Impact of pre-treatments on the brightness stability of a conventional and near neutral pH ECF-light bleaching sequence.

A study on Northern Bleached Softwood Kraft and the (OO) Q (OP) D (PO) bleaching sequence.

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Abstract

This is a study on Northern Bleached Softwood Kraft (NBSK) and the (OO) (OP) D/Dn (PO) bleaching sequence. The effects of a xylanase (X), mild acidic (A), DTPA (Q), and a combined DTPA & xylanase (Q+X) pre-treatments have been studied.

The results indicate that the Q+X pre-treatment most effectively reduced the presence of harmful metal ions in the pulp. The Q+X pre-treated pulp yielded the lowest kappa number and highest brightness values among the pre-treatments tested. Chemical analysis of this pulp also shows the highest reduction in xylans and lignin. The mild A stage was not effective in the removal of all essential harmful metal ions and showed no effect on the reduction of xylans or lignin. The X stage cannot meanwhile remove metals and is thus disadvantageous.

Subsequently, the Q+X pre-treated pulp as well as a Q-treated pulp stream were further bleached to study the effects of these pre-treatments on the final pulp quality as well as to compare these streams of pulp bleached using a conventional chlorine dioxide stage (D) and a near neutral pH chlorine dioxide (Dn) stage. The results confirmed that the Dn stage causes a reduced degree of AOX in the effluent. Furthermore, the brightness directly after the chlorine dioxide stage is higher for the Dn-treated pulps but the process is limited with regards to brightness stability which is a significant drawback.

The Q+X (OP) D (PO) bleaching sequence showed the highest brightness stability while the Q+X (OP) Dn (PO) bleaching sequence displayed no improvement over the Q (OP) Dn (OP) bleaching sequence. The conclusion can be made that the enzymatic boost in bleaching is not enough to compensate for the shortcomings of a Dn stage.

Sammanfattning

Syftet med denna studie är att undersöka påverkan av förbehandlingar på ljushetsstabiliteten av Northern Bleached Softwood Kraft (NBSK) som har blekts enligt (OO) (OP) D/Dn (PO) bleksekvensen. Effekten av förbehandling med xylanas (X), mild sur (A), DTPA (Q) samt ett kombinerad DTPA- & xylanassteg (Q+X) har studerats.

Resultaten indikerar att Q+X förbehandligen var mest effektiv i minskningen av skadliga metalljoner i massan. Den Q+X förbehandlade massan hade dessutom lägst kappa och högst ljushetsvärde bland förbehandlingarna. Kemisk sammansättningsanalys av de förbehandlade massorna visar vidare att den Q+X förbehandlingen ledde till den högsta minskningen av såväl xylan som lignin. Det milda A förbehandlingen var inte effektivt för att avlägsna alla viktiga skadliga metalljoner och visade ingen effekt på reduktionen av xylan eller lignin. Den X behandlade massan visade ingen förmåga att ta bort metaller och är därför ofördelaktigt.

Q och Q+X förbehandlade massaströmmar har blekts vidare för att studera effekterna av dessa förbehandlingar på den slutliga massakvaliteten samt för att jämföra ett konventionellt klordioxidsteg (D) och en nästan neutral pH klordioxidsteg (Dn). Resultaten bekräftar att Dn-steget ledder till en reducerad grad av AOX. Ljusheten direkt efter klordioxidsteget är vidare högre för de Dn-behandlade massorna, men processen är begränsad med avseende på ljushetsstabilitet, vilket är en viktig nackdel.

Q+X (OP) D (PO) blekningssekvensen visade den högsta ljushetsstabilitet, medan den Q+X (OP) Dn (PO) blekningssekvensen visade ingen förbättring jämfört med Q (OP) Dn (OP) blekningssekvensen. Slutsatsen är att den enzymatisk medförda kvalitetsförbättringen inte räcker för att kompensera för bristerna i ett Dn-steg.

Acknowledgments

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Abbreviations

(OO)	Two Staged Oxygen Delignification
(OP)	Initial Pressurised H_2O_2 and O_2 stage
(PO)	Second Pressurised H_2O_2 and O_2 stage
An	Acidic Stage
AOX	Absorbable Organic Halides
COD	Chemical Oxygen Demand
D	ClO_2 Stage
Dn	Near Neutral pH ClO_2 Stage
DP	Degree of Polymerisation
DTPA	Diethylenetriamine pentaacetic acid
ECF Light	Elemental Chlorine Free Bleaching Sequence with Low ClO_2 Charges
ECF	Elemental Chlorine Free Bleaching Sequence
EDTA	Ethylenediaminetetraacetic acid
LCC	Lignin-carbohydrate complexes
NBSK	Northern Bleached Softwood Kraft
ODT	Oven Dried Ton
Q	Chelating Agent Stage
Q+X	Combined Chelating Agent and Xylanase Stage
TCF	Totally Chlorine Free Bleaching Sequence
X	Xylanase Stage

Introduction

Wood is a unique, renewable, biodegradable, and versatile raw material. The utilization of forest raw materials predates civilization, and the way communities have utilized this raw material has changed throughout time in tangent with technological progress and societal needs. One of the many products to which forest materials can be processed is pulp which can be used for the manufacturing of various types of papers and textiles (Ek et al., 2009a).

The modern pulp mill can produce a range of biochemicals as well as energy through the use of lignocellulosic biomass, in addition to their main pulp product. The unique biobased & degradable, renewable, and recyclable characteristics of these chemicals place them in a key position in the transition towards reduced fossil fuel use. Consumers as well as policymakers furthermore show a preference for renewable and recyclable materials (Kymäläinen et al., 2022). Pulp mills are however required to function sustainably and incentivized to minimize their environmental impact (Starrsjö, 2021).

Softwoods are the most common source of feedstock for Scandinavian mills (Ek, et al., 2009b), and as many pulp and paper applications require or prefer bleached pulp, over 70% of the produced kraft pulp is bleached (Starrsjö, 2021). The pulping and bleaching process for pulp is the process in which wood or other lignocellulosic inputs are transformed away from their original natural form with certain chemical components separated and removed, yielding a white and cellulose-rich pulp. Fully bleached pulp is less susceptible to aging, softer, cleaner, and with minimal impact on the taste and smell (Ek, et al., 2009b).

Biomass → Debarking and Chipping → Pulping → Bleaching → Drying
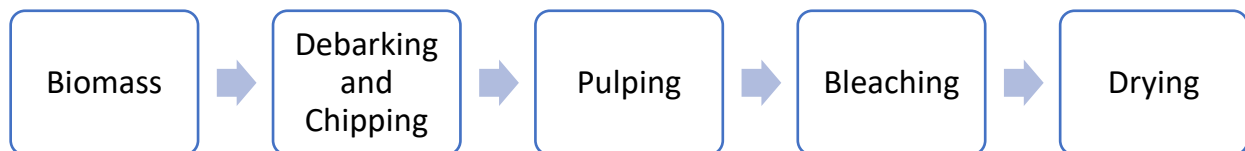
Figure 1 - Overview of the Manufacturing Process

Today, pulp is generally bleached through a combination of bleaching stages utilizing chlorine dioxide, ozone, and hydrogen peroxide which are considered environmentally friendly. The bleaching of pulp however leads to effluent that is harmful to the environment and that requires treatment before release to recipients (Ek, et al., 2009b).

When chlorine and chlorine derivates are used for bleaching, they give rise to a certain level of AOX pollution per tonne of pulp produced. However, the phasing out of elemental chlorine bleaching in favor of chlorine dioxide or TCF methods has led to a significant reduction in AOX per tonne pulp in Sweden (Sandström et al., 2016).

Although bleaching through TCF methods does not result in AOX pollution the bleaching of pulp using TCF methods yields different pulp characteristics than the more selective and still environmentally friendly ECF bleached pulp, indicating that ECF bleaching still has a role to play (Suhr et al., 2015). However, with industrial winds pointing towards larger pulp mills the pollution caused by ECF bleaching can become significant even though low pollution is produced per tonne (Starrsjö, 2021).

Thus, there has been a further effort towards the reduction of chlorine dioxide use in the overall bleaching system, known as ECF-light (Hart & Rudie, 2012). This causes a significantly lower AOX footprint as opposed to conventional three-stage chlorine dioxide bleaching systems for example, as less chlorine dioxide is employed.

Near neutral pH, chlorine dioxide bleaching has also been shown to reduce the AOX as well as improve the brightness of the pulp. This is due to the reactions between chlorine dioxide and the pulp suspension which is pH-dependent and thereby allowed to be controlled through the use of a buffer system (Starrsjö, 2021).

These modifications to the bleaching stage and system however change the characteristics of the bleached pulp. A study conducted on the ECF light bleaching sequence of (OO) (OP) D (PO) with a near neutral pH chlorine dioxide stage shows some limitations with regards to for example the brightness stability of the pulp compared to reference pulp bleached through a conventional chlorine dioxide stage. This difference is attributed to the persistence of hemicellulose-linked oxidizable structures in the pulp, namely hexenuronic acids (Starrsjö, 2021).

Hexenuronic acid side groups of xylans are formed during kraft cooking through the elimination of methanol and are shown to be a key accelerator of brightness reduction, the phenomenon whereby the color and quality of the pulp degrades with time and exposure to heat and humidity (Li, et al., 2002). Hexenuronic acids are stable in alkali environments and cannot be fully removed through the use of hydrogen peroxide and oxygen (Ek, et al., 2009b), and a recent study shows also near neutral pH chlorine dioxide treatments (Starrsjö, 2021).

The research suggests the use of enzymes or acidic pre-treatments to reduce the levels of xylan in the pulp and thus the hexenuronic acid content (Starrsjö, 2021). An acid treatment would theoretically enable the removal of hexenuronic acids which are more removable at acidic pH but a harsh acid treatment would also target the carbohydrates including the cellulose components of the pulp reducing fiber viscosity which is an important characteristic for softwood pulp (Ek, et al., 2009b).

Enzymes such as xylanase can be used to target the xylan components in the pulp and thereby reduce the hexenuronic acid content. The use of enzymes would be environmentally friendly as well as cost-effective and would not require any energy input (Buchert et al., 1994) (Viikari et al., 1996) (Chaurasia & Bhardwaj, 2019).

The use of pre-treatments to improve the brightness stability of softwood kraft pulp bleached according to the (OO) (OP) D/D_n (PO) is the topic of this study. This leads to the research questions presented below.

Research Question

The research question for this thesis is: Can the brightness stability of (OO) (OP) D_n (PO) bleached softwood pulp be improved through the use of a xylanase or a mild acidic pre-treatment?

Aim

This project aims to study the (OO) (OP) D (PO) bleaching system through experimental and theoretical analysis and to assess the impact of pre-treatments on pulp properties such as the brightness and brightness stability of the pulp.

For this project pulp, will be pre-treated with a chelating agent (as reference), xylanase, a combined chelating agent, and xylanase treatment as well as a mild acidic treatment and analyzed. The pre-treated pulp showing the most promising capability will be further bleached according to the (OO) (OP) D (PO) and (OO) (OP) Dn (PO) bleaching sequence and the impact on process and pulp characteristics will be analyzed.

Theory
Kraft Pulp

Pulp is a valuable intermediate product, manufactured at large industrial sites called pulp mills from the lignocellulosic materials of wood and annual plants. The pulp industry uses a variety of processing methods to obtain pulp, these methods have historically been either through harsh thermo-chemical, mechanical processes, or a combination of both and can be seen as a method of controlled and selective decomposition of the biomass (Ek et al., 2009b).

The kraft process developed in 1879 in Germany by Dahl has become an industrial staple due to its efficiency, and the strength of the produced pulp. Disadvantages as compared to other pulping methods include lower pulp yields, malodorous emissions, and enhanced bleaching requirements. The process was industrially introduced in the year 1890 in Sweden (Bajpai, 2018).

The efficiency is through an established chemical recovery and recycling system during which spent liquor and cooking chemicals are recycled, as well as the ability to utilize the dissolved segments of the wood during cooking for steam (Bajpai, 2018) (Ek et al., 2009b) and via the introduction of a steam turbine also electricity production (Siemens Energy, 2022).

Hydrogen sulfide is the main delignification agent while sodium hydroxide contributes is keeping the dissolved fragments of lignin in the solution. Lignin is a large hydrophobic polymer made up of the monolignol monomers shown in Figure 2. Hydrogen sulfide ions fragment the lignin by cleaving the β-O-4 linkages and hydroxyl groups are introduced to make it soluble as shown in Figure 3. Kraft chemical pulping is however not fully selective to lignin, with the process also degrading valuable carbohydrates in the wood fibers (Bajpai, 2018) (Ek et al., 2009b).
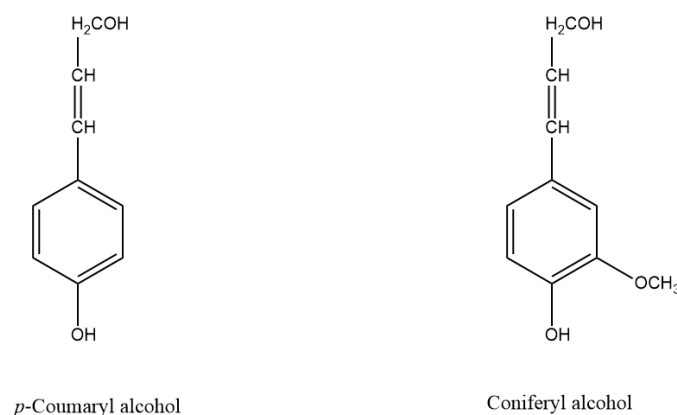

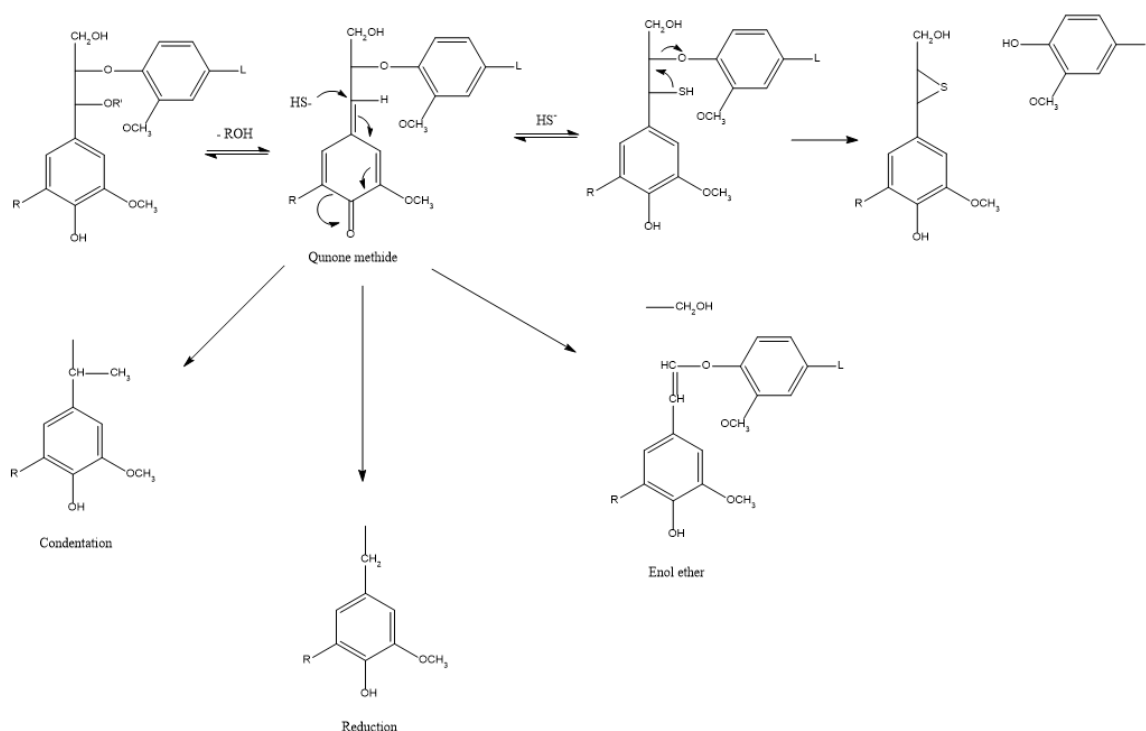*Figure 2- Softwood Monolignols (Ek et al., 2009a)*

Figure 3 - Depolymerisations of Lignin through β-O-4 Bond Cleavage (Ek et al., 2009b).

The kraft process is shown to work in three phases, including an initial, bulk, and final stage. The process is terminated before full delignification as the selectivity decreases once approximately 90% of the lignin is removed after the bulk depolymerization stage. The pulp at this stage is a dark brownish color and is highly susceptible to quality deterioration due to the presence of oxidizable structures such as residual lignin and hexenuronic acid (Ek et al., 2009b).

The Properties of Kraft Pulp

The thermo-chemical treatment leads to the modification of the natural polymers found in wood. The cooked wood chips are darker, physically softer, and chemically altered. During the kraft process, a large segment of the lignin is degraded and removed (Ek et al., 2009b).

The carbohydrate components of the cell wall notably the hemicelluloses and cellulose are furthermore also degraded to a certain degree and removed during kraft cooking. In the case of softwoods, the glucomannan component of hemicellulose is shown to be significantly reduced (Ek et al., 2009b).

With the bulk of the lignin removed, approximately +90% of the remaining lignin in softwoods is covalently bonded to carbohydrates. The kraft cooking process also leads to the formation of hexenuronic acid from hemicellulose xylan in the pulp which has detrimental effects on the pulp quality (Ek et al., 2009b).

Hexenuronic acid side groups of xylans are created during kraft delignification as methanol is eliminated from the 4-O-methyl glucuronic acids of xylan as shown in the figure below (Bajpai, 2018). Research furthermore suggests that due to the higher ingoing xylan content of hardwoods, more hexenuronic acids can be observed in hardwoods than in softwoods (Gellerstedt, 2007).
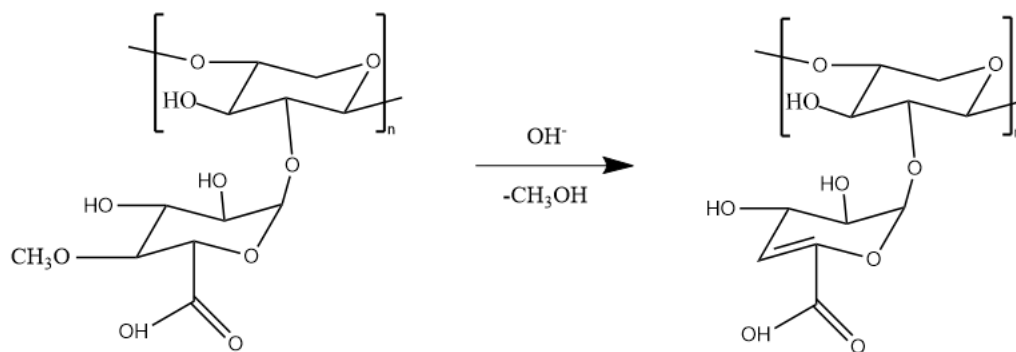
4

Figure 4 – Formation of Hexenuronic Acid from a Xylan chain with a 4-O-Methylglucoronic acid group (Ek et al., 2009b)

The Bleaching of Kraft Pulp

Unbleached Kraft pulp has a dark brown color mainly due to chromophores from residual lignin. It can furthermore contain shives, extractives, and dirt. The bleaching of pulp renders a brighter, whiter, and cleaner pulp with a higher cellulose content but also causes a reduced yield. This is critical for applications where for example:

- A good printing surface is desired.
- For packaging applications where the use of unbleached pulp would contaminate the smell and taste of the product being packaged.
- For sterile packaging applications where cleanliness is important.
- For pulp destined for biorefining applications.

(Bajpai, 2018) (Ek et al., 2009b).

As pulp is bleached certain hemicelluloses and residual lignin as well as dirt and shives are removed. To reach brightness, brightness stability, and cleanliness requirements the pulp is treated to remove the remaining lignin through further depolymerization and extraction. Furthermore, colored structures originating from bark, extractives, or carbohydrate derivates are to be removed through chemical treatments, although enzymes can also be used as a part of this process (Bajpai, 2018) (Ek et al., 2009b).

The bleaching of the pulp can be performed in several ways and conducted through a series of acidic and alkaline bleaching and washing stages. Bleaching however can also cause degradation of carbohydrates which is detrimental to yield and preferably reduced as much as possible (Bajpai, 2018) (Ek et al., 2009b). Technology developments during the late stages of the last century enabled the shift away from elemental chlorine bleaching with the implementation of TCF, ECF as well and hybrid bleaching systems (Gellerstedt, et al., 1995).

Oxygen Delignification

As the kraft pulping operation proceeds its selectivity gets reduced and thus it is advantageous to terminate the kraft process before all the lignin is removed to preserve production yield. Pulp bleached via early termination of the kraft and then oxygen delignified show a higher viscosity than pulp cooked until the same corresponding kappa number, meaning it functions more selectively (Ek et al., 2009b).

Oxygen delignification targets phenolic lignin molecules and causes depolymerization reactions. O_2 is a bi-radical with low solubility in water (Ek et al., 2009b). The oxygen delignification stage aims to reduce the kappa number of the pulp and thereby reduce the need for expensive and potentially toxic bleaching stages. Oxygen delignification causes an increase in the pulp brightness (Bajpai, 2018). This stage has become very common industrially ever since the addition of magnesium was shown to improve selectivity and is furthermore considered cheap and environmentally friendly as the effluent filtrate from the operations can be recycled (Ek et al., 2009b) (Hart & Brown, 2017).

Hydrogen Peroxide

Hydrogen peroxide can also be used in the bleaching of kraft pulps. This stage is alkaline and can be conducted with O_2 which would also pressurize the stage. Hydrogen peroxide can react with the residual lignin causing a delignification effect as well as react with chromophores present in the pulp suspension to brighten the pulp depending on its placement along the bleaching sequence (Ek et al., 2009b). Hydrogen peroxide bleaching stages play an important role in TCF bleaching sequences and also play a prominent role in ECF light bleaching sequences. An increase in temperature boosts the bleaching ability of hydrogen peroxide and employing a temperature of over 95°C would require pressurization (Hart & Rudie, 2012).

Once added to the pulp suspension, the hydrogen peroxide reacts through two main chemical reactions. The first reaction pathway is with the pulp yielding brightness improvement, where the HO_2^- anion reacts as a nucleophile with chromophores and phenolic lignin. The other reaction pathway is with itself, thereby it decomposes into water and oxygen. The decomposition of the hydrogen peroxide takes place in alkaline conditions and is catalyzed through the presence of the metal ions of manganese, iron, and copper. The degradation of hydrogen peroxide due to for example the presence of transition metal ions can cause the formation of hydroxyl radicals which can target nonphenolic compounds that can be seen as positive but are also damaging to the cellulose which is highly undesirable (Ek et al., 2009b) (Starrsjö, 2021).

As the presence of manganese, iron, and copper transmission ions is harmful for this process stage. It is thus common for pulps to be treated with a chelating agent before a hydrogen peroxide stage. Furthermore, the addition of magnesium ions to the suspension can improve the selectivity and this is thus added to the suspension along with the bleaching chemicals (Starrsjö, 2021) (Hart & Brown, 2017).

Metal Management

Metal ions are present in all woods and plants and if left unmanaged the manganese, iron, and copper ions will react to decompose H_2O_2 creating a costly situation whereby the bleaching agent is degraded before the pulp is sufficiently bleached (Ek et al., 2009b).

Metals in pulp can be removed through a series of methods, such as the sodium salts of ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) which are industrially utilized for their ability to bind these transition ions to themselves, facilitating their removal in subsequent washing operations (Ek et al., 2009b).

The creation of an acidic environment could also allow for the removal of metals from the pulp suspension. These conditions can be obtained through the use of an acidic chlorine dioxide stage in the bleaching sequence or generated acidic conditions (Hart & Rudie, 2012).

Bleaching with ClO_2

The ClO_2 stage has seen wide-scale application since the phasing out of elemental chlorine bleaching. Initially introduced due to its reducing agent qualities it can protect the carbohydrates

from peeling reactions with its radical scavenging ability. The D stage is effective in removing residual lignin and the reactions between ClO_2 and the pulp suspension will create an acidic environment which is beneficial for the removal of metals, as well as certain carbohydrates with oxidizable structures such as hexenuronic acid (Ek et al., 2009b) (Li et al., 2002).

ClO_2 is an electrophilic oxidant that can degrade both phenolic and non-phenolic lignin structures, hexenuronic acids as well and aromatic rings in residual lignin. An alkaline wash after the stage is required to remove the oxidized and fragmented components of the lignin in the pulp (Starrsjö, 2021).

The use of a chlorine derivative however causes the same type of pollution in mill effluent discharges as elemental chlorine (AOX) albeit at reduced levels per tonne of pulp produced. This creates the need for effluent stream separation and additional wastewater treatment to reduce the AOX content of wastewater before discharge (Suhr et al., 2015) (Starrsjö, 2021).

A bleaching sequence may contain one or more ClO_2 bleaching stages (Hart & Rudie, 2012). Mills that are eager to reduce AOX can seek to reduce the charge of the bleaching chemical used in each stage, reduce the number of ClO_2 stages in a given bleaching sequence, as well as to consider the placement of the stage within the sequence set-up.

The reactions of the ClO_2 with the pulp suspension are highly pH-dependent. The pH at which the stage is generally conducted is between 3.5 and 4. At pH ranges below 3, HOCl and Cl_2 are formed which is detrimental for AOX formation which arises from their reactions with residual lignin and hexenuronic acids. At higher pH ranges the delignification ability of the stage is reduced while brightness gain-inducing reactions are more common (Starrsjö, 2021) (Hart & Connel, 2008).

With the pH of the chlorine dioxide bleaching stage being important there is interest in controlling it for process optimisation. Mills can use NaOH and H_2SO_4 for pH regulation but there have also been studies that use buffer solutions as a cheaper alternative. The brightness gain can furthermore reduce the amount of chemicals required in the bleaching and thus reduce the AOX as well as ClO_2 demand (Starrsjö, 2021) (Jiang & Berry, 2008).

Near Neutral D pH stage
The pH of the Chlorine dioxide stage can be controlled through the addition of OH^- with NaOH added to the process or through the use of a buffer. The control of the pH allows practitioners to control the reaction environment and steer the reactions away from higher AOX-producing reactions which take place at lower pH ranges. The reactions between the pulp and chlorine dioxide at near neutral pH are furthermore shown to increase the brightness of the pulp which could result in chemical and energy savings for mills (Starrsjö, 2021) (Jiang & Berry, 2008). A near-neutral pH ClO_2 stage cannot however as effectively remove hexenuronic acids from the pulp suspension as these substances require lower pH treatments to be removed as shown in a recent study by Starrsjö (2021).

Jiang & Berry (2008), Ribeiro (2014), and Starrsjö (2021) show that near-neutral pH conditions could be obtained through the addition of CO_2 to the pulp suspension. This works by the in-situ creation of bicarbonate which acts as a buffer for the pH regulation of the system. The use of CO_2 is particularly interesting as it could provide mills with incentives to implement carbon capture and storage systems which could be possible due to the abundance of energy in for example non-integrated pulp mills.

The use of CO_2 to create a near-neutral D stage has been studied and works through the following buffer reaction.

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows HCO_3^- + H^+ \qquad (1)$$
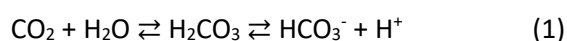
Xylanase
Xylanase is an enzyme that targets xylan chains in the hemicellulose component of the pulp. Xylanase treatment is seen as a cheap, environmentally friendly, and process-compatible bleaching booster. Mill trials run since the late 80's have proven its benefit, with numerous mills currently routinely employing the technology. Xylanase treatment can improve the bleachability of pulp which would in turn lead to reductions in bleaching chemical use and requirements which would yield direct financial as well as environmental benefits (Lundgren et al., 1994) (Ek et al., 2009b) (Viikari et al., 1996).

Xylanase can be said to function through the facilitation of the removal of hexenuronic acids and lignin bound to xylans by cleaving the xylan chains as well as facilitating the removal of residual lignin which may be entrapped by precipitated xylans. These improvements cause a reduced kappa number as hexenuronic acids and lignin are removed while at the same time improving the accessibility of bleaching chemicals and boosting bleachability (Ek et al., 2009b) (Roncero et al., 2000).

One key limiting factor is that the biological enzyme is not fully compatible with the harsh thermal and chemical conditions of kraft delignification (Ek et al., 2009a) (Viikari et al., 1996). Another limitation is that xylans which are carbohydrates are a component of the pulp yield and have been shown to contribute to the strength properties of the pulp and their complete removal could be seen as unwanted due to this. The enzymes are furthermore larger as compared to chemicals and cannot thus as effectively penetrate internal structures of the cell wall which will limit some of its effectiveness and limit it to a more topical effect.

Brightness Stability
The brightness of fully bleached pulp is reduced due to aging or exposure to heat, UV light, and humidity (Starrsjö, 2021). This effect will reduce the lifecycle of the pulp as well as cause issues during storage and shipping. Thus, the brightness stability of the pulp is a key characteristic of its application, storage, and lifecycle (Ek et al., 2009b).

Brightness reduction is attributed to the oxidizable structures in the pulp which are characterized as residual lignin, carbohydrates, as well as hexenuronic acids, which are shown to play a significant role in brightness reduction, as well as other oxidizable structures in the pulp. Transition metal ions furthermore play an important role in accelerating brightness loss (Buchert, et al. 1997) (Li, et al., 2002) (Starrsjö, 2021).

Hexenuronic acids are especially harmful to the brightness stability as during degradation into further oxidizable structures, hexenuronic acids furthermore are metal chelators and will release transition metal ions (Sevastyanova, et al. 2006).

TCF-bleached hardwoods show the highest degree of brightness reduction due to the limitation of these processes to effectively remove hexenuronic acids unless an ozone stage is employed as well as the higher xylan contents in the original biopolymer makeup which would naturally increase the hexenuronic acid content of these pulps. Softwoods have a lower degree of xylan in the original biopolymer make-up of natural wood, but hexenuronic acids are still prevalent in softwood pulps and cause issues with brightness stability (Li, et al., 2002) (Starrsjö, 2021) (Ek et al., 2009b).
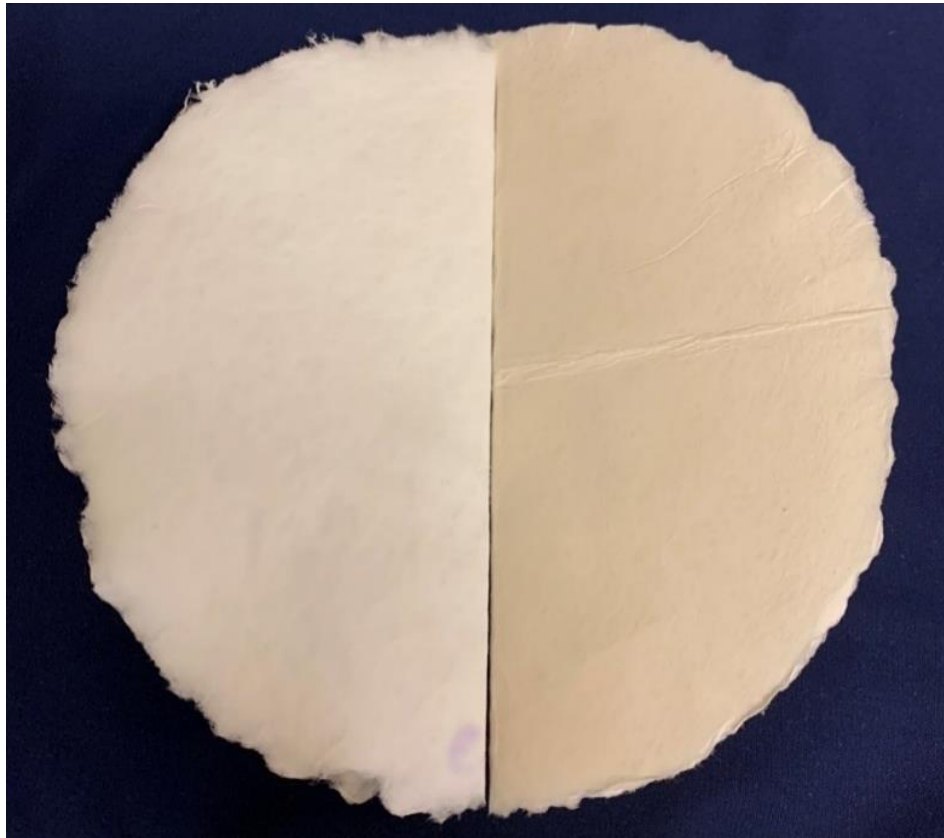
Figure 5- The effects of brightness reduction. The sample on the left is fully bleached pulp before brightness reduction and the right-hand side is after brightness reduction in a sealed environment within polyethylene bags and aged in a pre-heated water bath at 70° C for 10 days according to a method by Sevastyanova (2005).

Method

Pre-treatments

Industrial kraft and oxygen-delignified northern softwood pulp were kindly provided by SCA and constitute the raw material for this project. The pulp was washed on-site at the time of extraction as well as after transportation to the laboratory.

Pre-treatments were conducted according to the following laboratory parameters.

Table 1 – Laboratory Parameters for Pre-treatment

	Q	Q+X	X	A
H_2SO_4	0.24%	0.24%	-	Variable
DTPA	0.27%	0.27%	-	-
Xylanase	-	0.0025%	0.0025%	-
Time	60 min	60 min	20 min	30 min
Temp	90° C	87° C	87° C	25° C
Consistency	10%	10%	10%	3%
Final pH	6-6.4	6.7	8.9	3.0

The Q, Q+X, and X stages were conducted in preheated water baths. The chemicals were added to the pulp suspension in polyethylene bags which were sealed and mixed thoroughly using a mixer.

The xylanase used is a commercially available xylanase kindly provided by Novozymes which is heat and alkali resistant. The dosage of 0.0025% was decided upon to minimize the loss of xylans which are important to the yield. Furthermore, the temperature of 87° C was chosen for the Q+X stage to understand its compatibility with the current industrial Q stage, as well as to test the upper boundaries of the heat-resistant xylanase enzyme. However, due to a tendency of the water bath to lay ±3 °C of the input temperature the temperature of 87° C as opposed to 90° C was decided upon.

The low consistency mild acidic stage was conducted in a plastic container, mild acidic conditions and room temperature were chosen to reduce the risk of depolymerization of cellulose.

Further bleaching

Further bleaching was conducted in the laboratory according to the parameters displayed below, and according to the following bleaching sequences:

Q (OP) D (PO)

Q (OP) Dn (PO)

Q+X (OP) D (PO)

Q+X (OP) Dn (PO)

Table 2 - Laboratory Parameters for Further Bleaching

	(OP)	D	Dn	(PO)
O_2	0.5 MPa	-	-	0.5 MPa
NaOH	1%	-	-	1%
$MgSO_4$	0.1%	-	-	0.1%
ClO_2	-	0.76%	0.76%	-
$NaHCO_3$	-	-	2.5%	-
H_2O_2	0.6%	-	-	0.3%
Time	120 min	60 min	60 min	140 min
Temp	95° C	70° C	70° C	100° C
Consistency	12%	12%	12%	12%
Final pH	11-11.3	2.2-2.5	6.7-6.9	10.6-11.6

Pressurized Hydrogen Peroxide

The pressurized hydrogen peroxide stages were conducted in Teflon-coated autoclaves and inserted and rotated into a pre-heated polyethylene glycol (PEG) bath.

Chlorine dioxide

The chlorine dioxide stages were conducted using industrially sourced chlorine dioxide with a 7.9 grams per liter concentration. These steps were conducted in pre-heated water baths and sealed double polyethylene bags.

For the near neutral pH chlorine dioxide stages the buffering agent $NaHCO_3$ was selected for use instead of CO_2 which would have in-situ created the buffering agent, as the in-situ method of CO_2 addition to pulp has already been proven to work and the use of $NaHCO_3$ reduces the complexity as well as logistical requirements of this bleaching step.

This project will use a buffer, the dosage of which would equal the final release of 10 kg CO_2 per ODT pulp if a complete reaction were to be assumed where all of the CO_2 had been converted into a buffer on a molar basis. The buffering agent is added in liquid form and prepared with laboratory-grade $NaHCO_3$.

Analysis

Chemical component analysis was conducted according to SCAN-CM 71:09 to assess the effects of the chemical treatments on the biopolymers in the pulp. This analysis allows for a comparison and analysis of the ability of the pre-treatments to remove oxidizable structures in the pulp such as lignin as well as indirectly, hexenuronic acids.

Metal analysis was conducted through Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) to understand the effects of the metal removal from the pre-treatments as the metal content of the pulp enters further bleaching. Copper, Iron, and Manganese content in the pulp are to be measured and analyzed.

The brightness of the pulp is measured according to ISO 3688 (1999) through hand sheets and brightness measurements using an L&W Elrepho instrument. The brightness of the pulp can be an

indicator of the delignification and bleaching ability of each bleaching sequence and thus indicates how effective the stages have been.

The brightness stability measurement is another method of measurement employed in this project, as the brightness values alone can be misleading for comparison of different bleaching methods. Assessment has been done on pulp stored in a sealed environment within polyethylene bags and aged in a pre-heated water bath at 70° C for 10 days according to a method by Sevastyanova (2005). The brightness stability has furthermore been studied through the Tappi UM-200 method, conducted by placing hand sheets in a 105° C oven for 4 hours with the brightness values pre- and posttreatment compared.

The kappa number is another important metric for pulp quality and is measured as per ISO 302 (2004). Permanganate is used to assess the presence of oxidizable structures in the pulp with the kappa number indicating the content of oxidizable structures. The kappa number conveys a value correlating to the lignin, false lignin, and non-lignin oxidizable structures content of the pulp and is important for the assessment of pulping and bleaching effects. To measure the kappa number at certain ranges is however a resource-intensive measurement, thus kappa has only been measured for the initial bleaching stages of the pulp.

The COD values in the bleaching filtrate have also been studied using HACH LCK114 COD cuvette test-kit analysis as an indicator of organic content loss to monitor any process issues as well as to assess the effectiveness of the treatments.

AOX values from the chlorine dioxide stages have been measured using Hach Lange LCK 390 cuvette analysis kits. The purpose of these measurements was to assess the effects of the near-neutral pH chlorine dioxide stages as well as to confirm the reduced AOX potential from using a near-neutral pH stage.

The viscosity is a common analytical method employed by the pulp industry to indicate the degree of polymerization of the cellulose and was conducted in this project as per ISO 5351-2010 using a cupri-ethylenediamine (CED) solution.

Results & Discussion

Effects of Pre-Treatments on Chemical Composition

The chemical composition analysis conducted on the initial, untreated pulp as well as pulps having undergone pre-treatments are displayed in the table below.

Table 3 – Chemical Composition Results

Component	Ref.	Pre-treatments			
	(OO)	Q	A	Q+X	X
Lignin	1.9%	2.0%	2.1%	1.5%	1.6%
Xylan	9.1%	9.0%	9.1%	8.4%	8.6%
Galactogluco-mannan	0.3%	0.3%	0.3%	0.3%	0.3%
Glucomannan	5.6%	5.5%	5.6%	5.6%	5.6%
Cellulose	83.2%	83.2%	83.0%	84.1%	84.0%

From the data, it can be observed that the xylanase treatment is effective at the conditions chosen for this project as the xylan contents are reduced for the xylanase-treated pulps which indicate partial removal of xylans and in turn also reduces hexenuronic acids. Furthermore, the delignification effect can be observed through the reduction in lignin content in the xylanase-treated pulps as opposed to the initial reference as well as chelating agent and mild acid pre-treated pulps.

Additionally, it can be observed that the chelating agent does not inhibit the xylanase and that they are co-compatible. It can furthermore be observed that the mild acid treatment is not effective against hexenuronic acid side groups as no significant reductions in xylan can be observed.

Effects of Pre-treatments and (OP) on Kappa

The values obtained from kappa measurements are displayed below and re-enforce the data from the chemical analysis by displaying a reduction of kappa for pulps treated with xylanase, as well as a persisting kappa boost for the subsequent hydrogen peroxide-treated pulps which also show a lower kappa number as opposed to the chelating agent treated pulp. A significant reduction in kappa cannot however be seen from the mild acid pre-treatment.

Table 4- Effects of Pre-treatments and (OP) on Kappa

Pulp Sample	Kappa
(OO)	10.6
Q	10.1
A	10.0
Q+X	8.8
X	9.3
Q (OP)	6.3
Q+X (OP)	6.2

Effects of Pre-Treatments on Metals

The metal analysis results are displayed in the table below. The results reveal that the Q+X stage is the most efficient at removing the metals compared to the other pre-treatment steps. This can be due to the ability of xylanase to facilitate a greater activity area for the chelating agent, or due to the removal of hexenuronic acids which are metal chelators.

The mild acidic stage shows some effectivity in the removal of Mn; however, it cannot remove Fe ions. The xylanase treatment on the other hand shows no major significant ability to remove metals showing only a slight reduction in manganese content.

Table 5 - Metal Analysis Results (mg/kg)

Pulp Sample	Cu	Fe	Mn
(OO)	<2,1	6.6	64
Q	<2,1	3.3	3.1
Q+X	<2,1	2.5	2.5
X	<2,1	7.8	59
A	<2,1	7.2	12

## Effects of Pre-Treatments and Further Bleaching on Pulp Brightness

The brightness measurements from hand sheets are displayed below. The results show a mild increase from the Q+X pre-treatment which can be attributed to the stages' ability to facilitate the removal of carbohydrate-bound or entrapped residual lignin and hexenuronic acid. The chelating agent and mild acidic treatment furthermore show a very slight increase in the brightness which can be attributed to the increased washing of the pulp. Due to the results from the other analysis and limited time, the decision was taken to not create hand sheets for the X pre-treated pulp and to instead focus efforts on the Q+X sequence.

Table 6 – Brightness Results

Pulp Sample	% ISO Brightness
(OO)	43.17
Q	46.72
Q+X	49.04
A	46.9
X	N.A.

As for the brightness of the pulps having undergone further bleaching the following results have been obtained and displayed below. From the data, it can be observed that as stated above the Q+X treatment provided a brightness boost. Furthermore, it can be observed that the near-neutral chlorine dioxide stage provides a further boost to brightness when compared to the conventional chlorine dioxide stage.

The gained benefits in brightness after each stage are accumulative and the xylanase-treated pulp sequences seem to preserve the brightness advantage following subsequent treatment. This phenomenon however seems to disappear at the final stage where although the pulps are all treated similarly and with different ingoing brightness, the final brightness values fail to show preservation of the process long boost in brightness from the xylanase as well as near neutral pH chlorine dioxide treatment.
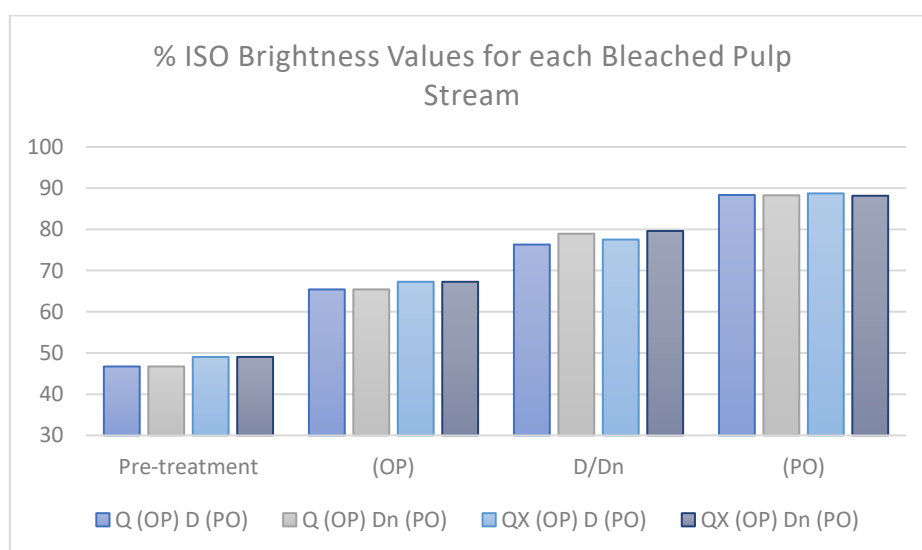
Figure 6 – % ISO Brightness Values for Pulp Sequences.

Effects on the Brightness Stability of the Fully Bleached Pulp

The brightness stability values obtained through heat-induced post-treatments of fully bleached pulps are displayed below for each of the methods of analysis. The Post-Colour (PC) number is an indication of the brightness stability with a higher value indicating reduced brightness stability.

Table 7 – Brightness Stability Results from Sevastyanova's (2005) method.

Bleaching Sequence	Initial (%ISO)	Final (%ISO)	% Reduction	PC number
Q (OP) D (PO)	88.3	79.8	10%	1.78
Q (OP) Dn (PO)	88.3	68.9	22%	6.25
Q+X (OP) D (PO)	88.7	80.6	9%	1.63
Q+X (OP) Dn (PO)	88.2	68.6	22%	6.41

Table 8 – Brightness Stability Results from the Tappi UM-200 Method

Bleaching Sequence	Initial (%ISO)	Final (%ISO)	% Reduction	PC number
Q (OP) D (PO)	88.1	86.2	2.2%	0.31
Q (OP) Dn (PO)	89.8	87.4	2.7%	0.33
Q+X (OP) D (PO)	89.1	87.4	1.9%	0.24
Q+X (OP) Dn (PO)	88.1	85.8	2.7%	0.38

The values from the two measurement methods are consistent with each other and indicate that the conventional chlorine dioxide stage is significantly more effective for brightness stability. The Q+X boosted conventional chlorine dioxide process shows the lowest post-colour number indicating the best brightness stability which could point towards chemical and power savings potential for pulp mills, due to the ability to potentially reduce the need for intensive bleaching.

A surprising revelation is that the Q+X (OP) Dn (PO) sequence shows the highest post-colour number among the sequences indicating the lowest brightness stability which appears to indicate that the xylanase treatment at the chosen dosage cannot remove hexenuronic acids to offset the limitations of the near neutral D stage when used as a pre-treatment.

Effects on COD

The COD, which is an indicator of the organic content in the effluent has been measured in the effluent of each bleaching stage. The COD value can be used to analyze bleaching stages by allowing an estimate of the bleaching effectivity. From the data obtained, it can be noted that the xylanase pre-treatments yield a significantly higher value of COD as opposed to the chelating agent treatment.

It can furthermore be observed that the COD value is higher after the first peroxide stage for the xylanase-boosted pulp which could be attributed to a boost in bleachability allowing for more substances to be reached by the bleaching chemicals and removed.

This trend cannot be seen for the subsequent chlorine dioxide and final hydrogen peroxide stages. As for the chlorine dioxide stages, it seems as though the COD is slightly lower for the near-neutral stages compared to the respective conventional bleaching stages. This can be attributed to the reduced bleaching effect of the near-neutral chlorine dioxide stage which although led to a higher brightness compared to the conventional chlorine dioxide stage cannot remove lignin and hexenuronic acid groups as effectively.

Table 9 – COD kg/ODT for each Pulp Sequence.

Bleaching Sequence	COD kg/ODT
Q (OP) D (PO)	28.6
Q (OP) Dn (PO)	30.1
Q+X (OP) D (PO)	38.5
Q+X (OP) Dn (PO)	36.6

From the COD values for the entire process, it can be noted that although a higher degree of organic materials has been removed during the bleaching process of the Q+X it fails to convert into brightness stability.
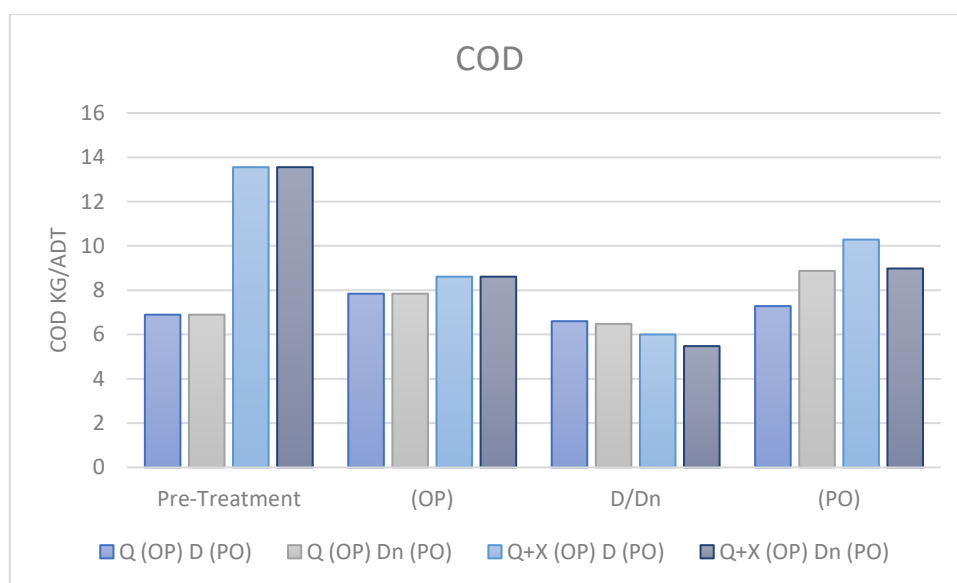

Figure 7 – COD kg/ ODT Development during Process

Effects of Near Neutral pH Chlorine Dioxide Bleaching on AOX

The values of AOX measurements of the pulp effluent are shown below. The measurements indicate an approximately 30% reduction in AOX values from the near neutral pH chlorine dioxide stage as opposed to the conventional chlorine dioxide stage, confirming the studies on the AOX reduction potential through pH regulation of the chlorine dioxide stage.

A further observation that can be made is that the AOX values are lower for the xylanase-treated pulp when compared to the pulp streams without xylanase the differences are however to a lower degree.

Table 10 - AOX kg/ODT values.

Bleaching Sequence	AOX kg/ ODT	Difference
Q (OP) D	0.19	31%
Q (OP) Dn	0.13	
Q+X (OP) D	0.17	29%
Q+X (OP) Dn	0.12	

Effects of Full Bleaching on the Viscosity

Viscosity data measurements on the fully bleached pulp streams are displayed below. The viscosity measurement can be used as a good indicator for assumptions on the bleaching stages as a method for the cellulose degree of polymerization.

The data here shows similar values for the intrinsic viscosity for each process sequence. It can be observed however that the xylanase-treated pulp streams show marginally lower values. There is furthermore a marginal difference between the pulps having undergone conventional and near-neutral pH chlorine dioxide bleaching.

Table 11 – Results from Viscosity Analysis on Fully Bleached Pulp from each Sequence.

Bleaching Sequence	Viscosity (ml/g)
Q (OP) D (PO)	799
Q (OP) Dn (PO)	811.5
Q+X (OP) D (PO)	797
Q+X (OP) Dn (PO)	800

Conclusion

To summarise the results and discussion it can be noted that a pre-treatment with xylanase together with a DTPA chelating agent successfully causes a reduction in the kappa number and boosts the brightness by reducing the amount of xylans and in turn hexenuronic acid groups in the pulp, as well as some lignin while also reducing the metal content.

The pulp stream having undergone a xylanase boosted pre-treatment and a conventional D stage shows the highest brightness stability among the tested sequences. This boost does however not convert into improvements for the Q+X (OP) Dn (PO) pulp stream as it seems that the xylanase treatment is not enough to compensate for the brightness stability shortcomings arising from using a Dn bleaching stage, which although results in lower AOX loads in the effluent and initially leads to a brightness boost over the conventional D stage, leads to brightness stability issues.

This can be because a low dosage of xylanase was applied and a higher degree of dosage might lead to some improvement as more xylan and in turn hexenuronic acids and lignin would be removed. Furthermore, the bleaching sequence in question would lack an acidic stage if Dn were to be used which could be a reason for the brightness stability issues with a Dn stage thus might be better suited for processes with more than one D stage where hexenuronic acids could be more effectively removed.

Further Research

For further analysis, it would be interesting to investigate the chemical functional group characteristics of the pulp using for example FTIR to better understand the development after each stage and to better understand the reasons for the brightness reduction. It would furthermore be interesting to compare the effects of this thesis to the application of xylanase at the end as a post-treatment as the prior bleaching would have increased the accessibility for the xylanase enzymes as well as reduced any risk where the xylanase-treated surface of the pulp gets degraded during bleaching reducing its effect.

Furthermore, it would be interesting to see the effects of a xylanase boosted pre-treatment on other bleaching sequences such as those with more than one chlorine dioxide stage as well as an alternatively placed chlorine dioxide stage along the sequence. Another interesting analysis would be to regulate the dosage of bleaching chemicals in each stage after the pre-treatment with xylanase and DTPA to assess the chemical savings potential that can be utilized.

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