LAPPEENRANTA-LAHTI UNIVERSITY OF TECHNOLOGY LUT
School of Engineering Science
Master's Programme in Chemical Engineering and Water Treatment

Meeri Häyrynen

REMOVAL OF HARMFUL IONS FROM PULP BLEACHING EFFLUENTS BY MEMBRANE TECHNOLOGY

Master's Thesis

Examiners: Arto Pihlajamäki, LUT University
Juhani Turunen, XAMK

ABSTRACT

LUT University
School of Engineering Science
Chemical Engineering

Meeri Häyrynen

Removal of Harmful Ions from Pulp Bleaching Effluents by Membrane Technology

Master’s thesis

2021

94 pages, 19 figures, 14 tables and 3 appendices

Examiners: Docent Arto Pihlajamäki
Lic.Sc. (Tech.) Juhani Turunen

Keywords: bleaching effluent, ion chromatography, ICP-OES, nanofiltration, ultrafiltration

Pulp bleaching is a major contributor to the freshwater consumption of kraft pulp mills. The main objective of this work was to investigate, how acidic and alkaline bleaching effluents can be purified by membrane technology in order to reduce the water consumption by closing water cycles. The bleaching effluents may contain certain cations, such as calcium, barium and transition metal ions, as well as anions including carbonate, oxalate, sulphate and chloride ions, which may have harmful impacts on bleaching processes. Therefore, to recycle the effluents, the concentrations of these ions typically need to be reduced. Promising results have been obtained by ultra- and nanofiltration. However, the filtration of the acidic effluents is typically considered more challenging than that of alkaline effluents. Additionally, the aim was to assess the suitability of ion chromatography for analysing the harmful ions in bleaching effluents.

Preliminary ultrafiltration experiments of the alkaline Eop stage bleaching effluent and the acidic D0 and D1 stage effluents from a Finnish kraft pulp mill were conducted using a stirred cell set-up with a polymeric ultrafiltration membrane (cut-off 5000 Da). Nanofiltration tests were carried out in a cross-flow unit, and four polymeric membranes with cut-off values in the range of 500-1000 Da were used to filter the three effluent samples. The anions and the most abundant cations in the feed solutions and permeates could be analysed by ion chromatography. For all the samples, most promising results were obtained using a sulphonated PES membrane with a cut-off value of 600-800 Da. Promising results were obtained also for the filtration of the acidic effluents. However, monovalent ions were poorly removed in the filtration, and therefore, further treatment is probably required in order to reuse the water streams to replace fresh water. Still, nanofiltration can have a remarkable role in further decreasing the water consumption in pulp mills.

TIIVISTELMÄ

Lappeenrannan-Lahden teknillinen yliopisto LUT
School of Engineering Science
Kemiantekniikka

Meeri Häyrynen

Haitallisten ionien poistaminen sellutehtaan valkaisun jätevesistä membraaniteknologian avulla

Diplomityö

2021

94 sivua, 19 kuvaa, 14 taulukkoa ja 3 liitettä

Tarkastajat: Dosentti Arto Pihlajamäki
Tekniikan lisensiaatti Juhani Turunen

Hakusanat: valkaisun jätevesi, ionikromatografia, ICP-OES, nanosuodatus, ultrasuodatus

Sulfaattisellun valmistuksessa merkittävä osa vedenkulutuksesta aiheutuu valkaisusta. Tämän työn tarkoituksena oli tutkia, miten valkaisun happamia ja alkalisia jätevesiä voitaisiin puhdistaa membraanitekniikalla vedenkulutuksen vähentämiseksi vesikiertoja sulkemalla. Nämä jätevedet voivat sisältää tiettyjä kationeja kuten kalsium-, barium- ja siirtymämetalli-ioneja sekä anioneja kuten karbonaatti-, oksalaatti-, sulfaatti- ja kloridi-ioneja, joilla voi olla haitallisia vaikutuksia valkaisuprosesseihin. Jotta valkaisun jätevesiä voitaisiin kierrättää prosesseissa, näiden ionien konsentraatioita täytyy yleensä vähentää, ja lupaavia tuloksia on saavutettu membraanitekniikalla. Happamien jakeiden suodattamista pidetään kuitenkin haastavampana kuin alkalisten. Lisäksi tarkoituksena oli tutkia ionikromatografian soveltuvuutta haitallisten ionien määrittämiseen valkaisun jätevesissä.

Erään suomalaisen sellutehtaan alkalisen Eop-vaiheen valkaisusuodoksen ja happamien D0- ja D1-vaiheiden suodosten alustavat ultrasuodatuskokeet tehtiin Stirred Cell-tyyppisellä suodatuslaitteistolla käyttäen polymeerimembraania (katkaisukoko 5000 Da). Nanosuodatuskokeet tehtiin käyttäen cross-flow suodatuslaitteistoa ja neljää polymeerimembraania, joiden katkaisukoot olivat välillä 500-1000 Da, käytettiin kolmen valkaisun jätevesinäytteen suodatukseen. Anionit ja ne kationit, joita liuoksissa oli eniten, voitiin määrittää ionikromatografisesti. Kaikkien näytteiden tapauksessa lupaavimmat tulokset saavutettiin käyttäen membraania katkaisukooltaan 600-800 Da ja jonka valmistusmateriaali on sulfonoitu PES. Lupaavia tuloksia saavutettiin myös happamien näytteiden suodatuksessa. Erityisesti kloridin määrä permeaateissa oli korkea, ja siksi jatkokäsittelyä todennäköisesti tarvittaisiin, jotta permeaattia voitaisiin käyttää prosessissa korvaamaan puhdasta vettä. Nanosuodatuksen rooli vedenkulutuksen vähentämisessä voi kuitenkin olla merkittävä.

ACKNOWLEDGEMENTS

This Master’s Thesis was conducted at Xamk Fiber Laboratory located in Savonlinna. I would like to thank the Fiber Laboratory, and especially my supervisor Juhani Turunen, for providing me with this opportunity and the interesting topic. I am also very grateful to Arto Pihlajamäki from LUT university for the supervision and valuable feedback. Special thanks to Mia who helped me a lot with the experimental part and with whom we made a great team solving the challenges I faced during this thesis project. I would also like to thank my other co-workers in Fiber Laboratory for contributing to the motivating work environment.

The end of this project also means the end of my studying journey in Lappeenranta, where I grew and learned a lot. During these five years I made new friends, spent many long nights studying, sang in Resonanssi choir and spent an amazing semester abroad in Lisbon. Thank you to my dear friends for making the good times even better and the hard times a lot easier. I am looking forward to new adventures with you.

Last but definitely not least, I would like to thank my parents, my sisters Mimmi and Helmi and my brother Elmer for always being there for me and supporting me during my studies. I am so lucky to have you as my family.

in Savonlinna, 2.10.2021
Meeri Häyrynen

TABLE OF CONTENTS

APPENDICES

LIST OF SYMBOLS AND ABBREVIATIONS

ABBREVIATIONS

ADt	Air dry ton
BOD	Biochemical oxygen demand
CE	Capillary electrophoresis
Da	Dalton (an atomic mass unit)
D0	First acidic ClO_2 bleaching stage
D1	Second acidic ClO_2 bleaching stage
Eop	Alkaline extraction stage where H_2O_2 and oxygen are used for reinforcement
ECF	Elemental chlorine-free bleaching
ED	Electrodialysis
FAAS	Flame atomic absorption spectroscopy
ETAAS	Electrothermal atomic absorption spectroscopy
IC	Ion chromatography
ICP-OES	Inductively coupled plasma-optical emission spectroscopy
NF	Nanofiltration
NPE	Non-process element
MF	Microfiltration
PES	Polyethersulphone
P&ID	Piping and instrumentation diagram
RO	Reverse osmosis
SI	Saturation index
TCF	Total chlorine-free bleaching
UF	Ultrafiltration

SYMBOLS

A	Absorbance	[-]
a	Absorptivity of a compound	$\left[\frac{\mathrm{L}}{\mathrm{g \cdot cm}}\right]$
A_m	Surface area of a membrane	$[\mathrm{m}^2]$
c	Concentration	$\left[\frac{\mathrm{g}}{\mathrm{L}}\right]$
$c_{i,p}$	Concentration of component i in permeate	$\left[\frac{\mathrm{g}}{\mathrm{L}}\right]$
$c_{i,r}$	Concentration of component i in retentate	$\left[\frac{\mathrm{g}}{\mathrm{L}}\right]$
d_h	Hydraulic diameter of the flow channel	[m]
J	Permeate flux	$\left[\frac{\mathrm{kg}}{m^2 h}\right]$
l	Length of the cuvette	[cm]
m	Mass of permeate	[kg]
PWF	Pure water flux	$\left[\frac{\mathrm{L}}{\mathrm{m^2 \cdot h}}\right]$
PWP	Pure water permeability	$\left[\frac{\mathrm{L}}{\mathrm{m^2 \cdot h \cdot bar}}\right]$
Q_P	Permeate flow	$\left[\frac{\mathrm{kg}}{h}\right]$
R	Rejection	[%]
Re	Reynolds number	[-]
v	Flow velocity	$\left[\frac{\mathrm{m}}{\mathrm{s}}\right]$
Δt	Collecting time of permeate	[h]
η	Dynamic viscosity	[Pa·s]
ρ	Density of water	$\left[\frac{\mathrm{kg}}{\mathrm{L}}\right]$

1 INTRODUCTION

In pulp and paper industry, substantial volumes of freshwater are consumed and effluents with varying compositions are generated in different processing stages. (Ashrafi, Yerushalmi & Haghighat, 2015) Bleaching of pulp is an essential contributor to the overall environmental effects of pulp production (Gavrilescu, Puitel, Dutuc et al., 2012). However, the environmental regulations concerning effluent generation and freshwater consumption have been tightening and acting as the driving force for the transition towards more sustainable bleaching systems (Pinto, Ascenso, Barros et al., 2013; Bajpai, 2012, p. 1). For instance, the consumption of conventional chlorine-based chemicals has been reduced and partially substituted by more environmentally friendly bleaching agents such as hydrogen peroxide (H_2O_2) (Bajpai, 2012, p. 1; Umgren, 1997).

Reusing the process water by closing water cycles in bleaching processes has led to lower levels of freshwater consumption. Consequently, accumulation of ions, such as calcium, barium, iron, manganese, and chloride ions, which may have adverse impacts on the bleaching processes or equipment, within the systems has increased. (Huber, Burnet & Petit-Conil, 2014) These ions may cause scale deposition and corrosion issues, and/or have detrimental impacts on hydrogen peroxide, oxygen, as well as ozone bleaching stages. Therefore, for to reuse different bleaching effluents in the process, the potential impacts on the process need to be assessed (Bajpai, 2012; p. 357). There are different methods for the management of these ions in bleaching processes, and promising results have been obtained by membrane filtration systems in the treatment of especially alkaline bleaching effluents (Pinto et al., 2013; Mänttäri, Kallioinen & Nyström, 2015).

This thesis is carried out for the Fiber Laboratory, a research unit at South-Eastern Finland University of Applied Sciences (Xamk), which is focused on the research and development of processes in pulp and paper industry. The aim of this work is to investigate the performance of ultra- and nanofiltration in the treatment of both alkaline and acidic bleaching effluents. In addition, the aim is to address the sources and behaviour of the ions that potentially have harmful impacts on bleaching processes. The suitability of ion chromatography for the determination of these ions is also examined.

The study consists of a literature part and an experimental part. In the literature part, the harmful ions and their sources and impacts on bleaching processes are addressed. Then, the interactions of metal ions with pulp fibres and dissolved organics in pulp suspensions, and the conditions that lead to precipitation of the most common sparingly soluble metal salts in bleaching systems, are discussed. In addition, different analytical methods for the characterisation of metals in bleaching effluents, such as ion chromatography and atomic adsorption spectroscopy, are compared with each other. Finally, a review of the previous studies on the purification of bleaching effluents especially by membrane technology is presented.

The experimental part contains a research report of the laboratory-scale experiments that were conducted to evaluate the performance of ultra- and nanofiltration in the removal of harmful ions from the acidic and alkaline bleaching effluents from a Finnish kraft pulp mill. Effluents from chlorine dioxide bleaching stages (D1 and D0) and alkaline extraction stage (Eop) were examined. Preliminary ultrafiltration experiments are carried out in a Stirred Cell type filtration unit using a tight polymeric ultrafiltration membrane. Nanofiltration experiments are conducted in a crossflow mode filtration system using four polymeric membranes. The filtration performance is evaluated based on the obtained rejections of the harmful ions and other pollutants and the permeate flux. The aim was to obtain high-quality permeate and to further assess the suitability of the permeates to be reused in bleaching processes to replace fresh water in the mill. Ion chromatography is used to determine certain anions and cations in the complex bleaching effluent samples.

LITERATURE PART

2 CLOSURE OF WATER CYCLES IN PULP BLEACHING SYSTEMS

Over recent decades, notable progress has been made in minimising the environmental impacts of the effluents and reducing the freshwater consumption in pulp mills. New systems that allow system closure, where the process water is recovered and reused in different operations in the pulp mill has had a central role in this development. Major advances have been made especially in delignification, bleaching and washing processes. (Stratton, Gleadow & Johnson, 2004)

However, in order to close water cycles by reusing process water, its potential effects on the process need to be assessed. The concentrations of non-process elements (NPEs) within the systems typically increase with the closure of water cycles, which may cause operational issues in the bleaching systems and adversely affect the pulp quality. (Bajpai, 2012; p. 357) Although a full cycle closure is not possible in most mills today, considerable advances have been made especially in the manufacturing of bleached kraft pulp, in the development of new systems for delignification and bleaching (Stratton et al., 2004).

2.1 A brief description of kraft pulping process

Worldwide, the most common wood pulp manufacturing process is kraft pulping. It has several advantages, including a high degree of chemical recovery and the strength of the resulting pulp. (Bajpai, 2015, p. 16) The first stages of the process are debarking and chipping of wood, after which the wood chips are cooked in a pressurised digester in high temperature. The digester contains highly alkaline solution called white liquor, which consists mainly of sodium hydroxide (NaOH) and sodium sulphide (Na_2S). (Gullichsen & Fogelholm, 1999, p. 39-40)

From the cooking stage, the mixture of pulp and liquor are discharged to a low-pressure tank. Then, the pulp from this blow tank is washed and screened. After washing, either bleaching is applied or the pulp is used as such for unbleached paper or board production (Gullichsen & Fogelholm, 1999, p. 40-41).

2.1.1 Chemical composition of wood

To understand the reactions of wood in different manufacturing and bleaching processes of pulp, it is important to have a general overview of its chemical composition. The composition and the structure of different constituents in the used wood raw material significantly affects the essential properties, such as strength and lignin content of the final pulp. (Koch, 2006, p. 21) Wood is an organic substance, which consists mainly of carbon, oxygen and hydrogen. It also contains small amounts of nitrogen and some other elements such as calcium, potassium and sodium. In table I, the relative amounts of these elements are shown. The elemental composition varies only slightly between different species of wood. (Koch, 2006, p. 22)

Table I An approximation of the chemical composition of wood (adapted from Koch, 2006, p. 22).

Element	Content, %
Carbon	49
Hydrogen	6
Oxygen	44
Nitrogen	<1
Inorganic elements (Ca, K, Na etc.)	<<1

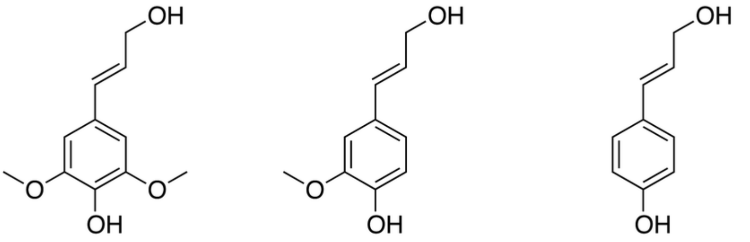
At molecular level, wood is mainly composed of cellulose, various hemicelluloses, and lignin. These three polymers are the major constituents of the cell wall of wood fibres. (Koch, 2006, p. 22) Cellulose and hemicelluloses play a major role in strengthening the cell wall, whereas lignin is typically present in high concentrations in middle lamella, which binds the fibres together (Sjöström, 1993, p. 13, 63).

The chemical composition and proportions of lignin and hemicelluloses differ between coniferous wood species (softwoods) and hardwoods, whereas in the case of cellulose, there is only a little variation. (Koch, 2006, p. 22) Generally, the cellulose content in wood is approximately 40-45 %, and the hemicellulose content between 25 and 30 % in softwoods, and between 30 and 35 % in hardwoods (Alén, 2000, p. 28; Sjöström, 1993, p. 54). The lignin content, in turn, is typically slightly higher in softwoods than in hardwoods (Sjöström, 1993, p. 72). In addition, smaller amounts of other polymeric compounds, including pectin, starch and proteins, are present (Alén, 2000, p. 28).

Wood also contains substances with lower molecular masses, including, for instance, metal compounds and wood extractives (Koch, 2006, p. 22). Wood extractives are a large group of organic constituents which can be classified into three main types, namely volatile oils, wood resins, and fats and waxes. (Koch, 2006, p. 34; Sjöström, 1993, p. 90)

Lignin

Lignin is a phenolic organic biopolymer, which is formed by radical coupling reactions (biosynthesis) of smaller structures called monolignols. The main monolignols are hydroxyphenyl, guaiacyl and syringyl alcohol (figure 1). They can be joined together in various ways and in different proportions, which leads to that the lignin polymer can have a very complex structure, and it occurs in various constitutions in wood. (Koch, 2006, p. 31-33)



sinapyl alcohol **(S)** **coniferyl alcohol** **(G)** ***p*-coumaryl alcohol** **(H)**

Figure 1 The main precursor constituents of lignin (Strassberger, Tanase & Rothenberg, 2014).

The monolignol units can be joined together either by carbon-carbon single bonds (C-C) or ether bonds. Also, different functional groups, such as methoxyl, carbonyl and/or hydroxyl groups, can be bound to lignin structure. (Sjöström, 1993, p. 81-83) In pulping and bleaching processes, lignin is released from wood to some extent and degraded into smaller compounds (Koch, 2006, p. 31).

2.1.2 Recovery of the pulping chemicals

The kraft process is a nearly closed process, where the pulping chemicals are recovered in the liquor cycle, and the lime that is needed in the recausticising process, is regenerated in the lime cycle. A schematic of the liquor cycle and the lime cycle is shown in figure 2.

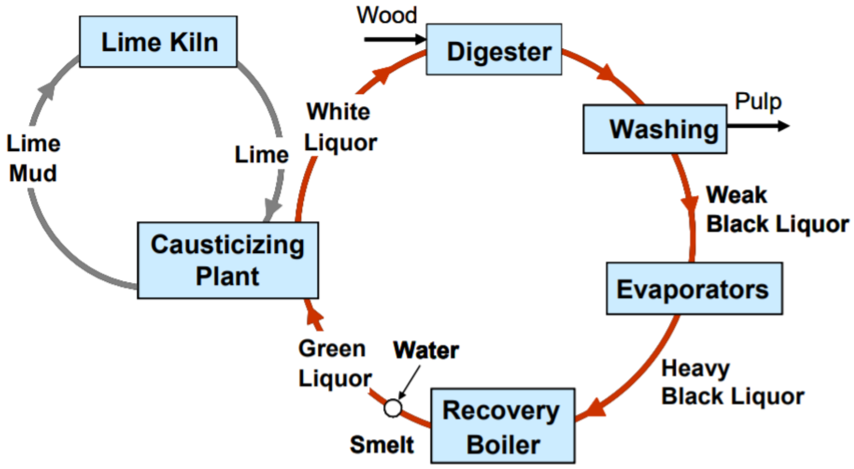


Figure 2 A schematic of a kraft pulping process (Tran & Vakkilainen, 2004).

The spent liquor, called weak black liquor, is recovered from washing and concentrated into heavy black liquor by evaporators (Gullichsen & Fogelholm, 1999, p. 41). It is incinerated in a recovery boiler to recover the cooking chemicals and generate heat. Moist salt smelt that contains primarily sodium sulphate (Na_2S) and sodium carbonate (Na_2CO_3), is produced. (Gullichsen & Fogelholm, 1999, p. 41; Bajpai, 2015, p. 27) It also contains small amounts of carbon that is not burned in the recovery boiler and different non-process elements (NPEs). These impurities are referred to as dregs. The smelt is diluted with weak white liquor from the recausticising stage, and the resulting solution is called green liquor. The dregs can then be removed from this liquor by clarification or filtration. (Arpalahti, Engdahl, Jäntti et al., 1999)

Subsequently, in the recausticising process, the Na_2CO_3 in green liquor reacts with lime (CaO) and water to form NaOH, generating white liquor according to the following chemical equation:

$$Na_2CO_3 + H_2O + CaO \rightarrow CaCO_3 + 2NaOH \qquad (1)$$

The produced lime mud, which mainly consists of calcium carbonate ($CaCO_3$), is burned in lime kiln in order to regenerate lime for the recausticising process. Also fresh lime usually needs to be added to the process. (Sanchez, 2000) External fuel, such as natural gas or fuel oil, is used to burn lime mud (Arpalahti et al., 1999).

The balance of sodium and sulphur in the process is essential for the operation of the mill. It is measured as a parameter called sulphidity, which is the relative concentration of sodium sulphide (Na_2S) compared to NaOH. (Saturnio, 2012) Thus, make-up chemicals need to be added to the system to compensate the sodium and sulphur losses (Bajpai, 2015, p. 27). For instance, the conversion of Na_2CO_3 to NaOH leads to losses in sodium, as full conversion is not possible to reach (Grace & Tran, 2007). Traditionally, Na_2SO_4 (make-up salt cake) has been the most commonly used chemical for maintaining a sufficient sodium concentration. However, with Na_2SO_4, excess sulphur is added to the system, and therefore, it has been partly replaced with NaOH. In kraft pulp mills, where chlorine dioxide (ClO_2) bleaching is applied, the salt cake that is generated in ClO_2 generators can also be added to the liquor cycle. (Tran & Vakkilainen, 2007; Saturnio, 2012)

2.2 Kraft pulp bleaching

The aim of bleaching is to remove residual lignin from pulp and thereby reduce its colour (Reeve, 1996; p. 3; Huber et al., 2014). Lignin is a complex organic molecule that contains various bonds, and therefore, several chemicals are needed for its degradation (KnowPulp). It degrades into various compounds with different molecular masses in different stages of the pulping and bleaching processes (Kojishima & Watanabe, 2003).

2.2.1 Bleaching chemicals and sequences

Generally, a bleaching sequence consists of both oxidative and alkaline bleaching stages and washing stages between them (KnowPulp). In oxidative stages, chemicals such as chlorine dioxide, hydrogen peroxide (H_2O_2) and ozone (O_3) are used to degrade the residual lignin into smaller and more soluble forms. Alkaline stages, where for instance sodium hydroxide is used, are needed to extract the alkali-soluble forms of lignin. In washing stages, the lignin is then removed. (Gavrilescu et al. 2012)

The phase-out of chlorine consumption over the past few decades has enhanced the development of new bleaching systems and increased the use of oxygen-based bleaching agents, such as oxygen, ozone and hydrogen peroxide (Bajpai, 2012, p. 1; Umgren, 1997). Bleaching sequences, where molecular chlorine is not used, are called elemental chlorine free (ECF) sequences, and they are currently most commonly used techniques worldwide. However, chlorine dioxide is used in these systems. If only oxygen-based oxidants are used instead of chlorine-based chemicals, the bleaching sequence is called totally chlorine free (TCF) system. (Bajpai, 2012, p. 263; KnowPulp).

Today, oxygen delignification is commonly applied in the beginning of bleaching sequences (Gavrilescu et al. 2012). In this process, oxygen is used together with an alkali to remove a major share of the residual lignin (Gullichsen & Fogelholm, 1999, p. 635). Through the transition towards ECF and TCF bleaching, the role of oxygen delignification has become very essential (Bajpai 2015, p. 87). In the following table, the commonly used symbols for different bleaching stages and the typical pH in the stages are shown.

Table II Symbols for different bleaching processes and the common operating pH (Huber et al. 2014; Reeve 1996, 16)

Bleaching stage/chemical	**Symbol**	**pH**
Oxygen delignification	O	10-11
Alkaline extraction (NaOH)	E	10-11
Hydrogen peroxide (H_2O_2)	P	10-11
Sodium hypochlorite (NaOCl)	H	10-11
Chelation	Q	3-5
Chlorine (Cl_2)	C	2-3
Chlorine dioxide (ClO_2)	D	2-4
Ozone (O_3)	Z	2-3

Chlorine dioxide is a very common bleaching chemical. It is a very strong oxidiser, and it does not degrade the other main wood constituents, cellulose and hemicellulose while reacting with lignin efficiently. Thus, in ClO_2 bleaching, the strength of the pulp is retained well. (Bajpai, 2012, p. 135) Among the oxygen-based bleaching agents, hydrogen peroxide is found to have several advantages, such as high delignification efficiency and minimal environmental impact of effluents (Li, Lee, Lee et al., 2011; Bajpai, 2012, p. 97). Bleaching by H_2O_2 is based on the formation of perhydroxyl radicals ($HO_2\bullet$) in alkaline conditions by the following decomposition reaction:

$$H_2O_2 + OH^- \rightleftarrows HO_2^- + H_2O \qquad (2)$$

The formed radicals then degrade chromophores from the pulp (Li et al., 2011). In kraft pulp bleaching, H_2O_2 is mostly used for reinforcement in stages where other chemicals are used as the main bleaching agents. (Bajpai, 2012, p. 97-98)

2.2.2 Counter-current washing systems

In pulp bleaching, most of the consumed water is used in washing stages. Water reuse in bleach plants is carried out by counter-current washing systems, where the used fresh water is mainly added to the final washing stage and reused in the previous stages. On average, 25-40 m^3 of effluent per air dry ton (ADt) of pulp was generated in a bleach plant in 1990s, but if counter-current systems are applied, a volume as low as 12 m^3/ADt can be achieved. (Histed, McCubbin & Gleadow, 1996; Suess, 2010)

There are several different approaches to counter-current washing, but usually, jump-stage and/or split-flow systems, where the acidic and alkaline washing filtrate streams are separated, are used (Huber et al. 2014). In jump-stage counter-current washing, the alkaline and acidic filtrates from subsequent bleaching stages are reused as washing water in the following stages. The principle of split-flow counter-current system is that washing of the pulp is first carried out with filtrate with similar pH to the bleaching stage where the pulp comes from, and then with filtrate with similar pH to the stage where the pulp is entering next. (Histed et al., 1996; Suess, 2010) An example of an ECF sequence, where a combination of the jump-stage and split-flow counter-current washing systems is applied, is illustrated in figure 3.

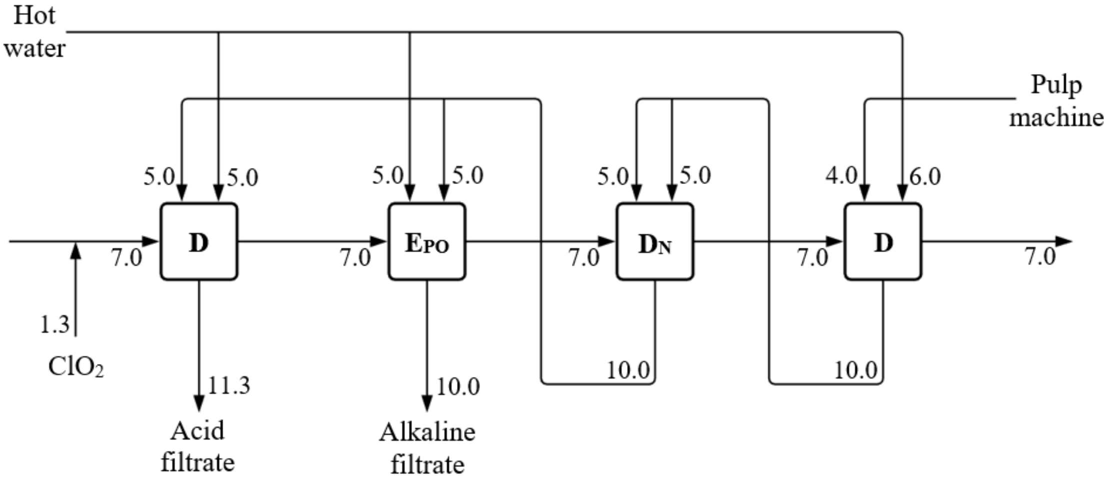


Figure 3 An ECF bleaching sequence with split-flow jump-stage counter-current washing and flows in m^3/ADt (adapted from Carter & Gleadow, 1994).

In this four-stage bleaching sequence (D0-(Eop)-D1D2), the pulp is first bleached with chlorine dioxide. Then there is an alkaline extraction stage where H_2O_2 and oxygen are used for reinforcement (E_{OP}), followed by two additional ClO_2 stages (Bajpai, 2012, p. 10, 155). Approximately 16 m^3/ADt of hot water is used in this sequence. In addition, whitewater, the process water that is used in paper machine systems, is reused in the process. (Carter and Gleadow, 1994)

2.2.3 Accumulation of NPEs in bleaching systems

Elements that are present in the pulping, bleaching or chemical recovery systems but do not actively take part in them are called non-process elements (NPEs) (Jemaa, Thompson, Paleologou et al., 1999). The accumulation of harmful NPEs, such as barium, iron, manganese and copper within kraft pulping processes is the most significant barrier for the further closure of the mills (Ulmgren, 1997; Suess, 2010, p. 196). Although calcium plays a significant role in the lime cycle, it can be considered as a NPE in the other processes, due to the adverse impacts of its accumulation (Jemaa et al., 2000). In table III, examples of different NPEs in bleached kraft pulp mills and their potential effects on the processes are shown.

Table III Adverse impacts of different NPEs in kraft pulping processes (Ulmgren, 1997).

Elements	Harmful impacts
Ca, Ba, Al, Si	Scaling
Cl, K, Mg	Corrosion
Cl, K	Recovery boiler plugging
P, Mg, Al, Si	Inert in lime cycle
Fe, Mn, Cu, etc.	Impacts on TCF bleaching processes
N, P, Cd, Pb, etc.	Environmental impacts

Most of the different NPEs that enter the bleaching processes originate from the wood raw material (Dahl, 1999). Their concentrations in wood vary over the tree species and the availability of metals in soil and groundwater. Generally, the metal content of hardwoods is higher than that of softwoods. (Rudie & Hart, 2012) Calcium, potassium, chloride, manganese and magnesium can be found in wood in relatively high concentrations, whereas the other NPEs are typically present only in trace amounts (Ulmgren, 1997). Bark contains more NPEs than the stemwood, and thus, the efficiency of the debarking process affects the amount of NPEs that enter the system (Gustafsson, Alén, Engström et al., 2012). Other possible sources for harmful ions that enter the bleaching processes are different chemical additives, the used process water and corrosion of the equipment (Ulmgren, 1997; Rudie & Hart, 2012).

In cooking, most of NPEs are partially released from the wood, after which they are carried to the liquor cycle with black liquor. (Ulmgren, 1997) Many of them can be removed from the process as precipitates with dregs and grits. The removal of green liquor dregs is the main purging point for less alkali-soluble elements such as calcium, magnesium, manganese and iron. (Arpalahti et al., 1999; Ulmgren, 1997) In current systems with open water cycles, some of the NPEs are removed with bleaching effluents. However, the elements, such as aluminium, magnesium, potassium and chloride, that are soluble in alkaline conditions, typically accumulate in the liquor cycle and/or lime cycle. (Ulmgren, 1997)

3 HARMFUL IONS IN PULP BLEACHING WATERS

In bleaching systems, for instance, scale deposition and corrosion problems may arise from the build-up of NPEs. It can also limit the bleaching efficiency and increase the required amounts of bleaching chemicals. (Umgren, 1997; Suess, 2010, p. 196) In this chapter, the sources, impacts and most important properties of certain ions that have been found to have adverse effects on kraft pulp bleaching processes, are discussed.

3.1 Anions

In bleaching systems, the process water and pulp contain various anions, including carbonate, oxalate and sulphate ions, that can either be formed in the process or added there (Ulmgren, 1997). Their accumulation in the water cycles reduces the possibilities for water recycling (Li, Du, Ge et al., 2020). Carbonate, oxalate and sulphate are divalent anions that tend to form insoluble precipitates with divalent metal ions and especially with barium and calcium ions (Rudie & Hart, 2012). In addition, chloride ions may cause corrosion of the equipment (Huber et al., 2014).

3.1.1 Carbonate

Carbonate anions (CO_3^{2-}) are formed in the degradation reactions of cellulose, hemicelluloses and lignin during cooking, and they enter the other processing stages with white liquor (Bryant, 1995; Ulmgren, 1997). Also, in alkaline bleaching stages, such as oxygen delignification and alkaline extraction stages, carbonates can be formed. With calcium ions, they tend to form poorly soluble calcium carbonate, which is one of the three main minerals that cause deposit problems in kraft pulp bleaching processes. (Ulmgren, 1997) The concentration of carbonate anions in a solution is affected by the following carbonic acid dissociation:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \tag{3}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \tag{4}$$

In aqueous solutions, carbon dioxide is converted into carbonic acid (H_2CO_3), which dissociates into bicarbonate (HCO_3^-) or carbonate ions (Loerting & Bernard, 2010). This dissociation is dependent on pH; at pH above 6, bicarbonate ions are formed, and at pH above 10, they are converted into carbonate ions according to reaction (4) (Rudie & Hart, 2006a). Thus, carbonate ions can be found in alkaline bleaching stages (Ulmgren, 1997).

3.1.2 Oxalate

Oxalate anions ($C_2O_4^{2-}$) present in the pulping processes are formed through the dissociation reactions of oxalic acid ($C_2H_2O_4$), according to reactions (5) and (6). Therefore, their availability is dependent on the extent to which oxalic acid is formed in different stages. (Häärä, Sundberg & Willför, 2011)

$$C_2O_4H_2 \rightleftharpoons C_2O_4H^- + H^+ \tag{5}$$

$$C_2O_4H^- \rightleftharpoons C_2O_4^{2-} + H^+ \tag{6}$$

The relative concentrations of oxalic acid, oxalate ions and hydrogen oxalate ions ($C_2O_4H^-$) are pH-dependent. When the pH is above 3, oxalate ions can be present. (Huber et al., 2014) Generally, a majority of oxalic acid in kraft pulping processes is formed in oxidative bleaching stages such as oxygen delignification and ozone stages, where it is generated in the oxidation reactions of lignin and hemicelluloses (Huber et al., 2014). It has been found that the amount of available lignin in the pulp largely affects the oxalic acid formation in bleaching (Elsander & Gellerstedt, 2000). In addition, a smaller share of it comes from the wood raw material (Häärä et al., 2011).

Oxalate ions can form poorly soluble precipitates by binding with alkaline earth metals such as calcium and barium (Li et al., 2020). Especially calcium oxalate causes scaling problems in bleaching processes. It can be deposited on the walls of pipes and the equipment, such as reactors and pumps in acidic bleaching stages (Ulmgren & Rådeström, 2001; Hu et al., 2014). For instance, fouling of washing filters by calcium oxalate is common (Huber et al., 2014; Hu et al., 2014).

However, oxalate ions can form also soluble complexes with various metal ions, such as Mg^{2+} and Mn^{2+}. Thus, it acts as a weak chelating agent for these ions. (Huber et al., 2014)

3.1.3 Sulphate

The concentration of sulphate anions (SO_4^{2-}) in bleaching filtrates is usually rather high. It is dependent on the second step of the sulphuric acid dissociation reaction (reaction 8).

Sulphuric acid is considered as a strong acid, and thus, the first dissociation step (reaction 7) into hydrogen sulphate (HSO_4^-) always takes place in water solutions. (Bryant, 1995; Rudie & Hart, 2006a)

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \tag{7}$$

$$HSO_4^- \rightleftharpoons +H^+ + SO_4^{2-} \tag{8}$$

Also the dissociation reaction of sulphuric acid is dependent on the pH. Sulphate ions are predominant over HSO_4^- ions when the pH value is higher than 2 (Rudie & Hart, 2006a).

The efficiencies of different bleaching processes are often strongly affected by the pH of the medium, which can be optimised by adding acid or alkali (Reeve, 1996). Sulphuric acid, which is most commonly used for acidification, is the most significant source of sulphate ions. Instead of sulphuric acid, also a salt by-product from ClO_2 production, sodium sesquisulfate, can be used for pH regulation, but in that case, substantially more sulphate ions are generated. (Rudie & Hart, 2006a) In addition to acidification, sulphate ions may end up to bleaching processes as carry-over from brownstock washing. Also, magnesium sulphate ($MgSO_4$) can be added to the oxygen delignification stage to decrease the degradation of cellulose, which also increases the sulphate ion concentration. (Huber et al., 2014)

By binding with barium, sulphate ions can form insoluble precipitates that are difficult to remove. Barium sulphate deposits cause issues especially in the operation of ECF bleaching systems and are commonly found in ClO_2 and ozone stages. (Bryant, 1995; Huber et al., 2014) Since sulphate ions are always present in bleaching systems, it is very difficult to prevent these deposits. In addition, in some areas, the soil contains radium, which may enter the pulping processes in small concentrations with the wood chips and tends to participate in the formation of radioactive radium-barium sulphate co-precipitates. (Rudie & Hart, 2006b) It has also been found out that sulphate ions can cause corrosion (Boffardi, 1992).

Sulphate ions can also participate in the formation of calcium sulphate and other soluble metal complexes, which reduces the amount of sulphate ions available for barium sulphate precipitation (Huber et al., 2014).

3.1.4 Chloride

Chloride anions (Cl^-) enter the kraft pulping processes mainly with wood chips and make-up chemicals such as lime and salt cake, in which chlorine is commonly present as an impurity. Chlorine is highly soluble in the alkaline pulping liquors, and therefore, it tends to accumulate in the liquor cycle. (Jemaa et al., 1999; Bajpai, 2015, p. 186)

Chloride ions are known to induce corrosion of the equipment. A decrease in pH increases this impact, and in highly alkaline conditions, they do not significantly contribute to corrosion (Ulmgren, 1997) In bleaching systems, where chlorine-based bleaching chemicals are used, the concentration of chloride ions is generally very high in the acidic washing filtrates. Reusing these filtrates to further close the water circuits is not yet viable. Due to their high chloride content, reusing them in the recovery cycle could lead to corrosion problems in the black liquor evaporators and recovery boiler.

3.2 Cations - Transition metal ions

Transition metal ions are known to catalyse the decomposition of hydrogen peroxide. Thereby, the presence of mainly iron, manganese and copper ions affects the efficiency of H_2O_2, oxygen and ozone bleaching. (Bryant, 1995) The catalysed decomposition may lead to an increased formation of very reactive hydroxyl radicals (OH•), which may lower the selectivity of the bleaching processes, since they can degrade also cellulose instead of lignin. This may result in poor strength of the pulp and increased consumption of the bleaching agents. (Bryant, 1995; Gullichsen & Fogelholm 1999, 203) In oxygen and ozone bleaching, H_2O_2 is formed in the reduction of oxygen and decomposition of ozone (Dahl, 1999; Puitel, Bordeianu & Gavrilescu, 2007).

3.2.1 Iron

Iron is an abundant transition metal in kraft pulping processes, originating mainly from the added make-up lime and the used process water. In addition, the wood raw material contains trace amounts of it, and corrosion of the equipment can lead to an increased iron concentration. (Jemaa, 1999) Most commonly, iron is present in two oxidation states, +2 and +3. In acidic conditions, the divalent ferrous ion (Fe^{2+}) is easily converted to ferric ion

(Fe^{3+}). (Wuorimaa, Jokela & Aksela, 2018) Some of the iron is removed from the process with dregs. (Jemaa et al., 1999)
It has been reported that the presence of iron ions decreases the viscosity of the pulp. Lachenal, Nguyen, Chirat et al. (1997) discovered that more radicals were formed as a consequence of the addition of Fe^{2+} ions in an alkaline H_2O_2 solution. This is known as the Fenton process. Even though the increase in radical formation has a good impact on the bleaching efficiency, the presence of iron ions also increases the consumption of H_2O_2 and thus the chemical costs. (Lachenal et al., 1997)

3.2.2 Copper

Copper ions (Cu^{2+}) are usually found in bleaching systems in smaller quantities than iron or manganese, and therefore, their impact on H_2O_2 decomposition is smaller (Wuorimaa et al. 2018; Bryant, 1995). They enter the pulping and bleaching processes mostly with the wood chips (Jemaa et al. 1999). In addition to catalysing the H_2O_2 decomposition, it has been discovered that copper ions can inhibit the precipitation of $CaCO_3$ and thus reduce deposit formation at bleach plants (Zeppenfeld, 2016).

It is thought that the catalysis of the H_2O_2 decomposition by copper ions occurs through similar mechanisms as by iron ions, but the presence of copper ions leads to the formation of more free radicals. With increasing pH, more copper-induced decomposition of H_2O_2 occurs. The increased generation of radicals, caused by the catalytic activity of copper ions, may lead to a notable viscosity drop in kraft pulp (Wuorimaa et al. 2018).

3.2.3 Manganese

Manganese originates mainly from the wood raw material. The process water can also carry small concentrations of it to bleach plants. Some of it is purged from the pulping process with dregs and grits. (Jemaa et al., 1999) Manganese occurs in nature in three oxidation states, Mn^{2+}, Mn^{3+} and Mn^{4+}. In alkaline conditions, Mn^{2+} is easily oxidised by air into Mn^{3+}. (Wuorimaa et al. 2019)

Manganese ion can be considered as the most effective transition metal ion as a catalyst for H_2O_2 decomposition, even at very low concentrations. The mechanisms of the catalysis differ from that induced by iron and copper in a way that hydroxyl radicals de not take part in the H_2O_2 decomposition (Wuorimaa et al. 2018). Both Mn^{2+} and Mn^{3+} ions are involved in the catalysis (Wekesa & Ni, 2003).

3.3 Cations – Earth alkali metal ions

Scale deposition problems in bleaching systems with reduced water consumption are typically caused by insoluble salts of calcium and barium, the most common ones being calcium carbonate, calcium oxalate and barium sulphate (Huber et al. 2014; Ulmgren, 1997).

3.3.1 Calcium

Calcium originates mainly from the wood raw material. Similarly to most trace elements, the concentration of calcium is higher in hardwoods than in softwoods. (Jemaa et al., 1999) In addition, calcium enters the system with white liquor and process water (Rudie, 2000). It is released from the wood in cooking and enters the bleaching systems as calcium ions (Ca^{2+}), adsorbed on the pulp, and as calcium carbonate precipitates. Most of the calcium that enters the kraft process is removed, for instance, with the green liquor dregs and thus does not reach the bleaching systems. (Huber et al., 2014; Ulmgren, 1997)

The two most common poorly soluble calcium salts that cause issues in bleaching systems are calcium carbonate ($CaCO_3$) and calcium oxalate (CaC_2O_4) (Ulmgren, 1997). $CaCO_3$ can be accumulated especially in the oxygen, alkaline extraction and H_2O_2 bleaching stages. It can be deposited on the pulp fibres or the surfaces of the equipment. CaC_2O_4 deposits can be found in the same bleaching stages as $CaCO_3$ deposits, and additionally in ClO_2 stages. As CaC_2O_4 precipitates in lower temperatures, it tends to cause plugging of filters in washing stages. (Huber et al., 2014)

Calcium ions can be present at any pH from 0 to 14. In addition to carbonate and oxalate, they can also form bonds with many other anions such as sulphate. Generally, in acidic conditions, a great amount of calcium is present in its ionic form. In alkaline conditions, calcium tends to form soluble complexes with different organics. (Huber et al., 2014)

3.3.2 Barium

Also the barium that enters the kraft process mainly originates from wood, but its concentration is substantially lower than that of calcium (Jemaa et al., 1999; Persson &

Ulmgren, 2002). Again, its concentration is generally higher in hardwoods than in softwoods. Debarking has a very essential role in limiting the amount of barium that enters the process. (Persson & Ulmgren, 2002; Rudie & Hart, 2006b) Barium ions (Ba^{2+}) are released from wood in cooking and partly removed from the process with the green liquor dregs (Persson & Ulmgren, 2002).

The barium sulphate ($BaSO_4$) precipitates are most commonly found in the D0 stage. In the later stages, the concentration of free barium ions is generally lower, as they tend to bind with fibres in alkaline conditions. (Persson & Ulmgren, 2002) In addition, $BaSO_4$ does not dissolve in the system once it is formed, and therefore, it is not common that it precipitates again in the later bleaching stages. Since barium is present in the system in very low concentrations, barium sulphate deposits are not of a great concern in most plants. (Rudie & Hart, 2012; Rudie & Hart, 2006b)

Similarly to calcium ions, also barium ions can be present at any pH. Both these cations can form bonds with various anions and dissolved wood constituents. (Huber et al., 2014) It is known that at pH above 4, a large share of the barium that is present is adsorbed on the fibres (Bryant, Samuelsson & Basta, 2003).

3.4 Other metal cations

In addition to barium and calcium ions, there can also be other divalent metal cations, such as cobalt, nickel, strontium and radium ions, which may form poorly soluble precipitates in the presence of divalent anions in kraft pulp mills. These ions are generally found in very low concentrations in bleaching systems, and thus, they do not significantly contribute to scale deposition problems. (Rudie & Hart, 2012) However, some of them may affect the precipitation of calcium and barium or form co-precipitates with them (Rudie & Hart, 2012; Zeppenfeld, 2016). Monovalent ions rarely contribute to scaling problems, since they typically form soluble salts (Rudie & Hart, 2005).

There can also be limit values for the discharge of heavy metals such as cadmium, zinc and lead, from the mills. They are of great environmental concern because of their potential toxic effects and tendency to accumulate in ecosystems. In today’s bleach plants, the alkaline bleaching filtrates are commonly recycled, but the possibilities for the reuse of acidic filtrates are poor, partly due to their high chloride and heavy metal content. (Bajpai, 2012, p. 341)

4 BEHAVIOUR OF METALS IN PULP SUSPENSIONS

In pulp suspensions, metals can be present as soluble ions, finely divided suspended particles, organic complex compounds, or attached to the acidic surface functional groups in fibres (Zhao, Wu, Hu et al., 2018; Sjöström, 1993, p. 175). The form of a metal affects its behaviour in bleaching filtrates (Wuorimaa et al. 2018).

4.1 Typical characteristics of bleaching effluents

Both the acidic and alkaline bleaching filtrates are extremely complex mixtures of chemical compounds. Their characteristics vary based on the used raw-material, process conditions and bleaching sequence. In addition to metal compounds, they may contain, for instance, cellulose fibres, residual lignin compounds with varying molecular mass and structure, wood extractives, and chlorinated organic compounds. (McCague & Carlberg, 1996, p. 751,759-760)

In order to evaluate the suitability of bleaching filtrates for reuse, and to assess the environmental impacts of their discharge to receiving water systems, it is necessary to characterise their chemical composition. Traditionally, the quality of these effluents has been assessed by indices such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), adsorbable organic halogens (AOX), total suspended solids (TSS) and colour. (Sjöström, 1993, p. 195) AOX is an approximate measure for all chlorinated organic compounds in the effluent. (McCague & Carlberg, 1996, p. 753) These compounds are of great environmental concern, as they may have toxic effects on the ecosystems and some of them tend to bioaccumulate in the receiving water bodies (Lindholm-Lehto, Knuutinen, Ahkola et al., 2015).

The effluents from the first extraction stage and the first chlorine dioxide stage (D0) contain most of the chlorinated organic compounds that are formed during bleaching. Thus, these effluents contribute significantly to the colour content and organic load of the final effluent of the bleach plant. (Ali & Sheekrishnan, 2001; Calvo, Gilarranz, Casas et al.,

2007) The alkaline filtrates have been reported to have higher organic load and colour content than the acidic filtrates (McKague & Carlberg, 1996).

4.2 Interactions between metal ions and pulp fibres

In pulp suspensions, the negatively charged fibre wall can attract metal cations. The interactions between the ions and the fibre wall are traditionally explained by Donnan equilibrium theory (Räsänen, 2003).

4.2.1 Donnan equilibrium theory

Pulp fibres consist of cellulose microfibrils, various hemicelluloses and lignin compounds. The dissociation of the functional groups that are present in hemicelluloses and residual lignin form a negative charge on the fibre surfaces. In water-fibre suspensions, the solution can be divided in two fractions, namely the external solution that surrounds the fibres and the water that is held by the fibre cell wall (figure 4). (Räsänen, 2003)

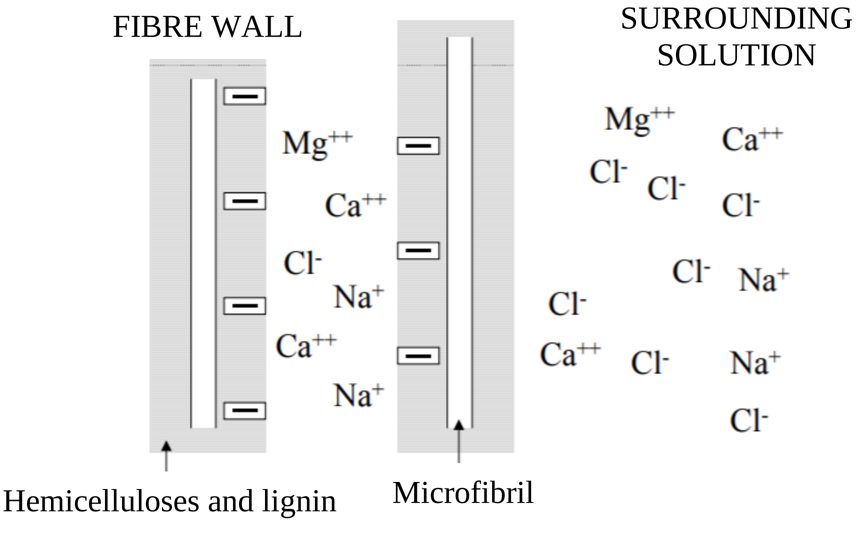


Figure 4 Ions in the negatively charged fibre wall and in the surrounding solution (Adapted from Räsänen, 2003).

Donnan theory can be applied to describe the partitioning of ions between the solution in the fibre wall and the external solution (Towers and Scallan, 1996). Some of the ions in the fibre wall are attached to the cellulose fibres. Therefore, there is excess charge in one phase, and to maintain a charge balance between the two phases, free ions are unevenly distributed between the phases. This distribution is expressed by an equilibrium constant (λ). (Räsänen, Stenius & Tervola, 2001; Räsänen, 2003)

Towers and Scallan (1996) introduced an equilibrium model based on the original Donnan theory, where it was presumed that all free ionic species are in a soluble form. The model was able to well describe the ionic distribution of calcium, sodium, magnesium and manganese ions between the external solution and fibre phase at pH range from 2 to 10 in an unbleached kraft pulp suspension. (Towers & Scallan, 1996) More recently, Räsänen (2003) developed a model, which considers also metal complex formation in the suspension.

4.2.2 Factors that affect the interactions between metal ions and pulp fibres

The charge of cellulose fibres strongly affects how the metal ions interact with them. It is determined by the types and amounts of the acidic functional groups on the fibre wall and the extent of their dissociation. (Athley & Ulmgren, 2001) Several ionisable groups are present in the polymeric wood constituents. Carboxylic groups in uronic acids that are mostly attached to xylan, are a major contributor for the generation of anionic sites on fibres. They are ionised in neutral or slightly acidic conditions. (Sjöström, 1993, p. 163) In addition, lignin contains ionisable phenolic hydroxyl groups and carbohydrates contain ionisable hydroxyl groups (Sjöström, 1993, p. 163; Räsänen, 2003). Metal ions have a notably higher affinity for lignin than to carbohydrates (Cardona-Barrau, Lachenal & Chirat, 2001). However, the reactions and dissolution of lignin, hemicellulloses and extractives, that take place in chemical delignification, reduce the net charge of the pulp fibres (Räsänen, 2003).

In addition, the charge of the cation and its concentration in relation to other ions in the system affect its distribution between the surrounding solution and the fibres (Athley & Ulmgren, 2001). It has been discovered that especially the trivalent iron ions (Fe^{3+}) bind to pulp very strongly (Granholm, Harju & Ivaska, 2010) Södö et al. (2007) studied the affinities of different metal ions for oxygen delignified hardwood pulp and discovered that copper and lead ions were the most tightly bound divalent cations. Monovalent cations were most weakly bound. (Södö et al., 2007) However, the monovalent Na^+ ion is typically the most abundant metal cation in process suspensions. Therefore, its concentration largely controls the partition of the other metal cations between the fibres and the surrounding solution (Athley & Ulmgren, 2001).

The main parameter that affects the ion exchange equilibrium in fibre suspensions is pH (Räsänen, 2003). The acidic groups in pulp fibre wall deprotonate with increasing pH, which leads to the formation of anionic sites on the fibres. Thus, at higher pH, the concentration of metal ions in fibres is higher. At very acidic conditions, this dissociation does not take place, and thus, the ion exchange capacity of the pulp is poor. (Towers & Scallan, 1996)

4.3 Interactions between metal ions and dissolved organic compounds

Especially in neutral and alkaline conditions, metal ions tend to bind to the anionic sites, such as carboxylic acid groups, of also certain ligands present in pulp suspensions, forming organic metal complexes (Dahlman, Reimann, Strömberg et al., 1995). This can occur either through inner-sphere or outer-sphere complexation. In the latter, the ion binds onto the surface with its hydration sphere purely through electrostatic forces, whereas in inner-sphere complexation, the ion binds directly to a specific site on the surface. (Merdy, Guillon & Aplincourt, 2002)

Monovalent metal ions such as K^+ and Na^+ can bind to the anionic sites in organic substances only through relatively weak electrostatic linkages. Also the divalent Ca^{2+} and Mg^{2+} ions tend to form outer-sphere complexes with organics. Dahlman et al. (1995) studied the affinities of different metal ions to the high-molecular mass fraction of bleaching effluents (molecular mass < 1000 Da) and reported that only small shares of the K^+ and Na^+ ions were associated with this fraction. The shares of the Ca^{2+} and Mg^{2+} ions associated with the high-molecular mass fraction were somewhat higher. Trivalent metal ions, in turn, form strong complexes with anionic organic compounds. (Dahlman et al., 1995)

4.3.1 Formation of organic metal-lignin complexes

In oxidative bleaching stages, residual lignin is oxidised into smaller structures with high acidic group content (Dahlman et al., 1995; Zhao et al., 2018). Especially transition metal ions typically form coordinate bonds with the carboxylic groups and especially phenolic hydroxyl groups in lignin structure, which leads to the formation of organic metal-lignin complexes (Zhao et al., 2018; Guo, Zhang & Shan, 2008). The formation of these complexes take place through oxidation-reduction (redox) reactions. The shares of different active functional groups in lignin structure, and the pH and the ionic strength of the solution affect their formation. (Merdy et al., 2002)

The divalent Mg^{2+} and Ca^{2+} ions form preferably outer-sphere complexes, whereas Fe^{3+} ions are known to form inner-sphere complexes with lignin-derived humic acids (Merdy et al., 2002). As free transition metal ions, also those that are bound to lignin contribute to catalytic decomposition of peroxide during bleaching. However, the catalytic activity of these complexes is lower than that of the free ions. The presence of different stabilisers can affect their formation. (Zhao et al., 2018) For instance, Ca^{2+} and K^{+} ions compete with manganese binding to the acid sites of lignin, and thus, their concentrations affect the extent of manganese complex formation. Also the presence of bicarbonate ions can inhibit the binding of Mn^{2+} ions on lignin, as they can form a negatively charged barrier between Mn^{2+} ions and the anionic sites in lignin. (Merdy et al., 2002)

5 CONDITIONS THAT LEAD TO PRECIPITATION OF METAL SALTS

As mentioned before, the three most common minerals that cause scale deposit problems at bleach plants with high degree of system closure are calcium oxalate (CaC_2O_4), calcium carbonate ($CaCO_3$) and barium sulphate ($BaSO_4$). For instance, pH, temperature, and concentrations of ions and organic substances are known to have an impact on their formation. (Ulmgren, 1997) Especially at high pH, the formation of soluble complexes with organics and other anions reduces the amount of available calcium and barium ions for the precipitation of these minerals in the systems. Also chelating agents such as ethylenediaminetetracetic acid (EDTA), which can be added to bind metal ions in bleaching solutions, lower the amounts of available metals. (Elsander et al., 2000; Huber et al., 2014)

Formation of precipitates takes place in two stages, namely nucleation and growth. In nucleation, crystal nuclei can be formed by precipitation in the solution (homogeneous nucleation) or on surfaces of, for instance, fibres, other suspended solids or the equipment (heterogeneous nucleation). (David & Klein, 2001; Huber et al., 2014). In the growth phase, the formed nuclei grow into larger precipitates. Formation of precipitates can occur only if the solution contains more solute than the maximum amount that can exist in a dissolved form in certain temperature. In this case, the solution is supersaturated. (Mersmann 2001) Saturation index (SI) can be used as an indicator of the level of saturation. If the SI value for a mineral is above zero, the solution is supersaturated.

5.1 Precipitation of calcium carbonate

The precipitation of $CaCO_3$ takes place in supersaturated solutions that contain calcium and carbonate ions. The equilibrium reaction for its formation is written as follows:

$$CaCO_3 \rightleftarrows Ca^{2+} + CO_3^{2-} \qquad (7)$$

In nature, $CaCO_3$ exists most commonly as calcite, which is its most stable crystalline form. For the nucleation of calcite to begin, high level of supersaturation ($SI < 1.5$) is required. However, even at a high level of supersaturation, a change in temperature or pH may be required to cause nucleation. Growth can take place at much lower supersaturation ($SI > 0$). Therefore, if there are calcite precipitates or nuclei already present in the bleaching equipment, growth occurs easily. However, in bleaching waters, the presence of dissolved organic compounds has been reported to inhibit crystal growth. (Huber et al., 2014)

Calcite is likely to be formed on fibres or the surfaces of, for instance, pipes by heterogeneous nucleation (Rudie, 2000). It is known that large amount of it is carried by fibres, which reduces the deposit formation on the equipment (Huber et al., 2014).

Calcite precipitates are formed in alkaline conditions, typically from pH 8 to pH 13. Free CO_3^{2-} ions available for precipitation can be found in alkaline bleaching stages. (Ulmgren, 1997) Typically, at pH below 8, their relative concentration is lower than the minimum that is required for the precipitation of calcite (Rudie, 2000). However, at high pH, calcium tends to form soluble complexes with different organic species (Huber et al., 2014). Also temperature affects the precipitation tendency, and calcite is likely to precipitate in high temperatures. (Huber et al., 2014; Ulmgren, 1997)

In addition to organic complexes, calcium can form soaps with fatty acids, which reduces the concentration of free calcium especially at brownstock washing. If carry-over of fatty acids to the bleach plant occurs, the formation of calcium soaps may also affect the precipitation of calcite on washers there (Huber et al. 2014).

It has been discovered that calcite scaling often takes place in aerated parts of pulp mills, where part of the inorganic carbon tends to be released to the atmosphere as CO_2 with the air bubbles that are leaving the system. Depletion in soluble CO_2 may lead to an increase in pH and thus also to increased saturation with respect to $CaCO_3$. (Huber, 2011) In bleaching systems, this can take place at points where the pulp and water are brought into contact with air, and especially on washers following alkaline extraction stages (Huber et al., 2014).

5.2 Precipitation of calcium oxalate

CaC_2O_4 precipitates are formed according to the following reaction equation:

$$Ca^{2+} + C_2O_4^{2-} + xH_2O \rightleftarrows CaC_2O_4 \cdot xH_2O(s), \qquad (1)$$

where the number of water molecules (x) can be one, two or three (Ulmgren & Rådeström, 2001; Huber et al. 2014). Its most stable and common form is calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$). However, Ulmgren & Rådeström (2001) discovered that also precipitation of the dehydrate form may occur in bleaching filtrates from chlorine dioxide stage. Only a low level of supersaturation is required for the precipitation of CaC_2O_4 in a solution (Huber et al. 2014).

Generally, CaC_2O_4 deposits are formed in acidic bleaching stages, on the walls of the equipment such as reactors and pumps (Ulmgren & Rådeström, 2001). It precipitates at temperatures lower than 40 to 50°C, and therefore, fouling of washing filters by calcium oxalate is very common, and temperature drops in bleaching systems may lead to its precipitation. (Huber et al., 2014)

Precipitation of CaC_2O_4 occurs likely in pH above 3, but in highly alkaline solutions, calcium tends to form soluble complexes with dissolved organic compounds and anions. The formation of soluble magnesium oxalate is more likely to occur than that of CaC_2O_4, and therefore, by partially substituting the NaOH that is commonly used as an alkali source, with $Mg(OH)_2$, the precipitation of calcium oxalate could be reduced. (Huber et al., 2014)

5.3 Precipitation of barium sulphate

Barium sulphate, which is also referred to as barite, is formed according to equilibrium reaction (5) in solutions that contain barium ions and sulphate ions in sufficient concentrations:

$$BaSO_4 \rightleftarrows Ba^{2+} + SO_4^{2-} \tag{5}$$

In bleaching systems, the concentration of barium is much smaller than that of calcium (Rudie & Hart, 2006b). However, high level of supersaturation is not required for barite to precipitate. (Huber et al., 2014)

Similarly to calcium oxalate, barite tends to precipitate in low temperatures. Therefore, temperature drops in bleaching systems and especially at washers can enhance the precipitation of barite. (Huber et al., 2014)

The availability of sulphate ions and thus also precipitation of barite depends on pH (Huber et al., 2014). Barium tends to enter the bleach plant as barium carbonate, which dissolves as the pH decreases below 7. (Rudie & Hart, 2006b) At pH below 4, most of barium is desorbed from the pulp and available for precipitation (Bryant et al., 2003). As also sulphate ions are always present in bleaching systems, it is usually difficult to control the formation of barite deposits in the first acidic bleaching stage. (Rudie and Hart, 2006a) It is known that barite typically precipitates at any pH above 2 (Huber et al., 2014). A summary of the pH ranges where the precipitation of $CaCO_3$, CaC_2O_4 and $BaSO_4$ take place is shown on top of figure 5.

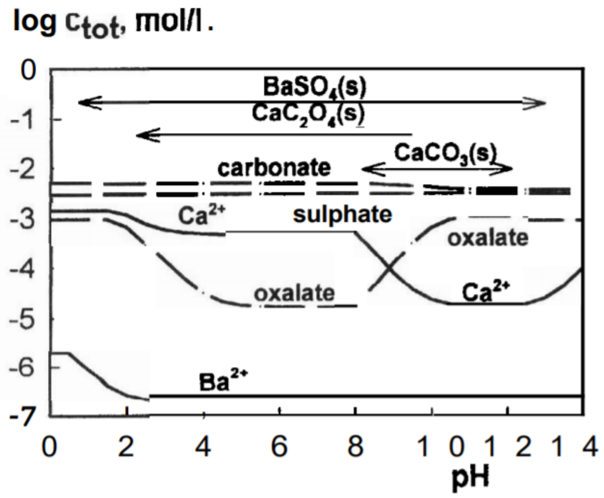


Figure 5 The pH ranges where the precipitation of $CaCO_3$, CaC_2O_4 and $BaSO_4$ can occur and the calcium, barium, carbonate, sulphate and oxalate ion concentrations with respect to pH (Ulmgren, 1997).

pH regulation affects barite scaling significantly (Huber et al., 2014). According to Rudie & Hart (2006b), when acidification is carried out using sulphuric acid, the sulphate ion concentration in the system keeps increasing even at extremely low pH. Thus, the precipitation of barite cannot be prevented by lowering the pH by adding sulphuric acid. (Rudie & Hart, 2006b) The use of spent acid for acidification instead of sulphuric acid further increases barite precipitation, as more sulphate ions are formed (Rudie & Hart, 2006a).

6 ANALYTICAL METHODS FOR THE DETERMINATION OF THE HARMFUL IONS

There are several different methods that can be used for the determination of metal cations in solutions. Today, spectroscopic methods including, for instance, atomic absorption spectroscopy (AAS) and inductively coupled plasma (ICP) spectroscopy, are most commonly used for metal analysis due to their sensitivity, rapidity and simplicity of their operation. Alternatively to these methods, ion chromatography (IC) can be used for metal analysis. (Michalski, 2009) In addition, different anions in water and wastewater samples can be analysed by IC (Fritz & Gjerde, 2009, p. 1; Michalski, 2010). Capillary electrophoresis (CE) has also been proven as a viable option for the determination of inorganic anions and cations (Valsecchi & Polesello, 1999).

6.1 Ion chromatography

Chromatography entails a wide range of analytical techniques, which are based on the interactions of different components of a sample with two phases. The other phase, the stationary phase, remains fixed, and the mobile phase carries the sample. (Higson 2004, p. 211-212) Liquid chromatography is a collective term for a variety of chromatographic methods, including ion chromatography (IC), where the mobile phase is a liquid and an ion exchanger is used as the stationary phase (Braithwaite & Smith 1985, p. 212). In ion chromatography, the separation occurs through ionic interactions between the analytes in the sample and the functional groups of opposite charge that are attached to the stationary phase material. (Nesterenko & Paull, 2017, p. 206)

IC is mostly used for analysing inorganic and relatively small organic cations and anions in wastewater samples. However, also larger ionic solutes, including metal complexes, low-molecular mass organic bases and acids such as carboxylic and sulphuric acids as well as carbohydrates, can be determined by IC (Fritz & Gjerde, 2009, p.1; Michalski, 2009).

6.1.1 Components of an ion chromatograph

An ion chromatography system typically consists of an eluent reservoir, a pump, a sample injection device, a separation column, a suppressor, a detector and a computer (Sinniah & Piers, 2001). The mobile phase or eluent is pumped at fixed rate to the system from the eluent container. A specific volume of the sample is injected to the eluent flow, after which it flows through a guard column to the analytical column, where the separation of the analytes in the sample takes place. The separated analytes are then transported by the eluent through a suppressor to a detector. The detector identifies and quantifies the analytes as they pass through it and sends data to the computer. (Fritz & Gjerde 2009, p. 21-22) A schematic of a typical configuration of ion chromatograph system is presented in figure 6.

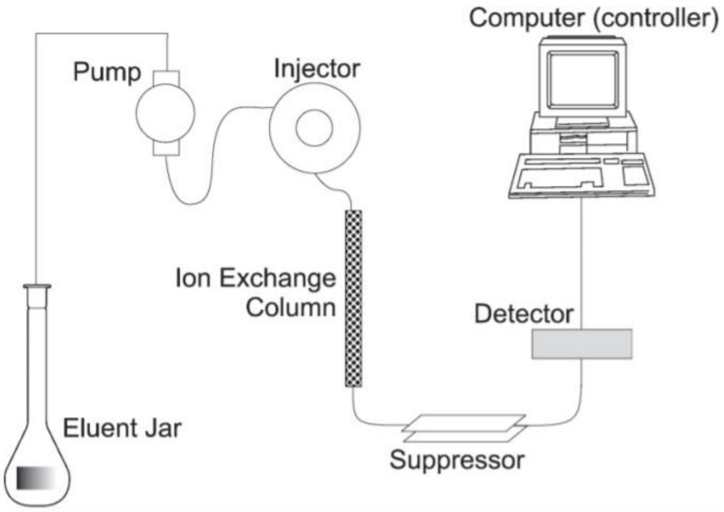


Figure 6 A schematic of an ion chromatograph (Sinniah & Piers, 2001).

The eluent contains ions that compete with the analyte ions to bind to the ion exchange material in the separation column. For the analysis of anions, typically a dilute solution containing sodium bicarbonate and sodium carbonate, or potassium hydroxide (KOH), is used as the eluent. The most common eluent for cation analysis is a dilute acid solution containing hydronium ions (H_3O^+). (Sinniah & Piers, 2001; Nesterenko & Paull, 2017, p. 164-165) During elution, the concentration of the eluent can either be kept constant (isocratic elution) or changed (gradient elution) (Nesterenko & Paull, 2017, p. 226).

The analyte ions move through the separation column at different rates (Sinniah & Piers, 2001). Most commonly, the used stationary phase consists of ion exchange resins, which are mainly organic silica- or styrene-based polymers that contain ionic groups attached to them (Small 1989, 42). In anion analysis, quaternary ammonium groups attached to the anion exchange resin typically function as positively charged ion exchange sites. In the case of cation analysis, the resin carries negatively charged sites, such as sulphonate and carboxylate groups. (Sinniah & Piers, 2001) To increase the lifetime of an analytical column, it can be protected by applying a guard column. As the sample first passes the guard column, the compounds that have a high affinity for the ion exchange material, are retained and do not contaminate the separation column. (Weiss, 2004, p. 835)

Different detectors, including, for instance, conductivity, UV/Vis and amperometric detectors, can be used in ion chromatography. Most commonly, a conductivity detector is used either with or without suppression. (Weiss, 2004, p. 6) In conductivity detection, identification and quantification of ions is carried out by measuring their electric conductivity, which depends on their type and concentration. (Fritze & Gjerde 2009, p. 33,71). A suppressor can be used to chemically lower the background conductivity caused by the ions in the eluent and to increase the conductivity of the analyte ions (Weiss, 2004, p. 6).

From the signals from the detector, a chromatogram is formed (Weiss, 2004, p. 550). If a conductivity detector is used, the chromatogram is a plot of electrical conductivity of the analyte versus time (Sinniah & Piers, 2001). The chromatogram usually consists of a series of peaks, that represent different ions, and the concentrations of the ions are defined based on the peak areas. The analytes in samples are quantified by preparing standard solutions of known concentrations and comparing the obtained peaks. (Weiss, 2004, p. 550, 957)

6.1.2 Applications of ion chromatography in pulp and paper industry

The process liquors and effluents from pulp and paper industry are typically extremely complex solutions, and thus, it is relatively difficult to analyse them by using ion chromatography (Weiss, 2004, p. 810). They may contain compounds, which interfere with the analysis or damage the instruments (Lacorte, Latorre, Barceló et al., 2003). For instance, humic acids tend to bind strongly to anion exchange resins (Weiss, 2004, p. 811). Therefore, appropriate pre-treatment needs to be applied for analysing these samples (Lacorte al., 2003). Typically, samples with high ionic strength are diluted to bring the concentration of the ions into the working range and filtered to remove solids (Jackson, 2000, p. 4).

In pulp and paper industry, IC has been used especially for analysing different anions in the process liquors (Michalski, 2009). The most essential ions that are commonly analysed are chloride, oxalate, and sulphur-containing anions such as sulphate (Weiss, 2004, p. 810).

In addition, carbonate ions can be determined in black liquor (TAPPI, 2009). However, the carbonate analysis requires rather complicated pre-treatment and lacks sensitivity compared to the titration method, which is typically used for the carbonate analysis in, for instance, white liquor and wastewaters (Chai, Zhu & Luo, 2001).

IC has been used for the quantitative determination of chloride and sulphur-containing ions also in the effluents from pulp and paper industry. Sullivan & Douek (1998) introduced a method for the analysis of inorganic chlorine-containing ions and other anions including sulphate in bleaching effluents. Prior to the analysis, the samples were sparged with helium to remove ClO_2. (Sullivan & Douek 1998) Žarković, Todorović, Krgovic et al. (2009) presented a method for the analysis of common inorganic anions including Cl^-, SO_4^{2-}, nitrate (NO_3^-) and phosphate (PO_4^{3-}) ions in process waters and effluents from a paperboard mill, and selective determination of the anions over a wide concentration range was obtained. (Žarković et al., 2009)

Sulphite ions (SO_3^{2-}) are easily oxidised to sulphate ions, which may cause erroneous results in sulphate analysis. The impacts of this oxidation reaction can, however, be reduced by analysing the samples immediately after dilution. (Douek et al., 1993; Easty & Johnsson, 1987) In the study conducted by Douek et al. (1993), isopropanol was added to process liquor samples and the dilution water to prevent the oxidation of sulphite.

There is a standardised method for the determination of dissolved and precipitated oxalate in bleaching waters by ion chromatography (SCAN-N 39:05). For the determination of dissolved oxalate ions, the samples are filtered with a syringe filter to remove CaC_2O_4 precipitates. After that, they are acidified to pH 2 or below by adding hydrochloric acid to avoid precipitation of CaC_2O_4. More recently, Sithole, Azeez & Ramjugernath (2014) described a rapid method in which soluble oxalate was determined directly, without chemical pre-treatment.

In addition, a method for the determination of carbohydrates such as glucose, xylose and mannose in wood, pulp, and various process liquors has been developed (Sullivan & Douek, 1994). Weiss (2004, p. 814) also listed the determination of alkali metals and ammonium ions as one of the applications of IC in pulp and paper industry.

6.2 Comparison of different methods for metal analysis

Most metals including, for instance, barium, are present in pulp mill effluents in very small concentrations, whereas the concentrations of some metals such as Na, Ca and K can be notably higher. For the routine analysis of metals, AAS methods, including flame atomic absorption spectroscopy (FAAS) and electrothermal atomic absorption spectroscopy (ETAAS), are most commonly used. (Hayes, 2017, 96, 104) In these methods, the concentration of a specific metal is determined by measuring the absorption of light by free ions. (Hill & Fischer, 1999)

More recently, inductively coupled plasma-optical emission spectroscopy (ICP-OES) has become another common spectroscopic technique for metal analysis. (Hayes, 2017, 96, 104) In ICP-OES, the determination of elements is based on measuring the wavelength of the electromagnetic radiation that excited ions and atoms release (Templeton, 1994).

In addition, capillary electrophoresis (CE) can be used for analysing various anions and metal cations from pulp and paper industry effluents and process waters (Lastra, Gómez & Romero, 2004; Sirén, Kokkonen, Hiissa et al., 2000). In CE, charged solutes can be separated based on their migration under an applied electric field, which takes place in a capillary, which contains buffer solution (Demarest, Monnot-Chase, Jiu et al., 1992). The most common detection mode is UV absorption. For ions that do not absorb UV radiation, indirect UV detection, where an oppositely charged co-ion, which absorbs the radiation, is added to the buffer solution, can be used. (de Jong, 2016)

Although there is strong competition with spectrometric methods, IC has some advantages over them (Michalski, 2009). The total content of different metals can be determined by AAS and ICP spectroscopy. However, the impacts of different metals usually depend on their form. Thus, a remarkable advantage of ion chromatography over these methods is that it gives information also on the speciation of metal ions. It is possible to distinguish their different oxidation states, such as ferric and ferrous states of iron. (Michalski, 2009) In addition, it is not possible to determine ammonium ions by spectroscopic methods (Michalski, 2018). However, very little information is available on the application of ion chromatography for the determination of metal cations in pulp and paper industry effluents and process waters.

A major advantage of IC and ICP spectroscopy compared to AAS techniques is that they can be used for simultaneous determination of multiple different metals (Weiss, 2004, 7; Hayes, 2017, 96). ICP-OES is a fast method with comparable detection limits to those of FAAS, but it is more expensive (Hayes, 2017, 96). IC has a broader dynamic range than AAS. It usually means that the required pre-treatment for samples is simpler, and lower analyte concentrations can be determined in complex solutions. (Kubáň, Guchardi, & Hauser, 2005) Whereas by AAS methods only one element can be determined per analysis, IC and ICP spectroscopy can be used (Weiss, 2004, 7).

Transition metals are usually analysed by spectroscopic methods (Michalski, 2009). They can also be analysed by ion chromatography with an UV/Vis detector. Prior to the analysis, 4-(2-pyridylazo)- resorcinol (PAR) reagent is added to the samples. With PAR, the transition metal ions form complexes, which can be determined by UV/Vis detector at certain wavelengths. (Weiss, 2004, p. 499-500)

However, there are challenges related to ion chromatography, including the development of new ion exchange materials, new sample pre-treatment and reference methods, the effectiveness of suppressors and lowering the detection limits of analyte ions. (Michalski, 2010) Capillary electrophoresis, as well as spectroscopic methods, has shown several advantages in relation to IC. In table IV, a comparison of different methods for metal analysis is shown.

Table IV The main advantages and disadvantages of the selected analytical methods (Michalski, 2009; Valsecchi & Polesello, 1999; Wilschefski & Baxter, 2019).

Analytical method	**Advantages**	**Disadvantages**
ICP-OES	Multi-element analysis Fast Large analytical range	High equipment and laboratory set-up costs High detection limit Skilled operation staff is required
FAAS	Low equipment and set-up costs Simple operation and sample pre-treatment Few interferences	Single-element analysis Limited analytical range High detection limit Flammable gases
ETAAS	Low equipment and set-up costs Simple sample pre-treatment in most cases Few interferences Low detection limit	Single-element analysis Limited analytical range Some elements require acid digestion pre-treatment
CE	Simple Shorter run times compared to IC Excellent separation efficiency Tolerant for complex matrices	High background noise with indirect UV detection
IC	Multi-element analysis Reliable for the analysis of several inorganic anions Provides information of metal speciation	Little information available on applications for metal analysis in P&P industry effluents High detection limits in some cases Long run times Complicated sample pre-treatment can be required

7 REMOVAL OF METAL COMPOUNDS

The reuse of bleaching effluents to substitute fresh water in the processes typically requires the removal of harmful metal compounds. In today’s bleaching systems, the filtrates with high metal content from acidic bleaching stages are typically removed from the system. (Huber et al., 2014)

The alkaline bleaching filtrate from oxygen bleaching can usually be reused in brownstock washing and in the recovery cycle after that. It can be evaporated and burned in the recovery boiler, since it contains high concentrations of dissolved organic compounds and its metal content is low. (Dence & Reeve, 1996) Also the suitability of alkaline extraction stage filtrate for reuse in the recovery cycle has been studied. After appropriate treatment, it could also be used to partially substitute fresh water that is needed in bleaching (Quezada, Silva, Hoffstedt et al., 2015). Promising results have been reported for the metal removal from alkaline bleaching filtrates by membrane separation processes such as ultra- (e.g. Fälth, Jönssön & Wimmerstedt, 2001) and nanofiltration (Lastra et al., 2004). However, in order to reach further cycle closure, also the acidic filtrates, which are typically more challenging to purify, should be utilised in the processes. For instance, nanofiltration and evaporation have been suggested for their purification (Dahl, 1999).

7.1 Evaporation

In evaporation processes, a solvent is vaporised by heating. Also the dissolved solids with lower vapour pressure than that of the solvent are removed. The vapour is then cooled and condensed. The suitability of evaporation for the removal of metals and chloride ions from acidic bleaching filtrates from ClO_2 and peracetic acid stages was studied by Dahl (1999). It was discovered that the quality of the condensates generated in the evaporation were sufficiently high for reuse in the same bleaching stages and did not contain transition metals. In order to burn the concentrate in the recovery boiler, it needed to be further treated to remove monovalent ions including Cl^-, Na^+ and K^+, which in high concentrations can cause problems in the boilers. Evaporation is a promising method for the metal removal from the acidic bleaching filtrates, but the energy consumption of the method is very high, which would lead to high costs at industrial scale (Dahl, 1999).

Johansson et al., (1995) proposed a totally effluent-free bleaching process involving evaporation and electrodialysis. In the process, the total effluent of an ECF bleach plant was first evaporated, and the condensate was reused in the bleaching process. The concentrate was flocculated to remove organic matter that could then be burned in the recovery boiler. The remaining suspension from flocculation was treated by electrodialysis to remove chloride ions. (Johansson et al., 1995)

7.2 Pressure-driven membrane separation processes

Pressure-driven membrane separation processes have shown promising results in purification of the effluents and process waters of pulp and paper industry. High temperatures and both highly alkaline and acidic conditions can prevail in bleaching systems, and these factors set certain requirements for the membrane systems. (Mänttäri et al., 2015)

7.2.1 Basic principles of membrane technology

Membranes are selective barriers between two phases, which are usually the feed phase and permeate, which passes the membrane. The phase that is rejected by the membrane is referred to as retentate. Either polymeric or inorganic materials can be used for the preparation of membranes. (Mulder, 1996, p. 5,7, 12) The driving force for membrane processes can be the difference in either pressure, concentration or electrical potential between the feed and the permeate sides of the membrane (Kapoor, Balasubramanian, Kavitha et al., 2021, p. 283-284).

Pressure-driven membrane processes, that are commonly used in water treatment applications, can be classified into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Their characteristics are shown in table V. By ultrafiltration, macromolecules with molecular mass of approximately 10 000 to 100 000 Da can be separated. For the separation of small compounds with molecular mass higher than 200 to 1000 Da, nanofiltration is typically used (Mulder, 1996, p. 16, 302).

Table V Typical characteristics of different pressure-driven membrane separation processes (adapted from (Shon et al., 2013)).

Quality	MF	UF	NF	RO
Typical pore size range [nm]	50-1000	5-20	1-5	-
Typical compounds to be separated	Solids	Colloids and macromolecules	Multivalent ions and small molecules	Mono- and multivalent ions and small molecules
Typical pure water flux [L/(m^{2}h)]	500-10 000	100-2000	20-200	10-100
Required pressure [bar]	0.5-5	1-10	7-30	20-100 (larger than osmotic pressure)

Membranes can also be characterised according to their molecular weight cut-off (MWCO). It is the molecular mass of a known compound, of which 90% is retained by the membrane. (Mulder, 1996, p. 6) Based on their configuration, membranes can be categorised in flat sheet type and cylindrical membranes. Typically, membranes are packed in a module in either plate-and-frame, spiral-wound, tubular or hollow-fibre configurations, and each of them is suitable for certain applications. The plate-and-frame and spiral-wound configurations are based on flat sheet-type membranes and the two latter ones on cylindrical membranes. (Kapoor et al., 2021, p. 284-285)

For ultra-, micro-, and nanofiltration systems, there are two operation modes that are cross-flow and dead-end filtration. In the dead-end mode, the feed flow is pushed through the membrane, whereas in the cross-flow mode, the flow is directed across the membrane surface. (Mulder, 1996, p. 291)

The effectivity of the membrane processes can be evaluated by measuring the permeate flux, rejection of analytes and fouling tendency (Mänttäri et al., 2015). Membrane fouling is a complicated phenomenon that hinders the performance of membrane processes, especially micro- and ultra- and nanofiltration, where porous membranes are employed. It can be defined as deposition and accumulation of undesirable compounds such as solids, colloidal substances, macromolecules and/or salts, on membrane surfaces. Fouling can occur through adsorption, blocking of pores, precipitation and cake formation mechanisms and lead to lower permeate flux. (Mulder, 1996, p. 448) In addition, biofouling, caused by micro-organisms and the extracellular polymers that they produce, can take place (Nguyen, Roddick & Fan, 2021). Fouling can occur either reversibly, when the impurities can be detached from the membrane surface by backflushing or other physical measures, or irreversibly, when chemical cleaning needs to be applied (Choi, Zhang, Dionysiou et al., 2005).

Another phenomenon that reduces the efficiency of membrane processes is concentration polarisation. It occurs when the concentration of retained solutes increase at the boundary layer between the feed solution and membrane. (Mulder, 1996, p. 418) Similarly to fouling, it may lead to flux decline. Concentration polarisation can be minimised by changing the feed flow rate or the design of the membrane module. However, controlling membrane fouling is more challenging. (Giorno & D'Agostino, 2016)

7.2.2 Membrane processes in pulp and paper industry effluent treatment

In pulp and paper industry, membrane processes have been used for the treatment of a broad range of process waters and effluents, including bleaching effluents (Mänttäri et al., 2015). In figure 7, the typical molar mass ranges of different effluent components and the typical molecular mass or size of the components that can be removed by different membrane processes are shown.

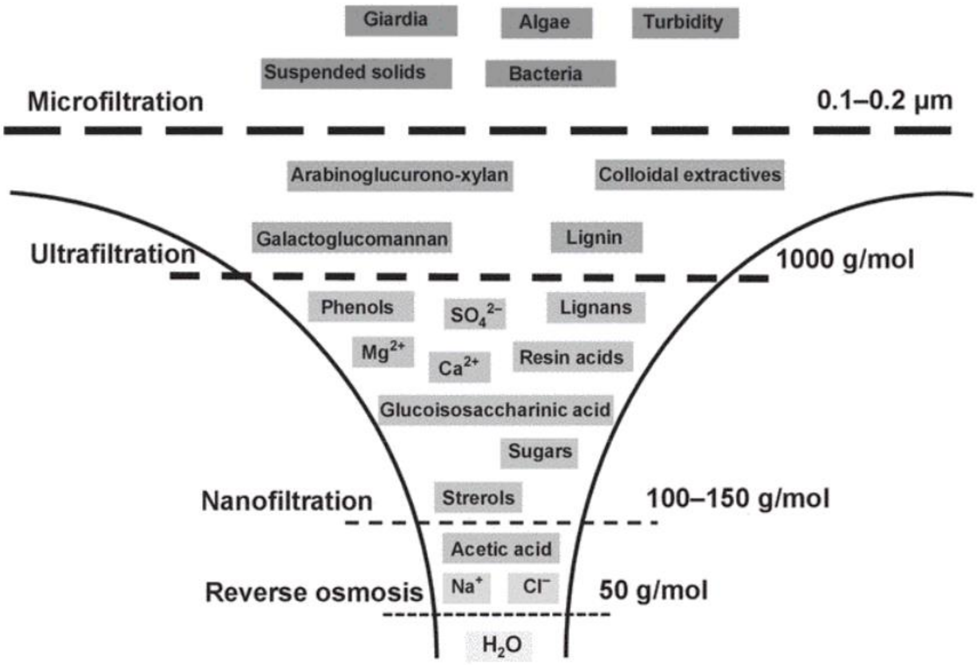


Figure 7 Typical size ranges of different components of pulp and paper industry effluents and the working ranges of different membrane systems (Mänttäri et al., 2015).

As shown in figure 7, nanofiltration can be used for the reducing the concentrations of multivalent ions such as barium, iron, manganese and sulphate. Monovalent ions can be removed by reverse osmosis, ion exchange or electrodialysis (ED). (Mänttäri et al., 2015) In ED, nonporous membranes with charged surface are used to separate ions from solutions (Kapoor et al., 2021, p. 284). However, the application of reverse osmosis in treating pulp and paper industry waters in plant-scale has been regarded economically non-viable, due to high investment costs and too low fluxes for the treatment of high volumes (Lastra et al., 2004).

Bleaching filtrates typically contain various different pollutants that may cause fouling of membranes. (Mänttäri et al., 2015) Therefore, the feed solution usually needs to be pre-treated prior to ultra- or nanofiltration. Additionally, especially spiral-wound modules are susceptible to blocking of the feed channel. Microfiltration is commonly used as pre-treatment for ultra- and nanofiltration. (Shukla, Kumar, Kim et al., 2013)

The membrane material needs to tolerate high temperatures, acids or alkalis, depending on the feed solution and have low fouling tendency. Surface charge, morphology and hydrophilicity of the membrane are the main characteristics that affect fouling. As pulp and paper mill effluents contain both negatively charged anions and positively charged cations, it has been discovered that fouling through electrostatic binding can be reduced by using membranes with low charge. (Puro, Kallioinen, Mänttäri et al., 2010) Divalent cations may also contribute to the development of a fouling layer by forming complexes with the colloidal compounds that are retained by the membrane (Chen, Mao, Wang et al., 2015). Typically, hydrophilic membranes have lower tendency to foul than hydrophobic membranes (Puro et al., 2010).

High shear stress is often generated on the membrane surfaces in order to minimise the flux reduction in the challenging conditions and to lower the requirements for pre-treatment. In tubular modules, shear forces can be generated, for instance, by increasing the flow rate of the feed or by vibrating the membrane. High-shear modules and spiral-wound modules have been used at industrial scale to treat the circulating water streams, such as whitewater and clear filtrates. However, as the shear forces wear the membranes, their lifetime may be shortened. (Mänttäri et al., 2015)

7.2.3 Ultrafiltration

Ultrafiltration has been proven effective in the treatment of alkaline kraft pulp bleaching effluents (Quezada, Silva, Rezende et al., 2014; Fälth et al., 2001). At plant-scale, UF has been used for the removal of colour and poorly biodegradable, high molecular mass compounds from the alkaline extraction stage filtrate. (Lastra et al., 2004) UF has also been applied for the purification of oxygen stage bleaching filtrate at Stora Enso's pulp and paper mill in Nymölla, Sweden. At the mill, polyethersulphone (PES) membranes with MWCO values of 4000 Da (softwood pulp line) and 6000 Da (hardwood pulp line) have been used. (Nordin & Jönssön, 2006)

In alkaline filtrates, a large fraction of inorganic substances such as metals is present as agglomerates bound to organic molecules or precipitates, rather than free ions. The size of these substances is larger, and therefore, a rather high separation efficiency for them can be obtained by UF. (Fälth et al., 2001) The purification of acidic bleaching filtrates is more challenging, mainly because the concentrations of chloride and soluble metal cations are higher in them. (Tirkkonen, Kallioinen & Mänttäri, 2014)

In a study carried out by Fälth et al. (2001), tubular PES membranes with cut-off values of 4000 Da and 6000 Da were used for the ultrafiltration of the alkaline effluents from ECF and TCF bleaching systems in a pilot-size cross-flow unit. A rather large fraction (70-80 %) of multivalent ions such as Ca and Mg ions was removed by the membranes, whereas monovalent cations including Na^+ and K^+ ions passed through them. (Fälth et al., 2001)

For metal removal from bleaching effluent, promising results have also been obtained in laboratory-scale studies by UF in conjunction with complexation (Tavares, Vieira, Petrus et al., 2001). Tavares et al. (2001) studied the efficiency of the addition of complexing agents, namely polyvinyl alcohol (PVA) and polyethyleneimine (PEI), followed by ultrafiltration, for the metal removal from TCF bleaching effluent. A dead-end type stirred module with a polyvinylidene fluoride membrane was used for the filtration. Ca, Fe, Mg and Mn could be effectively removed. PVA was found to be slightly more effective for the removal of metals than PEI. (Tavares et al., 2001)

Oliveira, Silva and Milanez (2007) examined the application of ultrafiltration combined with chemical precipitation for the metal removal from whitewater from a kraft pulp and paper mill. Precipitation of calcium as $CaCO_3$ was promoted by elevating the pH to 11 using NaOH solution (1 mol/L). Subsequently, the formed crystals were removed from the solution with a hollow-fibre UF module, which contained polymeric membranes with a mean pore size of 0.02 µm. The concentration of Ca^{2+} and Mg^{2+} ions could be reduced significantly. Laboratory-scale bleaching simulations were carried out to examine the suitability of the treated whitewater for reuse in the H_2O_2 bleaching stage, and it was concluded that it could be reused without formation of $CaCO_3$ precipitates. (Oliveira et al., 2007)

Quezada et al. (2014) compared the efficiencies of a NF membrane (350 Da), UF membranes (4000 Da and 1500 Da) and a combination of an UF and a NF membrane in the purification of Eop stage filtrate in a pilot plant. The highest removal efficiency of COD and colour as well as permeate flux was obtained by using ultrafiltration membranes (4000 Da and 1500 Da) in series. (Quezada et al., 2014)

In membrane separation processes, both a permeate stream and a retentate stream are always generated. To reduce the water consumption in a mill, both of these streams should be utilised in a way that the mill processes and product quality are not negatively affected. (Quezada et al., 2015) The feasibility of reusing the permeate and retentate streams produced in ultrafiltration of Eop stage effluent was studied by Quezada et al. (2015). Promising results were obtained on the permeate reuse in the Eop washing press. According to a simulation, hot water could be fully replaced by the permeate without critical accumulation of NPEs or $CaCO_3$ precipitate formation. The retentate could be reused in the black liquor recovery cycle with a minimal increase in the concentrations of harmful NPEs. (Quezada et al., 2015)

7.2.4 Nanofiltration

Nanofiltration has been applied for reducing the concentration of organic compounds (Tomani & Seisto, 1999) and AOX compounds (Afonso & Pinho, 1997) from alkaline bleaching effluents in laboratory-scale experiments. For instance, Geraldes & Pinho (1995) studied the application of NF, followed by ED for the removal of organics and salts from alkaline bleaching effluent, and a low NaCl concentration (350 ppm) was achieved.

Lastra et al. (2004) studied the economic feasibility of setting up a nanofiltration unit for the removal of metal complexes from chelation stage (Q) effluent in a TCF bleach plant to enable the reuse of the permeate in the Q stage. The efficiencies of polymeric (polyamide-polysulphone composite) and ceramic membranes were compared, and the polymeric membranes exhibited better rejection and less fouling in the pilot-scale experiments. By these membranes, Mn and Fe chelates could be fully removed (99-100 % rejection). According to the study, a membrane area of approximately 2400 m^2 would be needed to obtain a 90% recovery and a metal-free permeate stream. The investment could be economically feasible if the water consumption needed to be reduced due to more stringent environmental regulations. (Lastra et al., 2004)

The performance of NF in the purification of bleaching effluents depends strongly on the pH, as it affects the surface charge of the membrane (Afonso & Pinho, 1997). For instance, positively charged membranes reject multivalent cations more efficiently, whereas negatively charged membranes are preferable for the removal of multivalent anions (Mi, Liu, Jin et al., 2021). Promising rejections for different pollutants have been obtained also in acidic bleaching effluents by NF (Tirkkonen et al., 2014). In the study conducted by Tirkkonen et al. (2014), D0 stage filtrate was treated with polymeric NF membranes. High rejections were obtained for TOC (60-70 %) and lignin (80-90 %). The rejections for Ca, K and Na were higher than 80 %. In addition, the concentration of chloride ions was reduced to less than 50 %. Based on these findings, it was concluded that the water consumption could be reduced by nanofiltration of acidic bleaching effluents, but the utilization of these filtrates could be maximized by implementing additional treatment such as ED or evaporation. (Tirkkonen et al., 2014)

In a study conducted by Shukla et al. (2013), the acidic and alkaline bleaching effluents from a hardwood kraft pulp and paper mill with chlorine bleaching were treated by UF, NF and finally by RO in laboratory-scale. Spiral-wound modules with polysulphone and polyamide membranes were used to treat the effluents from chlorination and alkaline extraction stages. According to the results, the E stage effluent suited better for the filtration. Ultrafiltration was not efficient in the purification of the acidic effluent, probably due to that the acidic effluents are typically rich in low molecular mass compounds. However, by NF and RO, COD and AOX could be removed effectively also from the acidic effluent. (Shukla et al., 2013)

EXPERIMENTAL PART

8 OBJECTIVES OF THE EXPERIMENTAL PART

The aim of the experimental part was to investigate the performance of nano- and ultrafiltration in the removal of harmful metals (Ca, Ba, Fe, Mn and Cu) and anions (CO_3^{2-}, $C_2O_4^{2-}$, SO_4^{2-}, Cl^-) from acidic and alkaline kraft pulp bleaching filtrates. In addition, the suitability of ion chromatography for the determination of the harmful ions in bleaching filtrate samples was evaluated. The objective was to obtain high-quality permeate with low levels of the harmful ions, COD, lignin compounds and colour and to further estimate the suitability of the permeates to be reused in the bleaching processes.

The experimental part consisted of preliminary laboratory-scale ultrafiltration tests and nanofiltration tests. The ultrafiltration tests were conducted using a stirred ultrafiltration cell with polyethersulphone membranes. In the nanofiltration experiments, a pressurized filtration vessel with three polymeric nanofiltration membranes and a tight ultrafiltration membrane was employed. The retentions of the harmful anions and metals, COD and colour were determined for each nano- and ultrafiltration membrane that was tested. The performances of the different membranes were evaluated based on the measured retention and permeability values.

9 MATERIALS AND METHODS

9.1 Bleaching effluent samples

The samples were received from a Finnish softwood kraft pulp mill, where an ECF bleaching sequence is used. In the mill, oxygen delignification is employed prior to bleaching. The acidic and alkaline bleaching filtrate samples were collected after the washer following each stage. The acidic filtrate samples were collected from the first (D0) and the second (D1) ClO_2 bleaching stage, and the alkaline filtrate sample was collected from the alkaline extraction stage (Eop), which takes place between the D0 and D1 stages.

9.2 Ultra- and nanofiltration experiments

Preliminary ultrafiltration experiments were conducted to assess the performance of ultrafiltration in the removal of the harmful ions, COD, colour and lignin from the alkaline and acidic bleaching filtrate samples. Prior to both ultra- and nanofiltration experiments, the bleaching filtrate samples were filtered using a filter paper with a pore size of 1.6 µm and after that, through a 0.45 µm PES membrane.

9.2.1 Selection of membranes

Polymeric membranes with different cut-off values and the ability to tolerate a wide pH range, were selected for the experiments. In the preliminary ultrafiltration tests, a PES membrane with a MWCO value of 5000 Da was used. For the nanofiltration experiments, Nitto Denko NTR-7450, Microdyn Nadir NP030, Microdyn Nadir NP010 and Alfa Laval ETNA 01PP membranes were chosen. ETNA 01PP is considered as a tight ultrafiltration membrane. Characteristics of these membranes are given in table VI.

Table VI Characteristics of the membranes that were used in the ultra- and nanofiltration experiments.

Membrane	Manufacturer	MWCO [Da]	Material	pH range	Maximum temperature [°C]	Maximum pressure [bar]
NP030	Microdyn Nadir	500-600	PES	0-14	95	40
NTR-7450	Nitto Denko	600-800	Sulphonated PES	2-11	60	40
NP010	Microdyn Nadir	1000	PES	0-14	95	40
ETNA 01PP	Alfa Laval	1000	Composite fluoropolymer	1-11	60	1-10
Sartorius UF membrane	Sartorius	5000	PES	1-14	50	5 (filtration equipment)

9.2.2 Pure water permeability

Pure water permeability (PWP) was determined for each membrane prior to the experiments and after them to estimate the degree of fouling that occurs during the filtration. For the determination of PWP, pure water flux can be calculated by equation (3).

$$PWF = \frac{m}{\rho \cdot A_m \cdot \Delta t} \tag{3}$$

where		
	PWF	Pure water flux, L/(m^{2}h)
	m	Mass of permeate, kg
	ρ	Density of water, kg/L
	A_m	Surface area of membrane, m^2
	Δt	Collecting time of permeate, h

When pure water flux is plotted against the applied pressure, PWP is obtained from the slope of the straight line. After each nanofiltration test, the membranes were rinsed using deionised water at 30 bar for 15 minutes before the pure water flux measurements. In the preliminary ultrafiltration experiments, pure water flux measurements for the Sartorius ultrafiltration membranes were carried out by collecting permeate for three minutes at four different pressures, that were 1, 2, 3 and 4 bar.

In the nanofiltration experiments, pure water flux for each membrane was measured at pressures of 5, 10, 15 and 20 bar and the permeate was collected for 8 minutes. All the measurements were carried out at 50°C.

9.2.3 Preliminary ultrafiltration experiments

In the ultrafiltration experiments, the pre-filtered samples were filtered in a stirred ultrafiltration cell (Amicon, model 8400). A PES membrane (Sartorius) with a nominal MWCO of 5000 Da and a diameter of 76 mm was used and prepared according to the manufacturer's instructions, by filtering ultrapure water at approximately 4 bar pressure for at least five minutes prior to the experiments. The ultrafiltration equipment consisted of the N_2 source, a pressure regulating valve, a sample cell, a stir bar and a magnetic stirrer with heating, a cell base, the membrane and a container for collecting the permeate (figure 8). The upper operating pressure limit for the stirred ultrafiltration cell was 5 bar.

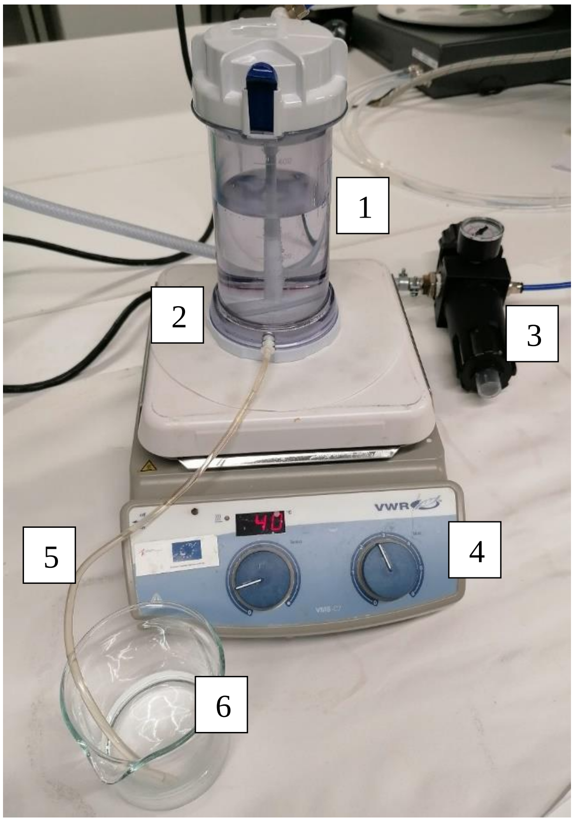


Figure 8 The used ultrafiltration equipment: 1. stirred ultrafiltration cell with a magnetic stir bar, 2. cell base and membrane, 3. pressure regulating valve, 4. magnetic stirrer with heating, 5. permeate outlet tube, 6. container for collecting the permeate.

Prior to the experiment, the samples were heated to 40°C in an oven to match the temperature of the bleaching filtrates in the mill. In fact, in the real process, their temperature can be notably higher, but the maximum operating temperature for the membranes was 50°C. During the experiments, the temperature of 40°C was maintained to the extent possible by using a magnetic stirrer with heating. In all the filtration experiments, the applied pressure was 4 bar, and the pressure was provided by a stream of N_2. The feed samples (volume 300 ml) were filtered until approximately 100-150 ml of permeate was collected. The experiments were repeated two to three times with similar results, and for each test, an unused membrane was employed. The rotation speed of the stirring bar was 250 rpm in all the experiments.

9.2.4 Nanofiltration experiments

The nanofiltration tests were conducted in cross-flow pressure filtration set-up with four parallel membrane modules. The filtration equipment consisted of a heated feed tank, a diaphragm pump, four parallel membrane modules, a pressure gauge and control valve and a variable area flowmeter (rotameter). A piping and instrumentation diagram (P&ID) of the system is presented in figure 9.

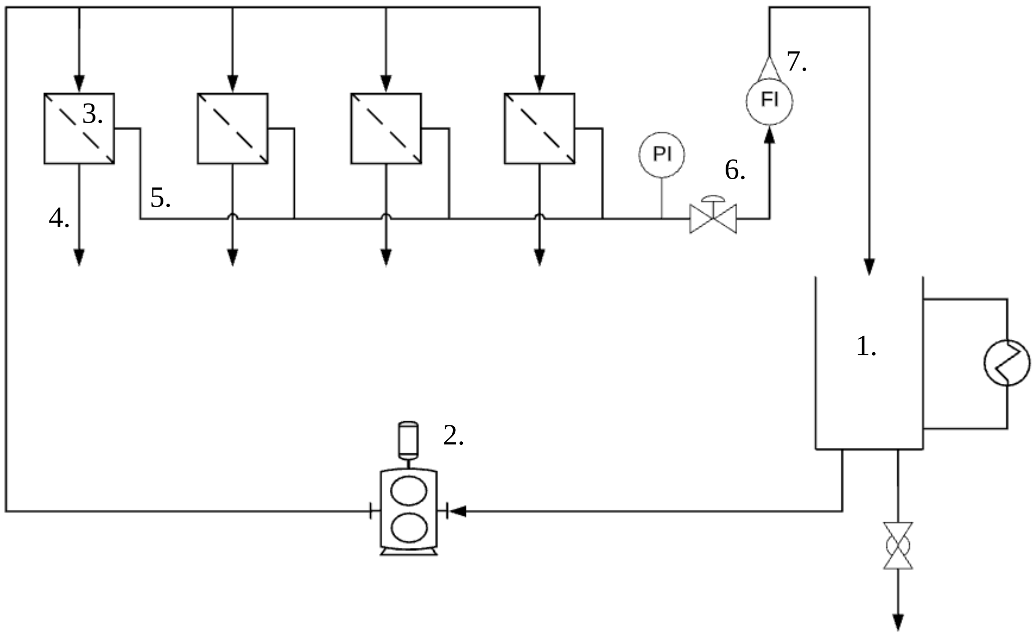


Figure 9 A P&ID of the used cross-flow pressure filtration set-up.

The temperature of the solution in the feed tank (1) was controlled with a water circulation heating system and monitored with a thermometer. The volume of the feed tank was approximately 4.5 liters. The feed solution was pumped with a Hydra-Cell diaphragm pump (model G03) (2), driven by an electric motor, which was controlled with a variable frequency drive, to the membrane modules (3). Each of the modules contained a membrane sheet with a filtration area of 0.0008 m^2 (40 mm x 20 mm). Approximately 100-150 ml of permeate (4) from each module was collected. After that, the permeate was re-circulated back to the feed tank in order to limit concentration of the feed solution. The retentate flow (5) was returned to the feed tank. The pressure inside the system was monitored with a pressure gauge and controlled with a valve (6). The retentate flow was directed through a rotameter (7) to measure its flowrate. The permeates and the pure water were weighed on a scale and a stopwatch was used to measure the collecting time.

In all the experiments, the feed temperature was set at 50 °C. Prior to the experiments, the membranes were immersed in dilute NaOH solution (pH < 11) for approximately 1 hour and pressurised at 30 bar for 15 minutes. The PWP of the membranes was measured before and after each test. The maximum feed flow rate for the system was 21,4 l/min, and in all experiments, a constant flow rate of 35% of the maximum was used. The permeate flux was determined at several pressures between 7 and 28 bar, and the experiments were carried out at the pressure after which the permeate flux did not increase with a further increase in pressure. The experiments where the D0 and D1 stage effluents were filtered, were carried out at 24 bar. The Eop stage effluent was filtered at 18 bar. All the experiments were repeated two to three times and rather similar results were obtained, and for each test, unused membranes were employed.

Permeate flux was determined by collecting permeate for 8 minutes at the same pressure as the nanofiltration experiments and weighing the collected solution. After weighing, the pressure was changed, and the flux was let to stabilise for 10 minutes before the following measurement. Permeate flux was measured in kg/m^2h by equation (4).

$$J = \frac{Q_P}{A_m} \tag{4}$$

where	J	Permeate flux, kg/m^{2}h
	Q_P	Permeate flow, kg/h
	Am	Surface area of a membrane, m^2

Reynolds number indicates whether the flow is laminar or turbulent. It is defined as follows (equation (5)).

$$Re = \frac{\rho \cdot v \cdot d_h}{\eta} \tag{5}$$

where	Re	Reynolds number, -
	v	Flow velocity, m/s
	d_h	Hydraulic diameter of the flow channel, m
	η	Dynamic viscosity, Pa s

9.2.5 Rejections

Rejection can be calculated to measure the extent to which a component is retained by a membrane. The rejections of different impurities and properties such as COD and colour were determined for the chosen membranes according to equation (6).

$$R = \left(1 - \frac{c_{i,p}}{c_{i,r}}\right) \cdot 100\% \tag{6}$$

where	R	Rejection, %
	$c_{i,p}$	Concentration of component i in permeate, g/L or mol/L
	$c_{i,r}$	Concentration of component i in retentate, g/L or mol/L

9.3 Analyses

The concentrations of the harmful anions, metals, lignin and colour and the COD values were determined in the feed solutions and in the permeates that were obtained in the ultra- and nanofiltration experiments. In addition, the pH values and the electrical conductivities of the samples were measured. The suitability of ion chromatography for measuring the concentrations of the anions and certain cations in the samples was examined.

9.3.1 Ion chromatographic analysis

The ion chromatographic analyses were performed using a Dionex ICS-6000 analytical IC system (Thermo Fisher Scientific Inc.) with two separate channels for the determination of anions and cations. The system was equipped with dual-piston pumps, an automatic sample injection system, a column oven and eluent generators. A suppressed conductivity detector was employed. The chromatographic separation of anions was achieved using a Dionex IonPac AS20 column with two IonPac AG20 guard columns connected in series. The stationary phase was composed of an anion exchange resin with quaternary ammonium groups attached to it. An aqueous solution of potassium hydroxide (KOH) was used as eluent.

The cation channel was equipped with an IonPac CS16 column with guard columns IonPac NG1 and IonPac CG16. The stationary phase was a weak cation exchange resin functionalised with carboxylic acid groups. As eluent, methanesulfonic acid (MSA) water solution was used.

For the analysis of both cations and anions, gradient elution where the eluent concentration was changed during the elution, was used. Five standard solutions with different concentrations of the wanted ions were prepared, and the calibration curves (peak area versus concentration) for each ion were automatically formed by the chromatograph to specify the peaks of the ions. The concentrations in the calibration solutions were dictated by the expected concentration range of the ions in the samples. Commercial calibration solutions were used for the standard solutions. Blank samples of ultrapure water were used in each analytical run.

Anions

The standard solutions, that were prepared for the anion analysis, contained Cl^- and SO_4^{2-} ions over the concentration range of 2-40 mg/L, and $C_2O_4^{2-}$ and CO_3^{2-} ions over the range of 0.5-10 mg/L and 10-50 mg/L, respectively. The samples were diluted with ultrapure water to two different concentrations (1:20 and 1:50) and, except the nanofiltered samples, filtered with a 0.2 µm syringe filter. They were analysed by a gradient elution sequence described in table VII. A flow rate of 0.3 mL/min was used, and the temperature of the column oven was set at 35°C.

Table VII The used gradient program for the determination of Cl^-, SO_4^{2-}, CO_3^{2-} and $C_2O_4^{2-}$ ions.

Step	Time [min]	Concentration of KOH [mM]
1	0	10.00
2	5	10.00
3	10	20.00
4	25	30.00
5	30	10.00

Cations

For the cation analysis, standard solutions over the concentration range of 0.2-5 mg/L for Ca^{2+}, K^+, Mg^{2+} and Ba^{2+} ions, and 2-25 mg/L for Na^+ ions were prepared. The samples were diluted to 1:10 of the original volume with ultrapure water and, except the nanofiltered samples, filtered with a 0.2 µm syringe filter. The gradient program that was used for the determination of the cations is shown in table VIII. A flow rate of 0.2 mL/min was used, and the temperature of the column oven was set at 40°C.

Table VIII The used gradient program for the determination of Ca^{2+}, Ba^{2+}, Na^+, K^+ and Mg^{2+} ions.

Step	Time [min]	Concentration of MSA [mM]
1	0	20.00
2	5	30.00
3	10	30.00
4	18	55.00
5	32	55.00
6	32	20.00
7	38	20.00

9.3.2 Metal and carbonate analyses

The concentrations of transition metals (Fe, Mn and Cu), calcium, barium, sodium and potassium were measured by ICP-OES. The concentrations obtained for Ca, Ba, Na and K analyses were compared with the results of the ion chromatographic analysis.

The concentrations of carbonate ions were estimated from total inorganic carbon (TIC) concentrations. TIC was determined with a TOC analyser, and the carbonate ion concentration was calculated from the obtained value by dividing it by five (SCAN-N 32:98). The analyses of metals and carbonate ions were carried out by an external laboratory.

9.3.3 Lignin

Lignin concentration in aqueous samples can be semiquantitatively determined by UV/Vis spectroscopy (Lu et al., 2017). Mettler Toledo UV5Bio spectrophotometer was used for the measurements. Prior to the analysis, the feed solution samples were filtered through PTFE (polytetrafluoroethylene) filters with a pore size of 0.45 μm to ensure that the lignin in the samples was in a soluble form. The lignin concentration was calculated from the absorbance values by using Lambert-Beer's law (equation 7).

$$c = \frac{A}{a \cdot l} \tag{7}$$

where c concentration, g/L

A absorbance, -

a absorptivity of a compound, L/(gcm)

l length of the cuvette, cm

For the alkaline samples, the absorbances were measured at a wavelength of 280 nm. According to Hansen, Pedersen-Bjergaard & Rasmussen (2012), the most accurate results are obtained when the absorbance values are between 0.2 and 0.8, which is the linear range of calibration curves of absorbance at 280 nm versus the concentration of lignin. To obtain absorbance values within this range for the samples, they were diluted using 0.1 M NaOH solution. The absorbances of the acidic samples were measured at 205 nm and 203 nm. Ultrapure water was used for their dilution to obtain absorbance values in the rage of 0.25-3.

The absorptivity coefficients were determined experimentally by preparing calibration curves of absorbance versus the concentration of a commercial alkali lignin (Sigma Aldrich, low sulphonate content) of the calibration solutions. For the determination of lignin content of the alkaline samples, solutions in the concentration range of 10-60 mg/L were prepared by dissolving the commercial lignin in 1 M NaOH solution, and the absorbances of these solutions were measured at 280 nm. For the lignin analyses of the acidic samples, calibration solutions in the concentration range of 3-40 mg/L were prepared by dissolving lignin in ultrapure water. The absorbances of these solutions were measured at wavelengths of 203 and 205 nm. The slopes of the calibration curves were used as the absorptivity coefficients.

9.3.4 COD and colour

COD was determined in a Merck Spectroquant NOVA 60 photometer. The samples were diluted with ultrapure water to obtain COD values below 1500 mg/L and a certain volume of each sample was pipetted to a cell containing chromosulphuric acid. The cells containing the samples and the test reagents were heated at 148°C for 120 minutes in a Spectroquant TR 420 thermoreactor, swirled and cooled to room temperature prior to the analysis. The measurement is based on oxidation of organic compounds using chromosulphuric acid and determination of chromate.

Also colour measurement was carried out by the Spectroquant NOVA 60 photometer. The samples were diluted with ultrapure water to obtain values below 500 Pt/Co. The glass cuvette containing the sample was placed into a cell compartment of the photometer. Color was measured at 340 nm by platinum-cobalt standard method and expressed as Pt/Co.

9.3.5 Conductivity and pH

Electrical conductivity was determined using a WTW inoLab Cond7110 conductivity meter to receive information of the overall ionic strength of the samples. The conductivity measurements were carried out at approximately 23°C. A SevenCompact pH meter (Mettler Toledo) was used to measure the pH of the samples.

10 RESULTS AND DISCUSSION

10.1 Feed solution quality

The feed solutions for the nano- and ultrafiltration experiments were analysed after the pre-filtration. The results of the analyses are presented in table IX. The concentrations of metals were determined with ICP-OES by an external laboratory.

Table IX Characteristics of the feed solutions.

	Eop stage filtrate	**D0 stage filtrate**	**D1 stage filtrate**
pH	11.3	2.4	3.4
Conductivity [mS/cm]	4.02	5.83	2.68
COD [mg/L]	2070	2363	917
Lignin [mg/L]	787	589	195
Colour [Pt/Co]	1324	852	120
Ca [mg/L]	17.8	120	20.9
Ba [mg/L]	0.18	0.44	0.16
Fe [mg/L]	<0.05	0.46	0.21
Mn [mg/L]	0.03	2.28	0.4
Cu [mg/L]	<0.05	<0.05	<0.05
Na [mg/L]	943	683	522
K [mg/L]	7.95	19.3	5.03
CO_3^{2-} [mg/L]	435	11	10
$C_2O_4^{2-}$ [mg/L]	87	147	21
SO_4^{2-} [mg/L]	177	399	441
Cl^- [mg/L]	237	938	372

The results show that the COD and colour values, as well as the lignin concentration, were notably higher for the Eop and D0 stage effluents than for the D1 stage effluent. Thus, it can be concluded that the organic loads of the Eop and D0 effluents were higher. For the D0 effluent, the concentrations of most metals, including Ca, Ba, Fe, Mn and K, were highest, whereas the concentration of Na was highest for the Eop effluent. The concentrations of copper were lower than the detection limit for the ICP-OES analysis. The detection limits and the mean values for the analysis are shown in appendix III. The concentration of chloride ions was highest in the D0 effluent, and the Eop effluent was rich in carbonate ions. The acidic filtrates contained most sulphate ions, as sulphuric acid is used for acidification in the mill. As mentioned before, the amount of oxalic acid formed in bleaching stages has been found to be influenced by the available lignin content of the pulp, which could partly explain the larger concentrations of oxalate ions in the Eop and D0 effluents, compared to those in the D1 effluent. These concentrations may fluctuate to some extent within the mill.

10.2 Results of the ultrafiltration experiments

The rejections of COD, lignin, colour, calcium, barium, sodium, potassium, carbonate, sulphate, oxalate and chloride ions were determined for the Sartorius PES membrane in the ultrafiltration experiments of Eop, D0 and D1 effluents. In the case of the acidic samples, also the rejections of iron and manganese were determined. For the pre-filtrered Eop filtrate, the concentrations of these metal ions were lower than the detection limit. In figure 10, the rejections of these compounds and parameters are expressed as percentages for the filtration of Eop effluent.

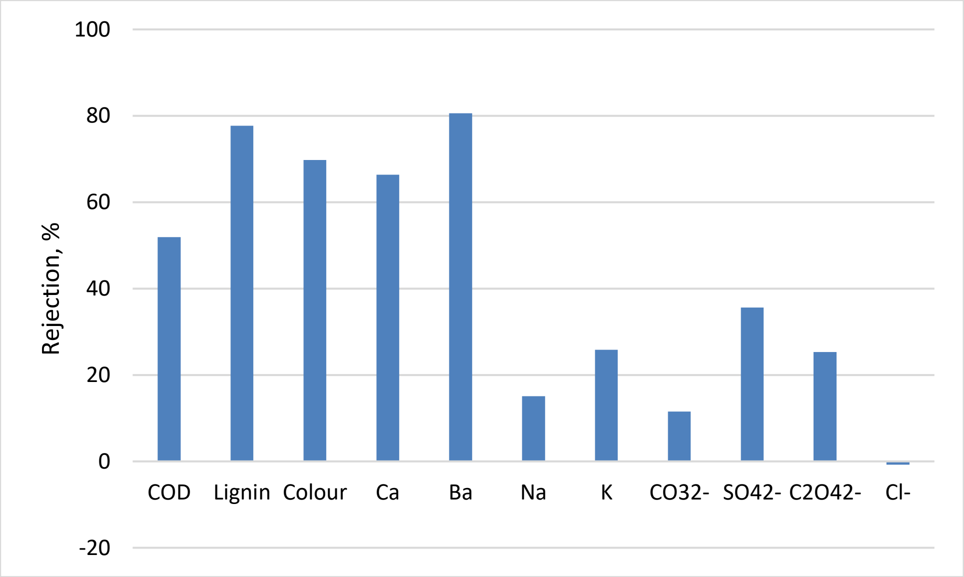


Figure 10 Rejections of COD, lignin, colour, calcium, barium, sodium, potassium, carbonate, sulphate, oxalate and chloride ions obtained for the Eop effluent permeate using Sartorius UF membrane (MWCO 5000 Da) at 40°C and at a pressure of 4 bar.

To obtain versatile possibilities for the reuse of the permeate, good rejections of the impurities are beneficial. Rejections higher than 60 % were obtained for lignin, colour, calcium and barium. For sodium and potassium, which occur as monovalent cations in soluble form, the rejections were considerably lower than those for the divalent calcium and barium. Also Fälth et al. (2000) and Quezada et al. (2015) reported that the Na^+ and K^+ ions easily passed the ultrafiltration membranes, whereas a major fraction of the multivalent ions could be removed. The rejections for the divalent anions, namely carbonate, sulphate and oxalate, were rather low, and chloride ions were not retained by the membrane. In figure 11, the rejections of the previously mentioned impurities in the filtration of the D0 effluent are shown.

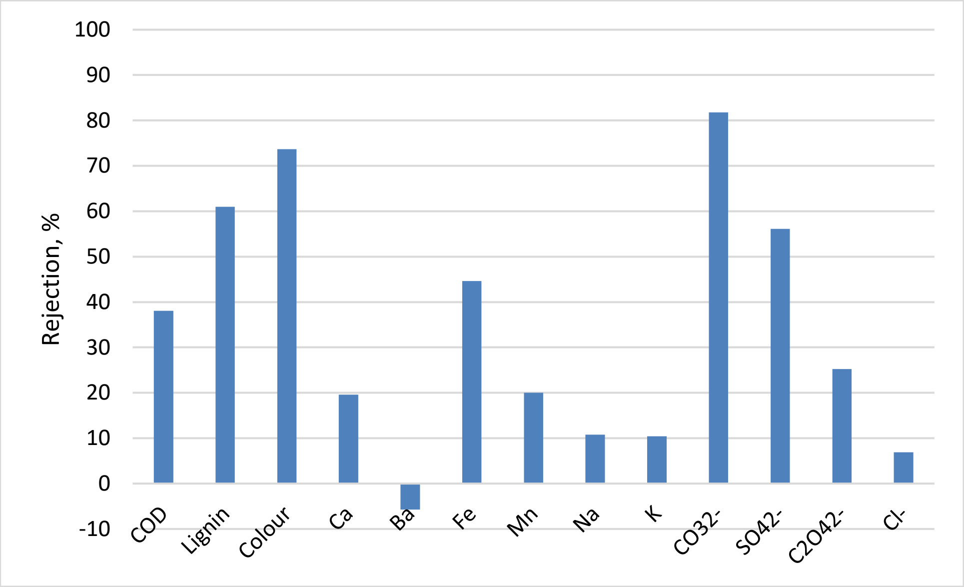


Figure 11 Rejections of COD, lignin, colour, calcium, barium, iron, manganese, sodium, potassium, carbonate, sulphate, oxalate and chloride ions obtained for D0 effluent permeates using Sartorius UF membrane (MWCO 5000 Da) at 40°C and at a pressure of 4 bar.

Lower rejections for metals were obtained when the acidic D0 effluent was filtered than in the filtration of the Eop filtrate. However, the rejections of the negatively charged ions were higher. Similarly as in the filtration of the Eop effluent, lower rejections were obtained for sodium and potassium than for the other metals. The rejections of lignin and COD were somewhat lower in the case of the D0 effluent, whereas the rejections of colour were similar in the two cases. The rejections of the different impurities in the filtration of the D1 effluent are shown in figure 12.

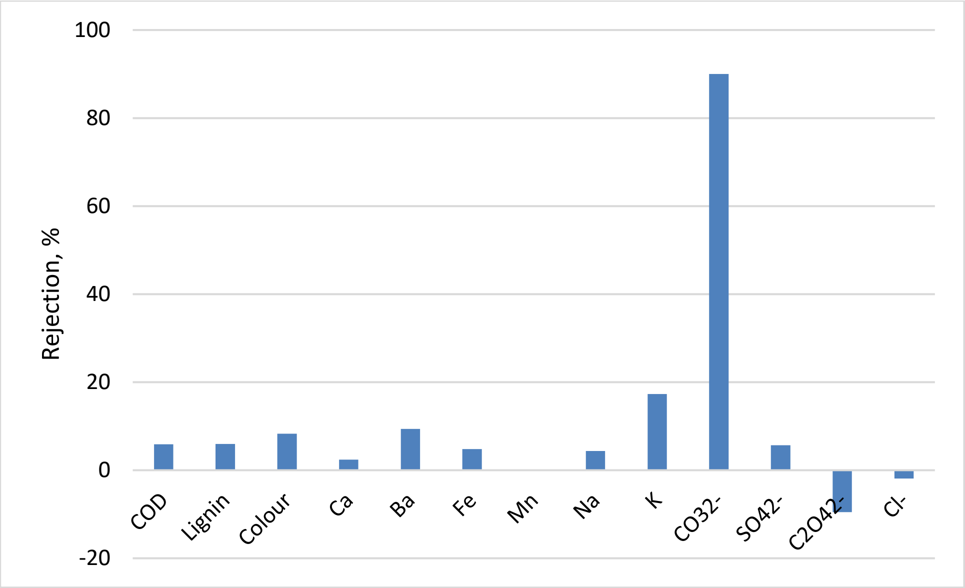


Figure 12 Rejections of COD, lignin, colour, calcium, barium, iron, manganese, sodium, potassium, carbonate, sulphate, oxalate and chloride ions obtained for D1 effluent permeates using Sartorius UF membrane (MWCO 5000 Da) at 40°C and at a pressure of 4 bar.

The rejections of COD, lignin and colour were significantly lower in the filtration of the D1 effluent compared to the two previous cases. Also the rejections of the metals and most anions were very low. The initial organic load of the D1 effluent was rather low and in acidic conditions, metals tend to occur in a soluble form. Thus, less metals were probably bound to larger organic compounds and therefore separated in ultrafiltration.

Pure water permeabilities were calculated for the Sartorius ultrafiltration membrane before and after the filtration experiments of the Eop, D0 and D1 effluent samples (figure 13). Lower values after filtration indicate fouling of the membrane.

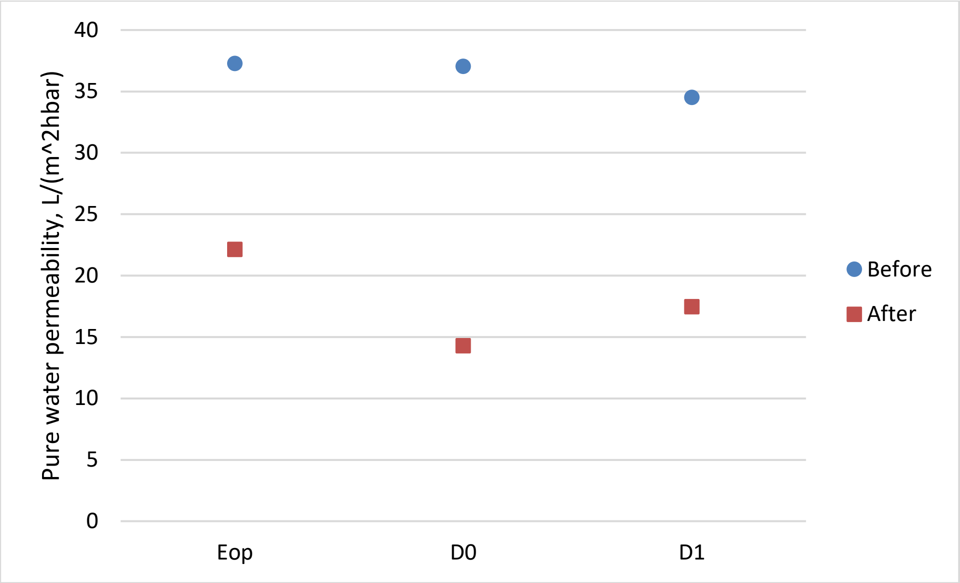


Figure 13 Pure water permeability values for the Sartorius UF membrane (MWCO 5000 Da) before and after the filtration experiments of the Eop, D0 and D1 effluents measured at 40°C.

In the experiments, the permeate collecting time was approximately 80 minutes. The pure water permeability was reduced significantly in all the tests. The reduction was most prominent in the case of the D0 stage effluent. It could have led to the reduction that the experiments lasted for a rather long time without washing the membrane, and that they were carried out in dead-end mode, even though stirring near the membrane surface was applied to reduce fouling.

10.3 Results of the nanofiltration experiments

To investigate the performance of nanofiltration for the removal of COD, lignin, colour, calcium, barium, sodium, potassium, carbonate, sulphate, oxalate and chloride ions, the rejections of these impurities were determined for each nanofiltration membrane used in the filtration experiments of Eop, D0 and D1 stage effluents. In the case of the acidic effluents, also the rejections of iron and manganese were determined. Pure water permeabilities were measured for each membrane before and after the filtrations to obtain information on membrane fouling during the experiments. Also the permeate flux was determined for each membrane. The Reynold’s number was calculated according to equation (5) and a value of 5368 was obtained. Thus, the flow in the feed channel was turbulent in all the experiments.

10.3.1 Nanofiltration of Eop stage effluent

The alkaline Eop stage effluent was filtered through the four membranes. The permeate flux was measured for the membranes in the beginning of the experiment and after collecting a sufficient amount of permeate for the analyses. The obtained values are shown in table X.

Table X Permeate fluxes measured in the beginning of the filtration experiment of the Eop effluent and after it at 50°C and at 18 bar.

Membrane	**Flux in the beginning [kg/m^{2}h]**	**Flux after [kg/m^{2}h]**
NP030	62.5	55.3
NTR-7450	194.1	178.1
NP010	467.3	361.2
ETNA 01PP	278.9	231.6

The permeate flux of the NP030 membrane was significantly lower than those of the other membranes. In all the cases, the permeate flux was lower after the experiment, which indicates that fouling and/or concentration polarisation occurred during the filtration. The impact of concentration polarisation, however, should be rather small, as the flow conditions were in the turbulent region at the membrane surfaces. The permeate flux reduced most significantly in the case of the NP010 membrane. Nevertheless, the filtration experiments were carried out continuously without backwashing or other methods, except for the pre-filtration, to limit fouling. To obtain information on irreversible fouling, the PWP values of the membranes measured before and after the nanofiltration experiments are shown in figure 14.

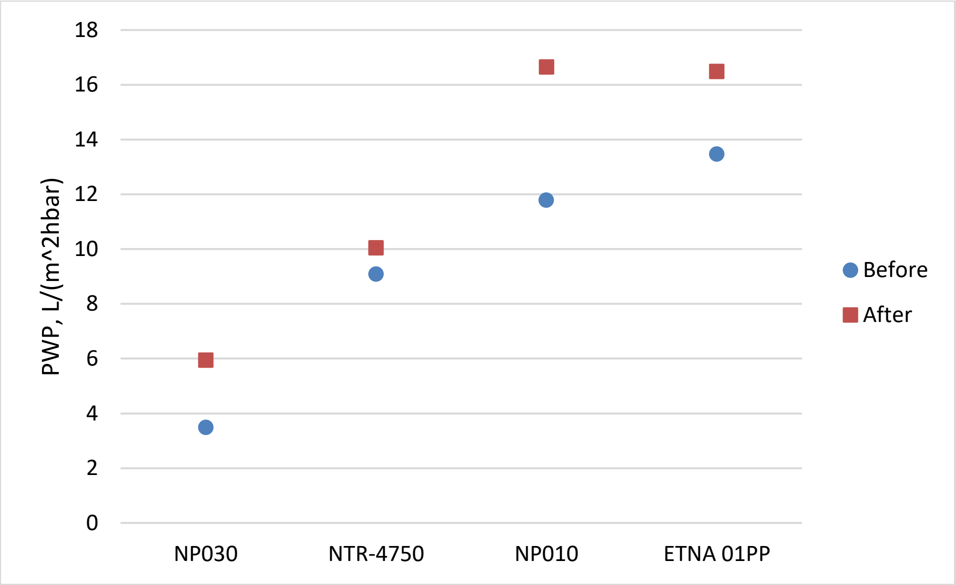


Figure 14 The PWP values of the membranes measured before and after the NF experiments of the Eop stage effluent at 50°C and at pressures of 5, 10, 15 and 20 bar.

For each membrane, a higher pure water permeability value was obtained after the experiments. For the NP010 membrane, the difference between the measured PWP values is comparatively large. Thus, comparison of the values obtained before and after the experiment poorly provides information on irreversible fouling in this case. The higher values obtained after the experiment may be due to the alkalinity of the sample, which might enhance the surface charge of the membranes during the filtration.

Figure 15 illustrates the rejections of COD, lignin, colour, calcium, barium, sodium, potassium, carbonate, sulphate, oxalate and chloride ions for each membrane.

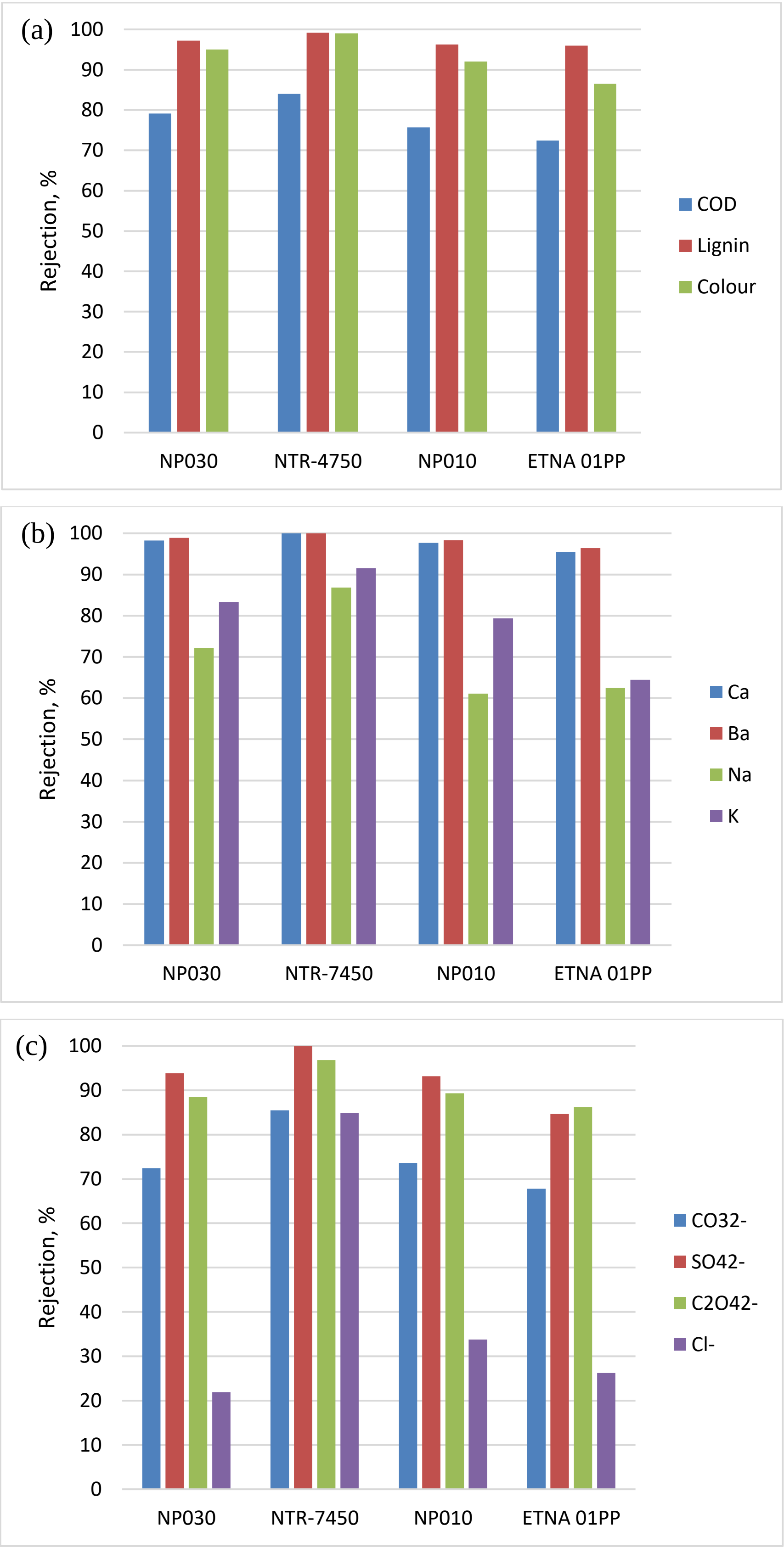


Figure 15 The obtained rejections toward a) COD, lignin and colour b) calcium, barium, sodium and potassium, c) carbonate, sulphate, oxalate and chloride ions when Eop stage effluent is filtrated at 50°C and a pressure of 18 bar.

The NTR-7450 membrane showed the highest rejections toward all the impurities and qualities of interest. A nearly complete removal was obtained for lignin, colour, calcium, barium and sulphate. For all the impurities, rejections higher than 80 % were obtained. The separation efficiency is affected by the membrane material. The surface of a sulphonated PES membrane carries more negative charges than that of a PES membrane (Zhao, Xue, Ran et al., 2013). Also for the NP030 membrane, rather high rejections for the impurities, except for chloride ions, were achieved. In addition, the rejections of sodium and carbonate for NP030 were only slightly higher than 70%. The rejections of most pollutants were somewhat lower for ETNA 01PP than for NP010. However, the applied pressure was higher than the typical operating pressure for ETNA 01PP, which may have affected its performance. The monovalent chloride ions were poorly separated in all the experiments. Again, the rejections for sodium and potassium were lower than those for calcium and barium. The qualities of the permeates are shown in appendix I, and the results of the external metal and carbonate analyses are shown in appendix III.

The pH of the Eop stage effluent was slightly higher than the maximum pH for the ETNA 01PP and NTR 4750 membranes. The contact time in these experiments was rather short, but the elevated temperature and the rather high pressures, together with the high pH could affect the performances of these membranes especially in the long term.

Shukla et al. (2013) reported notably lower rejections for COD in nanofiltration of Eop stage effluent, ranging approximately from 25 to 54 %. However, the reductions of colour were rather similar (75-96.5 %) to those obtained by the NP030, NTR 7450, NP010 and ETNA 01PP membranes.

10.3.2 Nanofiltration of D0 stage effluent

Compared to the filtration of the Eop effluent, that of the D0 effluent was more time-consuming. The permeate flux was measured for the different membranes in the beginning of the experiment and after a sufficient amount of permeate was collected (table XI).

Table XI Permeate flux measured in the beginning of the filtration experiment of the D0 stage effluent and after it at 50°C and at 24 bar.

Membrane	Flux in the beginning [kg/m^{2}h]	Flux after [kg/m^{2}h]
NP030	20.2	8.9
NTR-7450	152.4	81.1
NP010	45.6	28.8
ETNA 01PP	181.7	151.9

The permeate fluxes for the NP030 and NP010 membranes were notably lower than those for the NTR-7450 membrane. As separation efficiency, the flux is also affected by the membrane material. PES is a hydrophobic material, but by sulphonation, its hydrophilicity can be increased (Zhao et al., 2013). In these conditions, the measured fluxes of all the membranes and especially those of the NP030 and NP010 membranes were significantly lower than in the filtration experiments of the Eop effluent. In addition, a significant reduction in permeate flux during the filtration of the D0 effluent was observed for all the membranes. The D0 effluent has a high ionic strength, which could have increased the osmotic pressure in the feed side, leading to lower energy-efficiency and the requirement for higher pressures than the nanofiltration of the Eop effluent. The PWP values for each membrane before and after the filtration experiment are shown in figure 16.

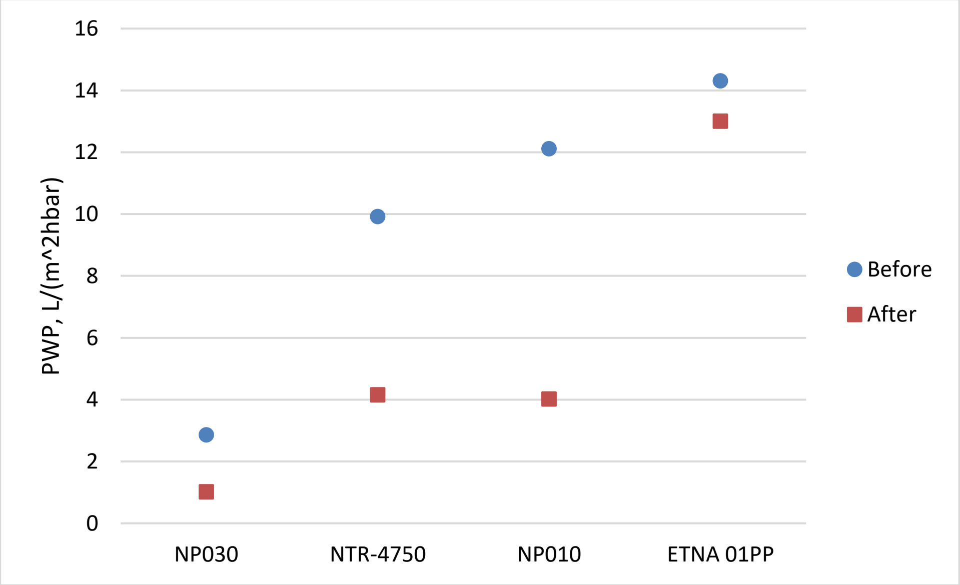


Figure 16 The PWP values for the membranes measured before and after the NF experiments of the D0 stage effluent at 50°C and at pressures of 5, 10, 15 and 20 bar.

For the NP030, NTR-7450 and NP010 membranes, PWP was significantly reduced after the experiment, which indicates that irreversible fouling occurred during filtration. For the ETNA 01PP membrane, the reduction was less significant. Due to the low permeate fluxes and the significant reduction in pure water permeability, the NP030 and NP010 PES membranes do not suit well for the nanofiltration of the D0 stage bleaching effluent. Figure 17 illustrates the rejections of the different impurities for the membranes obtained in the nanofiltration experiments of D0 stage effluent.

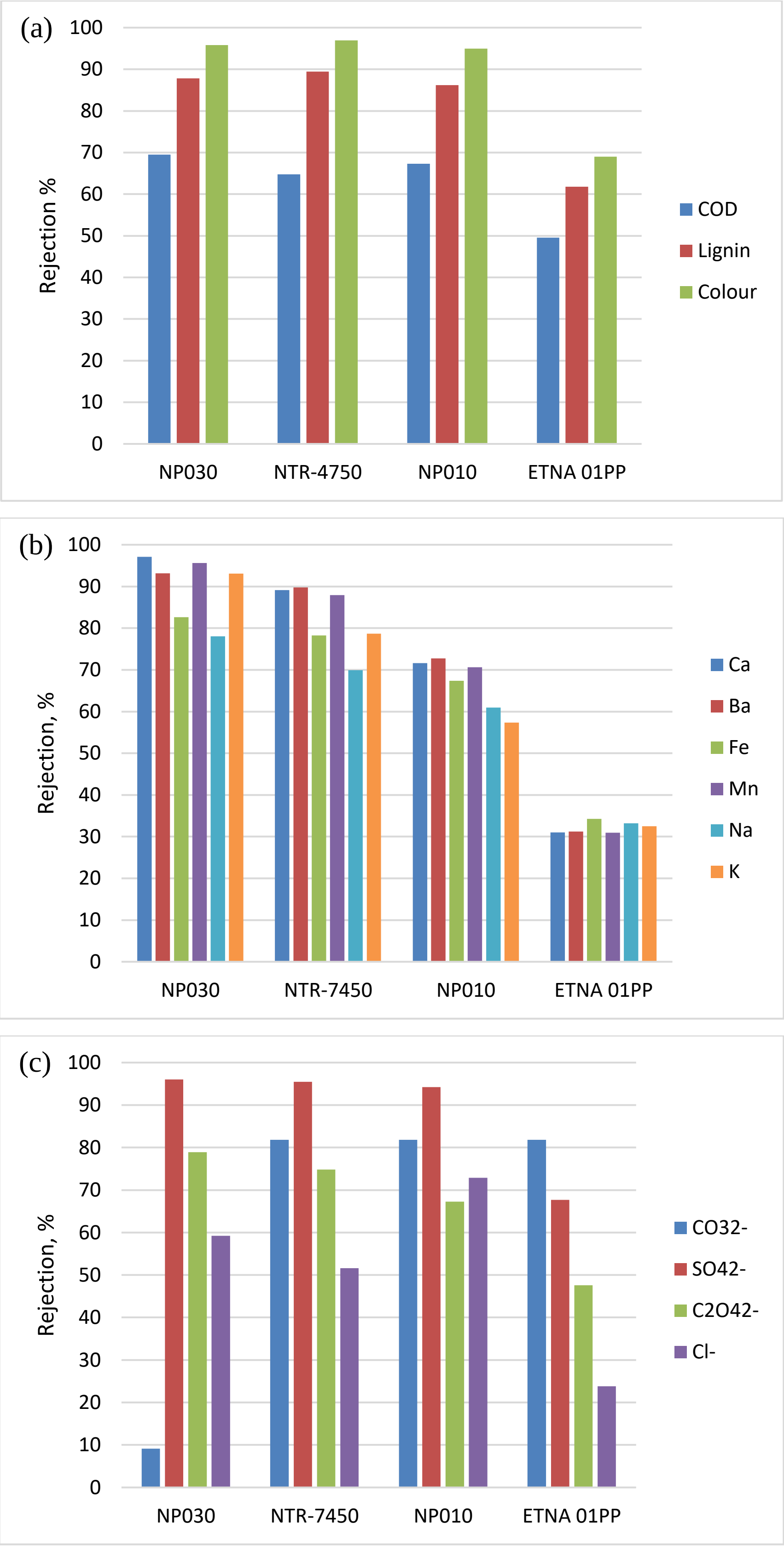


Figure 17 Rejections toward a) COD, lignin and colour b) calcium, barium, iron, manganese, sodium and potassium, c) carbonate, sulphate, oxalate and chloride ions when D0 effluent is filtrated at 50°C and a pressure of 24 bar.

Highest rejections for metals were obtained using the NP030 membrane with the smallest MWCO. For all the metals, rejections above 75% were reached. NTR-7450 showed the highest rejections for lignin, colour and sulphate ions, although in the case of sulphate, the differences between the rejections for NTR-7450, NP030 and NP010 were very small. ETNA 01PP showed lowest rejections for all the impurities, except for carbonate. By this membrane, the obtained rejections for the metals were poor, only around 30 %. The carbonate analysis in the case of the NP030 permeate could be erroneous, as the rejections of sulphate and oxalate for the NP030 were in the same order of magnitude as for the NTR-7450 and NP010 membranes. The obtained rejections of COD were lower than in the case of the Eop effluent. This could be due to that acidic bleaching effluents typically contain dissolved organic compounds over a wide molar mass range, and the small compounds may pass the membranes (Tirkkonen et al., 2014). Even for NP030, which showed the highest rejection toward COD, only a 69% rejection was reached. However, by the NF membranes, considerably higher COD rejections were obtained than by ultrafiltration membranes (Sartorius and ETNA 01PP) in acidic conditions. A similar conclusion was reported by Shukla et al. (2013).

The applied pressure was even higher than that in the nanofiltration experiments of Eop effluent, and thus notably higher than the typical operating pressure for ETNA 01PP. Based on the permeate flux and the rejections, the NTR-7450 membrane seemed most promising for the nanofiltration of the D0 stage effluent. The qualities of the permeates are shown in appendix I.

Tirkkonen et al. (2014) reported rejections higher than 80% for calcium, potassium and sodium. By the NP030 membrane, nearly as high rejections (over 75%) for these metals were obtained. Regarding the NP030, NTR 7450 and NP010 membranes, the rejections of lignin and chloride ions were rather similar to those obtained by Tirkkonen et al. (2014). 80-90% of lignin and over 50 % of chloride ions were rejected by these membranes.

According to Afonso & Pinho (1997), the performance of NF depends on the pH, as it has an impact on the surface charge of the membranes. The rejections of charged impurities and the fluxes can be largely affected by the membrane charge. In very acidic conditions, the negative surface charge of the membranes may be reduced, which also reduces the hydrophilicity of the membranes. Thus, the separation of negatively charged ions and the permeate fluxes can be lower at acidic pH.

10.3.3 Nanofiltration of D1 stage effluent

Also the filtration of the acidic D1 stage effluent was more time-consuming than that of the Eop stage effluent. The permeate flux was measured for each membrane in the beginning of the experiment and after it (table XII).

Table XII Permeate flux measured in the beginning of the filtration experiment of the D1 stage effluent and after it at 50°C and at 24 bar.

Membrane	Flux in the beginning [kg/m^{2}h]	Flux after [kg/m^{2}h]
NP030	20.6	15
NTR-7450	130.3	103.4
NP010	106.6	73.5
ETNA 01PP	254.1	202.5

Especially the permeate flux of the NP030 membrane was very low. In the beginning of the experiment, it was similar to the flux in the filtration experiment of D0 effluent, but it was reduced less during the filtration of D1 effluent. More fouling and/or concentration polarisation occurred during the filtration of the acidic effluents than during that of the Eop stage effluent. The PWP values measured before and after the filtration experiments are shown in figure 18.

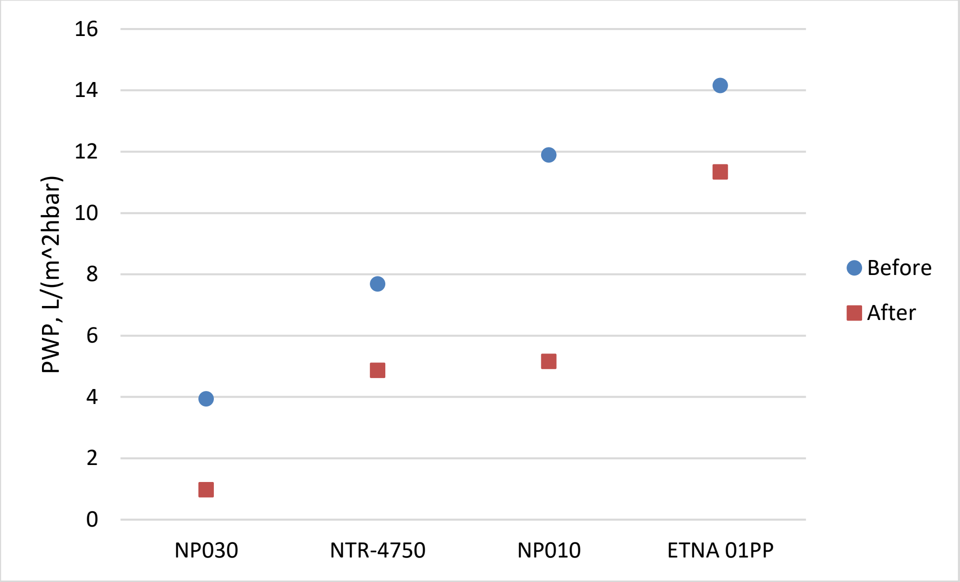


Figure 18 The PWP values for each membrane measured before and after the NF experiments of the D1 stage effluent at 50°C and at pressures of 5, 10, 15 and 20 bar.

The ETNA-01PP membrane showed highest values for pure water permeability and permeate flux. The PWP could not be restored by rinsing at high pressure, which indicates that irreversible fouling occurred during filtration in the cases of each membrane. For the NP010 membrane, the reduction in PWP was most significant. Also the pure water permeability measured after the filtration for the NP030 membrane was very low (approximately 1.0 L/(m^2hbar)). Based on the low permeate fluxes and the significant reduction in pure water permeability, the NP030 and NP010 PES membranes did not suit well for the nanofiltration of the acidic bleaching effluents.

The NP030 membrane was excluded from the comparison of the rejections, due to its very low permeate flux. For the other membranes, the rejections of different impurities are shown in figure 19.

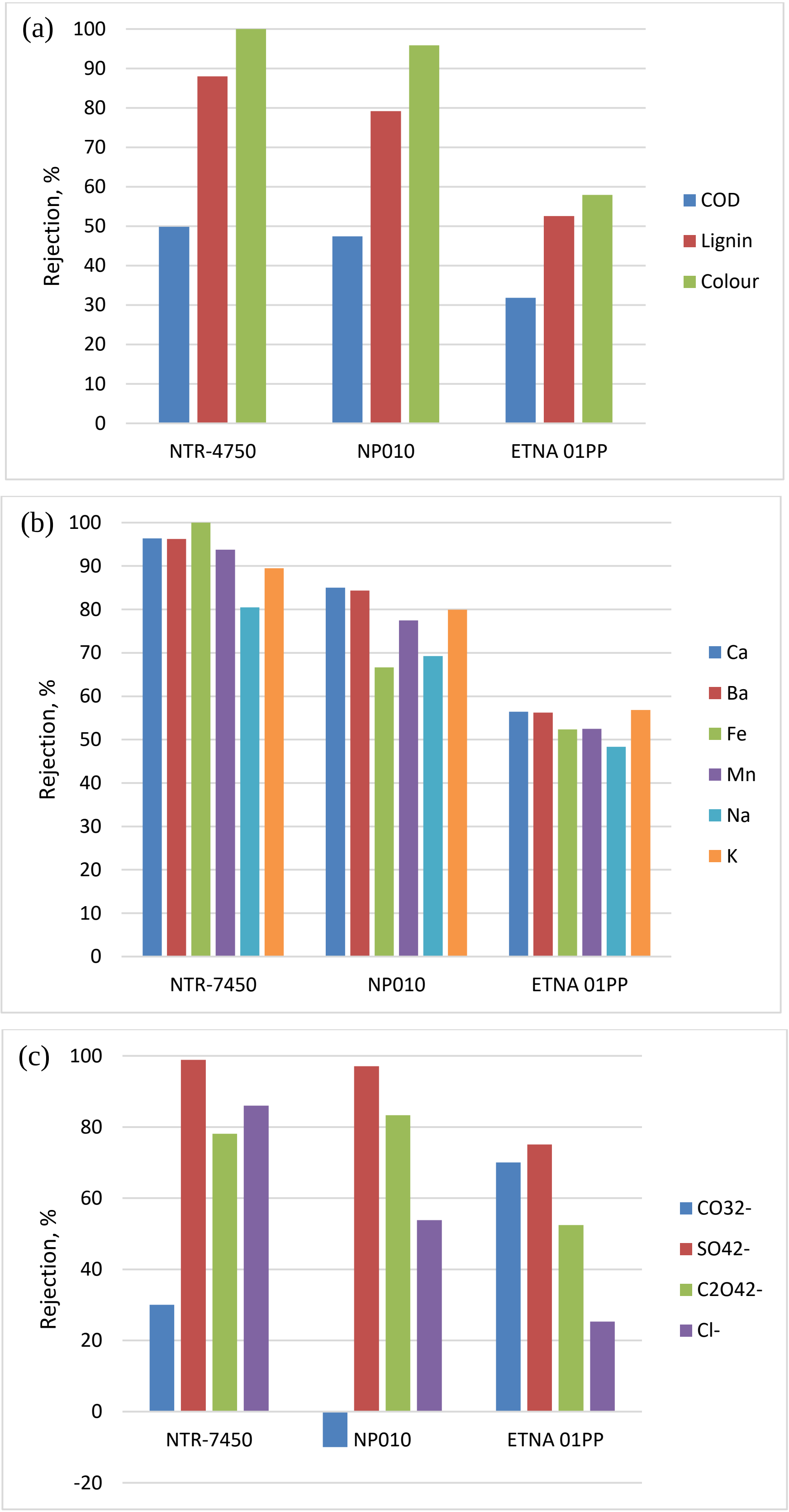


Figure 19 Rejections toward a) COD, lignin and colour b) calcium, barium, iron, manganese, sodium and potassium, c) carbonate, sulphate, oxalate and chloride ions when D0 effluent is filtrated at 50°C and a pressure of 24 bar.

NTR-7450 showed highest rejections for all the metals, as well as for COD, lignin and colour. The rejections of iron, calcium and barium were higher than 95 %. In addition, sulphate was nearly fully retained, and a chloride rejection of 86 % was obtained. Similarly as in the filtration experiments of the D0 effluent, ETNA 01PP showed lowest rejections for all the impurities, except for carbonate. The rejections of the metals were rather poor. The quality of the permeates obtained with different membranes, are shown in appendix I.

As mentioned by Tirkkonen et al. (2014), the possibilities for the reuse of the acidic effluents can be enhanced by applying additional treatment such as ED or evaporation after NF. Depending on the process in which the permeate is reused, nanofiltration might also be a sufficient technology. (Tirkkonen et al., 2014)

10.4 Performance of ion chromatography

The chromatograms of the cation and anion analyses of the original Eop, D0 and D1 effluent samples are shown in appendix II.

Analysis of anions

In order to reduce the error caused by the oxidation of sulphite ions (SO_3^{2-}) to sulphate ions, the samples were analysed immediately after dilution. The peaks of sulphate and chloride ions were clear and narrow, and there were no interfering peaks. The oxalate peak was comparatively wider. The shape of the peak indicated that the elution time of some other anion in the samples was similar to that of oxalate ion, which caused interference. Thus, the peak was manually split to separate the interfering peak from the oxalate peak. This may have caused small errors to the results.

By IC, the concentration of carbonate ions cannot be measured precisely. It was also determined with a TOC analyser by an external laboratory. However, the TIC procedure is also less precise than the titration method for the determination of carbonate. In the D0 and D1 feed solution and permeate samples, the carbonate concentrations were rather low and therefore could not be detected by IC. A comparison of the results obtained by IC and by the TIC procedure for Eop effluent feed solution and permeates from the NF experiments is shown in table XIII.

Table XIII Comparison of the carbonate concentrations obtained by TIC and IC procedures.

Sample	CO_3^{2-} [mg/L] (TIC)	CO_3^{2-} [mg/L] (IC)
Eop effluent	435	484
NP030 permeate	113	155
NTR-7450 permeate	63	46
NP010 permeate	115	125
ETNA 01PP permeate	140	145

The results obtained by the two analytical methods were within the same order of the magnitude, although some differences could be found. In the IC analysis, compared to the peaks of the other ions, the carbonate peak was wider and much lower. Also, the peak was very near to the sulphate peak. For the TIC procedure, the required sample volume was higher. The detection limit and the mean values for the carbonate concentrations in the feed solutions and permeates determined by the TIC procedure are shown in appendix III.

Analysis of cations

To evaluate the suitability of IC for the determination of sodium, potassium, calcium and barium ions in the bleaching effluents, the obtained results were compared with those from the ICP-OES analysis. In table XIV, the obtained results for the feed solutions are shown.

Table XIV The obtained metal and metal cation concentrations determined by ICP-OES and IC, respectively, for the Eop, D0 and D1 stage effluent feed solutions.

Feed solution	Na [mg/L]	Na^{2+} [mg/L]	K [mg/L]	K^+ [mg/L]	Ca [mg/L]	Ca^{2+} [mg/L]	Ba [mg/L]	Ba^{2+} [mg/L]
Eop	943	990	8	1.5	17.8	12.6	0.18	n.a.
D0	683	477	19.3	12.9	120	124	0.44	n.a.
D1	522	646	5	1.8	20.9	23.7	0.16	n.a.

In the case of sodium, for which the concentrations in the samples were higher compared to the other metals, comparable results with those from the ICP-OES analysis were obtained by IC. There were some differences, probably arising from the differences between the analytical methods and dilution of the samples. However, the concentrations of Na^+ ions in the standard solutions ranged from 2 to 25 mg/L, and in some of the diluted samples, their concentrations were higher than 25 mg/L. Therefore, for the determination of sodium ions by IC, the samples should be further diluted, for instance, to concentrations of 1:20 and 1:50.

For potassium, the results obtained by IC were systematically lower than those obtained by ICP-OES. For calcium, the results were within the same order of magnitude. However, as the concentration of these cations in the most dilute standard solution for the ion chromatographic analysis was 0.2 mg/L, and the samples were diluted to a concentration of 1:10, concentrations below 2 mg/L in the samples should be considered with precaution. The detection limits in the ICP-OES analysis were 0.5 for potassium, 0.1 mg/L for calcium and 0.002 mg/L for barium. The barium concentrations in the samples were very low, and in the most dilute standard solution prepared for the IC analysis, the concentration of Ba^{2+} ions was 0.2 mg/L. According to the ICP-OES analysis, the pre-filtered D1 stage effluent showed the highest barium concentration, 0.4 mg/L. Thus, Ba^{2+} ions could not be detected in any of the diluted samples by IC.

The equipment with the PAR reagent and an UV/Vis detector, which is required for the determination of transition metals by IC, was not installed. Thus, iron, copper and manganese were quantified only by ICP-OES. There is very little information available in the literature on the suitability of the PAR reagent equipment for analysing trace amounts of transition metals in the complex pulp and paper industry effluent samples.

10.5 Error inspection

Before the experiments, the samples were stored at approximately 6°C. They were cooled to this temperature rapidly, which may have resulted in precipitation of certain metals and differences in the surfaces of the pulp fibres in the samples. For instance, barium sulphate tends to precipitate in low temperatures. It is possible that barium sulphate was precipitated during storage and not dissolved when the samples were heated to the filtration temperature. In addition, sulphite ions are easily oxidised to sulphate ions, which may have affected the obtained sulphate concentrations. The sample containers were shaken to obtain representative samples.

All the membranes that were used in the nanofiltration experiments were pre-treated similarly. They were cut from a membrane sheet. Prior to each filtration, the filtration equipment was rinsed with the sample to remove the water. However, the feed solution may have been slightly diluted in the beginning of the filtration, as the rinsing solution could not be fully removed from the tubings. However, the feed solution concentrated to some extent during the filtration experiments, as permeate was collected. The feed solutions were analysed after the pre-filtration, and thus, their dilution and concentration were not taken into account. In the preliminary ultrafiltration experiments, the feed solution was notably concentrated during the experiment.

The dilution of the samples is a possible source of error in the analytical results, especially in the ion chromatographic analyses, where the dilution factors were comparatively large. The error that arises from the operation of the pipettes can be considered small, but when the results obtained for the diluted samples are multiplied to receive the concentrations in the original samples, the error is also increased. The lignin analysis by UV/Vis spectrophotometer and the carbonate analysis by IC are not precise. Lignin can be present in the samples in various forms, the UV absorptivity of which may significantly differ from the commercial alkali lignin. The carbonate concentrations were also estimated from TIC. In the COD analyses, parallel measurements were taken and similar results were obtained.

11 SUMMARY AND CONCLUSIONS

The main objective of this work was to identify the ions that typically have harmful impacts on kraft pulp bleaching processes, and to investigate how bleaching effluents could be purified by membrane technology. The literature part was focused on the origin and potential impacts of the harmful ions, their interactions with fibres and dissolved organic compounds, the conditions that lead to the formation of the typical metal precipitates in bleaching systems and the possibilities for the removal of metals from bleaching effluents. In addition, the suitability of ion chromatography for the analysis of the harmful ions was evaluated. Ultra- and nanofiltration experiments of alkaline Eop-stage effluent and acidic D0 and D1 stage effluents were carried out in laboratory-scale to examine the performance of nano- and ultrafiltration in the removal of harmful anions and metals, in order to possibly reduce the water use in the bleach plant.

Based on the literature, calcium, barium, transition metals (especially iron and manganese), carbonate, sulphate, oxalate and chloride ions typically cause issues in kraft pulp bleaching processes. Most of the harmful metal cations, including calcium, barium, manganese and copper entering the bleaching processes originate mainly from the wood raw material. Other sources for the harmful ions are the used process water, different chemical additives such as make-up lime and sulphuric acid, and corrosion of the equipment.

In ECF and TCF bleaching sequences, the most common salts to cause scale deposition problems are calcium carbonate, calcium oxalate and barium sulphate. Calcium carbonate deposits formed at high pH and at temperatures above 50°C. Calcium oxalate and barium sulphate precipitates are formed at relatively lower temperatures and, respectively, at pH ranging from 3.5 to 8.5 and from 1.5 to 4. The deposition of barium sulphate typically causes issues on the operation of the D0 and ozone stages. Transition metal ions, especially iron, manganese and copper ions, are known to act as catalysts for hydrogen peroxide decomposition, which may lead to poor strength of the final pulp and increased consumption of the bleaching agents. Magnesium can be considered as the most effective catalyst, even at very low concentrations. Chloride ions can cause corrosion of the equipment especially in acidic conditions.

In bleaching effluents, metals can be present as soluble ions, finely divided suspended particles, organic complexes, or attached to the acidic surface functional groups such as carboxylic groups in fibres. Mainly pH affects the ion exchange processes and complex formation in fibre suspensions. In addition, the charge of the cellulose fibre surface and the charge and concentration of the metal ion affects the partition of metal ions between the fibre wall and the surrounding solution. Especially transition metal ions have a tendency to form complexes with residual lignin. These complexes contribute to the catalytic decomposition of H_2O_2 during bleaching, although their impact is smaller than that of free transition metal ions.

Very little information is available on the application of ion chromatography for the determination of metal cations in pulp and paper industry effluents and process waters in the literature. However, in previous studies, IC has been used for the quantitative determination of chloride and sulphur-containing anions in these effluents. In the experimental part, sulphate, chloride, sodium and calcium ions were quantified by ion chromatography, and comparable results with the ICP-OES measurements were obtained in the samples with sufficiently high concentrations of these metals. However, the ICP-OES analysis is more rapid, and the concentrations of barium in all the samples were too low to be measured by IC.

Ultrafiltration is a feasible technology for the removal of colour and poorly biodegradable compounds in alkaline bleaching effluents. In this work, preliminary ultrafiltration experiments of alkaline Eop stage filtrate and acidic D0 and D1 stage filtrates from a Finnish kraft pulp mill were carried out in a stirred cell dead-end filtration unit using PES membranes with a MWCO of 5000 Da. Highest rejections for calcium and barium were obtained for the alkaline Eop stage effluent.

In previous studies, promising rejections for different pollutants have been obtained also in the treatment of acidic bleaching effluents by nanofiltration. The Eop, D0 and D1 stage effluents were filtrated using four polymeric membranes made of PES, sulphonated PES and composite fluoropolymer with MWCO values ranging from 500 to 1000 Da. Based on the rejections and permeate fluxes, the sulphonated PES NTR-7450 membrane showed the most promising results in the treatment of both the acidic and alkaline effluents. For the membranes made from PES, which is a more hydrophobic material, the permeate flux was low in the filtration of the acidic effluents. The metals that form divalent cations, including calcium and barium, could be effectively removed by nanofiltration. However, in the filtration experiments of the acidic effluents, more fouling occurred. In addition, the concentrations of monovalent ions, namely chloride and sodium in the permeates were high, and could cause issues when the permeate is reused in the processes. The removal of these monovalent ions would require, for instance, additional electrodialysis, reverse osmosis or evaporation treatment and thus more energy. There was more variation in the rejections of anions.

Bleaching is a major contributor to the overall freshwater consumption and effluent generation of pulp mills. However, the required volumes of fresh water and the amounts of discharged effluents can be decreased with increasing cycle closure. It is difficult to estimate, whether the quality of the obtained permeates is sufficiently high for their reuse in the bleaching processes to replace pure water. Therefore, additional research is required on the impacts of further closure of the water circuits in the mill. Due to the large volumes of the effluent to be treated, the required membrane area and costs may be high. However, the energy consumption of nano and ultrafiltration processes is lower than that of evaporation.

Filtration of the acidic bleaching effluents was more difficult, and more fouling occurred than in the filtration of the alkaline Eop stage effluent. Bleaching effluents are very complex mixtures, and there can be variation in their composition both between different mills and within the mill. Further investigation should be carried out to understand the phenomena such as fouling that take place during the filtration of these effluents and the factors that affect the poor filterability of the acidic effluents. Additionally, for instance, other membrane materials for the treatment of the acidic effluents and different methods such as backflushing, could be tested to prevent concentration polarisation and fouling of the membranes.

The ultra- and nanofiltration experiments were performed in laboratory-scale. To obtain information on the behaviour of these filtration systems on industrial scale, pilot-scale experiments should be conducted. Also, the long-term behaviour of especially the NTR-7450 membrane should be examined. In the experiments, the applied pressure was rather high and should be optimised, which affects the filtration capacity. In addition, the configuration of the filtration equipment affects, for instance, the permeate flux and fouling tendency, and therefore, module types such as spiral-wound modules or high-shear modules could be tested.

This work was focused on the quality of the obtained permeate. However, in membrane separation processes, also a retentate stream is produced and should be utilised. Different possibilities for the utilisation of the retentates should be evaluated. In addition, the bleaching filtrates may contain environmentally harmful substances such as heavy metals and chlorinated organic compounds, which needs to be taken into account in their discharge.

LIST OF REFERENCES

Afonso, M. & Pinho, M. 1997. Nanofiltration of Bleaching Pulp and Paper Effluents in Tubular Polymeric Membranes. *Separation Science and Technology*, 32(16), pp. 2641-2658.

Alén, R. 2000. Structure and chemical composition of wood. In: Stenius P. (ed.) Forest Products Chemistry. Helsinki: Fapet Oy. pp. 12-57. ISBN 952-5216-00-4.

Ali, M. & Sreekrishnan, T. 2001. Aquatic toxicity from pulp and paper mill effluents: a review. *Advances in Environmental Research*, 5(2), pp. 175–196.

Arpalahti, O., Engdahl, H., Jäntti, J., Kiiskilä, E., Liiri, O., Pekkinen, J., Puumalainen, R., Sankala, H. & Vehmaan-Kerula, J. 1999. White liquor preparation. In: P. Tikka, ed. Chemical Pulping Part 2, Recovery of Chemicals and Energy. Helsinki, Finland: Paperi ja Puu Oy, pp. 133-202.

Ashrafi, O., Yerushalmi, L. & Haghighat, F. 2015. Wastewater treatment in the pulp and-paper industry: A review of treatment processes and the associated greenhouse gas emission. *Journal of environmental management*, 158, pp. 146-157.

Athley, K., & Ulmgren, P., 2001. Interaction between divalent metal ions and oxygen-delignified kraft pulps. *Nordic Pulp And Paper Research Journal*, 16(3), pp. 204-214.

Bajpai, P., 2012. Environmentally benign approaches for pulp bleaching. 2nd edition. Amsterdam, Netherlands: Elsevier Science. 416 p. ISBN: 978-0-444-59421-1.

Bajpai, P., 2015. Green Chemistry and Sustainability in Pulp and Paper Industry. Springer International Publishing AG. ISBN: 978-3-319-18744-0.

Boffardi, B. P. 1992. Corrosion and deposit control in mill supply water [Conference paper]. Tappi Engineering Conference, Boston, USA. 953-974.

Braithwaite, A. & Smith, F., 1985. Chromatographic Methods. 4th edition. London, UK: Chapman & Hall. 414 p. ISBN 0-412-26770-5.

Bryant, P. 1995. Metals Management in the Fiberline [Technical paper]. TAPPI Minimum Effluent Mill Symposium, Atlanta, Georgia. IPST Technical Paper Series Number 599.

Bryant, P., Samuelsson, Å. & Basta, J. 2003. Minimizing BaSO4 scale formation in ECF bleach plants. TAPPI Journal, 2(3), pp. 3-7.

Calvo, L., Gilarranz, M., Casas, J., Mohedano, A., & Rodríguez, J., 2007. Detoxification of Kraft pulp ECF bleaching effluents by catalytic hydrotreatment. *Water Research*, 41(4), pp. 915–923.

Cardona-Barrau, D., Lachenal, D. & Chirat, C., 2001. Affinity of Metal Ions for Kraft Pulps Studied by ESR. Inhibition of Their Catalytic Action in Oxygen Bleaching. *Journal of Wood Chemistry and Technology*, 21(3), pp. 247-261.

Carter, D. & Gleadow, P. 1994. Water use reduction in chemical pulp mills. In: Turner, P., Williamson, P. & Wadham, K. (eds.). Water Use Reduction in the Pulp and Paper Industry 1994. Montreal, Canada: Canadian Pulp and Paper Association. pp. 53-80.

Chai, X., Zhu, J. & Luo, Q. 2001. Carbonate analysis in black liquors from pulping and evaporation process [Conference paper]. International Chemical Recovery Conference, Whistler, British Columbia, Canada, June 11-14, 2001.

Chen, C., Mao, S., Wang, J., Bao, J., Xu, H., Su, W., and Dai, H. 2015. Application of ultrafiltration in a paper mill: Process water reuse and membrane fouling analysis, *BioResources*, 10(2), pp. 2376-2391.

Choi, H., Zhang, K., Dionysiou, D., Oerther, D., & Sorial, G. 2005. Effect of permeate flux and tangential flow on membrane fouling for wastewater treatment. *Separation and Purification Technology*, 45(1), pp. 68–78.

Dahl, O., 1999. Evaporation of Acidic Effluent from Kraft Pulp Bleaching, Reuse of the Condensate and Further Processing of the Concentrate. Doctoral dissertation. University of Oulu, Faculty of Technology.

Dahlman, O., Reimann, A., Strömberg, L. & Mörck, R. 1995. High-molecular-weight effluent materials from modern ECF and TCF bleaching. *TAPPI Journal*, 78(12), pp. 99-109.

David, R. & Klein, J. 2001. Reaction Crystallization. In: Mersmann, A. (ed.) Crystallization Technology Handbook, 2nd edition. Marcel Dekker: New York, Basel, Switzerland. ISBN 0-8247-0528-9.

de Jong, G. 2016. Detection in Capillary Electrophoresis – An Introduction. In: de Jong, G. (ed.) Capillary Electrophoresis–Mass Spectrometry (CE-MS): Principles and Applications. 1st Edition. pp. 1-5. Wiley-VCH Verlag GmbH & Co. KGaA. ISBN: 9783527693801.

Demarest, C., Monnot-Chase, E., Jiu, J. & Weinberger, R. 1992. Separation of Small Molecules by High Performance Capillary Electrophoresis. In: Grossman, P. & Colburn, J. (eds.) Capillary Electrophoresis: Theory and Practice. California, USA: Academic Pess, Inc. ISBN 0-12-304250-X.

Douek, M., Sullivan, J. & Ing, J. 1993. Effect of Sample-Related Sources of Error on the Analysis of Pulp and Paper Mill Process Liquids by Ion Chromatography: Part I — Determination of Sulphur Species. *Journal of Wood Chemistry and Technology*, 13(3), pp. 439-462.

Elsander, A., Ek, M. & Gellerstedt, G. 2000. Oxalic Acid Formation During ECF and TCF Bleaching of Kraft Pulp. *TAPPI Journal*, 83(2), pp. 73-77.

Fälth, F., Jönsson, A. & Wimmerstedt, R. 2001. Ultrafiltration of effluents from chlorine-free, kraft pulp bleach plants. *Desalination*, 133(2), pp. 155-165.

Gavrilescu, D., Puitel, A., Dutuc, G. & Craciun, G. 2012. Environmental impact of pulp and paper mills. *Environmental Engineering and Management Journal*, 11(1), pp. 81-85.

Geraldes, V. & Pinho, M. 1995. Process water recovery from pulp bleaching effluents by an NF/ED hybrid process. *Journal of Membrane Science*, 102, pp. 209-221.

Giorno, L. & D'Agostino, N. 2016. Fouling. In: Drioli, E. & Giorno, L. (eds.). Encyclopedia of Membranes. Springer, Berlin, Heidelberg. ISBN: 978-3-662-44324-8.

Grace, T. & Tran, E. 2007. The effect of dead load chemicals in the kraft pulping and recovery system. *TAPPI Journal*, 3(7), pp. 2031-2064.

Granholm, K., Harju, L. & Ivaska, A. 2010. Desorption of Metal Ions from Kraft Pulps. Part 1. Chelation of Hardwood and Softwood Kraft Pulp with EDTA. *BioResources*, 5(1), pp. 206-226.

Gullichsen, J. & Fogelholm, C. (eds.). 1999. Papermaking science and technology. Book 6A, Chemical pulping. Helsinki, Finland: Fapet. 693 p. ISBN 952-5216-06-3.

Guo, X., Zhang, S., & Shan, X. 2008. Adsorption of metal ions on lignin. *Journal of Hazardous Materials*, 151(1), pp. 134-142.

Hayes, C. 2017. Atomic Spectroscopy, Forestry and Wood Products Applications. In: Encyclopedia of Spectroscopy and Spectrometry. 3rd Edition. pp. 96-104. ISBN 978-0-12-803224-4

Higson, S. 2004. Analytical chemistry. New York, USA: Oxford University Press. 453 p. ISBN 978-0-19-850289-0.

Hill, S. & Fisher, A. 1999. Atomic Absorption, Methods and Instrumentation. In: Lindon, J. (ed.) Encyclopedia of Spectroscopy and Spectrometry. pp. 37-43. Elsevier Ltd. ISBN 978-0-12-803224-4.

Huber, P. 2011. Kinetics of CO_2 Stripping and Its Effect on the Saturation State of $CaCO_3$ upon Aeration of a $CaCO_3$–CO_2–H_2O System: Application to Scaling in the Papermaking Process. *Industrial & engineering chemistry research*, *50*(24), pp. 13655–13661.

Häärä, M., Sundberg, A. & Willför, S. 2011. Paper chemistry: Calcium oxalate - a source of "hickey" problems - A literature review on oxalate formation, analysis and scale control. *Nordic Pulp & Paper Research Journal*, 26 (3), pp. 263-282.

Jackson, P. 2000. Ion Chromatography in Environmental Analysis. In: Meyers, R. (ed.) Encyclopedia of Analytical Chemistry, pp. 2779–2801. John Wiley & Sons Ltd, Chichester.

Johansson, N., Clark, F. & Fletcher, D. 1995. New technology developments for the closed cycle bleach plant [Conference paper]. Proc. 1995 International Non-Chlorine Bleaching Conference, March 5-9, 1995, Amelia Island Florida.

Koch, G., 2006. Raw Material for Pulp. In: Sixta, H. (ed.) Handbook of Pulp. pp. 21–68. Wiley-VCH Verlag GmbH. ISBN: 978-3-527-30999-3.

Kubáň, P., Guchardi, R., & Hauser, P., 2005. Trace-metal analysis with separation methods. *TrAC Trends in Analytical Chemistry,* 24(3), pp. 192–198.

Sjöström, E., 1993. Wood chemistry: fundamentals and applications. 2nd edition. Academic Press. 277 p. Online ISBN: 978-0-08-092589-9.

Kapoor, A., Balasubramanian, S., Kavitha, E., Poonguzhali, E. & Prabhakar, S. 2021. Role of Membranes in Wastewater Treatment. In: Inamuddin, A. & Lichtfouse, E. (eds.) Water Pollution and Remediation: Photocatalysis. Environmental Chemistry for a Sustainable World, vol 57. Springer, Cham. ISBN: 978-3030547226

KnowPulp. Bleaching sequences [online]. Available at: http://www.knowpulp.com/www_demo_version/english/pulping/bleaching/4_sequences/frame.htm [Accessed 8.2.2021].

Lachenal, D., Nguyen T., Chirat, C. and Soria, L. 1997. Optimum use of H_2O_2 in kraft pulp delignification. *Paperi Puu*, 79(4), pp. 252-256.

Lacorte, S., Latorre, A., Barceló, D., Rigol, A., Malmqvist, A. & Welander, T. 2003. Organic compounds in paper-mill process waters and effluents. *Trends in Analytical Chemistry,* 22(10), pp. 725-737.

Li, H., Du, C., Ge, S. & Liu, M. 2020. Oxalate formation during ClO_2 bleaching of bamboo kraft pulp. *Nordic Pulp & Paper Research Journal*, 35(1), pp. 18-24.

Li, L., Lee, S., Lee, H. & Youn, H. 2011. Hydrogen peroxide bleaching of hardwood kraft pulp with adsorbed birch xylan and its effect on paper properties. *BioResources*, 6.

Lindholm-Lehto, P., Knuutinen, J., Ahkola, H., & Herve, S. 2015. Refractory organic pollutants and toxicity in pulp and paper mill wastewaters. *Environmental Science and Pollution Research,* 22 (9), pp. 6473-6499.

Loerting, T. & Bernard, J. 2010. Aqueous Carbonic Acid (H_2CO_3). *Chemphyschem*, 11, pp. 2305-2309.

McKague, A. & Carlberg, G. 1996. Effluent Characteristics and composition. In: Pulp Bleaching – Principles And Practice. Dence, C. W. & Reeve, D. (eds.), Atlanta, USA: TAPPI Press. pp. 749-765. ISBN: 9780898520637.

Merdy, P., Guillon, E., & Aplincourt, M. 2002. Iron and manganese surface complex formation with extracted lignin. Part 1: Adsorption isotherm experiments and EPR spectroscopy analysis. *New Journal of Chemistry*, 26(11), pp. 1638–1645.

Mersmann, A. 2001. Physical and Chemical Properties of Crystalline System. In: Mersmann, A. (ed.) Crystallization Technology Handbook. 2nd edition. Marcel Dekker: New York, Basel, Switzerland. pp. 1-44. ISBN 0-8247-0528-9.

Mi, Z., Liu, Z., Jin, S., Zhang, D. & Wang, D. 2021. Positively Charged Nanofiltration Membrane Prepared by Polydopamine Deposition Followed by Crosslinking for High Efficiency Cation Separation. *Polymer Testing*, 93.

Michalski, R. 2009. Applications of Ion Chromatography for the Determination of Inorganic Cations. *Reviews in Analytical Chemistry*, 39(4), pp. 230-250.

Michalski, R. 2010. Environmental Applications of Ion Chromatography in Eastern and Central Europe. *Journal of Chromatographic Science*, 48(7), pp. 559-565.

Michalski, R. 2018. Ion Chromatography Applications in Wastewater Analysis. *Separations*, 5(1), 16.

Mulder, M. 1996. Basic Principles of Membrane Technology. 2nd edition. Springer Netherlands. 575 p. Online ISBN: 9789400917668.

Mänttäri, M., Kallioinen, M. & Nyström, M. 2015. Membrane technologies for water treatment and reuse in the pulp and paper industries. In: Basile, A., Cassano, A., Rastogi, N. (eds.) & Ang, W. (cont.). Advances in membrane technologies for water treatment: materials, processes and applications. Amsterdam, Netherlands: Woodhead Publishing. pp. 581-603. ISBN: 9781782421214.

Nguyen, T., Roddick, F. & Fan, L. 2012. Biofouling of Water Treatment Membranes: A Review of the Underlying Causes, Monitoring Techniques and Control Measures. *Membranes*, 2(4), pp. 804–840.

Nordin, A. & Jönssön, A. 2009. Case study of an ultrafiltration plant treating bleach plant effluent from a pulp and paper mill. *Desalination*, 201(1), pp. 277-289.

Puitel, A., Bordeianu, A. & Gavrilescu, D. 2007. Review on Lignin Reactions in TCF Kraft Pulp Bleaching. *Cellulose Chem. Technol.*, 41(4-6), pp. 219-234.

Sinniah, K., & Piers, K. 2001. Ion Chromatography: Analysis of Ions in Pond Waters. *Journal of Chemical Education*, 78(3), pp. 358-362.

Stratton, S., Gleadow, P. & Johnson, A. 2004. Pulp mill process closure: a review of global technology developments and mill experiences in the 1990s. *Water science and technology*, 50 (3), pp. 183–194.

Strassberger, Z., Tanase, S. & Rothenberg, G. 2014. The pros and cons of lignin valorisation in an integrated biorefinery. *RSC Advances*, 4, pp. 25310-25318.

Suess, H. 2010. Pulp Bleaching Today. Berlin: De Gruyter. ISBN: 9783110207378.

Histed, J., McCubbin, N. & Gleadow, P. 1996. Water Reuse and Recycle. In: Pulp Bleaching – Principles And Practice. Dence, C. W. & Reeve, D. (eds.), Atlanta, USA: TAPPI Press. pp. 647-673. ISBN: 9780898520637.

Hu, H., Jin, H. & Chai, X. 2014. A practical headspace gas chromatographic method for the determination of oxalate in bleaching effluents. *Journal of industrial and engineering chemistry,* 20 (1), pp. 13–16.

Huber, P., Burnet, A. & Petit-Conil, M. 2014. Scale deposits in kraft pulp bleach plants with reduced water consumption: A review. *Journal of environmental management,* 141, pp. 36-50.

Jemaa, N., Thompson, R., Paleologou, M. & Berry, R. 1999. Non-process elements in the kraft cycle, part 1: sources, levels and process effects. *Pulp & Paper Canada,* 100(9).

Lastra, A., Gómez, D., Romero, J., Francisco, J., Luque, S. & Álvarez, J. 2004. Removal of metal complexes by nanofiltration in a TCF pulp mill: technical and economic feasibility. *Journal of Membrane Science*, 242(1), p. 97–105.

Nesterenko, P. & Paull, B. 2017. Ion Chromatography. In: Fanali, S., Haddad, P., Poole, C., & Riekkola, M. (eds.) Liquid Chromatography - Fundamentals and Instrumentation, Volume 1. 2nd edition. Elsevier. pp. 205-244. ISBN: 9780128053935.

Oliveira, C., Silva, C. & Milanez, A. 2007. Application of ultrafiltration in the pulp and paper industry: Metals removal and whitewater reuse. *Water science and technology,* 55, pp. 117-23.

Persson, M. & Ulmgren, P. 2002. Deposition of barium sulfate in bleach plants. Part 1: solubility and factors affecting the precipitation in D (chlorine dioxide)-filtrates. *Nordic Pulp & Paper Research Journal*, 17, pp. 280-287.

Pinto, I., Ascenso, O., Barros, M. & Soares, H. 2013. Pre-treatment of the paper pulp in the bleaching process using biodegradable chelating agents. *International journal of environmental science and technology*, 12(3), pp. 975-982.

Puro, L., Kallioinen, M., Mänttäri, M., Natarajan, G., Cameron, D. & Nyström, M. 2010. Performance of RC and PES ultrafiltration membranes in filtration of pulp mill process waters. *Desalination*, 264 (3), pp. 249-255.

Quezada, R., Silva, C., Rezende, A., Nilsson, L. & Manfredi, M. 2014. Membrane treatment of the bleaching plant (EPO) filtrate of a kraft pulp mill. *Water Science & Technology,* 70(5), pp. 843-850.

Quezada, R., Silva, C., Hoffstedt, C., Berglin, N. & Rezende, A. 2015. Reuse of ultrafiltration membrane permeate and retentate of (EPO) filtrates from a kraft pulp mill bleaching plant. *Appita Journal*, 68(4), pp. 338-343.

Reeve, D. 1996. Introduction to the principles and practice of pulp bleaching. In: Pulp Bleaching – Principles And Practice. Dence, C. W. & Reeve, D. (eds.), Atlanta, USA: TAPPI Press. pp. 1-24. ISBN: 9780898520637.

Rudie, A. 2000. Calcium in Pulping And Bleaching. *TAPPI Journal*, 83(12), pp. 36-37.

Rudie, A. & Hart, P. 2005. Managing calcium oxalate scale in the bleach plant. *Solutions*, 88(6).

Rudie, A. & Hart, P. 2006a. Mineral Scale Management Part II. Fundamental Chemistry. *TAPPI Journal*, 5(7), pp. 17-23.

Rudie, A. & Hart, P. 2006b. Modeling and minimization of barium sulfate scale [Conference paper]. TAPPI Engineering, Pulping, and Environmental Conference, 5.-8. November 2006, Atlanta, GA.

Rudie, A. & Hart, P. 2012. Mineral Scale Management. In: Hart, P. & Rudie, A. (eds.). The Bleaching of Pulp. 5th edition. TAPPI Press. ISBN: 9781595102096.

Räsänen E. (2003) Modelling ion exchange and flow in pulp suspensions. Doctoral thesis. VTT Publications 495, VTT Technical research centre of Finland.

Räsänen, E., Stenius, P. & Tervola, P. 2001. Model describing Donnan equilibrium, pH and complexation equilibria in fibre suspensions. *Nordic Pulp and Paper Research Journal*, 16(2), pp. 130-139.

Saturnio, D. 2012. Modeling of Kraft Mill Chemical Balance. Doctoral dissertation. University of Toronto, Graduate Department of Chemical Engineering and Applied Chemistry.

SCAN-N 32:98, 1998. Carbonate Content [Standard procedure]. Stockholm, Sweden: Scandinavian pulp, paper and board testing committee.

SCAN-N 39:05, 2005. Dissolved and Precipitated Oxalate [Standard procedure]. Stockholm, Sweden: Scandinavian pulp, paper and board testing committee.

Shon, H., Phuntsho, S., Chaudhary, D., Vigneswaran, S. & Cho, J. 2013. Nanofiltration for water and wastewater treatment –a mini review. *Drinking Water Engineering and Science*, 6(1), pp. 47-53.

Shukla, S., Kumar, V., Kim, T. & Bansal, M. 2013. Membrane filtration of chlorination and extraction stage bleach plant effluent in Indian paper Industry. *Clean Technologies and Environmental Policy*, 15, pp. 235–243.

Sirén, H., Kokkonen, R., Hiissa, T., Särme, T., Rimpinen, O. & Laitinen, R. 2000. Determination of soluble anions and cations from waters of pulp and paper mills with on-line coupled capillary electrophoresis. *Journal of Chromatography A*, 895, pp. 189–196.

Sithole, B., Azeez, M.& Ramjugernath, D. 2014. A New Method for the Analysis of Soluble and Insoluble Oxalate in Pulp and Paper Matrices. *Journal of Wood Chemistry and Technology*, 34, pp. 55-66.

Sullivan, J. & Douek, M. 1998. Determination of inorganic chlorine species in kraft mill bleach effluents by ion chromatography. *Journal of Chromatography A*, 804(1-2), pp. 113-121.

Sullivan, J. & Douek, M. 1994. Determination of carbohydrates in wood, pulp and process liquor samples by high-performance anion-exchange chromatography with pulsed amperometric detection. *Journal of Chromatography A*, 671(1-2), pp. 339-350.

Södö, M., Su, P., Granholm, K., Harju, L. & Ivaska, A. 2007. Study on metal ion affinities to oxygen delignified hardwood kraft pulp by a column chromatographic method. *Nordic Pulp & Paper Research*, 22(4), pp. 462–467.

TAPPI (Technical Association of the Pulp and Paper Industry), 2009. Analysis of pulping liquors by suppressed ion chromatography, Test Method T 699 om-09.

Tavares, C., Vieira, M., Petrus, J., Bortoletto, E. & Ceravollo, F., 2001. Ultrafiltration-complexation process for metal removal from pulp and paper industry wastewater. *Desalination*, 144(1-3), pp. 261-265.

Templeton, D. 1994. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) In: Seiler, H., Sigel, A., Sigel, H. (eds.). Handbook on metals in clinical and analytical chemistry. New York: Marcel Dekker, Inc. pp. 167–80. Online ISBN: 9780585399812.

Tirkkonen, K., Kallioinen, M. & Mänttäri, M. 2014. Recycling of acidic bleaching effluents of a kraft pulp mill with nanofiltration [Conference paper]. October 2014. International Pulp Bleaching Conference, October 2014.

Tomani, P. & Seisto, A. 1999. Separation methods for closed-loop manufacture of bleached kraft pulp overview of an EU project. *Desalination*, 124, pp. 217-223.

Towers, M. & Scallan, A. 1996. Predicting the ion exchange of kraft pulps using the Donnan theory. *Journal of Pulp Paper Science*, 22(9), pp. 332-337.

Tran, H. & Vakkilainen, E. 2004. The Kraft Chemcial Recovery Process [Conference paper]. International Chemical Recovery Conference Charleston, SC, Tappi/PAPTAC,June 2004.

Ulmgren, P. 1997. Non-process elements in a bleached kraft pulp mill with a high degree of system closure-state of the art. *Nordic Pulp And Paper Research Journal*, 12(1), pp. 32-41.

Ulmgren, P. & Rådeström, R. 2001. A steady state model describing the solubility of calcium oxalate in D (chlorine dioxide stage) -filtrates. *Nordic Pulp and Paper Research Journal*, 16(4).

Valsecchi, S. & Polesello, S. 1999. Analysis of inorganic species in environmental samples by capillary electrophoresis. *Journal of Chromatography A*, 834, pp. 363–385.

Wekesa, M. & Ni, Y. 2003. Further Understanding of the Chemistry of Manganese-Induced Peroxide Decomposition. *Canadian journal of chemical engineering*, 81(5), pp. 968–972.

Weiss, J. 2004. Handbook of Ion Chromatography, Third, completely revised and updated edition. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. 902 p. Online ISBN:9783527619610.

Wilschefski, S. & Baxter, M. 2019. Inductively Coupled Plasma Mass Spectrometry: Introduction to Analytical Aspects. *Clinical Biochemist Reviews*, 40(3), pp. 115–133.

Wuorimaa, A., Jokela, R. & Aksela, R. 2018. Recent developments in the stabilization of hydrogen peroxide bleaching of pulps: An overview. *Nordic Pulp & Paper Research Journal*, 21(4), pp. 435-443.

Zeppenfeld, K. 2016. Inhibition of CaCO3 scaling by zinc (II) and copper (II): A comparative review. In: Ende, D. (ed.). Physikalische und Energetische Wasserbehandlungsverfahren für Wärmeübertrager und 16 Rohrleitungen in der gewerblichen und industriellen Anwendung, 2nd edition. Essen, Germany: PP Publico Publications, pp. 4-20.

Zhao, C., Xue, J., Ran, F. & Sun, S. 2013. Modification of polyethersulfone membranes – A review of methods. *Progress in Materials Science,* 58, pp. 76-150.

Zhao, H., Wu, H., Hu, H., Li, Y., Jing, L. & Zhang, X. 2018. Cooperative Decomposition of Hydrogen Peroxide by Lignin-combined Transition Metals in Pulp Bleaching. *Bioresources*, 13(2), pp. 3922-3931.

Žarković, D., Todorović, Ž., Krgovic, M. & Rajakovic, L., 2009. Determination of inorganic anions in papermaking waters by ion chromatography. *Journal of the Serbian Chemical Society*, 74(3).

CHEMICAL COMPOSITION OF THE PERMEATES

Table I The permeate quality from the nanofiltration experiments of Eop effluent using NP030, NTR 7450, NP010 and ETNA 01PP membranes.

Membrane	**NP030**	**NTR 7450**	**NP010**	**ETNA 01PP**
pH	10.4	10.4	10.6	11.1
Conductivity [mS/cm]	1.34	0.65	1.76	1.90
COD [mg/L]	431	332	503	570
Lignin [g/L]	22.1	6.3	29.2	31.9
Colour [Pt/Co]	66	12	105	179
Ca [mg/L]	0.32	<0.01	0.42	0.81
Ba [mg/L]	0.002	<0.002	0.003	0.007
Fe [mg/L]	<0.05	<0.05	<0.05	<0.05
Mn [mg/L]	<0.01	<0.01	<0.01	<0.01
Cu [mg/L]	<0.05	<0.05	<0.05	<0.05
Na [mg/L]	262	124	367	354
K [mg/L]	1.32	0.68	1.64	2.83
CO_3^{2-} [mg/L]	113	63	115	140
$C_2O_4^{2-}$ [mg/L]	10	2.8	9.3	12
SO_4^{2-} [mg/L]	11	0.2	12	27
Cl^- [mg/L]	185	36	157	175

Table II The permeate quality from the nanofiltration experiments of D0 stage effluent using NP030, NTR 7450, NP010 and ETNA 01PP membranes.

Membrane	**NP030**	**NTR 7450**	**NP010**	**ETNA 01PP**
pH	2.7	2.8	2.7	2.6
Conductivity [mS/cm]	2.53	1.64	2.62	4.13
COD [mg/L]	721	832	772	1193
Lignin [g/L]	72	62	81	225
Colour [Pt/Co]	36	26	43	257
Ca [mg/L]	3.15	13.01	34.1	82.8
Ba [mg/L]	0.03	0.05	0.12	0.3
Fe [mg/L]	0.08	0.1	0.15	0.3
Mn [mg/L]	0.1	0.28	0.67	1.58
Cu [mg/L]	<0.05	<0.05	<0.05	<0.05
Na [mg/L]	150	206	267	456
K [mg/L]	1.34	4.99	8.23	13.03
CO_3^{2-} [mg/L]	10	2	2	2
$C_2O_4^{2-}$ [mg/L]	31	37	48	77
SO_4^{2-} [mg/L]	16	18	23	129
Cl^- [mg/L]	383	454	254	715

Table III The permeate quality from the nanofiltration experiments of D1 stage effluent using NP030, NTR 7450, NP010 and ETNA 01PP membranes

Membrane	**NP030**	**NTR 7450**	**NP010**	**ETNA 01PP**
pH	3.2	3.8	3.5	3.5
Conductivity [mS/cm]	1.17	0.60	1.30	1.69
COD [mg/L]	458	460	482	624
Lignin [g/L]	38	23	40	92
Colour [Pt/Co]	4.5	0	5.0	50.5
Ca [mg/L]	3.2	0.8	3.1	9.1
Ba [mg/L]	0.02	0.006	0.03	0.07
Fe [mg/L]	0.21	<0.05	0.07	0.1
Mn [mg/L]	0.09	0.03	0.09	0.19
Cu [mg/L]	<0.05	<0.05	<0.05	<0.05
Na [mg/L]	157	102	161	270
K [mg/L]	1.48	0.53	1.01	2.17
CO_3^{2-} [mg/L]	10	7	11	3
$C_2O_4^{2-}$ [mg/L]	2	5	4	10
SO_4^{2-} [mg/L]	11	5	13	110
Cl^- [mg/L]	156	52	172	278

CHROMATOGRAMS FROM THE ION CHROMATOGRAPHIC ANALYSES

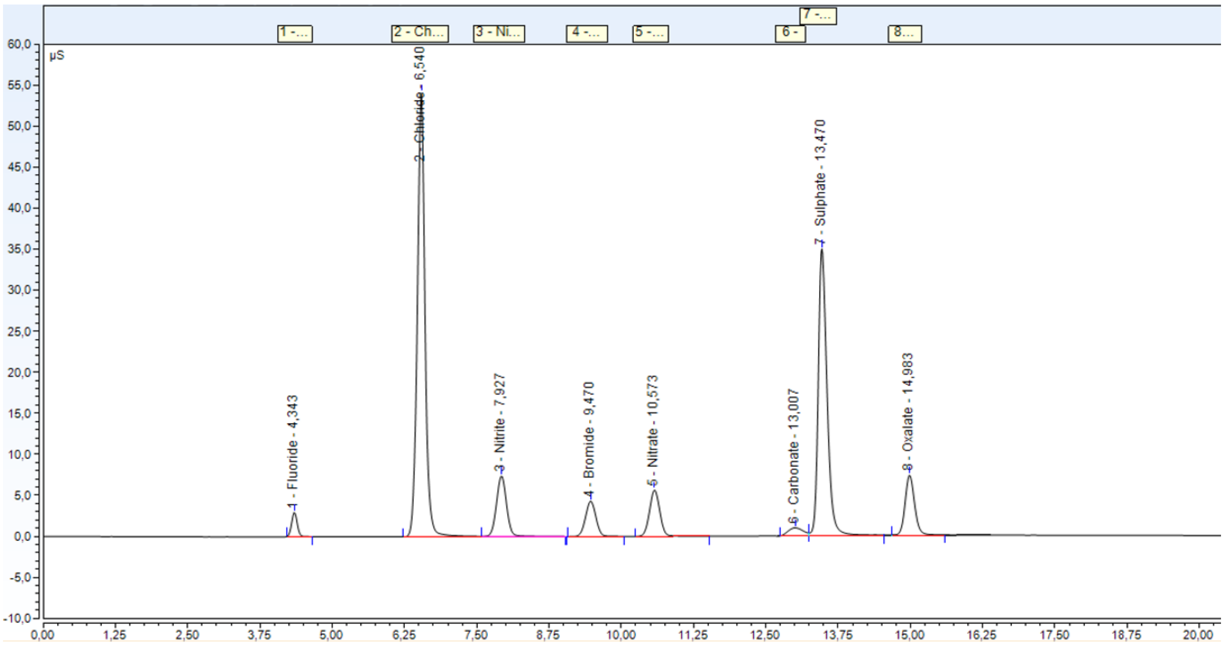


Figure 1 Chromatogram of anions in the standard solution (level 5: 40 mg/L Cl-, 40 mg/L SO_4^{2-}, 10 mg/L $C_2O_4^{2-}$ and 50 mg/L CO_3^{2-}).

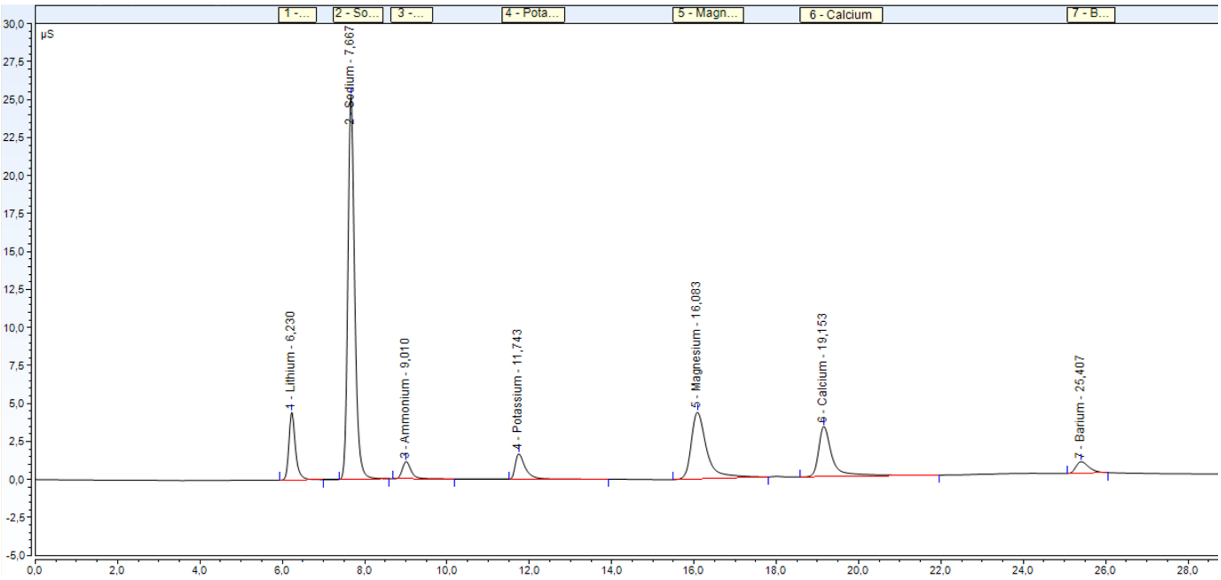


Figure 2 Chromatogram of cations in the standard solution (level 4: 15 mg/L Na^+, 2 mg/L K^+, 2 mg/L Mg^{2+}, 2 mg/L Ca^{2+} and 2 mg/L Ba^{2+}).

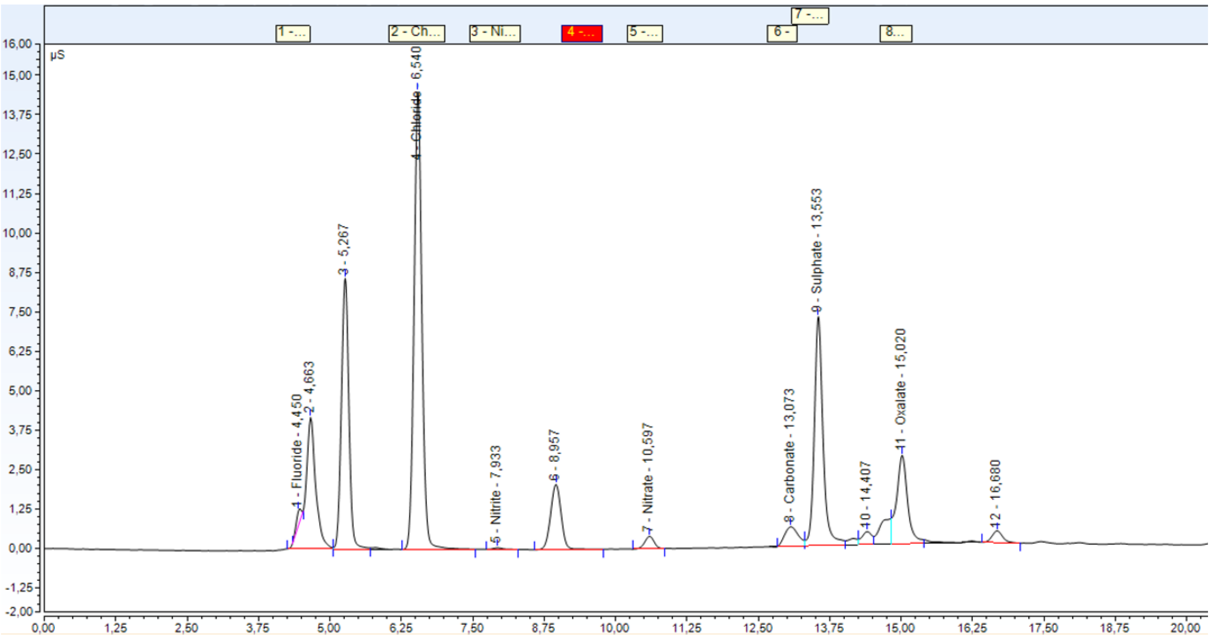


Figure 3 Chromatogram of anions in the Eop stage effluent sample (dilution 1:20).

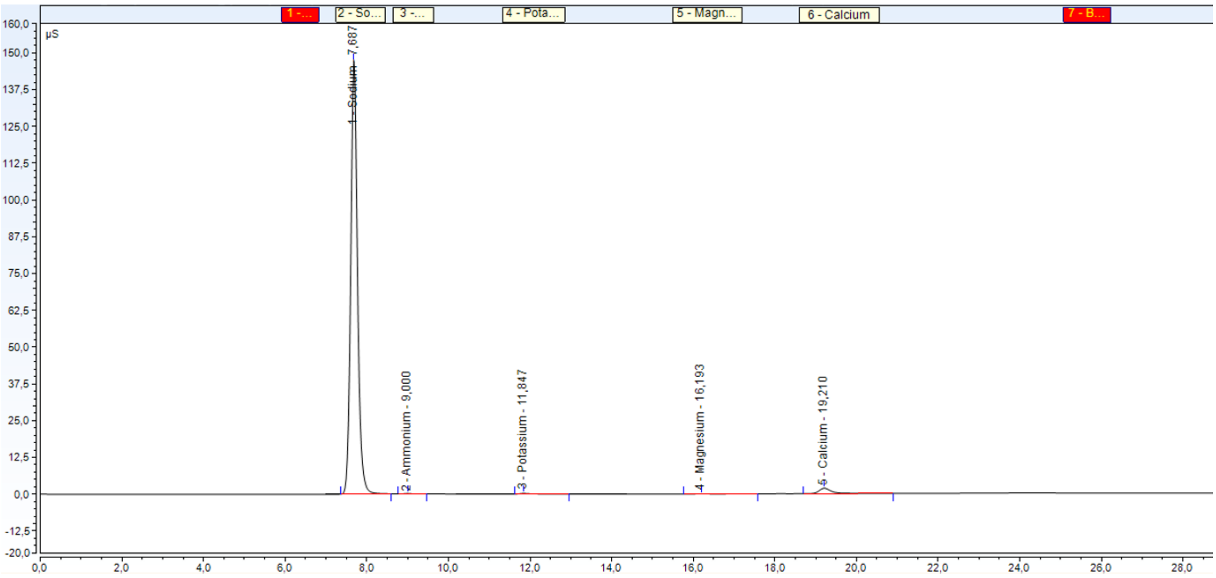


Figure 4 Chromatogram of cations in the Eop stage effluent sample (dilution 1:10).

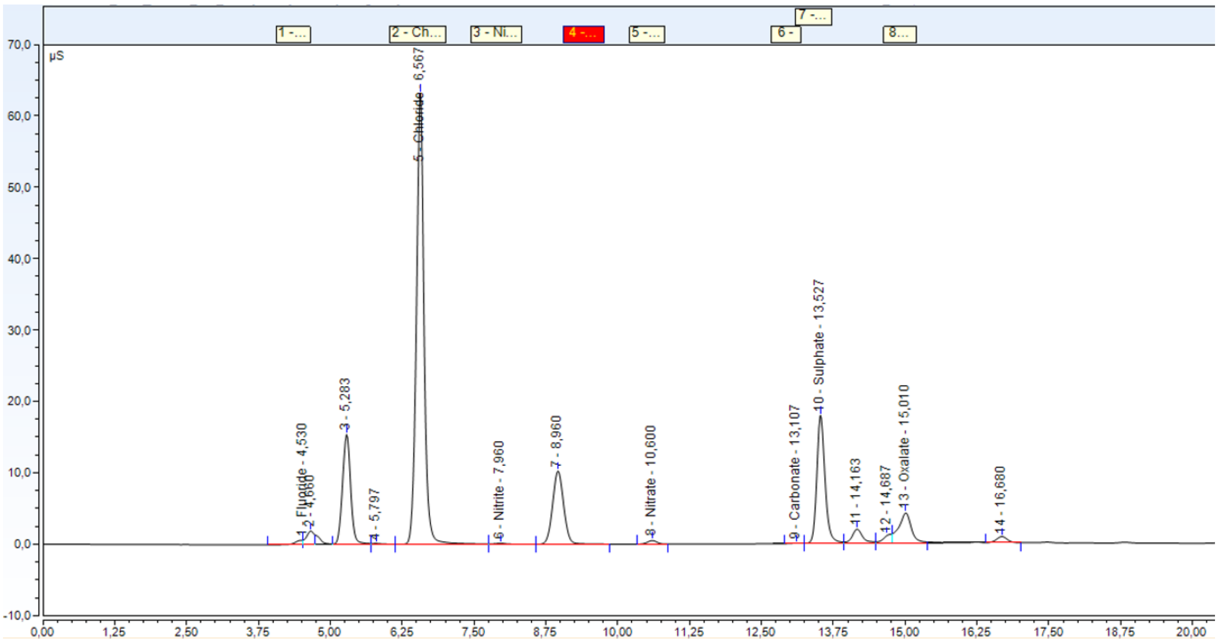


Figure 5 Chromatogram of anions in the D0 stage effluent sample (dilution 1:20).

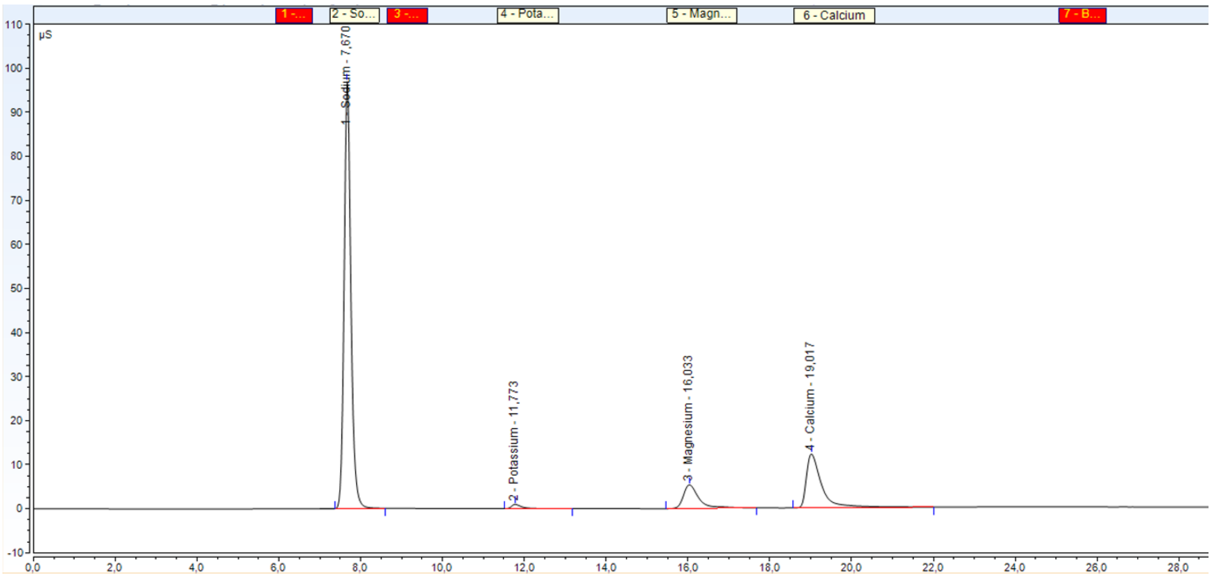


Figure 6 Chromatogram of cations in the D0 stage effluent sample (dilution 1:10).

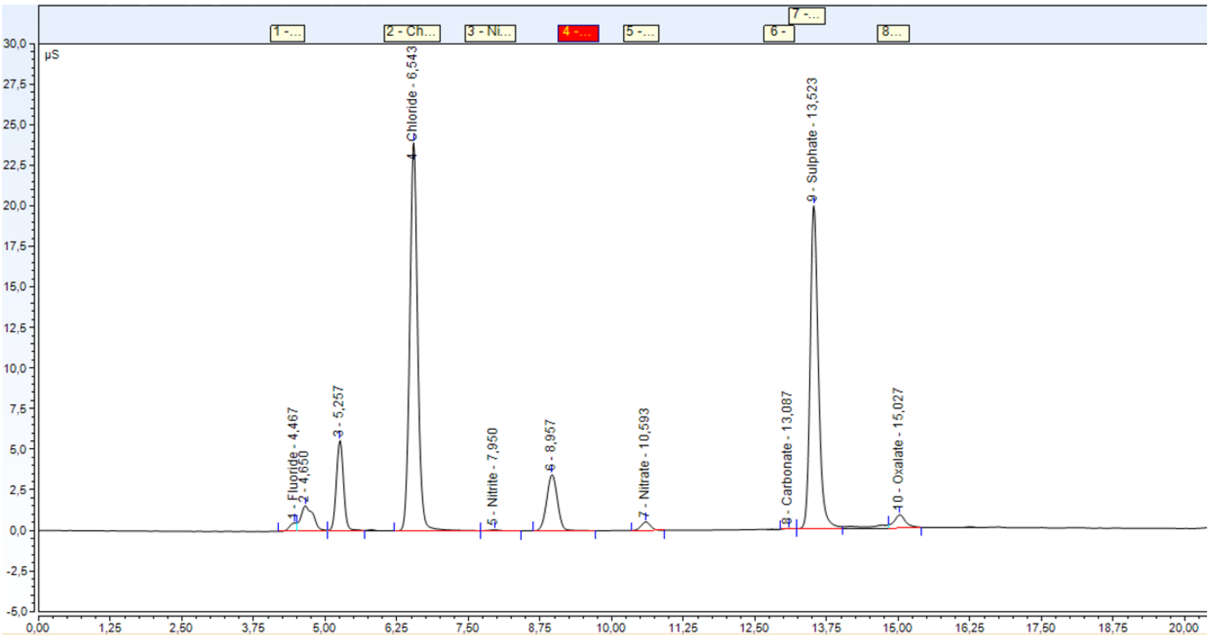


Figure 7 Chromatogram of anions in the D1 stage effluent sample (dilution 1:20).

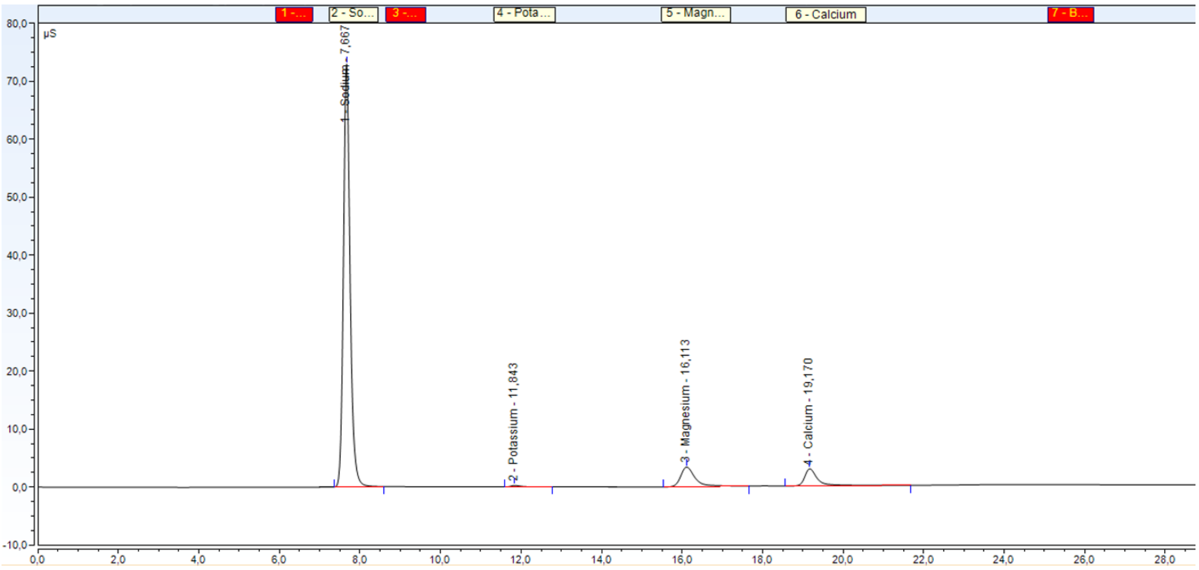


Figure 8 Chromatogram of cations in the D1 stage effluent sample (dilution 1:10).

RESULTS FROM THE ICP-OES AND TIC ANALYSES

Table I The detection limits and the mean values for the concentrations received from the external laboratory for the Eop stage effluent and the permeates from its nanofiltration experiments using NP030, NTR 7450, NP010, ETNA 01PP and Sartorius membranes.

	Detection limit	**Eop effluent**	**NP030 permeate**	**NTR 7450 permeate**	**NP010 permeate**	**ETNA 01PP permeate**	**Sartorius (5 kDa) permeate**
Ca [mg/L]	0.1	17.8	0.32	<0.01	0.42	0.81	5.98
Ba [mg/L]	0.002	0.18	<0.002	<0.002	0.003	0.007	0.04
Fe [mg/L]	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Mn [mg/L]	0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.01
Cu [mg/L]	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Na [mg/L]	1	943	262	124	367	354	801
K [mg/L]	0.5	7.95	1.32	0.68	1.64	2.83	5.90
TIC [mg/L]	0.2	87	22.5	12.5	23	28	77
CO_3 [mg/L]	1	435	112.5	62.5	115	140	385

Table II The detection limits and the mean values for the concentrations received from the external laboratory for the D0 stage effluent and the permeates from its nanofiltration experiments using NP030, NTR 7450, NP010, ETNA 01PP and Sartorius membranes.

	Detection limit	**D0 effluent**	**NP030 permeate**	**NTR 7450 permeate**	**NP010 permeate**	**ETNA 01PP permeate**	**Sartorius (5 kDa) permeate**
Ca [mg/L]	0.1	120	3.15	13.01	34.1	82.8	96.5
Ba [mg/L]	0.002	0.44	0.03	0.05	0.12	0.31	0.47
Fe [mg/L]	0.05	0.46	0.08	0.10	0.15	0.30	0.26
Mn [mg/L]	0.01	2.28	0.10	0.28	0.67	1.58	1.83
Cu [mg/L]	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Na [mg/L]	1	682.5	150	206	267	456	609
K [mg/L]	0.5	19.3	1.34	4.99	8.23	13.03	17.3
TIC [mg/L]	0.2	2.1	2.0	0.25	0.31	0.48	0.45
CO_3 [mg/L]	1	10.5	10	2.4	1.6	2.4	2.2

Table III The detection limits and the mean values for the concentrations received from the external laboratory for the D1 stage effluent and the permeates from its nanofiltration experiments using NP030, NTR 7450, NP010, ETNA 01PP and Sartorius membranes.

	Detection limit	**D1 effluent**	**NP030 permeate**	**NTR 7450 permeate**	**NP010 permeate**	**ETNA 01PP permeate**	**Sartorius (5 kDa) permeate**
Ca [mg/L]	0.1	20.9	3.15	0.76	3.14	9.10	20.4
Ba [mg/L]	0.002	0.16	0.02	0.006	0.03	0.07	0.15
Fe [mg/L]	0.05	0.21	0.21	<0.05	0.07	0.10	0.20
Mn [mg/L]	0.01	0.40	0.09	0.03	0.09	0.19	0.40
Cu [mg/L]	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Na [mg/L]	1	522	157	102	161	270	499
K [mg/L]	0.5	5.03	1.48	0.53	1.01	2.17	4.16
TIC [mg/L]	0.2	1.90	2.05	1.33	2.18	0.85	0.22
CO_3 [mg/L]	1	9.5	10.3	6.7	10.9	4.3	1.1