



Sorption of Metal Ions to Wood, Pulp and Bark Materials

Pingping Su



Laboratory of Analytical Chemistry
Process Chemistry Centre
Department of Chemical Engineering
Åbo Akademi University
Åbo, Finland
2012

Sorption of Metal Ions to Wood, Pulp and Bark Materials

Pingping Su



Laboratory of Analytical Chemistry
Process Chemistry Centre
Department of Chemical Engineering
Åbo Akademi University
Åbo, 2012

Supervised by

Professor Ari Ivaska

Laboratory of Analytical Chemistry
Process Chemistry Centre
Åbo Akademi University
Åbo, Finland

and

Docent Leo Harju

Laboratory of Analytical Chemistry
Process Chemistry Centre
Åbo Akademi University
Åbo, Finland

Reviewed by

Professor Raimo Alén

Laboratory of Applied Chemistry
Department of Chemistry
University of Jyväskylä
Jyväskylä, Finland

and

Professor Yang Gao

Key Laboratory of Pulp and Paper
Science & Technology
Shandong Polytechnic University
Jinan, Shandong, China

Taishan Scholar (Research Chair)
R&D Center, Huatai Group Co. Ltd.
Dongying, Shandong, China

Research Scientist
Limerick Pulp and Paper Centre
University of New Brunswick
Fredericton, NB, Canada

Opponent

Professor Raimo Alén

Laboratory of Applied Chemistry
Department of Chemistry
University of Jyväskylä
Jyväskylä, Finland

ISBN 978-952-12-2777-6

Painosalama Oy – Turku, Finland 2012

Table of contents

<i>Table of contents</i>	<i>i</i>
<i>Preface</i>	<i>iii</i>
<i>List of publications</i>	<i>v</i>
<i>Abbreviations</i>	<i>vii</i>
<i>Abstract</i>	<i>ix</i>
1. Introduction	1
2. Fundamentals of wood, pulp and bark	3
2.1. Macroscopic structure of a tree stem	3
2.2. Ultrastructure of wood cell wall	4
2.3. Chemical composition of wood	4
2.3.1. Cellulose.....	5
2.3.2. Hemicelluloses.....	6
2.3.3. Pectin.....	8
2.3.4. Lignin.....	8
2.3.5. Extractives.....	9
2.3.6. Inorganic components.....	10
2.4. Wood pulping	12
2.4.1. Mechanical pulping.....	12
2.4.2. Chemical pulping.....	13
2.5. Bleaching	13
2.5.1. Oxygen delignification.....	14
2.5.2. Hydrogen peroxide bleaching.....	15
2.6. Bark	16
3. Metal sorption to wood, pulp and bark materials	17
3.1. Functional groups in wood, pulp and bark	17
3.2. Characterization of the functional groups	19
3.2.1. General aspects.....	19
3.2.2. Acid-base titration of the functional groups.....	20
3.3. Theory of ion exchange reactions	23
3.4. Interaction of metal ions with wood, pulp and bark	24
4. Analytical techniques	27
4.1. Acid-base titrator	27
4.2. Ion exchange techniques	28
4.3. ICP-OES technique	30
4.4. LA-ICP-MS technique	31
5. Experimental	33
5.1. Materials	33
5.2. Main chemicals	34
5.3. Methods	34

5.3.1. Batch method	34
5.3.2. Column method.....	34
6. Results and discussion	36
6.1. Protonation constants and concentrations of acid groups in wood, pulp and bark.....	36
6.2. Equilibration time for sorption of metal ions to wood and bark.....	41
6.3. Results of metal ion sorption using the column chromatographic technique.....	42
6.3.1. Sorption of Ba, Sr, Ca and Mg ions.....	43
6.3.2. Sorption of Cd, Zn, Ni, Mn, Ba, Sr, Ca, Mg, Rb, K, Na and Li ions.....	46
6.3.3. Sorption of Pb, Cu, Cd, Zn, Ni, Mn, Ba, Sr, Ca, Mg, Rb, K, Na and Li ions	50
6.3.4. Sorption of Fe, Pb, Cu, Cd, Zn, Ni, Mn, Ba, Sr, Ca, Mg, K, Na and Li ions.....	55
6.3.5. Sorption of Rb, K, Na and Li ions.....	59
6.3.6. Sorption of metal ions to a synthetic cation exchanger and to pure cotton fibers	59
6.3.7. Effect of pH on metal ion sorption.....	65
6.3.8. Effect of particle size on metal ion sorption	66
6.3.9. Effect of mass of materials on metal ion sorption	66
6.3.10. Competitive sorption of metal ions	66
6.3.11. Regeneration of tree-related materials for metal sorption.....	67
6.3.12. Mass balance in sorption experiments	67
6.4. Distribution of metal ions in single fibers	68
7. Conclusion.....	70
8. References	73

Preface

The research work presented in this thesis was carried out at the Laboratory of Analytical Chemistry, Åbo Akademi University, Finland. This work is a part of the activities of the Process Chemistry Centre within the national Centre of Excellence programme (2000-2011) appointed by the Academy of Finland. Financial support from the National Technology Agency (TEKES), the Bioraff project, the Process Chemistry Centre and the Research Institute of Åbo Akademi Foundation are gratefully acknowledged.

First of all, I designate my sincere gratitude to my supervisor, Professor Ari Ivaska, for giving me the opportunity to work at his laboratory. His great enthusiasm and extensive knowledge in science as well as in scientific writing/presenting have inspired me throughout these years. Dear Professor Ari Ivaska, thank you for your support, guidance and encouragement during my thesis work. Moreover your thorough review and comments on this thesis have been greatly appreciated.

I would also like to express my deepest appreciation to my second supervisor Docent Leo Harju for his guidance, tireless advice and great patience throughout the work. Thank you for your beautiful words on my experimental work and your critical comments in the discussion as well as your comments on my writing. I also owe my gratitude to Dr. Kim Granholm for outstanding cooperation in our small research group. Heartful thanks for your enthusiastic help both inside and outside the research work. I would also like to thank all colleagues from our laboratory for their kind help both in my study and in my private life. It has been a great pleasure to be a member of the big happy family at our laboratory. I enjoy the friendly atmosphere and the jolly good moments we have shared together.

I also deeply appreciate Professor Bjarne Holmbom and Docent Andrey Pranovich from the Laboratory of Wood and Paper Chemistry for fruitful discussions. I particularly thank Andrey Pranovich for preparing some samples which I have used in my work. That sample preparation has been a labor-intensive process. I would like to express my gratitude to Professor Menghua Qin, from Shandong Institute of Light Industry, for giving me the opportunity to study abroad.

To my best friends: thank you for always being there, bringing me laugh, giving me joy and sharing amazing experiences with me. Thanks for your care, help and advice during my stay in Finland. Life would have been extremely boring without you. These beautiful moments we have shared will be kept in my heart forever.

Finally, my deepest love goes to my family. Thank all of you for the love, support and encouragement you have given me in my studies and personal life.

感谢陪伴我一路走来的图尔库的中国朋友们！真的很高兴认识你们，感谢你们的关心鼓励支持，给我留些的那些永不磨灭的美好回忆！少霞春林端木周珍刘洋，感谢你们陪我一起度过初来芬兰时那段艰难困苦的日子，谢谢你们的扶持鼓励，那段时光虽然艰苦但也是那么的温馨难忘！涛涛德德谢谢你们经常邀请我一起度周末假期，和我分享生活的点滴！你们层出不穷的点子让我们的聚会总是那么的美妙欢乐，和你们在一起时间总是过得那么快！尤其特别感谢你们带来了天真无邪的小天使诺诺！娜娜浩林谢谢你们在我工作晚归时温馨的晚餐！怀念一起共享的悠闲舒适的清晨咖啡时光！菊菊谢谢你在论文修改的日子里，倾听我的不安焦躁抱怨谢谢你和我分享你的经验心得给我建议。感谢所有的朋友们：炳之小琛小昕徐谦何宁于凯志强彦曦等等，谢谢你们陪我午饭约我钓鱼陪我踏青约我野餐约我烧烤陪我开点陪我升级陪我麻将，谢谢你们让图尔库暗沉漫长的冬日不是那么的单调难熬，给图尔库转瞬即逝的夏日留下更多的美好回忆！和你们一起的快乐不是简单几句就可倾尽的，对你的感谢不是仅仅几句话就能表达的！千言汇一语：亲爱的朋友们谢谢你们，很幸运能够认识你们，祝愿我们的友情长久！

感谢念兴，在我无助时给我的安慰和鼓励，在我最忙碌的日子里，给我的悉心照顾，以及对我的包容和理解。感谢你的陪伴你的照顾你的体贴和你带给我的那些喜悦和幸福！尤其感谢我亲爱敬爱的亲人们，是你们无私的付出才有今日的我，是你们毫无保留的理解、包容、鼓励和支持才让我日渐成熟，学有所成！你们的绵绵亲情是我一生中最为宝贵的财富！感谢所有关心我，爱护我的亲人，祝福你们身体健康，万事如意！

感谢生活给予我的一切，不论快乐幸福，还是悲伤失望，所有这些都将成为我人生路上最珍贵的记忆，让我积极生活，乐观坚强！

Åbo, 2012
Pingping Su

Pingping Su

苏萍萍

List of publications

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

- Paper I** Pingping Su, Kim Granholm, Andrey Pranovich, Leo Harju, Bjarne Holmbom, Ari Ivaska (2012) **Metal ion sorption to birch and spruce wood.** *BioResources*, 7(2), 2141-2155.
- Paper II** Pingping Su, Kim Granholm, Andrey Pranovich, Leo Harju, Bjarne Holmbom, Ari Ivaska (2010) **Sorption of metal ions to untreated, alkali-treated and peroxide-bleached TMP.** *Cellulose*, 17:1033-1044.
- Paper III** Pingping Su, Kim Granholm, Leo Harju, Ari Ivaska (2010) **Study of metal ion binding to unbleached softwood kraft pulp by column chromatography.** *Appita*, 63:143-149.
- Paper IV** Pingping Su, Kim Granholm, Leo Harju, Ari Ivaska (2011) **Binding affinities of different metal ions to unbleached hardwood kraft pulp.** *Holzforschung*, 65(4):619-622
- Paper V** Pingping Su, Paul Ek, Ari Ivaska (2012) **Determination of metal ions in single wood fiber by LA-ICP-MS,** *Holzforschung*, *in press*
- Paper VI** Pingping Su, Kim Granholm, Andrey Pranovich, Leo Harju, Bjarne Holmbom, Ari Ivaska (2012) **Sorption of metal ions to spruce bark.** *Submitted to Wood Science and Technology.*

Contributions of the Author

Paper I, II, III and V: The author did all the experimental work, wrote the first draft of the manuscript and finalized it together with the co-authors.

Paper IV: The author planned the experimental work, evaluated the results, wrote the first draft of the manuscript and finalized it together with the co-authors. The laboratory work was done by an exchange student.

Paper VI: The author planned and did the experimental work, evaluated the results, wrote the first draft of the manuscript and finalized it together with the co-authors. The laboratory work was partially performed by a summer trainee.

Supporting publications

- [1] Maria Södö, Pingping Su, Kim Granholm, Leo Harju, Ari Ivaska (2007) **Study on metal ion affinities to oxygen delignified hardwood kraft pulp by a column chromatographic method.** *Nordic Pulp & Paper Research Journal*, 22(4):462-467.

- [2] Pingping Su, Kim Granholm, Leo Harju, Ari Ivaska (2008) **Use of column chromatography for the study of metal ion binding to oxygen bleached softwood pulp.** *Proceeding of 2nd international papermaking & Environment conference (B)*:242-245.

- [3] Kim Granholm, Pingping Su, Leo Harju, Ari Ivaska (2009) **Study on desorption of Mn, Fe, and Mg from TMP and evaluation of the complexing strength of different chelating agents using side reaction coefficients.** *Holzforschung*, 63:785-790.

Abbreviations

bdl	below detection limit
C	total capacity, i.e. total concentration of functional groups in materials
C_{OH}	concentration of a strong base
CMP	chemimechanical pulp
CTMP	chemi-thermomechanical pulp
d.m.	oven-dried mass
DP	degree of polymerization
ESCA	electron spectroscopy for chemical analysis
HexA	hexenuronic acid
$[H^+]$	concentration of protons in the liquid phase
HR	protonated form of functional groups in tree-related materials
$[HR]$	concentration of protons bound to the solid phase
ICP-OES	inductively coupled plasma optical emission spectrometry
GalA	galacturonic acid
Glc	glucose
GlcA	glucuronic acid
K_a	dissociation constant of HR
$K_{HR}^{H,R}$	protonation constant of R
K_w	ionic product of water
L	load, i.e. how much acid groups in materials are occupied by metal ions of interest
LA-ICP-MS	laser ablation inductively coupled plasma mass spectrometry
M	metal
M^{n+}	metal ion with valence n+
$[M]$	concentration of the metal ion M^{n+} in the solution phase
Man	mannose
MB	methylene blue
ML	middle lamella
$[MR_n]$	concentration of the metal ion M^{n+} in the solid phase
N^+	metal ion with valence 1+
OC	operating capacity, i.e. total concentration of metal ions adsorbed to materials of study
P	primary wall of wood cell
PGW	pressure groundwood
PIXE	particle induced x-ray emission
pK_a	negative logarithm of acid protonation constant
ppm	parts per million (mg/kg)
R-	coordinating groups in wood, pulp or bark matrix
S	secondary wall of wood cell

S ₁	outer layer of secondary wall
S ₂	middle layer of secondary wall
S ₃	inner layer of secondary wall
SGW	stone groundwood
TMP	thermomechanical pulp
V	volume of a strong base added
V ₀	initial volume of a mixture
Xyl	xylose

Abstract

In this thesis different tree-related materials were characterized for their acid-base and metal ion sorption properties. The materials studied in the work include: 1) birch and spruce wood particles, 2) untreated, alkali-treated and peroxide-bleached mechanical pulps, 3) unbleached and oxygen-delignified hardwood and softwood kraft pulps, and 4) inner and outer bark of spruce. The results of this study provide new information of the fundamental knowledge about interactions of metal ions with tree-related materials.

The functional groups (acid groups) in wood, pulp and bark materials were determined for their concentrations and protonation constants by a potentiometric acid-base titration method. The FITEQL program was used to treat the experimental data, and it was found that a model with four acid groups best satisfied the potentiometric titration data. Results showed that of the materials studied wood materials generally have the acid groups of the lowest concentration. The mechanical and chemical pulping processes slightly increase the total concentration of acid groups. The chemical pulps have more carboxylic acid groups than the mechanical pulps. Bark in turn contains much more acid groups than wood and pulp materials.

The sorption/desorption time of metal ions to wood and bark particles were investigated in a batch system by using wood and spruce outer bark. It was found that the sorption/desorption of metal ions to wood and bark samples is quite fast. The equilibrium of sorption of metal ions to wood particles usually was reached within 20 min and to bark materials within 5 min.

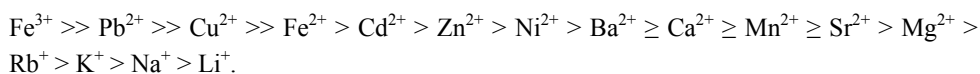
The metal sorption capacities of different tree-related materials and the affinities of different metal ions were characterized by a column chromatographic method. The sorption process is dominated by ion exchange reactions mainly by complexation between metal ions and carboxyl groups. Based on the experimental results, the concentrations of different metal ions adsorbed to different materials have been obtained. The operating capacities of different tree-related materials have been determined. It was found that the bark materials have the highest sorption capacities for metal ions and the wood particles (sawdust) generally exhibit the lowest sorption capacities. In general the mechanical and chemical treatments of the original materials increase their sorption capacities. These sorption results correspond well with the total concentrations of acid groups found in the materials. All the tree-related materials studied show a rather clear selectivity for different metal ions. By combining the results from several sorption experiments using different metal ion loading solutions, the affinity order of metal ions to the studied tree-related materials was established in the following general sequence: $\text{Fe}^{3+} \gg \text{Pb}^{2+} \gg \text{Cu}^{2+} \gg \text{Fe}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Ba}^{2+} \geq \text{Ca}^{2+} \geq \text{Mn}^{2+} \geq \text{Sr}^{2+} > \text{Mg}^{2+} > \text{Rb}^{+} > \text{K}^{+} > \text{Na}^{+} > \text{Li}^{+}$.

The distribution of metal ions in single kraft pulp fibers was investigated by the laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) technique. Results showed that the distribution pattern of metal ions varies. Iron ions are rather uneven distributed, but the other metal ions studied, e.g. Cu, Zn, Mn, K, are quite smoothly distributed in single fibers.

Referat

I denna avhandling har sorptionsreaktioner mellan metalljoner och ved, massafibrer och bark undersökts. Protonisationskonstanter och kapaciteter för de funktionella grupperna i de olika materialen bestämdes med potentiometriska syra-bas titrerings. De teoretiska beräkningarna gjordes med ett FITEQL program. En jämviktsmodell med fyra syra-bas grupper, d.v.s. två karboxylgrupper och två fenoliska hydroxylgrupper, satisfierade bäst experimentella titrerdata.

Metalljoner binds till de funktionella grupperna i den fasta fasen via jonbyte, främst genom komplexbildning. Metalljoners affiniteter till de olika trädbaserade materialen undersöktes med en kolonnkromatografisk metod. Genom att använda olika blandningar av metalljoner vid sorptionsförsöken kunde följande affinitets serie bestämmas, som med några få undantag gäller samtliga material:



Trevärt järn binds starkast och förekommer delvis som svårösliga salter i de olika materialen. Också de toxiska tungmetallerna Pb^{2+} , Cu^{2+} och Cd^{2+} binds relativt starkt. De envärda alkalimetalljonerna binds mycket svagt till alla de undersökta materialen. Vattenfasens pH är den viktigaste parametern och bestämmer den totala halten av metalljoner som binds till materialen. Ju högre pH desto högre halt av metalljoner är bundet till den fasta fasen. De trädbaserade materialens jonbytesegenskaper jämfördes med en syntetisk svagt sur katjonbytare. Den syntetiska jonbytare, som har karboxylgrupper som funktionella grupper, uppvisade en mycket liknande affinitetsordning som de naturliga materialen.

Resultatet i denna avhandling kan delvis betraktas som grundforskning, men är också av stor praktisk betydelse vid t.ex. kontroll av metalljoner när man strävar mot mera slutna processer i massafabriker. Ved och speciellt bark kan i framtiden få stor betydelse som potentiella material för bio-sorption av tungmetaller från avfallsvatten. Materialen är billiga, lätt tillgängliga i stora volymer, kan regenereras och användas på nytt i flera sorption-desorption cykler. För granbark bestämdes en jonbyteskapacitet på ca 1 mekv/g, vilket är av samma storleksordning som för syntetiska jonbytare.

1. Introduction

Metal ions are known to play an important role in the pulping and bleaching processes when they are accumulated in the process liquors in a closed-cycle mill. Some metal ions are harmful to the processes causing operational problems and lowering the quality of products (Jemaa et al. 1999, 2000). Some metal ions, however, have beneficial effects in the processes (Gupta 1970; Lapierre et al. 1995). Metal ions like Ba, Ca, Mg, Al and Si tend to cause scaling in digesters and evaporators. Accumulation of K and Mg may increase tendency for fouling, plugging and corrosion in recovery boilers (Fiskari 2002; Lundqvist et al. 2006; Doldán et al. 2011). In the bleaching processes, however, the alkaline earth metal ions (Ca, Mg, Ba) can improve significantly the bleachability and color reversion of groundwood pulps (Gupta 1970; Prasakis et al. 1996). Transition metal ions, such as Cu, Fe and Mn, have detrimental effects on the bleaching processes. These metal ions can catalyze the decomposition of bleaching agents, e.g. hydrogen peroxide, increasing the consumption of bleaching chemicals in the bleaching sequences (Bryant and Edwards 1994; Devenyns et al. 1994; Lapierre et al. 1995; Prasakis et al. 1996; Fiskari 2002; Lastra et al. 2004). This undesirable effect can be inhibited to a large extent by having magnesium and silicate ions in the bleaching system (Lundqvist et al. 2006; Doldán et al. 2011). In addition, the presence of Fe and Cu in bleached mechanical pulps may also cause significant decrease in the brightness of pulps because of the formation of highly colored transition metal complexes with lignin (Gupta 1970; Prasakis et al. 1996; Ni et al. 1998). Metal ions, such as Cr, Al and Ca, present at high concentration are also harmful to pulp brightness and cause color reversion. Lead in small quantities has a beneficial effect on hydrosulphite bleaching but becomes extremely harmful if present in larger amounts (Gupta 1970).

Therefore metal management in paper mills is critical as mills close up their bleaching processes and reduce chlorine containing bleaching chemicals (Bryant and Edwards 1996). An important aspect of paper mills is to find an efficient treatment for removal of the “harmful” metal ions and management of the “good” metal ions. Two methods have proven to be successful for control of metal ion contents in pulps prior to peroxide bleaching: 1) metal chelation at pH 4-7, followed by standard water wash, 2) thorough acid wash at pH 1.5-3.0, followed by replenishment of magnesium ions (Bryant and Edwards 1994; Lapierre et al. 1995; Granholm et al. 2010a, b). The success of removing metal ions from pulps depends on the method applied and also on the binding mechanism of metal ions to pulps.

With the development of industrialization and human activities, the discharge of heavy metal ions into the environment has been increasing. When the concentration of heavy metal ions exceeds a certain level, most of them become very harmful. They can

accumulate in living organisms, causing serious health problems in plants, animals and human beings. For example, the lead exposure may cause brain damage and affect kidneys, hearing and nervous system (Järup 2003; Bulut and Baysal 2006; Naiya et al. 2008; Gundogdu et al. 2009; Munagapati et al. 2010). An excessive intake of copper may lead to skin itching, liver irritation, stomach intestinal distress and kidney damage (Ajmal et al. 1998; Rahman and Islam 2009). The exposure to cadmium may cause kidney and skeletal damage, and may also affect nervous system and liver system (Semerjian 2010). The intake of nickel may cause vomiting, chest pain and rapid respiration (Subbaiah et al. 2009).

As a consequence from the environmental point of view, the heavy metal ions in the wastewater must be removed or be reduced to the minimum level before discharged to the environment. Recently many researchers have been interested in studying the potential use of biomass as the bio-sorbent for removal of various metal ions from aqueous solution (Hubbe et al. 2011). In the past decade, large number of scientific articles have been published on this subject (Babel and Kurniawan 2003; Sud et al. 2008; Wan Ngah and Hanafiah 2008; Febrianto et al. 2009; Gupta and Suhas 2009; Farooq et al. 2010; Fu and Wang 2011). Many different types of biomass have been found to be successful bio-sorbents for removal of metal ions from single, binary, ternary and quaternary metal ion systems in the laboratory scale experiments. Various biomass materials have also been modified in different ways to improve their sorption capacities. However there are not so many studies investigating the sorption of metal ions by using biomass from multi-metal ion solutions. The success of the removal of metal ions from aqueous solutions, whether in the pulping/bleaching processes or in the environment, depends on the method applied, on the materials used and also on the types of metal ions of interest.

The objective of this work is to study the interactions of metal ions with tree-related materials (wood, pulp and bark). The acid groups (functional groups) in these materials are acting as the metal binding sites and their concentrations were determined by potentiometric acid-base titrations. A column chromatographic technique was used to find the differences in affinity and content of different metal ions bound to the studied materials in multi-metal ion loading solutions. The results in this thesis are of importance. They may complement the fundamental knowledge of optimal metal management in paper mills. The results also may contribute to the applications of biomass for removal of heavy metal ions from aqueous solutions in environmental management.

In the following chapters, the tree-related materials used in this work, the fundamental principles of ion-exchange reactions, the main analytical techniques as well as the main conclusions of the results will be discussed and summarized. The results are based on the six publications included in the thesis.

2. Fundamentals of wood, pulp and bark

2.1. Macroscopic structure of a tree stem

Figure 1 presents the cross section view of a tree stem with different areas, e.g. pith, heartwood, sapwood, earlywood, latewood, inner bark and outer bark. The pith represents the tissue formed during the first year of growth and can be seen as a dark stripe in the middle of the stem (Sjöström 1993). The heartwood is located in the middle of a tree and it has dark color. It consists of dead cells, which were once sapwood in the beginning of tree growth. The heartwood gives the support and stiffness to the tree. The sapwood surrounds the heartwood and it is lightly colored. It contains primarily dead cells, but also some living cells for water and nutrient transportation.

The growth ring is a new additional layer of wood stem, which is produced annually. The width of the growth ring varies largely, mainly depending on the tree species and climatic conditions (Alén 2000a). The age of a tree can be roughly calculated from the number of the growth rings. Within a growth ring, the earlywood and the latewood are formed during the growth season. The earlywood is formed normally in the spring and is composed of large and thin-walled cells. The latewood is produced later in the summer, and has small and thick cell wall. The latewood is darker and denser than the earlywood (Sjöström 1993).

Bark is the outermost protective layer surrounding wood stem and is roughly divided into inner bark and outer bark. The inner bark is a narrow layer of living cells, which has the function to transport the liquid and nutrients to the tree (Alén 2000a). The outer bark consists of dead cells, which once were part of the inner bark. The function of the outer bark is to protect the tree from mechanical injury, microbiological attacks and desiccation (Fengel and Wegener 1989; Sjöström 1993).

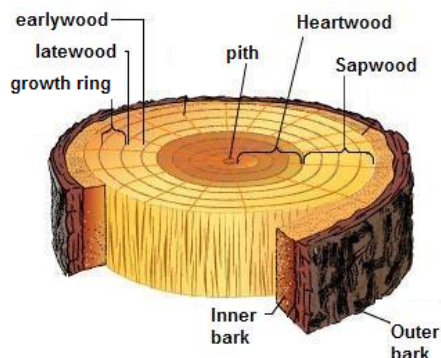


Figure 1. Cross-section of a tree stem (© Merriam-Webster Inc.).

2.2. Ultrastructure of wood cell wall

The cell wall of wood is composed of several layers, mainly including primary wall (P), secondary wall (S) and middle lamella (ML) as shown in Figure 2. These layers differ in their structure and chemical composition (Sjöström 1993). The primary wall is a thin layer first formed, in which the microfibrils are loosely packed and arranged in a random pattern (Thomas 1991). The secondary wall (S) is subsequently formed, in which the microfibrils are closely packed and exhibit a helical winding pattern (Hill 2006). Based on the different microfibrils orientation, the secondary wall is further divided into the outer layer (S₁), the middle layer (S₂) and the inner layer (S₃). Of these, the outer layer (S₁) is formed first and has a crossed fibrillar structure (Koch 2006). The middle layer (S₂) is generally the thickest portion of the cell wall and its microfibrils angle varies between 5-30°. The inner layer (S₃) is the thinnest layer containing microfibrils with an angle of 50-90° (Sjöström 1993). The middle lamella (ML) is located between the cells, which are adjacent to the primary walls on both side and has the function to glue the cells together (Alén 2000a). The middle lamella (ML) is difficult to be distinguished from the adjacent primary walls (P). The concentration (% in each layer) of lignin is high in the primary wall and middle lamella (Gullichsen 2000). The secondary wall (S) contains the highest concentration of polysaccharides (Alén 2000a).

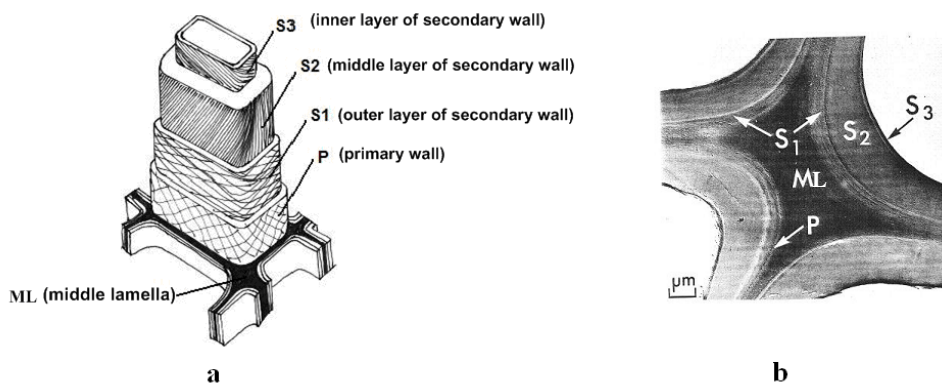


Figure 2. Ultrastructure of a wood cell wall schematically showing a) microfibrils orientation (Hill 2006), b) transverse section view (Sjöström 1993).

2.3. Chemical composition of wood

Wood is a natural fiber raw material with varying properties in morphology and chemical composition. The major chemical constituents of all wood species are cellulose, hemicelluloses and lignin. Cellulose is the main component in wood cell walls surrounded by hemicelluloses and lignin. In addition to these three components, wood also contains pectin, starch and other various compounds of low molecular masses, such

as extractives and inorganics, in varying small concentrations. Distribution and concentration of the chemical constituents in wood are varying from species to species, from tree to tree and even within the same tree. Table 1 lists the average concentrations of the main wood constituents in hardwood and softwood stem (Gullichsen 2000).

Table 1. Average chemical composition (% of dry wood weight) of softwood and hardwood (Gullichsen 2000).

<i>Component</i>	<i>Softwood</i>	<i>Hardwood</i>
<i>Cellulose</i>	41-46	42-49
<i>Hemicelluloses</i>	25-32	23-34
<i>Lignin</i>	26-31	20-26
<i>Extractives</i>	1-2.5	3-8

2.3.1. Cellulose

Cellulose is the main chemical constituent of wood and is serving as the supporting material in the wood cells. It approximately accounts for 40-45% of the dry substance (d.m.) in most wood species (Sjöström 1993). The cellulose molecules are built up of β -D-glucopyranose units which are linked together by (1 \rightarrow 4)-glycosidic bonds as show in Figure 3. Wood cellulose in the native state consists of about 10,000 glucose units and the length of native cellulose molecules is at least 5000 nm (Gardner et al. 2008). Cellulose has both reducing and non-reducing ends in its molecular structure (Alén 2000a; Sundberg and Holmbom 2002).

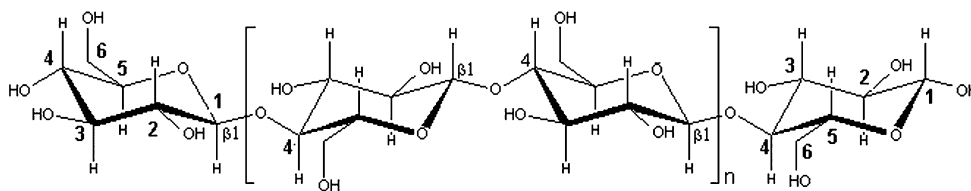


Figure 3. Structure of wood cellulose (Sjöström 1993; Gardner et al. 2008).

Of the three main wood components, cellulose molecules are completely linear and have a strong tendency to form hydrogen bonds between intra- and inter- molecules, resulting in the high strength of cellulose fibers. Bundles of some hundred cellulose molecules

associate to form elementary fibrils (Meier 1962). These elementary fibrils aggregate together in the form of microfibrils, which then form fibers joined with other wood constituents, e.g. hemicelluloses and lignin (Sjöström 1993; Taipale et al. 2010). Cellulose in wood has 50-70% crystalline structure, which make cellulose resistant to chemical attack and degradation (Biermann 1996; Hill 2006). Cellulose is predominantly located in the secondary cell wall (S) of wood, for example 48% in poplar wood, 41% in pine wood and 94% in cotton fiber (Zhong and Ye 2009).

2.3.2. Hemicelluloses

Hemicelluloses are a group of heterogeneous polysaccharides, which are mostly branched and essentially amorphous. The amount of hemicelluloses in wood is usually 20-30 % of the dry weight of wood (Sjöström 1993). Hemicelluloses have lower molecular mass with degree of polymerization (DP) of only 100-200 (Alén 2000a). The main chain of hemicelluloses consists of one or several sugar (monosaccharide) units. Hemicelluloses are generally less ordered than cellulose, and are relatively easily hydrolyzed by acid to their monomeric components, such as glucose (Glu), mannose (Man), xylose (Xyl), glucuronic acid (GlcA), and galacturonic acid (GalA) (Sjöström 1993; Biermann 1996). The structure and the content of hemicelluloses in softwood and hardwood are significantly different (Sjöström 1993; Sixta 2006). Even within the same species, their contents and compositions are also considerably different between stems, branches and roots. Like cellulose, the main function of hemicelluloses is also to act as supporting material in the cell wall.

In softwood the principal hemicelluloses are galactoglucomannans (15-20%, d.m.) and arabinoglucuronoxylan (5-10%, d.m.) (Sjöström 1993). Galactoglucomannans are often called glucomannans and the structure is shown in Figure 4a. It has a linear chain built up of glucopyranose and mannopyranose units or possibly slightly branched with side groups of galactose by (1→6)-bonds (Alén 2000a). The hydroxyl groups at C2 and C3 positions in the chain units of glucomannans are partially acetylated, which are easily cleaved by alkali (Sjöström 1993). Arabinoglucuronoxylan is often called xylan and its principal structure is shown in Figure 4b. Arabinoglucuronoxylan is composed of (1→4)-linked β -D-xylopyranose units which are partially substituted by side chains of 4-O-methyl- α -D-glucuronic acid groups at C2 position (Alén 2000a). On the average every ten xylose units carry two glucuronic acid residues at the C2 position. These uronic acid substituents protect the xylan chain against alkali-catalyzed degradation (Hill 2006).

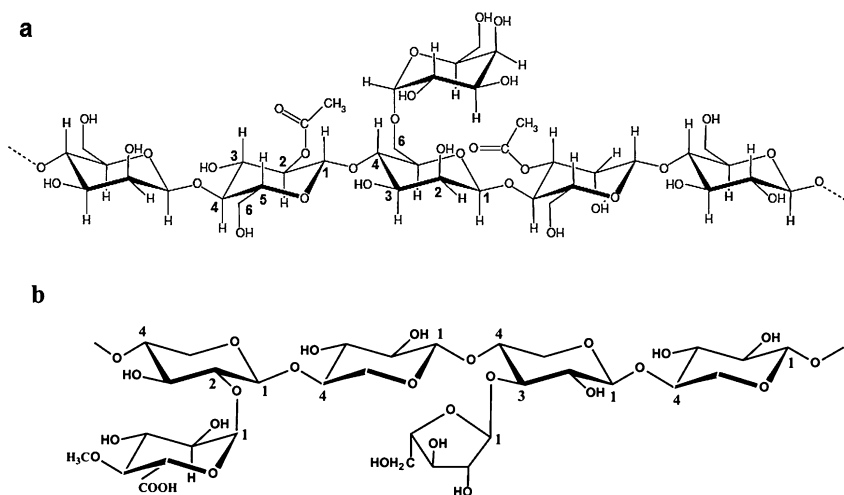


Figure 4. Principal hemicelluloses structure in softwood, a) Galactoglucomannans, b) Arabinoglucuronoxylan (Sjöström 1993; Hill 2006).

In hardwood the major hemicelluloses are glucuronoxylan, which backbone composes of β -D-xylopyranose units, linked by (1 \rightarrow 4)-bonds (Sjöström 1993). The content of glucuronoxylan in hardwood is approximately 20-30% of the dry wood mass. Figure 5 shows the principal structure of glucuronoxylan. Within the xylan chain, the hydroxyl groups at C2 and C3 positions are partly substituted by acetyl groups which are easily cleaved by alkali to form acetate. The xylose units in xylan chain also contain 4-O-methyl-glucuronic acid residues. The linkages between the uronic acid groups and xylose units are very acid resistant. The distribution of the uronic acid units is uneven within the xylan chain, and on the average there is one uronic acid unit present in every ten xylose units (Sjöström 1993; Alén 2000a). Therefore the number of uronic acid substituents in hardwood xylan chain is much lower than in softwood.

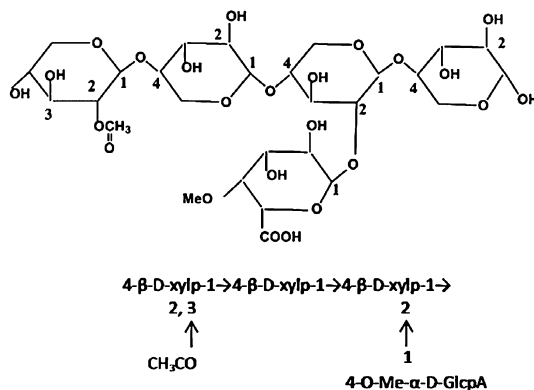


Figure 5. Principal structure of glucuronoxylan in hardwood (Sundberg and Holmbom 2002).

2.3.3. Pectin

Beside cellulose and hemicelluloses, wood also contains other polysaccharides, e.g. pectin and starch. Pectin is a group of heterogenous acidic structural polysaccharides, which provide the flexibility and mechanical strength to the cell wall (Fengel and Wegener 1989; Sjöström 1993). Both in softwood and hardwood cells the dominant structure of pectin is made up of galacturonic acid (GalA) units, which are linked by (1→4)-bonds as shown in Figure 6. In native wood most of the carboxyl groups in galacturonic acid units are methyl esterified (Hafren and Daniel 2003; Putoczki et al. 2008). The protonation constants ($\lg K_{HR}^{H,R}$) of pectin acids are in the range of 3.5-4.5, depending on the de-esterification (ionization) degree of the pectin (Sundberg et al. 2000; Ralet et al. 2001; Monge et al. 2007; Saarimaa 2007). Generally the content of pectin in both softwood and hardwood is less than 1-2% (d.m.). The pectin is mainly located in the primary cell wall (P) and the middle lamella (ML) (Hafren and Daniel 2003; Putoczki et al. 2008).

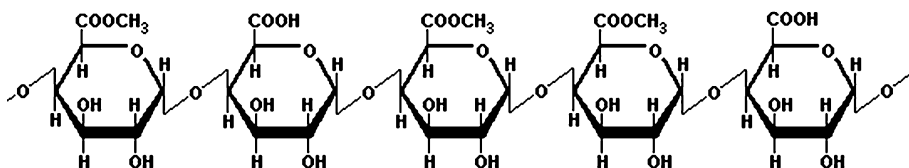


Figure 6. An example structure of pectin (Zamora 2012).

2.3.4. Lignin

Next to cellulose, lignin is the most abundant and important polymeric substance in wood. Lignin is an amorphous polymer which is built up of phenylpropane units with many different linkages. Lignin glues the fibers together in the cell wall, and provides the mechanical strength and stiffness to the wood. The content of lignin is quite variable in different tree species and also within the same tree. Softwood contains 26-32% (d.m.) lignin while hardwood contains 20-25% (d.m.) lignin (Sjöström 1993). Native lignin is very complex and it is not possible to isolate it completely for analysis. Therefore the structure of lignin molecule has not yet been completely indentified. Several lignin models have been proposed. The structure model for lignin commonly used was presented by Freudenberg in 1968 for spruce lignin, and later developed by Adler and others researchers (Adler 1977). A representative lignin structure is shown in Figure 7 (Biermann 1996). The lignin polymer contains characteristic methoxyl groups and phenolic hydroxyl groups (Sjöström 1993). The content of phenolic hydroxyl groups is 15-30% in softwood lignin and 10-15% in hardwood lignin. Figure 7 represents only a

segment of the lignin macromolecule and shows some of the most important linkages in the structure (Dence and Lin 1992). Lignin is present in all parts of the cell wall. The concentration of lignin is highest in the middle lamella (65%, of the dry matter of the layer), whereas most of the lignin (79%, of the total amount of the constituent) is located in the secondary cell wall because of its thickness (Beall 1969; Alén 2000a). The native lignin has a very low solubility in most solvents.

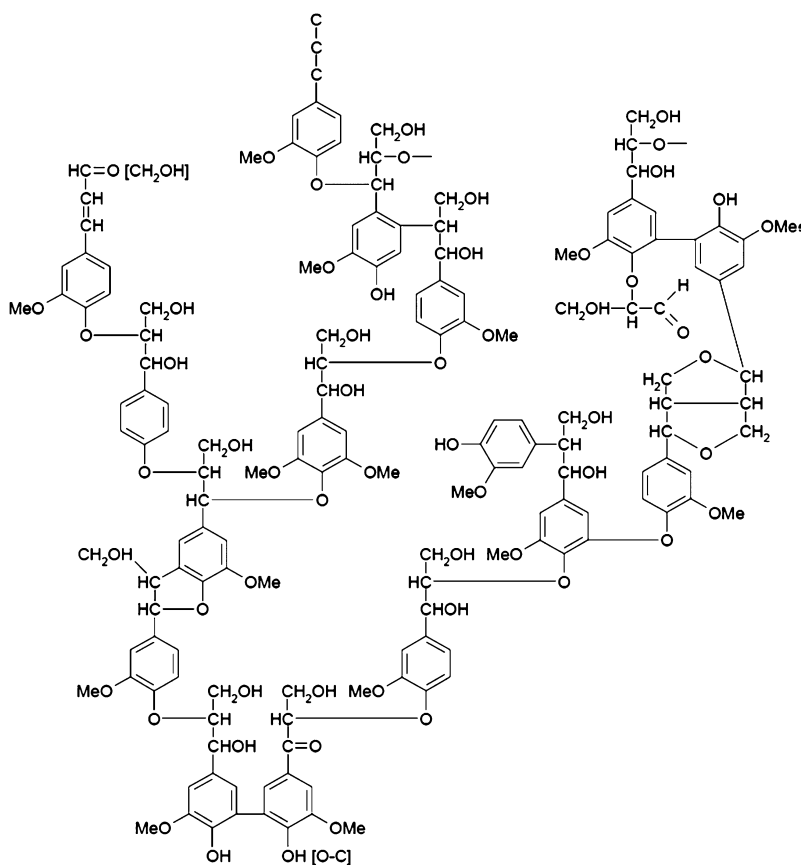


Figure 7. A structural model for softwood lignin (Adler 1977).

2.3.5. Extractives

In addition to the major components, wood also contains a minor fraction of extractives. Extractives in wood are of large variety and almost entirely composed of compounds of low molecular weight. They mainly serve as an energy source for wood cells and protect wood against insect attacks. These compounds are soluble in organic solvents or in hot water. The content of extractive is usually less than 10% of the dry wood mass.

2.3.6. Inorganic components

Wood contains only rather low concentrations of inorganic components, often measured as ash content (0.1-5%, d.m.) (Sjöström 1993; Saarela et al. 2005). The inorganic components are mainly composed of various metal salts, such as carbonates, silicates, oxalates and phosphates, deposited in the cell walls and lumina. Table 2 shows the occurrence of metal ions and their concentration ranges in stem wood of a Scots pine (Ivaska and Harju 1999). The most abundant metal ions in stem wood are Ca, K and Mg amounting up to 100 ppm. Some metal ions, for example Fe, Mn and Na, present in wood are in concentrations less than 100 ppm. Most of the other metal ions usually occur only at trace levels below 10 ppm. The metals in wood are partially bound as cations to the acid groups present in xylan and pectins. These metal ions can only be displaced and washed out from wood by acids or by chelating agents (Sjöström 1993). Some of the metal ions are present in inaccessible regions in the wood structure and are in form of sparingly soluble salts. Therefore the wood materials are difficult to wash completely free from metal ions.

Table 2. Occurrence of metal ions and their concentration ranges in stem wood of a Scots pine (*Pinus sylvestris*) tree (Ivaska and Harju 1999).

<i>Concentration range, ppm (mg/kg)</i>	<i>Elements</i>
100-1000	Ca, K, Mg
10-100	Fe, Mn, Na
1-10	Zn, Sr, Al, Si, Ti
0.1-1	Cu, Cd, Ba, Ni, Rb, Ag, Cr, Sn
0.01-0.1	Pb, Li, Bi, Br, Co, Se, La
0.001-0.01	Hg, Mo, As, Sb, Nd, Sc, Gd

The content of inorganic components largely depends on the wood species, the location in the tree and the environmental conditions (temperature, soil, fertilization and air pollution) (Koch 2006; Saarela 2009). Saarela et al. (2005) analyzed over 160 wood samples of birch, pine and spruce in Finland and found their inorganic components as the ash content in the range 0.2-0.5%. They showed that the mean ash content for spruce is higher than for birch and then for pine. The inorganic content also varies within the tree itself. Saarela (2009) has studied the distribution of elements from pith to bark of pine wood. The concentrations of metal ions are clearly highest in pith. In the rest of stem wood the elements are quite evenly distributed. Harju et al. (1996) have studied seasonal variations of trace element concentrations within annual tree rings by thick-target particle induced x-

ray emission (PIXE). The highest concentrations for most elements were found in earlywood in the beginning of the growth season. Werkelin (2008) investigated the inorganic elements in different parts of a tree by chemical fractionation analysis. The results showed that the contents of inorganic elements in the samples range over several orders of magnitude and the element concentrations are highest in the foliage, followed by needles, twigs, bark and then wood. Tokareva et al. (2007) studied the spatial distribution of metal ions on the surfaces of the spruce and aspen stem woods and found the distribution patterns of metal ions in ray cells, vessels and fibers were different.

2.4. Wood pulping

The main purpose of wood pulping processes is to separate the fibers from the wood and to make the fibers suitable for papermaking (Salmén et al. 1999). There are two technological principles to produce wood pulps, i.e. mechanical process and chemical process. All the main chemical constituents in wood behave differently during pulping processes (Alén 2000b). In the mechanical pulping, the lignin and hemicelluloses are more or less softened. In the chemical pulping, however, the lignin is removed or dissolved to a large extent as well as hemicelluloses. On a global scale, the chemical pulping has become the predominating process and most of the chemical pulps are produced by the kraft cooking process. The pulps used in this work are of thermomechanical pulp (TMP) and kraft pulp. A brief description of the mechanical and kraft pulping processes are given in this chapter.

2.4.1. Mechanical pulping

Mechanical pulping is to separate the fibers from wood by mechanical force. The main mechanical pulps of today are the thermomechanical pulps (TMP), chemimechanical pulps (CMP), pressure groundwood (PGW) and stone groundwood (SGW) pulps. There are two major ways to produce mechanical pulps, including a grinding process and a refining process. The thermomechanical pulping process is the dominating refiner-based mechanical pulping process (Tienvieri et al. 1999). Figure 8 illustrates the basic principle of TMP refining. The wood raw material is cut into chips and then fed into the refining zone between two metal discs which are rotating with high speed (Salmén et al. 1999; Tienvieri et al. 1999). The chips are steamed and pressurized on their way to the refiners. During their passage through the unit the chips are ground and broken up to small fragments and fibers.

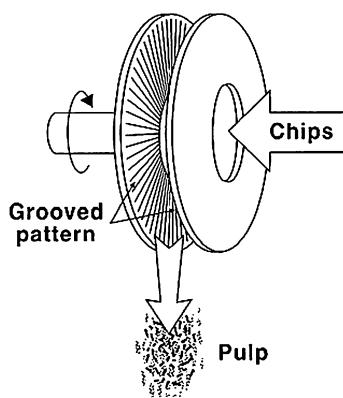


Figure 8. Principle of refiner mechanical pulping (Tienvieri et al. 1999).

The mechanical pulps contain all components of the wood raw material in about the same ratios as in wood. The yield of mechanical pulping is high, normally 80-95%, while that of chemical pulping is normally 45-50%. Mechanical pulping usually causes physical damage on the fibers and the strength of the mechanical pulps thus is rather low. Mechanical pulps are mainly used for the production of non-permanent papers, like newspapers and magazine papers. Mechanical pulping process demands high energy and requires high-quality wood raw materials, mainly spruce wood (Tienvieri et al. 1999; Blechschmidt et al. 2006).

2.4.2. Chemical pulping

The principle of chemical pulping is to dissolve lignin from wood to such an extent that the fibers are easily liberated from wood matrix without being too damaged. The chemical pulping is mainly based on the sulfite and sulfate pulping processes, of which the latter predominates (Sjöström 1993). Sulphite pulps are produced by cooking wood chips in a pressurized vessel in the presence of bisulphite ($NaHSO_3$) liquor. In sulfite pulping mills the cooking chemicals are costly and difficult to be completely recovered, and the emission can cause serious environmental problems. Thus the number of sulfite processes has clearly decreased during the recent decades.

Sulfate pulps (kraft pulps) are produced by cooking wood chips in a pressurized digester with a solution containing sodium hydroxide ($NaOH$) and sodium sulfide (Na_2S). The process is performed at high pH (>12) and high temperature (160-180°C) (Gullichsen 2000). The lignin in wood is broken down by cleavage of the ether linkages and then dissolved in the cooking liquor. The delignification in the chemical pulping, however, is unfortunately not a selective process. In addition to the removal of lignin, a significant part of hemicelluloses and some cellulose are also degraded. As a consequence the yield of cellulose in chemical pulping is lower than in mechanical pulping, i.e. the average yield in the range 45-55% (Alén 2000b). The sulfate pulping process is the dominating method in the world today to produce chemical pulps. The spent liquor can be clarified and recovered as the white liquor containing $NaOH$ and Na_2S . The kraft pulps are used widespread, for instance, with bleached pulps particularly for graphic papers, tissue and carton boards. Unbleached pulps are commonly used in liner for corrugated boards, wrappings, sacks, bag papers and envelopes (Leithe-Eriksen 2001).

2.5. Bleaching

The purpose of bleaching is to brighten the pulps and also to improve the cleanliness of the pulps (Sjöström 1993; Lindholm 1999). The color of the pulps is mainly due to the lignin remained in pulps after pulping. Figure 9 shows the most common chromophores

in lignin residues. To reach an acceptable brightness, the residual lignin should be removed from pulps (delignifying), or the strongly light-absorbing groups should be converted to non-chromophores (lignin-preserving). The delignifying bleaching is commonly applicable to chemical pulps, which results in both high and reasonably permanent brightness. Bleaching of chemical pulps is usually performed in a bleaching sequence consisting of several treatment stages with bleaching chemicals and sodium hydroxide. The bleaching chemicals commonly used are chlorine, chlorine dioxide and oxygen. Due to the environmental reasons, the chlorine-containing bleaching chemicals are gradually replaced with chlorine-free chemicals, such as oxygen, hydrogen peroxide and ozone. Lignin-preserving bleaching is the appropriate method for mechanical pulps, which usually gives a moderate brightness increase. The typical bleaching chemicals used are sodium dithionite ($Na_2S_2O_4$) and hydrogen peroxide. The oxygen delignification and the peroxide bleaching will be described briefly in the following sections.

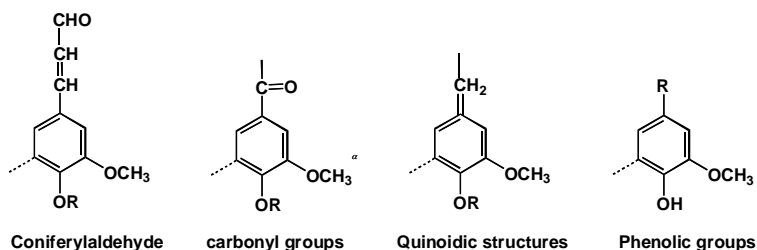


Figure 9. Various groups in lignin contributing to the pulp color (Lindholm 1999; Sundberg and Holmbom 2002).

2.5.1. Oxygen delignification

Oxygen delignification can be considered as an extended delignification step that is used after the pulping process but before the traditional bleaching steps (Gullichsen 2000). It can also be regarded as a bleaching stage combined with other bleaching chemicals in the subsequent stages. The basic process involving oxygen delignification in pulp bleaching is shown in Figure 10.

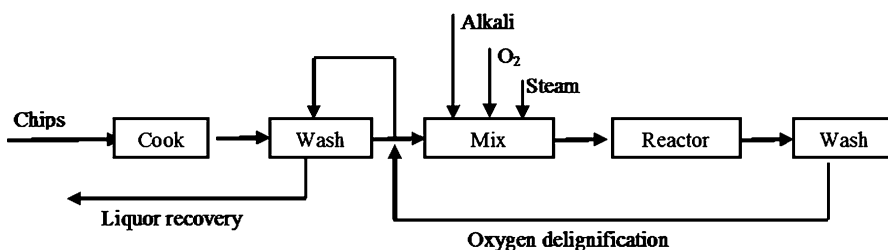


Figure 10. Incorporation of oxygen delignification in pulp lines (Gullichsen 2000).

Oxygen delignification is normally performed in alkaline conditions. The aromatic rings substituted with free phenolic hydroxyl groups in the residual lignin are primarily attacked and cleaved to unsaturated dicarboxylic acid structures (Sjöström 1993; Sundberg and Holmbom 2002). Introduction of oxygen delignification stage is to lower the demand of other bleaching chemicals in the subsequent stages and to reduce the environmental impact of the bleaching plant effluents. Oxygen delignification, however, is less selective toward lignin removal than other bleaching chemicals. Carbohydrates are also attacked during alkaline oxygen delignification process. For example, cellulose is degraded by random chain cleavages and peeling reactions. Thus oxygen delignification has to be stopped when about 50% of the residual lignin has been dissolved. The severe degradation of polysaccharides can be inhibited to some extent by the presence of magnesium salts in the oxygen delignification process (Alén 2000b; Gullichsen 2000; Sixta et al. 2006).

2.5.2. Hydrogen peroxide bleaching

Hydrogen peroxide bleaching is usually used for brightening mechanical pulps, via modifying chromophonic groups in wood lignin (Gullichsen 2000). The condition for hydrogen peroxide bleaching is similar to those used for oxygen delignification. Hydrogen peroxide bleaching is only a complementary bleaching stage to be used in combination with other bleaching chemicals for production of fully bleached pulps (Sjöström 1993). The transition metals, such as copper, manganese and iron, can induce severe decomposition of hydrogen peroxide. The concentration of metal ions in pulps, therefore, has to be reduced prior to the peroxide bleaching stage by treatment with acid or chelating agents (Lindholm 1999). The hydroxyl radicals formed after peroxide decomposition are powerful lignin oxidants, but they are nonspecific, attacking carbohydrates as well (Sjöström 1993). To avoid or limit the decomposition of hydrogen peroxide, the bleaching must be performed under carefully controlled conditions by using stabilizing agents. Normally sodium silicate (Na_2SiO_3) and magnesium salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) are added to the bleaching liquor in order to stabilize the hydrogen peroxide.

2.6. Bark

Bark is the outmost layer surrounding the wood stem, branches and root. The bark constituents amounts to 10-20% of the total weight of the tree, depending on the species and on growing conditions (Fengel and Wegener 1989; Mun et al. 2010). The structure and chemical composition of bark are more complicated in comparison with wood. They vary not only among the different tree species but even within the same species depending on, e.g. the age, the height and the growth conditions of the tree (Laver 1991; Sjöström 1993; Biermann 1996). Bark has negative effects on pulping and papermaking processes, and thus has to be removed from stem wood prior to pulping.

Bark contains some constituents similar as in wood, such as cellulose, hemicelluloses and lignin, but in very different proportions (Sjöström 1993). The polysaccharides are present in bark by a lower percentage. Typically the content of cellulose in bark is roughly 20-30% and the lignin content in the range 15-40%, of the dry weight of bark (Mun et al. 2010). The contents of extractives, pectins and phenolic compounds are much higher in bark than in wood, for instant, the content of extractive in spruce bark is 20-40% and the pectin 5.7-7.1% (Mun et al. 2010; Krogell et al. 2012). Bark contains a much higher content of inorganic components than wood. Saarela et al. (2005) analyzed 25 spruce samples from south-western Finland and showed that the mean content of inorganics (ash-%) in bark is 9 times higher than in stem wood, i.e. 3.85 vs 0.42. The main metal ions and their mean contents (mg/g) in spruce bark were: Ca 20, K 5.0, Mn 0.39, Zn 0.15 and Fe 0.073. Calcium is the predominant metal ion and it is mainly in form of calcium oxalate crystals deposited in lumina (Fengel and Wegener 1989).

In addition to the same components as present in wood, bark also contains significant high concentrations of other complex constituents. Tannins are one of the complex compounds occurring in the bark. They have similar structure as lignin and are present as condensed polyphenolics possessing free phenolic functional groups. The molecular weight of tannins varies in the range 1600-5500 (Laver 1991). The content of tannins in barks varies widely from 5-50% (Fengel and Wegener 1989). The condensed tannins do not readily break down under mild condition of hydrolysis, but the low molecular-weight tannins are readily hydrolyzed into a phenol carboxylic acid (Laver 1991).

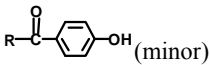
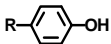
3. Metal sorption to wood, pulp and bark materials

3.1. Functional groups in wood, pulp and bark

Wood, pulp and bark materials can exhibit ion-exchange properties due to the presence of certain type of functional groups (anionic groups). In this thesis, the functional groups in wood, pulp and bark materials are defined as the negatively charged acid groups. These acid groups are mainly the carboxyl groups and the phenolic hydroxyl groups, acting as the binding sites for sorption of metal ions to wood, pulp and bark materials. The functional groups partly originate from the constituents in the materials themselves, and some are formed during the pulping and bleaching processes (Fardim and Holmbom 2003). The total content of acid groups and their distribution in pulps differ with wood raw materials, and also with processes in which the mechanical or chemical treatments are applied. In general, the total concentration of functional groups in mechanical pulps is higher than that in chemical pulps, particular because mechanical pulps contain much more lignin carrying phenolic hydroxyl groups. The distribution of acid groups is expected to be very uneven in mechanical pulps, but in chemical pulps they are more uniformly distributed (Fardim and Holmbom 2005).

In native wood there are various types of acid groups, e.g. carboxyl and phenolic hydroxyl groups as shown in Table 3 (Sjöström 1993). Most of the carboxyl groups are of the uronic acid type, mainly chemically bound to the xylan in hemicelluloses. Some of them are present in pectic substances. In addition, carboxyl groups may also be present in native lignin and extractives, but their concentrations in these compounds are relatively low (Bhardwaj et al. 2004). The phenolic hydroxyl groups are mainly related to lignin. In both softwood and hardwood the main uronic acid groups originate from 4-O-methyl glucuronic acid units (GlcA) in xylan and D-galaturonic acid units (GalA) in pectins, and to minor extent D-glucuronic acid units in arabinogalactan (Laine et al. 1996; Koljonen et al. 2004). Their chemical structures are shown in Figures 4 and 5 in the previous chapter. These groups are mostly methyl-esterified and lactonized to various degrees in different wood species (Konn et al. 2007). In softwood the molar ratio of glucuronic acid to xylan is roughly 1:5 and in hardwood it is 1:10 (Fengel and Wegener 1989; Sjöström 1989; Lindström 1992). Thus the number of these acid groups in softwood xylan is two times higher than that in hardwood xylan. Hardwood species, however, contain in average 1.5 times more hemicelluloses than softwood species. The total amount of the carboxyl groups in hardwood and softwood is approximately the same. During pulping and bleaching operations these original acid groups in wood will be exposed to the chemicals and converted to other forms or even removed from the original molecules.

Table 3. Types of acid groups in wood (Sjöström 1993).

Acid group	Structure	pK _a	Degree of ionization at pH 7 (%)
Carboxylic	R-CH(OR ⁺)COOH	3-4	99.9-99.99
	R-CO ₂ H (minor)	4-5	99-99.9
Phenolic	 (minor)	7-8	10-50
		9.5-10.5	0.03-0.3
Alcoholic	R-CH(OR ⁺)CH(OH)-R ⁺	13.5-15	10 ⁻⁶ -3·10 ⁻⁵

During mechanical pulping, the chemical components in wood are mainly maintained. Thus the acid groups in untreated mechanical pulps are similar to those originally in native wood, i.e. mainly the carboxyl groups of 4-O-methyl-glucuronic acid (GlcA), galacturonic (GalA) and glucuronic acids (Fardim and Holmbom 2005). During grinding or refining, some carboxyl groups are lost from wood due to the dissolution of xylan in hemicelluloses and fatty acids in extractives (Diniz 1995). Only few new carboxyl groups are generated during mechanical treatments (Koljonen et al. 2004). The alkaline treatment of mechanical pulps increases the content of free carboxyl groups due to the hydrolysis of the methyl-ester groups in pectin (i.e. exposure of galacturonic acid groups in pectin) (Fardim and Holmbom 2005).

During kraft pulping, most of the lignin and part of the hemicelluloses are removed. The acid groups in kraft pulps are mainly the hexenuronic acids (HexA), the glucuronic acids (GlcA) on the remaining xylan and the carboxyl groups in the lignin residue, as well as the phenolic hydroxyl groups in the residue lignin (Fengel and Wegener 1989; Sjöström 1989; Lindström 1992). Part of the initial 4-O-methyl glucuronic acid groups in native wood xylan are dissolved along with the degradation of xylan chain and the cleavage of glycosidic bonds between xylose units (Simão et al. 2005). Part of them is converted to hexenuronic acid groups (HexA) (Laine et al. 1996). In alkaline condition the HexA was observed to be dissolved along with the degradation of xylan chain and with the degradation of HexA itself, by alkaline splitting of HexA from the xylan backbone (Simão et al. 2005). The formation and the degradation of the HexA are strongly influenced by the temperature and the alkaline concentration. On the other hand, some new carboxyl groups are formed during alkaline pulping, i.e. formation of alkali stable saccharinic acids or other types of alkali stable carboxyl groups by peeling reactions of cellulose (or hemicelluloses) chains (Sjöström 1993; Athley et al. 2001; Fardim and Holmbom 2005). Carboxyl groups are also introduced into lignin fractions through

alkaline oxidation during kraft pulping, but only to a minor extent (Sjöström 1989; Lindström 1992; Laine et al. 1994; Laine et al. 1996). Stenius and Laine (1994) confirmed the formation of the acid groups bound to lignin during alkaline pulping by ESCA characterization. It has been reported that kraft pulping processes reduce the total number of carboxylic acid groups present in wood pulps (Diniz 1995; Laine et al. 1996). The content of these acid groups in hardwood kraft pulps is higher than in softwood kraft pulps due to higher content of hemicelluloses in the hardwood pulps (Horvath and Lindström 2007). During kraft pulping, a significant proportion of lignin with phenolic units are degraded and new phenolic groups are formed to a large extent (Liitiä and Tamminen 2007). It has been reported that the total content of acid groups depends on the kappa number of kraft pulps and it increases with increasing kappa number of unbleached kraft pulps (Stenius and Laine 1994).

During bleaching processes oxidizing agents, such as oxygen and hydrogen peroxide, introduce new anionic groups into pulps. During peroxide bleaching of mechanical pulps, the methyl-esterified galacturonic units in pectin may be demethylated and thus new galacturonic acids are formed (Diniz 1995; Mosbye et al. 2001; Fardim and Holmbom 2005). In addition, some new carboxyl groups also are generated in lignin structures by oxidation of the lignin moieties (Diniz 1995; Fardim and Holmbom 2005). Goulet and Stratton (1990) reported that peroxide bleaching of TMP increased the total content of weak acid groups. However, Fardim and Holmbom (2005) reported that the peroxide bleaching reduced the amount of acid groups in TMP, probably due to removal of hemicelluloses and lignin as well as degradation of saccharinic acid units by oxidative reactions. For kraft pulps, the oxygen delignification and bleaching introduce some new phenolic groups to lignin residues (Liitiä and Tamminen 2007). The formed hexenuronic acids and the remaining 4-O-methylglucuronic acids in kraft pulps are not degraded during the oxygen delignification. Athley et al. (2001) reported that the hexenuronic acid is the main contributor to the acid groups in the oxygen-delignified kraft pulps.

3.2. Characterization of the functional groups

3.2.1. General aspects

As described in a previous section, wood, pulp and bark materials contain different types of weak acid groups as functional groups participating in ion exchange reactions with metal ions. The protonation of the functional groups (acid groups) depends on the pH of the medium in which they are dispersed. Generally the carboxyl groups are dissociated in neutral or weakly acidic conditions. However, the ionization of phenolic hydroxyl groups demands rather alkaline conditions. The degree of dissociation of the functional groups in wood, pulp and bark materials has been modeled by using one or more dissociation constants (Stenius and Laine 1994; Laine et al. 1996). Studies have shown a relatively

rapid increase in the negative charge on the fibers when the pH of the surrounding solution was increased (Wang and Hubbe 2002).

The total content of acid groups (anionic groups) on fibers have been investigated by different titration and sorption methods, such as potentiometric titration, conductometric titration, polyelectrolyte titration, methylene blue (MB) sorption as well as ion exchange methods. These methods have been compared in several studies (Holmbom et al. 2002; Fardim and Holmbom 2005; Fardim et al. 2005). The potentiometric, conductometric and polyelectrolyte titration methods are very time-consuming. The MB sorption method is fast, simple and repeatable (Fardim and Holmbom 2003). The content of total acid groups obtained from the conductometric and the potentiometric titrations were rather similar. However, the potentiometric titration can also be used to determine the protonation constants of acid groups. The polyelectrolyte titration gave consistently larger values for the number of carboxyl groups than the potentiometric titration method (Stenius and Laine 1994; Fardim et al. 2005). The polyelectrolyte adsorption strongly depends on the molar mass of the polyelectrolyte used and the ionic strength of the solution. Thus, it has also been reported in some studies that the polyelectrolyte adsorption gave lower values than the conductometric or potentiometric titration for the total content of acid groups (Lloyd and Horne 1993; Koljonen et al. 2004; Zemljič et al. 2008). The polyelectrolyte titration also gave information of accessibility of the carboxyl groups by using different molecular weights of polyelectrolytes. The methylene blue sorption gave similar results as the conductometric titration, but lower than the polyelectrolyte titration (Fardim et al. 2005; Holmbom et al. 2002). The MB sorption can be used for a fast determination of the total content of anionic groups. The ion exchange method gave clearly lower values for the number of carboxyl groups and the obtained results varied very much depending on which metal ions were used in the experiments.

In this thesis, the potentiometric acid-base titration method has been used to determine the protonation constants and the concentrations of acid groups in tree-related materials. The principle of the acid-base titration method will be described in the following section, as well as the methods used to evaluate the titration data.

3.2.2. Acid-base titration of the functional groups

The protonation of functional groups in wood, pulps and bark can be described by the following general reaction, where R refers to functional groups in the sample matrix and HR is its protonated form.



The protonation constant, $K_{HR}^{H,R}$, is defined by:

$$K_{HR}^{H,R} = \frac{[HR]}{[H^+][R^-]} \quad (2)$$

or in the logarithmic form:

$$\lg K_{HR}^{H,R} = \lg \frac{[HR]}{[H^+][R^-]} = pK_a \quad (3)$$

where pK_a is the negative logarithm of the dissociation constant K_a of HR .

The traditional way to treat the titration data is to plot the measured pH as function of the added volume, i.e. V , of a strong base. For a sample solution containing several acids, such analysis will be successful only if the titration curve has clearly distinguished pH jumps for each of the acid groups in the sample. To fulfill these requirements the protonation constants ($K_{HR}^{H,R}$) of the acids should be less than 10^7 and the difference between the constants larger than 10^4 (Ingman and Still 1966). These requirements will guarantee that the equivalence point of the stronger acid is the starting point for titration of the weaker acid. However, such requirements are not fulfilled in the titration of acid groups in wood, pulp and bark materials, because the acid groups in these tree-related materials have rather similar values of $K_{HR}^{H,R}$. In order to obtain the concentration of the acid groups in wood, pulp and bark materials, two different methods were employed to evaluate the titration data in this thesis work, i.e. the FITEQL program and the method of linear titration curves, the so called Gran method.

The FITEQL program

The FITEQL program is designed to calculate the optimal values for the protonation constants and the total concentrations of different species from experimental data based on equations of chemical equilibria (Herbelin and Westall 1999). Experimental data (concentration of the strong base C_{OH^-} , pH, dilution factor, ionic strength) can be used as parameters in the computer program. The unknown protonation constants $\lg K_{HR}^{H,R}$ and concentrations of the different species are initially guessed for the equilibrium calculation. The protonation constant and the concentration of each species are then optimized by an iterative procedure on the adjustable parameters in the FITEQL computer program (Herbelin and Westall 1999). The procedure when using the FITEQL program comprises the following basic steps:

1. Definition and input of the chemical equilibrium model
2. Input of free concentration, total concentrations and $K_{HR}^{H,R}$ values of known species
3. Input of the initial guesses for concentrations and $K_{HR}^{H,R}$ values of unknown species
4. Input of the experimental titration data, i.e. C_{OH^-} , pH, dilution factor, ionic strength
5. Start the FITEQL calculations
6. The initial guesses are set to the equilibrium values by proceeding the iterations on the adjustable parameters in the FITEQL computer program
7. Output of optimum values for the concentrations and the protonation constants, $\lg K_{HR}^{H,R}$

The Gran method

The potentiometric titration data can also be evaluated by the Gran method to obtain the total concentration of acid groups. The Gran method is a graphical method to determine the equivalence point in potentiometric acid-base titration by converting the titration curve to straight lines (Gran 1950, 1952). This method was improved by Ingman and Still (1966) and Johansson (1970) to determine more accurately the equivalence point in titrations of very weak acids. Ivaska has further developed the method for titration of weak acids and their mixtures (Ivaska 1974; Ivaska and Wänninen 1974).

In this work the equations (4) and (5) were used to convert the titration data, V and pH data pairs, to the linear lines for determination of the total concentration of weak acid groups in tree-related materials. The concentration of strong acid in the mixture is determined by equation (4) and the total concentration of all acids is determined by equation (5). These equations are based on the expression made by Johansson (1970).

$$f(V) = \frac{(V_0 + V)}{C_{OH}} 10^{-pH} \quad \text{on the acid side of the equivalence point} \quad (4)$$

$$f(V) = \frac{(V_0 + V)}{C_{OH}} 10^{pH - K_w} \quad \text{on the alkaline side of the equivalence point} \quad (5)$$

V_0 is the initial volume of the mixture. V is the volume of the added strong base with concentration of C_{OH} , and K_w is the ionic product of water. Two straight lines are obtained by plotting $f(V)$ as a function of the volume, V , of the added standard base solution. These lines intersect with the x-axis, separately. The point of intersection of the line obtained with equation (4) gives the concentration of strong acid present in the sample suspension. The point of intersection of the line obtained with equation (5) gives

the total concentration of acids in the sample suspension. The difference between the two intersection points gives the volume of strong base consumed by the weak acids in the sample. The total concentration of acids calculated with the Gran method is mostly in good agreement with the values obtained with the FITEQL program.

3.3. Theory of ion exchange reactions

Ringbom (1963) has given a thorough description of the theory of complexation in cation and anion exchange reactions. As described by Ringbom ion exchange is a reversible process in which the ions in the solid phase are exchanged with the ions in the solution phase. An ion exchanger can be any insoluble material that has the ability to take up ions from a solution, with the simultaneous releasing of a chemically equivalent number of ions into the solution. The ion exchange reaction of a binary system, involving hydrogen ions and metal ions, can be expressed by the following general equation:



where R^- is the anionic group in the solid matrix. In this work it is the functional groups present in wood, pulp or bark material. M^{2+} is a metal ion with divalent charge, which undergoes ion exchange reaction with the hydrogen ions and is bound to the solid phase.

The degree to which this process takes place depends on the ion exchange equilibrium constant (Ringbom 1963), which is given by the following equation:

$$K_{2H}^M = \frac{[MR_2][H^+]^2}{[M^{2+}][HR]^2} \quad (7)$$

where $[MR_2]$ and $[HR]$ are the concentrations of metal ions and protons bound to the solid phase. $[M^{2+}]$ respective $[H^+]$ are their concentrations in the aqueous phase. In general, when discussing the ion exchange processes it is more convenient to express concentrations in solid phase in milli-equivalents per gram (*meq/g*) or micro-equivalents (*μeq/g*) per gram. These units take into consideration the reaction stoichiometry.

The total number of exchange sites in the solid phase in general is defined as the total capacity of the ion exchanger and is denoted by C (on dry weight basis). In practice all of the functional sites in an exchanger are not completely occupied by the ions of interest. The number of these sites taken up by the ions of interest can be defined as the operating

capacity, i.e. OC , of the ion exchanger under the particular experimental conditions. Load of the ion exchangers, L , is used to indicate the percentage of exchange sites that are occupied by the particular ions under experimental conditions. It can be expressed by equation (8):

$$L = \frac{OC}{C} \cdot 100\% = \frac{n [MR_n]}{C} \cdot 100\% \quad (8)$$

where n is the charge of the ion M and $[MR_n]$ the concentration of M bound to the solid phase.

3.4. Interaction of metal ions with wood, pulp and bark

As mentioned in an earlier section, metal ions may deposit in wood and bark materials in salt forms, such as hydroxides, oxalates, sulfates, phosphates and carbonates. Most metal ions are, however, supposed to be associated to the functional groups like carboxyl groups and phenolic hydroxyl groups in wood, pulp and bark. In this thesis, the interaction of metal ions with these tree-related materials was studied under weak acidic or neutral experimental conditions. The functional groups involved in the reactions are mainly the carboxyl groups, because they partially dissociate in the pH range used in the experiments. The metal ions are bound to the tree-related materials mainly by ion-exchange reactions. Figure 11 illustrates a simplified model of ion-exchange reactions occurring between the metal ions in the solution and the hydrogen ions in carboxyl groups in the solid phase. The ion exchange that may take place between two metal ions with different valences is also involved in this figure. It has been expected that the divalent metal ions have a higher affinity to the acidic sites (carboxyl groups) in comparison with the monovalent cations. The equilibrium reactions of these ion exchange reactions are stoichiometric, i.e. approximately 1:2 for exchange of divalent metal ions to hydrogen ions and ca. 1:1 for exchange of monovalent metal ions to hydrogen ions. This has been demonstrated in few studies (Karhu et al. 2002; Crist et al. 2003).

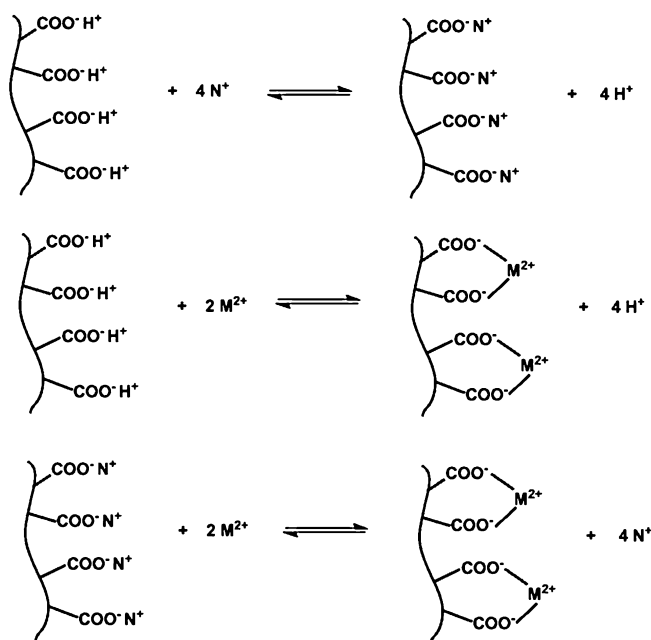


Figure 11. Ion exchange of metal ions with hydrogen ions to carboxyl groups.

Many studies have demonstrated the importance of the carboxyl groups in the sorption of metal ions to biomass materials (Merdy et al. 2002; Bakir et al. 2009; Hubbe et al. 2011). The capacity of sorption of metal ions to the biomass materials is mainly due to the concentration of the carboxyl groups. The interaction of metal ions with the carboxyl groups takes mainly place by ion exchange. The sorption of metal ions is also pH-dependent and an increase in the sorption capacity has been found when the pH of the aqueous solution was increased (Ofomaja et al. 2010; Semerjian 2010; Reddy et al. 2011; Rafatullah et al. 2012). This can be explained by increasing dissociation of functional groups with increasing pH, in turn resulting in an increase in the ion exchange capacity of the materials (Hubbe et al. 2011). It has also been reported that the sorption of metal ions is not only based on the ion-exchange mechanism, but also the unspecific Donnan adsorption is involved (Pesavento et al. 1994; Towers and Scallan 1996; Bygrave and Englezos 1998; Yantasee and Rorrer 2002; Duong et al. 2004; Sundman et al. 2008).

Many different biomass materials have been studied for the sorption of metal ions from aqueous single, binary, ternary or quaternary metal ion batch systems. The sorption capacity varies with the materials and the metal ions studied. The hardwood sawdust showed sorption capacities in the range 10-100 $\mu\text{mol/g}$ and the softwood sawdust in the range 27-80 $\mu\text{mol/g}$, depending on the tree species and the metal ions studied. The unbleached kraft pulps showed sorption capacities of 20-50 $\mu\text{mol/g}$ for Ca^{2+} and 90

$\mu\text{mol/g}$ for Fe^{2+} (Duong et al. 2004; Chia et al. 2007). The sorption capacities of bark for different metal ions were reported to vary from 36-2100 $\mu\text{mol/g}$. These values have been summarized in an extensive review paper (Hubbe et al. 2011). In the studies listed in the review paper the ion-exchange sorption mechanism has also been confirmed by measuring the amount of hydrogen ions released from the biomass and it was found that that number matched the total number of metal ions adsorbed from the solution.

4. Analytical techniques

This chapter briefly describes the main analytical techniques used in this thesis. An automatic titrator was used for the acid-base titrations of wood, pulp and bark materials. A column chromatographic method was developed to study the sorption of metal ions to the wood, pulp and bark samples. The inductively coupled plasma optical emission spectrometry (ICP-OES) technique was applied to determine the concentrations of metal ions in the liquid samples. The laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) technique was used to study the distribution of metal ions in the solid samples.

4.1. Acid-base titrator

In this thesis an automatic titrator (Mettler Toledo DL 50, Schwerzenbach, Switzerland) was used in determination of the concentration of the functional groups in the wood, pulp and bark materials (Figure 12). This titrator is a microprocessor-controlled analytical instrument which includes a DG111 combined glass-reference electrode with a ground-glass sleeve junction for potentiometric measurement (Toledo 1997).



Figure 12. Mettler Toledo DL 50 titrator (© Mettler-Toledo International Inc.).

The standard *KOH* solution used as the titrant is pumped from a sealed bottle to the burette, and then delivered to the sample vessel. The titration is controlled by a program in which the measurement conditions, i.e. the potential change within preset time, the volume of the titrant added within a defined potential difference and waiting time up to the next increment addition etc., can be defined (Toledo 1997). The equilibrium potential and the volume of the titrant added are recorded after each addition. These data are transferred to a computer after the titration, and are used to calculate the concentration of acid groups in samples by the FITEQL program and the Gran method.

4.2. Ion exchange techniques

The ion exchange analysis is generally performed by two techniques: batch operation and column technique. In the batch operation, the ion exchanger is mixed with the solution containing ions of interest in a suitable vessel. The suspension is stirred until reaction equilibrium has been reached. After mixing, the two phases are then separated by filtration for further chemical analysis. This operation is simple and quite suitable for the basic study of a specific ion exchange reaction.

In the column chromatography the ion exchange material is packed in a column, usually in a glass column. Solution containing metal ions of interest is loaded to the column. The metal ions pass through the ion exchanger inside the column and are bound to the solid phase of the exchanger according to their selectivity. After this step the bound ions can be eluted out from the column with some suitable solutions. The eluate is collected in small fractions for analysis of metal ions that were bound to the materials in the column. The column technique is the most frequently used ion exchange method (Willard et al. 1988; Bobleter and Bonn 1991). This method is more effective than the batch method, and gives far better separations. However this method is more time consuming because a large number of eluate fractions must be collected and analyzed.

In column operations, the following terms are commonly used: influent, eluent, effluent, eluate and elution (shown in Figure 13). Influent refers to the solution entering the column. If it is used to remove the ions adsorbed on the solid phase of the ion exchanger, it is called the eluent. The solution coming out from a column is called the effluent. If it contains the ions that were bound to the ion exchanger, it is called the eluate. The whole process of removing adsorbed ions is called elution (Ringbom 1963).

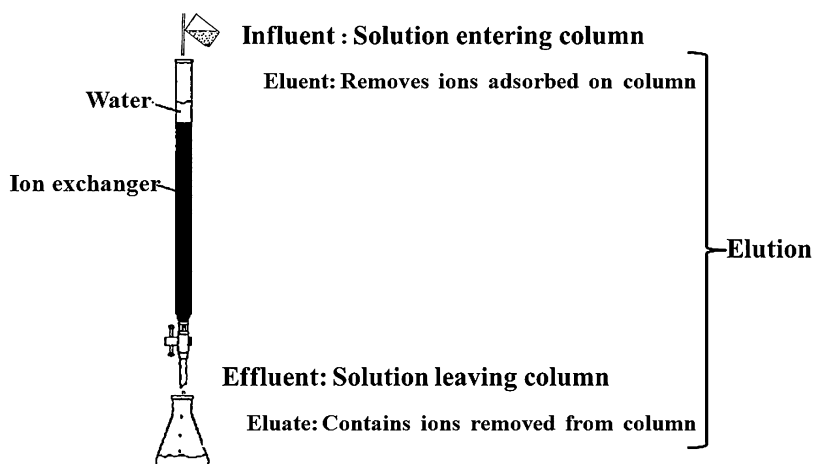


Figure 13. Important chromatographic terms related to the column technique.

During the ion exchange process, when the metal ions pass through the solid phase in the column, their rate of movement (elution) is affected by their sorption tendency to the solid phase. The metal ions having the highest selectivity to the solid phase are firstly bound and eluted out last from the column. The metal ions having the lowest affinity are weakly bound and they are eluted first from the column. A schematic diagram of a chromatographic process is shown in Figure 14a. The loading solution applied to the column contains metal ions of A, B and C; they have different affinity to the solid phase of the ion exchanger. Of them, A has the highest bounding strength and C has the lowest bounding strength. If the difference between their selectivity is large enough, their elution curves are separated and the metal ions come out one by one as shown in the chromatogram (Figure 14b). In the ideal case the elution curves of the metal ions are Gaussian (symmetric).

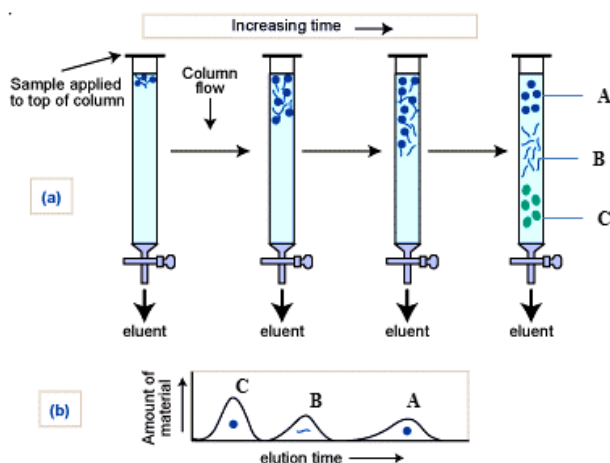


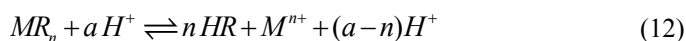
Figure 14. Elution of a metal mixture from a chromatographic column, a) a solution containing 3 different ions (A, B and C) is loaded to a column, b) the chromatogram of these three ions (Seidman and Mowery 2006).

In this thesis work, the wood, pulp and bark materials studied have functional groups with negative charges that can react with metal ions mainly by ion exchange. These functional groups are generally protonated at acidic pH values with dilute nitric acid. When a solution containing metal ions of interest is mixed with or loaded to these tree-related materials, the metal ions are exchanged with the hydrogen ions in the solid phase of the material studied. That process can be described by the following general ion exchange equilibria (9)-(11):



N and M are metal ions with the charge $1+$ and $n+$. The hydrogen ions released from the material are stoichiometrically equivalent to the total number of metal ions bound to materials. The ion exchange reactions between the functional groups in the solid phase and the metal ions in the solution phase are not simple processes, mainly due to the complexity of the ion binding sites in wood, pulp and bark materials. In addition, the metal ions participating in the reactions can have mono-, di- or even trivalent charge. During the course of interaction of metal ions with tree-related materials, the metal ions having the higher affinity replace the metal ions having the lower affinity.

In the column operations, dilute solutions of nitric acid are commonly used as the eluent and the bound metal ions are replaced by the hydrogen ions. When the metal ions bound to the solid phase are eluted out from the column with diluted nitric acid solution, an excess of hydrogen ions, $(a-n)H^+$, are also simultaneously eluted out from the column. This is described by the following general ion exchange equilibrium:



In this thesis, the batch method was used to investigate the equilibration time for the sorption of metal ions to the materials studied under particular experimental conditions. The column chromatographic method was used to study the ion exchange reactions of metal ions with different tree-related materials. The operating capacity and the affinity order of metal ions adsorbed to wood, pulp and bark materials were established by column technique.

4.3. ICP-OES technique

The ICP-OES technique is an atomic spectroscopic method and commonly used for determination of the concentrations of elements in liquid samples. In principle, ICP-OES can be used to determine over 70 elements simultaneously and it can be performed over a wide concentration range.

The main components included in the ICP-OES system are the nebulizer, the ICP torch and the spectrometer as shown in Figure 15 (Boss and Fredeen 1997). The sample is usually a liquid sample; it is transported into the nebulizer through a very thin tube by a pump. A high-speed argon gas flows through the nebulizer and the liquid is broken up to droplets and converted into an aerosol. The created sample aerosol is then transported into a spray chamber, which is placed between the nebulizer and the torch. Inside the spray chamber, the large droplets in the sample aerosol are removed, and only small droplets of uniform size are injected into the plasma. Inside the ICP torch, the atoms and ions of the elements are excited by the high temperature argon plasma (as high as 10000 K). The

excited atoms and ions emit their characteristic radiations at specific wavelengths. A monochromator is used to separate the wavelengths and the intensities of the radiations are measured with a detector system. The measured emissions intensities are then converted into concentration information using the calibration curves obtained with standard reference solutions. In this thesis, the ICP-OES (Optima 5300 DV, PerkinElmer, Ontario, Canada) was used to determine the concentration of metal ions in liquid samples collected in the experimental work.

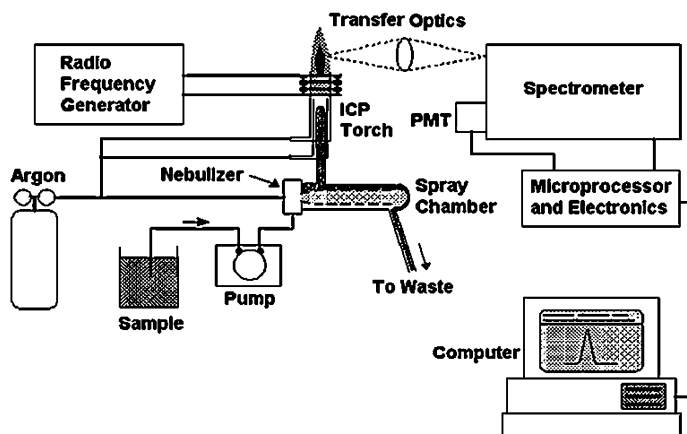


Figure 15. The principle and major components of a typical ICP-OES instrument (Boss and Fredeen 1997).

4.4. LA-ICP-MS technique

LA-ICP-MS is a powerful and versatile technique for direct analysis of solid samples to determine trace element concentrations and their distributions. With the mass spectrometer as the detector even the different isotopes of the elements can be detected. The general layout of a laser ablation inductively coupled plasma mass spectrometer system is shown in Figure 16.

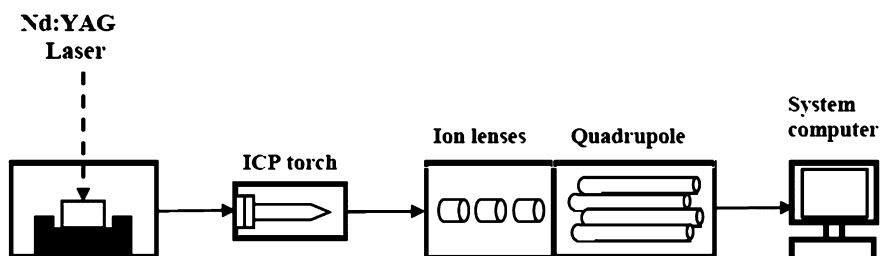


Figure 16. Schematical configuration of a LA-ICP-MS system (Figure 1 in Paper V).

A solid sample is placed inside an ablation chamber and a laser beam is focused directly on the surface of the solid sample. A certain amount of sample is ablated, i.e. partially vaporized and ionized to form a dry aerosol. The ablated sample is then transported to the ICP-MS instrument by a carrier gas, usually by the argon gas. The sample aerosol is firstly atomized or ionized by the high temperature plasma in the ICP torch. The ions produced in the ICP-torch pass through the ion lenses and then enter the mass spectrometer. In the MS part of the instrument, the ions are separated and analyzed based on their specific mass-to-charge ratio (m/z).

There are many advantages to use the LA-ICP-MS technique, including direct analysis of solid sample, reducing sample preparation and minimizing the risk of sample contamination (Masters and Sharp 1997; Durrant 1999; Hoffmann et al. 2000; Heinrich et al. 2003; Lee et al. 2003). Due to the unique advantages, LA-ICP-MS technique has been widely applied to analyze a variety of solid materials, such as human hair and nails, wood and archaeological samples (Prohaska et al. 1998; Devos et al. 2000; Hoffmann et al. 2000; Rodushkin and Axelsson 2000; Tokareva et al. 2010). However the quantification of the analytical results are rather difficult due to a number of problems (Cromwell and Arrowsmith 1995; Bellotto and Miekeley 2000; Ødegård et al. 2001; Ohata et al. 2002). Therefore LA-ICP-MS technique is mostly commonly used to investigate the distribution of elements by surface mapping, providing semi-quantitative analytical data.

In this thesis, The LA-ICP-MS was used to study the distribution of metal ions in single pulp fibers. The analytical results were quantified by using calibration curves obtained both with prepared standard single fibers and with standard cellulose pellets.

5. Experimental

5.1. Materials

The materials studied in this work include wood particles from spruce and birch, thermomechanical pulps (TMP) treated with different chemicals, unbleached/oxygen-delignified hardwood and softwood kraft pulps, and inner and outer bark of spruce. A synthetic weakly acidic cation exchanger and pure cotton fibers were also studied for the comparison of the sorption properties. The wood, pulp and bark materials were stored in a freezer until used in the experiments. Their water content was determined by oven drying at 105°C for ca. 24 hours. All results presented in this thesis are given on oven dry weight (d.m.) of the solid samples.

The wood samples were prepared from Norway spruce (*Picea abies*, 47-years old) and birch (*Betula pendula*, 25-years old) trees. Of Norway spruce, the sapwood and heartwood were separated for the study. The wood materials were milled to particles of 1-mm and 2-mm. Before used in the sorption experiments, all the wood samples were extracted with acetone in a Soxhlet apparatus. The preparation procedure for wood samples is presented in detail in the experimental part in *Paper I*.

The original TMP, made from Norway spruce (*Picea abies*), was taken out from a second refiner in a Finnish pulp mill. Different treatments were done in the laboratory on the original TMP. The TMP samples used for experiments are untreated TMP, alkali-treated TMP and peroxide-bleached TMP. The treatment processes are described in detail in the experimental part in *Paper II*. The unbleached/oxygen-delignified hardwood and softwood kraft pulps were obtained from a Finnish kraft mill. The preparations of unbleached kraft pulps for metal sorption experiments are presented in *Papers III* and *IV*. The preparations of single fibers for the LA-ICP-MS analysis are described in *Paper V*.

Bark samples were taken from Norway spruce (*Picea abies*) trees and milled to particles of 0.5-mm in a laboratory mill. Inner bark and outer bark were separated manually for the study. Prior to sorption experiments, the bark samples were treated with acetone, ethanol, distilled water and distilled hot water. The details for the sample preparation are described in the experimental part in *Paper VI*.

The commercial weakly acidic cation exchanger is Amberlite IRC-76 in hydrogen form (Sigma, St Louis, USA). The cotton fibers are of 100% pure cotton for medical purposes (Tamro Oyj, Finland). These samples were acid washed until free from metal ions, before used for further sorption experiments.

5.2. Main chemicals

The stock solutions (0.1 M) of most metal ions used in this work were prepared from their respective nitrate salts (Merck, Darmstadt, Germany). The divalent iron stock solution (0.1 M) was prepared by dissolving $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in deionized water. All the salts used were of *pro analysi* grade. Deionized water ($\geq 18.2 \text{ M}\Omega \cdot \text{cm}$, Purelab Ultra MK2, ELGA) was used throughout this work.

5.3. Methods

5.3.1. Batch method

The batch method was used for the characterization of sorption properties of different tree-related materials in this work, including potentiometric acid-base titration and batch metal sorption method. The potentiometric acid-base titration method was used to determine the concentrations of functional groups and their protonation constants in all the materials studied in this work. All the samples for the titrations were prepared by washing with 0.01 M HNO_3 , deionized water and 0.1 M KNO_3 in sequential order. Accurately weighed samples were dispersed in a 0.1 M KNO_3 solution and then acidified to pH 2 with a solution containing 1 M HNO_3 and 0.1 M KNO_3 . The potentiometric titrations were carried out up to pH ca. 12.5. The sample preparation and titration procedure are described in detail in *Papers II* and *III*.

The batch method was also used to study the equilibrium time for the sorption of metal ions to wood and bark materials. Before the batch metal sorption experiments, the sample had to be washed free from the naturally occurring metal ions. An accurately weighed sample (ca. 4 g, d.m.) was mixed with 100 ml deionized water in a glass beaker. In the adsorption experiments, a mixture of metal ions studied was added to react with the acid groups in the sample and the pH in the suspension was recorded as the function of time during the course of the adsorption. In the desorption experiments, the sample was first loaded with the metal ions of interest. A nitric acid solution was added to release the metal ions from the samples. The pH of the suspension was recorded as the function of time during the desorption course. The experimental procedures are described in detail in *Papers I* and *VI*.

5.3.2. Column method

The column chromatographic method was used to investigate the sorption capacities (operating capacities) of the materials studied and to establish the orders of affinity of different metal ions bound to these materials, as well as the contributions of each metal ion to the sorption capacities. A glass column was used in the column chromatographic

experiments for metal sorption studies. The size of the glass column used, e.g. diameter and length, varied in the course of this thesis. The mass (d.m.) of sample packed in the column also varied in different sorption experiments. The steps for the column chromatographic sorption experiments are presented schematically in Figure 17. The details for the whole procedure are described in the experimental parts in *Papers II and III*.

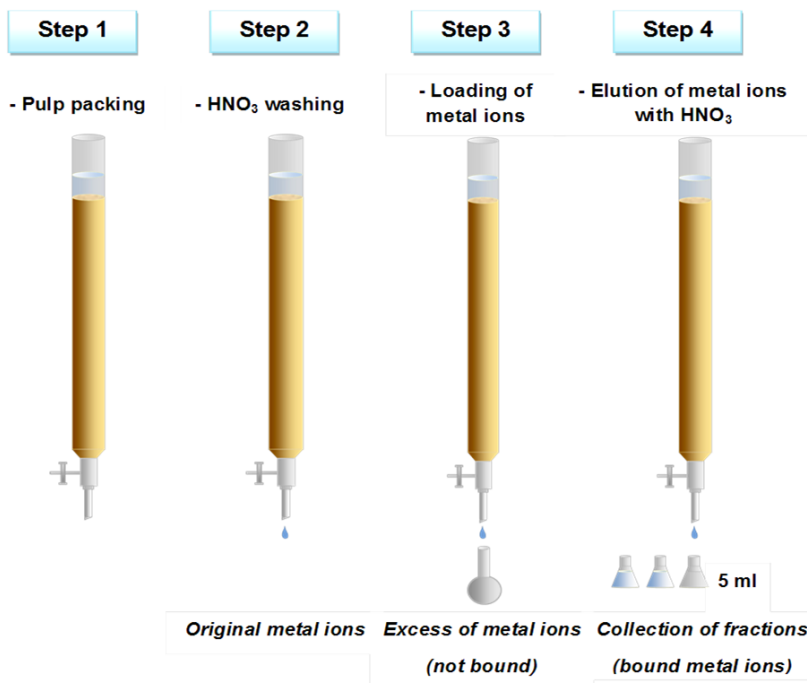


Figure 17. Column chromatographic procedure for metal sorption experiments (Figure 1 in *Papers II and VI*).

6. Results and discussion

6.1. Protonation constants and concentrations of acid groups in wood, pulp and bark

Protonation constants of the functional groups in wood, pulp and bark materials and their concentrations have been determined in *Papers I-IV* and *Paper VI*. At the beginning of this thesis work, a model with three acid groups was used in the FITEQL program in running the experimental data obtained in titrations of the unbleached softwood kraft pulps (*Paper III*). Later, a model with four acid groups was found to give a slightly better fitness to the recorded potentiometric titration data. The protonation constants of the acid groups and their concentrations in all the materials studied in this thesis are summarized in Tables 4 and 5. The sums of these concentrations, given in the last line of Table 5, are regarded as the total sorption capacity of the materials studied.

Of the acid groups determined in wood and pulp samples, two are of carboxyl types and the other two are of phenolic hydroxyl type. The protonation constants ($\lg K_{HR}^{H,R}$) for the strongest carboxyl groups (HR_1) are in the range 3.3-4.2. These groups can be assigned to uronic acids contained in hemicelluloses and pectin substances. The second carboxyl groups (HR_2) have protonation constants in the range of $\lg K_{HR}^{H,R} \sim 4.7-5.9$, and they may be the carboxyl groups associated with lignin structure. Those two groups with the protonation constants in the range of $\lg K_{HR}^{H,R} \sim 6.5-8.0$ and 8.4-10.4 are obviously phenolic hydroxyl groups in lignin.

The value of the protonation constants of the acid groups in wood and pulp depends on the side groups conjugated to them. The side groups vary with the type of the materials and with the chemical treatments of the samples. The protonation constants of the acid groups in the untreated mechanical pulps are close to those in the native wood, because the main components in native wood are maintained in the mechanical pulping. Chemical treatments of TMP, e.g. the alkaline treatment and the peroxide bleaching, change the acid groups and increase the strength of the acid groups. The kraft pulps contain stronger acid groups compared to the native wood, since the acid groups in the native wood are changed and converted during kraft pulping, for instance, methylglucuronic acid groups in xylan are converted to hexenuronic acid units. The oxygen delignification further increases the strength of these acid groups. This is more pronounced for oxygen delignification of hardwood kraft pulps (Table 4).

The strongest carboxyl groups (HR_1) present in spruce bark are similar to those in native wood. These groups have the $\lg K_{HR}^{H,R}$ value of 3.9. They might mainly be of uronic acid

type in the pectin substances which are present both in native wood and bark. The other three acid groups in bark slightly differ from those in the native wood. The second acid groups, HR_2 , is most probably also a carboxyl group with $\lg K_{HR}^{H,R}$ values of 5.9-6.1. The HR_3 and HR_4 are phenolic hydroxyl groups having $\lg K_{HR}^{H,R}$ values in the range 8.2-10.7. The bark contains tannins, which probably contribute to the contents of carboxyl and especially the phenolic hydroxyl groups.

Sjöström (1993) has reported pK_a values ($\lg K_{HR}^{H,R}$) in wood of around 3-4 for major carboxyl groups, 4-5 for minor carboxyl groups, 7-8 for minor phenolic acidic groups and 9.5-10.5 for major phenolic hydroxyl groups. Koljonen et al. (2004) found carboxyl groups in CTMP pulps with $pK_a \sim 3-5$ and $pK_a \sim 5-6$. Both in native wood and in mechanical pulps the majority of the carboxyl groups are of uronic acid types mainly attached to the xylan. Some of the carboxyl groups originated from pectin substances and a relatively small amount was also found in lignins. Laine et al. (1996) found that both unbleached softwood and hardwood kraft pulps contained two types of carboxyl groups, with $pK_a \sim 3.3$ and $pK_a \sim 5.5$. For the unbleached softwood (pine) kraft pulps two different carboxyl groups with the pK_a values of 3.6 and 5.7 have also been reported (Stenius and Laine 1994). Karhu (2008) and Karhu et al. (2000) have determined protonation constants and concentrations of both the carboxyl and phenol groups at different temperatures (25, 45, 65 and 85°C) for unbleached and oxygen-delignified softwood and hardwood kraft pulps. They reported protonation constants ($\lg K_{HR}^{H,R}$) of carboxyl groups in the range 3-6 and $\lg K_{HR}^{H,R}$ of phenol groups in the range 9-10. The temperature was found to have a remarkable influence on the concentration of phenolic groups. So far quite a few studies have been done on the protonation of phenol groups in pulps. Karhu (2008) has also shown that during potentiometric re-titration of pulps at 25°C the components containing both carboxyl and phenol groups were dissolved to the solution phase. The dissolved compounds have the similar protonation constants as the original pulp sample. The phenolic acid groups in particular were found to dissolve in the solution during both first and second titrations, and the total content of acid groups in the two phase system increased.

Table 4. Protonation constants ($\lg K_{HR}^{H,R}$) of functional groups in wood, pulp and bark samples.

Acid groups	Wood		TMP		Kraft pulp		Spruce Bark			
	Spruce	Birch	Un-treated	Alkali-treated	Softwood	Hardwood	Inner	Outer		
	Heartwood	Sapwood	Peroxide-bleached		Un-bleached	Oxygen-delignified	Un-bleached	Oxygen-delignified		
HR_1	4.0	3.9	4.2	3.6	3.7	3.6	3.6	3.3	3.9	3.9
HR_2	5.6	5.7	5.9	4.9	5.5	5.2	5.1	4.7	6.1	5.9
HR_3	7.9	7.9	7.9	7.4	7.5	7.0	7.3	6.5	8.4	8.2
HR_4	10.1	9.9	10.2	10.0	9.3	8.8	8.7	8.4	10.7	10.5

Table 5. Concentrations ($\mu\text{eq/g, d.m.}$) of functional groups in wood, pulp and bark samples.

Acid groups	Wood		TMP		Kraft pulp		Spruce Bark			
	Spruce	Birch	Un-treated	Alkali-treated	Softwood	Hardwood	Inner	Outer		
	Heartwood	Sapwood	Peroxide-bleached		Un-bleached	Oxygen-delignified	Un-bleached	Oxygen-delignified		
HR_1	56	55	42	87	67	69	110	130	440	270
HR_2	20	18	11	37	20	22	23	40	66	74
HR_3	17	14	11	15	19	18	10	18	98	120
HR_4	50	43	72	48	30	19	10	18	590	520
Total	143	130	191	187	136	128	153	206	1194	984

A comparison of the concentrations of acid groups in different samples shows that the total content of acid groups in native woods, unbleached mechanical pulps and unbleached kraft pulps are quite similar (Table 5). The alkaline treatment and peroxide bleaching of mechanical pulps significantly increase the total content of acid groups in samples. Both inner bark and outer spruce bark contains much more acid groups than wood and pulp samples.

The native hardwood (birch) contains more acid groups than the native softwood (spruce), mainly due to the higher concentration of phenolic hydroxyl groups (HR_4). Concentration of the phenolic hydroxyl groups in hardwood is almost double that in softwood. The spruce heartwood contains somewhat more acid groups than the spruce sapwood, also mainly due to the higher concentration of HR_4 . Concentrations of the two strongest acid groups, HR_1 and HR_2 types, in hardwood and softwood are almost the same. The uronic type of acid groups (HR_1) contributes to the total acid groups by 39-42% in softwood, and by 30% in hardwood.

During the mechanical pulping, some acid groups of uronic type and of phenolic type are decreased due to partial dissolution of hemicelluloses and lignin. Some new free phenolic hydroxyl groups are simultaneously formed in the lignin structure, mainly due to the fragmentation of lignin during the mechanical treatment. On the whole, the concentration of HR_1 type acid groups in the mechanical pulps (untreated TMP) decreased by 24% and the concentration of HR_4 type acid groups increased by 59%, compared with their average concentration in the native wood (spruce). Total concentration of all the four acid groups in the untreated TMP has a similar value as that in the spruce native wood.

The chemical treatments (i.e. alkaline treatment and peroxide bleaching) of spruce TMP increase the concentration of carboxyl groups, especially the peroxide bleaching. The concentration of carboxyl groups ($HR_1 + HR_2$) in the alkali-treated TMP is twice, and in the peroxide-bleached TMP almost three times, higher than that in the untreated TMP. Koljonen et al. (2004) revealed that alkaline treatment of TMP mainly hydrolyzes the methyl ester groups in pectin, while peroxide bleaching increases also the amount of lignin-bound carboxyl groups. The concentration of phenolic hydroxyl groups decreases during these chemical processes. Approximately 33% of the phenolic hydroxyl groups (HR_4) was eliminated from the untreated-TMP during alkaline treatment, and about 47% of HR_4 was released during peroxide bleaching. In general the alkaline treatment and peroxide bleaching of spruce TMP increases the total content of the acid groups. This was also found by Goulet and Stratton (1990).

Kraft pulping creates some new acid groups, but some acid groups are simultaneously lost. In general, the total content of acid groups in unbleached kraft pulps is slightly higher than that in native wood. The concentration of uronic type of acid groups HR_1 increased during kraft pulping, accounting for 49-72% of the total content of acid groups in unbleached kraft pulps (30-43% in wood, Table 5). Oxygen delignification of kraft pulps slightly increases the concentration of this type of acid groups. It can also be observed in Table 5 that the concentration of the hydroxyl groups, as HR_4 type, decreased to a large extent during kraft pulping obviously due to the removal of lignin. Comparing hardwood kraft pulps with softwood kraft pulps, more acid groups were found in hardwood kraft pulps. This is mainly due to the higher concentration of the uronic acid carboxyl groups (HR_1) in hardwood kraft pulps. Similar results have also been observed by other groups (Herrington and Petzold 1992; Athley et al. 2001). Holmbom et al. (2002) found that in unbleached kraft pulps about 50% of the total acid group consisted of the uronic acids and in bleached kraft pulps uronic acid groups was 20-40% of the total content of acid groups.

Spruce bark contains much more acid groups, especially much higher content of the HR_1 and HR_4 type acid groups, compared with spruce stem wood. The higher HR_1 content is mainly due to high content of pectin substances abundant in bark. The higher HR_4 content in bark probably can be assigned to the higher content of phenolic compounds associated with lignin and also tannins. The total concentration of the acid groups determined in bark of spruce is approximately 7~9 times higher than that in stem wood of spruce. Of spruce bark, inner bark contains higher concentrations of HR_1 and HR_4 types of acid groups than outer bark. The concentration of HR_1 in inner bark of spruce is almost double that in outer bark, indicating a higher content of pectin in inner bark. The concentration of HR_4 type groups is ca. 13% higher in inner bark than in outer bark. The total concentration of functional groups in inner bark of spruce is higher than that in outer bark (Table 5).

6.2. Equilibration time for sorption of metal ions to wood and bark

The metal sorption experiments were carried out in a batch system to investigate the minimum time required to reach the reaction equilibrium. The details of the experiments are described in *Papers I and VI*. In these papers the time required for sorption respective desorption of metal ions to wood and bark materials has been studied. The sorption of metal ions to bark particles was found to be faster than to wood particles under the same experimental conditions. In *Paper I* it was shown that the reaction of metal ions with wood particle is quite fast during both sorption and desorption processes. The equilibrium of these reactions was attained within ca. 20 min for all the wood samples studied. During the first few minutes, the sorption/desorption was fast, then the rate gradually decreased and after ca. 20 min reaction equilibrium was reached. In *Paper VI* where spruce outer bark was studied it was shown that the equilibrium of these reactions was attained within ca. 5 min.

When the sorption of metal ions to tree-related materials were studied by column chromatographic technique in this thesis, the loading time (when all metal ions loaded to column pass through the sample inside) and the elution time (when metal ions bound are nearly completely washed out from column) were approximately 3-5 h. These times depend on the type and the mass of samples in the packed column. These results indicate that the time of the column chromatographic experiments was long enough for sorption equilibrium to be reached in the column.

The effect of the size of wood particles on the sorption time was also studied by using the batch technique. The birch wood was milled to particles with sizes of 1-mm and 2-mm. The sorption/desorption process was followed by measuring the pH of the solution phase (Figure 18). When metal ions are adsorbed or desorbed, hydrogen ions are released or taken-up, respectively. It was found that the reaction rate of metal ions with the smaller size wood particles is slightly faster than with the larger size particles in the beginning of the adsorption experiments. A similar result was also found in the desorption process. A possible explanation for this may be that the sample with the smaller particle size offers a larger total surface area, and therefore the accessibility of the binding sites on the sample surface is higher. Studies by other researchers also showed that the particle size and the available sorption sites on the materials affected the time needed to reach the sorption equilibrium (Naiya et al. 2008; Subbaiah et al. 2009; Reddy et al. 2010).

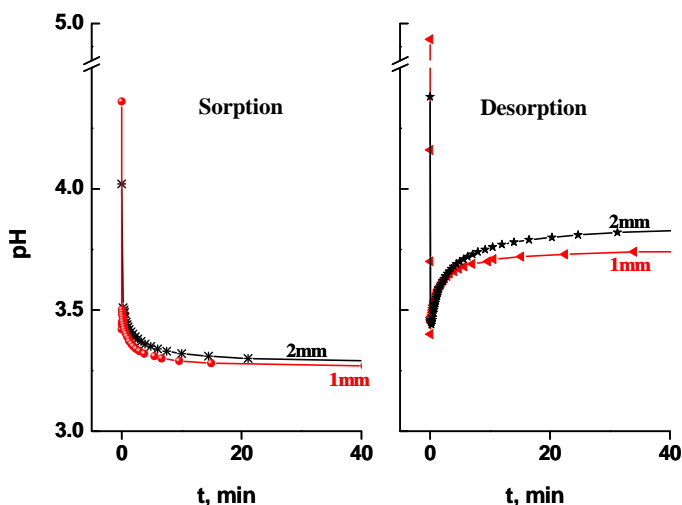


Figure 18. Reaction time for sorption respective desorption of metal ions to birch wood particles of different sizes.

6.3. Results of metal ion sorption using the column chromatographic technique

In this thesis work the materials studied included: spruce and birch wood particles (*Paper I*); untreated, alkali-treated and peroxide-bleached TMP (*Paper II*); unbleached/oxygen-delignified hardwood and softwood kraft pulps (*Papers III-IV*); spruce inner and outer bark (*Paper VI*); and synthetic weakly acidic cation exchanger (Amberlite IRC-76) and pure cotton fibers. Different metal ion mixtures, given in Table 1 in *Paper II*, were used to load the solid phase of samples in the chromatographic column. The affinity orders of metal ions to these materials were established by combining the results from several sorption experiments. The sorption capacities of materials (operating capacities) were also calculated by summing the concentration of each metal ion adsorbed to the materials.

Because the natural properties of the materials studied and their total capacities varied a lot (see Table 5), columns of different sizes were used in the experimental work in this thesis. The weight (d.m.) of the samples used and the height of the packed bed in the column (packed-bed height) also varied between the sorption experiments. In every experiment, the number equivalents of each metal ion in the loading mixtures were in excess compared to the total capacity of the material determined by the acid-base potentiometric titration method. In this chapter, the results from sorption experiments with different materials are summarized and briefly discussed, according to the different metal ion mixtures loaded to column. More detailed information about the experimental conditions and results can be found in *Papers I-IV* and *VI*.

6.3.1. Sorption of Ba, Sr, Ca and Mg ions

The elution curves of the sorption experiments with alkaline earth metal ions (Ba^{2+} , Sr^{2+} , Ca^{2+} and Mg^{2+}) performed on pulp and bark materials are summarized in Figure 19. The x-axis is the volume of the eluate (ml) and y-axis is the concentrations of the metal ions in each eluted fraction collected in Step 4 (Figure 17). The pH of eluate in each fraction is given to the right on the y-axis. The elution curves in Figure 19 show that the metal ions have been adsorbed by different strength to the samples in the sorption process (Step 3 in Figure 17).

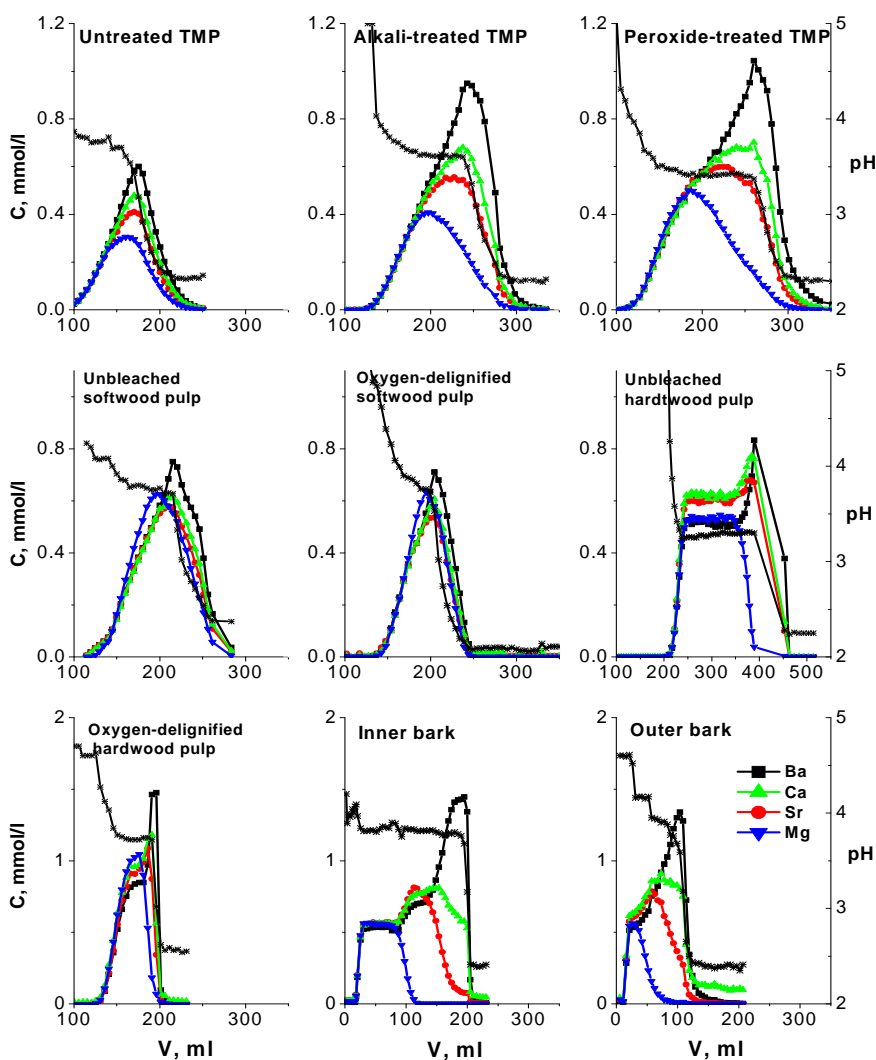


Figure 19. Concentrations of alkaline earth metal ions and pH in the collected fractions as function of the elution volume for different pulp and bark samples.

As can be seen in Figure 19, the alkaline earth metal ions generally show elution curves of different shapes. For all the samples studied barium ions show the broadest elution curves and highest concentration peaks compared with the other three alkaline earth metal ions. Thus of the alkaline earth metal ions barium is the most strongly bound to pulp and bark materials. Magnesium ions show the smallest concentration peaks and has the narrowest elution curves. Magnesium ions thus are most weakly adsorbed to pulp and bark materials. The affinity order can also be established as these metal ions were eluted out at different elution volumes. In all the sorption experiments with alkaline earth metal ions, magnesium ions were first completely eluted out from the column and barium ions were the last to be eluted from the column. This is most pronounced in those sorption experiments with TMP and bark samples. The following affinity sequence can be obtained from the elution curves in Figure 19: $Ba^{2+} > Ca^{2+} > Sr^{2+} > Mg^{2+}$.

The shapes of the elution curves of the alkaline earth metal ions differ with the type of materials studied. The elution curves of each metal ion are rather well separated for the TMP and bark samples. However, the elution curves of these metal ions are rather similar and not so well separated for the kraft pulps. Variations of the elution curves may be due to the variable total capacities of different materials studied and also to the different types of functional groups in the materials. Of the mechanical pulps (TMP) studied, the peroxide-bleached TMP shows the broader elution curves and higher concentration peaks for each alkaline earth metal ion. This can be explained by a higher content of acid groups in the peroxide-bleached TMP. Of the kraft pulps studied, the unbleached kraft pulps show broader elution curves than the oxygen-delignified pulps. A most probable reason for this is that in these sorption experiments more unbleached kraft pulps were packed, e.g. 16.1 g of unbleached hardwood pulps vs 7.9 g of oxygen-delignified hardwood pulps, in the column.

It also can be observed in Figure 19 that the volumes of breakthrough of the elution curves vary a lot with different samples. This is mainly due to the different length of samples packed in the column and the diameter of the column used, and also due to the variable mass of samples used in the experiments. Other studies found that the breakthrough volume and time of elution curves were dependent on bed height and flow rate (Chen et al. 2011; Ramesh et al. 2011; Chowdhury et al. 2012; Nwabanne and Igbokwe 2012). The steeper curves were obtained after breakthrough volume with lower bed height and the breakthrough time decreased with increasing flow rates.

The amount of samples (d.m.) packed in the column varied from experiment to experiment, thus the contents of the metal ions adsorbed to the materials cannot directly be read and compared from the elution curves. Table 6 summarizes the operating

capacities of the materials studied and the concentrations of each alkaline earth metal ion adsorbed under the experimental conditions.

Table 6. Operating capacities and concentrations of each metal ion adsorbed to pulp and bark samples. Weights (d.m.) of samples packed in column also included in the table.

<i>Materials</i>	<i>Weight</i> <i>g</i>	<i>Ba</i> <i>μeq/g</i>	<i>Ca</i> <i>μeq/g</i>	<i>Sr</i> <i>μeq/g</i>	<i>Mg</i> <i>μeq/g</i>	<i>Operating</i> <i>Capacity</i> <i>μeq/g</i>
<i>Untreated TMP</i>	5.0	15	13	11	8.9	48
<i>Alkali-treated TMP</i>	6.6	24	19	16	11	70
<i>Peroxide-bleached TMP</i>	7.7	27	22	19	13	81
<i>Unbleached softwood pulp</i>	11.7	9.6	8.4	8.1	8.2	34
<i>Oxygen-delignified softwood pulp</i>	6.0	13	12	11	11	47
<i>Unbleached hardwood pulp</i>	16.1	14	14	13	9.6	51
<i>Oxygen- delignified hardwood pulp</i>	7.9	13	13	11	10	47
<i>Inner bark of spruce</i>	2.1	140	120	89	41	390
<i>Outer bark of spruce</i>	2.0	90	88	58	21	257

It can be seen in Table 6 that different materials show different sorption capacities (operating capacities) for alkaline earth metal ions in these sorption experiments. The peroxide-bleached TMP has a higher operating capacity than the alkali-treated TMP, followed by the untreated TMP. This indicates that of the mechanical pulps studied the peroxide-bleached TMP has highest number of binding sites (acid groups). This agrees well with the results obtained from potentiometric acid-base titrations given in Table 5. In those sorption experiments with chemical pulps, the operating capacity of the softwood kraft pulps (unbleached) is lower than that of the hardwood kraft pulps (unbleached). The oxygen-delignified softwood pulps show a higher sorption capacity than the unbleached softwood pulps. However for hardwood pulps, the sorption capacities of the unbleached and oxygen-delignified pulps are similar. In the experiments with spruce bark, the inner bark of spruce has a higher operating capacity for the alkaline earth metal ions than its outer bark, but both the inner bark and the out bark show much higher operating capacity than the wood and pulp materials. The results in this part show that the operating capacities of the materials are generally related to the total concentrations of their acid groups. The more acid groups are in the material, the higher is the operating capacity.

From Table 6 it can also be observed that in the all sorption experiments with alkaline earth metal ions the concentrations of barium adsorbed to pulp and bark are the highest

and the concentrations of magnesium are the lowest. Calcium and strontium are adsorbed approximately in equal amounts to pulp samples, but in clearly different amounts to bark samples. The concentration of calcium ions in bark is much higher than that of strontium ions. Of the alkaline metal ions, therefore, barium is the strongest bound and magnesium the weakest bound to the pulp and bark materials. Calcium ions are bound stronger than strontium ions to bark sample, but their affinity to kraft pulps is similar. From Table 6 the following general affinity order can also be estimated:

For mechanical and kraft pulps: $Ba^{2+} \geq Ca^{2+} \geq Sr^{2+} > Mg^{2+}$

For spruce bark: $Ba^{2+} > Ca^{2+} > Sr^{2+} > Mg^{2+}$.

6.3.2. Sorption of Cd, Zn, Ni, Mn, Ba, Sr, Ca, Mg, Rb, K, Na and Li ions

Figure 20 shows the elution curves obtained from the sorption experiments with wood, pulp and bark materials using a solution containing Cd^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} , Rb^+ , K^+ , Na^+ and Li^+ . It can clearly be observed in this figure that for all the materials studied cadmium ions have the broadest elution curves and the highest concentration peaks, followed by Zn^{2+} and then Ni^{2+} . Thus these metal ions are most strongly bound in these sorption experiments. The differences in the elution curves of alkaline earth metal ions are not as clear as they showed in Figure 19. This is due to the competition with the strongly binding metal ions, e.g. Cd^{2+} and Zn^{2+} , to the functional groups in samples. Of the divalent metal ions, magnesium shows the narrowest elution curves with the lowest concentration peaks. The alkali metal ions, i.e. Rb^+ , K^+ , Na^+ and Li^+ , show the smallest concentration peaks in the elution curves. With the scale used for the y-axis, their elution curves are almost invisible for some samples, e.g. the untreated and the alkali-treated TMP. They were first completely eluted out from the column and thus most weakly bound to the materials studied in these experiments. From the elution curves in Figure 20 the following affinity order can roughly be established for all materials studied: $Cd^{2+} > Zn^{2+} > Ni^{2+} > Ba^{2+}$, Mn^{2+} , Sr^{2+} , $Ca^{2+} > Mg^{2+} > Rb^+$, K^+ , Na^+ , Li^+ .

Comparing the different types of materials studied, the elution curves of Cd^{2+} and Zn^{2+} are quite well separated from those of the other metal ions for wood and bark materials (Figure 20). This might be mainly due to the type of acid groups and also the total content of acid groups involved in the sorption experiments. The masses of wood samples packed in the column were much higher than of other samples (Table 7), leading to higher total number of binding sites participating in the sorption experiments. The bark materials have much higher contents of acid groups than the other materials used (Table 5), also leading to more binding sites involved in the column sorption experiments. For the unbleached softwood pulps the differences in the elution curves of metal ions studied are less noticeable, since the concentration of acid groups in this type of pulps is lower and also a lower amount of sample was used for the sorption experiments.

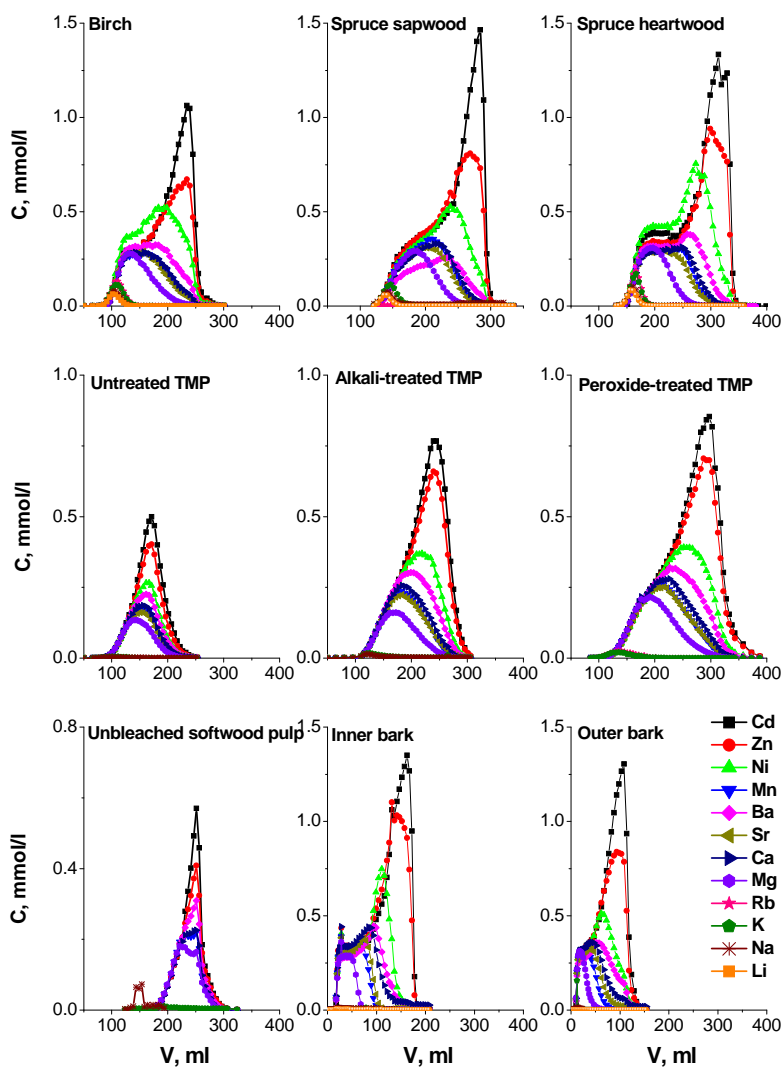


Figure 20. Concentrations of 12 metal ions in the collected fractions as function of the elution volume for wood, pulp and bark samples.

In the experiments with the wood materials (same amount of birch and spruce samples were used), birch shows the lowest concentration peaks in the elution curves of the heavy metal ions, i.e. Cd^{2+} , Zn^{2+} and Ni^{2+} . In the experiments with the mechanical pulps, the untreated TMP bound lower content of metal ions and shows the smallest elution curves for all the metal ions studied. This means that the total number of metal ion binding sites is lower in the sorption experiment with the untreated TMP, compared to that in the experiments with the alkaline-treated and peroxide-bleached TMP. In the experiments with bark materials, the outer bark bound less metal ions and shows the smaller elution

curves compared to the inner bark. This result indicates that the outer bark has the lower concentration of acid groups than the inner bark. This was also shown by the potentiometric pH titrations (Table 5).

Table 7 summarizes the operating capacities of different materials studied and the concentrations of the 12 metal ions bound in these sorption experiments. The dry masses of the samples used in the column sorption experiments are also included in Table 7. In these sorption experiments the operating capacity of spruce is slightly higher than that of birch. The native wood of spruce shows the lower operating capacity than its mechanical pulps (untreated TMP) and its kraft pulps (unbleached softwood pulps). Of the mechanical pulps, the operating capacity of the untreated TMP is 51 µeq/g. The alkaline treatment and the peroxide bleaching of the untreated TMP increased the sorption capacity by 59% and 84%, respectively. Both the inner bark and outer bark of spruce show much higher sorption capability than the wood and pulp materials. The operating capacity of inner bark of spruce is higher than that of outer bark. The operating capacities of most materials obtained in these experiments with 12 metal ions (Table 7) are higher than the results obtained in the sorption experiments with alkaline earth metal ions (Table 6).

From Table 7 it can be seen that for all the studied materials Cd^{2+} , followed by Zn^{2+} and Ni^{2+} , are strongest bound. For other divalent metal ions in these sorption experiments, the differences in their binding strength are quite small, but can still be distinguished in Table 7. The sorption of monovalent metal ions to materials is minimal when also divalent metal ions are present in the loading solution. The concentrations of alkali metal ions bound to samples are thus very low, in some cases even lower than the detection limit of the analytical method used. According to the concentrations of metal ions bound to the materials (Table 7), the following affinity orders were obtained:

For wood particles: $\text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \underline{\text{Ba}^{2+} > \text{Ca}^{2+} \geq \text{Mn}^{2+} \geq \text{Sr}^{2+}} > \text{Mg}^{2+} > \text{Rb}^+ \sim \text{K}^+ \sim \text{Na}^+ \sim \text{Li}^+$

For mechanical pulps: $\text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \underline{\text{Ba}^{2+} > \text{Ca}^{2+} > \text{Mn}^{2+} \geq \text{Sr}^{2+}} > \text{Mg}^{2+} > \text{Rb}^+ \sim \text{K}^+ \sim \text{Na}^+ \sim \text{Li}^+$

For chemical pulps: $\text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \underline{\text{Ba}^{2+} > \text{Mn}^{2+} \geq \text{Ca}^{2+}} > \text{Mg}^{2+} > \text{Rb}^+ \sim \text{K}^+ \sim \text{Na}^+ \sim \text{Li}^+$

For bark materials: $\text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \underline{\text{Ba}^{2+} \geq \text{Ca}^{2+} > \text{Sr}^{2+}} > \text{Mn}^{2+} > \text{Mg}^{2+} > \text{Rb}^+ \sim \text{K}^+ \sim \text{Na}^+ \sim \text{Li}^+$

Table 7. Operating capacities and concentrations of 12 different metal ions adsorbed to wood, pulp and bark samples. Weights (d.m.) of samples packed in column also included in the table.

<i>Materials</i>	<i>Weight</i> g	<i>Cd</i> μeq/g	<i>Zn</i> μeq/g	<i>Ni</i> μeq/g	<i>Mn</i> μeq/g	<i>Ba</i> μeq/g	<i>Sr</i> μeq/g	<i>Ca</i> μeq/g	<i>Mg</i> μeq/g	<i>Rb</i> μeq/g	<i>K</i> μeq/g	<i>Na</i> μeq/g	<i>Li</i> μeq/g	<i>Operating Capacity</i> μeq/g
<i>Birch</i>	18.2	8.6	7.0	6.6	3.1	4.1	3.0	3.2	2.2	0.2	0.2	0.1	0.1	38
<i>Spruce sapwood</i>	18.1	9.9	8.2	5.7	3.5	3.0	3.1	3.4	2.3	0.0	0.2	0.1	0.1	40
<i>Spruce heartwood</i>	18.2	12	9.8	8.6	3.8	5.0	3.3	3.8	2.3	0.3	0.2	0.2	0.1	49
<i>Untreated TMP</i>	5.0	11	9.2	6.7	4.7	6.0	4.4	5.0	3.6	bdl	0.0	0.1	bdl	51
<i>Alkali-treated TMP</i>	6.6	19	17	11	6.3	9.3	6.2	7.2	4.1	bdl	0.2	0.2	bdl	81
<i>Peroxide-bleached TMP</i>	7.7	22	19	13	7.5	11	7.3	8.6	5.4	bdl	0.2	0.1	bdl	94
<i>Unbleached softwood pulp</i>	3.0	14	12	/	8.6	10	/	8.4	7.3	bdl	0.3	0.5	bdl	61
<i>Inner bark of spruce</i>	2.1	97	90	52	22	35	24	36	11	/	0.3	0.5	0.1	368
<i>Outer bark of spruce</i>	2.0	75	60	36	13	27	17	23	7.0	/	0.2	0.1	0.0	258

bdl - below detection limit

/ - not included in the mixtures

6.3.3. Sorption of Pb, Cu, Cd, Zn, Ni, Mn, Ba, Sr, Ca, Mg, Rb, K, Na and Li ions

In this section, the sorption results will be discussed when Pb^{2+} and Cu^{2+} were added to the loading solution described in the previous section. In these experiments, there will be a sorption competition between 14 different metal ions. Figure 21 shows the elution curves obtained for wood, pulp and bark materials. Of the 14 metal ions studied Pb^{2+} and Cu^{2+} are clearly most strongly bound to all the samples studied. They dominate the sorption process in these sorption experiments. The presence of lead and copper ions radically decrease the sorption of the other metal ions in the mixture. With the scale used on the y-axis in Figure 21 the elution curves for the other 12 metal ions are small and somewhat overlap. The affinity order of the twelve other metal ions thus cannot accurately be established from these experiments. From the elution curves obtained in these sorption experiments, only the following affinity order can be established: $\text{Pb}^{2+} \gg \text{Cu}^{2+} \gg \text{Cd}^{2+}$.

It can also be observed in Figure 21 that for bark materials the separation of the elution curves of Pb^{2+} and Cu^{2+} is not as big as observed between the elution curves of these two metal ions obtained for wood and pulp materials, even though bark has much higher concentration of acid groups (binding sites, Table 5). The reason might be that the functional groups participating in the sorption reactions in bark are different from that in wood and pulp materials. It has been stated that bark tannins were active species in the metal sorption processes (Randall et al. 1974; Vázquez et al. 1994).

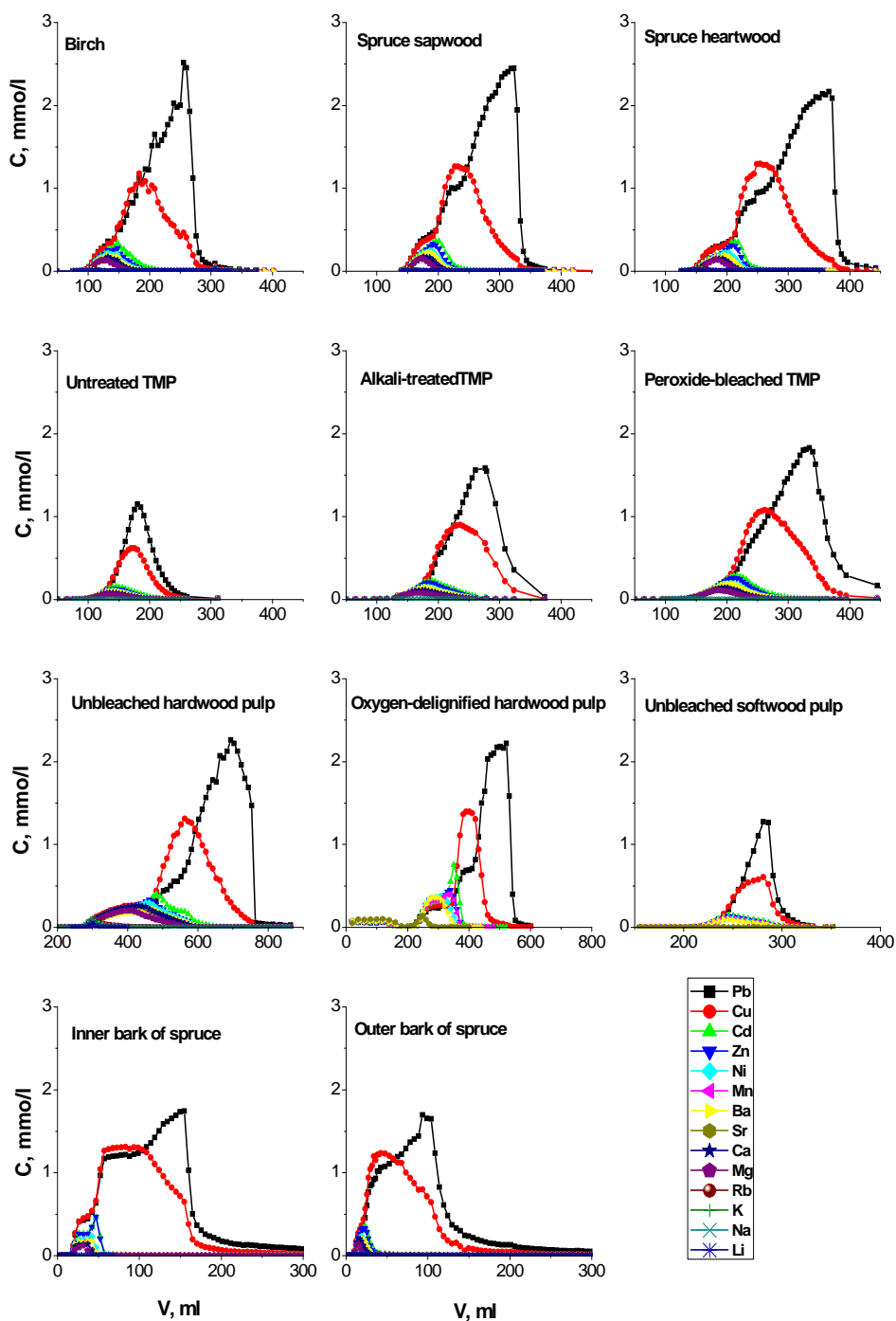


Figure 21. Concentrations of 14 metal ions in the collected fractions as function of the elution volume for wood, pulp and bark materials.

Table 8 summarizes the operating capacities of the materials studied and the concentrations of different metal ions adsorbed to the samples in the sorption experiments with 14 metal ions. It can be seen that the operating capacity of spruce heartwood is slightly higher than that of spruce sapwood. This is mainly due to the higher concentration of acid groups in the heartwood of spruce. Both the heartwood and sapwood of spruce exhibit slightly higher operating capacities than birch. In these sorption experiments with 14 metal ions the operating capacities of wood materials are lower than these of their mechanical pulps and chemical pulps. Of the mechanical pulps, the untreated TMP shows a lower operating capacity than the alkali-treated and peroxidized-bleached TMP. The alkaline treatment of mechanical pulps increases the content of acid groups, thus resulting in a higher operating capacity of the alkaline-treated TMP than the untreated TMP. Peroxide bleaching of mechanical pulps in alkaline condition further increases the operating capacity by producing some new acid groups. It can be seen in these sorption experiments that the alkaline treatment increased the operating capacity by 52% and the peroxide bleaching by 94%. Of the chemical pulps, the hardwood kraft pulps show higher operating capacities than the softwood kraft pulps when using similar metal ion mixtures to load the samples. This is most probably because of that the hardwood kraft pulps have a higher concentration of acid groups. The operating capacities of the unbleached and oxygen-delignified kraft pulps do not differ significantly in these sorption experiments.

The operating capacities of bark materials are much higher than those of wood and pulp materials. This is due to the fact that much more acid groups were found in bark (Table 5). Of the spruce bark, the inner bark shows stronger adsorption tendency to most metal ions than the outer bark, since more acid groups were found in the inner bark of spruce.

For all the materials studied in these experiments, Pb^{2+} and Cu^{2+} are strongly bound and they clearly dominate the sorption process. The other metal ions are adsorbed to the materials in rather low concentrations (Table 8). Approximately 51-54% of the active binding sites (operating capacity) in wood materials are occupied by lead, in TMP materials 44-46%, in kraft pulp materials 40-55 % and in bark materials 51-53%. The concentrations of copper adsorbed stands for 23-29% of the operating capacities of wood and pulp materials, and 37-38% of bark materials. From Table 8, the following affinity order can be established for all the materials studied: $Pb^{2+} \gg Cu^{2+} \gg Cd^{2+} > Zn^{2+} > Ni^{2+}$. For the rest of the metal ions studied in these experiments, their affinity order cannot accurately be distinguished from each other because their sorption is so much decreased by the presence of Pb^{2+} and Cu^{2+} . However their affinity order has already been established with loading solutions described in the previous sections (Tables 6 and 7).

Table 8. Operating capacities and concentrations of 14 different metal ions adsorbed to wood, pulp and bark samples. Weights (d.m.) of samples packed in the column are also included in the table.

Materials	Weight g	Pb μeq/g	Cu μeq/g	Cd μeq/g	Zn μeq/g	Ni μeq/g	Mn μeq/g	Ba μeq/g	Sr μeq/g	Ca μeq/g	Mg μeq/g	Rb μeq/g	K μeq/g	Na μeq/g	Li μeq/g	Operating capacity μeq/g
Birch	18.2	22	12	2.0	1.6	1.2	0.9	1.1	0.8	0.8	0.6	0.1	bdl	bdl	0.1	43
Spruce sapwood	18.1	26	13	2.0	1.7	1.2	0.8	1.1	0.7	0.8	0.6	bdl	bdl	bdl	bdl	48
Spruce heartwood	18.2	28	15	2.0	1.8	1.3	0.8	1.1	0.8	0.8	0.6	0.1	0.1	bdl	0.1	53
Untreated TMP	5.0	27	16	3.7	3.1	2.5	2.0	2.4	1.9	1.9	1.5	/	bdl	bdl	/	62
Alkali-treated TMP	6.6	42	27	5.1	4.6	3.4	2.6	3.3	2.4	2.5	1.9	/	0.1	0.1	/	94
Peroxide-bleached TMP	7.7	55	33	5.7	5.1	3.8	2.8	3.7	2.7	2.5	2.0	/	bdl	bdl	/	120
Unbleached softwood pulp	3.5	26	16	4.0	3.8	/	2.9	3.2	/	/	2.6	/	/	0.1	/	58
Oxygen-delignified softwood pulp	6.0	33	17	4.2	3.3	3.4	/	/	/	/	/	/	/	/	/	60
Unbleached hardwood pulp	13.6	31	18	4.9	4.3	3.9	3.3	3.1	3.4	3.5	2.4	0.2	0.2	0.1	bdl	78
Oxygen-delignified hardwood pulp	18.3	32	16	5.7	4.8	/	3.7	4.3	/	/	3.3	/	/	0.5	/	70
Inner bark of spruce	2.1	190	140	10	9.8	5.0	3.0	4.0	2.7	2.7	1.6	/	0.1	bdl	0.1	370
Outer bark of spruce	2.0	140	99	6.0	5.7	3.4	1.9	3.0	2.1	3.3	1.1	/	bdl	0.1	0.1	270

bdl - below detection limit
/ - not included in the mixtures

The affinity series obtained for various tree-related materials in this thesis are in good agreement with those presented by other authors in literatures. Saeed et al. (2005) studied adsorption of metal ions from contaminated water by papaya wood. They found the following sorption order: $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$. Lim et al. (2008) found the affinity order of metal ions to the sawdust of *Pinus koraiensis*: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$. A very similar affinity orders for spruce wood were also obtained by Marin and Ayele (2002; 2003): $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$. Pine bark has been reported to have the following order for uptake of metal ions: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$ (Gundogdu et al. 2009). The affinity of Pb^{2+} to *Moringa oleifera* bark was also found to be much higher than that of Ca^{2+} and Mg^{2+} (Reddy et al. 2010).

6.3.4. Sorption of Fe, Pb, Cu, Cd, Zn, Ni, Mn, Ba, Sr, Ca, Mg, K, Na and Li ions

The sorption of Fe^{3+} and Fe^{2+} , respectively together with the other 14 metal ions discussed earlier, is discussed in this section. Figure 22 shows the elution curves obtained from sorption experiments with trivalent iron on wood and bark samples. The elution profiles of Fe^{3+} differ clearly from the elution curves of the other metal ions. A huge concentration peak with a strong tailing can be seen in the elution curves of Fe^{3+} . The elution curves of Pb^{2+} and Cu^{2+} are small, however, for the rest of the metal ions the elution curves are hardly visible with the scales used in Figure 22. It can be concluded from these elution curves obtained in the sorption experiments that trivalent iron ions are most strongly bound to all the materials studied, much stronger than Pb^{2+} and Cu^{2+} . The long Fe^{3+} tails at the end of the chromatogram may be due to the presence of trivalent iron hydroxide and other precipitates formed on the solid phase of samples. The remaining trivalent iron ions in the column are difficult to remove completely, even with a large volume of nitric acid. From these elution curves in Figure 22, the following affinity order can be obtained: $\text{Fe}^{3+} \gg \text{Pb}^{2+} \gg \text{Cu}^{2+} > \text{Cd}^{2+}$.

A sorption experiment including divalent iron (Fe^{2+}) with spruce sapwood is presented in Figure 23. It can be seen that the elution curves obtained in this experiment completely differs from those obtained in sorption experiments including Fe^{3+} . In this column experiment Fe^{2+} was found to have a lower affinity than Cu^{2+} . A clear tailing is also observed in the elution curve of Fe^{2+} , which probably is due to the oxidization of a part of Fe^{2+} to Fe^{3+} . The trivalent iron ions then form salts of low solubility in the column, as discussed in the previous paragraph. The sorption experiment including Fe^{2+} gave the following affinity order for spruce sapwood (Figure 23): $\text{Pb}^{2+} \gg \text{Cu}^{2+} \gg \text{Fe}^{2+} > \text{Cd}^{2+}$.

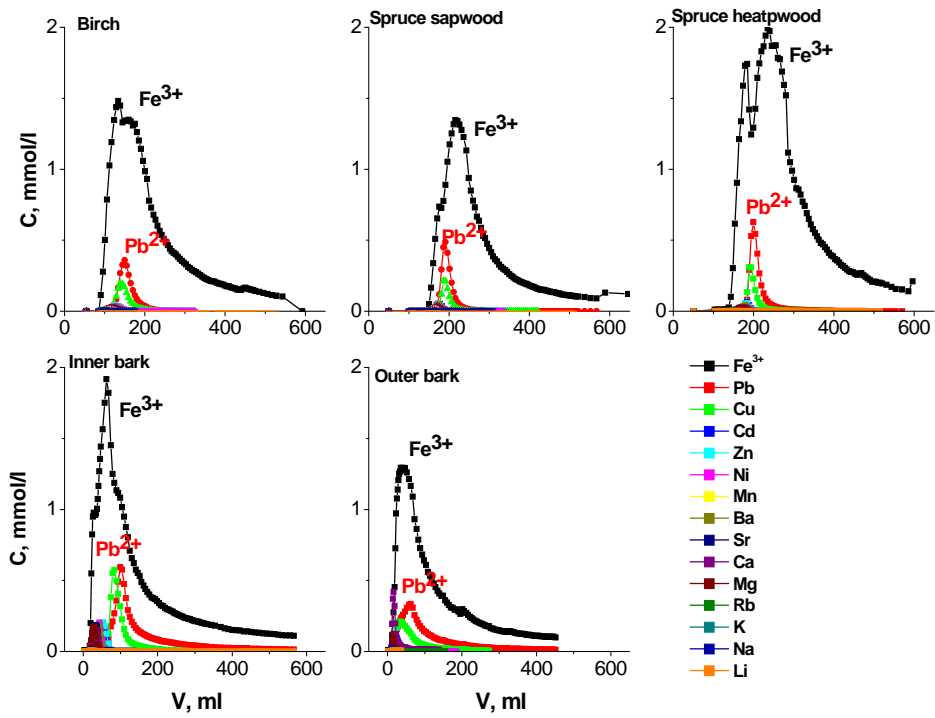


Figure 22. Concentrations of trivalent iron and 14 other metal ions in the collected fractions as function of the elution volume for wood and bark samples.

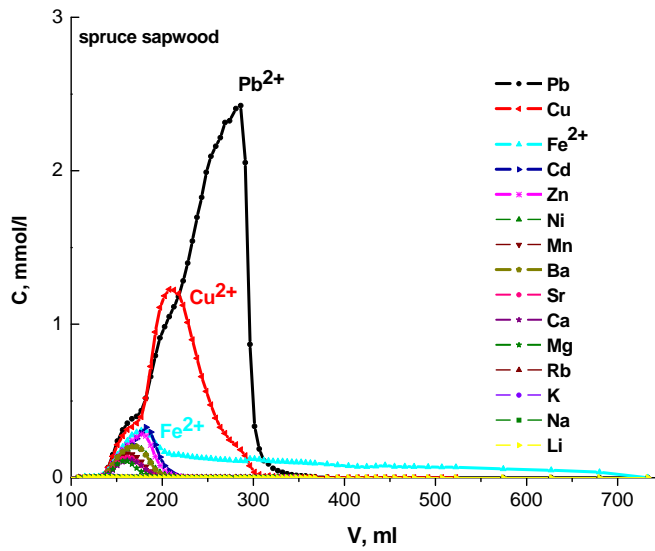


Figure 23. Concentrations of divalent iron and 14 other metal ions in the collected fractions as function of the elution volume for spruce sapwood.

Table 9 summarizes the operating capacities of the materials studied and the concentrations of each metal ion bound in the sorption experiments described in this chapter. In the sorption experiments with Fe^{3+} , the trivalent iron ions dominate the sorption process and very strongly adsorbed to the wood and bark materials. The operating capacity of wood materials is in the range 40-61 $\mu\text{eq/g}$, and over 90% is due to the sorption of trivalent iron. Inner bark and outer bark of spruce have the operating capacities of 427 and 303 $\mu\text{eq/g}$, respectively, and approximately 78% originates from the sorption of Fe^{3+} . The presence of Fe^{3+} in the loading solution depresses to a large extent the sorption of the other 14 metal ions. Even lead and copper generally having relatively strong affinity become less competitive in these experiments. For wood material, lead and copper ions stand for only ca. 4% respectively ca. 2% of the operating capacity. Their contributions to the sorption capacity of bark materials are somewhat higher, ca. 10% and ca. 5% respectively. In these sorption experiments, the affinity of the metal ions studied has the following order to the wood and bark materials: $\text{Fe}^{3+} \gg \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+}$ etc.

Table 9 also summarizes the results obtained from the sorption experiment with spruce sapwood in which Fe^{2+} was included in the loading solution. The sorption capacity of spruce wood for Fe^{2+} is much less than for Fe^{3+} (5.8 $\mu\text{eq/g}$ for Fe^{2+} and 33 $\mu\text{eq/g}$ for Fe^{3+}). In this experiment, Pb^{2+} and Cu^{2+} are the main metal ions bound to the spruce sapwood. Based on the results in Table 9 the following affinity order of metal ions in this loading mixture can be established for spruce sapwood: $\text{Pb}^{2+} \gg \text{Cu}^{2+} \gg \text{Fe}^{2+} > \text{Cd}^{2+}$ etc.

Table 9. Operating capacities and concentrations of iron (II, III) and 14 other metal ions adsorbed to wood and bark samples. The weights (d.m.) of samples packed in the column are also included in this table.

Materials	Weight g	Fe³⁺ μeq/g	Pb μeq/g	Cu μeq/g	Cd μeq/g	Zn μeq/g	Ni μeq/g	Mn μeq/g	Ba μeq/g	Sr μeq/g	Ca μeq/g	Mg μeq/g	Rb μeq/g	K μeq/g	Na μeq/g	Li μeq/g	Operating capacity μeq/g	
Birch wood	18.2	37	1.6	0.8	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1	bdl	bdl	bdl	bdl	bdl	40
Spruce sapwood	18.1	33	1.6	0.6	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	bdl	bdl	bdl	0 bdl	0 bdl	36
Spruce heartwood	18.2	57	2.1	0.9	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	bdl	bdl	bdl	0 bdl	0 bdl	61
Inner bark of spruce	2.1	330	43	22	5.5	5.8	4.3	3.0	3.8	3.9	2.7	2.2	/	0.1	0.1	0.1	0.1	427
Outer bark of spruce	2.0	239	32	13	1.5	1.6	1.4	1.0	1.4	1.2	9.6	0.7	/	0.1	0.2	0.7	0.7	303

Materials	Weight g	Fe²⁺ μeq/g	Pb μeq/g	Cu μeq/g	Cd μeq/g	Zn μeq/g	Ni μeq/g	Mn μeq/g	Ba μeq/g	Sr μeq/g	Ca μeq/g	Mg μeq/g	Rb μeq/g	K μeq/g	Na μeq/g	Li μeq/g	Operating capacity μeq/g
Spruce sapwood	18.2	5.8	23	10	1.4	1.3	0.9	0.6	0.9	0.5	0.4	0.4	bdl	bdl	bdl	bdl	45

bdl - below detection limit

/ - not included in the mixtures

6.3.5. Sorption of Rb, K, Na and Li ions

As discussed earlier the alkali metal ions are the most weakly bound ions to tree-related materials and are first eluted from the column. When divalent metal ions are present in the loading solutions, the concentration of alkali metal ions bound to the solid phase is too low to obtain any reliable order of affinity between them. The alkali metal ions were therefore studied in separate sorption experiments with TMP materials containing only these metal ions (*Paper II*). The elution curves are shown in Figure 24 (Figure 3 in *Paper II*). For the untreated TMP, the shapes of the elution curves are almost symmetrical (Gaussian). For the alkali-treated and peroxide-bleached TMP, the elution curves of the alkali metal ions, however, are distorted and not symmetrical any more. The asymmetry is even more pronounced for the peroxide-bleached TMP. These experiments gave the following affinity order: $\text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$.

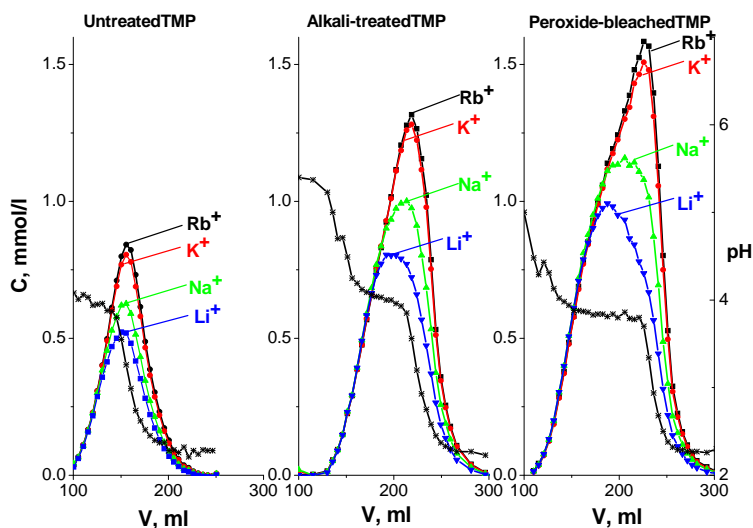


Figure 24. Concentrations of alkali metal ions in the collected fractions as function of the elution volume for TMP (Figure 3 in *Paper II*).

6.3.6. Sorption of metal ions to a synthetic cation exchanger and to pure cotton fibers

The sorption properties of a synthetic weakly acidic cation exchanger and pure cotton fiber were studied in order to compare with the sorption properties of wood, pulp and bark materials. The weakly acidic cation exchanger used is Amberlite IRC-76 (Sigma, USA), which contains carboxyl groups as the functional groups. The cotton fibers (Tamro

Oyj, Finland) used are of chemically purified cotton bud and are used for medical purposes. Due to the higher capacities of Amberlite IRC-76 (11 meq/g) compared to the wood, pulp and bark materials, the concentration of each metal ions in loading solution was 0.05 M. The concentration of nitric acid used to elute the bound metal ions was 0.01 M. A comparison between the ion-exchange properties of wood materials and a synthetic weakly acidic cation exchanger was made in *Paper I*.

The elution curves of metal ions obtained with the weakly acidic cation exchanger is shown in Figure 25. Three different sorption experiments were done with the synthetic resin. Both similarities and differences compared with the sorption data obtained for the wood, pulp and bark materials can be observed. The elution curves of the alkaline earth metal ions (Figure 25a) are more separated and the content of the metal ions bound are clearly different. The affinity order of the metal ions for the synthetic resin is: $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$, which is quite similar to that obtained for the tree-related materials, only the order between Sr^{2+} and Ca^{2+} is exchanged. Figure 25b presents the elution curves for the sorption experiment with a metal ion mixture containing Cd^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} , K^+ , Na^+ and Li^+ . It can be seen that Cd^{2+} are clearly most strongly bound to the weakly acidic cation exchanger. The elution curves of the monovalent metal ions can be distinguished from each other and are more separated than when wood, pulp and bark materials were studied. Their maximum concentration peaks occur in the beginning of the elution and they were eluted out from column before the divalent metal ions. Figure 25c presents the elution curves for the sorption experiment with a metal ion mixture containing Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} , K^+ , Na^+ and Li^+ . In this experiment Pb^{2+} and Cu^{2+} are clearly most strongly bound to the synthetic weakly acidic cation exchanger. The elution curve of barium is below of cadmium, but higher than of other metal ions in the mixture. By combining the results from the experiments with these three different metal ion mixtures, the following affinity order can be obtained for sorption of metal ions to the weakly acidic cation exchanger: $\text{Pb}^{2+} \gg \text{Cu}^{2+} \gg \text{Cd}^{2+} \gg \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Zn}^{2+}, \text{Ca}^{2+}, \text{Ni}^{2+}, \text{Mn}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+ > \text{Li}^+$.

By comparing the above order with the affinity series determined for wood, pulp and bark materials in the present work, it can be observed that the affinity of the alkaline earth metal ions of Ba^{2+} and Sr^{2+} to the synthetic weakly acidic cation exchanger are stronger than the affinity of Zn^{2+} and Ni^{2+} . The differences in affinities for the natural materials (i.e. wood, pulp and bark) and the synthetic exchanger are probably best explained by their different types of functional groups. The synthetic resin contains only one type of carboxyl groups. Wood, pulp and bark as natural materials contain more than one type of carboxyl groups, and also contains different phenolic hydroxyl groups (Tables 4 and 5). The complexity of functional groups in natural materials probably increases their relative affinity to the transition metal ions, such as Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , and Ni^{2+} , compared to

the alkaline earth metal ions. In addition, the big differences in the concentrations of the acid groups (total capacities) can also affect the sorption properties of the materials studied.

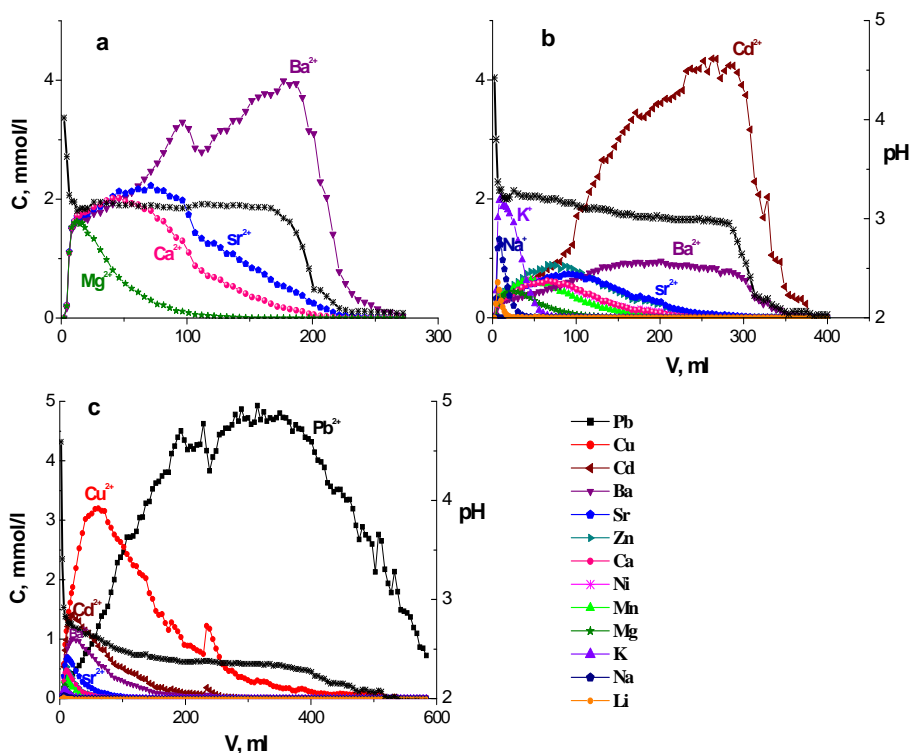


Figure 25. Concentrations of metal ions and pH in the collected fractions as function of the elution volume for the weakly acidic cation exchanger Amberlite IRC-76.

Figure 26 shows the elution curves of metal ions from a column filled with the pure cotton fibers. The elution curves have similar shapes and the retention times of the metal ions are the same. The concentration of adsorbed metal ions is, however, different for each cation. For the alkaline earth metal ions the affinity order to the cotton fibers can be established to: $\text{Ba}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Mg}^{2+}$, which is same as that obtained for the wood, pulp and bark materials. For the metal ions in the experiment shown in Figure 26b the affinity order is: $\text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Ba}^{2+} > \text{Ca}^{2+} > \text{Mn}^{2+} \sim \text{Sr}^{2+} > \text{Mg}^{2+}$. The concentrations of the eluted alkali metal ions of K^+ , Na^+ and Li^+ were below the detection limit of the analytical method used. Figure 26c shows the elution curves for sorption experiment with a metal ion mixture containing Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , Ba^{2+} ,

Sr^{2+} , Ca^{2+} , Mg^{2+} , K^+ , Na^+ and Li^+ . It can be seen that the highest affinity to the pure cotton fibers is shown by Pb^{2+} and then by Cu^{2+} . The elution profiles in Figure 26c are slightly tilted and not strictly symmetrical anymore. The elution curves of lead and copper ion in Figure 26c are clearly shifted from the rest of the curves due to much stronger sorption of these ions to cotton fibers. In all these three experiments the pH drops from ca. 4.5 to 2.4 during elution of the metal ions from the column.

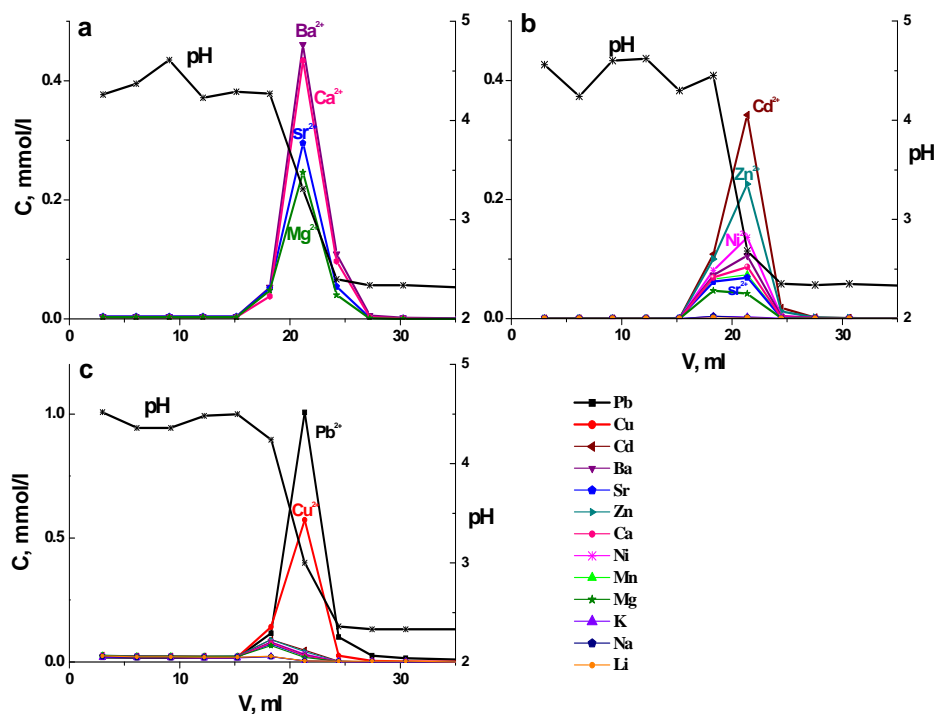


Figure 26. Concentrations of metal ions and pH in collected fractions as function of the elution volume for pure cotton fibers.

Table 10 summarizes the concentrations of metal ions adsorbed to the weakly acidic cation exchanger (Amberlite IRC-76) and to pure cotton fibers. The operating capacities of these materials obtained in the different experiments are also shown in this table. For the experiments with alkaline earth metal ions, the pH of the loading solution is ca. 5.4 and approximately 1.2 meq metal ions in total are bound to per gram of the weakly acidic cation exchanger (ca. 11% of the total capacity of 11 meq/g). For the experiments with mixture 4 (Table 10) the pH of the loading solution is ca. 3.2 and approximately 2.7 meq/g of metal ions is adsorbed (ca. 25% of the total capacity). The operating capacity

obtained from experiments with mixture 3 (Table 10) is ca. 1.7 meq/g (ca. 15% of the total capacity). All the values of the operating capacities are clearly below the total capacity of the weakly acidic cation exchanger, ca. 11 meq/g. From the results showed in Table 10, the following affinity order can be obtained for the synthetic acidic cation exchanger: $\text{Pb}^{2+} \gg \text{Cu}^{2+} \gg \text{Cd}^{2+} \gg \text{Ba}^{2+} > \text{Sr}^{2+} > \text{Zn}^{2+} > \text{Ca}^{2+} \geq \text{Ni}^{2+} > \text{Mn}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+ > \text{Li}^+$.

Cotton fibers are mainly of cellulose, except of small amount of pectin. They only contain a small amount of acid groups, resulting in very low sorption capacities (only 6-15 $\mu\text{eq/g}$, Table 10). The affinity order obtained for the pure cotton fibers is quite similar to the order obtained for the wood, pulp and bark materials, i.e. $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Ba}^{2+} > \text{Ca}^{2+} > \text{Mn}^{2+} \sim \text{Sr}^{2+} > \text{Mg}^{2+}$.

Table 10. Operating capacities and concentrations of each metal ion adsorbed to weakly acidic cation exchanger Amberlite IRC-76 and pure cotton fibers. Weights (d.m.) of sample packed in the column are included.

Materials	Weight g	Loading solution	pH	Pb $\mu\text{eq/g}$	Cu $\mu\text{eq/g}$	Cd $\mu\text{eq/g}$	Zn $\mu\text{eq/g}$	Ni $\mu\text{eq/g}$	Mn $\mu\text{eq/g}$	Ba $\mu\text{eq/g}$	Sr $\mu\text{eq/g}$	Ca $\mu\text{eq/g}$	Mg $\mu\text{eq/g}$	K $\mu\text{eq/g}$	Na $\mu\text{eq/g}$	Li $\mu\text{eq/g}$	Operating capacity $\mu\text{eq/g}$
	1.9	Mix.2	5.4						630	290	220	70					1210
Amberlite	1.9	Mix.3	4.4		900	130	80	64	230	120	76	27	30	9.1	2.2		1668
IRC-76	1.9	Mix.4	3.2	1910	530	130	13	9.3	8.0	81	24	12	3.0	1.0	0.5	0.1	2722
	1.8	Mix.2	5.4						2.2	1.4	2.0	1.2					7
Cotton	1.8	Mix.3	4.4		1.6	1.2	0.8	0.5	0.6	0.5	0.6	0.3	bdl	bdl	bdl	bdl	6
fibers	1.8	Mix.4	3.2	4.7	2.9	0.9	0.9	0.8	0.8	0.8	0.7	0.8	0.7	0.2	0.2	0.2	15

bdl – below detection limit

6.3.7. Effect of pH on metal ion sorption

Dissociation of the acid groups in the solid phase of samples is associated with the pH of the surrounding solution. Therefore the content of metal ions adsorbed to the materials studied is expected to be affected by the pH of the loading solution in Step 3 (Figure 17). The effect of pH on the metal sorption has been studied in *Paper II*. The sorption experiments were carried out at pH 4.5, 8 and 10, by applying the loading solution of Ba^{2+} , Sr^{2+} , Ca^{2+} and Mg^{2+} to the peroxide-bleached TMP. The study shows that the adsorption capacity increases with increasing pH of the loading solution. This is due to the fact that the competition of hydrogen ions to the binding sites on the material is reduced with the increasing pH of the solution. The sorption capacity of the untreated TMP is 80 $\mu\text{eq/g}$ at pH 4.5. It increased by ca. 2.5% to 82 $\mu\text{eq/g}$ at pH 8, and at pH 10 increased by ca. 21% to 97 $\mu\text{eq/g}$. The higher capacity at pH 10 is also probably due to the contribution of phenolic groups to the metal complexation in the pulp phase. The effect of pH on the sorption of metal ions to the peroxide-bleached TMP was also studied with only one metal ion, i.e. Mg^{2+} , present in the loading solution. The experiments were performed at pH 5.5 and 8. The operating capacity obtained at pH 5.5 is 77 $\mu\text{eq/g}$ and it increased by 47% to 110 $\mu\text{eq/g}$ when the pH of the Mg^{2+} solution was increased to 8.

There are several studies reporting that the pH of aqueous solution is the most important parameter governing the sorption process (Saeed et al. 2005; Shukla and Pai 2005; Acar and Eren 2006; Ahmad et al. 2007; Argun et al. 2007; Reddy et al. 2010; Semerjian 2010; Reddy et al. 2011). These studies showed that the sorption of metal ions is favored by increasing pH in the solution phase (Ajmal et al. 1998; Gundogdu et al. 2009; Rafatullah et al. 2012) and was, in general, explained by the fact that dissociation of the acid groups in the solid phase increase with increasing pH, resulting in an increasing sorption capacity of the materials (Srinivasa Rao et al. 2007; Öztürk et al. 2009; Ofomaja et al. 2010; Hubbe et al. 2011).

The sorption capacities are generally affected by the pH of the loading solution, and the sorption capacity for one specific cation is also significantly affected by the presence of other cations in the solution. It has been reported earlier that in the experiments with bark the optimum pH for Pb^{2+} sorption was 4, for Cu^{2+} 6, for Cd^{2+} and Ni^{2+} 5 and for Zn^{2+} 6.5 (Vázquez et al. 1994; Subbaiah et al. 2009). Ahmad et al. (2007) found that in a single-metal batch system the metal uptake capacity of *Pinus roxburghii* at pH 6.5 was in the order: $\text{Zn}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$. When all the metal ions were present in equal concentrations in the same solution, the selectivity order of these metal ions on the adsorbent was: $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} \sim \text{Ni}^{2+}$. Al-Asheh and Duvnjak (1997) reported that in a single-metal system at pH 4 the uptake of metal ions by pine bark was observed in the

order: $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Ni}^{2+}$. In a mixed metal ions system, however, the relative affinity of different metal ions was: $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$.

6.3.8. Effect of particle size on metal ion sorption

Birch wood was ground to two different particle sizes of 1-mm and 2-mm, and was used to study the effect of particle size of the materials on the metal sorption. A metal solution containing Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} , Rb^+ , K^+ , Na^+ and Li^+ was used as the loading solution in column chromatographic experiments. The results of the study show that there is no any notable changing in sorption capacity when the particle sizes of the birch were decreased from 2-mm to 1-mm. It has been reported in literatures, however, that a decrease in particle size in batch sorption experiments resulted in an increase in adsorption capacity, due to a larger available surface area of finely ground samples (Al-Asheh and Duvnjak 1997; Ajmal et al. 1998; Ahmad et al. 2005; Bulut and Baysal 2006; Naiya et al. 2008). Such an observation was not found in the current study with our column sorption experiments.

6.3.9. Effect of mass of materials on metal ion sorption

Unbleached softwood pulps were used to study the effect of the mass of the materials on the metal sorption in the column experiments. The loading solution used for this study contained Pb^{2+} , Cu^{2+} , Cd^{2+} , Zn^{2+} , Ba^{2+} , Mn^{2+} , Mg^{2+} and Na^+ . Two experiments were performed with different adsorbent masses: 13.2 g and 3.5 g. The unbleached softwood pulps were found to show a lower operating capacity when more material was packed in the column (43 $\mu\text{eq/g}$ vs 58 $\mu\text{eq/g}$, respectively). The shapes of the elution curves obtained for these two experiments, however, were similar. Acar and Eren (2006) have shown an increase in the sorption capacity with the increasing material dosage in batch system. This may be due to the availability of more adsorption sites on the increased surface area. This is in contradiction with our results obtained with column chromatographic method.

6.3.10. Competitive sorption of metal ions

A series of experiments were carried out to investigate the sorption ability of the materials in the presence of different combinations of metal ions. Unbleached softwood pulps were used for this study. The operating capacity of the unbleached softwood pulps is 59 $\mu\text{eq/g}$ when the loading solution contained Zn^{2+} , Ba^{2+} , Mn^{2+} , Ca^{2+} , Sr^{2+} , Mg^{2+} , K^+ and Na^+ . When Ba^{2+} was absent from the loading solution, the corresponding operating capacity decreased by 8% to 54 $\mu\text{eq/g}$. When both Zn^{2+} and Ba^{2+} were absent, the corresponding operating capacity decreased more (15%) to 47 $\mu\text{eq/g}$. Results of these experiments indicate that the operating capacity of the studied material is slightly decreased when Ba^{2+}

being the second in the affinity series of these metal ions was absent. The operating capacity decreased further when Zn^{2+} having highest affinity in the mixture was not present in the loading solution. Results reveal that the sorption capacity of the materials obtained is related to the metal ions present in the loading solution. The concentrations of each metal ion adsorbed are also influenced by the presence of other metal ions in the mixed metal ion system. Similar conclusions have also been obtained in other studies (Al-Asheh and Duvnjak 1997; Igwe et al. 2005; Gundogdu et al. 2009; Ofomaja et al. 2010).

6.3.11. Regeneration of tree-related materials for metal sorption

The metal ions bound to the solid phase of tree-related materials are replaced by hydrogen ions when the column is eluted with dilute nitric acid. Several consecutive sorption experiments performed on the same packing of the materials in column show the possibility to regenerate the materials used. The metal ions bound to the materials could nearly completely be desorbed with a 0.005 M HNO_3 solution. During repeated sorption-desorption experiments for at least three cycles, the sorption capacities of the materials remained unchanged or in some cases slightly decreased. Thus from this aspect the materials studied could be regarded as potential bio-sorbents for treatments of water contaminated with metal ions. The tree-related materials, however, cannot be reused after the sorption of iron ions because the insoluble iron precipitates are formed in the solid phase, and it is not easy to completely remove all iron ions from the solid phase (Figures 22 and 23).

Saeed et al. (2005) have found a negligible loss in the sorption capacity of papaya wood after several experiments. In some studies, a decrease in the adsorption capacity with an increase in the number of loading cycles, relative to the original capacity, has also been observed (Bulut and Baysal 2006; Reddy et al. 2011). This might be due to the damages of the metal binding sites or the release of small amounts of dissolved organics to aqueous phase during sorption processes (Khokhotva and Waara 2010). Gundogdu et al. (2009) have found that higher concentration of acid was more efficient in releasing metal ions. Some studies have demonstrated that regeneration of sorbing materials can also be achieved by using strong base (Shukla and Pai 2005; Chen et al. 2011).

6.3.12. Mass balance in sorption experiments

In the column experiments, the hydrogen ions that were exchanged by metal ions in sorption step (Step 2 in Figure 17) were collected and their total concentration was determined by the acid-base titrations. It was found that the number of hydrogen ions released to the aqueous phase is equal to the equivalent amount of metal ions bound to the solid phase of materials. This confirms that the ion exchange is the main reaction mechanism for the sorption of metal ions to tree related-materials.

During sorption-desorption experiments, the number of each metal ion that was loaded to the column (Step 2 in Figure17), not bound in the collected solution in Step 3 (Figure17) and bound to the solid phase in the column (Step 4 in Figure17) were determined. Results show the mass balance for “input” metal ions and “output” metal ions, i.e. the number of the equivalents of the metal ions poured through the materials is equal to the sum of equivalents of the metal ions bound and not bound to the materials. This confirms the validity of the analytical method and the quality of the ion exchange procedure used. An example of the mass balance of a column sorption-desorption experiment is shown in Table 11. The experiment was conducted by using the peroxide-bleached TMP and a loading solution containing 14 metal ions.

Table 11. Numbers of moles of metal ions that were loaded to the column, not bound detected in the collected solution and bound to the solid phase in experiments with peroxide-bleached TMP.

Metal ions in loading solution	Pb	Cu	Cd	Zn	Ni	Mn	Ba	Sr	Ca	Mg	K	Na
C_{load} (mmol)	1.28	1.24	1.34	1.38	1.31	1.29	1.33	1.31	1.26	1.28	1.04	1.06
$C_{unbound}$ (mmol)	1.05	1.11	1.31	1.37	1.29	1.27	1.35	1.25	1.29	1.27	1.06	1.08
C_{bound} (umol)	211	125	22	19	15	11	14	10	10	8	bdl	bdl
C_{sum} (mmol)	1.26	1.24	1.33	1.38	1.30	1.28	1.36	1.26	1.30	1.27	1.06	1.08

C_{load} - content of metal ions loaded to the column

C_{bound} - content of metal ion bound to the solid phase of pulp

$C_{unbound}$ - content of metal ions not bound

C_{sum} - sum of content of metal ions bound and not bound

6.4. Distribution of metal ions in single fibers

In *Paper V* the distribution of metal ions in single fibers was investigated by the laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). The single fibers studied were of softwood kraft pulps sampled from a Finnish pulp mill. The metal ions of interest are K, Mg, Mn, Zn, Cu and Fe. Figure 27 presents the distribution patterns of metal ions in single unbleached and oxygen-delignified softwood kraft pulp fibers. As can be seen in these figures, the metal ions of K, Mn, Zn and Cu are quite smoothly distributed. The even distribution patterns indicate that the metal ions are mainly attached to the acid groups in fibers, for example to the carboxylic groups. Magnesium ions are also quite evenly distributed, but several distinct peaks can even be observed in the distribution curves. Snickars et al. (2001) have explained that this is probably due to particles deposited on the fiber when magnesium salts were added to the pulping process. It also might result from the fiber fragments from the bulk of fibers.

The distribution of iron ions is rather uneven with quite sharp peaks, which obviously is due to the formation of iron oxide deposits on fibers. Iron-containing particles originating from the process equipments may also be found in fibers and caused the distribution peaks. The distribution pattern of metal ions varies between different single fibers, due to the inhomogeneous characteristics of pulps.

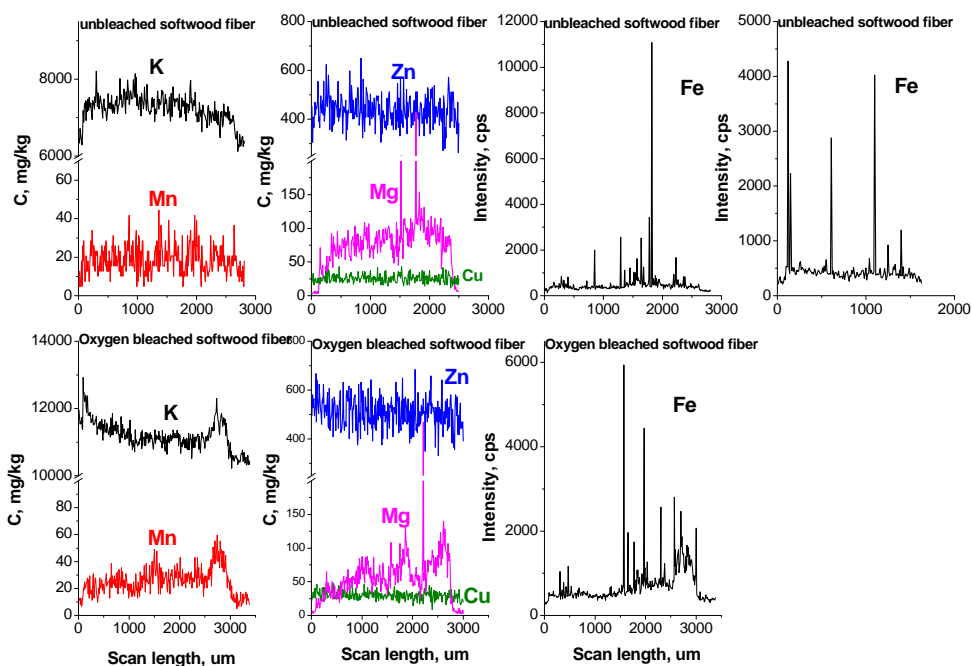


Figure 27. Concentrations and distribution of metal ions in single softwood kraft pulp fibers determined by LA-ICP-MS.

Among the metal ion studied, potassium was found in the highest concentration. The concentration of zinc is higher than that of magnesium, followed by copper. The concentration of copper is slightly higher than that of manganese. Comparing the metal distribution patterns in Figure 27, the concentrations of metal ions in single oxygen-delignified softwood fibers are in general higher than those in single unbleached softwood fibers. This may be explained by the formation of some new carboxylic acid groups during bleaching processes resulting in increased amount of metal ion adsorbed on fibers.

7. Conclusion

Metal ions are known to have detrimental effects on the processes in the papermaking mills. From the environmental point of view they also are harmful to human beings and other living organisms when their concentrations exceed certain thresholds. In this thesis, different tree-related materials (wood, pulp and bark) were investigated for their concentrations of acid groups and their sorption capacities for different metal ions. Both batch and column chromatographic methods were used for sorption/desorption experiments.

The functional groups (acid groups) in the materials studied are key units in the sorption processes of metal ions to wood, pulp and bark materials. The sum of the concentrations of all the acid groups in the materials is regarded as the total sorption capacity. Potentiometric titrations and model calculations showed that tree-related materials contain four main types of acid groups, of carboxylic and phenolic types. The total concentrations of acid groups in wood materials, untreated mechanical pulps and unbleached chemical pulps are not in big difference. The mechanical pulps contain less carboxylic acid groups but more phenolic groups than the chemical pulps. The chemical treatments of original pulps generally increase the content of their acid groups. It was found that the alkali-treated and peroxide-bleached TMP contain more acid groups than the untreated TMP. The oxygen delignification of chemical kraft pulps increases the content of carboxyl groups. Inner bark and outer bark of spruce show the highest total concentrations of acid groups (1.2 mmeq/g and 0.99 meq/g, respectively).

The operating capacity of the tree-related materials in the sorption experiments were determined by the column chromatographic techniques by using different metal ion loading solutions. The bark materials show the highest sorption capacity for metal ions, and wood sawdust (particles) exhibits the lowest sorption capacity. The mechanical and chemical treatments of the original materials generally increase their operating capacities. All the results showed that the operating capacities of the materials are generally related to the concentration of their acid groups.

The operating capacity also depends on the pH of the loading solution and the type of metal ions adsorbed on the materials. It was shown that a higher pH favors the adsorption of metal ion to materials, resulting in higher operating capacities. The operating capacities also increase when metal ions with higher binding affinity are present in the solution.

Studies have shown correlations between the total numbers of weak acid groups in materials and the content of all metal ions that can be adsorbed on their solid phase. The total sorption capacity (total content of acid groups) obtained by acid-base titrations is

usually higher than the operating capacity obtained in sorption experiments. The lower operating capacity is mainly due to the fact that the hydrogen ions are competing effectively with metal ions for the binding sites on the solid phase of materials, especially at lower pH. The phenolic hydroxyl groups are only partially dissociated even at higher pH values. Therefore all functional groups are not coordinated by metal ions at slightly acidic and neutral pH values. Results from the column sorption experiments showed that in the column ion-exchange process the load of the wood particles by metal ions is in the range 20-43%, of the mechanical pulps 22-50%, of the bark materials 26-38%, and of the synthetic cation exchanger 11-25%.

The sorption-desorption experiments done in this work showed that various metal ions are bound to tree-related materials with different strengths. The column chromatographic method is a method of competition between metal ions, and even small differences in affinities can be detected. Results obtained in this work showed that all materials studied have clear selectivity for different metal ions. By combining several sorption experiments performed with different metal ions mixtures, the following orders of metal affinities for the studied materials were obtained:

For wood samples: $Fe^{3+} \gg Pb^{2+} \gg Cu^{2+} \gg Fe^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+} > \underline{Ba^{2+}} \geq \underline{Ca^{2+}}$
 $\geq \underline{Mn^{2+}} \geq \underline{Sr^{2+}} > Mg^{2+} > Rb^+ \sim K^+ \sim Na^+ \sim Li^+$

For mechanical pulps: $Pb^{2+} \gg Cu^{2+} \gg Cd^{2+} > Zn^{2+} > Ni^{2+} > \underline{Ba^{2+}} > \underline{Ca^{2+}} > \underline{Mn^{2+}} \geq \underline{Sr^{2+}} > Mg^{2+} > Rb^+ > K^+ > Na^+ > Li^+$

For chemical pulps: $Pb^{2+} \gg Cu^{2+} \gg Cd^{2+} > Zn^{2+} > Ni^{2+} > \underline{Ba^{2+}} > \underline{Mn^{2+}} \geq \underline{Ca^{2+}} \geq \underline{Sr^{2+}} > Mg^{2+} > Rb^+ \sim K^+ \sim Na^+ \sim Li^+$

For bark materials: $Fe^{3+} \gg Pb^{2+} > Cu^{2+} \gg Cd^{2+} > Zn^{2+} > Ni^{2+} > \underline{Ba^{2+}} > \underline{Ca^{2+}} > \underline{Sr^{2+}} > \underline{Mn^{2+}} > Mg^{2+} > K^+ \sim Na^+ \sim Li^+$

The metal ions studied appear to have quite similar affinity orders to all the tree-related materials. It can thus be concluded that the main mechanism for sorption of metal ion are the same for all the tree-related materials studied. The differences in binding strength of metal ions to different materials, however, slightly vary.

It can be seen from the above affinity series that for all the materials studied the monovalent metal ions, i.e. alkali metal ions, show the weakest binding affinity. Of divalent metal ions, lead and copper ions are most strongly bound. Trivalent irons have the highest binding strength. They show completely different sorption behavior to the materials compared to the other metal ions studied in this work. In the column experiments, trivalent irons could not completely be removed from the materials. This is most probably due to that a part of iron ions in the sample is present in salts of low solubility.

The wood, pulp and bark materials have good metal sorption capacities and the operating capacities almost remain unchanged even after several adsorption-desorption cycles. These results indicated that the tree-related materials would be promising bio-sorbents for removal of metal ions from aqueous solutions. When metal ions are adsorbed to a protonated sample, an equivalent amount of hydrogen ions are released. This confirmed that ion exchange is the main mechanism involved in the sorption processes of metal ions to tree-related materials.

For comparison, the sorption properties of a commercial synthetic cation exchanger (Amberlite IRC-76) and pure cotton fibers were also studied. The adsorption capacities of the tree-related materials are lower than that of the synthetic cation acid exchanger resins, but much higher than that of the pure cotton fibers. The following affinity order was obtained:

For Amberlite IRC-76: $Pb^{2+} \gg Cu^{2+} \gg Cd^{2+} \gg Ba^{2+} > Sr^{2+} > Zn^{2+} > Ca^{2+} \geq Ni^{2+} > Mn^{2+} > Mg^{2+} > K^+ > Na^+ > Li^+$
For cotton fibers: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+} > Ba^{2+} > Ca^{2+} > Mn^{2+} \geq Sr^{2+} > Mg^{2+} > K^+ \sim Na^+ \sim Li^+$.

By comparing the above orders with the affinity series determined for wood, pulp and bark materials, both similarities and differences can be found. The affinity order of some metal ions to the synthetic cation exchanger differs to some degree from the affinity series which have been determined for the different tree-related materials. The binding strength of different metal ions to the synthetic cation exchanger is distinctly different. The affinity order obtained for cotton fibers is similar to that for tree-related materials. However, the differences in the affinity of most metal ions to the pure cotton fibers are not quite clear.

I hope that the results presented in this thesis have provided new information about sorption reactions of metal ions to tree-related materials, i.e. wood, pulp and bark. This new information may be of a great use for the metal management in pulping/bleaching processes and can also contribute to the application of biomass for removal of heavy metal ions in environmental management.

8. References

- Acar, F. N., Eren, Z. (2006). "Removal of Cu(II) ions by activated poplar sawdust (Samsun Clone) from aqueous solutions." *Journal of Hazardous Materials*, 137(2): 909-914.
- Adler, E. (1977). "Lignin chemistry-past, present and future." *Wood Science and Technology*, 11(3): 169-218.
- Ahmad, A., Rafatullah, M., Danish, M. (2007). "Sorption studies of Zn(II)- and Cd(II) ions from aqueous solution on treated sawdust of sissoo wood." *Holz Als Roh-Und Werkstoff*, 65(6): 429-436.
- Ahmad, R., Rao, R. A. K., Masood, M. M. (2005). "Removal and recovery of Cr(VI) from synthetic and industrial wastewater using bark of Pinus roxburghii as an adsorbent." *Water Quality Research Journal of Canada* 40(4): 462-468.
- Ajmal, M., Khan, A. H., Ahmad, S., Ahmad, A. (1998). "Role of sawdust in the removal of copper(II) from industrial wastes." *Water Research*, 32(10): 3085-3091.
- Al-Asheh, S., Duvnjak, Z. (1997). "Sorption of cadmium and other heavy metals by pine bark." *Journal of Hazardous Materials*, 56(1-2): 35-51.
- Alén, R. (2000a). "Structure and chemical composition of wood." In *Forest Products Chemistry* / edited by Stenius P., Fapet Oy, Helsinki: 12-57.
- Alén, R. (2000b). "Basic chemistry of wood delignification." In *Forest Products Chemistry* / edited by Stenius P., Fapet Oy, Helsinki: 59-103.
- Argun, M. E., Dursun, S., Ozdemir, C., Karatas, M. (2007). "Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics." *Journal of Hazardous Materials*, 141(1): 77-85.
- Athley, K., Ulmgren, P., Ohman, L.-O. (2001). "Acid-base properties of oxygen-delignified kraft pulps." *Nordic Pulp and Paper Research Journal*, 16(3): 195-203.
- Babel, S., Kurniawan, T. A. (2003). "Low-cost adsorbents for heavy metals uptake from contaminated water: a review." *Journal of Hazardous Materials*, 97(1-3): 219-243.
- Bakir, A., McLoughlin, P., Tofail, S. A. M., Fitzgerald, E. (2009). "Competitive Sorption of Antimony with Zinc, Nickel, and Aluminum in a Seaweed Based Fixed-bed Sorption Column." *CLEAN – Soil, Air, Water*, 37(9): 712-719.
- Beall, F. C. (1969). "Thermogravimetric Analysis of Wood Lignin and Hemicelluloses" *Wood and Fiber Science*, 1(3): 215-226.
- Bellotto, V. R., Miekeley, N. (2000). "Improvements in calibration procedures for the quantitative determination of trace elements in carbonate material (mussel shells) by laser ablation ICP-MS." *Fresenius' Journal of Analytical Chemistry*, 367(7): 635-640.
- Bhardwaj, N. K., Duong, T. D., Hoang, V., Nguyen, K. L. (2004). "Determination of fiber charge components of Lo-solids unbleached kraft pulps." *Journal of Colloid and Interface Science*, 274(2): 543-9.
- Biermann, C. J. (1996). "Wood and fiber fundamentals." In *Handbook of Pulping and Papermaking* / edited by Biermann C. J., Academic Press, California, USA: 13-54.
- Blechsmidt, J., Heinemann, S., Suss, H.-U. (2006). "Mechanical Pulping." In *Handbook of Pulp* / edited by Sixta H., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim: 1069-1134.
- Bobleter, O., Bonn, G. (1991). "Ion exchange chromatography." In *Ion Exchange* / edited by Dorfner K., Walter De Gruyter, Berlin; New York: 1187-1124.
- Boss, C. B., Fredeen, K. J. (1997). Concepts, instrumentation and techniques in inductively coupled plasma optical emission spectrometry, Perkin-Elmer, California, USA
- Bryant, P. S., Edwards, L. L. (1994). "Manganese removal in closed kraft mill bleach plants." *Tappi Journal*, 77(2): 137-148.
- Bryant, P. S., Edwards, L. L. (1996). "Cation exchange of metals on kraft pulp." *Journal of Pulp and Paper Science*, 22(1): 37-42.

- Bulut, Y., Baysal, Z. (2006). "Removal of Pb(II) from wastewater using wheat bran." *Journal of Environmental Management*, 78(2): 107-113.
- Bygrave, G., Englezos, P. (1998). "Fiber charge from potentiometric titration of kraft pulp and Donnan equilibrium theory." *Nordic Pulp and Paper Research Journal*, 13(3): 220-224.
- Chen, N., Zhang, Z., Feng, C., Li, M., Chen, R., Sugiura, N. (2011). "Investigations on the batch and fixed-bed column performance of fluoride adsorption by Kanuma mud." *Desalination*, 268(1-3): 76-82.
- Chia, C. H., Duong, T. D., Nguyen, K. L., Zakaria, S. (2007). "Thermodynamic aspects of sorption of Fe²⁺ onto unbleached kraft fibres." *Journal of Colloid and Interface Science*, 307(1): 29-33.
- Chowdhury, Z. Z., Zain, S. M., Rashid, A. K., Rafique, R. F., Khalid, K. (2012). "Breakthrough Curve Analysis for Column Dynamics Sorption of Mn(II) Ions from Wastewater by Using Mangostana garcinia Peel-Based Granular-Activated Carbon." *Journal of Chemistry*, 2013: 8.
- Crist, D. R., Crist, R. H., Martin, J. R. (2003). "A new process for toxic metal uptake by a kraft lignin." *Journal of Chemical Technology & Biotechnology*, 78(2-3): 199-202.
- Cromwell, E. F., Arrowsmith, P. (1995). "Semiquantitative Analysis with Laser-Ablation Inductively-Coupled Plasma-Mass Spectrometry." *Analytical Chemistry*, 67(1): 131-138.
- Dence, C. W., Lin, S. Y. (1992). "Introduction." In *Methods in Lignin Chemistry* / edited by Lin S. Y. and Dence C. W., Springer-Verlag, Berlin: 3-19.
- Devenyns, J., Desprez, F., Troughton, N., Plumet, L. (1994). "Metals control in TCF bleaching - Implication for kraft bleaching sequence design." *Tappi Pulping Conference Proceedings*, Atlanta: 381-389.
- Devos, W., Senn-Luder, M., Moor, C., Salter, C. (2000). "Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for spatially resolved trace analysis of early-medieval archaeological iron finds." *Fresenius' Journal of Analytical Chemistry*, 366(8): 873-880.
- Diniz, J. M. B. F. (1995). "Distribution of Charge in Wood Pulp." *Langmuir*, 11(10): 3617-3619.
- Doldán, J., Poukka, O., Salmenoja, K., Battezzore, M., Fernandez, V., Eluén, I. (2011). "Evaluation of sources and routes of non-process elements in a modern Eucalyptus kraft pulp mill." *PAPEL* 72(7): 47-52.
- Duong, T. D., Hoang, M., Nguyen, K. L. (2004). "Extension of Donnan theory to predict calcium ion exchange on phenolic hydroxyl sites of unbleached kraft fibers." *Journal of Colloid and Interface Science*, 276(1): 6-12.
- Durrant, S. F. (1999). "Laser ablation inductively coupled plasma mass spectrometry: achievements, problems, prospects." *Journal of Analytical Atomic Spectrometry*, 14(9): 1385-1403.
- Fardim, P., Holmbom, B. (2003). "Fast determination of anionic groups in different pulp fiber by methylene blue sorption." *Tappi Journal*, 2(10): 28-32.
- Fardim, P., Holmbom, B. (2005). "Origin and surface distribution of anionic groups in different papermaking fibres." *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 252(2-3): 237-242.
- Fardim, P., Moreno, T., Holmbom, B. (2005). "Anionic groups on cellulosic fiber surfaces investigated by XPS, FTIR-ATR, and different sorption methods." *Journal of Colloid and Interface Science*, 290(2): 383-91.
- Farooq, U., Kozinski, J. A., Khan, M. A., Athar, M. (2010). "Biosorption of heavy metal ions using wheat based biosorbents - a review of the recent literature." *Bioresource Technology*, 101(14): 5043-53.

- Febrianto, J., Kosasih, A. N., Sunarso, J., Ju, Y.-H., Indraswati, N., Ismadji, S. (2009). "Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies." *Journal of Hazardous Materials*, 162(2-3): 616-645.
- Fengel, D., Wegener, G. (1989). Wood - Chemistry, Ultrastructure, Reactions, Walter de Gruyter, Berlin, New York.
- Fiskari, J. (2002). "Metals buildup in TCF bleach plant closure: laboratory simulation." *Tappi Journal*, 1(3): 22-25.
- Fu, F. L., Wang, Q. (2011). "Removal of heavy metal ions from wastewaters: A review." *Journal of Environmental Management*, 92(3): 407-418.
- Gardner, D. J., Oporto, G. S., Mills, R., Samir, M. A. S. A. (2008). "Adhesion and Surface Issues in Cellulose and Nanocellulose." *Journal of Adhesion Science and Technology* 22: 545-567
- Goulet, M. T., Stratton, R. A. (1990). "The effect of pulping, bleaching, and refining operations on the electrokinetic properties of wood fiber fines." *Nordic Pulp and Paper Research Journal*, 5(3): 118-125.
- Gran, G. (1950). "Determination of the equivalent point in potentiometric titrations." *Acta Chemica Scandinavica* 4: 559-577.
- Gran, G. (1952). "Determination of the equivalence point in potentiometric titrations. Part II." *Analyst*, 77: 661-671.
- Granhölm, K., Harju, L., Ivaska, A. (2010a). "Desorption of metal ions from kraft pulps, Part 1: Chelation of hardwood and softwood kraft pulp with EDTA." *BioResources*, 5 106-116
- Granhölm, K., Harju, L., Ivaska, A. (2010b). "Desorption of metal ions from kraft pulps, Part 2: Chelation of kraft pulps with different complexing agents and with EDTA in a reducing environment." *BioResources* 5: 227-243
- Gullichsen, J. (2000). "Fiber line operations." In *Chemical Pulping* / edited by Gullichsen J. and Fogelholm C.-J., Fapet Oy, Helsinki: 19-231.
- Gundogdu, A., Ozdes, D., Duran, C., Bulut, V. N., Soylak, M., Senturk, H. B. (2009). "Biosorption of Pb(II) ions from aqueous solution by pine bark (Pinus brutia Ten.)." *Chemical Engineering Journal*, 153(1-3): 62-69.
- Gupta, V. K., Suhas (2009). "Application of low-cost adsorbents for dye removal - A review." *Journal of Environmental Management*, 90(8): 2313-42.
- Gupta, V. N. (1970). "Effect of metal ions on brightness, bleachability and colour reversion of groundwood." *Pulp and Paper Magazine of Canadian*, 71(18): 69-77.
- Hafren, J., Daniel, G. (2003). "Distribution of methyl-esterified galacturonan in chemical and mechanical pulp fibers." *Journal of Wood Science*, 49(4): 361-365.
- Harju, L., Lill, J.-O., Saarela, K.-E., Heselius, S.-J., Hernberg, F. J., Lindroos, A. (1996). "Study of seasonal variations of trace-element concentrations within tree rings by thick-target PIXE analyses." *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 109-110: 536-541.
- Heinrich, C. A., Pettke, T., Halter, W. E., Aigner-Torres, M., Audétat, A., Günther, D., Hattendorf, B., Bleiner, D., Guillong, M., Horn, I. (2003). "Quantitative multi-element analysis of minerals, fluid and melt inclusions by laser-ablation inductively-coupled-plasma mass-spectrometry." *Geochimica et Cosmochimica Acta*, 67(18): 3473-3497.
- Herbelin, A., Westall, J. C. (1999). "FITEQL: A computer program for determination of chemical equilibrium constants from experimental data [computer program], v. 4.0." Dept. of Chemistry, Oregon State University, Corvallis, OR.
- Herrington, T. M., Petzold, J. C. (1992). "An Investigation into the Nature of Charge on the Surface of Papermaking Woodpulp. 1. Charge/pH Isotherms." *Colloids and Surfaces*, 64(2): 97-108.

- Hill, C. A. S. (2006). "Modifying the Properties of Wood." In *Wood Modification: Chemical, Thermal and Other processes* / edited by Hill C. A. S., John Wiley & Sons, Ltd, West Sussex, England: 19-44.
- Hoffmann, E., Lüdke, C., Skole, J., Stephanowitz, H., Ullrich, E., Colditz, D. (2000). "Spatial determination of elements in green leaves of oak trees (Quercus robur) by laser ablation-ICP-MS." *Fresenius' Journal of Analytical Chemistry*, 367(6): 579-585.
- Holmbom, B., Ivaska, A., Karhu, J., Mortha, G., Laine, J. (2002). "Critical comparison and validation of methods for determination of anionic groups in pulp fibres." *Nordic Pulp and Paper Research Journal*, 17(3): 346-351.
- Horvath, A. E., Lindström, T. (2007). "Indirect polyelectrolyte titration of cellulosic fibers - surface and bulk charges of cellulosic fibers." *Nordic Pulp and Paper Research Journal*, 22(1): 87-92.
- Hubbe, M. A., Hasan, S. H., Ducoste, J. J. (2011). "Cellulosic substrates for removal of pollutants from aqueous systems: A review. 1. Metals." *BioResources* 6(2): 2161-2287.
- Igwe, J. C., Ogunewe, D. N., Abia, A. A. (2005). "Competitive adsorption of Zn (II), Cd (II) and Pb (II) ions from aqueous and non- aqueous solution by maize cob and husk." *African Journal of Biotechnology* 4(10): 1113-1116.
- Ingman, F., Still, E. (1966). "Graphic method for the determination of titration end-points." *Talanta*, 13(10): 1431-1442.
- Ivaska, A. (1974). "Graphic determination of equivalence volumes in potentiometric titrations of mixtures of weak acids--I Two monobasic acids." *Talanta*, 21(11): 1167-1173.
- Ivaska, A., Harju, L. (1999). "Analysis of inorganic constituents." In *Analytical Methods in Wood Chemistry, Pulping and Papermaking* / edited by Sjöström E. and Alén R., Springer-Verlag, Berlin Heidelberg: 287-304.
- Ivaska, A., Wänninen, E. (1974). "Potentiometric titration of weak acids." *Analytical Letters*, 6(11): 961-967.
- Järup, L. (2003). "Hazards of heavy metal contamination." *British Medical Bulletin*, 68: 167-182.
- Jemaa, N., Thompson, R., Paleologou, M., Berry, R. M. (1999). "Non-process elements in the kraft cycle. Part I. Sources, levels, and process effects." *Pulp and Paper Canada*, 100(9): 47-51.
- Jemaa, N., Thompson, R., Paleologou, M., Berry, R. M. (2000). "Non-process elements in the kraft recovery cycle. Part II. Control and removal options." *Pulp and Paper Canada*, 101(2): 41-46.
- Johansson, A. (1970). "Automatic titration by stepwise addition of equal volumes of titrant. Part I. Basic principles." *Analyst*, 95: 535-540.
- Karhu, J. (2008). "Equilibria and balances of metal ions in kraft pulping." *Doctoral thesis*, Åbo Akademi University, Åbo.
- Karhu, J., Forslund, J., Harju, L., Ivaska, A. (2000). "Characterization of carboxyl and phenol groups in kraft pulps at different temperatures." In *Cellulosic Pulps, Fibres and Materials* / edited by Kennedy J. F., Philips G. O., Williams P. A., and Lönnberg B., Woodhead Publishing, Cambridge: 129-135.
- Karhu, J. T., Snickars, P. M., Harju, L. U., Ivaska, A. U. (2002). "Cation exchange of alkali and alkaline earth metal ions on hardwood kraft pulp." *Appita Journal*, 55(5): 392-397.
- Khokhotva, O., Waara, S. (2010). "The influence of dissolved organic carbon on sorption of heavy metals on urea-treated pine bark." *Journal of Hazardous Materials*, 173(1-3): 689-696.
- Koch, G. (2006). "Raw material for pulp." In *Handbook of Pulp* / edited by Sixta H., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim: 21-61.

- Koljonen, K., Mustranta, A., Stenius, P. (2004). "Surface characterisation of mechanical pulps by polyelectrolyte adsorption." *Nordic Pulp and Paper Research Journal*, 19(4): 495-505.
- Konn, J., Pranovich, A., Fardim, P., Holmbom, B. (2007). "Characterisation and effects of new anionic groups formed during chemithermomechanical pulping of spruce." *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 296(1-3): 1-7.
- Krogell, J., Holmbom, B., Pranovich, A., Hemming, J., Willför, S. (2012). "Extraction and chemical characterization of Norway spruce inner and outer bark." *Nordic Pulp and Paper Research Journal*, 27(1).
- Laine, J., Stenius, P., Carlsson, G., Ström, G. (1994). "Surface characterization of unbleached kraft pulps by means of ESCA." *Cellulose*, 1(2): 145-160.
- Laine, J., Buchert, J., Viikari, L., Stenius, P. (1996). "Characterization of unbleached kraft pulps by enzymic treatment, potentiometric titration and polyelectrolyte adsorption." *Holzforschung*, 50(3): 208-214.
- Lapierre, L., Bouchard, J., Berry, R. M., Van Lierop, B. (1995). "Chelation prior to hydrogen peroxide bleaching of kraft pulps: an overview." *Journal of Pulp and Paper Science* 21(8): 268-273.
- Lastra, A., Gómez, D., Romero, J., Francisco, J. L., Luque, S., Álvarez, J. R. (2004). "Removal of metal complexes by nanofiltration in a TCF pulp mill: technical and economic feasibility." *Journal of Membrane Science*, 242(1-2): 97-105.
- Laver, M. L. (1991). "Bark." In *Wood Structure and Composition* / edited by Lewin M. and Goldstein I. S., Marcel Dekker, Inc., New York: 409-434.
- Lee, Y. L., Chang, C. C., Jiang, S. J. (2003). "Laser ablation inductively coupled plasma mass spectrometry for the determination of trace elements in soil." *Spectrochimica Acta Part B-Atomic Spectroscopy*, 58(3): 523-530.
- Leithe-Eriksen, R. (2001). "Pulp bleaching around the Baltic Sea." *Ecology & Pioneering*, Gothenburg.
- Liitiä, T., Tamminen, T. (2007). "Direct method for the determination of phenolic hydroxyl groups in pulp." *Holzforschung*, 61(6): 623-627.
- Lim, J., Kang, H.-M., Kim, L.-H., Ko, S.-O. (2008). "Removal of heavy metals by sawdust adsorption: equilibrium and kinetic studies." *Environmental Engineering Research*, 13(2): 79-84.
- Lindholm, C.-A. (1999). "Bleaching." In *Mechanical Pulping* / edited by Sundholm J., Fapet Oy, Helsinki: 313-344.
- Lindström, T. (1992). "Chemical factors affecting the behaviour of fibres during papermaking." *Nordic Pulp and Paper Research Journal*, 7: 181-192.
- Lloyd, J. A., Horne, C. W. (1993). "The determination of fibre charge and acidic groups of radiata pine pulps." *Nordic Pulp and Paper Research Journal* 8(1): 48-52.
- Lundqvist, F., Brelid, H., Saltberg, A., Gellersted, G., Tomani, P. (2006). "Removal of non-process elements from hardwood chips prior to kraft cooking." *Appita Journal*, 59(6): 493-499.
- Marin, J., Ayele, J. (2002). "Removal of Some Heavy Metal Cations from Aqueous Solutions by Spruce Sawdust. I. Study of the Binding Mechanism through Batch Experiments." *Environmental Technology*, 23(10): 1157-1171.
- Marin, J., Ayele, J. (2003). "Removal of some heavy metal cations from aqueous solutions by spruce sawdust. II. Adsorption-desorption through column experiments." *Environmental Technology*, 24(4): 491-502.
- Masters, B. J., Sharp, B. L. (1997). "Universal calibration strategy for laser ablation inductively coupled plasma mass spectrometry based on the use of aqueous standards with modified absorption coefficients." *Analytical Communications*, 34(9): 237-239.
- Meier, H. (1962). "Chemical and morphological aspects of the fine structure of wood." *Pure and Applied Chemistry*, 5(1-2): 37-52.

- Merdy, P., Guillon, E., Aplincourt, M., Dumonceau, J., Vezin, H. (2002). "Copper Sorption on a Straw Lignin: Experiments and EPR Characterization." *Journal of Colloid and Interface Science*, 245(1): 24-31.
- Merriam Webster Inc. (2012). "Wood Art Britannica Online for Kids." from <http://kids.britannica.com/elementary/art-66141>.
- Mettler Toledo International Inc. (2007). "DL50 Graphix." from http://us.mt.com/us/en/home/phased_out_products/PhaseOut_Ana/DL50_Graphix.html.
- Monge, M. E., Negri, R. M., Kolender, A. A., Erra-Balsells, R. (2007). "Structural characterization of native high-methoxylated pectin using nuclear magnetic resonance spectroscopy and ultraviolet matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. Comparative use of 2,5-dihydroxybenzoic acid and nor-harmaline as UV-MALDI matrices." *Rapid Communications in Mass Spectrometry*, 21(16): 2638-2646.
- Mosbye, J., Moe, S., Laine, J. (2001). "The Charge of Fines Originating from Different Parts of the Fibre Wall." *11th International Symposium on Wood and Pulping Chemistry*, Nice, France: 169-172.
- Mun, S., Ku, C., Kim, J. (2010). "Adsorption of metal and uranyl ions onto amidoximated *Pinus densiflora* bark." *Wood Science and Technology*, 44(2): 283-299.
- Munagapati, V. S., Yarramuthi, V., Nadavala, S. K., Alla, S. R., Abburi, K. (2010). "Biosorption of Cu(II), Cd(II) and Pb(II) by *Acacia leucocephala* bark powder: Kinetics, equilibrium and thermodynamics." *Chemical Engineering Journal*, 157(2-3): 357-365.
- Naiya, T. K., Bhattacharya, A. K., Das, S. K. (2008). "Adsorption of Pb(II) by sawdust and neem bark from aqueous solutions." *Environmental Progress*, 27(3): 313-328.
- Ni, Y., Ghosh, A., Li, Z., Heitner, C., McGarry, P. (1998). "Photostabilization of bleached mechanical pulps with DTPA treatment." *Journal of Pulp and Paper Science*, 24(8): 259-263.
- Nwabanne, J. T., Igbokwe, P. K. (2012). "Adsorption Performance of Packed Bed Column for the removal of Lead (II) using oil Palm Fibre." *International Journal of Applied Science and Technology*, 2(5): 2221-1004.
- Ødegård, M., Mansfeld, J., Dundas, S. H. (2001). "Preparation of calibration materials for microanalysis of Ti minerals by direct fusion of synthetic and natural materials: Experience with LA-ICP-MS analysis of some important minor and trace elements in ilmenite and rutile." *Fresenius' Journal of Analytical Chemistry*, 370(7): 819-827.
- Öztürk, H. B., Vu-Manh, H., Bechtold, T. (2009). "Interaction of cellulose with alkali metal ions and complexed heavy metals." *Lenzinger Berichte* 87: 142-150.
- Ofomaja, A. E., Unuabonah, E. I., Oladoja, N. A. (2010). "Competitive modeling for the biosorptive removal of copper and lead ions from aqueous solution by *Mansonia* wood sawdust." *Bioresource Technology*, 101(11): 3844-3852.
- Ohata, M., Yasuda, H., Namai, Y., Furuta, N. (2002). "Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS): Comparison of different internal standardization methods using laser-induced plasma (LIP) emission and LA-ICP-MS signals." *Analytical Sciences*, 18(10): 1105-1110.
- Pesavento, M., Biesuz, R., Cortina, J. L. (1994). "Sorption of metal ions on a weak acid cation-exchange resin containing carboxylic groups." *Analytica Chimica Acta*, 298(2): 225-232.
- Prasakis, J., Sain, M., Daneault, C. (1996). "Metal management improves peroxide bleaching of TMP." *Tappi Journal*, 79(10): 161-166.
- Prohaska, T., Stadlbauer, C., Wimmer, R., Stinger, G., Latkoczy, C., Hoffmann, E., Stephanowitz, H. (1998). "Investigation of element variability in tree rings of young

- Norway spruce by laser-ablation-ICP-MS." *Science of the Total Environment*, 219(1): 29-39.
- Putoczki, T. L., Gerrard, J. A., Butterfield, B. G., Jackson, S. L. (2008). "The distribution of un-esterified and methyl-esterified pectic polysaccharides in *Pinus radiata*." *Iawa Journal*, 29(2): 115-127.
- Rafatullah, M., Sulaiman, O., Hashim, R., Ahmad, A. (2012). "Removal of cadmium (II) from aqueous solutions by adsorption using meranti wood." *Wood Science and Technology*, 46(1): 221-241.
- Rahman, M. S., Islam, M. R. (2009). "Effects of pH on isotherms modeling for Cu(II) ions adsorption using maple wood sawdust." *Chemical Engineering Journal*, 149(1-3): 273-280.
- Ralet, M.-C., Dronnet, V., Buchholt, H. C., Thibault, J.-F. (2001). "Enzymatically and chemically de-esterified lime pectins: characterisation, polyelectrolyte behaviour and calcium binding properties." *Carbohydrate Research*, 336(2): 117-125.
- Ramesh, S. T., Gandhimathi, R., Nidheesh, P. V., Badabhagni, N., Bharathi, K. S. (2011). "Breakthrough data analysis of adsorption of Cd (II) on Coir pith column." *Electronic Journal of Environmental, Agricultural and Food Chemistry*, 10(7): 2487-2505.
- Randall, J. M., Garret, V., Bermann, R. L., Waiss, A. C. (1974). "Use of bark to remove heavy metal ions from waste solutions." *Forest Products Journal*, 24(9): 80-84.
- Reddy, D. H. K., Ramana, D. K. V., Sessaiah, K., Reddy, A. V. R. (2011). "Biosorption of Ni(II) from aqueous phase by *Moringa oleifera* bark, a low cost biosorbent." *Desalination*, 268(1-3): 150-157.
- Reddy, D. H. K., Sessaiah, K., Reddy, A. V., Rao, M. M., Wang, M. C. (2010). "Biosorption of Pb²⁺ from aqueous solutions by *Moringa oleifera* bark: equilibrium and kinetic studies." *Journal of Hazardous Materials*, 174(1-3): 831-8.
- Ringbom, A. (1963). Complexation in analytical chemistry, Wiley, New York.
- Rodushkin, I., Axelsson, M. D. (2000). "Application of double focusing sector field ICP-MS for multielemental characterization of human hair and nails. Part I. Analytical methodology." *Science of the Total Environment*, 250(1-3): 83-100.
- Saarela, K.-E. (2009). "Element analysis of wood materials by external millibeam thick target PIXE." *Doctoral thesis*, Åbo Akademi University, Turku.
- Saarela, K.-E., Harju, L., Lill, J.-O., Heselius, S.-J., Rajander, J., Lindroos, A. (2005). "Quantitative elemental analysis of dry-ashed bark and wood samples of birch, spruce and pine from south-western Finland using PIXE." *Acta Academiae Aboensis. Ser. B*, 65(4): 1-27.
- Saarimaa, V. (2007). "Pectin acids in mechanical pulping and papermaking." *Doctor thesis*, Åbo Akademi University, Åbo.
- Saeed, A., Akhter, M. W., Iqbal, M. (2005). "Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent." *Separation and Purification Technology*, 45(1): 25-31.
- Salmén, L., Lucander, M., Härkönen, E., Sundholm, J. (1999). "Fundamentals of mechanical pulping." In *Mechanical Pulping* / edited by Sundholm J., Fapet Oy, Helsinki.
- Seidman, L., Mowery, J. (2006). "Ion Chromatography." from http://serc.carleton.edu/microbelife/research_methods/biogeochemical/ic.html.
- Semerjian, L. (2010). "Equilibrium and kinetics of cadmium adsorption from aqueous solutions using untreated *Pinus halepensis* sawdust." *Journal of Hazardous Materials*, 173(1-3): 236-242.
- Shukla, S. R., Pai, R. S. (2005). "Adsorption of Cu(II), Ni(II) and Zn(II) on dye loaded groundnut shells and sawdust." *Separation and Purification Technology*, 43(1): 1-8.
- Simão, J. P. F., Egas, A. P. V., Baptista, C. M. S. G., Carvalho, M. G., Castro, J. A. A. M. (2005). "Evolution of Methylglucuronic and Hexenuronic Acid Contents of

- Eucalyptus globulus Pulp during Kraft Delignification. *Industrial & Engineering Chemistry Research*, 44(9): 2990-2996.
- Sixta, H. (2006). Handbook of Pulp. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
- Sixta, H., Suss, H.-U., Potthast, A., Schwanninger, M., Krotscheck, A. W. (2006). Pulp bleaching. In *Handbook of Pulp* / edited by Sixta H., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim: 609-731.
- Sjöström, E. (1989). The origin of charge on cellulosic fibers. *Nordic Pulp and Paper Research Journal*, 4(2): 90-93.
- Sjöström, E. (1993). Wood chemistry: fundamentals and applications ". Academic Press, San Diego, Calif.
- Snickars, P., EK, P., Harju, L., Ivaska, A. (2001). Application of laser ablation ICP-MS for analysis of metal ions in single pulp fibers. *11th International Symposium on Wood and Pulping Chemistry*, Nice, France: 641-643.
- Srinivasa Rao, P., Suresh Reddy, K., Kalyani, S., Krishnaiah, A. (2007). Comparative sorption of copper and nickel from aqueous solutions by natural neem (Azadirachta indica) sawdust and acid treated sawdust. *Wood Science and Technology*, 41(5): 427-442.
- Stenius, P., Laine, J. (1994). Studies of cellulose surfaces by titration and ESCA. *Applied Surface Science*, 75: 213-219.
- Subbaiah, M. V., Vijaya, Y., Kumar, N. S., Reddy, A. S., Krishnaiah, A. (2009). Biosorption of nickel from aqueous solutions by Acacia leucocephala bark: Kinetics and equilibrium studies. *Colloids and Surfaces B: Biointerfaces*, 74(1): 260-265.
- Sud, D., Mahajan, G., Kaur, M. P. (2008). Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions – A review. *Bioresource Technology*, 99(14): 6017-6027.
- Sundberg, A., Holmbom, B. (2002). Wood and fibre chemistry. Laboratory of Forest Products Chemistry, Faculty of Chemical Engineering, Åbo Akademi University, Åbo.
- Sundberg, A., Pranovich, A., Holmbom, B. (2000). Distribution of Anionic Groups in TMP Suspensions. *Journal of Wood Chemistry and Technology*, 20(1): 71-92.
- Sundman, O., Persson, P., Ohman, L. O. (2008). A multitechnique study of the interactions between H⁺, Na⁺, Ca²⁺ and Cu²⁺ and two types of softwood Kraft fibre materials. *Journal of Colloid and Interface Science*, 328(2): 248-56.
- Taipale, T., Österberg, M., Nykänen, A., Ruokolainen, J., Laine, J. (2010). Effect of microfibrillated cellulose and fines on the drainage of kraft pulp suspension and paper strength. *Cellulose*, 17(5): 1005-1020.
- Thomas, R. J. (1991). Wood: formation and morphology. In *Wood Structure and Composition* / edited by Lewin M. and Goldstein I. S., Marcel Dekker, Inc, New York: 7-47.
- Tienvieri, T., Huusari, E., Sundholm, J., Vuorio, P., Kortelainen, J., Nystedt, H., Artamo, A. (1999). Thermomechanical pulping. In *Mechanical Pulping* / edited by Sundholm J., Fapet Oy, Helsinki: 159-219.
- Tokareva, E. N., Pranovich, A. V., Ek, P., Holmbom, B. (2010). Determination of anionic groups in wood by time-of-flight secondary ion mass spectrometry and laser ablation-inductively coupled plasma-mass spectrometry. *Holzforschung*, 64(1): 35-43.
- Tokareva, E. N., Pranovich, A. V., Fardim, P., Daniel, G., Holmbom, B. (2007). Analysis of wood tissues by time-of-flight secondary ion mass spectrometry. *Holzforschung*, 61(6): 647-655.
- Toledo, M. (1997). Reference handbook: DL50/DL53/DL55/DL58 Titrators Mettler Toledo GmbH, Switzerland.
- Towers, M., Scallan, A. M. (1996). Predicting the ion-exchange of kraft pulps using donnan theory. *Journal of Pulp and Paper Science*, 22(9): 332-337.

- Wan Ngah, W. S., Hanafiah, M. A. K. M. (2008). "Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review." *Bioresource Technology*, 99(10): 3935-3948.
- Wang, F., Hubbe, M. A. (2002). "Charge Properties of Fibers in the Paper Mill Environment. 1. Effect of Electrical Conductivity." *Journal of Pulp and Paper Science* 28(10): 347-353.
- Vázquez, G., Antorrena, G., González, J., Doval, M. D. (1994). "Adsorption of heavy metal ions by chemically modified Pinus pinaster bark." *Bioresource Technology*, 48(3): 251-255.
- Werkelin, J. (2008). "Ash-forming elements and their chemical forms in woody biomass fuels." *Doctoral thesis*, Åbo Akademi University, Åbo-Turku.
- Willard, H. H., Merritt, L. L., Dean, J. A., Settle, F. A. (1988). "Chromatography: general principles." In *Instrumental Methods of Analysis* / edited by Carey J., Wadsworth, USA: 513-539.
- Yantasee, W., Rorrer, G. L. (2002). "Comparison of ion exchange and donnan equilibrium models for the pH-dependent adsorption of sodium and calcium ions onto kraft wood pulp fibers." *Journal of Wood Chemistry and Technology*, 22(2-3): 157-185.
- Zamora, A. (2012). "Carbohydrates - Chemical Structure." from <http://www.scientificpsychic.com/fitness/carbohydrates2.html>.
- Zemljčić, L. F., Peršin, Z., Stenius, P., Kleinschek, K. S. (2008). "Carboxyl groups in pre-treated regenerated cellulose fibres." *Cellulose*, 15(5): 681-690.
- Zhong, R., Ye, Z.-H. (2009). "Secondary Cell Walls." *Encyclopedia of Life Sciences (ELS)*, John Wiley & Sons, Ltd. Chichester.

ISBN 978-952-12-2777-6
Painosalama Oy – Turku, Finland 2012