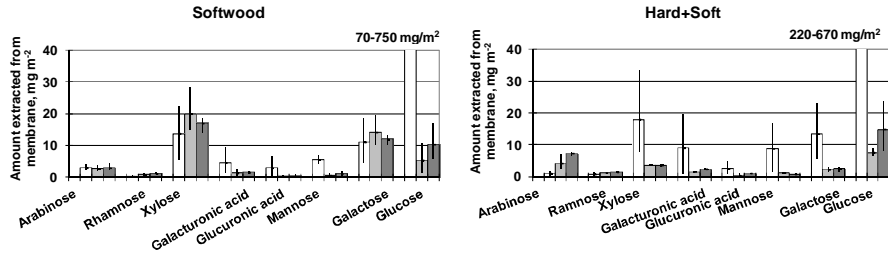


Fig.8.17 Average amount of monosaccharide and uronic acid units found in the UC030 (□), UH030P (■) and UH050P (■) membranes at 40 °C after adsorption tests of softwood and hardwood+softwood process effluents at 0 bar pressure. There are three replicates of each membrane.

8.4.4 Influence of membrane characteristics and process water

Fouling of xylose, galactose and arabinose units depends on the process water characteristics because their fouling behavior was different in filtration of softwood and hardwood+softwood process effluents (Fig. 8.18). Membrane characteristics such as material, hydrophilicity and/or cut-off value affected fouling in UF of hardwood+softwood process water because there were more xylose and galactose units but less arabinose units in the RC membrane than in the PES membranes.

Mannose and galacturonic and glucuronic acid units showed similar fouling behavior in UF of softwood and hardwood+softwood process effluents (Fig. 8.19). Thus, it can be concluded that process water characteristics did not influence their fouling behavior. Membrane characteristics, however, had an influence on fouling; the RC membrane was fouled more with mannose and galacturonic and glucuronic acid units than the PES membranes.

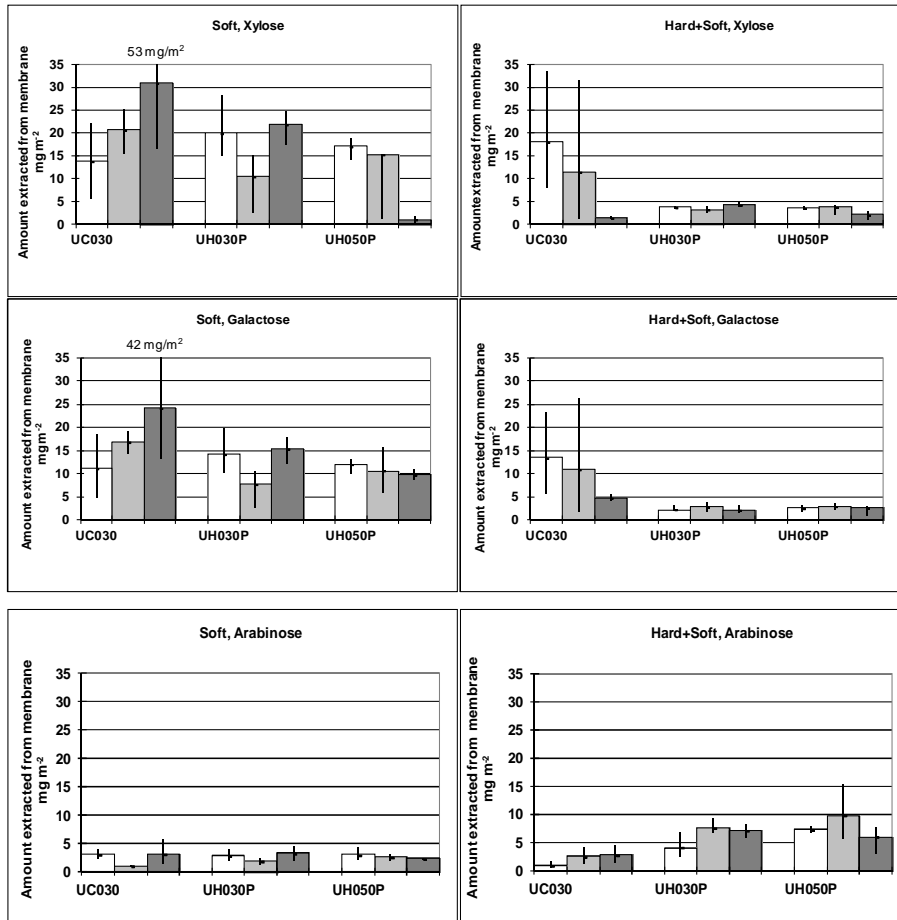


Fig.8.18 Average amount of xylose, galactose and arabinose units found in the UC030, UH030P and UH050P membranes at 40 °C and at pressures of 0 (□), 1 (▨) and 2 (■) bar in UF of softwood and hardwood+softwood process water. There are three replicates of each filtration.

The PES membrane UH050P fouled more with glucose units than the PES membrane UH030P in UF of hardwood+softwood process water. It seems, thus, that the cut-off value of the membrane had an impact on fouling. The amount of glucose and glucuronic acid units in the RC membrane UC030 shown in Fig. 8.19 cannot be considered because the measurements contain membrane material and thus no conclusions can be drawn about their fouling potential on the RC membrane .

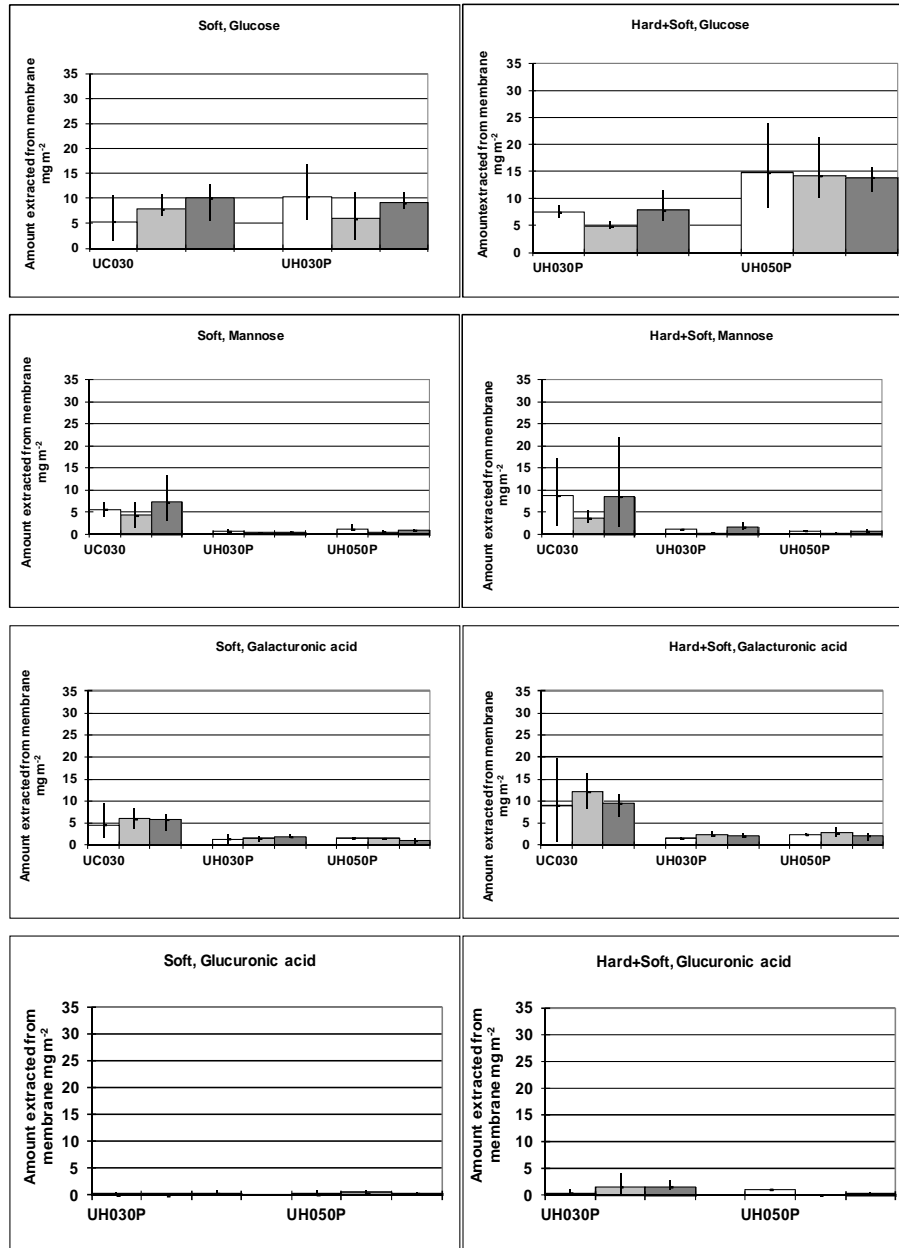


Fig.8.19 Average amount of glucose, mannose, galacturonic and glucuronic acid units found in the UC030, UH030P and UH050P membranes at 40 °C and at pressures of 0 (\square), 1 (\blacksquare) and 2 (\blacksquare) bar in UF of softwood and hardwood+softwood process water. There are three replicates of each filtration.

If the amount of monosaccharide and uronic acid units at 0 bar pressure is compared to that at 1 and 2 bar pressures (Figs. 8.18 and 8.19) it is noticed that in many cases the pressure had a negligible influence on the amount of monosaccharide and uronic acid units. It can, thus, be concluded that carbohydrate fouling is mostly due to adsorption.

8.4.5 Acid methanolysis versus Soxtec extraction

Hemicelluloses were analyzed as monosaccharide and uronic acid units both from the Soxtec acetone:water extracts and by performing acid methanolysis for the fouled membrane pieces according to Sundberg et al. [106]. The amount of monosaccharide and uronic acid units analyzed from the membranes fouled in UF of softwood and hardwood+softwood process effluents is illustrated in Fig. 8.20. The amount of glucose and glucuronic acid units in the RC membrane UC030 is ignored because these units partly come from the membrane material. It can be seen from Fig 8.20 that the isolation technique may influence the content and amount of monosaccharide and uronic acid units found in the membranes in UF of softwood and hardwood+softwood process effluents. The difference in the monosaccharide amount could also be due to the membrane area used in the analysis. The membrane area used in Soxtec extraction was 0.00314 m^2 while the membrane area in direct acid methanolysis was less than a third of that area, 0.00086 m^2 . It is thus possible that the membrane area used in the direct acid methanolysis was not representative enough as a sample of the fouled membrane. Based on the results obtained, it seems that both methods can be used in the isolation of hemicelluloses as monosaccharide units from fouled membranes if qualitative analysis alone is required. However, the optimum membrane area for the analysis should be verified first.

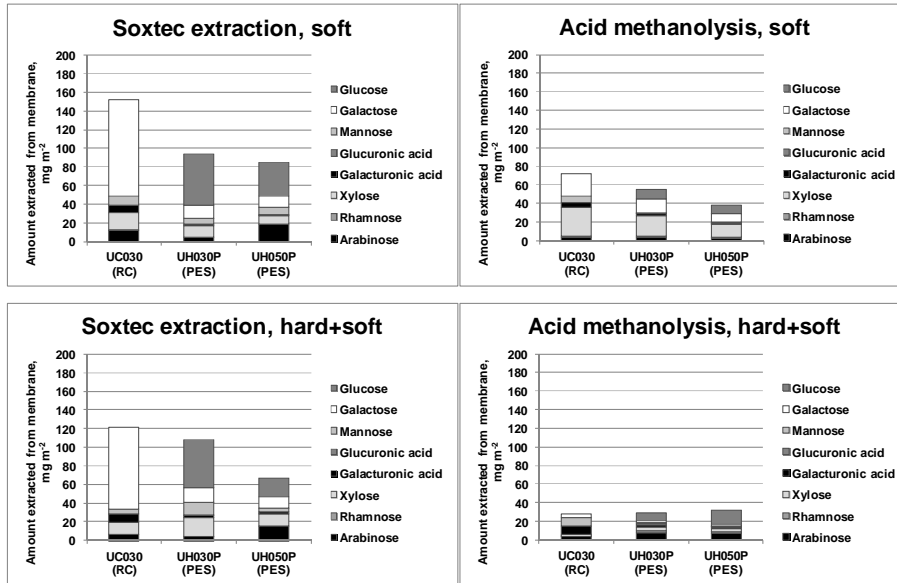


Fig.8.20 Average amount of monosaccharide and uronic acid units found in the UC030, UH030P and UH050P membranes at 40 °C and at a pressure of 2 bar in UF of softwood and hardwood+softwood process water. Monosaccharides and uronic acid units were isolated from the fouled membranes with Soxtec extraction and direct acid methanolysis. There are three replicates of each membrane. The amount of glucose and glucuronic acid units in RC membrane UC030 is ignored.

8.4.6 Conclusions

From the results presented and the above discussion, it is clear that it is possible to extract and analyze carbohydrate foulants from membranes. They can be isolated from the fouled membranes by Soxtec extraction or by direct acid methanolysis. It is, however, impossible to analyze the amount of glucose and glucuronic acid units from the RC membranes because RC membranes break down in the Soxtec extraction and in the acid methanolysis.

9 CONCLUSIONS

This thesis focused on the estimation of hemicellulose fouling by polysaccharides in model solution filtrations and on the identification and characterization of wood extractives and hemicelluloses as foulants in pulp and paper mill applications. The identification and characterization of wood extractives and hemicelluloses as foulants was based on; 1) their extraction from the fouled membrane, and 2) their analysis with gas chromatography.

The model solution filtrations performed in the thesis showed that each polysaccharide had its own fouling mechanism which depended on the membrane used. A secondary layer formed in NF of locust bean gum with a NTR-7450 membrane while in NF of karaya gum there was no secondary layer formation. There was no fouling in NF of karaya gum with Desal-5 DK. In NF of locust bean gum, irreversible fouling and concentration polarization were minor for the more hydrophilic Desal-5 DK and the fouling was more severe at higher flow velocity with the NTR-7450 membrane.

The model substance study revealed that polysaccharides can foul the membranes by adsorption and not only by gel and/or cake layer formation on the membrane surface. Neutral locust bean gum was adsorbed more than negatively charged karaya gum on the membranes at pH 4-5. In the binary mixture filtrations performed, the polysaccharides interacted, which makes fouling evaluation of certain compounds very challenging. Moreover, the concentration of the model substance may influence the severity of the fouling. Therefore, the right choice of model substance and concentration for fouling experiments is critical.

An extraction procedure for fouled membrane analysis was developed in this thesis. With this procedure, it is possible to extract and identify wood extractives from membranes fouled in filtration of pulp and paper mill streams. The most effective solvent for the extraction of wood extractives was found to be acetone:water (9:1 v/v) because it extracted both lipophilic extractives and lignans sufficiently and it was suitable for the membrane materials. A one-hour extraction time was enough to extract wood extractives with Soxtec extraction from membrane samples with an area

of less than 0.008 m^2 . A simplification of the extraction procedure was tested to speed up the analysis. Results from these tests revealed that this simplification of the extraction procedure is not recommended if the quantitative amount of wood extractives is important. If only qualitative results are needed then the simplified extraction procedure could be used.

The identification of the wood extractives as foulants revealed that mostly fatty and resin acids were the reason for fouling, while fouling by steryl esters and triglycerides was negligible. Thus, fouling was seen to be mainly due to dissolved fatty and resin acids and colloidal fouling was negligible. However, colloidal fouling increased as the filtration pressure increased. Results in this thesis indicate that adsorption is the main fouling mechanism in extractives-induced fouling, with at least 50% of the fouling due to adsorption. Over 60% of this adsorptive fouling is due to fatty and resin acids. Both process water characteristics and membrane characteristics had an impact on extractives-induced fouling. Regardless of the process water used, there was a general trend that the more hydrophilic RC membrane contained less wood extractives than the hydrophobic PES and PA membranes. No correlation was found between sessile drop contact angle and the amount of wood extractives extracted from the membrane. This finding suggests the presence of other foulants, such as lignins and hemicelluloses, which also influence on contact angle.

Based on the results of this thesis, it is clearly possible to identify carbohydrates as monosaccharide and uronic acid units from the fouled membranes. While it was possible to analyze all the carbohydrate units for synthetic polymeric membranes, it was impossible to analyze glucose and glucuronic acid units for the RC membrane because their amount obtained contained degraded membrane material, regenerated cellulose.

One of the fouling mechanisms of carbohydrates was adsorption. The amount of monosaccharide and uronic acid units in the adsorptive fouled membranes was however significantly lower than the amount of wood extractives. Thus, carbohydrates are not potent adsorptive foulants to the same extent as wood extractives.

Process water and membrane characteristics had an influence on fouling of certain monosaccharide units. The membranes used fouled differently in UF of the softwood and hardwood+softwood process effluents and the RC and PES membranes behaved differently. Fouling of xylose, galactose and arabinose units depended on the process water characteristics because their fouling behavior was different in UF of softwood and hardwood+softwood process effluents. There were more xylose and galactose units but fewer arabinose units in the RC membrane than in the PES membranes in UF of hardwood+softwood process water, whereas in UF of softwood water, the monosaccharide unit amount of the RC and PES membranes was similar. Furthermore, membrane characteristics had an impact on fouling of mannose and galacturonic and glucuronic acid units. There were more of these hydrophilic carbohydrate units in the RC membrane UC030 than in the PES membranes UH030P and UH050P. Thus, membrane characteristics, i.e. material, hydrophilicity and/or cut-off value, can be seen to have affected fouling.

The results of this thesis demonstrated that Soxtec extraction and direct acid methanolysis methods could be used in the isolation of carbohydrates from fouled membranes. The results obtained from these methods showed that the isolation technique may influence the monosaccharide and uronic acid units content and amount found in the membranes. The membrane area for both methods should be optimized to ensure a representative sample of the fouled membrane for both of the isolation procedures.

10 SUGGESTIONS FOR FUTURE WORK

The literature search performed for the thesis showed that little information on analytical characterization of foulants in pulp and paper mill applications is available. There is considerable demand for membrane applications in the pulp and paper mill industry due to the movement towards biorefinery development. In the future, a variety of new foulant compounds may exist because biorefinery process effluents have different compound composition than traditional effluents. Thus, knowledge of foulants is crucial for finding the right membrane for a certain application to maximize the operational lifetime of the membrane. In further studies, potential

foulants other than wood extractives and hemicelluloses should be studied, such as lignin, and the fouling potential of different process streams should be evaluated.

Procedures for the analysis of carbohydrates from fouled membranes should be developed further such that it would also be possible to analyze glucose and glucuronic acid units from RC membranes. Moreover, the optimum membrane area required for a representative sample for analysis should be studied. As should the molar mass of carbohydrate foulants.

The results of this thesis showed that wood extractives and carbohydrates could be characterized from fouled membranes, but their composition and amount varied depending on the process water filtered and the membrane used. These analysis procedures are, however, time-consuming, and therefore, fast and easy analyses should be developed. A fast analysis of a certain potential foulant group would be useful. Methods suitable for faster-analysis of fouled membranes might be, for instance, ATR-FTIR, UV/VIS reflectance and foulant staining. A huge amount of analysis data could be obtained if both the process water and the fouled membrane are analyzed thoroughly with different analysis techniques. Usually, only univariate examination is used to explain obtained results; the weakness of this approach is that some information may be ignored in the data analysis. Therefore, treating large amounts of analysis data with the use of multivariate methods may increase the information obtained from experimental filtration results compared to traditional univariate examination.

One major problem in the study of fouling is the time needed to obtain reliable results. Analysis of membranes fouled in industrial applications give reliable results but how such results could be obtained in a laboratory setting with a short experiment is still a question. Thus, testing procedures need to be developed to obtain correlative results with industrial applications.

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