# Dispersion and flocculation affinity of anionically charged kraft lignin

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## Dedications

I would like to dedicate this work to my parents for their love, encouragement, and their endless prayer for me.

A special dedication of this work with thanks to my kids and my wife as she took my place as being a father while I was not home and was busy with my entire MSc work, thanks for making home comfortable, warm and joyful.

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# Abstract

Softwood kraft lignin is a biodegradable, renewable, and environmentally friendly natural polymer. Although kraft lignin is widely produced in Canada, it is predominantly underutilized as fuel because it is only soluble in alkaline pH that limits its application as a value-added product.

The main objective of this MSc study was to enhance the water solubility of softwood kraft lignin to be used as dispersants and flocculants. In one set of experiments, softwood kraft lignin was modified through a sulfonation reaction with sodium sulfite to produce water soluble sulfonated lignin with an anionic charge density. Alternatively, the kraft lignin was oxidized via hydrogen peroxide or nitric acid to improve its water solubility and charge density. The results confirmed that the modifications generated water soluble products with anionic charge densities. The modified lignin samples were also characterized via FTIR, TGA, DSC, GPC and elemental analyses. Furthermore, the performance of the modified lignin samples was studied and compared with a commercial lignosulfonate as a flocculant and dispersant.

The results confirmed that the adsorption of modified lignin samples was higher than that of commercial lignosulfonate on alumina, bentonite, and kaolin. The oxidized lignin with nitric acid exhibited a greater adsorption capacity than other modified lignin samples on all types of particles studied. Generally, the modified lignin reduced the zeta potential of suspensions and the change was more pronounced for the oxidized lignin via nitric acid treatment. The dispersion studies confirmed that the modified lignin with nitric acid was more effective than other samples, but its flocculation performance was not as good.

Furthermore, the efficiency of the lignin samples in removing basic blue and ethyl violet dyes from solutions were studied, and the results confirmed that the lignin samples modified with nitric acid had a higher efficiency than other samples. The higher charge density of the lignin sample modified with nitric acid (2.6 meq/g) was claimed to be the main factor for its better performance; whereas the lower charge density of commercial lignosulfonate (1.4 meq/g) was its main drawback for its application as a flocculant.

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| | |
|---|---|
| Softwood kraft lignin | SKL |
| Sulfonate softwood kraft lignin via sodium sulfite | SSKL |
| Oxidized softwood kraft lignin via hydrogen peroxide | OSKL |
| Oxidized softwood kraft lignin via nitric acid | OOSKL |
| Commercial lignosulfonic acid sodium salt | CLS |
| Particle charge detector | PCD |
| Gel permeation chromatography | GPC |
| Fourier transform infrared spectrophotometer | FTIR |
| Photometric dispersion analyzer | PDA |
| Dynamic drainage jar | DDJ |
| Thermogravimetric analysis | TGA |
| Differential scanning calorimetry | DSC |

# List of Equations

# Introduction

Dispersants are widely used in suspensions and colloids to improve the separation of particles and prevent their settling (Ouyang et al., 2009; Pang et al., 2008). They could be used in cement admixture or froth flotations of the mining industry to reduce the interaction between the particles and increase their surface charge. Flocculants are added to suspensions to improve the sedimentation of a small particles and have wide industrial applications, such as in wastewater treatment and pulp and paper (Inwood, 2014; Liu et al., 2011). However, currently industrial dispersants and/or flocculants are expensive and toxic due to their non-biodegradable nature. In this respect, the incentives for producing more environmentally friendly dispersants and flocculants from biodegradable polymers are high in industry (Cotana et al., 2014; Dilling & Huguenin, 1998; Liu et al., 2011).

Cellulose, hemicelluloses, and lignin are three main components of wood plants (Gabrielii et al., 2000), which can be used to produce value-added products. However, most of lignin is currently burnt in pulp and paper industry and has limited industrial use (Konduri & Fatehi, 2015). On the other hand, kraft lignin can be separated from black liquor of kraft pulping process through various methods investigated in the literature to produce value added products. Among different treatments studied to extract lignin from pulping spent liquors, it was claimed that acidification could be an industrially reliable option; based on which LignoBoost and LignoForce technologies were designed and practiced (Fatehi & Chen, 2016). The production of kraft lignin at commercial scales facilitate the generation of other kraft lignin based value added products.

Colloidal suspensions are heterogeneous mixtures in which the solute particles are suspended throughout the bulk of the media. In addition, colloidal suspensions are generally thermodynamically unstable as a result of their lyophobic nature and tend to accumulate (Ampian, 1985; Zaman et al., 2002). However, colloidal particles may be stabilized by electrostatic repulsions. Colloidal suspensions including kaolin, bentonite, which have a negative charge, and alumina suspensions, which have a positive charge, contain mixture of different minerals that make clay suspensions with different chemistry (Adamis & Williams, 2005).

In this MSc thesis, softwood kraft lignin was received from industry and rendered water soluble and anionically charged via chemical modification for producing dispersants and flocculants. Furthermore, FTIR, TGA, DSC, GPC, and elemental analyses were used to characterize the modified lignin samples. Herein, the overall aspects of this MSc work are discussed. It illustrates a synopsis of the thesis chapters, and explains the hypotheses, objectives and novelty of this work.

In chapter one, the literature relevant to this work was discussed. The discussion included information about lignin structure and extraction methods as well as the modification and application of lignin as dispersants. In chapter two, the modification of softwood kraft lignin via sulfonation and oxidation (through hydrogen peroxide and nitric acid) was discussed. The characterization of the modified lignin products was also investigated and discussed using advanced tools such as FTIR, elemental analyzer, GPC, TGA and DSC. In chapter three, the performance of the modified lignin samples as dispersants and flocculants were studied in kaolin, bentonite, alumina suspensions, and dye solutions. The results of modified lignin samples were compared with those of commercial lignosulfonate. Finally, in the fourth chapter, the overall conclusions and recommendations for future work were elaborated.

## Hypothesis

It is hypothesized that softwood kraft lignin can be chemically modified to produce water soluble lignin based products. In this regard, sulfonation and oxidation will provide anionic charge density and enhance the water solubility of kraft lignin. The products can be adsorbed on particles, and thus change the overall chemistry of suspensions. As a result, water soluble lignin based products can be produced and used as dispersants for kaolin and bentonite suspensions, and as flocculants for alumina suspensions.

## Objectives

The objectives of this thesis were to:

1. increase the solubility, charge density, and functional groups of softwood kraft lignin with sulfonation via sodium sulfite, oxidation through nitric acid, and oxidation with hydrogen peroxide;
2. investigate the properties of sulfonated and oxidized lignin using charge density analyzer, FTIR, TGA, DSC, and molecular weight analyses;

3. investigate the adsorption of modified lignin products on alumina, bentonite and kaolin suspension;
4. investigate the dispersion performance of the modified lignin in bentonite and kaolin suspensions,
5. assess the flocculation performance of lignin samples in alumina suspension;
6. investigate the zeta potential of alumina, bentonite, and kaolin suspensions;
7. investigate the impact of modified lignin products in removing ethyl violet and blue basic 41 dyes from solutions; and to
8. compare the dispersion and flocculation performance of the modified lignin products from this work with commercial lignosulfonate.

## Novelty of the study

The aim of this work is to produce modified sulfonated and oxidized softwood kraft lignin via sodium sulfate treatment, nitric acid oxidation and hydrogen peroxide oxidation. The dispersion (kaolin and bentonite) and flocculation (alumina) performance of these water soluble kraft lignin based products will be assessed systematically for the first time; in addition to investigating their performance to remove dyes including ethyl violet and blue basic 41 from solutions.

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# 1 Chapter 1: Literature review

## 1.1 Introduction

The depletion of natural resources and climate change have changed the focus of research to more environmentally friendly approaches (Borrero-López et al., 2017), such as biorefining that allows for the production of platform chemicals from biomass (Filiciotto et al., 2017). Lignocellulosic materials, composed of cellulose, hemicellulose and lignin, are considered as natural and renewable energy resources that might be alternatives for fossil fuels (Shafaghat et al., 2017). Table 1.1 lists some applications of these materials.

Table 1.1: Applications of hemicelluloses, cellulose and lignin

| Type of polymer | Application | Reference |
|---|---|---|
| Hemicelluloses | Food (xylitol and sugar) | (Otieno & Ahring, 2012; Yi & Zhang, 2012) |
| | Medicine (Xylooligosaccharides) | (Bian et al., 2013) |
| | Energy (fuel and $H_2$) | (Olcay et al., 2013) |
| | Chemical industry (furfural) | (Gürbüz et al., 2012) |
| | Polymeric materials (film, hydrogel) | (Karaaslan et al., 2011; Ruiz et al., 2013) |
| | Biosurfactant (glycolipids) | (Foley et al., 2011) |
| | Papermaking (strength additives and flocculants) | (Filho et al., 2013). |
| Cellulose | Finishing of textile | (Gorgieva & Kokol, 2011) |
| | Thickening paints | (Dal-Bó et al., 2011) |
| | Thickener in cement mortar | (Patural et al., 2011) |
| | Sizing agent in paper making | (Kugge et al., 2004) |
| | Pharmaceutical industries (drug delivery system) | (Shokri & Adibki, 2013) |
| Lignin | Carriers for fertilizers and pesticides | (Ramirez et al., 1997; Zhang, 2008) |
| | Carbon fibers | (Kubo et al., 1998; Kadla et al., 2002) |
| | Blends with thermoplastic polymers | (Cazacu et al., 2004; Gosselink et al., 2005) |
| | Binders and resins | (Alonso et al., 2004; Turunen et al., 2003; Tejado et al., 2007) |
| | Ion-exchange resins | (Zoumpoulakis & Simitzis 2001; Dizhbite et al., 1999) |
| | Activated carbons | (Fierro et al., 2003; Carrott & Carrott, 2007) |

Lignin is the second abundant organic polymer in nature after cellulose (Vanholme et al., 2010), which plays important roles in woody plants including 1) adding strength to the cell walls, 2) controlling fluid flow of liquid in plants, and 3) protecting plants from the enzymatic degradation. It was claimed that all vascular plants contain lignin in different amounts depending on the type of plant and growing conditions (Smook, 2000). For example, it was reported that lignin content is greater in softwood species (25-32 wt.%) than in hardwood species (18-25 wt.%) (Sixta, 2006).

It is worth mentioning that lignin has been an area of interest in research and development since 1970s. According to a study, over 70 million tons of lignin has been produced annually as a by-product of the pulping industry (Kumar et al., 2009). Although a considerable amount of lignin has been utilized as fuel, a small amount (1%- 2%) has been used to generate value-added products (Kubo & Kalda, 2005). Lignin can be modified through different methods to make it applicable in many industrial fields. To produce lignin based value-added products, lignin derivatives should be separated from pulping spent liquors, which are dilute in lignin and impure. In this chapter, the literature studies on lignin structure and modification are reviewed.

## 1.2 Lignin structure

Lignin has a three-dimensional multi-branched structure connected through ether and C–C bonds (Lewinsky, 2006), as shown in Figure 1.1. Lignin is built up from three phenylpropanoid monomers units of p-coumaryl alcohol-hydroxyphenyl (H-type), coniferyl alcohol-guaiacyl (G-type), and sinapyl alcohol-syringyl (S-type) (Desch & Dinwoodie, 1996) (Figure 1.1).

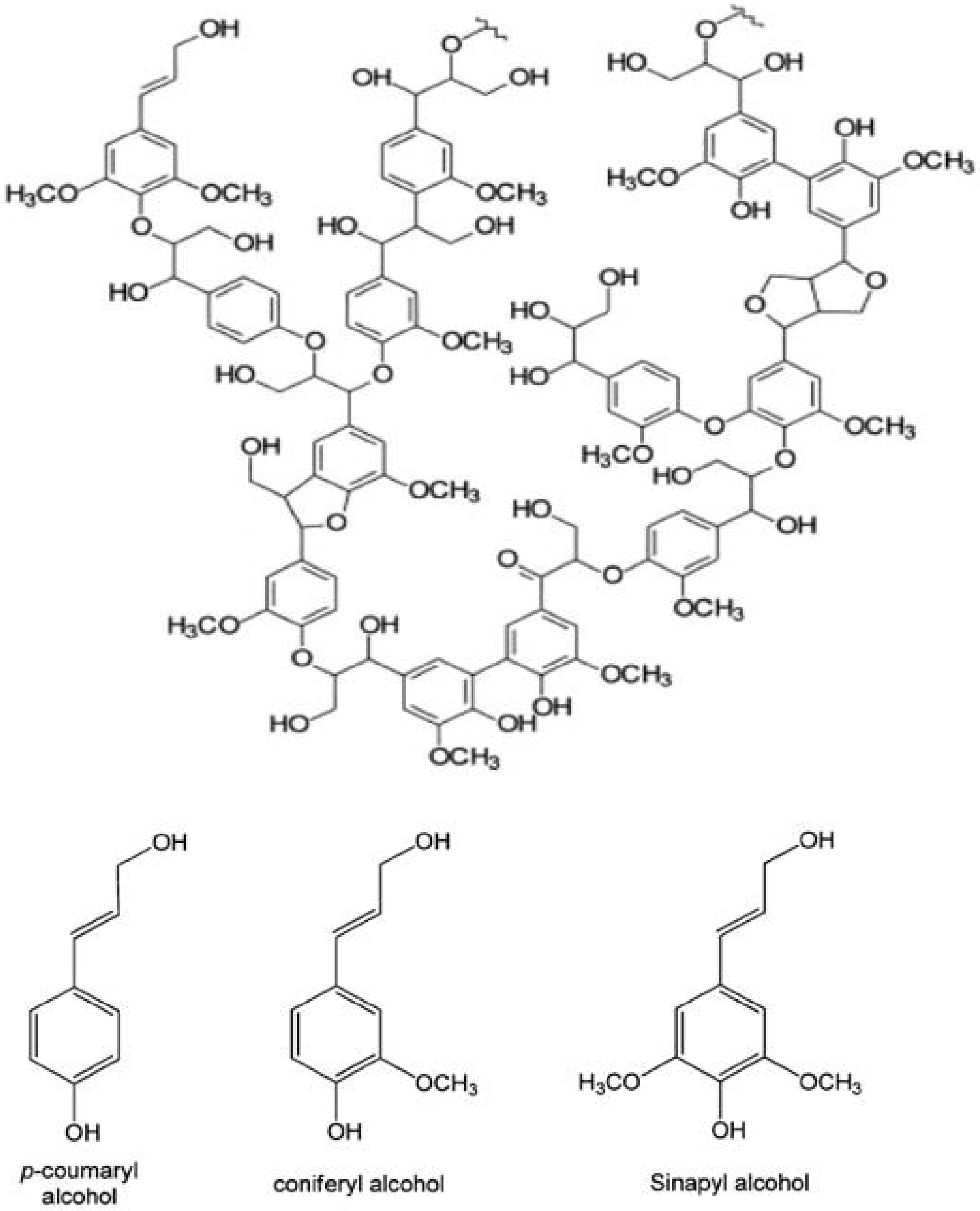

Figure 1.1: Lignin structure (Lewinsky, 2006)

The phenylpropanoid monomer units are different quantitatively from species to species and contain a variety of functional groups (e.g., methoxyl group and phenolic groups). Softwood lignin contains a large amount of coniferyl alcohol. For example, it was reported that spruce species contained 94 wt. % guaiacyl, 1 wt.% sinapyl, and 5 wt.% p-coumaryl alcohol-hydroxyphenyl (Sixta, 2006). In another study, it was reported that pine species contained 85 wt.% guaiacyl, 2 wt.% sinapyl and 13 wt.% p-coumaryl alcohol-hydroxyphenyl (Glasser et al., 1981). Hardwood lignin contains different amounts of sinapyl and guaiacyl units. In one study, beech species contained 56 wt.% guaiacyl, 40 wt.% sinapyl, and 4 wt.% p-coumaryl alcohol-hydroxyphenyl (Choi et al., 2001).

## 1.3 Lignin extraction from black liquor

As mentioned earlier, lignin has the potential to be converted to a value-added product after being separated from pulping liquors. Kraft lignin is produced in the black liquor of kraft pulping in pH of 12-13 (Velez & Thies, 2016; Arkal et al., 2014; Manttari et al., 2015; Zhu & Theliander, 2015) with the use of sodium hydroxide (NaOH) and sodium sulphide ($Na_2S$). The liquor contains a complex mixture of organic and inorganic molecules with lignin content of 30-45% (Tian et al., 2015). Precipitation and ultrafiltration are basically the main methods of separating kraft lignin from black liquor. Kraft lignin can be isolated from black liquor with the help of acidification, membrane electrolysis or solvents. In 1942, Westvaco Company used the acidification method to produce lignin particles from black liquor by reducing the pH of the black liquor and filtering the liquor (Zhu & Theliander, 2015). The pH reduction led to protonation of phenolic structure of lignin molecules, and thus reducing the electrostatic repulsive force between them, which facilitated the lignin agglomeration (Gilardi & Cass, 1993; Sundin, 2000; Vainio et al., 2004).

At laboratory scales, various investigations have been carried out on lignin precipitation via acidification. In one study, the effect of pH of acidification (using hydrochloric acid) (HCl of black liquor was studied (Table 1.2) (Lourençon et al., 2015). It is observable that decreasing the pH reduced the molecular weight of the precipitated lignin in both hardwood and softwood species, which decreased the yield of lignin extraction, but increased the sulfur content of the precipitates. In another study, lignin precipitation yields were increased to 90% via acidifying the black liquor to pH 2 using sulfuric acid (Alen et al., 1979). In addition, an increase in the pressure decreased the carbonation time and increased the lignin yields with a total dry solid content around 30% and 35% for softwood and hardwood species, respectively (Alen et al., 1985). Moreover, it was reported that the pH of precipitation and temperature improved the filtration properties (Ohman & Theliander, 2007). However, the traditional acidification had poor filtration performance and produced impure lignin (Tomani, 2010).

Membrane filtrations, using microfiters, ultrafilters, and nanofilters, were also suggested as methods to extract lignin from black liquor (Arkal et al., 2014; Alén et al., 1986; Wallberg et al., 2003; Kouisni et al., 2011; Zhu & Theliander, 2015; Humpert et al., 2016). Polymeric and ceramic membranes are the most common membrane materials suggested for lignin extraction. Comparingly, the ceramic membrane has the ability to stand extreme pH value, while the polymeric membrane is less expensive (Arkal et al., 2014; Humpert et al., 2016). However, lignin has a wide molecular weight distribution, which causes filtration problems (Pakkanen & Alén, 2012; Ringena et al., 2006). As a drawback, since membrane technology was based on size separation, hemicelluloses were collected with lignin and led to lignin impurity (Fatehi & Chen, 2016).

Table 1.2: Properties of softwood and hardwood species obtained by acidification of black liquor at different pHs adopted from (Lourençon et al., 2015).

| Lignin type | Hardwood | | | | | | Softwood | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Yield % | $M_W$ | Elemental analysis | | | | Yield % | $M_W$ | Elemental analysis | | | |
| | | | C % | H% | O% | S% | | | C % | H % | O % | S % |
| pH 9 | 51.70 | 5316 | 53.20 | 4.90 | 38.70 | 2.50 | 49.90 | 13895 | 54.10 | 5.00 | 37.90 | 2.40 |
| pH 5 | 33.70 | 4352 | 56.90 | 5.30 | 34.40 | 2.90 | 11.00 | 12643 | 52.30 | 4.80 | 38.60 | 3.51 |
| pH 1 | 1.50 | 3630 | 71.40 | 8.60 | 14.00 | 2.90 | 1.00 | 3464 | 43.80 | 4.50 | 26.10 | 24.60 |

Electrolysis is another method to extract lignin from black liquor. In this method, lignin is precipitated via oxidation on the anode side and oxygen gas is formed, while sodium hydroxide is produced in the cathode side. Black liquor consisting of different ions including $K^+$ and $Ca^{+2}$ at a very small amount while $Na^+$ ions are the principle cation (Clayton et al., 1983; Venkatesh & Nguyen, 1992). As a result, hydrogen gas is produced at the cathode, when black liquor is exposed to electrolysis. The electrolysis reduces the overall costs of this process by generating sodium hydroxide, oxygen and hydrogen gases as value-added by-products. However, the cost of electric requirement and membrane foaling/cleaning are challenges of this process (Davy et al., 1998).

Solvents have also been introduced as separation methods for lignin isolation. In this respect, chloroform, dichloromethane, ethanol, methanol, and isopropanol were used for isolating lignin (Whalen, 1975; Villar, 1996). Basically, this method relies on the disruption of hydrogen bonding development between lignin molecules and water in black liquor, causing lignin to precipitate (Whalen, 1975). However, this method requires solvent recovery, which would increase the operation cost of kraft pulping, and thus hampers its practical application in industry (Fatehi & Chen, 2016).

Two processes were commercialized to extract kraft lignin from black liquor namely LignoForce, ™ developed by FPInnovations, and LignoBoost™ process that was developed by Innventia (Kouisni et al., 2011; Tomani, 2010). They are based on the acidification theory and produce highly pure lignin.

LignoBoost technology was introduced in 2013, and commercialized by Domtar in the USA with an annual production of 25000 tons of lignin (Zhu, 2015). It consists of four steps of precipitation, re-dispersion, filtration and washing. Through this process, black liquor from kraft pulping process is acidified with carbon dioxide to reduce its pH to 9, which causes lignin to precipitate (Tomani, 2010). The precipitated lignin then disperses and being washed with acid before the second stage of filtration. Compared to the traditional method of acidification, LignoBoost has a reduced operation cost as it uses filters with small surface area and less amount of sulfuric acid for washing lignin after precipitation. This process has a higher yield of lignin recovery, and contains lower ash and carbohydrate (Tomani, 2010).

The most recent commercial process for lignin extraction from black liquor of kraft pulping is LignoForce process, which was commercialized in 2016 by WestFraser Inc. in Canada (Fatehi & Chen, 2016; Kouisni et al., 2012). In this system, after oxidizing black liquor with $O_2$, lignin is precipitated with the addition of carbon dioxide to pH 9 in the temperature range of 70 and 75 °C. Then, lignin is washed with sulfuric acid and water in a filter press and finally air dried (Kouisni et al., 2016). LignoForce system improves the filterability of the precipitated kraft lignin and the dry content of the produced lignin. This process has low acid requirement and produces less sulfur emission.

## 1.4 Lignin extraction from spent liquor

The spent liquor of sulfite pulping process is usually in the pH range of 3 and 4 and contains lignosulfonates, sugars, and other chemical residuals (Marques et al., 2009; Restolho et al., 2009). Lignosulfonates are produced around 1 million ton annually in the sulfite pulping process

(Mansouri & Salvadó, 2007). Considering that sulfite pulping is conducted under acidic conditions and lignosulfonate is soluble in acidic environment (Neytzell-De Wilde, 1987), the extraction of lignosulfonates from its spent liquor cannot be conducted via acidification (Fatehi et al., 2011b).

The most respected method for extracting lignosulfonates is membrane technology (Areskogh, 2011). Lignosulfonates have a higher molecular weight than other components in the spent liquors, and membranes were found to be suitable for extracting lignosulfonates from spent liquors (Restolho et al., 2009). In one study, it was found that 95 % of pure lignosulfonate was extracted from calcium bisulfate pulping spent liquors by using a polysulfone-based ultrafilter with a molecular weight cut off of 20,000 g/mol (Manttari & Nystrom, 2008; Kuzmenko, 2010). The Howard method is an alternative for extracting lignosulfonate from spent liquor (Stoklosa and Hodge, 2014). In the Howard method, the addition of calcium hydroxide to the spent liquor makes lignosulfonate precipitated as calcium lignosulfonate at pH 8.5. The precipitated product can be further dried and then mixed with water prior to filtration to be purified. The yield of this process is in the range of 90 % to 95 % (Areskogh, 2011; Aro & Fatehi, 2017). However, ion exchange, amine extraction, and electrolysis were also reported to be effective in lignosulfonate isolation.

In the amine extraction, lignosulfonate is isolated from the spent liquor via liquid-liquid extraction by reacting lignosulfonate with a long-chain alkyl amine to form lignosulfonate acid-amine that is water insoluble (Aro & Fatehi, 2017). This process has many challenges, such as the incomplete elimination of the amine, formation of the salt, time consuming, and solvent consumption (Ringena et al., 2006).

Electrolysis requires demineralization, desalination, in addition to a high usage of electric, which makes it a costly process, and this hampers its application in industry (Ringena et al., 2005; Fatehi & Chen, 2016).

## 1.5 Lignin modifications and applications

Modification of kraft lignin is challenging due to its structural complexity (Sjostrom, 1993; Košíková et al., 2000). Although the α position and/or phenolic OH groups of the phenyl propene subunits of kraft lignin present the most reactive sites for any reaction (Sjostrom, 1993; Košíková et al., 2000). The β-O-4 aryl ether linkage bonds occupy these reactive sites or create a steric hindrance, which limits the reactivity of kraft lignin for modification (Wu et al., 2012; Ouyang et al., 2009). Chemical modification may change the properties of softwood kraft lignin to desirable ones. In one study, the molecular weight of lignin decreased and resulted in increasing the reactivity of lignin by removing the methoxyl and phenolic hydroxyl groups from its aromatic ring (Mansouri & Salvado, 2007). In another study, the reactivity of lignin was increased through the addition of formaldehyde to the aromatic ring on the para position (Yasuda et al.,1998). In other work, the carboxymethylation of hardwood kraft lignin introduced carboxyl groups to the para-position on the aromatic ring, and yielded lignin with a higher charge density (Konduri & Fatehi, 2015).

In the past, lignosulfonates have been used in different applications, such as dispersant in cement admixture. However, the amount of lignosulfonate produced is limited in Canada. Kraft lignin can be used in many important applications, such as an emulsifying agent, stabilizer, binder in mortar and construction structures, additive in agriculture and oil field applications (Calvo-Flores et al., 2015; Chiellini & Solaro, 2012; Stewart et al., 2008). Lignin has also been used in metal sequestrations and plastic composites (Stewart et al., 2008). In addition, lignin can be utilized in the manufacturing of flexible polyurethane foam and as a raw material for producing adhesives and elastomers (Bernardini et al., 2015). In another study, the polymerization of kraft lignin produced a product to be used as a tanning agent in the process of leather tanning (Suparno et al., 2005). However, the main objective of this MSc studies was to modify kraft lignin to increase its water solubility to be used as dispersants for clay suspensions.

Various methods were reported to be applied for this purpose including demethylation, hydroxymethylation and phenolation (Hu et al., 2011; Ouyang et al., 2009; Inwood, 2014). For example, the demethylation of lignin could remove the methyl group from the phenolic hydroxyl groups of lignin (Hu et al., 2011), which resulted in increasing the free phenolic groups and thus its reactivity (Okamoto et al., 1996). In one study, the demethylation of wheat straw soda lignin reduced the molecular weight and increased the phenolic content of lignin (Wu et al., 2001). In another work, the hydroxymethylation of pine kraft lignin by formaldehyde in alkaline medium introduced hydroxymethyl group to the aromatic ring (Hu et al., 2011), which improved its reactivity (Malutan et al., 2008). Similarly, the hydroxymethylation of calcium lignosulfonate improved its properties (i.e., solubility, charge density and reactive groups), in a work by Pang and coworkers (2008).

Phenolation was also reported to improve the properties of lignin by increasing the phenolic content of lignin (Hu et al., 2011; Inwood, 2014). Although demethylation, hydroxymethylation, and phenolation were able to improve the properties of lignin, they were not favorable for improving the properties of lignin to be used as dispersants. For example, hydroxymethylation reduced the dispersive ability of the production (Pang et al., 2008). Alternatively, oxidation and sulfonation were proposed to improve the water solubility of softwood kraft lignin as dispersants in cement admixtures and were considered to produce anionic lignin similar to lignosulfonates. In another study, grafted sulfonated alkali lignin was prepared with hydrophilic side chain and used as a dispersant in coal-water slurry (Qin et al., 2015). The sulfonation of kraft lignin enhanced its charge density to -1.6 meq/g, and produced a water-soluble product (Gargulak et al., 1999). When softwood kraft lignin was utilized as a dispersant in cement, it increased the cement dispersibility from 65 mm to 200 mm with the addition of 0.5 wt.%. In this study, softwood kraft lignin was oxidized with nitric acid followed by sulfomethylation, which produced a modified lignin with a negative charge of 2.05 meq/g, under the conditions of 100 °C, 3 h treatment, formaldehyde to lignin molar ratio of 1/1, sodium metabisulfite to lignin molar ratio of 0.5/1, and 4.0 wt% sodium hydroxide (He & Fatehi, 2015).

In the past, various studies were carried out on lignin modification by oxidation reaction using hydrogen peroxide (Pang et al., 2008; He & Fatehi, 2015), nitric acid (He & Fatehi, 2015), metal oxides and nitrobenzene (Villar et al., 1997) and oxygen with metals (Villar et al., 2001) to improve its water solubility and reactivity. Generally, oxidation improves the solubility of lignin by increasing the negative charge density of lignin via increasing the number of carboxylate groups (Meister, 2002; Pang et al., 2008). In one study, lignosulfonate was reacted with hydrogen peroxide under the optimum conditions of 80 °C, molar ratio of 0.12 $H_2O_2$/lignosulfonate for 1.5 h. It was concluded that the addition of oxidized lignosulfonate improved the dispersion performance of cement by 34 % (Pang et al., 2008). On the other hand, oxidizing lignin with nitric acid was reported to increase the number of carboxylate group which in turn improved the hydrophilicity and anionicity of lignin (He & Fatehi, 2015). One of the advantages of using nitric acid is that it could be recycled (Morrow et al., 1988). According to He and Fatehi (2015), the oxidation of kraft lignin via nitric acid was found to eliminate the methoxy and phenolic groups from lignin and reduce the steric hindrance of lignin, while improving its reactivity and water solubility.

## 1.6 Dispersant

Dispersants have a wide range of applications in industry (Table 1.3). They are either non-surface-active polymers or surface-active substances added to a suspension. Dispersants are important components in concrete for reducing the amount of water and improving the workability of concrete (Lou et al., 2013). In addition, dispersants were reported to advance the strength and durability of cement structures (Plank et al., 2010). They could be used in the mining and oil-sand industries. However, the current dispersants that used in industry are oil-based, which are environmentally unfriendly and expensive. Lignin-based dispersants can be used in industry due to their low production costs, as well as excellent performance (Tomita & Hirata, 2005). In other words, the future of lignin dispersants is promising because lignin makes dispersants more environmental friendly and biodegradable (Cotana et al., 2014).

Table 1.3: Various applications of dispersant

| Dispersant application | Type of lignin | Reference |
|---|---|---|
| Cement admixtures | Alkali lignin sulfonated | Ouyang et al., 2009 |
| | Kraft lignin | Aso et al., 2013 |
| | Sulfomethylated lignin | He & Fatehi, 2015 |
| Coal-water slurry | Sodium lignosulfonate | Zhou et al., 2008 |
| | Grafted sulfonated alkali lignin | Qin et al., 2015 |
| Dyeing industrial | Hydroxypropyl sulfonated alkali lignin | Qin et al., 2015 |
| Aqueous graphite suspension | Carboxymethylated lignin | Gan et al., 2013 |
| Drilling fluid | Grafted copolymerized Lignosulfonate | Zahran et al., 2014 |
| Plasterboards | Ammonium lignosulfonate | Plank, 2010 |

## 1.7 Lignin applications as dispersants

### 1.7.1 Cement admixture

Sulfonated lignin and lignosulfonate were considered to be used as dispersants for cement due to their appropriate molecular weight, anionic charge density, and presence of functional (i.e., sulfonate) groups (Meister, 2002; Vishtal & Kraslawski, 2011).

In one study, alkali lignin was oxidized, and then hydroxymethylated prior to sulfonation for sulfonated lignin production that was more reactive with a molecular weight of 9688 g/mol (Ouyang et al., 2009). The sulfonated lignin was evaluated as a dispersant in cement and compared with commercial lignosulfonate. It was found that the adsorption of sulfonated lignin on cement particles was 8.5 mg/g, which was higher than that of commercial lignosulfonate (5.9 mg/g). The fluidity of cement (ability to flow easily) was measured by adding the modified lignin and mixing it with the cement prior to spreading it in a truncated flow cone to flow for 30 seconds. Then, the maximum diameter ($d_1$) of the spread and the diameter of perpendicular ($d_2$) were measured to report the fluidity of cement as the average value ($d_1$+$d_2$/2) (He & Fatehi, 2015). The addition of sulfonated lignin samples increased the fluidity of cement admixture to 200 mm, which was higher than that when lignosulfonate was used (190 mm), while the fluidity of the cement admixture without lignosulfonate was 70 mm. He and Fatehi (2015) also reported that sulfomethylated kraft lignin had 200 mm fluidity, which was higher than that of lignosulfonate at fluidity of 165 mm. Alternatively, sulfomethylated kraft lignin with the sulfonate group content of 2.05 meq/g was produced via oxidation and sulfomethylation of kraft lignin, which had an adsorption of 6.5 mg/g on cement particles and improved the fluidity of cement pastes from 65 mm to 200 mm. These results were better than those of commercial lignosulfonic acidic sodium salt, in which the adsorption and fluidity were 4.0 mg/g and180 mm, respectively. Another conclusion of this study was that the increment in sulfonation degree of lignin would increase its dispersion performance (He & Fatehi, 2015). In another study on sulfonated phenolic resins, the fluidity of cement increased as the sulfonation degree increased to the maximum degree of 0.36 g/g sulfur/carbon ratio (Hsu et al., 2000). Moreover, Li et al. (2011) showed that the sulfonation of wheat straw lignin, which was produced via hydroxymethyltion and sulfonation of lignin extracted via ethanol pulping, reduced the water use of cement by 14.9 wt.%.

It was claimed that the charge density and molecular weight of dispersants could impact their performance (Ouyang et al., 2009). In one study, the oxidation, hydroxymethylation and sulfonation of wheat straw lignin yielded a sulfonated lignin with 1.49 meq/g sulfonate content and 9688 g/mol molecular weight ($M_w$). This product reduced the surface tension of water to 47 mN/m, while having an adsorption of 8.5 mg/g on cement particles, and a higher dispersability (216 mm) compared to commercial lignosulfonate (210 mm).

### 1.7.2 Dye solutions

In the past, lignin was modified and used as a dye dispersant in various studies (Qin et al., 2015; Meister, 2002; Ouyang et al., 2009). For example, Qin et al. (2015) evaluated the effect of molecular weight of hydroxypropyl sulfonated lignin as a dye dispersant. This investigation performed a comparison between the hydroxypropyl sulfonated lignin with three different molecular weights and commercial dispersants as dye dispersants. It was found that the molecular weight of all the hydroxypropyl sulfonated lignin samples (8750, 11020 and 14830 g/mol) was higher than that of the commercial dye dispersant (8050 g/mol). However, the hydroxylpropyl sulfonated lignin with the lowest molecular weight (8750 g/mol) had the highest hydroxyl phenol group (2.32 mmol/g), suggesting its best performance to interact with epichlorohydrin (Qin et al., 2015). The results revealed less thermal stability and less sediment formation when hydroxypropyl sulfonated lignin was used in comparison with lignosulfonate. Moreover, dye uptake in this study confirmed that hydroxylpropyl sulfonate had higher temperature stability than commercial lignosulfonate. In another study, lignosulfonate was reacted with 1-methanolylphenol, which increased its molecular weight, and resulted in better thermal stability and dispersion in comparison with lignosulfonate (Meister, 2002).

On the other hand, the charge density of the modified lignin influenced its performance for dispersing dye pigments. The highest content of hydroxyl phenol group increased the electrostatic repulsion between the samples and the surface of dyes due to their similar charges (Qin et al., 2015). According to a study on the sulfonation of alkali lignin, sulfonated lignin was produced with a negatively charged sulfonation degree of 1.49 mmol/g, compared with a commercial lignosulfonate, which had a negative sulfonation degree of 1.39 mmol/g (Ouyang et al., 2009). The negative charge of sulfonic group in the sulfonated lignin molecule was higher than the commercial lignosulfonate molecule. Accordingly, it could be concluded that the sulfonated lignin had a higher adsorption amount of 9 mg/g on particles than commercial lignosulfonate (5.9 mg/g) (Ouyang et al., 2009). Therefore, the adsorption amount and charge density increased the zeta potential (-30 mV) of cement particle (-26 mV); accordingly, a better dispersion effect to the cement admixtures could be found (Ouyang et al., 2009).

However, it was unclear how oxidized kraft lignin could act as a dispersant in comparison with lignosulfonate. For this aim, in the present work, kraft lignin was chemically modified by three methods of oxidation by hydrogen peroxide, nitric acid treatment, and sulfonation via sodium sulfite treatment, and then the performance of the products was compared systematically with commercial lignosulfonate.

## 1.8 Methodology

### 1.8.1 Charge density analysis

Charge density of polymers play important roles in colloidal system, as it is responsible for interaction of particles in suspensions (Nasser & James, 2006; Zhou et al., 2008). The charge density of polymers was measured in many studies using a particle charge detector (PCD) (Li et al., 2011; Lou et al., 2013; Plank et al., 2010). The fundamental of PCD is based on neutralization of charged polymers by a standard solution of polymers with an opposite charge. When a streaming current is 0 mV, all existing charges in the sample are neutralized. For quantitate charge density measurement, a polyelectrolyte titration is used to determine the neutralization point (0 mV). In this study, polydailyldimethylammonium chloride (PDADMAC) was used as a standard polymer to neutralize the modified lignin. By considering the amount of PDADMAC added for neutralizing, and the amount of dried polymer added to the cell of PCD, the charge density of the polymer can be calculated (Li et al., 2011; Lou et al., 2013; Plank et al., 2010).

### 1.8.2 Molecular weight determination (GPC)

Gel permeation chromatography is one of the most powerful technique for characterizing the molecular weight of polymers (Kostanski et al., 2004). Some important characteristics, such as weight average molecular weight ($M_w$), number average molecular weight ($M_n$), and polydispersity ($M_w/M_n$) can be identified by GPC (Choi et al., 2001). In GPC analysis, polymers should pass through of a column of porous beads. The polymers with smaller size should pass through more pores to pass through the column, while the larger polymers cannot pass through very small pores and thus pass through the column more quickly than small polymers (Brend, 1995). By using standard polymers in GPC analysis, a calibration curve can be generated for correlating the size of polymers and retention time it takes for polymers to pass through the column. The elution behavior of sample is displayed as a retention time, which represents the time of a fraction to exit from the column in a chromatogram. Standard polyethylene oxide samples were used as standard for calibrating the GPC. 0.1 mol/L $NaNO_3$ solution was used as solvent and eluent with flow rate of 0.70 mL/min. The retention time of samples can help identify their sizes according to the calibration curve. The molecules eluted from the column may be detected by different detectors including refractive index (RI), ultraviolet (UV) viscometer, and a multi angel laser detector (Bernd, 1995). Furthermore, $M_w$ and $M_n$ can be calculated using following equations 1.1 and 1.2 (Ward, 1981).

$$M_w = \Sigma \frac{W_i M_i}{\Sigma W_i} \qquad 1.1$$

$$M_n = \Sigma N_i \frac{M_i}{\Sigma N_i} \qquad 1.2$$

Where N refers to the number of polymer chains having molecular weight of $M_i$ and $W_i$ refers to weight fraction distribution, while $M_n$ represents the number average molecular weight, and $M_w$ represents the weight average molecular weight.

In addition, polydispersity index (PDI) provides information about the distribution of the chain lengths, which can be calculated using equation 1.3 (Ward, 1981).

$$PDI = \frac{M_w}{M_n} \qquad 1.3$$

### 1.8.3 Fourier transform infrared spectrophotometer (FTIR)

FTIR is one of the methods to characterize the properties of polymers to identify the functional groups, bonding vibration of compounds and specify the structure of polymers (Mansouri & Savado, 2007; Griffiths & De Haseth, 1986; Li & Ge, 2011). According to the literature, FTIR spectroscopy was used to determine the structural and functional groups of lignin (Wegener & Strobel, 1992) and the relative content of phenolic hydroxyl groups (Faix & Bottcher, 1993). FTIR analysis depends on the fact that most of the molecules adsorb light in the infrared region of the electromagnetic spectrum, which represents a fingerprint information on the chemical composition of materials (Zhang & Cresswell, 2016; Griffiths & De Haseth, 2007).

### 1.8.4 Elemental analysis

Elemental analysis is a process through which the elemental compositions of polymers are determined (Das et al., 2013; Li & Ge, 2011; Thompson, 2008). Elemental analysis includes determination of carbon, hydrogen, nitrogen, and sulfur elements in different samples in wide range of applications, such as polymers, chemicals, food, and pharmaceuticals (Fadeeva et al., 2008; Aiken et al., 2007). The analysis requires a high temperature (1200 ºC) of combusting materials in a furnace in the presence of oxygen gas to convert carbon to carbon dioxide, nitrogen to nitrogen gas, sulphur to sulphur dioxide, and hydrogen to water (Fadeeva et al., 2008; Thompson, 2008; Käldström et al., 2014). Afterwards, the combustion gases pass through an adsorbent trap with an inert gas (helium) to ensure that there are only carbon dioxide, water, nitrogen and sulphur dioxide (Thompson, 2008; Aiken et al., 2007).

In addition, the oxygen content of a sample could be measured separately using pyrolysis and reduction methods (Skoog et al., 1998). In many studies, elemental analysis was used to investigate the oxygen content of unmodified lignin and modified lignin (Meister, 2002; Helander et al., 2013; Konduri & Fatehi, 2015; Wang et al., 2016). In this thesis, elemental analysis was conducted to investigate the compositions of unmodified lignin and modified lignin, where lignin samples were combusted at a high temperature of 1200 ºC.

### 1.8.5 Zeta potential

Zeta potential is used to measure the electrical charge of suspensions, the charge repulsion/attraction or the magnitude of the electrostatic charge between particles. Colloidal particles gain charges because of dissolution of surface functional groups in suspensions. The net surface charges, which are promoted at the surface, influence the distribution of ions in the neighboring interfacial regions, causing an increased concentration of counter ions close to the surface of particles. Therefore, an electrical double layer exists around each particle (Riddick, 1968), as shown in Figure 1.2, which contains inner and outer regions. In the inner region, called stern layer, ions are strongly attached to the particle surface, whereas the ions in the outer region, called diffused layer, are less firmly attached. Furthermore, a boundary, called slipping plane, occurs in the diffuse layer, where ions and particles form a stable system, and the electric potential corresponding to the slipping plane is zeta potential (Riddick, 1968; Araki et al., 1998). As zeta potential indicates the stability of colloidal particles, the particles with high zeta potential lean to repel each other and no aggregation of particles is performed in the suspensions. It was reported that particles with zeta potential higher than ±30 mV are reflected to be stable (Araki et al., 1998; Sharma et al., 2014). This suggests that when a charged polymer (negative or positive one) is added to the suspension, it changes the zeta potential of the particles in suspension, which affect the stability of the suspension. However, the effect of modified lignin on zeta potential of kaolin, bentonite and alumina colloid suspensions was not investigated in detail, which was addressed in the present work.

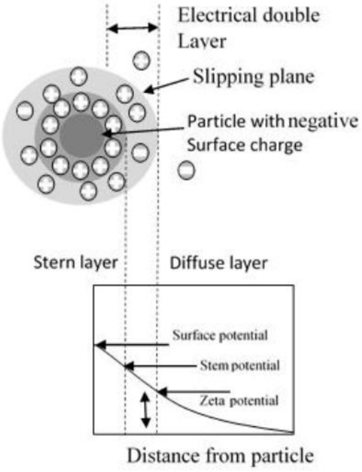

Figure 1.2: Electrical double layer surrounding the particle

### 1.8.6 Thermo-gravimetric analysis (TGA)

Thermo gravimetric analysis (TGA) assesses the thermal stability of a polymer, in which a sample is burned over time as the temperature increased in a controlled atmosphere (Li & Ge, 2011; Stodghill, 2010; Gabbott et al., 2008). In another word, in TGA, the sample's weight is monitored as it is burned in a furnace (Gabbott et al., 2008). Generally, TGA consists of sample pan which is supported by micro-thermal balance to monitor the mass changes during the process and the burning environment is controlled by the presence of $N_2$ or $O_2$ for pyrolysis and combustion experiment (Gabbott et al., 2008). Degradation of lignin will be determined by indicating the mass loss (as a percentage of the initial mass) during the temperature change (Gabbott et al., 2008). The result of TGA analysis is reported in this work for modified lignin samples.

### 1.8.7 Differential scanning calorimetry (DSC)

DSC is a technique in which the difference in the amount of heat absorbed or released for samples compared with a reference is determined as a function of temperature (Gabrielii et al., 2000). DSC investigates the thermal behavior of lignin, such as glass transition and heat capacity. The fundamental of DSC is that when the sample undergoes a physical change such as glass transition, a higher heat is required to flow the sample than the reference material. The glass transition of lignin occurs when the polymer transits from a glassy state into a rubbery state (Khaldi et al., 2016). Whereas, heat capacity (Cp) is the amount of energy to raise the temperature of sample by 1ºC and measured in the unit of (J/g ºC). DSC consists of two pans; the first pan is sample pan containing the lignin that is being investigated, while the second one contains a reference. In this set of experiments, the two pans are heated separately at the same rate, while the heat flow of the pans are monitored and recorded to keep their temperature difference close to each other, when the temperature is increased in the DSC furnace (Gabbott et al., 2008).

### 1.8.8 Turbidity analysis

Turbidity analysis is one of the method for studying the dispensability (clarity) of suspensions (He & Fatehi, 2015; Wu et al., 2012) as a function of flocculant or dispersant concentration. Due to the charge density of particles, dispersion occurs between the particles in suspensions when the repulsion force between the particles increases, which in turn raises the turbidity of the suspension. On the other hand, flocculation occurs when the repulsion force between the particles in suspension decreases and the particles agglomerate, which results in a decrease in the turbidity of the suspension.

One of the most widely used methods to study the dispensability of suspension is photometric dispersion analyzer (PDA). In this analysis, the turbidity of a suspension passing through a tube is monitored by a detector as a function of direct current voltage of the suspension (DC) (Petzold et al., 2005). In this analysis, distilled water is transferred to DDJ. The suspension passes through a tube and PDA then circulated to the DDJ. The DC voltage value of the suspension will be read by the PDA. The DC voltage of unflocculated suspension is denoted by $V_i$, while the DC of final suspension is represented by $V_f$, while $\tau_f$ and $\tau_i$ are the final and initial suspension turbidities, respectively and $V_0$ is the initial base DC voltage (Wang et al., 2016; Li & Ge, 2011; Konduri & Fatehi, 2017).

$$\text{Relative turbidity} = \frac{\tau_f}{\tau_i} = \frac{\ln(V_0/V_f)}{\ln(V_0/V_i)} \qquad 1.4$$

### 1.8.9 Surface area of particles

The surface area of kaolin, bentonite, and alumina particles was determined by using Quantachrome surface area analyzer, NOVA-2200e using Branuer-Emmett-Teller. BET method was used in many studies to determine the surface area of porous materials (Tombácz and

Szekeres, 2006; Gupta et al., 2015; Grishechko et al., 2013; Sing, 2001). This method is based on the adsorption of an inert gas (usually $N_2$) with a known surface coverage on a porous material. Physical adsorption between the gas molecules (the adsorbate) and the surface area of the porous material (the adsorbent) is the result of van der Waals interaction (Reible, 1999).

### 1.8.10 Particle size of suspensions

Particle size analyzer (Mastersizer 2000, Malvern), which is a laser diffraction instrument, have been used in many studies to determine the particle size distribution of a colloidal suspension (Wang et al., 2016; Storti & Balsamo, 2010; Loginov et al., 2008; Ryzak et al., 2007). In this thesis, alumina, kaolin, and bentonite suspensions were prepared in aqueous conditions and characterized by Mastersizer 2000 laser diffraction. This laser diffraction particle size analyzer is designed for determining particles in the range of 0.02 to 2000 µm. The principle of laser diffraction is based on the Mie theory (Mccave et al., 1986; Boer et al., 1987). In other word, when a laser beam passes through particle suspension, the light is scattered, the angular variation intensity of the scattered light is received by the detector of the machines and then analyzed. Thus, large particles scatter light at small angles relative to the laser beam and small particles scatter light at large angles (Mccave et al., 1986). The size of particles that is responsible for light scattering at different angles is calculated using the Mie theory as shown in equation 1.5 (Andrews et al., 2010; Fu & Sun, 2001).

$$\mathrm{I} = \frac{2\pi \mathrm{r} N_m}{\lambda} \qquad 1.5$$

where I denoted the intensity of incident of light, r is the radius of the particles (nm), Nm is the refractive index of the medium and $\lambda$ is the wavelength of incident light (nm).

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# 2 Chapter 2. Sulfonation and oxidation of softwood kraft lignin

## 2.1 Abstract

In this study, the modification of softwood kraft lignin (SKL) through sulfonation and oxidation was investigated. The sulfonation was studied via sodium sulfite reaction under various conditions, including $Na_2SO_3$/ kraft lignin ratio, temperature, time and lignin concentration. The FTIR analysis confirmed that the self-condensation of the guaiacyl phenyl propane subunits of kraft lignin occurred in the sulfonation. The selected conditions for sulfonation were 90 °C, 1 h and 3/1 $Na_2SO_3$/lignin molar ratio. Oxidation of softwood kraft lignin via nitric acid treatment improved the water solubility of kraft lignin and increased the anionic charge density of lignin. The selected conditions were found to be 20 % wt. nitric acid concentration at 90 °C for 1 h. The oxidation with hydrogen peroxide indicated that the oxidation enhanced the solubility and charge density of kraft lignin. The selected conditions were found to be 0.5 $H_2O_2$/lignin molar ratio at 80 °C for 2 h. Overall, the charge densities of 1.63, 1.31, and 3.2 meq/g were obtained for sulfonated lignin (SSKL), oxidized lignin via hydrogen peroxide (OSKL) and oxidized lignin via nitric acid (OOSKL) treatments, respectively. The molecular weights (Mw) were determined to be 17890 g/mol for SKL, 27295 g/mol for SSKL, 24539 g/mol for OSKL and 14725 g/mol for OOSKL. In addition, the characteristics of SSKL, OSKL, and OOSKL were evaluated using particle charge detector, gel permeation chromatography, FTIR and an element analyzer.

## 2.2 Introduction

After cellulose, lignin is the most abundant renewable biopolymer that may provide a premium source for producing value-added products (Pouteau et al., 2003; Inwood, 2014). However, lignin is not very reactive due to its complex structure. There is a great number (plurality) of ether bonds including β-O-4, α-O-4, 4-O-5 and carbon linkages on lignin. In addition, lignin has different types of functional groups such as methoxyl, carboxylic, phenolic hydroxyl, aliphatic and carbonyl groups, which can facilitate the reaction of lignin with other reagents if being modified. Sulfonation and oxidation are popular procedures for improving the properties of lignocellulosic biomass (Coughlin et al., 2013; Yu et al., 2013; He & Fatehi, 2015).

In different studies, sulfonation was conducted to alter lignocelluloses (Shin & Rowell, 2005) and cellulose (Zhang et al., 2014) to produce polyelectrolyte reactive products. Sulfonation was practiced using different reagents including sulfuric acid (Kaandorp et al., 1962; Kim et al., 1990) and chlorosulfonic acid (Xie & Shi, 2011). In addition, concentrated sulfuric acid was used to sulfonate toluene (Kaandorp et al., 1963a) and tertbutyl benzene (Kaandorp et al., 1963b), while vapour sulfuric acid was used for sulfonating polystyrene beads (Kim et al., 1990). However, sulfuric acid may be dangerous and chlorosulfonic acid must be performed in a solvent, which is challenging and not economical.

On the other hand, oxidation was reported to introduce a reactive group on lignin, and thus enhancing the charge density and solubility of lignin (Meister et al., 2002; Pang et al., 2008). It was reported previously that the oxidation of kraft lignin decreased the steric hindrance of kraft lignin via removing the methoxyl and phenolic groups of lignin, which improved its solubility and reactivity (He & Fatehi, 2015). In the past, oxidation was used for modifying lignin via various pathways including hydrogen peroxide (Pang et al., 2008), metal oxides (Villar et al., 1997), nitrobenzene (Villar et al., 1997), and oxygen with catalyst (Villar et al., 2001) as an attempt to improve its properties. In one study, lignosulfonate was oxidized with hydrogen peroxide to improve its performance as a dispersant (Pang et al., 2008), where adding 4 g/L of modified lignosulfonate improved its dispersion performance by 34.2%. It was also concluded that increase in the carboxylate groups and anionic charge density of the lignosulfonate had a great effect on its performance as a dispersant on cement admixtures (Pang et al., 2008).

However, to produce water soluble products, oxidation reaction may not be favorable in mild condition (Morrow et al., 1988). Alternatively, nitric acid (Alvarez et al., 2003; Tchoul et al., 2007; He & Fatehi, 2015), sodium periodate (Kim et al., 2000), potassium permanganate (Javor et al., 2003), chlorine (Meister, 2002), and chlorine dioxide or hypochlorite (Meister, 2002) were used to oxidize organic materials and kraft lignin. According to Alvarez et al. (2003), the oxidation of low rank coal via nitric acid helped remove sulphur and increased the carboxylate and amino groups of coals, which increased the hydrophilicity of the coal. In another study, chemical modification of carbon nanotubes via nitric acid improved its dispersion performance in polar solvents (Tchoul et al., 2007).

In this work, SKL was modified by sulfonation via sodium sulfite, in addition to oxidation via nitric acid and hydrogen peroxide oxidation. To our knowledge, there is no literature describing these modifications to softwood kraft lignin. The products of these modifications were evaluated by a particle charge detector, FTIR, GPC, and TGA. Also, the results were compared with those of commercial lignosulfonic acid salt. The solubility of modified lignin was also assessed. Based on the results, the conditions that yielded a sulfonated lignin and oxidized lignin with the highest charge density and solubility were determined.

## 2.3 Experimental

### 2.3.1 Raw materials

Acid washed and dried softwood kraft lignin (SKL) was supplied by FPInnovations' facilities in Thunder Bay, ON, and used as received. Sodium sulfite was purchased from Sigma-Aldrich. Kaolin, bentonite, blue basic 44 dye and alumina particles were all purchased from Sigma-Aldrich and used as received. Sodium hydroxide (0.1M), hydrochloric acid (0.1M), commercial lignosulfonic acid sodium salt (CLS), with a molecular weight of 52,000 g/mol and a sulfonation degree of 1.68 meq/g, and poly diallyldimethylammonium chloride solution (PDADMAC), with a molecular weight of 100,000-200,000 g/mol (20 wt.% in water), were all purchased from Sigma-Aldrich.

### 2.3.2 Sulfonation of softwood kraft lignin (SSKL)

A specific amount of SKL was reacted with sodium sulfite under different conditions in a 500 mL three-neck flask assembled with graham condenser in an effort to eliminate the loss of sulfonation reagent through evaporation. The reaction parameters were temperature (50-90 °C), lignin concentration (5-20 g/L), time (1-4 h), and $Na_2SO_3$/lignin molar ratio. In all reactions, magnetic stirrer was set at 300 rpm, and the temperature was controlled with a hot plate equipped with a thermometer. Once the reaction was completed, the solution was cooled slowly to room temperature (25 $^{o}$C), the pH was then adjusted to 7 using NaOH or HCl solution. The sulfonated SKL was dialyzed with membrane with a molecular weight cut off of 1000 g/mol to separate unreacted sodium sulfite and other unwanted contaminants, while changing water every 2 hours for the first 6 hours and then every 12 h for 2 days. Afterward, the sulfonated SKL was separated and dried in an oven overnight at 105 °C and the product was denoted as SSKL.

### 2.3.3 Oxidation of SKL via nitric acid (OOSKL)

A specific amount of SKL was added to a 500 mL three-neck glass flask and mixed with water at room temperature. Then, nitric acid was added slowly to the solution by mixing at 300 rpm. The oxidation reaction was conducted at different temperatures (60 °C, 70 °C, 80 °C, and 90 °C) and different concentrations of nitric acid (10 %, 15 %, 20 %, and 25 %) for 1 h. After completion, the reaction medium was cooled slowly to room temperature and adjusted to pH 7 with the help of NaOH solution. The product was purified using the membrane with the molecular weight cut off of 1000 g/mol, as described earlier. Finally, the product was dried in the oven at 105 °C overnight and the product was denoted as OOSKL.

### 2.3.4 Oxidation of SKL via hydrogen peroxide (OSKL)

Firstly, a specific amount of SKL was mixed with water in a 500 mL three-neck flask at room temperature and brought to pH 12 with the aid of NaOH. The temperature and stirring were controlled using a hot plate equipped with a thermometer. Once completed, the mixture allowed to cool slowly to room temperature and the pH was adjusted to neutral. Finally, the mixture was transferred into the membrane with a molecular weight cut off 1000 g/mol to purify the produced oxidized SKL as described earlier, and then dried in the oven over night at temperature 105 ºC. The product was denoted as OSKL.

## 2.4 Characterization

### 2.4.1 Solubility

The solubility of the modified lignin was measured using the following steps. First, 0.2 g of SSKL, OSKL and OOSKL were added to 19.8 g of distilled deionized water to make 1 wt.% solutions at room temperature and neutral pH. Then, the solutions were treated in a water bath shaker (New Brunswick Scientific, NJ) for 1 h at 30 ºC and 150 rpm. Generally, the modified lignin would dissolve completely after 10 min, but the samples were kept for 1 h in the water bath to ensure that all sample parts had sufficient time to dissolve in water. Afterwards, all solutions were centrifuged using a centrifuge (Thermo Scientific, Sorvall, ST 16) for 5 min at 1000 rpm to separate the soluble part from the insoluble one. Finally, the soluble part was dried in the oven and its solubility (%) was measured by using equation 2.1:

$$Water\ solubility\ (wt.\%) = \frac{\text{mass of dissolved lignin}}{\text{intial mass of lignin}} \times 100 \tag{2.1}$$

### 2.4.2 Charge density

The surface charge density of the soluble part of the modified lignin was measured using a particle charge detector Mutek (PCD-T3). In this set of experiments, 1 mL of 1 wt.% of modified lignin was added into PCD titrator cell using a glass pipette and deionized water. Titration was performed using a standard solution of PDADMAC (0.005M) to neutralize the negative charge of the modified lignin in the solutions. Finally, the charge density was calculated according to equation 2.2:

$$Charge\ density\ of\ soluble\ \left(\frac{meq}{g}\right) = \frac{\text{Volume of titrant(mL)}\times \text{concentration of titrant }(\frac{\text{mol}}{\text{L}})}{\text{mass of dried soluble(g)}} \times \text{ dilution factor (if any)}$$

(2.2)

### 2.4.3 Molecule weight analysis

Molecular weight analysis of the samples was carried out using a gel permeation chromatography (GPC) system, Malvern GPCmax VE2001 Module + Viscotek TDA305 with multi-detectors (UV, RI, viscometer, low angle and right angle laser detectors). For unmodifed lignin measurement, the organic columns of PolyAnalytic PAS106M, PAS103 and PAS102.5 were used, and HPLC-grade tetrahydrofuran (THF) was used as solvent and eluent. The flow rate was set at 1.0 mL/min. For modifed lignin measurement, the columns of PolyAnalytic PAA206 and PAA203 were used, and 0.1 mol/l $NaNO_3$ solution was used as solvent and eluent. The flow rate was set at 0.70 mL/min. The column temperature was set up at 35 °C for both systems. Polystyrene polymers were used as standards for the organic system and polyethylene oxide for the aqueous system.

### 2.4.4 Elemental analysis

The elemental analysis for unmodified and modified lignin samples was performed using an Elementar Vario EL Cube elemental analyzer following a combustion method (Sarwar et al., 2012). For preparing the samples, any moisture must be removed from the samples. Approximately, 2-4 mg of all samples were dried in an oven overnight at 105 °C and used in this analysis for determining carbon, hydrogen and nitrogen contents of all samples (Fadeeva et al., 2008). The oxygen content of the samples was calculated based on mass balance.

### 2.4.5 Fourier transform infrared (FTIR) analysis

FTIR analysis was conducted on unmodified and modified lignin using 0.05 g of the samples. All samples were first dried in the oven at 105 °C overnight to remove any moisture before using FTIR analysis (Bruker Tensor 37, Germany, ATR accessory). The spectra were recorded in transmittance mode in the range of 800 $cm^{-1}$ and 4000 $cm^{-1}$, and each sample was scanned 32 times with a 4 $cm^{-1}$ resolution.

### 2.4.6 Thermo-gravimetric analysis

A thermogravimetric analyzer, (TGA)-i1000 (Instrument Specialist Inc.), was used to determine the thermal behavior of lignin samples. The samples were first dried overnight in the oven at 105 °C. Then, they were inserted into the thermogravimetric analyzer at a heating rate of 10 °C/min in the range of 25 °C and 800 °C in nitrogen at the flow rate of 30 mL/min.

### 2.4.7 Differential scanning analysis

Thermal behavior of unmodified lignin, modified lignin, and commercial lignosulfonate were examined using a differential scanning calorimeter (DSC), TA instrument Q2000, using an RC standard cell. All samples were dried in the oven over night at 105 ºC to remove any moisture, then 7 – 10 mg of the dried samples were placed into a Tzero aluminum pan, and analyzed in the range of 50 – 250 ºC at 50 mL/min nitrogen and 5 ºC/min.

## 2.5 Results and discussion

### 2.5.1 Sulfonation of SKL

Figure 2.1 illustrates the sulfonation reaction of lignin with sodium sulfite. The sulfite group was reacted with the α position on softwood kraft lignin (Meister et al., 2002). However, sulfite ions could react at the ortho position next to the hydroxide group, but in a stronger condition as needed for aromatic substitution (Cerfontain et al., 1985).

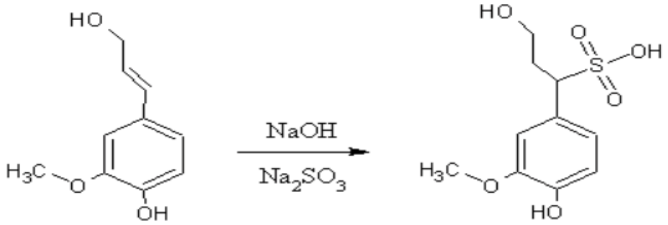


Figure 2.1: Scheme of sulfonation reaction of kraft lignin with sodium sulfite (Inwood, 2014).

Figure 2.2 shows the charge density and solubility of SSKL as a function of molar ratio of $Na_2SO_3$ to lignin. The solubility of the sulfonated lignin depended on mole ratio as the solubility was 100 % at mole ratio of 1 to 3 $Na_2SO_3$/lignin. Additionally, the charge density reached the highest value of 1.63 meq/g at a molar ratio of 3. It was claimed in a previous study that $Na_2SO_3$/lignin molar ratio was important in the modification reaction via sodium sulfate (Inwood, 2014; Yu et al., 2013).

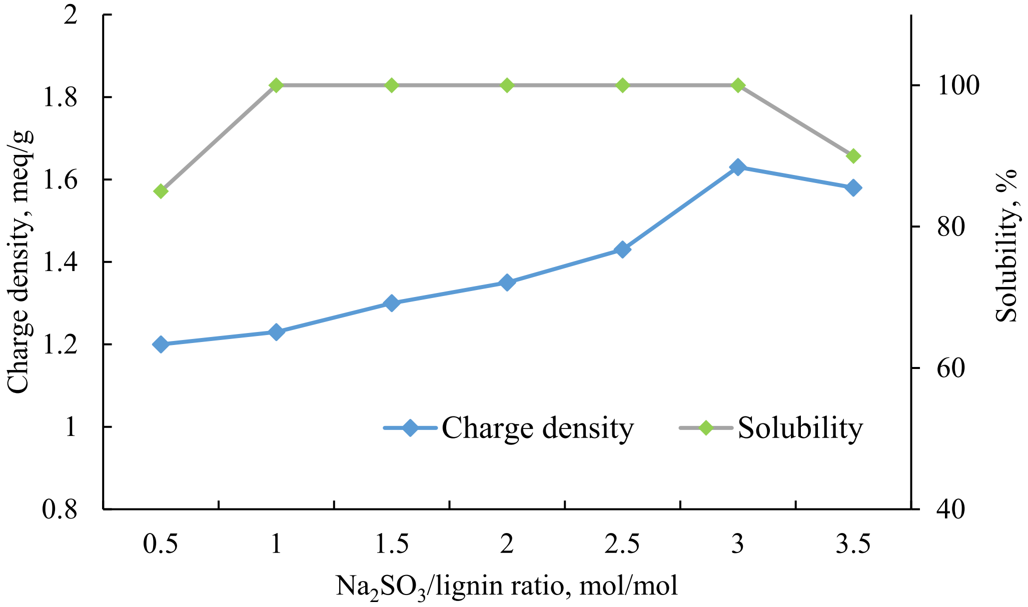


Figure 2.2: Charge density of soluble lignin and solubility of SSKL as a function of $Na_2SO_3$/lignin molar ratio. Other experimental conditions were 90 °C, 1 h and lignin concentration of 17 g/L.

Figure 2.3 shows the impact of temperature on the solubility of solutions and the charge density of the soluble part. The results illustrated that there was a correlation between the reaction temperature and both the solubility and the charge density of soluble lignin product. The lowest value of the charge density of soluble part was 1.5 meq/g obtained at 60 °C. The solubility of the sulfonated lignin progressively improved from 80 wt.% at 60 °C to the highest (100 wt.%) at 90 °C. At temperature, greater than 80 °C, the condensation of the guaiacyl subunit were reported to become more prominent (Xie & Shi, 2011; Gierer et al., 1964; Gierer & Petterson, 1977).

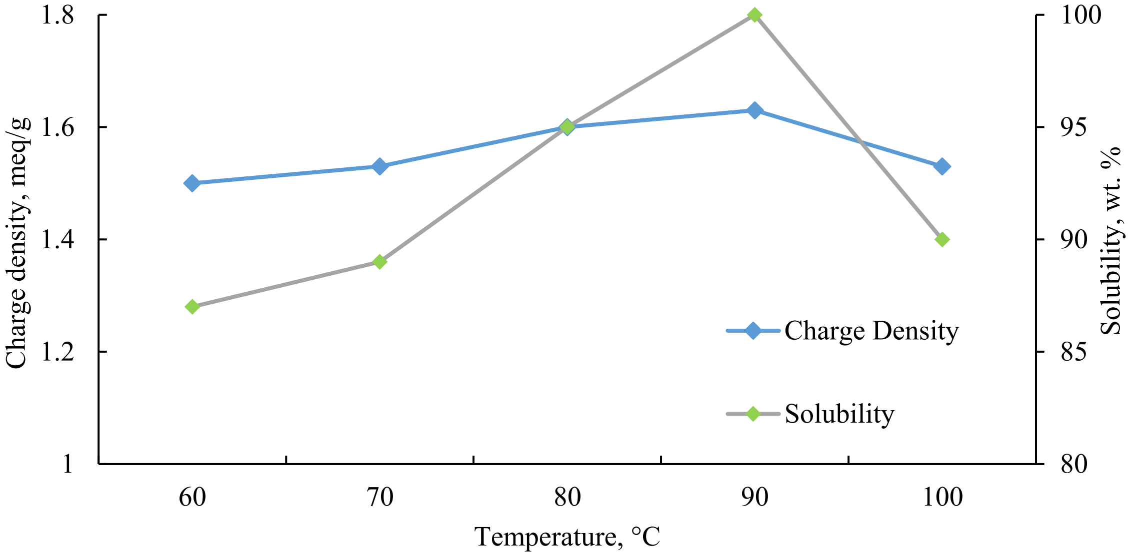


Figure 2.3: Charge density of soluble lignin and solubility of SKL as a function of temperature. Other experimental conditions were $Na_2SO_3$/lignin molar ratio of 3, 1 h and lignin concentration of 17 g/L.

### 2.5.2 Oxidation of SKL via nitric acid (OOSKL)

Figure 2.4 shows the reaction scheme between nitric acid and SKL. Oxidation of lignin with nitric acid resulted in generation of active sites within the lignin's aliphatic parts (Sjostrom, 1993). In addition, the high acidity may cause lignin segments to decompose to low molecular weight molecules (Ouyang et al., 2009; Wu et al., 2012). The oxidation generally results in forming vanillin (4- Hydroxyl-3-methoxybenzaldehyde) and small amounts of acetovanillone (4′-Hydroxy-3′-methoxyacetophenone) (Wong et al., 2010; He & Fatehi, 2015). Also, most of the methoxy and phenolic groups can be removed via oxidation with nitric acid (Meister et al., 2002; Gonzalez et al., 1992; He & Fatehi, 2015). Figure 2.4 also shows the reaction scheme of nitric acid and SKL. In case of excess nitric acid, the addition of nitro groups ($-NO_2$) and nitrate ester groups ($-ONO_2$) to lignin is expected (Wool & Sun, 2005; Meister, 2002).

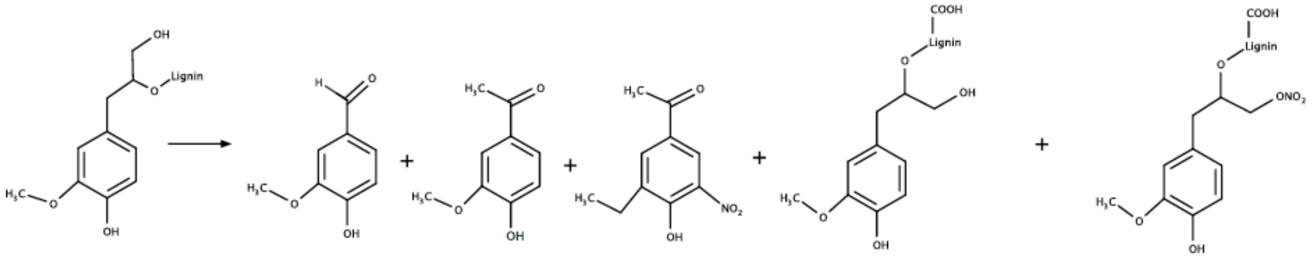


Figure 2.4: Reaction scheme of oxidation reaction of SKL via nitric acid (Couch et al., 2016)

The impact of nitric acid concentration on the charge density and solubility of oxidized lignin are shown in Figure 2.5. As seen, the charge density and solubility increased from 2.3 meq/g and 70 wt.%, respectively, at 10 wt.% nitric acid concentration, to 3.2 meq/g charge density and 100 wt.% solubility at 20 wt.% nitric acid. However, at concentration higher than 20 wt.% nitric acid, both charge density and solubility decreased, due to the dealkylation of lignin with an excess amount of nitric acid. In another work, an increase in nitric acid concentration from 20 wt.% to 30 wt.% improved the charge density and solubility of lignin, but a higher concentration of nitric acid decomposed lignin and reduced its charge density (Meister, 2002; Couch et al., 2016). The difference in the results of the present work and those reported in the literature was most probably due to varied lignin species used in these studies. The treatment with a 20 wt.% nitric acid concentration was selected for further investigation as it generated a charge density of 3.2 meq/g and solubility of 100 wt.%.

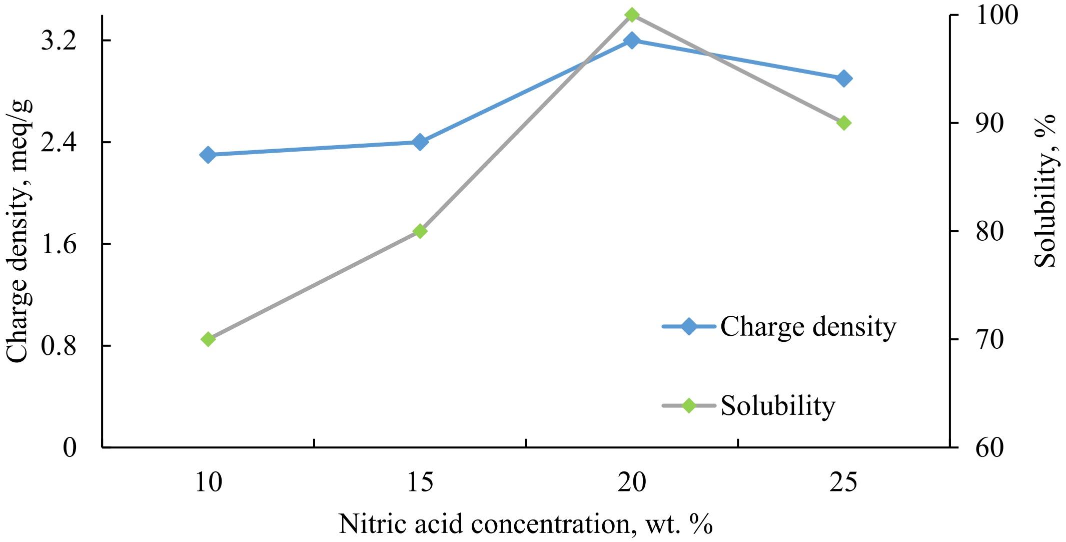


Figure 2.5: Charge density and solubility of OOSKL as a function of nitric acid concentration. Other experimental conditions were 90 °C and 1 h reaction time.

Figure 2.6 presents the influence of temperature on the charge density and solubility of lignin at a 20 wt.% nitric acid concentration. The results depicted that there was a correlation between the reaction temperature and both charge density and solubility with the lowest charge density of 2.51 meq/g at 60 °C. The solubility of the oxidized lignin gradually improved from 89 wt.% at 60 °C to the highest (100 wt.%) at 90 °C. It was reported in other studies that increasing the reaction temperature from 60 to 100 °C increased the charge density from 3.2 to 3.9 meq/g, due to the fact that oxidation of lignin is an endothermic process (He & Fatehi, 2015; Rovio et al., 2011). Also, lignin depolymerization increased by raising the temperature due to the decomposition of lignin with nitric acid under stronger conditions (Shimizu et al., 2012; He & Fatehi, 2015).

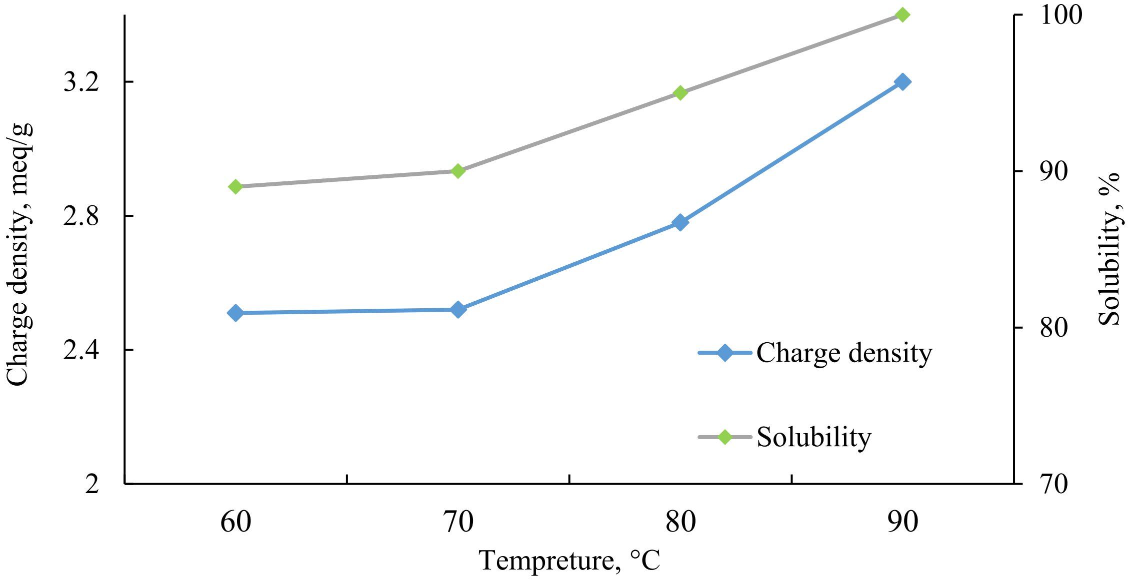


Figure 2.6: Charge density and solubility of OOSKL as a function of temperature. Other experimental conditions were 20 wt.% nitric acid concentrations and 1 h reaction time.

### 2.5.3 Oxidation of SKL via hydrogen peroxide

Figure 2.7 illustrates the reaction between lignin and hydrogen peroxide. As gauiacyl units exceed 95% of the phenyl propane units of softwood kraft lignin, most of R within the structure of lignin in Figure 2.7 will be $OCH_3$ (Wong et al., 2010; Laurichesse & Averous, 2014). Hydrogen peroxide under alkaline conditions may attack the aromatic ring and/or introduce a carboxylate group to lignin (Kubo & Kadla, 2005).

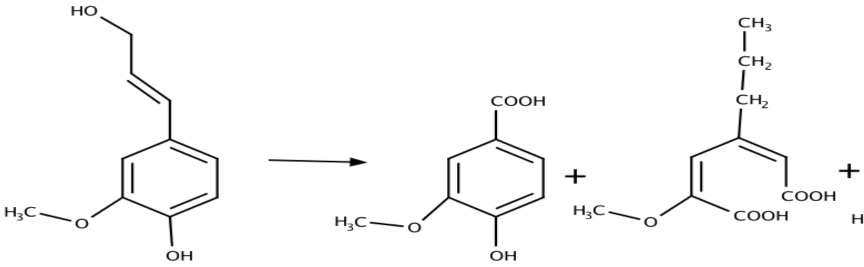


Figure 2.7: Reaction scheme of oxidation of SKL via hydrogen peroxide

Figure 2.8 shows the impact of $H_2O_2$/lignin molar ratio on the charge density and solubility of lignin. It illustrates that at 0.5 $H_2O_2$/lignin molar ratio, by increasing the temperature from 60 °C to 80 °C, the charge density and solubility increased to 1.31 meq/g and 100 %, respectively (Figure 2.9). In addition, by increasing the molar ratio of $H_2O_2$/lignin, the charge density of the products raised. It was stated in a previous study that increasing the concentration of hydrogen peroxide in the reaction would generate more perhydroxyl anions and facilitate the oxidation of lignin (Suss et al., 1997).

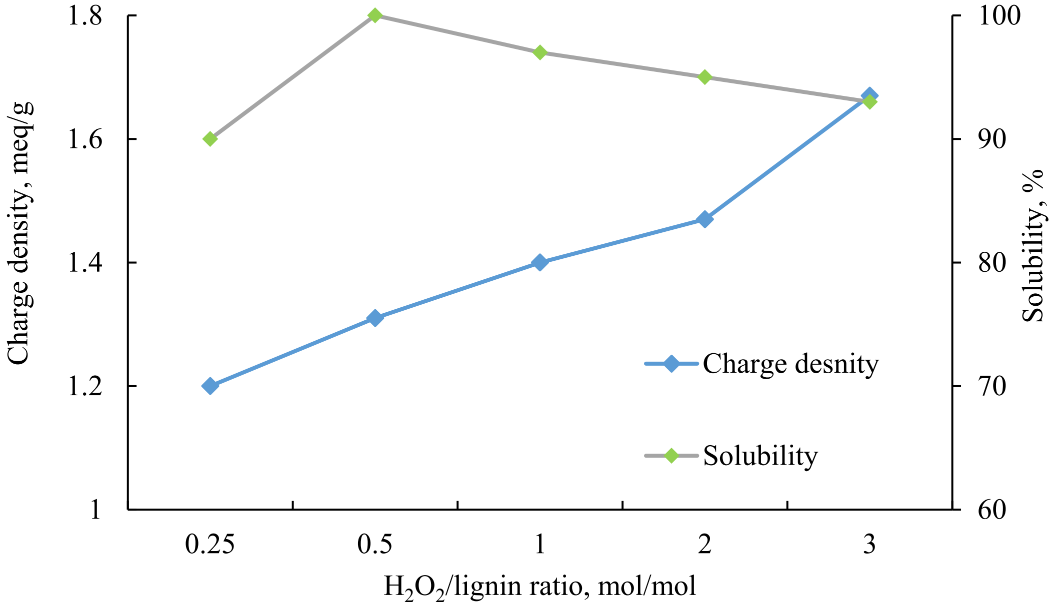


Figure 2.7: Charge density of soluble lignin and solubility of OSKL as a function of $H_2O_2$/lignin molar ratio. Other experimental conditions were 80 °C and 2 h reaction time.

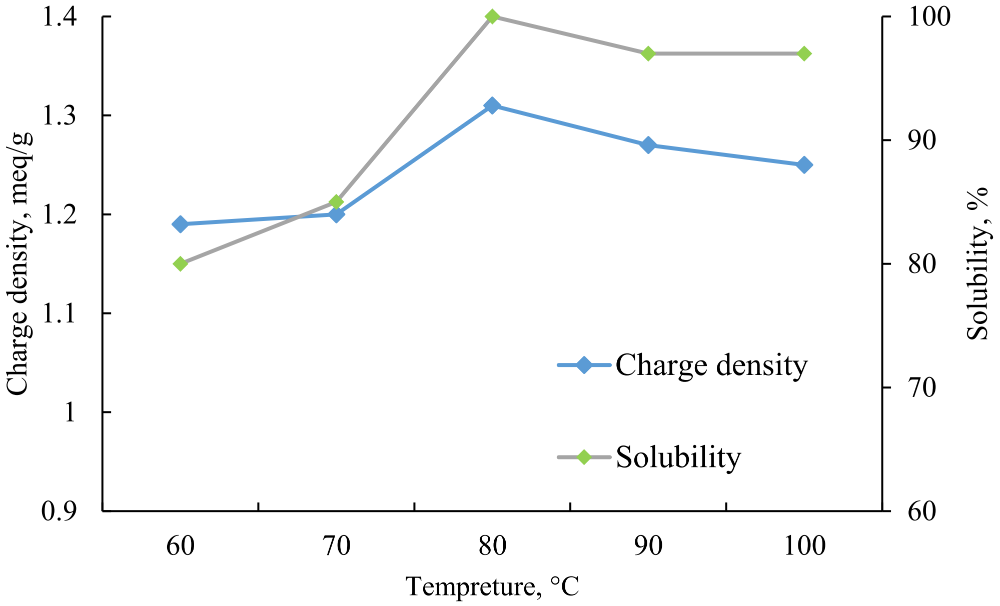


Figure 2.8: Charge density of soluble lignin and solubility of OSKL as a function of $H_2O_2$/lignin molar ratio. Other experimental conditions were 0.5 $H_2O_2$/lignin molar ratio and 2 h reaction time.

## 2.6 Characterization

### 2.6.1 Molecular weight analysis

The properties of SKL, SSKL, OSKL and OOSKL, prepared under selected conditions, are shown in Table 2.1. The weight average molecular weight ($M_w$) of softwood kraft lignin (SKL) was 17,890 g/mol, while it was 14,725 g/mol, 24,539 g/mol, 27,295 g/mol and 16,426 g/mol for OOSKL, OSKL, SSKL and CLS, respectively. As can be seen, the molecular weight of OSKL and SSKL increased while it decreased for OOSKL. The slight increase in the molecular weight could be attributed to the grafting of carboxylate or sulfonate groups on lignin, and a slight decrease in molecular weight was ascribed to the decomposition of lignin under severe reaction conditions (Wu et al., 2012; He & Fatehi, 2015). In a previous study, the $M_w$ of softwood kraft lignin, which was produced using the LignoForce technology, was reported to be 16,770 g/mol, which decreased to 13,845 g/mol after oxidation with nitric acid (He & Fatehi, 2015).

Table 2.1: Molecular weight of SKL, SSKL, OSKL, OOSKL and CLS analyzed by GPC.

| Sample | $M_w$ (g/mol) | $M_n$ (g/mol) | $M_w/M_n$ | Reference |
|---|---|---|---|---|
| SKL | 17890 | 7612 | 2.35 | PS* |
| SSKL | 27295 | 16745 | 1.63 | PS |
| OSKL | 24539 | 18732 | 1.31 | PS |
| OOSKL | 14725 | 10748 | 1.37 | PS |
| CLS | 16426 | 9332 | 1.76 | PS |
| Kraft lignin | 16770 | 5457 | 3.07 | He & Fatehi, 2015 |
| Thermomechanical pulping lignin | 6270 | NR | NR | Couch et al., 2016 |
| Oxidized kraft lignin | 13845 | 7500 | 1.85 | He & Fatehi, 2015 |

*PS: Present work.

### 2.6.2 Elemental analysis

The elemental compositions of SKL, SSKL, OSKL and OOSKL are shown in Table 2.2. Kraft lignin found to have 65.26 wt.% carbon, 5.66 wt.% hydrogen, and 1.73 wt.% sulfur. In the past, softwood kraft lignin was reported to have 65.28 wt.% carbon, 5.69 wt.% hydrogen, and 28.64 wt.% oxygen (Zhou et al., 2014), which are similar to those presented in this work. In another work, softwood kraft lignin contained 52.0 wt.% carbon, 4.9 wt.% hydrogen, 3.4 wt.% sulfur, and 38.9 wt.% oxygen (Lourencon et al., 2015; Lv et al., 2012).

Furthermore, SSKL, OSKL, and OOSKL contain 62.58 %, 62.99 %, and 45.55 % of carbon, respectively (Hu et al., 2006; Zhou et al., 2014). The hydrogen content of SSKL, OSKL and OOSKL was reported to be 5.42 %, 5.36 %, and 3.19 %, respectively (Hu et al., 2006; Zhou et al., 2014). The results showed that the carbon and hydrogen contents of lignin were decreased after modification (especially for OOSKL sample); whereas, their oxygen content increased, probably due to the addition of carboxylate and sulfonated groups in SSKL. The nitrogen content of SSKL and OSKL did not change but the nitrogen content of OOSKL increased to 4.37% as a result of nitro groups addition to lignin.

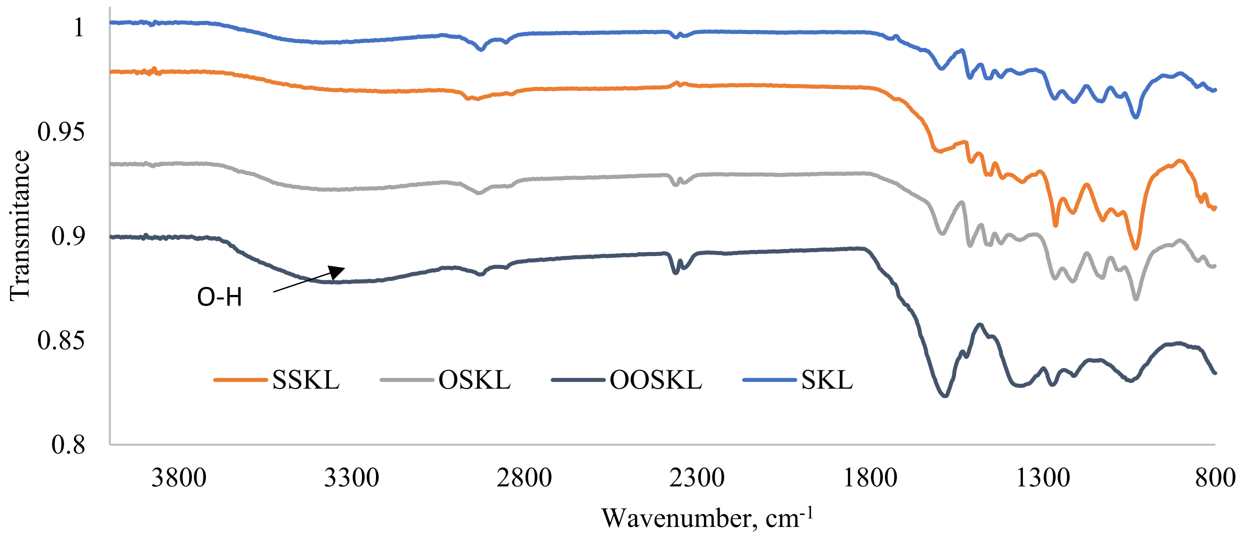
Table 2.2: Element compositions of SKL, SSKL, OSKL and OOSKL at pH 7.

| Sample | N (wt.%) | C (wt.%) | H (wt.%) | S (wt.%) | O (wt.%) | Reference |
|---|---|---|---|---|---|---|
| SKL | 0 | 65.26 | 5.66 | 1.73 | 27.35 | PS |
| SSKL | 0.07 | 62.58 | 5.42 | 2.35 | 29.58 | PS |
| OSKL | 0 | 62.99 | 5.36 | 1.31 | 30.34 | PS |
| OOSKL | 4.37 | 45.55 | 3.19 | 0.49 | 46.40 | PS |
| Softwood kraft lignin | 0.39 | 65.28 | 5.69 | - | 28.64 | Zhou et al., 2014 |
| Milled wood lignin | 0.02 | 65.00 | 5.80 | - | 29.20 | Hu et al., 2006 |
| Softwood kraft lignin | - | 52.00 | 4.90 | 3.40 | 38.90 | Lourençon et al., 2015 |

*PS: present work

### 2.6.3 Fourier transform infrared spectroscopy analysis

The FTIR spectra of unmodified lignin and modified lignin are presented in Figure 2.10. The broad peak around 3400 cm$^{-1}$ is attributed to O-H band of phenolic groups (Ibrahim et al., 2004; Inwood, 2014). The peaks around 2930 cm$^{-1}$ correspond to C-H stretching. The absorption peak at 1470-1600 cm$^{-1}$ in all samples assigned to the aromatic ring vibrations (Bykov, 2008). In all four lignin samples, C-H stretching of methyl groups are present and located at 2900 cm$^{-1}$. The relative intensity of the absorption peak around 1600 cm$^{-1}$ belongs to C=O deformation (Mohebby, 2008; Inwood, 2014; He & Fatehi, 2015), which was significantly larger in oxidized lignin via nitric acid and hydrogen peroxide than lignin, thus indicating the increment of carboxylate group (-COOH) (He & Fatehi, 2015). The addition peak at 1352 cm$^{-1}$, which did not appear in SKL, was caused by the addition of nitro group, belonging to N=O stretching presented in the oxidized lignin via nitric acid (Pavia et al., 2001; Meister, 2002; Couch et al., 2016). Furthermore, the absorption peak at 1032 cm$^{-1}$ attributed to sulfate groups, which is large in the sulfonated lignin and confirms the addition of the sulfate group to lignin (Inwood, 2014).



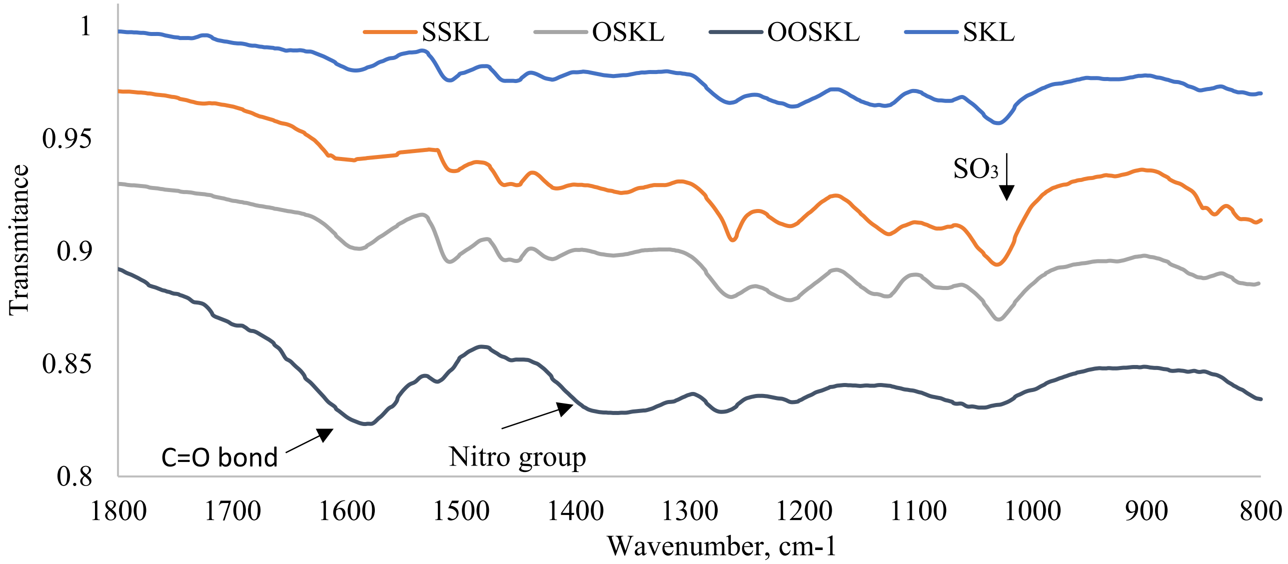
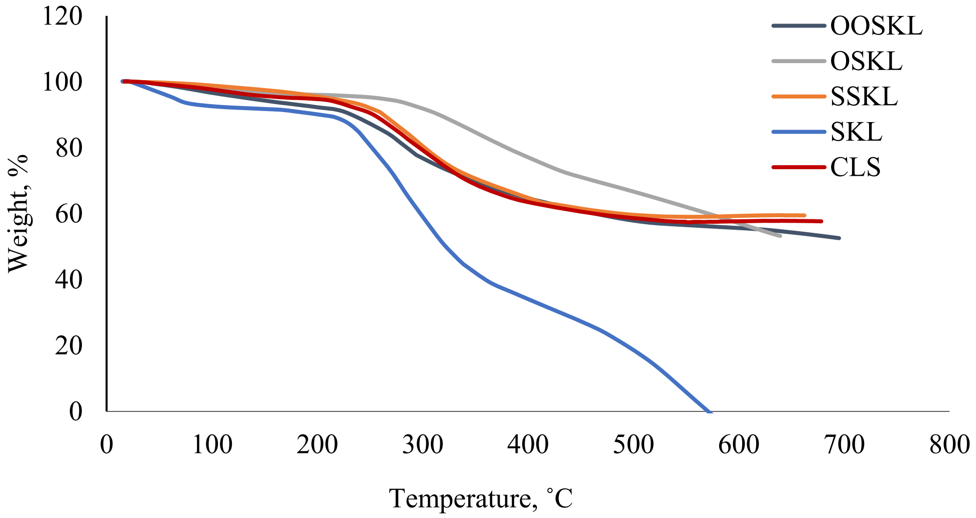


Figure 2.9: FTIR of SKL, SSKL, OSKL and OOKL top) in range of 800 and 4000 cm$^{-1}$ and bottom) in the range of 800 and 1800 cm$^{-1}$.

### 2.6.4 Thermogravimetric (TGA) Analysis

Figure 2.11 shows the weight loss of lignin samples as a function of temperature. The weight loss below 100 ºC in all samples, may due to the elimination of moisture adsorbed on samples at room temperature during the preparation of the samples. It is observed that kraft lignin decomposes completely at a temperature lower than 600 ºC, while modified lignin samples and commercial lignosulfonate exhibit thermal resistance. A 20% weight loss occurred at temperature of 270 ºC for kraft lignin, 380 ºC for oxidized lignin via hydrogen peroxide and around 300 ºC for other samples. After heating to a temperature greater than 600 ºC, the remaining char was around 55% for all modified lignin samples and commercial lignosulfonate. It was also noted that unmodified kraft lignin had a lower thermal resistance than other samples (Inwood, 2014). These results suggest that modified lignin and commercial lignosulfonate needed higher energy than unmodified kraft lignin to be degraded (Couch et al., 2016). In addition, oxidized lignin via hydrogen peroxide had a higher thermal stability than other samples at temperature between 250 and 500 ºC. The increase in thermal stability of lignin can be considered as an advantage for its end-use application as a dispersant and flocculants (Wu et al., 2012). Figure 2.11 also presents weight loss rate of kraft lignin, modified lignin and commercial lignosulfonate. A noticeable increase occurred at in the temperature range of 220 and 350 °C in all samples, with kraft lignin representing the highest. The smaller peaks at 270 to 320 °C show that the modified lignin samples exhibited a less weight loss that is similar to commercial lignosulfonate, which may be due the improved intramolecular linkages (Ma et al., 2011).



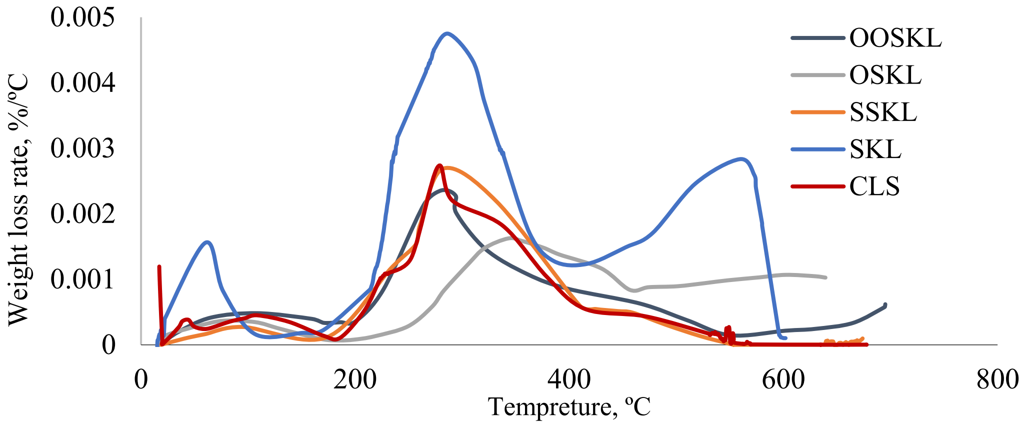


Figure 2.10: Weight loss and weight loss rate of SKL, SSKL, OKL, OOKL and CLS conducted in $N_2$ at 30 mL/min heated at 10 °C/min.

### 2.6.5 Differential scanning analysis

Polymers, such as lignin, are amorphous and solid at room temperature. They may undergo a transition from a rigid state into a flexible state (rubbery) at a specific temperature, which is called a glass transition temperature ($T_g$) (Fox & Mcdonlad, 2010). DSC is the most accepted technique for indicating the glass transition temperature of lignin or altered lignin (Gabrielii et al., 2000). Figure 2.12 shows the DSC of softwood kraft lignin, commercial lignosulfonate, and modified lignin samples as a function of temperature. The $T_g$ obtained from figure is listed in Table 2.3. The $T_g$ of softwood kraft lignin was reported to be 172.7 °C. In literature, it was reported that the glass transition of softwood kraft lignin was in the range of 140 and 180 °C (Laurichesse & Averous, 2014; Gellerstedt, 2015; Fox & Mcdonlad, 2010; Passoni et al., 2016). It can be illustrated that the glass transition temperature of SSKL and OOSKL was reduced from 172.7 °C (for unmodified lignin) to 155.5 ˚C and 126.1 °C, respectively, while that of OSKL increased to 188.6 °C. It was reported previously that $T_g$ increased by decreasing the molecular weight of the polymer (Passoni et al., 201), which can be a reason for the higher $T_g$ of this sample. On the other hand, the $T_g$ change of SSKL and OOSKL may be due to the changes in the structure, functional groups, and morphology of lignin via modification processes, but more investigation is needed to find the exact reason for this behavior (Wen et al., 2013; Yoshida et al., 1990). The $T_g$ of commercial lignosulfonate was higher than other samples (except for OSKL); therefore, a lower temperature is required to change the morphology of these modified samples than the commercial ones. All samples had a small peak below 100 ºC, which may be due to the evaporation of inherent moisture inform the samples (Kundu, 2014; Quajai et al., 2005).

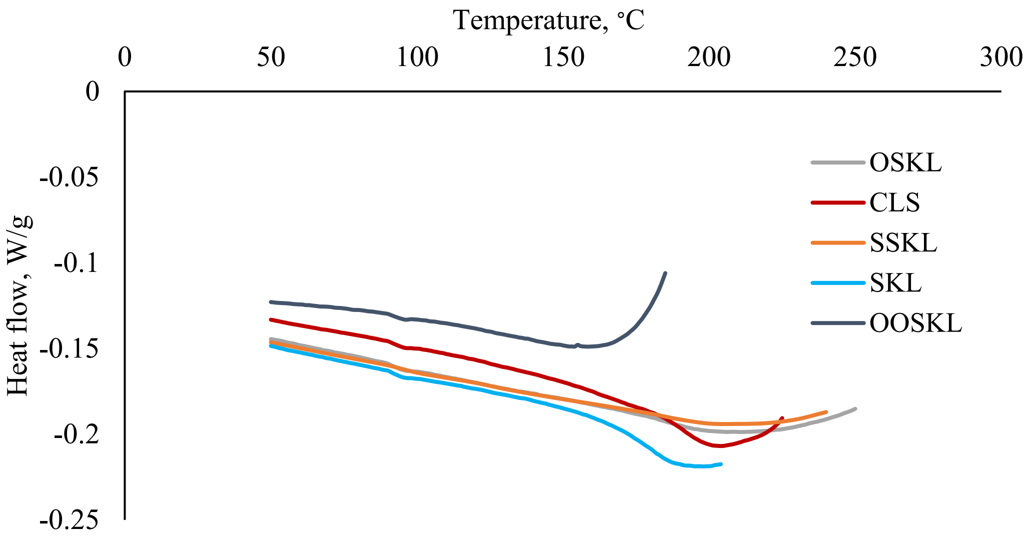


Figure 2.11: The DSC analysis of SKL, SSKL, OSKL, OOSKL, and CLS. Conditions of 50 – 250 °C at 50 mL/min nitrogen and 5 °C/min.

In addition to $T_g$, heat capacity ($C_p$) of lignin samples can be determined in DSC (Table 2.3). $C_p$ is a measure of heat required to raise the temperature of substance by 1 °C. The $C_p$ of SKL was 0.162 J/g °C. It can be illustrated that the $C_p$ of SSKL and OOSKL increased to 0.297 and 0.291 J/g °C, respectively, while it was reduced to 0.138 J/g °C for OSKL. Due to different chemical modifications, the $C_p$ of lignin may increase or decrease (Hatakeyama & Quinn, 1995). The results showed that the oxidation reaction of SKL via hydrogen peroxide increased the mobility of the OSKL via decreasing the interaction between lignin molecules. On the other hand, sulfonation and oxidation via nitric acid increased the interaction between lignin molecules, thus the mobility of SSKL and OOSKL samples decreased. However, more investigation is needed to understand the fundamentals associated with the changes in $C_p$.

Table 2.3: Glass transition temperature and heat capacity of SKL, SSKL, OSKL, OOSKL and CLS.

| Lignin | $T_g$ (°C) | Heat capacity, $\Delta C_p$ (J/g. °C) |
|---|---|---|
| SKL | 172.69 | 0.1626 |
| SSKL | 155.55 | 0.2976 |
| OSKL | 188.63 | 0.1385 |
| OOSKL | 126.10 | 0.2911 |
| CLS | 178.39 | 0.3801 |

## 2.7 Conclusions

The chemical modification of softwood kraft lignin has been successfully conducted through sulfonation and oxidation reactions. It was achieved via sodium sulfite reaction under the conditions of 1 h, 90 °C and 3/1 $Na_2SO_3$/lignin molar ratio. Under these conditions, the resulted sulfonated lignin had a charge density of 1.63 meq/g and 100 % water solubility. The oxidation of softwood kraft lignin via nitric acid was obtained under the conditions of 20% nitric acid concentration, 1 h, 90 °C, while the oxidation reaction via hydrogen peroxide was performed under the conditions of 2 h, 80 °C and 0.5 $H_2O_2$/lignin molar ratio. Accordingly, the charge density was determined to be 3.2 and 1.31 meq/g for oxidized lignin with nitric acid and hydrogen peroxide, respectively, and both samples were water soluble. GPC analysis indicated that the molecular weights of SSKL, OSK and OOSKL were 27295, 24539 and 14725 g/mol, respectively, while it was 25100 g/mol for softwood kraft lignin. FTIR results confirmed the addition of nitro, sulfonate and carboxylate groups at peaks of 1350 $cm^{-1}$, 1030 $cm^{-1}$ and 1226 $cm^{-1}$ for OOSKL, SSKL and OSKL, respectively. The TGA analysis determined that kraft lignin exhibited a large decomposition peak at 520 °C, and was completely consumed at 570 °C, while modified lignin samples as well as commercial lignosulfonate had a peak around 500 °C, and had resistance to thermal degradation. In addition, DSC analysis indicated the change in $T_g$ and $C_p$ of lignin samples due to the chemical modifications. It was found that OSKL had the highest $T_g$ and the lowest $C_p$ among all samples.

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# 3 Chapter 3. Applications of modified lignin

## 3.1 Abstract

In this chapter, the performance of sulfonated kraft lignin (SSKL), oxidized kraft lignin via hydrogen peroxide treatment (OSKL) and oxidized kraft lignin via nitric acid treatment (OOSKL) was analyzed for different applications. Specifically, the dispersion performance of these polymers in kaolin and bentonite suspensions and the flocculation performance of these polymers in alumina suspension were studied. The adsorption of SSKL, OSKL, OOSKL, and commercial lignosulfonate (CLS) on kaolin, bentonite and alumina particles showed that OOSKL had a higher adsorption on particles. The relative turbidity of kaolin and bentonite suspensions was increased with the addition of polymers, and OOSKL depicted a higher impact. On the other hand, OOSKL was a weaker polymer compared with others to affect the relative turbidity of alumina suspensions. Furthermore, the addition of polymers to alumina suspensions reversed the zeta potential of the suspension, from positive to a negative value. The removal of ethyl violet and blue basic dyes was successfully achieved with the addition of all polymers and OOSKL showed the best results of removing ethyl violet and blue basic 41 dyes.

## 3.2 Introduction

The need for readily available, cheap, nontoxic and renewable value- added biobased chemicals is high in industry (Qin et al., 2015; Inwood, 2014). Although lignin can be modified to produce value-added chemicals, only 2% of it is used for different applications (Inwood, 2014; Kubo & Kalda, 2005).

Current chemical dispersants are toxic and pose threat to the environment. However, lignin based dispersants can be produced as an alternative resource to serve the environment (Swannell & Daniel, 1999). In the past, different types of lignin were modified and utilized as dispersants in various applications. In one study, lignin was modified through oxidation, hydroxymethylation and then sulfonation and the product was an effective dispersant for cement admixtures (Ouyang et al., 2009). It was found that the adsorption of sulfonated lignin (9.2 mg/g) was higher than that of commercial lignosulfonates (5.9 mg/g) on cement particles, which facilitated its dispersion performance (Ouyang et al., 2009). A similar result was obtained for lignosulfonate after oxidation and hydroxymethylation or sulfomethylation (Pang et al., 2008). In another study, wheat straw ethanol lignin was modified via hydroxymethylation and sulfonation to produce a dispersant for cement particles; in which the addition of sulfonated lignin in cement admixture reduced the water requirement of cement admixtures by 14.9 % (Li et al., 2011). On the other hand, the addition of sulfonated lignin to cement admixtures improved the workability and the fluidity of cement admixtures (Hsu et al., 2000). In another work, sugar cane bagasse lignin was modified through oxidation, hydroxymethylation and sulfonation, and then utilized as a dispersant for pesticide formulation (Li & Ge, 2011). In another study, sodium lignosulfonate was evaluated as a dispersant in cola water slurry lignin (Yang et al., 2007). These literature results show that the adsorption of lignin may vary after modification and thus affect its behavior as a dispersant or flocculant.

Flocculants have been used widely in the pulp and paper, oil and mining to remove undesirable compounds from different solutions or in the wastewater treatments processes. Flocculants are used to precipitate colloidal suspensions. Currently, chemical flocculants, such as alum, ferric and synthetic organic flocculants are used in industry (Li et al., 2008), which are expensive or may affect the environment and human as they are considered to be toxic (Banks et al., 2006; Gonzalez-Domidguez et al., 2014; Shih et al., 2001). On the other hand, lignin has the potential to be used as environmentally friendly flocculants (You et al., 2009). Lignin has been studied extensively to be used as flocculants (Zhang et al., 2013; Fang et al., 2010; Wang et al., 2014). Previously, lignosulfonate was used as a flocculent to remove talc and other insoluble phyllosilicate from molybdenum concentrates (Hiscox et al., 1975). In another work, lignin was modified to create a cationic flocculant (Zhang et al., 2014).

Furthermore, dyes are chemical pollutants present in the wastewater from the textile, tannery, pulp and paper and paint industries on a large scale (Gupta & Suhas, 2009; Couch et al., 2016). Many studies focused on the removal of various dyes from the effluents using different methods (Annadurai et al., 2002; Tang & Chen, 2002; Tahir & Rauf, 2006). Membrane was used as an alternative for dye removal, but blockage and high maintenance operation of these methods are barriers for their use in industry (Couch et al., 2016; Meriç et al., 2004). On the other hand, modified lignin may be used as a coagulant to remove dyes from effluents (Suteu et al., 2010). The removal of dyes from simulated wastewater was assessed using oxidized lignin in the past (Couch et al., 2016) and charge neutralization was proposed as the main mechanism for dye removal (Fang et al., 2010; Wang et al., 2014). It was reported that oxidized lignin was able to remove 77 % of ethyl violet dye and 88 % of basic blue 41 dye from a solution at 100 mg/L concentration (Couch et al., 2016). In another study, lignin was modified to produce a cationic modified lignin to be used as a flocculant in anionic dye solution (Zhang et al., 2013). In 2014, Wang and his colleagues produced an animated lignin and used as a flocculant, where 96% of the anionic dye was removed after 48 h treatment (Wang et al., 2014).

In this chapter, the performance of modified lignin as well as the commercial lignosulfonic acid salt as dispersants/flocculants for different applications are studied and compared. The novelty of this chapter is the investigation on the performance of these lignin samples as dispersants or flocculants in different suspensions (including alumina, bentonite and kaolin).

## 3.3 Experimental

### 3.3.1 Raw materials

In this study, acid washed and dried softwood kraft lignin (SKL) was supplied by FPInnovations' pilot plant facilities in Thunder Bay mill, ON, and used as received. Basic blue 44 dye, ethyl violate, aluminum oxide particles, kaolin, and bentonite particles were all purchased from Sigma-Aldrich and used as received. Sodium hydroxide and hydrochloric acid were purchased from Sigma-Aldrich and prepared at the concentration of 0.1 M. Commercial lignosulfonic acid sodium salt (CLS) with a sulfonate degree of 1.39 meq/g and a molecular weight of 16,426 g/mol was purchased from Sigma-Aldrich and used as received. SSKL was prepared as described in Chapter 3 under the conditions of 3/1 $Na_2SO_3$/lignin molar ratio, lignin concentration of 16 g/L for 1 h and a reaction temperature of 90 °C, which had the charge density and solubility of 1.63 meq/g and 100 wt.%, respectively, and a molecular weight of 27,295 g/mol. OSKL was prepared as explained in chapter 3 under the conditions of 0.5 mol/mol $H_2O_2$/lignin at temperature of 80 °C and reaction time of 2 h, which had the charge density and solubility of 1.31 meq/g and 100 wt.%, respectively, with a molecular weight of 24,539 g/mol. OOSKL was prepared based on the procedure established in chapter 3 under the conditions of 20% nitric acid concentration, 90 °C and 1 h reaction time, which had the charge density and solubility of 3.2 meq/g and 100 wt.%, respectively, and a molecular weight of 14,725 g/mol.

### 3.3.2 Properties of kaolin, bentonite, and alumina particles

The surface area of kaolin, bentonite, and alumina particles was determined by using a Quantachrome surface area analyzer, Nova2200e. In this set of experiments, the samples were initially dried in an oven at 105 °C overnight and approximately 0.05 g of sample was pretreated for 4 h at 250 °C prior to analysis. The specific surface area of the samples was then analyzed according to Branuer-Emmett-Teller (BET) method via adsorption-desorption isotherms using nitrogen gas at 180 °C in the relative pressure range of 0.01 to 0.99 (Wang et al., 2016). The hydrodynamic diameter of aluminum oxide particles in the suspensions was determined by a particle size analyzer (Mastersizer 2000, Malvern). About 10 mL of 5 g/L aluminum oxide suspension was added to 600 mL of deionized water by stirring at 250 rpm to make a 0.08 g/L concentration, then the measurement was conducted at the wavelength of 633 nm with red laser light. Afterward, the hydrodynamic diameter ($d_h$) of the particles was determined. The mean value of $d_h$ was determined as the average value of the volumetric distribution of three parallel measurements.

### 3.3.3 Adsorption analysis

In this set of experiments, the adsorption of SSKL, OSKL, OOSKL, and CLS on kaolin, bentonite and alumina particles at pH 7 was investigated. Different dosages of SSKL, OSKL, OOSKL and CLS (0 – 25 mg/L) were added to kaolin and bentonite having a 20 g/L concentration and the mixtures were stirred at 200 rpm for 30 min at room temperature. All samples were prepared in 125 mL Erlenmeyer glass flasks. Subsequently, the samples were transferred into centrifuge tubes and centrifuged at 1500 rpm for 10 min using Thermo Scientific Sorvall ST 16 centrifuge and then the samples were filtered using Whatman filters#1. The concentration of the polymers remaining in the filtrate samples was measured using a UV-Vis spectrophotometer (Genesys 10S, Thermo Scientific) at room temperature and 280 mm. The adsorption amount was calculated by the difference in the concentrations of solutions before and after filtration following equation 3.1:

$$\text{Adsorbed amount}\left(\frac{\text{mg}}{\text{g}}\right) = \frac{v(C_0-\text{C})}{m} \tag{3.1}$$

where $C_o$ and C are the concentrations of the lignin samples (mg/L) in the suspensions before and after filtering, v is the initial volume of the polymer (mL) and m is the weight of clay (g).

The adsorption performance of different lignin samples on alumina particles was also measured. In this case, different dosages of SSKL, OSKL, OOSKL and CLS (0 – 25 mg/L and 2- 100 mg/L) were added to alumina suspension having a 1 g/L concentration and the mixtures were stirred at 200 rpm for 30 min at room temperature. All samples were prepared in 125 mL Erlenmeyer glass flasks. Subsequently, the samples were transferred into centrifuge tubes and centrifuged at 1500 rpm for 10 min using Thermo Scientific Sorvall ST 16 centrifuge and then filtered using Whatman filters#1. The concentration of the polymers remaining in the filtrate were assessed as above and the adsorption amount calculated following equation 3.1.

### 3.3.4 Zeta potential analysis

The zeta potential of the suspensions was analyzed using a NanoBrook Zeta PALS (Brookhaven Instruments Corp, USA). In this study, different concentrations of SSKL, OSKL, OOSKL, and CLS (2 mg/L to 20 mg/L) were added into 50 mL of kaolin and/or bentonite suspension (20 g/L) at pH 7, followed by stirring the suspensions for 30 min. Subsequently, 1 mL of the sample was collected and mixed with 20 mL of KCl solution (1mM) prior to zeta potential analysis. In another set of experiments, SSKL, OSKL, OOSKL, and CLS, with different concentrations varying from 2 mg/L to 20 mg/L, were added into 50 mL of alumina suspension (1 g/L) at pH 7. After stirring for 30 min, 1 mL of the sample was collected and mixed with 20 mL of KCl solution (1mM) prior to zeta potential analysis.

### 3.3.5 Turbidity analysis

Turbidity analysis was carried out using a photometer dispersion analyzer (PDA 3000, Rank Brother Ltd.), which was connected to a dynamic drainage jar (DDJ) with a 70-mesh screen (Ramphal & Sibiya, 2014). Turbidity analysis was conducted on all of alumina, kaolin, and bentonite suspensions at neutral pH.

In case of kaolin and bentonite experiments, 450 mL of deionized water was transferred into a DDJ container and recycled through a 3-mm plastic tube from DDJ to PDA and the DC value was measured and used as a background ($V_0$). Peristaltic pump was used to maintain the flow rate at 20 mL/min. Afterward, 50 mL of clay suspension (kaolin or bentonite at 200 g/L) was added into the DDJ, resulting in a clay concentration of 20 g/L, which was stirred at 300 rpm. The addition of clay (kaolin or bentonite) caused a decrease in the initial base DC voltage ($V_0$) of the PDA to a new voltage ($V_i$). After 300 seconds, different amounts of lignin-based polymers were added to the suspension in the DDJ to simulate 1 mg/g to 20 mg/g adsorption, causing a change in the recorded voltage ($V_i$ to $V_f$). The dispersion performance of lignin-based polymer suspensions was calculated according to equation 3.2 (Wang et al., 2009; Li & Ge, 2011; Konduri & Fatehi, 2017):

$$\text{Relative turbidity, } \tau_r = \frac{\tau_f}{\tau_i} = \frac{ln(\frac{V0}{Vf})}{ln(\frac{V0}{Vi})} \tag{3.2}$$

where $\tau_f$ and $\tau_i$ are the final and initial suspension turbidities, respectively, $V_i$ denotes unflocculated suspension DC voltage, and $V_f$ stands for final suspension DC voltage, while $V_0$ is the initial base DC voltage.

The flocculation performance of lignin-based polymers in the alumina suspension was also assessed using the same procedure under different conditions. In this set of experiments, 490 mL of deionized water was added into the DDJ and circulated from the DDJ to the PDA through a 3 mm plastic tube with a flow rate of 20 mL/min, and the initial DC was recorded. Then, 10 mL of a 200 g/L of alumina suspension was added into the DDJ to make a 1 g/L of alumina concentration at 300 rpm, and DC ($V_i$) was recoded. After 300 seconds of stirring, the polymers of varying concentrations were added to the alumina suspension to make 1 mg/g to 20 mg/g adsorption in the DDJ causing in a decrease in the recorded voltage ($V_i$ to $V_f$). The relative turbidity of alumina flocculation was measured using equation 3.2.

### 3.3.6 Stability analysis

A vertical scan analyzer, Turbiscan Lab Expert, was used in this study to investigate the stability analysis of the colloidal suspension (kaolin, bentonite and alumina) without polymer and with SSKL, OSKL, OOSKL and CLS. In this set of experiments, colloidal suspensions, in the presence and absence of lignin samples were prepared to investigate the changes in the suspensions stability under condition of 30 min, single scan of every 2 seconds and pH of 7 at 30 °C. With the help of Turbisoft 2.1 software, the transmittance and backscattering zones of the suspension was recorded as a percentage of transmittance signals in regard to silicon oil which was used as a standard (Mengual et al., 1999; He et al., 2016). Destabilization index of suspensions was calculated using the Turbisoft software using equation 3.3 (He et al., 2015):

$$\mathrm{DSI} = \sum_i \frac{\sum_h |\mathrm{scan}_i(h) - \mathrm{scan}_{i-1}(h)|}{H} \tag{3.3}$$

Where $scan_i$ (h) and $scan_{i-1}$ (h) are the transmission signals for two consecutive time intervals at a given height and H is the total height of sample.

### 3.3.7 Dye removal analysis

In this set of experiments, ethyl violet and blue basic 41 dye solutions were prepared at the concentration of 250 mg/L and their pH was adjusted to neutral (using HCl or NaOH). SSKL, OSKL and CLS were prepared at 2 g/L as standard solutions. Firstly, a specific amount of dye solutions was transferred into a 125-mL flask and diluted with desired amount of deionized water to make different concentrations. Different dosages of lignin samples were added to the flasks and the samples were shaken at 100 rpm in a water bath shaker (New Brunswick Scientific, USA) at 30 °C for 10 min. Afterwards, all samples were transferred from the flasks into 50 mL centrifuge tubes and centrifuged (Thermo Scientific Sorvall ST 16 Centrifuge) at 1000 rpm for 5 min. Supernatants were collected from top of each tube to measure the dye concentration. The concentration of dyes was determined using a UV/vis spectrophotometer (Genesys 10s UV-Vis spectrophotometer, Madison, WI) at 595 nm wavelength for ethyle violte and at 617 nm wavelength for blue basic 41 and the removal of dyes was calculated following equation 3.4:

$$\text{Dye removal (\%)} = \frac{C_o - \text{C}}{C_o} \times 100 \tag{3.4}$$

where $C_o$ and C were the dye concentrations (mg/g) in the supernatants with and without the addition of lignin-based polymers, respectively. All measurements were carried out in triplicate and the mean values were reported.

## 3.4 Results and discussion

### 3.4.1 Properties of kaolin, bentonite and alumina particles

Table 3.1 lists the surface area, pore size and surface charge density of the particles. It is observable that the surface charge density of bentonite was more negative than kaolin, which may be related to the montmorillonite layer structure of bentonite due to a greater percentage of oxide anions on the bentonite surface (Loginov et al., 2008). Alumina particles had slightly cationic charge density. In addition, bentonite particles were larger than kaolin, but had a smaller surface area and pore volumes than kaolin particles. The surface area of alumina was 100.3 $m^2$/g.

Table 3.1: Properties of kaolin, bentonite and alumina suspensions

| Sample | Surface charge, μeq/g | Particle size, μm | Surface area, $m^2/g$ |
|---|---|---|---|
| Kaolin | -5.5 | 4.7 | 55.64 |
| Bentonite | -9.4 | 6.1 | 20.12 |
| Alumina | 0.0031 | 2.7 | 100.3 |

### 3.4.2 Adsorption performance

The adsorption performance of modified lignin and lignosulfonate on kaolin, bentonite and alumina particles are shown in Figures 3.1 and 3.2. It is observable that the adsorption of modified lignin on bentonite was much more than on kaolin particles, which is attributed to the more negative charge of bentonite than kaolin (Alvarez et al., 2003; Chai et al., 2016). Also, OOSKL had the highest adsorption, and lignosulfonate (CLS) the lowest, regardless of particle type. OOSKL had the highest charge density, but smallest molecular weight among all samples (Table 3.1). Also, CLS had the lowest charge density among all samples. In the past, it was stated that the adsorption of polymers would be increased by increasing their charge density (He & Fatehi, 2015; Ouyang et al., 2009; Paria & Khilar, 2004). Also, by increasing the molecular weight of polymers, the area that they occupy on the surface of particles is increased, thus less of larger polymers can adsorb on the particles (Matsushita & Yasuda, 2005; Inwood, 2014; Sakkayawong et al., 2005). It is noted that charge density plays a more important role than molecular weight as OSKL and SSKL have higher charge densities than CLS, but their adsorption was higher.

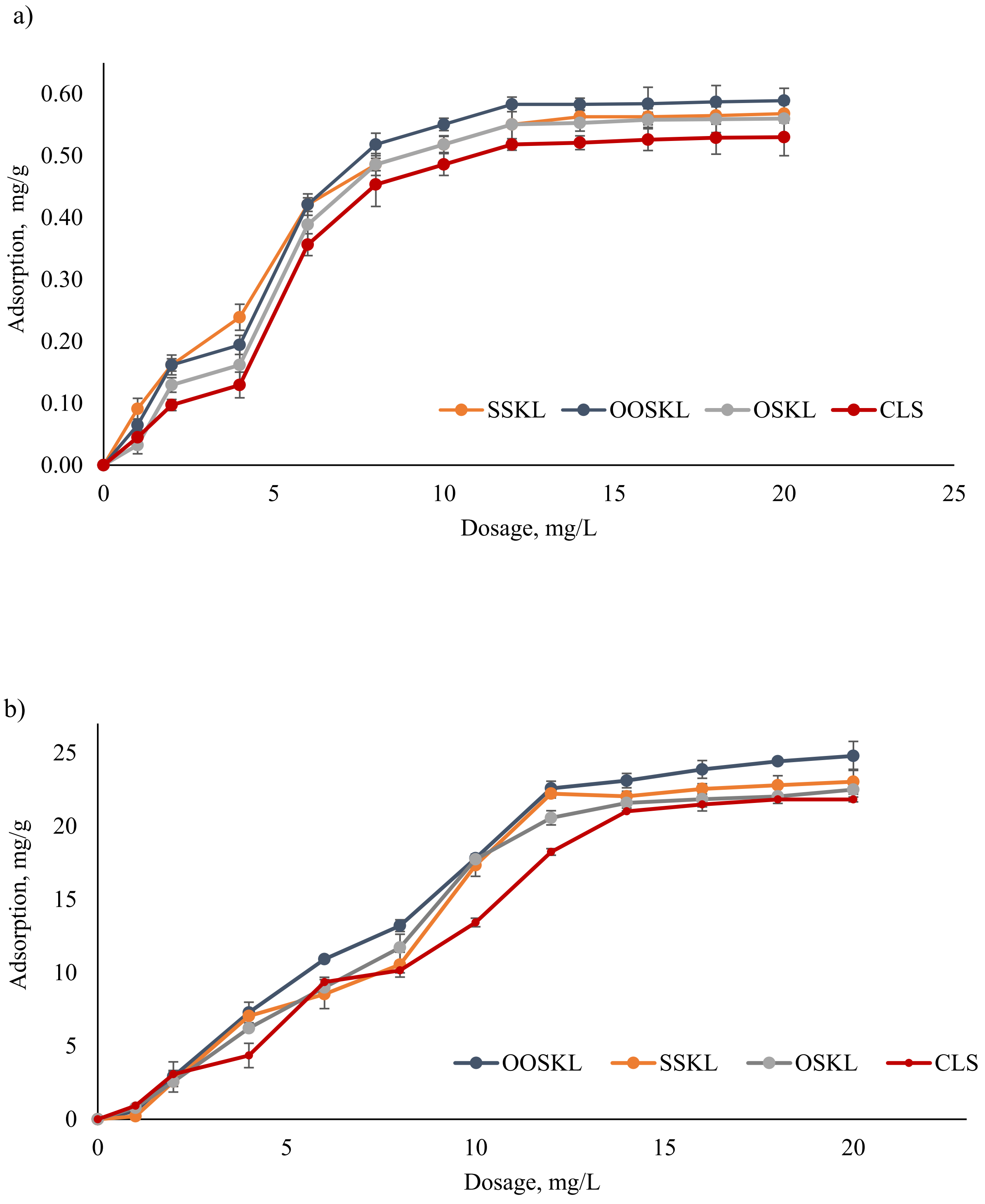


Figure 3.1: Adsorption isotherms of SSKL, OSKL, OOSKL and CLS on a) kaolin and b) bentonite particles. Other experimental conditions were pH 7 at 30 °C.

Figure 3.2 shows the adsorption of lignin samples on alumina particles. As can be seen, the adsorption of lignin samples increased by increasing their concentration in the suspensions, and no saturation was reached for any of the samples within the scope of adsorption studies. Interestingly, OOSKL and SSKL had higher, and CLS had lower adsorption than other samples. These results again confirmed that charge density played more important role than molecular weight on the adsorption of lignin samples on particles. One reason for this behavior may be the limited variations in molecular weight of lignin samples but more significant alterations in their charge density (Table 2.1).

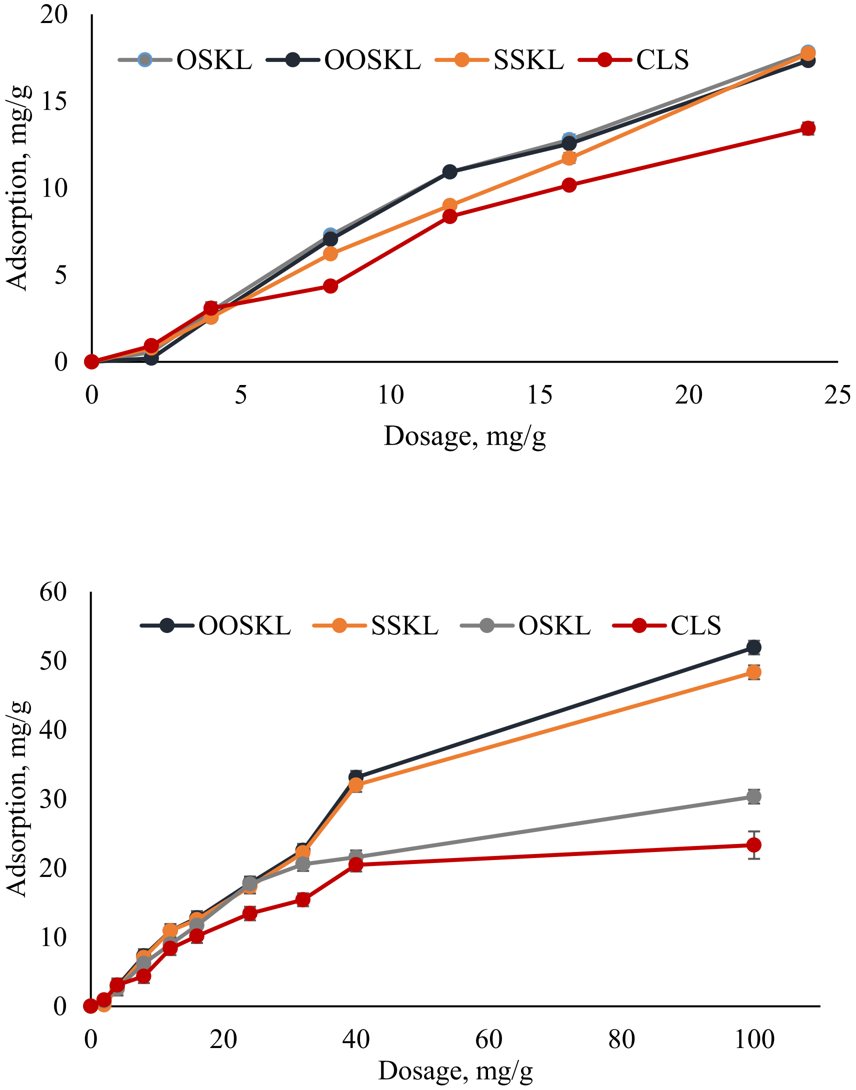


Figure 3.2: Adsorption isotherms of SSKL, OSKL, OOSKL and CLS on alumina particles a) at lower lignin concentration and b) at higher lignin concentration. Other experimental conditions were pH 7 at 30 °C.

### 3.4.3 Zeta Potential

Figure 3.3 shows the zeta potential of the suspensions as a function of lignin dosage, while Figure 3.4 shows the zeta potential of the suspension as a function of adsorbed polymers. Generally, kaolin and bentonite suspensions had a negative zeta potential of approximately -34 mV, but the alumina suspension had a positive zeta potential of 30 mV. The negative zeta potential of kaolin and bentonite suspensions was due to their negatively charged surface, whereas the positive zeta potential of alumina suspension was due to its positively charged surface (Table 3.1). Generally, by adding more lignin samples, the zeta potential of the suspensions dropped to more negative values. The drop was more significant for OOSKL than other samples. The impact of lignin type on zeta potential was more observable on alumina suspension as 7.5 mg/L of CLS, but 3 mg/L of other lignin samples were needed to neutralize the suspensions (Figures 3.3 and 3.4). The zeta potential was affected by the charge density of lignin molecules and the amount of adsorbed lignin on particles (Perez et al., 2016; Konduri & Fatehi, 2017). As OOSKL had higher adsorption and negative charge density (Figure 3.1), it affected the zeta potential of the suspensions more significantly. In one study, the addition of carboxymethylated lignin reduced the zeta potential of ceramic suspension from -30 mV to -50 mV as its concentration was increased from 0.1 to 0.2 wt.% (Cerrutti et al., 2012). In another study, an increase in the concentration of sulfonated lignin from 1 to 5 g/L led to a decrease in zeta potential of cement particles from 10 to -30 mV at neutral pH (Ouyang et al., 2010).

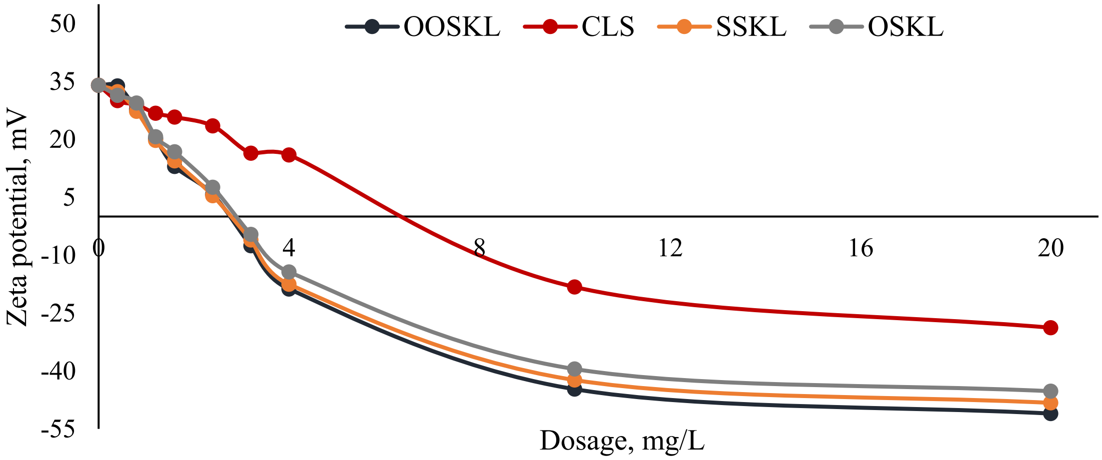
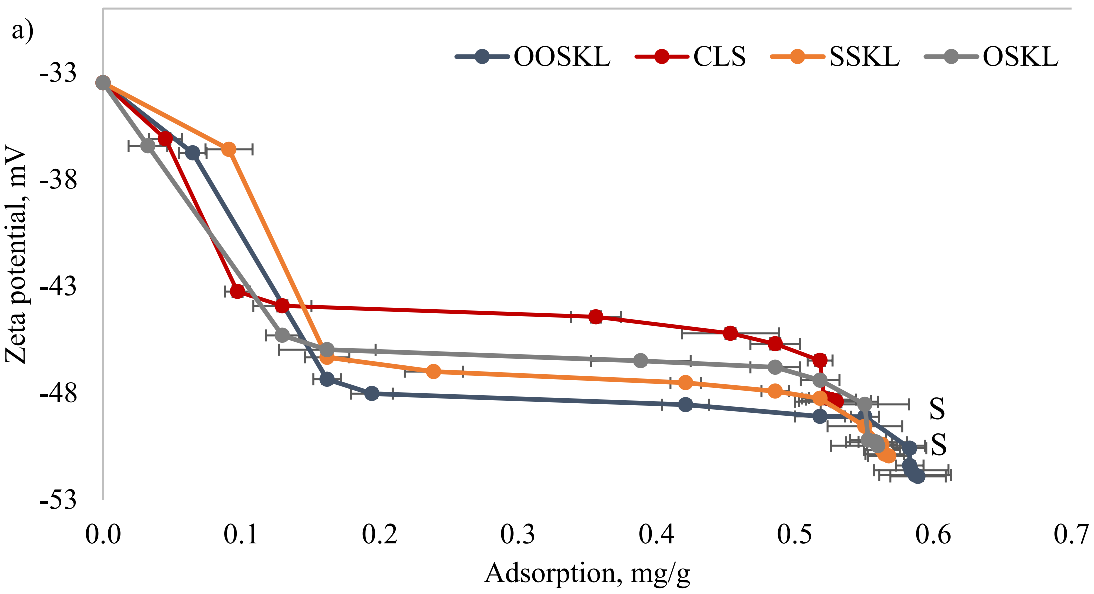
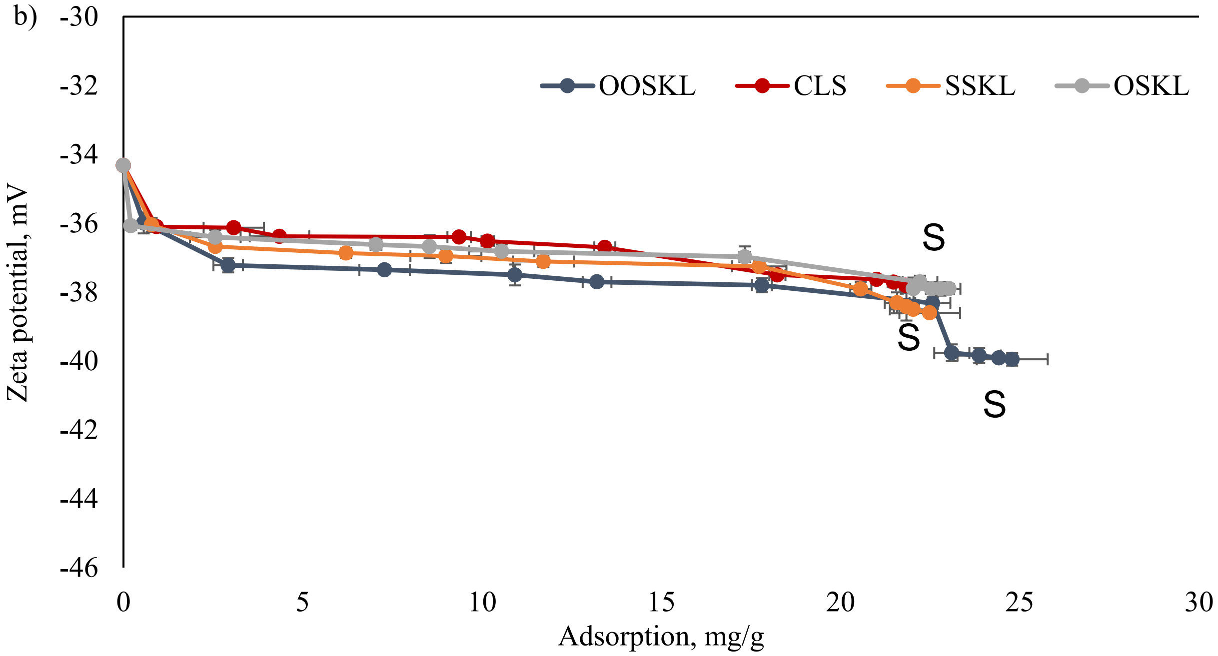


Figure 3.3: Zeta potential of alumina suspension as a function of lignin dosage. Other experimental conditions were pH 7 and room temperature.


a)
OOSKL
CLS
SSKL
OSKL
Zeta potential, mV
-33
-38
-43
-48
-53
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Adsorption, mg/g
S
S


b)
OOSKL
CLS
SSKL
OSKL
Zeta potential, mV
-30
-32
-34
-36
-38
-40
-42
-44
-46
0
5
10
15
20
25
30
Adsorption, mg/g
S
S
S

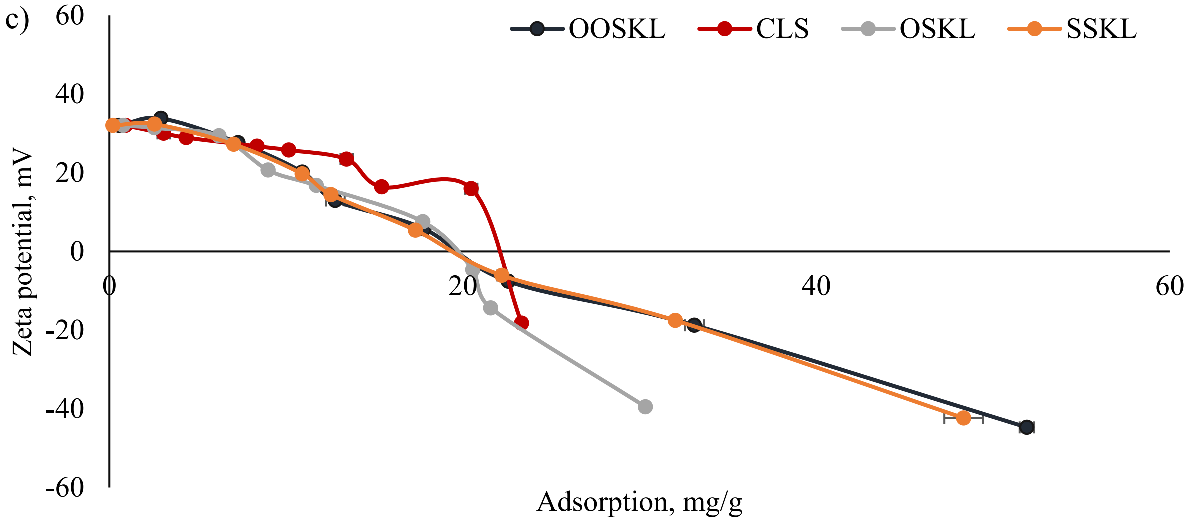


Figure 3.4: Zeta potential of a) kaolin, b) bentonite and c) alumina suspensions as a function of adsorbed lignin samples. Other experimental conditions were pH 7 and room temperature.

### 3.4.4 Dispersion analysis

The influence of polymers dosage on the relative turbidity of kaolin and bentonite suspensions are shown in Figure 3.5. Generally, by increasing the adsorption of lignin samples, the relative turbidity of the suspensions increased, which was more observable for kaolin suspension. These trends show that the lignin samples acted as dispersants for the suspensions, and the reason for this behavior could be attributed to the rise in the overall negativity of the suspension (Figure 3.4), which accordingly elevated the repulsion between the particles in the suspensions (Shine et al., 2006). Furthermore, increasing the adsorption of lignin samples on kaolin particles improved the relative turbidity from 1.0 to 1.3, 1.19, 1.15 and 1.09 for OOSKL, SSKL, OSKL and CLS, respectively. Similarly, the relative turbidity of bentonite suspension increased from 1 to 1.1, 1.05, 1.04 and 1.03 for OOSKL, SKL, OSKL and CLS, respectively. The reason for better performance of lignin samples in kaolin suspensions is ascribed to its larger surface area and higher adsorption (Figure 3.1).

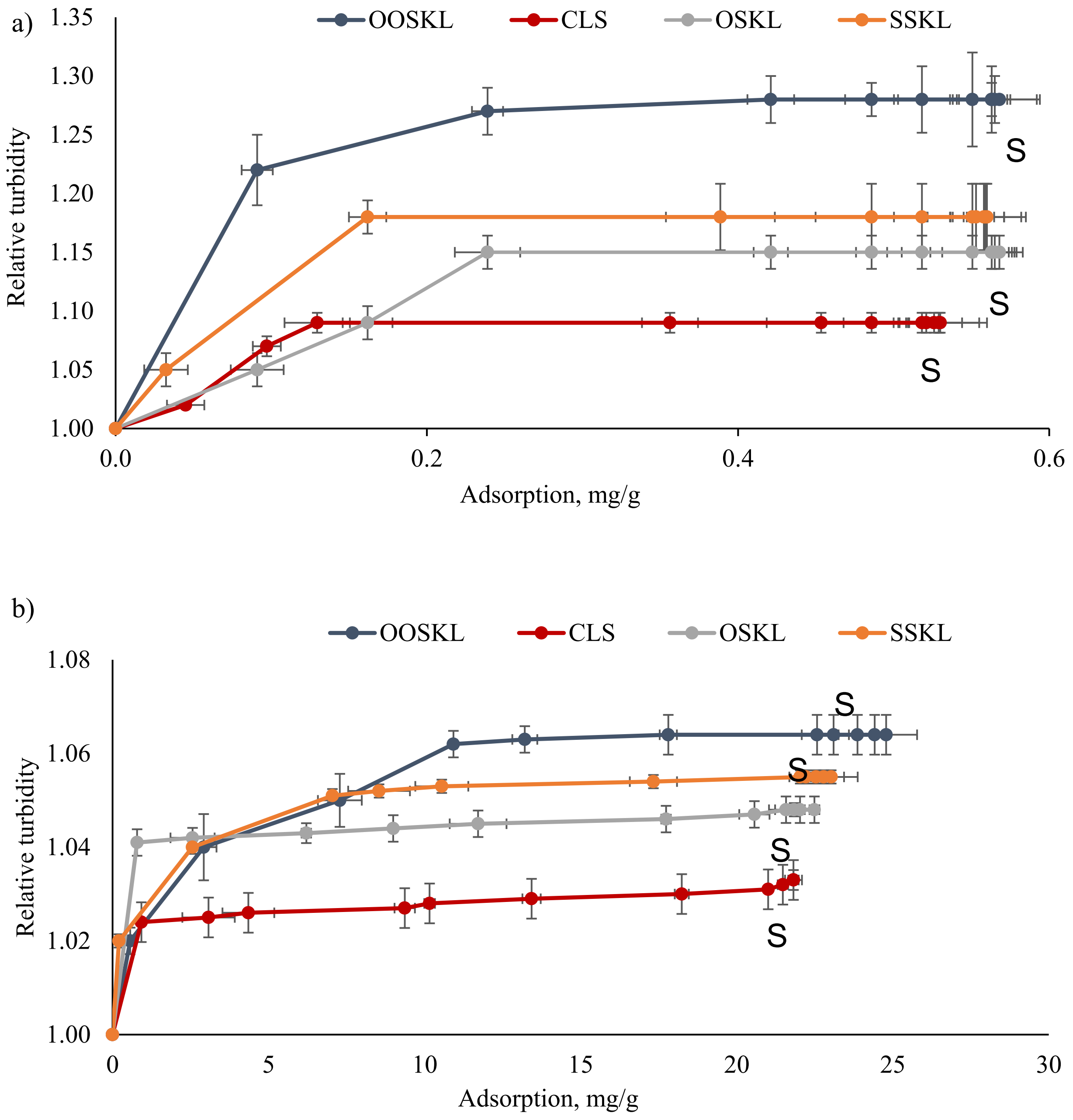


Figure 3.5: Effect of lignin adsorption on the relative turbidity of a) kaolin and b) bentonite suspensions. Other experimental conditions were experimentation at room temperature for 30 min and pH 7.

### 3.4.5 Flocculation analysis

The relative turbidity of the suspension was used to determine the flocculation affinity of lignin samples on the alumina suspension (Farrokhpay, 2009; Nsib et al., 2006). The effect of lignin dosage on the relative turbidity of alumina suspension is shown in Figure 3.6. Generally, an adsorption of 2 mg/g was sufficient to obtain the minimum relative turbidity. A higher adsorption than optimum generated repulsion force among particles and hampered the flocculation affinity of lignin samples. It is also seen that SSKL had the best flocculation performance and OOSKL had the worst one. The reason for this behavior is attributed to the higher molecular weight of SSKL and lower molecular weight of OOSKL (Wiśniewska et al., 2009; Viota et al., 2004; Wiśniewska et al., 2013).

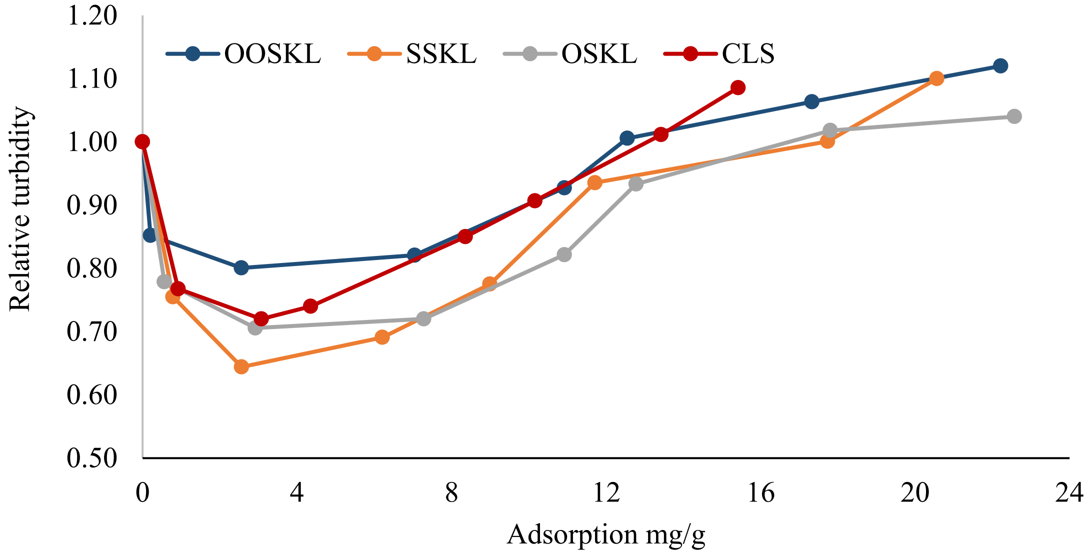


Figure 3.6: Effect of lignin adsorption on the relative turbidity of alumina suspension. Other conditions of experiments were mixing at 300 rpm at room temperature for 30 min and pH 7.

### 3.4.6 Correlation between zeta potential and relative turbidity

The relationship between the relative turbidity and zeta potential of the kaolin and bentonite suspensions is shown in Figure 3.7. As seen in Figure 3.7, the relative turbidity of kaolin and bentonite suspension increased slowly with a decrease in the zeta potential of particles. Figure 3.7a indicates that the relative turbidity of kaolin suspension increased to 1.07, 1.06, 1.05, and 1.03 as its zeta potential decreased to -40, -38, -38.60 and -37.8 mV, respectively. Figure 3.7b shows that the relative turbidity of bentonite suspension increased to 1.28, 1.18, 1.15, and 1.09, while its zeta potential decreased to -52, -51, -50, and -48 mV with addition of OOSKL, SSKL, OSKL and CLS, respectively. These results are attributed to the higher adsorption and charge density of OOSKL than other samples, which introduced electrostatic repulsion between particles and increased the relative turbidity of the suspensions to a greater extent than other samples. The S points in each curve represent the relative turbidity of kaolin and bentonite suspension at maximum adsorption in Figure 3.1, and minimum zeta potential in Figure 3.7. When there was no change in the adsorption amount (Figure 3.1), the relative turbidity of kaolin and bentonite suspensions and the zeta potential of kaolin and bentonite particles remained the same with no changes; implying that the unabsorbed polymers did not play a role in zeta potential and relative turbidity of the suspensions.

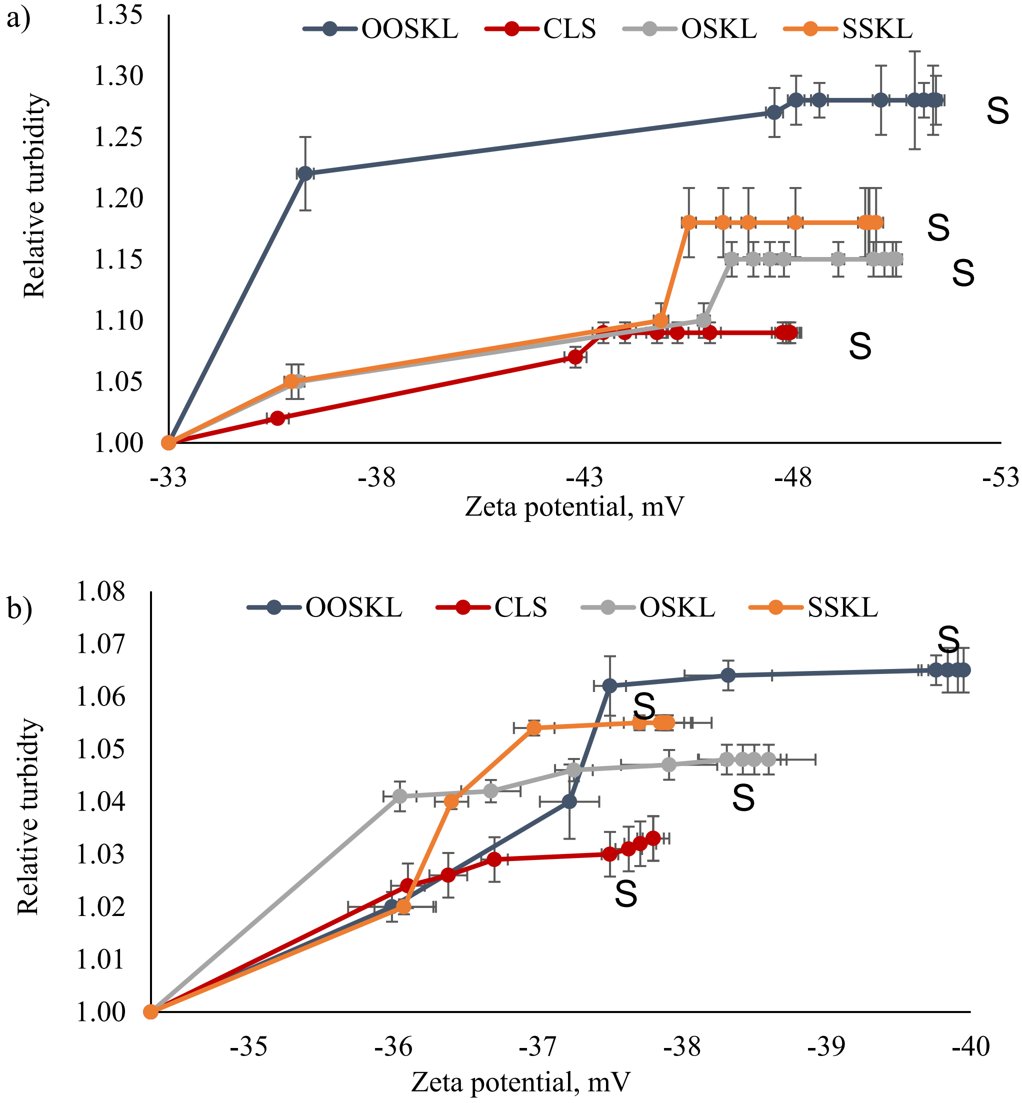


Figure 3.7: The relation between relative turbidity and zeta potential of a) kaolin suspension and b) bentonite suspension (20 g/L) at pH 7 and room temperature.

Furthermore, the relationship between the relative turbidity and zeta potential of alumina suspension is shown in Figure 3.8. The data suggest that by reducing the zeta potential, the relative turbidity dropped. The minimum relative turbidity of 0.64, 0.71, 0.80, and 0.72 for SSKL, OSKL, OOSKL, and CLS were observed at the zeta potential of 19.7, 20.6, 20.1, and 28.9, respectively. In addition, at a lower zeta potential of 20 mV, the adsorption of SSKL, OSKL, OOSKL, and CLS started to raise, thus the relative turbidity started to increase with further addition of polymers (Gregory & Barany, 2011; Viota et al., 2004).

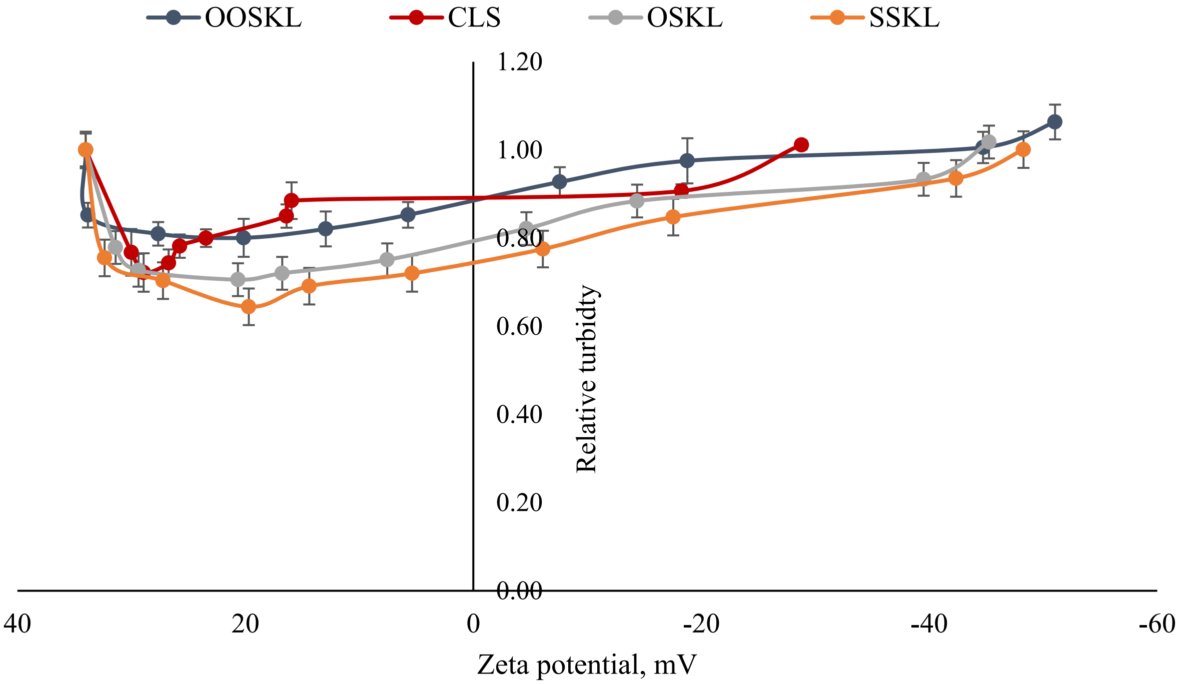


Figure 3.8: The relationship between relative turbidity and zeta potential of alumina suspension (1 g/L) at pH 7 and room temperature.

### 3.4.7 Dispersion stability

The dispersion stability of kaolin and bentonite suspensions with and without the addition of polymers was assessed with destabilization index analysis (Gan et al., 2013; Wisńiewska, 2010). The reported value of destabilization index was related to transmission and backscattering light intensity of a dispersion. A decrease in the destabilization index means that the particle sedimentation was slow. Therefore, a high destabilization index value indicated that the suspension had a low stability (Gan et al., 2013; Qin et al., 2016; Wiśniewska, 2010). The destabilization index of a blank kaolin suspension (without polymers) increased rapidly with time to approximately 80 after 30 min (not shown in Figure 3.9), while the destabilization index of blank bentonite suspension increased slightly to 0.4 after 30 min (Figure 3.10). The higher destabilization index value of kaolin suspension showed that these particles were less stable than bentonite particles (Qin et al., 2016). The addition of OSKL, SSKL, and OOSKL decreased the destabilization index of kaolin and bentonite suspension more than CLS addition, which caused the suspension to become more stable, compared to CLS addition.

Figure 3.11 shows that the destabilization index of blank alumina suspension increased from 0 to approximately 30 after 30 min. The data in Figure 3.11 suggested that with the addition of polymers to the alumina suspension, the destabilization index value increased to 40 implying that the polymers accelerated the flocculation and settling of particles. In addition, OOSKL was found to decrease the destabilization index more than did CLS as a result of its higher charge density, which improved its flocculation performance (Qin et al., 2016). OSKL has decreased the destabilization index of alumina suspension more than CLS as a result of its higher $M_w$.

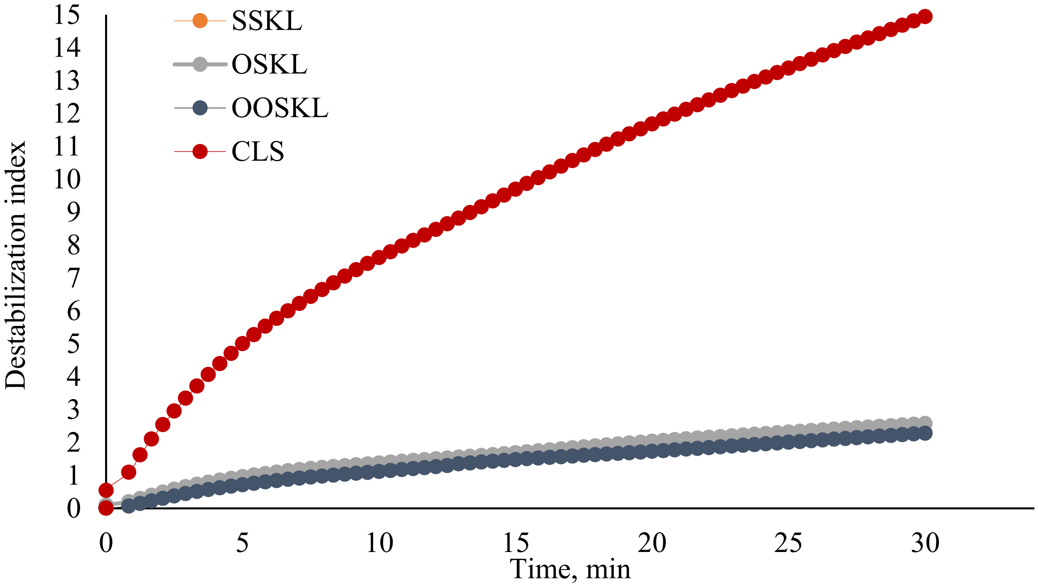


Figure 3.9: Effect of polymers on the destabilization index of kaolin suspension (20 g/L) at pH 7 and room temperature. Date reported as a function of time (0-30 min).

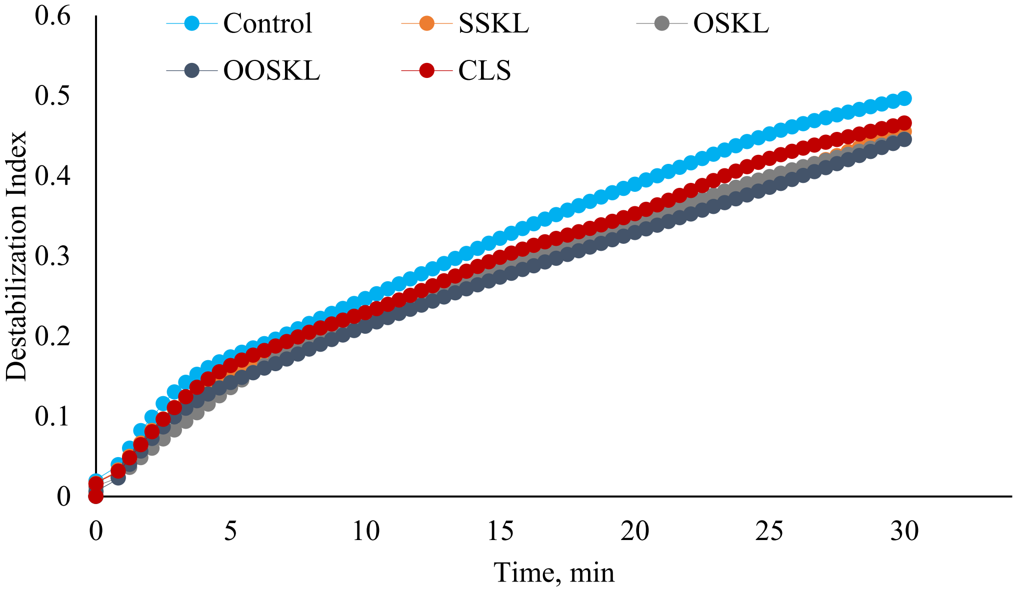


Figure 3.10: Effect of polymers on the destabilization index of bentonite suspension (20 g/L) at pH 7 and room temperature. Date reported as a function of time (0-30 min).

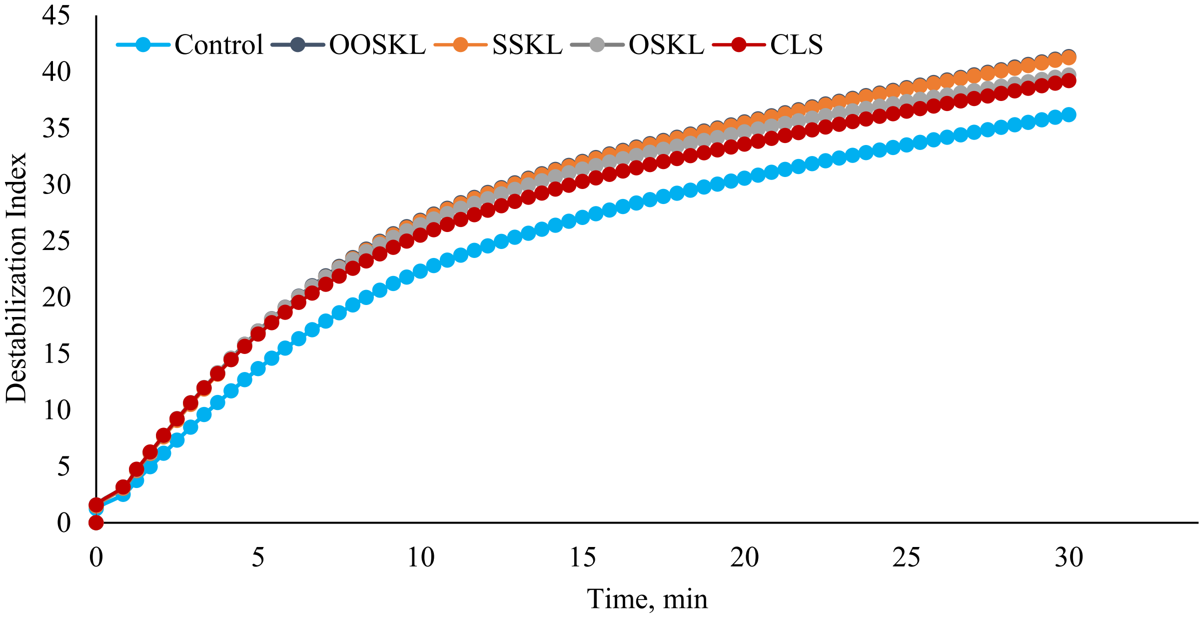


Figure 3.11: Effect of polymers on the destabilization index of alumina suspension (1 g/L) at pH 7 and room temperature. Date reported as a function of time (0-30 min).

### 3.4.8 Dye removal

In this set of experiments, the removal of dyes as a function of dosages of lignin polymers was investigated. Ethyl violet and basic blue 41 are cationic dyes with the structures shown in Figures

3.12 and 3.13. They would interact with the anionic lignin samples to form complexes. The properties of dye samples are listed in Table 3.2. It is seen that the dye samples had a charge density of 2.6-3 meq/g, with small molecular weight.

Table 3.2: Charge density and molecular weight of ethyl violet and basic blue dyes

| Cationic dye | Charge density, meq/g | Molecular weight ($M_w$), g/mol |
|---|---|---|
| Ethyl violet | 2.57 | 492.14 |
| Basic blue 41 | 2.9 | 359.19 |

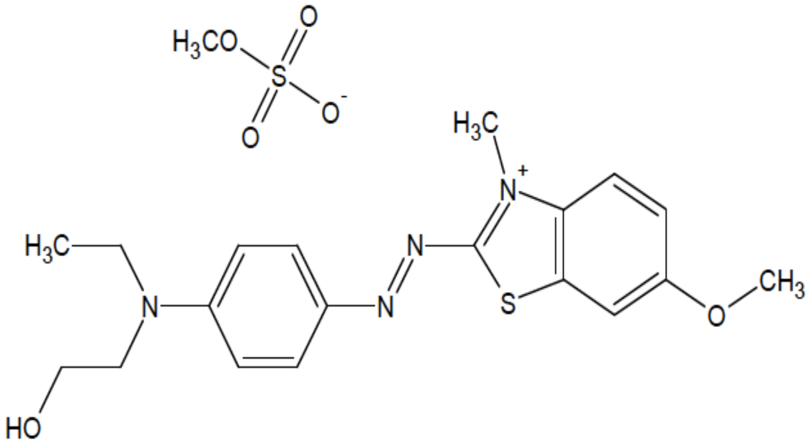


Figure 3.12: Chemical structure of blue basic 41 (Baldo et al., 2014)

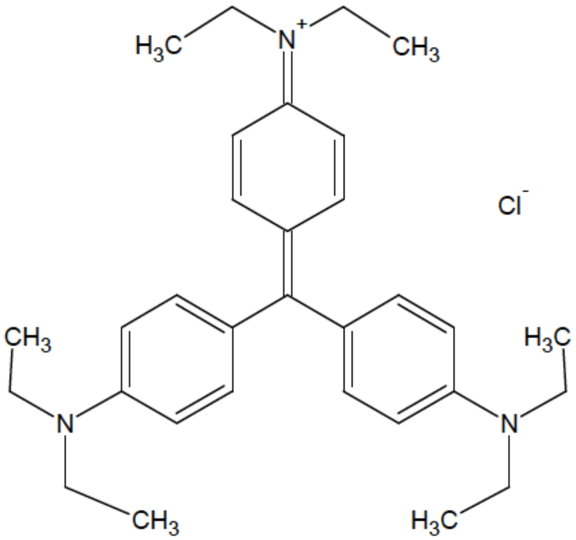


Figure 3.13: Chemical structure of ethyl violet (He et al., 2016)

Figure 3.14 shows the removal of basic blue dye as a function of lignin polymer dosage. It is noted that OOSKL and SSKL required a lower dosage than other lignin samples to remove the dye, thus these samples had the best performance. It is also seen that CLS required more dosage for the removal. OOSKL and SSKL had a higher charge density than other samples (Table 2.1), and the results confirmed that the charge density played a major role in the removal (Fang et al., 2010). In a previous study, the addition of the cationic copolymerized lignin to an anionic acid black 1, reactive red 2 and direct red 2 led to 95%, 94% and 95% dye removals, respectively (Fang et al., 2010). In another study, oxidized lignin was found to remove 70% of ethyl violet and 85 % of blue basic dyes at concentration of 100 mg/L of dye (Couch et al., 2016). It is also seen that when the lignin concentration exceeded the optimal dosage, the dye removal declined. It was reported previously that charge neutralization is the main mechanism of polymer and dye interaction (Wang et al., 2014; Fang et al., 2010). Therefore, the excess amount of lignin samples would promote charge reversal and re-dispersion of dye particles in solutions (Rojas & Hubbe, 2005; López-Maldonado et al., 2014).

Furthermore, the results in Figure 3.14 depict that the lignin samples were more effective in removing ethyl violet than basic blue dye, as lower dosages of them removed more dyes. The reason for this behavior is attributed to the lower charge density of ethyl violet dye than basic blue 41 dye as shown in Table 3.2. Ethyl violet dye needed a lower dosage of polymer to neutralize its charge, while blue basic needed a higher dosage of polymer.

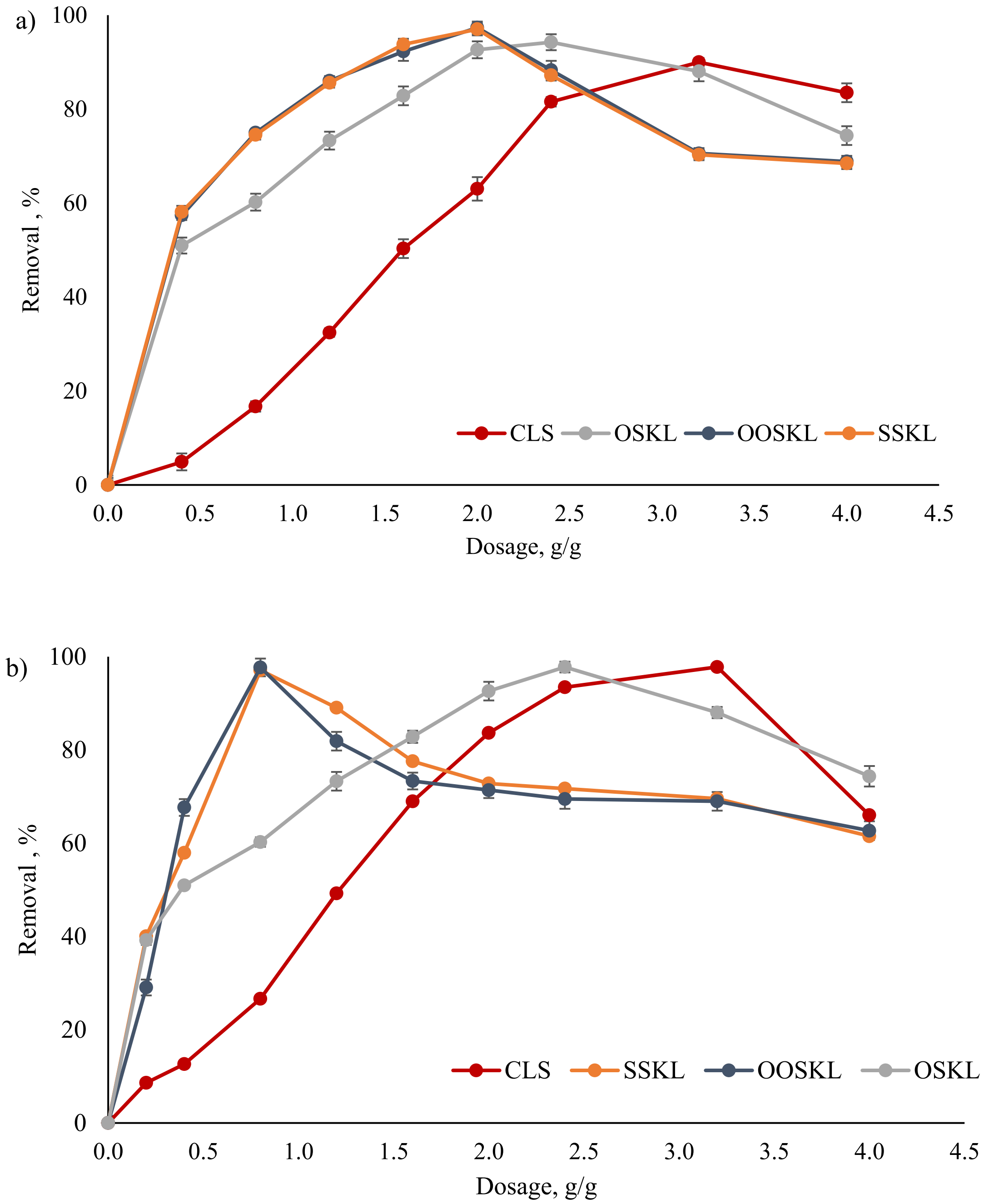


Figure 3.14: Effect of lignin dosage on removal of a) basic blue 41 and b) ethyl violet dyes from solutions. Experiments were conducted under the conditions of pH 7 and room temperature.

## 3.5 Conclusions

In this chapter, the adsorption of modified lignin samples and commercial lignosulfonate on kaolin, bentonite and alumina particles was examined. It was observed that all modified lignin samples were adsorbed more than commercial lignosulfonate on the particles, and OOSKL had the highest adsorption level. OOSKL changed the zeta potential and relative turbidity of the clay particles more than other samples (thus a more effective dispersant), because of its higher charge density. SSKL and OSKL were more effective flocculants than other samples. Charge density played a major role on the adsorption, dispersion and flocculation of particles. Generally, the adsorption of lignin samples was more on kaolin than on bentonite, but lignin samples dispersed bentonite particles more effectively. OOSKL was more effective than other lignin samples in removing dye segments and CLS was the least effective. Furthermore, more variations in the efficiency of lignin samples were observed for removing ethyl violet than basic blue dyes from the solution. Furthermore, the addition of OOSKL and SSKL and OSKL in kaolin and bentonite stabilized the suspension more than did CLS.

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# 4 Chapter 4. Conclusions and recommendations

## 4.1 Conclusions

In this MSc thesis, kraft lignin was modified via SSKL, OSKL and OOSKL in order produce anionic modified lignin and their dispersion and/or flocculation performance in different colloidal suspensions were studied. The produced modified lignin samples were characterized by PCD, GPC, elemental analysis, FTIR. The thermal stability of produced modified lignin samples was evaluated and compared with CLS. The adsorption behavior of all anionic modified lignin was investigated in different colloidal suspensions and compared with CLS. The effect of anionic lignin polymers on the dispersion of kaolin and bentonite and on the flocculation of alumina suspension was investigated and compared with CLS at room temperature and pH 7. The influence of anionic modified lignin on the turbidity and the stability of kaolin, bentonite and alumina suspension was analyzed and compared with CLS. Furthermore, the impact of the anionic modified lignin was evaluated in removing ethyl violet and blue basic 41 dyes.

The selected SSKL had a charge density of -1.63 meq/g, 100 % solubility, and molecular weight of 27295 g/mol, which was produced under conditions of 90 °C, 3/1 mol/mol $Na_2SO_3$/lignin, 16 g/L lignin concentration and pH 12.

The selected oxidized lignin (OSKL) had a charge density of -1.31 meq/g, 100 % water solubility with molecular weight of 24539 g/mol, which was produced under the conditions of pH 12, 0.5 $H_2O_2$/lignin molar ratio, 2 h reaction time at temperature of 80 °C.

The selected OOSKL lignin had a charge density of -3.2 meq/g, 100% water solubility and 14725 g/mol molecular weight, which was produced at 20 wt. % nitric acid concentration, 90 °C and 1 h reaction time.

The elemental analysis and FTIR confirmed the success of sulfonation and oxidation reactions. The oxygen content of OSKL and OOSKL was increased as a result of carboxylate groups addition to SKL via oxidation reactions. Also, the addition of nitro groups to lignin in OOSKL resulted in an increase in its nitrogen content. In addition, SSKL was found to have a higher sulfur content than other samples.

Thermal behavior of lignin samples was studied by TGA and DSC analyses. TGA analysis showed an increase in thermal stability of SKL via sulfonation and oxidation treatment due to the improvement of intermolecular linkages in SSKL, OSKL and OOSKL. In addition, the results showed that SKL was completely decomposed at 570 °C while modified lignin and CLS samples resisted the thermal degradation at higher temperature than 600 °C. On the other hand, DSC results showed that $T_g$ and $C_p$ of modified lignin changed due to changing in chemical structure of lignin. Among all samples, OSKL had the highest $T_g$ value and the lowest $C_p$ value.

The adsorption of SSKL, OSKL, OOSKL on bentonite was 22.49 mg/g, 21.82 mg/g and 24.79 mg/g, respectively, which were higher than that of CLS (21 mg/g). In addition, the adsorption of SSKL (48.34 mg/g), OSKL (30.34 mg/g) and OOSKL (51.92 mg/g) was higher than CLS (32.33 mg/g) on kaolin. Moreover, SSKL, OSKL, and OSKL found to affect the relative turbidity of kaolin, bentonite and alumina suspensions more than did CLS. The zeta potential of kaolin, bentonite and alumina was also influenced by the addition of SSKL, OSKL and OOSKL more greatly than by that of CLS. The relative turbidities of SSKL, OSKL, OOSKL and CLS were found to be 1.80, 1.15, 1.28, and 1.09 on kaolin suspension, respectively. Also, the relative turbidities of bentonite suspension containing SSKL, OSKL, OOSKL, and CLS were 1.06, 1.04, 1.07, and 1.03, respectively. The adsorption, relative turbidity and zeta potential studies (dispersion studies) of polymers on kaolin and bentonite suspension indicated that SSKL, OSKL and OOSKL influenced the dispersion performance more significantly than CLS. In the same vein; adsorption, relative turbidity and zeta potential studies (flocculation studies) of polymers on alumina suspension indicated that SSKL, OSKL, and OOSKL were more influential than CLS as a flocculant. The addition of OOSKL, SSKL, and OSKL in kaolin and bentonite stabilized the suspension more than did CLS. In addition of SSKL, OSKL, and OOSKL stabilized the colloidal suspension better than CLS.

The studies on the application of polymers in removing ethyl violet and blue basic 41 dyes from solutions suggested that OOSKL and SSKL were more effective in removing ethyl violet and blue basic at a lower dosage (2 g/g for blue basic 41 and 0.8 g/g for ethyl violet), which was higher than that for CLS (3.2 g/g in ethyl violet and blue basic 41 solutions).

## 4.2 Recommendations

To understand the structural differences between softwood kraft lignin, oxidized lignin, and sulfonated lignin samples, nuclear magnetic resonance spectroscopy of the samples should be studied comprehensively. This study can be further continued via analyzing the dispersion and flocculation performance of the modified lignin samples in different industrially produced suspensions such as cement admixtures and industrial and municipal wastewater effluents. Thermal mobility and morphology of lignin samples should be studied to understand the thermal behavior of lignin samples.