Thesis for the degree of Doctor of Technology, Sundsvall 2014

SELECTIVE SEPARATION OF WOOD COMPONENTS IN INTERNAL PROCESS WATERS ORIGINATING FROM MECHANICAL PULPING

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ISSN 1652-893X,
Mid Sweden University Doctoral Thesis 184
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Printed by Kopieringen Mittuniversitetet, Sundsvall, Sweden, 2014
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ABSTRACT

Dissolved and Colloidal substances (DSC) and metals are released from wood during thermomechanical pulp (TMP) production. These components have a tendency to accumulate in process waters, as the water circulation systems in integrated paper mills are closed. Disturbances such as pitch depositions in the paper machine (pitch problems), specks in the paper, decreased wet and dry strength, interference with cationic process chemicals, and impaired sheet brightness and friction properties appear when DSC are present. Transition metal ions such as manganese results in higher consumption of bleaching chemicals (hydrogen peroxide) and lowers the optical quality of the final product, and addition of complexing agents, such as EDTA or DTPA, to prevent this is needed. The never ending trends to decrease water consumption and increase process efficiency in pulp and paper production emphasizes that it is very important both to know the effects of wood substances on pulping and papermaking and to be able to remove them in an efficient way. From a biorefinery point of view, DSC components can be promising renewable raw materials for biofuels, bio-based chemicals and materials.

In this thesis, a new approach using induced air flotation (IAF) without a cationic polyelectrolyte addition for the removal of pitch and metal ions from mechanical pulp mill process waters is presented. The induced air flotation of different process waters is facilitated by the addition of a chelating surfactant and different foaming agents. The influence of the pH value, temperature and foaming agent concentration on the flotation efficiency has been investigated. The investigations
presented show that the disturbing components can be removed from TMP press water to a high extent. A 90% decrease in turbidity and a 91% removal of lipophilic extractives (i.e. resin and fatty acids, triglycerides, sterols and steryl esters) from unbleached and bleached TMP process water can be obtained by addition of a cationic surfactant as foaming agent during flotation. Lower amount of foaming agent is needed to purify efficiently bleached TMP process water, than unbleached. Additionally, fibres located in TMP press water are not removed with the foam fraction but purified. A retained concentration of hydrophilic extractives (i.e. hemicelluloses and lignans) in the process water indicates that the flotation is selective. Moreover, by introduction of a new recoverable surface active complexing agent, a chelating surfactant, manganese ions in the form of chelates can be successfully removed from the pulp fibres and separated from the process water in the same flotation process. Furthermore, from the purified unbleached TMP process water a 90% recovery of dissolved hemicelluloses by anti-solvent precipitation was obtained.

The findings presented above indicate new possibilities for the internal water cleaning stage to decrease DSC emissions to recipient and for recovery of valuable raw materials from purified process water if flotation technology is applied in an integrated mechanical pulp mill.

Keywords: flotation, foaming agents, chelating surfactant, TMP process water, pitch control, internal cleaning stage, hemicellulose recovery, anti-solvents, solvents, precipitation
SAMMANFATTNING


De studier som ligger till grund för denna avhandling visar att hydrofoba ämnen som löses ut från veden kan avlägsnas från TMP pressvatten i stor utsträckning. Med hjälp av flotation tillsammans med katjonisk skumbildare har en minskning av vattengrämskillingen med 90 % och en borttagning av hydrofoba ämnen från TMP pressvatten på 91 % uppnås. Fibrer som finns i TMP pressvatten tas inte bort med skumfraktion utan rengörs. Hydrofilla extraktivämnen finns kvar i processvattnet efter behandlingen och indikerar att flotionen är selektiv. Dessutom, med hjälp av en ny typ av ytaktiv och separerbar komplexbildare kanSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSS

De ovan beskrivna resultaten visar på nya möjligheter för intern vattenrening och möjliggör minskade utsläpp till vatten vid och återvinning av värdefulla komponenter om flotion av processvatten tillämpas i ett integrerat massa- och pappersbruk.
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LIST OF PAPERS

This thesis is mainly based on the following six papers, herein referred to by their Roman numerals:

Paper I  Brightness development of a hydrogen peroxide bleached spruce TMP. Comparisons of pre-treatments with DTPA and a separable chelating surfactant
Ida Högbom, Dariusz Zasadowski, Anette Karlsson, Bengt Wikman, Fredrik Andersson, Erik Hedenström, Håkan Edlund, and Magnus Norgren

Paper II  Removal of lipophilic extractives and manganese ions from Spruce TMP waters in a customized flotation cell
Dariusz Zasadowski, Erik Hedenström, Håkan Edlund, Magnus Norgren

Paper III  Use of a Voith flotation cell for removal of lipophilic extractives and Mn ions from spruce thermomechanical pulping process waters
Dariusz Zasadowski, Erik Hedenström, Håkan Edlund, Magnus Norgren

Paper IV  Selective flotation of pitch components from TMP water
Anders Strand, Dariusz Zasadowski, Magnus Norgren, Erik Hedenström, Stefan Willför, Anna Sundberg

Paper V  Selective purification of bleached spruce TMP process water by induced air flotation (IAF)
Dariusz Zasadowski, Anders Strand, Anna Sundberg, Håkan Edlund, Magnus Norgren
THE AUTHOR’S CONTRIBUTION TO THE MANUSCRIPTS

The author’s contributions to the papers in the thesis are as follows:

Paper I  Performing a part of the experimental work and interpretation of results

Paper II  Planning and performing the experimental work, interpretation of results and writing the article

Paper III Planning and performing the experimental work, interpretation of results and writing the article

Paper IV  Planning and performing the experimental work, interpretation of results in co-operation with Anders Strand

Paper V  Planning and performing the experimental work, interpretation of results in co-operation with Anders Strand, writing the article

Paper VI  Planning and performing the experimental work, interpretation of results and writing the article
RELATED PUBLICATIONS

Use of chelating surfactants as complexing agents for removal of manganese from mechanical pulp fibres prior to hydrogen peroxide bleaching
Ida Högb erg, Dariusz Zasadowski, Anette Karlsson, Bengt Wikman, Fredrik Andersson, Erik Hedenström, Håkan Edlund, Magnus Norgren

Removal of dissolved and colloidal substances from mechanical pulping white waters by flotation
Dariusz Zasadowski, Fredrik Andersson, Håkan Edlund, Ann Almesåker, Erik Hedenström, Magnus Norgren

Recovery of water-soluble hemicelluloses from TMP process water after selective flotation
Dariusz Zasadowski, Magnus Norgren, Håkan Edlund

Selective froth flotation of pitch components from spruce TMP process water
Dariusz Zasadowski, Magnus Norgren, Erik Hedenström, Stefan Willför, Anders Strand, Anna Sundberg
ABBREVIATIONS

TMP            Thermo mechanical pulp
CTMP           Chemithermo mechanical pulp
CP             Chemical pulp
DCS            Dissolved and colloidal substances
RFA            Resin and Fatty acid
EDTA           Ethylenediaminetetraacetic acid
DTPA           Diethylenetriaminepentaacetic acid
4-C12-DTPA     2-Dodecyldiethylenetriaminepentaacetic acid
pK_w           pH value where 50% of an acid is associated with lipophilic droplets
               (l) and 50% found in the water phase
DDAO           N,N-dimethyl dodecylamine-N-oxide
DoTAC          Dodecytrimethylammoniumchloride
SDS            Sodium dodecyl sulfate
Chitosan       2-Amino-2-deoxy-(1→4)-β-D-glucopyranan
ICP            Inductively coupled plasma
AAS            Atomic absorption spectrometry
GC             Gas chromatography
GGM            Galactoglucomannan
PeA            Pectic acids
NMR            Nuclear magnetic resonance
GPC            Gel permeation chromatography
1. INTRODUCTION

Society’s increasing environmental awareness has become an important factor in recent decades affecting legislation, commerce and industry as well as research and development to a great extent. Our climate is always changing. Global warming is either due to increased heat let into the Earth or a decrease in the amount of heat that is let out of the atmosphere. Various factors are said to influence the Earth’s climate. An increased release of carbon dioxide into the atmosphere causes a greenhouse effect. Forest fires and volcanic eruptions are sending CO₂ and ash particles into atmosphere that affect the temperature on Earth. Human activities use huge quantities of fuels that release carbon dioxide, currently far more greenhouse gases are produced than consumed, contributing to global warming. Another greenhouse gas called nitrous oxide is produced when nitrate and ammonium in human-produced fertilizers breakdown in the soil. Furthermore, chemicals and additives used in various production processes are unrecoverable which means that they may be transported with water streams to recipients. All of the above mentioned and more influence our surrounding environment significantly. Powerful winds and storms, destroying whole towns and killing hundreds people are a consequence of long-term abuses.

We can decrease the amount of greenhouse gases that we release into the atmosphere by stopping the use of fossil fuel to power all parts of our lives and by changing our way of thinking and investigating in green renewable sources of energy. Wind and solar energy are the fastest-growing sources of power. At the same time biomass has gained more supporters appreciating this way of receiving the green energy where a main component is a wood material. This tendency has also been noticed by the European Community, which supports numerous project promoting innovative solutions leading to a sustainable economy. Three such projects of the Seventh Framework Programme with overlapping scopes, Biostruct (www.biostructproject.eu), Forbioplast (www.e.europa.eu) and Woody (www.woodyproject.eu), are focused on the valorization of forest-derived resources for the production of bio-based products such as polymers, additives, composites and so on. New chemicals which can be recovered, regenerated and reused in the process are of great importance. The awareness of irreversible climate changes is well anchored in our minds and it is clearly noticeable in the pillars of the new EU framework on climate and energy for 2030 which was recently presented by the European Commission.
Sweden has Europe’s second biggest afforested area after Russia. Approximately 66% of the whole land area is covered by forests which correspond to about 28.3 million hectares. The forestry business is therefore of importance for the Swedish national economy. It is more important than in any other EU country, apart from Finland (www.nordicforestry.org and www.slu.se).

Water is an inseparable factor in the pulp and paper industry. It is known that pulp and paper mills consume large amounts of water. Our environmental awareness about the influence of industries on nature has resulted in increased demands on what and how much can be released in waste streams. With the development of new techniques and other improvements the consumption of fresh water has been decreased by closure of water systems in paper mills. With the reduction of fresh water consumption new disturbances have been found. The main problem is correlated to accumulation of various substances released and added during pulp and paper production, having negative effects on both production process and final product properties. In addition, the possibility to use recovered material as a source to produce new chemicals or electricity can be the next step in an effective exploitation of the biomass.

1.1. Objective

This research is an effect of the CLEAN (chemical engineering for active metal control and neat process water purification) and FORE (forest as resource) projects where a versatile of thermomechanical pulping is emphasized as shown in Figure 1.

The overall aim of the projects is to show the synergetic possibilities and to investigate opportunities related to the forest industry through the production systems, with improved efficiency to a large range of sustainable bio-based new and existing products.

The objective reported in this thesis was to develop a method in an internal cleaning stage approach to purification of TMP process water before and after flotation. Furthermore, a recovery process of valuable raw materials from purified TMP process water has been developed. The method presented in this study is a combination of a well-known separation technique, “flotation”, together with chemicals. The recovery process of valuable materials is based on precipitation and adsorption. The original TMP waters and water produced at a laboratory were investigated. Various analytical methods were used to characterize the flotation
process efficiency and both chemical composition and purity of recovered materials.

Figure 1. A multi-product mill based on mechanical processes

2. BACKGROUND

This section presents a general description of the structure and constituents of wood. More detailed information can be found in Back and Allen (2000), Sjöström (1993), Sjöström and Allen (1998) and Sundbom (1999).

Wood is a complex material, having a seasonal growth pattern, which has a wide field of applications due to its unique properties. The properties of wood vary depending on wood species, i.e. hardwood or softwood, the part of the tree, i.e. stem, branches, roots, or bark and also on the element of the part of the tree, i.e. pith, heartwood, sapwood, or cambium. The main chemical components are cellulose, lignin and hemicelluloses that form fibres glued together in the wood tissue. Table 1 shows composition of dry wood and Figure 3 presents layered cell wall construction; the primary wall (P), the three layers of the secondary wall (S1, S2 and S3).

The primary wall contains oriented cellulose fibrils whereas the secondary wall has different orientations of the cellulose fibrils. The thicknesses of the layer are different; S2 has the thickest wall and P and S3 the thinnest. The hollow centre inside the fibre is called lumen. Figure 3 illustrates an approximate distribution of
the most important components in the different layers of softwood. **Figure 4** shows a distribution of the most important components in the different layers of softwood wood fibre wall.

**Table 1. Composition (%) of dry wood [1]**

<table>
<thead>
<tr>
<th></th>
<th>Cellulose</th>
<th>Glucomannan</th>
<th>Xylan</th>
<th>Other polysaccharides</th>
<th>Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood</td>
<td>33-42</td>
<td>14-20</td>
<td>5-11</td>
<td>3-9</td>
<td>27-32</td>
</tr>
<tr>
<td>Hardwood</td>
<td>38-51</td>
<td>1-4</td>
<td>14-30</td>
<td>2-4</td>
<td>21-31</td>
</tr>
</tbody>
</table>

**Cellulose** is the dominating cell wall components and makes up 40-45% of the wood. Cellulose is composed of β-D-glucopyranose units linked together by (1 → 4) glycosidic bonds as shown in **Figure 2**. The molecules are completely linear and have a strong tendency to form hydrogen bonds. The individual cellulose chains are arranged in the form of microfibrils which are the building blocks of fibrils, the units of fibres.

![Cellulose structure](image)

**Figure 2. Structure of cellulose**

![Wood fibre structure](image)

**Figure 3. A schematic illustration of the wood fibre, showing the primary wall (P) and the secondary wall layers (S1, S2 and S3)**
**Figure 4.** A distribution of the most important components in the different layers of a softwood fibre [2]

**Hemicelluloses** are heterogeneous polysaccharides which consist of the following monomers: D-glucose, D-mannose, D-galactose, D-xylene, L-arabinose and L-rhamnose and smaller amounts of the hexuronic acids, D-glucuronic acid, 4-O-methyl-D-glucuronic acid and D-galacturonic acid as illustrated in Figure 5. The galactoglucomannan, arabinogalacturonoxylans and arabinogalacturonogalactans are the main hemicelluloses in softwood which are relatively easily hydrolyzed to their monomeric components by acid hydrolysis. O-acetyl-galactoglucomannan (AcGGM) 16.3% and arabinono-(4-O-methylgalurono)-xylan 8.6% are the major hemicelluloses in *Picea abies* (spruce softwood). Softwood also contains other hemicelluloses such as xyloglucans in the primary cell wall and galactans in compression wood.

The backbone of GGMs comprises \((1\rightarrow 2)\)-linked β-D-mannopyranosyl and \((1\rightarrow 6)\)-linked β-D-glucopyranosyl units at a ratio of approximately 10:1.9-2.6, with side units of \(\alpha-(1\rightarrow 5)\)-D-galactopyranosyl [3]. The mannopyranosyl units contain acetyl groups at the C-2 and C-3 positions, which gives a degree of acetylation of about 0.5 in of GGM spruce wood [4] and 0.28-0.37 for GGMs dissolved in spruce TMP water [5].
Figure 5. Structure of AcGGM and arabino-(4-O-methylglucurono)xylan [6].
(GAL=galactose, GLC=glucose, MAN=mannose, Ac=acetyl group, XYL=xylose, GlcA=methylglucuronic acid, ARA=arabinose)

The backbone of arabino-(4-O-methylglucurono)-xylans consist of (1-4)-linked β-D-xylose units which are partially substituted at C2 by 4-O-α-D-methylglucuronic acid groups, on average two residues per ten xylose units [3]. No substitution by acetyl groups has been found.

Lignin is a complex high-molecular-weight polymer composed of the phenylpropane units as p-coumaryl alcohols, coniferyl alcohol and sinapyl alcohol. The amount of lignin in softwoods varies between 26% and 32%. The main precursor of lignin in softwood is trans-coniferyl alcohol, presented in Figure 6. This natural polymer gives stiffness to the cell walls, glues cells together, prevents attacks from micro-organisms, and acts as a barrier to enzymatic degradation of the cell walls. The lignin is considered to be one of the main sources of colour in wood and pulp.
Figure 6. Structure of trans-coniferyl alcohol

Ether bonds and carbon-carbon bonds are typical linkages between lignin units. The most common functional groups in lignin are methoxy, phenoxyl, hydroxyl, benzyloxy and carbonyl groups which are usually expressed per 100 phenylpropane units.

A hypothesis about chemical the connection between lignin and carbohydrates was presented in 1866 by Erdmann [7]. An alkaline degradation, acid degradation and Smith degradation was used to confirm the chemical bonds between lignin and carbohydrates [8]. Reduction, methylation analysis, chromatography, spectroscopy and electron microscopy have also delivered some evidence for lignin-carbohydrate bonds. Potential lignin-carbohydrate bonds have recently been reviewed and presented [9]:

- a benzylic ether type between the α-hydroxyl group of a lignin unit and a hydroxyl group of a carbohydrate
- a benzylic ester type between the α-hydroxyl group of a lignin unit and a carboxylic acid group of a carbohydrate
- a glycoside type between an aliphatic or aromatic hydroxyl group and the reducing end group of carbohydrates
- an acetal type between two hydroxyl groups of carbohydrates and a carbonyl group of lignin
**Extractives** consist of lipophilic and hydrophilic components which are soluble in non-polar and polar solvents. The composition and amount varies between tree species parts of the same tree and between elements of the same part. The lipophilic extractives comprise oleoresin, fats and waxes. A composition of lipophilic extractives from Norway Spruce is presented in Figure 7.

![Figure 7](image)

**Figure 7.** A composition of lipophilic extractives in Norway Spruce (Picea abies) (adapted from “Extractives”, lecture notes, Åbo Akademi, Finland)

The resin acids (diterpenes) and terpenes are the main components of the oleoresin that are located in resin canals. The fats can be found in ray cells and consist of triglycerides, fatty acids, sterols and steryl esters. Long-chain alcohols and their esters descend from a group called waxes. The hydrophilic, water-soluble extractives comprise of phenols, polyphenols and sugars.

The extractives have various functions in a tree. The fats are a physiological food reserve whereas the resin acids and the phenolic substances are said to give both chemical and physical protection against attacks, e.g. by bacteria, fungi, and insects.

Wood contains a low amount of inorganic material, 0.1 – 1%. Calcium, potassium and magnesium provide over 50% of the inorganic components. The metal concentration varies within a tree as well. Needles, leaves, branches and roots have different levels of metals and heartwood has higher metal content compared with sapwood. Up to about 100 mg/kg of manganese and trace amounts of other metals can be found in the wood. The mechanism of connection between metals and wood tissues is not completely understood. The metal ions are most likely bound to
anionic sites such as carboxylates or phenolates in the wood structure, or can be found in strongly chelated complexes with e.g. phenolic moieties in lignin.

3. ON DISTURBANCES IN THE TMP PROCESS

Mechanical pulping provides a high pulp yield of 85-95% compared to only about 45% obtained from chemical pulping. The process uses very little or no chemicals but is very energy intensive. The breaking down of the wood into fibres can be done by either grinding the logs against a stone which results in a groundwood pulp or by passing wood chips between one rotating (rotor) and one stationary (stator) metal discs or two rotating discs. Heat can also be used in mechanical pulping to produce thermomechanical pulp (TMP). Mechanical pulps are characterized by high light-scattering ability, high smoothness, good formation and high bulk. The application range of mechanical pulps is very wide. Newsprint and uncoated (SC) and coated (LWC) printing paper are produced from mechanical pulp but also wallpaper, soft tissue and board paper [10, 11].

Dissolved and Colloidal Substances (DCS) are released from wood by mechanical pretreatment and refining in TMP pulp production. The goal of pretreatment is to open up the wood structure to minimize variation in moisture content, maximize the removal of extractives, reduce variation in bulk density and reduce the energy consumption during subsequent refining whereas in the refining wood chips are separated into individual fibres [12, 13].

During the TMP production process DCS have an increased tendency to accumulate in the process water, as the water circulation systems in paper mills are being closed [14, 15]. The future pulp and paper industry will attempt to decrease water consumption and increase process efficiency in pulp and paper production. Therefore it is very important to know the effects of wood substances on pulping and papermaking. The most important, but not main compounds of DCS, are lipophilic extractives which are said to cause significant technical and economic troubles in pulp and paper manufacture [16]. The lipophilic part of the extractives is also called “pitch” or “resin”. Disturbances such as pitch depositions on the paper machine (pitch problems), specks in the paper, odour, decreased wet strength, interference with cationic process chemicals, and impaired sheet brightness, paper strength and friction properties are caused by lipophilic substances [17-30]. Thus, removing detrimental substances from water system is a natural step to increase pulp and paper quality and process efficiency. The lipophilic extractives can be found in the production process in form of colloidal
dispersion and can be adsorbed on the fibres surface and encapsulated in the fibres.

The influence of the hydrophilic extractives is not as well-described as the influence of lipophilic extractives, but there are more and more publications describing their positive effects on the production process. Some of the dissolved substances in the process water are said to stabilize pitch dispersions stERICally which may prevent formation of uncontrolled aggregations [20, 21, 31-33].

With the development of new chlorine free bleaching techniques, such as hydrogen peroxide bleaching, new disturbances were observed as coming from metal ions bound to acidic groups in the fibre walls. To avoid this, complexing agents (chelating agents) were added to the pulp. The main task of a chelating agent is to form chelates by association of metal ions, especially transition metal ions such as manganese, copper and iron that negatively affect the bleaching efficiency due to catalysis of both the decomposition of the bleaching chemicals and the heat and light induced formation of chromophores [34-37]. When the decomposition of the hydrogen peroxide takes place, the consumption of the H₂O₂ increases and the optical properties of the final product may be impaired. The transition metal ions promote the rapid transformation of H₂O₂ to hydroxyl radicals that increase manufacturing costs. In addition to the pulp and paper industry, chelating agents are commonly used in a production of textiles, rubbers, polymers and in a soil washing process as well. They can also be found in soaps, cosmetics, detergents and in developer baths.

Furthermore, all these substances released and added during the pulping process are not easily biodegradable [38-41]. This means that the residual non-adsorbed components may increase the toxicity of the effluent and may increase the risk of uncontrolled pitch aggregation and other disturbances [41-47]. On the other hand, chelates with high resistance to (bio)degradation is often necessary for the stability of various technical processes [48] Thus, the demands on chelating agents being stable at various process conditions and having low impact on the environment after use is wishful. Furthermore, a selective removal of the colloidal substances from the process with the help of new methods, decreasing harmful effects both on paper properties and on the environment, is of great importance [18, 49-51].

3.1. Colloidal stability of pitch

A key to successful pitch control is an understanding of the colloidal stability of the released substances. Increased closure of process water circuits in paper mills leads
to accumulation of these components which in turn leads to occurrences of “pitch problems”. Since it is known that the pitch droplets have a two-layered construction with triglycerides and steryl esters located in the core of the droplets and fatty and resin acids located in the outer layer, investigations of the influence of pH on the pitch droplet behaviour become more complex [52-54]. Sundberg et al. [53] and Strand et al. [54] showed that the pH has a significant influence on the phase distribution of the fatty and resin acids in water solution. According to these studies, the phase distribution of fatty and resin acid can be characterized by the parameter pKw. pKw is defined as the pH value where 50% of an acid is associated with pitch droplets (l) and 50% found in the water phase (w). At low pH most of these compounds are insoluble in water and a transition of resin and fatty acid between colloidal phase and water phase take place very fast at drastic pH changes as shown in Figure 8. It is extremely important to emphasize that the sudden changes in pH will immediately change the concentration of lipophilic extractives in the water phase and its stability.

![Figure 8](attachment:image.png)

**Figure 8.** Distribution of resin and fatty acids (RFAs) between colloidal phase and water phase after **a)** sudden pH increase from 5 to 8 and **b)** sudden pH decrease from 11 to 5 at 50 °C. The dotted lines represent the distribution at equilibrium (after 3 h) [53, 54].

The lipophilic extractives can be found adsorbed on the surface of fibres, encapsulated in fibres and in the form of colloidal droplets in the size range 0.1 – 1 μm [55]. The latter form is the most detrimental since a delicate balance of attractive and repulsive interactions between particles is decisive whether the colloidal pitch dispersion remains stable or not. When attraction dominates, the particles will adhere and finally the entire dispersion may coagulate. When repulsion dominates, the system will be stable and remain in a dispersed state. The attraction forces between colloidal particles are possible due to van der Waals forces and therefore, a colloidal dispersion will be stable only when the other repulsive interactions counteract the van der Waals forces [15, 56, 57].
Since there are always strong, long-range attractive forces between similar colloidal particles, it is necessary to provide long range repulsion between the particles to impart stability. This repulsion should be at least as strong as the attractive force and comparable in range of the attractive interaction. Stability can be obtained by surrounding colloidal particles using:
- an electrical double layer (electrostatic or charge stabilization).
- adsorbed or chemically attached polymeric molecules (steric stabilization).
- free polymer in the dispersion medium (depletion stabilization).

A combination of the first two stabilization mechanisms leads to electrosteric stabilization. The latter two types of stabilization are often realized by the addition of polymers to stabilize dispersions and are called polymeric stabilization.

A phenomenon providing a fundamental understanding of the electrostatic stabilization of colloids is based on so-called Electric Double layer that surrounds a colloid and consists of counter ions in exponentially increasing concentration when approaching an oppositely charged particle surface and a layer of ions exponentially decreasing in concentration during the approach, due to the electric potential and the electrical field strength arising from the surface [58, 59]. The negative surface charges and the diffuse layer of counter ions appear after dissociation of fatty and resin acids at the surface of the pitch droplets. The diffuse layers provide protection in case of particle collision which could lead to a growth of aggregates and uncontrolled depositions. An interaction between two particles in a colloidal system can be explained by the DLVO theory. The theory states that the colloidal stability is determined by a potential energy of the particles which consists of two parts: potential energy of the attractive interaction due to van der Waals force and potential energy of the repulsive electrostatic interaction. The electrostatic stabilization is sensitive to a presence of metal ions; i.e. the main contribution to the ionic strength.

Both steric stabilization and depletion are polymeric stabilizations of colloids. Steric stabilization of colloidal particles is achieved by attaching macromolecules to the surface of particles as shown in Figure 9a. Depletion stabilization of colloidal particles is imparted by macromolecules that are free in solution. The macromolecules create repulsive forces between the approaching particles as presented in Figure 9b. It is not unusual that an electrostatic and steric stabilization protect a system at the same time. This phenomenon is called as electrosteric stabilization.
Figure 9. Schematic a) steric and b) depletion stabilizations of colloids [60]

A destabilization of electrostatically stabilized colloids can take place at a relatively low electrolyte concentration [31]. Steric stabilization is a result of adsorption of a soluble polymer on a pitch surface which provides an efficient protection even at high salt concentrations. In the TMP process colloids before the bleaching stage are sterically stabilized as a result of adsorption of dissolved hemicelluloses on the particles surfaces which prevents the colloids from aggregating [61, 62].

3.2. Path and behaviour of pitch colloids in TMP process

After release during mechanical treatment of wood material, lipophilic extractives form a colloidal dispersion in the process water, which is both electrostatically and sterically stabilized. A schematically illustrated change in the appearance of pitch droplets in the TMP mill is shown in Figure 10.

Figure 10. Schematically illustrated change in the appearance of pitch in the TMP mill
The behaviour of pitch colloids in a TMP mill depends on the location in the process. Before bleaching the pitch droplets have electrostatic stabilization. The electrostatic stabilization comes partly from dissociated resin and fatty acids located in the outer layer of the pitch droplet due to the pH of the process water that is within 5-5.5. From earlier studies it is known that the pH where 50% of an acid is associated with lipophilic droplets and 50% is found in the water phase for resin acids and fatty acids is 6.1 and 9.1, respectively [53, 54]. The steric stabilization is given by adsorbed hemicelluloses on the pitch droplets. O-acetylglactoglucomannan is the dominating dissolved hemicelluloses type in softwood in refining.

After the bleaching that is performed at alkaline conditions the colloids stability changes drastically. The steric stabilization disappears and the hemicellulose composition changes. Acetic acid is released due to deacetylation of O-acetylglactoglucommanan and methanol forms as result of demethylation of pectins. Only electrostatic prevents against uncontrolled aggregating of the pitch that is sensitive to a presence of electrolytes in the system. The bleaching increases the anionic load of both the water and fibres [27]. Only a slight decrease in the turbidity indicating aggregation of pitch colloids was observed after the electrolyte additions in the case of unbleached TMP whereas the pitch colloids from after peroxide bleached TMP was completely aggregated. The higher valence of the cations of the electrolyte the lower concentration is needed to make the pitch colloids unstable [31].

3.3. Ways of pitch control

As mentioned earlier, the concentration of colloidal substances in process water from a closed water system is higher than the concentration in process water from an open system. There is a tendency in the development of pulp and paper production to decreases fresh water consumption.

Our awareness of environmental risks as result of a release of these components to recipients has increased and new approaches of pitch control have been developed or are in the test phase. Nowadays, a pitch control relies on an adsorption of lipophilic extractives to fibre surfaces using fixation agents [63]. However, the results of Johansen and Stenius show that only about 30% of the pitch can be retained in the paper, and the residual pitch remains in the process water [19]. Apart from fixing them to the paper web, lipophilic extractives can be removed by sedimentation, membrane filtration and flotation with flocculants [64]. The difference in density between solid particles and water is utilized in sedimentation.
Thompson et al. showed that up to 80% of suspended material can be removed in the paper mill [65]. Filtration as another way of removal of colloids from process water may be inefficient for water with high concentration of colloids and fibres that may block the membrane filters [66]. Flotation proceeded by a flocculation stage seems to be the most suitable method of removal of colloidal substances from process waters that is being used in an internal cleaning stage approach. The choice of purification method depends on the location in the production process and on the concentration of lipophilic extractives in process waters.

An internal cleaning stage is a relatively new approach of purification of process water in paper mills where flotation is a promising solution [67]. The flotation process has already been applied in the area of mining for over 80 years. In general, flotation is based on the control of the surface hydrophobicity / hydrophilicity of dispersed materials in the water which has made it possible to rapidly transfer to the paper industry and to the deinking of waste paper and to an internal cleaning stage [67-71]. The functioning of flotation relies on attachment of particles to air bubbles that can be generated by injection of air or by stirring. After a flotation process two fractions are received in form of cleaned water and foam. Sizes of particles and air bubbles are the main factors determining if a flotation is efficient or not [72, 73].

Also the amount of foam fraction determines flotation efficiency. Turbidity measurement, focused beam reflectance measurements, chemical oxygen demand (COD), GC analysis and total organic carbon (TOC) are usually used to determine flotation efficiency. The application of flotation to remove lipophilic extractives is a challenge due to the small size of colloids. It is well known that flotation of small particles is inefficient. Thus, the lipophilic extractives in form of colloidal dispersion should be aggregated before flotation [49, 74]. Successful flotation of lipophilic extractives has been carried out preceded by cationic polyelectrolyte flocculation. Common cationic chemicals include polyacrylamide (C-PAM) and poly-(N-N-dimethylallyl-3-4-ethylpyrrolidinium)-chloride (poly-DADMAC). Molecular mass and charge density of a polyelectrolyte are important for aggregation efficiency. An aggregation process is based on a charge neutralization and bridging flocculation when a single polyelectrolyte chain is adsorbed on more than one particle at the same time. Miranda et al. describes the application of the flotation to purify the process water from paper mill producing newsprint from 100% recovered paper, where lipophilic extractives are aggregated with the help of cationic polyelectrolytes and are then removed in the flotation process [69]. Negro et al. show that the aggregation of the lipophilic extractives with polyelectrolyte and flotation can be used successfully in the purification of eucalyptus process
water as well [75]. Opedal et al. achieved a removal of 70% lipophilic and 60% dissolved extractives by DAF from water pressates of Norway spruce chips [76, 77]. Richardson and Grubb reported that up to 90% of lipophilic extractives can be removed from newsprint mill process waters derived from Pinus radiata in a DAF unit [78]. Process water from a paper mill not only contains colloids but also fibre and fines material that is flocculated together with colloids using cationic polyelectrolytes. In this way controlling colloids by addition of cationic polyelectrolytes may introduce disturbances in the further utilization of the removed material due to the fact that polyelectrolyte adsorption is in general irreversible [57].

3.4. Metal ions disturbances and their control

The concentration of metals in wood mainly depends on the geographic location e.g. pH of soil, climate and surrounding industrialization. The uptake of metals takes place through the roots and then the metals are transported further into the tree [79, 80].

The concentration of metals is different in leaves, needles, branches and roots. Heartwood has higher concentration of metals compared with sapwood, and earlywood contains more metals than latewood. The binding mechanisms of metal ions to wood tissue are most likely based on metals ions and anionic sites interactions and on chelated complexes of metal ions with e.g. phenolic moieties in lignin [81]. In addition to lignins, chelates of metal ions can be formed as well with cellulose materials, hemicelluloses and tannins. Some metals can be presented as insoluble salts or oxides [82, 83].

Transition metal ions such as manganese, iron, copper and other may negatively affect the mechanical pulp process. They catalyze decomposition of bleaching agents such as hydrogen peroxide and dithionite giving radicals which results in decreased brightness of pulp [35]. An oxidation of some structural elements, e.g. phenolic groups to chromophores, takes place in the presence of transition metal ions [84]. The metal ions increase the rate of autoxidation of hydroquinones, and catechols which may lead to discoloration. Cellulose degradation upon ageing may occur due to metal ions. Iron ions catalyze a cleavage of 1-4-β-glucosidic bond of cellulose, whereas the oxidation on the anhydroglucose ring can be caused by copper ions [85]. Various precipitates and scales may be formed during peroxide bleaching of mechanical pulp when sodium silicate interacts with Ca²⁺ and hydroxylized magnesium cation (MgOH⁺) [86].
The reason behind hydrogen peroxide decomposition under bleaching is not completely clear. Several mechanisms are usually proposed to account for the H$_2$O$_2$ decomposition: a base-catalyzed ionic mechanism [87]; a base-catalyzed free radical mechanism [88]; a transition metal reaction with perhydroxyl anions to form unstable peroxides [89] and a transition metal-catalyzed free radical mechanism [90]. Special attention is paid to the hydrogen peroxide decomposition catalyzed by manganese and iron, as these metals are present in relatively high amounts in wood fibres. A proposed four-step mechanism of transition metal ion-catalyzed H$_2$O$_2$ decomposition is presented in Figure 11.

$$
\begin{align*}
M^{n} + H_{2}O_{2} & \rightarrow M^{(n+1)} + HO^{*} + HO^{-} \quad [1] \\
M^{(n+1)} + HO_{2}^{-} + HO^{-} & \rightarrow M^{n} + O_{2}^{*} + H_{2}O \quad [2] \\
M^{(n+1)} + O_{2}^{*} & \rightarrow M^{n} + O_{2} \quad [3] \\
O_{2}^{*} + HO^{*} & \rightarrow O_{2} + HO^{-} \quad [4]
\end{align*}
$$

**Figure 11.** Metal ions catalyzed free radical mechanism of peroxide decomposition [35]

As presented previously, manganese ions decrease the efficiency of bleaching by the decomposition of H$_2$O$_2$ which increases chemical consumption. Colodette et al. show that manganese ions are more detrimental than iron and copper in the pH range 9.8-10.3, which are typical conditions of hydrogen peroxide bleaching. Only 0.5 ppm of manganese is sufficient for complete decomposition of H$_2$O$_2$ [35].

In this context an efficient removal of the transition metal is necessary to prevent hydrogen peroxide decomposition. There are two main methods used in the industry today. The first one is based on an acid washing at pH 2.5 or less which is not preferable since a lot of alkali is then spent to reach and maintain the optimum pH-value. The second method relies on a chelation of metal ions by using chelating agents. DTPA (diethylenetriaminepentaacetic acid) and EDTA (ethylenediaminetetraacetic acid) are the main chelating agents used in mechanical pulping. DTPA and EDTA form water-soluble chelates mainly with harmful manganese, iron and copper whereas at correct additions, magnesium and calcium are not bonded to any large extent due to much lower conditional stability constants of the latter chelates. The chelates are stable at oxidative conditions. Stability constants for DTPA and EDTA are comparable in a range of pH 5 to pH 7. At higher pH the stability constants for DTPA are higher than EDTA [48].

The chelates of transition metal ions stay in the process water which may increase toxicity of effluents from paper mills due to low DTPA biodegradation [38, 39].
Furthermore, a removal of problematic substances from the process with the help of new methods, decreasing harmful effects both on paper properties and on the environment, is desired.

4. ON PROMISING RENEWABLE RAW MATERIALS FROM TMP PROCESS WATER

During the last decades, an outstanding increase in interest from scientists at universities, research institutes as well as industrial companies in research of biopolymers from renewable sources can be noted. Shortage of natural energy sources and replacement of petroleum-based products, which is connected with demands of a solution of the worldwide environmental problems, are the main driving forces behind these activities.

TMP provides great opportunities to recover valuable natural components released into process water during these turbulent conditions since the process is mild in terms of chemical application when comparing with CP or CTMP. This means that the nature and composition of these components is unchanged at certain production stages, which makes it possible to recover them. A crude estimation of potential benefits from a biorefinery point of view, after recovery of 100% of process water, at spruce TMP production of 500,000 ton per year, is presented in Table 2.

Table 2. A rough value estimation of benefits after 100% recovery of raw material

<table>
<thead>
<tr>
<th>Targeted substances*</th>
<th>Amount recovered** (ton)</th>
<th>Estimated value*** (MEUR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty acids</td>
<td>44 – 111</td>
<td>0.04 – 0.12</td>
</tr>
<tr>
<td>Resin acids</td>
<td>86 – 250</td>
<td>0.09 – 0.28</td>
</tr>
<tr>
<td>Galactoglucomannans</td>
<td>6440 – 8678</td>
<td>6.5 – 8.7</td>
</tr>
<tr>
<td>Lignans</td>
<td>933 – 1012</td>
<td>9.3 – 10.1</td>
</tr>
<tr>
<td>Σ</td>
<td></td>
<td>15.8 – 19.2</td>
</tr>
</tbody>
</table>

* neutrals, uronic acids and pectins not included  
** the interval reflects variations in white water composition  
*** based on 1,000 EUR/ton in general, and 10,000 EUR/ton for lignans

4.1. Hemicelluloses

Wood polysaccharides (70-75% b.o. wood) consisting mainly of cellulose, hemicelluloses and pectins [1] belong to the building components of the cell walls of the plants. Depending on the plant species and the location of the same plants, the properties of wood polysaccharides vary. These components can be a
promising renewable raw material for biofuels, materials and bio-based chemicals [91]. Hemicelluloses are also attractive as bioplastics and biopolymers, which can be utilized in their native or modified form in various areas including food and non-food application [92, 93]. The hemicelluloses can serve as a source of sugars for fermentation to fuel (bioethanol), or chemicals, such as 1,2,4-butanetriol, a less hazardous alternative to glycerine as a substrate to nitroglycerin production [94].

Various methods for isolation of hemicelluloses have been widely investigated. Extraction of GGMs from spruce wood by hot-water [95], by microwave heat-fractionation [96], by alkaline extraction [97] and by pressurized hot-water extraction [98, 99], has been extensively presented.

Filtration approach, based on microfiltration, ultrafiltration and nanofiltration, has been widely discussed and results presented shows that this technique can be used to fractionation of the TMP process waters into several products. GGM was efficiently concentrated in the ultrafiltration stage to over 60 g/L with lignin content over 20% [100-104].

Precipitation with ethanol seems to be a promising way to recover GGM from the water stream. Peng et al. investigated graded ethanol precipitation to recover hemicelluloses from Sugarcane Bagasse [105, 106]. It was noted that with an increasing ethanol concentration from 15% to 60% the recovery yield of hemicelluloses increases and the weight-average molecular (Mw) weights of hemicelluloses increased as well from 42,430 g/mol to 85,510 g/mol. Bian et al. used ethanol precipitation to fractionate of hemicelluloses from Caragana Korshinskii and confirms that recovery of hemicelluloses is higher at higher ethanol contents [107, 108]. The results revealed that an increase in ethanol content from 10% to 30% resulted in growth in Mw from 28,950 to 58,900 g/mol, while further increasing ethanol content from 45% to 80% led to a decrease in Mw from 44,000 to 15,000 g/mol. It has been reported in several studies that a combination of various separation techniques such as ultrafiltration and precipitation can be a good way to recover hemicelluloses from various water streams. Xu et al. investigated properties of ethanol precipitated and spray-dried water-soluble spruce galactoglucamannans, concentrated firstly by ultrafiltration [109, 110]. It was reported that recovered hemicelluloses by ethanol precipitation had higher content of GGM and had higher average molar mass than spray-dried GGM i.e. 46,000 and 39,000 respectively. Willför et al. proposes a recovery procedure of hemicelluloses from TMP waters based on ultrafiltration, ethanol precipitation and vacuum evaporation concentration [111]. It was observed that GGM was the main carbohydrate with Mw of 29,000.
4.2. Lignin

Lignin has been considered for a long time as a waste from the pulp and paper industry that can be used only as fuel to power paper mills. A black liquor (containing between 35 and 45% of lignin) during kraft pulping is used for the production of steam, electricity and inorganic chemicals for internal mill use [112]. When an excess of lignin increased more studies were performed on lignin conversion into various chemicals. The availability of lignin is over 300 billion tons and increases annually by around 20 billion tons [113]. The extraction of lignin in the pulp and paper industry was about 50 million tons. But only 2% has been commercialized for the formulation of dispersants, adhesives and surfactants or as antioxidants in plastics and rubbers. Lignin through the functionalization of its hydroxyl groups, becomes a good candidate for a building block unit for polymer synthesis including polyhydroxystyrene derivatives, polyethers, polyesters and polyurethanes. The functional groups of lignin can be modified by the following reactions: esterification, etherification, oxidation and reduction, phenolation, silylation and reaction with isocyanates.

4.3. Phenolic antioxidants

Considerable worldwide attention has been given to natural phenolic antioxidants found in many fruits, vegetables, red wine, and trees. The literature on antioxidants has expanded widely because of accumulating evidence that they may contribute to the nutritional benefits of foods and beverages containing phenolic compounds. According to Kroon and Williamson, there are strong evidences for polyphenols role in preventing cardiovascular disease and cancer [114]. The consumption of fruits and vegetables is associated with reduced coronary heart diseases, cancer and other age-related diseases and the natural antioxidants can be a reason for this. However, there are few studies that have provided direct evidence of these benefits.

The first report concerning natural phenolic antioxidants (lignans) in wood was published more than 100 years ago by Lindsey and Tollens. It was noted in the report that a substance can be extracted by diethyl ether from spent liquor of sulphite pulping of Norway spruce. Furthermore, [115, 116] established their composition to that of conidendrin, that was found to be the acidic cyclisation product of 7-hydroxymatairesinol (HMR) which is the predominant lignan in Norway spruce wood [117]. Freudenberg and Knof isolated HMR and determined its structure [117]. They also determined other lignans from Norway spruce wood.
The presence of conidendrin, HMR, matairesinol, oxomatairesinol and pinoresin in spruce oleoresin was reported by Goldschmid et al. [118].

Several reports can be found on extractives in stemwood, branches and knots of spruce. However, the knots extractives were not analyzed in detail with the exception of radiate pine (Pinus radiata) [119] and parana pine (Araucaria angustifolia) [120]. A research group at Åbo Akademi University analyzed and reported that knots, i.e. the branch bases inside the stem, normally contain 5-10% (w/w) of lignans. Norway spruce knots contain as much as 6-24% of lignans, with 7-hydroxymatairesinol (HMR) as the main lignan (65-85%) as shown in Figure 12.

![Figure 12](image_url)

**Figure 12.** Concentration of lignans, excluding oligolignans, in Norway spruce trees and the structure of two isomers of the main lignan, HMR [121, 122]

It was also revealed that the lignans occur in knots of pines although in lower amounts than in spruce. The amount of lignans in Scots pine is estimated to 0.4-3%.

During the thermomechanical pulping process (TMP) the lignans are washed out. Hydroxymatairesinol and α-conidendric acid are the most common lignans in wood and effluent. The concentration of lignans in water from pulp screening in TMP production is reported to be 85-200 mg/L [123-126]. This indicates that TMP effluents can be a valuable source of lignans.
5. MATERIALS

5.1. Chemicals used to reduce disturbing substances and recover hemicelluloses

In this study influence of various chemicals on flotation and precipitation efficiency was studied. The following chemicals were used:

**Foaming agents:** zwitterionic N,N-dimethyl dodecylamine-N-oxide (i.e. DDAO, Sigma-Aldrich), cationic dodecyltrimethyl-ammoniumchloride (i.e. DoTAC, Fluka), and anionic sodium dodecyl sulfate (i.e. SDS, Calbiochem)

**Cationic polyelectrolytes:** polyacrylamide (i.e. Fennopol K1384, Kemira), poly-diallyldimethylammonium chloride (i.e. Fennofix 40, Kemira), and poly-(D)glucosamine (i.e. Chitosan, Sigma-Aldrich)

**Complexing agents:** 2-Dodecyl diethylenetriaminepentaaetic acid (i.e. 4-C12-DTPA, Mid Sweden University) and diethylenetriamine-pentaacetic acid (i.e. DTPA, Fluka)

**Anti-solvents:** methanol (VMP PROLAB®), ethanol (Solveco) and acetone (VMP PROLAB®)

5.2. Process waters used in the investigations

The initial process parameters and chemical characteristics of the waters studied are shown in Figure 13.

The original pH and turbidity for TMP process water before bleaching was 5.0 and 2400 NTU. The corresponding characteristics for bleached TMP process water were 7.6 and 3600 NTU.

The concentration of pitch components and lignans for laboratory water was more and less 10 times lower compared to TMP process water before bleaching and pH was 5.5.
Figure 13. Initial concentrations of components in TMP process water before and after bleaching. a) Pitch components (i.e. resin acids, fatty acids, oxidized resin acids, diglycerides, steryl esters, triglycerides) and lignans. b) Carbohydrates as sugars after methanolysis.

6. PROCEDURES APPLIED IN THE INVESTIGATIONS

6.1. Preparation of laboratory process water from unbleached TMP

The laboratory water from unbleached TMP was prepared using a method developed by Örså and Holmbom [127]. Unbleached TMP was diluted with distilled water to 1% consistency and agitated (150 rpm) at 60 °C for 4 h. The final pH was around 5.5. The suspension was centrifuged at 500g, and the supernatant containing the dissolved and colloidal substances was separated by decantation and stored in a refrigerator at 10 °C. The samples of the TMP water were taken from the wire press section before the bleaching tower at SCA Graphic Sundsvall, Ortviken mill, Sweden. The pulp consistency after the wire press was 32.5%.

6.2. Flotation process

Flotation trials were carried out with water produced at the laboratory and real industrial waters e.g. TMP process waters “before” and “after” bleaching.
The flotation of the water samples were carried out in two different flotation units; a 1 litre customized flotation cell and in a 20 L conventional Voith flotation cell.

![Flotation Cell Images](image)

**Figure 14.** A 1 L customized flotation cell and a 20 L Voith flotation cell

A customized flotation cell with a volume of 1.6 L, consisting of a plexiglass cylinder and a sintered glass frit of a diameter of 60 mm (porosity 4, VWR, Sweden) mounted at the bottom of the cell is presented in **Figure 14.** The rate of the foam, induced by nitrogen gas injection with flow of 5 L/min, was controlled by valve on the top of the cell.

The Voith flotation cell consists of a plexiglass cube with a 30 cm long side. In addition, the cell is equipped with a motor delivering an impeller rotational speed of 1340 rpm. In each corner of the cube 6 cm × 13 cm plexiglass plates are located. The flotations were induced only by switching on the impeller.

The flotation was continued until the formation of stable foam ended. The flotation time was found to correlate to the amount of added foaming agent and varied between 35 min for the lowest additions and 70 min for the highest addition. For the original TMP process water the flotation was continued to the end of the foam forming process as well. The flotation times were from 40 min at 80 ppm of DoTAC up to 240 min at 400 ppm of the foaming agent concentration.

In the Voith 20 L flotation cell TMP process water “before” and “after” bleaching was tested.
Six-litre samples of the waters were poured into a glass beaker and stirred vigorously at 20 °C or 50 °C. The pH was adjusted to 3.5, 5.1, or 7.3 with HCl. The DoTAC concentrations were adjusted to values between 40 and 80 ppm for the water “before” bleaching and between 0 and 40 ppm for the water “after” bleaching. CaCl\(_2\) was added to some of the flotation experiments. The mixture was then poured into the flotation cell, preconditioned for 30 min, and the flotation was conducted for 60 min. The foam generated during the flotation was collected using a suction flask, and the collapsed foam volume was measured after the flotation. The turbidity of the waters was measured after the flotation. The water samples were stored in a freezer to determine pitch and carbohydrate content at a later point.

6.3. Recovery of hemicelluloses

Precipitation of hemicelluloses from the purified TMP process water samples before and after concentration was performed at different weight fractions of methanol, ethanol, and acetone. The anti-solvents were added at two different pH-values; 3.8 and 5.1, and precipitation was carried out at 7 °C, 20 °C and 50 °C. After 4 h of sedimentation at each temperature, the samples were shaken vigorously and the turbidity was measured. Turbidity measurement was applied only on the anti-solvent treated samples from unconcentrated process water since the concentrated water samples showed values out of the measuring range. For the unconcentrated water, the GGM precipitation was repeated at some of the anti-solvent/water ratios found more interesting from the turbidity study to collect enough precipitates for more extensive chemical analysis. The samples were centrifugated at 500g for 15 min and the supernatants were carefully separated. The precipitates were transferred into 25 ml beakers, freeze-dried over night and weighed. In further analyses, solutions were prepared from the freeze-dried precipitates by dissolving 25 mg in 25 ml distilled water.

7. ANALYSES APPLIED IN THE INVESTIGATIONS

7.1. Carbohydrate analyses

7.1.1. The orcinol method

The carbohydrate content was determined using the Orcinol method based on a colour reaction of carbohydrates with 0.2% orcinol reagent solution in concentrated sulphuric acid. A water sample (5 mL) after addition of 10 mL of orcinol reagent was heated for 25 min in a water bath. The solution was cooled down to room
temperature and analyzed according to SCA-F W 15:77 on a Varian 100 Bio UV-Vis spectrophotometer at 540 nm of wavelength.

7.1.2. Acid methanolysis

The content of carbohydrates in the water samples and the anti-solvent precipitated hemicelluloses was determined by GC after acid methanolysis [91, 126]. The samples were filtered through 0.22-µm nylon filters (MS NY Syringe filter, Membrane Solutions) to completely remove fines, remained colloids or non-dissolved precipitates. The filtered samples were frozen and freeze-dried. Water-free 2 M HCl in methanol was added to the dry samples. The samples were placed in an oven at 100 °C for 3 h and then neutralized with pyridine. Sorbitol in methanol was added as internal standard. The samples were silylated using pyridine, hexamethyldisilazane (HMDS) and TMCS at room temperature. The analysis of sugar units was conducted by long column GC (HP-1, 25 m by 0.20 mm) with split injection and detection by a FID detector.

7.1.3. Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy was used to characterize main functional groups of anti-solvent precipitated carbohydrates. The FTIR spectra were recorded in the wavelength range of 4000-400 1/cm on a Nicolet 6700 FTIR from Thermo Scientific equipped with OMNIC software. Before data collection, a background scanning was performed for background correction.

7.2. Lipophilic extractive analyses

7.2.1. Solid-phase extraction (SFE)

The total concentration of extractives in TMP process waters was determined gravimetrically, according to the SCA-F W 35:97 method based on a solid-phase extraction (SPE) that was preceded by the addition of methanol to a concentration of 15% in the water sample and pH adjustment to pH 2. Before extraction, a SPE disc (3M Empore, SDB-XC, 47 mm, Scantec Lab) was washed with 10 mL of MTBE, 10 mL of methanol, and 10 mL of distilled water. During the extraction, small amounts of water samples were added so that the flow did not exceed 2 mL/min. After the extraction, the SPE disc was washed with 2 portions of 10 mL of 40% methanol and vacuum dried for 30 min. The disc was eluted with 3 portions of 10 mL of MTBE. The solution obtained was vacuum-dried at 40 °C for 3 h and weighed.
7.2.2. MTBE extraction and silylation of lipophilic extractives

The TMP process water samples were pipetted through a coarse metallic 20-mesh wire to remove most of the fines in the samples. The anti-solvent precipitated hemicelluloses were analyzed without further preparation. H$_2$SO$_4$ was added to acidify the water samples. An internal standard mixture containing equal amounts of heneicosanoic acid, betulinol, cholesteryl heptadecanoate, and 1,3-dipalmitoyl-2-oleyl glycerol in (tert-butyl)methylether (MTBE) was added to the samples [127]. The pitch components were extracted from the water samples with MTBE. The extractives in MTBE were then dried under N$_2$ gas, and silylated with pyridine, N,O-bis(trimethylsilyl) trifluoroacetamide (BSTFA), and trimethylchlorosilane (TMCS) for 45 min at 70 °C. The silylated extractives were analysed by gas chromatography (GC) on a short column (HP-1, 7 m by 0.53 mm or DB-1, 5 m by 0.53) with on-column injection and detection by a flame ionization detector (FID). Individual resin and fatty acids were analyzed on a long column (HP-1, 25 m by 0.20 mm) with split injection and detection by a FID detector.

7.2.3. Analysis of lipophilic extractives in fibre fractions

The fibre fraction was separated from spruce TMP process water by filtration through a plastic Büchner funnel having a diameter of 24 cm equipped with a 100 mesh as a filter. A small amount of water was used at once to avoid formation of a fibre filter which may influence the concentration of lipophilic extractives in the fibre fraction. The fibre fraction was freeze-dried overnight before extraction. The total concentration of extractives was determined gravimetrically according to the SCAN-CM 67:03 method. The extraction of fibre fraction was carried out in a Soxhlet apparatus with a cyclohexane:acetone ratio of 9:1. The extract was transported to an aluminium container, evaporated for 30 min at 105 °C, and weighed. The main groups of lipophilic extractives in fibre fraction from spruce TMP process water were investigated according to Örså and Holmbron [127].

7.2.4. Particle content estimation in different waters by turbidity measurements

The turbidity measurement was used as an indirect measurement of the content of lipophilic extractives due to a good linear correlation between them [19, 129, 130]. The turbidity was analyzed using a HACH RATIO/XR 43900 turbidimeter. TMP water contained fibres and fines that significantly influenced the turbidity measurements. The measurements of the water before and after flotation were carried out after 1 h of sedimentation.
7.3. Lignin determinations

Lignin determination in the water samples and the hemicelluloses solutions after MTBE extraction was based on measurements of ultraviolet (UV) absorption at 280 nm. The measurements were performed on a Shimadzu UV-1800 spectrophotometer. QS cuvettes for measurements in UV-range produced by VWR International were used and the extinction coefficient, used for quantification of lignin, was 0.0145 L/mg cm according to the SCA-F W17:81 method.

7.4. Determination of residual foaming agent

The residual foaming agent content in the water samples after flotation experiments was determined by mass spectrometry measurements on an electrospray ionization mass spectrometry (ESI-MS) Quattro II instrument equipped with the software MasslyxTM 4.0. The following (instrument) parameters were used during measurements: source temperature 60 °C, drying gas flow 250 L/h, nebulising gas flow 10 L/h, capillary voltage 4.5 kV, HV Lens 0.5 kV, and sample cone voltage 30 V. The fibres and fines from the water samples were removed by filtration through a MILLEX®-GS filter of 0.22 μm. The methanol was added to a concentration of 50% in the water samples; 3 standard solutions of DoTAC were prepared consisting of concentrations 1.1 ppm, 2.2 ppm, and 5.5 ppm. The coefficient of determination of the chart equation was R²=0.997. The water samples were measured in ES+ mode and a strong signal at m/z 228.1 was obtained.

7.5. Metal analyses

A water sample of 10 mL was refluxed for 5 minutes with 2.5 mL of concentrated nitric acid and 2 mL of 30% hydrogen peroxide in order to digest the fibre fraction. The solution was filtered through a Munktell 00H paper filter and adjusted to 25 mL. The metal ion content in water before and after flotation was analyzed according to the SCAN standard method CM 38:96 on a Varian ICP-OES 720 inductively coupled plasma spectrometer (ICP) and an atomic absorption spectrometry (AAS).

7.6. Images of foam fraction

Two droplets of each water sample were placed on a microscope slide (76 × 26 mm Geschnitten) and covered by a microscope glass cover slip (18 × 18 mm Chance Proper). The images of the foam fractions after flotation with DoTAC and cationic
polyelectrolyte were taken with the help of a Leica DMRX light microscope and DFC 320 Camera equipped with the software LAC V3.8.

7.7. Measurement of fibre distributions

Optical measurements to determine the geometry of each fibre were made in the Metso Automation FibreLab™ equipped with a sampling carousel and software display. The measurements were made using two CCD cameras that measured the fibres in a 50-μm-wide chamber. The procedures for fibre and image processing needed to determine the fibre properties are described in detail elsewhere (Metso Automation 2001).

7.8. Molecular mass determination analyses

7.8.1. Self-diffusion NMR

PFG NMR self-diffusion measurements were performed on a Bruker Avance DPX 250 MHz spectrometer equipped with a Bruker self-diffusion probe, able to provide 18 T/m at 60 A (Bruker Biospin AG, Karlsruhe, Germany). Samples of freeze-dried polysaccharides were dissolved in deuterium oxide to a concentration of 1 wt% and mixed overnight. The resulting self-diffusion coefficients for the polysaccharides were obtained after fitting the echo decays to a lognormal distribution function as described elsewhere [131-133]. Dextran standards were used to obtain the scaling parameters (K and α) needed to calculate the approximate molecular mass distribution from the Mark-Houwink relationship between the self-diffusion coefficient (D) and the molar mass (M), D = KM^α.

The relation between the weight-averaged median self-diffusion coefficient and the weight-averaged median molecular mass of the dextran standards is linear with a correlation of R²=0.998.

7.8.2. Gel permeation chromatography (GPC)

GPC measurements were performed on a OHpak SB-800HQ and Ultimate 3000 from Dionex equipped with a PAD, UV and RI detector at MoRe Research AB. Pullulan standards from Shodex were used for the molecular mass calibration. Samples of 10 mg were transformed to 10 mL of water and ultrasonicated twice for 30 min. Prior to injection, the samples were filtrated by a 0.45 μm filter.
8. RESULTS AND DISCUSSION

8.1. Flotation in a 1 L customized flotation cell (Paper I and II)

In this study flotation trials of TMP water produced at laboratory and TMP process water from the paper mill was carried out in a customized flotation cell, consisting of a plexiglass cylinder and a sintered glass frit mounted at the bottom of the cell. The rate of the foam was controlled by valve on the top of the cell. Flotations proceeded until the formation of stable foam was stopped. The influence of a chelating surfactant, different foaming agents and cationic polyelectrolytes, pH value and temperature on the purification efficiency of the TMP waters mill have been studied.

8.1.1. Laboratory water

Two complexing agents in combination with various foaming agents were studied during flotation, which are DTPA, a common complexing agent used in the paper industry and a recoverable chelating surfactant, 4-C12-DTPA synthesized at Mid Sweden University. 4-C12-DTPA has surface active properties due to an introduction of a carbon chain to its structure and its affinity to metal ions is not affected. In Figure 15 the chemical structures of the above mentioned complexing agents are shown. Metal ions bound with 4-C12-DTPA can easily be removed in a simple flotation process by the interaction of the chelating surfactant with the surface of air-bubbles. As it was shown in Paper I, the chelating surfactant studied can be efficiently used as a complexing agent in the metal ion removal of the spruce thermomechanical pulp (TMP) investigated prior to hydrogen peroxide bleaching. No significant differences in either the brightness development or the hydrogen peroxide consumption could be detected in comparison to pulp treated with the conventional complexing agent diethylenetriamine pentaacetic acid (DTPA) ([134, 135]).

![Figure 15. Chemical structure of the studied of a) recoverable chelating surfactant (4-C12-DTPA) and b) conventional complexing agent (DTPA)](image)

The results shown in Table 3 and Table 4 indicate that 4-C12-DTPA is more efficient in regards to the removal of manganese ions and the reduction in turbidity
in laboratory water compared with DTPA. The higher removal of Mn²⁺ ions after application of 4-C12-DTPA is correlated to the adsorption at air-water interfaces of the chelating surfactant which results in the efficient foam formation ability compared to regular DTPA. The flotations with both 4-C12-DTPA and DTPA in combination with DoTAC resulted in high reductions in turbidity. The decrease in turbidity increased with an increase in DoTAC concentration. This phenomenon was not observed after additions of SDS and DDAO. A reason why DoTAC is more efficient in the removal of lipophilic extractives than other foaming agents is correlated to the chemical character of DoTAC. DoTAC is a cationic foaming agent that is most likely adsorbed on negatively charged double-layered pitch droplets and creates stronger interactions than both DDAO, which is a zwitterionic foaming agent, and SDS, which is an anionic foaming agent [57].

Table 3. The removal of Mn²⁺/4-C12-DTPA chelates (%), the decrease in turbidity (%) and the amount of foam fraction (wt%) of laboratory water at different foaming agents additions (pH 5.5 and 20 °C).

<table>
<thead>
<tr>
<th>Foaming agent (ppm)</th>
<th>8</th>
<th>16</th>
<th>40</th>
<th>80</th>
<th>160</th>
<th>320</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDAO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn²⁺ (%)</td>
<td>48.1</td>
<td>53.1</td>
<td>68.7</td>
<td>73.9</td>
<td>81.5</td>
<td></td>
</tr>
<tr>
<td>Turbidity (%)</td>
<td>12.5</td>
<td>13.1</td>
<td>15.1</td>
<td>19.0</td>
<td>19.0</td>
<td></td>
</tr>
<tr>
<td>Foam F. (%)</td>
<td>1.2</td>
<td>1.3</td>
<td>4.0</td>
<td>2.8</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>SDS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn²⁺ (%)</td>
<td>7.3</td>
<td>12.7</td>
<td>27.9</td>
<td>28.9</td>
<td>30.6</td>
<td></td>
</tr>
<tr>
<td>Turbidity (%)</td>
<td>5.3</td>
<td>12.6</td>
<td>22.6</td>
<td>27.8</td>
<td>34.3</td>
<td></td>
</tr>
<tr>
<td>Foam F. (%)</td>
<td>0.8</td>
<td>0.5</td>
<td>7.8</td>
<td>13.6</td>
<td>21.7</td>
<td></td>
</tr>
<tr>
<td>DoTAC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn²⁺ (%)</td>
<td>6.2</td>
<td>21.9</td>
<td>36.5</td>
<td>42.1</td>
<td>65.8</td>
<td>99.8</td>
</tr>
<tr>
<td>Turbidity (%)</td>
<td>20.1</td>
<td>37.2</td>
<td>46.2</td>
<td>47.8</td>
<td>57.1</td>
<td>94.5</td>
</tr>
<tr>
<td>Foam F. (%)</td>
<td>0.8</td>
<td>0.8</td>
<td>1.1</td>
<td>3.2</td>
<td>6.4</td>
<td>9.2</td>
</tr>
</tbody>
</table>

The investigation of pH and temperature influence on the flotation efficiency has been carried out and the results indicate that these two parameters are extremely important for pitch control. It was shown that the influence of pH on the removal of pitch colloids is significant and depends on the colloids' composition and structure.

At pH 3 the flotation was most efficient, with regards to the reduction of turbidity. With an increase in pH a lower decrease in turbidity was observed. A potential explanation for a more efficient flotation at lower pH may be correlated to the phase distribution between colloids pitch droplets and the water phase [53]. A high amount of the foam fraction at high pH was observed. The removal of the manganese ions increases as the pH value increases. With the increase in pH, the amount of potential attachment sides for metal ions in form of deprotonated
carboxylic groups increases. It can be noted that with the increase in temperature, the removal efficiency of Mn²⁺ and the decrease in turbidity increase for both 4-C12-DTPA and DTPA.

**Table 4.** The removal of Mn²⁺/DTPA chelates (%), the decrease in turbidity (%) and the amount of foam fraction (wt%) of L-water at different foaming agents additions (pH 5.5 and 20 °C)

<table>
<thead>
<tr>
<th>Foaming agent (ppm)</th>
<th>8</th>
<th>16</th>
<th>40</th>
<th>80</th>
<th>160</th>
<th>320</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDAO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn²⁺ (%)</td>
<td>0.0</td>
<td>0.0</td>
<td>7.1</td>
<td>11.3</td>
<td>19.4</td>
<td></td>
</tr>
<tr>
<td>Turbidity (%)</td>
<td>18.6</td>
<td>21.9</td>
<td>30.4</td>
<td>21.1</td>
<td>31.2</td>
<td></td>
</tr>
<tr>
<td>Foam F. (%)</td>
<td>0.1</td>
<td>0.1</td>
<td>3.0</td>
<td>9.5</td>
<td>7.4</td>
<td></td>
</tr>
<tr>
<td>SDS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn²⁺ (%)</td>
<td>3.8</td>
<td>8.1</td>
<td>12.4</td>
<td>15.8</td>
<td>20.2</td>
<td></td>
</tr>
<tr>
<td>Turbidity (%)</td>
<td>18.1</td>
<td>20.4</td>
<td>25.0</td>
<td>28.0</td>
<td>32.0</td>
<td></td>
</tr>
<tr>
<td>Foam F. (%)</td>
<td>1.0</td>
<td>0.6</td>
<td>1.1</td>
<td>8.5</td>
<td>9.9</td>
<td></td>
</tr>
<tr>
<td>DoTAC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn²⁺ (%)</td>
<td>9.6</td>
<td>7.0</td>
<td>6.0</td>
<td>7.2</td>
<td>17.9</td>
<td>34.6</td>
</tr>
<tr>
<td>Turbidity (%)</td>
<td>17.4</td>
<td>26.5</td>
<td>28.9</td>
<td>36.3</td>
<td>46.5</td>
<td>85.4</td>
</tr>
<tr>
<td>Foam F. (%)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>1.0</td>
<td>2.0</td>
<td>4.9</td>
</tr>
</tbody>
</table>

A more detailed discussion on DoTAC influence on the flotation efficiency of colloids will be carried out later on in the thesis and a potential mechanism will be presented as well as discussed.

**8.1.2. TMP process water BEFORE bleaching**

There is a huge difference between laboratory water and TMP process water regarding chemical composition and concentration in dissolved and colloidal components (DCC). Additionally, TMP process water contains 0.1% of fibres as well as DTPA, which introduces certain limitations for adding 4-C12-DTPA.

In **Figure 16**, a decrease in the turbidity (%) and the amount of the foam fraction (wt%) in TMP process water as a function of different DoTAC concentrations after flotation is shown. As it can be observed a 91% decrease in the turbidity of water was obtained and the amount of the foam fraction was within 20% at DoTAC concentration of 320 ppm. When further increasing the DoTAC concentration, the turbidity and the amount of the foam fraction were almost unchanged. This means that an optimal dose of DoTAC is important for the flotation efficiency with regards to both removal of colloids and the amount of foam fraction.
Figure 16. The decrease in the turbidity (%) and the amount of the foam fraction (wt%) in TMP process water as a function of different DoTAC concentrations after flotation.

An investigation of the effect of pH on the purification efficiency of TMP process water was carried as well and the results show that a change in pH significantly affects the amount of the foam fraction and the turbidity, as was seen in the case of laboratory water flotations.

A difference in turbidity changes at pH 3 between TMP and laboratory water was observed which is correlated to a variation in chemical composition and the amount of colloids in the waters. This may influence the colloids' behaviour. A higher concentration of colloids, gives a higher number of potential attachment sites for DoTAC in the form of pitch charges which may affect DoTAC/pitch interactions. The effect of temperature on the flotation was insignificant; the turbidity and the amount of foam fraction were not affected. Changes in temperature, pH value, or DoTAC concentration did not affect the Mn²⁺ ion removal.

Another important parameter, which should be paid some attention, is the residual concentration of foaming agent in the water after flotation. Boonyasuwat et al. showed that a cationic surfactant (ethylpyridinium chloride) is easier to recover from water than an anionic surfactant (sodium dodecyl sulfate) and furthermore, it was more rapid in more turbulent conditions which resulted in an extremely high wetness of the foam fraction [136].

At an initial concentration of 320 ppm of DoTAC before the flotation, only 2.6 ppm was detected in the water after the flotation. This indicates that DoTAC was attached to the pitch droplets and removed during flotation. Furthermore a part of DoTAC molecules can be attached to fibres which remained in the purified water.
It is known that to increase the removal efficiency of colloids from process water, a flotation process should be preceded by an aggregation of colloids, using a cationic polyelectrolyte [31, 33]. Moreover, the particles sized 15-25 μm can be removed by flotation most efficiently which means that the amount of additives used in the release of ink from fibres has to be controlled so that not too many small particles are formed [72]. In this study an initial comparison between application of cationic foaming agent (DoTAC) and different cationic polyelectrolytes (conventional and unconventional) in an internal cleaning stage based on flotation was performed.

The results in Table 5 indicate that DoTAC can be successfully used in the purification of the water. Chitosan, an unconventional cationic polyelectrolyte in this context, gave slightly better removal of lipophilic extractives compared to DoTAC. Over 92% of all lipophilic extractives could be removed and a 91% decrease in turbidity could be obtained by adding both chitosan and DoTAC. The concentration of lignans was probably higher than is shown in Table 5 and this issue is further described and discussed in Paper II.

Table 5. The decrease in turbidity (%), the decrease of both total concentration of extractives (mg/L) and major groups extractives concentrations (mg/L) in TMP process water before and after flotation at different purification conditions (pH 5 and temp. 20°C)

<table>
<thead>
<tr>
<th>Analysis</th>
<th>TMP process water</th>
<th>Chitosan/SDS 150 ppm/40 ppm</th>
<th>DoTAC 320 ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Decrease in Turbidity (%)</strong></td>
<td>-</td>
<td>99</td>
<td>91</td>
</tr>
<tr>
<td><strong>Total concentration of extractives (mg/L)</strong></td>
<td>738</td>
<td>103</td>
<td>149</td>
</tr>
<tr>
<td>Fatty and resin acids (mg/L)</td>
<td>73.1</td>
<td>2.9</td>
<td>2.8</td>
</tr>
<tr>
<td>Lignans (mg/L)</td>
<td>10</td>
<td>3.5</td>
<td>9.3</td>
</tr>
<tr>
<td>Betasitosterols (mg/L)</td>
<td>11.8</td>
<td>2.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Sterylicesters (mg/L)</td>
<td>88.2</td>
<td>2.4</td>
<td>7.6</td>
</tr>
<tr>
<td>Triglycerides (mg/L)</td>
<td>137</td>
<td>0.1</td>
<td>7.7</td>
</tr>
</tbody>
</table>

The ability of chitosan to form large and compact flocks facilitates the removal of disturbing substances from the water. The cationic foaming agent can only be adsorbed onto individual pitch droplets and fibres, which changes their surface properties so that the lipophilic extractives are easily removed from the process waters by flotation. The difference in the behaviour of the cationic polyelectrolyte compared to DoTAC is shown in Figure 17 and Figure 18. As can be noted, chitosan binds the pitch droplets together with the fibres in huge and tight flocks,
which can lead to considerable fibre losses. The binding mechanism of fibres and pitch droplets is based on a bridging flocculation when a single chain of the polyelectrolyte is attached to several pitch droplets and fibres [75].

**Figure 17.** Light microscope image of a foam fraction after flotation of TMP process water with 150 ppm Chitosan and 40 ppm SDS. Dark areas represent aggregates of pitch and fibres

**Figure 18.** Light microscope image of a foam fraction after flotation of TMP process water with 320 ppm DoTAC. Dark areas represent aggregates of pitch and fibres

Moreover, compared with a cationic foaming agent as DoTAC, the interaction between cationic polyelectrolyte and the lipophilic extractives are probably irreversible; this may introduce limitations in further use of the removed material. Small pitch aggregates appear after the addition of DoTAC due to neutralization of the charges on the pitch droplets which make possible to remove them efficiently by flotation. Wu et al. also tested cationic foaming agents in deinking flotation and noticed that the particle size distribution of toners increased with an increase in cationic foaming agents concentrations [137].

The flotation trials with chitosan resulted in an extensive deposition of “dirt” on the equipment. The flocks adhered to the surfaces of the flotation unit were very
tacky and formed a layer difficult to remove. After the trials with DoTAC the flotation unit was much cleaner.

8.1.3. Conclusions

It can be concluded that DoTAC functions selectively. A 90% decrease in turbidity in laboratory and TMP process water was observed by flotation. The temperature and the pH value have significant influence on the flotation efficiency. A 99% removal of manganese ions from the laboratory water can be obtained by the introduction of 4-C12-DTPA (chelating surfactant) to the system. The flotation units were much cleaner after flotation with DoTAC than after a cationic polyelectrolyte application.

8.2. Flotation in a Voith flotation cell (Paper III, IV, and V)

Flotations of TMP process water “before” and “after” bleaching were performed in a 20 L Voith flotation cell, equipped with a rotor-based air dispersing system. The investigation of the influence of foaming agent concentration, pH, temperature and concentration of calcium ions on the removal of both DCS components from TMP process water “before” and “after” bleaching were carried out. The flotations were continued until the formation of stable foam ended (Paper III) or for 1 hour (Paper IV and V). A comparison between the Voith cell and the 1 L cell was carried out as well due to a significant difference noticed in the influence of the cell construction on both the decrease in turbidity and the removal of extractives. The results from the 1 L cell investigation in the comparison of the cells refers to paper I.

8.2.1. TMP process water BEFORE bleaching

The difference in froth generation of the Voith cell and the 1 L cell affects the removal efficiency of colloids from the water. The Voith cell delivers more turbulent conditions compared with the 1 L cell. In the Voith cell the air-bubbles are formed and mixed into the solutions via an impeller, whereas in the customized 1 L cell the air-bubbles are generated only by direct injection of air through a glass filter as shown in Figure 19. The Voith cell gives a better distribution of driving forces which increases removal of colloids from the water. The outcome of a comparison between these two flotation cells are shown in Figure 20. A higher removal of the colloids was obtained for the Voith flotation cell than for the 1 L cell. A 90% decrease in the turbidity could be obtained at lower DoTAC concentration and at shorter flotation time in the Voith flotation cell than in the 1 L cell. Additionally, the amount of the foam fraction within 5% of the
initial volume indicated that the flotation process may be used successfully in the purification of the water.

**Figure 19.** A difference in the driving forces distribution between 1 L and Voith flotation cell

**Figure 20.** The decrease in turbidity (%) and the amount of foam fraction (wt%) in TMP process water before bleaching as a function of different DoTAC concentrations (ppm) after flotation in the Voith cell and in the 1 L cell at pH 5.0 and 21 °C (Paper III)

In addition to DCS components, TMP process water contains fibres and fines in amounts of 0.05-0.1%. During flotation only individual fibres were removed using the foam fraction. GC analysis of lipophilic extractives on fibres and fines before and after flotation shows that fibres and fines can be purified. A large part of the lipophilic extractives was removed from the surfaces as presented in **Table 6**.
Table 6. Concentration of major groups of extractives (mg/L) and total extract concentration (%) in the fibres and fines from TMP process water before and after flotation at a DoTAC concentration of 160 ppm, pH 5.0 and 21 °C

<table>
<thead>
<tr>
<th>Extractives</th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fatty and resin acids</td>
<td>15900</td>
<td>3110</td>
</tr>
<tr>
<td>(mg/kg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lignans (mg/kg)</td>
<td>698</td>
<td>781</td>
</tr>
<tr>
<td>Betasitosterols (mg/kg)</td>
<td>1360</td>
<td>832</td>
</tr>
<tr>
<td>Sterolesters (mg/kg)</td>
<td>9060</td>
<td>5250</td>
</tr>
<tr>
<td>Triglycerides (mg/kg)</td>
<td>15100</td>
<td>6720</td>
</tr>
<tr>
<td>Extract concentration</td>
<td>4.2</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Wu et al. investigated brightness gain obtained from hand-sheets made of deinked fibres as a function of different foaming agents concentration [137]. It was noted that that cationic surfactants gave much higher brightness gains than TX-100 which is a non-ionic surfactant.

The promising results obtained in Paper III were an inspiration for the next study where the influence of pH, temperature, cationic foaming agent concentration, calcium concentration and air flow on flotation efficiency was investigated. This resulted in Paper IV.

Based on the results presented in Figure 21 it can be noted that pH has a significant influence on the flotation efficiency of lipophilic extractives. The residual concentration of lipophilic extractives i.e. fatty and resin acids and neutrals, was 37% at pH 5.1 and 14% at pH 3.5. About 20% of the neutral substances remained after the flotation at pH 3.5 while at pH 5.1 the residual of neutral substances was 50%. At pH 7.6, the residual concentration of neutral substances was 125% whereas the residual concentration of resin and fatty acids was 20% and 40% respectively. A similar trend can be noted in the residual turbidity presented in Table 7. At pH 7.6 at 20 °C and 80 ppm DoTAC, the residual turbidity was 50% while the turbidity at pH 5.1 was 25% and 10% at pH 3.5. A reason why the flotation is more efficient at a lower pH than at a higher is correlated to the phase distribution between colloidal pitch droplets and the water phase. RFAs are mostly attached to the colloidal droplets at low pH and a potential mechanism behind the flotation process is shown in Figure 22.
Figure 21. Residual extractives after flotation of TMP water, with 80 ppm DoTAC at 20 °C

Figure 22. A model of colloidal pitch, RFAs and DoTAC at different pH levels

Nylund et al. stated as shown in Figure 23 that only 5% of the carboxylic groups in RFAs are dissociated at pH 3 [52]. Furthermore, it can be observed that the RFAs are mostly attached to the colloidal droplets at pH 3 as a surface layer. This could be a reason why the flotation process is more efficient at low pH. At pH 5.1, the
RFAs were not associated with the colloidal pitch droplets to the same extent as at pH 3.5 and about 90% of the carboxylic groups in RFAs are dissociated which decreased the pitch removal. The increase in pH shifted the phase distribution of RFAs from the colloidal pitch droplets further towards the water phase. Moreover, at pH 8 the degree of dissociation of carboxylic group in RFAs is 100% as shown in Figure 23.

**Figure 23.** Degree of dissociation [52] and phase distribution [53] of RFAs in pitch emulsion at various pH values.

From Figure 21 it can be also concluded that the pH variations did not affect the lignan concentrations which are hydrophilic extractives.

The residual concentration of water soluble galactoglucomanan (GGM) and uronic acids (PeA) at 20 °C and 80 ppm DoTAC is almost unchanged at all conditions or even higher than 100%. The uronic acids consists mainly of galacturonic acids units which are methylesterified to a high degree in unbleached TMP of Norway spruce [138]. This means that PeAs are not charged and therefore not removed by flotation with DoTAC at all pHs. The observation that GGM remained in the water after flotation can be interpreted as a result of its high water solubility. The fibres in the process water were already beaten in a refiner, and this facilitates washing out of the different components during the turbulent flotation conditions [139].

Since high pH is inefficient in the removal of lipophilic extractives by flotation a further investigation of DoTAC concentration and temperature on flotation efficiency was only performed at pH 5.1 and pH 3.5 as shown in Figure 24 and Table 7. The residual concentration of lipophilic extractives decreases with an increase in DoTAC concentration from 40 to 80 ppm at all conditions. A higher decrease was observed at pH 3.5 than at pH 5.1. An increase in temperature from
20 °C to 50 °C resulted in a higher decrease of lipophilic extractives which can be clearly seen in GC analysis in Figure 24 and in the turbidity measurements in Table 7.

Table 7. Characteristics of the unbleached TMP process water after 60-min flotations at 20 °C and 50 °C at different pHs and various DoTAC concentrations

<table>
<thead>
<tr>
<th>pH</th>
<th>DoTAC (ppm)</th>
<th>Residual turbidity (%)</th>
<th>GGM (%)</th>
<th>PeA (%)</th>
<th>Foam fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.6</td>
<td>80</td>
<td>50</td>
<td>108</td>
<td>112</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>53</td>
<td>86</td>
<td>81</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>38</td>
<td>93</td>
<td>87</td>
<td>2</td>
</tr>
<tr>
<td>5.1</td>
<td>80</td>
<td>25</td>
<td>110</td>
<td>101</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>35</td>
<td>96</td>
<td>85</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>21</td>
<td>95</td>
<td>84</td>
<td>9</td>
</tr>
<tr>
<td>3.5</td>
<td>80</td>
<td>10</td>
<td>115</td>
<td>84</td>
<td>5</td>
</tr>
</tbody>
</table>

It can be noted that resin acids were removed more efficiently than the fatty acids in flotations which may indicate that the resin acids were more accessible for DoTAC. Sundberg et al. (2009) showed by phase distribution experiments that resin acids are released from colloidal pitch droplets at lower pH than fatty acids [53]. It was also stated that fatty acids may be packed closer to the core of pitch droplets than resin acids which could explain why the resin acids were removed more extensively than fatty acids [140].

The residual concentration of water soluble GGM and PeA is almost unchanged during flotations with except for PeA at pH 3.5, 80 ppm DoTAC and 50 °C where an almost 60% decrease in PeA was observed.

The foam fraction was within 2% with exception of high pH and low pH at high DoTAC concentration and at 50 °C. The released resin and fatty acids at higher pH contribute to higher foamability. At low pH, where the number of potential attachment sides is low, it is easy to overdose DoTAC which results in high foam forming.

The results presented in Table 8 (not published) confirm that the pitch components were efficiently removed from the water and concentrated in the foam fraction whereas the concentration of lignans and carbohydrates was low. Original water compositions, an amount of extractives in the fibre fraction and flotation
parameters are the main factors determining the foam fraction content. This may explain variations, especially in pitch components which are not well-correlated to the results presented in Table 7 and Figure 24.

![Graphs showing residuals](image)

**Figure 24.** Residual extractives in unbleached TMP process water after 60-min flotation at 20 °C and 50 °C as a function of DoTAC concentration at pH 3.5 and 5.1. Neutrals mean diglycerides, triglycerides and steryl esters.

It is well-known that calcium content is an important factor in the pulp and paper industry so the influence of calcium on the flotation was also investigated at pH 5.1, temperature 20 °C and DoTAC 80 ppm. The calcium concentration was increased from 0.5 mM, which is an original concentration in delivered water, to 3 mM. The residual concentration of total lipophilic extractives was unaffected whereas the concentration of GGM and PeA decreased with an increase to 3 mM calcium concentration. A redeposition of the hemicellulose chains onto fines in the water is likely behind the removal of GGM. The decrease in concentration of uronic acids may have been caused by co-aggregation with colloidal pitch [141].
Table 8. Chemical composition and amount of extractives and carbohydrates in collapsed foam fractions (mg/L)

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>pH</th>
<th>DoTAC (ppm)</th>
<th>Fatty acids</th>
<th>Resin acids</th>
<th>Neutrals</th>
<th>Lignans</th>
<th>GGM</th>
<th>PeA</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>7.6</td>
<td>80</td>
<td>50</td>
<td>143</td>
<td>137</td>
<td>161</td>
<td>1590</td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>5.1</td>
<td>40</td>
<td>86</td>
<td>297</td>
<td>485</td>
<td>187</td>
<td>1600</td>
<td>208</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>153</td>
<td>499</td>
<td>958</td>
<td>167</td>
<td>1610</td>
<td>233</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>252</td>
<td>781</td>
<td>1370</td>
<td>184</td>
<td>1930</td>
<td>301</td>
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<tr>
<td></td>
<td>3.5</td>
<td>40</td>
<td>73</td>
<td>211</td>
<td>495</td>
<td>170</td>
<td>1710</td>
<td>230</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>56</td>
<td>155</td>
<td>397</td>
<td>171</td>
<td>1950</td>
<td>298</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>92</td>
<td>233</td>
<td>583</td>
<td>174</td>
<td>1920</td>
<td>359</td>
</tr>
<tr>
<td>50°C</td>
<td>5.1</td>
<td>40</td>
<td>135</td>
<td>271</td>
<td>896</td>
<td>38</td>
<td>1720</td>
<td>217</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>96</td>
<td>187</td>
<td>713</td>
<td>43</td>
<td>1750</td>
<td>229</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>157</td>
<td>415</td>
<td>825</td>
<td>181</td>
<td>2150</td>
<td>311</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>40</td>
<td>136</td>
<td>372</td>
<td>676</td>
<td>148</td>
<td>2000</td>
<td>356</td>
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<tr>
<td></td>
<td></td>
<td>60</td>
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<td>142</td>
<td>792</td>
<td>47</td>
<td>1810</td>
<td>284</td>
</tr>
<tr>
<td></td>
<td></td>
<td>80</td>
<td>21</td>
<td>40</td>
<td>250</td>
<td>47</td>
<td>1580</td>
<td>202</td>
</tr>
</tbody>
</table>

It has been reported that the precise air control can be key to efficient flotation [73]. In our study an increase in air flow to 9 L/min had no significant effect on the removal of lipophilic extractives.

The residual DoTAC concentrations were equally low at all conditions.

8.2.2. TMP process water AFTER bleaching

A similar study, as was also the case for the unbleached TMP process water, was performed for TMP process water after bleaching since various water purification systems are originally applied after the bleaching stage. The bleaching stage is the most critical stage for the behaviour of DSC released to the TMP process water after the refining stage. Figure 13 found in the Material part emphasizes changes in concentration and composition of DSC which occurs when high alkali and temperature are applied. It can be noted that the concentration and composition of lipophilic extractives is unaffected during bleaching whereas the concentration of lignans was drastically decreased due to oxidation and degradation [142]. The concentration of dissolved hemicelluloses analysed as monomeric sugars from (mannose, glucose, galactose, arabinose, xylose and rhamnose) decreased...
significantly. The concentration of GGM calculated from a mannose/glucose/galactose unit ratio of 4:1:0.5 was lowered by about 85% [111]. This is explained by the deacetylation of GGM, leading to a decreased solubility in water and re-adsorption of deacetylated GGMS onto the fibres [143, 144]. The concentration of PeAs increased which is due to the hydrolytic cleavage of pectins under alkaline conditions. This leads to shorter segments of PeAs and facilitates their release from the fibres.

From the result presented in Table 9 and Figure 25 it can easily be claimed that the flotation is more efficient at low pH as was also the case for TMP process water before bleaching. The residual pitch concentration decreases with an increase in DoTAC concentration at pH 5.1 and 3.7 whereas it is almost unchanged at higher pH. Obviously, there is a pH-dependent phase distribution of resin and FaA between pitch droplets and water. The influence of pH at pitch removal by flotation has been discussed in the previous chapter. Furthermore it can be noted that an increase in temperature from 20 °C to 50 °C gives higher removal of pitch.

Table 9. Characteristics of the bleached TMP process water after 60-min flotations at 20 °C and 50 °C at different pHs and various DoTAC concentrations

<table>
<thead>
<tr>
<th>pH</th>
<th>DoTAC (ppm)</th>
<th>Residual turbidity (%)</th>
<th>GGM(%)</th>
<th>PeA (%)</th>
<th>Foam fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.6</td>
<td>0</td>
<td>30 34</td>
<td>109 100</td>
<td>102 93</td>
<td>1 1</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>30 33</td>
<td>119 123</td>
<td>102 112</td>
<td>2 2</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>34 27</td>
<td>144 155</td>
<td>121 122</td>
<td>4 3</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>25 38</td>
<td>159 165</td>
<td>12 139</td>
<td>5 4</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>23 26</td>
<td>129 123</td>
<td>114 105</td>
<td>6 7</td>
</tr>
<tr>
<td>5.1</td>
<td>0</td>
<td>25 10</td>
<td>118 99</td>
<td>99 64</td>
<td>3 7</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>11 14</td>
<td>156 70</td>
<td>118 71</td>
<td>8 4</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>30 17</td>
<td>112 162</td>
<td>109 97</td>
<td>3 4</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>21 17</td>
<td>115 125</td>
<td>101 70</td>
<td>3 3</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>13 8</td>
<td>105 120</td>
<td>100 68</td>
<td>4 10</td>
</tr>
<tr>
<td>3.5</td>
<td>0</td>
<td>17 10</td>
<td>117 124</td>
<td>58 31</td>
<td>7 5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>25 8</td>
<td>161 141</td>
<td>114 35</td>
<td>7 4</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>16 10</td>
<td>171 147</td>
<td>128 43</td>
<td>8 3</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>13 7</td>
<td>168 126</td>
<td>126 39</td>
<td>17 4</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>10 11</td>
<td>123 98</td>
<td>100 31</td>
<td>15 9</td>
</tr>
</tbody>
</table>

The concentration of dissolved GGM was >100% at all DoTAC concentrations and at both temperatures. GGM is washed out from fibres during flotation.
Furthermore, GGM remains in the water after flotation due to high water solubility of GGM. The concentration of PeA is unchanged or even higher at 20 °C at all pHs. When increasing temperature and lowering pH at the same time, the concentration of PeA began to decrease. It can be explained by the easier formation of PeA aggregates with Ca²⁺ under these conditions and the solubility decrement of the formed aggregates. Saarimaa et al. (2006) found that PeA isolated from bleached TMP can be completely precipitated by Ca²⁺ [141]. Furthermore, MacDougall et al. (1996) noted that the stiffness of the gel formed by pectic polysaccharides in the presence of Ca²⁺ increases at higher temperature [145]. When increasing Ca²⁺ concentration small changes in flotation efficiency was observed.

**Figure 25.** Residual pitch concentration after 60-min flotation at 20 °C and 50 °C as a function of DoTAC concentration at various pH values
When comparing TMP process water before and after bleaching it can be noted that a lower DoTAC concentration is needed to remove the pitch for bleached TMP process water which is correlated to a lack of steric stabilization given by GGM dissolved in the water. The dissolved GGM in the accept was close to or above 100% for both waters. The concentration of PeA remained unchanged during the flotation of unbleached TMP process water, whereas in the bleached TMP process water, a high removal of PeA can be observed at low pH and 50 °C. The foam fraction is larger after bleaching than before, indicating substantial changes in the water composition.

8.2.3. Conclusions

Foam flotation can selectively remove colloidal pitch from both unbleached and bleached TMP process waters. The pH value and temperature are the most important factors for the efficiency and selectivity of flotation with regard to DCS removal and amount of foam fraction. DoTAC concentration is also important for flotation especially for unbleached TMP process water. The flotation selectivity is further confirmed by unchanged concentration of dissolved GGM in the accept.

8.3. Recovery of hemicelluloses (Paper VI)

As presented in Paper IV and V the flotation can be successfully used to selectively remove lipophilic extractives from the unbleached and bleached TMP process water while the concentration of dissolved GGM remains unchanged. In further studies recovery trials of hemicelluloses from purified TMP process water were performed. The hemicelluloses were recovered only from purified unbleached TMP process water since the substantial changes of hemicelluloses during the bleaching stage occurred which affected their concentration and chemical composition. A precipitation procedure with various anti-solvents was used to recover GGM from unconcentrated as well as concentrated waters. The influence of anti-solvents such as methanol, ethanol and acetone was investigated. Moreover, effects of pH, temperature and different electrolytes were also taken into consideration.

8.3.1. Precipitation yield determination by turbidity and gravimetric analysis

Figure 26 shows the influence of the solutions conditions, such as weight fraction of different anti-solvents, pH and temperature, on the phase separation of hemicelluloses monitored by turbidity measurements.
At low methanol weight fraction (up to 60%) small changes in the turbidity was observed at all temperatures. When increasing the methanol fraction, the turbidity increases at all conditions. It can also be noted from the same figure that precipitation of hemicelluloses is more efficient with ethanol than methanol. Based on the results presented in Figure 26, it can be clearly seen that among the anti-solvents studied, acetone is the most efficient in precipitating hemicelluloses.

Figure 26. Turbidity changes (NTU) during anti-solvent induced phase separation of hemicelluloses from unconcentrated TMP process water at various temperatures

The reasons behind hemicelluloses starting to precipitate under the conditions investigated can be qualitatively described by using the Flory-Huggins approach [146]. A large difference in the interaction energy between segments of the polymer...
and solvent molecules, when compared to the interaction energy between segment-segment and solvent-solvent molecules, leads to polymer precipitation (phase separation) from the solution. For entropy reasons, at lower anti-solvent addition likely the high molecular species will separate out first, leaving the lower molecular weight species in solution. When increasing the addition of anti-solvent also the species with lower molecular weight starts separating which is described by Flory and Huggins [57]. Moreover, since ethanol is slightly more hydrophobic than methanol due to the additional methylene group, ethanol increases the hemicellulose phase separation more than methanol. A similar carbon chain dependency has also been reported for the phase separation of salt-free EHEC solutions [147].

He et al. investigated the solubility parameters of polysaccharides (polydextrose and spruce galactoglucomannan) for various solvents (ethanol, acetone and DMSO) [148]. It was noticed that when increasing the solvent weight fraction, the solubility parameter decreases and the hydrophobicity in the polymer-solvent system increases. Moreover, the solubility parameters for mixtures of water-acetone are lower compared to the mixtures of water-ethanol. Furthermore, acetone is an aprotic solvent, which means that acetone may weaken or even break down hydrogen bonds between water and hemicellulose. This may contribute to a lower solubility of the species in solution and may accelerate the phase separation. Ethanol and methanol are protic solvents that decrease the solubility of the species in solutions to a lower extent, since they can form hydrogen bonds with dissolved material. It can be observed that higher amounts of ethanol and methanol than acetone are needed to precipitate hemicellulose from the studied process water.

Mass analysis presented in Figure 27 confirms that methanol is less efficient anti-solvent than ethanol and acetone. The similar trends were obtained when hemicelluloses were recovered from concentrated water as shown in Figure 28. The main difference observed between un-concentrated and concentrated waters is that a lower amount of anti-solvent is needed to receive high precipitation yields for concentrated water than for un-concentrated. The optimum for un-concentrated water is from 65% to 75% of acetone, whereas for concentrated water the optimum is found within the range of 50% to 55%.
Figure 27. Mass of precipitated hemicelluloses received for uncentrated water after precipitation with various anti-solvents at various conditioning temperatures.

An influence of some electrolytes, such as KAc, Na₂SO₄ and MgSO₄ at added concentration of 0.01 M, 0.05 M and 0.1 M with mentioned anti-solvents and temperatures, on the precipitation efficiency of hemicelluloses from uncentrated water was evaluated. Also Borax (Na₂B₄O₇·10H₂O) impact on hemicellulose yield was taken into considerations. From these results (not published) it was concluded that neither electrolytes nor borax influenced the hemicelluloses precipitation from the water at all tested conditions.
**Figure 28.** Mass of precipitated hemicelluloses received from 10 mL of concentrated purified TMP process water after precipitation with various antisolvents at various conditioning temperatures

### 8.3.2. Chemical composition of hemicelluloses precipitates and impurities

The chemical composition of precipitates was determined by GC analysis. It was noted that mannose, galactose and glucose are the main components, contributing to over 80% of total carbohydrate content regardless of precipitation conditions both for unconcentrated and concentrated TMP process water. The GGM content calculated from a mannose/glucose/galactose unit ratio of 4:1:0.5 [111] increases with a increase in anti-solvent weight fractions. The concentration of arabinose and xylose was about 10% and 7% for unconcentrated and about 6.5% and 2% for concentrated waters at all temperatures and decrease with an increase in the anti-solvent addition. The concentration of rhamnose is low at all conditions.

FTIR spectroscopy was used to identify main functional groups of carbohydrates. A strong hydrogen bond O-H stretching absorption at 3400 1/cm and a C-H stretching vibration absorption in the region of 2950-2980 1/cm were found. Strong signals defined in the range of 2500-2900 1/cm derived from the vibration in O-H located in the carboxylic groups. The bands at 1580 1/cm, 1456 1/cm and 1370 1/cm are assigned to C-H vibrations of carbohydrates. The wavenumber at 1260 1/cm was indicative of carboxylic acid vibrations which were due to glucuronic acids side groups. In addition, a specific band in the 1200-1000 1/cm region is dominated by ring vibrations overlapped with stretching vibration identified for the OH group in uronic acids, xylene and glucose units in galactoglucomannans and the C-O-C glycosidic bond vibration [149]. The absorbance at 873 1/cm is likely to derive from the pyranose rings of glucose, galactose and mannose [150].
As an important part of the following study is an investigation of the impurities of precipitates. A content of lignin and extractives was determined and the results are presented below.

It was observed that the precipitates obtained from unconcentrated water after methanol addition, contain more impurities at all conditions than the hemicelluloses precipitated with ethanol or acetone. The content of the lipophilic part of impurities in precipitates from concentrated TMP water was low at all conditions. The content of lignans was below 0.01% in all the precipitates for unconcentrated water. For concentrated water the content of lignans was much higher especially at lower anti-solvent addition. The lignin content for precipitates originating from concentrated water is much higher at low anti-solvent addition and starts to decrease with an increase of the anti-solvent addition.

As reported previously, the lignin content can be lowered by 30-40% by through selective flotation, which may contribute to low residual lignin content in the precipitates. The residual amounts of lignin are likely to originate lignin-carbohydrate complexes (LCC) [151, 152]. It is important to emphasize that the water samples extracted with MTBE contain not only lignin but also dissolved hemicelluloses that may contribute to the absorption at 280 nm and then introduce an overestimation of the lignin content [127]. During the same flotation a high decrease in the concentration of lipophilic extractives was obtained and confirmed by a 90% decrease in turbidity which contributed to their low amounts in the precipitates. The content of metal ions in the precipitates was found regardless of anti-solvent addition; Na 0.8%, Ca 0.7%, Mn 0.2%, Cu 0.1% and Fe 0.1% regardless of the ethanol weight fraction.

A precipitation efficiency determination was investigated and analysis of both fractions i.e. precipitates and water after precipitation and anti-solvent recovery was performed. It can be noted that at 54.5% of ethanol, a 60% yield was obtained whereas for the same acetone content the yield increased to 80%. When increasing the anti-solvents content to 58.3% the yield increased to around 70% and 90% for ethanol and acetone, respectively. GGM was still the main hemicellulose in the precipitates.

8.3.3. Molecular mass distribution in hemicellulose precipitates

Molecular mass determinations of some of the hemicellulose fractions obtained by anti-solvent precipitation were performed by GPC and PFG NMR measurements.
The two methods display complementary information on the physical properties of the samples. GPC gives size distribution of molecules and particles based on obstruction effects caused by the highly porous packing material in the chromatography column that affect the retention of differently sized molecules and particles differently. PFG NMR detects self-diffusion of truly dissolved molecules based on differences in the decay of proton signals when a magnetic field-gradient applied to the sample is varied. In Figure 29, it can be noted that there are GPC peaks showing a fraction of molecules having very low molecular mass, approximately in the range of tens to some hundred grams per mole. There is also a main distribution with a peak situated at some tens of thousands, and finally a third distribution is observed with peak molecular mass at several hundred thousand grams per mole.

Figure 29. Molecular mass distribution of precipitates from concentrated TMP process water after precipitation with various anti-solvents at 7°C.

The peaks of the distributions observed in the intermediate molecular mass region in all the GPC curves are assigned as representing precipitated hemicelluloses when considering previously reported values [106, 108]. PFG NMR measurements
support also these results. PFG NMR is only able to detect signals from truly dissolved molecules, and the fitting procedure applied is based on an assumption that the molecules in the samples can be represented by unimodal lognormal distribution curves. On the hand, if the high molecular mass peaks in GPC would represent dissolved hemicelluloses, the peak value and the distribution curves obtained from PFG NMR would be shifted to higher molecular mass. This should be especially visible for the precipitates obtained at the higher anti-solvent concentration, since the populations of the lowest molecular mass fractions determined by GPC are significantly smaller. On the other hand, the relatively large fractions of low molecular mass species detected by GPC in the precipitates obtained at the lowest concentration of anti-solvents are indeed detected by PFG NMR and contribute to shift the peak values of the dotted curves to lower molecular mass values, as well as slightly broadening the distribution. Determined values of hemicellulose peak (median) molecular mass of precipitates obtained from GPC and PFG NMR measurements are presented in Table 10.

**Table 10.** Peak molecular weight of the precipitated hemicellulose at 7 °C from GPC and PFG NMR determination

<table>
<thead>
<tr>
<th>Anti-solvent</th>
<th>Anti-solvent concentration (%)</th>
<th>Peak molecular weight (g/mol)</th>
<th>GPC</th>
<th>PFG NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>66.7%</td>
<td>30400</td>
<td>16600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>37.5%</td>
<td>36600</td>
<td>29800</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>66.7%</td>
<td>32300</td>
<td>20300</td>
<td></td>
</tr>
<tr>
<td></td>
<td>37.5%</td>
<td>33900</td>
<td>34300</td>
<td></td>
</tr>
</tbody>
</table>

From the results it can be concluded that higher molecular mass hemicelluloses precipitate at the lower anti-solvent weight fractions than lower molecular mass hemicelluloses. This confirms what is expected from the theory and some earlier investigations [57]. What is still unclear, however, is the chemistry of the particles that give rise to the highest molecular mass peaks displayed in the GPC measurements.

### 8.3.4. Conclusions

An anti-solvent precipitation can be a promising way to recover hemicelluloses from pre-purified and concentrated TMP process water. Water evaporation is an interesting approach for concentration of hemicelluloses from TMP process water. At all investigated solution conditions, the precipitation was found to be governed by the aprotic solvent and the efficiency correlates to the inverse of the anti-solvent's dielectric constant as: acetone > ethanol > methanol. Moreover, acetone
has the lowest boiling point and does not form azeotropes with the water, which may facilitate its recovery. To increase the overall purity of the hemicellulose to be recovered, flotation of the process water before anti-solvent precipitation was found efficient. The obtained precipitates contained low amounts of impurities such as lipophilic extractives and lignin. GGM was the main hemicellulose in the precipitates.

8.4. Recovery of phenolic antioxidants

Lignans which are a desirable natural raw material, recognized as phenolic antioxidants, can be efficiently recovered from purified TMP process water. More than 90% of lipophilic extractives are removed by selective flotation and over 90% of hemicelluloses can be recovered by anti-solvent precipitation.

A basic trial of lignans recovery is presented below. The hemicellulose was firstly recovered by anti-solvent precipitation with 70% of acetone. After acetone recovery, an absorbent XAD-2 was added to the water and the mixture was stirred for a long time. Then, the XAD-2 fraction was separated and washed with methanol. The methanol fraction was further analysed. HMR and allo-HMR were found to be the main fractions. Other lignans in much lower concentrations were detected in the methanol fraction as well.
9. GENERAL CONCLUSIONS

Accumulation of non-adsorbed lipophilic substances increases the risk of uncontrolled pitch aggregation and process disturbances. Johnsen et al. (2007) show that only about 30% of the pitch can be retained in the paper [19]. From this perspective, treatment methods that reduce the harmful effects of lipophilic substances in the process and decrease the emissions of chemicals and released wood substances to the environment are desired.

Flotation used as a way of internal cleaning is a promising solution for purification of process waters in integrated pulp mills providing opportunities for an efficient and selective removal of pitch colloids. It was noted that the choice of equipment plays an important role for the efficiency of the flotation. Compared to the 1 L cell, a decrease in turbidity of 90% could be obtained in the Voith cell at shorter flotation time and at lower concentration of foaming agents. The application of a cationic foaming agent, DoTAC, gives a 90% removal of lipophilic extractives from laboratory water, original and bleached TMP process water. pH and temperature has a significant influence on the flotation. Selective flotation and probably reversible interaction between DoTAC and colloids may create opportunities to further investigate material recovery from purified water and foam fractions. Water evaporation seems to be a promising way to concentrate raw materials in pre-purified TMP process water before recovery. An 85-90% recovery of hemicelluloses with low impurities content could be obtained by anti-solvent precipitation. In a further step, lignans recovery may be performed.

By introducing a new separable complexing agent (4-C12-DTPA), manganese ion chelates could be removed successfully from L- and O-water in both the 1 L and the Voith flotation cells. A 98% removal of manganese ions could be obtained in both flotation units.
10. FURTHER PERSPECTIVES

Since it is known that DoTAC can be successfully applied in purification of unbleached and bleached TMP press water, a more extensive optimization of the flotation conditions and a deeper chemical analysis and characterization of the individual components removed and present in the water after the flotation should be carried out.

A low residual concentration of DoTAC in waters after flotation indicates a good DoTAC separation but it should be noted that due to its cationic character, DoTAC can be expected to adsorb on fibres that have negative charges. Therefore, investigations of the adsorption of DoTAC on fibres should be carried out.

Flotation with the cationic foaming agent changes the properties of the whole TMP water, e.g. water and fibre fraction, which may influence both paper properties and production process. An investigation of both strength and optical properties of the final product is necessary to indicate the influence on paper manufacturing.

A preliminary attempt to recover lignans from purified TMP process water was performed. An extensive investigation and optimization of the recovery conditions for lignans should be implemented.

An investigation of potential applications of recovered hemicelluloses and lignans is an important part of further studies.

An investigation of different protocols for recovery and purification of complexing agent and DSC components from foaming fraction will be also evaluated.

An application of the presented method for purification of process water derived from CTMP could be an interesting part of further method development. Especially removal of components contributing to bad odour and test could be of great importance.
11. ACKNOWLEDGEMENTS

I would like to thank my supervisor Magnus Norgren, Erik Hedenström and Håkan Edlund for guidance and continuous support.

SCA R&D Centre in Sundsvall is greatly acknowledged for carrying out a part of the analytical analysis.

SCA Ortviken is greatly acknowledged for providing pulp and process water.

All my colleagues at Mid Sweden University are acknowledged.

Financial support was given from the Bo Rydin Foundation for Scientific Research, the Administrative Board of the County of Västernorrland and the EU Structural Funds, Objective 2.

Slutligen vill jag tacka min familj för att Ni alltid tror på mig och är villiga att ge en hjälpande hand. Tack Aniu, Antosiu i tobie Maluszku.

Dziękuję też wam, Mamo, Tato i Mańku za wiarmę we mnie, wsparcie i pomoc.
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