IMPACT OF DEGREE OF SULPHONATION OF LIGNOSULPHONIC ACID ON MOLECULAR WEIGHT DISTRIBUTION OF SPENT LIQUOURS

by

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Submitted in fulfilment of the academic requirement for the degree of Master of Science in Chemical Engineering, at the School of Engineering, College of Agriculture, Engineering, and Science, University of KwaZulu-Natal,
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PREFACE

The research contained in this thesis was completed by the candidate for a master's degree while based in the Discipline of Chemical Engineering, School of Engineering, of the College of Agriculture, Engineering and Science, University of KwaZulu-Natal, Howard College Campus, South Africa.

The contents of this work have not been submitted in any form to another university for a degree, and except where the work of others is acknowledged in the text, the results reported are due to investigations by the candidate.

As the candidate's supervisor, I approve this thesis for submission.

[redacted]_____ 13 June 2024

Signed: Prof. B. Sithole (Supervisor) Date:

DECLARATION

I, Bonisile Mokoena, declare that:

1. The research reported in this thesis, except where otherwise indicated, and is my original research.

2. This thesis has not been submitted for any degree or examination at any other university.

3. This thesis does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.

4. This thesis does not contain other persons' writing, unless specifically acknowledged as being sourced from other researchers. Where other written sources have been quoted, then

    a. Their words have been re-written, but the general information attributed to them has been referenced.

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ABSTRACT

Lignosulphonates are produced during the chemical pulping of wood species through acid sulphite or neutral sulphite semi-chemical processes. Lignosulphonates are applied in several commercial products, including but not limited to dispersants, resins, binders, concrete admixtures, water treatment aids (coagulants), etc. These complex macromolecular structures exhibit different chemical properties, depending on the pulping process and tree species used. How lignosulphonates are valorised will, therefore, depend on their inherent chemical properties. The molecular weight and the sulphonic acid content in particular are two properties that will affect how lignosulphonates are used. In this study, the molecular weight and sulphonic acid of magnesium lignosulphonate (MgLS) and sodium lignosulphonate (NaLS) were studied. Due to the processing contaminants that interfere with molecular weight and sulphonic acid measurements of spent liquors purification of the MgLS and NaLS streams was carried out using a combination of Dowex 50wx8 and XAD-7 resins. The Dowex resin was used for de-ashing, and the XAD-7 resin to adsorb the lignosulphonate molecule. Ultrafiltration was also included as a comparison for the Dowex-XAD-7 purification. Approximately; 5 % ash was retained on samples purified by ultrafiltration and less than 3% ash was retained by samples purified by Dowex-XAD-7. The sample yield after Dowex-XAD-7 and ultrafiltration was similar for MgLS samples, between 32 and 36% sample was extracted . There was, however, a difference in sample yield when NaLS liquor was purified. A 24 and 32 % sample recovery was achieved using Dowex-XAD-7 and ultrafiltration, respectively. The yield was higher for the ultrafiltrated product than for the XAD-7 product. Samples purified by ultrafiltration generally showed high molecular weight and sulphonic acid content. The molecular weight for NaLS and MgLS samples purified by ultrafiltration measured approximately 6 and 20 kDa, respectively. Where as NaLS and MgLS samples purified by Dowex-XAD-7 reported a molecular weight of 3 and 12 kDa, respectively. The sulphonic acid content ranged between 3 and 5% for ultrafiltrated samples where as the Dowex-XAD-7 extracted samples ranged between 2 and 3%.

The samples purified by XAD-7 resins were then sequentially fractionated using ultrafiltration with molecular weight cut-off (MWCO) sizes between 100 kDa to 1kDa. The molecular weight of the fractionated products decreased with a decrease in MWCO size ranging between 100 and 1kDa. This decrease was from 17.6 to 0.6 kDa and 14.8 to 0.8 for MgLS and NaLS samples, respectively. For the MgLS, the sulphonic acid content increased from 0.93 to 1.25 mmol/g

with a decrease in molecular weight, whereas the fractions from the NaLS feed seemed to decrease with a decrease in molecular weight.

ACKNOWLEDGEMENTS

My heartfelt gratitude goes to the group at Sappi, BOKU, and UKZN who made this work possible. Prof A. Potthast, Ivan and Gregory offered guidance throughout the study. Berdine, Sanet for your honest opinions, reviews and needed pep talks. Thank you to Prof. Sithole for your contribution and guidance

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NOMENCLATURE

ATR	Attenuated total reflection
$Ba(OH)_2$	Barium hydroxide
BOKU	University of Natural Resources and Life Sciences (Universität für Bodenkultur Wien, BOKU), Vienna, Austria.
Ca	Calcium
Ca^{2+}	Calcium cation
DMAc	Dimethylacetamide
DMF	dimethylformamide
DMSO	Dimethyl sulfoxide
DoS	Degree of sulphonation
DOW-XAD-7	
FTIR	Fourier Transform Infrared
G	Guaiacyl unit
GPC	Gel permeation chromatography
H_2SO_4	Sulphuric acid
H units	p-hydroxyphenyl
H^+	hydrogen cation
HCl	Hydrochloric acid
HSO_3^-	Sulphurous acid
ICP-OES	Inductive Coupled Plasma- Optical Emission Spectrometry
K	Potassium
K^+	Potassium Cation
LCC	Lignin-carbohydrate complex
LiBr	Lithium bromide
LiCl	Lithium chloride
LiOH	Lithium hydroxide
LS	Lignosulphonates
MALS	Multi-angle light scattering
Mg	Magnesium
Mg^{2+}	Magnesium ion
Mg^{2+}	Magnesium cation
MgLS	Magnesium lignosulphonate
$MgSO_3$	Magnesium sulphite
MWCO	Molecular weight cut-off
Na	Sodium
Na^+	Sodium cation
Na_2SO_3	Sodium sulphite
NaLS	Sodium lignosulphonate
NaOH	Sodium hydroxide
NH^{4+}	Ammonia cation
NH_4LS	Ammonia-based spent liquor
NSSC	Neutral Sulphite Semi-Chemical
OH^-	Hydroxide
PDI	Polydispersity index
PF	Phenol formaldehyde
PS	Polystyrene
PSS	Polystyrene sulphonate

PTFE	Polytetrafluoroethylene
RI	Refractive index
S unit	Syringyl,
SEC	Size exclusion chromatography
TDS	Total dry solid
THF	Tetrahydrofuran
UF	Ultrafiltration
UV-VIS	Ultraviolet-visible
α	Alpha
β	Beta

Units of measurement

%	Percentage
°C	Degree Celsius
µm	Micrometre
cm^{-1}	Reciprocal centimetre (or wavenumber)
Đ	Polydispersity index
g	Gram
g/kg	Gram per kilogram
h	Hours
kDa	Kilodalton
L	Litre
M	Molar concentration
M	Weight-average molecular weight
mA/cm^2	Milliampere per square centimetre
mbar	Millibar
mg	Milligram
mg/L	Milligram per litre
min	Minute
ml	Millilitre
ml/min	Millilitre per minute
mm	Millimetre
mmol/g	Millimole per gram
Mn	Number-average molecular weight
mS/cm	milliSiemen per centimetre
Ni	The number of chains of that specific molar weight
nm	Nanometre
rpm	Revolutions per minute
v/v	Volume by volume
w/w	Weight by weight
ε	Adsorption coefficient

CHAPTER 1

1. INTRODUCTION

1.1. Thesis: General Overview

Technical lignosulphonate liquors are by-products of the chemical pulping processes of wood chips in the production of paper grade and dissolving wood pulp using sulphite pulping chemicals. These liquors contain residual components of the cooking chemicals (inorganic materials) and degraded wood constituents such as lignin, degraded cellulose and hemicellulose, organic acids, as well as extractives (Li and Takkellapati, 2018). Most pulp mills usually burn the lignosulphonate liquor to recover pulping chemicals and to produce energy that can be used by the mill.

The chemical structure of the lignosulphonate molecule is complex and differs depending on the pulping process and tree species used. This variation, therefore, introduces differences in the chemical and physical properties of the lignosulphonates obtained from the different pulping processes.

The title for this study was suggested by Sappi. Sappi wanted to get a better understanding of the molecular weight and sulphonic acid properties of their MgLS and NaLS when they are sequentially fractionated. The molecular weight and sulphonic acids of lignosulphonates are important parameter for a company like Sappi that not only sells their lignosulphonate commercially but also aim to modify these liquors for high value added products . Sappi has in the past worked with the University of Natural Resources and Life Sciences (Universität für Bodenkultur Wien, BOKU), Vienna, Austria in order to characterise their various lignosulphonate streams. This previous work however only concentrated at extraction of lignosulphonate using resins or ultrafiltration. These extracted lignosulphonate were then characterising for molecular weight and sulphonic acids and other parameters.
By understanding the degree of sulphonation (by determining sulphonic acid content) of lignosulphonate at the different molecular weight size distribution can help estimate the best way to valorise spent liquors. Since NaLS and MgLS are produced from different pulping processes, this study will also assist Sappi in identifying these differences.

Sappi was then interested in the characterisation (molecular weight and sulphonic acid content) of the fractionated components of their MgLS and NaLS streams. They also wanted these two

liquor streams to be compared to each other. This research study was therefore carried out at BOKU since they already had the experimental setup and the knowhow. BOKU has already developed the method to extract lignosulphonate from spent liquor using resins (Sumerskii et al., 2015). They also went a step further and sequential fractionated the extracted sample (Musl et al., 2020).

In this research study, the relationship between molecular weight and degree of sulphonation of sulphite spent liquors obtained from different wood pulping processes was explored. The following questions were also answered:

- How effective are polymeric adsorbents compared to ultrafiltration in extracting lignosulphonate from neutral sulphite semi-chemical (NSSC) spent liquors? This was achieved by comparing the yield of lignosulphonate (from NaLS) extracted by the resin to that using ultrafiltration.
- How effective are polymeric adsorbents compared to ultrafiltration in extracting lignosulphonate from acid sulphite spent liquors? This was achieved by comparing the yield of lignosulphonate (from MgLS) extracted by the resin to that using ultrafiltration.
- Determine the difference in lignosulphonate yields, molecular weight and sulphonic acids between MgLS and NaLS.
- How does the degree of sulphonation of NSSC and acid sulphite spent liquors vary at different lignosulphonate molecular weights? The molecular weight and sulphonic content of sequentially fractionated NaLS and MgLS samples were plotted and their trend discussed.
- From this study the purity of the extracted lignosulphonates should also be determined. This was by measuring the lignosulphonate and inorganic content in the extracted products
- Other observation noticed during the study should be noted and discussed

The biggest limitation to this study was the amount of time it took to carry out ultrafiltration. Due to limited availability to ultrafiltration equipment, there wasn't enough time to conduct the sequential fractionation in replicate. The sequential fractionation was therefore conducted in single fold.

1.2 Chapter Overview

This thesis is divided into four chapters. The first chapter gives an introduction into the research study. Chapter 2 is the literature review and Chapter 3 and 4 discusses the laboratory experiments, results discussion, conclusions, and recommendations for future experiments.

CHAPTER 2

2. LITERATURE REVIEW

In this literature review the following topics were explored:

- The structure of wood lignin
- How sulphonation of lignin takes place during different sulphite pulping processes
- Methods that are used to purify lignosulphonates from spent liquors
- Analytical methods that are used to quantify the degree of sulphonation of lignosulphonates
- Analytical methods used to measure molecular weight of lignosulphonates
- The degree of sulphonation of lignosulphonate compounds fractionated into different molecular weight fractions

2.1 Structure of wood lignin

Wood is made up of cellulose, hemicellulose, lignin, and extractives, (Koch, 2006). Lignin is found in hardwood and softwood tree species and in non-woody sources like grass, wheat, and straw (Sixta, 2006[a]; Todorciuc *et al.,* 2009). The lignin content of softwood tree species is higher (25 to 31%) than that of hardwood species (16 to 24%) (Sixta, 2006[a]). In wood, lignin is known for its protective properties, the mechanical strength it provides to the plant, and the role it plays as a transporter of nutrients (Koch, 2006). Its location between the cellulose fibres makes it easy for lignin to fulfil these roles (Figure 2.1) Doherty et al., (2011).

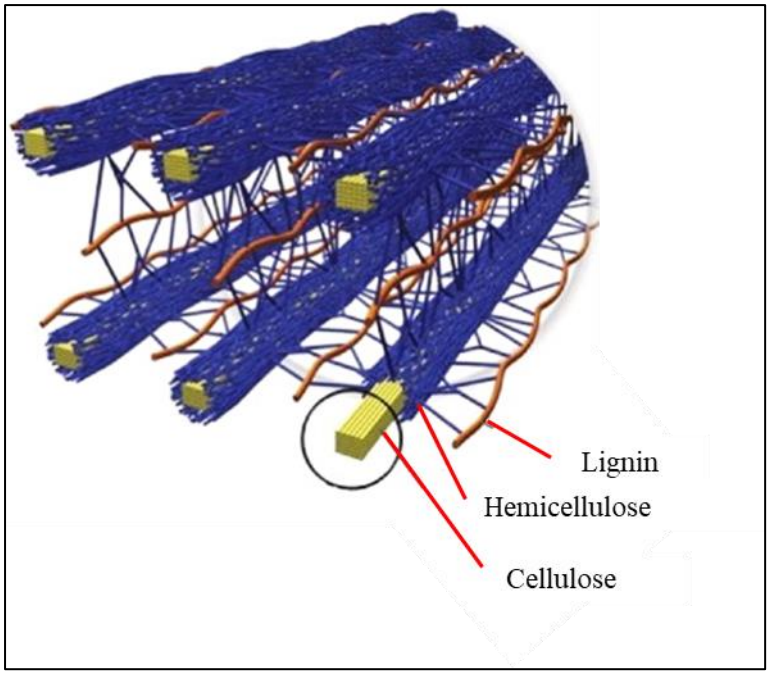

Figure 2.1: Illustration of the location of lignin, hemicellulose, and cellulose in the wood structure. Image obtained from Doherty *et al.,* (2011).

The lignin structure in wood is a product of the polymerisation of three types of alcohol precursors, namely p-coumaryl, coniferyl, and synapyl alcohols (Koch, 2006). These alcohol precursors which are also referred to as guaiacyl, syringyl, and hydrophenyl sub-units (Figure 2.2) are also denoted as G, S and H units respectively. In softwoods, the lignin structure is mainly made up of repeating G units (up to 95 %) (Figure 2.3). Softwood lignin is, therefore, also known as guaiacyl lignin. Softwood lignin only contains trace amounts of H units and S units. Hardwood lignin contains G and S units and is, therefore, referred to as guaiacyl-syringyl lignin (Koch, 2006). The syringyl to guaiacyl (S/G) ratio in lignin is an important parameter to measure since it will influence the delignification rate in chemical pulping processes (Sixta *et al.,* 2006).

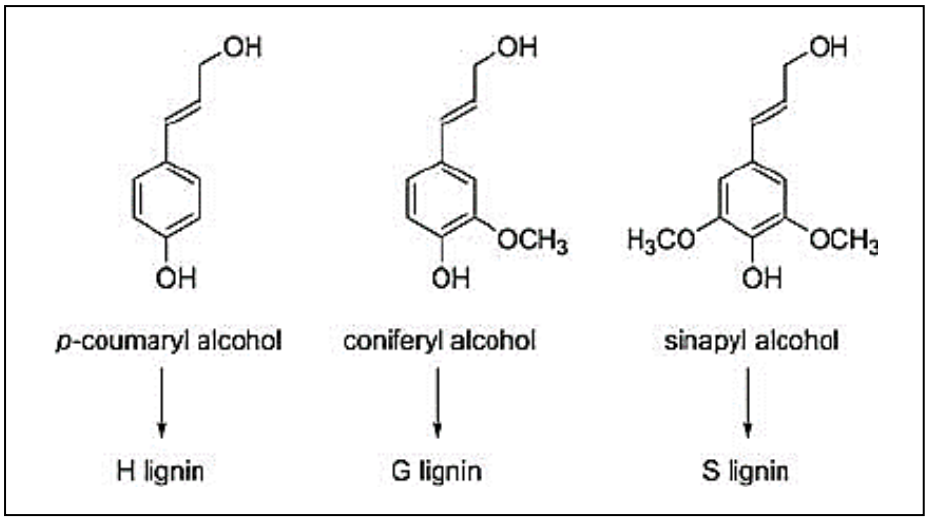

Figure 2.2: Illustration of the three alcohols that make up the lignin macromolecule. The coniferyl, synapyl and p-coumaryl alcohols are also referred to as guaiacyl (G), syringyl (S) and hydrophenyl (H) units; respectively. Image obtained from Stark *et al.*, (2016).

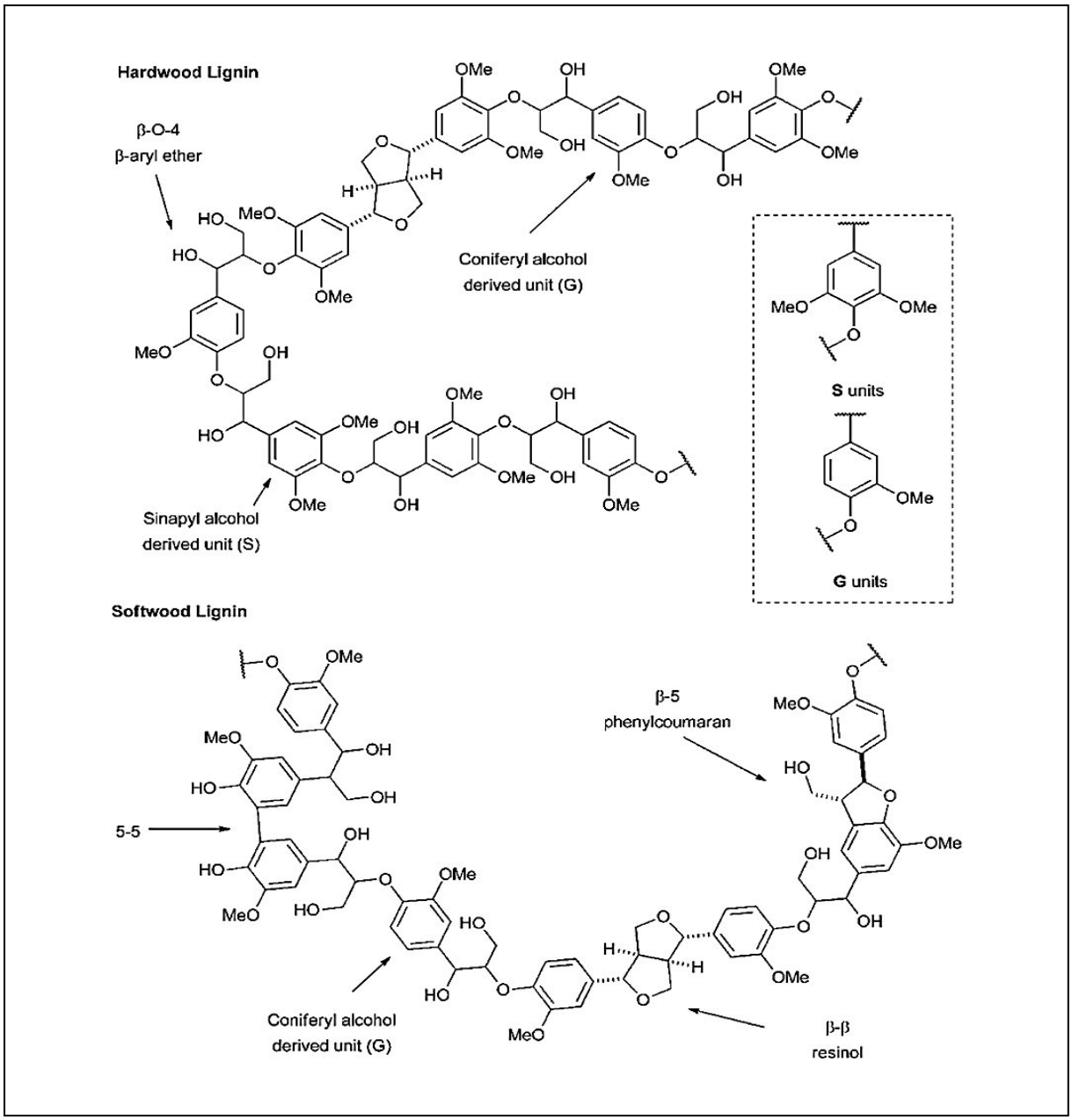

Figure 2.3: Illustration of the structure of hardwood and softwood lignins and the distribution of the different units (S and G) throughout. Image obtained from Lancefield *et al*., (2015).

The lignin structure is not only made up of repetitive units of the S, G or H units but can also have polysaccharides attached to it. This structure is then named the lignin-carbohydrate-complex (LCC). Several authors have identified the different LCC linkages that exist in wood. They claim that the lignin polymer can be chemically bound to the hemicellulose via several sites e.g. phenyl glycosides, benzyl ethers and ester linkages (Nishimura *et al*., 2018; Tribot *et al*., 2019; Tarasov *et al.*, 2018). In Figure 2.4 these phenyl glycosides, benzyl ethers and ester linkages are illustrated in (a), (b) and (c) respectively (Du *et al*., 2014).

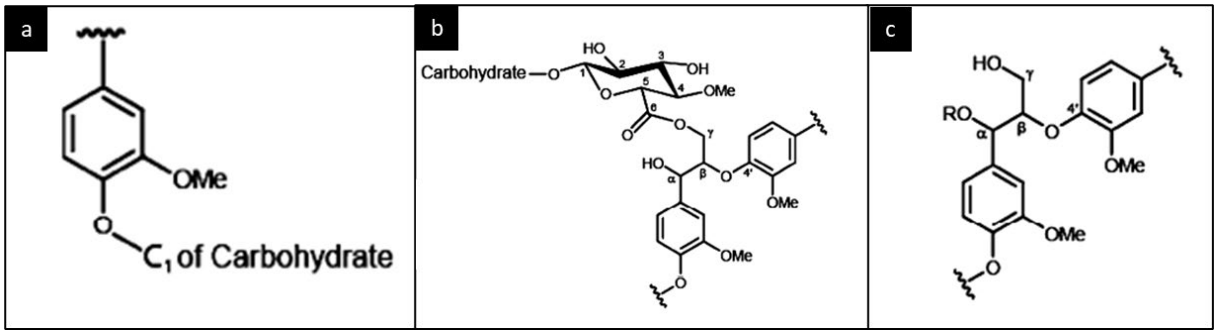

Figure 2.4: Illustrations of the possible LCC structures where lignin molecule is bound to phenyl glycoside (a), ester of 4-O-methylglucuronic acid on lignin Cγ (b), benzyl ether (c), with different sugar units linked on lignin Cα (R = C6 in Glu, Man, Gal, or C5 in Ara). Image obtained from Du *et al.,* (2014).

The lignin-carbohydrate-complex poses a challenge during the pulping processes. For example, a low pulp yield in kraft pulping can be attributed to LCC bonds (Sixta *et al.,* 2006). In spent liquors, extraction of pure lignosulphonate could also be challenging if LCC compounds are present.

2.2 Production of lignosulphonate

2.2.1 Pulping conditions used to produce sulphonated spent liquors

In the pulp and paper manufacturing industry, wood chips are put through chemical pulping and refining processes to produce cellulose-based pulp and paper products. The removal of lignin in sulphite pulping processes is facilitated by sulphonation (Sixta, 2006[b]). The sulphonation process solubilises the lignin molecule in the sulphite-containing cooking liquor, and thus, enables the separation of the lignin from the wood. There are three sulphite cooking processes currently used in the pulp and paper industry, namely, neutral sulphite semi-chemical (NSSC) pulping, acid sulphite pulping and bisulphite pulping. One of the major differences between these pulping processes is the pH range at which the cooking is carried out. The acid sulphite pulping process operates at lower pH values (1 to 3) compared to the other processes (Table 2.1). The bisulphite process operates at a slightly higher pH range (3 to 5) compared to the acid sulphite while the NSSC process is conducted closer to a neutral pH range (5 to 7) (Table 2.1). Since the active cooking reagents (e.g., sulphurous acid, HSO_3^-) are highly reactive, base cations e.g., calcium, sodium, magnesium or ammonia (Ca^{2+}, Na^+, Mg^{2+} and NH^{4+}) are used as buffers. The base cations used in the NSSC process are typically Na^+ or NH^{4+} while Ca^{2+}, Mg^{2+}, Na^+ and NH^{4+}can be used during acid sulphite pulping. Ca^{2+} is not used in sulphite cooking processes carried out at a pH above 2.5, due to its solubility limitation at higher pH values (Sixta, 2006[b]).

Table 2.1: Differences between NSSC, bisulphite and acid sulphite pulping conditions (Sixta, 2006[b]).

Pulping process	Cooking liquor active reagents	Base cation	pH	Temperature (°C)
NSSC	HSO_3^-/SO_3^{2-}	Na^+ or $NH4^+$	5-7	150-175
Acid sulphite	SO_2/HSO_3^-	Mg^{2+}, Na^+, NH^{4+}	1-2	125-145
Bisulphite	HSO_3^-	Mg^{2+}, Na^+, NH^{4+}	3-5	150-175

2.2.2 Sulphonation of lignin

Sulphonation of lignin in NSSC pulping

Sixta, 2006[b] reported that the sulphonation of lignin in the NSSC pulping process occurs through the dissociation of the β-O-4-ether bonds of the lignin structure (Figure 2.5). The author further claimed that the sulphonation in the NSSC process occurs at a lower rate (due to the neutral pH) compared to other processes and thus, fewer of the lignin structures react (about 20%) (Lin and Dence, 2012). Therefore, residual lignin is left in the pulp that is further processed to paper products. Pulp products from NSSC pulping are known for their strength properties and are used in the manufacture of corrugated boxes and board products. Sappi Tugela Mill uses pulp produced during the NSSC process to produce containerboard products (Sappi, 2022[b]).

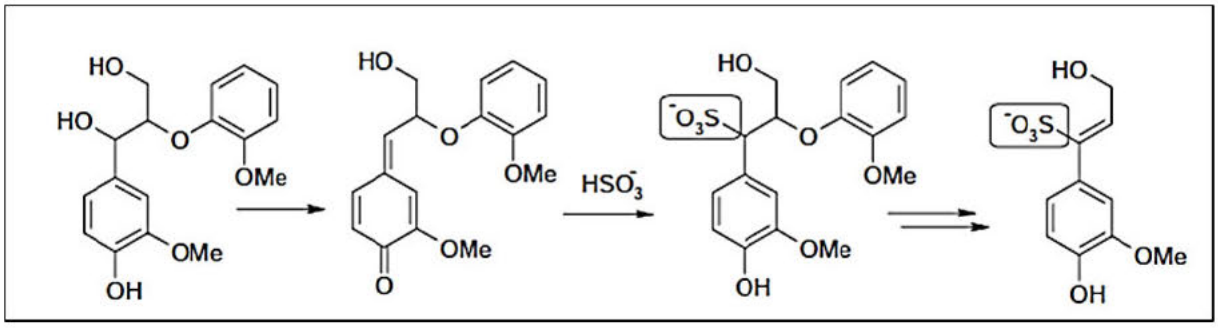

Figure 2.5: Illustration of how lignin sulphonation occurs during NSSC pulping. Image obtained from Sixta, (2006[b])

Lignin sulphonation in acid sulphite pulping

During acid sulphite pulping, the oxygen atom of the OR-group located at the α-region of the lignin molecule gets protonated by a hydrogen cation (H^+) that originates from the acidic cooking liquor, and thus, is eliminated as water or alcohol. This results in the formation of a benzylium cation intermediate (Figure 2.6, 3a), which then reacts with the sulphonic acid group of the cooking liquor through a nucleophile addition reaction, to form a sulphonated lignin

compound. The benzylium cation is susceptible to reactions with other nucleophiles that compete with the sulphonation reaction. Hydrolysis reactions between lignin and carbohydrates also occur under acid sulphite pulping conditions. These reactions occur at a slower rate than that of sulphonation (Sixta, 2006[b]).

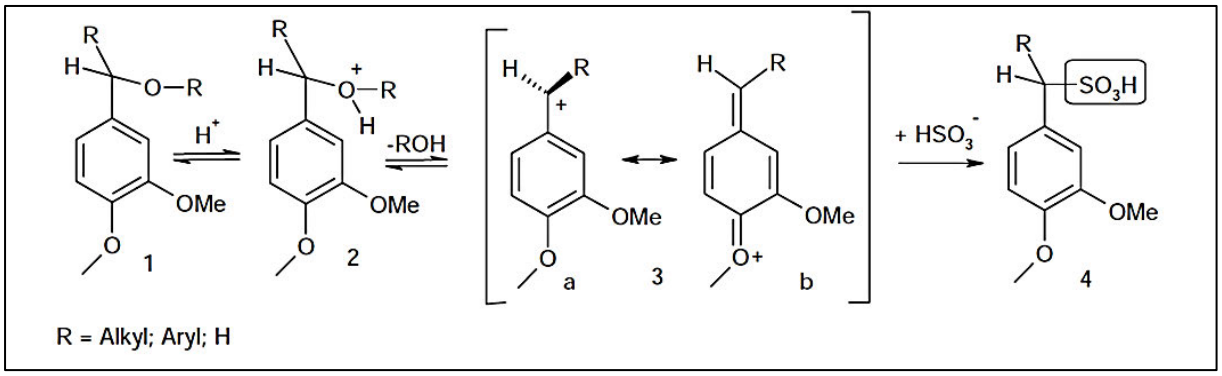

Figure 2.6: Illustration of how lignin sulphonation occurs under acid sulphite pulping conditions. Image obtained from Sixta, (2006[b]).

Condensation reactions occur when the benzylium cation intermediate reacts with a nucleophile from the lignin molecule. Condensation reactions are unfavourable in the pulping process as they compete with sulphonation reactions that promote delignification (Sixta, 2006[b]). According to Sixta, (2006[b]), condensation reactions are favoured by an increase in the acidity at a later stage of the cooking process.

The condensation reaction occurs by first forming a benzylium ion at the C1 or C6 position of the phenyl structure, by removal of the hydroxyl (OH^-) group. The benzylium ion then reacts with a nucleophile to form a condensed lignin structure (Figure 2.7). Condensation reactions can, however, be reduced during pulping by increasing the bisulphite concentration. This reaction is not limited to lignin nucleophiles, however, and Sixta, (2006**[b]**) outlined that other nucleophiles (carbohydrates and extractives) can also react with the benzylium ion.

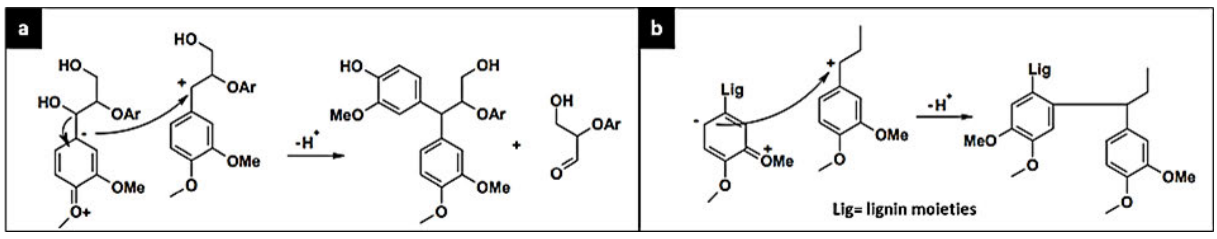

Figure 2.7: Illustration of how lignin condensation reactions of benzylium ion with a nucleophile at C1 (a) and C6 (b) occurs. Image obtained from Sixta, (2006[b]).

2.3 Extraction of lignosulphonate from spent liquor

Most spent cooking liquor contains residual cooking chemicals and degraded wood components (lignin, organic acids, carbohydrates, inorganic material, *etc*.). The carbohydrates can be present as dissolved entities in the liquor or attached to the lignin molecule as LCCs. The non-lignin structures can interfere with the characterisation of the lignin molecule and must therefore, be removed prior to analysis.

Purification techniques used to extract lignin and lignosulphonates from their spent liquors for analytical quantification measurements and/or industrial application, have been extensively investigated. Fatehi and Chen, (2016) compiled a summary of lignin and lignosulphonate extraction techniques from spent liquors originating from Kraft, NSSC and acid sulphite pulping processes. The authors identified several lignin isolation techniques, including polymeric resin adsorbents, amine extraction, ultrafiltration, electrolysis, and combinations of these, that could be suitable for the removal of lignosulphonate from the acid sulphite pulping spent liquor. Only two types of lignin isolation techniques, namely solvent extraction and a combination of adsorption, flocculation and coagulation steps were identified for lignin separation from NSSC spent liquor (Fatehi and Chen, 2016).

The extraction of lignin from Kraft spent liquor is achieved by simple acidification to precipitate the lignin. However, the extraction of lignosulphonates from sulphite-based spent liquors is more complicated. Acidification of Kraft lignin has already been commercialised by Domtar, using the LignoBoost^{TM} Technology (Tomani, 2010). Since this research study only focuses on sulphite spent liquors, this technique was not explored further.

According to Lin and Dence, (2012) the selection of the lignosulphonate isolation technique should consider various criteria, including the yield and purity of the product, as well as the simplicity of the technique. For a good lignosulphonate yield, the quantity of the purified product should closely resemble the quantity of lignosulphonate contained in the spent liquor. High purity is also required, and the extracted product should, therefore, only contain lignosulphonate. Finally, the selected extraction techniques should be easy to use and not time consuming. For certain analytical applications, the quality of the extracted lignosulphonate product (purity) could surpass the quantity (yield) requirement. This could, however, be the opposite for industrial applications.

Since this study focused on analytical characterisation of purified lignosulphonate, flocculation and coagulation were not included in the review, since these techniques are more suited for industrial applications. Flocculation and coagulation techniques result a product with a significant number of contaminants. Instead, only amine extraction, membrane filtration and adsorption resins were included in this literature review.

2.3.1 Lignosulphonate extraction using amines

The use of amines for extraction of lignosulphonates was explored by Ringena *et al*., (2005[a]). This extraction process is a multistep approach as depicted in Figure 2.8 (Ringena *et al*., 2005[a]). The first step involves treating the acidic magnesium lignosulphonate (MgLS) spent liquor with 2% $Ba(OH)_2$, to reach a pH of 3. The lignosulphonate-amine complex is then formed by addition of the amine (dicyclohexylamine in *n*-butanol), followed by the isolation of the complex using liquid-liquid extraction with different solvents (Figure 2.8). According to Ringena *et al*., (2005[a]) this technique was time consuming, and the extracted lignosulphonate product did not produce pure lignosulphonate. The authors also noted that amine extraction altered the solubility properties of the extracted product. Other challenges when using amines to extract lignosulphonates include foaming and the formation of an emulsion (Lin and Dence, 2012). Amine extraction was, therefore, not recommended as an isolation technique for the qualitative analysis of lignosulphonate.

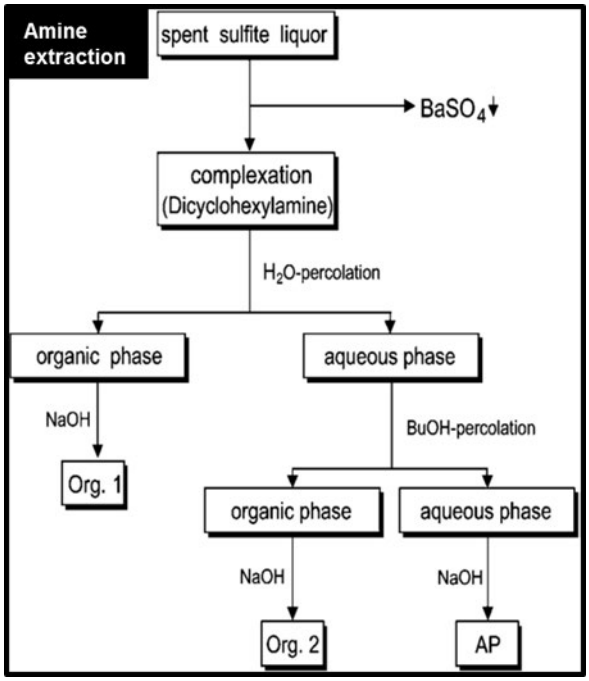

Figure 2.8: Illustration of the process flow for isolating lignosulphonate using amine extraction. Image obtained from Ringena *et al*., (2005[a]).

2.3.2 Membrane fractionation

Membrane fractionation uses a membrane to separate compounds in the spent liquor according to their molecular weights. The advantage of using membrane filtration is that the extracted lignosulphonate will be representative of the lignosulphonate in the original spent liquor (feed). Since membrane filtration does not make use of chemicals to extract lignosulphonate, it will not change the properties of the lignosulphonate, as seen with amine extraction (Ringena *et al*., 2005[a]). The disadvantages of using membrane filtration (especially ultrafiltration), include the time-consuming nature of the method (Sumerskii *et al*., 2015) and fouling of the membrane (Area *et al*., 1999).

Area *et al*., 1999 evaluated ultrafiltration membranes with different molecular weight cut-off (MWCO) sizes (0.5, 2, 3 and 10 kDa) that was produced from different materials, including regenerated cellulose, cellulose acetate and polyethersulfone. It was found that regenerated cellulose membranes with 2 and 3 kDa MWCO sizes, recovered the most lignosulphonate. Sumerskii *et al.*, 2015 also evaluated ultrafiltration with a 1 kDa MWCO size membrane from regenerated cellulose as a reference when they were investigating the use of adsorption resin as an alternative lignosulphonate isolation technique.

Membrane filtration can be further used as a characterisation tool for molecular weight distribution within a batch of spent liquor. This is done by sequentially fractionating the lignosulphonate from the highest MWCO size to the lowest. Ringena *et al*., 2005[a] used a sequential technique when they compared amine extraction to ultrafiltration. The membranes were arranged in decreasing MWCO sizes, and the spent liquor was first passed through the membrane with the largest MWCO size (100 kDa). The resulting retentate was then collected while the permeate was fed to a membrane of the next MWCO size (50 kDa). This process was repeated until the permeate was passed through the membrane with the smallest MWCO size (1 kDa), (Figure 2.9).

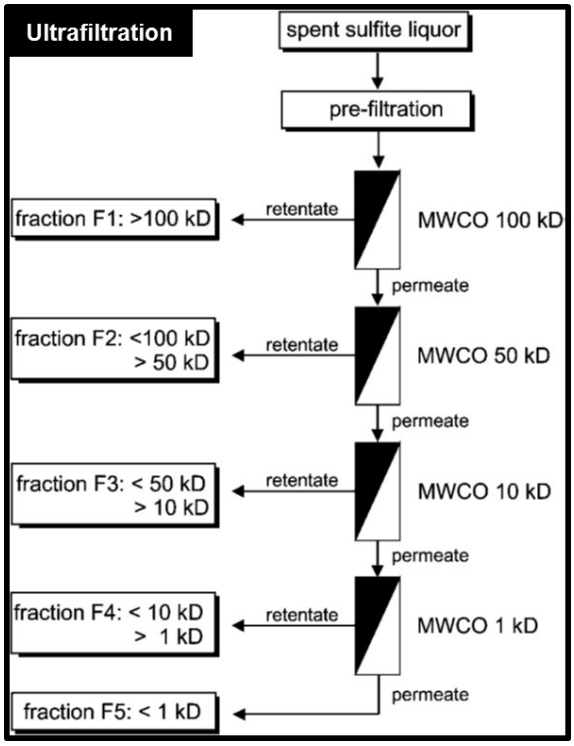

Figure 2. 9: Illustration of the process flow for the sequential fractionation of lignosulphonate spent liquor using ultrafiltration. Image obtained from Ringena *et al*., (2005[a]).

Sequential ultrafiltration was also used by Musl *et al*., (2020) on MgLS spent liquor previously purified by adsorption resins. Both Ringena *et al*., (2005[a]) and Musl *et al*., (2020) confirmed that, spent liquors contain lignosulphonates of varying molecular weights within the same batch.

2.3.3 Polymeric adsorption resins

Sumerskii *et al*., (2015) compared the use of a resin adsorbent and ultrafiltration with a 1 kDa membrane to extract lignosulphonates from sulphite spent liquors. They identified Amberlite™ XAD7HP (XAD-7) as the most suitable resin for this process. According to the XAD-7 product information sheet (Sigma Aldrich, 2022), the resin is made from an acrylic ester and is a weakly polar adsorbent resin that adsorbs compounds with a molecular weight (MW) of up to 60 kDa.

Prior to adsorbing the lignosulphonate onto the XAD-7 resin, the spent liquor is treated with Dowex® 50WX8, which is cation exchange resin to remove inorganic material. The Dowex resin is strongly acidic (H^+) with a 50 to100 mesh size (Lenntech, 1998-2022). The liquor/Dowex mixture is filtered, and the XAD-7 resin is added to the filtrate. The lignosulphonate is then extracted from the XAD-7 resin using an alcohol solvent. Sumerskii *et al*., (2015) claimed that treatment of magnesium-based spent liquors with either ultrafiltration

or adsorption onto XAD-7 resin produced similar purified product yields (a 25 to 39% yield using ultrafiltration and a 24 to 40% yield using XAD-7 resin).

When the carbohydrate content of the purified lignosulphonate products were compared, it was found that both ultrafiltration and XAD-7 treatment resulted in less than 1% carbohydrates. In their study, Sumerskii *et al*., (2015) also found that the lignosulphonate extracted with XAD-7 resin was purer compared to the product treated with ultrafiltration. This was confirmed by measuring and comparing the methoxy-group content. Lignosulphonate purified by XAD-7 resin contained more methoxy groups compared to the ultrafiltrated product. The authors claimed that the methoxy groups are an indication of phenylpropane units (syringyl and coniferyl units), which are the building blocks of the lignin molecule. They also claimed that the XAD-7 isolation technique is faster than the ultrafiltration method (Sumerskii et al., 2015).

2.3.4 Solvent extraction

Tarasov *et al*., (2015) used solvent extraction to remove lignosulphonate from an NSSC spent liquor. This was done by mixing the NSSC spent liquor at room temperature with the organic solvents acetone, ethanol, or isopropyl alcohol at spent liquor to solvent ratios (w/w) of 33:66, 50:50, 25:75 and 20:80. These mixtures were then centrifuged at a speed of 3000 rpm for 15 min. The supernatants from these reactions were decanted and analysed for hemicellulose and lignosulphonate content (Tarasov *et al*., 2015). The maximum amount of lignosulphonate extracted (60 %) was obtained with isopropyl alcohol at a 20:80 spent liquor to solvent ratio. Tarasov *et al*., (2015) also reported that, regardless of the solvent used, approximately 30% of the hemicelluloses were also extracted with the lignosulphonate (Tarasov *et al*., 2015). Solvent extraction is, therefore, not an ideal lignosulphonate isolation technique when a high lignosulphonate purity is required.

2.3.5 Lignosulphonate extraction using electrolysis

Ringena *et al.*, 2005[b] evaluated the application of electrolysis on MgLS to purify lignosulphonate. This experiment was carried out in an electrolysis cell where the MgLS spent liquor and sulphuric acid (H_2SO_4) were placed in the anolyte and catholyte compartments, respectively. A cation exchange membrane was used to separate the compartments. Electrolysis was then applied galvanostatically at 60°C and at a constant current density of 125 mA/cm^2 (Ringena *et al.*, 2005[b]). From this study it was concluded that electrolysis can be used to recover process chemicals, since a reduction in the ash content was observed when the Mg^{2+} ions

migrated to the catholyte compartment. Since all the hemicellulose were still present after electrolysis, it was concluded that this technique cannot be used for qualitative lignosulphonate isolation.

2.4 The degree of sulphonation and molecular weight

Lignosulphonates possess amphiphilic properties which, when taken advantage of, can be of use in different industries. Sappi (Johannesburg, South Africa), a pulp and paper manufacturing company, lists several applications for the lignosulphonate spent liquors they produce, including pelletising, dispersants, admixtures and resins (Sappi, 2022[a]). Borregaard (Sarpsborg, Norway) also produces lignosulphonate-based biopolymers that are sold into different markets as binders, dispersants and complexing agents (Borregaard, 2021).

Calvo-Flores *et al.*, (2015) explored the various uses of lignosulphonate in detail and separated these according to products that use lignosulphonates as-is and those that need modification prior application. The use of lignosulphonates in industries that do not require prior modification, relies on the inherent properties of the molecule as given by the functional groups present on the structure. The sulphonic acid content, carboxylic acid groups and phenolic hydroxyl groups are some of the functional groups that are responsible for the hydrophilic properties of lignosulphonates (Aro, and Fatehi., 2017). Applications of lignosulphonates where modifications are necessary, include production of phenol formaldehyde (PF), epoxy resins and polyurethane foams (Calvo-Flores *et al.*, 2015). During lignosulphonate modification, several properties, including solubility, reactivity, degree of sulphoation and molecular weight can be enhanced in order to meet the requirements of the new product (Aro, and Fatehi., 2017).

The sulphonic acid content and the molecular weight of the lignosulphonate molecule should be understood before it can be valorised to obtain new products. There are several test methods available to measure the sulphonic acid content and molecular weight of lignosulphonate and these are explored below.

2.4.1 Determination of the degree of sulphonation

The degree of sulphonation (DoS) of lignosulphonate is determined by measuring the sulphonic acid content. Prior to sulphonic acid measurement, the lignosulphonate sample must be purified, since the only sulphur present in the sample must be in the form of sulphonic acid groups attached to the lignin structure (Beatson, 1992). The sample should, therefore, be free

of all contaminants including organic acids, hemicellulose and free sulphur (originating from residual pulping chemicals).

This purification step is crucial, especially since some of the DoS methods do not differentiate between the different sulphur groups present in the spent liquor. The purification of lignosulphonates is detailed in section 2.3. Methods that measure the sum total of all sulphur compounds in the spent liquor, are referred to as indirect methods (Beatson, 1992). Examples of these methods include X-ray fluorescence spectroscopy, combustion/ion chromatography and elemental analysis (Beatson, 1992).

Conductometric and potentiometric titrations are considered direct methods, as these methods measure only the sulphonic acid content (Beatson, 1992). For both titration methods, the purified sample is titrated against a base, which can be sodium hydroxide (NaOH) or lithium hydroxide (LiOH), from which a titration curve is drawn, and the end point determined.

Another direct method to measure DoS is the quantitation of retained benzidinium ions by UV-spectroscopy (Beatson, 1992). Beatson, (1992) claims that Katz *et al*.,(1984) suggested that conductometric titration is the most convenient method for the direct measurement of sulphonate content, as it can differentiate between the sulphonic and carboxylic groups.

Conductometric titration

The conductometric titration method is described by Beatson, (1992) in detail and is also accepted by the Scandinavian Pulp, Paper and Board Committee (Standards Scandinavia, 2002) to measure sulphonic acid content in liquors. This method is based on the measurement of sulphonic acid content in pulp where the pulp is protonated by soaking it in hydrochloric acid (HCl), followed by titration with 0.1 M NaOH (added at 0.5 ml aliquots). During the addition of each aliquot of NaOH the conductivity is measured. A calibration curve is then constructed and the total acids content in the pulp determined from the strong and weak acids (Beatson, 1992) claims that the strong acids are due to the presence of sulphonic acids while the weak acids are from the carboxylic acids.

Korntner *et al.,* (2018) applied this method to determine the sulphonic acid content in lignosulphonate spent liquors. The lignosulphonate that was purified using XAD-7 resin was titrated using 0.1 M LiOH as a base. This was immediately followed by back-titration with HCl. Each titrant was added in 0.05 ml aliquots until a total volume of 6 ml was reached. A titration curve was drawn. The measured conductivity is plotted on the y - axis and the volume

of titrant added is on the x-axis.

For the LiOH titration, the conductivity gradually decreases, and the curve almost flattens. A sharp increase in conductivity is then seen when all the acid has reacted with the LiOH. When the linear regions of the curve are extrapolated, these inflection points in the curve can be properly identified. Korntner *et al.,* (2018), denotes these points as **a** and b and describes them as the volumes (LiOH added) that can be used to calculate the concentration of strong acids and weak acids, respectively. Korntner *et al.,* (2018) correlates the strong acids to sulphonic acids and attributes the weak acids to carboxylic acids and phenolic hydroxyls. Beatson, (1992) expresses these intersections as end points. Korntner *et al.,* (2018) further identifies **c** as the excess amount of LiOH added. The titration curve where 0.1M HCL is used as the titrant represents the back titration. This curve is a mirror image of the base titration (Korntner *et al.,* 2018).

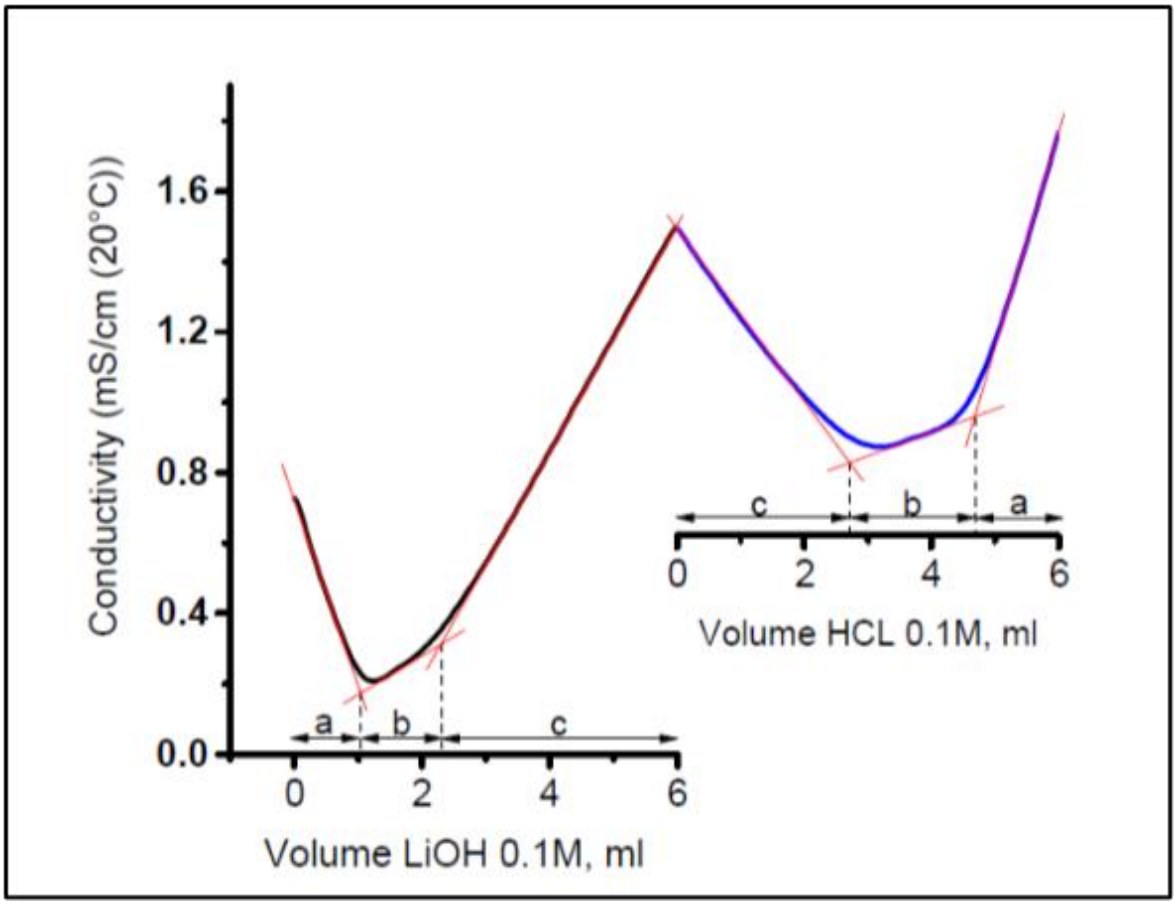

Figure 2.10: Illustration of the titration curve that is obtained during the conductometric titration of a purified lignosulphonate sample using 0.1 M LiOH as the base and back-titration with 0.1 M HCl. **a and b** are intersection points that represents volume of titrant than can be used to calculate concentration of strong acids and weak acids. **c** is the excess LiOH volume added. Image obtained from Korntner *et al*., 2018.

Using the volumes at the endpoint **a,** the sulphonic acid content is calculated using Equation 1.

$$Sulfonic\ acid\ content = \frac{End\ point\ (mL) \times concentration\ of\ titrant\ (M)}{Weight\ of\ sample(dry)}$$ **Equation 1** (Beatson, 1992)

Korntner *et al*., (2018) expressed the sulphonic acid content as the millimolar content of sulphonic acid per gram of purified lignosulphonate (mmol/g). The carboxylic acid content can be calculated with Equation 1 using the end point **b** of the calibration curve.

2.4.2 The molecular weight measurement of lignosulphonate

The use of gel permeation chromatography (GPC) or size exclusion chromatography (SEC) to measure the molecular weight of lignin and lignosulphonates is well described in literature. On their website, Waters (Massachusetts, USA) (Waters, 2022[a]) illustrates that a basic GPC instrument (Figure 2.11) is fitted with an injection port, solvent delivery system (pump), columns, detector and a solvent supply, that contains the mobile phase (Figure 2.11). The function of the pump is to deliver a consistent flow rate throughout analysis. The sample is introduced into the instrument by injection. It is then transported by the mobile phase to the column (stationary phase) where analyte separation occurs. The data system then captures the chromatogram and the resulting data.

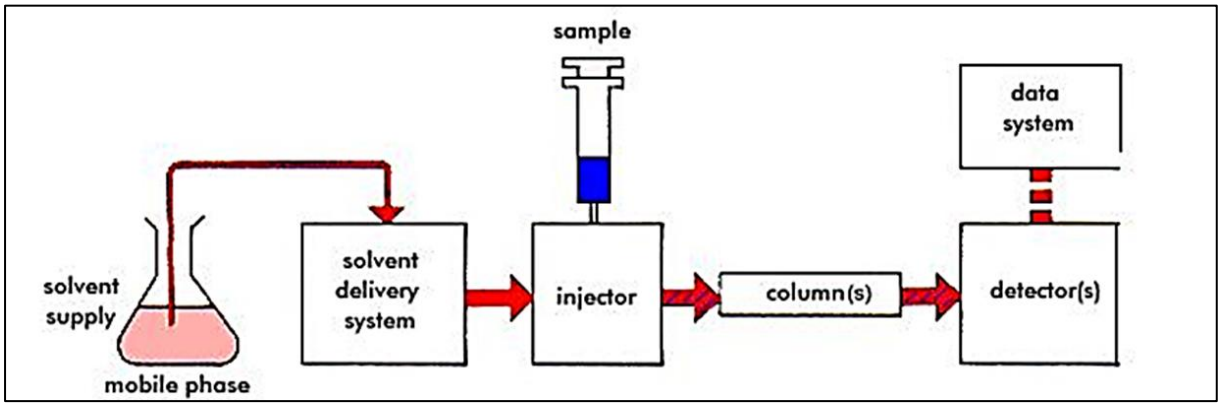

Figure 2.11: Typical GPC instrument setup as illustrated by Waters (Waters, 2022[a]).

The GPC system used for lignosulphonates can be aqueous, organic or a mixture of both (Phenomenex, 2022; Agilent, 2022). Tetrahydrofuran (THF), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dimethylacetamide (DMAc) and sodium hydroxide (NaOH) are some of the solvents used (Sulaeva *et al*., 2017, Baumberger *et al*., 2007). Sulaeva *et al*., (2017) claimed that lignosulphonates are not completely soluble in THF and that sample derivatisation would be required. DMSO and DMAc can be used on lignosulphonates without derivatisation.

Zinovyev *et al*., (2018) highlighted that DMSO is a universal solvent and can dissolve most lignosulphonates. Lithium halides like lithium bromide (LiBr) and lithium chloride (LiCl) are usually added to DMAc, DMF and DMSO, to overcome the associative and/or aggregation properties encountered with lignins and lignosulphonates (Sulaeva *et al*., 2017, Chum *et al*., 1987). The type of GPC system selected is, therefore, influenced by the solubility of the spent liquor that will be analysed.

It is of critical importance to always select a lignosulphonate purification technique that does not adversely change the solubility properties of the lignosulphonate molecule being analysed. For example, it was observed that the resultant product was less soluble in the solvent used for molecular weight analysis (DMSO) when amines were used in extracting lignosulphonates (Ringena *et al*., 2005). This occurred due to the amine adducts that were retained with the purified lignosulphonate (Ringena *et al*., 2005).

Waters (Massachusetts, USA), Agilent (California, USA), Phenomenex (California, USA) and other suppliers sell columns for different GPC systems (aqueous, organic and polar organic) with different molecular weight limits (Waters, 2022[b]; Agilent, 2022; Phenomenex, 2022). As indicated in Figure 2.12, separation in a column is determined by molecular size as well as the presence of molecules that are not retained by the column's stationary phase, which will elute first (Ludwig *et al*.**,** 2019). These are usually the molecules that are larger than the pores of the stationary phase. The smaller molecules, which can permeate through the pores of the stationary phase, are retained longer. These molecules will then elute at a later retention time than the larger molecules. As the molecules elute at different retention times, their response is then recorded by a detector (Figure 2.12). Usually, a series of columns with different cut-off sizes are used. This is particularly important for technical spent liquors, since their molecular weight size distribution could range between high, middle and low, depending on the pulping process used. Using columns of different sizes also ensures that all the molecular size fractions within the spent liquor are accounted for.

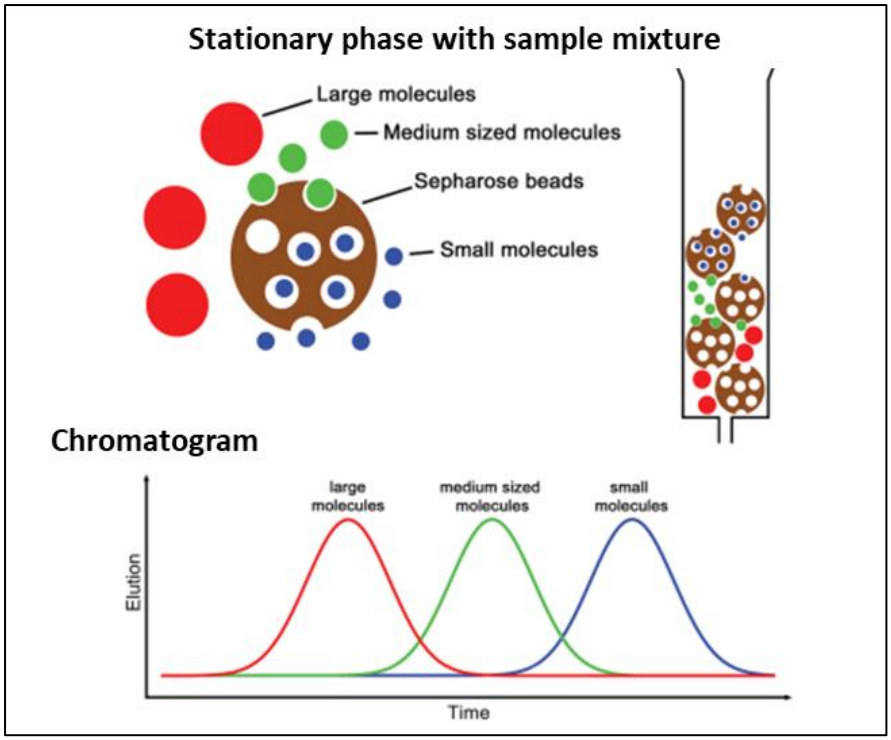

Figure 2.12: Illustration of the GPC/SEC column stationary phase (Sepharose® beads) with sample mixture (large medium and small molecules) and its resultant chromatogram. Image from Ludwig *et al*., 2019

Calibration standards of different molecular sizes are injected into the GPC system to construct a calibration curve. Since there are no commercially available calibration standards for lignosulphonate, polystyrene (PS) and polystyrene sulphonate (PSS) of different molecular weights are used (Baumberger *et al*., 2007). The PS standards are not soluble in water and DMSO, but are soluble in THF (Baumberger *et al*., 2007, Zinovyev *et al*., 2018). The PSS standards are, however, soluble in DMSO (Zinovyev *et al*., 2018).

Ultraviolet-visible (UV-VIS), multi-angle light scattering (MALS) and refractive index (RI) detectors are typically employed in spectroscopic molecular weight detection of lignosulphonate (Zinovyev *et al*., 2017, Zinovyev *et al*., 2018) . RI detectors are not as selective as UV detectors, since all sample components (sugar, alcohol, and inorganic ions) are measured, even those that can't adsorb light in the UV spectrum. UV-VIS detection is selective in its measurement as it measures compounds at a specific wavelength (lignosulphonates absorb at 280nm) (Lu., *et al* 2021).

MALS detectors outperform UV-VIS and RI detectors since these can measure the absolute molecular weight of a lignosulphonate sample, therefore, MALS detectors do not require calibration standards (Zinovyev *et al*., 2018). The main limitation of MALS detection is the

possible overestimation of the molecular weight of a sample due to the close proximity of UV absorption and fluorescence to that of the wavelength of the MALS laser (Zinovyev *et al*., 2018).

During molecular weight measurement the following parameters can be calculated:

a) Weight-average molecular weight (Mw) (Waters, 2022[b]; Agilent, 2015)

$$Mw = \frac{\Sigma NiMi^2}{\Sigma \mathrm{N}i\mathrm{Mi}} \qquad \textbf{\textit{Equation 2}}$$

Where: *Ni is the number of chains of that specific molar weight*

Mi= molecular weight of a chain

b) Number-average molecular weight (Mn) (Agilent, 2015)

$$Mn = \frac{\Sigma NiMi}{\Sigma \mathrm{Ni}} \qquad \textbf{\textit{Equation 3}}$$

Where: *Ni is the number of chains of that specific molar weight*

Mi= molecular weight of a chain

c) Polydispersity index (Đ) (Agilent, 2015):

$$Đ = \frac{Mw}{Mn} \qquad \textbf{\textit{Equation 4}}$$

Where: *Mw is the weight average molecular weight*

Mn is the number average molecular weight

With this parameter (Đ), the molecular weight size distribution of the lignosulphonate sample is calculated. A sample with similarly sized molecules will have Đ close to one whereas a sample with a wide range of molecular sizes will have a higher Đ value (Agilent, 2015). The polydispersity index is calculated by dividing the molecular weight with the number average molecular weight (Equation 4).

2.5 Conclusion

The lignin molecule is complex in structure and have different functional groups, depending on the type of wood species it originates from. The molecule is altered during the sulphite pulping processes when a sulphonated lignin or lignosulphonate is produced as by-product to the pulping process.

An understanding of the relationship between the molecular weight and the DoS of the lignosulphonate structure will assist researchers to determine how to best valorise this molecule to produce high value products for industrial applications. Since the lignosulphonate fractions contained in a spent liquor consist of different molecular sizes, their characterisation at a

molecular size level will extend our understanding of these complex structures and how to apply them.

Resin adsorption, amine extraction, ultrafiltration, dialysis, electrolysis and solvent extraction were reviewed as possible lignin extraction techniques. Since spent liquors contain other components that can interfere with these measurements, this literature review has assisted in identifying the best isolation techniques for acid sulphite and NSSC liquors.

The yield and purity of the extracted lignosulphonate product were identified as key characteristics to considering during the evaluation of different extraction techniques. Literature indicated that amine extraction resulted in the highest yield of lignosulphonate but with the lowest purity. Lignosulphonates purified using solvent extraction and electrolysis displayed the lowest purity, while isolation with membrane fractionation (ultrafiltration) and resin isolation resulted in products of high purity. Overall, lignosulphonates isolated with XAD-7 resin resulted in the highest purity, which makes it the method of choice.

According to literature (Beatson, 1992; Sulaeva *et al*., 2017; and Zinovyev *et al*., 2018), conductometric titration and GPC proved to be the best methods to measure the sulphonic acid content and molecular weight of lignosulphonates, respectively. The molecular weight and sulphonic acid content of lignosulphonate in spent liquors influence how spent liquors can be valorised. There are several sulphonic acid test methods available. Conductometric titration was found to be the most convenient of all the methods that were reviewed. Molecular weight analysis of lignosulphonates can be carried out either in aqueous or organic solvents, or a mixture of these in a GPC system, that will consist of the appropriate solvent, columns and standards). The solubility properties of the lignosulphonate molecule will determine the selection of the correct GPC system and detector. UV-VIS, IR and MALS detectors are the most widely used in lignosulphonate molecular weight analyses

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CHAPTER 3

3. CHARACTERISATION OF PURIFIED LIGNOSULPHONATE SPENT LIQUOURS

ABSTRACT

Lignosulphonate was purified from sodium lignosulphonate (NaLS) and magnesium lignosulphonate (MgLS) spent liquors using XAD-7 resin and ultrafiltration (1 kDa membrane). Not all the lignosulphonate was extracted from the raw NaLS and MgLS liquor samples, however. Only 45% lignosulphonate was purified from NaLS and MgLS spent liquor using ultrafiltration. The use of XAD-7 resin allowed the extraction of 24.5 and 36.4 % lignosulphonate from NaLS and MgLS, respectively. The purified MgLS samples had a higher molecular weight compared to the NaLS samples. The sulphonic acid content of samples extracted both from NaLS and MgLS was considerably lower than what is reported in literature. The samples purified by XAD-7 resin had the highest purity, as they contained the least inorganic material. It was recommended that the sugar content of the extracted lignosulphonates should be measured to further ascertain their purity. The lignosulphonate not retained by either isolation technique should also be also characterised as a substantial amount was lost during purification.

3.1 Introduction

The properties of technical lignosulphonates (LS) differ, depending on tree species and pulping processes used to produce the lignosulphonate in the spent liquor (Aro and Fatehi, 2017; Schorr *et al*., 2014; Zainab et al., 2018). It is, therefore, important to have the spent liquor characterised before deciding on how to valorise the lignosulphonate. By modifying the lignosulphonate properties, e.g. phenol formaldehyde resins, polyols and many other high-value lignin-based products can be produced (Calvo-Flores *et al*., 2015; Aro and Fatehi, 2017; Ibrahim *et al*., 2011; Li and Takkellapati, 2018). The physico-chemical properties of lignosulphonates, including molecular weight and sulphonic acid content as well as other functional groups, can be manipulated to produce various products (Calvo-Flores *et al*., 2015; Aro and Fatehi, 2017). These properties play a central role in the solubility, dispersion and reactivity and reactivity of lignosulphonates (Calvo-Flores *et al*., 2015; Aro and Fatehi, 2017).

Prior to molecular weight and sulphonic acid measurements, the spent liquor containing the lignosulphonate needs to be purified. Spent liquors contain residual, inorganic cooking chemicals and degraded wood components, including hemicellulose, organic acids and furfural, that can interfere with analysis, especially degree of sulphonation (DoS) (Lin and Dence, 2012). Chapter 2 discussed the different lignosulphonate purification techniques that can be used. Polymeric resins and ultrafiltration were identified as the most suitable techniques to purify lignosulphonate from spent liquors. Polymeric resins and ultrafiltration outperformed the other isolation techniques in terms of product purity (section 2.3). In this chapter, the isolation of lignosulphonate from acid sulphite liquor and neutral sulphite semi-chemical (NSSC) liquor, using polymeric resins and ultrafiltration will be compared.

3.2 Materials

3.2.1 Lignosulphonate spent liquors

The sodium lignosulphonate (NaLS) spent liquor used during the current study was supplied by a South African pulp and paper mill that uses hardwood as its raw material in a NSSC pulping process. The magnesium lignosulphonate (MgLS) spent liquor was supplied by a German pulp and paper mill that also used a hardwood tree species that is prevalent to Europe as their raw material in an acid sulphite pulping process. These spent liquors were sampled at the mills prior to evaporation and, therefore, had a low dry solids content.

3.2.2 Ultrafiltration membranes

All membranes (1 kDa) used for ultrafiltration were made from regenerated cellulose and were purchased from Merck (Darmstadt, Germany).

3.2.3 Reagents

All reagents used in this study were purchased from Sigma-Aldrich (St. Louis, USA) and were of analytical grade.

3.3 Extraction of lignosulphonate with ion exchange resins

3.3.1 Preparation of Dowex and XAD-7 resins

The Dowex® 50W X8 (Dowex) and Amberlite™ XAD7HP (XAD-7) resins were prepared according to Sumerskii *et al*., (2015). The Dowex resin was first washed in distilled water by stirring it for 20 min using a mechanical stirrer. The water was then removed by filtration. This wash stage was repeated three times until the filtrate was considered clean. The washed resin was then regenerated by hydrochloric acid (HCl) treatment. It was sequentially stirred for 10

min in 0.5, 1.0 and 2.0 M HCl solutions, respectively. Each acid wash was repeated three times. The resin was then filtered and stored in a glass bottle and washed with distilled water before use.

The XAD-7 resin was prepared by an exhaustive Soxhlet extraction process using methanol, acetone, methyl tert-butyl ether, followed by methanol again. The Soxhlet-extracted resin was then stirred in 0.1 M sodium hydroxide (NaOH) with a mechanical stirrer at a low speed (200 rpm) setting for 60 min. This was followed with a washing step, where the resin was rinsed three times with distilled water in 5-min intervals. The resin was then washed three times with 0.1 M HCl in 60-min intervals. Thereafter acid was drained off and the resin washed with ethanol.

3.3.2 Treatment of MgLS and NaLS spent liquors with resin

The spent liquors were protonated using the regenerated Dowex resin prepared as described previously (section 3.3.1). The Dowex resin was dosed at the recommended ratio of 4 to 5 g Dowex resin per 1 g of dry solids (TDS) of the spent liquor. The dry solids content of the liquors was determined according to the method detailed in section 3.5.1. To achieve this ratio, 70 g and 75 g Dowex resin were transferred to glass bottles containing 100 g of NaLS and MgLS each, which represented approximately 13 and 14 g dry solids, respectively. These mixtures were shaken for three hours at 200 revolutions per minute (rpm). After shaking, the mixtures were filtrated using borosilicate POR 3 glass filters. All samples were prepared in triplicate.

The filtrates from the Dowex treatment were then adsorbed onto the XAD-7 resin. This was done at the recommended application rate of 10 g XAD-7 resin per 1 g TDS lignosulphonic acid, as described by Sumerskii *et al.*, 2015. To achieve this ratio, 140 g and 150 g XAD-7 resin were added to the Dowex filtrates from the NaLS and MgLS samples, respectively. The solutions were shaken overnight (16 h) at 200 rpm. The mixtures were then filtrated, and the resins washed three times with acidified water (170 ml) and distilled water (170 ml), respectively. The acidified water was adjusted to pH 2 with HCl.

A volume of 225 ml ethanol was then used to desorb the lignosulphonic acid from the XAD-7 resins. After desorption, the ethanol fraction was removed by rotary evaporation using a Heidolph Hei-VAP Precision Rotavap (Schwabach, Switzerland). This was done by transferring the samples into to 2 L evaporation flasks and attaching each flask to the rotary

evaporator filled with deionised water. Also attached to the equipment was a 2 L catching flask. The flask containing the sample was immersed into the water bath that was set to 40 ºC. The pressure was lowered to below 180 mbar and the evaporated ethanol was collected in the catching flask. The sample that remained in the evaporation flask was freeze-dried at -80ºC and vacuum-dried in a Telstar Lyoquest Freeze Dryer (Madrid, Spain). The mass percentage of purified sample was calculated using Equation 2 as described in Section 3.4. The lignosulphonate products obtained using the resin treatment were annotated as DOW-XAD-7.

3.4 Extraction of lignosulphonate using ultrafiltration

Aliquots of 151.97 g MgLS and 153.47 g NaLS were weighed and transferred into the ultrafiltration cell (Amicon 8200, Merck, Darmstadt, Germany) fitted with a 1 kDa membrane. The cell was then placed on a stirring plate and stirred at 200 rpm. A 2.0 L water reservoir tank, filled with deionised water, was attached to the cell. The tank was connected to a nitrogen gas line and 2.5 to 3.0 bar pressure was applied. The pressurised water from the reservoir tank was fed into the cell and all the components that were permeable through the 1 kDa membrane were collected in a 2 L glass Schott bottle, as the permeate. The components remaining in the ultrafiltration cell (retentate) were collected and freeze-dried.

The permeate was concentrated using a rotary evaporator. The temperature on the rotary evaporator was set at 40°C and pressure below 70 mbar to remove the water portion. Both the retentate and the concentrated permeate were freeze-dried and the dried powders were then left in the vacuum drier (40°C) to remove residual moisture. The masses of the dried powders were determined gravimetrically. The lignosulphonate products obtained from ultrafiltration were annotated as UF.

3.5 Analysis of spent liquors and extracted lignosulphonate

3.5.1 Determination of dry solids content of samples

The dry solids contents (Coetzee, 2016 unpublished test method) of samples were determined by weighing approximately 5 g of the samples into crucibles and drying them in an oven at 105°C for 16 h (Coetzee, 2016 unpublished test method). The dried samples were cooled and weighed again and the mass before and after oven-drying was used to calculate percentage dry solids (Equation 1).

$$Dry\ solids\ (\%) = \frac{Mass\ of\ dry\ sample\ (g)}{Mass\ of\ wet\ sample\ (g)} \times 100 \qquad \textbf{\textit{Equation 1}}$$

3.5.2 Sample yield

The yield of each sample extracted from the MgLS and NaLS spent liquors was calculated using Equation 2.

$$Yield\ (\%) = \frac{Dry\ mass\ of\ isolated\ sample\ (g)}{Dry\ mass\ of\ spent\ liquour\ used(g)} \times 100 \qquad \textbf{\textit{Equation 2}}$$

3.5.3 Ash contents

The inorganic content of the spent liquors were determined by incineration (Coetzee, 2016 unpublished test method). The spent liquors were weighed into crucibles and transferred into a muffle furnace. The samples were then incinerated at 800°C for 2 h. The mass before (bone-dry) and after incineration was used to calculate the percentage ash (Equation 4) in the liquor sample. The bone-dry mass of the weighed sample was used (Equation 3).

$$Bone\ dry\ sample\ weight = (\frac{Weighed\ sample\ (g) \times Dry\ solids\ (\%)}{100}) \qquad \textbf{\textit{Equation3}}$$

$$Ash\ \%\ of\ solids = (\frac{Ash\ (g)}{Bone{-}dry\ sample\ weight\ (g)}) \times 100 \qquad \textbf{\textit{Equation 4}}$$

3.5.4 Cations

The cation composition of the two spent liquors was determined by Inductive Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Agilent (5110), California, USA), prior to purification. Calibration standards (1 to 200 mg/L) for the elements calcium (Ca), potassium (K), magnesium (Mg) and sodium (Na) were prepared from 1000 mg/L stock solutions. The stock solution for these elements were prepared from commercially available standard solutions. Calibration standards (0.1 to 2 mg/L) for transition elements (aluminium, barium, beryllium, copper, cobalt, cadmium, chromium, iron, manganese, nickel, strontium and zinc) were also prepared from a commercially available multi-element solution. The MgLS and NaLS liquor samples were prepared by dilution in deionised water. The samples and calibration standards were then quantified using the ICP-OES. The absorbance values of the standards were used to construct calibration curves and the concentrations (mg/L) of the unknown samples were determined from the regression equations (Ndlovu, 2018 unpublished test method).

3.5.5 Lignosulphonate content determination using UV spectrometer

The lignosulphonate content of the spent liquors and the purified lignosulphonate samples were determined by ultra-violet (UV) spectrophotometry (Helios β (Unicam) spectrophotometer,

Thermo). Samples were appropriately diluted, and absorbance values determined at a wavelength of 280 nm.

The lignosulphonate content was calculated and expressed as percentage solids by first determining lignosulphonate content (g/kg) using Equation 5 and then converting it to the percentage solids using Equation 6 (Coetzee, 2017 unpublished test method). The LS (%solids) gives an indication of the purity of the extracted sample. The extinction coefficient (ε) in Equation 5 was previously determined by Coetzee, (2017 unpublished test method).

$$LS\ (g/kg) = \left(\frac{\text{Absorbance (g/kg)}}{\varepsilon\ (g/kg/cm)}\right) \times Dilution\ factor \qquad \textbf{Equation 5}$$

$$LS\ (\%\ solids) = \left(\frac{Lignosulfonate\ (g/kg)}{Dry\ solids\ (g/kg)}\right) \times 100 \qquad \textbf{Equation 6}$$

During the experiment there were samples in which a lignosulphonate content of more than 100% yield was measured. The lignosulphonate (% solids) was then adjusted to 100% for samples measuring LS content over 100% by deducting the ash content (Equation 7).

$$LS\ adjusted\ (\%\ solids) = 100\% - ash\ content(\%) \qquad \textbf{Equation 7}$$

To calculate the lignosulphonate content extracted from the original sample the calculation steps outlined below were followed.

Firstly, the lignosulphonate content (g) of the raw spent liquor was calculated:

$$LS\ content\ (g) = sample\ bone\ dry\ mass\ (g)\ \times \left(\frac{LS\ (\%solids)}{100}\right) \qquad \textbf{Equation 8}$$

The next step was to determine the mass of lignosulphonate in the extracted sample:

$$LS\ content\ (g) = extracted\ sample(g) \times \left(\frac{LS\ (\%solids)}{100}\right) \qquad \textbf{Equation 9}$$

Finally, the LS from extracted sample was divided by the LS in the raw spent liquor, to obtain the actual LS extracted from the sampled spent liquor*:*

$$LS\ content\ (\%) = \left(\frac{LS\ in\ extracted\ sample(g)}{LS\ in\ raw\ spent\ liquor(g)}\right) \times 100 \qquad \textbf{Equation 10}$$

3.5.6 Fourier-Transform Infrared spectroscopy

A Fourier Transform Infrared (FTIR) spectroscopic scan (400 to 4000 cm^{-1}) of the two spent liquors, the purified lignosulphonates and the wastes (generated during purification) were conducted. Samples were scanned on a Bruker ALPHA-P FTIR spectrometer (Anton Paar, Graz, Austria) (Marake, 2020 unpublished test method). The dried samples were placed on an

attenuated total reflection (ATR) crystal surface. The scans were captured using the OPUS Touch software.

3.5.7 Molecular weight analysis using Gel Permeation Chromatography

Only the purified and fractionated samples were analysed for molecular weight distribution for this study. The molecular weight analysis was conducted by gel permeation chromatography (GPC) as described by Sulaeva *et al*., (2017). A GPC instrument (Kontron 420 HPLC pump, pulse damper, Ultimate 3000 autosampler and column oven) equipped with Agilent PolarGel M columns 7.5 x 300 mm (5 um particle size) and a guard column (7.5 x 50 mm) was used. The GPC system was equipped with Ultraviolet-visible (UV-VIS) and Shodex RI-101 reflective index (RI) detectors. The column oven was set at 40°C.

The instrument was calibrated using poly-(styrene sulphonate) sodium salt standards (Mp between 891 and 152 kDa). The standards were pre-treated with a cation exchange resin (Dowex® 50W X8) by adding 2 to 3 g of the resin to the standard solution and shaking overnight. The standard solution was prepared by dissolving the standard into 10 ml distilled water. After shaking, the mixture was filtered, and the filtrate was freeze-dried to remove the water portion. A solution of dimethyl sulfoxide (DMSO) and lithium bromide (70/30, v/v) was prepared and used as the mobile phase and as a solvent for the protonated standards and sample. The protonated standards were prepared by weighing out 15 mg and dissolving them in 1 ml of the mobile phase. The samples (8 mg) were prepared by also dissolving them in the solvent. Samples were shaken overnight and then filtered through a 0.45 mm PTFE filter.

Samples (10 ml) were injected and analysed at 40°C. The different molecular weight fractions were separated using DMSO/LiBr (70/30, v/v) as eluent at a flow rate of 0.5 ml/min for 65 min. The UV-VIS detector was set at 280 nm. Data acquisition and evaluation was done using Chromeleon software (version 6.80).

3.5.8 DoS: Conductometric titration

The DoS of the purified samples were determined according to the method described by Kortner *et al*., (2018) using conductometric titration. A Titrando titration unit from Metrohm (Herisau, Switzerland) equipped with an 856-conductivity module and an electrode with a 5-ring conductivity cell combined with a PT1000 thermo sensor was used. Approximately 40 mg of sample was dissolved in 40 ml ultrapure water. This sample solution was then titrated with a 0.1 M lithium hydroxide (LiOH) solution. In total 6 ml of the LiOH solution was added in

0.05 ml aliquots. This solution was then back-titrated using 0.1 M HCl. The same titrant volume addition of 6 ml HCl added in 0.05 ml aliquots was followed.

The Tiamo™ software from Metrohm was used for data acquisition. A titration curve was plotted using the data obtained from the titration, and the sulphonic acid groups were calculated as described in Chapter 2 using Equation 1.

3.6 Results and discussion

3.6.1 Observations during sample extraction

It was observed that the colour of the XAD-7 resins changed from white to brownish as the resins were mixed with Dowex filtrates (Figures 3.1 and 3.2). This change in colour was more pronounced for the filtrate from the NaLS liquor (Figure 3.1b) compared to the MgLS (Figure 3.2b) liquor. It was observed that the NaLS liquor was originally much darker in colour compared to MgLS. The XAD-7 resin was then filtered and washed with acidified water. The wash water filtrate were discarded (Figure 3.1c and 3.2c). The lignosulphonate portions adsorbed on the XAD-7 resins from the MgLS and NaLS liquor sources were desorbed using ethanol and collected as the products (Figure 3.1d and 3.2d). The product from the MgLS source had a reddish to brown colour (Figure 3.2d), whereas that from the NaLS source was dark brown (Figure 3.1d). After freeze drying the products were obtained as fine brown powders (Figure 3.1e and 3.2e).

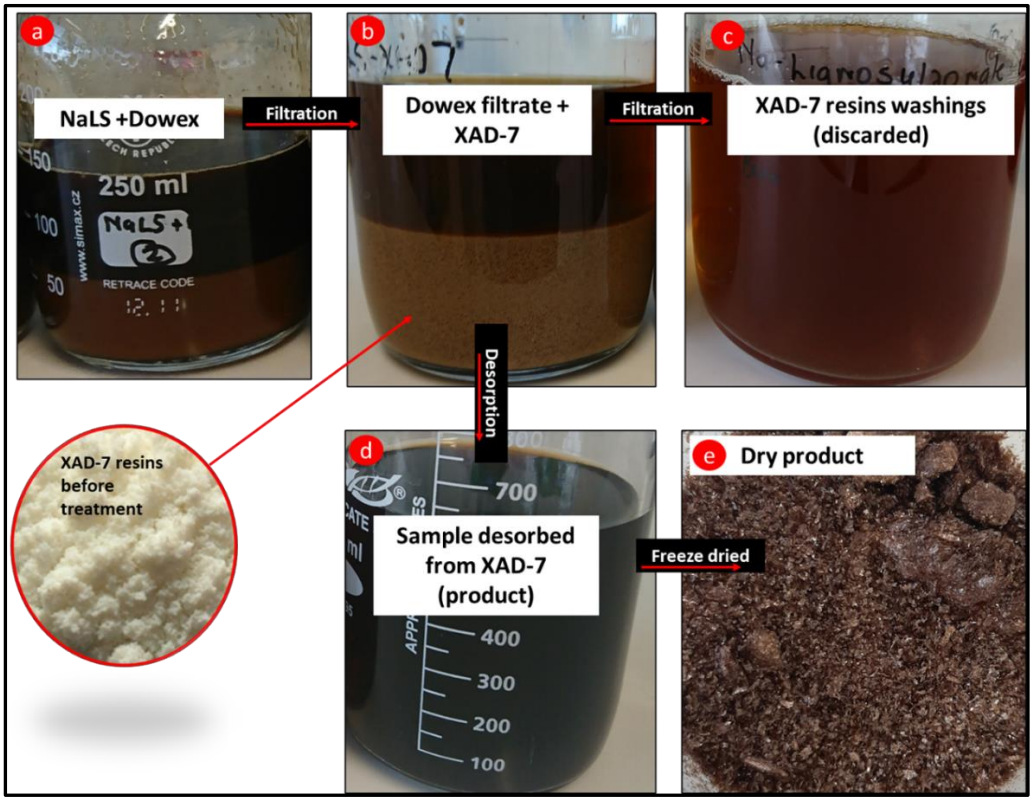

Figure 3.1: Treatment of NaLS with Dowex and XAD-7 resins. (a) NaLS treated with Dowex resins, (b) Dowex filtrate treated with XAD-7 resins, (c) XAD-7 waste, (d) liquor extracted product, (e) dried extracted product.

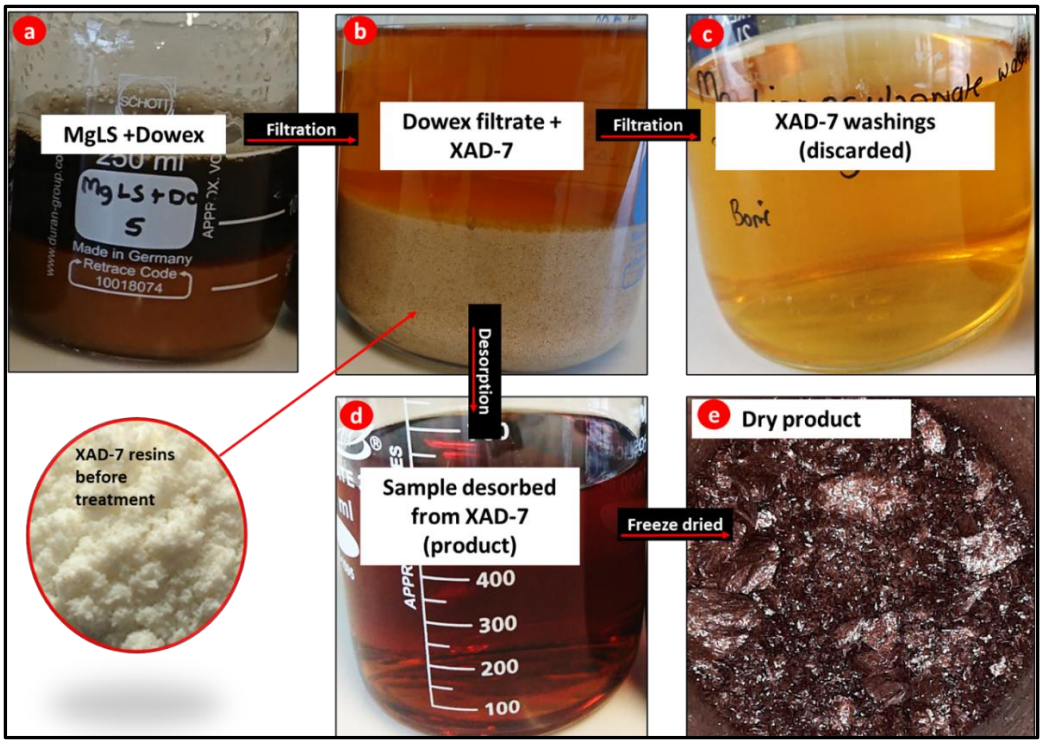

Figure 3.2: Treatment of MgLS with Dowex and XAD-7 resins. (a) MgLS treated with Dowex resins, (b) Dowex filtrate treated with XAD-7 resins, (c) XAD-7 waste, (d) liquor extracted product, (e) dried extracted product.

3.6.2 Effect of isolation technique on ash removal

The spent liquors were sampled prior to the evaporation step at the different mills and the solids contents were relatively low at 13.9 and 15.0% for the NaLS and MgLS, respectively (Table 3.1). Due to differences in the pulping processes, the NaLS liquor contained a notably higher concentration of ash compared the MgLS liquor (35.3 and 12.4 % of solids, respectively). As expected, the Mg^{2+} was the predominant cation in the MgLS liquor and Na^{+} in the NaLS spent liquor (Table 3). The cooking liquors contained magnesium sulphite ($MgSO_3$) and sodium sulphite (Na_2SO_3), respectively. Ca^{2+} and K^{+} were also detected in considerable amounts (Table 3.1). The cations that were detected in low concentrations were included in the appendices (Appendix A).

Table 3.1: Solids (% of sample) and ash (% of solids) content and composition of the spent liquors and the lignosulphonate products purified using resin treatment (DOW-XAD-7) and ultrafiltration (UF).

Sample		Solids (% of sample)	Ash (% of solids)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)
NaLS	Spent liquor	13.9	35.3	78.2	17854	258.4	39.0
	DOW-XAD-7	*100	2.3	ND	ND	ND	ND
	UF	*100	5.3	ND	ND	ND	ND
MgLS	Spent liquor	15.0	12.4	4889	29.7	350.7	402.5
	DOW-XAD-7	*100	2.8	ND	ND	ND	ND
	UF	*100	4.7	ND	ND	ND	ND

* = Purified lignosulphonate freeze dried and vacuum dried to complete dryness
ND = not determined

Both purification techniques resulted in notable decreases in the ash content with the ash content of the purified samples ranging between 2.3 and 5.3 % of the total solids (Table 3.1). The ash contents of the lignosulphonates purified with DOW-XAD-7 resin were also lower (2.3 and 2.8 % of solids) compared to the that obtained from ultrafiltration (5.3 and 4.7 % of solids) for the NaLS and MgLS liquors, respectively (Table 3.1). This indicates that lignosulphonate isolation using resins was more successful in removing inorganic material from the spent liquors compared to ultrafiltration. The results also indicated that the initial ash content of the samples did not influence ash removal capacity of the two isolation techniques, since similar concentrations of ash remained in the purified samples of NaLS and MgLS (2.3 and 2.8 % of solids for DOW-XAD-7 and 5.3 and 4.7 % of solids for ultrafiltration) (Table 3.1).

The removal of inorganic content during the isolation of NaLS and MgLS from the spent liquors was also confirmed by FTIR data (Figure 3.3 and Figure 3.4). According to Rodríguez-Lucena *et. al*., (2009), the sulphonic groups of the lignosulphonate molecules are expected to report in the 620 to 660 cm^{-1} range. Peaks at approximately 650 cm^{-1} represent the sulphoyl groups bound to the lignosulphonate molecules, while peaks at approximately 619 cm^{-1} represent the unbound sulphur present in the spent liquor.

For the NaLS spent liquor two peaks, namely at 651 and 619 cm^{-1} were present in the 620 to 660 cm^{-1} region (Figure 3.3). The high ash content (35%) of the NaLS spent liquor was confirmed by the pronounced peak at 619.17 cm^{1}. After the purification step with DOW-XAD-7 resin and ultrafiltration, the peak at 619.17 cm^{-1} almost disappeared, indicating the removal

of unbound sulphur as part of the ash content. The peak at 651.4 cm^{-1} represented the sulfonyl group attached to the aromatic ring of the lignosulphonate structure. The DOW-XAD-7-purified sample showed a more pronounced peak at the 651.4 cm^{-1} compared to the NaLS spent liquor and the lignosulphonate purified with ultrafiltration (Figure 3.3).

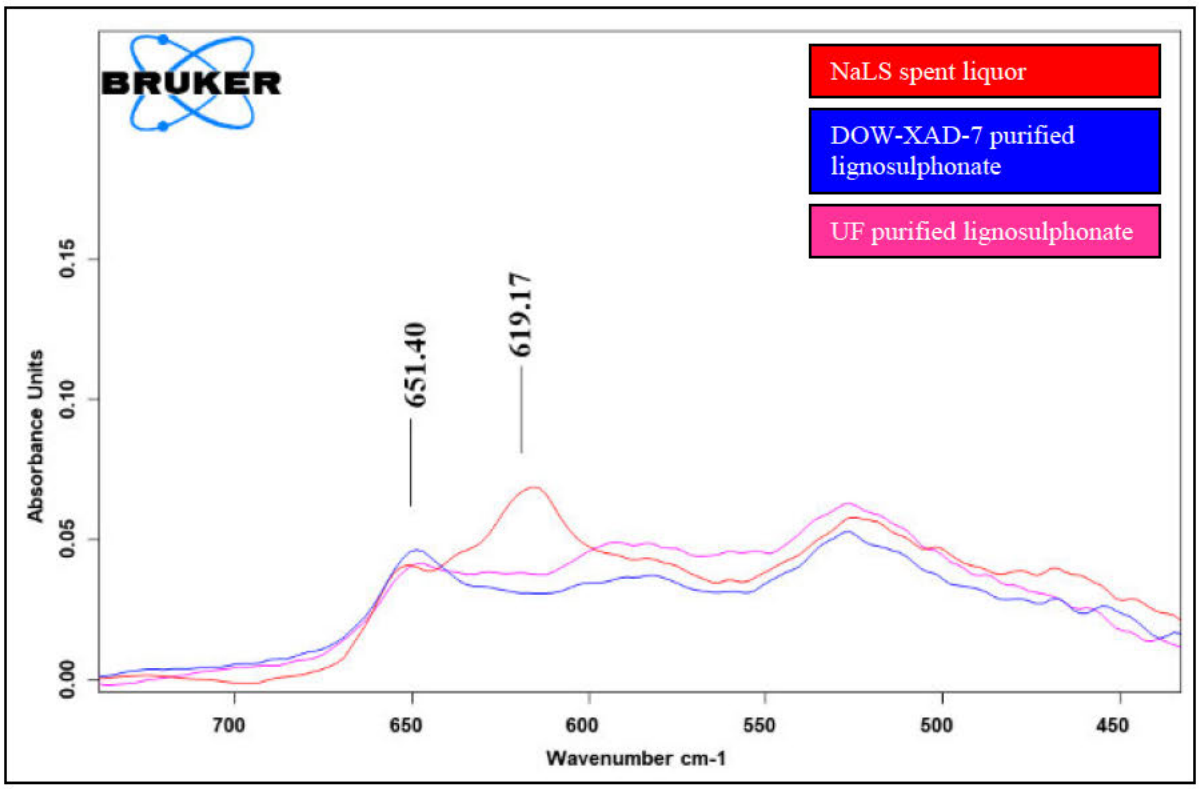

Figure 3.3: FTIR scan comparison of spent NaLS liquor (red) with the lignosulphonate purified with DOW-XAD-7 resin (blue) and lignosulphonate purified with ultrafiltration (pink).

The FTIR spectra for the MgLS spent liquor were also compared to that of the lignosulphonates that were purified using the DOW-XAD-7 resin and ultrafiltration, respectively (Figure 3.4). The peak corresponding to the unbound sulphoyl groups (619.7 cm^{-1}) was not as distinctive for the MgLS spent liquor as that of the NaLS spent liquor (Figure 3.3), confirming its lower ash content (12.4 % of solids) compared to the NaLS spent liquor (35.3 % of solids) (Table 3.1). The small peak observed at 626 cm^{-1} in the MgLS spent liquor represented the Mg^{2+} of the spent liquor. Similar to the NaLS sample, the peak at 619.7 cm^{-1} was not observed when the spent liquor was treated with both DOW-XAD-7 resin and ultrafiltration to purify the MgLS, indicating the removal of the unbound sulphur. The peaks observed at 650cm^{-1} for the lignosulphonate purified using the DOW-XAD-7 resin and ultrafiltration showed similar intensities (Figure 3.4).

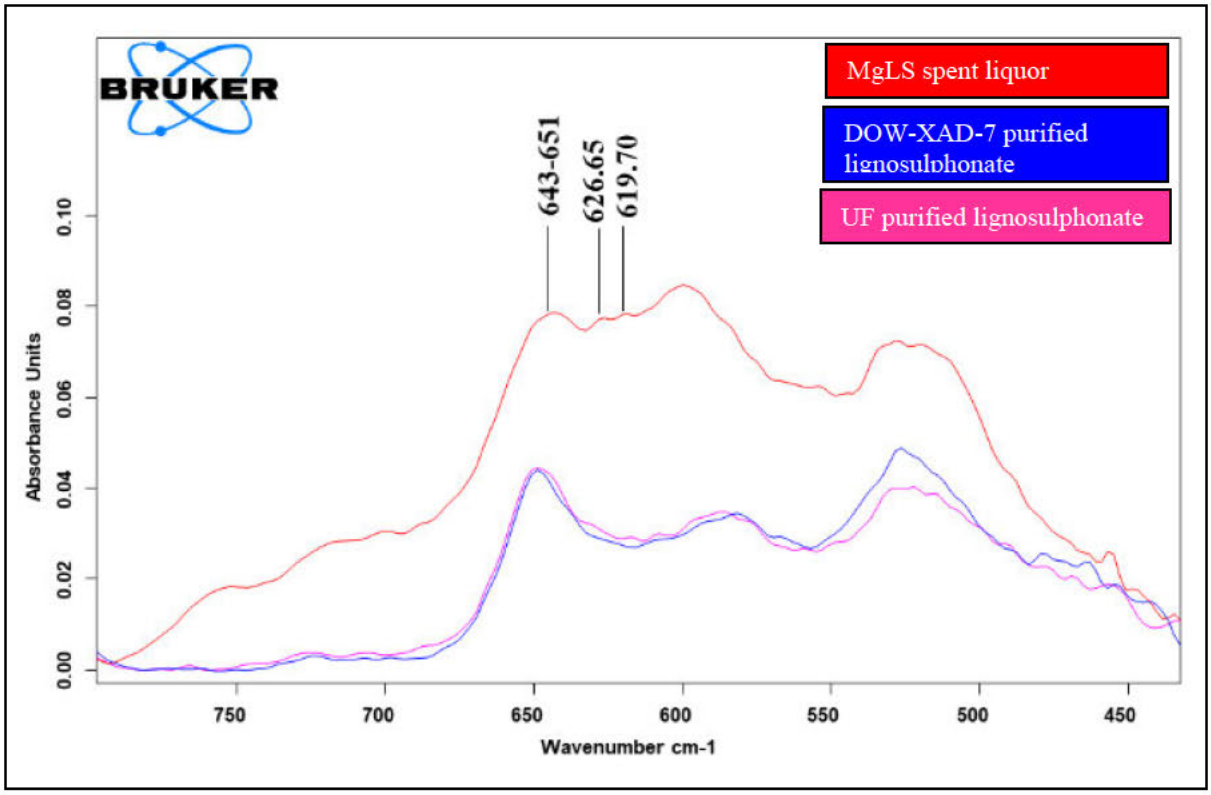

Figure 3.4: FTIR scan comparison of spent NaLS liquor (red) with the lignosulphonate purified with DOW-XAD-7 resin (blue) and lignosulphonate purified with ultrafiltration (pink).

3.6.3 Effect of isolation technique on sugar removal

The sugar content of the spent liquors and the purified lignosulphonates were not measured for this study. However, Sumerskii *et al*., (2015) reported that lignosulphonates that were purified from MgLS liquor using both DOW-XAD-7 and ultrafiltration contained very low sugar concentrations (less than one percent by weight). It was also reported by the University of Natural Resources and Life Sciences [Universität für Bodenkultur Wien, in Vienna, Austria, (BOKU)], that the sugar content of a lignosulphonate purified with DOW-XAD-7 resin from a NaLS liquor (similar to the sample used in the current study), contained a negligible amount of sugar (Sumerskii, 2017 - 2018, unpublish data). However, Area *et.al*., (1999) measured substantial amounts of sugar in lignosulphonate purified from a of NSSC liquor that was ultrafiltrated using membranes of several MWCO sizes (10 to 2 kDa). Results from studies conducted at the Sappi Technology Centre (Pretoria South Africa) also indicate that most of the sugar in NaLS spent liquor (between 10 and 15 % of the solids content) is oligomeric sugar that is bound to the lignosulphonate to form lignin-carbohydrate complexes (LCC) (Grant, 2021, unpublished data). It was, therefore, possible that the sugar was retained with the lignosulphonate during ultrafiltration during this study.

3.6.4 Effect of isolation technique on sample yield and lignosulphonate yield

The yields were also calculated for the samples obtained from treatment of the two spent liquors with DOW-XAD-7 resin and ultrafiltration. The sample yield was expressed as the percentage of the solids of the treated spent liquor that was recovered. The lignosulphonate yield was expressed as the percentage of available lignosulphonate that was recovered during each isolation.

It was observed that the sample yields obtained from the NaLS spent liquor were different when DOW-XAD-7 resin and ultrafiltration were compared (12.9% and 20.6%, respectively) (Table 3.2). The lignosulphonate yields for these treatments were calculated as 24.4 and 32.3%, respectively.

Similar results were reported previously by the University of Natural Resources and Life Sciences (Universität für Bodenkultur Wien, BOKU) in Vienna, Austria, when a similar NaLS was analysed. At the time BOKU also compared the DOW-XAD-7 resin and ultrafiltration as techniques to purify lignosulphonate from NaLS spent liquors. They also found that isolation with DOW-XAD-7 resin resulted in a lower sample yield (between 12 and 16%) compared to the sample yield achieved with ultrafiltration (between 18 and 27%) (Sumerskii, 2017 - 2018,

unpublish data). This trend was also observed for an ammonia-based spent liquor (NH_4LS), as reported by Sumerskii *et.al.* (2015) where the sample yield was 47% for DOW-XAD-7 resin and 62% when ultrafiltration was used.

Table 3. 2: Sample yield, lignosulphonate yield and lignosulphonate purity obtained after treatment of NaLS and MgLS spent liquors with DOW-XAD-7 resin and ultrafiltration, respectively.

Sample		Sample yield (% of solids treated)	LS yield (% of LS recovered)	*LS purity (% of solids recovered	#LS purity (% of solids recovered
NaLS	Spent liquor	NA	NA	51.6	NA
	DOW-XAD-7	12.9	24.4	153.4	97.7
	UF	20.6	32.3	80.8	80.8
MgLS	Spent liquor	NA	NA	50.0	NA
	DOW-XAD-7	18.7	36.4	108.0	97.2
	UF	17.1	32.6	104.4	95.3

* = Measured lignosulphonate purity (measured at 280 nm and calculated using adsorption coefficient of ε = 10.4)
# = Calculated lignosulphonate purity. Values of LS >100 % were assumed as 100% and ash content subtracted calculated to calculate purity
NA = not applicable

The cause of the differences in the sample and lignosulphonate yields achieved when NaLS spent liquor was treated using DOW-XAD-7 and ultrafiltration, was not investigated during this study. However, Sumerskii *et al.*, (2015) speculated that the XAD-7 resin is very selective in the compounds it adsorbs in spent liquor. It was found that XAD-7 resin adsorption favoured less sulphonated compounds when its capacity to adsorb potassium guaiacolsulphonate and phenol were compared since it adsorbed more phenol than potassium guaiacolsulphonate. Therefore, it was suggested that the low adsorption of potassium guaiacolsulphonate could be due to a combination of the sulphonation degree and molecular weight of the compound being purified (Sumerskii *et.al.*, 2015). Therefore, it is possible that the XAD-7 resin adsorbed less sulphonated compounds in the NaLS spent liquor, although this need to be confirmed by characterising the liquor component not adsorbed by the resin as well.

When the MgLS spent liquor was treated, the sample yields recovered after DOW-XAD-7 treatment and ultrafiltration were comparable (18.7 and 17.1%, respectively), representing lignosulphonate yields of 36.4 and 32.6 %, respectively (Table 3.2). Sumerskii *et.al.*, (2015) also purified two different MgLS spent liquors originating from an acid sulphite pulping process, using DOW-XAD-7 resin and ultrafiltration (1 kDa), respectively. The sample yields

obtained were similar for the two isolation techniques for both samples, namely 24 and 25% for the one sample and 40 and 39% for the other (Sumerskii *et.al.*, 2015).

The low lignosulphonate yields that were achieved with the DOW-XAD-7 resin (24.4 % and 36.4 % respectively for NaLS and MgLS) can be ascribed to lignosulphonate losses that were incurred during the Dowex pre-treatment and XAD-7 resin treatment. This was confirmed by FTIR analyses of the filtrates that were removed after the resin treatments of the NaLS spent liquor (Figure 3.5) and MgLS spent liquor (Figure 3.6).

Peaks in the 650 cm^{-1} regions of the spectra indicated that the two waste streams contained notable portions of the bound sulphoyl group for both NaLS and MgLS liquor sources. Since the bound sulfonyl groups represented lignosulphonate, it indicated that not all the lignosulphonates were retained by the resins and a large portion was lost with filtrates. It can also be deduced that the Dowex resin extracted some of the lignosulphonate and it was, therefore, not selective to the cations from the inorganic compounds (ash) only.

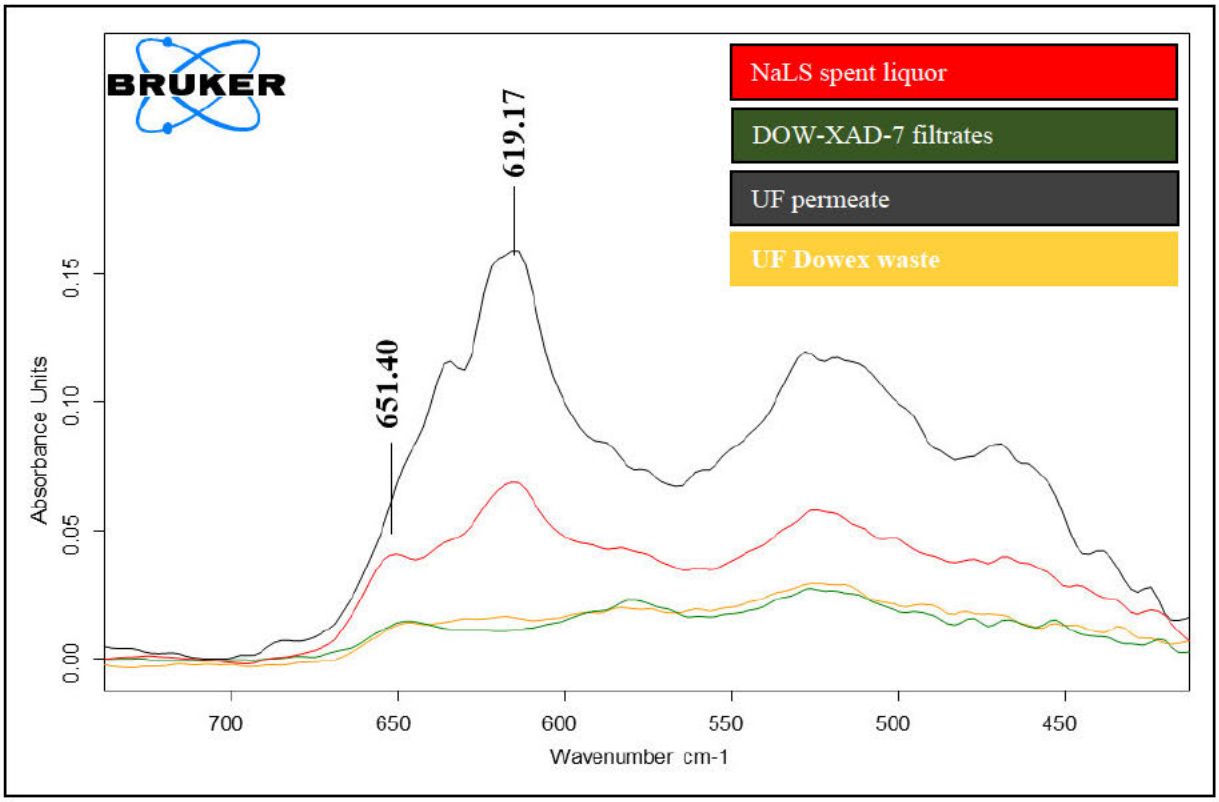

Figure 3.5: FTIR comparative scan of spent NaLS liquor (red) with the filtrates removed during DOW-XAD-7 resin treatments (green). Dowex waste after deashing ultrafiltration retentate(orange) and permeate from ultrafiltration (grey).

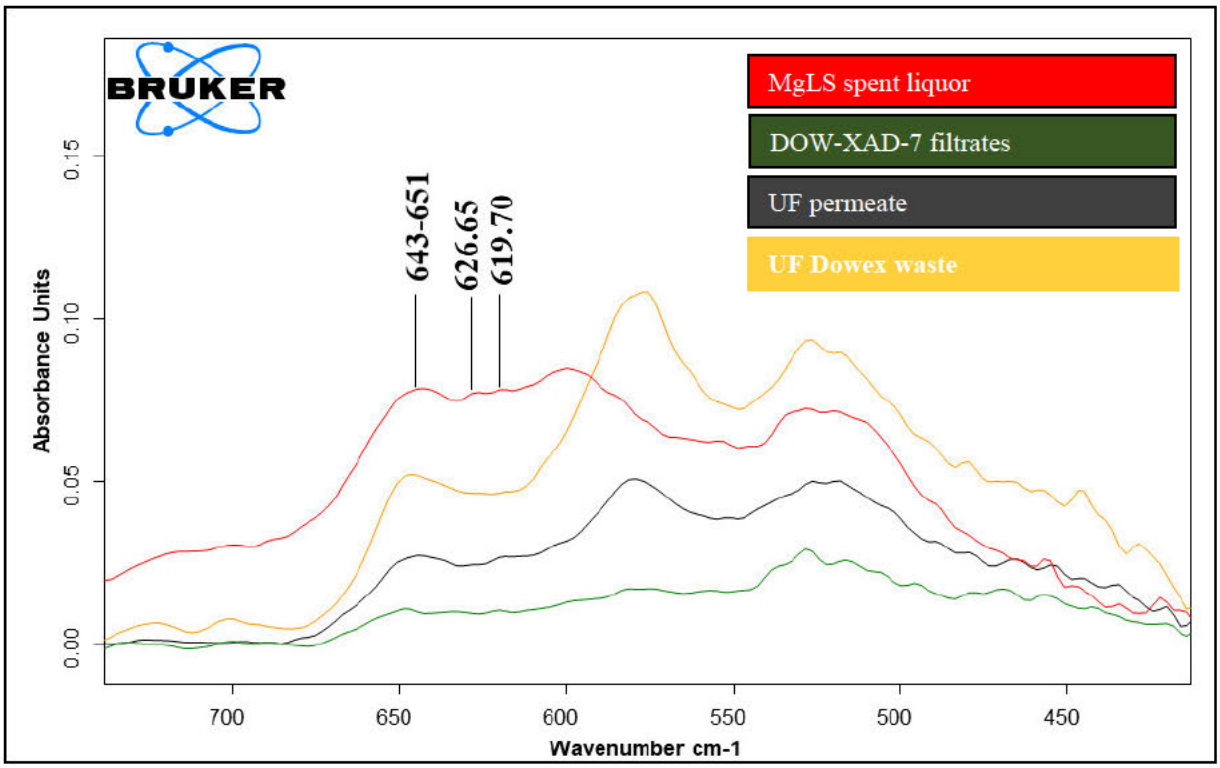

Figure 3.6: FTIR comparative scan of spent MgLS liquor (red) with the filtrates removed during DOW-XAD-7 resin treatments (green). Dowex waste after deashing ultrafiltration retentate(orange) and permeate from ultrafiltration (grey)

It was, however, unclear why such low lignosulphonate yields were achieved when the lignosulphonates were purified from NaLS and MgLS spent liquor using ultrafiltration (32.2 and 32.6 %, respectively). It is possible that low molecular weight lignosulphonate fractions (< 1 kDa) present in the spent liquors were removed together with the ash in the permeates. This was confirmed by the presence of peaks in the 650 cm^{-1} region of the FTIR spectra of the permeates that was collected during ultrafiltration (Figure 3.5 and Figure 3.6).

3.6.5 Effect of isolation technique on lignosulphonate purity

The lignosulphonate contents of the purified samples were also measured to determine the purity of the samples (Table 3.2). The lignosulphonate content of the sample that was purified from the NaLS spent liquor using ultrafiltration, was measured as 80.8 % of the solids. Therefore, 19.2 % of the solids content of the purified sample was assumed to consist of ash (measured as 5.3% of solids), and sugars. As discussed previously in Section 3.6.3, it is clear from literature that a notable amount of sugar could be present in samples purified from NSSC liquor with ultrafiltration Area *et.al.*, 1999. The sugar content on the samples purified by ultrafiltration will however need to be confirmed as the experimental conditions for this study and Area *et.al.*, 1999 differ.

The lignosulphonate content of the sample that was purified from NaLS using a DOW-XAD-7 resin was calculated as 153 % of total solids content, which was s a clear overestimation. This overestimation of the lignosulphonate content could be ascribed to the fact that the absorption coefficient that was used for all calculations were based on a lignosulphonate sample that was purified from a NSSC hardwood spent liquor, using ultrafiltration. A lignosulphonate concentration of more than 100 % indicated that this absorption coefficient was not suitable to calculate the lignosulphonate content of samples purified using DOW-XAD-7 treatment.

It is, therefore, recommended that individual adsorption coefficients be determined for each liquor type and each isolation technique to calculate the lignosulphonate content more accurately in future. For this reason, the purity of the DOW-XAD-7 extracted lignosulphonate was expressed as 97.7 % (Table 3.2). This value was calculated as the difference between 100 % and the ash content (2.3 % of solids) by the using Equation 8.

The lignosulphonate contents of the samples purified from MgLS using both DOW-XAD-7 treatment and ultrafiltration, were also calculated as higher than 100 % of total solids content (108.0 and 104.4 % of solids, respectively). It was concluded that these values were also overestimated since an absorption coefficient for NaLS was used that was not representative for MgLS liquor. The purity of the lignosulphonate samples were therefore, calculated as 95.3 % and 97.2 % of the total solids content for DOW-XAD-7 resin treatment and ultrafiltration, respectively.

3.6.6 Effect of isolation technique on molecular weight and sulphonic acid content

Weight-average molecular weights (Mw) of 3.1 and 5.9 kDa were measured for the lignosulphonates that were purified from NaLS spent liquor using DOW-XAD-7 treatment and ultrafiltration, respectively (Table 3.3). These Mw values were much lower compared to the lignosulphonates purified from the MgLS spent liquor using DOW-XAD-7 treatment (12.0 kDa) and ultrafiltration (19.5 kDa) (Table 3.3). Instead, these results were comparable to previous reports stating that the Mw of Sappi MgLS ranges between 12 and 20 kDa and that of NaLS between 2 and 7 kDa (Sumerskii, 2017-2018 unpublished data, Sumerskii, 2014- 2015 unpublished data). The polydispersity index (PDI) (Mw/Mn) of the two samples purified from the MgLS spent liquor (8.4 and 7.6 for DOW-XAD-7 resin and ultrafiltration) were also higher than that from the NaLS (3.0 and 4.6, respectively) (Table 3.3). This higher calculated PDI indicated that the samples extracted from the MgLS spent liquor contained fractions with a wider range of molecular weight sizes, compared to those extracted from the NaLS spent

liquor. The vast difference in the molecular weight properties of these two spent liquors indicated that the two pulping processes (NSSC and acid sulphite) produced lignosulphonates of different molecular weights.

For each spent liquor, the samples purified by DOW-XAD-7 displayed a lower Mw than those purified by ultrafiltration (Table 3.3). Several studies carried out by BOKU confirmed that the Mw for NaLS samples purified by XAD-7 resin was between 2 and 3 kDa, whereas NaLS samples purified by ultrafiltration (1 kDa) were reported as between 4 and 7 kDa (Sumerskii, 2017-2018 unpublished data; Sumerskii, 2014- 2015 unpublished data, Sumerskii; 2019-2020 unpublished data). These differences could be ascribed to the selectivity of the XAD-7 resin for compounds of a specific molecular weight and DoS, compared to ultrafiltration.

Table 3.3: Molecular weights (expressed as Mw, Mn and Mw/Mn) and degrees of sulphonation (expressed as mmol/g lignosulphonate and % of lignosulphonate), of NaLS and MgLS spent liquors that were treated with DOW-XAD-7 resin and ultrafiltration, respectively. Results summarised from Appendices A and B.

Sample		Molecular weights			DoS	
		Mw (kDa)	Mn (kDa)	Mw/Mn	mmol/g LS	% of LS
NaLS	DOW-XAD-7	3.1	1045	3.0	0.29	2.36
	UF	5.9	1302	4.6	0.37	3.00
MgLS	DOW-XAD-7	12.0	1432	8.4	0.41	3.35
	UF	19.5	2562	7.6	0.57	4.60

The lignosulphonates that were purified from the NaLS and MgLS spent liquor using DOW-XAD-7 displayed a slightly lower degree of sulphonation (2.36 and 3.35 % of lignosulphonate, respectively) than the lignosulphonates that were purified using ultrafiltration (3.00 and 4.60 % of lignosulphonate, respectively) (Table3.3). Sumerskii *et al.*, (2015) found that the sulphonic acid content of magnesium-based lignosulphonate purified by DOW-XAD-7 resin was lower compared to ultrafiltration. The difference in sulphonic acid content between the two isolation techniques was between 2 and 4 % (Sumerskii *et al.*, 2015). As previously noted, the authors speculated that the XAD-7 resin had less affinity to highly sulphonated lignosulphonates and would, therefore, not adsorb these highly sulphonated moieties. Overall, the degree of sulphonation for the two lignosulphonate samples purified from the NaLS spent liquor were lower than that of the MgLS (Table 3.3). This difference in DoS could be ascribed to differences in the NSSC and acid sulphite pulping processes.

The sulphonic acid content reported in this study was lower than what was previously reported in literature. Sumerskii *et al*. (2015) measured a sulphonic acid content of 9 and 14 % of LS content respectively, for lignosulphonates purified from two MgLS spent liquors when using DOW-XAD-7 treatment, while 13 and 17% of LS content were reported for lignosulphonates purified by ultrafiltration.

BOKU reported the sulphonic acid content for NaLS streams purified with DOW-XAD-7 resins to range between 0.50 and 1.23 mmol/g (Sumerskii, 2017-2018 unpublished data). When ultrafiltration was used as the purification technique, the sulphonic acid content ranged between 0.93 to 1.47 mmol/g (Sumerskii, 2017-2018 unpublished data). In this study the sulphonic acid content for the samples purified from NaLS spent liquor was 0.29 and 0.37 mmol/g respectively using DOW-XAD-7 and ultrafiltration, (Table 3.3). The differences between the sulphonic acid content reported in literature compared to those found in this study were not explored further.

3.7 Conclusion

The use of polymeric adsorbents (Dowex and XAD-7 resins) and ultrafiltration as purification techniques for NaLS from the NSSC spent liquors and MgLS from acid-sulphite spent liquors were compared. The sample yield when using XAD-7 resins was similar to ultrafiltration when purifying MgLS spent liquor streams. However, the polymeric resins investigated for this study, resulted in higher purity samples in terms of inorganic content, compared to ultrafiltration.

The sample yield for NaLS samples purified by XAD-resins was, however, lower than those purified by ultrafiltration. None of the isolation techniques were able to extract all the lignosulphonate contained in either spent liquors.

The Mw of the samples purified from MgLS was higher compared to the Mw of samples isolated from the NaLS spent liquor stream, irrespective of the purification technique. Overall, it was observed that samples purified by ultrafiltration had a higher Mw than those purified by XAD-7 resins. The sulphonic acid content between ultrafiltration and XAD-7 was not markedly different for either spent liquor.

3.8 Recommendation

During this study it was observed that, when analysing the lignosulphonate content of purified samples, the lignosulphonate content was over-estimated, therefore, it is recommended that the extinction coefficient is determined for each individual purification technique.

This study also showed that neither ultrafiltration nor a XAD-7 resin extracted all the lignosulphonate present in the spent liquor. Other isolation techniques, that also target the lignosulphonate not adsorbed or retained by the XAD-7 resins and ultrafiltration membranes, should be investigated in future.

It is also recommended that the sugar content be determined before and after purification of spent liquors. This is especially important if the lignosulphonate compound still contain a carbohydrate complex since the presence of a LCC will lead to an overestimation of the molecular weight size and an underestimation of the sulphonic acid content of the purified spent liquor.

Finally, it is recommended that the selectivity of XAD-7 resins towards lignosulphonate molecules should be investigated. Limited absorption due to the presence of polar groups on the molecule may affect the sample yield of lignosulphonates with different molecular weights and sulphonic acid content.

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CHAPTER 4

4. DEGREE OF SULPHONATION OF LIGNOSULPHONIC ACID AT VARIOUS MOLECULAR WEIGHT DISTRIBUTION

ABSTRACT

Sequential fractionation was used to separate the lignosulphonate compounds according to different molecular weight sizes. The sequential fractionation of lignosulphonates previously extracted with DOW-XAD-7 resins from NaLS and MgLS liquors was carried out using membranes with molecular cut-off (MWCO) sizes ranging between 1 and 100 kDa. The molecular weight distribution for samples fractionated between 100 to 1 kDa were 14 to 0.7 and 17 to 0.6 kDa for NaLS and MgLS liquor streams, respectively. The samples fractionated from the MgLS source showed an increase in sulphonic acid content with a decrease in molecular weight. For the NaLS source, the sulphonic acid content increased from the 100 to the 10 kDa fractions, then reduced from 10 to 1 kDa. It should be noted that the differences in sulphonic acid content within each fraction weren't large for both the NaLS and MgLS spent liquors.

4.1. Introduction

Sequential ultrafiltration of lignosulphonates (LS) separates the lignosulphonate into different molecular weight fractions. Characterisation of these fractions allows for a deeper understanding of how the molecular weight of the lignosulphonate molecules is distributed within the same batch of spent liquor. Quantification of the sulphonic acid content of these different molecular weight fractions also provides details about the sulphonic acid content of the lignosulphonate molecule at a molecular level.

Using sequential fractionation, the variations in the molecular weight of kraft lignin and lignosulphonates present in sodium lignosulphonate (NaLS) and magnesium lignosulphonate (MgLS) spent liquors were reported in literature by several authors (Madad *et al.*, 2011; Ringena *et al*., 2005; Musl *et al*., 2020; Zinovyev et al., 2017). Understanding these variations within a spent liquor assist in making an informed decision on how the liquor should be modified for application in different industries. The molecular weight and solubility properties, which include the sulphonic acid content, can be modified using alkaline hydrolysis, hydroxypropyl sulphonation and sulphomethylation (Aro and Fatehi, 2017). Lignosulphonate

modification reactions are further discussed by several authors (Ruwoldt., 2020; Ye *et al*., 2017; Wysocka *et al*., 2016).

It was reported in Chapter 3 that the lignosulphonates that was extracted from NaLS and MgLS spent liquors using DOW-XAD-7 resins displayed molecular weights of 3.1 and 12.0 kDa, respectively, with a polydispersity index (PDI) of 3.0 and 8.4 (Table 4). These PDI values indicate that there is substantial variation in molecular weight of the extracted lignosulphonate, especially that of the MgLS liquor source. This chapter will, therefore, focus on characterising lignosulphonate molecules according to their molecular size distribution.

4.2. Materials

The NaLS and MgLS samples that were purified as described in Chapter 3, using Dowex® 50W X8 (Dowex) and Amberlite™ XAD7HP (XAD-7) resins, were put through a sequential ultrafiltration process using regenerated cellulose membranes of various molecular weight cut-off (MWCO) sizes (100 to 1kDa). The membranes were purchased from Merck (Darmstadt, Germany). The ultrafiltration unit that was used for sequential ultrafiltration was also described in Chapter 3. Throughout the study, deionised water was used.

4.3. Methods

Lignosulphonates were purified from the NaLS and MgLS spent liquors samples using DOW-XAD-7 resins as described in Chapter 3. The purified samples were then fractionated into different molecular sizes using sequential ultrafiltration as described by Ringena *et al*., (2005) and Musl *et al.,* (2020).

During sequential filtration of purified NaLS, 1.9656 g of the extracted sample was dissolved in 150 ml deionised water. This solution was then transferred into the ultrafiltration cell fitted with a 100 kDa cut-off size membrane. The cell was placed on a stirring plate and stirred at 200 rpm. A water reservoir tank filled with deionised water (2 L) was attached to the cell. The tank was connected to a nitrogen gas line and 2.5 to 3.0 bar pressure was applied. The pressurised water from the reservoir tank was fed into the cell and all the components that were permeable through the 100 kDa membrane were then collected in a 2 L glass Schott bottle as the permeate. This was continued until all the water in the reservoir tank was fed through and contents in the cell were reduced to 40 ml.

The components in the cell (retentate) were collected and freeze-dried in a Telstar Lyoquest Freeze Dryer (Madrid, Spain). The permeate, which was collected into the Schott bottle was concentrated to 150 ml (to fit into the ultrafiltration cell) using a Heidolph Hei-VAP Precision Rotavap (Schwabach, Germany) rotary evaporator set to a temperature of 40°C and a pressure maintained below 70 mbar. The concentrated permeate was then transferred into the ultrafiltration cell, now fitted with a 30 kDa membrane. The same filtration process described for the 100 kDa membrane was followed. The permeate of the 30 kDa membrane was then fed to the next membrane (10 kDa). This process was repeated for the 5 and 1 kDa membranes as well. This fractionation sequence is depicted in Figure 19. All collected retentate samples were freeze-dried and the dried powders were then vacuum dried (40ºC) to remove residual moisture. The masses of the dried powders were determined gravimetrically.

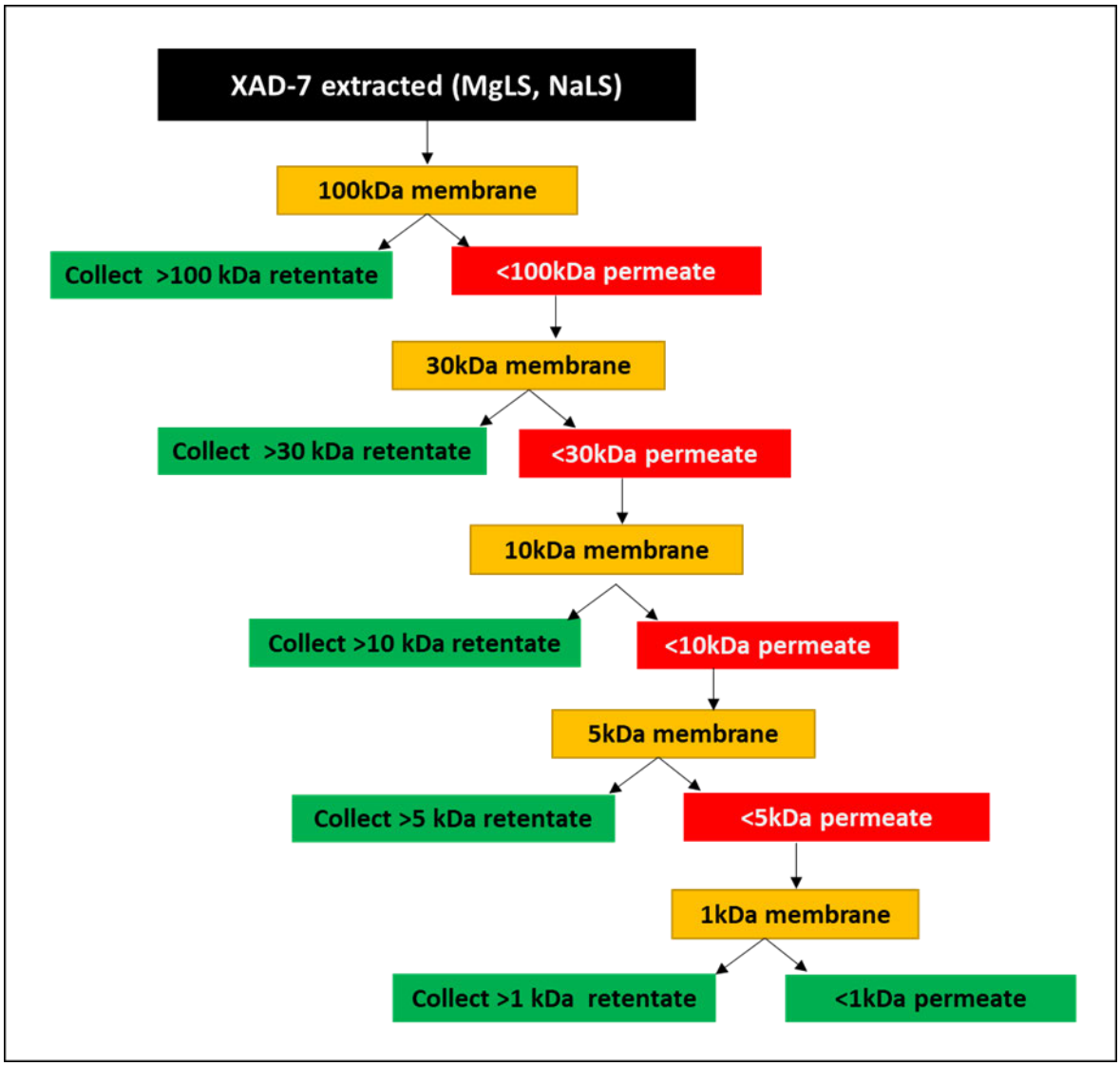

Figure 4.1: Illustration of the sequential ultrafiltration process that was conducted to separate the lignosulphonate fractions of the MgLS and NaLS liquors.

For the sequential filtration of the lignosulphonate purified from the MgLS spent liquor, 1.9743 g of the extracted sample was dissolved in 150 ml distilled water. The same fractionation procedure described for the NaLS sample was carried out using the purified MgLS material. The only difference was that the cell was directly connected to the gas supply and the feed water (2 L) was manually fed. The reason for this was the limited availability of the reservoir tanks at the time, therefore, fractionation of the NaLS and MgLS material were carried out concurrently. The permeates from all the fractions were collected and freeze-dried. The dried powders were then left in the vacuum drier to remove any residual moisture. The dried powder masses were determined gravimetrically.

4.4. Test methods

The purified samples were tested for sample yield (using Equation 2 in Chapter 3), molecular weight and sulphonic acid content. Molecular weight and sulphonic acid content measurements were carried out as described in Sections 3.5.7 and 3.5.8 of Chapter 3, respectively.

4.5. Results and discussion

4.5.1. Effect of sequentially fractionation on sample yield and molecular weight

The sample yield (% of dry sample recovered) and molecular weight properties of the sequentially filtrated fractions are reported in Table 4.1. When comparing the measured molecular weight (Mw) of the fractions retained by each membrane, to the membrane specifications, these values did not correlate. The ultrafiltration membranes retained compounds that were smaller than their stated MWCO sizes.

For example, the Mw of the fractions retained by the 100 kDa membrane were measured as 14.8 and 17.6 kDa in the purified NaLS and MgLS sources, while the 30 kDa membrane also retained lower Mw (15.6 kDa) for the MgLS (Table 4.1). This difference in sizes was seen for all the membranes with smaller MWCO sizes as well (10, 5 and 1 kDa) for both lignosulphonate sources.

Table 4.1: Extracted sample yield expressed as % of dry solids and molecular weights (kDa) measured in the retentates (R) and permeates (P) of the two spent lignosulphonate liquors that were sequentially fractionated. Results summarised from Appendix B.

Fraction	NaLS			MgLS		
	Dry sample yield (%)	Mw (kDa)	Mw/Mn	Dry sample yield (%)	Mw (kDa)	Mw/Mn
100 kDa R	31.7	14.787	7.4	12.4	17.577	10.0
30 kDa R	4.4	NES	NES	38.6	15.605	5.4
10 kDa R	8.2	4.330	3.0	8.4	4.047	2.5
5 kDa R	22.2	2.315	2.0	10.2	2.172	1.8
1 kDa R	10.4	1.362	1.7	11.4	1.192	1.5
1 kDa P	22.9	0.765	1.5	18.4	0.635	1.5
Recovery	99.8	NA	NA	99.4	NA	NA

NES = not enough sample; NA = not applicable

The samples retained by each membrane were still able to give important information, however, regarding the sample yield of each fraction and their Mw distributions. Fractionation of both spent liquors resulted in similar sample yields for the 10 kDa membrane (approximately 8% for both NaLS and MgLS). The sample yields for the 1 kDa retentate were also similar, with only a one percentage point difference between the two spent liquors (10.4% for the NaLS and 11.4% MgLS).

Marked differences in the sample yields of the two spent liquors were seen for the 100, 30 and 5 kDa fractions (Table 4.1). For the NaLS source, sample yields of 31.7, 4.4 and 22.2% were calculated for the 100, 30 and 5 kDa fractions, respectively. In contrast, for the MgLS source sample yields of 12.4, 38.6 and 10.2% were reported for the 100, 30 and 5 kDa fractions, respectively. The overall recovery achieved for both samples, were close to 100% (Table 4.1). The small sample losses were incurred during sample preparation.

When the purified NaLS was sequentially fractionated, the highest sample yield was recovered in the retentate of the 100 kDa membrane (31.7%) followed by the permeate of the 1 kDa membrane (22.9%) and the retentate of the 5 kDa membrane (22.1%). Sample yields of 10% and lower were measured in the retentates of the 1, 10 and 30 kDa membranes (10.4, 8.2 and 4.4%, respectively (Table 4.1).

The fractionation profile of the purified MgLS liquor was notably different compared to the NaLS liquor. The highest yield was recovered in the retentate of the 30 kD membrane (38.6%), followed by the permeate of the 1 kDa membrane (18.4%) and the retentate of the 100 kDa

membrane (12.4%). Lower yields were recovered in the retentates of the 1, 5 and 10 kDa membranes (11.4, 10.2 and 8.4%, respectively) (Table 4.1).

The Mw and polydispersity (Mw/Mn) of the lignosulphonates in the different fractions were also determined (Table 4.1). As expected, the fractionated samples' Mw decreased with decreasing membrane MWCO size (Table 4.1). The Mw of the lignosulphonates fractionated from purified MgLS spent liquor, ranged between 17.6 and 1.5 kDa (Table 4.1). Musl *et al*., (2020) found that the Mw of a MgLS (previously purified by Dowex and XAD-7 resin) ranged between 86 and 4 kDa when using membranes with 100 to 3 kDa MWCO sizes for fractionation.

The Mw of the lignosulphonates fractionated from purified NaLS spent liquor ranged between 14.8 and 0.7 kDa (Table 4.1). Madad *et al*., (2011) also found that the Mw of NaLS sequentially fractionated by ultrafiltration ranged between 19.5 to 2.3 kDa.

When the Mw sizes of the lignosulphonates that were recovered from the retentates of membranes with different MWCO sizes were compared for the two liquors sources, differences were seen for the 100 and 30 kDa membranes. The Mw of lignosulphonate purified from NaLS in the retentate of the 100 kDa membrane, was lower than that from the MgLS source (14.8 and 17.6 kDa, respectively). However, the Mw of the lignosulphonate in the 30 kDa fraction of the MgLS source (15.6 kDa) were close to that of the 100 kDa fraction of the NaLS (14.8 kDa). This observation corroborates the finding that the membrane MWCO size cannot be used solely as an estimate for Mw size.

Unfortunately, not enough sample was available to determine the Mw of the 30 kDa retentate fraction from the NaLS source. The fraction sizes of the other NaLS retentates were, however, similar to the retentates obtained for the MgLS liquor (Table 4.1).

Previously, it was found that the Mw of lignosulphonate obtained from the MgLS spent liquor using DOW-XAD-7 was 12.0 kDa (Table 3.3 of Chapter 3). This value corresponded to the Mw of the 30 kDa membrane's retentate (15.6 kDa) (Table 4.1).

The Mw of the lignosulphonate fractions in the 30 kDa and 100 kDa retentates were similar. When these fractions' sample yields were added, an overall yield of 51% was obtained, indicating that approximately half of the lignosulphonates purified from the MgLS using DOW-XAD-7 treatment consisted of higher Mw fractions.

For NaLS, the retentate of the 100 kDa membrane had a sample yield of 32% and a Mw of 14.8 kDa. The sum of the of the 10 kDa retentate and 1 kDa retentate and permeate yields were more than 60% of the total sample yield. This indicated that the largest fraction of the purified NaLS consisted of lower Mw fractions compared to the MgLS. The lower Mw of the lignosulphonates isolated from NaLS during this study was corroborated by the Mw reported for the lignosulphonate that was purified from the NaLS spent liquor using DOW-XAD-7 (3.1 kDa) (Table 3.3 of Chapter 3).

The polydispersity (Mw/Mn) of the lignosulphonate fractions decreased with the decrease in the membrane MWCO size (Table 4.1). For both purified spent liquors, the 100 kDa membrane resulted in a high polydispersity (7.4 and 10.0 for NaLS and MgLS, respectively), indicating that within that fraction the lignosulphonate molecule consisted of different Mw sizes. As the permeates passed through the successively smaller membranes, the polydispersity was further reduced. For the 1 kDa membranes the lowest polydispersity values were calculated (1.5), indicating that the lignosulphonate molecules retained by this fraction were similar in size.

4.5.2. Effect of sequential fractionation on solubility

When the 100 kDa retentate from the MgLS source was prepared for conductometry titration to determine sulphonic acid content, the sample did not completely dissolve in water. The sample was nonetheless put through the titration process. As the LiOH titrant was added, the solubility started improving and when the acidic titration (back-titration with HCl) commenced, the sample appeared completely dissolved.

Due to the insolubility of the 100 kDa retentate, the LiOH titration curve was not usable (Figure 4.2a). However, the titration curve obtained from HCl titration (Figure 4.2) was more representative of a titration curve as described by Kortner *et al.,* (2018). Therefore, from Figure 4.2b, the end point for sulphonic acid (point ii) could easily be determined.

When the lignosulphonate was purified from MgLS spent liquor using DOW-XAD-7 (without sequential fractionation) no insolubility in the liquor was not observed. Fractionating the samples according to different Mw, therefore, gave solubility information that could be otherwise overlooked, if lignosulphonate samples were only tested as is and not at a molecular level. For consistency, all sulphonic acid values reported were, therefore, calculated from the HCl titration curves. All sulphonic acid data using both LiOH and HCl are included in the appendices (Appendix B1and B2).

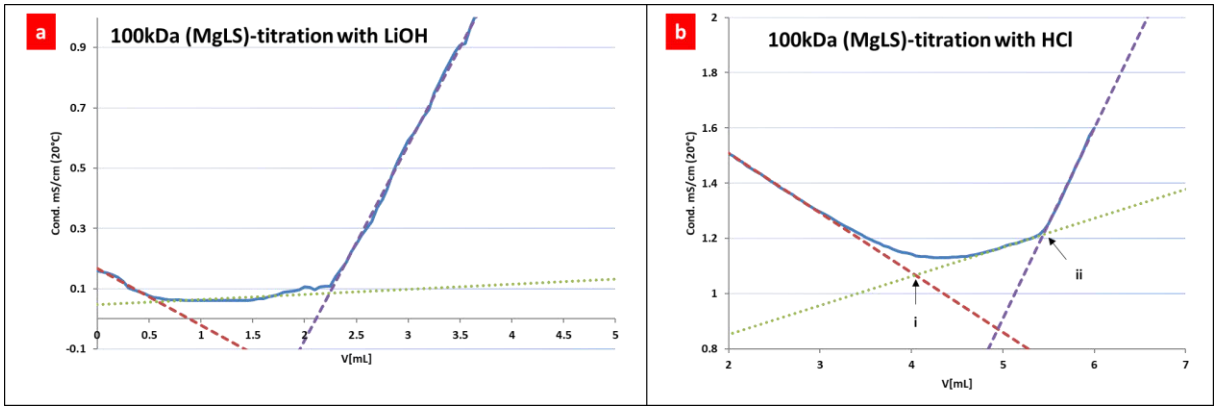

Figure 4.2: LiOH (a) and HCl (b) titration curves obtained for the 100 kDa retentate after fractionation of MgLS, where i represented the end point for weak acids and ii represented the end point for the strong acids (sulphonic acids).

4.5.3. Influence of molecular weight on the sulphonic acid content

The relationship between the sulphonic acid content and the Mw of fractions from the purified and ultrafiltrated MgLS spent liquor is depicted in Figure 4.3. An increase in sulphonic acid content was observed with a decrease in Mw for the lignosulphonate molecules in the retentates of the 100 to 5 kDa membranes (increased from 0.93 to 1.31 mmol/g for fractions with Mw between 17.6 and 2.2 kDa).

The sulphonic acid content of the 1.2 kDa fraction (1 kDa retentate) then dropped to 1.12 mmol/g, after which it increased again to 1.25 mmol for the 0.6 kDa fraction (1 kDa permeate). Musl *et. al*., (2020) found a similar trend when MgLS, purified with DOW-XAD-7 resin, was sequentially fractionated. The authors reported the sulphonic acid content increasing from 1.66 to 1.83 mmol/g with decreasing Mw fractions, as measured between 85.7 to 5.2 kDa (Musl *et. al*., 2020).

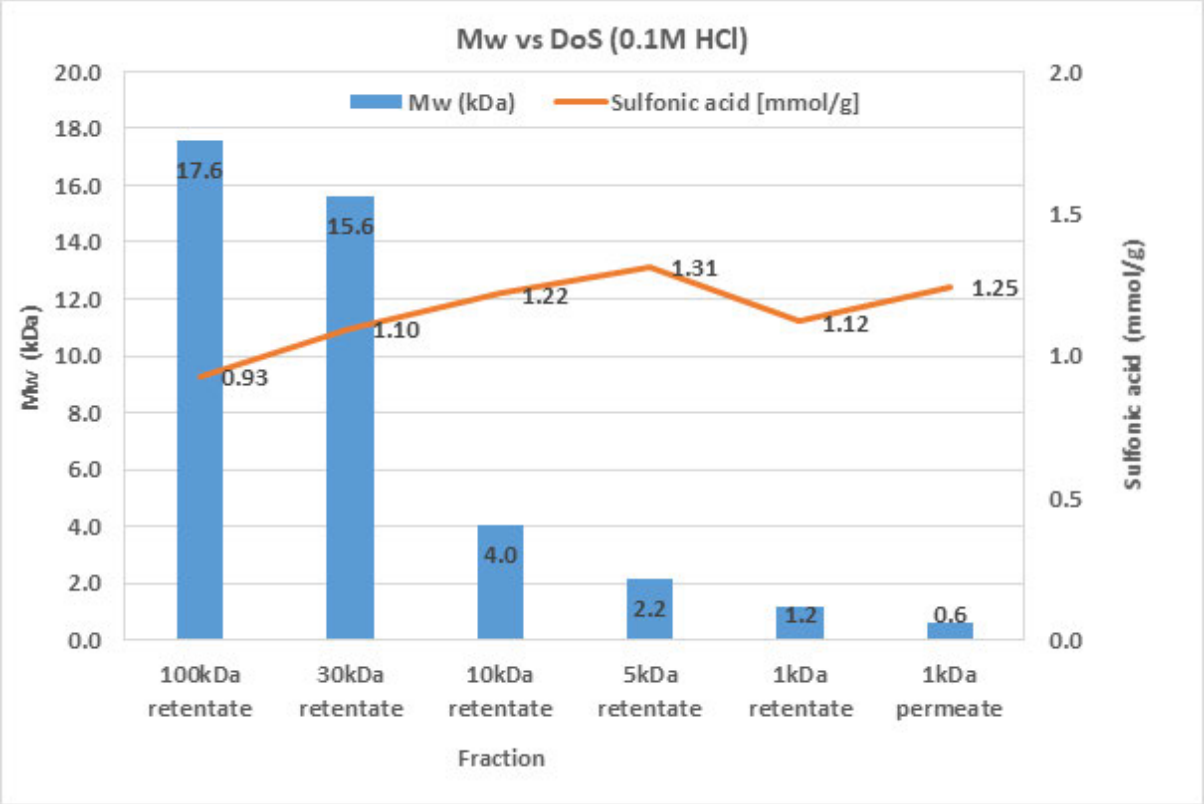

Figure 4.3: Comparison between the sulphonic acid content (mmol/g lignosulphonate) and the Mw (kDa) of lignosulphonate in the retentates obtained during the sequential ultrafiltration of purified MgLS spent liquor.

For the lignosulphonate fractions obtained from sequential ultrafiltration of purified NaLS spent liquor (Figure 4.4), the 30 kDa retentate sample was not enough for molecular weight and sulphonic acid determination. An increase in the sulphonic acid content was only observed between the 100 and 10 MWCO sizes with a concomitant decrease in Mw. A steady decrease in the sulphonic acid content was observed for the retentates of the 10, 5 and 1 kDa membranes (1.19 to 0.74 mmol/g) which also resulted in a decrease in the Mw of the lignosulphonate fractions.

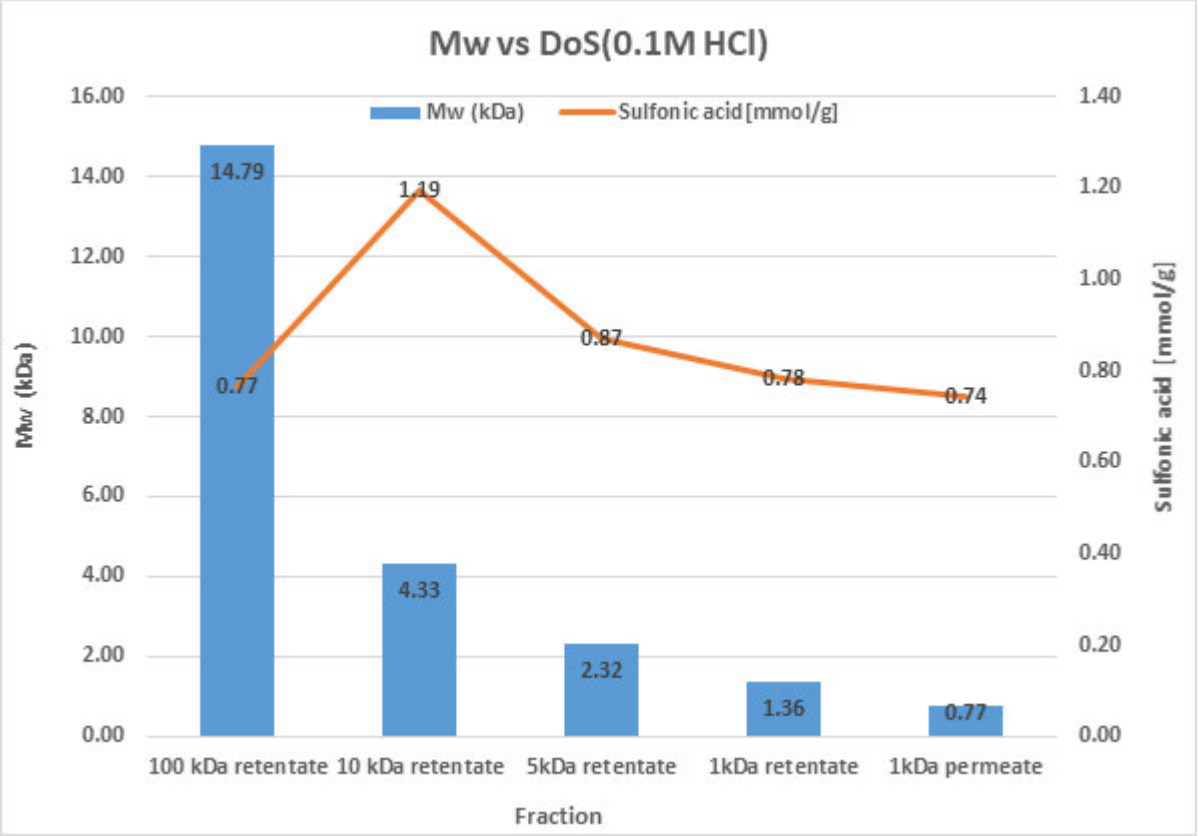

Figure 4.4: Comparison between the sulphonic acid content (mmol/g lignosulphonate) and the Mw (kDa) of lignosulphonate in the retentates obtained during the sequential ultra-filtration of purified NaLS spent liquor.

The sulphonic acid content of the purified lignosulphonate samples reported in Table 3.3 of Chapter 3 did not show the same extent of sulphonation as the samples fractionated by ultra-filtration in the current study. The sulphonic acid content measured for the lignosulphonates purified from MgLS and NaLS with DOW-XAD-7 were 0.41 and 0.29 mmol/g lignosulphonate, respectively. These values were lower compared to the sulphonic acid contents reported for any of the fractionated samples in Figure 4.3 and 4.4.

4.6. Conclusion

Purified NaLS and MgLS samples were fractionated by sequential ultra-filtration with membranes of decreasing MWCO sizes and the resulting lignosulphonate fractions' Mw and sulphonic acid content were measured and compared. For the MgLS stream, the retentate of the 100kDa membrane was not soluble in water. The Mw of both spent liquor sources (MgLS and NaLS) were similar at that membrane cut-off size, however.

When the sulphonic acid contents of the MgLS and NaLS sources were compared, the purified MgLS stream had a slightly higher sulphonic content compared to the NaLS. When compared to literature, however, both spent liquors had a markedly lower sulphonic acid content.

It was observed that, with sequential ultra-filtration to fractionate the purified MgLS, the sulphonic acid content increased with a decrease in the Mw size. In contrast when purified Na-LS was fractionated the sulphonic acid content decreased with a decrease in Mw for the smaller MWCO sizes.

The vast difference between the sulphonic acid content in sequentially fractionated samples to those that were only purified further justifies this study. It indicates that differences in sulphonic acids content can be measured in samples extracted from different cooking process (MgLS and NaLS). This result however can not be definitely used to assume that all the lignosulphonate fractions in a specific liquor are similar.

4.7. Recommendation

In order to ascertain that the results obtained are reproducible; the sequential fractionation experiment should be repeated and carried out in triplicate. This will also assist in determining statistical data for all the tests and experiment processes

It is recommended that this study is repeated with a larger sample size in order for sufficient sample volumes to be extracted after each fraction step. It is also recommended that the portion of the sample removed by the Dowex resin during purification is characterised to determine the ash and lignosulphonate contents. Understanding to organic/inorganic ratio of the contents removed by the resin will inform future studies how much lignosulphonate is lost- during the purification step.

In order to properly quantify the lignosulphonate content, the extinction coefficient of XAD-7 purified spent liquor should also be determined. This will give a more accurate value when measuring lignosulphonate content using UV-VIS.

Since it was seen from literature that ligno-carbohydrate complexes (LCC) may be present in spent lignosulphonate liquor streams, sugar analyses of the purified and fractionated samples should be included in future studies. The sugar content in the lignosulphonate spent liquors will have influence the amount of sample weighed for sulphonic acids determination If the purified sample should contain oligomeric carbohydrates, the sugar content should be deducted

from the mass used for sulphonic acid determination. However, the Mw will unfortunately be influenced by the LLC compound, depending on the type of detector used, and this will also have to be taken into consideration when analysing and comparing Mw values.

During this study it was observed that purification with XAD-7 resin, followed by ultrafiltration did not extract all the lignosulphonate contained in the spent liquors analysed. It is, therefore, recommended that the portion of the samples not retained by the XAD resin or ultrafiltration is also assessed. This will enable a better understanding of the overall chemistry of the spent liquor, which is especially important for Sappi, since the entire NaLS spent liquor stream is typically used when developing new products.

4.8. References

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5. APPENDICES

Appendix A: ICP results of cations in MgLS and NaLS spent liquors

Determinant (mg/L) liquor as received	MgLS	NaLS
Calcium as Ca	402.5	39.04
Potassium as K	350.7	258.4
Magnesium as Mg	4 889	78.24
Sodium as Na	29.66	17 854
Aluminium as Al	1.75	3.13
Barium as Ba	0.74	1.01
Beryllium as Be	< 0.010	< 0.010
Cadmium as Cd	0.03	0.01
Cobalt as Co	0.1	< 0.010
Chromium as Cr	0.08	0.16
Copper as Cu	0.3	0.21
Iron as Fe	30.36	11.02
Manganese as Mn	148.7	1.95
Nickel as Ni	0.72	0.29
Lead as Pb	1.23	0.67
Silicon as Si	8.36	5.43
Strontium as Sr	1.67	0.89
Zinc as Zn	1.82	0.21

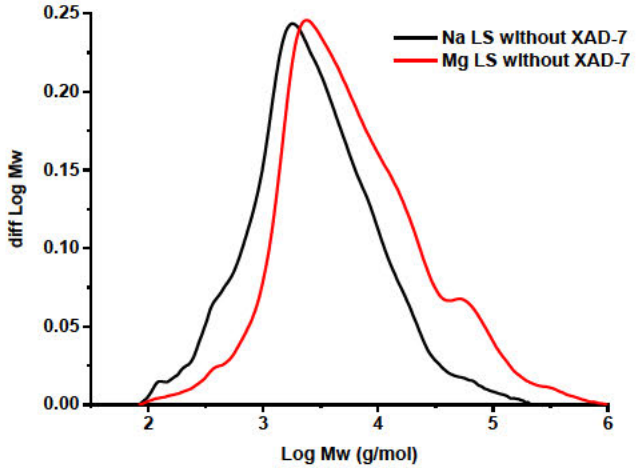
Appendix B2: Sulphonic acid and aromatic hydroxyl content of the MgLS spent liquor, the lignosulphonates purified from this liquor using resins (DOW-XAD-7) and ultrafiltration (UF), as well as that of the lignosulphonates in the retentates and permeates obtained during the sequential fractionation of the MgLS spent liquor.

Sample ID	Titrated with LiOH				Titrated with HCL				Average			
	Sulphonic acid		Aromatic hydroxyl		Sulphonic acid		Aromatic hydroxyl		Sulphonic acid		Aromatic hydroxyl	
	(mmol/g LS)	(% of LS)	(mmol/g LS)	(% of LS)	(mmol/g LS)	(% of LS)	(mmol/g LS)	(% of LS)	(mmol/g LS)	(% of LS)	(mmol/g LS)	(% of LS)
MgLS spent liquor	0.99	8.03	1.05	1.78	1.02	8.25	2.87	4.87	1.00	8.14	1.96	3.33
MgLS UF	0.52	4.20	0.79	1.34	0.57	4.59	2.26	3.84	0.54	4.39	1.52	2.59
MgLS DOW-XAD 7	0.50	4.07	1.13	1.92	0.41	3.35	2.57	4.37	0.46	3.71	1.85	3.15
100 kDa retentate	IW	IW	IW	IW	0.93	7.53	2.36	4.0	0.93	7.53	2.36	4.01
30 kDa retentate	0.75	6.05	0.73	1.24	1.10	8.88	2.96	5.0	0.92	7.46	1.84	3.13
10 kDa retentate	0.93	7.51	1.41	2.40	1.22	9.89	3.25	5.5	1.08	8.71	1.96	3.33
5 kDa retentate	0.93	7.53	0.67	1.14	1.31	10.65	3.25	5.5	1.12	9.08	2.33	3.97
1 kDa retentate	0.72	5.85	0.75	1.28	1.12	9.07	3.72	6.3	0.92	7.46	2.24	3.80
1 kDa permeate	0.79	6.44	2.71	4.61	1.25	10.09	5.16	8.8	1.02	8.26	3.94	6.69
IW = insoluble in water												

Appendix B3: Sulphonic acid and aromatic hydroxyl content of the NaLS spent liquor, the lignosulphonates purified from this liquor using resins (DOW-XAD-7) and ultrafiltration (UF), as well as that of the lignosulphonates in the retentates and permeates obtained during the sequential fractionation of the MgLS spent liquor.

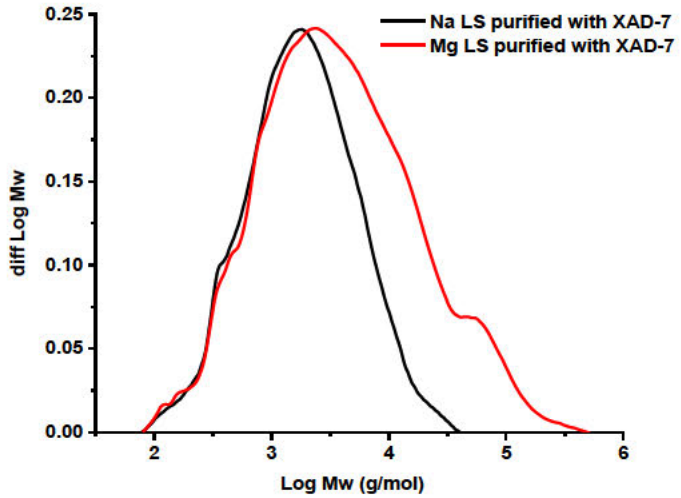
Sample ID	Titrated with LiOH				Titrated with HCL				Average			
	Sulphonic acid		Aromatic hydroxyl		Sulphonic acid		Aromatic hydroxyl		Sulphonic acid		Aromatic hydroxyl	
	(mmol/g LS)	(% of LS)	(mmol/g LS)	(% of LS)	(mmol/g LS)	(% of LS)	(mmol/g LS)	(% of LS)	(mmol/g LS)	(% of LS)	(mmol/g LS)	(% of LS)
NaLS spent liquor	0.89	7.23	0.87	1.49	0.84	6.84	3.28	5.57	0.87	7.04	2.07	3.53
NaLS UF	0.59	4.76	0.68	1.15	0.37	3.03	1.75	2.97	0.48	3.89	1.21	2.06
NaLS DOW-XAD 7	0.46	3.72	0.49	0.84	0.29	2.36	2.54	4.31	0.38	3.04	1.51	2.57
100 kDa retentate	1.06	8.55	1.00	1.71	0.77	6.20	2.42	4.12	0.91	7.37	1.71	2.91
30 kDa retentate	NES	NES	NES	NES	NES	NES	NES	NES	NES	NES	NES	NES
10 kDa retentate	0.82	6.61	1.67	2.84	1.19	9.68	3.52	5.98	1.01	8.15	2.59	4.41
5 kDa retentate	0.50	4.02	2.08	3.54	0.87	7.07	4.08	6.94	0.68	5.54	3.08	5.24
1 kDa retentate	0.43	3.48	1.84	3.13	0.78	6.34	4.12	7.01	0.61	4.91	2.98	5.07
1 kDa permeate	0.42	3.44	2.98	5.07	0.74	6.02	5.18	8.81	0.58	4.73	4.08	6.94
NES = not enough sample												

Appendix C1 : Molecular weight distribution of lignosulphonates purified from NaLS and MgLS spent liquors using ultrafiltration



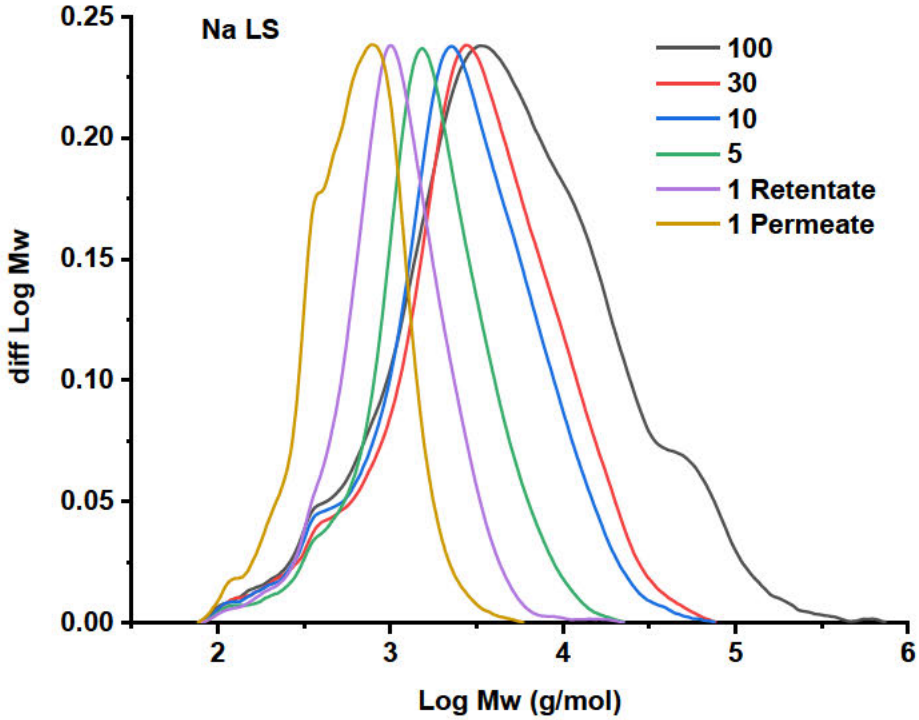
Sample ID	GPC data				
	Mn (Da)	Mp (Da)	Mw (Da)	Mz (Da)	Mw/Mn
Na LS (UF) w/o XAD	1302	1752	5920	27900	4.6
Mg LS (UF) w/o XAD	2562	2440	19490	153180	7.6

Appendix C2a: Molecular weight distribution of lignosulphonates purified from NaLS and MgLS spent liquors using DOW-XAD-7 resin.

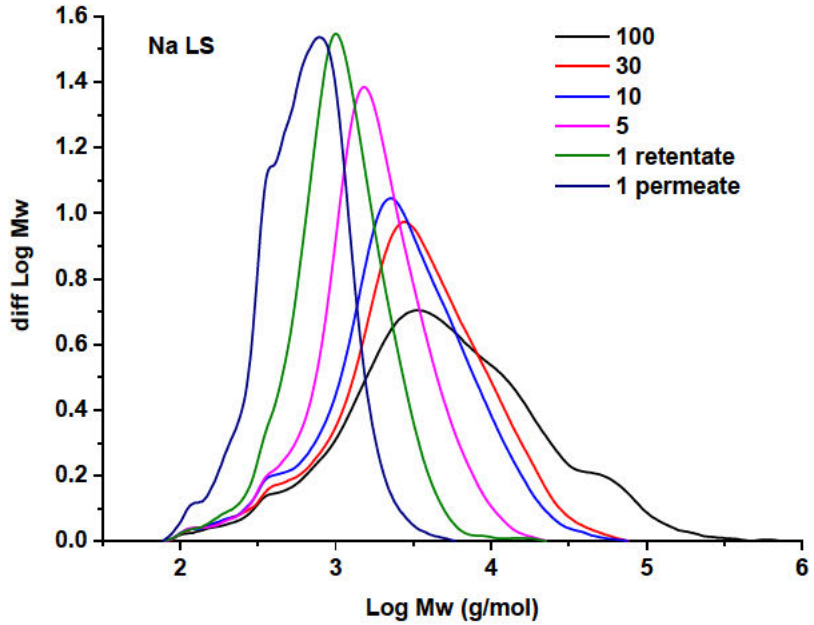


Sample ID	GPC data				
	Mn (Da)	Mp (Da)	Mw (Da)	Mz (Da)	Mw/Mn
Na LS purified with XAD	1045	1817	3135	7907	3.0
Mg LS purified with XAD	1432	2485	12022	71495	8.4

Appendix C3a: Molecular weight distribution of lignosulphonates purified from NaLS spent liquor using DOW-XAD-7 resin followed by the sequential ultrafiltration set of cut-off membranes (100, 30, 10, 5, 1 kDa). Values were normalised by 1.



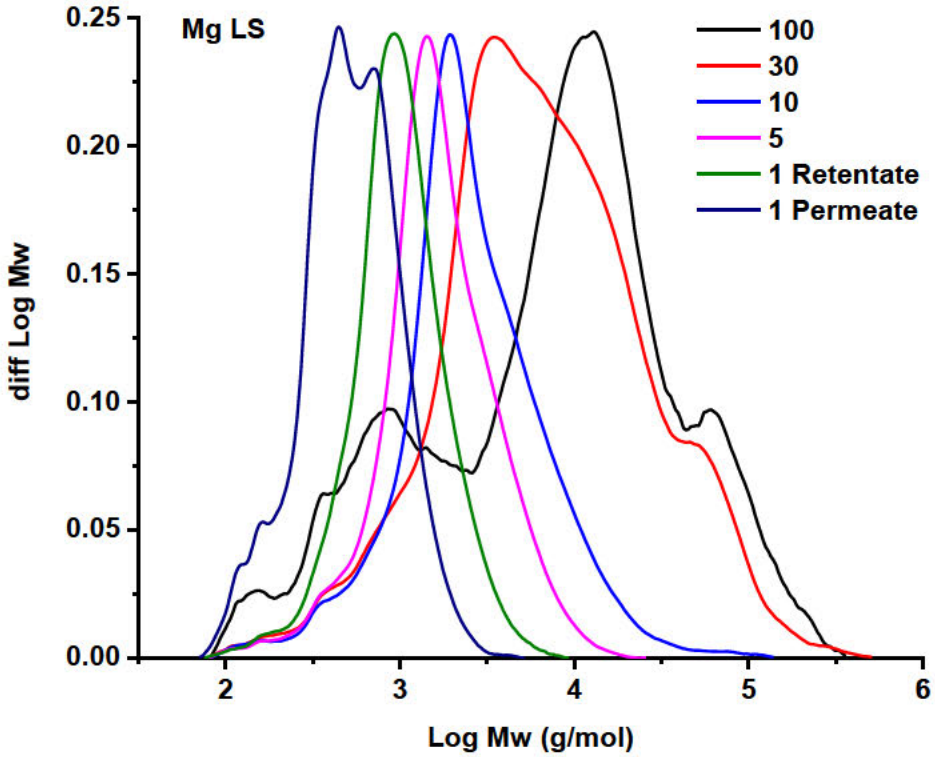
Appendix C3b: Molecular weight distribution of lignosulphonates purified from NaLS spent liquor using DOW-XAD-7 resin followed by the sequential ultrafiltration set of cut-off membranes (100, 30, 10, 5, 1 kDa). Values were normalised by peak area.



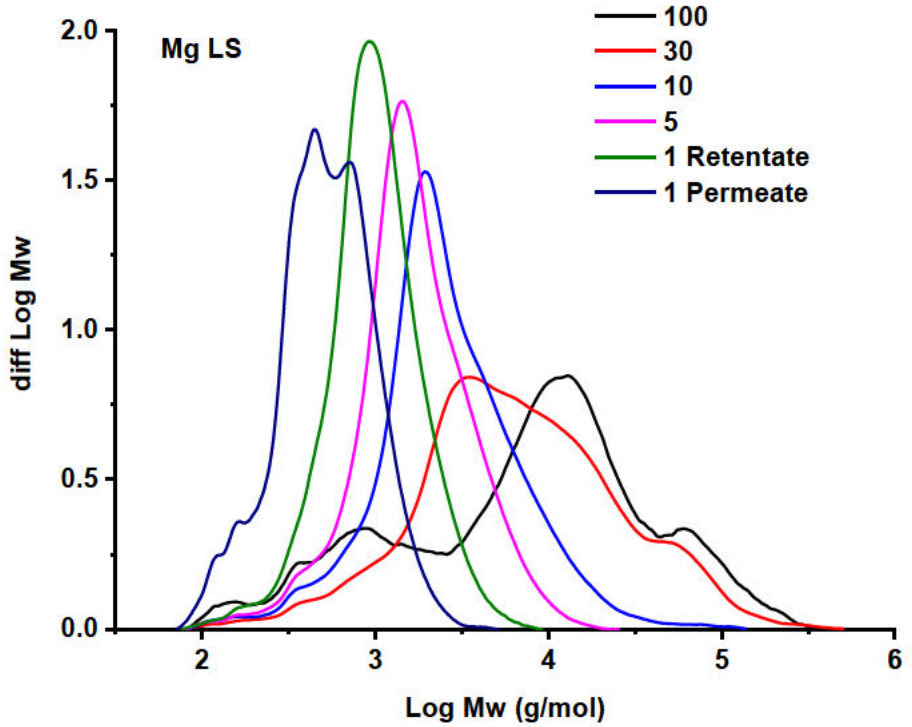
Sample ID (NaLS)	GPC data				
	Mn (Da)	Mp (Da)	Mw (Da)	Mz (Da)	Mw/Mn
100 kDa	1980	3380	14787	96602	7.4
30 kDa	1562	2775	5640	15372	3.6
10 kDa	1432	2285	4330	10967	3

5 kDa	1157	1532	2315	4215	2
Retentate 1 kDa	815	1002	1362	2262	1.7
Permeate 1 kDa	507	785	765	1140	1.5

Appendix B3a: Molecular weight distribution of lignosulphonates purified from MgLS spent liquor using DOW-XAD-7 resin followed by the sequential ultrafiltration set of cut-off membranes (100, 30, 10, 5, 1 kDa). Values were normalised by 1.



Appendix C3b: Molecular weight distribution of lignosulphonates purified from MgLS spent liquor using DOW-XAD-7 resin followed by the sequential ultrafiltration set of cut-off membranes (100, 30, 10, 5, 1 kDa). Values were normalised by peak area.



Sample ID (MgLS)	GPC data				
	Mn (Da)	Mp (Da)	Mw (Da)	Mz (Da)	Mw/Mn
100 kDa	1792	12230	17577	58675	10
30 kDa	2925	3445	15605	61450	5.4

10 kDa	1647	1975	4047	12097	2.5
5 kDa	1220	1420	2172	3775	1.8
Retentate 1 kDa	800	932	1192	1750	1.5
Permeate 1 kDa	422	450	635	910	1.5

Appendix D: Molecular weight distribution of lignosulphonates purified from MgLS and NaLS injected in duplicate

Sample ID	GPC data				
	Mn (Da)	Mp (Da)	Mw (Da)	Mz (Da)	Mw/Mn
Na LS without XAD (1)	1315	1800	6500	35800	5
Na LS without XAD (2)	1290	1705	5340	20000	4.2
Mg LS without XAD (1)	2520	2450	19560	152800	7.8
Mg LS without XAD (2)	2605	2430	19420	153560	7.5
Na LS with XAD (1)	1030	1830	3100	7900	3
Na LS with XAD (2)	1060	1805	3170	7915	3
Mg LS with XAD (1)	1445	2370	12600	76845	8.7
Mg LS with XAD (2)	1420	2600	11445	66145	8.1
Na LS - 100 kDa (1)	1920	3270	14015	84990	7.3
Na LS - 100 kDa (2)	2040	3490	15560	108215	7.6
Na LS - 30 kDa (1)	1600	2770	5370	13415	3.4
Na LS - 30 kDa (2)	1525	2780	5910	17330	3.9
Na LS - 10 kDa (1)	1425	2280	4300	10835	3
Na LS - 10 kDa (2)	1440	2290	4360	11100	3
Na LS - 5 kDa (1)	1150	1525	2300	4200	2
Na LS - 5 kDa (2)	1165	1540	2330	4230	2
Na LS Ret. 1 kDa (1)	820	1000	1400	2460	1.7
Na LS Ret. 1 kDa (2)	810	1005	1325	2065	1.6
Na LS Perm. 1 kDa (1)	510	790	760	1100	1.5

Na LS Perm. 1 kDa (2)	505	780	770	1180	1.5
Mg LS - 100 kDa (1)	1705	12950	21110	77700	12.4
Mg LS - 100 kDa (2)	1880	11510	14045	39650	7.5
Mg LS - 30 kDa (1)	2725	3500	16080	67840	5.9
Mg LS - 30 kDa (2)	3125	3390	15130	55060	4.8
Mg LS - 10 kDa (1)	1590	1940	4240	15475	2.7
Mg LS - 10 kDa (2)	1705	2010	3855	8720	2.3
Mg LS - 5 kDa (1)	1200	1425	2180	3800	1.8
Mg LS - 5 kDa (2)	1240	1415	2165	3750	1.8
Mg LS - Ret. 1 kDa (1)	800	935	1190	1745	1.5
Mg LS - Ret. 1 kDa (2)	800	930	1195	1755	1.5
Mg LS - Perm. 1 kDa (1)	420	445	630	900	1.5
Mg LS - Perm. 1 kDa (2)	425	455	640	920	1.5
(1) first injection (2) second injection					