

Tiina Leiviskä

COAGULATION AND SIZE
FRACTIONATION STUDIES
ON PULP AND PAPER MILL
PROCESS AND WASTEWATER
STREAMS

FACULTY OF TECHNOLOGY,
DEPARTMENT OF PROCESS AND ENVIRONMENTAL ENGINEERING,
UNIVERSITY OF OULU



ACTA UNIVERSITATIS OULUENSIS
C Technica 348

TIINA LEIVISKÄ

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PULP AND PAPER MILL PROCESS
AND WASTEWATER STREAMS**

Academic dissertation to be presented with the assent of
the Faculty of Technology of the University of Oulu for
public defence in Raahensali (Auditorium L10), Linnanmaa,
on 15 January 2010, at 12 noon

OULUN YLIOPISTO, OULU 2009

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Acta Univ. Oul. C 348, 2009

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ISBN 978-951-42-6087-2 (Paperback)
ISBN 978-951-42-6088-9 (PDF)
<http://herkules.oulu.fi/isbn9789514260889/>
ISSN 0355-3213 (Printed)
ISSN 1796-2226 (Online)
<http://herkules.oulu.fi/issn03553213/>

Cover design
Raimo Ahonen

OULU UNIVERSITY PRESS
OULU 2009

Leiviskä, Tiina, Coagulation and size fractionation studies on pulp and paper mill process and wastewater streams.

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Acta Univ. Oul. C 348, 2009

Oulu, Finland

Abstract

This thesis aims to increase our knowledge about the characteristics of chemical pulp process and wastewaters and how problematic substances, e.g. wood extractives, could be removed effectively and selectively by coagulation–flocculation with either internal or external water treatment. Characterization was performed by investigating kraft pulp bleaching filtrates, as well as wastewater, before (influent) and after (effluent) the activated sludge treatment by means of a range of chemical analyses and by carrying out size fractionation studies. Cationic polyelectrolytes were used to purify oxygen stage bleaching filtrate, and charge analyses (zeta potential, charge quantity) were carried out in order to understand the coagulation phenomenon. In activated sludge treatment, the enhancement of particle removal, either by filtration or using a chemical in the primary clarifier, would lead to savings in aeration costs and result in a more stable process. Microfiltration already with a large pore size (8 µm) removed 30–50% of the wood extractives from the influent. Separate treatment stages for certain wastewater fractions, e.g. debarking plant effluent, would ensure cost-efficiency. After the activated sludge process, the wood extractives were present as particles (18%) and < 3 kDa fraction (82%). β-sitosterol occurred only in particles in the effluent. The release of harmful components into the environment could be decreased by microfiltration (e.g. 0.45 µm) of the final effluent or using a chemical in the secondary clarifier. Interestingly a huge increase in BOD was realized in the 3 kDa fraction of both influent and effluent, which indicated the presence of toxic substances in the larger fractions. After passing the effluent into the water system, there might be a similar jump in the BOD because the effluent is diluted many-fold. This would contribute to the formation of areas with an oxygen deficit. In the coagulation–flocculation studies, effective and selective removal of wood extractives (92%) from the oxygen stage filtrate was obtained with a cationic polyelectrolyte of medium molecular weight and medium charge density at 72 °C and pH 5–6. The multimodal zeta potential distribution gave more information than the average zeta potential. Aggregation of colloidal particles occurred when only one zeta potential was observed. The number of different zeta potentials diminished with decreasing pH and after exceeding a certain polyelectrolyte dosage level.

Keywords: activated sludge treatment, cationic polyelectrolytes, chemical pulp mill, coagulation, wood extractives, zeta potential

To my children

Acknowledgements

This study was carried out in the Department of Process and Environmental Engineering, University of Oulu, during the years 2003–2009. First of all, I owe my deep respect and sincere gratitude to my supervisor, Dr. Jaakko Rämö, for the professional, patient and friendly guidance during this work. Professor Mika Sillanpää deserves my deep gratitude for his encouraging support in the beginning of my work.

The study has been financially supported by the Walter Ahlström Foundation, the Kemira Foundation, the Tauno Tönning Foundation, Maa- ja vesitekniikan tuki ry., the Oulu University Scholarship Foundation, Kemira and Stora Enso, all of which I gratefully acknowledge. The pre-examiners of this thesis, Professor Simon Parsons and Professor Mika Mänttari, are greatly acknowledged for the revision and valuable advice. I also express my appreciation to Dr. John Derome for careful revision of the language of this thesis.

I am very grateful to everyone in the Water Resources and Environmental Engineering Laboratory who has supported this work, or just been good company at coffee breaks. Special thanks to Tuomo Reinikka for his expertise and kind support during my experimental work. I wish to thank the staff of Kemira who contributed to this study, especially Heikki Palonen, Jussi Nikkarinen, Kaisu Jukuri, Mari Zabihian, Jukka Jokela, Tiina Sarja, Kati Matula and Marjatta Piironen. Ilkka Laakso and Esa Ruonala from Stora Enso are acknowledged for guiding me in practical matters related to samples and process knowledge. Docent Hannu Nurmesniemi from Stora Enso and Docent Risto Pöykiö from the City of Kemi are gratefully acknowledged for providing an interesting research topic and their invaluable contribution to the last two papers of this research. Warm thanks also to Docent Toivo Kuokkanen, Jaakko Pellinen and Veli-Matti Vuorenpalo for their valuable contribution as co-authors. I am also grateful to many people from the University of Oulu for their support in practical matters.

I warmly thank my cousin Reija for supporting me in my life despite our distance. I also want to thank Jaana, the members of our senior high school girl group: Iris, Miia, Minna and Tanja, and other friends for support.

My warmest gratitude go to my family; my mother Leena, my father Kari, and brothers Pekka and Tapio with their families, and my husband Juha and my admirable children Perttu, Tuulia and Viljami.

Oulu, December 2009

Tiina Leiviskä

Abbreviations

AOX	absorbable organic halogens
BOD	biological oxygen demand
BOD _n	biological oxygen demand after n days
COD	chemical oxygen demand
COD _{Cr}	chemical oxygen demand, oxidation with potassium dichromate
C-PAM	cationic copolymers formed of methacrylates and acrylamides
D	chlorine dioxide stage
Da	dalton
DC	average transmitted light intensity
DOC	dissolved organic carbon
E	extraction stage
ECF	elemental chlorine-free
ELS	electrophoretic light scattering
E _{op}	extraction stage fortified with oxygen and hydrogen peroxide
E _p	extraction stage fortified hydrogen peroxide
ELSD	evaporative light scattering detector
eq/L	equivalents/litre
GC	gas chromatography
GC-MS	gas chromatography-mass spectrometry
GW	groundwood
HE	hexamethylene diamine epichlorohydrin polycondensate
HPLC	high performance liquid chromatography
Hz	hertz
kDa	kilodalton
L/(g·cm)	litre/(gram·centimetre)
LS	laser diffraction
mA	milliampere
meq/g	milli-equivalents/gram
MF	microfiltration
MTBE	methyl <i>tert</i> -butyl ether
mV	millivolt
MW	molecular weight
MWD	molecular weight distribution

n	number of measurements
n.d.	not determined
NMWL	nominal molecular weight limit
NTU	nephelometric turbidity unit
O	oxygen delignification or oxygen stage
Op/O	oxygen stage reinforced with hydrogen peroxide
Paa	peracetic acid stage
PAC	polyaluminium chloride
PAE	epichlorohydrindimethylamine copolymer
PALS	phase analysis light scattering
PAM	polyacrylamide
PDA	photodispersion analyser
PEI	polyethyleneimine
Poly-DADMAC	polydiallyldimethylammonium chloride
PO ₄ -P	phosphate phosphorus
RFA	resin and fatty acids
RMS	root mean square value of the fluctuating signal
RPM	revolutions per minute
RSD	relative standard deviation
SC	supercalendered
SD	standard deviation
SEC	size exclusion chromatography
t	tonne
TCF	total chlorine-free
TOC	total organic carbon
Tot-P	total phosphorus
TSS	total suspended solids
UF	ultrafiltration
UV	ultraviolet
V	volt
W	washing stage
WWTP	wastewater treatment plant
XQ	enzyme treatment + chelation stage

List of original papers

This thesis is based on the following publications, which are referred to in the text by their Roman numerals:

- I Leiviskä T, Rämö J, Sillanpää M & Vuorenvalo V-M (2005) Multimodal zeta potential distributions in chemical pulp bleaching filtrates. *Journal of Pulp and Paper Science* 31: 167–174.
- II Leiviskä T & Rämö J (2008) Coagulation of wood extractives in chemical pulp bleaching filtrate by cationic polyelectrolytes. *Journal of Hazardous Materials* 153: 525–531.
- III Leiviskä T & Rämö J (2007) Investigation of multimodal zeta potential and size distribution in chemical pulp process water. *Water Science & Technology* 56: 123–129.
- IV Leiviskä T, Nurmesniemi H, Pöykiö R, Rämö J, Kuokkanen T & Pellinen J (2008) Effect of biological wastewater treatment on the molecular weight distribution of soluble organic compounds and on the reduction of BOD, COD and P in pulp and paper mill effluent. *Water Research* 42: 3952–3960.
- V Leiviskä T, Rämö J, Nurmesniemi H, Pöykiö R & Kuokkanen T (2009) Size fractionation of wood extractives, lignin and trace elements in pulp and paper mill wastewater before and after biological treatment. *Water Research* 43: 3199–3206.

The author of this thesis was the corresponding author in all the papers, and the co-authors participated in writing the articles by making valuable comments. The experimental work presented in Papers I–III was designed by the author of this thesis. The experimental work presented in Papers IV and V was designed by the author together with the co-authors.

Contents

Abstract	
Acknowledgements	7
Abbreviations	9
List of original papers	11
Contents	13
1 Introduction	15
2 Wood extractives in the chemical pulp process	17
3 Coagulation–flocculation	25
3.1 Introduction.....	25
3.2 Coagulation–flocculation of chemical pulp process and wastewaters.....	27
3.3 Investigation of coagulation–flocculation.....	30
3.3.1 Turbidity.....	30
3.3.2 Zeta potential.....	31
3.3.3 Charge quantity.....	34
3.3.4 Floc structure characteristics.....	36
4 Materials and methods	39
4.1 Bleaching filtrates.....	39
4.2 Model water.....	39
4.3 Wastewater.....	40
4.4 Cationic polyelectrolytes.....	41
4.5 Repeatability studies on DELSA zeta potential measurement.....	42
4.6 Coagulation experiments.....	42
4.7 Sequential filtration.....	43
4.7.1 O ₂ birch pulp filtrate.....	43
4.7.2 Wastewater.....	44
4.8 Analytical techniques.....	46
4.8.1 Zeta potential.....	46
4.8.2 Charge quantity.....	49
4.8.3 Particle size.....	51
4.8.4 TOC, COD and BOD.....	51
4.8.5 Wood extractives and lignin.....	52
4.8.6 Carbohydrates and hydroxyl carboxylic acids.....	53
4.8.7 Turbidity, conductivity and pH.....	54
4.8.8 Elements.....	54

4.8.9	Molecular weight distribution	55
4.8.10	Tot-P and PO ₄ -P	55
5	Results and Discussion	57
5.1	Characterization of the chemical pulp process waters and wastewaters	57
5.1.1	Multimodal zeta potential distribution.....	57
5.1.2	Components in the chemical pulp process waters	61
5.1.3	Size fractionation of wastewater.....	66
5.2	Selective coagulation–flocculation of wood extractives	83
5.2.1	Model water.....	83
5.2.2	Process water	88
6	Conclusions	95
	References	99
	Original papers	111

1 Introduction

The pulp and paper industry has been faced with ever-more stringent limitations on its discharges during the last few decades and the same trend will continue in the future. In Finland, the pulp and paper industry has been markedly successful in reducing discharges (the biochemical oxygen demand (BOD), phosphorus and chemical oxygen demand (COD)) even though the production of pulp and paper has increased considerably. In the 1980s, the activated sludge treatment was introduced in many mills. The oxygen delignification stage reduced the wastewater load because water used in this stage is recycled to the recovery system. The replacement of chlorine (Cl_2) in bleaching by elemental chlorine-free (ECF) bleaching or with only a minor amount of total chlorine-free (TCF) bleaching, has drastically cut down discharges of absorbable organic halogens (AOX). Furthermore, the increasing need to reduce water consumption has forced pulp mills to develop more efficient techniques for pulp washing. The circulation of filtrates has increased and internal water treatment is also nowadays used. A shortage of water is already a major problem in many countries.

In spite of the major process investments in environmental protection, the supplementary treatment of wastewater will become ever-more important in the future due to the large quantities of wastewater that are generated. The decolourization of effluents, at least, should be performed. Conventional biological treatment processes have little or no effect on wastewater decolourization. The brownish colour is mainly attributable to lignin and its derivatives, which are difficult to degrade naturally. It has even been proposed that lignin may have an inhibitory effect on living organisms (Pessala *et al.* 2004). Wood extractives can cause toxic and hormonal effects in aquatic environments at very low concentrations (Oikari *et al.* 1983, Mörck *et al.* 2000, Lehtinen *et al.* 1999). Biological treatment removes most of the wood extractives (Kostamo & Kukkonen 2003) and the effluent is highly diluted in the receiving water system. However, wood extractives (e.g. resin acids and sterols) can be transformed to other toxic compounds during biological treatment. Furthermore, there is no guarantee that biological treatment will always work properly, and serious toxicity breakthroughs may occasionally occur. Wood extractives adsorbed to sedimenting particles may later be desorbed from sediments (e.g. due to dredging or shipping) into the surrounding water and pose a serious threat to the aquatic environment.

Besides being toxic to aquatic life, wood extractives also cause production problems in the pulp and paper industry, such as pitch deposits on process equipment and pulp quality problems. Intensive water recirculation in pulp mills leads to an accumulation of wood extractives in the water cycles, as well as other harmful substances such as non-process elements. Non-process elements, which are an unintended component of the pulping and bleaching chemicals, enter the process as trace elements in wood and impurities in process chemicals and raw water. Among other things, these elements cause corrosion (mainly Cl), deposits on equipment (Al, Ba, Ca, and Si), increase the consumption of bleaching chemicals (Mn, Fe, and Cu) and have a negative impact on the environment (N, P, and heavy metals) (Ulmgren 1997).

This research aims to increase our knowledge about the characteristics of chemical pulp process and wastewaters and about how problematic substances could be removed effectively and selectively by means of either internal or external treatment. Detailed information about the characteristics of wastewater is essential for optimizing existing treatment methods and for developing new ones. The efficient removal of problematic substances from process waters will make it possible to close the water circuits. This would also decrease the amount of wastewater. Supplemental treatment of wastewater would, in turn, lower the amount of detrimental compounds and their access to the water system. Furthermore, pretreatment before biological wastewater treatment could have a positive impact on the performance of the biological process.

In this study the characterization of process waters and wastewaters was performed by conducting a range of analyses and performing size fractionation on these water streams by means of microfiltration and ultrafiltration. The coagulation–flocculation method was used to remove wood extractives. The coagulation–flocculation process effectively removes suspended solids and colloidal particles. In coagulation–flocculation studies, the measurement of zeta potential and charge quantity provide important information about the prevailing colloidal system. The zeta potential describes the stability of a colloidal system, whereas the charge quantity describes the cationic (or anionic) demand of the sample for neutralization. These two analyses complement one another, and using just one of them does not provide a proper understanding of colloidal systems. Understanding colloidal systems is considerably enhanced if we could distinguish between populations with distinctly different zeta potentials. This is possible with multi-angle analysis on a Doppler electrophoretic light scattering analyser, which was also used in this study.

2 Wood extractives in the chemical pulp process

Wood consists of carbohydrates (typically 65–80%), lignin (20–30%), extractives (2–5%), proteins (< 0.5%) and inorganics (0.1–1%). While the carbohydrates and lignin function as structural substances, wood extractives are needed for protecting wood against insect and fungal attack. Wood extractives can also serve as an energy source (fats and waxes) and they give wood its colour, odor and taste. (Alén 2000)

Wood extractives are components that are extractable from wood with various solvents, either nonpolarized organic solvents or water. Wood extractives can be grouped into aliphatic and alicyclic compounds, phenolic compounds and other compounds (Table 1). Lipophilic wood extractives (called wood resin or pitch) are components that can be extracted from wood with nonpolar organic solvents but are insoluble in water. Lignans and other phenolic compounds are relatively soluble in water and thus they are not included in lipophilic extractives. (Alén 2000, Back & Ekman 2000)

Table 1. Wood extractives (Alén 2000, published by permission of the Finnish Paper Engineers' Association).

Aliphatic and alicyclic compounds	Phenolic compounds	Other compounds
Terpenes and terpenoids (including resin acids and steroids)	Simple phenols Stilbenes	Sugars Cyclitols
Esters of fatty acids (fats and waxes)	Lignans Isoflavones	Tropolones Amino acids
Fatty acids and alcohols	Condensed tannins	Alkaloids
Alkanes	Flavonoids Hyrolyzable tannins	Coumarins Quinones

Terpenes, terpenoids, fatty acids and their esters are lipophilic extractives. Terpenes are biosynthesized from isoprene units (C_5H_8 , 2-methyl-1,3-butadiene). Terpenoids are terpenes substituted with one or more oxygen-containing functional groups (alcohols, ketones, aldehydes or acids). Monoterpenes and monoterpenoids are volatile compounds. The common resin acids such as abietic acid are diterpenoids. Betulinol and lupeol are triterpenyl alcohols. Their fatty acid esters are triterpenyl esters. Steroids are structurally close to triterpenoids. Sterols have a tetracyclic ring, a hydroxyl group at the C-3 position, and a side chain at the C-17 position. Their fatty acid esters are steryl esters. Fig. 1 shows

the chemical structures of abietic acid, betulinol and sitosterol. (Back & Ekman 2000)

Fatty acids are carboxylic acids which usually have a long unbranched chain. They are either saturated or unsaturated. Unsaturated fatty acids have double bonds in the chain. Fats (mainly triglycerides) are glycerides in which the glycerol is esterified with fatty acids. Waxes are long-chain alcohols and their acid esters (mainly fatty acid esters). (Back & Ekman 2000)

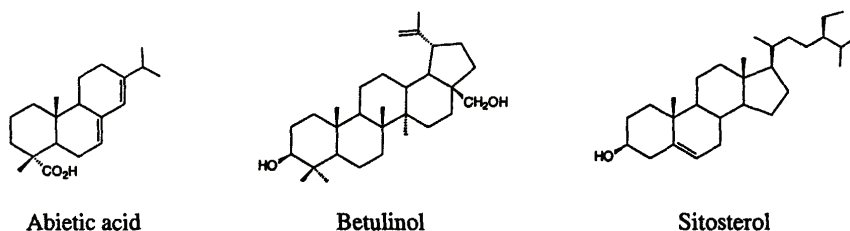


Fig. 1. Chemical structure of abietic acid, betulinol and sitosterol (Alén 2000, published by permission of the Finnish Paper Engineers' Association).

Glycerides, steryl esters, triterpenyl esters and free fatty and resin acids are saponifiable compounds i.e. they form soaps during the alkaline treatment of wood. Unsaponifiables include hydrocarbons, fatty alcohols, sterols and triterpenyl alcohols. (Back & Ekman 2000)

The amount and composition of wood resin can vary considerably between wood species, between the same species, between sapwood and heartwood, between injured and damaged wood and also within a tree from butt to top (Ekman & Holmbom 2000). Pitch control must be started in the beginning of the whole production process. Many factors affect the composition of wood resin during wood handling, such as wood storage time and conditions, and especially temperature.

Fig. 2 shows the effect of wood extractives during the chemical pulp process. Before felling the trees, terpenes and other volatile compounds are released naturally into the air. The terpene emissions increase after the tree is felled. Volatile terpenes evaporate into the air and non-volatile terpenoid compounds start to cover the cut surface. Terpenes may contribute to the local production of photochemical oxidants (i.e. ground-level ozone, hydrogen peroxide, organic peroxides, organic nitrates and aerosols) due to their high chemical reactivity. (Strömvall & Petersson 2000)

Pitch deposits problems in the pulping processes are traditionally reduced by natural seasoning of the wood or wood chips. In addition to seasoning, the pitch content can be decreased by biological treatment of the wood chips with fungi. Several reactions take place during wood storage, and they are accelerated with increasing temperature and ventilation. The most important reactions are: hydrolysis of triglycerides and steryl esters; oxidation, degradation or polymerization of resin acids and liberated unsaturated fatty acids; evaporation of volatile terpenoids. The water solubility of the compounds increases as a result of hydrolysis and oxidation reactions, whereas polymerized components have a lower solubility. Polymerization reactions also reduce the amount of free acids, which are important in pulping. (Ekman 2000, Back 2000a)

Softwoods and most hardwoods should be pulped as soon as possible after felling (Ekman 2000). The reason for this is that fresh wood contains the greatest amount of triglycerides that saponify during kraft pulping. Pitch problems are more likely to occur in the production of kraft pulp from birch than from pine. Hardwoods (e.g. birch and aspen) contain greater amounts of sterols and other unsaponifiables than softwoods. The lack of resin acids in hardwoods makes the deresination (chemical or mechanical removal of wood resin) of pulp problematic (Laamanen 1984). Storage would decrease the content of wood extractives because fatty acids and steryl esters are degraded during longer storage times (Ekman 2000). Deresination can be improved, or the need for storage can even be eliminated, by adding tall oil during the digestion of birch. Tall oil is a by-product of the sulphate pulping of resinous woods, and mainly consists of resin acids and fatty acids. The physical reason for the lower deresination of birch kraft pulp during cooking is that most of the birch extractives are located inside the small ray cells, which have very small pores (Laamanen 1984). In contrast, most of the pine extractives are located between the cells, and the cells containing extractives have larger pores than those of birch.

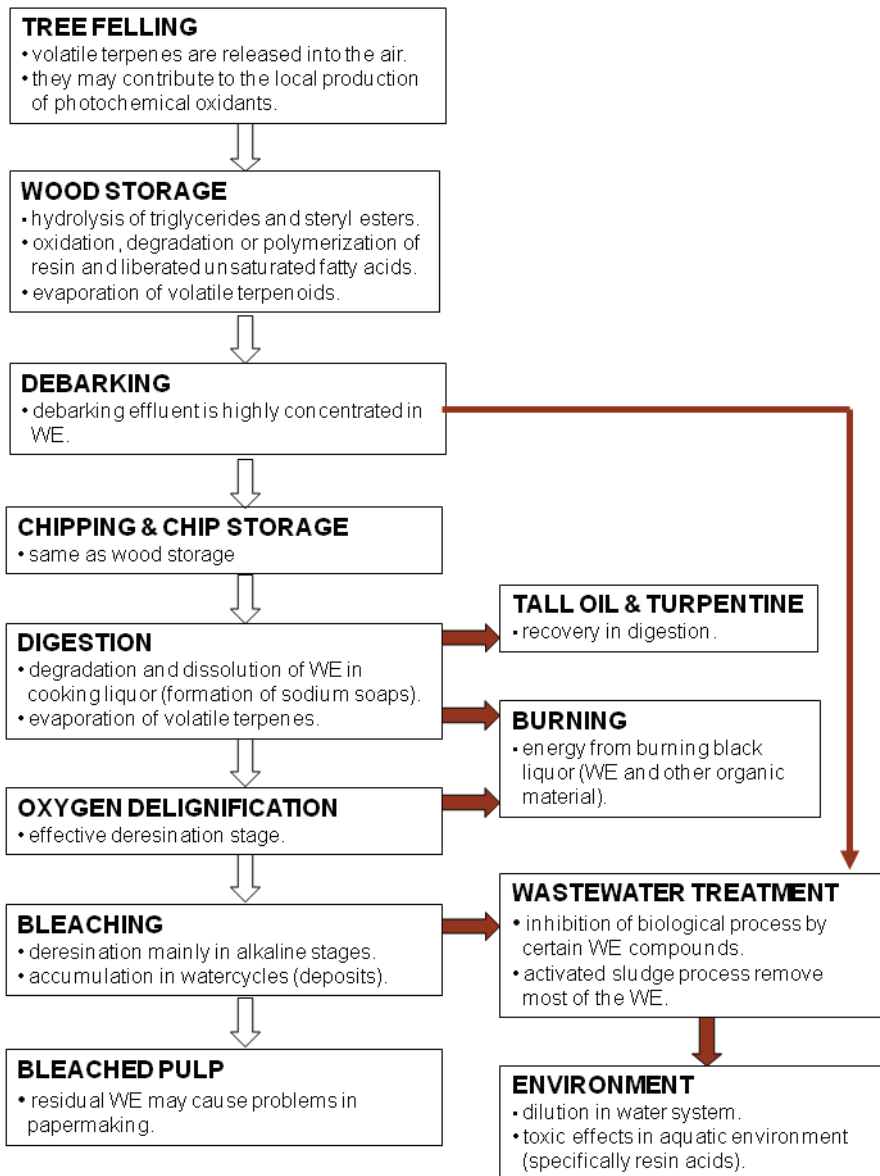


Fig. 2. Effect of wood extractives (WE) in the chemical pulp process.

Efficient debarking is important especially in the case of hardwoods with smooth bark; bark can contain five to ten times more extractives than wood (Back 2000a). This is the case especially with silver birch, the resin in the outer bark mainly consisting of betulinol. The inner bark of birch does not contain any betulinol and the wood contains only small amount or none at all (Back 2000a). As debarking is never 100% complete, some betulinol is always found in bleached birch kraft pulp. The debarking effluent is usually conveyed to the wastewater treatment plant, and contains large amounts of wood extractives.

In kraft pulping, the chips are digested in white liquor (sodium hydroxide and sodium sulphide) in order to separate the fibres and dissolve lignin. About half of the wood substances degrades and dissolves in the cooking liquor. Free fatty and resin acids form sodium soaps, fats (mainly di- or triglycerides) form sodium soaps and glycerol, and steryl esters form sodium soaps and sterols. The dissolved fatty and resin acid soaps form micelles that can promote the dispersion and solubilization of unsaponifiable components. The reaction rates are the highest with free acids, and the lowest with steryl esters. The reaction rates are strongly affected by the alkali concentration and temperature during cooking. The tall oil and turpentine (released terpenes) that are formed during digestion are recovered. After digestion, the spent liquor (black liquor) is separated from the pulp by washing, evaporated, and finally burnt in the recovery furnace for the recovery of chemicals and energy. (Alén 2000, Back 2000a)

The oxygen delignification stage (O), or the oxygen stage in short, and the following bleaching stages are designed to remove residual lignin from the pulp. Oxygen delignification is usually performed as a two-stage process, with intermediate washing under pressure at a high temperature (90–110 °C) under alkaline conditions (Alén 2000). The O stage effluents are recycled back to the recovery system. Bleaching is a multistage process with intermediate washings cycles using oxygen and chemicals such as ozone, hydrogen peroxide and chlorine dioxide. The alkaline bleaching effluents are usually recycled countercurrently in the bleaching stage, and finally dissipated with the acid bleaching effluent to the wastewater treatment plant.

The pitch in unbleached pulp is located in several places: on fibre surfaces, inside the parenchyma cells, as colloids, and in dissolved form (Allen 1975). Deresination in bleaching is achieved mainly by dissolving and dispersing the resin in the bleaching liquors followed by removal with the washing liquids. Alkaline conditions favour this process. Deresination is efficient in the O stage and in the alkaline press washing step that follows the O stage (Holmbom 2000).

For example, Bergelin and Holmbom (2003) reported deresination of 63–68% for birch in the O stage and press washers of kraft pulp ECF bleaching. An overall deresination of over 90% was achieved in the bleach plant in question. The deresination of betulinol mainly occurred as a result of washing in the O stage, and some in the E_{op} (extraction fortified with oxygen and hydrogen peroxide) stage. The overall reduction for betulinol was relatively low (80%). (Bergelin & Holmbom 2003) Efficient washing of the dispersed resin is needed in order to avoid agglomeration in the acidic stages. Synthetic surfactants are sometimes used to prevent agglomeration (Holmbom 2000).

Another mechanism for deresination is the oxidation of resin components; this results in more hydrophilic components, which can be removed by washing (Holmbom 2000). In ECF birch pulp bleaching, the resin content decreases in each bleaching stage, but no longer significantly in the D₂ (chlorine dioxide) stage (Bergelin & Holmbom 2003).

The composition of pitch deposits and extractives in process waters depends on the bleaching sequence. In the ECF bleaching of *Eucalyptus globules* pulp, saturated sterols and sterolesters were found to be present in the deposits that were collected after chlorine dioxide bleaching, whereas unsaturated sterols and sterolesters, mainly β -sitosterol and β -sitosterol esters, were completely degraded (del Río *et al.* 1998). The deposit collected after the O stage during the TCF kraft pulping of *Eucalyptus globulus* mainly contained steroids and waxes (del Río *et al.* 2000), and the deposit collected after hydrogen peroxide bleaching contained steroids, fatty acids and lower amounts of waxes. Sitosterol was the dominant sterol in all the deposits and in *Eucalyptus globulus* wood extractives. Sterols, sterol esters, steroid ketones and steroid hydrocarbons were the main compounds in the process waters, pitch deposits and eucalyptus wood after kraft pulping and during TCF bleaching (Gutiérrez *et al.* 2001).

The residual resin in bleached pulp may cause problems in paper mills, such as the accumulation of deposits in equipment and pitch dirt in paper. Pitch control in paper mills is performed by optimizing the process conditions and using additives such as dispersants and retention aids (Allen 2000a). The amount of residual resin in ECF and TCF bleached birch pulps were 0.7–2 kg/t pulp (Bergelin & Holmbom 2003), and betulinol, lupeol and saturated fatty acids the main residual components.

The wood extractives in pulp and paper mill wastewaters mainly originate from the debarking plant and the bleaching plant. Activated sludge treatment generally removes most of the wood extractives (Kostamo & Kukkonen 2003).

During treatment, the wood extractives are degraded, transformed into other compounds or adsorbed on the biosludge (Kostamo *et al.* 2004). Biooxidation by micro-organisms is the main mechanism in the removal of resin and fatty acids, whereas adsorption is important when the treatment time is short (Liu *et al.* 1996). Oxidation by air is the third, but less important, mechanism. pH has an influence on resin acid bioavailability and thus on the success of biooxidation. The solubility, and therefore also the bioavailability of resin acids increases under alkaline conditions. (Werker & Hall 1999) Toxicity breakthroughs may occur in some situations, resulting in the release of larger amounts of extractives. For example, a sudden increase in the concentration of resin acids in incoming wastewater will probably result in toxicity breakthrough due to the long acclimation time of the microbial community (Werker & Hall 1999). The rest of the wood extractives and their metabolites in the effluent will pass into the receiving water systems and associated sediments.

Wood extractives can cause toxic and hormonal effects in aquatic environments even at very low concentrations. Toxic effects of dehydroabietic acid on rainbow trout have been observed at a concentration of 20 µg/L (Oikari *et al.* 1983). Pimaric-type resin acids (isopimaric, sandaracopimaric and pimaric acid) are even more toxic, but less soluble than abietic-type resin acids (palustric, neoabietic, levopimaric, abietic acid and dehydroabietic acid) (Peng & Roberts 2000). Fatty acids have also been reported to be toxic to fish; unsaturated fatty acids are more toxic than saturated, but not as much as resin acids (Mörck *et al.* 2000). Sterols can have an effect on the reproduction and growth of fish (Lehtinen *et al.* 1999). β -sitosterol is the dominating sterol in effluents from kraft mills (Mörck *et al.* 2000). The transformation of β -sitosterol into androgens can occur during biotreatment (Stahlschmidt-Allner *et al.* 1997). Wood extractives in sediments may desorb and pass into the surrounding water, e.g. due to mechanical disturbance of sediments (Meriläinen *et al.* 2006) and cause adverse effects on aquatic species.

3 Coagulation–flocculation

3.1 Introduction

Aqueous particles generally have a net negative charge and they repel each other in water. In addition, colloidal particles (approximately 1 nm – 1 µm) do not settle without help in a reasonable time or at all. The surface charge of particles can be reduced by adding a chemical (a coagulant) carrying positive charges, like iron and aluminium salts or polyelectrolytes, and they will destabilize and separate. Coagulant is added under rapid mixing in order to ensure effective dispersion. In the flocculation stage, destabilized particles aggregate under slow mixing and form flocs. Another chemical (a flocculant) can be added to improve floc quality, e.g. to obtain larger, stronger flocs. When mixing is stopped, the flocs settle out in a few minutes. Flotation and filtration are also widely used for floc separation.

The coagulation–flocculation processes effectively remove suspended solids and colloidal particles. Some soluble compounds with a net negative charge (such as fulvic and humic acids and orthophosphate) can also be removed. Non-charged substances e.g. carbohydrates are ineffectively removed. (Lindquist 2003)

Aluminium and iron salts are available with a range of basicities and counter ions (e.g. sulphate, chloride, and nitrate). Besides inorganic chemicals, organic polymers (mainly synthetic) are also extensively used in coagulation–flocculation, either alone or together with an inorganic coagulant. Polymers are available in a range of molecular weights (MW) and charge densities. The following grouping for MW is used: low MW < 10⁵, medium MW 10⁵–10⁶, and high MW > 10⁶ (Bolto & Gregory 2007). Ionic polymers are called polyelectrolytes.

When Al and Fe salts are used in water treatment, the dosage requirements, sludge formation, and the residual ion concentrations (Al³⁺, Fe³⁺ and counter ions) in the purified water may be high. The required dosage of polymers and, therefore, the amount of precipitates, are lower than with inorganic chemicals. If the precipitate is burned to produce energy, the organic polymers themselves do not form any ash. The floc properties are also improved. On the negative side, however, organic polymers are more expensive. As is the case with Al and Fe, the residual concentration of polymers in purified water should be controlled due to their potential toxicity. Cationic polyelectrolytes are more toxic to aquatic organisms than anionic or non-ionic (Bolto & Gregory 2007).

There are different mechanisms involved in coagulation–flocculation, i.e. how different types of particle are removed. The most important are charge neutralization, sweep coagulation, patching and bridging. In charge neutralization, the surface charge of the particles is neutralized by the coagulant, and aggregation is possible. For example, Al^{3+} forms different positive aluminium species in water; they are adsorbed on negative particles, resulting in neutralization. Overdosing of the coagulant leads to restabilization. In sweep coagulation or flocculation, insoluble aluminium or iron hydroxide precipitates sweep down the suspended material. In the patch mechanism (Fig. 3a), the polymer adsorbs on the surface of an anionic particle and forms local positively charged regions (patches). The differently charged regions on particles then create strong interaction between particles, thereby initiating flocculation. In bridging flocculation (Fig. 3b), a long-chain polymer is adsorbed on the surface of a particle and the loops and tails of the polymer are free to attach themselves to other particles.

In addition to electrostatic interaction, a polymer can adsorb via hydrogen bonds (e.g. PAM and polyethylene oxide) or ion binding (Bolto & Gregory 2007). In ion binding, the anionic polyelectrolyte becomes adsorbed on negatively-charged surfaces in the presence of divalent positive metal ions, which probably form a bridge between the anionic polyelectrolyte and negative surface (Berg *et al.* 1993).

The pH value has a major influence on the coagulation process, because the charge of the particles is dependent on the pH. Typically, with increasing pH the number of negative charges increases while the number of positive charges decreases. Coagulants also have an optimum pH range. The residual concentration of aluminium and iron in purified water depends on the pH, and thus needs to be determined for each type of water and metal salt (Lindquist 2003).

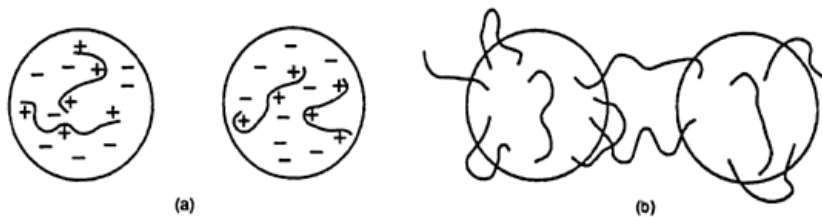


Fig. 3. Patching (a) and bridging (b) flocculation mechanisms (Eklund & Lindström 1991, published by permission of DT Paper Science Oy Ab).

The main disadvantage of coagulation–flocculation is that an additional technique, such as settling, filtration, or dissolved air flotation, is needed to separate the precipitate from the purified water, and the precipitate itself then has to be treated. Real-time dosing control, based for example on measurements of turbidity or charge quantity, is needed for an influent with a highly variable quality.

3.2 Coagulation–flocculation of chemical pulp process and wastewaters

In the internal water treatment of pulp mills, process waters are purified in order to circulate water to the other stages. The methods that have been studied for internal water treatment in kraft pulp mills include at least evaporation (Dahl 1999), membrane processes (Rosa & Pinho 1995, Reid *et al.* 1997, Svard *et al.* 1998, Fälth *et al.* 2001, Tavares *et al.* 2002, Cortiñas *et al.* 2002), ion exchange (Knocke *et al.* 1986, Brown *et al.* 1999), adsorption (Knocke *et al.* 1986), coagulation–flocculation (Knocke *et al.* 1986, Beulker & Jekel 1993, Rampotas 1999, Lombardo *et al.* 1997, Järvinen *et al.* 1994, Välttilä *et al.* 1996), and electrolytic flocculation (Dahl *et al.* 1998).

In external wastewater treatment, wastewater is purified before it is released into the receiving water system. Various treatment processes, such as sedimentation, coagulation–flocculation, adsorption, chemical oxidation, and membrane processes, as well as biological (both aerobic and anaerobic) processes and fungal treatment, have been studied for the treatment of pulp and paper mill wastewaters (Pokhrel & Viraraghavan 2004). Wastewater treatment in pulp and paper mills is typically carried out using sedimentation as the primary treatment, and activated sludge process as the secondary treatment. The activated sludge process is designed to remove organics from wastewater using micro-organisms under aerobic conditions, and thereby producing well settleable sludge. Due to the

inability to remove non-biodegradable organics and its vulnerability to disturbances, there is a need for a tertiary treatment stage or supplemental treatment steps in pulp and paper mill wastewater treatment. The coagulation–flocculation processes studied in the internal or external wastewater treatment of kraft pulp mills are discussed below in more detail.

The use of aluminium, polyaluminium and ferric salts with bleaching filtrates, as well as with wastewater, has been studied widely. Beulker & Jekel (1993) found that an aluminium salt was the most effective chemical against lime and magnesium hydroxide in the effluents from the oxygen and chlorine stages of a bleach plant. Aluminium removed only high MW substances from oxygen bleaching effluent, whereas low MW substances were also partly removed from chlorine bleaching effluent. Barton *et al.* (1992) reported 50–70% AOX removal from softwood bleach plant filtrates with aluminium sulphate, while chlorinated phenolic compounds were not effectively removed.

Ferric chloride and polyaluminium salts removed 70–80% COD from alkaline ECF bleaching effluent (Lombardo *et al.* 1997). The alkaline effluent included organic molecules with the following main molecular weights: 64,000; 23,000; 6100; 3300 and 700. The molecular weights of acidic effluent were near 1500 and 500. As aluminium polychloride primarily precipitated molecules larger than 2000, the molecular structure of the acidic effluent meant that it could not be cleaned. Garcia-Heras and Forster (1989) reported high colour removal (99%) with ferric chloride from eucalyptus kraft pulp bleaching effluent (mixture of wastewater from chlorination and caustic extraction stages). However, there was poor settling velocity and a high sludge volume.

More efficient removal can be attained using aluminium or ferric coagulants together with flocculants. Chou *et al.* (1998) used polyaluminium chloride (PAC) together with cationic polyelectrolyte (dimethyl diallyl ammonium chloride) and obtained a higher solid removal efficiency in the coagulation of pulp wastewater than using PAC alone, due to the better floc formation. With 2 mg/L polyelectrolyte, the PAC dosage could be decreased from 35 mg/L to 20 mg/L. Lombardo *et al.* (1997) reported a slight increase in COD reduction and a substantial improvement in floc settling when bentonite or organic flocculants were used together with ferric chloride or polyaluminium salts. Furthermore, enhanced reduction of turbidity, total suspended solids (TSS) and COD was obtained when an aluminium salt and PAC were used together with polyacrylamide (PAM) in the treatment of pulp and paper mill wastewater

(Ahmad *et al.* 2008). Cationic PAM performed better than anionic PAM in that it resulted in a lower sludge volume.

Frizzo *et al.* (1996) studied the use of solid residues from the kraft pulp industry (dregs, grit and heavy ash) and of active carbon as a flocculating aid, in the coagulation of kraft pulp bleaching effluent with ferric chloride and aluminium sulphate. This gave an appreciable reduction in the colour and AOX content of the final effluent.

Synthetic cationic polymers (hexamethylene diamine epichlorohydrin polycondensate (HE) and polyethyleneimine (PEI)) resulted in better removal of TOC and colour from kraft mill black liquor wastewater compared to non-ionic PAMs (Ganjidoust *et al.* 1997). A natural polymer, chitosan, was found to be the best coagulant compared to aluminium sulphate, HE, PEI and non-ionic PAM, but the chitosan coagulation process was associated with poor sludge settling. In addition, the suitable coagulant dose for HE and PEI was much lower than that for aluminium sulphate or chitosan. Rohella *et al.* (2001) reported better removal of turbidity, COD and colour from pulp and paper mill wastewater with polyelectrolytes than with a aluminium salt. Wong *et al.* (2006) showed, that on the basis of turbidity, TSS and COD values, that PAM alone effectively purified pulp and paper mill wastewater. Cationic polyacrylamide with a very high MW and low charge density proved to give the best result.

When using coagulation–flocculation to purify process water before circulation, the residual coagulant concentration in the filtrate has to be taken into account. For example, aluminium can have a negative effect on peroxide bleaching by increasing the consumption of peroxide. In order to avoid this, the aluminium dosage should be so small that the residual aluminium concentration in the filtrate is at the most 20 mg/L (Terelius *et al.* 1999). With iron these problems are more serious.

A combined coagulation and photocatalysis method gave good results when used for effluent samples collected after cellulose pulp bleaching (Rodrigues *et al.* 2008). Coagulation with ferric chloride together with chitosan, effectively removed turbidity, nitrogen compounds, phosphate and sulphate, as well as aromatic and aliphatic compounds. Photocatalysis performed with ultraviolet (UV) radiation/TiO₂/H₂O₂ resulted in a colourless effluent with a very high biodegradability (0.71; after 4 h photocatalysis). For an untreated sample the value was only 0.14, and after coagulation 0.50.

Overall, most of the studies dealing with the coagulation–flocculation of organic material from kraft pulp bleaching filtrates or wastewater have evaluated

the success of purification by measuring colour reduction, UV absorbance, or parameters such as total organic carbon (TOC), dissolved organic carbon (DOC), COD and AOX. Results for residual wood extractives have seldom been reported. The deresination of filtrates by flocculation with polyethylene oxide has been demonstrated in pilot plant and full-scale studies at chemical and mechanical pulp mills (Rampotas *et al.* 1996, Rampotas 1999). Removal of more than 90% of wood extractives was achieved, along with high removal efficiencies of non-process metals. In another study, aluminium sulphate and cationic PAM effectively removed wood extractives from softwood TCF pulp process water (alkaline oxygen/peroxide stage) at a pH of 4.5–5 (Vuorenpallo 2000). The total lignin content was reduced by over 70%.

3.3 Investigation of coagulation–flocculation

Performance of the coagulation–flocculation process can be determined by measuring purification results such as turbidity, TOC, COD or any other sum parameter or component of interest. Charge analyses are important in determining the stability of colloidal particles and the mechanisms underlying the coagulation–flocculation phenomenon. The physical characteristics of flocs can be measured, e.g. with laser diffraction techniques, by monitoring the settling behaviour of particles or by image analysis. Some of the techniques, with the main focus on charge analyses, are discussed below. A review of techniques (mainly scattering, settling and imaging) for the measurement of fractal dimension of aggregates has been published by Bushell *et al.* (2002).

3.3.1 Turbidity

Turbidity is an important analysis in investigations on coagulation–flocculation. When the aim of coagulation–flocculation is to remove colloidal and suspended solids from water, the residual turbidity provides an indicator of how well the treatment has succeeded. Turbidity can be measured either as a reduction in the intensity of transmitted light or as an increase in the scattered light intensity at a selected angle, for example 90 degrees. Also a combination of both methods can be used (Ratio method). Light scattering depends on the size of the particles relative to the wavelength of the light, the shape of the particles and the refractive index of the particles relative to that of the suspension medium (Gregory 2006).

Particles of size 0.4–0.7 μm (similar to the wavelength of light) have a large effect on turbidity (Lindquist 2003).

The fact that many different turbidity units are used is sometimes misleading. Instruments using 90 degrees are called nephelometers and the unit used is then NTU (Nephelometric Turbidity Unit). If one wants to emphasize what calibration standards have been used, FTU (Formazin Turbidity Unit) and FNU (Formazin Nephelometric Unit) can be used when calibration of the instrument is performed with formazin standards. Polymer bead suspensions are also used in calibration. The light scattering behaviour of polymer bead standards differs from the formazin standards, so this should be taken into account when comparing the results in different studies. (Arnerich 2003) FAU (Formazin Attenuation unit) is used when turbidity is measured with transmission technique and calibration is performed with formazin standards.

3.3.2 Zeta potential

The zeta potential describes the stability of colloidal systems. If the magnitude of the particle zeta potential is large, the colloidal system is stable. When the zeta potential is close to zero, particles will generally aggregate. In water and wastewater treatment and in the paper industry, colloidal systems are destabilized by adding a chemical, i.e. aggregation is meant to take place. In contrast, some industries want to prepare stable colloidal systems like inks and paints. (Oja & Sugrue) The zeta potential correlates closely with the concentration of residual suspended solids in bleached kraft effluent (Dorica & Wong 1981).

The Fig. 4 presents the structure of an electrical double layer. In this case, the particle has a net negative surface charge. Ions of opposite charge (counter ions) are attracted to the surface where they become tightly bound to the surface. The Stern layer consists of inner and outer Helmholtz planes (not shown in Fig. 4). The inner Helmholtz plane consists of ions, which are specifically adsorbed to the surface. The outer Helmholtz plane consists of the closest hydrated counter ions in the solution. Outside the Stern Layer there is a diffuse layer, or Gouy layer, in which ions are more loosely bound. While the ions in the Stern layer move together with the particle, the ions in the diffuse layer do not. The electrical double layer consists of a surface charge, the counter ions of the Stern layer and the ions in the diffuse layer. The zeta potential describes the potential difference between the shear plane of the particle and the solution. The shear plane lies just outside the Stern layer. In addition to the surface charge, the concentrations and

valencies of the surrounding ions and the dielectric constant of the continuous phase also affect the magnitude of the zeta potential. (Oja & Sugrue)

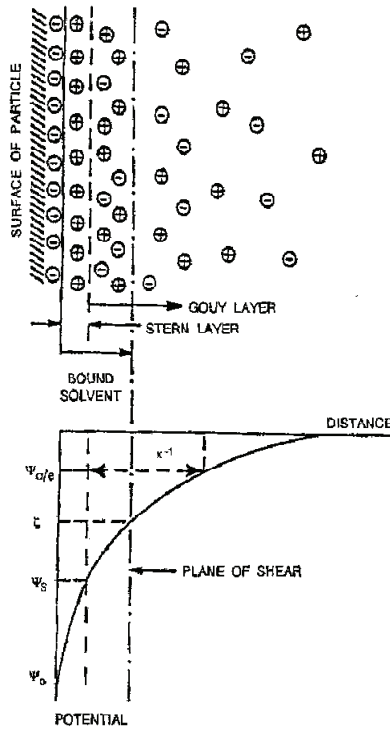


Fig. 4. Structure of the electrical double layer (Eklund & Lindström 1991, published by permission of DT Paper Science Oy Ab).

When an electric field is applied, the electrical charges on the surface of the particles interact. This electrokinetic effect can be measured with different techniques, which differ from each other in the way the motion is induced. In electro-osmosis the movement of a liquid is measured relative to a stationary surface. In streaming potential, the liquid is forced to move under a pressure gradient through a capillary or porous plug with charged walls (see Subchapter 4.3.3). In the sedimentation potential technique, an electric field is generated when charged particles sediment. In electrophoresis the movement of charged particle is measured relative to the liquid. Electrophoresis is described below in more detail. (Hunter 1981)

Electrophoretic mobility is proportional to the surface charge density of the particle. Different techniques can be used to measure the electrophoresis of particles like microelectrophoresis, moving boundary methods, tracer electrophoresis, the mass transport method and electrophoretic light scattering (ELS) (Hunter 1981). In microelectrophoresis, image analysis has recently been used instead of manual microscopy (van Merode *et al.* 2007, van Merode *et al.* 2006, Liu *et al.* 2007, Kim *et al.* 2008).

In the ELS technique, which was used in this study, electrophoretic mobility is measured by analysing Doppler shifts of scattered light from a moving particle in an applied electric field. Laser light is directed onto particles moving in the electric field. Some light is scattered from the particles and the frequency of the detected light is Doppler shifted from the incident frequency by an amount proportional to the particles' velocities (Coulter DELSA Reference Manual). Electrophoretic mobilities are calculated from the frequency shifts of scattered light. Electrophoretic mobility is calculated as:

$$U = V / E , \quad (1)$$

where U is the electrophoretic mobility ($\mu\text{m}\cdot\text{cm}/\text{V}\cdot\text{s}$), V the velocity ($\mu\text{m}/\text{s}$) and E the electric field (V/cm). The zeta potential is approximated from the electrophoretic mobility according to the Smoluchowski equation, which assumes that the double layer thickness is small compared with the colloid particle diameter:

$$\zeta = U\eta / \varepsilon_0 D , \quad (2)$$

where ζ represents the zeta potential (mV), η the viscosity (Pa·s), ε_0 the permittivity of free space (F/m) and D the dielectric constant. The dielectric constant and viscosity can usually be approximated by values for water. At the isoelectric point, the zeta potential is zero, i.e. no electrokinetic effects are observed.

Electrophoretic mobility measurements must be performed at the stationary level of the measurement cell where electro-osmotic flow of the liquid is zero. Electro-osmotic flow derives from the difference in electrical potential between the sample cell walls and the bulk solution. When the electric field is applied parallel to the channel, the liquid starts to flow. In a closed system, there is a zero net flow of liquid. The direction of flow in the centre of the channel is opposite to that in the direction of the cell walls. Thus there are two regions (upper and lower

stationary levels) where the liquid flow is zero. (Coulter DELSA Reference Manual)

In a single-angle measurement system like that employed in Malvern Zetamaster ZEM 5002, there is one laser beam source, from which the light is split into two beams. The reference beam is aligned directly onto a receiver assembly, while the other passes through the sample. (Zetamaster Hardware Reference Manual 1993)

In the multi-angle measurement technique (Coulter DELSA 440SX) measurements are made simultaneously at four scattering angles i.e. the angles between the incident light and the scattered light of detector (see also Subchapter 4.8.1). Multi-angle measurement makes it possible to detect particle populations of different zeta potential. The zeta potential distributions can also be measured by microelectrophoresis (Dong 2002, van der Mei & Busscher 2001, van Merode *et al.* 2007, van Merode *et al.* 2006, Liu *et al.* 2007, Kim *et al.* 2008) and capillary electrophoresis instruments (Duffy *et al.* 2002, Glynn *et al.* 1998), as well as with the relatively new Malvern Zetasizer Nano instrument, which uses a combination of laser Doppler velocimetry and phase analysis light scattering (PALS) (Davydova *et al.* 2008). Very low mobilities and their distributions can be measured with PALS.

There are few publications describing the multimodal zeta potential distribution in the field of microbiology (Dong 2002, van der Mei & Busscher 2001, van Merode *et al.* 2007, van Merode *et al.* 2006, Duffy *et al.* 2002, Glynn *et al.* 1998, Davydova *et al.* 2008), particle suspension characterization (Liu *et al.* 2007, Kim *et al.* 2008), and in the pulp and paper industry (Heikkinen 2005, Leiviskä *et al.* 2005, Leiviskä & Rämö 2007, Leiviskä *et al.* 2008).

3.3.3 Charge quantity

The charge quantity is the total amount of surface charge. Determination of the charge quantity is based on the streaming current principle. Fig. 5 shows a typical instrument. The sample is added to the teflon measuring cell containing a fitted displacement piston. Oscillation of the piston inside the measuring cell gives the liquid a high flow rate in the cell. Charged colloidal particles will be adsorbed at the plastic surface of the piston and on the walls of the cell through the action of van der Waals forces. Counter ions are separated from the adsorbed material, thereby creating a streaming current, which can be measured with two electrodes. The streaming potential is converted from the current and displayed on the

instrument. A quantitative measurement of the total charge is made by titrating the sample with a titrant of opposite charge until the point of zero charge is reached. The charge quantity is calculated from the consumption of titrant. (Mütek Instruction manual 2000)

In the streaming current method, one must assume that the materials under investigation are adsorbed (Phipps 1999). Different sample preparation methods give different results (Mütek Instruction Manual 2000). For example, a sample treated by screening gives the total charge of the sample (fines, fillers, colloiddally dissolved material). A sample treated by centrifuging gives only the charge of the colloiddally dissolved system (anionic trash).

Charge analysis is an invaluable tool when dosing and the behaviour of the additives are to be evaluated. Charge analysis is already used in wet-end applications in paper mills (Patton & Lee 1993) and in sewage treatment plants (Sailer 2002). The optimum dosage of the coagulant or flocculant is usually close to that required to neutralize the surface charge carried by the particles, and thus it can be used in determining the coagulant/flocculant dosage (Beulker & Jekel 1993, Lombardo *et al.* 1997). Determination of the charge density of synthetic polyelectrolytes is also very important, especially in the case of polymeric flocculants (Kam & Gregory 1999). By choosing a chemical with a suitable charge density, the dosage level needed to achieve complete destabilization can be minimized (Bobacka & Eklund 1999).

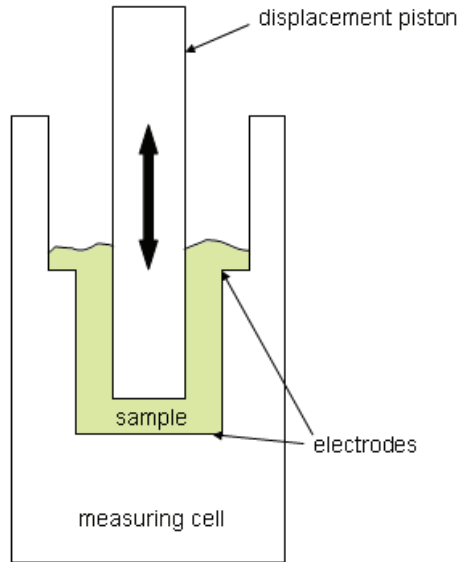


Fig. 5. Streaming current detector.

Zeta potential and charge quantity analyses complement one another, and using just one of them does not provide a proper understanding of colloidal systems (e.g. Leiviskä & Rämö 2008, Leiviskä *et al.* 2008). To simplify, the charge quantity describes the total amount of positive or negative charges and the zeta potential the magnitude of the charges. Thus it is not surprising if they do not always correlate well with each other. Liu and Wu (1997) found a good correlation between the zeta potential and the streaming current in the coagulation of synthetic raw water prepared from kaolinite, when ferric chloride was used as coagulant.

3.3.4 Floc structure characteristics

The relative floc size, formation, breakage and re-formation can be studied by means of a photodispersion analyser (PDA). In this method (Rank Brothers Ltd.), the flowing suspension is illuminated by a narrow beam of light perpendicular to the direction of flow. The PDA gives a ratio value, which is the proportion between the root mean square value (RMS) of the fluctuating signal and the

average transmitted light intensity (DC). RMS is related to the average number concentration and size of the suspended particles. The value increases when aggregation occurs. DC is dependent on the turbidity of the suspension and is less sensitive to changes in the state of aggregation. (Rank Brothers Ltd.)

PDA has mainly been used in studying and monitoring coagulation processes, e.g. when comparing different coagulants and conditions (Gregory & Nelson 1986, Chou *et al.* 1998, Graham *et al.* 2008, Moussas & Zouboulis 2008, Zouboulis & Tzoupanos 2009). Too large flocs can result in clogging (Chou *et al.* 1998).

The floc properties (size, shape and fractal dimension), and formation during flocculation, can also be examined by image analysis (Chakraborti *et al.* 2003, Honkanen *et al.* 2004). Image analysis is carried out with a digital camera and image processing software. There is no sample handling during the analysis so disturbance of the flocs is avoided. The fractal dimension of the flocs indicates how the particles in the aggregate occupy space (Kim *et al.* 2001). The fractal dimension decreases as the structure of the aggregate becomes more open and irregular. Sometimes it may be difficult for the software to identify flocs, for example in strongly coloured waters. The imaging of aggregates can also be performed by various microscope techniques such as scanning electron microscopy, transmission electron microscopy and X-ray microscopy (e.g. Cornelissen *et al.* 1997, El Samrani *et al.* 2004, Siéliéchi *et al.* 2008).

In laser diffraction measurement, the particles pass through a laser beam and scatter the light at an angle inversely proportional to their size (Malvern Instruments 2005). The angular intensity of the scattered light is then measured with photosensitive detectors. Kim *et al.* (2001) concluded that the fractal dimensions of flocs determined by the small angle laser light scattering method were more reliable than those obtained with image analysis. Jarvis *et al.* (2006) and Wei *et al.* (2009) used a laser diffraction instrument (Mastersizer 2000) to monitor floc size during coagulation. The sample in a jar was recirculated through the sample cell of the Mastersizer by a peristaltic pump with a 5 mm internal diameter tube.

4 Materials and methods

4.1 Bleaching filtrates

Bleaching filtrates were taken from two Finnish pulp mills performing ECF bleaching of birch (*Betula verrucosa*). The sequence of Mill A (Stora Enso Oyj Oulu Mill) consists of the oxygen stages O₁ and O₂, i.e. oxygen delignification, and displacement bleaching. The bleaching comprises a chlorine dioxide stage (D₀) followed by two alkaline extraction stages (E₀ and E₁) and washing (W), with the E₀ stage fortified with oxygen, a second chlorine dioxide stage (D₂) and, finally, a peracetic acid stage (Paa). The bleaching filtrates are extensively recycled. The volume of the discharged bleach plant effluent was approximately 13.5 m³/t of pulp.

The sequence of Mill B (Stora Enso Oyj Veitsiluoto Mill) consists of oxygen delignification, an enzyme treatment and a chelation stage (XQ), oxygen stage reinforced with hydrogen peroxide (Op/O), a chlorine dioxide stage (D₁), an E_p stage fortified with hydrogen peroxide, a second chlorine dioxide stage (D₂), and a peracetic acid stage. The volume of the discharged bleach plant effluent was approximately 23 m³/t of pulp.

4.2 Model water

Model water was prepared from birch kraft pulp (Mill A, Subchapter 4.1) in order to ensure similar material throughout the preliminary coagulation studies. The pulp, which was sampled after the O₂ stage, had a consistency of about 28% and was stored in a freezer (−20 °C) until use.

The model water was prepared from thawed pulp by diluting it to 2% consistency with deionized water. The suspension was heated to 60 °C and mixed for 1 h (400 rpm). It was then centrifuged (Jouan C412 centrifuge) at 1950 rpm (revolutions per minute) for 10 min to remove fibres and large particles. The supernatant was used to dilute the pulp back to 2% consistency. The new suspension was also heated to 60 °C, mixed for 1 h, and centrifuged at 1950 rpm, but in this case for 25 min. The second stage supernatant was used as model water. The model water contained dissolved and colloidal material and some micro-fines. Its composition can be considered to be an intermediate form between a real and a synthetic water sample.

4.3 Wastewater

For the size fractionation studies, wastewater samples were taken from Stora Enso Oyj Veitsiluoto Mill, which is an integrated pulp and paper mill located in Northern Finland (Table 2).

Table 2. Information of the Veitsiluoto Mill (Papers IV and V).

Integrated pulp and paper mill	
Production in 2007	
ECF kraft pulp (t)	371,566
uncoated fine papers(t)	514,385
coated printing papers (t)	394,779
sawn goods (t)	149,566
Wood species and consumption in 2007	
pulp mill (million m ³)	0.44 softwood (80% pine, 20% spruce), 0.94 hardwood (100% birch in July 2007) and 0.36 sawmill chips
groundwood mill (million m ³)	0.35 spruce
saw mill (million m ³)	0.31 pine
Water consumption in 2007	
in pulp mill (m ³ water/t of pulp)	48
in paper mill and GW mill (water/t of paper)	8
Wastewater composition in July 2007	
pulp mill	73%
emergency basin (mainly from pulp mill)	2%
debarking plant	1%
SC printing paper machines and GW mill	10%
fine paper machines	14%
Design wastewater discharge (m ³ /d)	60,000
Hydraulic retention time	
in aeration (h)	35
in WWTP (h)	48

GW = groundwood, SC = supercalendered, WWTP = wastewater treatment plant.

The wastewater from the pulp mill, the debarking plant and the emergency basin, wastewater from the supercalendered (SC) printing paper machines and the groundwood (GW) mill, and the disc filters of the fine paper machines, are treated biologically by the activated sludge method. Other wastewaters from the paper mill are treated by flotation.

Grab samples were taken on two different occasions (May 7, 2007 and July 30, 2007), before (influent) and after (effluent) activated sludge treatment during

stable operating conditions in the wastewater treatment plant (WWTP). The influent sample was taken immediately before aeration. The effluent sample was taken after the secondary clarifier.

4.4 Cationic polyelectrolytes

Short-chain cationic polyelectrolytes, namely epichlorohydrindimethylamine copolymer (PAE), polydiallyldimethylammonium chloride (Poly-DADMAC), and two cationic copolymers formed of methacrylates and acrylamides with different charge densities (C-PAM1 and C-PAM2), were obtained from Kemira Oyj (Table 3). Fresh 0.1% and 1% solutions were prepared daily. Dosages throughout the study are given as effective polyelectrolyte dosages, not as a product.

Table 3. Properties of the polyelectrolytes (data provided in October 2006 by the supplier, reprinted and revised from Paper II with permission from Elsevier).

Polyelectrolyte	Molecular weight (g/mol)	Charge density (meq/g) ^b
PAE	20,000 ^a	+7–8
Poly-DADMAC	100,000	+6.2
C-PAM1	200,000	+4.2
C-PAM2	200,000	+1.2

^a 75,000 with a new measurement technique (June 2008). ^b The unit is corrected in this summary.

Charge densities are given against dry product and they can vary to some extent. The MW can also vary to some extent in different batches. It was stated in Paper I that the charge density of Poly-DADMAC was higher than that of PAE; numerical values for the MW and charge densities were not available while writing Paper I. Nonetheless, this has no effect on the interpretation of the results. PAE and Poly-DADMAC had considerable higher charge densities and lower MWs than C-PAMs. According to the results, however, the Poly-DADMAC was a more effective neutralizer in chemical pulp model water. It should also be taken into account that the MW was probably underestimated in the case with PAE. After the measurement technique had been changed, a higher MW was subsequently given by the supplier for the same product (Table 3).

4.5 Repeatability studies on DELSA zeta potential measurement

The repeatability of the DELSA zeta potential measurement was studied with bentonite slurry and two process waters (Op/O and XQ) taken from Mill B. Commercial bentonite (Altonit SF, supplied by Kemira Oyj) was used as a 2% slurry. The bentonite particles have a negative charge on their surface. Bentonite was dispersed in warm deionized water (50 °C) by mixing the suspension at 2500 rpm with an IKA Werk for 30 min. After that, mixing was continued with a magnetic stirrer (800 rpm and 40 °C) for 90 min. The slurry was left to equilibrate for 24 h before performing the repeatability studies. The 2% slurry was centrifuged (Jouan C412 centrifuge) for 30 min at different rates (1100, 1930, 2600 and 3760 rpm), and a sample was then pipetted for zeta potential analysis. Two parallel samples were prepared with the same centrifugation speed, and two analyses were carried for each sample. Centrifugation is a good alternative for the pretreatment of samples with too large a particle concentration in zeta potential measurement (See Subchapter 4.8.1).

The process waters were also centrifuged on a Jouan C412 centrifuge for 30 min at different rates (1100, 1950, 2600 and 3960 rpm) and then sampled for the zeta potential analysis. Two parallel samples were prepared at the same centrifugation speed, and four analyses carried out on each sample. The process waters were also measured directly without the centrifugation stage. The results are presented in the Subchapter 4.8.1.

4.6 Coagulation experiments

Coagulation was performed in jar tests in a beaker either at room temperature or in a water bath (Fig. 6). In some of the experiments, sample pH was adjusted with 1 M HCl or 1 M NaOH. The polyelectrolyte solution was added and the sample then rapidly mixed for 1 min and slowly mixed for 9 min. After centrifugation (1950 rpm for 15 min, Jouan C412 centrifuge), the supernatant was sampled for analysis. The coagulation experiments are described in more detail in Papers I and II.

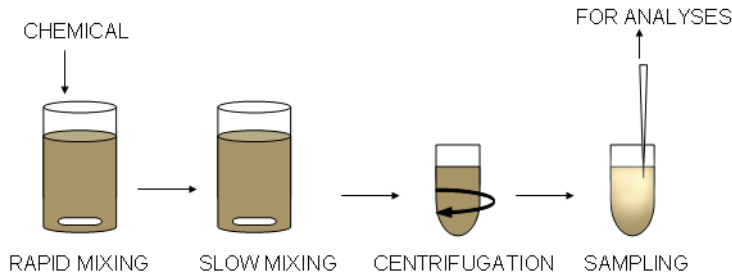


Fig. 6. Procedure used in the coagulation experiments.

The effect of pH on the multimodal zeta potential distribution was studied by adjusting the pH of the water sample and carrying out the coagulation experiment as described above but without adding coagulant. The zeta potential measurements, as well as the charge quantity measurements, were carried out on the supernatant.

4.7 Sequential filtration

4.7.1 *O₂ birch pulp filtrate*

Birch kraft pulp process water sampled after the O₂ stage (Mill A, Subchapter 4.1) was filtrated using suction Millipore filtration equipment with a 47-mm diameter filter paper with pore sizes of 12 μm, 1.6 μm, 1.2 μm, 0.45 μm and 0.1 μm (Paper III). Fig. 7 shows the sequential microfiltration procedure and the analyses conducted on the filtered fractions. The characteristics of the membrane filters are given in Paper III. The membranes used were hydrophilic, except the borosilicate glass fibre material used in 1.6 and 1.2 μm filtration. However, the structure of the filter is such that capillary action allows aqueous liquids to flow easily (Barton 2009). Hence the filters are hydrophilic even though the fibres are not.

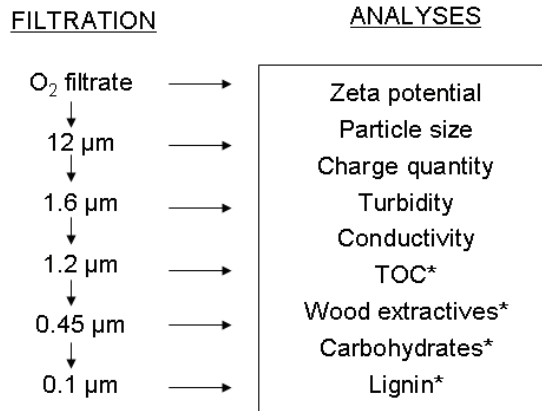


Fig. 7. The sequential microfiltration procedure and the analyses conducted on the O₂ filtrate. * Not for 12 μm and 0.45 μm filtrates.

The sampling, filtration and a part of the analyses (zeta potential, conductivity and particle size (by DELSA) and turbidity) were performed during the same day. The particle size measurements by laser diffraction (LS) and charge quantity measurements were performed after a few days. The determination of organic substances was performed on samples stored in a freezer (-20 °C) until analysis.

4.7.2 Wastewater

Fig. 8 shows the sequential microfiltration/ultrafiltration procedure and the analyses conducted on the filtered fractions. Wastewater filtration was started on the same day as sampling (Subchapter 4.3). The samples were first passed through a 4 mm plastic sieve. They were then filtered sequentially, first by using a suction Millipore filtration device with a 47-mm diameter filter paper with pore sizes of 8, 3, 0.45, and 0.22 μm. Subsequent ultrafiltrations were performed with a stirred cell (Amicon, Model 8400) using Millipore ultrafiltration (UF) membranes with nominal molecular weight limits (NMWL) of 100, 50, 30, and 3 kilodalton (kDa). The volume of the stirred cell was 400 mL and it was pressurized with nitrogen gas (99.5%). The operating pressures were 66 kPa for 100 kDa membranes, 111–132 kPa for 50 and 30 kDa membranes, and 132–223 kPa for 3 kDa membranes. The stirring rate was adjusted according to the operating instructions: the vortex created was approximately one-third the depth of the liquid volume. The membranes were cleaned according to the instructions of the manufacturer (restoration with 0.1 M NaOH and storage in a 10%

ethanol/water solution. The sample flow rate was followed during filtration and a clean membrane was inserted at intervals in order to avoid fouling. The effect of fouling was not quantified by comparing pure water permeability before and after filtration of the influent and effluent. The filtration procedure was time-consuming due to the sequential filtration (high sample volume) and because there was only one ultrafiltration device available. Because some of the analyses (especially BOD and COD) have to be carried out as soon as possible, delays between sampling and analyses/preservation had to be avoided.

The characteristics of the different filters and membranes are given in Papers IV and V. All the membranes were hydrophilic. However the hydrophilic nature of the membranes decreases in the order: regenerated cellulose (Ultracell) > cellulose nitrate \approx mixed cellulose esters > polyethersulfone (Biomax). Mixed cellulose esters are 85% cellulose nitrate. (Blomqvist 2009)

Prior to analysis, the samples were stored in a refrigerator (molecular weight distribution (MWD), TOC, COD_{Cr}, Tot-P, PO₄-P, conductivity, pH, turbidity, charge quantity, zeta potential) or in a freezer (BOD₇, lignin, wood extractives, and trace elements). Freezing was performed immediately after filtration. The effect of freezing on the results of the BOD₇ analysis was tested on the influent sampled in July. BOD₇ analysis of the four largest fractions (sieved, 8 μ m, 3 μ m, 0.45 μ m) was also started, without any freezing, immediately after filtration.

Some of the results are presented as cumulative values for a given filter or membrane size. For example, the 0.45 fraction of influent or effluent includes all the compounds that were not retained on a 0.45 μ m filter. Some of the results are presented as differential values for selected size categories, e.g. particles (> 0.45 μ m), colloids (0.45 μ m – 3 kDa) and the < 3 kDa fraction.

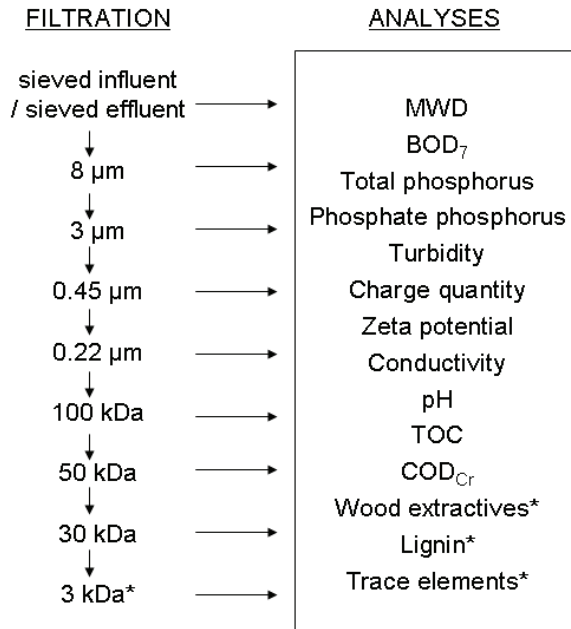


Fig. 8. The sequential microfiltration/ultrafiltration procedure and the analyses carried out on wastewater. * July only.

4.8 Analytical techniques

4.8.1 Zeta potential

Single-angle measurements

Single-angle measurements (in Paper I) were made with a Malvern Zetamaster ZEM 5002 analyser (Malvern Instruments, United Kingdom), which is based on the Doppler ELS technique. The system has one laser beam source, from which the light is split into two beams. The reference beam is aligned directly onto a receiver assembly, while the other passes through the sample. The angle at which the two beams cross in the cell is known. Measurements were carried out in the stationary layer (21.1% of the height of the cell from the cell wall). The

Zetamaster is suitable for particles in the size range of 0.005–5 μm . (Zetamaster Hardware Reference Manual 1993)

Multi-angle measurements

Multi-angle zeta potential measurements were made with the Coulter DELSA 440SX (Beckman Coulter, USA), which is likewise based on the Doppler ELS technique. The measurements were made simultaneously at four scattering angles (the angles between the incident light and the detector of scattered light). The average of the four angles (8.9°, 17.6°, 26.3°, and 35.2°; the refractive index of water was taken into account) was taken as the result. If the zeta potential values obtained from the four different angles are the same, the peaks are real peaks, not artifacts. The dielectric constant and viscosity were approximated with values for water. The measurements were performed at the upper stationary level of measurement cell.

The front and back temperatures of the sample cell were within 1% of the set temperature (25.0 °C) during the measurements. The measurements were usually performed using a 500 Hz frequency range and 60–100 s run time. The strength and mode (voltage or current) of the electric field were chosen according to the conductivity of the sample. The voltage was used when the conductivity was less than 1 mS/cm and the current when it was greater. The applied electric field (on-time 2.5 s and off-time 0.5 s) was chosen such that it produced a frequency shift of -10 Hz at the first scattering angle (8.9°). The calibration of DELSA 440SX was carried out using a Coulter mobility standard.

DELSA calculates the zeta potentials of particles in the size range 0.01–30 μm . If the particle concentration is too high, which is typically the case with process waters from the pulp and paper industry, measurement without pretreatment is impossible. The appropriate sample concentration can be checked by measuring the heterodyne ratio, which is the strength of the reference beam divided by the strength of the scattered beam on the detector (Coulter DELSA Reference Manual). Light from the reference beam should be of greater intensity and the heterodyne ratio should be in the range of 2 to 30. When too low a heterodyne ratio is obtained and the beam intensity adjustment does not improve the ratio, the particle concentration of the sample has to be reduced. Suitable methods for lowering the particle concentration include sedimentation, centrifugation and filtration. Dilution with water is usually not acceptable because the sample pH, conductivity and viscosity may change, with the result that the

zeta potential also changes. With filtration, the filter material containing extractables or surfactants must be carefully flushed with clean water in order to avoid changes in the particles' surface chemistry (Coulter DELSA Reference Manual). Centrifugation was used in the coagulation studies in this research. The process waters were either centrifuged or sedimentated before performing the zeta potential measurements. In the size fractionation studies, the filtered fractions of the process or wastewaters were measured directly.

The repeatability of the zeta potential measurement with DELSA was studied with a bentonite suspension and process waters (XQ and Op/O). According to the heterodyne ratio, the particle concentration was too high in the 2% bentonite suspension at a speed of 1100 rpm (Table 4). The Op/O filtrate had a poor heterodyne ratio without pre-treatment (Table 5), whereas the XQ filtrate could be measured directly (Table 6).

Table 4. Repeatability of the zeta potential measurement of DELSA with a 2% bentonite suspension. Voltage = 10–14 V, frequency range 500 Hz, time 60 s (unpublished data).

Speed of rotation (rpm)	Turbidity (NTU)	Average ZP (mV)	Standard deviation (n = 2)
1100	1628	-24.0 ^a	1.56
1100	1651	-22.8 ^a	1.20
1930	899	-25.7	0.64
1930	880	-22.4	0.00
2600	630	-26.8	0.42
2600	590	-27.6	0.00
3760	279	-27.3	0.42
3760	291	-26.3	1.13

^a Too low heterodyne ratio.

On the whole, the measurements were reproducible. With the XQ filtrate, usually one or two populations were observed. During the measurement of the same sample, however, this pattern changed. Some changes may have occurred in the sample between measurements. For example, sedimentation of large particles can occur, with the result that they are no longer detected in the upper stationary level. Multimodal zeta potential distributions are challenging to measure on real chemical pulp process waters. Higher resolution can be obtained by lowering the frequency range from 500 Hz to 250 Hz. However, the measuring time must then be increased from 60 s to 120 s or even to 240 s in order to obtain good precision.

Table 5. Repeatability of the zeta potential measurement of DELSA with Op/O process water. Current = 2.0–2.7 mA, frequency range 500 Hz, time 60 s (unpublished data).

Speed of rotation (rpm)	Turbidity (NTU)	Average ZP (mV)	Standard deviation (n = 4)
-	155	-37.3 ^a	0.63
-	161	-42.0 ^a	0.85
1100	153	-42.5	2.09
1100	154	-40.2	1.96
1950	153	-40.0	0.79
1950	153	-39.1	0.78
2600	151	-44.9	4.46
2600	152	-44.6	0.44
3960	149	-45.1	0.69
3960	148	-48.0	0.84

^a Too low heterodyne ratio.

Table 6. Repeatability of the zeta potential measurement of DELSA with XQ process water. Current = 2.0–2.7 mA, frequency range 500 Hz, time 60 s (unpublished data).

Speed of rotation (rpm)	Turbidity (NTU)	1		2		3		4	
		ZPI (mV)	ZPII (mV)	ZPI (mV)	ZPII (mV)	ZPI (mV)	ZPII (mV)	ZPI (mV)	ZPII (mV)
-	86	-17.8	-31.3	-19.4	-30.3	-	-30.3	-	-27.8
-	89	-	-31.2	-21.9	-31.1	-	-28.8	-26.1	-31.3
1100	80	-24.3	-33.0	-21.9	-36.3 ^a	-	-30.4	-	-30.7
1100	82	-	-28.8	-22.6	-32.7	-22.6	-30.6	-	-30.5
1950	78	-	-30.2	-	-30.8	-	-29.1	-	-28.3
1950	78	-	-29.8	-24.9	-29.4	-	-27.2	-10.3	-28.5
2600	89	-21.6	-29.7	-10.5	-30.2	-22.4	-30.5	-23.4	-31.8
2600	82	-22.7	-30.9	-20.7	-32.3	-15.4	-26.5	-22.6	-28.4
3960	78	-25.8	-30.9	-	-33.9	-24.5	-31.4	-22.2	-28.9
3960	80	-24.2	-31.3	-	-31.1	-	-31.2	-	-30.6

^a Also third population was observed (-48.7 mV).

4.8.2 Charge quantity

The charge quantity (eq/L = equivalent/litre) was measured with a Mütek Particle Charge Detector PCD 03 pH (Mütek Analytic GmbH, Germany). The samples were titrated with 0.001 eq/L cationic (Poly-DADMAC) or 0.001 eq/L anionic

(polyethylene sodium sulphonate (PES-Na)) polyelectrolyte until the charges in the sample were neutralized. For centrifuged samples, the method gives the charge of the colloiddally dissolved system (anionic trash). Two replicate measurements were usually performed and the repeatability was good.

When measuring charge quantity, the streaming potential can be read directly from the instrument. Figs. 9 and 10 shows the streaming potential in the beginning of the titration, together with the charge quantity and zeta potential, as a function of the Poly-DADMAC dosage when coagulation of the O₂ filtrate (Mill A, Subchapter 4.1) was performed at 72 °C and pH 5.5. According to the results, streaming potential had a relatively good correlation with the charge quantity, and somewhat poorer with the zeta potential in this type of process water.

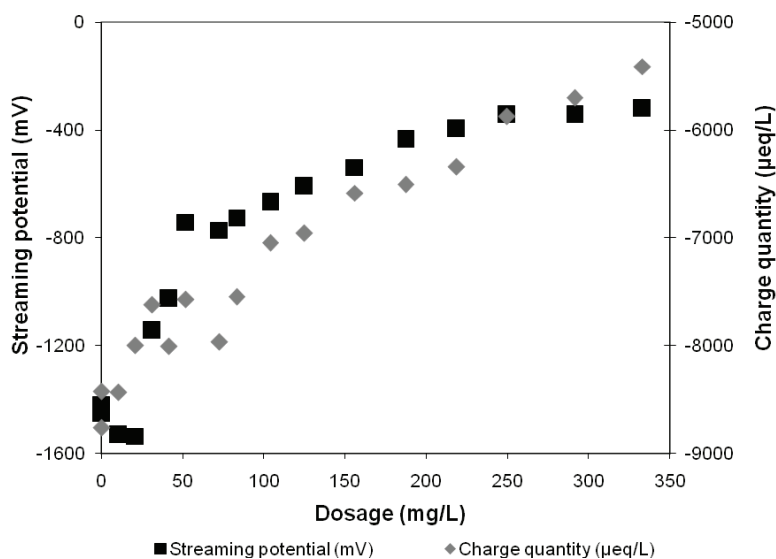


Fig. 9. Streaming potential and charge quantity as a function of Poly-DADMAC dosage when coagulation of the O₂ filtrate was performed at 72 °C and pH 5.5 (unpublished data).

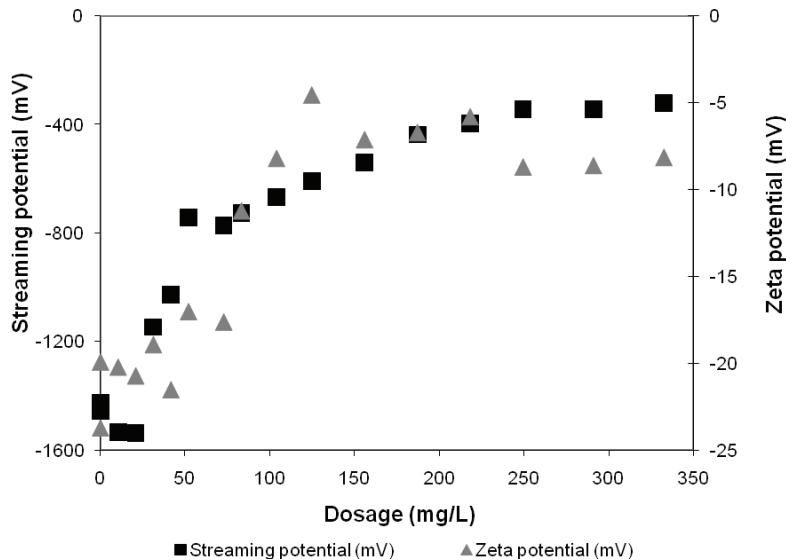


Fig. 10. Streaming potential and zeta potential as a function of Poly-DADMAC dosage when coagulation of the oxygen-bleached process water was performed at 72 °C and pH 5.5 (unpublished data).

4.8.3 Particle size

In Paper III, the particle size measurements were performed with the LS 13320 Laser Diffraction Particle Size Analyzer (Beckman Coulter, USA) equipped with a universal liquid module, and by using the Fraunhofer model (including PIDS, Polarization Intensity Differential Scattering) for data analysis. The LS measures the size of particles ranging from 0.04 μm to 2000 μm .

4.8.4 TOC, COD and BOD

In Papers I–III, TOC was measured with a Shimadzu TOC 5000A analyser (Shimadzu Corporation, Japan), in which combustion is followed by non-dispersive, infrared gas analysis.

In Paper IV, TOC was measured with a Sievers 900 Portable Total Organic Carbon Analyzer (GE Analytical Instruments, USA), which is based on the oxidation of organic compounds to carbon dioxide (CO_2) using UV radiation and

a chemical oxidizing agent (ammonium persulphate). Automated reagent adjustment was used, and three replicates were measured.

The content of TOC (Paper I) was roughly calculated by assuming that lignin-like substances contain 55% (Gellerstedt & Heuts 1997), wood extractives 80%, and carbohydrates 40% carbon. The unidentified carbon component is the difference between the analysed TOC value and the sum of the identified carbon.

COD_{Cr} was measured by oxidation with dichromate according to standard method SFS 5504 (SFS 1988). The analysing laboratory reported that the detection limit of the measurement is 30 mg/L. Two or three replicates were performed for each fraction in the size fractionation studies.

BOD₇ was measured by the dilution and seeding method with allylthiourea addition (to prevent nitrification) according to SFS-EN 1899-1 (SFS 1998) (referred to as the chemical method later on in the text). The seed was generated by sampling mechanically cleaned municipal wastewater, which was left to stand for one day at room temperature and after that in a refrigerator. The seed was pipetted from the surface and used within one week. Municipal wastewater seed was used in order to ensure stable activity of the seed in spite of a probable lower activity in pulp and paper mill wastewater. The dissolved oxygen concentration was measured at the beginning and after 7 days by the electrotechnical probe method according to SFS-EN 25814 (SFS 1995). The probe was a WTW Multi 350i (Wissenschaftlich-Technische Werkstätten (WTW), Germany).

Biodegradability was also investigated by the manometric respirometric Oxitop® method (WTW, Germany), with allylthiourea addition and thermostating at 20.0 °C for 7 days. The determination is based on pressure measurement in a closed system. Micro-organisms consume oxygen while degrading organic material and form CO₂, which is absorbed by NaOH. BOD can be calculated from the pressure change. Standard SFS-EN 1899-1 (SFS, 1998) was followed in the sample preparation.

4.8.5 Wood extractives and lignin

Lipophilic extractives (fatty acids, resin acids, sitosterols, steryl esters, triglycerides) and lignans were determined (in Papers I–III) by extraction with methyl *tert*-butyl ether (MTBE), followed by silylation and gas chromatography (GC) analysis (Perkin Elmer GC autosystem XL, USA) (Örså & Holmbom 1994).

In Paper V, the extraction method was similar but detection was carried out on a Hewlett Packard 6890 GC (Germany) coupled to a Hewlett Packard 5973

Mass Selective Detector (USA), with a capillary column DB-1HT (Dimethylpolysiloxane, 15 m length \times 0.25 mm internal diameter \times 0.1 μ m film thickness, J&W Scientific, Folsom, CA, USA). The internal standards were heneicosanoic acid (99%, Sigma) for fatty and resin acids, heptadecanoate acid (Merck) for lignans, cholesterol (Merck) for sterols, cholesteryl heptadecanoate (Sigma) for steryl esters, and 1,3-dipalmitoyl-2-oleyl-glycerol (99%, Sigma) for triglycerides. The extraction and GC-MS (gas chromatography-mass spectrometry) analysis were performed twice on each sample. Some compounds of interest were identified in the individual fractions of wastewater by matching their retention times and mass spectra with the mass spectra of a Database (Wiley 275.1 1998). Only compounds with reliable identification are discussed in the text.

The concentration of lignin (in Papers I–III and unpublished data in Table 8) was determined on the water phase after MTBE extraction by UV measurement at 280 nm (UV-visible recording spectrophotometer UV-240, Shimadzu Corporation), and using absorptivity values of 19.8 L/(g \cdot cm) for the O₂ and XQ stages (Lahdelma 2002), and 16.3 L/(g \cdot cm) for the E_o, and Op/O and for the E_p stages (Ristolainen 1999). UV absorption at 280 nm is mainly due to the presence of lignin-like material (Örså and Holmbom, 1994).

In Paper V, the concentration of lignin was determined on the water phase, after MTBE extraction by high performance liquid chromatography (HPLC, Shimadzu LC-10AD, Shimadzu, Japan) and UV measurement at 280 nm (Shimadzu SPD-10A, Shimadzu, Japan). The columns were PolySep-GFC-P Guard column (35 \times 7.80 mm, Phenomenex, Torrance, CA, USA), and a PolySep-GFC-P Linear column with a fractionation range of 1–10,000 kDa (hydrophilic synthetic polymer phase, 300 \times 7.80 mm, Phenomenex, Torrance, CA, USA). Lignin (alkal, Sigma, USA) was used as calibration standard, and quantitative data were obtained from the sample peak areas. The chromatogram was registered using the LC solution version 1.03 SP6 software (Lab Solutions, Germany) of the HPLC system.

4.8.6 Carbohydrates and hydroxyl carboxylic acids

Carbohydrates were determined by sample freeze-drying and methanolysis (Eckerman & Ekman 1990, Sundberg *et al.* 1996). Methanolysis was used to degrade hemicelluloses into their monomeric units of methyl glycosides. After silylation, the monomers were analysed by GC (Perkin Elmer GC autosystem XL, USA).

The hydroxy carboxylic acids were determined as their per(trimethylsilyl)ated derivatives by GC (Perkin Elmer GC autosystem XL, USA) (Alén *et al.* 1984). Oxalic acid was determined by ion chromatography (IC Dionex DX500, Dionex Corporation, USA) (Reimann *et al.* 2000). Formic acid and acetic acid were determined by capillary electrophoresis (HP^{3D} capillary electrophoresis, Agilent Technologies, Germany) using indirect UV detection and an external standard method (Ollanketo 1997).

4.8.7 Turbidity, conductivity and pH

Turbidity was measured with a Hach Ratio XR turbidimeter (Hach Company, USA) by ISO method 7027 (SFS 2000). In the instrument, the nephelometric measurement (90°) is compensated by the measurement of transmitted light and forward scatter light.

In Paper I conductivity was measured with a Radiometer CDM3 (Radiometer, Denmark) according to SFS-EN 27888 (SFS 1994). In Paper III conductivity was measured with a Coulter DELSA 440 SX (Beckman Coulter, USA). In Paper IV conductivity was measured using a Kemotron Tetramatic conductivity meter (Kemotron a/s, Denmark) in accordance with SFS-EN 27888 (SFS 1994).

pH was determined with a Radiometer PHM82 (Radiometer, Denmark) according to SFS 3021 (SFS 1979).

4.8.8 Elements

Ca, Mn, and Fe (in Paper I) were determined by flame atomic absorption spectrometry (Perkin Elmer 4100, Germany) according to SFS 3044, SFS 3018, SFS 3048, and SFS 3047 (SFS 1980a, SFS 1982a, SFS 1982b, SFS 1980b). Al and Si (in Paper I) were determined by graphite furnace atomic absorption spectrometry (Perkin Elmer AAnalyst 600, Germany) according to SFS-EN ISO 15586 (SFS 2004).

Mn, Fe, Zn, Al and Si were determined in Paper V by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 5300 DV, USA).

4.8.9 Molecular weight distribution

The MWDs were determined by HPLC (Shimadzu LC-10AD, Shimadzu, Japan) using a size exclusion chromatography (SEC) column and an evaporative light scattering detector (ELSD, PL-ELS 2100, Polymer Laboratories, UK). UV detection (Shimadzu SPD-10A, Shimadzu, Japan) at 280 nm and 254 nm was also used for the sieved influent and effluent sampled in May. The columns were PolySep-GFC-P Guard column (35 × 7.80 mm, Phenomenex, USA), PolySep-GFC-P 2000 column with a fractionation range of 100–10,000 Da (hydrophilic synthetic polymer phase, 300 × 7.80 mm, Phenomenex, USA), and a PolySep-GFC-P Linear column with a fractionation range of 1–10,000 kDa (hydrophilic synthetic polymer phase, 300 × 7.80 mm, Phenomenex, USA). Dextran 50000 standard (Fluka), polyvinyl alcohol standard 7200 (Fluka), α -cyclodextrin (> 98%, Merck, Germany) and dextran 1000 standard (Fluka) were used for molecular weight calibration of the chromatograms (weight-average molecular weight).

4.8.10 Tot-P and PO₄-P

Total phosphorus (Tot-P) and phosphate phosphorus (PO₄-P) were determined by flow injection analysis (LACHAT FIA QC 8000, Zellweger analytics, USA). The analysing laboratory reported that the extended uncertainty of measurement (including systematic error and random error) is 10% for both analyses at the studied concentration level.

5 Results and Discussion

5.1 Characterization of the chemical pulp process waters and wastewaters

5.1.1 Multimodal zeta potential distribution

In the birch pulp model water (preparation in Subchapter 4.2) there were repeatedly three particle populations of different zeta potential (Fig. 11). The average zeta potentials of the model water were -33 ± 5 mV, -51 ± 5 mV, and -74 ± 10 mV ($n = 13$). The pH had a pronounced effect on the multimodal zeta potential distribution. The number of populations diminished with decreasing pH and, at a low pH level, only one zeta potential was observed (Fig. 12, upper part). The number of populations increased when the pH of the model water was increased. At pH 11.1, as many as five well-distinguished populations of different zeta potential were detected (Fig. 12, lower part).

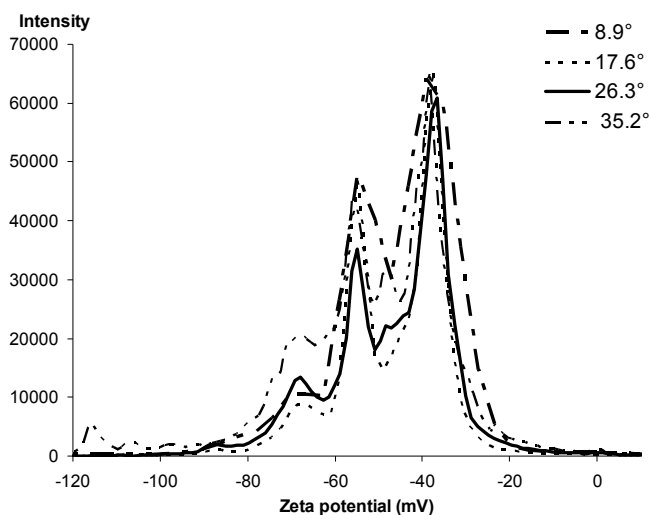


Fig. 11. Multimodal zeta potential distribution for birch pulp model water at pH 9.6 (reprinted and revised from Paper I with permission from Pulp and Paper Technical Association of Canada).

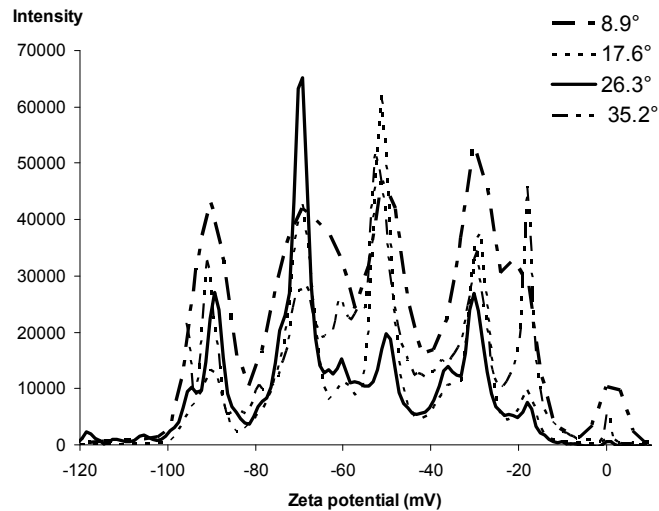
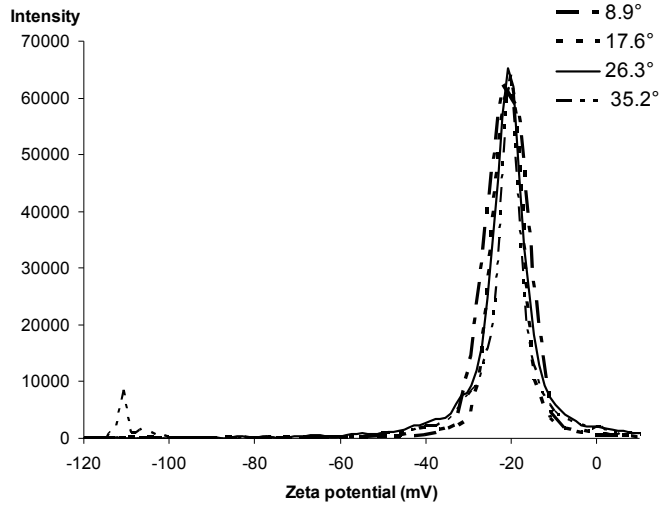


Fig. 12. Effect of pH on the multimodal zeta potential distribution of birch pulp model water: pH 4.8 (upper) and pH 11.1 (lower) (reprinted and revised from Paper I with permission from Pulp and Paper Technical Association of Canada).

The same pH effect was observed with the real process water (Paper I). The zeta potential and charge quantity were increased (approached zero) by the hydrogen ions (Dorica & Wong 1981) when the pH was decreased. At low pH levels, repulsion between particles of different charge is minor because there are abundant neutralizing hydrogen ions present. Thus small, nonsettleable

aggregates were probably formed. It is also likely that, at low pH, the multi-angle ELS technique may not be able to distinguish small differences in charges and therefore give only the mean zeta potential.

A comparison of the two zeta potential analyses showed that the mean of the multiple zeta potential values measured in the assay water by the multi-angle ELS technique was approximately equal to the zeta potential measured by the single-angle ELS technique (Paper I). Subchapter 5.2.1 includes a discussion about the effect of short-chain cationic polyelectrolytes on the multimodal zeta potential distribution of the chemical pulp model water.

The multimodal zeta potential distribution was next studied by filtering the birch pulp process water after the O₂ stage (pH 10.6) into fractions, and by measuring various parameters (see Fig. 7 for the filtration procedure and analyses). With unfiltered process water (sedimented for a short period), the 12 μm and 1.6 μm filtrates had three or even four different zeta potentials (Fig. 13). When the filtration was performed with a 1.2 μm membrane or smaller, the number of populations was reduced to two. Conductivity was nearly the same for all the filtrates as well as for the process water (7.2–7.4 mS/cm).

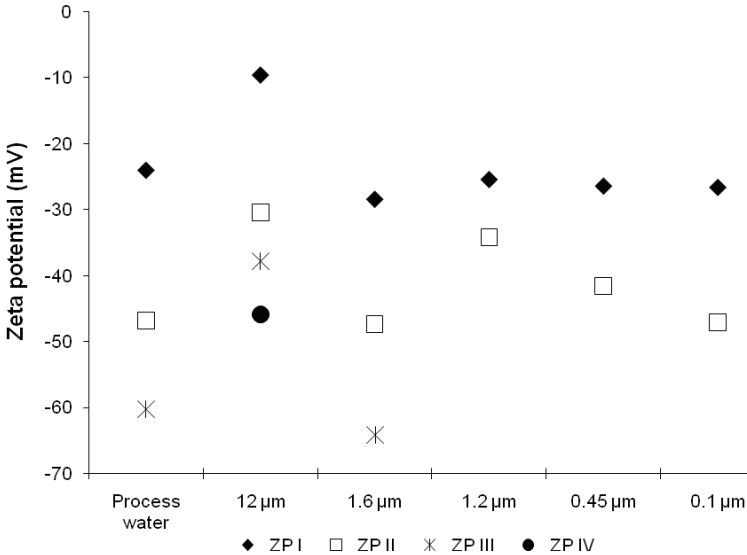


Fig. 13. Effect of filtration on the multimodal zeta potential distribution in birch pulp process water after the O₂ stage (reprinted and revised from Paper III with permission from IWA Publishing).

The particle size distribution of the process water determined by LS contained three main fractions: 1.45 μm , 28.7 μm and 66.4 μm (Paper III). Over half of the substances that caused a charge quantity were removed by 1.6 μm filtration (Fig. 14). Subsequently, the charge quantity remained relatively constant (approximately -8000 $\mu\text{eq/L}$). The use of filtration, e.g. as a pretreatment for coagulation, could be advantageous in order to minimize the coagulant dosage. However, floc formation and the settling behaviour could also be affected. Turbidity decreased relatively linearly with decreasing membrane size, from 136 NTU in process water to 4 NTU in 0.1 μm filtrate (Fig. 14).

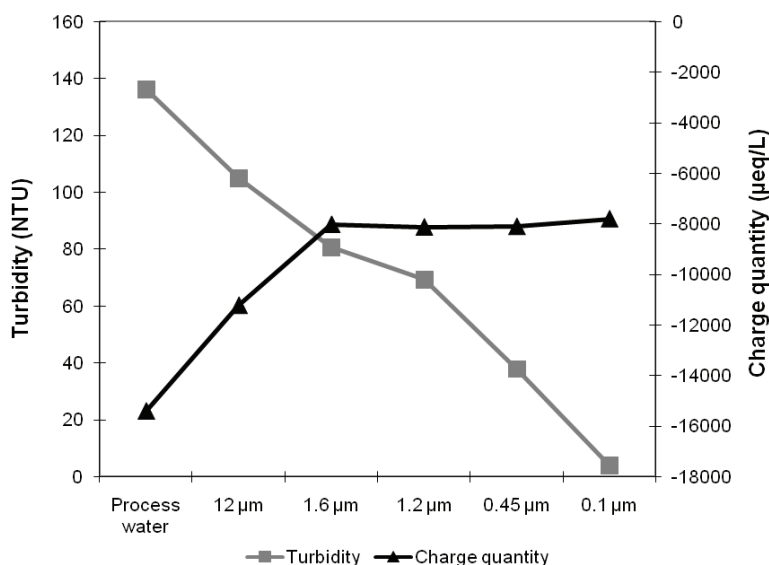


Fig. 14. Effect of filtration on turbidity and charge quantity in birch pulp process water after the O_2 stage (reprinted and revised from Paper III with permission from IWA Publishing).

TOC data proved that the bulk of the organic material was well dissolved, with material under a size of 0.1 μm (Paper III). There was no significant difference in the concentrations of carbohydrates and lignin between the filtrated fractions and unfiltrated water (Paper III). However, methanolysis degrades only dissolved hemicelluloses. It does not take into account those carbohydrates that could occur in existing agglomerates, which are formed from carbohydrates and wood

extractives. Over half of the lipophilic extractives were absent when applying 0.1 μm filtration (Paper III). Even with 1.2 μm filtration, they were still all present (138 mg/L), indicating that the size of the colloidal extractives was mainly between 0.1–1.2 μm . Due to the high pH of the process water (10.6), resin acids and fatty acids would be dissolved to a high extent (Ström 2000). Decreasing pH would give more large colloidal extractives, and they would be removed more effectively with coagulation–flocculation.

5.1.2 Components in the chemical pulp process waters

Table 7 presents the concentrations of wood extractives and Table 8 some other characteristics in the model water and in process waters from ECF birch pulp bleaching in two Finnish pulp mills (Papers I and II including also unpublished data). The model water contained a relatively small amount of extractives, but the amount is typical of process waters taken from the various bleaching stages of kraft birch pulp, with the exception of the O₂ stage. The larger amounts of extractives in the oxygen stages are as expected because the deresination of pulp in bleaching occurs mainly in the oxygen stage (Holmbom 2000).

Resin acids occur exclusively in softwoods and are not found in birch. The process water sampled during birch pulp bleaching nevertheless contained as much as 107 mg/L resin acids in Mill A and 56 mg/L in Mill B after the O₂ stage. This can be explained by the mill's alternate pulping of birch and pine during a cycle lasting for a few-days and by the addition of tall oil in the digestion of birch.

The wastewater going to wastewater treatment consists mainly of D₀ and some E₀ in Mill A. In Mill B, the wastewater consists of XQ filtrate and some Op/O and D₁ filtrates. The counter-current circulation results in the carry-over of compounds from previous stages, which makes detailed analysis difficult (Ristolainen 1999).

The model water and process waters contained large amounts of xylose relative to other monosaccharides (Table 8). The proportion of xylose units is typically high in hardwoods (Sjöström 1993). The major hemicellulose in hardwood species is O-acetyl-4-O-methylglucuronoxylan, or simply xylan, which is relatively stable under alkaline conditions. On the average, every tenth xylose unit of xylan is linked to a side group of 4-O-methylglucuronic acid (Fengel & Wegener 1989). Most of the OH groups at C-2 and C-3 of the xylose units contain an O-acetyl group, which is readily cleaved by alkali (Sjöström 1993). A significant amount of xylan dissolves in the cooking liquor as a polysaccharide

rather than degrading, and readsorption of xylan into fibres occurs to some extent. Because of the higher proportion and readsorption of xylan, the yield of hardwood kraft pulp is higher than that of softwood kraft pulp (Sjöström 1993). A large amount of xylose (641 mg/L) was found in the model water. However, the model water had a low concentration of 4-O-methylglucuronic acid relative to that of xylose. Apparently, some of the 4-O-methylglucuronic acid groups had been stripped off.

Table 7. Concentration of wood extractives (mg/L) in model water and in process waters from ECF birch pulp bleaching in two Finnish pulp mills.

Bleaching stage	Fatty acids	Resin acids	Sitosterols	Steryl esters	Triglycerides	Total
Model water						
O ₂ [†]	7	2	< 1	< 1	< 1	9
Mill A						
O ₂	259	107	2	8	1	377
D ₀	4	< 1	< 1	< 1	< 1	4
E ₀	2	4	< 1	< 1	< 1	6
E ₁	3	3	< 1	< 1	< 1	6
W	4	4	< 1	< 1	< 1	8
D ₂ [‡]	6	1	< 1	< 1	< 1	7
Mill B						
O ₂ [‡]	190	56	23	6	< 1	275
XQ	6	< 1	< 1	< 1	< 1	6
Op/O	37	9	< 1	1	< 1	47
D ₁	1	< 1	< 1	< 1	< 1	1
E _P	8	8	< 1	< 1	< 1	16
D ₂	< 1	< 1	< 1	< 1	< 1	< 1

[†] Model water prepared of oxygen bleached pulp from Mill A. [‡] Samples were not taken on the same day as the others.

Table 8. Characteristics of model water and process waters from two kraft pulp mills carrying out elemental chlorine-free (ECF) bleaching of birch (*Betula verrucosa*) (reprinted and revised from Paper I with permission from Pulp and Paper Technical Association of Canada including also unpublished data).

	Model water					Mill A					Mill B												
	O ₂ [†]	O ₂	D ₀	E ₀	E ₁	W	XQ [‡]	Op/O	D ₁	E _P	D ₂	O ₂ [†]	O ₂	D ₀	E ₀	E ₁	W	XQ [‡]	Op/O	D ₁	E _P	D ₂	
pH	9.6	10.6	4.2	9.4	11.8	11.7	4.2	11.7	3.5	11.2	3.1												
Conductivity (mS/m)	31	905	485	780	1190	810	335	490	320	440	230												
Turbidity (NTU)	26	367	361	95	98	87	88	70	47	40	26												
TOC (mg/L)	320	2900	900	1100	1300	1300	700	1000	700	900	300												
Carbohydrates (mg/L)	688	488	326	180	204	238	360	450	233	176	64												
Arabinose	2	37	12	19	24	26	12	21	13	15	6												
Xylose	641	307	175	86	92	122	265	339	120	111	42												
Rhamnose	1	16	4	3	6	6	3	6	2	3	1												
Mannose	1	11	7	2	3	3	2	3	3	2	1												
Glucose	17	42	22	26	37	40	11	27	8	16	5												
Galactose	2	52	29	28	28	28	16	27	22	17	6												
4-O-Methyl-Glucuronic acid	22	13	5	5	7	7	8	14	2	4	1												
Glucuronic acid	1	2	1	1	1	1	2	1	1	1	1												
Galacturonic acid	1	8	71	10	6	5	41	12	62	7	1												
Hydroxy carboxylic acids (mg/L)	< 10	467	47	44	147	164	53	173	48	125	31												
Lactic acid	-	47	4	3	5	6	3	7	3	8	2												
Glycolic acid	-	8	3	2	4	8	3	17	8	17	4												
2-Hydroxybutanoic acid	-	40	2	2	3	3	2	3	2	8	2												
Methylsuccinic acid	-	2	-	-	-	-	-	2	4	7	7												
Glyceric acid	-	3	4	3	6	7	4	7	4	6	2												
2,4-Dihydroxybutanoic acid	-	42	10	10	54	59	12	42	8	27	4												
3,4-Dihydroxybutanoic acid	-	18	8	4	16	19	7	21	6	11	3												

	Model water				Mill A				Mill B			
	O ₂ [†]	O ₂	D ₀	E ₀	E ₁	W	XQ [‡]	Op/O	D ₁	E _P	D ₂	
Adipic acid	-	-	1	-	1	2	1	1	-	-	-	
Malic acid	-	1	-	-	-	-	-	1	1	2	2	
2,5-Dihydroxypentanoic acid	-	52	2	2	2	2	2	1	-	1	-	
Xyloisosaccharinic acid	-	33	3	8	33	34	9	34	5	20	3	
2,4,5-Trihydroxypentanoic acid	-	78	7	6	16	16	6	22	4	11	2	
β-Glucosisosaccharinic acid	-	106	3	3	5	6	3	11	2	5	-	
α-Glucosisosaccharinic acid	-	37	-	1	2	2	1	4	-	2	-	
Lignin (mg/L)	110	2640	n.d.	1020	n.d.	n.d.	430	865	n.d.	840	n.d.	
Lignan (mg/L)	<1	18	<1	<1	<1	<1	2	4	<1	2	<1	
Oxalic acid (mg/L)	2	150	70	20	90	90	45	90	50	70	20	
Formic acid (mg/L)	10	205	90	200	200	215	5	130	55	130	140	
Acetic acid (mg/L)	10	220	35	25	45	45	10	30	35	45	40	
Ca (mg/L)	1.6	14.3	83.3	27.8	25.3	20.6	n.d.	n.d.	n.d.	n.d.	n.d.	
Mn (mg/L) [†]	0.1	1.1	3.8	2.1	1.1	1.1	n.d.	n.d.	n.d.	n.d.	n.d.	
Fe (mg/L) [†]	<0.02	0.1	0.5	0.5	0.2	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	
Si (mg/L)	0.6	1.8	8.0	5.7	7.6	7.4	n.d.	n.d.	n.d.	n.d.	n.d.	
Al (mg/L)	0.2	0.3	0.7	0.5	0.3	0.3	n.d.	n.d.	n.d.	n.d.	n.d.	

n.d. = not determined. [†] Model water prepared from oxygen bleached pulp from Mill A. [‡] The concentration of lignin was calculated using the absorptivity value of the O₂ stage (19.8 L/(g·cm)). ¹ Filtration with a 0.45 µm membrane before analysis.

Hydroxy carboxylic acids were not detected in the model water (Table 8). The O₂ filtrate contained a large amount of these acids (467 mg/L), the predominant acids being β-glucoisosaccharinic acid and 2,4,5-trihydroxypentanoic acid. 2,4-dihydroxybutanoic acid, 3,4-dihydroxybutanoic acid, xyloisosaccharinic acid and 2,4,5-trihydroxypentanoic acid were the main hydroxy carboxylic acids in almost all the filtrates.

The concentration of lignin-derived material was low in the model water (110 mg/L) compared to that in the O₂ process water (Table 8). The concentration of lignin is not given for E₁, W and different D filtrates due to the lack of absorptivity value for these stages. It should be noted also that the absorptivity value used for the XQ filtrate has been determined for the O₂ filtrate. Overall, accurate determination of lignin is difficult due to the absorptivity value, the magnitude of which depends on structural changes in lignin during the different process stages. Determination of the absorptivity value is not trouble-free (Lahdelma 2002). Furthermore, water samples taken after extraction with MTBE contain small amounts of non-lignin substances (like polysaccharides) having UV-absorbance at 280 nm (Örså & Holmbom 1994).

For Mill A, a high concentration of Ca was observed in acidic stage D₀ (Table 8). Calcium oxalate scales have been detected in Mill A due to extensive water circulation in the mill. Calcium dissolves from the pulp in the acid stages, and oxalate ions are formed in the oxidative stages (Ulmgren 1997). Calcium carbonate scale has also been observed in the E stages in Mill A.

The content of TOC (according to data in Table 8) in the birch pulp process water after the oxygen stage is illustrated in Fig. 15. As much as 80.6% of the TOC in the O₂ filtrate was identified (Mill A). Lignin-derived material accounted for one a half of the TOC composition. The unidentified substances (19.4%) mainly comprised polysaccharide and lignin fragments that were not separately identified.

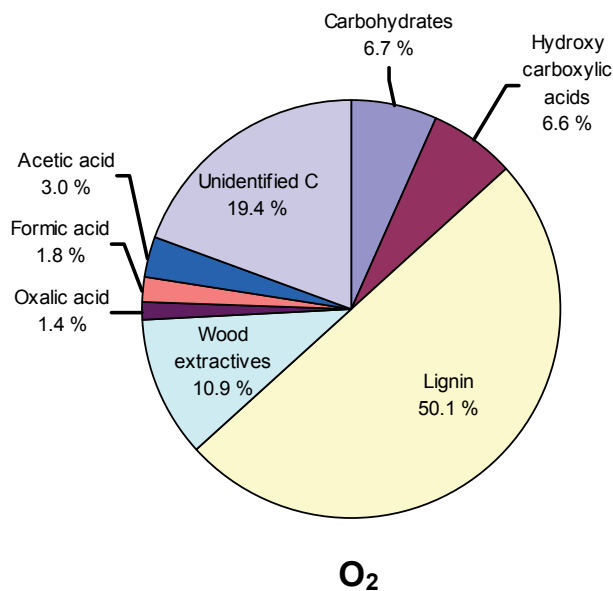


Fig. 15. The content of TOC in birch pulp filtrate sampled after the O₂ stage (Mill A). 80.6% of the TOC was identified (reprinted and revised from Paper I with permission from Pulp and Paper Technical Association of Canada).

5.1.3 Size fractionation of wastewater

The aim in the size fractionation of wastewater was to determine the size fractions in which the main pollutants occur, and then to investigate the effect of biological treatment on their distribution (Papers IV and V). The fractionation was performed on two different occasions (May and July 2007) by microfiltration and ultrafiltration of the wastewater taken from an integrated pulp and paper mill before (referred to as influent) and after (effluent) the activated sludge treatment process (See Subchapter 4.7.2).

Molecular weight distribution and lignin

Most of the organic material (detected with ELSD) in both the influent and effluent samples was in the medium MW range (< 10 kDa), with three main sub-

fractions (Fig. 16). The distributions were relatively repeatable. Only the influent sampled in May had a middle peak (7400 Da) of higher intensity. The magnitude of MWD in the effluent was about one half that in the influent. Moreover, the lower MW compounds proved to be more biodegradable.

The effluent sampled in May had a broader MWD than the influent sampled on the same day. Degradation of some of the fractions into smaller compounds was indicated by the peak at around 5700 Da. There was no corresponding feature in the influent and effluent sampled in July.

The sieved influent and effluent samples contained only a small amount of larger compounds (lignin and its derivatives) with a MW range of approximately 20 to 28 kDa. The ELSD did not, however, register them, but they were detected under UV at 280 nm and 254 nm using the linear column with a fractionation range of 1–10,000 kDa.

Since the major part of the compounds in the May had a MW of between 5700 Da and 8600 Da, a 3 kDa membrane was added to the UF procedure on the July samples in order to verify the effect of UF. However, the 3 kDa fractions still included compounds with a MW higher than 3 kDa. The MWD of the influent was reduced to some extent by 3 kDa ultrafiltration. In contrast, the 3 kDa ultrafiltration had no marked effect on the effluent.

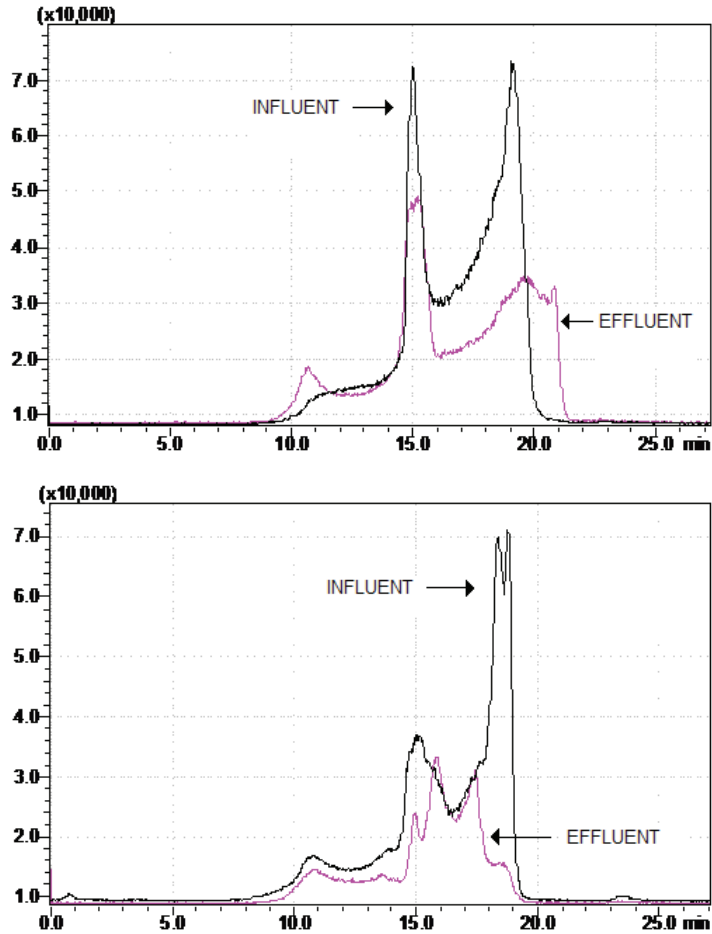


Fig. 16. MWDs of the sieved influent and effluent sampled in May (upper) and in July (lower). Retention time 10 min \approx 8800 Da, 20 min \approx 6000 Da; Column: PolySep-GFC-P 2000; ELSD (reprinted from Paper IV with permission from Elsevier).

According to the MWD data, the ultrafiltration method did not provide complete separation of the components on the basis of their molecular weight. Millipore’s definition of NMWL is that a UF membrane with a given NMWL will retain at least 90% of a globular solute of that MW in Daltons (Millipore 1999). UF membranes have a distribution of pore diameters, not just pores of one diameter. Different types of membrane have a diverse microstructure (open–tight). In addition to the size and shape of the solute, as well as membrane type, there are

also other factors, e.g. the solute concentration, that affect the retention of UF membranes (Cheryan 1986). Concentration polarization due to retained solutes causes membrane fouling. If the retained solute concentration is high, then the passage of solutes with a lower molecular size than the NMWL used may be impeded due to the formation of a secondary membrane. Membrane fouling will cause a drop in the flux during filtration. The presence of other solutes also has an effect on the success of separation. The retention of a solute in a complex mixture is different to that in a simple solution. Separation between two macromolecules should be possible if there is at least a 10-fold difference in their molecular weight and if there is an UF membrane available with an NMWL between the molecular weights of the two molecules (Cheryan 1986). The solution conditions (e.g. pH and ionic strength) also affect solute retention, because these parameters also influence the conformation and shape of the solutes (Cheryan 1986). It is also possible that hydrophobic extractives with a size smaller than the membrane pore diameter can adsorb on the membranes or material retained on the membrane. In this study, adsorption and fouling were minimized by performing sequential filtration, stirring the liquid during filtration, replacement with a clean membrane at intervals, and using hydrophilic membranes. Cleaning the membranes was performed with 0.1 M NaOH solution, and this should remove any attached resin and fatty acids. Thus, in this research, membrane fouling was probably not a major problem. However, there was a slight but gradual decrease in peak intensities in MWD (compounds under 10 kDa) with decreasing pore size, starting already from the 8 μm membrane, which could be due to the secondary membrane. In addition to problems that can arise during the ultrafiltration procedure, MW determination using SEC also has limitations that sometimes lead to over- or underestimation of compounds due to interaction with the column packing (Knuutinen *et al.* 1998).

The sieved influent contained about 200 mg/L of lignin material, of which 40% of the lignin was present in the colloids and 55% in the < 3 kDa fraction (Paper V). Filtration had no effect on the concentration of lignins in the effluent. The effluent contained approximately 100 mg/L of completely dissolved lignin material. Lignin fragments in fact typically consist of phenyl propane chains with molecular weights of 1000–10,000 (Sjöström & Alén 1998). The chain-like structure of lignin, which is presumably the main component of MWD, may allow it to permeate even the 3 kDa ultrafiltration, and some decomposition may also take place during the filtration process. A brownish colour, which is mainly attributable to lignin and its derivatives, was clearly observed in all the fractions.

BOD, TOC and COD

Fig. 17 shows the BOD₇ in the influent and effluent fractions measured with the conventional chemical method (both May and July) and with the manometric respirometric method (July only). The activated sludge treatment reduced BOD₇ by 98% in May and by 96% in July (according to the chemical method). The respirometric method gave between 15–51% lower BOD₇ values for the influent than the chemical method; however, the trend of the curves was very similar. Thus, the difference presumably originated from dilution in the chemical method, indicating the presence of considerable amounts of inhibitive substances in the wastewater. For the influent, BOD₇ decreased gradually as a function of pore size. For the effluent, too, the BOD₇ values decreased to some extent with decreasing pore size. Interestingly, however, the 3 kDa fractions of both the influent and effluent showed a significant increase in BOD₇. The same phenomenon was observed with both methods. The BOD₇ value for the 3 kDa fraction of the effluent measured with the chemical method was even higher than that presented in Fig. 17 because, due to inadequate dilution, the oxygen concentration after seven days was zero and there was no sample left to repeat the analysis. Analysis of the 3 kDa fraction of the influent was repeated afterwards on a frozen sample with the chemical method, and the BOD₇ value was very close to the BOD₇ value measured on the first occasion (835 and 839 mg/L, respectively). The repeatability was evaluated by means of a glucose-glutaminic acid standard prepared according to the standard method, and it was good. A small amount of sample was available for BOD measurement, and many dilutions were performed on each sample in order to obtain a result for each fraction.

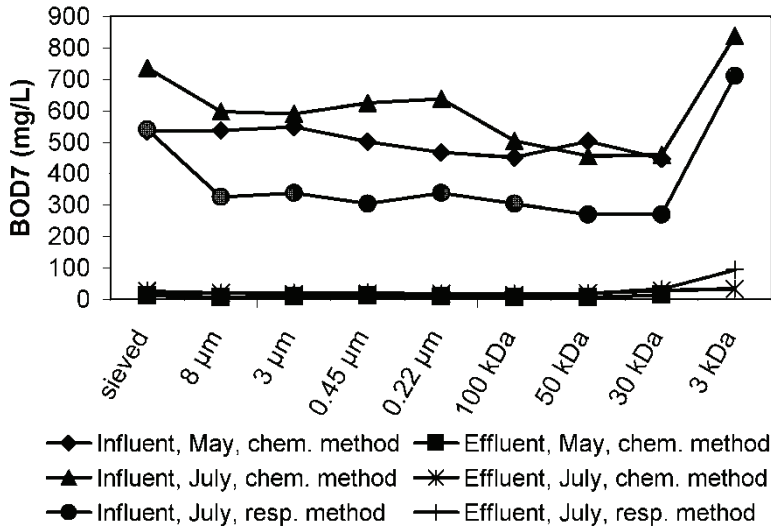


Fig. 17. BOD₇ in the influent and effluent fractions measured with the conventional chemical method (sampled in May and in July) and with the manometric respirometric method (only in July) (reprinted and revised from Paper IV with permission from Elsevier).

Fig. 18 shows the BOD development measured by the manometric respirometric method on the influent (upper) and effluent (lower) and their filtered fractions. The initial slope for the influent was much steeper than for all the filtered fractions. The 3 kDa fraction of the influent showed a significant increase in BOD after 3 days. The 3 kDa fraction of the effluent showed a marked increase in BOD even during the first day of the BOD determination. The initial slope for the 30 kDa fraction of the effluent was similar to that for the 3 kDa fraction, but then rapidly decreased.

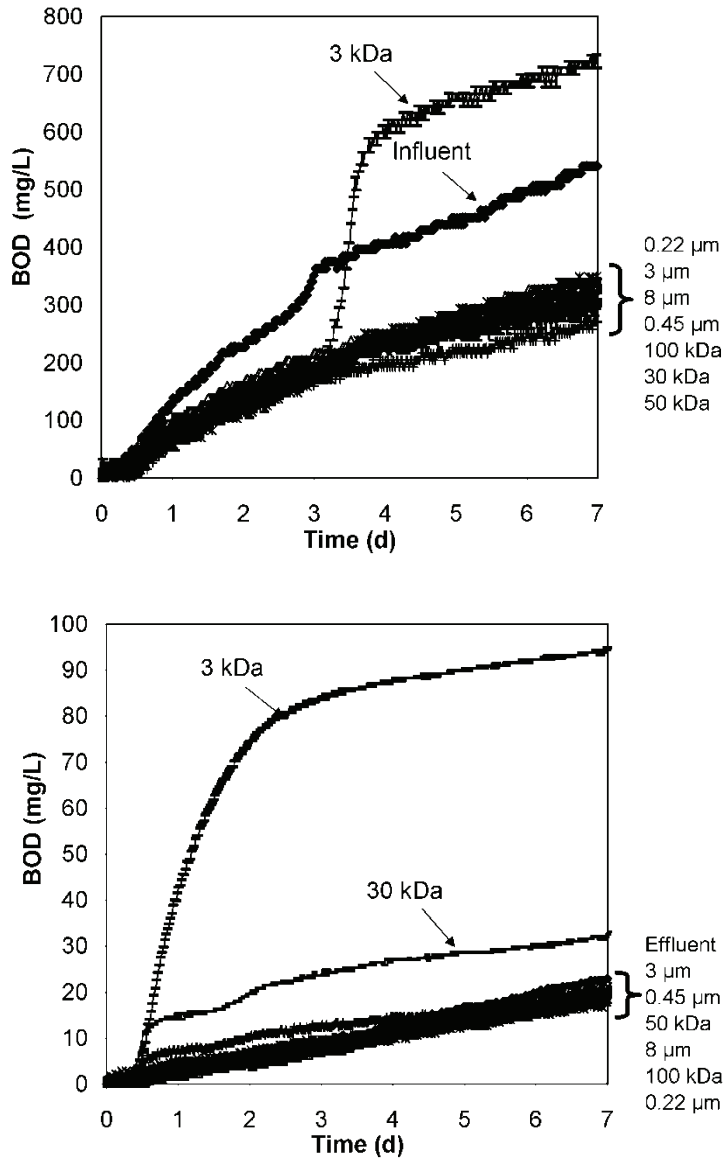


Fig. 18. BOD (mg/L) development measured with the manometric respirometric method on the sieved influent (upper) and sieved effluent (lower) and all the filtered fractions sampled in July (reprinted from Paper IV with permission from Elsevier).

The high BOD₇ in the 3 kDa fractions could not be due to nitrification because allylthiourea was used to prevent nitrification (SFS 1998). Furthermore, the MWD data showed that degradation of compounds to a more bioavailable form did not occur in the 3 kDa filtration. The TOC results also showed that there was no contamination from the membranes (Paper IV), thus ruling out the possibility that contamination was the reason for the higher BOD₇ values. Thus the highly likely explanation for the high BOD₇ in the 3 kDa fractions is that compounds toxic to bacteria were removed only in the 3 kDa, and to some extent also in the 30 kDa ultrafiltration. The effect of dilution on the BOD₇ values (Fig. 17) already indicated the presence of inhibiting substances. Toxic compounds known to reduce biological activity at elevated concentrations include arsenic, chromium, copper, cyanide, iron, lead, manganese, mercury, nickel, silver, zinc, some waste organics (Gaetano 2000) and aluminium in different monomeric, polymeric or colloidal forms. Besides being toxic to aquatic life, wood extractives can also be inhibitory to the biomass of the activated sludge treatment. A sudden increase in resin acid concentration can affect biomass viability (Werker & Hall 1999).

After this kind of effluent passes into the water system, there may be a similar jump in the biochemical oxygen demand, because the effluent is diluted many-fold thereby reducing the concentrations of inhibiting substances, in addition to the biodegradable material itself. Oxygen consumption caused by the effluent in natural water may thus be considerably higher than has earlier been thought. In other words, the BOD₇ values may be much too low when it is determined in the presence of compounds harmful to bacteria.

TOC decreased somewhat in the influent samples when smaller pore sizes were used (Paper IV). However, TOC in the 50 and 30 kDa fractions of the influent sampled in May was even higher than that in the sieved influent. This was also the case for the 3 kDa fraction of the influent sampled in July; TOC was considerably higher than for the 30 kDa fraction of the same influent sample. The analysis probably could not measure all the organic carbon in the larger fractions. It is possible that the mechanical strain caused by tight ultrafiltration at high pressure converted some of the compounds into a more oxidizable form. Contamination from the filters and membranes was ruled out, because the same effect should have been found with the effluent samples, but this was not the case. Repeatability of the TOC measurements was excellent; the standard deviation (SD) of three replicates was in most cases under 10 mg/L (relative standard deviation (RSD) < 1.2%). In two cases it was higher: for the 3 µm fraction of

effluent sampled in May the SD was 15 mg/L (RSD 4.8%), and for the 50 kDa fraction of influent sampled in July the SD was 24 mg/L (RSD 4.5%).

The COD_{Cr} in the influent and effluent fractions decreased slightly on moving to the smaller fractions (Paper IV). As was the case with the TOC results, COD_{Cr} increased to some extent in the smaller fractions of the influents, probably due to similar analytical problems as the inhibited oxidation with the larger fractions. However, the results indicate that the major part of the sieved influent and effluent COD_{Cr} was within the soluble range (< 30 kDa).

The repeatability of the COD_{Cr} measurements was good; the SD of two (or three) replicates varied in most cases from 0 to 21 mg/L (RSD < 3.9%). It was higher only for three samples (influent May 3 µm fraction SD = 60 mg/L (RSD = 4.1%, n = 2), influent May 0.22 µm fraction SD = 130 mg/L (RSD = 10.4%, n = 2), effluent May 0.45 µm fraction SD = 30 mg/L (RSD = 5.2%, n = 2).

The BOD:COD ratio is used as a biodegradability index, which depicts the proportion of easily biodegradable organic material. A component with a BOD₅:COD ratio of at least 0.40 can be considered biodegradable (Chamarro *et al.* 2001). When calculating the biodegradability index, it is essential to take into account the fact that dilution and freezing of sample when measuring BOD, and using BOD₇ instead of BOD₅, increases the value of the index. According to the results from the conventional chemical method on frozen samples, the BOD₇:COD_{Cr} ratio for the influent sampled in May was 0.34 and in July 0.43. Freezing presumably changed the composition of the sample and made it more readily decomposable by bacteria. The BOD₇ of unfrozen influent was lower, thus resulting in a lower index value, 0.34 (July). When the results obtained with the manometric respirometric method were used in the calculation, the biodegradability was even lower, 0.32 in July (frozen sample). When the BOD₅:COD_{Cr} ratio was calculated according to the results with the manometric respirometric method, the biodegradability index was as low as 0.26 in July (frozen sample). Thus the influent had a relatively low biodegradability. Since municipal wastewater seed was used in this study to measure BOD₇ (both chemical and respirometric method), the BOD₇ value may be underestimated due to the inability of micro-organisms present in the seeding material to degrade certain compounds, which would otherwise be readily degradable by the micro-organisms present in the activated sludge of the pulp and paper mill wastewater treatment plant. However, higher BOD values have been reported for pulp and paper mill wastewater with municipal wastewater seed than with the mill's own return sludge (Prokkola 2007).

The efficiency of biological treatment could be improved by increasing the biodegradability of wastewater before biological treatment, e.g. by the degradation of refractory lignin in the wastewater. Advanced oxidation processes (AOP) would degrade organic compounds into smaller fragments or even completely mineralize them (e.g. Andreozzi *et al.* 1999, Bijan & Mohseni 2005, Makhotkina *et al.* 2008). According to a life cycle assessment carried out by Muños *et al.* (2006), however, the high energy requirements of some AOPs is the main environmental impact. Selective oxidation of wastewater fractions containing a high proportion of complex nonbiodegradable substances would be economically feasible because the consumption of chemicals required for the degradation of simple compounds would be much lower (Mohammed & Smith 1992). The effluent quality could also be improved by performing the degradation of refractory lignin after biological treatment. It has been even suggested that lignin, in this case most probably the high MW lignin, may have an inhibitory effect on living organisms (Pessala *et al.* 2004). Improved biodegradability and decolourization of an effluent was achieved, for example, by ozonating pulp and paper mill wastewater after the biological process (Kreetachat *et al.* 2007). It should be noted, however, that the toxicity of certain compounds can even increase as a result of oxidation due to the formation of toxic intermediates and products, as has been reported for the ozonation of abietic acid (El-Din *et al.* 2006).

Wood extractives

The sieved influent contained about 14.3 mg/L of wood extractives, of which 12.8 mg/L were resin and fatty acids and 1.5 mg/L sterols (Paper V). The concentration of total wood extractives in the influent decreased with decreasing pore size down to 0.22 µm filtration. 44% of the resin and fatty acids in the influent were found in particles, 20% as colloids and 36% in the < 3 kDa fraction. The values for sterols were only 5% in particles, 46% as colloids and 49% in the < 3 kDa fraction (Fig. 19). The standard deviation of the measurement was the highest for the sieved influent (SD = 3.88 mg/L, RSD = 27%) and for the 3 kDa fraction of the effluent (SD = 0.41 mg/L, RSD = 29%). For other fractions the SD was between 0 and 1.36 mg/L (RSD < 19%). The particle fraction may contain dispersed extractives, as well as extractives adsorbed on fibrous material and other particles (Mörck *et al.* 2000).

The sieved effluent contained 1.7 mg/L of wood extractives, of which 1.45 mg/L were resin and fatty acids (reduction 89%) and 0.26 mg/L sterols (reduction 83%). They were mainly present in the < 3 kDa (82%) fraction as well as, to some extent, in particles (18%) (Fig. 19). Our result deviated from that earlier reported (Kostamo *et al.*, 2004), according to which 74–99% of the extractives were discharged attached to particles (retained on Whatman GF-C filters). This further indicates that, in the present case, the adsorption of dispersed extractives was highly unlikely. The membranes with a NMWL of 100 kDa, 50 kDa and 30 kDa were the least hydrophilic (polyethersulphone) and therefore, if adsorption had occurred, it probably would have occurred on these membranes. The concentrations of wood extractives were at the same level as reported previously (Verta *et al.* 1996, Kaplin *et al.* 1997, Kostamo *et al.* 2004).

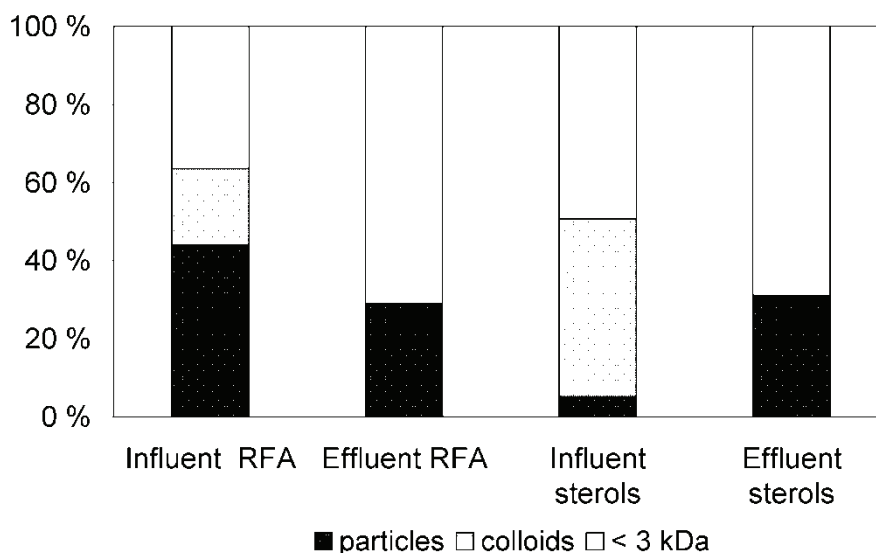


Fig. 19. Distribution of resin and fatty acids (RFA) and sterols in the influent and the effluent from the activated sludge plant (particles > 0.45 μm , colloids = 0.45 μm –3 kDa) (reprinted and revised from Paper V with permission from Elsevier).

The sieved influent contained $220 \pm 54 \mu\text{g/L}$ β -sitosterol and the sieved effluent $88 \pm 50 \mu\text{g/L}$ β -sitosterol. This compound occurred mainly in particles (34%) and as colloids (66%) in the influent, but totally in particles (100%) in the effluent.

According to the results, β -sitosterol is thus completely removable by microfiltration after the activated sludge process.

The sieved influent contained 514 ± 193 $\mu\text{g/L}$ dehydroabietic acid, and it was partitioned in all three fractions: particles (16%), colloids (40%), as well as in the < 3 kDa fraction (44%). The sieved influent contained 200 ± 27 $\mu\text{g/L}$ abietic acid, and it occurred only in particles (47%) and as colloids (53%). Isopimaric acid was reliably identified only in the 3 and 0.45 μm fractions. The 3 μm fraction of the influent contained 86 ± 4 $\mu\text{g/L}$ isopimaric acid, and the 0.45 μm fraction 80 \pm 6 $\mu\text{g/L}$ isopimaric acid. Pimaric-type resin acids are less soluble than abietic-type resin acids (Peng & Roberts 2000). Individual resin acids in the effluent fractions could not be identified with a high degree of certainty. Using a longer column (30 m) instead of the 15 m column would have helped identification.

Palmitic acid and oleic acid were reliably identified in both the influent and effluent. The influent contained 1374 ± 659 $\mu\text{g/L}$ palmitic acid and 1228 ± 520 $\mu\text{g/L}$ oleic acid, and the effluent correspondingly 209 ± 10 $\mu\text{g/L}$ and 81 ± 23 $\mu\text{g/L}$. These compounds were mainly present in particles (75% palmitic acid, 72% oleic acid) in the influent, but completely dissolved in the effluent.

Linoleic acid was found and successfully identified only in the influent. The sieved influent contained 1990 ± 777 $\mu\text{g/L}$ linoleic acid and it was mainly present in particles (73%) and, to a lesser extent, also as colloids (27%). Apidic acid was also found only in the influent (60 ± 35 $\mu\text{g/L}$), where it was completely dissolved (< 3 kDa fraction).

Lignans, steryl esters and triglycerides were not found. Steryl esters and triglycerides typically occur in small concentrations in pulp mill wastewaters (Kostamo *et al.* 2004, Mörck *et al.* 2000). Triglycerides are saponified during alkaline cooking, resulting in the release of free fatty acids and glycerol.

It is notable that a substantial amount of wood extractives was removed even with 8 μm filtration of the influent. Due to the high volume of wastewater (60,000 m^3/d in this case), however, it is too costly to treat the whole wastewater load with filtration. Separate treatment stages for certain wastewater fractions are more economically feasible. For example, the debarking plant effluent contains very high concentrations of wood extractives, tannins and lignin material (Verenich *et al.* 2005). The toxicity of wood extractives and lignin has earlier been verified, and it has also been demonstrated that condensed tannins from spruce bark are also toxic to aquatic organisms like fish (Temmink *et al.* 1989) while the oxidative polymerization of tannins into high MW compounds will completely eliminate the aquatic toxicity. Pretreatment of debarking effluent could be both

cost-effective and beneficial for the biological process. During sampling in this study, the debarking plant effluent load was 350 m³/d and it was discharged into the primary clarifier.

Another option for enhanced particle removal before the biological process would be coagulation–flocculation, which could remove a considerable amount of wood extractives and, for example, also particulate phosphorus (19–29 % of total phosphorus). Even though both microfiltration and ultrafiltration were used in this study for characterization purposes, an evaluation and comparison of the costs of coagulation–flocculation and of micro/ultrafiltration would probably interest many people. In this study, however, coagulant addition was not tested on wastewater. Thus, the only cost evaluation that was performed is that presented in Subchapter 5.2.2 for the O₂ filtrate treatment by coagulation–flocculation. Comparing the characteristics of the O₂ filtrate and influent provides only a rough estimate of the chemical costs of influent pretreatment. Probably only a small coagulant addition would be sufficient to remove the largest particles (e.g. > 8 µm) because the average charge quantity of the influent was -1100 µeq/L (for the O₂ filtrate it was about -8000 µeq/L). As the influent pH was about 7, this pH is suitable for cationic polyelectrolytes. The average conductivity of the influent was 0.26 S/m, but for the O₂ filtrate 0.905 S/m. The lower conductivity of the influent may have an influence on polymer conformation as well as on particle interactions. The effect of a high conductivity value on coagulation–flocculation is discussed in Subchapter 5.2.2. Cationic polymers would also perform better at the lower influent temperatures (about 37 °C before aeration) than in the high temperature of process water.

Turbidity, charge quantity and zeta potential

Turbidity was well partitioned from the sieved influent into the 0.22 µm fraction (Paper IV). The turbidity of the 100 kDa and smaller fractions of the influent was under 6 NTU. The turbidity of the sieved effluent was at a low level in May (4 NTU), but somewhat higher in July (16 NTU).

In contrast to turbidity, the charge quantity (Fig. 20 and 21) remained very constant from the sieved to the 0.22 µm fraction (Paper IV). In May the effluent fractions had a higher charge quantity than the influent, whereas in July it was the opposite. Actually the effluents were relatively similar, but the influents clearly differed from each other. The influent in July had a considerable higher charge

quantity than in May. The relative standard deviation was, on an average, 1.2% when two replicates were measured for each sample.

With 100 kDa filtration, the charge quantity started to approach zero in all cases. However, a relatively large increase in the charge quantity was observed again in the 30 kDa fraction of the influent (-659 $\mu\text{eq/L}$) sampled in July to the 3 kDa fraction of the same sample (-955 $\mu\text{eq/L}$). Neutralization of the charges started to occur as the turbidity disappeared. There was a large amount of colloidal anionic compounds between 100 kDa – 0.22 μm in both the influent and effluent.

There was no clear trend in the zeta potential results (Fig. 20 and 21). On the whole, the zeta potentials were clearly negative, as was the case with the charge quantities. The values were more negative in the influent samples than in the effluent samples. One to three different zeta potentials were detected for the larger influent fractions, but a maximum of two for the larger effluent fractions. The change that emerged in the charge quantity and turbidity after filtration with 100 kDa membrane (with nominal size 7.9 nm) was not observed in the zeta potential measurements, because DELSA calculates the zeta potential of particles in the size range of 0.01 μm to 30 μm . The sieved influent samples were, on the other hand, too concentrated to be properly measured with DELSA. To sum up, the influent samples contained weakly negative particles (low negative zeta potential) but also strongly negative particles (high negative zeta potential), whereas the effluent samples contained a lot weakly negative particles (high anionic charge quantity and low negative zeta potential). Anionic particles can, for example, be organic colloids containing ionizing groups like $-\text{COOH}$, or certain bacteria whose surface contain proteins and thus ionizing groups (Sincero & Sincero 2003).

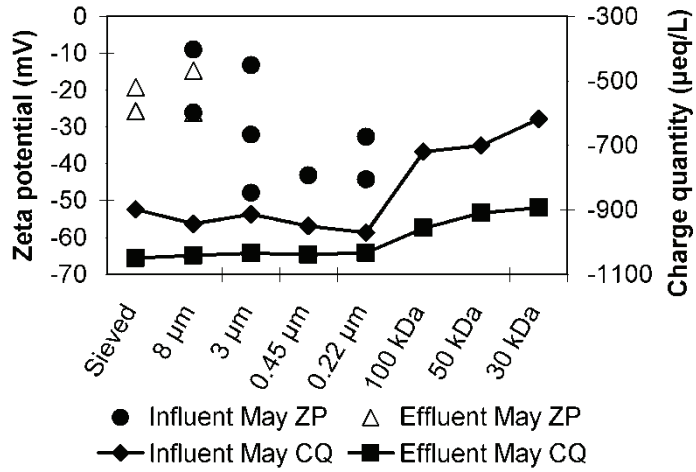


Fig. 20. Charge quantity and zeta potential in the different fractions of the influent and effluent from the activated sludge treatment plant sampled in May (reprinted and revised from Paper IV with permission from Elsevier).

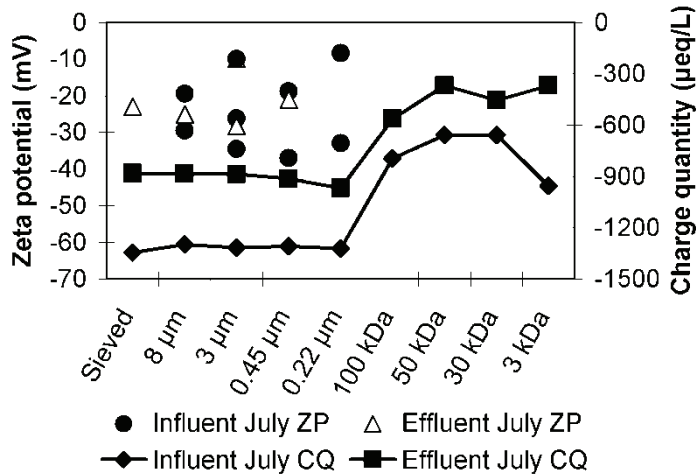


Fig. 21. Charge quantity and zeta potential in the different fractions of the influent and effluent from the activated sludge treatment plant sampled in July (reprinted and revised from Paper IV with permission from Elsevier).

The clearly negative surface charges (Fig. 20 and 21) also indicate that coagulants and flocculants with a high positive charge could be used. Carrying out a chemical treatment before or after the biological treatment would enhance the removal of COD and TOC. For instance, Engström & Gytel (2000) reported that a combination of biological and chemical treatment at the pilot plant scale removed 97% of COD, 92% of TOC and 84% of colour from a TCF pulp mill effluent. For the biological treatment alone, the results were similar to those obtained here; 71% of COD (63–71% in this study) and 72% of TOC (60–67% in this study) was removed.

Phosphorus, conductivity and pH

Due to the low level of nutrients in the pulp and paper mill wastewater, the mill in question adds phosphorus as phosphoric acid and nitrogen as urea to the aeration process in order to improve the efficiency of the treatment process. According to size fractionation, 14–30 % of the Tot-P was attached to particles larger than 0.45 µm (Paper IV). The main phosphorus fraction in the influent and the effluent samples consisted of soluble phosphate. The reduction in Tot-P in the activated sludge treatment was 73% in May and 57% in July, resulting in a low residual phosphorus concentration (mainly as soluble phosphate) of 0.66 mg/L in May and 0.41 mg/L in July. The influent sampled in May had a notably higher Tot-P concentration (2.4 mg/L) than the influent sampled in July (0.95 mg/L).

Conductivity remained at the same level in all the filtered fractions (Paper IV). pH showed a continuous increase in larger fractions, but a decrease in some smaller ultrafiltered fractions (Paper IV).

Trace elements

Fig. 22 shows the distribution of Mn, Fe, Zn, Al and Si in the influent and the effluent. In the influent, Mn (2.5 mg/L), Zn (0.32 mg/L) and Si (5.2 mg/L) were mainly present in the < 3 kDa fraction, whereas a significant proportion of Fe (0.69 mg/L) and Al (0.85 mg/L) were also found in the particle and colloidal fractions. In the effluent, Fe (0.61 mg/L) and Al (0.33 mg/L) were mainly present in the colloidal fraction; in contrast, Mn (1.1 mg/L), Zn (0.58 mg/L) and Si (4.8 mg/L) were mainly in the < 3 kDa fraction. The higher concentration of Zn in the effluent than in the influent was probably due to variations in the Zn concentration of the wastewater. The repeatability of the measurements was good,

except for the ultrafiltered fractions of aluminium. Skipperud *et al.* (1998) reported a similar result for Fe (0.5 mg/L) and for Zn (0.21 mg/L) for settled, discharged wastewater from a pulp plant.

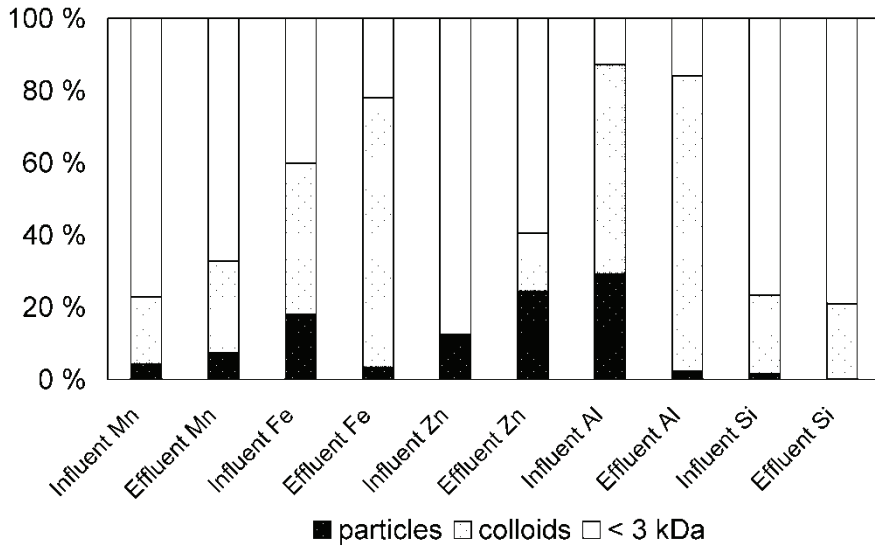


Fig. 22. Distribution of trace elements (Mn, Fe, Zn, Al and Si) in the influent and the effluent from the activated sludge treatment plant (particles > 0.45 μm , colloids = 0.45 μm – 3 kDa) (reprinted and revised from Paper V with permission from Elsevier).

Due to the high volume of wastewater discharged annually, the amounts of discharged trace elements can be considered as significant. The toxicity and potential bioavailability of elements in the environment depends largely on the prevailing conditions, and the concentration and form in which the element exists. Metal cations or labile complexes are generally more harmful, because they are readily absorbed and pass into and bioaccumulate in the tissue of marine organisms (Øygaard *et al.* 2007, Stumm & Morgan 1996). Mn and Fe are micronutrients, but they may also have toxic effects in plants and animal organisms under certain conditions, for example in very acidic soil solution (Låg 1994). An acidic aluminium-rich environment has been reported to be toxic to freshwater fish species (Poléo *et al.* 1997). The toxicity of Al is mainly attributed to monomeric species, Al^{3+} , $\text{Al}(\text{OH})^{2+}$ and $\text{Al}(\text{OH})_2^+$, as well as to polynuclear aluminium species, like Al_{13} . These polynuclear species may bind strongly to

phosphate groups on the cell membrane, thereby decreasing membrane fluidity (Flaten 1994). As a result, the membrane becomes more fragile and the entry of Al and other harmful substances into cells increases.

5.2 Selective coagulation–flocculation of wood extractives

The performance of polyelectrolytes is mainly governed by pH, impurities in the water, and temperature. Of these, the prevailing pH probably has the major influence on functionality. Not only the polyelectrolyte charge, but also the solubility of the target compounds depends on pH. At high pH levels, wood extractives (resin and fatty acids) are mainly dissolved in a form that makes their removal by coagulation with cationic polyelectrolytes difficult, if not impossible. Certain multivalent metal ions have proved useful in precipitating resin acids out of solution under alkaline conditions (Eklund & Lindström 1991). Another way to reduce the solubility of wood extractives is to reduce the pH. Coagulation–flocculation studies were first performed with model water prepared from oxygen bleached birch pulp (Subchapter 5.2.1) and, after that, with real birch pulp filtrate taken after the O₂ stage (Mill A, Subchapter 5.2.2).

5.2.1 Model water

Chemical pulp model water proved to be a good material for testing the short-chain cationic polyelectrolytes (Poly-DADMAC, PAE, C-PAM1 and C-PAM2) and their effect on the multimodal zeta potential distribution. Figure 23 shows the turbidity of the supernatant at different polyelectrolyte dosages, when the experiments were carried out at pH 9.6. An increase in turbidity at low dosage was observed with all the polyelectrolytes except C-PAM2. Wågberg and Ödberg (1991) reported that, at low levels of Poly-DADMAC addition, the dissolved wood polymers are precipitated, giving particles in the size range of 0.1–0.4 µm. The size of the particles is such that they have a strong influence on turbidity (Lindquist 2003). At higher levels of Poly-DADMAC addition, these precipitates, together with the original colloidal material, are neutralized and start to form larger settleable flocs in the size range of 1–10 µm.

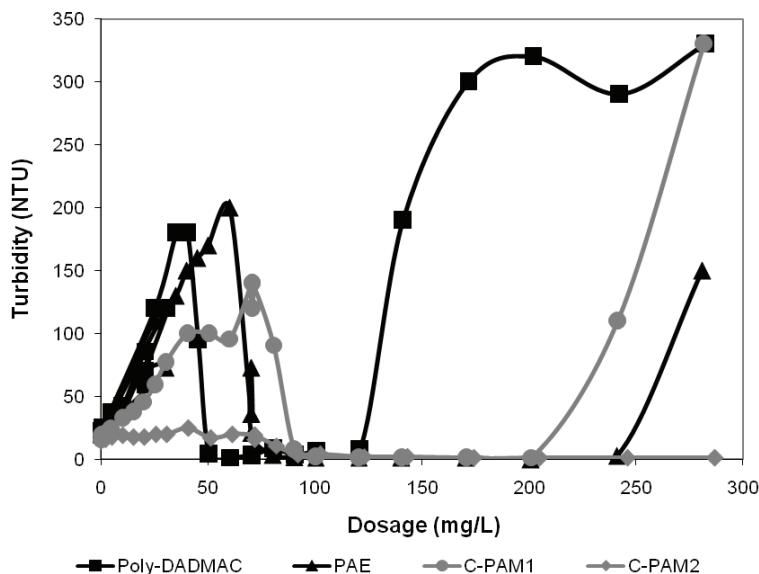


Fig. 23. Coagulation of the chemical pulp model water (pH 9.6, at room temperature) with cationic polyelectrolytes. The initial turbidity of the model water was as low as 26 NTU (reprinted and revised from Paper I with permission from Pulp and Paper Technical Association of Canada).

The charge quantity began to neutralize as a function of polyelectrolyte dosage, except in the case of C-PAM2 (Paper I). When the charge quantity reached zero with Poly-DADMAC and PAE (Fig. 24), the zeta potential started to approach zero. With C-PAM1 (Fig. 25) and C-PAM2 the charge quantity and zeta potential remained negative. The addition of polyelectrolyte did not affect the pH of the solution.

At very low dosages, there were two to three populations in the supernatant with different zeta potentials (Paper I). It is likely that, at low levels of polyelectrolyte addition, the particles carrying higher negative charges were only or mainly affected by the cationic polyelectrolyte. As the chemical dosage was increased, the magnitude of the differences between the charges decreased until only one zeta potential was observed. This means that aggregation of particles had occurred.

The optimum chemical dosage determined by turbidity (maximum flocculation) was achieved when the zeta potential was still negative (-21 mV

with Poly-DADMAC and -15 mV with PAE). When Poly-DADMAC and PAE were added in overdose, the colloidal particles were restabilized, i.e. the flocculation efficiency was decreased (Fig. 23). A patch coagulation mechanism most probably plays the most important role. With a low molecular weight polymer, there is a tendency for each polymer molecule to adsorb on a single particle (Forbes 2000). At dosages of 62 and 103 mg/L of Poly-DADMAC, the zeta potential was measured with DELSA also during the coagulation–flocculation process of the model water (unpublished data). It was observed that only one zeta potential was left immediately after the rapid mixing stage. The zeta potential could be readily measured well without pre-treatment. This proved that the reaction was rapid.

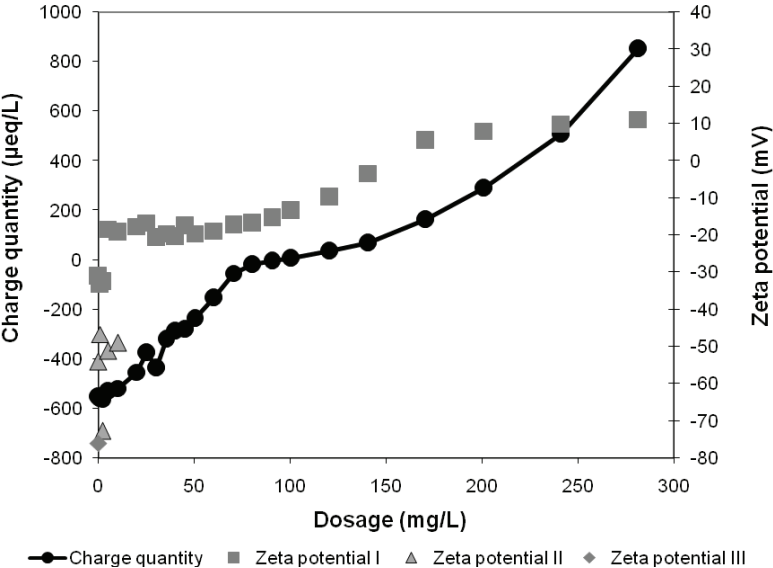


Fig. 24. Effect of PAE on the multimodal zeta potential distribution and charge quantity in the chemical pulp model water (pH 9.6, room temperature) (reprinted and revised from Paper I with permission from Pulp and Paper Technical Association of Canada).

Fig. 24 and 25 confirm the earlier established (Brouwer 1991) existence of constant zeta potential plateaus when cationic polyelectrolytes are added to the pulp. One explanation for these plateaus is that soluble anionic material interacts the most strongly with the added cationic polyelectrolyte (Brouwer 1991). In the

case of Poly-DADMAC, PAE, and C-PAM1, these kinds of plateaus also occurred (the negative zeta potential I was still present) after the soluble anionic trash had been neutralized. This means that the most recalcitrant group against destabilization (particles no longer adsorb any polyelectrolyte) had a size range above $0.01\ \mu\text{m}$, which is the detection limit of the zeta potential equipment used. Brouwer (1991) showed that, under wet-end conditions, the most pertinent component preventing Poly-DADMAC destabilization was in the colloidal range.

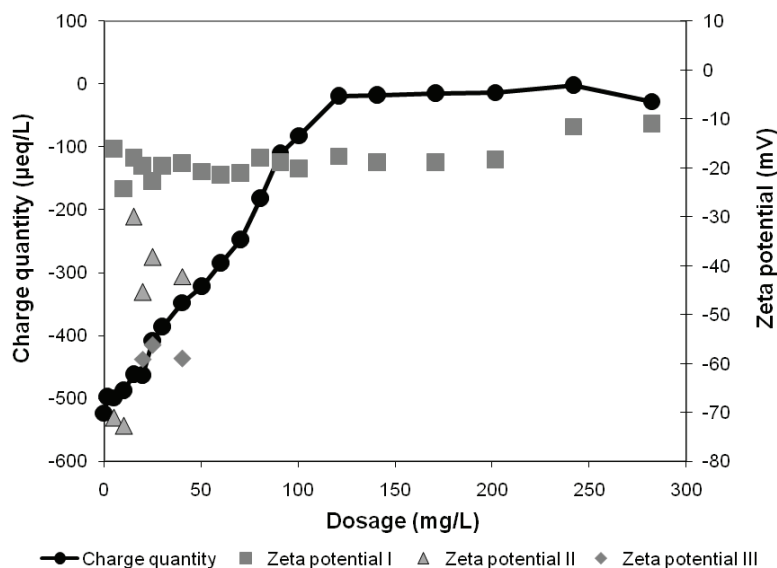


Fig. 25. Effect of C-PAM1 on the multimodal zeta potential distribution and charge quantity in the chemical pulp model water (pH 9.6, room temperature) (reprinted and revised from Paper I with permission from Pulp and Paper Technical Association of Canada).

The polyelectrolyte with the lowest charge density, C-PAM2, only interacted with the populations carrying higher negative charges (Paper I). Zeta potential I did not change even with larger additions. Clearly, C-PAM2 lost its cationicity at the original pH (9.6) of the model water. Also C-PAM1 had only a minor effect on the zeta potential: the populations with a higher zeta potential initially disappeared, and only at very high dosages of polyelectrolyte did the zeta potential approach zero. However, C-PAM1 did in fact contribute to the charge quantity. Furthermore,

there was one clear region for maximum flocculation, 100–200 mg/L, in the case of C-PAM1 (Fig. 23).

As the pH of 9.6 was too high for C-PAM2, experiments were also carried at lower pH values. C-PAM2 worked well when the pH was decreased to pH 8 or lower (Fig. 26). In addition to working well at lower pH (C-PAM2), a lower dosage of polyelectrolytes was also required. For example, C-PAM1 worked well at a dosage of 70 mg/L at pH 6.6, whereas at least 100 mg/L was required at pH 9.6 (unpublished data). Decreasing the pH decreases the amount of negative charges and thus the cationic demand.

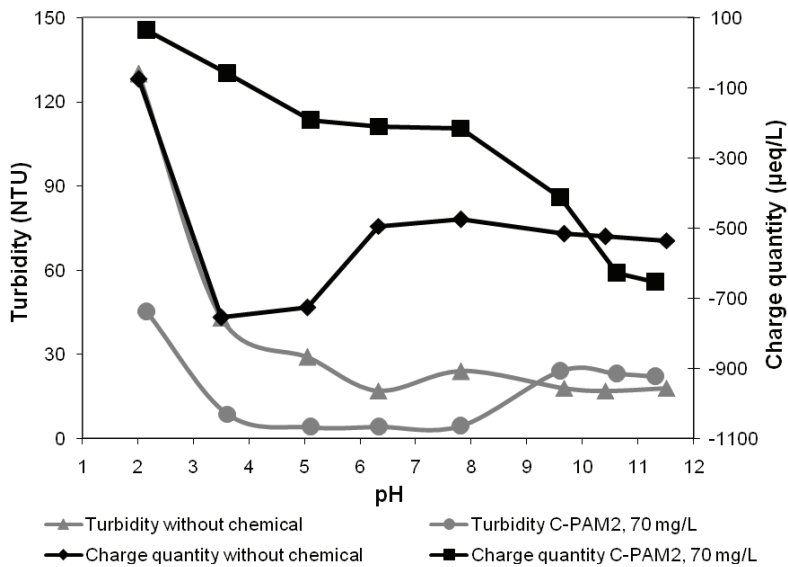


Fig. 26. Effect of pH on the performance of cationic polyelectrolyte, C-PAM2. Experiments with model water were carried out at room temperature (unpublished data).

The residual Ca, Si and Al concentrations were determined on some samples and it was observed that (unpublished data), over the optimum dosage range, Poly-DADMAC and C-PAM1 most effectively removed Ca (reduction of 50–70%). Less Si and Al were removed.

5.2.2 Process water

O₂ stage filtrate from Mill A was selected for coagulation–flocculation studies due to its high content of wood extractives (Table 7). In the experiments the pH had to be reduced to 5.5 due to the restricted performance of the polyelectrolytes at high pH (Paper II). As the temperatures of the filtrates in the bleaching process are high, the polyelectrolytes were tested at high temperatures.

Fig. 27 shows the residual turbidity obtained with different dosages of the cationic polyelectrolytes when the experiments were carried out at pH 5.5 and a temperature of 72 °C. Only C-PAM1 significantly lowered the turbidity. For C-PAM1, the optimum dosage range was relatively narrow, 102–142 mg/L, and the lowest turbidity value, 60 NTU, was recorded at a dosage of 142 mg/L. Up to 92% of the wood extractives was removed at this dosage. The same initial increase in turbidity at low dosage levels occurred as with the model water experiments (Fig. 23). The charge quantity (Fig. 28) gradually, but only slightly, decreased with increased dosage of C-PAM1. Within the optimum C-PAM1 dosage range, the zeta potential (Fig. 29) was clearly neutralized but still negative (-6 mV with 142 mg/L C-PAM1). With higher dosages the zeta potential also remained negative.

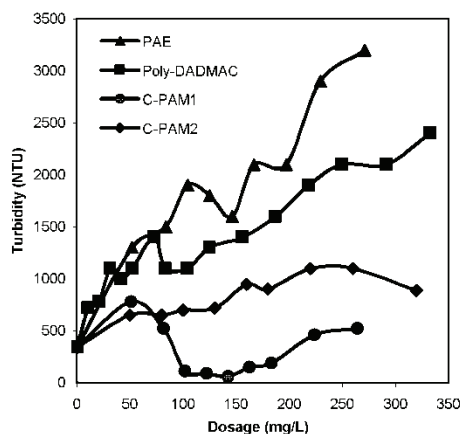


Fig. 27. Effect of polyelectrolyte dosage on the residual turbidity in the coagulation of oxygen-bleached process water at 72 °C and pH 5.5 (reprinted from Paper II with permission from Elsevier).

In terms of turbidity reduction, the other polyelectrolytes did not function over the studied dosage range and at 72 °C (Fig. 27). The addition of flocculant (a long-chain organic polymer), together with a short-chain polyelectrolyte, might improve the formation of settleable floc. The supernatants from the C-PAM2 experiments (> 100 mg/L) were, nevertheless, strongly post-precipitated after one-day storage under refrigeration, and the precipitate settled out well to give a clear solution. It would appear that the poor functioning was due to the high temperature. Centrifugation was performed immediately after coagulation–floculation. In addition, C-PAM2 had the strongest influence of all the polyelectrolytes on the charge quantity (Fig. 28) and zeta potential (Fig. 29). The dosage of C-PAM2 required to obtain zero zeta potential and plateau zeta potential was the same, 100 mg/L. To sum up, C-PAM2 appears to be an effective neutralizer of surface charge under the conditions investigated, but lower temperatures, as well as more time, are needed for agglomeration to occur.

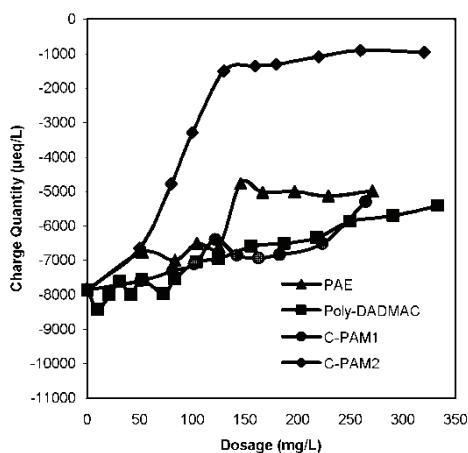


Fig. 28. Effect of polyelectrolyte dosage on the charge quantity in the coagulation of oxygen-bleached process water at 72 °C and pH 5.5 (reprinted from Paper II with permission from Elsevier).

The O₂ filtrate contained a large amount of lignin-derived material. The reduction in lignin (at 72 °C and pH 5.5) achieved with the tested cationic polyelectrolytes was 40% with 125 mg/L PAE, 21% with 125 mg/L Poly-DADMAC, 17% with 142 mg/L C-PAM1, and 2% with 130 mg/L C-PAM2 (Paper II).

As the removal of extractives was high with C-PAM1 at 72 °C and pH 5.5, and poor with PAE and Poly-DADMAC (Paper II, Fig. 4), the concentration of extractives was actually even higher following the addition of C-PAM2 (130 mg/L) compared to the reference sample (without polyelectrolyte addition). The effect of temperature, studied using reference samples (pH 5.5) at 18, 57, and 80 °C, was found to be similar to the effect of C-PAM2. The TOC concentration increased with temperature: from 2100 mg/L (18 °C) to 2300 mg/L (80 °C). The concentration of some carbohydrates increased significantly, particularly that of xylose (Paper II, Fig. 5). The concentrations of some extractives also increased with temperature (Paper II, Fig. 6).

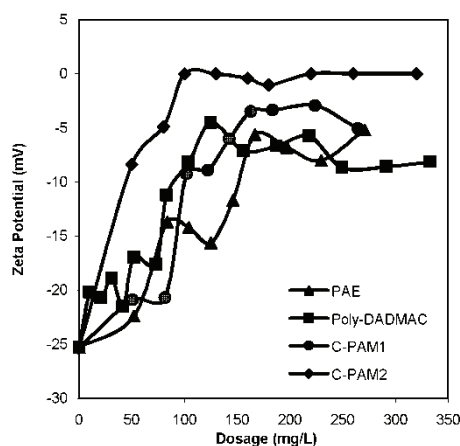


Fig. 29. Effect of polyelectrolyte dosage on the zeta potential in the coagulation of oxygen-bleached process water at 72 °C and pH 5.5 (reprinted from Paper II with permission from Elsevier).

The probable explanation for this is that a part of the carbohydrates became agglomerated with the wood extractives during refrigerated storage of the O₂ filtrate before the coagulation experiments. In the case of the reference sample prepared at 18 °C, the agglomerates may have been removed in the centrifugation stage or else they were not detected in the analysis (carbohydrates). At higher temperatures most of the agglomerates may have decomposed. Those agglomerates that were not significantly affected by temperature might have been decomposed upon addition of C-PAM2, thus explaining the higher concentration of extractives. The presence of C-PAM2 in the sample may prevent new agglomeration between carbohydrates and wood extractives. However, the reason

why reagglomeration in reference samples investigated at 57 and 80 °C did not occur after the new storage period before analyses is not known. The water solubility of extractives depends on temperature and ionic strength, in addition to pH and the presence of multivalent metal ions (Back 2000b). Differences in the components themselves (e.g. chain length, unsaturated/saturated) also contribute to the solubility. It should also be kept in mind that the repeatability of wood extractive analyses is lower for samples containing larger particles. However, the difference between the reference sample and C-PAM2 (Paper II, Fig. 4) was relatively high (66 mg/L).

The conformation of a polyelectrolyte is strongly dependent on the electrolyte concentration. Normally, polyelectrolytes assume an expanded conformation so that repulsion between groups with equal charge is minimized (Eklund & Lindström 1991). The repulsion decreases as the ionic strength of the solution increases until, at a higher electrolyte concentration, the conformation of a polyelectrolyte changes from an expanded to a collapsed, coil-like conformation. The filtrate used in this study was of a very high conductivity so the polyelectrolytes formed a tight coil in solution.

Greenwood & Kendall (2000) demonstrated with Poly-DADMAC-based polyelectrolytes that the optimum concentration for flocculation was strongly affected by ionic strength and weakly affected by polyelectrolyte molecular weight. The amounts of polyelectrolyte adsorbed onto alumina particles were much less at 50 mmol/L than at 10 mmol/L electrolyte concentration. The final plateau value of the zeta potential decreased as the salt concentration increased due to screening of the polyelectrolyte and particle charges by the electrolyte. The flocculation mechanism was concluded to be electrostatic patching.

Short-chain cationic polyelectrolytes with high charge density such as PAE and Poly-DADMAC are well suited for patch flocculation, where oppositely charged patches of a particle are attracted to each other. At very high electrolyte concentrations, the cationic polyelectrolyte may desorb from the particles, leading to lower aggregation (Eklund & Lindström 1991).

Patching (Fig. 3a) may also be the main aggregation mechanism for C-PAM1 and C-PAM2 owing to the short-chain structure. However, the interaction between these polyelectrolytes and surfaces is weaker than for PAE and Poly-DADMAC due to the lower charge densities, and they may not be adsorbed as a flat conformation on the surface but instead form loops and tails, even short ones, able to attach to other particles (bridge flocculation). Compared with PAE and Poly-DADMAC, moreover, the chain lengths of C-PAM1 and C-PAM2 are

slightly longer (Table 3). The bridging may be enhanced by a total electrolyte concentration sufficient to suppress the thickness of the diffuse layer and to shorten the mean distance between particles. Conversely, high ionic strength may impair the ability to form bridges due to coil conformation (Eklund & Lindström 1991). No charge reversal took place with a high dosage of C-PAM1. The zeta potential remained negative (Fig. 29). It has been shown (Bremmell *et al.* 1998) that, at low polyelectrolyte concentrations, bridging between particles occurs with a moderately charged cationic copolymer of acrylamide and 2(methacryloxy)ethyltrimethyl ammonium chloride.

The charge density of the polyelectrolyte also affects the floc structure: the flocs formed with highly charged polyelectrolytes are more open and thus less shear resistant than those formed with polyelectrolytes of lower charge (Eriksson *et al.* 1995). Temperature, in turn, affects floc stability. Probably the lower temperature during storage allowed aggregation to occur with C-PAM2. One explanation for the stable floc formation at lower temperature could be a decrease in the collision frequency due to Brownian (thermal) motion (Eklund & Lindström 1991), which controls the collision frequency for small particles (< 1µm).

Not only electrolyte concentration, but also temperature affects the conformation of polyelectrolyte. An earlier study has shown that the temperature effect is more pronounced for non-ionic polyethylene oxide (PEO) than for anionic PAM (Mpofu *et al.* 2004). At high temperatures, a coil conformation with fewer loops and tails is preferred. In the case of Poly-DADMAC and PAE, post-precipitation did not occur during refrigerated storage. From the findings of this study, it is difficult to say whether the high electrolyte concentration was the reason for the poor aggregation with PAE and Poly-DADMAC. Degradation of these polyelectrolytes due to the high temperature is also possible (Nikkarinen 2003).

When the polyelectrolytes were also tested at lower temperatures, it was found that C-PAM2 worked well at temperatures between 18–58 °C (unpublished data). The experiments were performed at constant dosage, approximately 210 mg/L, and at pH 5.5. The residual turbidity was under 30 NTU. At 58 °C wood extractives were selectively removed (Fig. 30). According to the residual amount of extractives, the other polyelectrolytes also worked well at a temperature of 58 °C; however the residual turbidities were higher than with C-PAM2 (Fig. 30), probably due to the fact that the dosages were not within the optimum range. Beneficially, carbohydrates were not removed; the amount was even slightly

higher probably due to degradation of aggregates, as was earlier discussed in this subchapter. Poly-DADMAC, PAE and C-PAM1 removed some colour, too.

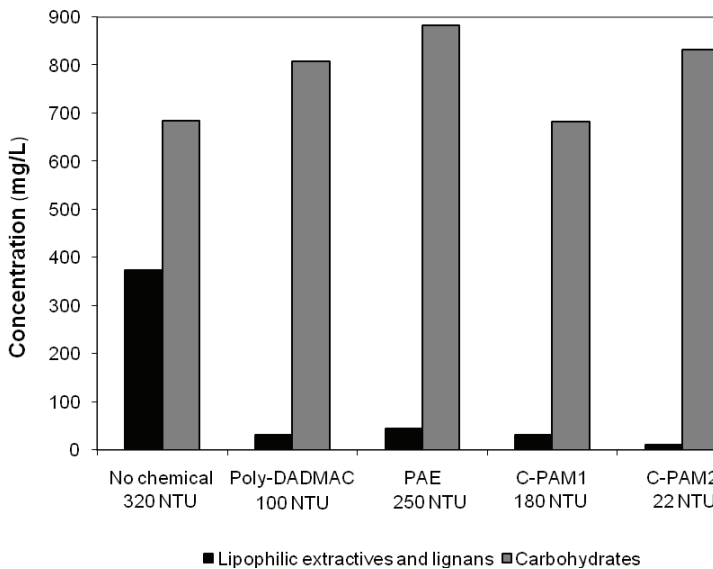


Fig. 30. Residual lipophilic extractives and lignans and carbohydrates after coagulation with cationic polyelectrolytes at a constant dosage of 210 mg/L, at pH 5.5 and a temperature of 58 °C. The residual turbidity is shown below the chemical name (unpublished data).

The earlier experiments showed that the optimum dosage range determined by turbidity is very wide for C-PAM2, whereas Poly-DADMAC at least is more sensitive for overdose. Because of this, C-PAM2 has a significant additional advantage for the treatment of process water of highly changeable quality. Furthermore, as the coagulation studies with process water were performed at different pH values, the residual turbidity and charge quantity values showed that C-PAM2 worked well already at pH 8 (unpublished data). The same result was earlier obtained with model water (Fig. 26). Thus purified filtrate could be better circulated into the alkaline stages, for example at the post-oxygen washers, if the pH did not have to be decreased very much. Oxygen stage filtrates are usually recycled back to the recovery system. In such cases, the mill recovery system may even suffer from overload (Allen 2000b). Thus it would be preferable to circulate

this filtrate also to other stages. However, the costs are still too high if cationic polyelectrolytes are used alone. It was estimated that process water treatment with cationic polyelectrolytes would cost about 1.1 € / 1 m³, which is approximately five times more expensive than using the mill's own purified raw water. Moreover, the calculated costs included only chemical costs (pH adjustment by sulphuric acid to 5.5, and using either C-PAM1 or C-PAM2 100 mg/L (as effective agent)). At pH 8 the costs would be even higher due to the increasing cationic demand, and also because the costs consisted to a large degree of cationic polyelectrolyte. The addition of small doses of flocculant (long-chain organic polymer), which is able to bridge more effectively, would probably decrease the demand for coagulant. Moreover, cost analysis would identify the lowest costs for the treatment.

6 Conclusions

This thesis focused on characterization of chemical pulp process and wastewaters, and investigated how coagulation–flocculation could be used either in internal process water treatment or as a supplemental treatment for the activated sludge process.

In the size fractionation studies on wastewater before (influent) and after (effluent) the activated sludge process, it was found that enhancing particle removal in both the influent and effluent, either by filtration or using a chemical, would have considerable benefits. Enhanced particle removal before the activated sludge process would represent savings in aeration costs, and result in a more stable process due to the decrease in toxic extractives. Microfiltration with a large pore size (8 μm) already removed, for example, 18–25% of the phosphorus, 60% of the turbidity and 30–50% of the wood extractives from the influent. Separate treatment stages for certain wastewater fractions e.g. debarking plant effluent, would ensure cost-efficiency. After the activated sludge process, the wood extractives were present as particles (18%) and < 3 kDa fraction (82%). β -sitosterol occurred only in particles in the effluent. The release of harmful components into the environment could be decreased or prevented, especially during process disturbances, by microfiltrating (e.g. 0.45 μm) the effluent or by using a chemical in the secondary clarifier. The charge quantity and zeta potential results also indicate that cationic coagulants could be used in both the primary and secondary clarifier. A high proportion of the colloidal anionic compounds were between 100 kDa – 0.22 μm in both the influent and effluent.

In the size fractionation of wastewater there was a huge increase in BOD according to two different BOD analysis methods in the 3 kDa fraction of the influent and effluent, which indicated the presence of toxic substances in the larger fractions. After this kind of effluent passes into the water system, there might be a similar jump in the BOD, because the effluent (and thus toxicity) is diluted many-fold. The manometric respirometric method gave lower BOD₇ values for the influent than the conventional chemical method; however, the trend of the curves was very similar. The difference presumably originated from dilution in the conventional chemical method, resulting in a lower amount of inhibitive substances, and thus higher BOD value than that obtained by the manometric respirometric method. Thus the manometric respirometric method better describes the situation in wastewater, whereas both BOD methods may underestimate the BOD effect of pulp and paper mill effluent in the aquatic

environment. As the oxygen consumption is higher in the water environment, it will contribute to the formation of areas with an oxygen deficit.

The birch kraft pulp filtrate after the O₂ stage contained huge amounts of wood extractives and was thus selected for the coagulation–flocculation studies. Our knowledge of the behaviour of short-chain cationic polyelectrolytes at a high temperature and a high electrolyte concentration was deepened in this study. With the O₂ filtrate, effective and selective removal of wood extractives (92%) was obtained with a cationic polyelectrolyte of medium molecular weight and medium charge density (C-PAM2) at 72 °C and pH 5–6. The optimum dosage range, based on the turbidity reduction, was 102–142 mg/L. Bridging flocculation was considered to be another suitable mechanism in flocculation, besides patching, at a high electrolyte concentration. The other studied polyelectrolytes worked better when the temperature during coagulation–flocculation was decreased. Decreasing the pH from the original pH of the O₂ filtrate (10.6) is necessary. If the pH is decreased less (C-PAM2 worked well already at pH 8), the purified O₂ filtrate could be better circulated to alkaline stages, for example, at the post-oxygen washers. However, further studies should be performed in order to bring also the total costs lower.

In the coagulation–flocculation studies, charge analyses give important information about coagulation–flocculation mechanisms. The charge quantity based on the streaming current principle describes the total amount of positive or negative charges and is an invaluable tool in dosing systems. The zeta potential, on the other hand, describes the magnitude of the charges. Moreover, the multimodal zeta potential distribution gives more information in coagulation–flocculation studies than the average zeta potential. If there are two or more zeta potentials in the solution, then the components are not coagulated with each other, i.e. dispersion is stable. In this study it was observed that pH and cationic polyelectrolyte addition had an effect on the multimodal zeta potential distribution of the bleaching filtrates. The number of different zeta potentials diminished with decreasing pH, as well as after exceeding a certain dosage level of polyelectrolyte. Aggregation of the colloidal particles took place when only one zeta potential was observed.

Despite the large investments made by the pulp and paper industry, case-specific supplementary treatments will be needed in the future, e.g. to increase water circulation due to the growing water shortage, to increase the biodegradability of wastewater before biological treatment, to decolour the wastewater and to eliminate the toxic effects of effluents completely. Detailed

characterization of different wastewaters streams should first be performed, for example by size fractionation, in order to identify different size fractions in which the harmful components exist. A possible treatment method could then be evaluated by taking into account the total costs and possible savings in other treatment stages. And of course without forgetting how much our planet earth would benefit from this, too.

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ISBN 978-951-42-6087-2 (Paperback)

ISBN 978-951-42-6088-9 (PDF)

ISSN 0355-3213 (Print)

ISSN 1796-2226 (Online)

