Tampereen yliopisto

Hanna Romppanen

REMOVAL OF METALS FROM PULP MILL WASTEWATER WITH WOOD-BASED MATERIALS

Master's Thesis
Faculty of Engineering and Natural sciences
Examiners:
Riikka Lahtinen
Marja Palmroth
06/2022

ABSTRACT

Hanna Romppanen: Removal of Metals from Pulp Mill Wastewater with Wood-Based Materials
Master of Science Thesis
Tampere University
Master's Degree Programme in Science and Engineering
June 2022

Reducing the amount of water used in pulp mills is one important topic in making pulp mills more environmentally friendly. To establish a closed water cycle, the water needs to be purified by removing harmful compounds. One of the biggest sources of wastewater at a pulp mill is wood handling. The aim of this thesis was to study the ability of different wood-based materials to act as an adsorbent for metals dissolved in the debarking water of a pulp mill.

Adsorption is a chemical process in which components in liquid are separated using a solid surface that has attraction for some of the components. Important properties for adsorbent are surface area, volume of pores, and the total charge. The properties of wood, such as the total charge and the amount of metals it contains, affect its ability to act as an adsorbent. During pulp process, these properties change. Adsorption conditions also affect the efficiency of adsorption. The wastewater from wood handling is slightly acidic (pH 5) due to the dissolved wood material.

In this thesis, the metals studied were sodium, potassium, magnesium, and calcium. The adsorbents and debarking water used in the studies were obtained from Finnish softwood pulp mills. Used adsorbents were sawdust, brown stock pulp, mechanical pulp, and bleached pulp. The amount of acid groups in the adsorbents were determined by acid-base titration. Adsorption was studied by stirring the debarking water and the pulp for two minutes to half an hour at pH values of two to eleven. After mixing, the debarking water was analyzed by cation chromatography and the concentrations were compared to the metal concentrations of the original debarking water. In addition, it was investigated whether the studied adsorption could be modelled with Donnan equilibrium theory.

From the titration results, the amounts of acid groups for each adsorbent were calculated. The total charges of sawdust, brown stock pulp, mechanical pulp, and bleached pulp were 0.161 mol/kg, 0.104 mol/kg, 125 mol/kg, and 0.049 mol/kg. In the adsorption tests, it was found that the reaction is highly dependent on the pH. The results showed that sodium adsorption was most efficient at pH 5 or less. When pH was raised above 5, sodium was desorbed back into water. For potassium, magnesium, and calcium, the higher the pH was raised, the better the adsorption was. On the other hand, when pH was below 6, these metals were desorbed back into water. Of the adsorbents studied, untreated sawdust proved to be the best adsorbent by removing almost 24% of sodium from the debarking water at pH 5 and approximately 60% of other metals studied from the debarking water at pH 11.

The modelling of the reactions with Donnan theory was quite successful. The effect of the amount of acid groups on the adsorption efficiency was observed in modelling. The modelling of monovalent cations corresponded well to the results of laboratory experiments, but Donnan theory did not model the adsorption of divalent cations at high pH values correctly. With the modelling, it was found that the more sawdust was added to the debarking water, the more efficient the adsorption was. On the other hand, by increasing the mass of brown stock pulp, the adsorption decreased.

The results of this thesis showed that metals can be removed from wastewater with adsorption to wood-based materials by changing the pH. However, results also indicate that metals are also removed with brown stock pulp, which is not suitable as an adsorbent without treatment. Thus, the removal of metals also takes place in other ways than by adsorption on the wood material.

Keywords: Adsorption, debarking water, Donnan theory, pulp, wastewater

TIIVISTELMÄ

Hanna Romppanen: Metallien poisto sellutehtaan jätevesistä puupohjaisten materiaalien avulla
Diplomityö
Tampereen yliopisto
Teknis-luonnontieteellinen tutkinto-ohjelma
Kesäkuu 2022

Sellutehtaiden vedenkäytön vähentäminen on tärkeää tehtaiden ympäristöystävällisyyden kannalta. Suljetun vesikierron aikaansaamiseksi vesi on puhdistettava haitallisista yhdisteistä. Yksi sellutehtaan suurimmista jäteveden lähteistä sekä tilavuudeltaan että kuormittavuudeltaan on puunkäsittely. Tämän diplomityön tavoitteena oli tutkia eri sellumassojen kykyä toimia adsorbenttina sellutehtaan kuorimoveteen liuenneille metalleille.

Adsorptio on kemiallinen prosessi, jossa nesteen sisältämiä komponentteja erotetaan käyttämällä kiinteää pintaa, joka vetää puoleensa tiettyjä komponentteja. Adsorbentin tärkeitä ominaisuuksia ovat pinta-ala, huokosten tilavuus ja kokonaisvaraus. Puun ominaisuudet, kuten kokonaisvaraus ja sen sisältämien metallien määrä vaikuttavat sen kykyyn toimia adsorbenttina. Myös adsorptio-olosuhteet vaikuttavat adsorption tehokkuuteen. Sellutehtaan kuorimojätevesi on lievästi hapanta (pH 5) liuenneen puumateriaalin takia.

Tässä diplomityössä tutkitut metallit olivat natrium, kalium, magnesium ja kalsium. Tutkimuksissa käytetyt adsorbentit ja kuorimovesi saatiin suomalaisilta sellutehtailta. Käytetyt adsorbentit olivat sahanpuru, ruskea massa, mekaaninen massa ja valkaistu massa. Happoryhmien määrä adsorbenteissa määritettiin happo-emäs-titrauksella. Adsorptiota tutkittiin sekoittamalla kuorimovettä ja adsorbenttia kahdesta minuutista puoleen tuntiin pH-arvoissa kahdesta yhteentoista. Sekoituksen jälkeen kuorimovesi analysoitiin kationikromatografilla ja pitoisuuksia verrattiin alkuperäisen kuorimoveden metallipitoisuuksiin. Lisäksi selvitettiin, voidaanko tutkittua adsorptiota mallintaa Donnan tasapainoteorialla.

Kokeellisessa osuudessa määritettiin massojen sisältämien happoryhmien määrä happo-emäs titrauksella. Adsorptiota tutkittiin sekoittamalla kuorimovettä ja massaa kahdesta minuutista puoleen tuntiin pH arvoilla kahdesta kymmeneen. Sekoituksen jälkeen kuorimovesi analysoitiin kationikromatografilla ja tuloksia verrattiin alkuperäisen kuorimoveden metallipitoisuuksiin. Lisäksi selvitettiin, pystytäänkö tutkittua adsorptiota mallintamaan Donnan teorialla.

Titraustuloksista laskettiin kunkin adsorbentin happoryhmien määrät. Sahanpurun, ruskean massan, mekaanisen massan ja valkaistun massan kokonaisvaraukset olivat 0,161 mol/kg, 0,104 mol/kg, 125 mol/kg ja 0,049 mol/kg. Adsorptiotesteissä havaittiin, että reaktio on pH-riippuvainen. Tulokset osoittivat, että natriumin adsorptio oli tehokkainta, kun pH oli 5 tai pienempi. Kun pH oli yli 5, natrium desorptoitui takaisin veteen. Kaliumin, magnesiumin ja kalsiumin kohdalla adsorptio lisääntyi mitä korkeammalle pH:ta nostettiin. Kun pH oli alle 6, nämä metallit desorptioituivat takaisin veteen. Tutkituista adsorbenteista käsittelemätön sahanpuru osoittautui parhaaksi adsorbenttiksi poistamalla lähes 24 % natriumista pH:ssa 5 ja noin 60 % muista tutkituista metalleista pH:ssa 11.

Reaktioiden mallintaminen Donnan teorialla onnistui varsin hyvin. Mallinnuksessa havaittiin selvästi happoryhmien määrän vaikutus adsorptiotehokkuuteen. Yksiarvoisten kationien mallintaminen vastasi hyvin laboratoriokokeiden tuloksia, mutta Donnan teoria ei mallintanut oikein kaksiarvoisten kationien adsorptiota korkeissa pH-arvoissa. Mallinnuksen avulla havaittiin, että mitä enemmän sahanpurua kuorimoveteen lisättiin, sitä tehokkaampaa adsorptio oli. Toisaalta lisäämällä ruskeaa massaa adsorptio väheni.

Diplomityön tulokset osoittivat, että metalleja voidaan poistaa jätevedestä adsorptiolla muuttamalla pH:ta. Tuloksista havaittiin myös se, että metalleja pystytään poistamaan myös ruskealla massalla, joka ei sovellu adsorbentiksi ilman käsittelyä. Näin ollen metalleja poistuu jätevedestä myös muilla tavoin kuin adsorptiolla puumateriaaliin.

Avainsanat: Adsorptio, Donnan teoria, kuorimovesi, sellu, jätevesi

PREFACE

I want to thank Andritz for this opportunity to study an interesting topic as my Master’s thesis. I would also like to thank all my colleagues, professors and other people who helped me during this spring. Especially I want to thank my family and friends for their support.

Tampere, 16.6.2022

Hanna Romppanen

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ABBREVIATIONS AND SYMBOLS

ADt	*Air dry tonne of pulp product*
BOD_5	*Biological Oxygen Demand*
COD	*Chemical Oxygen Demand*
DTPA	*diethylenetriaminepentaacetic acid*
EDTA	*ethylenediaminepentaacetic acid*
NPE	*non process element*
ppm	*parts per million*
Tot-P	*total phosphorus*

A	*adsorbate*
A_f	*molar amount of acid in fiber*
AS	*reserved adsorption site*
E_r	*relative error*
$_f$	*subscript denoting fiber phase*
K	*equilibrium constant for the adsorption reaction*
K_i	*dissociation constant of acid in fiber*
K_{sp}	*solubility product constant*
m	*weight*
M^+X^-	*ion exchanger*
$_s$	*subscript denoting external phase*
S	*free adsorption site on the surface*
V_T	*total volume*
V_f	*fiber phase volume (l/kg)*
x_E	*experimental concentration of a cation*
x_D	*concentration of a cation according to Donnan theory*
X_i	*molar amount of ion i*
$[X_i]$	*concentration of ion i*
$[X_i]_1$	*intial concentration of ion i*
$[X_i]_2$	*final concentration of ion i*
z	*charge of ion*
λ	*Donnan distribution coefficient*
θ	*degree of coverage*

1. INTRODUCTION

Reducing the amount of water used in the pulp mills is one important topic in making pulp mills more environmentally friendly. To establish a closed water cycle, the water needs to be purified by removing harmful compounds. This will reduce the amount of fresh water intake in the pulp mill. On the other hand, it's noteworthy that all reusable materials could be recovered from the water [1]. One of the biggest wastewater producers in pulp mills is the debarking plant.

This master's thesis aims to research the capability of four different wood masses from different stages in a pulp mill as an adsorbent for removing unwanted metal ions like sodium, potassium, calcium, and magnesium from pulp mills debarking water. With adsorption, components in an external solution are separated using a solid surface. A solid surface has a charge and attracts some of the components. Donnan theory can be used to model the adsorption of metals from water to fibrous material. Donnan theory explains the movement of ions between fiber and external solution. Dissociated acidic groups create a negative charge on the fiber. The mobile ions in the system are distributed unevenly so, that cations are attracted, and anions are repelled by the fiber to establish an equilibrium. [2]

The structure of wood, the processes of a pulp mill and the changes in fiber in the various processes of a pulp mill affect the ability of wood material to act as an adsorbent. Debarking water is naturally slightly acidic due to the wood materials dissolved in it, which affects the adsorption efficiency. The adsorbents studied in this thesis are collected from Finnish softwood mills and include sawdust, brown stock pulp, mechanical pulp, and bleached pulp. In the experimental part, the amount of organic acid groups in different adsorbents are determined. The amounts of acid groups are used to determine the potential of the fibrous material to adsorb positively charged metal ions. In addition, it is necessary to find out the reaction time and pH value where the adsorption is most efficient. The amount of acid groups in the adsorbents are determined by acid-base titration. Adsorption is studied by stirring the adsorbents and debarking water for varying time periods at different pH values. It is also investigated whether the adsorption takes place according to Donnan theory.

In the second chapter, the general properties and structures of wood are presented. The next chapter introduces the basic principles of pulp mill, how the pulp changes at a certain stage and what chemicals are used. The fourth chapter discusses the wastewaters produced in pulp mills. The final chapter before the experimental part is about the chemical metal removal techniques, Donnan theory, and previous research on the topic. The materials and methods chapter reviews the laboratory tests and calculation methods, the results of which are discussed in chapter 7. Conclusions of the thesis are discussed in chapter 8.

2. PROPERTIES OF WOOD

This chapter reviews the structure of wood at both general and detailed levels. The purpose is to clarify the chemical structures present in wood and how they affect its pulping properties. Pulping properties include the wood type, fiber length, and contents of lignin, hemicellulose, extractives, and inorganic compounds. Pulp is chemically or mechanically modified wood, in which the cellulose fibers are separated [3].

2.1 Wood structure in general

The outer part of the wood is called sapwood and it contains living cells. In the center, there are dead cells, and the wood is drier than the outer part. This center part of the wood is called heartwood. Heartwood is formulated when the inner parts of a wood dies with a corresponding deposition of extractives. Extractives are compounds with small molecular mass that are soluble in organic solvents. [4] Heartwood has many polyphenols that do not exist in sapwood, giving heartwoods dark colour and resistance to decay. [3] Because of the low moisture content, the heartwood is more difficult to pulp than sapwood.

The fiber wall is divided into nested layers consisting of lamels. The thickest, secondary wall (S2-layer) of the fiber determines the properties of the fiber and the outer layer of the fiber determines its surface chemical properties. The intermediate lamel connects the cells. It is amorphous and consists of lignin. [5]

Bark consists of inner and outer bark. The outer bark is made from three layers. The chemical structure of bark varies between different species. There are four groups that the chemical structures can be classified: polysaccharides, lignin and polyphenols, hydroxy acid complexes, and extractives. [3]

The chemical structure of bark is 10-30 % of extractives, 15-45% cellulose, and 15-40% lignin. Leftover parts of barks mainly consist of different kinds of carbohydrates. Outer bark consists of waxes. When the bark is burned to ash, the main components are oxalate salts of calcium, potassium, silicates, and phosphates. [3]

2.2 Organic compounds in wood

The chemical structure of wood can be divided into macromolecular and low-molecular-weight substances. Low-molecular-weight substances include organic and inorganic matter, which can be further specified in extractives and ash (Figure 1). Macromolecular substances include polysaccharides, like cellulose and polyoses, and lignin. [6]

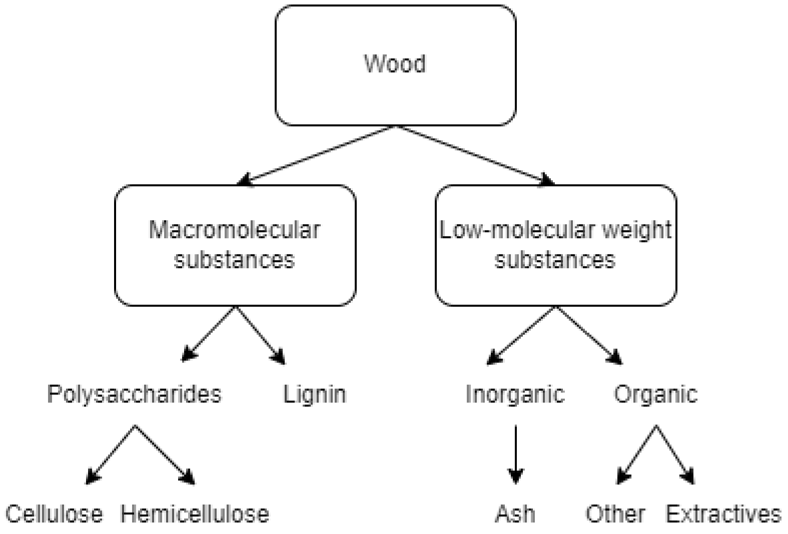

Figure 1. *Classification of woods chemical structure.* [6]

Most of the wood is cellulose (40-45%) and hemicellulose (15-25%) polymers. As combined, they are called holocellulose.[7] Sugars are one of the minor polymers in wood. [7] Holocellulose is mainly made from d-glucose, d-mannose, d-galactose, d-xylose, l-arabinose, d-glucuronic acid.[8]

There are non-specific and specific interactions between the functional groups of the fibers and the free ions. Non-specific interactions are electrostatic attraction or repulsion between ions and the fiber cell wall matrix. Specific interactions include the complexation of metal cations with the functional groups of fibers and the adsorption of ions on polarized surfaces. The interaction of ions with cellulosic fibers depends on the charge properties of the fibers.[9] The pH of press-extracted wood fluid is approximately 4.7 so it’s naturally slightly acidic [8].

The pK_a value of a carboxylic acid depends on the origin of it. In fibers, carboxylic acids are from lignin and carbohydrate. Different pK_a values of acidic groups present in fibers are shown in Table 1.

Table 1. *The* pK_a *values of acidic groups in fiber* [10].

Functional group	**pK_a**
Carboxylic acid, carbohydrate	3.1 – 3.3
Carboxylic acid, lignin	5 - 6
Phenol	7.3 – 10.3

The main charge in wood is caused by the carboxylic acid with pK_a values of 3.1-3.3 [11].

2.2.1 Cellulose

Cellulose is the most common biopolymer in the world. [10] It is a polydispersed linear glucan polymer of d-glucopyranose units linked by β-(1,4)-glycosidic bonds. [11] The backbone of cellulose is made up of chains of cellulose molecules (Figure 2) consisting of glucose anhydride units $C_5H_{10}O_5$ arranged in bundles.

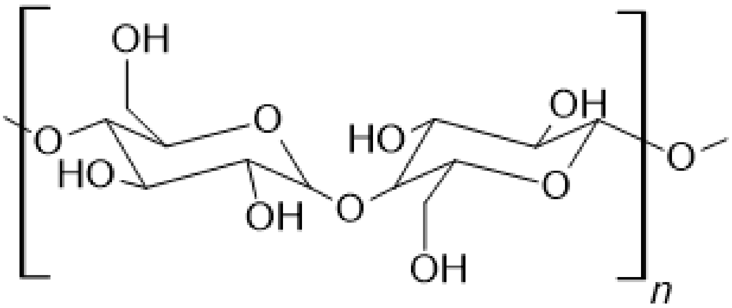

Figure 2. *Structural formula of cellulose. [10]*

The degree of polymerization of cellulose is approximately 10 000. [12] In each glucopyranose unit there are three hydroxyl groups. Due to these groups, polymer tends to form both internal and external hydrogen bonds. As a result of bonding, cellulose molecule bundles are aggregated into microfibrils, which may form crystalline and amorphous areas. Further merging of microfibrils into fibrils and cellulose fibers a high degree of crystallinity (60-75%) is formed. A high degree of crystallinity makes the polymer chemically very persistent material. [11]

Native cellulose is insoluble in most solvents. When treated with alkali, cellulose does not dissolve but swells [3]. Cellulose derivatives are mainly made from so-called cellulose 2, which is formed by treating native cellulose with alkali. Highly bleached cellulose has less than 1000 glucose units, whereas untreated cellulose has over 10 000 units. [3]

2.2.2 Hemicellulose

Hemicellulose makes up 20-35 % of the dry weight of wood. [13] It is a heteropolymer that consists of polysaccharide polymers. The structure of hemicellulose is formed of a few types of sugars, from hexosis, pentoses or from deoxyhexosis. [4], [12] Hemicellulose also contains acetyl- and methyl-substituted groups, and small amounts of uronic acids. [4] In hardwood, hemicelluloses are formed from O-acetyl-4-O-methyl-glucuronoxylan. Softwood hemicellulose contains a backbone polymer of d-galactose, d-glucose, and d-mannose [12]. One typical hemicellulose is xylan, which is a compound that has pentoses bonded to each other (Fig. 3) [14]

Figure 3. *Primary structure of a β-(1-3)-D-xylan* [15]

Hemicelluloses are in the cell walls of the fibers where they act as wall support materials. [16] They form internal bonds with cellulose and lignin in the wood material.

The branched and amorphous structure as well as the low polymerization degree of hemicellulose makes hemicelluloses more unstable than cellulose. [4] Hemicelluloses are reactive in different conditions. In alkaline solutions, hemicelluloses are soluble, whereas acidic conditions hydrolyse hemicellulose. The acetyl groups are hydrolyzed to give free acetic acid in alkaline conditions [3]. This free acetic acid consumes a great amount of alkali that is used in cooking. In pulp and paper process, cellulose can be cleaved by two different reactions, which are indiscriminate chain cleavage and terminal cleavage. The more common reaction mechanism is indiscriminate chain cleavage. Transition metals in the process increase the cleavage reactions and thus reduce the yield.[17]

2.2.3 Lignin

Lignin is a heterogeneous branched polymer, where propyl benzene derivates are attached via covalent bonds forming a grid like structure [5]. The linkages in the polymers are C-O-C and C-C. The most common linkage type in lignin is β-O-4 ether bond. The structure of lignin consists of three aromatic phenylpropane units: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. [4] The initial stage of softwood lignin is mainly coniferyl alcohol, whereas in hardwood lignin, the main initial stage is sinapyl alcohol. [18] Lignin also contains methoxyl groups. [3]

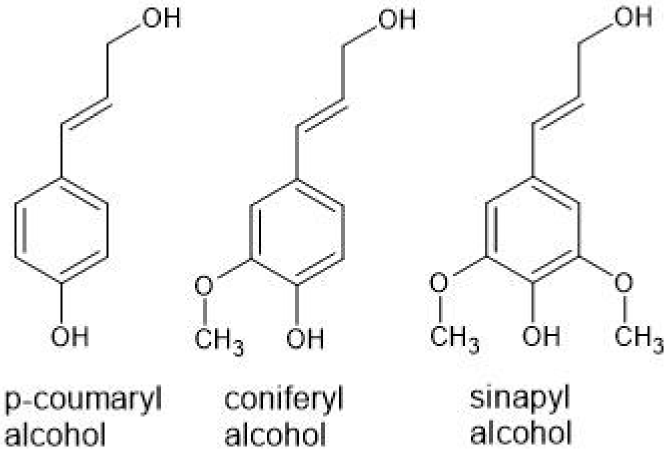

Figure 4. *The precursors of lignin.* [19]–[21]

Lignin's primary role is to support the wood's structure by filling the intermidiate lamella. [12] There are several groups in lignin that contribute to the colour of the pulp, for example coniferylaldehyde, carbonyl groups, quinonic structures and phenolic groups. [22] These groups are removed from the pulp when lignin is removed, which also changes the colour of the pulp. Only free phenolic groups in lignin can react with oxygen in pulp and paper processes. The ionized lignin structure decomposes and dissolves under alkaline conditions due to a chain reaction. [17] The high electron density required for the first impulse of oxygen reactions is provided by addition of alkali. [17]

2.2.4 Extractives

The highest concentrations of extractives are found in the heartwood and bark. The main extractives can be divided into three groups: aliphatic compounds, terpenes, and phenolic compounds. [23] Most of the aliphatic compounds in wood are fatty acids, fatty alcohols, and hydrocarbons. The fatty acids occur in wood as esters, unlike fatty alcohols, which can be found as free compounds. [24] Terpenes have a high concentration in softwoods whereas, in hardwoods, the concentration of terpenes is small. [3] Terpenes are cyclic compounds built from the condensation of several isoprene units in a linear or cyclic structure. [25] Monoterpenes, sesquiterpenes, diterpenes, and triterpenes are the four major terpen groups present in wood. [24] The occurrence of terpenes in softwoods and hardwoods is different. In softwoods, main terpenes are mono-sesqui-, and diterpenes, as well as sterols. In hardwoods, terpenes occur as higher terpenes, sterols, and triterpenoids, which are terpenes with oxygen in the structure. [24] Phenolic compounds are water soluble compounds that usually function as fungicides in heartwood and bark. Most of the phenolic extractives are removed in cooking, but they can be found in acetone extracts in wood and mechanical pulp. [11]

2.3 Inorganic compounds in wood

There are always some inorganic compounds in wood. They are important for the growth. The inorganic compounds are carried into the tree in aqueous solution where metals appear as cations. [26] After the elements have entered the wood, they can be organically associated or precipitate as inorganic salts to form a part of the solid tissues. Some of the compounds are left in aqueous solution present in the living cells.[26] The inorganic compounds in wood are determined from the wood ash using atomic absorption spectroscopy (AAS).

Usually, the concentration of inorganic compounds in wood is 0.3-1.5 m-%. Content of inorganic compounds can be large if there is a lot of silica. Usually, it is less than 0.5 %. [27] Ca, Mg, and K are the most common metals found in wood. They appear as oxalates, carbonates, and sulphates, or bound to carboxyl groups in pectic materials [28]. Other inorganic compounds found in wood are Na, Si, B, Mn, Fe, Mo, Cu, Zn, Ag, Al, Ba, Co, Cr, Ni, Pb, Rb, Sr, Ti, Au, Ga, In, La, Li, Sn, V, and Zr [29]. In pulp process, inorganic compounds, especially metals cause carbohydrates to break. Therefore, efforts are made to remove inorganic compounds from the pulp with chelating agents. The most used chelating agents are ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) [17].

Werkelin et al. [30] studied four Finnish wood species, spruce, pine, birch, and aspen. From each wood, they analyzed wood, bark, and foliage. Their results for wood and bark are presented in Table 2 which are the relevant results for this thesis.

Table 2. *The main elements and their amount found in Finnish wood species.* [30]

	Wood (ppm)	**Bark (ppm)**
Ca	410-1340	4800-19100
K	200-1310	1600-6400
Mg	70-290	210-2400
Mn	15-240	110-1100
P	0-350	210-1200

They discovered that the ash content was highest in bark, and lowest in wood. Calcium had the highest concentration in both wood and bark. In foliage, potassium had the highest content. Their results were very similar to those of previous studies [31]–[34].

3. BASIC OPERATION OF A PULP MILL

The basic operations of a pulp mill are wood handling, cooking, washing, and screening, oxygen delignification, and bleaching. Of these, the operations that chemically modify the fiber are cooking, oxygen delignification, and bleaching. This chapter introduces the chemicals typically used in the operations, as well as their chemical reactions with the fibers. Knowing how the fibrous material changes in the basic processes enables the evaluation of its ability to act as an adsorbent. Knowledge of the chemicals used is important in order to know the source of the metals in the fibers and in the water.

3.1 Cooking

Cooking aims to remove lignin, which is a natural compound of wood that keeps fibers together. Due to the removal of lignin, the wood starts to defibrate. Lignin is removed with heat and chemicals. [17] When lignin is removed, it also decreases the amount of acid groups in pulp [35]. The most common method of cooking is sulphate cooking in which the main chemical used is white liquor. White liquor is a mixture of sodium hydroxide, NaOH, and sodium sulphide, Na_2S. White liquor gives the process solution a basic pH of 10-14. [14] Another type of cooking is sulphite cooking, in which sulphite and hydrogen sulphite solutions are used as an extraction reagent. [14]

In sulphate cooking, the most important reaction of lignin is cleavage of β-O-4 structures. For carbohydrates, important reactions are the peeling reaction, alkaline hydrolysis, and the formation of hexenuronic acid. [36] The cleavage reaction of phenolic β-O-4 structure is shown in Figure 5. The formed episulphide structure is unstable, so reaction continues forming hydrosulphide and thiosulphate ions as products. [37] If no free phenolic groups are available, cleavage happens with an ionization of α-hydroxyl groups with OH^-. [38]

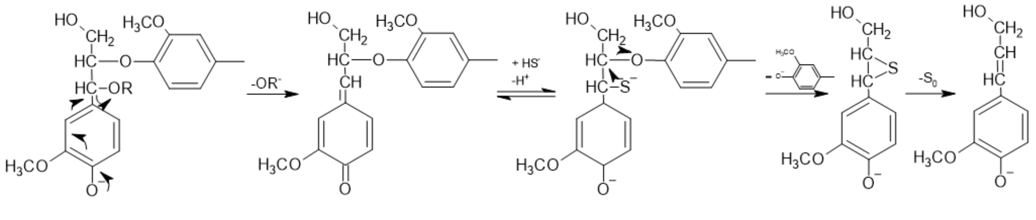

Figure 5. *Cleavage of phenolic β-O-4 structures in lignin. Modified from* [39].

Carbohydrates react via peeling reaction (Figure 6). In this reaction depolymerization of the polysaccharides occurs in stages, beginning with the reducing end group. In the beginning of the reaction, equilibrium is established between hemiacetal and open aldehyde form. Also, further equilibrium of aldehyde and keto structure will be established. These structures undergo a β-elimination reaction. After β-elimination has happened, the product will react via benzylic acid rearrangement and form an isosaccharinic acid. [40]

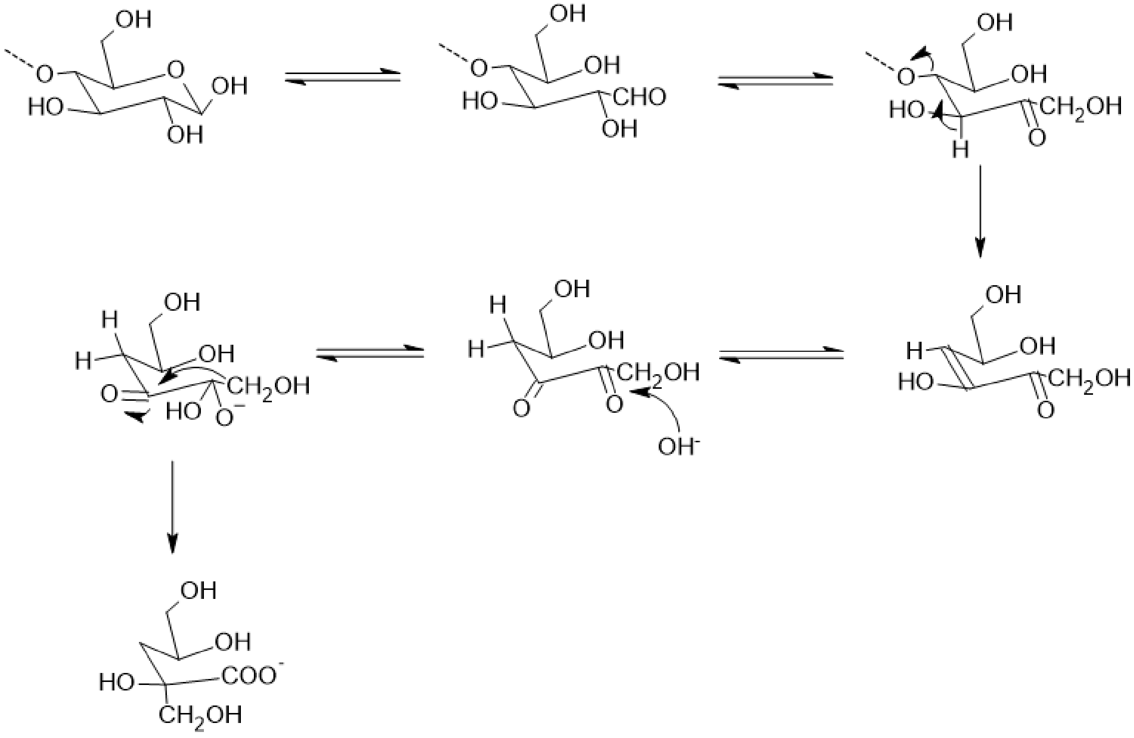

Figure 6. *Peeling reaction in sulphate pulping.*[40]

The alkaline hydrolysis causes a cleavage of the cellulose chain. Due to the reaction, cellulose loss increases. The reaction mechanism is illustrated in Figure 7. [41]

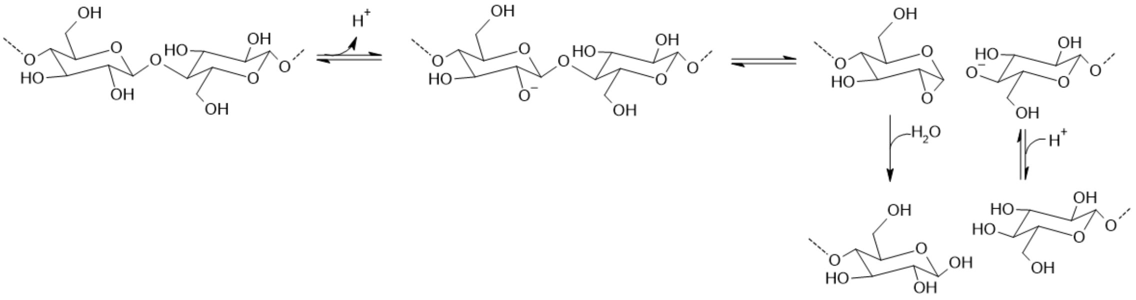

Figure 7. *Alkaline hydrolysis. Modified from* [41]

The hexenuronic acid is formed by the reaction of xylan in alkaline conditions. Xylan is substituted with 4-O-methylglucuronic acid groups linked through an alfa-glucosidic linkage. With alkaline, methoxyl group is eliminated as methanol forming a product of hexenuronic acid (HexA) (Fig. 8). [40]

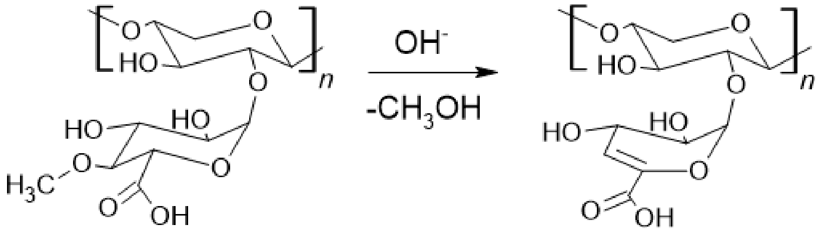

Figure 8. *Formation of hexenuronic acid. Modified from* [42]

Because hexenuronic acid is more stable than xylan, after cooking, most of the xylan left is in hexenuronic acid form. [40]

From an environmental point of view, one important reaction during cooking is the cleavage of the methyl-aryl ether linkages in lignin. This reaction is minor, but the products constitute the origin of the smell from kraft mills. Like described in Figure 9, methyl mercaptan is formed. This can react further in alkaline conditions and form a methylmercaptide anion and further dimethylsulfide. These products are volatile and toxic compounds.[40]

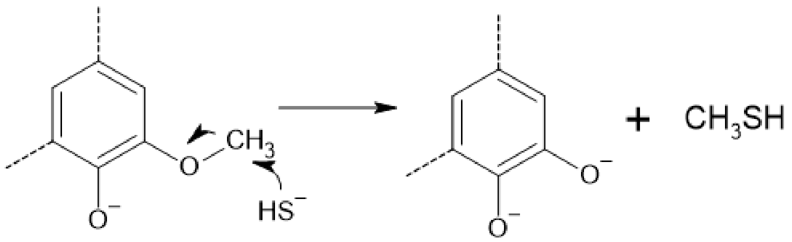

Figure 9. *The formation of methylmercaptan.*[40]

In sulphite process, the ether bonds in lignin goes through hydrolysis reaction. [14] Sodium sulphite Na_2SO_3 is one of the most important chemical used in sulphite cooking. It is used as an aqueous SO_2 with a base. In sulphite processes, sulfonic groups are introduced into the partially hydrolyzed lignin resulting a fully water-soluble lignosulfonate. Figure 10 shows the sulphonation of lignin under acidic conditions. [40]

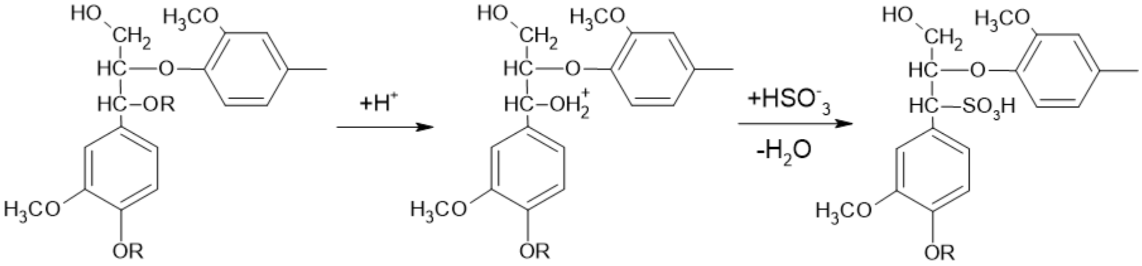

Figure 10. *Sulphonation of lignin in sulphite cooking.* [40]

In acidic conditions, condensation reaction of lignin can also take place with acid acting as a catalyst. In this reaction, the existence of free aromatic carbons in the para position to methoxyl group allows the production of C-C-bond to a neighbouring benzylic carbon. Linkage can be formed only if methoxyl group is formed via protonation and elimination. [40]

3.2 Oxygen Delignification

Oxygen delignification is performed in-between cooking and bleaching. It uses oxygen and alkali to remove residual lignin remaining in pulp after cooking. [17] The reaction breaks and oxidizes lignin into a form that can be dissolved in alkali, eliminates the lignin's colour components, and removes resin from the pulp. [17] Oxygen delignification can be performed in a lower kappa number than pulping, which results in decrease of bleaching chemical consumption. [17]

In oxygen delignification, the main reaction of lignin with a phenolic hydroxyl group is an oxidation of aromatic units like shown in Figure 11. [43]

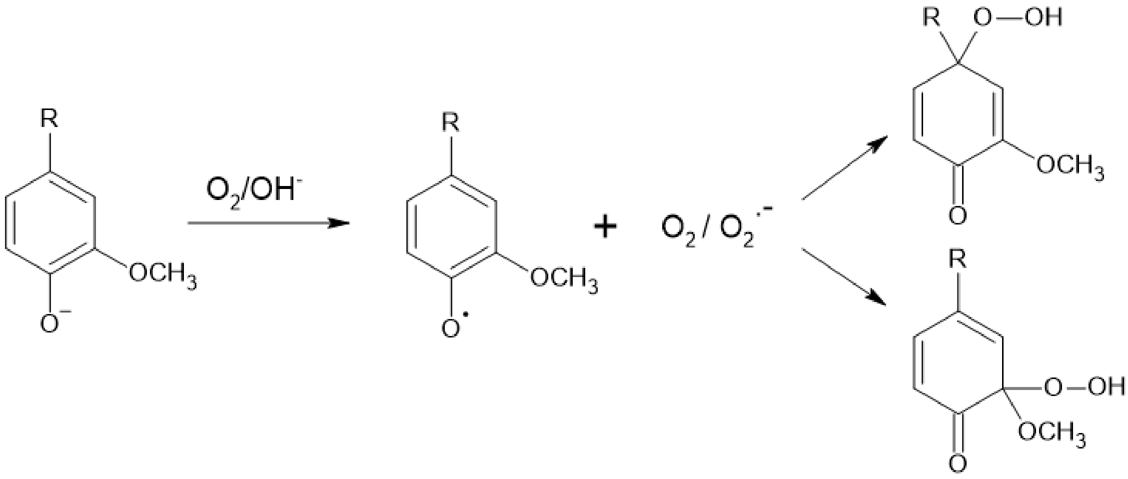

Figure 11. *Oxidation of lignin.*[43]

After the reactions of phenolic end-groups, there are three ways the lignin can react: via sidechain elimination, ring splitting or demethoxylation. In oxygen delignification, reducing end groups in carbohydrates are oxidized to an aldonic acid group. These aldonic acid groups inhibit the endwise degradation. [43] In oxygen delignification, heavy metals cause harmful chain cleavage. To prevent this reaction, magnesium sulphate, $MgSO_4$, is used to the treat the pulp, which slows down the decrease in viscosity up to a certain lignin content. [44]

3.3 Bleaching

Bleaching is done to decrease the darkness of pulp. It aims to dissolve and remove lignin. It also decreases the amount of fiber bundles, shives, and bark and removes extractives from pulp. [45] When hemicellulose and lignin dissolves during bleaching, the acid content of pulp decreases from unbleached pulp. [35] Bleaching is done with multiple stages by delignification and dissolved material extraction phases. [46] The delignification process breaks down the lignin and dissolves it in water. [3]

The most used bleaching chemicals are chlorine dioxide, sodium hydroxide, ozone, hydrogen peroxide, sodium dithionite, peracetic acid, peroxymonosulfuric acid and chelating agents. Different bleaching chemicals tend to react with different groups. Main bleaching chemicals are divided into three groups in the Table 3. [46]

Table 3. *The main bleaching chemicals and their reactivity.*[46]

Group	**Chemicals**	**Reactivity**
1	O_3	All aromatic lignin units with phenolic groups
2	O_2, ClO_2	Free phenolic hydroxy groups
3	H_2O_2, NaOCl	Carbobyl groups from lignin

In the production of mechanical pulp, bleaching is performed in two stages using peroxide and dithionite.

In bleaching, the residual lignin left after pulping is removed. This is done by oxidating the pulp several times. The basic reaction of lignin during bleaching is presented below.

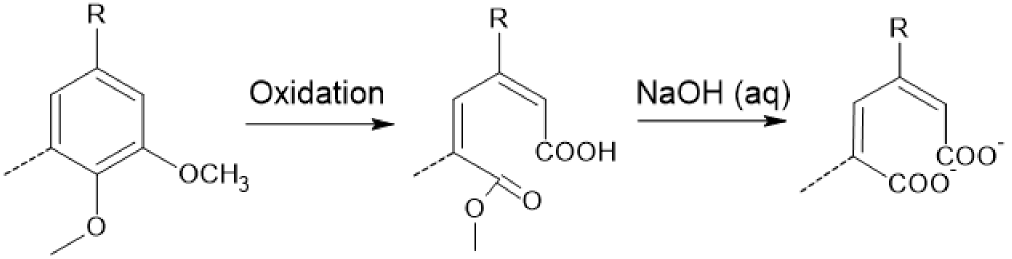

Figure 12. *The basic principle of lignin reactions during bleaching.*[43]

Chlorine dioxide bleaching is done under acidic conditions. ClO_2 attacks to lignin groups and degrades most of the residual phenolic groups in lignin. The oxidation mechanism for lignin reacting with chlorine dioxide is presented in Figure 13.

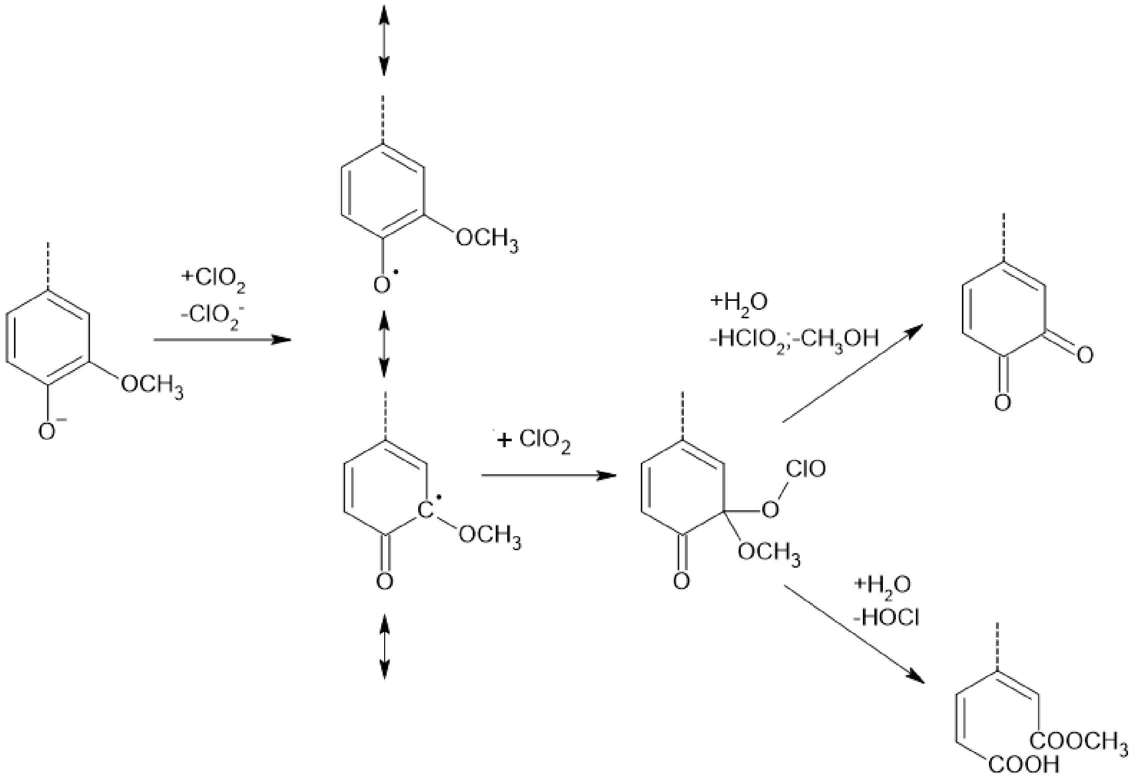

Figure 13. *The main reactions of chlorine dioxide and phenolic lignin.*[47]

For mechanical pulps, bleaching is done in two stages with peroxide and dithionite $S_2O_4^-$. [17] In dithionite bleaching, dithionite and pulp react to reduce double bonds and carbonyl structures, like orto- and para quinones. As a product of this reaction, partly bleached pulp is produced. Partly bleached product is obtained due to coniferaldehyde, which is still partly present in the structure. [48] The reaction mechanism of dithionite bleaching is presented below. [49]

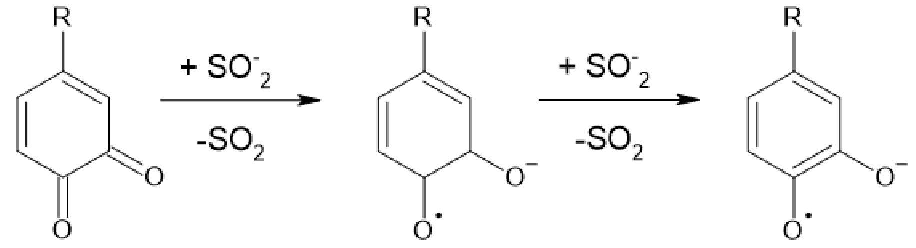

Figure 14. *The mechanism of dithionite bleaching.* [49]

Hydroxyl radical reacts with lignin's side chains and with the aromatic rings, thus, in pH values higher than pK_a 11,9, only side chain cleavage occurs (Figure 15). [50]

Hydroxyl radical present in the reactions can be formed from homolytic cleavage of hydrogen peroxide or by decomposition catalysed by metal ions.

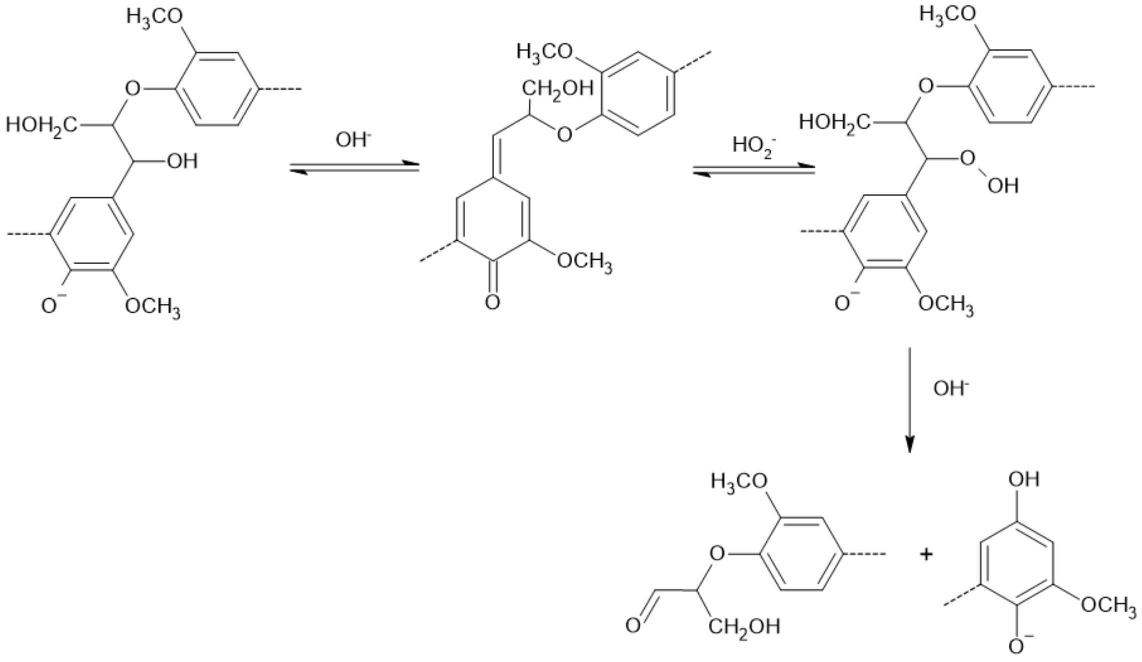

Figure 15. *Cleavage of residual phenolic β-O-4 structure with hydrogen peroxide***.** [51]

When bleaching with hydrogen peroxide, it is noteworthy that hydrogen peroxide decomposes easily into water and oxygen. Especially copper, iron, and manganese-ions speed up the reaction. That is why pulp is usually prepared with chelant before bleaching with peroxide. [48]

4. WASTEWATERS IN PULP MILL

Water plays a major role in the pulp and paper industry. In recent years, water usage and reduction have improved. As a result, various wastewater treatment methods are being developed. [52] The chemical content of wastewaters varies between different pulp mills. Differences are caused by the wood used and differences in pulping processes. [53] Wastewater is produced in multiple stages of a pulp mill. For bleached kraft pulp mills, the wastewater flow is approximately 20-90 m^3/ADt [52]. ADt is a term used in pulp industry to describe an air-dry ton of pulp product. Main emissions to water are dissolved organic compounds, chlorine compounds, extractive compounds, metals, and salts. [45] More specified classification of emissions in different stages is presented in Figure 16.

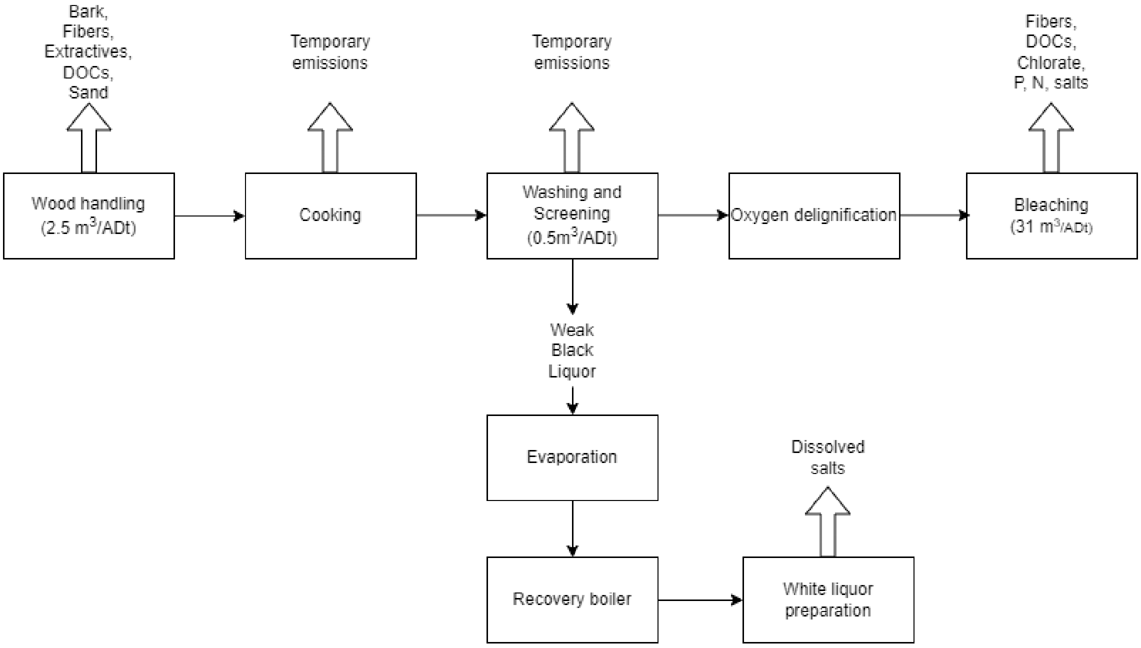

***Figure 16.** Emissions to water from pulp mills.*[52]

Metals that do not participate in the pulping process are called Non process elements (NPEs). [54] In addition to wood, NPE compounds are entered to pulp mill with make-up chemicals and process waters [55]. NPEs in water can cause problems such as scaling, plugging, fouling and corrosion. Table 4 shows the harms of some NPEs for a pulp mill.

Table 4. *NPEs and their effects in pulping process.*[54]

NPE	Digester	Bleaching	Evaporators	Recovery boiler	Causticizing	Lime kiln
K, Cl				Plugging and corrosion		
Ca	Scaling of heating surface and screens	Scaling of wash equipment	Scaling of heating surfaces			
Mg					Poor lime mud filterability, plugging of filters	High dead load in lime cycle
Al			Sodium aluminium silicate scaling			
Mn, Fe		Peroxide decomposition				High dead load in lime cycle

The amount of water utilized is directly proportional to the pulp mill's wastewater load. There are many ways to reduce the water consumption, all of which aim to increase water recirculation in the pulp and paper mill. However, when reducing water usage, the whole pulp mill must be considered. Considerations include scaling, corrosion, and accumulation of salts or non-process elements in process waters. [52]

Wood handling is the pulp mill's second largest producer of wastewater after bleaching with effluent flow of 0.5-10 m^3/ADt [52]. Most of the wastewater from wood handling is caused by debarking. Debarking is usually done by wet debarking. In debarking, bark and dirt from the wood is removed with water flow. In winters, the water consumption of debarking increases, as water is used for de-icing in addition to debarking. The water consumption of the debarking can be reduced by converting the wet debarking to a dry debarking. [17] When using dry debarking, the effluent flow can be reduced to 95 %. Reduction of biological oxygen demand (BOD), and chemical oxygen demand (COD) can be 97 %. For total phosphorus content (Tot-P) the reduction percentage can be 71 %. Pollution loads of wet and dry debarking processes are presented in Table 5.

Table 5. *Pollution loads of wet and dry debarking.* [52]

	Effluent flow (m^3/ADt)	**BOD_5 (kg/ADt)**	**COD (kg/ADt)**	**Tot-P (g/ADt)**
Wet debarking	3-10	5-15	20-30	25-35
Dry debarking	0.5-2.5	0.5-2.5	1-10	10-20

The colour of compressed debarking water is dark. The colour changes depending on the pH and is caused by the oxidation products of substances dissolved from bark. Typical pH of debarking water is approximately 5, which is due to extractives dissolved from wood and bark. [56] As explained in Chapter 2.3, wood and bark contain metals that will dissolve to debarking water. Calcium has the highest concentration of metals in wood. Water solids consist of, for example, lignin, tannin, fatty and resin acids, and carbohydrates. Fatty acids and resin acids are proved to be toxic before treatment. Nowadays, the most efficient way to reduce toxicity is biological treatment. [45] 30-50% of debarking effluent contains COD emissions, about half of which is due to tannins. [57]

The amount of effluent from cooking is small compared to the amount of effluent from debarking and bleaching. The effluent produced is usually condensed water and black liquor leaked from the process. Condensation waters may contain volatile and highly odorous compounds such as methyl mercaptan. In kraft cooking, COD-emissions are about 1000-33 600 mg/L. Most of this is due to methanol. [58] In sulphite cooking, COD- emissions range from 7500-50 000 mg/L. From this, 30-60% is due to acetic acid, and 10-25% from methanol. [59]

Bleaching causes most of the pulp mill wastewater (approximately 85%). The amount of wastewater produced is proportional to the amount of lignin in the pulp to be bleached. The more lignin the pulp contains, the more bleaching chemicals are needed, and the more wastewater is produced. [60] Wastewater from bleaching contains toxic compounds, such as dissolved organic compounds and chlorine compounds. In the delignification phase, lignin enters to the water. [53]

5. METAL REMOVAL METHODS AND THEORIES

This chapter discusses traditional metal removal methods, ion exchange, and adsorption. In addition, Donnan equilibrium theory is presented, which is used to model the results of the laboratory work.

5.1 Ion exchange

Ion exchange is a chemical reaction in which the ion in external solution is exchanged with the same charged free mobile ion from the solid material. Ion exchange is often considered as a separate but similar process to adsorption. [61] The exchange occurs when ion diffuses from the external solution into the solid material and ion from the solid material diffuses into the external solution. According to the basic principle of ion exchange, the movements of external ions and their counterions must always fulfil the electroneutrality principle. [62] The solid material, ion-exchangers are typically resins. Ion-exchangers can be cation-exchangers, anion-exchangers or amphoteric exchangers that exchange both anions and cations. [63] Cation exchange can be written as equation (Eq. 1):

$$\mathrm{M^+X^-(s) + N^+(aq) \rightarrow N^+X^-(s) + M^+(aq)} \tag{1}$$

Where ion exchanger $\mathrm{M^+X^-}$ is ionized with soluble ion $\mathrm{M^+}$, and $\mathrm{N^+}$ is an ion in the external solution. A similar equation can also be written for the anion exchanger with the difference that the ion of the insoluble exchanger has a positive charge. [62]

5.2 Adsorption

Adsorption is a chemical process in which components in liquid are separated with solid surface which has attraction for some of the components. The adhesion of particles to the surface of a substance by adsorption is because the surface molecules of the material tend to enter a lower energy state. The incorporation of particles into the surface of the substance reduces the surface energy. The adhesion of particles to the surface of a substance can be classified into chemisorption and physisorption. In chemsorption, coupling occurs through chemically generated bonds, and in physisorption, coupling is caused by weak van der Waals forces. [64] The amount of adsorption depends on the properties of the material acting as the adsorbent. These properties are for example the surface area, the conditions where the adsorbent is used, and the volume of pores. [65] Typically used adsorbents are activated alumina and carbon, silica gel, which have numerous fine pores. [66]

Adsorption can be described by several different models and equations. In this thesis, adsorption is modelled using Donnan equilibrium theory, which is presented in more detailed in the next subsection. However, the most common method is Langmuir's adsorption isotherm, in which adsorption is described by the equilibrium reaction [67]

$$\mathrm{A\ (s) + S\ (s) \rightleftharpoons\ AS\ (s)} \tag{2}$$

where A is the adsorbate, S is the free adsorption site on the surface of the substance and AS is the reserved adsorption site. According to Langmuir's assumptions: the enthalpy of adsorption is independent of the degree of surface coverage θ, the molecules adsorb to a certain point and do not move on the surface, and a certain point of the surface of a substance can adsorb only one molecule, so the resulting layer is monomolecular. [68] The degree of coverage θ, describes the proportion of the surface of the substance that is already filled with the adsorbent. The degree of coverage can be represented as an equation

$$\theta = \frac{Kc_{eq}}{1+Kc_{eq}} \tag{3}$$

where K is the equilibrium constant for the adsorption reaction and c_{eq} is the equilibrium concentration of the adsorbent. From Equation 3, we note that when K is small, the coverage $\theta \approx Kc_{eq}$ and when K is large $\theta \rightarrow 1$. [68]

5.3 Donnan Equilibrium theory

Donnan theory describes the ion equilibrium between two phases. Donnan effect was first presented in 1911 after Frederick George Donnan and it was used to describe sol concentration effects of electrochemical cells.[69] Afterwards the theory has been applied to, for example, the characterization of colloids and the characterization of electrolyte intercactions with fibers [70], [71].

According to Donnan theory, ions pass through the membrane due to a charge gradient, and back to the original side to balance the concentration. This phenomenon is illustrated in Figure 17. [72] Donnan theory combines the structural properties and charge properties of the fiber, and the ionic composition of the whole system [73].

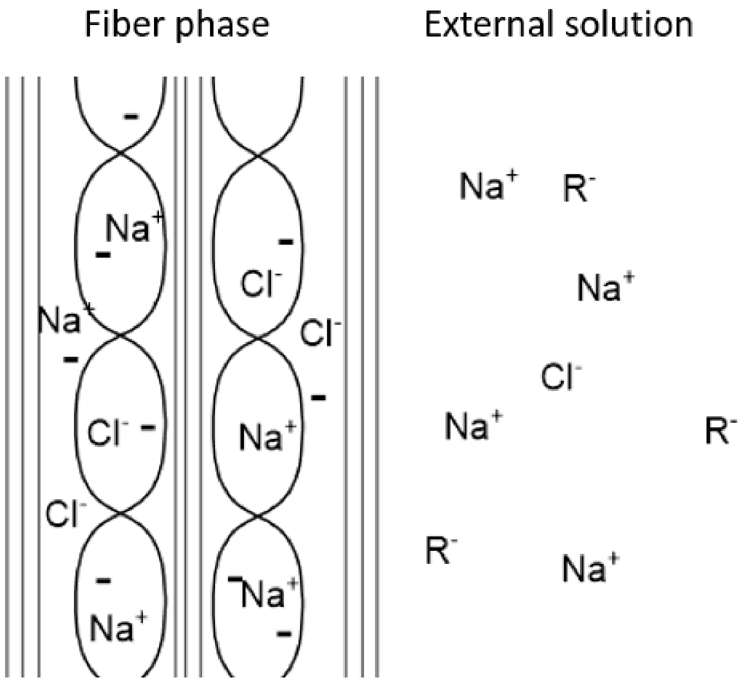

Figure 17. *The principle of Donnan equilibrium theory. Modified from* [74].

Donnan theory can be easily explained by thinking of NaCl solution and a semipermeable membrane which divides the NaCl solution into two equal volumes. Na^+ and Cl^- ions in the solution can cross the membrane. When another electrolyte NaR is added, Na^+ ion can cross the membrane, but R^- ion cannot. The reason can be that it is adsorbed on a surface or carrier, or it is simply too big molecule to cross the membrane. The equilibrium will be established when Na+ and Cl- will diffuse across the membrane. At the equilibrium, the energy needed to transport reversibly and isothermally Na^+ to the other side of the membrane equals the energy which can be gained by the equal reversible and isothermal transport of Cl^-. So, the energy gained in the system must be zero. [72]

The interaction of ions with the cellulose fibers depends on the charge properties of the fibers. Fibers are naturally slightly acidic so Donnan equilibrium theory can be applied to understand the reactions. The most important factor for ion exchange is the pH of the suspension. [75] On fibers, there are phenolic hydroxyl groups and carboxylic acid groups to use as cation exchangers. [76] The dissociated acidic groups, carboxylic acid, and phenol groups create a negative charge on the fiber and mobile ions are distributed unevenly. This means, that fibers repel anions and attach cations to them. When equilibrium is established, the distribution of any freely mobile ion between two phases can be calculated by multiplying the known concentration of an ion in the external phase with Donnan distribution coefficient. This basic principle can be written in the form of an equation as follows

$$[X]_f = \lambda^{z_i}[X]_s \qquad (4)$$

Where the subscripts *f* and *s* denote the fiber phase and the external solution phase. λ is the Donnan distribution coeffiecient and z_i is the charge of the ion. From eq. 4, the distribution coefficient can be determined as

$$\lambda^{z_i} = \frac{[X]_f}{[X]_s} \qquad (5)$$

The electroneutrality condition for the external solution can be written as

$$10^{-pH} - 10^{-14+pH} + \sum_{i=1}^{n} \frac{z_i X_{T,i}}{V_T + V_f(\lambda^{z_i} - 1)} = 0 \qquad (6)$$

Where $X_{T,I}$ is the total molar amount of cations i, V_T is the total volume of the system (l) and V_f is the water content in wood (l/kg). [66] The electroneutrality for the whole system is

$$\left(V_T + V_f(\lambda - 1)\right) 10^{-pH} - \left(V_T + V_f(\lambda^{-1} - 1)\right) 10^{-14+pH} + \cdots$$

$$\ldots + \sum_{i=1}^{n} z_i X_{T,i} - V_f \sum_{i=1}^{n} \frac{K_i[A_{f,i}^{-}]}{K_i + \lambda 10^{-pH}} = 0 \qquad (7)$$

Where K_i is the dissociation constant of acid i, and $[A_{f,i}^{-}]$ is the concentration of acid i (mol/kg). [66]

Towers and Scallan combined the Donnan distribution conditions, mass balances of ions between phases, and electroneutrality conditions in their model which is written in one equation, see eq. 8 [77]

$$(\lambda^2 - 1) \cdot 10^{-pH} + z_i \cdot (\lambda^{z_i+1} - 1) \cdot \frac{\sum_i [X_i^{z_i}]_T \cdot V}{V_T + V_f \cdot (\lambda^{z_i} - 1)} - \sum_i [A_{f,i}^-]_T = 0 \tag{8}$$

Where λ is the Donnan distribution coefficient, z_i is the charge of cation i, $[X_i^{z_i}]_T$ is the concentration of metal cation i (mol/kg), V_T is the total volume of water (l/kg), F is the water content in pulp (l/kg), and $[A_{f,i}^-]_T$ is the amount of of acid groups i in pulp. In equation 8, the sum of acid groups in adsorbent is calculated as

$$[A_f^-]_T = \frac{K_\mathrm{i}[A_{i,f}]}{K_\mathrm{i} + \lambda \cdot 10^{-pH_s}} \tag{9}$$

Where $K_{A_{i,f}}$ is the dissociation constant of acid group i (mol/L) and $[A_{i,f}]$ is the concentration of acid group i (mol/kg). The Donnan distribution coefficient can be numerically determined from equation 8. The coefficient depends on several parameters: volumes of the fiber and external solution phase, the number of acidic groups in fiber and this pK_a values, pH of the solution, and ionic strength of the suspension.

When the Donnan distribution coefficient is calculated from equation 8, the concentration of ions in external phase can be calculated according to eq. 10.

$$[X_i]_s = \frac{X_i}{(V_T + F(\lambda^{z_i} - 1))} \tag{10}$$

Laivins and Scallan [78] extended the theory made by Towers and Scallan [74] about partitioning of cations between fiber and external phases to study ion-exchange of pulps. According to their study, higher valency cations bind to the pulp quickly even in dilute solutions. To exchange higher valency cations by monovalent cations, higher concentration of cations is required. Also, when pulp was washed with acid, all cations were replaced with hydrogen.

Räsänen has studied ion exchange of fibers and water solutions using Donnan theory in four different articles [79]–[82]. The first study was about Donnan equilibrium model and the relationship with pH and complexation equilibrium in fiber suspension. [79] Second publication studied the complexation of metal ions[80], and the last two were about displacement flow and ionic equilibrium in pulp beds with laboratory experiments and mathematical modelling [81], [82]. Räsänen developed an extension to Donnan theory models, which are the equations that facilitate the calculation of pH and combine

Donnan theory with complexation models. The experimental part verified the assumptions by determinating acidic and basic properties and metal ion sorption of hardwood kraft fibers at different ionic strengths in the presence of a chelant and by modifying the fiber charge by selective hydrolysis of hexenuronic acids. The developed model predicts quantitatively the ionic equilibria in all systems investigated. [73] He also presented the electroneutrality conditions earlier presented in two different equations for both phases in one. [75]

Athley et al.[83] investigated the interactions of divalent metal ions and oxygen-delignified pulps. The study was done by comparing a classical complex formation model and Donnan theory. Their results were that manganese ions had higher affinity for the pulp tan calcium ions. Also, Donnan model gave 10-45% lower prediction of metals in pulp than amounts determined in laboratory tests.

Yantaase et al. [84] compared ion exhange and Donnan equilibrium models to study adsorption of sodium and calcium ions into pulp fibers. In this study, they found that the Donnan model predicted adsorption better than multi-component ion exchange model in the pH range 2.7-6. At pH value higher than 6, both models failed to predict the adsorption of calcium to brown stock pulp. At higher pH, calcium adsorped to brown stock pulp more than what the carboxylate ions were providing.

Interactions between calcium, copper and aluminium ions and wood fibers were studied by J. Lindgren et al. [85] They were also capable to find equilibrium model for pH ≤ 6. Using IR measurements, they determined that Donnan equilibrium model is incapable to model molecular-level interactions between fibers and metal ions. They concluded that there were specific interactions between fibers and metals in the system. An equilibrium model was derived for the equilibrium reaction between two fibers and one metal ion, which explains the results of the study.

6. MATERIALS AND METHODS

This chapter introduces the methods of the experimental part, as well as the substances and analytical methods used. In addition, formulas used to calculate the results are presented.

6.1 Preparation of the adsorbents

The four adsorbents examined in this thesis were sawdust, brownstock pulp, mechanical pulp, and bleached pulp. The initial metal concentrations of the adsorbents are shown in Table 6.

Table 6. *The amounts of metals in the adsorbents (mg/kg). Measured according to Tappi standard T 266 om-02* [86].

Sample Description	Sawdust	Brown stock pulp	Mechanical Pulp	Bleached Pulp
Aluminum, Al	4.79	8.73	5.64	1.99
Barium, Ba	6.81	12.6	4.7	0.47
Boron, B	1.30	0.84	9.30	<0.1
Cadmium, Cd	0.12	0.14	<0.1	0.11
Calcium, Ca	661	1252	1289	568
Chromium, Cr	0.15	0.15	0.24	0.11
Cobalt, Co	<0.1	<0.1	<0.1	<0.1
Copper, Cu	1.18	0.23	26.7	71.1
Iron, Fe	9.88	6.36	5.06	2.75
Magnesium, Mg	154	159	1071	36.0
Manganese, Mn	62.8	58.5	3.24	0.45
Molybdenum, Mo	0.15	0.10	0.12	<0.1
Nickel, Ni	0.29	0.23	0.49	0.27
Potassium, K	369	422	36.5	19.4
Silicon, Si	16.0	56.3	86.7	16.5
Sodium, Na	3.10	3463	352	72.3
Strontium, Sr	3.69	7.10	4.97	0.86
Titanium, Ti	<0.1	0.17	0.28	<0.1
Vanadium, V	0.29	0.30	3.47	<0.1
Zinc, Zn	7.34	6.43	3.06	3.69

Sawdust was produced as follows. Chip samples were dried under a controlled temperature of 35 degrees. The chips were then milled to 1mm particle size to increase the surface area using a Wiley mill M02. Wiley mill is a common mill used in pulp and paper industry laboratories. The sample is loaded into a funnel and into spinning four-blade-rotor which works against stationary knives. Grinded samples that passed the screen are collected into container below the mill. [87]

Collected sawdust was then stored under –20 degrees Celsius. Brown stock pulp was first centrifuged and then stored in freezer in 0 degrees Celsius. The wood samples were stored in the cold, as changes in the properties of the wood samples can be observed when stored at room temperature. When stored at room temperature, for example, the pH of the pulp has been found to decrease significantly. [88]

Before laboratory tests, brown stock pulp, bleached pulp, and mechanical pulp were further wet disintegrated. [89] The disintegrator is used for pulp samples to separate fibers without altering their structural qualities. [90]

6.2 Acid-base titration

Acid-base titration is a quantitative analysis method to determine the concentration of acid or base. In this thesis, acid-base titration was used to determine the concentrations and pK_a values of different acid groups in sawdust and pulp samples. With acid-base titration, all the acid groups in the adsorbent can be determined with a single measurement.

Before titration, 3-5 g of adsorbent was washed with distilled water and filtered with a Büchner funnel. The adsorbent was washed again with 0.1 M HCl so, that the pH is approximately 2. The final wash was then done with distilled water. 1 g of acid-washed adsorbent was added to 490 ml of distilled water and 10 ml of 0.05 M NaCl was added. The solution was stirred and titrated with 0.05M NaOH. The addition of NaOH was done every 30 seconds and the pH was measured after every addition. From the measurements, a diagram of pH as a function of the volume of NaOH was drawn.

The equivalent points of the titration curves were determined with first and second derivatives. The first derivative is calculated from the data to observe equivalent points according to Eq. 11

$$\frac{\mathrm{d}}{\mathrm{dV}}\mathrm{pH} = \frac{\mathrm{d(pH)}}{\mathrm{dV}} \approx \frac{\Delta\mathrm{pH}}{\Delta\mathrm{V}} \tag{11}$$

The first derivative pH-values are plotted as a function of volume mean. The equivalence points are the maximum values.

The second derivative can be calculated according to Equation 12.

$$\frac{d^2}{dV}pH = \frac{d^2(pH)}{dV^2} \approx \frac{\Delta\left(\frac{\Delta pH}{\Delta V}\right)}{\Delta V} \tag{12}$$

The resulting derivative values are further plotted as a function of the volume derivatives. The equivalence points are then solved from a linear equation.

The acid groups in pulps and NaOH react in a molar ratio 1:1. The amount of acid group (mol/kg) can be calculated from the equivalence point (Eq. 13-14)

$$n(OH^-) = n(acid) \tag{13}$$

$$c(acid) = \frac{n(acid)}{m(pulp)} \cdot \text{pulp dry matter content} \tag{14}$$

p*Ka* values of weak organic acids can be calculated from the titration curve. At the half-equivalencepoint, pH=pK_a.

6.3 Cation chromatography

The determination of the metal ions in debarking water after adsorption tests were carried out with cation chromatography. As chromatography, Dionex ICS-6000 was used with IonPac CS16-4 um 2*250 mm analytical column and precolumns CG16-4 µm 2*50 mm and NG12*50 mm. Eluent in use was methane sulphonic acid. Measurement ranges of the ion chromatography used for K^+, Mg^{2+}, and Ca^{2+} were from 0.2 mg/L to 5 mg/L. For Na^+ the measurement range was from 2 mg/L to 25 mg/L.

6.4 Determination of metal concentration and moisture degree of the adsorbents

From each pulp type, the dry matter content was measured with a thermogravimetric moisture analyzer Precisa XM 60. Moisture degrees of the adsorbents were measured to calculate the number of acid groups according to the weight of dry adsorbent. This makes comparison of acid groups more straightforward.

Metal concentrations in adsorbents were determined according to TAPPI T266 –method. According to this standard pulp samples are ashed in the oven and then diluted to HCl solution. [86] In order to apply Donnan theory to modelling, it is necessary to know the amounts of metals in both the external solution and in the fiber. This gives information about how much metals are in the adsorbent in relation to the acid groups it contains, as well as how much metals may move to the external phase in equilibrium. Known metal concentrations in the debarking water were used in all adsorption-related calculations to determine removal efficiency.

6.5 Determination of reaction time of pulp and metal solution

Before tests with debarking water and adsorbents, the optimal contact time is determined with synthetic wastewater. The reaction time was determined to know how the metals move between the phases at different times. With the information obtained from this study, the debarking water and adsorbents were allowed to react for an optimal time. Synthetic wastewaters were prepared from distilled water and metal chlorides. $4.69 \cdot 10^{-4}$ mol/L of $CaCl_2$, $5.76 \cdot 10^{-5}$ mol/L of $MgCl_2$, and $7.30 \cdot 10^{-2}$ mol/L of NaCl were weighed to a flask and mixed with 250 ml of distilled water. pH was adjusted to 5 with 0.1M HCl. 1 g of pulp and 50 ml of synthetic wastewater was pipetted into five flasks. Flasks were then mixed for 2, 5, 10, and 30 minutes. After each period, the sample was filtered with a Büchner funnel and syringe filter. Samples were analyzed with cation chromatography. The filtration with the Büchner funnel was intended to stop the sorption and separate most of the solids from the debarking water. Because the filtered debarking water samples were analyzed with cation chromatography, the samples still had to be filtered using a syringe filter. A syringe filter was used to ensure that the debarking water samples did not contain solids and thus plug the chromatography. The results obtained from the cation chromatography (mg/L) were converted to concentration per the mass of sawdust to give an idea of how the cations reacted with the pulp. An average was taken from each pair of duplicates.

6.6 Adsorption tests with debarking water

For the actual adsorption test, samples were prepared from 1 g of adsorbent and 50 ml of debarking water for six different flasks. Samples' pH was then adjusted with 0.05M NaOH and 0.1M HCl so, that the pH varied from 2 to 10. Also, one blank sample is made from only debarking water. After mixing time, the samples are filtered first with a Büchner funnel and then with a syringe filter. Samples were analyzed with cation chromatography.

Removal efficiencies were calculated by subtracting the final cation concentration from initial cation concentration in debarking water. The change was further divided by the initial cation concentration in debarking water and multiplied by 100 to give the removal efficiency as a percentage. The calculations are presented as equations below.

$$\Delta[X_i] = [X_i]_1 - [X_i]_2 \tag{15}$$

$$\Delta[X_i] - \% = \frac{\Delta[X_i]}{[X_i]_1} \cdot 100\% \tag{16}$$

In the Equations 15 and 16 $[X_i]_1$ is the initial concentration of cation i (mg/L) in debarking water, $[X_i]_2$ is the final concentration of cation i (mg/L) in debarking water.

6.7 Donnan Theory calculations

For every adsorbent and debarking water, concentration of divalent anions were calculated using Donnan theory and Excel solver-command. This was done, because it was assumed that there are some anions in the adsorbents that were not determined in chromatography. For adsorbents, the determination of anion concentration was done using Equations 6 and 7.

Titration results were used to solve the equations for the pulp samples and sawdust, as the compounds used in the titration and their amounts were known. The solution were no acid or base additions had been made was used to solve equations. In this case, the only ions present in the solution were the Na^+ and Cl^- initially added to the solution.

The concentration of anion was first solved from the equation so that the solution of each equation approached zero. The Excel Solver command was then used to resolve pH and Donnan distribution coefficient λ for entire titration data.

The knowledge of the original pH of debarking water was used to determine the anion concentration in debarking water. When no pulp is added, the Donnan equilibrium concentrates only on external solution and the concentration can be calculated using Equation 6.

In the case of debarking water alone, the Donnan distribution coefficient is 1. Therefore, Equation 6 can be simplified to

$$10^{-pH} - 10^{-14+pH} + \sum_{i=1}^{n} \frac{z_i X_{T,i}}{V_T} = 0 \tag{17}$$

When solving the equation 19. It was considered that the metals in the solution without pulp addition are originated only from the debarking water.

The adsorption results of the metals were also modelled using Donnan theory. All known values were inserted in the Equation 8. In addition, the previously solved amount of anions in both the debarking water and pulp were taken into account. The only unknown term in the equation was Donnan distribution coefficient, which was solved using Excel's goal seek command. When Donnan distribution coefficients λ were solved for each pH value, the cation concentrations in the external solution could be solved using Equation 10.

With Equation 10, the concentration of any desired cation can be calculated when its total molar amount, total volume of the system, and Donnan distribution coefficient λ are known. In this thesis, concentrations were calculated as the sum of potassium and sodium, and magnesium and calcium. In addition, concentration of potassium was further calculated separately to model its adsorption without a high concentration of sodium. The concentration values obtained were plotted as a function of pH and compared with the experimental results.

The relative errors between Donnan theory and experimental results were calculated as follows:

$$E_r = \frac{x_E - x_D}{x_E} \cdot 100\% \tag{18}$$

Where E_r is the relative error, x_E is the experimental concentration of a cation, and x_D is the concentration according to Donnan theory.

Donnan theory was further used to calculate theoretical metal concentrations in external solution with different adsorbent weights. The initial mass of the adsorbent (~1g) was multiplied by 0.1-15 and the new weight was placed in Equations 8 and 10. This provided a theoretical estimate of how metals are removed at different volume-weight ratios and which ratio would be best for metal removal.

7. RESULTS AND DISCUSSION

The results are presented in this chapter. This chapter also discusses the reasons for the results and possible ways to improve them.

7.1 Determination of acid groups in pulp adsorbents

For each adsorbent, the titration curve was derived twice as described in chapter 6.2. To find out the different acid groups, the values of NaOH consumption were determined for each maximum value of the derivative and subtracted from the corresponding blank consumption. Titration curves and first derivatives are shown in Figure 18.

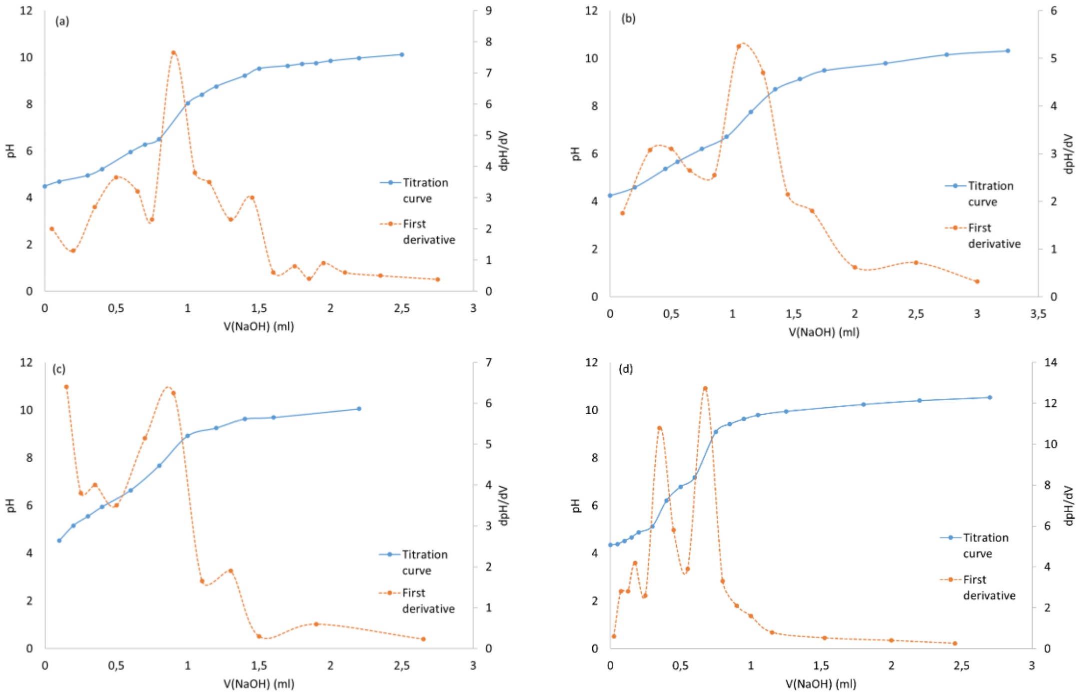

Figure 18. *Acid-base titration curves and the first derivatives for a) sawdust b) brown stock pulp c) mechanical pulp and d) bleached pulp. The titration curves are shown as pH as a function of NaOH consumption. The first derivatives are shown according to the second axis (V(NaOH), dpH/dV).*

Based on the titration curves, the titration could be assumed to be successful. All curves clearly show rapid changes in pH. The pK_a value and concentration of each acid group as mol/kg dry pulp were calculated from the derivatives. Resulting values for pK_a values and amounts of acid groups are presented in Table 7.

Table 7. *pKa values and acid concentrations for the adsorbents used in the thesis.*

	Sawdust		**Brown stock pulp**		**Mechanical pulp**		**Bleached pulp**	
	pK_a value	c(acid) (mol/kg)	pK_a value	c(acid) (mol/kg)	pK_a value	c(acid) (mol/kg)	pK_a value	c(acid) (mol/kg)
pK_{a1}	3.11	0.002	3.04	0.032	4.10	0.006	4.48	0.003
pK_{a2}	5.42	0.029	4.62	0.004	5.02	0.019	4.79	0.014
pK_{a3}	7.91	0.042	5.69	0.020	6.27	0.065	5.53	0.032
pK_{a4}	10.50	0.088	8.46	0.047	9.22	0.035		
Total		0.161		0.104		0.125		0.049

The pKa values listed in Table 7 are like those in previous studies. Sjöströms study showed that the pK_a values of major carboxyl groups in wood vary between 3-4, and pK_a values for the minor carboxyl groups 4-5. The pK_a values referring to phenolic acid groups vary between 7-8 and 9.5-10.5.[10] According to Koljonen et al. the carboxylic acids present in the mechanical pulp have pK_a values between 3-5 and 5-6. All studies revealed that the major source of carboxylic acids are uronic acids attached to xylan.[91] Stenius and Laine found that kraft pulps contain carboxyl groups with pK_a values of 3.6 and 5.7 [92]. Similar pK_a values were found by Laine et al. as the pK_a values of kraft pulp carboxyl groups were 3.3 and 5.5 [93]. Karhu et al. studied the acid groups contained in pulps and the relationship between their amount and temperature. According to them, the pK_a values of the carboxyl groups range from 3 to 6 and the phenolic groups from 9 to 10. The results also showed that temperature is a significant factor in concentrations. [94]

a pK_a value of 3.4 indicates the presence of uronic acids, and 5.5 a weaker acid due to residual lignin in the pulp. Lignin also contains guaiacyl and syringyl phenols with pKa value 6.2-11. [93] In mechanical pulp, pK_a values 3-5 and 5-6 indicate the presence of carboxyl groups. Hexenuronic acid hydrolysis during bleaching like described in chapter 3.3. Therefore, there are no indications of hexenuronic acid pKa of 3 in the titration results of the bleached pulp.

7.2 Reaction time for adsorption

The reaction time for adsorption was determined by stirring synthetic wastewater and sawdust for different times. From Figure 19, it can be seen that during the first five minutes at pH 5, adsorption to sawdust is most efficient. Within ten minutes, the metals have dissolved back into the water, showing a rise in the curves. After 15 minutes, some of the metals have adsorbed back into the sawdust, but after this time the metals again dissolve back into the water. This phenomenon is due to the equilibrium of the system, with the ions in the sawdust and external water moving between the phases to find equilibrium, as explained in chapter 4. From the results, a clear equilibrium was not observed.

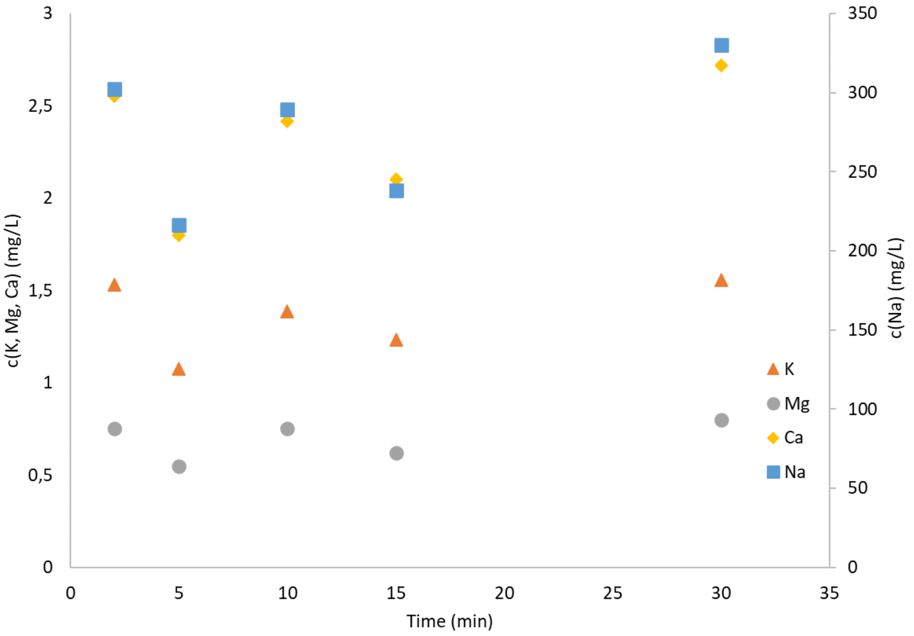

Figure 19. *Concentrations of metals in synthetic wastewater at pH 5 from 2 to 30 minutes.*

Table 8 shows the exact concentrations of the studied metal cations in synthetic wastewater from 2 to 30 minutes in pH 5.

Table 8. *Concentrations of each metal cation in pH 5 with reactions times 2-5 minutes.*

Time (min)	Na (mg/L/g)	K (mg/L/g)	Mg (mg/L/g)	Ca (mg/L/g)
2	304.01	1.54	0.76	2.57
5	218.25	1.09	0.55	1.82
10	286.91	1.38	0.74	2.40
15	231.80	1.20	0.61	2.05
30	325.51	1.54	0.79	2.68

In Ala-Kaila and Aléns study, the best removal efficiency occurred in 5 minutes, which is in line with the results of this work. However, after 5 minutes, the concentration remained almost constant. [95]

7.3 Adsorption capability of adsorbents and pH dependence

The ability to act as an adsorbent was examined using debarking water ang 1g adsorbent. The metal concentrations of the original debarking water were measured using cation chromatography. Metal concentrations and other important water properties for the thesis are listed in Table 9.

Table 9. *Properties of used debarking water.*

Property	Value
pH	5.05
COD, mg/L COD	1255
Na, mg/L	55.184
K, mg/L	23.932
Mg, mg/L	4.176
Ca, mg/L	8.42

The adsorption test showed that different metals react differently at different pH values. Sodium was adsorbed at low pH values, but when pH was above 5, sodium was desorbed back into water. Potassium and magnesium reacted stably, and both were removed from the water at high pH. Calcium was desorbed into water especially when sawdust was used at low pH but adsorbed on the pulp at pH above 6. Graphs showing the adsorption and desorption of each cation at different adsorbents are shown in Figure 20 as removal percentages as a function of pH. A quartic polynomial function was fitted to the data points.

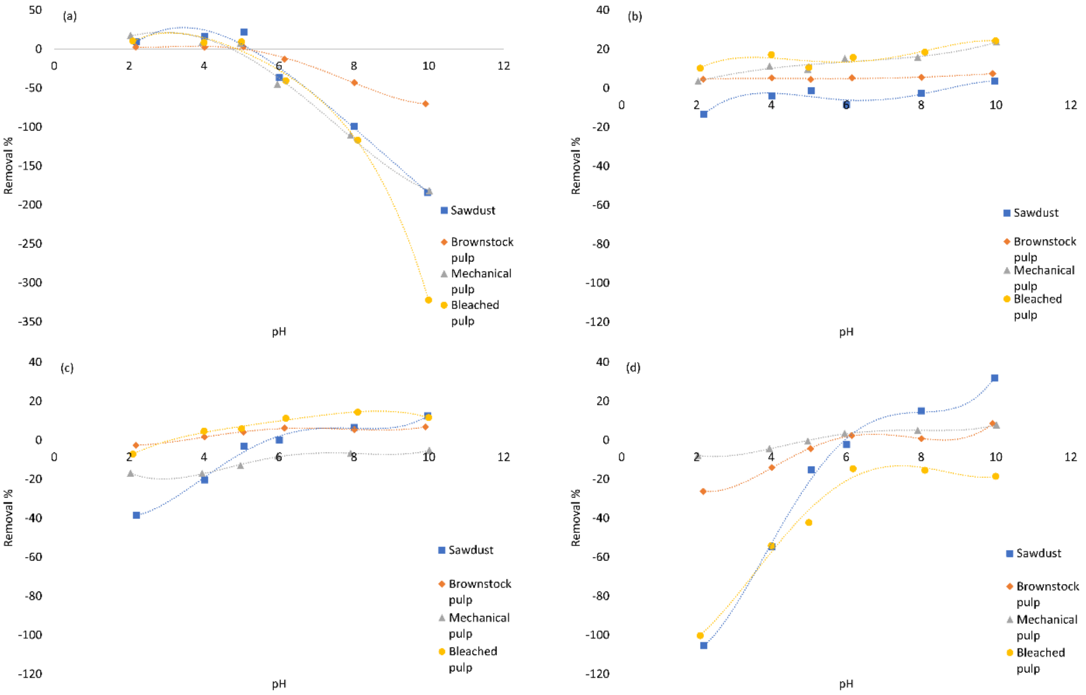

Figure 20. *Removal percentages of a) Na$^+$ b) K$^+$ c) Mg^{2+} and d) Ca^{2+} plotted with fitted quartic polynomial function at pH 2-10.*

The test shows that the adsorption of sodium from water to pulp takes place most efficiently at a pH of 5 (Fig. 20). At pH values above this, sodium is desorbed into water, whereby calcium and magnesium are adsorbed on the pulp. As shown in Figure 20, sodium adsorption was most efficient when sawdust was used. Sodium removal efficiency was calculated relative to the initial sodium content of the debarking water. The removal percentages at pH 5 for all adsorbents are shown in Table 10.

Table 10. *Sodium removal efficiencies at pH 5 per 1g of dry pulp.*

Adsorbent	Na (%)
Sawdust	21.82
Brown stock pulp	2.81
Mechanical pulp	7.18
Bleached pulp	9.29

K, Ca, and Mg reacted similarly. At low pH values, these metals were released from pulp into water. At higher pH values, these metals are adsorbed on pulp. The higher the pH was raised the more divalent metals were removed from the water (Fig. 20).

From Table 11, potassium was most efficiently removed by bleached pulp at pH 10 by 24.3%. Bleached pulp also removed magnesium by 11.6% at pH 10. The corresponding value for sawdust was 11.4%. Bleached pulp, however, did not remove calcium at all. Sawdust was the most efficient in removing calcium by 29.4% at pH 10.

Table 11. *K, Mg, and Ca removal percentages at pH 10 per 1 g of dry pulp.*

Adsorbent	K (%)	Mg (%)	Ca (%)
Sawdust	3.57	11.35	29.36
Brown stock pulp	7.43	6.82	8.51
Mechanical pulp	23.62	-5.20	4.98
Bleached pulp	24.31	11.61	-18.60

Wood chip and brown stock pulp samples were also tested for pH 11. Under these conditions, 485.09% of sodium was desorbed into water, while 4.81% of potassium, 12.47% of magnesium, and 41.70% of calcium were adsorbed on wood. The release of cations and adsorption into pulp was considerably more moderate with brown stock pulp. 143.01% of sodium was desorbed into water, 8.27% of potassium, 6.66% of magnesium, and 12.10% of calcium were adsorbed into pulp. The results clearly show that the efficiency of adsorption increases especially with divalent cations the higher the pH is raised with NaOH. When NaOH is added, the amount of Na^+ ions and OH^- ions increases in the external solution with increasing pH. One explanation for the removal percentages of magnesium and calcium is that they react with OH^- in the external solution and precipitate as hydroxides. This reaction is called hydroxide precipitation, in which metals precipitate into hydroxides at their characteristic pH values. [96]

Yantaase and Rorrer studied the adsorption of Na^+ and Ca^{2+} to hydrogen exchanged bleached pulp and unbleached brown stock pulp. In their study, sodium adsorption was 0.005 mmol/g dry bleached pulp and 0.01 mmol/g dry brown stock pulp at pH 10. Calcium adsorption at pH 10 was 0.020 mmol/g dry bleached pulp and 0.05 mmol/g dry brown stock pulp. [84] Differences in results clearly show the importance of hydrogen exchange. In this work at pH 10, sodium was not adsorbed to the bleached pulp or brown stock pulp. Calcium was also not adsorbed on the bleached pulp, but the adsorption on the brown stock pulp was about 0.02 mmol/g dry brown stock pulp. In Sus study, an acid washed spruce adsorbed Ca 76 mg/g, Mg 27.9 mg/g, K 7.8 mg/g and Na 4.6 mg/g. Acid washed brown stock pulp adsorbed Ca 168 mg/g, Mg 89 mg/g, K 11.7 mg/g and Na 11.5 mg/g. Acid washed peroxide bleached mechanical pulp adsorbed Ca 172 mg/g, Mg 65.61 mg/g, K 7.8 mg/g and Na 2.3 mg/g. [97] These values are much higher than the results of this thesis. Significant differences in the results are most likely due to acid washing.

The efficiency of sawdust as an adsorbent can be explained by the amount of acid groups relative to the amount of metals it contains. Sawdust contains approximately 0.035 mol/kg of metals, and the organic acid group content is approximately 0.161 mol/kg (Table 12). Although bleached pulp contains almost half amount of metals, it also contains almost three times less acid groups than sawdust. Therefore, the potential for metal adsorption relative to the metals already existing in sawdust is greater than with bleached pulp.

Table 12. *Amount of organic acid groups (mol/kg) relative to initial metal content (mol/kg) for all adsorbents.*

	Sawdust	**Brown stock pulp**	**Mechanical pulp**	**Bleached pulp**
Metal content (mol/kg)	0.035	0.203	0.097	0.021
Organic acid content (mol/kg)	0.161	0.104	0.076	0.049
Organic acids/metals	4.623	0.512	1.283	2.735

The results show that sawdust contain more than 4.5 times more acid groups than metals. This means that even if internal metals are not removed, sawdust still have the potential to adsorb metals. On the other hand, brown stock pulp contains almost twice as many metals as acid groups, so if brown stock pulp is to be used as an adsorbent, the metals it contains must first be removed by acid washing. However, the laboratory experiments showed that even with brown stock pulp, it is possible to remove Na, K, Mg, and Ca from the debarking water. This may be due to the fact, that when equilibrium is established, the mass desorbs the metals it contains into water, freeing acid binding sites for the metals studied. Another option is that the removal of metals happens otherwise than through adsorption. For example, the metals can react with the sulphates in the system and precipitate.

7.4 Modelling of the adsorption with Donnan Theory

Donnan theory was used to model the adsorption between debarking water and sawdust. Initially, it was assumed that sawdust and debarking water contained anions that had not been analyzed. When solving the amount of anions, it was assumed that all the metals in wood were removed in the acid wash performed before titration. Donnan theory was used to find the anion content that was close to the pH values of the initial titration. (Fig. 21) The molar amount of anions in sawdust was $6.67 \cdot 10^{-6}$ mol, in brown stock pulp $1.96 \cdot 10^{-6}$ mol, in mechanical pulp $5.02 \cdot 10^{-6}$ mol, and in bleached pulp $4.81 \cdot 10^{-6}$ mol.

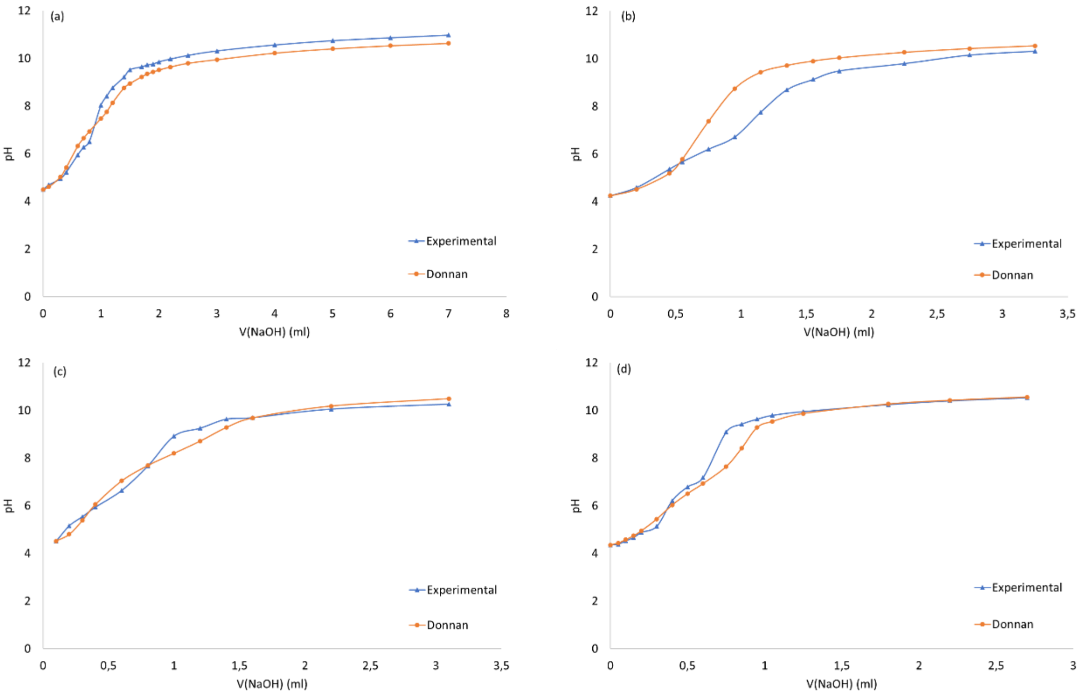

Figure 21. *Titration curves calculated with Donnan theory and experimental titration curves a) sawdust b) brown stock pulp c) mechanical pulp and d) bleached pulp.*

The same methods were used to determine the amount of anionic groups in debarking water. In laboratory experiments, the pH of debarking water was adjusted before the sawdust was mixed with the water. Thus, the anion content of water could be calculated considering only the cations and pH contained in the debarking water. The calculated amount of anions in debarking water was $7.12 \cdot 10^{-4}$ mol/L.

The calculated amount of anions were used to determine the values of Donnan distribution coefficient in different pH values (Figure 22). The parameters used in the calculation are presented in Table 13.

Table 13. *Parameters and values used to determine Donnan distribution coefficient.*

Parameter	Value
Total volume, V (mL)	50-61
Water content of wall, F (mL/g dry pulp)	1.4
Dissociation constant of acid, K_a	$10^{-3.04}$-$10^{-10.5}$
Acid group content, $[A_f]_T$ (mol/kg dry pulp)	0.049-0.161
Hydrogen ion concentration $[H^+]_s$	$10^{-2.19}$-10^{-11}
Total amount of monovalent metal ions, $[M^+]$ (mol/kg)	0.0126-0.0131
Total amount of divalent metal ions, $[M^{2+}]$ (mol/kg)	0.0234
Total amount of trivalent metal ions, $[M^{3+}]$ (mol/kg)	0.0018
Total amount of tetravalent metal ions, $[M^{4+}]$ (mol/kg)	0.0006
Total amount of anions in fiber phase (mol/kg)	$7.12 \cdot 10^{-4}$
Total amount of anions in external phase (mol/L)	$1.96 \cdot 10^{-6}$ – $6.67 \cdot 10^{-6}$

The resulting Donnan distribution coefficients were plotted as a function of pH (Fig. 22).

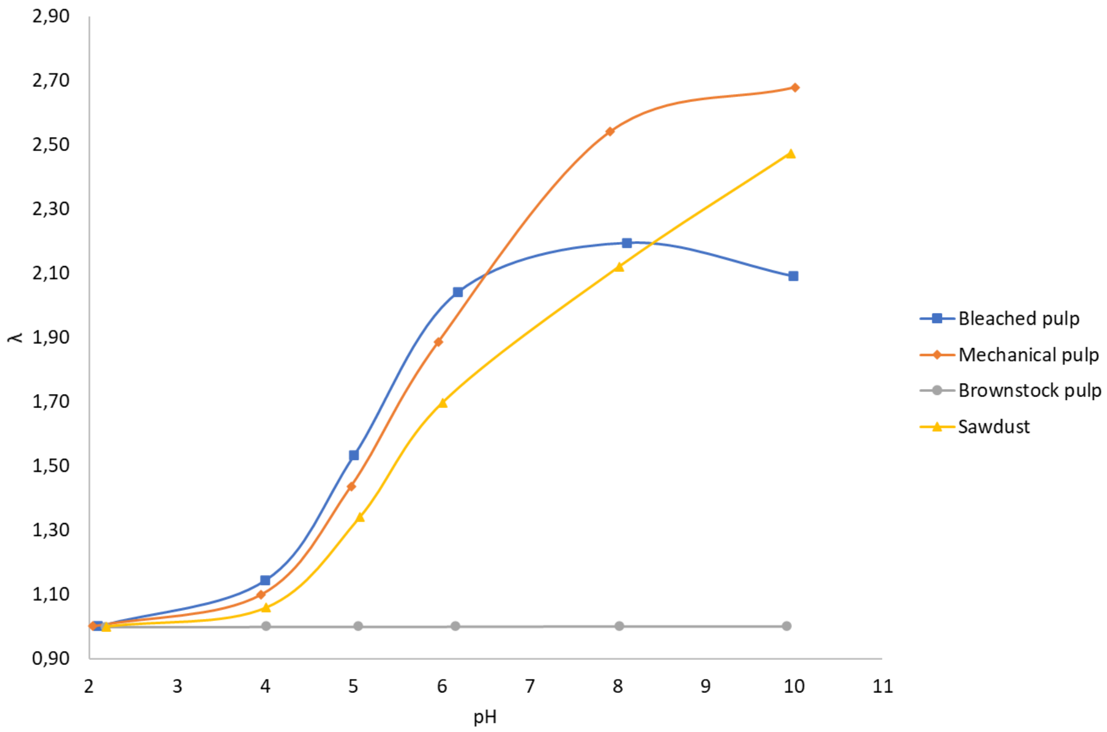

Figure 22. *Donnan distribution coefficient as a function of pH.*

With saw dust mass of 1g and the volume of debarking water 50 ml, the Donnan distribution coefficients got values from 1 to 2.69. These values are in line with previous studies. [84] At low pH, the value of Donnan distribution coefficient is around one. As the pH is raised, the metal cations adsorb to pulp, increasing the value of the coefficient. These values were further used to determine cation concentrations in different pH values according to Equation 9 (Table 14).

Table 14. *Calculated Donnan distribution coefficients at different pH values.*

			λ	
pH	Saw-dust	Brown stock pulp	Mechani-cal pulp	Bleached pulp
2	1.00	1.00	1.00	1.00
4	1.06	1.00	1.10	1.15
5	1.34	1.00	1.44	1.53
6	1.70	1.00	1.89	2.04
8	2.12	1.00	2.53	2.19
10	2.47	1.00	2.68	2.09

In Yantaase and Rorrers study, the Donnan distribution coefficient values for brownstock pulp ranged from 1.46 to 2.84 when the pH was 2.64 to 10.9. For bleached pulp, the Donnan distribution coefficient got values from 1.45 to 2.64 with pH from 2.67 to 11.11. [84] These results also indicate that the acid washing of the pulp is important for the adsorption.

When modelling the adsorption of monovalent cations, the relative error to the experimental value ranged from 0 % - 48 %. Donnan theory failed to calculate cation adsorption, and relative errors ranged from 0 % to 123 %. In addition to the calculations, the errors are most likely due to inaccuracies in laboratory work. The adsorption results modelled with Donnan theory, and the experimental results are presented in Figure 23 and 24 as a function of pH.

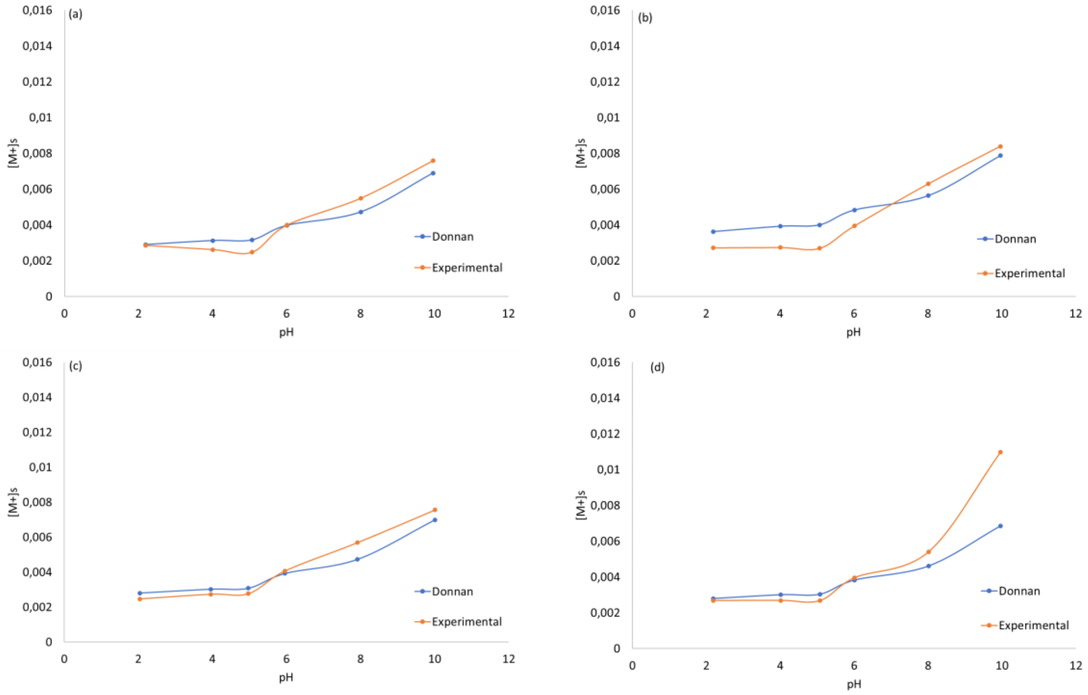

Figure 23. *Concentration of monovalent cations in debarking water at pH 2-10 modelled with Donnan Theory and experimental values with a) saw dust b) brown stock pulp c) mechanical pulp and d) bleached pulp.*

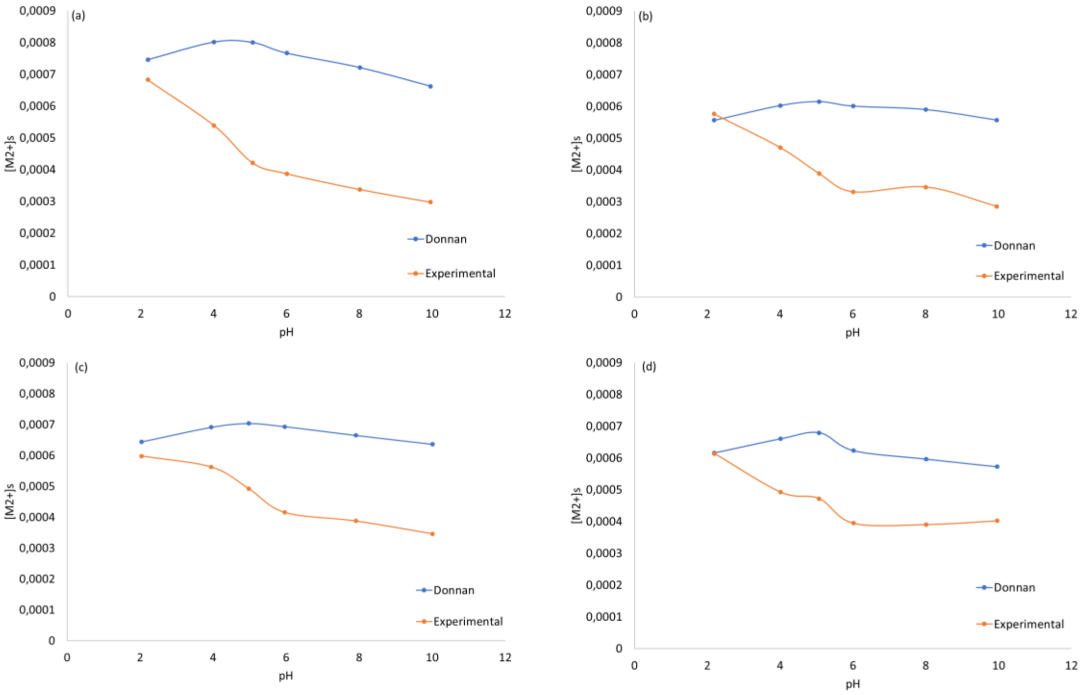

Figure 24. *Concentration of divalent cations in debarking water at pH 2-10 modelled with Donnan Theory and experimental values with a) saw dust b) brown stock pulp c) mechanical pulp and d) bleached pulp.*

As Figures 23 and 24 indicate, Donnan theory modelled the initial concentrations of cations in adsorbents and debarking water well. The Theory did not model the adsorption of divalent cations with its actual efficiency. However, the graphs show that the curves are quite similar in shape. Donnan theory modelled adsorption and desorption of monovalent cations with good accuracy. Similar results from modelling are observed in the Yantaase and Rorrers study. In their results, sodium adsorption could be modelled with good accuracy. Calcium adsorption was also weaker in their work when modelled at high pH values than in reality. [84]

From the modelled results, the adsorption efficiency with different mass to external liquid ratios was further calculated. The mass was changed from 0.1 grams to 15 grams, keeping the volume of debarking water constant. The resulting cation concentrations as a function of mass are shown in Figure 25 and 26.

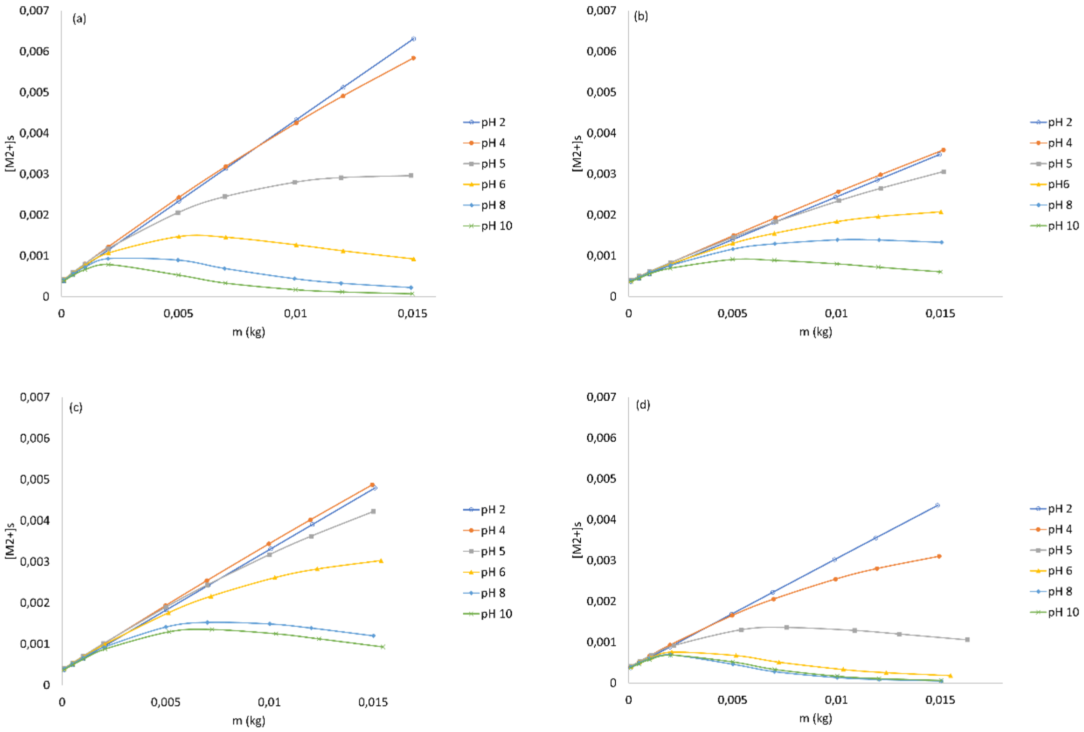

Figure 25. *Concentration of divalent cations in debarking water with a) sawdust b) brown stock pulp c) mechanical pulp and d) bleached pulp in pH 2-10 with different mass-volume ratio.*

The results show that the efficiencies of divalent cation removal and the amounts of organic acid groups in the pulps are related. Sawdust and bleached pulp had the highest acid-metal ratio of 4.62 and 2.74. These adsorbents also remove metals with the best efficiency. The metal removal efficiency of these adsorbentss increases at high pH values as more pulp is added. This means that the amount of free acid groups in the adsorbent increases, allowing more cations to be removed. The acid-metal ratio of brown stock pulp was approximately 0.51 which means that in brown stock pulp, there is half the amount acid than metals. It is also reflected in the results, as the brown stock pulp is not able to remove cations from the debarking water according to the model.

The initial concentration of calcium and magnesium in debarking water was $2.2\cdot10^{-4}$ mol/L. The concentration of divalent cations in debarking water increases at low pH. At pH 10 and with 15 g of sawdust in 50 ml of debarking water, sawdust removes 66.8 % of divalent cations, as the final concentration was $7.15\cdot10^{-5}$ mol/L. The bleached pulp would remove approximately 71.1% under the same conditions. It can be assumed that in reality sawdust removes divalent cations more efficiently. The reason for the calculated result may be that Donnan theory modelled more accurately the experimental results with bleached pulp (see Figure 22). The modelled results show that sawdust is able to remove divalent cations on at pH 10 or higher. However, it can be seen from the results of the experimental work that the removal of divalent cations already takes place at a pH 8. In addition, it is assumed that the more sawdust is used in relation to the amount of debarking water, the more efficient the removal of cations. This is because when the weight of sawdust is increased, the amount of organic acid groups in sawdust increases.

The same phenomenon is also seen when modelling the adsorption of monovalent cations. The sawdust and bleached pulp remove cations, especially at high pH values and with increasing pulp amount. With mechanical pulp, the concentration of metals in the external liquid remains almost constant, and in the case of brown pulp, the concentration of monovalent cations increases considerably (Fig 26).

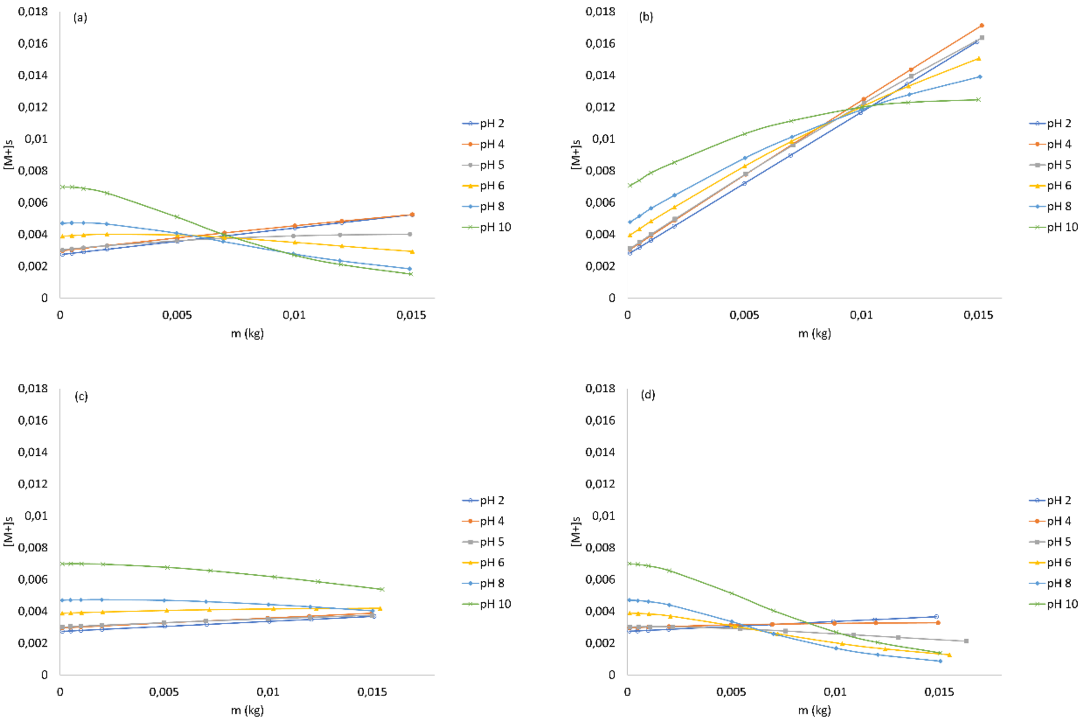

Figure 26. *Concentration of monovalent cations in debarking water with a) sawdust b) brown stock pulp c) mechanical pulp and d) bleached pulp in pH 2-10 with different mass-volume ratio.*

When modelling the reaction of potassium and sodium, sodium is the dominant cation. For this reason, adsorption of potassium was modelled also separately. It can be seen from the graphs (Fig. 27) that the concentration of potassium in external solution is different with different weights than in Figure 26. This is due to the high amount of sodium compared to the amount of potassium.

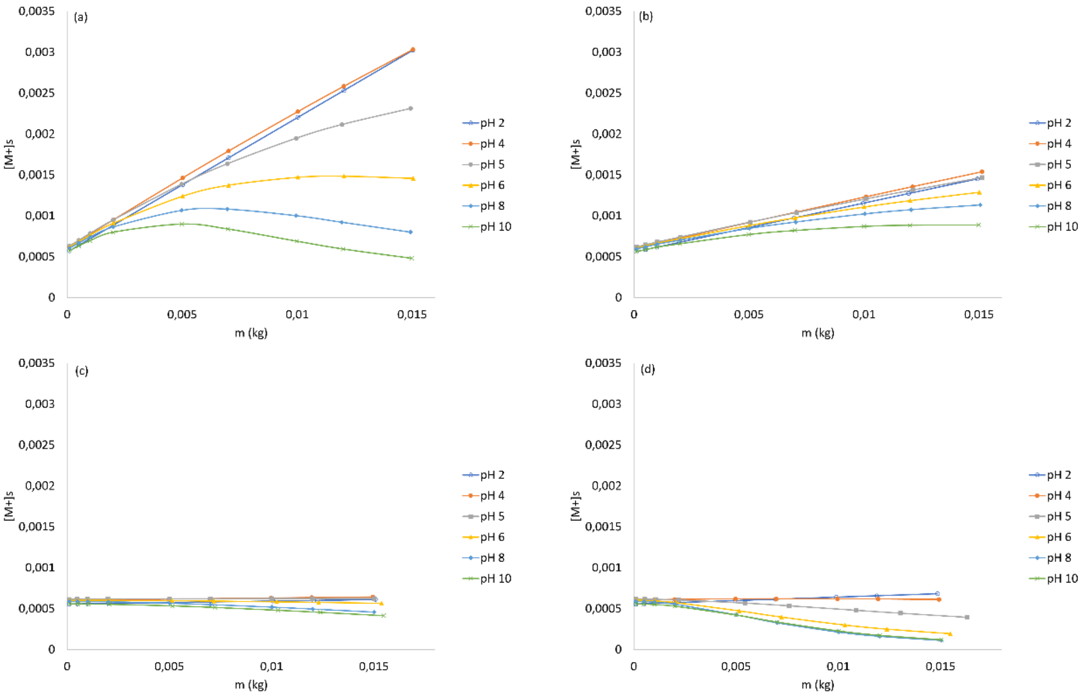

Figure 27. *Concentration of potassium in debarking water with a) sawdust b) brown stock pulp c) mechanical pulp and d) bleached pulp in pH 2-10 with different mass-volume ratio.*

The removal efficiencies were also calculated from the ratio of the concentrations of the modelled cations in externals solution to the initial concentrations of cations of debarking water. Table 15 shows the removal efficiencies at pH 10.

Table 15. *Removal efficiencies of monovalent and divalent cations at pH 10.*

	Removal efficiency (%) of monovalent cations			
m (g)	Sawdust	Brown stock pulp	Mechanical pulp	Bleached pulp
0.1	-131.92	-134.57	-131.82	-132.42
0.5	-131.57	-145.67	-132.09	-130.73
1	-128.95	-161.38	-132.02	-127.70
2	-119.19	-183.24	-131.17	-117.96
5	-69.08	-242.51	-124.53	-70.36
7	-32.74	-269.59	-117.62	-34.32
10	10.11	-298.17	-104.66	10.65
12	29.93	-308.23	-94.76	32.20
15	50.01	-313.71	-78.80	53.90
m (g)	Removal efficiency (%) of divalent cations			
0.1	-79.41	-71.14	-75.56	-73.94
0.5	-144.84	-108.18	-130.26	-119.66
1	-207.83	-158.97	-194.77	-166.12
2	-265.99	-222.49	-308.57	-218.18
5	-146.40	-322.91	-504.64	-140.33
7	-55.18	-313.02	-530.18	-54.98
10	19.99	-273.01	-482.12	22.44
12	45.57	-235.03	-424.92	49.30
15	66.77	-181.46	-333.25	71.07

It is clear from the calculated removal percentages that theoretically only sawdust and bleached pulp can remove all the metals studied at pH 10 when the weight of adsorbent is above 10 g and volume of debarking water is 50 ml. The ratio of adsorbent to debarking water is then 1:5. The removal efficiency increases when the weight of these adsorbents increases. According to Donnan Theory, the reason for this is the increasing amount of acid groups. Sawdust and bleached pulp have more acid groups than metals (Table 12), which increases the acid groups active in adsorption as more sawdust or bleached pulp is added.

Results of the laboratory work show that it is possible to remove metals using sawdust and pulp. Of the four adsorbents studied, sawdust had the best metal removal efficiency. Using sawdust, removal of sodium was the most efficient at pH 5 (23.77 %), potassium, magnesium and calcium was most efficiently removed at pH 11 with 58.98 %. The efficiency of sawdust was assumed, as the untreated wood contains a lot of acid groups and no metals from the pulp process have been attached to it. However, when considering the use of sawdust in water purification, its overall impact on water must be considered. The removal efficiency increases when more sawdust is used. Because of that, the easiest way to use sawdust could be to pack it into a fine bed and let water flow through it. Natural wood contains resin acids and their derivatives, which are toxic to fish species. [98] In addition to toxic compounds, more organic compounds dissolve in water from the sawdust, which increases the need of filtering, requiring additional investments. In addition, the adsorption is highly pH dependent, so the pH must be changed with some base. One area of future research could be the removal of metals by hydroxide precipitation. The challenges of the method are that the precipitation pH for each metal is slightly different, and the solubilities varies for different metals. This means when one metal precipitates, the other may dissolve back into liquid. Sodium and potassium hydroxides are very soluble in water so they cannot be easily removed by precipitation. The method can be used to remove calcium and magnesium. Calcium hydroxides solubility product constant value, K_{sp}, is approximately $5.5 \cdot 10^{-6}$ at 25 °C, so the concentration of calcium in water needs to be quite high for the removal. The solubility product constant indicates the level at which the substance dissolves in water. The higher the K_{sp} value, the better the substance is soluble in water. [99] For magnesium hydroxide, the K_{sp} value at 25 °C is $1.8 \cdot 10^{-11}$, which means that magnesium hydroxide can be easily precipitated from water. [100] The benefit of the method would be that no additional organic matter would need to be added to the wastewater. In addition, the pH change could be made using lime or caustic soda, which are already used in the pulp mill. [101]

8. CONCLUSIONS

In this thesis, the ability of sawdust, brown stock pulp, mechanical pulp, and bleached pulp to act as an adsorbent to remove metals from debarking water was examined. The theoretical part studied what properties of wood affect the ability to act as an adsorbent and how the properties change during pulp process. The most important properties for the adsorbents were the amount of acid groups in the adsorbents and the amount of metals they contained. The metals studied in this thesis were sodium, potassium, magnesium, and calcium. The adsorption of metals on wood and pulp samples was modelled using Donnan theory. Donnan theory describes the movement of metal cations through a semipermeable membrane, combining both ionic and mass equilibrium.

Sodium was removed from the wastewater at significantly lower pH values than the other metals studied. The most efficient removal of sodium was at pH 5. At higher pH, it dissolved back into water. Potassium removal was uniform at all pH values. Divalent calcium and magnesium, in turn, are removed more efficiently when pH is raised. Of the adsorbents, untreated sawdust was the most efficient in removing metals. The highest sodium removal efficiency, 23.77 %, was obtained using sawdust at pH 5. At pH 11, sawdust solution removed almost 42 % of calcium, and 13% of magnesium. Potassium was removed by about 5 %. The efficiency of sawdust in removing metals can be explained by the amount of organic acid groups compared to the initial metal concentration of sawdust.

Donnan theory was able to model adsorption quite well. The modelled results for the adsorption of monovalent metals and the laboratory results corresponded well to each other. According to Donnan theory, the adsorption of divalent metals is lower than shown by the results of laboratory experiments. However, the shapes of the graphs of the results were similar. According to the experimental results, some removal of metals is also possible with brown stock pulp and mechanical pulp, which, according to Donnan theory, could not remove metals. This indicates that when reacting with debarking water, metals are also removed for example by precipitation, which could be one future research topic. When modelling adsorption using a different amount of sawdust, it was found that theoretically, by increasing the amount of sawdust, more metals can be removed. If sawdust is used in the future for the removal of metals from pulp mill wastewaters, the overall impact of its use must be studied.

REFERENCES

[1] “Paper Mills’ Thirst for Water – RecycleNation.” https://recyclenation.com/2010/09/paper-mills-recycle-water/ (accessed Apr. 22, 2022).

[2] G. J. Vervelde, “The Donnan-principle in the ionic relations of plant roots on ,” *Plant and soil IV*, vol. 4, May 1953, Accessed: Jun. 13, 2022. [Online]. Available: https://www.jstor.org/stable/42931620

[3] C. J. Biermann, *Handbook of Pulping and Papermaking*. San Diego: Elsevier Science & Technology, 1996.

[4] Raimo. Alén, “Structure and chemical composition of wood.,” in *Forest Products Chemistry*, P. Stenius, Ed. Helsinki: Fapet Oy, 2000.

[5] L. Serrano, R. Luque, and B. F. Sels, *Lignin Chemistry*. Cham: Springer International Publishing AG, 2020.

[6] Dietrich. Fengel, *Wood chemistry, ultrastructure, reactions*, Reprint 2011. Berlin ; Walter de Gruyter, 1989. doi: 10.1515/9783110839654.

[7] A. Stamm, *Wood and cellulose science*. New York: Ronald Press Co., 1964.

[8] R. M. Rowell, R. Pettersen, and M. A. Tshabalala, “Cell Wall Chemistry,” *Handbook of Wood Chemistry and Wood Composites, Second Edition*, pp. 33–72, 2012.

[9] F. Asadi, H. Shariatmadari, and N. Mirghaffari, “Modification of rice hull and sawdust sorptive characteristics for remove heavy metals from synthetic solutions and wastewater,” *Journal of Hazardous Materials*, vol. 154, no. 1–3, pp. 451–458, Jun. 2008.

[10] E. Sjostrom, *Wood Chemistry*. Saint Louis: Elsevier Science & Technology, 1993.

[11] Monica. Ek, G. Gellerstedt, and Gunnar. Henriksson, *Pulp and paper chemistry and technology. Volume 1, Wood chemistry and wood biotechnology*. Berlin: De Gruyter, 2009. doi: 10.1515/9783110213409.

[12] E. Sjöström and U. Westermark, “Chemical Composition of Wood and Pulps: Basic Constituents and Their Distribution,” in *Analytical Methods in Wood Chemistry, Pulping, and Papermaking*, Berlin, Heidelberg: Springer Berlin Heidelberg, pp. 1–19. doi: 10.1007/978-3-662-03898-7_1.

[13] M. Asif, “Sustainability of timber, wood and bamboo in construction,” in *Sustainability of Construction Materials*, Elsevier, 2009, pp. 31–54. doi: 10.1533/9781845695842.31.

[14] A. Behr, *Chemistry of renewables : an introduction*, 1st ed. 2020. Berlin, Germany ; Springer-Verlag, 2020. doi: 10.1007/978-3-662-61430-3.

[15] A. Ebringerová, Z. Hromádková, and T. Heinze, “Hemicellulose,” in *Polysaccharides I*, Berlin/Heidelberg: Springer-Verlag, pp. 1–67. doi: 10.1007/b136816.

[16] Eero. Sjöström, *Wood chemistry : fundamentals and applications*. New York: Academic press, 1981.

[17] “KnowPulp.” http://www.knowpulp.com/extranet/suomi/kps/ui/knowpulp.htm (accessed Apr. 03, 2022).

[18] L. Donaldson, B. Nanayakkara, and J. Harrington, “Wood Growth and Development,” *Encyclopedia of Applied Plant Sciences*, vol. 1, pp. 203–210, Jan. 2017.

[19] “p-Coumaryl alcohol | C9H10O2 - PubChem.” https://pubchem.ncbi.nlm.nih.gov/compound/p-Coumaryl-alcohol (accessed Feb. 21, 2022).

[20] “Coniferyl alcohol | C10H12O3 - PubChem.” https://pubchem.ncbi.nlm.nih.gov/compound/1549095 (accessed Feb. 21, 2022).

[21] “Sinapyl alcohol | C11H14O4 - PubChem.” https://pubchem.ncbi.nlm.nih.gov/compound/5280507 (accessed Feb. 21, 2022).

[22] A. Sundberg and B. Holmbom, “Wood and fibre chemistry,” *Laboratory of Forest Products Chemistry, Faculty of Chemical Engineering, Åbo Akademi University, Åbo*, 2002.

[23] Monica. Ek, G. Gellerstedt, and Gunnar. Henriksson, *Pulp and paper chemistry and technology. Volume 1, Wood chemistry and wood biotechnology*. Berlin: De Gruyter, 2009. doi: 10.1515/9783110213409.

[24] M. Björklund Jansson and N.-O. Nilvebrant, “7. Wood Extractives,” *Wood Chemistry and Wood Biotechnology*, pp. 147–172, Oct. 2009, Accessed: Apr. 13, 2022. [Online]. Available: https://www.degruyter.com/document/doi/10.1515/9783110213409.147/html

[25] T. R. Seshadri and T. N. C. Vedantham, “Chemical examination of the barks and heartwoods of betula species of american origin,” *Phytochemistry (Oxford)*, vol. 10, no. 4, pp. 897–898, 1971.

[26] T. W. Sudia, “Translation of a Translation Plant Physiology Henrich Lundegardh F. M. Irvine W. O. James,” *Bioscience*, vol. 17, no. 10, pp. 752–752, 1967.

[27] C. Schuerch, “Methods of wood chemistry. vol. II. B. L. Browning, Ed., Wiley, New York, 1967. 498 pp. $18.75,” *Journal of Polymer Science Part A-2: Polymer Physics*, vol. 6, no. 11, pp. 1943–1944, Nov. 1968.

[28] Hon-David-N-S and Shiraishi-Nobuo-1936, *Wood and cellulosic chemistry*, 2nd ed., rev. And... 2001.

[29] E. L. Ellis, “Cellular Ultrastructure of Woody Plants,” *W.A. Côté Jr. (ed), New York: Syracuse University Press*, pp. 181–189, 1965.

[30] J. Werkelin, B.-J. Skrifvars, and M. Hupa, “Ash-forming elements in four Scandinavian wood species. Part 1: Summer harvest,” *Biomass and Bioenergy*, vol. 29, no. 6, pp. 451–466, Dec. 2005.

[31] V. G. Semenova, “Chemical composition of bark and wood of spruce, birch and lime trees,” *Lesovedenie*, vol. 6, pp. 71–74, 1971.

[32] R. D. Gibbs, “Studies of wood: II. On the water content of certain canadian trees and on changes in the water-gas system during seasoning and flotation,” *Canadian Journal of Research*, vol. 12, no. 6, pp. 727–760, Jun. 1935.

[33] H. G. Basham and E. B. Cowling, “Distribution of essential elements in forest trees and their role in wood deterioration.,” *Beihefte zu Material und Organismen*, pp. 155–165, 1976.

[34] A. Berglund, H. Brelid, A. Rindby, and P. Engström, “Spatial distribution of metal ions in spruce wood by synchrotron radiation microbeam X-ray fluorescence analysis,” *Holzforschung*, vol. 53, no. 5, pp. 474–480, Sep. 1999, Accessed: Apr. 22, 2022. [Online]. Available: https://www.degruyter.com/document/doi/10.1515/HF.1999.078/html

[35] J. C. (John C. Roberts, *The chemistry of paper*. Cambridge: Royal Society of Chemistry, 1996.

[36] O. Fearon *et al.*, “Detailed modeling of the kraft pulping chemistry: carbohydrate reactions,” *AIChE Journal*, vol. 66, no. 8, Aug. 2020, doi: 10.1002/aic.16252.

[37] G. Gellerstedt, “3. Mechanical Pulping Chemistry,” in *Pulping Chemistry and Technology*, De Gruyter, 2009, pp. 35–56. doi: 10.1515/9783110213423.35.

[38] “Chemistry of Chemical Pulping,” in *Pulping Chemistry and Technology*, vol. 2, Berlin, New York: Walter de Gruyter, 2009. doi: 10.1515/9783110213423.91.

[39] E. Windeisen and G. Wegener, “Lignin as Building Unit for Polymers,” *Polymer Science: A Comprehensive Reference, 10 Volume Set*, vol. 10, pp. 255–265, Jan. 2012.

[40] G. Gellerstedt, “Chemistry of Chemical Pulping,” in *Pulping Chemistry and Technology*, De Gruyter, 2009, pp. 91–120. doi: 10.1515/9783110213423.91.

[41] J. Berglund *et al.*, “The structure of galactoglucomannan impacts the degradation under alkaline conditions,” *Cellulose*, vol. 26, no. 3, pp. 2155–2175, Feb. 2019.

[42] A. Ragauskas, “Influence of Hexenuronic Acids on Kraft Bleaching,” *Tappi Journal*, vol. 83, Jan. 2000.

[43] G. Gellerstedt, “Chemistry of Bleaching of Chemical Pulp,” in *Pulping Chemistry and Technology*, De Gruyter, 2009, pp. 201–238. doi: 10.1515/9783110213423.201.

[44] L. Lucia, “High Selectivity Oxygen Delignification,” 2005.

[45] P. (Pratima) Bajpai, “Environmentally friendly production of pulp and paper.” Wiley, Hoboken, N.J, 2010.

[46] P. (Pratima) Bajpai, *Pulp and paper industry : chemicals*. Amsterdam, Netherlands: Elsevier, 2015.

[47] T. Eriksson, “Reactions of ozone and chlorine dioxide in bleaching. ,” 1993.

[48] M. Ek, G. Gellerstedt, and G. Henriksson, *Pulp and paper chemistry and technology. Volume 2, Pulping chemistry and technology*. Berlin: De Gruyter, 2009.

[49] J. Gierer, “Basic principles of bleaching,” *Holzforschung*, vol. 44, no. 5, pp. 387–394, 1990.

[50] C. Heitner, Don. Dimmel, and J. A. Schmidt, *Lignin and lignans : advances in chemistry*. Boca Raton: Taylor & Francis, 2010. doi: 10.1201/EBK1574444865.

[51] G. Gellerstedt, “The chemistry of bleaching and post-color formation in kraft pulps”.

[52] Michael. Suhr *et al.*, “Best Available Techniques (BAT) reference document for the production of pulp, paper and board.,” 2015.

[53] R. Toczyłowska-Mamińska, “Limits and perspectives of pulp and paper industry wastewater treatment – A review,” *Renewable & sustainable energy reviews*, vol. 78, pp. 764–772, 2017.

[54] K. Salmenoja, O. Poukka, and M. Battegazorre, “Management of non-process elements in eucalyptus kraft pulp mills,” 2009.

[55] W. B. A. SHARP, “Anticipated effects of system closure on corrosion in chemical recovery equipment,” *Tappi J*, vol. 79, no. 8, pp. 161–165, 1996.

[56] “The Finnish Background Report for the EC Documentation of Best Available Techniques for Pulp and Paper Industry - Valto.” https://julkaisut.valtioneuvosto.fi/handle/10138/40277 (accessed Jun. 10, 2022).

[57] V. Peck and R. Daley, “Toward a ‘greener’ pulp and paper industry,” *Environ Sci Technol*, vol. 28, no. 12, pp. 524A-527A, 1994.

[58] M. Mänttäri and M. Nyström, “Water Treatment in the Pulp and Paper Industry,” in *Membrane Technology*, Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, 2010, pp. 169–192. doi: 10.1002/9783527631407.ch6.

[59] X. Jiang, “Anaerobic Batch Treatment of Carbon Dioxide in Pulp and Paper Effluent,” 2013.

[60] M. N. Cabrera, “Pulp Mill Wastewater: Characteristics and Treatment,” in *Biological Wastewater Treatment and Resource Recovery*, InTech, 2017. doi: 10.5772/67537.

[61] E. Worch, “Adsorption Technology in Water Treatment: Fundamentals, Processes, and Modeling,” *Adsorption Technology in Water Treatment: Fundamentals, Processes, and Modeling*, pp. 1–356, Apr. 2021, doi: 10.1515/9783110240238/PDF.

[62] S. Kumar and S. Jain, “History, introduction, and kinetics of ion exchange materials,” *Journal of Chemistry*, 2013, doi: 10.1155/2013/957647.

[63] Y. Dahman, “Nanopolymers,” *Nanotechnology and Functional Materials for Engineers*, pp. 121–144, Jan. 2017, doi: 10.1016/B978-0-323-51256-5.00006-X.

[64] T. (Thomas) Engel, *Physical chemistry*. San Fancisco: Pearson, 2005.

[65] “Adsorption and Ion Exchange,” *Chemical Process Equipment*, pp. 523–554, Jan. 2005, doi: 10.1016/B978-075067510-9/50047-4.

[66] “Adsorption - Types of Adsorbents.” http://www.separationprocesses.com/Adsorption/AD_Chp01a.htm (accessed Jun. 07, 2022).

[67] “Derivation of the Langmuir isotherm.” https://pages.jh.edu/chem/fairbr/teach/BET/lang.html (accessed Jun. 12, 2022).

[68] E. Worch, *Adsorption Technology in Water Treatment*, 1. Aufl. Berlin/Boston: Walter de Gruyter GmbH Co.KG, 2012.

[69] F. G. Donnan and A. B. Harris, “The osmotic pressure and conductivity of aqueous solutions of congo-red, and reversible membrane equilibria,” *Journal of the Chemical Society, Transactions*, vol. 99, no. 0, pp. 1554–1577, Jan. 1911, doi: 10.1039/CT9119901554.

[70] F. G. Donnan, “The theory of membrane equilibrium in presence of a non-dialyzable electrolyte,” *Z. Elektrochem.*, vol. 17, no. 572, 1911.

[71] H. R. Procter and J. A. Wilson, “The acid–gelatin equilibrium,” *Journal of the Chemical Society, Transactions*, vol. 109, no. 0, pp. 307–319, Jan. 1916, Accessed: Jun. 12, 2022. [Online]. Available: https://pubs.rsc.org/en/content/articlehtml/1916/ct/ct9160900307

[72] F. G. Donnan, “Theory of membrane equilibria and membrane potentials in the presence of non-dialysing electrolytes. A contribution to physical-chemical physiology,” *Journal of Membrane Science*, vol. 100, pp. 45–55, 1995.

[73] P. Stenius and P. Tervola, “Model describing Donnan equilibrium, pH and complexation equilibria in fibre suspensions,” 2001. [Online]. Available: https://www.researchgate.net/publication/279553434

[74] M. Towers and A. M. Scallan, “Predicting the ion-exchange of kraft pulps using donnan theory,” *Journal of pulp and paper science*, vol. 22, no. 9, pp. J332–J337, 1996.

[75] E. Räsänen, “Modelling ion exchange and flow in pulp suspensions,” 2003, Accessed: Feb. 15, 2022. [Online]. Available: http://www.vtt.fi/inf/pdf/

[76] T. A. Davis, “Membrane separations | Donnan Dialysis,” in *Encyclopedia of Separation Science*, Elsevier, 2000, pp. 1701–1707. doi: 10.1016/B0-12-226770-2/05331-X.

[77] M. Towers and A. M. Scallan, “Predicting the ion-exchange of kraft pulps using donnan theory,” *Journal of pulp and paper science*, vol. 22, no. 9, pp. J332–J337, 1996.

[78] G. V. Laivins and A. M. Scallan, “The exchange and removal of the metal cations in pulps,” in *Fundamentals of Papermaking Materials*, 1997, vol. 2, pp. 837–858.

[79] E. Räsänen, P. Stenius, and P. Tervola, “Model describing Donnan equilibrium, pH and complexation equilibria in fibre suspensions,” *Nordic Pulp and Paper Research Journal*, vol. 16, pp. 130–139, Jan. 2001.

[80] E. Räsänen and L. Kärkkäinen, “Modelling of Complexation of Metal Ions in Pulp Suspensions,” *Journal of Pulp and Paper Science*, vol. 29, pp. 196–203, Jun. 2003.

[81] E. Räsänen, A. R. P. van Heiningen, P. Koukkari, R. Pajarre, and R. Aksela, “Modelling displacement flow and ionic equilibria in pulp beds. Part 1: Laboratory experiments,” *Paperi ja puu*, vol. 86, no. 4, pp. 279–288, 2004.

[82] E. Räsänen, A. R. P. van Heiningen, P. Koukkari, R. Pajarre, and R. Aksela, “Modelling Displacement Flow and Ionic Equilibria in Pulp Beds, Part 2 - Mathematical Model,” *Paperi ja puu*.

[83] K. Athley and P. Ulmgren, “Interaction between divalent metal ions and oxygen-delignified kraft pulps,” *Nordic pulp & paper research*, vol. 16, no. 3, pp. 204–214, 2001.

[84] W. Yantasee and G. L. Rorrer, “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*, vol. 22, no. 2–3, pp. 157–185, Jan. 2002.

[85] J. Lindgren, P. Persson, and L.-O. Öhman, “Interactions of calcium(II), copper(II) and aluminium(III) ions with two chemically modified wood fibres,” *Nordic pulp & paper research*, vol. 16, no. 3, pp. 225–234, 2001.

[86] “TAPPI T 266 : Determination of sodium, calcium, copper, iron and manganese in pulp and paper by atomic absorption spectroscopy.” https://global.ihs.com/doc_detail.cfm?document_name=TAPPI%20T%20266&item_s_key=00349346 (accessed Apr. 03, 2022).

[87] C. E. Dunn, “Biogeochemistry in mineral exploration.,” pp. 159–160, 2007.

[88] “Laboratory Analysis of Mechanical Pulp - The Effects of Storage Conditions and Time on Measured Tech.” https://imisrise.tappi.org/TAPPI/Products/PM/PM00135.aspx (accessed May 30, 2022).

[89] “ISO - ISO 5263-1:2004 - Pulps — Laboratory wet disintegration — Part 1: Disintegration of chemical pulps.” https://www.iso.org/standard/37893.html (accessed Apr. 03, 2022).

[90] “T-100 Pulp Disintegrator | Thwing Albert.” https://www.thwingalbert.com/product/disintegrator-t-100/ (accessed May 30, 2022).

[91] K. Koljonen, A. Mustranta, and P. Stenius, “Surface characterisation of mechanical pulps by polyelectrolyte adsorption,” *Nordic Pulp and Paper Research Journal*, vol. 19, no. 4, pp. 495–505, 2004, doi: 10.3183/NPPRJ-2004-19-04-P495-505.

[92] P. Stenius and J. Laine, “Studies of cellulose surfaces by titration and ESCA,” *Applied Surface Science*, vol. 75, no. 1–4, pp. 213–219, Jan. 1994.

[93] J. Laine, J. Buchert, L. Viikari, and P. Stenius, “Characterization of Unbleached Kraft Pulps by Enzymatic Treatment, Potentiometric Titration and Polyelectrolyte Adsorption,” *hfsg*, vol. 50, no. 3, pp. 208–214, 1996.

[94] J. Karhu, P. Forslund, L. Harju, and A. Ivaska, “Characterization of carboxyl and phenol groups in kraft pulps at different temperatures,” *Cellulosic Pulps, Fibres and Materials*, pp. 129–135, Jan. 2000, doi: 10.1533/9781845698546.129.

[95] K. Ala-Kaila and R. Alén, “Dynamic response in pH and the transient behavior of some chemical elements in pulp-water suspensions,” *Nordic Pulp and Paper Research Journal*, vol. 14, no. 2, pp. 149–157, May 1999, Accessed: Jun. 06, 2022. [Online]. Available: https://www.degruyter.com/document/doi/10.3183/npprj-1999-14-02-p149-157/html

[96] “Hydroxide Precipitation - Industrial Wastes - Climate Policy Watcher.” https://www.climate-policy-watcher.org/industrial-wastes/hydroxide-precipitation.html (accessed Jun. 16, 2022).

[97] P. Su, “Sorption of Metal Ions to Wood, Pulp and Bark Materials”.

[98] R. Sierra-Alvarez, F. W. Claassen, J. Dorado, T. A. van Beek, G. Lenon, and H. B. P. A. Wijnberg, “Removal and transformation of toxic resin acids by wood-inhabiting fungi,” in *TAPPI Pulping/Process and Product Quality Conference*, 2000, pp. 1241–1245.

[99] “Solubility Product Constant, Ksp - Chemistry LibreTexts.” https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Equilibria/Solubilty/Solubility_Product_Constant%2C_Ksp (accessed Jun. 16, 2022).

[100] “Ksp Table.” https://www.chm.uri.edu/weuler/chm112/refmater/KspTable.html (accessed Jun. 16, 2022).

[101] M. N. Rao, R. Sultana, and S. H. Kota, “Hazardous Waste,” *Solid and Hazardous Waste Management*, pp. 159–207, Jan. 2017, doi: 10.1016/B978-0-12-809734-2.00005-5.