Copolymerization of pretreated kraft lignin and acrylic acid to produce flocculants for suspension and solution systems

by:

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Thesis Presented to the Faculty of Graduate Studies
of Lakehead University of Thunder Bay
in Partial Fulfillment
of the Requirements
for the Degree of
Master of Science in Chemistry

Lakehead University
April 2017

Abstract

The presence of dyes in the wastewater of textile industry poses a number of environmental concerns due to their toxic nature and the removal of dyes from the wastewater is a major challenge nowadays. Synthetic polymers are commonly used in the flocculation of various colloidal systems. However, these synthetic polymers cause environmental concerns due to their non-biodegradability and toxicity to human and animals. Their high costs also limit their use in many applications. These disadvantages may be overcome by using polymers derived from natural sources. Lignin is the most abundant renewable resource after cellulose, and is an inexpensive raw material that can be used to produce high-value products, such as flocculants, dispersants, phenols etc. Native lignin does not possess suitable properties to be used as is, however, its attributes can be changed by means of chemical modifications. In this thesis, kraft lignin was initially modified via sulfation, sulfomethylation or phenolation methods and subsequently copolymerized with acrylic acid. The resulting copolymers were characterised using a variety of methods including NMR, FTIR, TGA, molecular weight analysis, and elemental analysis, all of which demonstrated remarkable changes in the chemical and physical structure of lignin after modification. The flocculant property of the produced copolymers was investigated in alumina suspensions via studying a) the adsorption behaviour of copolymers on alumina particles b) changes in the zeta potential of alumina particles, and c) the ability of the copolymers to alter the relative turbidity of alumina colloids. The results demonstrated that the copolymers could indeed act as effective flocculants, with their performance being partly dependent on their charge density, molecular weight and their ability to decrease the zeta potential of the alumina particles. Indeed, the copolymers with the highest charge density and molecular weight adsorbed more dye. This work demonstrated the potential of using widely available, inexpensive, and renewable kraft lignin as a flocculant after modification. It also provided information on the flocculation of ethyl violet dyes from synthetic solutions. The data also provides further information about the mechanism and best ways to chemically modify lignin, as well as how these products function as flocculants.

Acknowledgements

I would like to thank my supervisor Dr. P. Fatehi for his help and guidance.

I would also like to thank my committee Dr. C. Gottardo and Dr. B. Liao for their support.

I would specifically like to thank my family, friends, Dr. Fatehi's lab members for helping me through my graduate studies and making this thesis possible.

Dedication

I would like to dedicate my thesis to my parents and my daughters for their love, endless support and encouragement.

I also would like to dedicate this work and give special thanks to my husband for being there for me throughout the entire master program. Most of all, thank you for being my best friend. I couldn’t have done this without you.

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lists of abbreviations

Products

Unmodified lignin-1	UL1
Sulfated lignin-1	SL1
Sulfomethylated lignin-1	SML1
Phenolated lignin-1	PL1
Unmodified lignin-2	UL2
Sulfated lignin-2	SL2
Sulfomethylated lignin-2	SML2
Phenolated lignin-2	PL2
Unmodified lignin-1 with acrylic acid	UL1A
Sulfated lignin-1 with acrylic acid	SL1A
Sulfomethylated lignin-1 with acrylic acid	SML1A
Phenolated lignin-1 with acrylic acid	PL1A
Unmodified lignin-2 with acrylic acid	UL2A
Sulfated lignin-2 with acrylic acid	SL2A
Sulfomethylated lignin-2 with acrylic acid	SML2A
Phenolated lignin-2 with acrylic acid	PL2A
Purified unmodified lignin-1 with acrylic acid	PUL1A
Purified sulfated lignin-1 with acrylic acid	PSL1A
Purified sulfomehylated lignin-1 with acrylic acid	PSML1A
Purified phenolated lignin-1 with acrylic acid	PPL1A
Purified unmodified lignin-2 with acrylic acid	PUL2A
Purified sulfated lignin-2 with acrylic acid	PSL2A
Purified sulfomehylated lignin-2 with acrylic acid	PSML2A
Purified phenolated lignin-2 with acrylic acid	PPL2A

Chapter 1: Introduction

1.1. Overview

Nowadays, flocculants are widely used in the mining, oil, pulp and paper industries to remove tailings present in the processing water or in wastewater treatment processes. Specifically, flocculants are used to destabilize colloidal systems viz., clay, coal, and aluminum oxide suspensions.

Currently, inorganic chemicals or synthetic polymers or combination of both are used as flocculants. These are commonly petroleum-based materials which can be themselves detrimental to the environment, are expensive and are non-biodegradable. This has led to the consideration of alternative flocculants made from renewable and natural resources, which are biodegradable and more environmentally friendly.

Woody plants are mainly composed of three natural polymer constituents; cellulose, hemicelluloses, and lignin, all of which can be used to produce value-added materials, such as biofuels, dispersants, phenols, and flocculants. However, the studies on preparation and application of these polymers as flocculants are limited. Lignin, in particular is an abundant natural polymer generated mainly as a by product of the pulp and paper industry. In its native state, lignin interacts poorly with colloidal particles, including those of alumina suspensions due to its limited types of functional groups. To improve its application properties, various functional groups are grafted on to kraft lignin via sulfation, sulfomethylation, phenolation and copolymerization with acrylic acid, causing them to interact with alumina particles.

So far very few studies were reported on effect of polymer characteristics on flocculation of clay suspensions. Thus, in this study, the effect of charge density and molecular weight of produced polymers on their flocculation ability was investigated. Adsorption of polymers on alumina particles is important, because the adsorbed polymer may change the surface properties of alumina particles and in turn their flocculation behaviour. Thus, it is significant to study the impact of polymer concentration on the time of adsorption of polymers on alumina particles. The adsorbed charged polymer on alumina particles also affects the electrokinetic potential of alumina particles, which further contributes to flocculation behaviour of alumina suspensions Thus in this study the effect of polymer concentration on zeta potential of alumina particles was also studied.

The objectives of this study were to:

1. improve the functional properties of kraft lignin with sulfation, sulfomethylation, and phenolation methods;
2. to enhance the functional properties of modified kraft lignin by copolymerization with acrylic acid;
3. investigate the adsorption of anionic lignin copolymers onto alumina particles;
4. investigate the performance of the copolymer as a flocculant for alumina suspensions;
5. investigate the impact of the copolymers in flocculating ethyl violet dye from synthetic solutions

Chapter one, includes the summary of the work, hypothesis, objectives and novelty of the study.

Chapter two discuss the literature review on the modification and copolymerization of lignin and also the methods to characterize the properties of lignin.

Chapter three describes modification of kraft lignin via phenolation, sulfomethylation, and sulfation for improving the functional properties of kraft lignin. This chapter also includes the optimization of process conditions to produce modified kraft lignin with targeted properties. The techniques used to characterize the modified kraft lignin were also described.

Chapter four represents the copolymerization of modified lignin with acrylic acid. In this chapter, the impact of process conditions on the copolymerization of modified lignin was investigated and the reaction conditions to produce modified lignin copolymer with high charge density and solubility were determined. The characteristics of the products were also investigated using elemental analyzer, FTIR, ^{1}H-NMR, and TGA.

Chapter five describes the flocculation studies of produced copolymers products before and after purification in alumina suspensions. The flocculation performance of produced copolymers was investigated by adsorption, zeta potential and turbidity studies. The ability of copolymers to remove dyes from a synthetic solution was also investigated.

Chapter six includes the overall conclusions of all the chapters and some recommendations for future work

1.2. Questions to investigate

- What process conditions will affect the synthesis of pretreated anionic lignin copolymers?
- What structural or chemical properties of modified anionic lignin copolymers will affect their flocculation performance in alumina suspensions?

- How the flocculation performance of modified anionic lignin copolymers will differ in suspensions and solutions?

1.3. Novelty of study

The study is novel as it will result in:

1. The production of a novel product via copolymerization of phenolated or sulfomethylated, or sulfonated kraft lignin with acrylic acid
2. An investigation of the potential of lignin copolymers to flocculate alumina particles and dye segments from suspension and solution systems.

Chapter 2: Literature review

2.1. Introduction

A desire to protect our environment, air, water, flora and fauna has led many governments to introduce a variety of new environmental regulations and safeguards. These new polices have forced chemical industries to either produce fewer waste products, and/or to treat their wastes to reduce or eliminate their environmental impacts. Not least amongst these producers is the chemical industry, which is exploring and implementing ways to replace petrochemical feedstocks with sustainably produced biologically-based alternatives, one of which is wood based products.

Woody plants are mainly composed of three constituents; cellulose, hemicelluloses, and lignin, which could be utilized in the production of biofuels and other value-added products by means of a process termed biorefining (Kamm, 2004). Biorefining utilizes a variety of processes including thermal, thermochemical, or biochemical conversion, either singly or in combination, to turn biomass into value-added products. Currently, most biorefining processes focus on the use of cellulose and hemicelluloses. Lignin, on the other hand, has been paid less attention (ElMekawy et al., 2013).

Lignin is a natural polymer with a complex structure as shown in Figure 2.1. It is made up of three phenyl propane monomeric units viz., *p*-coumaryl alcohol, coniferyl alcohol, or sinapyl alcohol (Figure 2.2). These monomeric units are joined together by several types of ether and carbon and carbon linkages(Chien et al., 2012). Now-a-days, the majority of lignin is obtained as a by-product of the kraft pulping processes or from cellulosic ethanol plants. Million tonnes of lignin are produced annually with only 1–2% of lignin estimated to be used in the production of value-added products, the rest being burned as a fuel (Lewinsky, 2006).

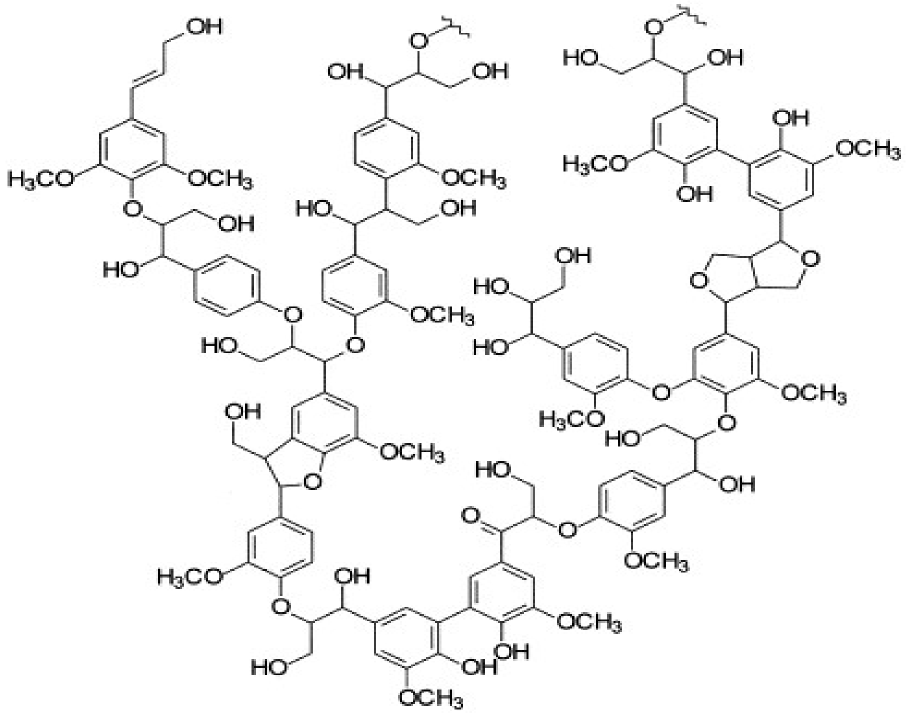
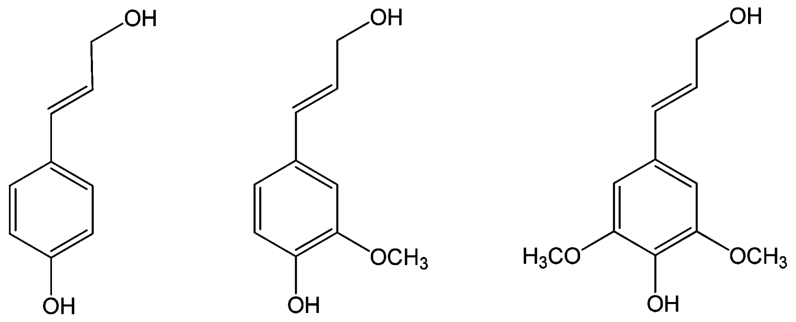


Figure 2.1: Structure of lignin (Lewinsky, 2006)



p-coumaryl alcohol

coniferyl alcohol

Sinapyl alcohol

Figure 2.2: Three phenyl propane monomers in lignin (Lewinsky, 2006)

Limited solubility and reactivity of native lignin hampers its application potential. However, lignin can be modified to improve its chemical and physical properties in order to be employed in many different applications such as dye dispersant, water reducing agent for cement admixture, chelating agent and flocculation water treatment. For example, various lignin types were chemically altered using different techniques including the oxidization of calcium lignosulfonate and softwood kraft lignin (Pang et al., 2008; He & Fatehi, 2015), hydroxymethanlation and sulfonation of alkali lignin (Ouyang et al., 2009; Inwood, 2014), phenolation of softwood lignin, and carboxymethlation of hardwood kraft lignin (Inwood, 2014; Konduri et al., 2015). Such modifications introduce desirable properties to lignin. For example, the oxidation of lignin can selectively remove methoxyl and phenolic hydroxyl groups from its aromatic ring (Mansouri & Salvado, 2006), which results in decreasing the molecular weight and increasing the reactivity of the lignin by means of reducing steric hindance. Therefore, oxidation can increase the reactivity of lignin and enhance its ability to undergo further chemical processing (He & Fatehi, 2015). Similarly, hydroxymethylation increases the reactivity of lignin (Inwood, 2014), through the addition of formaldehyde to the aromatic ring which increases the reactivity of the *para*- or -positions of lignin (Yasuda et al., 1998).

Sulfonation by sulphuric acid treatment was exploited as a method to sulfonate alkali lignin derived from olive stone biomass, with the product being incorporated into a phenol/formaldehyde resin (Zoumpoulakis & Simitzis, 2001). The phenolation of lignin increased its reactivity through grafting a phenol group at the α-position of the lignin structure. The phenolation added two more reactive sites to the lignin structure, facilitating the reaction mechanisms that targeted the aromatic ring of lignin (Inwood, 2014; Alonso et al., 2005; Gosselink et al., 2004).

Carboxymethylation has been employed to modify wheat straw alkali lignin. In this method, carboxylate groups were added to the phenolic hydroxyl group of lignin, where the active site of $Na^{+}O^{-}$ in the aromatic ring exist along with sodium acetate groups that are replaced by the carboxymethyl groups (Vishtal & Kraslawski, 2011). In other work, carboxymethylation of hardwood kraft lignin introduced carboxyl groups to the *para*-position on the aromatic ring, resulting in a lignin with a higher charge density (Konduri et al., 2015).

However, these chemical modifications did not significantly modified lignins with properties that favour their use as flocculants in wastewater systems. For example, such modifications only moderately change the charge density of the polymer or its solubility, thereby limiting its potential use in industry. To overcome these difficulties, copolymerization of lignin has been introduced as an alternative. The copolymerization of lignin with other monomers has achieved greater success than the methods described above in producing materials with broader industrial applications, because the copolymerization of lignin can result in high charge density, molecular weight, and solubility, which would promote lignin copolymers application as flocculants for wastewater systems (Wang et al., 2016), thickening and thinning of suspensions, and dewatering sludge (Hüttermann et al., 2001). In the following sections, the synthesis and use of lignin copolymers to produce anionic lignin copolymers are discussed.

2.2. Copolymerization of lignin

2.2.1. Copolymerization of lignin with acrylamide

The copolymerization of lignin and vinyl monomers, such as acrylamide (AM), acrylonitrile, and methyl methacrylate can occur in environmentally benign aqueous solvents (Meister et al., 1984). Acrylamide is particularly attractive given its low cost and high reactivity (Wang et al., 2014). Used alone, its resulting homopolymer, polyacrylamide, has been applied in wastewater systems as a flocculant (Wang et al., 2014), and as a versatile strength additive in various papermaking processes (Mihara et al., 2008). The copolymerization of acrylamide with various bio-based materials is of growing importance. The reaction scheme of lignin and acrylamide is shown in Figure 2.3. In this reaction, potassium persulphate acts as a source of sulphate radicals which leads to the formation of phenoxy radicals within the lignin backbone. The phenoxy radicals then react with acrylamide monomers to form copolymers. The free radical also provides a variety of side reactions, including the homopolymerization of acrylamide (Wang et al., 2016).

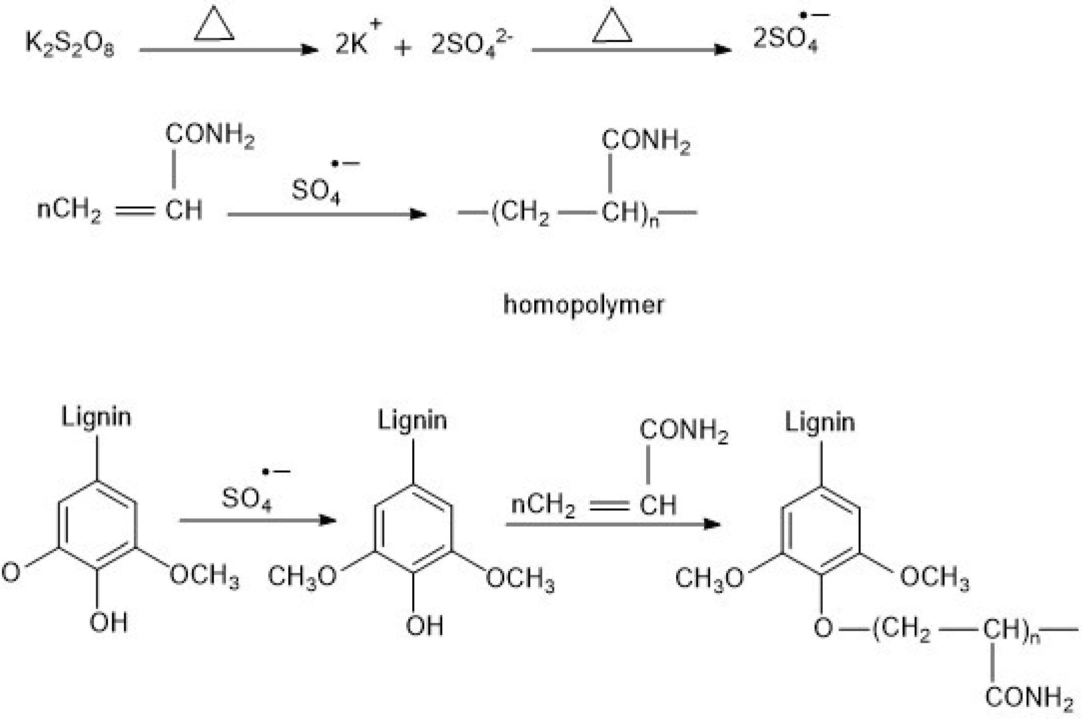


Figure 2.3: Reaction mechanism of copolymerization of AM with lignin (Wang et al., 2016)

In one research study, the copolymerization of soda lignin and acrylamide (AM) was investigated and the results indicated that the soda lignin-acrylamide copolymer could be used as an effective dry strength additive in papermaking applications (Wang et al., 2016). The optimal reaction conditions for the copolymerization of soda lignin and acrylamide were found to be incubating at

90 °C for 4 h with acrylamide/soda lignin molar ratio of 7.5 mol/mol, lignin concentration of 2 g/L, and potassium persulphate 3.0 wt. % as an initiator. The reaction conditions and the properties of lignin-acrylamide products are listed in Table 2.1. The optimized reaction conditions produced a soda lignin-acrylamide copolymer with 100% solubility and a molecular weight of 194,000 g/mol (Wang et al., 2016).

In another report, the optimal reaction conditions for the copolymerization of enzymatically hydrolyzed (EH) lignin with acrylamide were found to be EH-lignin/acrylamide molar ratio of 2/3 mol/mol in a 1% NaOH aqueous solution in the presence of $K_2S_2O_8$-$Na_2S_2O_8$ at 50 °C for 4 h. The copolymerization reaction was confirmed by Fourier transform infrared spectroscopy (FTIR) analysis in which an absorbance peak of 1700 cm^{-1} of C=O was observed for the copolymer.

In the same vein, sodium lignosulfonate has been copolymerized with acrylamide using 3.5 wt.% of hydrogen peroxide (acting as an initiator), and 20 mol% of acrylic monomers/sodium lignosulfonate at 70°C and 4 h. The analysis showed that the viscosity of the final products could be varied over the range 0.65 to 3 Pa/s by changing the monomer concentration, which illustrated the flexibility of the copolymerization process (Abdel et al., 2015) and how it may be tailored to particular applications.

Table 2.1: Copolymerization of lignin with acrylamide

Lignin type	**Reaction condition**				**References**
	Molar ratio, AM/lignin	Initiator, wt%	Time, h	Temperature, °C	
Soda	15/2	$K_2S_2O_8$ at 3.0	4	90	(Wang, 2016)
EH	2/3	$K_2S_2O_8$ $Na_2S_2O_3$ at 3.0	4	50	(Fang, 2009)
Sodium lignosulfonates	2/10	3.5	4	70	(Abdel, 2015)

2.2.2. Applications of acrylamide/lignin copolymers

As stated above, acrylamide is both an inexpensive and highly reactive monomer. As such, it is widely used for the copolymerization of different bio-based materials (Isikgor et al., 2015). Similar to polyacrylamine, acrylamide-based copolymers have a wide range of applications, including being used as flocculants in wastewater treatment, sugar manufacture, soil erosion prevention, and in the production of grout, concrete, cosmetics, and plastics (Smith et al., 1991). Lignin-acrylamide based copolymers have also been used as dry strength agents for papermaking (Wang et al., 2016). For example, by adding 1 wt.% of soda lignin-acrylamide copolymer to soda pulping, the dry strength of the resulting paper was increased by 15.2 % (Wang et al., 2016). This was mainly attributed to an increase in hydrogen bonding between the amide groups of the copolymer and the hydroxyl groups of the cellulose fibers (Mihara et al., 2008). Previously, enzymatically hydrolyzed lignin-acrylamide copolymer was used to remove dye present in waste water effluents. As the copolymer concentration was increased from 50 to 200 mg/L, the removal of the dye (Acid Red 274) in aqueous solution increased from 30 to 85 % (Fang et al., 2009). In other work, sodium lignosulfonate was polymerized with acrylamide monomer under the conditions of hydrogen peroxide concentration of 3.5 % and the temperature of 70 °C for 4 h, where the resulting product was proposed to be used as a thinner for drilling mud. As a result, the copolymerization increased the viscosity of the final product by 50 % relative to the unmodified lignin due to the fact that amide groups in acrylamide polymer were less hydrophilic than carboxylic groups in acrylic acid polymer, and the feature was found to be advantageous in this particular application (Abdel, 2015).

2.2.3. Copolymerization of lignin with acrylic acid

Acrylate monomers are extensively used for producing polymers, with polyacrylates being widely employed in the surface coating industry, polymer film manufacturing, and as adhesives in many applications, including adhesive resins, pressure-sensitive adhesives, and water-based coatings (Todica et al., 2015). However, they are oil based chemicals, which are both expensive and toxic (Isikgor et al., 2015). Efforts have been put into generating more environmentally friendly acrylate-based copolymers including those with lignin (Kong et al., 2015). Figure 2.4 shows the reaction mechanisms of lignin and acrylic acid.

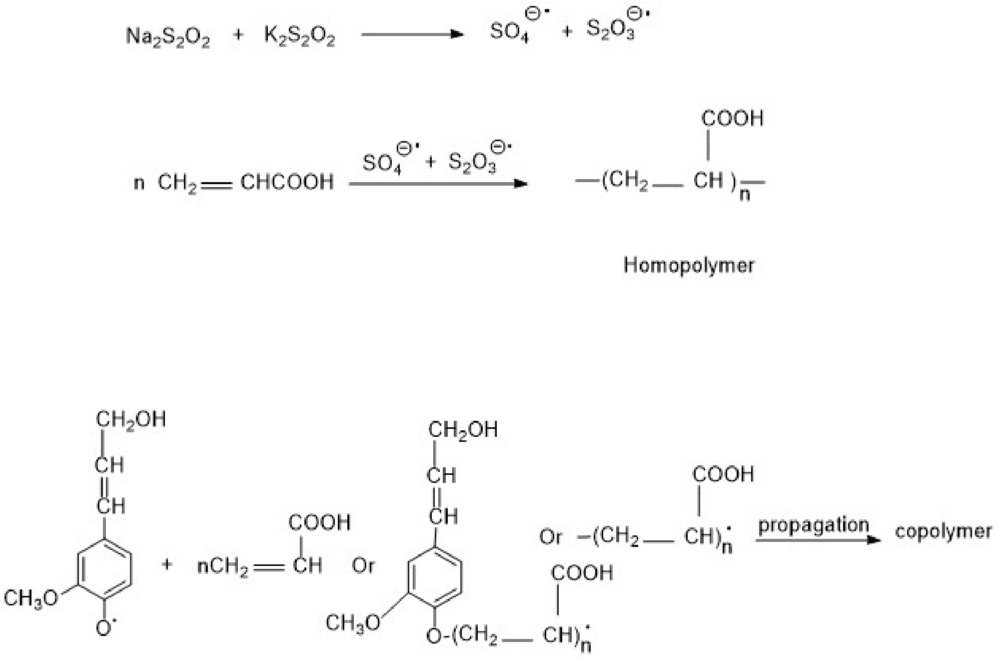


Figure 2.4: Reaction mechanism of copolymerization of acrylic acid with Kraft lignin (Kong et al., 2015)

In this reaction, which is similar to that of the acrylamide copolymerization reaction, the initiators, $Na_2S_2O_3$ and $K_2S_2O_8$, form sulphate radicals via a redox mechanism, which accelerates the polymerization of vinyl monomers and lignin. The sulphate radicals then react with the phenol group of kraft lignin to generate a phenoxy radical, which can participate in the copolymerization reaction (Kong et al., 2015). The copolymerization of lignin and acrylic acid has received some attention by other researchers (Table 2.2). In one study, lignosulfonate was copolymerized with acrylate to produce dispersants for drilling mud. The copolymerization of lignosulfonate with acrylate monomer under the conditions of 3.5 wt.% initiator, incubation at 70 °C for 4 h, and a lignin/acrylic acid molar ratio of 2/3 resulted in a copolymer with a high viscosity of 1.2 Pa/s and high molecular weight. Furthermore, the solubility of the copolymer was increased as monomer concentration and reaction time increased (Zahran et al., 2014).

Kraft lignin has also been modified with acrylic acid to produce lignin-acrylic acid copolymers. In one report, the copolymer was found to be highly water soluble, being produced under the conditions of kraft lignin concentration of 0.024 mol/L, acrylic acid concentration of 0.94 mol/L, 0.001 mol/L of *p*-toluenesulfonic as a catalyst, and incubated at 80 °C for 12 h (Ibrahim et al., 2006). In another study, the copolymerization of lignosulfonate with acrylic acid was performed for 2 h at 50 °C under the conditions of lignosulfonate/acrylic acid molar ratio of 1/1, an initiator dosage of hydrogen peroxide and potassium persulfate of 1.5 wt.% (Ye et al., 2014). Finally, kraft lignin was copolymerized with acrylic acid under the conditions of acrylic acid/lignin mole ratio of 8.0 mol/mol, an initiator dosage ($K_2S_2O_8$– $Na_2S_2O_3$) of 1.5 wt.% for 3 h at 70 °C. The resultant copolymer had a charge density of 1.86 meq/g and was water soluble at the concentration of 100 g/L (Kong et al., 2015).

Table 2.2: Copolymerization of different types of lignin with acrylic acid

Lignin type	Reaction conditions Lingin/AA molar ratio	Initiator, wt. %	Time, h	Temperature, ^{o}C	References
Lignosulfonate	2:3	3.5	4	70	(Zahran et al., 2014)
Kraft lignin	1:22	0.25 g	12	80	(Ibrahim et al., 2006)
Lignosulfonate	4:11	0.40g	2	50	(Ye et al., 2014).
Kraft lignin	1:8	1.5	3	70	(Kong et al., 2015)

2.2.4. Applications of acrylate/lignin copolymers

The lignin-based acrylate copolymer has been used in a variety of applications including as a flame retardant, drilling mud thinner, binder, hydrophobic and high water resistant composite, as well as aniline absorbent (Ibrahim et al., 2006). Lignosulfonate and acrylic acid copolymer were also used as dispersants for drilling mud (Zahran et al., 2014). In the latter application, the addition of the copolymer remarkably increased the viscosity of the solutions from 0.36 to 3.30 Pa/s, when present at a concentration of 30 % in water (Zahran et al., 2014).

In another study, kraft lignin was modified to be used as an additive in hydrocarbon drilling operations suitable for high temperature and high pressure operating conditions (Ibrahim et al, 2006). The water soluble lignin-based graft copolymer was prepared by means of a bulk copolymerization technique using *p*-toluenesulfonic acid (PTS) as a catalyst, producing a material with excellent thermal stability (Ibrahim et al., 2006). In addition, the copolymerization of acrylic acid and eucalyptus lignosulfonate calcium (by using Fenton's reagent, H_2O_2 and $FeCl_2$ as an initiators) led to a polymer, which could be applied as a dust depressant (Ye et al., 2012). By adding the eucalyptus lignosulfonate calcium to the copolymer, the Ph-OH group of lignin acted as the active center in the grafting reaction (Ye et al., 2014).

2.3. Pretreatment of lignin prior to acrylate copolymerization

Although the above section illustrates the promise of lignin copolymers, the chemical and physical properties often need to be matched more closely with the needs of a particular application. To do so, a number of researchers have studied how the modification of lignin prior to copolymerization can be used to enhance the performance of lignin-acrylate-based copolymers. The following section will detail some of the pretreatment methods, which have been described in Table 2.3.

2.3.1. Oxidized lignin and acrylic acid copolymers

The complicated structure of lignin impedes modification reactions (Matsushita, 2015). To alleviate this problem, hydrogen peroxide has been used to pretreat kraft lignin in order to break the structure of the lignin, and to remove existing carbonyl groups, resulting in a significant decrease in lignin molecular weight (He et al., 2015). As a result, resonance forms of phenoxyl radicals were produced and involved in the copolymerization reactions. In one study, the pretreatment conditions were a kraft lignin concentration of 0.2 mol/L, hydrogen peroxide concentration of 0.05 mol/L, and pH 10.5 for 2 h at 70 °C. The pretreated sample was then copolymerized under the conditions of kraft lignin/acrylic acid molar ratio of 8.0 mol/mol, 1.5 wt.% initiator (based on lignin mass), and pH 10.5 for 3 h at 70 °C (Rojith, 2013). The results showed that the pretreated lignin copolymer produced from oxidized lignin contained the expected carbonyl group peak at 1710 cm^{-1}. A similar result was reported in the copolymerization of softwood lignosulfonate with acrylic acid (Ye et al., 2012), indicating the general utility of this technique.

2.3.2. Methylated kraft lignin with acrylic acid

Similar to oxidation, kraft lignin can be methylated according to the method utilized by Sadeghifar et al. (2012). A mixture of lignin/dimethyl sulphate at the molar ratio of 1/1.5 was heated to 80 °C for 2 h, and the pH of the mixture was kept at 11–11.5 (Sadeghifar et al., 2012). The methylated and unmodified kraft lignin was copolymerized under the conditions of lignin/acrylic acid molar ratio of 8.0 mol/mol for 3 h at 70 °C with 1.5 wt.% initiator. This reaction occured when the lignin radicals driven from phenolic hydroxyl group participated in the copolymerization with acrylic acid. The results showed that the phenolic hydroxyl group content of methylated kraft lignin decreased from 1.73 meq/g to 0.87 meq/g after copolymerization. Acrylic acid was not able to graft onto lignin that does not have phenolic hydroxyl group, and the presence of aliphatic hydroxyl groups of kraft lignin didn’t facilitate the grafting of acrylic acid on kraft lignin, which indicated that the phenolic hydroxyl group of kraft lignin participated in the reaction, although the implcations of this finding remain unclear (Kong et al., 2015).

2.3.3. Acetylated kraft lignin with acrylic acid

Kraft lignin has also been acetylated prior to copolymerization under the conditions of 0.05 mol/L kraft lignin, 1.17 mol/L pyridine acetic anhydride concentration at 25 °C and then incubated in the dark for 72 h at room temperature. The pretreated samples were copolymerized under the conditions of lignin/acrylic acid molar ratio of 8.0 mol/mol, 1.5 wt.% initiator, for 3 h at 70 °C. The results demonstrated that the acetylation protected both the phenolic and aliphatic hydroxyl groups of lignin without impacting the other parts of lignin structure (Lundquist, 1980; Andes, 2006). The reaction of the acetylated lignin with acrylic acid did not proceed, which illustrated the occurrence of acrylic acid reaction on phenolic and aliphatic hydroxyl groups (Kong et al., 2015).

Table 2.3: Pretreated lignin followed by copolymerization

Lignin type	Reaction conditions						References
	Lignin/reagent molar ratio	Reagent	Initiator, wt.%	Time, h	Temperature, °C	pH	
Kraft lignin	2/5	Hydrogen peroxide	-	2	70	10.5	(Rojith, 2013)
Oxidized Kraft lignin	1/8	Acrylic acid	$K_2S_2O_8$ $Na_2S_2O_3$	3	70	-	(Kong et al, 2015)
Kraft lignin	1/1.5	Dimethyl sulphate	-	2	80	11 – 11.5	(Sadeghifar et al., 2012).
Methylated Kraft lignin	1/8	Acrylic acid	$K_2S_2O_8$ $Na_2S_2O_3$	3	70	-	(Kong et al, 2015)
Kraft lignin	1/21	Pyridine acetic	-	72	25	-	(Lundquist, 1980), (Andes, 2006)
Acetylated Kraft lignin	1:8	Acrylic acid	$K_2S_2O_8$ $Na_2S_2O_3$	3	70		(Kong et al, 2015)

2.3.4. Applications of pretreated lignin copolymers

The pretreatment of lignin impacts its properties and hence its end-use applications (Ouyang et al., 2009). For example, a lignin was modified by oxidation with hydrogen peroxide and the product was then copolymerized with acrylic acid (Chen et al., 1986). During the copolymerization, the carboxylic acid groups from acrylic acid reacted with the oxidized lignin copolymer molecules, which resulted in increased water solubility, charge density, and molecular weight. However, the application of the products was not assessed (Kong et al., 2015). In another study, the methylated copolymerized lignin was proposed to be used as a concrete water-reducer, water–coal–slurry dispersant, and pesticide adjuvant (Sadeghifar et al., 2012). Finally, acetylated lignin copolymerized with acrylic acid was used as dispersion modifier. The results showed that the acetylated lignin had a reduced brittleness without a sacrifice in the modulus of elasticity (Chung et al., 2013).

2.4. Methods to analyze the reaction performance

In the following sections the methods used to determine chemical reactions and the characteristics of the resulting polymers are reviewed. Understanding the polymerization reaction is the key to both designing and optimizing the reaction performance, with three methods; NMR, FTIR, and elemental analysis being commonly used by researchers.

2.4.1. NMR

Nuclear magnetic resonance (NMR) spectroscopy has been utilized to investigate the primary structure of lignin (Ede & Ralph, 1996). In NMR, the chemical compound is exposed to a oscillating magnetic field in the presence of a static magnetic field in order to determine the resonant frequency of the nuclei it contains. The structure of the material can be illucidated based on the the bonding arrangment in atoms. For example, the resonance of ^{1}H and ^{13}C has been used in monitoring reaction performance and the structure of chemicals, by which the types of ether and carbon-carbon linkages can be identified between the phenyl propene groups of lignin. Recently, phosphorus ^{31}P NMR was introduced to determine the amounts of the phenyl propene subunits of lignin (Pas et al., 2014).

2.4.2. FTIR

Fourier transform infrared spectroscopy (FTIR) provides a means to investigate the chemcial bonds present in various substiances (Dai et al., 2011). In lignin analysis, FTIR is a technique utilized to determine the functional groups attached to lignin and the relative content of phenolic hydroxyl groups (Faix and Bottcher, 1993).

2.4.3. Elemental analysis

Elemental analysis determines the organic elements present in the samples by means of their combustion. In this method, samples are burned in excess oxygen and the products of combustion, including carbon dioxide, water, nitric oxide and sulphur are collected and used for identifying the composition of the samples (Käldström et al., 2014). The analysis aids at obtaining an accurate determination of elemental composition (C/H/N/S) in a wide variety of chemical compounds. In lignin analysis, it allows for the investigation of the chemical formula of lignin before and after treatment by considering the weight percentage and atomic weight of each element (Fadeeva et al., 2008).

2.5. Methods to determine the properties of lignin-based copolymers

The chemical composition of the polymers is of great importance determining the applications of the product. The following sections briefly describe some of the key chemical and physical properties of polymers used in this study.

2.5.1. Charge density and functional group measurement

Charge density is defined as the quantity of electric charge attached to the sample (Pienta, 2001). It can be used to determine the charge of lignin products. It can also determine the efficiency of reactions, and if charged groups are attached to or detached from lignin during reactions, such as those occurring during sulfonation, carboxylation and amination. Conductometric titration is a preferred method used to determine the number of moles of the sulfonated group attached to lignin before and after copolymerization (Kong et al., 2015). Also, the aqueous conductometric titration method was used to measure the amount of carboxylated and phenolated groups attached to unmodified or modified lignin samples (Inwood, 2014).

2.5.2. Molecular weight determination (GPC and DLS)

Gel permeation chromatography (GPC) is one of the analytical techniques available for understanding the molecular weight of polymers. It can be utilized to characterize the composition of the phenyl propene monomers of lignin by which the weight average molecular weight (M_w), the number average molecular weight (M_n), polydispersity (M_w/M_n) and the most fundamental characteristic of a polymer; its molecular weight distribution, can be identified (Choi et al., 2001).

2.6. Methods to determine the performance of lignin-based products

In this section, some key aspects of polymer performance that influence their use are assessed. In the literature, little information is available regarding the impact of lignin based copolymers as flocculants which is the topic of this thesis.

2.6.1. Adsorption

Adsorption is extensively used in industry to separate dissolved chemicals from solutions. For example, it is used in wastewater treatment for minimizing heavy metal concentrations in surface waters (Suhas et al. 2007). Adsorbents can also change the surface chemistry of particles and facilitate their removal from suspensions. In this regard, it is notable that modified lignin can be adsorbed on the surface of suspended particles and facilitate their agglomeration, and accordingly, their removal. In one study, sulfonated lignin was adsorbed around 8.5 mg/g to cement particles, which was higher than that of commercial lignosulfonate (5.9 mg/g) (Ouyang et al., 2009). Another report demonstrated that modified lignin has a high adsorption capacity and can remove heavy metal ions of Zn^{2+}, Pb^{2+}, and Cd^{2+} (Celik & Demirbaş, 2005). Similarly, Wu and associates reported that lignin can be used in removing Cr(III) from wastewater (Wu et al., 2008). The literature gives little information regarding the adsorption characteristics of lignin copolymers. Therefore, one topic of this thesis is to study the adsorption performance of lignin copolymer on various suspended particles.

2.6.2. Zeta potential

Zeta potential is used to measure the electrical charge of suspensions, as well as the charge repulsion/attraction or the magnitude of the electrostatic charge between particles. This is of importance given that the zeta potential is one of the main parameters affecting the stability of suspensions. Furthermore, it is widely used when investigating the mechanism of flocculation and dispersion as it provides data regarding the stability of colloidal dispersions. As well, it relates the adsorption, zeta potential and flocculation performance of polymers. One report showed that the zeta potential absolute value of sulfonated lignin in cement particles was around 30 mV, which was higher than the zeta potential of lignosulfonate in cement particles of 26 mV. This is indicative of the presence of sulfonated lignin contributing to electrostatic repulsion forces among the cement particles more than lignosulfonate, making it a better option for use as a dispersant for the cement matrix (Ouyang et al., 2009). In another report, the zeta potential of a ceramic suspension was reduced from -20 mV to -30 mV at pH 6 by the addition of carboxymethylated lignin (Traiphol et al., 2010). However, it is unclear how sulfonated and copolymerized lignin will impact the zeta potential of suspensions as this has not previously been investigated.

2.6.3. Turbidity analysis

One method to assess the efficiency of flocculation is to monitor the clarity (turbidity) of suspensions as a function of flocculant concentration, given that turbidity is influenced by the size and number of particles suspended in solutions. For example, the addition of 25 mg/g carboxymethylated xylan to a clay suspension showed an increase in the relative turbidity of 1.25. Furthermore, by increasing the concentration of carboxymethylated xylan, the stability of clay suspension was increased (Konduri et al., 2015). In another study, the flocculation efficiency of lignin (methacryloyloxy)ethyl] trimethylammonium chloride (METAC) copolymer and lignin poly(methacryloyloxy)ethyl] trimethylammonium chloride (PMETAC) copolymer increased in a concentration dependent manner (Fatehi et al., 2016). This data is encouraging as it may show a potential application for lignin-copolymers. However, how sulfonated and copolymerzed lignin alter the turbidity of suspensions has not been investigated yet.

2.6.4. Dye Removal

Dye is a pollutant commonly present in the effluents of the textile industry. The removal of dyes from wastewater is therefore important for addressing concerns associated with discharge of often toxic dyes into the environment. Modified lignin has the potential to be used in the removal of pollutants due to their fundamental characteristics, such as hydrophobic nature and charge density (Suteu et al., 2010). The removal of dye from simulated wastewater was assessed using hydroxymethylated lignin. It was shown that charge neutralization was the main mechanism affecting the flocculation of dye particles (Fang et al., 2010). Charge neutralization would occur between the charges of modified lignin and cationic charges of dyes. Moreover, oxidized lignin has been utilized for removing cationic dyes from simulated wastewater (Couch et al., 2016) with ethyl violet and basic blue concentration being reduced by 70−80 wt.% and 80−95 wt.% respectively, when the dye concentration was 100 mg/L (Couch et al., 2016). In another study aminated lignin was produced, and its application as a flocculant led to 96 % removal of an anionic dye from the wastewater effluents (Wang et al., 2014). Moreover, Fang et al. (2010) used enzymatically generated lignin and rendered it cationic for anionic dye removal. The lignin-based product removed more than 95 % of dyes from the effluent with the dye present at a concentration of 50−250 mg/L (Fang et al., 2010). However, it is not clear how well sulfonated and copolymerized lignin is able to remove cationic dyes.

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Chapter 3: Sulfation, sulfomethylation and phenolation of softwood kraft lignin

Abstract

In this work, the modifications of softwood kraft lignin through sulfomethylation, phenolation, and sulfation were investigated. The sulfation was studied via sulfuric acid treatment under different conditions of reaction temperature and time as well as H_2SO_4/lignin molar ratio. The results indicated that the self-condensation of the guaiacyl phenyl propane subunits of lignin occured via sulfation. The optimum conditions for sulfation were at 160 °C, 3 h, and 6.5 molar ratio of H_2SO_4/lignin. The sulfomethylation of softwood kraft lignin with formaldehyde and sodium sulfite under various conditions, i.e. different lignin/sodium hydroxymethylsulfonate ratio, lignin concentration, and temperature was studied. Sulfomethylation enhanced the solubility and charge density of kraft lignin. The optimum conditions of sulfomethylation were found to be 0.5M NaOH concentration, 0.1 mol/mol lignin/sodium hydroxymethylsulfonate, 50 °C, 1 h and lignin concentration of 20 g/L. Moreover, softwood kraft lignin was phenolated with liquefied phenol in a sulphuric acid solution under the conditions of liquefied phenol/lignin molar ratio of 7.3, 4 h, 80 °C, and 60 wt.% H_2SO_4. Phenolation proved to be detrimental to solubility, and self-condensation of guaiacyl phenyl propane subunits of lignin during phenolation aided by sulphuric acid catalyst seemed to affect the reactivity of lignin.These reaction conditions were applicable to both types of lignin suggesting their general applicability to softwood kraft lignin.

3.1. Introduction

Lignin is the most abundant renewable resource after cellulose and provides an excellent source of inexpensive material available to create high-value products. However, kraft lignin has a low reactivity due to its complex structure. There is a multitude of inter-unit bonds of ether, which include β-O-4, α-O-4, 4-O-5 and carbon linkages on lignin. Approximately 50% of these bonds are β-O-4 ether linkages. Lignin is a highly-branched polymer containing a variety of functional groups including, but not limited to, aliphatic, phenolic hydroxyls, carboxylic, carbonyl and methoxyl groups. Lignin can be modified through these groups to improve its reactivity.

There are several methods to increase the reactivity of lignin including oxidation, hydroxymethylation, carboxymethylation, sulfation, sulfomethylation, and phenolation. Oxidation reduces the steric hindrances of lignin, while produces lignin with lower molecular weight and higher reactivity (He and Fatehi, 2015). The oxidation of lignin was also reported to form reactive catechol groups (Nagieb and Egypt, 1985; Olivares et al., 1988). The oxidation reaction caused non-uniformity in the structure of lignin which would affect its subsequent modification process. Nevertheless, the lower molecular weight lignin produced by oxidation could not be used as dispersants or flocculants (Matsushita & Yasuda, 2005). The hydroxymethylation adds a methoxy group to the aromatic ring, which increases the reaction sites and thus enhances the reactivity of lignin (Inwood, 2014). Carboxymethylation introduces carboxyl groups into lignin structure effectively, which improves its reactivity (Konduri et al., 2015). However, the aforementioned method might be expensive and/or complicated to industrially exploit.

Sulfomethylation and sulfation are more popular methods to modify lignin, and they are considered as industrially friendly procedures compared to hydroxymethylation and carboxymethylation (Yu et al., 2013). In the past, sulfation was used for modifying lignocellulosic materials (Shin and Rowell, 2005) and cellulose (Zhang et al., 2007) in order to create polyelectrolyte reactive products. Previously, the sulfonation reaction was conducted on polymers with aromatic rings or woody materials under different conditions by using a multitude of sulfonation agents including concentrated sulfuric acid for sulfonation of tertbutyl benzene (Kaandorp et al., 1963b), and benzene (Kaandorp et al., 1962), sulfonation of toluene (Kaandorp et al., 1963a), and polystyrene (Akovali and Ozkan, 1986). In another work, sulphuric acid (in vapor form) was used for sulfonating polystyrene beads (Kim et al., 1990). Moreover, a concentrated sulfuric acid was used as a catalyst on a macronet polystyrene backbone (Theodoropoulos et al., 1993) and chlorosulfonic acid to wood materials (Xie and Shi, 2011). The sulfomethylation reaction by using formaldehyde and sodium sulfite can introduce the methylene sulfonic group to lignin. Sulfomethylated lignin has been obtained from treating sugarcane bagasse lignin, esparto grass lignin or hardwood kraft lignin with sodium sulfite and formaldehyde (Li and Ge, 2011; Kamoun et al., 2003; Konduri and Fatehi, 2015). However, the sulfomethylation of softwood kraft lignin has not been studied, but it will provide an opportunity for producing reactive and water soluble products from softwood lignin, which is greatly available in the pulping industry.

In the past, the phenolation of lignin has also been proven to increase the number of phenolate groups on lignin and thus its reactivity (Alonso et al., 2005). Phenolation of lignin using liquid phenol would provide more sites on the aromatic structure of lignin. The phenolation of ammonium lignosulfonate was practiced for reparing phenolic resins (Alonso et al., 2005). Another study dealt with the phenolation of lignosulfonate to increase the content of phenolic hydroxyl groups and to simplify the structure of lignosulfonate (Zhao et al., 2000). Phenolation could increase the reactivity of softwood kraft lignin by introducing more sites.

In this chapter, the sulfation, sulfomethylation and phenolation were conducted on softwood kraft lignin under different conditions. Although these methods were investigated in other lignin types, available literature would not be very useful as the structure of lignin is different from source to source. In other words, as the properties of lignin impacts its modification performance, the results available in the literature cannot be expected for different lignin samples. In this work, the properties of the raw materials and products were evaluated using different tools. The solubility of the modified lignin products was also assessed. The main aim of this chapter was to explore the sulfation, sulfomethylation and phenolation of softwood kraft lignin as means to pretreat kraft lignin prior to copolymerization that is discussed in the next chapter.

3.2. Experimental

3.2.1. Raw materials

In this work, two samples of softwood kraft lignin were used. The first was extracted from black liquor using Lignoforce technologies (kraft lignin-1) and the second one was extracted via acidification of black liquor (kraft lignin-2). Sodium hydroxide, liquefied phenol (>89% purity), formaldehyde solution (30%), and poly (diallyldimethylammonium chloride) solution (PDADMAC) with a molecular weight (MW) of 100,000-200,000 g/mol (20 wt.% in water) were all purchased from Sigma-Aldrich. Anionic polyvinyl sulfate (PVSK) with a MW of 100,000-200,000 g/mol (98.4 wt.% esterified) was purchased from Sigma-Aldrich. Tetrahydrofuran (99.9 wt. %), acetyl bromide (99 wt. %), acetic acid (99.7 wt. %) and sodium sulfite, sulfuric acid (98% purity) were obtained from Sigma Aldrich and used as received.

3.2.2. Sulfation of lignin

Different types of lignin (5 g) were reacted with 17– 80 g of H_2SO_4 (72 wt.%) in a glass flask, vortexed for 1 min at 2900 rpm with a Fisher Scientific Mini Vortexor (to ensure homogenous mixture). Then, the samples were placed in an oil bath and the reaction repeated under different temperatures ranging 140-160 °C, and time ranging 1-3 h. The reaction factors were lignin/$H_2SO_{4\,(aq)}$ molar ratios of 6.5-30, reaction times of 1-3 h at the temperature of 140°C- 160 °C. After the reactions, the sulfation reaction was stopped by neutralizing the sample with NaOH (2.5 M). The reaction mixtures were cooled to room temperature, and unreacted chemicals and salts were separated by dialysis membranes with a molecular weight cut-off of 1000 g/mol, while changing the water every 2 h for the first day and then twice a day for 2 days. Then, the product was dried in an oven at 105 °C overnight.

3.2.3. Sulfomethylation of lignin

The sulfomethylation of lignin samples was performed via mixing kraft lignin (1-5 g) with formaldehyde and sodium sulfite under various conditions. The reaction parameters were lignin/sodium hydroxymethylsulfonate ratios of 0.02- 0.1 mol/mol, NaOH concentration of 0.5 molar concentration, reaction temperature of 30-50 °C, reaction time 1 h, and lignin concentration of 20 g/L. All of the reactions were carried out in a 250 mL three-neck glass flask under a constant stirring of 180 rpm. After reaction, the reaction media were cooled to the room temperature, then the reaction was neutralized with 1 M sulfuric acid. Unreacted sodium hydroxide, sodium sulfite and formaldehyde were separated from sulfomethylated lignin by dialysis membranes with the molecular weight cut-off of 1,000 g/mol in 2 days while changing water twice a day for for purification. The dialysed samples were dried in an oven at 105 °C overnight.

3.2.4. Phenolation of lignin

The phenolation of kraft lignin was conducted as described in the literature on the softwood kraft lignin (Inwood, 2014). In this study, 2g of kraft lignin was mixed with liquefied phenol under the conditions of liquefied phenol/lignin molar ratio of 7.3, 4 h and 80 °C. The reaction was performed with 90 mL of 60% H_2SO_4, which followed by a dilution to 1500 mL of water and boiling for two hours. Then, the product was dried in an oven at 105 °C overnight.

3.2.5. Solubility and charge density analyses

To measure the solubility of lignin samples, 0.2 g of modified lignin was suspended in 20 mL of deionized water by shaking at 150 rpm at 30 °C for 2 h in a water bath shaker. Afterwards, samples were centrifuged at 1500 rpm for 10 min in order to separate soluble and insoluble lignin from the solution. The solution section was taken for charge density analysis of the soluble lignin, while the supernatant was dried at 60 °C overnight in an oven. Then, the concentration of lignin in the supernatants was determined, which helped measure the solubility of lignin samples via equation 1:

$$\text{Water Solubility (wt. \%)} = \frac{\text{Mass of dissolved lignin}}{\text{Initial mass of lignin}} \times 100 \qquad (1)$$

To measure the charge density of lignin samples, the modified lignin was initially dried at 105 °C overnight to remove moisture. Then, 0.2 g of lignin samples were dissolved in 20 mL of deionized water and incubated for 2 h at 30 °C in a water bath shaker at 150 rpm. After the incubation, the samples were centrifuged at 1500 rpm for 10 min to separate soluble and insoluble lignin from the solution. The solution section was taken for charge density analysis of soluble lignin, while precipitated lignin was dried in the oven at 60 °C for charge density analysis of insoluble lignin samples. The charge density of soluble lignin samples was determined by direct titration, while the charge density of insoluble samples was identified by back titration. The charge of soluble samples was measured by Mutek PCD-04 titrator (Herrsching, Germany), where 1 mL of lignin sample solutions was added to the cell of the particle charge detector, and titrated against PDADMAC standard solution (~0.005M). The volume of PDADMAC solution titrated against the samples was considered for measuring the charge density using equation 2:

$$\text{Charge Density (meq/g)} = \frac{\text{vol of titrant} \times \text{concentration of titrant}}{\text{mass of lignin}} \times \text{dilution factor } (if\ any) \quad (2)$$

To measure the charge density of insoluble samples, 0.05 g of dried insoluble lignin samples was mixed with PVSK standard solution (~0.005M) and stirred at 150 rpm and 30 °C for 1 h. The samples were then filtered and the concentration of PVSK solutions before and after mixing with lignin samples in the filtrates was determined by titrating with the standard solution PDADMAC, and the charge density of insoluble lignin sample was determined using equation 3:

$$\text{Insoluble lignin charge density (meq/g)} = \frac{(\text{vol.PVSK for control} - \text{vol.PVSK for sample}) \times \text{conc.PVSK}}{\text{mass of lignin}} \times \frac{\text{total mass PDADMAC}}{\text{mass PDADMAC}} \quad (3)$$

3.2.6. Degree of sulfation

A conductometric titration was used for measuring the number of moles of sulfonated group attached to lignin before and after sulfation. In this method, a 1% wt. solution of samples was prepared with distilled water and the samples were shaken in a Boekel Scientific water bath operating at a temperature of 30 °C and 100 rpm for 1 h. Then, 100 mL of deionized water was added to the mixtures and the pH of the solutions were then adjusted to 3. The mixtures were titrated with the 0.1 M NaOH standard solution using an automatic potentiometer, Metrohm, 905 Titrado, Switzerland. Finally, the sulfonation degree was calculated following equation 4:

$$\text{Degree of sulfonation} = \frac{C1V1 - C2V2}{M} \quad (4)$$

where C_1 is the concentration of NaOH, V_1 is the volume of NaOH, C_2 is the concentration of HCl, V_2 is the volume of HCl, and M is mass of the of lignin samples (0.06 g).

3.2.7. Phenolic hydroxyl and carboxyl group analyses

A conductometric titration was considered to determine the number of moles of phenolic hydroxyl and the carboxyl groups attached to lignin before and after modification. In this method, a 0.06 g of sample was mixed with 1mL of 0.8M potassium acid and 4 mL of 0.5% *para*-hydroxybenzoic acid (as an internal standard sample). Then, 100 mL of deionized water was added to the mixture. The mixture was titrated with 0.1 M HCl standard solution using an automatic potentiometer, Metrohm, 905 Titrado, Switzerland. The amounts of phenolic hydroxyl and carboxyl groups in the modified lignin were calculated based on equations 5 and 6 :

$$\text{Phenolic hydroxyl group (mmol/g)} = \frac{[(V2'-V1')-(V2-V1)]\times C}{m} \tag{5}$$

$$\text{Carboxyl group (mmol/g)} = \frac{[(V3'-V2')-(V3-V2)]\times C}{m} \tag{6}$$

where *C* is the molar concentration of HCl standard solution, *m* is the dried weight of lignin samples (g), V_1,V_2,V_3 are the first, second and third endpoint volume of HCl (mL), and V_1’,V_2’,V_3’ are the first, second and third endpoint volume of HCl standard solution (mL) used for lignin samples.

3.2.8. Elemental analysis

The elemental analysis of the lignin samples was conducted using an elemental analyzer (Elementar, Vario Micro, Germans) as stated in the literature (Fadeeva et al., 2008). In this set of experiments, the samples were first dried in an oven at 105 °C overnight in order to remove any moisture. Approximately, 2 mg of unmodified, sulfated, sulfomethylated and phenolated lignin samples were used in this analysis for measuring their carbon, hydrogen, nitrogen and oxygen contents by following a method described elsewhere (Jahan et al., 2012). The elemental analysis helped investigate the theoretical chemical formula of the samples before and after the modification reactions.

3.2.9. Molecular weight analysis

Unmodified lignin, sulfated lignin, sulfomethylated, and phenolated lignin samples were not soluble in water. Thus, the determination of molecular weight of the samples was not possible with a gel permeation chromatography. Therefore, the molecular weight of these samples was analyzed with a static light scattering (SLS) instrument, which was attached to a goniometer, Brookhaven BI-200SM, Holtsville, NY, USA. In this analysis, the solutions of the samples were first prepared at different concentrations of 0.2, 0.4, 0.6, 0.8 and 1.0 wt.% in alkaline aqueous solutions (NaOH solution) at pH 12 (samples were soluble at this pH) and room temperature. The solutions were filtered using a nylon syringe filter with 0.45μm pore size and 30 mm diameter (Celltreat Scientific Products). In the measurement, the laser polarized light wavelength was set at 637 nm, and the intensities of the scattered light were measured at different angles (from 15 ° to 155 °) for each solution. The data was compiled and analyzed using BIC Zimm Plot software (Couch et al, 2016).

3.3. Results and discussion

3.3.1. Properties of unmodified lignin

The properties of softwood kraft lignin samples are shown in Table 3.1. The results demonstrated that UL1 had a molecular weight of 35000 g/mol, which is higher than reported values and will be attributed to variations in the origins of tress lignin samples are from and pulping process conditions. The molecular weight of UL2 was 17000 g/mol. One study reports that the molecular weight of kraft lignin was 17,890 g/mol, while M_w was 5,150 g/mol, and M_n of the kraft lignin was 3,473 (Kong et al., 2015). Another study showed that the hardwood kraft lignin's molecular weight, M_w, was between 5,000 to 15,000 g/mol (Luque et al., 1994); whereas the M_w and M_n of softwood kraft lignin recovered by Lignotech from black liquor were reported to be 8,900-11,119 g/mol and 200 to 2,755 g/mol, respectively (Baumberger et al., 2007). In one report, the molecular weight of lignin generated from milled softwood was 10,700 g/mol (Meister, 2002). Another work on softwood lignosulfonate reported an average molecular weight of 36,000 – 61,000 g/mol.

It is evident that UL1 contained 47.7% carbon, 4.7% hydrogen, 46.27% oxygen, and 1.26% sulfur, while UL2 contained 61.6% carbon, 5.6% hydrogen, 31.02% oxygen, and 1.69% sulfur. In another study, 61.26% carbon, 5.9% hydrogen and 8.7% sulfur were reported for softwood kraft lignin (Helander et al., 2013). In the past, the elemental analysis of hardwood kraft lignin was reported to have 64.76% carbon, 5.78% hydrogen, 26.78% oxygen and 1.05 % sulfur (Konduri et al., 2015). Soda lignin contained 54.39% carbon, 5.72% hydrogen, and 39.25% oxegen (Wang et al., 2016). Moreover, the carboxylation degree of UL1&2 samples were found to be 0.8 meq/g, and 0.9 meq/g, respectively. Similarly, the phenolation degree for both unmodified lignin was 0.7meq/g, while the charge density of UL1 was 0.29 meq/g, and 0.72 meq/g for UL2.

Table 3.1. Properties of unmodified lignin studied in this work and reported in literature

Lignin	**^{1}MW, g/mol**	**Elemental Analysis**					**Charge density meq/g**	**Carboxylate (mmol/g)**	**Phenolated group (mmol/g)**	**Reference**
		C%	H%	O%	N%	S%				

UL1	35000	47.77	4.70	46.27[a]	0	1.26	0.29	0.8	0.7	[2]PS
UL2	17000	61.63	5.66	31.02	0	1.69	0.72	0.9	0.6	PS
Hardwood kraft lignin	22,746	64.76	5.78	26.78	0.03	1.05	[3]NR	0.03	NR	(Konduri et al., 2015)
Soda lignin	NR	54.39	5.72	39.25	0.03	ND	NR	NR	NR	(Wang et al., 2016)
Softwood kraft lignin	NR	61.26	5.9	NR	NR	8.7	NR	NR	NR	(Helander et al., 2013)
Kraft lignin	17,890	NR	NR	NR	NR	NR	NR	NR	NR	(Kong et al., 2015)
Softwood kraft lignin	10,700	NR	NR	NR	NR	NR	NR	NR	NR	(Meister, 2002)
Softwood lignosulfonate	36,000 - 61,000	NR	NR	NR	NR	NR	NR	NR	NR	(Luque et al., 1994)
Hardwood kraft lignin	5000-15,000	NR	NR	NR	NR	NR	NR	NR	NR	(Luque et al., 1994)
Softwood kraft lignin	8,900-11,119	NR	NR	NR	NR	NR	NR	NR	NR	(Baumberger et al., 2007)

[1]MW: Molecular weight, [2]PS: Present work, [3]NR: Not reported, a: By difference.

3.3.2. Sulfation of lignin

Figure 3.1 illustrates the condensation of lignin under acidic conditions, the α position and the aromatic *ortho* position in kraft lignin could react with strong sulfonating agent (Cerfontain et al., 1985).

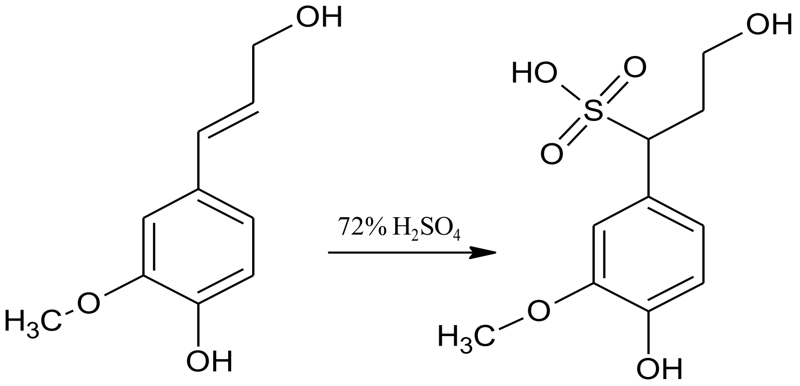


Figure 3.1. The scheme of sulfation of lignin (Inwood, 2014)

The effect of the reaction conditions on the charge density and solubility of SL was investigated to determine how to best conduct the modification. Table 3.2 illustrates the charge density of soluble lignin (CDSL), the charge density of insoluble lignin (CDIL), and the solubility of sulfuric acid treated lignin SL. The CDSL, CDIL, and the solubility were decreased by increasing the mole ratio of sulfuric acid to lignin. Conversely, by increasing the acid/lignin ratio (6.5 to 13), the amount of ion-exchange capacity increased due to an increase in a sulfonated group attached to novolac-lignin and novolac-hydroxymethylated lignin in another study (Zoumpoulakis et al., 2001). As the condensation and sulfation may occur simultaneously, the product with a greater stability will dominate. The self-condensed guaiacyl provided a product with greater stability, which was the main product of this process (Shimada et al., 1997).

Table 3.2. The charge density of soluble lignin (CDSL), the charge density of insoluble lignin (CDIL), and solubility of SL1, and SL2 as a function of H_2SO_4/lignin molar ratio, temperature and time.

H_2SO_4/lignin, mol/mol	**Time, h**	**Temperature, °C**	**CDSL, meq/g**		**CDIL, meq/g**		**Solubility, wt.%**	
			SL1	SL2	SL1	SL2	SL1	SL2
6.5	1	140	0.81	0.85	0.24	0.25	14.90	15.90
6.5	1	160	1.90	1.95	0.26	0.26	12.80	12.30
15	1	160	0.17	0.17	0.13	0.15	15.24	16.50
30	1	160	0.16	0.17	0.24	0.20	9.20	9.50
6.5	3	160	0.09	0.10	0.18	0.19	34.73	35.00

The results also show that, as temperature enhanced, the charge density of soluble lignin increased from 0.8 meq/g to 1.9 meq/g. Evidently, by extending the reaction time, the charge density of soluble lignin decreased from 0.2 meq/g to 0.09 meq/g. However, the solubility increased from 15.2 wt.% to 34.7 wt.%. Also, SL2 had the same results of charge density and solubility of SL1. In the literature, the time extension will provide conditions for the production of a more stable product; which could be the self-condensed guaiacyl product in this case (Shimada et al., 1997). This experiment was repeated using lignin type 2 and gave largely similar results (as data shown in lignin-2).

3.3.3. Sulfomethylation of lignin

The sulfomethylation is a reaction where the methylene sulfonic group is added to lignin. Figure 3.2 shows the reaction scheme for the sulfomethylation of lignin. In this reaction, methylene sulfonic group was mainly introduced to ortho position of the phenolic hydroxyl group because the group acted as an activator in the reaction. The sulfomethylation of lignin was performed under alkali conditions, while formaldehyde provided methyl group, and sodium sulfite contained sulfonated group for sulfomethylation. In this reaction, in Figure 3.2. (a) the OH group of lignin could react with strong base such as NaOH to generate the alkoxide group (Figure 3.2a). Simultaneously, sodium hydroxymethane was sulfonated, which was formed as a result of the reaction of sodium sulfite and formaldehyde. Then, sodium hydroxymethane reacted with the generated nucleophile, which introduced sodium sulfomethyl group by replacing Na^+O^- in the lignin, and produced sulfomethylated lignin. As seen in Figure 3.2. (b), NaOH reacted with sodium sulfite to produce sodium thiosulfate, which would be a by-product of this reaction (Gordin, 1913).

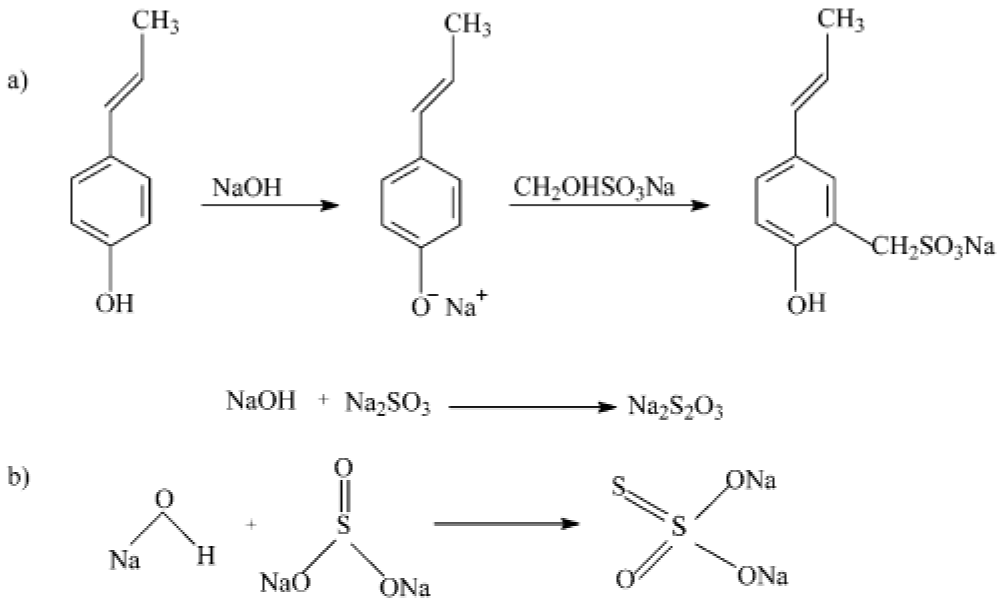


Figure 3.2. a) Sulfomethylation of lignin and b) undesired sodium thiosulfate production (Konduri & Fatehi, 2015)

Table 3.3 lists the charge density and solubility of SML samples that were produced under different temperatures and sodium hydroxymethylsulfonate ratios. By increasing the reaction temperature from 30 to 50 °C, the charge density and the solubility of kraft lignin increased to 1.50 meq/g and almost 100 wt.%, respectively. This is a lower reaction temperature than previously reported in the literature by Pang and his coworkers on the sulfomethylation of calcium lignosulfonate, in which the maximum sulfonation degree of 1.23 mmol/g was obtained at 90 °C (Pang et al., 2008). In another work, the modification of hardwood lignin with formaldehyde and sodium sulfite was obtained at 100 °C, and showed the charge density of -1.60 meq/g with sulfonated group content of 1.48 meq/g (Konduri and Fatehi, 2015). Similarly, the treatment of softwood kraft lignin with formaldehyde and sodium sulfite at (100 °C) resulted in the sulfonation degree of 1.45 meq/g (Hu, 2002). Additionally, the sulfonation of wheat straw hydroxymethyl ethanol lignin with sodium sulfite increased the solubility of lignin from 1 wt.% to 60 wt.% (Li et al., 2011).

Furthermore, the maximum charge density and solubility of 1.50 meq/g and 100 wt. % were obtained at 0.1 mol ratio (i.e. the highest ratio studied). Improving the reaction efficiency by increasing sodium hydroxymethylsulfonate in the solution led to the increase in charge density and solubility of lignin. In the literature, the molar ratio of 0.6 lignin to sodium hydroxymethylsulfonate was found to be the optimum ratio for producing a dispersant for gypsum (Matsushita et al., 2005). In the past, the sulfomethylation of alkali lignin from corn stalk resulted in the maximum sulfonic group content of 1.29 mmol/g at 1/1/0.5 weight ratio of lignin/sodium sulfite/formaldehyde (Wu et al., 2012). Previously, hardwood kraft lignin was modified with formaldehyde and sodium sulfite under an alkali condition, and the sulfomethylated lignin had 1.48 mmol/g of the sulfonated group at 0.6 mol/mol lignin/sodium hydroxymethylsulfonate ratio (Konduri and Fatehi, 2015).

Table 3.3. Effect of temperature and mole ratio of lignin/sodium hydroxymethylsulfonate on the charge density (CDSL) and solubility of SML1 and SML2.

Conc. mol/mol	**Temperature, °C**	**CDSL meq/g**		**CDIL meq/g**		**Solubility, wt.%**	
		SML1	SML2	SML1	SML2	SML1	SML2
0.1	30	1.08	1.00	0.09	0.09	4.41	5.11
0.1	40	0.82	0.99	0.04	0.06	7.98	8.08
0.1	50	1.50	1.55	-	-	99.0	99.0
0.05	50	0.93	0.97	-	-	96.0	96.5
0.02	50	0.91	0.93	-	-	96.5	96.5

The results demonstrated that the maximum charge density of 1.50 meq/g and solubility of 99 wt. % were obtained at 0.1 mol/mol sodium hydroxymethylsulfonate/lignin concentration. The increase in the charge density and solubility was due to more collisions of reagents at higher concentrations (Elkin and Shorygina, 1966). Also, by increasing the reaction temperature from 30 to 50 °C, the charge density and solubility of kraft lignin increased to 1.50 meq/g and 99 wt. %, respectively. Raising the temperature not only reduced the viscosity of reaction mixture (Thirumaleshwar, 2009), but also impacted the diffusion and collision of reagents and kraft lignin, which resulted in a decrease in reaction efficiency and thus charge density and solubility (Bruden and Schoenmakers, 2010). As with SL, SML2 resulted in similar results to that of SML1 (as data shown in lignin-2).

3.3.4. Phenolation of lignin

Figure 3.3 shows the reaction scheme of phenolation of lignin. It is clear that the phenolation of lignin would increase the reaction sites by adding two more sites ortho relative to hydroxide groups on the attached phenol. In other words, the phenol group attached to the α position in the double bond of lignin and provided more sites on the aromatic part for reaction.

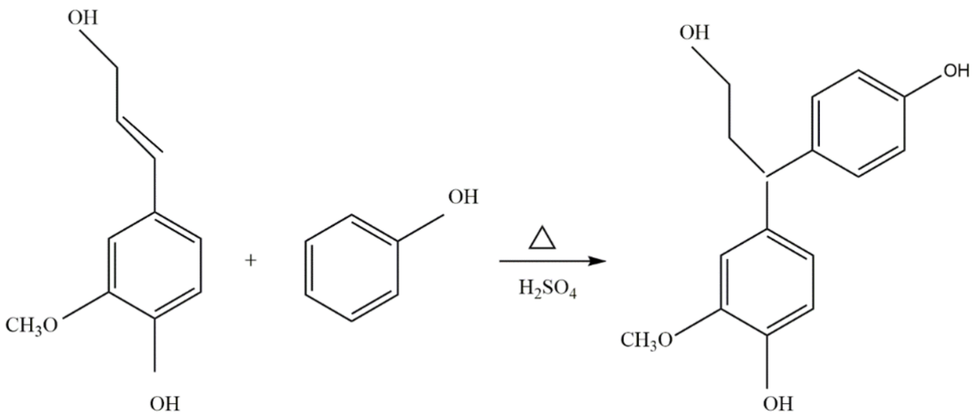


Figure 3.3. The scheme of phenolation of lignin (Inwood, 2014)

The results of the phenolation were increased the solubility of both types of kraft lignin from 5.25 wt.% to 81.34 wt.%; while the charge density remained the same because no charged group was added to lignin. In the past, the phenolation of lignin was performed with 72% and 60% H_2SO_4 (Matsushita et al., 2003; Yasuda et al., 1980). Previosuly on the phenolation of lignin, the optimum conditions were a phenol/lignin molar ratio of 7.3 mol/mol, 4 h, 80 °C, reacting in a 90 mL of 60 wt.% H_2SO_4, which generated lignin with high reactivity (Inwood, 2014).

3.3.5. Selected conditions

The results indicated that softwood kraft lignin is successfully modified to produce SL, SML, or PL but, the particular reaction conditions required vary from those in the literature derived from other lignin. In this study, the following reaction conditions were chosen: The optimum reaction conditions for SL were a temperature of 160 °C, the reaction time of 3 h, and H_2SO_4/lignin molar ratio of 6.5. The optimum reaction conditions for the SML were a temperature of 50°C, the reaction time of 1 h, 0.5 moles NaOH concentration, 0.1 mol/mol lignin/sodium hydroxymethylsulfonate, and 20 g/L lignin concentration. The selected conditions for the synthesis of PL were a phenol/lignin molar ratio of 7.3, the temperature of 80°C, the reaction time of 4 h (Inwood, 2014).

3.3.6. Properties of sulfated, sulfomethylated and phenolated lignin

The results of molecular weight analysis for unmodified and modified kraft lignin samples are provided in Table 3.4. The MW of SL1 was 68,000 g/mol, while SL2 was 51000 g/mol. The SML1 96,000 g/mol, SML2 97,000 g/mol. The higher molecular weight of sulfomethylated lignin than unmodified lignin was due to the replacement of hydroxyl groups with sulfomethyl groups in the reaction, which lead to increased molecular weight (Konduri & Fatehi, 2015; Ouyang et al., 2009).

In the past, formaldehyde and sodium sulfite increased the molecular weight of lignin after modification (20,650 g/mol versus 2,378 g/mol) (Yu et al., 2013). The molecular weight of phenolated lignin-1 & 2 were 23,000 g/mol and 21,000 g/mol, respectively. The drop in molecular weight can be attributed to the cleaving of ether bonds (Hu et al., 2011b). As can be seen, the molecular weight of SL, SML and PL were detected by SLS, due to solubility issues on tetrahydrofuran after acetylation and as such Mn was not possible to determine.

The results of the elemental analysis of unmodified and modified lignin are also provided in Table 3.4. It is seen that sulfur contents of lignin were increased and the amount of hydrogen decreased in SL and SML. Based on these results, the sulfonate group of lignin samples of both types of lignin was estimated to be higher in SL, and SML than UL, and PL. (Madzhidova, 1998). The results in Table 3.4 facilitated the determination of chemical formula of lignin as $C_9H_{10.62}S_{0.007}$ for UL1 as $C_9H_{8.01}S_{0.009}$ for UL2, $C_9H_{8.10}S_{0.03}$ for SL1, $C_9H_{7.92}S_{0.03}$ for SL2, $C_9H_{9.72}S_{0.03}$ for SML1, $C_9H_{9.72}S_{0.03}$ for SML2, $C_9H_{9.91}S_{0.009}$ for PL1, and $C_9H_{9.81}S_{0.008}$ for PL2.

The sulfonation amount of of SL1 and SL2 were determined to be 1.72 and 1.66 mmol/g respectively, which are close to the charge density of SL1 of 1.90 meq/g and SL2 of 1.88 meq/g. Also, The sulfonation amount of both SML1 and SML2 were 1.32 mmol/g and the charge density of both were 1.50 meq/g.SL1, SML1, and PL1 and SL2, SML2, and SL2 showed an increase in carboxylate group content from 0.2 to 1.90 mmol/g.

Table 3.4. Properties of modified lignin studied in this work.

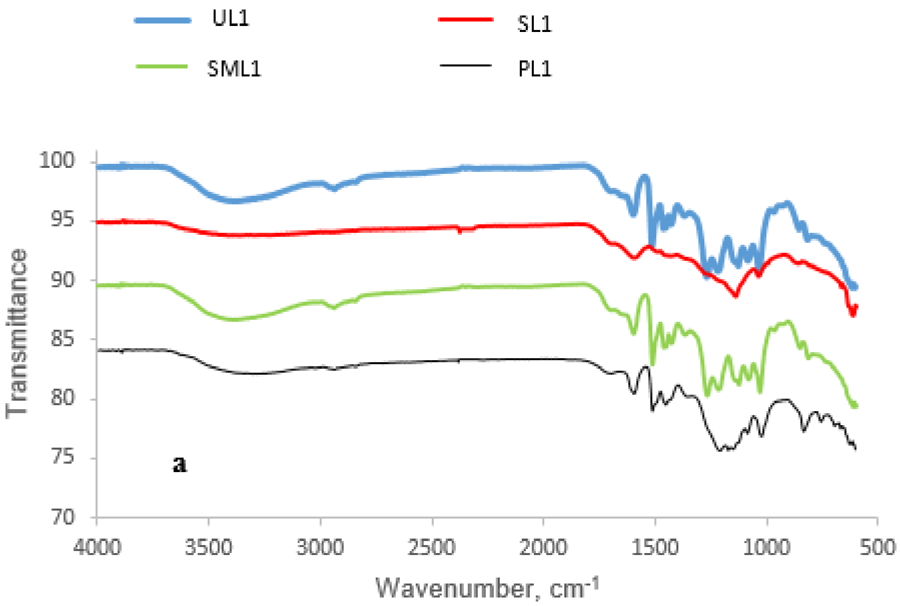
Lignin	**[1]MW, g/mol**	**Elemental Analysis**					**Charge density meq/g**	**COOH(mmol/g)**	**Phenolated group (mmol/g)**	**SO_3^- group (mmol/g)**	**Reference**
		C%	H%	O%	N%	S%					
UL1	35000	47.77	4.70	[3]NR	0	1.26	0.29	0.8	0.7	-	[2]PS
UL2	17000	61.63	4.66	NR	0	1.69	0.72	0.9	0.6	-	PS
SL1	68000	48.04	3.65	NR	0	4.45	1.90	2.05	2.25	1.72	PS
SL2	51000	51.35	3.84	NR	0	4.18	1.88	2.80	1.70	1.66	PS
SML1	96000	54.42	4.94	NR	0	5.21	1.50	2.05	1.60	1.32	PS
SML2	97000	54.14	4.92	NR	0	5.01	1.55	2.30	1.20	1.33	PS

PL1	23000	60.00	5.53	NR	0.16	1.99	2.02	1.25	1.30	-	PS
PL2	21000	61.62	5.62	NR	0.19	1.44	1.89	1.97	0.98	-	PS

[1]MW: Molecular weight, [2]PS: Present work, [3]NR: Not reported.

3.3.7. FTIR analysis

The FTIR spectra of UL1, SL1, SML1, and PL1 (a) andUL2, SL2, SML2, and PL2 (b) are presented in Figure 3.4. There exists a strong and broad signal at around 3416 cm^{-1}, which is the characteristic of the hydroxide group or phenolic compounds (Ibrahim et al., 2004). The peaks in the sulfomethylation sample SML at 2380 cm^{-1} and 2303 cm^{-1} were associated with C-H stretching of methyl or methylene groups. In all samples, the increase in absorption peaks at 1597 cm^{-1} and 1510 cm^{-1} was attributed to the aromatic skeletal vibration (Yu et al., 2013). The peaks at 1448 cm^{-1} and 1379 cm^{-1} corresponded to C-H bending and C-H stretching of methylene groups, were significantly increase in SML sample and decrease in PL sample and is lesser in SL sample. The peak at 1269 cm^{-1} could be attributed to guaiacyl breathing with C=O stretching and with the stretching of aromatic C-O bond (Malutan et al., 2008). The absorption peaks at 1032 cm^{-1} and 1018 cm^{-1} of SL, PL, and SMLwere attributed to sulfate groups, which were not present in UL and confirmed the grafting of sulfonated groups to the modified lignin during sulfation, sulfomethylation, and phenolation reactions.



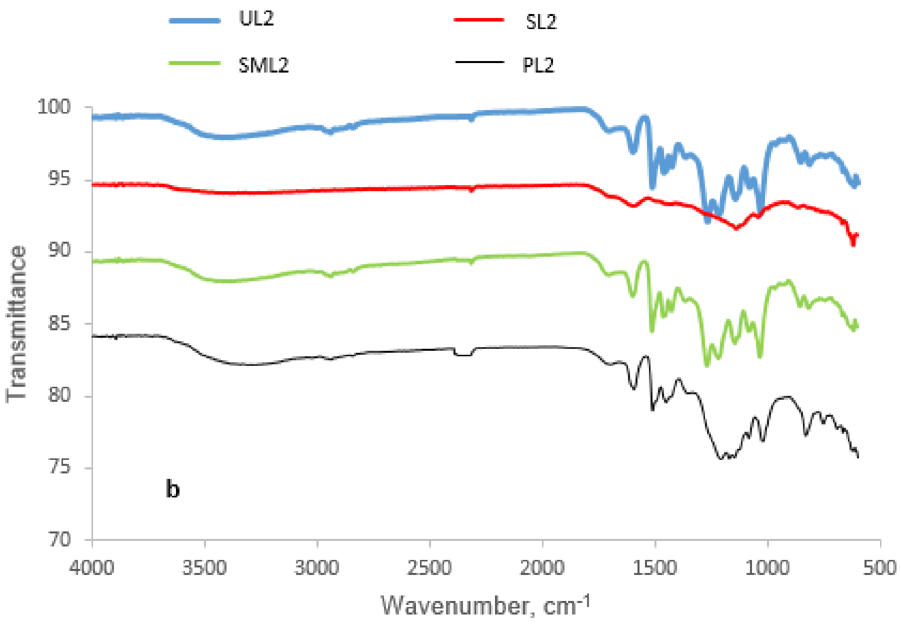


Figure 3.4. FTIR spectra of (a) UL1 and SL1, SML1 and PL1, and (b) UL2, SL2, SML2 and PL2.

3.4. Conclusions

SL exhibited a solubility of 15.2% and was obtained under the conditions of 160 °C, 3 h, and 6.5 molar ratio of H_2SO_4/lignin. SML exhibited a solubility of 99% and was obtained under the conditions of 50 °C, time of 1 h and 20 g/L lignin concentration, 0.5 moles NaOH concentration, and 0.1 mol/mol lignin/sodium hydroxymethylsulfonate. PL exhibited a solubility of 81.34% and was obtained under the conditions of 80 °C, 4 h, 14.55 phenol/lignin molar ratio with a 60% sulfuric acid. The SLS analysis demonstrated that the molecular weight of SL1 and SL2 were 68,000 g/mol, 51,000 g/mol. The molecular weight of SML1 and SML2 96,000 g/mol, 97,000 were greater than the molecular weight of UL1 and UL2, 35,000 g/mol, and 17,000 due to the replacement of hydroxyl groups with sulfomethyl groups in sulfomethylated lignin. The molecular weight of PL1&2 was determined to be smaller than kraft lignin, with a molecular weight 23,000 g/mol and 21,000 g/mol, respectively. The decrease in molecular weight is associated with hydrolysis underneath acidic conditions. The charge density of the SL, SML, and PL were 1.90, 1.50, 0.25 meq/g, respectively. Moreover, the number of reactive functional groups was increased by phenolation. All such findings support the conclusion that lignin was successfully modified, which was also confirmed by FTIR. These lignin samples will be utilized to studies lignin copolymers in next chapter.

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Chapter 4: Copolymerization of modified lignin with acrylic acid

Abstract

In this chapter, the copolymerization of UL, SL, SML, and PL with acrylic acid was investigated under various reaction conditions. The main objective of this chapter was to investigate the copolymerization of modified kraft lignin to produce water soluble kraft lignin with an anionic charge density. The mechanism of the copolymerization of unmodified/modified kraft lignin with acrylic acid was also discussed. SL, SML, and PL lignin were copolymerized under the conditions of 0.35 mol/L KL, 8 mol/mol AA/KL, 1.5 wt.% initiator, 70 ºC, 3 h and pH 2. The lignin copolymer was characterized by a particle charge detector, conductometric titrator, GPC, Fourier transform infrared (FTIR) spectrophotometry and TGA. The results showed the maximum charge densities of 11.64, 10.03, 10.57 and 10.30 meq/g and maximum solubilities of 85.5%, 100%, 100% and 100% for SLA, SMLA, PLA and ULA copolymers, respectively. The molecular weights (Mw) of SLA, SMLA, PLA, and ULA were determined to be 95276, 146201, 139330, and 133426 g/mol, respectively.

4.1. Introduction

Lignin is the second most abundant biopolymers after cellulose. Since lignin is non-toxic and renewable, it has potential to be widely used in industry (Pouteau et al., 2003). Annually, over 50 million tons of lignin are produced in the pulp and paper industry (Wei et al., 2015). It is usually seen as a waste product of the pulp and paper industry and is often used as fuel source (Pouteau et al., 2003). The major challenge in lignin utilization is to find and develop new applications, such as composites, adsorbents, carbon fibers, flocculants and dispersants, for lignin (Setteet al., 2013). Lignin's modification is limited by its resistance to chemical modificaiton, which is in part due to its low molecular weight and reactivity. Substantial reseach has been conducted on improving lignin's reactivity through oxidiation, hydrolysis, hydroxymethylation, carboxymethylation, phenolation, sulfomethylation, and sulfation (Laurichesse and Avérous, 2014).

It was reported that pretreatment of lignin enhanced its reactivity (Alonso et al., 2005). A variety of pretreatment steps have been investigated in literature including sulfation, sulfomethylation, oxidation, hydrosymethylation, carboxymethylation and phenolation. The sulfation, sulfomethylation, and phenolation of lignin has been reported to be more effective than oxidation, hydroxymethylation, and carboxymethylation for lignin modification (Yu et al., 2013; Alonso et al., 2005), as they reported to improve the reactivity of lignin (Alonso et al., 2005; Konduri and Fatehi, 2015; Inwood, 2014).

The sulfation of lignin using sulfuric acid results in the self-condensation of lignin, which improves the occurrence of its copolymerization with aromatic ring (Inwood, 2014). The sulfomethylation of lignin occurs at the *ortho* position of a phenolic hydroxyl group, which increases its charge density (He and Fatehi, 2015). The phenolation of lignin would provide two other sites at ortho position and allow for more sites for copolymerization, which ultimately improves the reactivity of lignin for copolymerization (Inwood, 2014).

Copolymerization of lignin with vinyl monomers is a promising method to increase its molecular weight and charge density (Kong et al., 2015; Zahran et al., 2014). The copolymerization of lignin and vinyl monomers utilizing acrylonitrile and methyl methacrylate was assessed in aqueous or natural solvents (Meister et al., 1984). The results showed that the copolymerization of soda lignin performed under the conditions of 90 °C for 4 h with acrylamide/soda lignin molar ratio of 7.5 mol/mol generated water soluble lignin copolymer with the molecular weight of 194,000 g/mol (Wang et al., 2016). In another study, the copolymerization of lignosulfonate with acrylic acid was performed for 2 h at 50 °C under the conditions of lignosulfonate/acrylic acid molar ratio of 11 mol/mol and an initiator dosage of hydrogen peroxide and potassium persulfate of 1.5 wt.% (Ye et al., 2012). In this reaction, the phenolic hydroxide groups of lignin participated in the reaction (Ye et al., 2014). In other work, hydrogen peroxide (3.5 wt.%) was used as a initiator for the copolymerization of sodium lignosulfanate and acrylamide, under the conditions of the mole ratio of acrylic acid/lignosulfonate of 20 mol/mol at 70°C and 4 h, which generated a product with the viscosity ranging from 0.65 to 3 Pa/s by changing the monomer concentration, which illustrated the flexibility of the copolymerization process (Abdel et al., 2015). Similarly, the copolymerization of kraft lignin with acrylic aid was performed previously by controlling acrylic acid/lignin molar ratio of 8.0 mol/mol, an initiator dosage ($K_2S_2O_8$– $Na_2S_2O_3$) of 1.5 wt.% for 3 h at 70 °C. The resultant copolymer had a charge density of 1.86 meq/g and was water soluble at the concentration of 100 g/L (Kong et al., 2015). However, it is still unclear how pretreated kraft lignin can be copolymerized with acrylic acid. This is because the pretreatment processes would affect the properties of kraft lignin. On one hand, it may facilitate the copolymerization reaction via improving the water solublity of lignin. On the other hand, it may introduce steric hinderance and space constraints for copolymerization reaction. The objective of this chapter was to analyze the performance of pretreated lignin in copolymerization reactions.

In this chapter, the previously synthesised SL, SML, and PLA were copolymerized with acrylic acid under various conditions. The performance of pretreated lignin in the copolymerization reactions were evaluated and the results were compared. This is the first report to state the copolymerization of pretreated kraft lignin for the production of water soluble lignin based products. The produced copolymers were then characterized by a particle charge detector, FTIR, conductometric titrator, GPC, and TGA.

4.2. Experimental

4.2.1. Raw materials

In this work, two samples of softwood kraft lignin were used. The first one was extracted from black liquor using LignoForce technologies and the second one was extracted via acidification of black liquor. Formaldehyde solution (30%), sulfuric acid (98% purity), sodium sulfite, liquefied phenol (>89% purity), acrylic acid (AA), polydiallyldimethyl-ammonium chloride (PDADMAC, 100,000-200,000 g/mol), sodium hydroxide (97%, reagent grade), sodium thiosulfate ($Na_2S_2O_3$) (analytical grades), and potassium persulfate ($K_2S_2O_8$) (analytical grades) were all purchased from Sigma-Aldrich. Dialysis membranes with the molecular weight cut-off of 1000 g/mol was obtained from Spectrum Labs.

4.2.2. Pretreatments of lignin

Pretreatment of kraft lignin prior to copolymerization was discussed in the previous chapter. The phenolation of kraft lignin was performed by adding 3 g of kraft lignin, 18 mL of liquefied phenol and 90 mL of 60% w/w $H_2SO_{4(aq)}$ in a three- neck glass flask. The solution was allowed to react for 4 h at 80 °C under stirring conditions at 280 rpm. The soltuions were diluted to 1500 mL of water and boiled for 2 h. The product was then dried in an oven at 105 °C overnight.

The sulfomethylation of lignin was performed by adding 5 g of kraft lignin, 0.5 moles NaOH, and 0.1 molar ratio of lignin/sodium hydroxymethylsulfonate to a three- neck glass flask. The solution was allowed to react at 50 °C for 1 h under stirring conditions at 280 rpm. The product was neutralized using sodium hydroxide and purified with membrane dialysis for two days. Water was changed every 2 h in the first 6 h and then twice a day for 2 days for purification. The purified solution was dried at 150°C in an oven.

The sulfation of softwood kraft lignin was performed by adding 5 g of kraft lignin, and 6.5 molar ratios of H_2SO_4/lignin in a three neck glass flask. The reaction was allowed to react at 160 °C for 3 h. The resulting products was neutralized and purified with a membrane dialysis for two days as stated above. The purified solution was dried at 150°C in an oven.

4.2.3. Copolymerization of lignin

UL and pretreated (SL, SML, and PL) samples (0.5 - 5.0 g) were dissolved into 50 mL of 1.0 % sodium hydroxide solution at 280 rpm and different temperatures and placed in a three neck glass flask. The solution was purged with nitrogen for 15 min. Subsequently, the initiator was added to three neck flasks with 2/1 wt./wt. ratio of $K_2S_2O_8$/$Na_2S_2O_3$(based on lignin mass), the pH of the solution was adjusted to 2 in order to optimize the reaction conditions of sulfated lignin samples. The optimized reaction conditions of sulfation reactions were followed for SML and PL samples.The reaction solution was cooled to room temperature, and then the pH of the reaction solution was adjusted to 7.0 ± 0.2 using a solution of NaOH. The copolymerized lignin was then placed in dialysis membranes and purfied as stated above. The solution was dried in an oven at 150°C.

4.2.4. Purifying lignin copolymer

To separate copolymers from homopolymers, the samples were acidified to pH 1.5 after cooling to room temperature. After 10 min, they were centrifuged at 3500 rpm for 10 min. As poly acrylic acid is soluble under acidic pH, only lignin copolymer would precipitate if the reaction product is acidified to a low pH of 2, for example. This procedure was established previously and has been used extensively in previous work (Kong et al., 2015; Wang et al., 2015).To remove unreacted monomer from the copolymer, the precipiates were mixed with 50 mL of water, and dialyzed with the membrances for 2 days as explained earlier. After dialysis, the solution was dried at 105 °C, and the dried samples were considered as the purified lignin copolymer products.

4.2.5. Charge density analysis

In preparing the samples for analysis, 0.2 g of dried copolymer lignin was added to 20 mL of deionized water to generate a suspension in a 50 mL centrifuge tube. The suspension was immersed into a water bath shaker (Innova 3100, Brunswick Scientific, Edison, NJ, USA) and shaken (150 rpm) at 30 °C for 2 h. The samples were centrifuged at 2500 rpm for 10 min and supernatants were collected for the charge density analysis by using a particle charge detector (Mutek, PCD 04, Germany) and titrated against a PDADMAC standard solution (0.005 M) for measuring the charge density using equation 1:

$$\text{Charge Density (meq/g)} = \frac{\text{vol of titrant}\times\text{concentration of titrant}}{\text{mass of lignin}} \times\text{dilution factor } (if\ any) \quad (1)$$

To measure the charge density of insoluble samples, 0.05 g of dried insoluble lignin samples were mixed with PVSK standard solution (~0.005M) for 1 h at 30 °C. Then, the concentration of PVSK solutions before and after mixing with lignin samples was determined by titrating againt standard PDADMAC solution and the charge density of insoluble lignin sample was determined using equation 2:

Insoluble lignin charge density (meq/g)

$$= \frac{(\text{vol.PVSK for control}-\text{vol.PVSK for sample})\times\text{conc.PVSK}}{\text{mass of lignin}} \times \frac{\text{total mass PDADMAC}}{\text{mass PDADMAC}} \quad (2)$$

4.2.6. Solubility of unmodified, phenolated, sulfomethylated, sulfated lignin copolymer

The solubility of the modified lignin samples was determined based on a previous work (Konduri et al., 2015). To measure the solubility of lignin samples, 0.2 g of modified lignin was mixed with 20 mL of deionized water by stirring at 150 rpm at 30 °C for 2 h in a water bath shaker. Afterward, the samples were centrifuged at 1500 rpm for 10 min to separate soluble (filtrate) and insoluble (precipiate) lignin from the solution. The filtrates was taken for charge density analysis. The solubility of lignin samples were determined using the following equation 3:

$$\text{Water Solubility (wt. \%)} = \frac{\text{Mass of dissolved lignin}}{\text{Initial mass of lignin}} \times 100 \quad (3)$$

4.2.7. Determination of phenolic hydroxyl group and carboxyl group

A conductometric titration was used for determining the amount of phenolic hydroxyl group and carboxylic acid groups of lignin before and after modification. In this method, 0.06 g of samples was mixed with 1 mL of 0.8 M potassium acid and 4 mL of 0.5 % para-hydroxybenzoic acid (as an internal standard sample). Deionized water (100 mL) was then added to the mixture. The mixture was titrated against a 0.1 M HCl standard solution using a Metrohm, 905 Titrado, Switzerland. The amounts of phenolic hydroxyl and carboxylic acid groups were calculated based on equations 4 and 5:

$$\text{Phenolic hydroxyl group (mmol/g)} = \frac{[(V2'-V1')-(V2-V1)]\times C}{m} \quad (4)$$

$$\text{Carboxyl group (mmol/g)} = \frac{[(V3'-V2')-(V3-V2)]\times C}{m} \quad (5)$$

where C is the molar concentration of HCl standard solution as titrating solution (0.1 M), m is the dried weight of lignin samples (g), V_1,V_2,V_3 are the first, second and third endpoint volumes of HCl (mL), while V_1',V_2',V_3' are the first, second and third endpoint volumes of HCl standard solution (mL) used for lignin samples.

4.2.8. Elemental analysis

The elemental analyses of unmodified and modified lignin samples were determined using an elemental analyzer (Elementar, Vario Micro, Germany) as stated in the literature (Fadeeva et al., 2008). In this set of experiments, the samples were first dried in an oven at 105 °C overnight in order to remove any moisture. Approximately, 2 mg of ULA, SLA, SMLA and PLA copolymers were used in this analysis to measure their carbon, hydrogen, nitrogen and oxygen contents by following a previously established method (Jahan et al., 2012).

4.2.9. Molecular weight analysis

In this set of experiments, the molecular wieght of modified lignin copolymer was measured using gel permeation chromatography (Malven, GPCmax VE2001 Module + Viscotek TDA305) with UV, RI and viscometer detectors. The columns of Polyanalytic PAC000101 and PAC000103 were used, and 5% acetic acid solution was used as an eluent and mobile phase at the flow rate of 0.7 ml/min. Polyethylene oxide was used as standard samples for calibrating the instrument. 50 mg of dried modified samples was dissolved in 5 mL of 5% acetic acid solution by stirring at 200 rpm for 24 h and room temperature, and then the sample was filtered with a nylon 0.2 µm filter (13 mm diameter).

The molecular weight of unmodified copolymers was measured by using Malvern GPCmax VE2001 Module + Viscotek TDA305 equipped with RI and viscometer detectors using polyethylene oxide as standard samples. 100 mg of sample was dissolved in 10 mL of a 0.1 mol/L $NaNO_3$ solution and filtered with a nylon 0.2 mm filter (13 mm diameter). Then, the solutions were used for molecular weight analysis. The columns of PolyAnalytic PAA206 and PAA203 were used for analysis. Also, 0.1 mol/L of $NaNO_3$ solution was used as solvent and eluent and the flow rate was set at 0.70 mL/min. The column temperature was set up at 35 °C for the systems.

4.2.10. Fourier Transform Infrared (FTIR)

The Fourier transform infrared spectroscopy (FTIR) analysis was used for evaluating the struture of lignin samples. The lignin samples (0.05 g) were firstly dried in an oven at 105 °C overnight to remove any moisture before analysis (Bruker Tensor 37, Germany, ATR accessory). The spectra were recorded in transmittance mode in the range of 600 cm^{-1} to 4000 cm^{-1} with 4 cm^{-1} resolution. Each sample was scanned 32 times for consistency.

4.2.11. ^{1}H-NMR analysis

The ^{1}H-NMR analysis of unmodified kraft lignin and sulfated, sulfomethylated, and phenolated kraft lignin was also carried out. Samples of ULA, SLA, SMLA, and PLA in purified forms were dissolved into D_2O at 25-35 mg/L concentration. The solution was stirred for 30 min to fully dissolve the materials. The spectra of these samples were recorded using an INOVA-500 MHz instrument (Varian, USA) with a 45° pulse and relaxation delay time of 1.0 s.

4.2.12. Thermo-gravimetric analysis

A thermogravimetric analyzer (TGA, i-1000 series, Instrument Specialist Inc) was used for determining the thermal stability of the unmodified and modified lignin samples. The samples were dried in an oven at 105 °C overnight and 8 mg of unmodified and modified lignin copolymer samples were used in the TGA analysis. The analysis was carried out under N_2 at a steady flow rate of 30 mL/min. The samples were heated from room temperature to 800 °C at the rate of 10 °C/min.

4.3. Results and Discussion

4.3.1. Mechanism of copolymerization of unmodified/modified lignin with acrylic acid

In this set of reactions, $K_2S_2O_8$ and $Na_2S_2O_3$ were used to initiate the copolymerization reaction and form the sulphate radicals via a redox mechanism (Figure 4.1 (1)). The sulphate radicals then react with the phenol group of kraft lignin to generate a phenoxy radical, which can participate in the copolymerization reaction (Kong et al., 2015).

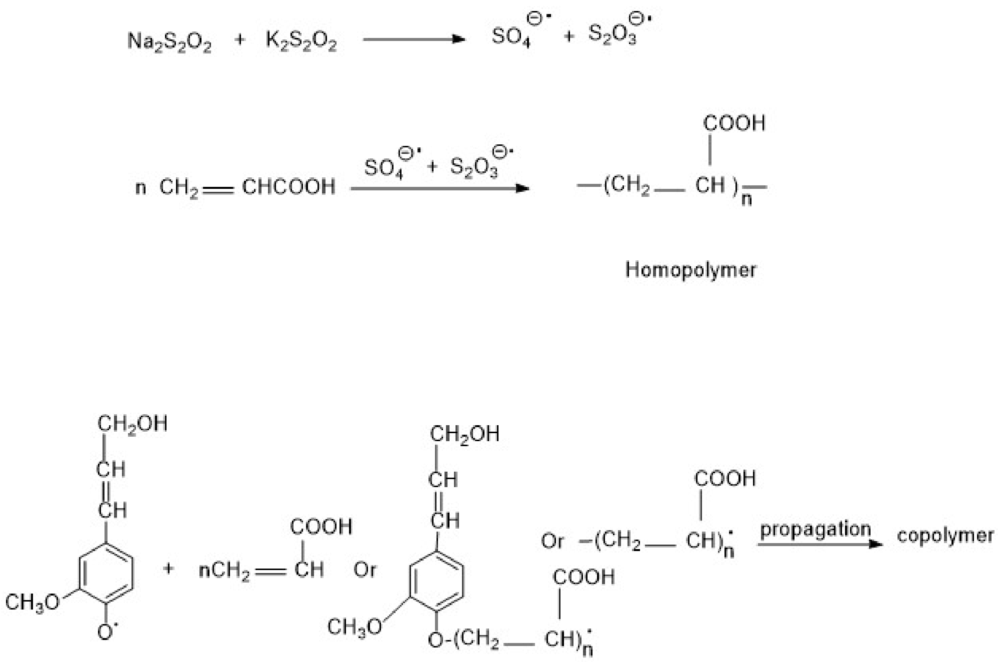
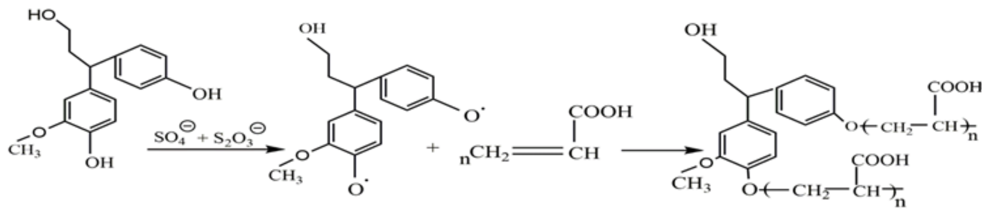


Fig.4.1. Reaction mechanism of copolymerization of unmodified lignin with AA (Kong et al., 2015).

The copolymerization of phenolated lignin can occur as shown in Figure 4.2. It can be seen that free radicals can be formed on the original and newly attached phenolic strutrue of lignin, which enhances its reactivity in the copolymerization reaction. In this case, the extension of acrylic acid chain will start on the phenolic sites. As phenolated lignin contains more phenolic groups, it may be expected that acrylic acid copolymerization would be more pronounced on phenolated lignin than unmodified lignin (Kaur et al., 2010).



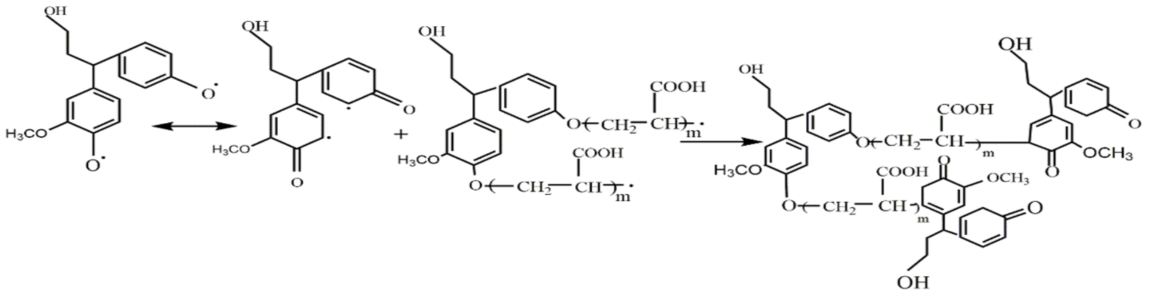


Fig.4.2. The proposed mechanism of copolymerization of phenolated lignin with acrylic acid.

Figure 4.3 depicts the reaction mechanism of sulfomethylated lignin with acrylic acid. The copolymerization of sulfomethylated lignin is similar to that of unmodified kraft lignin with acrylic acid. However, the sulfomethylated lignin has a sulfonate group on the aromatic *ortho*-position (relative to the hydroxide group) (Cerfontain et al., 1985). This charged group would not chemically interfere in the copolymerization of lignin with acrylic acid, but as it makes lignin more water soluble, it may faciliate the reaction, or may provide steric hinderance for the copolymerization reaction (Hong et al., 2016).

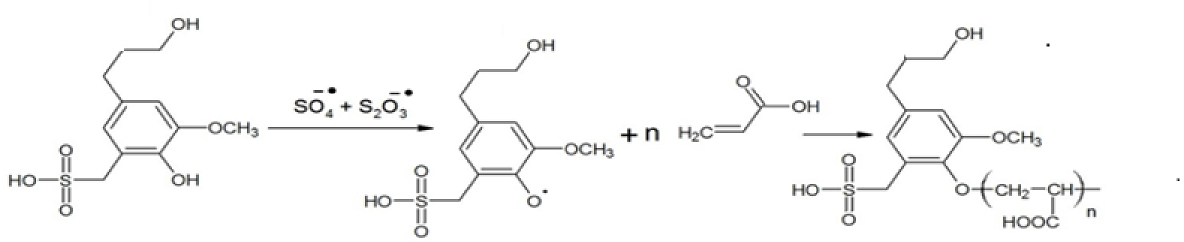


Fig.4.3. The proposed mechanism of copolymerization of sulfomethylated lignin with acrylic acid.

Figure 4.4 illustrates the mechanism of copolymerization of sulfated lignin with acrylic acid.The copolymerization of sulfated lignin would be similar to that of unmodified lignin with acrylic acid. Moreover, sulfated lignin has sulfated group in both the α position in kraft lignin . As stated above for sulfomethylated lignin with acrylic acid, the charge group makes lignin more water soluble, and may faciliate the reaction, or may provide steric hinderance for the copolymerization reaction (Hong et al., 2016).

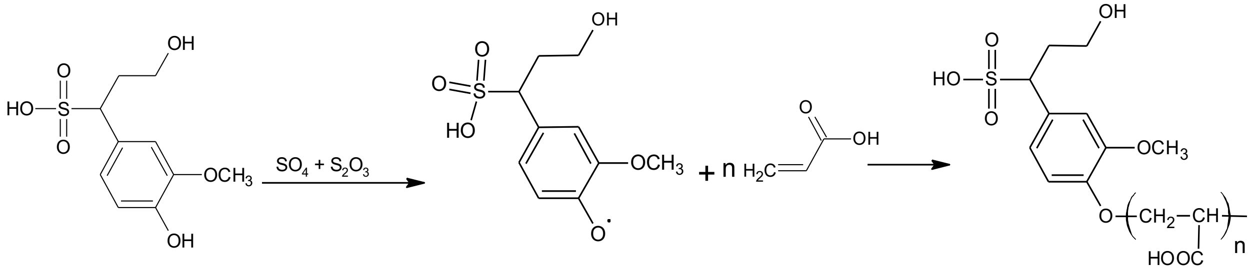


Fig.4.4. The proposed mechanism of copolymerization of sulfated lignin with acrylic acid.

4.3.2. The copolymerization of unmodified and modified lignin with acrylic acid

4.3.2.1. AA/modified lignin effect

Figure 4.5 (a) shows the charge density and solubility of unpurified SL1A product as a function of mole ratio of acrylic acid to SL1. The results revealed that the charge density and solubility of the reaction products were dependent on the molar ratio of acrylic acid to lignin in the reaction. At the ratio of 8, the charge density and solubility reached the highest values of 12.72 meq/g and 85.5 wt.%, respectively. The increases in charge density and solubility are attributed to the production of more homopolymer or copolymers (Witono et al., 2012). The graft copolymerization of cassava starch with acrylic acid under the conditions of an initiator dosage (Fe^{2+}/H_2O_2) of 10 wt.% for 3 h at 40 °C was reported to produce a copolymer with the charge density of 1.5 meq/g. It was reported that the product could be decomposed in high acid concentrations, suggesting that the decrease in charge density at high acrylic acid concentrations may be due to the degradation of the product (Meister, 2002). Figure 4.5 (b) shows the the charge density and solubility of the purified copolymerized PSL1A as a function of molar ratio of acrylic acid to SL1. At the molar ratio of 8, the charge density and solubility reached the highest values of 3.12 meq/g and 82.45 wt.%, respectively. Compared with unpurified products, it is observable that the charge density of soluble lignin copolymers decreased to 2.0 meq/g, while the charge density of insoluble and solubility of the modified lignin did not change. These results implied that homopolymers contributed significantly to the charge density of unpurified SL1A products, and lignin copolymer with a lower charge density can be obtained if purified.

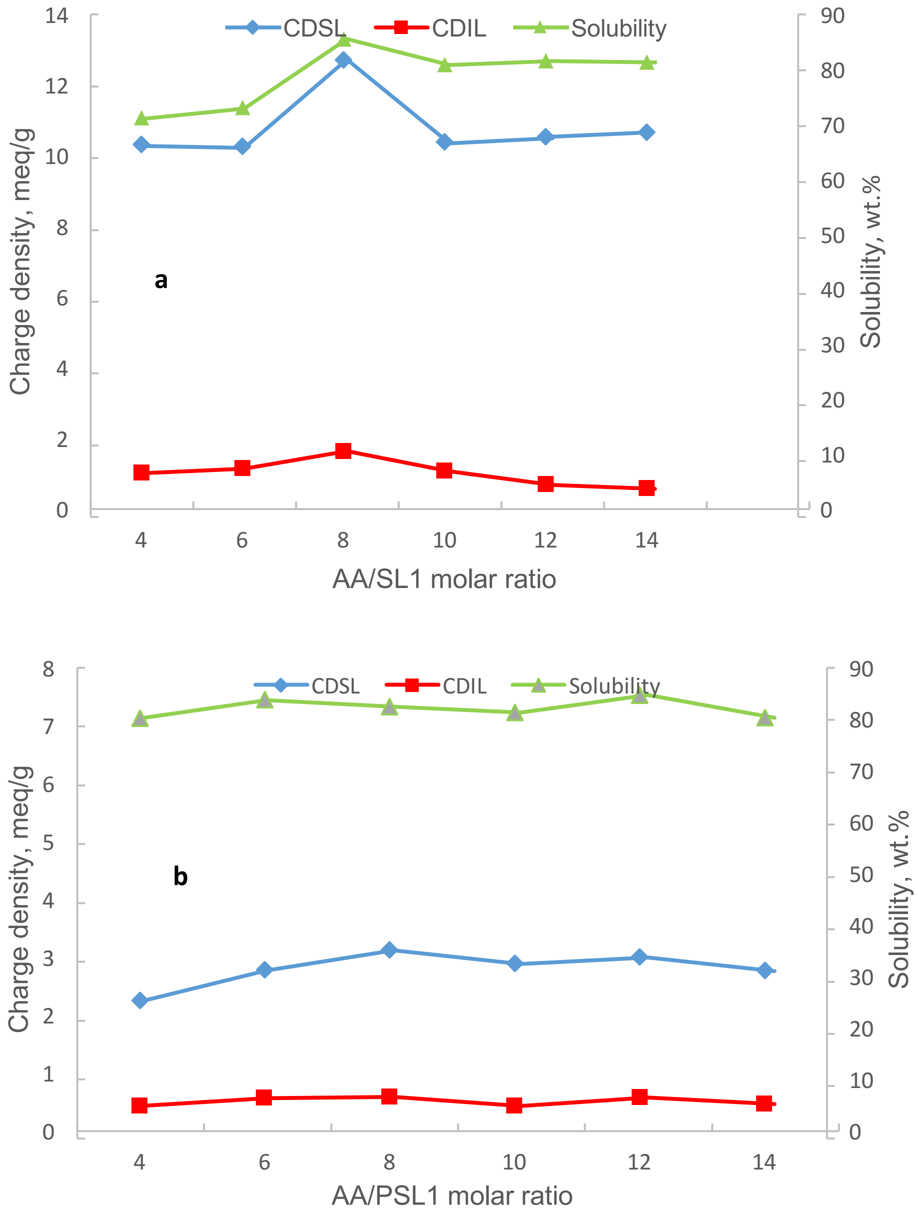


Figure 4.5. The charge density of soluble lignin (CDSL), the charge density of insoluble lignin (CDIL), and solubility of a) SL1A and b) PSL1A copolymer as a function of AA/lignin molar ratio. experiments were conducted at 70 °C, 3 h and pH 2.

4.3.2.2. pH effect

Copolymerization reactions have been reported to be influenced by pH (Yin et al., 2006). Lignin acrylic acid copolymerization was conducted at various pHs to determine the impact of pH on reaction. Figure 4.6 (a) shows the impact of pH on the charge density and solublity of the products. By increasing pH to 6, the charge density of the products dropped significantly, while the charge density of insoluble products was not affected. In the literature, the solubility of the modifie lignin was impacted by pH, and the product became insoluble at pH 6 (Pinkert et al 2011). The solubility and charge density of lignin copolymer after purification are presented as a function of pH in Figure 4.6 (b). The charge density of soluble lignin was higher at pH 2, while the solubility was low in all the samples of PSL1A copolymer. As the charge density and solublity of PSL1A were insiginificantly affected by pH while that of SL1A dropped significantly, it can be claimed that the production and solubility of the homopolymer was affected by pH significantly.

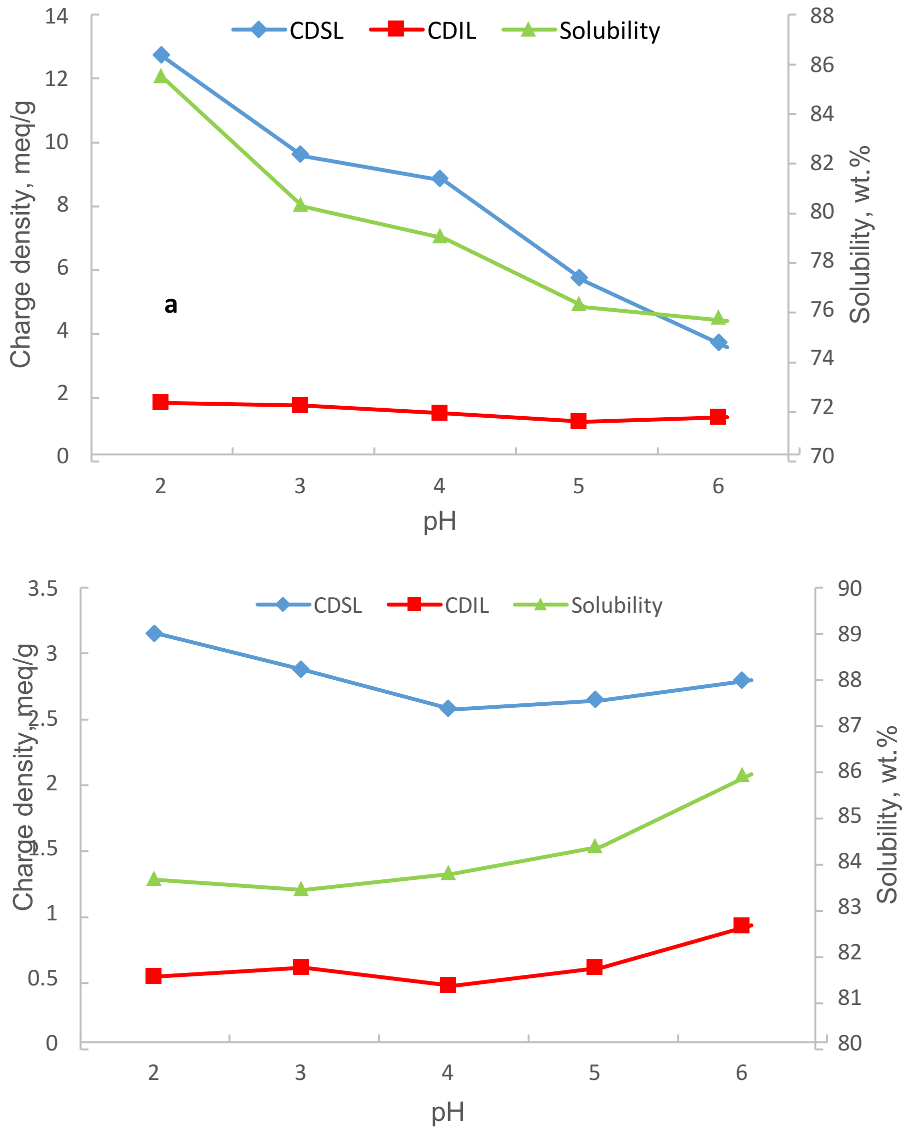


Figure 4.6. The charge density of soluble lignin (CDSL), the charge density of insoluble lignin (CDIL), and solubility of a) SL1A and b) PSL1A. The experiments were performed at a temperature of 70 °C, 3 h, and AA/modified lignin molar ratio of 8.

4.3.3. Characterization of copolymerized lignin

The properties of copolymerized lignin (PLA, SMLA, SLA, and ULA), which were prepared under the conditions of 0.35 mol/L modified lignin, AA/modified lignin ratio of 8.0 mol/mol, 1.5 wt.% initiator ($K_2S_2O_8$-$Na_2S_2O_3$), 70 ºC at 3 h and pH 2 are listed in Table 4.1. In this study, the M_w of PL1A, SML1A, SL1A and UL1A were 139,771 g/mol, 146,201 g/mol, 95,276 g/mol, and 133,426 g/mol, respectively. Moreover, the M_w of PL2A, SML2A, SL2A and UL2A were 139,331 g/mol, 135,221 g/mol, 89,116 g/mol and 132,883 g/mol, respectively. In one study, it was found that kraft lignin copolymered with acrylic acid had a molecular weight M_w of 46,420 g/mol (Kong et al., 2015). Another study reported that the M_w of copolymerized soda lignin- acrylmide was 194,000 g/mol (Wang et al., 2016). After purification, the M_w of PSML1A, PSL1A, PPL1A and PUL1A copolymers were 532,816 g/mol, 898,328 g/mol, 543,211 g/mol, and 335,290 g/mol, respectively. Also, the M_w of PSML2A, PSL2A, and PUL2A were 515,290 g/mol, 513,251 g/mol, and 330,705 g/mol, respectively. It is clear that the molecular weight of PSLA, PSMLA, PPLA of both types of lignin were higher than the molecular weight of PULA implying that the homopolymers probably had a lower molecular weight and they reduced the overal molecular weight of the product prior to purification.

The elemental compositions of the lignin copolymers are also included in Table 4.1. In the past, the elemental analysis of soda lignin with acrylamide had 44.89% carbon, 8.11% hydrogen, 16.39% nitrogen and 30.61% oxygen (Wang et al., 2016). Alternatively, kraft lignin-acrylic acid copolymer contained 59.07% carbon, 6.44% hydrogen, 32.96% oxygen, 0.36% nitrogen, and 1.17% sulfur (Podkościelna et al., 2015). As seen in Table 4.1, SLA, SMLA, PLA, and ULA had a similar carbon content (57%). The copolymerization degree of lignin can be measured by the change in the oxygen content of lignin, as carboxylate group would contribute to the overall oxygen content of modified lignin. The oxygen content of the acrylic acid treated lignin samples were 32.9%, 35.3%, 34.5% and 31.0%, for SL1A, SML1A, PL1A, and UL1A, respectively. Also, the oxygen content of SL2A, SML2A, PL2A, and UL2A were 34.3%, 35.4%, 33.9%, 31.9%, respectively. After purification, the oxygen content of the copolymerized samples were 38.2%, 39.3%, 35.1%, 39.94%, 36.8%, 38.4%, and 34.7% for PSL1A, PSML1A, PPL1A, PUL1A, PSL2A, PSML2A, and PUL2A, respectively. Based on this analysis, the copolymerization of SLA was more sucessful, while SMLA and PLA had similar results.

Based on the results tabulated in Table 4.1, a proposed chemical formula can be derived for each lignin copolymer. To allow for ease of comparison, a basis of 9 units of carbon was used. The chemical formula of kraft lignin was determined to be $C_9H_{8.545}O_{2.994}S_{0.075}$. Modified kraft lignin, SL, SML and PL had $C_9H_{9.986}O\ S_{0.075}$, $C_9H_{9.989}O\ S_{0.045}$ and $C_9H_{9.992}O\ S_{0.045}$ chemical formulas. The derived chemical formula of UL1A, SL1A, SML1A, and PL1A were $C_{5.02}H_{8.45}O_{1.94}S_{0.005}$, $C_{4.81}H_{8.71}O_{2.06}S_{0.018}$, $C_{4.64}H_{8.39}O_{2.20}S_{0.016}$, and $C_{4.69}H_{8.71}O_{2.14}S_{0.002}$, respectively. Additionally, the chemical formulas of UL2A, SL2A, SML2A, and PL2A were $C_{4.94.}H_{8.54}O_{1.99}S_{0.006}$, $C_{4.75}H_{8.15}O_{2.14}S_{0.015}$, $C_{4.64}H_{8.29}O_{2.21}S_{0.016}$, and $C_{4.74}H_{8.70}O_{2.12}S_{0.012}$, respectively. It should be stated that nitrogen was removed from the formula due to its trace amount. The chemical formula of PSL1A, PSML1A, PPL1A and PUL1A were $C_{4.42}H_{8.17}O_{2.38}S_{0.017}$, $C_{4.31}H_{8.43}O_{2.45}S_{0.015}$, $C_{4.29}H_{8.73}O_{2.46}S_{0.006}$, and $C_{4.66}H_{8.77}O_{2.19}S_{0.003}$, respectively. The chemical formula of PSL2A was $C_{4.51}H_{8.08}O_{2.30}S_{0.106}$, PSML2A was $C_{4.39}H_{8.36}O_{2.40}S_{0.015}$, and PUL2A was $C_{4.68}H_{8.89}O_{2.17}S_{0.00}$.

The charge density of lignin samples are also included in Table 4.1. Previously, the charge density of kraft lignin with acrylic acid was 1.86 meq/g (Kong et al., 2015). In this study, SLA had higher than 12.0 meq/g, while SMLA, PLA, and ULA of both types of lignin had a similar charge density of 10.0 meq/g. Moreover, PSLA and PSMLA had approxiamtely 3.0 meq/g charge density for both types of lignin, while PPLA and PULA had a similar charge density of 2.50 meq/g.

The results in Table 4.1 also depicted that the highest carboxylic acid amount of SLA of both types of lignin was 6.10 mmol/g, while after purification the carboxylate acid amount of PSLA and PSMLAwere 4.30 mmol/g.

Therefore, based on these analysis of the samples, the unpurified SMLA and SLA had higher molecular wieght and charge density, while the purified PSLA had a higher molecular wieght and charge density. The results may also show that the the amount of homopolymers in sulfomethylation reaction was significant.

Table 4.1. Properties of lignin copolymer in the present work and those reported in literature.

Lignin	Mw, g/mol	Mn, g/mol	Mw/ Mn	CHNOS					Charge density of	Charge density of	COOH mmol/g	Refer ence
				C%	H%	O%	N%	S%				

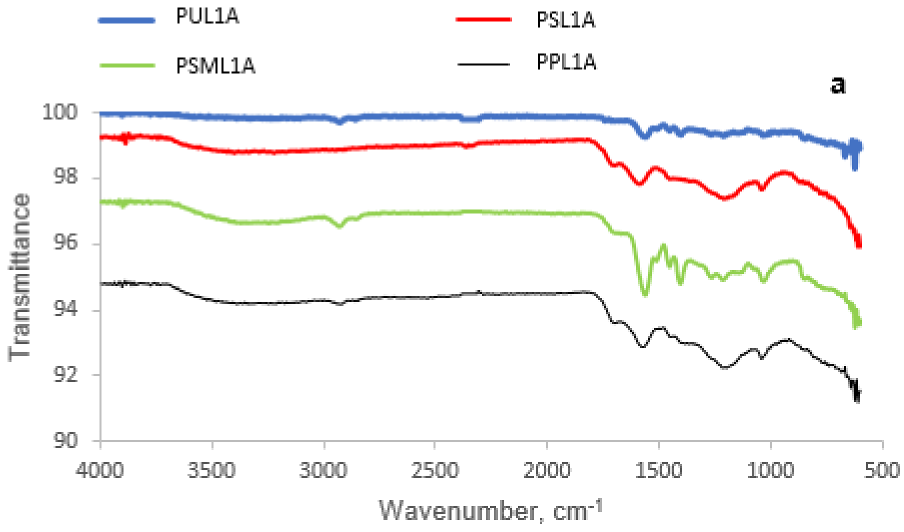
									soluble lignin meq/g	insoluble lignin meq/g		
SL1A	95276	51456	1.852	57.72	8.71	32.97	0.00	0.60	12.72	1.67	6.11	[1]PS
SML1A	146201	88115	1.659	55.75	8.39	35.33	0.00	0.53	10.03	-	5.91	PS
PL1A	139771	83449	1.675	56.30	8.71	34.52	0.00	0.07	10.57	-	4.29	PS
UL1A	133426	88604	1.732	60.35	8.45	31.04	0.00	0.16	10.31	-	3.44	PS
SL2A	89116	50969	1.748	57.03	8.15	34.33	0.00	0.49	11.61		6.09	PS
SML2A	135221	85966	1.650	55.74	8.29	35.44	0.00	0.53	10.00	-	5.87	PS
PL2A	139331	96204	1.864	56.90	8.70	33.99	0.00	0.41	9.78	-	4.66	PS
UL2A	132883	94994	1.715	59.29	8.54	31.96	0.00	0.21	10.05	-	3.65	PS
PSL1A	898328	180603	4.974	53.07	8.17	38.2	0.00	0.56	3.17	-	4.13	PS
PSML1A	532816	419013	1.272	51.76	8.43	39.3	0.00	0.48	3.01	-	4.71	PS
PPL1A	543211	408091	1.346	51.56	8.73	39.49	0.00	0.22	2.57	-	4.05	PS
PUL1A	335290	105654	3.173	55.98	8.77	35.15	0.00	0.12	2.54	-	3.98	PS
PSL2A	513251	228881	2.242	54.51	8.08	36.88	0.00	0.53	3.31		4.09	PS
PSML2A	515290	328991	2.532	52.70	8.36	38.44	0.00	0.50	3.42	-	4.32	PS
PUL2A	330705	95919	3.448	56.21	8.89	34.76	0.00	0.14	2.50	-	3.65	PS
Kraft lignin-AA	46420	21360	2.173	NR[2]	NR	NR	NR	NR	1.86	-	4.35	(Kong et al., 2015)

Soda lignin-AM	194000	NR	NR	44.89	8.11	30.61	16.39	NR	NR	-	NR	(Wang et al., 2016)
Kraft lignin-AA	NR	NR	NR	59.07	6.44	32.96	0.36	1.17	NR	NR	NR	(Podkościelna et al., 2015)

[1]PS: Present work, [2]NR: Not reported.

4.3.4. FTIR analysis

The FTIR spectra of PUL1A, and PSL1A, PSML1A, and PPL1A copolymers as well as PUL2A, PSL2A, and PSML2A copolymers are presented in Figure 4.7. The peak at 3346 cm^{-1} is attributed to OH groups of the products (Ibrahim et al., 2004). The absorption of two peaks at 1553 and 1400 cm^{-1} in all the samples are attributed to the carboxylic acids (symmetrical stretching vibrations of carboxyl anions –COO^{-}) (Kong et al., 2015). These peaks demonstrate that the copolymerization of lignin with AA was successful (McCluskey et al., 1989). The peak at 1040 cm^{-1} in PSLA is attributed to sulfate group attached to lignin. Also, PSMLA had the adsorption peak at 1032 cm^{-1} corresponding to the sulfonated acid group. However, no observable peak was noticed at 1028 cm^{-1}. As this peak represents phenolic OH group, its absence may provide evidence for occurrence of the copolymerization reaction through phenolic group of lignin (Kong et al., 2015).



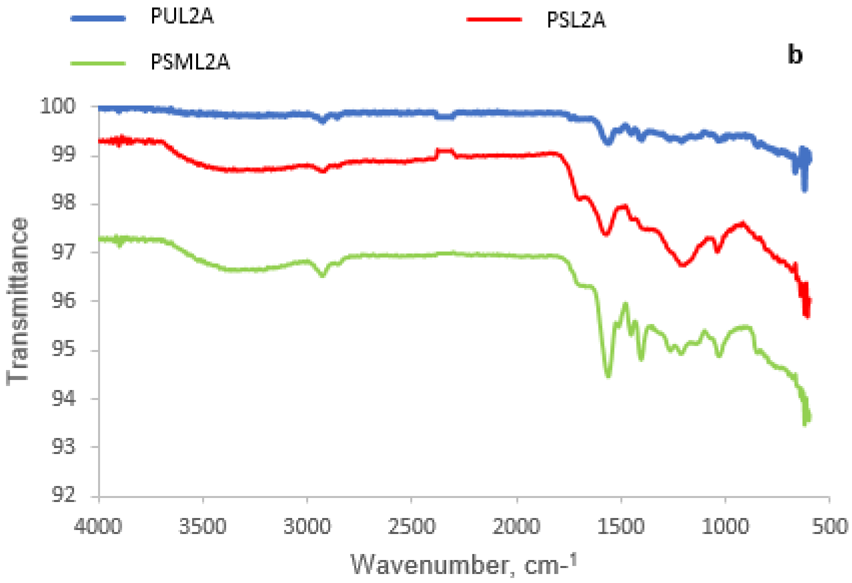


Figure 4.7. FTIR spectra of purified samples (a) PUL1A, PSL1A, PSML1A, and PPL1A (b) PUL2A, PSL2A, and PSML2A.

4.3.5. ^{1}HNMR analysis

The H^1 NMR spectra of PULA, PSLA, PSMLA, and PPLA after purification are presented in Figure 4.8. The peak at 6.15 ppm is attributed to aromatic protons including certain vinyl protons on the carbons adjacent to aromatic rings and at 5.75-5.15 ppm is attributed to aliphatic protons including H_α and H_β (Nagy et al., 2010; Lundquist, 1981). The peak at 4.3 ppm is observed in the spectrum of the lignin copolymer, which is absent in that of kraft lignin. This is attributed to the protons of CH_2 in the structure of $–CH_2COC_6H_5$ (Kong et al., 2014; Xiong et al., 2003). This also confirms that the phenolic hydroxyl groups were the active sites that participated in the copolymerization reaction as showed in the FTIR. The small peaks at 1.7 ppm and 2.6 ppm are assigned to the aliphatic protons in lignin (Hu et al., 2013). This experiment was repeated using lignin type 2, which generated similar results (as shown in Figure 4.9).

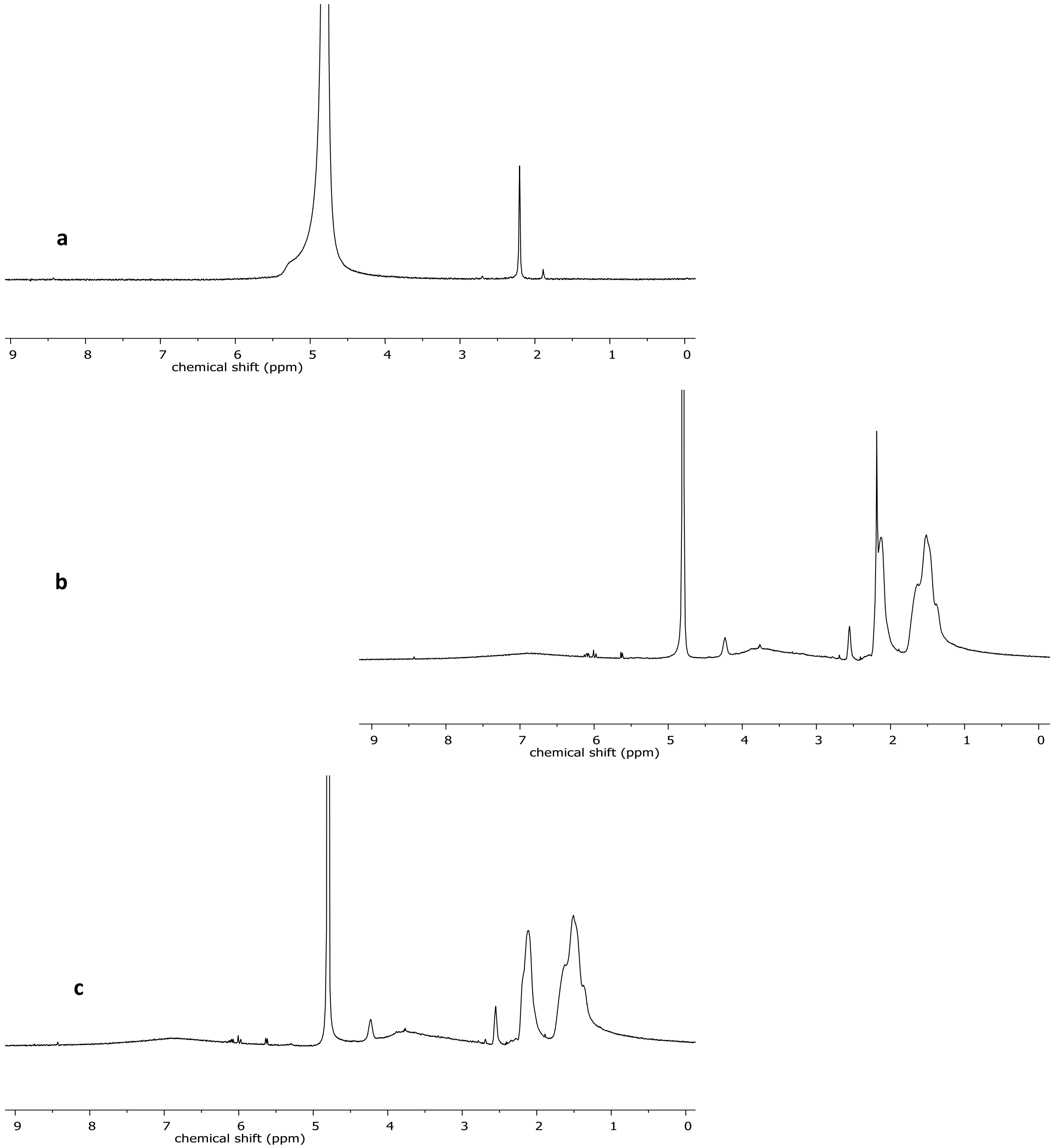


Figure 4.8. The H-NMR spectra of lignin-1 after purification (a) PSL1A, (b), PSML1, and (c) PUL1A.

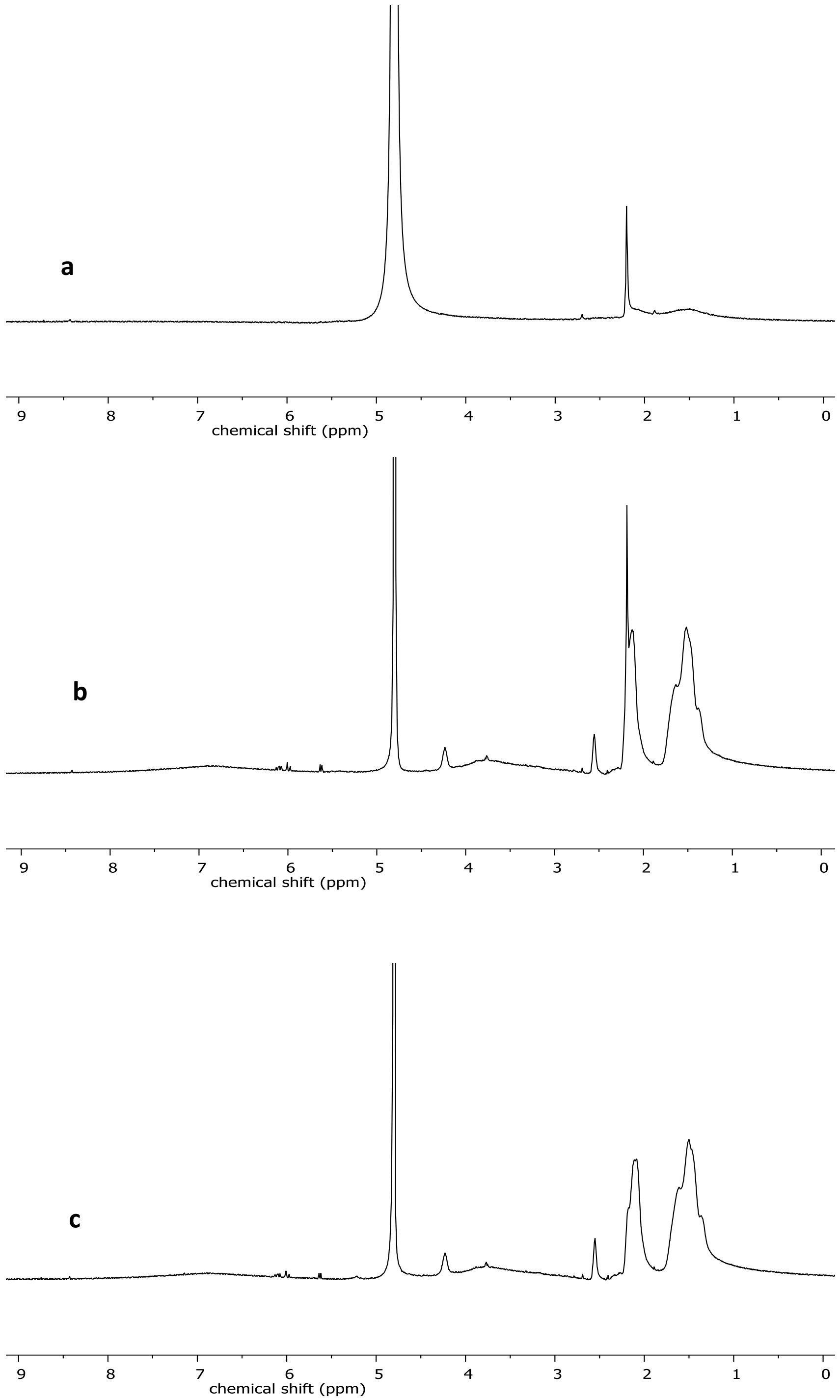
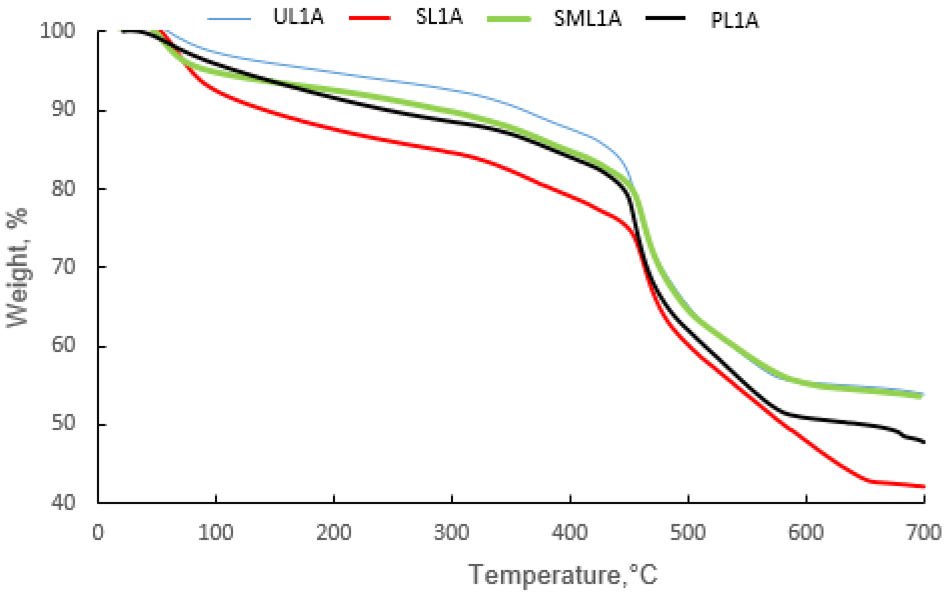


Figure 4.9. The H-NMR spectra of lignin-2 after purification (a) PSL2A, (b), PSML2A, and (c) PUL2A.

4.3.6. Thermogravimetric (TGA) Analysis

Thermogravimetric analysis (TGA) can provide information on the thermal decomposition/stability of lignin copolymer (Yang and Wu, 2009). Figure 4.10 shows the results of TGA analysis for unmodified/modified copolymerized lignin samples. It is observable that modified copolymerized lignin decomposed faster than unmodified lignin. The weight change below 100 °C is attributed to the elimination of moisture in all samples. Also, the decomposition step occurred in the range of 420 to 525 °C, with 20% weight loss corresponding to the decomposition of ULA, SMLA, and PLA (Yang et al., 2007; Dominguez et al., 2008). The main decomposition temeprature was in the range of 440 °C and 600 °C, which is ascribed to the decomposition of intermolecular bonding of lignin (Zhang et al., 2014). The results also suggest that SLA was the less stable sample, and this less stability is attributed to the decompostion of the condensed structure of intramolecular bonds of lignin (Lv et al., 2013). In another work, the sulfonated lignin was less stable than unmodified lignin due to the decomposition of its condensed structures at a lower temperature of 350 °C (Inwood, 2014). Based on the results, the lignin copolymers were stable at temperatures lower than 450 °C. The increase in the thermal stability of lignin can be regarded as an advantage for its end-use applications in composites or as a dispersant and flocculant in solution and suspension systems (Wu et al., 2012). This experiment was repeated using lignin type 2 and similar results were obtained as shown in Figure 4.11.



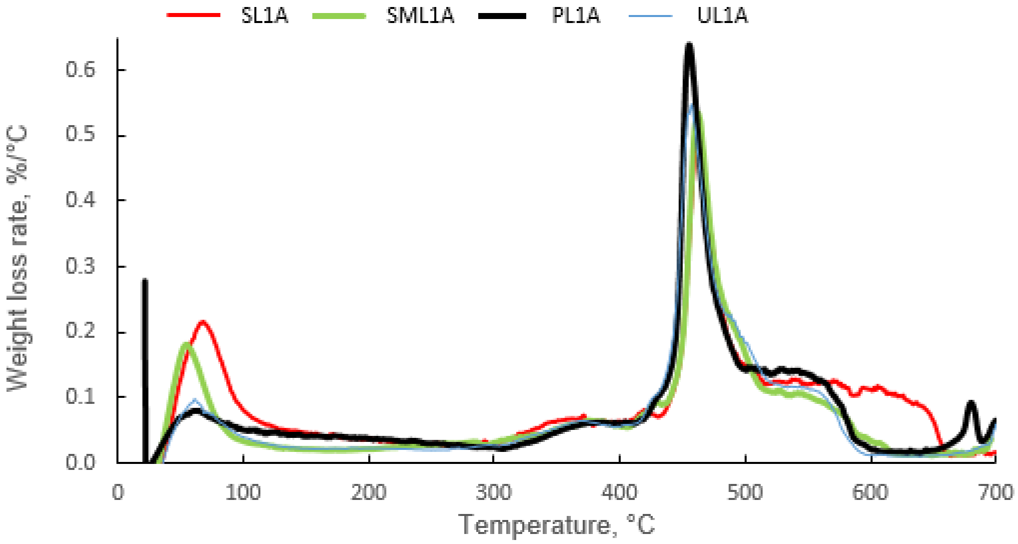
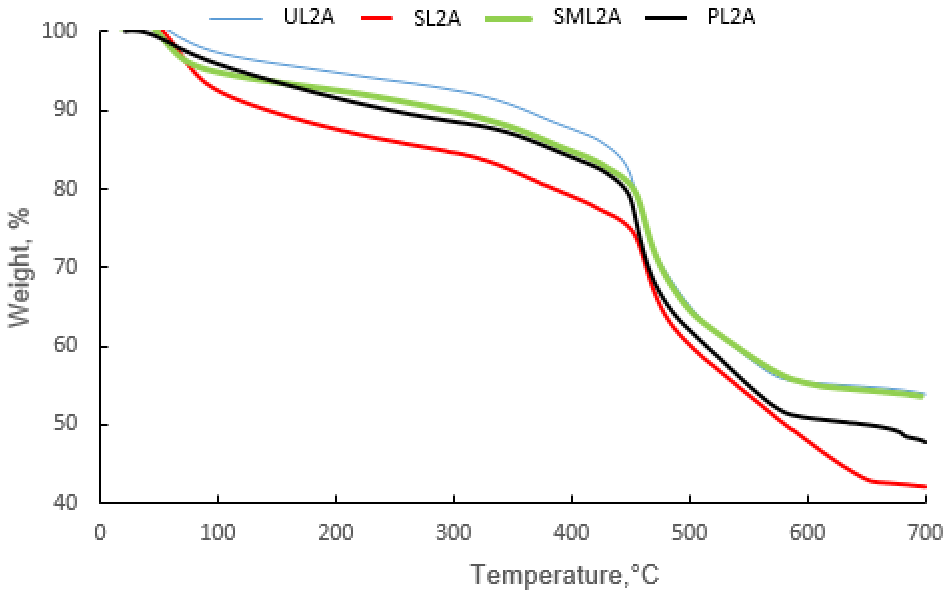


Figure 4.10. Weight loss rate of UL1A, SL1A, SML1A, and PL1A copolymer conducted under N_2 with the flow rate of 30 mL/min heated at 10 °C/min.



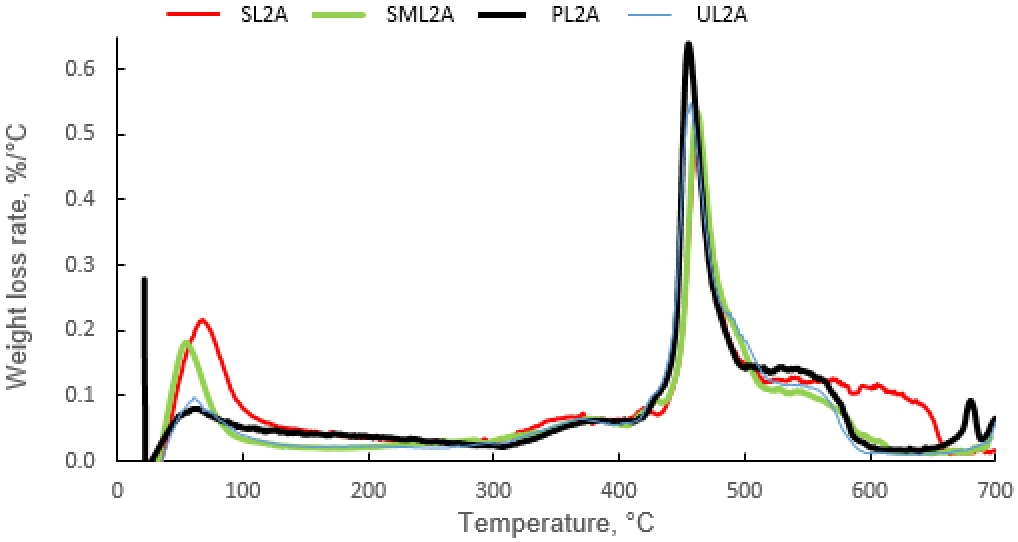


Figure 4.11. Weight loss rate of UL2A, SL2A, SML2A, and PL2A copolymers conducted under N_2 with the flow rate of 30 mL/min heated at 10 °C/min.

4.5. Conclusions

UL, SL, SML and PL were sucessufully copolymerized with acrylic acid. SLA, SMLA, PLA and ULA products had a charge density of 11.6, 10.0, 10.5 and 10.30 meq/g and the solubility of 85.5%, 100%, 100% and 100%, respectively. However, PSLA, PSMLA, PPLA and ULA had the charge density of 3.30, 3.42, 2.50 and 2.50 meq/g and solubility of 83.65%, 100%, 98%, and 97% respectively. The FTIR, ^{1}HNMR and elemental analyses confirmed the copolymerization of modified lignin and AA. Also, the molecular weights of SLA, SMLA and PLA were determined to be 95,276, 146,201 and 139,330 and 133,426 g/mol, respectively, before purification. After purification, the molecular weight of PSMLA, PSLA, PPLA and PULA copolymers were 532,816 g/mol, 898,328 g/mol, 543,211 and 335,290 g/mol, respectively. TGA results showed a reduction in the thermal stability of the unmodified/modified lignin copolymers samples. For lignin 1, the results showed that SLA had a high charge density and solubility, which makes it more successful product than other products. For lignin 2, the results of SMLA had a higher molecular weight and solubility, which makes it a more promising product. Also, the analysis on purified copolymers confirmed that PSLA and PSMLA were the most successful pretreatment in making lignin copolymers.

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Chapter 5: Applications of copolymerized lignin as a flocculant in different colloidal systems

Abstract

Copolymers of lignin may be used as flocculants for different wastewater systems. This chapter discusses the efficiency of eight lignin-acrylic acid copolymers produced in chapter 4 to flocculate particles from an aluminum oxide suspension and ethyl violet from a dye solution. In this analysis, the products of the copolymerization reaction were used without and with purification to 1) understand if purification of the products is necessary for their industrial use and 2) determine the impact of homopolymers/copolymers in flocculation of aluminum oxide particles (as a suspension model) and ethyl violet dye (as a solution model). Without purification, the product could reduce the relative turbidity of the suspension by 5-50%, and with purification, the copolymers could reduce the relative turbidity by 70%. With the exception of phenolated lignin copolymers, all other copolymers could adsorb onto the aluminum oxide particles, reverse the zeta potential of the suspension from a positive to a negative value, and could effectively remove the dye from the solution. Among the products, sulfated lignin copolymer with acrylic acid SLA led to the highest removals of aluminum oxide particles and dye from the systems. The SLA and sulfomethylated lignin copolymer with acrylic acid SMLA functioned more effectively for the suspension and solution systems.

5.1. Introduction

The pollution of water resources by heavy metals is a serious and widespread environmental concern, which threatens both human health and ecosystems (Merian, 1980). Mineral processing activity is a major source of heavy metal pollution of water resources. The removal of heavy metals is of great importance, but is challenging due their stability in colloidal systems (Pearse et al., 2001; Lee et al., 1991). The metals can, however, be removed by coagulation and flocculation processes (Menezes et al., 1996). Coagulation is the destabilization of colloids by the chemical interaction between the coagulant and the colloidal particles, while flocculation is the clumping of the particles (Alther, 2008; Gregory, 1985). The coagulation and flocculation process can be used to assist the removal of particles from wastewater, which can be conducted by the addition of polymers (Guo et al., 2009: Sabah et al., 2004). However, some of the polymers used for this purpose are expensive and inefficient (Pearse et al., 2001; Pradip et al., 1991; Gao et al., 2007). Interestingly, lignocellulosic materials can be converted to flocculants (Suteu et al.,2006).

Lignin is an abundant component of plant biomass (16% to 33%), and is an inexpensive by-product of the pulp and paper industry (Windt et al., 2009; Voitl and Von Roh, 2010). Unmodified lignin, however, is not well suited to be used as a flocculant. Lignin can be chemically modified to be used as a flocculant (Kindsigo and Kallas, 2006). For example, enzymatically produced lignin was rendered cationic, which was capable of removing 95% of azo-dyes (Congo red, Eriochrome blue black R, Acid Black, Reactive Red and Direct Red) from wastewater (Fang et al., 2010; Wang et al., 2014). Li and colleagues (Li et al., 2015) reported that aminated alkali lignin removed 54.12% of humic acids from simulated wastewaters. Although these results are promising, the use of lignin-derived flocculants for removing particles from suspension systems have not been studied in detail (Tripathy and De, 2006; Sabah et al., 2004). In the previous chapter, the impact of lignin functionalization on the properties of lignin copolymers was discussed. Furthermore, the performance of the copolymers as flocculants for both suspension and solution systems are discussed.

5.2. Experimental

5.2.1. Materials

Potassium chloride and sulfuric acid (95-98%) were received from Fisher scientific, USA. Sodium hydroxide (97%, reagent grade), aluminum oxide (Al_2O_3) and ethyl violet cationic triarylmethane dye were obtained from Sigma-Aldrich Company. Ethyl violet had molecular weights of 492.14 g/mol, and the chemical formula of $C_{31}H_{42}N_3Cl$. Ethyl violet had an absorption wavelength (λ_{max}) at 595 nm.

5.2.2. Lignin based flocculants

The products of copolymerization reactions for SL1A, SL2A, SML1A, SML2A, PL1A, PL2A, UL1A, UL2A copolymers (purified and unpurified) stated in previous chapters were used as flocculants in this chapter. The full name of these copolymers is defined in abbreviation Table at the beginning of this thesis.

5.2.3. Adsorption analysis

Alumina suspensions were prepared via mixing aluminum oxide particles in 50 mL of deionized water to make 1 g/L concentrations. Different dosages (2 – 110 mg/g) of lignin based products were added to the suspensions at pH 6. The suspensions were stirred at 250 rpm for 30 min and room temperature, centrifuged at 3000 rpm for 10 min, and the supernatants were then filtered using Whatman filter papers (Theng, 1970). Deionized water was used as a control sample and the absorbance of all the filtered samples under 280 nm were tested by UV-Vis spectrophotometer (Genesys 10S, Thermo Scientific) at room temperature. A series of lignin solution with concentrations of 10, 20, 30, 40, 50, and 100 mg/L were prepared and their UV absorbance under 280 nm were tested and the relationship between their concentration and UV absorbance was used as standard curve. All measurements were carried out in triplicate and the mean values were reported.

5.2.4. Zeta potential analysis

The zeta potential analysis of the alumina particles was performed using a NanoBrook Zeta PALS analyzer (Brookhaven Instruments Corp, USA). Different concentrations of lignin copolymer (2 to 110 mg/g) were maintained in 50 mL of an alumina suspension (20 g/L) at pH 6. After stirring at 250 rpm and room temperature for 10 min, 1 mL of the sample was collected and then mixed with 20 mL of KCl solution (1 mM) prior to zeta potential analysis. All measurements were carried out in triplicate and the mean values were reported.

5.2.5. Turbidity analysis

The flocculation of alumina suspensions was assessed using a photometric dispersion analyzer (PDA 3000, Rank Brothers Ltd), which was connected to a dynamic drainage jar (DDJ) fitted with a 70 mm mesh screen (Ramphal and Sibiya, 2014). In this set of experiments, 490 mL of distilled water was poured into the DDJ container and circulated from the DDJ to the PDA through a 3 mm plastic tube at a steady flow rate of 20 mL/min with the help of a peristaltic pump. Afterward, 10 mL of a 200 g/L alumina suspension was added into the DDJ resulting in an aluminum oxide concentration of 1 g/L, which was stirred at 300 rpm. The presence of the alumina reduced the initial base DC voltage (V_0) of the PDA to a new voltage (V_i). After 60 s of stirring, lignin copolymers of varying concentrations (2 to 110 mg/g) were added to the suspension in the DDJ resulting in an increase in the recorded voltage (V_i to V_f). The flocculation performance of lignin copolymer in the aluminum oxide suspension, as assessed by the relative turbidity, τ_r, was calculated according to equation 1 (Wang et al., 2009; Xiao et al., 2010):

$$\text{Relative turbidity, } \tau r = \frac{\tau f}{\tau i} = \frac{ln(\frac{V0}{Vf})}{ln(\frac{V0}{Vi})} \qquad (1)$$

where τ_f and τ_i are the final and initial suspension turbidities, respectively. All measurements were carried out in triplicate and the mean values were reported.

5.2.6. Dye removal

Different concentrations (0.2 – 1.6 g/L) of dye solutions were prepared by dissolving ethyl violet dye in 50 mL of deionized waster with, or without, the addition of lignin copolymers. After preparing the dye solutions, they were placed into centrifugal tubes. The tubes were placed in a water bath shaker for 10 min at 30 °C and 150 rpm. The tubes were then centrifuged at 2500 rpm for 10 min. The dye content of supernatants in each tube was quantified using a UV/vis spectrophotometer (Genesys 10s UV-Vis spectrophotometer, Madison, WI) at 595 nm wavelength (i.e. absorbance peak for ethyl violet). The extinction coefficient of the dye was calculated and used to determine the dye concentration in the systems. Dye removal was calculated using equation (2):

$$\text{Dye Removal (\%)} = \frac{C_0 - C}{C_0} \times 100 \qquad (2)$$

where C_0 and C were the dye concentrations in the supernatants with and without the addition of lignin copolymer, respectively. All measurements were carried out in triplicate and the mean values were reported.

5.3. Results and Discussion

5.3.1. Adsorption analysis

Figure 1 shows the adsorption of lignin copolymer products without purification on aluminum oxide particles at pH 6. SL1A, SML1A, PL1A, and UL1A exhibited a maximum adsorption of 43.3, 33.99, 30.60 mg/g, and 29.62 mg/g on aluminum oxide particles, respectively (Figure 1). Similarly, SL2A, PL2A, SML2A, and UL2A had adsorption of 33.98, 18.70, 17.53, and 18.70 mg/g. Interestingly, the adsorption behavior of lignin-1 and lignin-2 copolymers were similar, but they had different adsorption levels. As stated in Table 4.1 in the previous chapter, SL1A and SL2A had a higher charge density of 12.72 meq/g, which led to their increased adsorption onto alumina particles (Durand-Piana et al., 1987) via electrostatic interaction (Ryan and Gschwend, 1994).

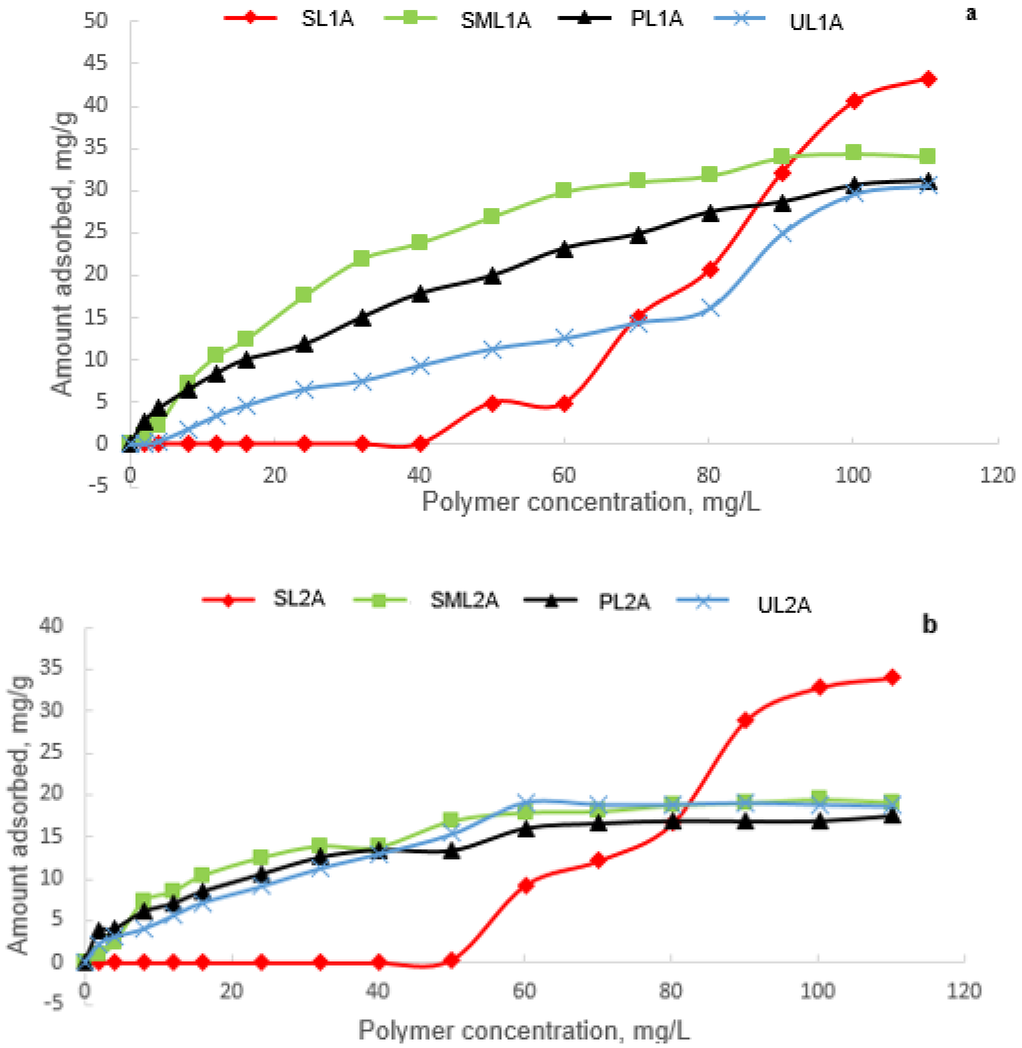


Figure 5.1. (a) adsorption isotherms of unpurified SL1A, SML1A, PL1A and unmodified UL1A, and (b) adsorption isotherms of SL2A, SML2A, PL2A, and UL2A onto aluminum oxide (1g/L) conducted at room temperature for 30 min.

5.3.2. Adsorption of purified lignin copolymers

The adsorption of purified copolymers on aluminum oxide particles is shown in Figure 5.2. PPLA did not adsorb onto the particles (Figure 5.2 (a) and 5.2 (b)). This behaviour is attributed to the limited copolymerization of phenolated lignin with AA, as discussed in the previous chapter. Other purified copolymers were significantly adsorbed onto the particles, which is in opposition to those of unpurified samples. In another work, the adsorption of cationic starch on the clay surface at pH 5 was increased from 2 to 18 mg/g, when cationic starch concentration was increased from 30 to 260 mg/L in a clay suspension (Lundström-Hämälä et al., 2010). The difference between the purified and unpurified samples revealed that lignin based copolymers had indeed better adsorption than homopolymers on the particles, and this difference should be due to the high charge of unpurified product. It is well known that polymers with a high charge have a limited adsorption on surfaces as small adsorption of these polymers would create a significant repulsion force for other polymers for adsorption, and thus prevent their adsorption (Durand-Piana et al., 1987; Chen et al., 2007).

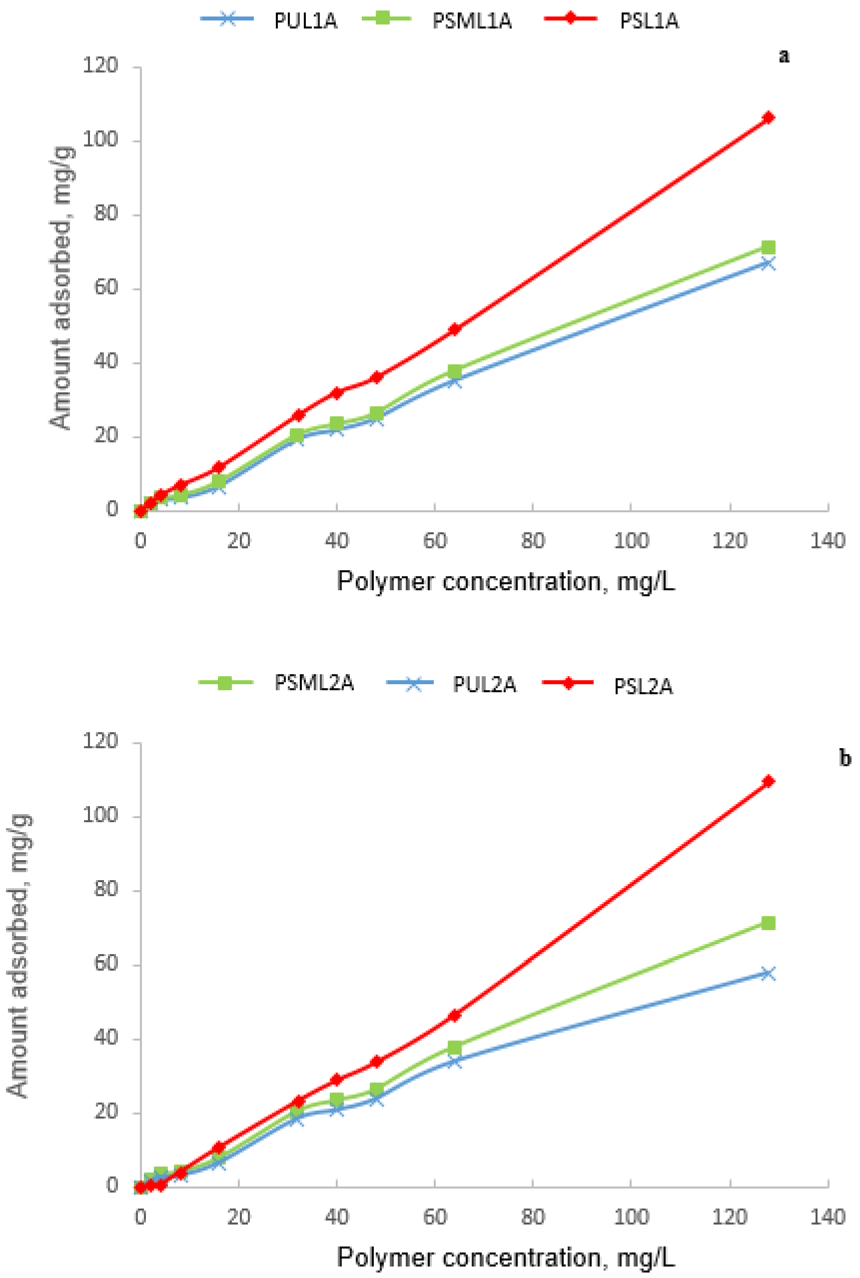


Figure 5.2. (a) adsorption isotherms of purified PSL1A, PSML1A, and PUL1A (b) Adsorption isotherms of PSL2A, PSML2A, and PUL2A, onto aluminum oxide particles, which was conducted at room temperature for 30 min.

5.3.3. Modeling analysis

To understand the adsorption mechanisms of the copolymers on the particles, the experimental values presented in Figures 1 and 2 were fitted into Langmuir and Freundlich models. Equations (3) and (4) present the Langmuir and Freundlich Adsorption models (Li et al., 2007; Tekin et al., 2005):

$$\frac{Ce}{\text{Qe}} = \frac{1}{\text{KlQmax}} + \frac{\text{Ce}}{\text{Qmax}} \qquad (3)$$

$$\log Q_e = \log K_f - \frac{1}{n} \log C_e \qquad (4)$$

where C_e is a concentration of copolymers at equilibrium (mg/L), Q_e is the number of copolymers adsorbed on alumina particles at equilibrium (mg/g), Q_{max} is the maximum adsorption of copolymers on alumina particles (mg/g), and K_l, K_f and n are Langmuir and Freundlich constants. Table 5.1 list the parameters of adsorption isotherms obtained by fitting the experimental data of Figures 5,1 and 5.2 into equations 3 (Langmuir) and 4 (Freundlich). the results obtained represents that the adsorption isotherms of unpurified and purified products fitted into both Langmuir and Freundlich isotherms models, however, Langmuir isotherm model fitted the data better than Freundlich isotherm model which explained that the adsorption of the experimental system is caused by the monolayer adsorption (Durand-Piana et al., 1987).

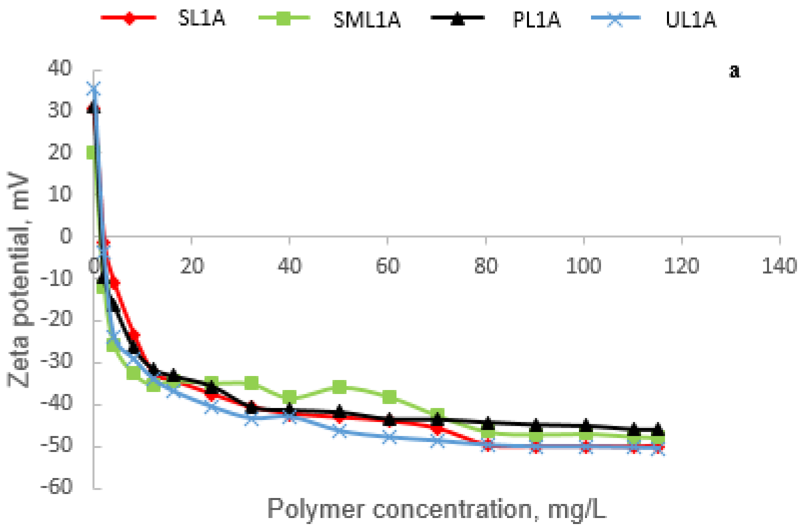
Table 5.1. Parameters of Langmuir and Freundlich adsorption isotherms of modified lignin copolymers on aluminum oxide.

Sample	**Langmuir**			**Freundlich**		
	K_l	Q_{max}	R^2	K_f	n	R^2
SL1A	0.68	40.59	0.992	1.34	1.87	0.891
SML1A	0.60	33.99	0.985	1.40	1.77	0.904
PL1A	0.63	29.6	0.973	1.45	1.70	0.918
UL1A	0.62	29.6	0.966	1.46	1.70	0.932
SL2A	0.66	28.89	0.992	1.49	1.71	0.905
SML2A	0.57	18.91	0.971	1.56	1.63	0.933
PL2A	0.39	16.91	0.987	1.61	1.41	0.995

UL2A	0.60	18.91	0.964	1.54	1.63	0.935
PSL1A	0.66	48.82	0.987	1.44	1.71	0.918
PSML1A	0.63	37.70	0.977	1.50	1.65	0.907
PUL1A	0.60	37.70	0.951	1.52	1.60	0.887
PSL2A	0.65	46.54	0.997	1.46	1.70	0.891
PSML2A	0.56	37.71	0.930	1.52	1.66	0.895
PUL2A	0.65	33.90	0.972	1.53	1.63	0.932

5.3.4. Zeta potential for use of unpurified lignin copolymers

Figure 5.3 shows the zeta potential of the suspension as a function of the dosage of unpurified copolymers. Increasing the concentration of copolymers over the range 1 to 20 mg/L reduced the zeta potential of the suspension from +30 to -40 and -50 mV. In another study, the concentration of carboxymethylated lignin from 0.1 to 0.2 wt.% decreased the zeta potential of ceramic suspensions to -50 mV (Cerrutti et al., 2012). An increase in the concentration of polyacrylic acid from 0.1 to 0.8 wt.% led to a decrease in the zeta potential of suspended kaolinite particles from -20 to -40 mV at pH 7 (Amoros et al., 2010; Cerrutti et al., 2012). It is seen that the zeta potential of the suspension dropped independent of the copolymer type. These results suggest that the structure of the copolymer may not impact the zeta potential of the suspension (Wang et al., 2016).



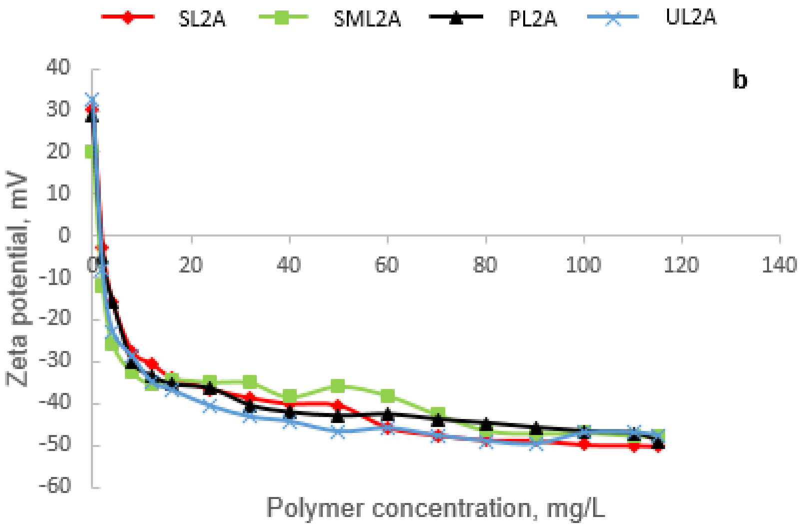


Figure 5.3. (a) zeta potential of unpurified SL1A, SML1A, PL1A and UL1A (b) zeta potential of unpurified SL2A, SML2A, PL2A, and UL2A, as a function of copolymer concentration, which was conducted under the conditions of pH 6, 30 min incubation at 30 °C, and 1 g/L of alumina concentration.

5.3.5. Zeta potential for use of purified lignin copolymer

Figure 5.4 shows the impact of lignin copolymer dosage on the zeta potential of the suspensions. Interestingly, the purification showed no significant effect on the zeta potential of the suspensions, which was also observed in a previous study (Nabzar et al., 1998).

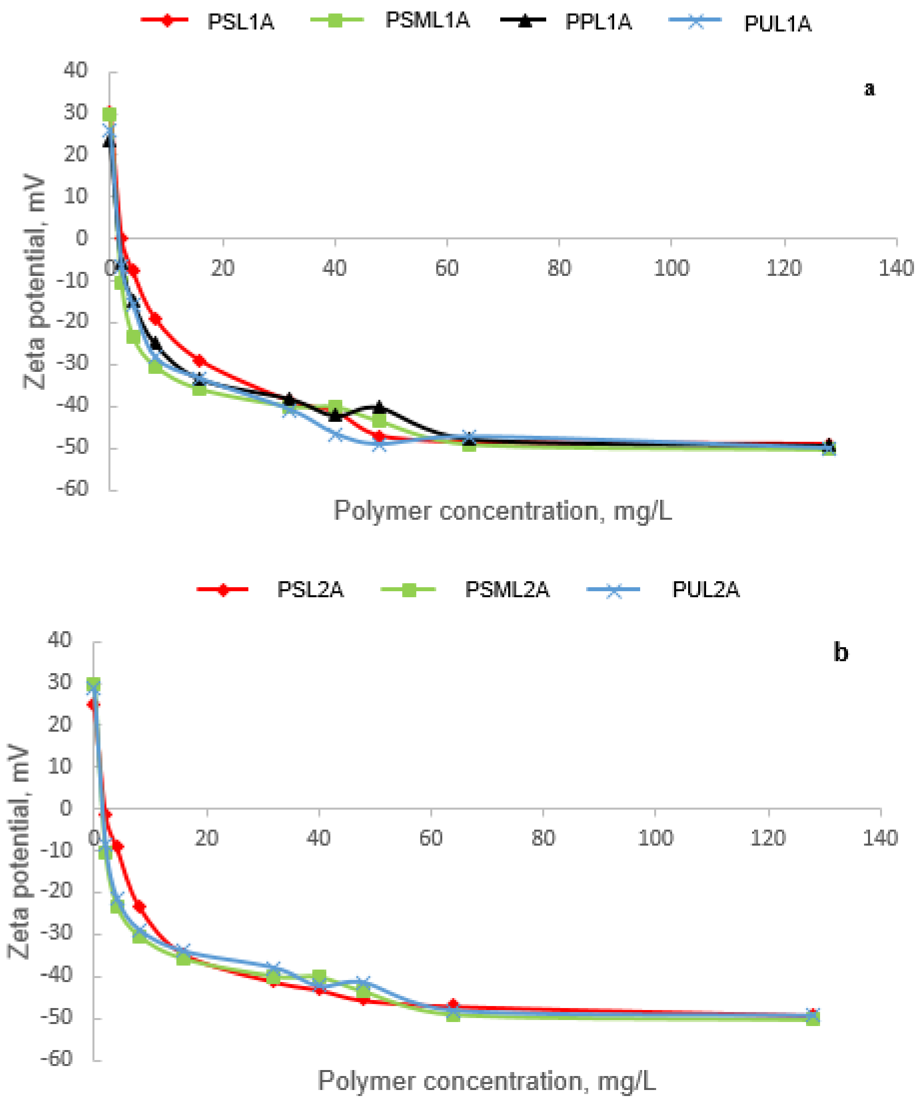


Figure 5.4. (a) zeta potential of purified PSL1A, PSML1A, PPL1A, and PUL1A, (b) zeta potential of purified PSL2A, PSML2A, and PUL2A as a function of polymer concentration conducted under the conditions of pH 6, 30 min of incubation at 30 °C and 1 g/L of alumina concentration.

5.3.6. Flocculation for use of unpurified lignin copolymer

The relative turbidity of the suspended alumina was used to determine the optimum polymer dosage required for flocculating alumina particles in the past (Farrokhpay, 2009; Nsib et al., 2006). Figure 5.5 shows the relative turbidity of the suspension as a function of copolymer dosage (unpurified samples). It is seen that SMLA copolymers reduced the relative turbidity of the suspension more efficiently, while SLA and PLA samples had a similar effectiveness but still higher than that of ULA copolymer. These results are attributed to the large size, higher charge density (Table 4.1), and/or higher adsorption of them on particles that induced flocculation more effectively (Chen, 1998).

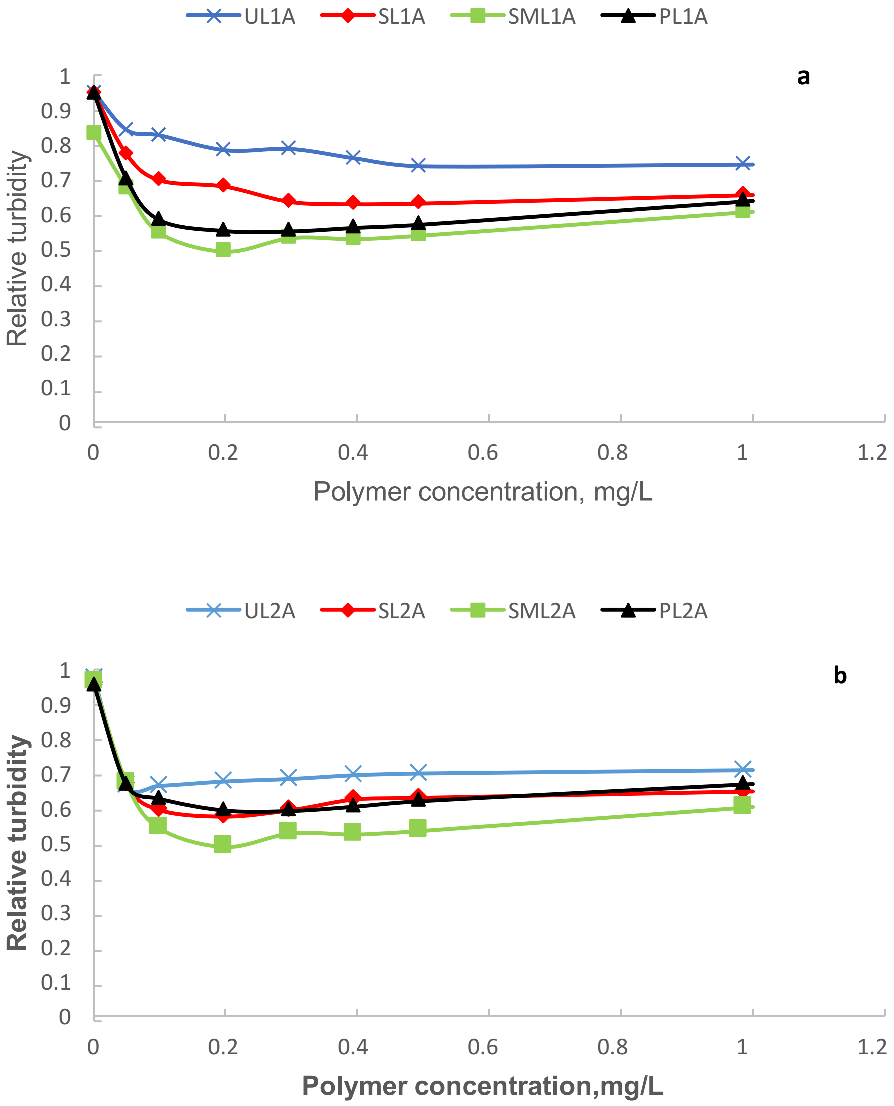


Figure 5.5. the relative turbidity of aluminum oxide suspension as a function of dosage of (a) unpurified UL1A, SL1A, SML1A, and PL1A, (b) UL2A, SL2A, SML2A, PL2A. The experiments were conducted under the conditions of 25 °C for 30 minutes at pH 6 with stirring at 300 rpm.

5.3.7. Flocculation for use of purified lignin copolymers

The relative turbidity of aluminum oxide suspension is plotted as a function of purified lignin copolymers in Figure 5.6. Interestingly, purified PSLA copolymer functioned more effectively in reducing the relative turbidity of the suspension. PULA copolymer was not effective in reducing the relative turbidity, while PSMLA and PPLA copolymers were more influential in reducing in the relative turbidity, these results are attributed to the higher adsorption amount of the copolymers on particles.

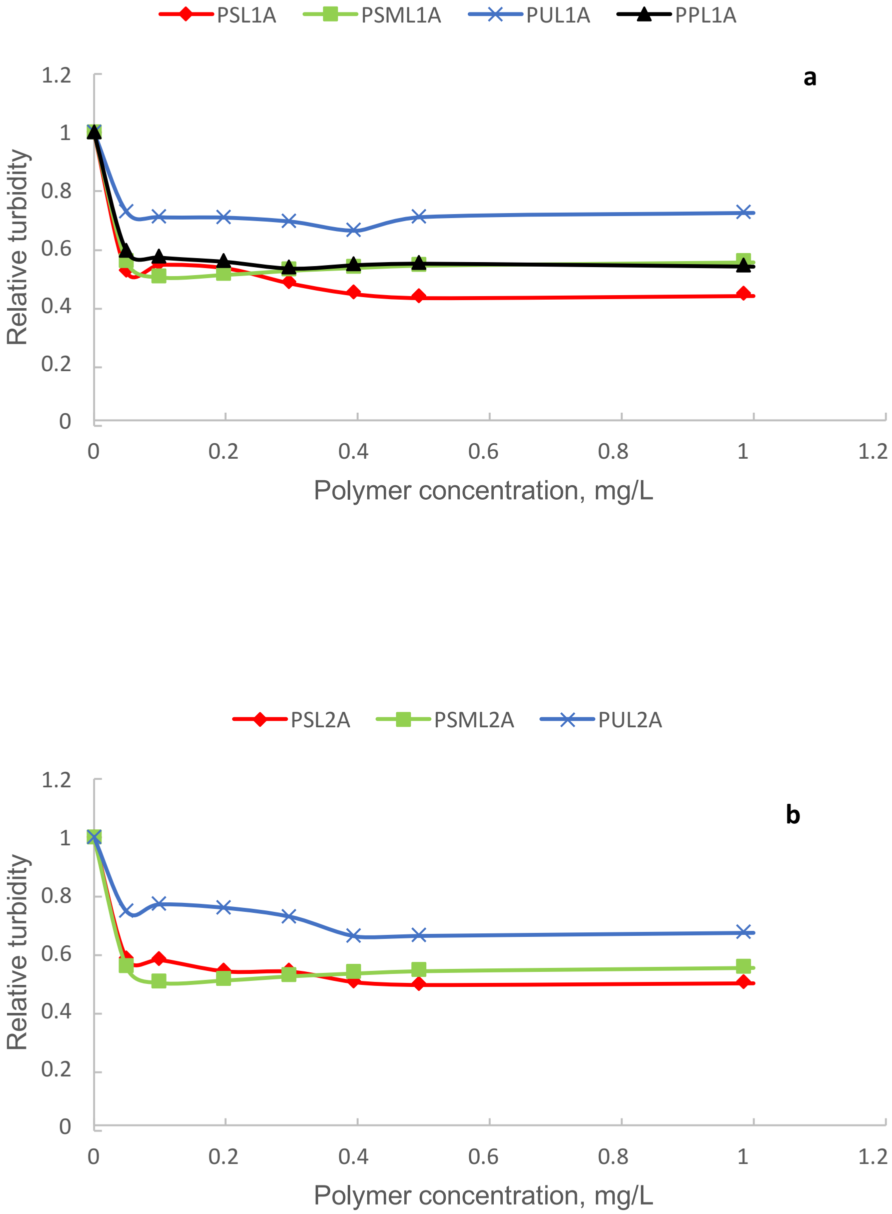
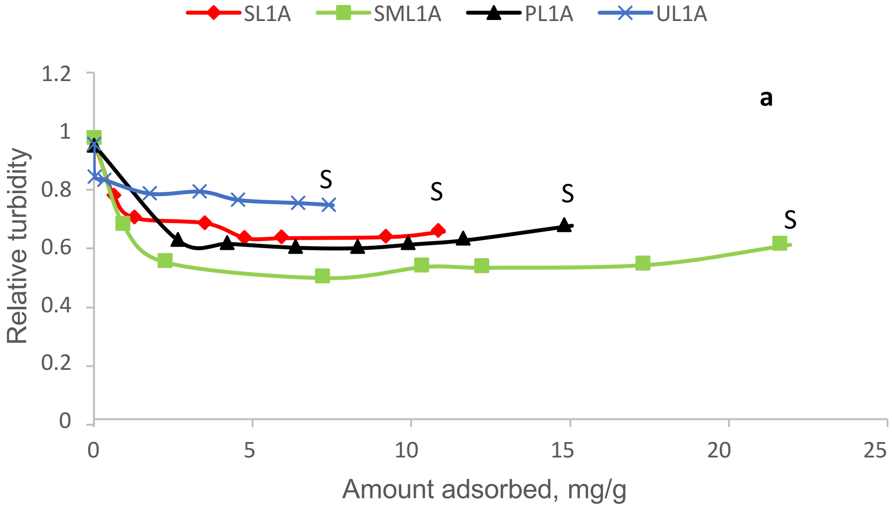


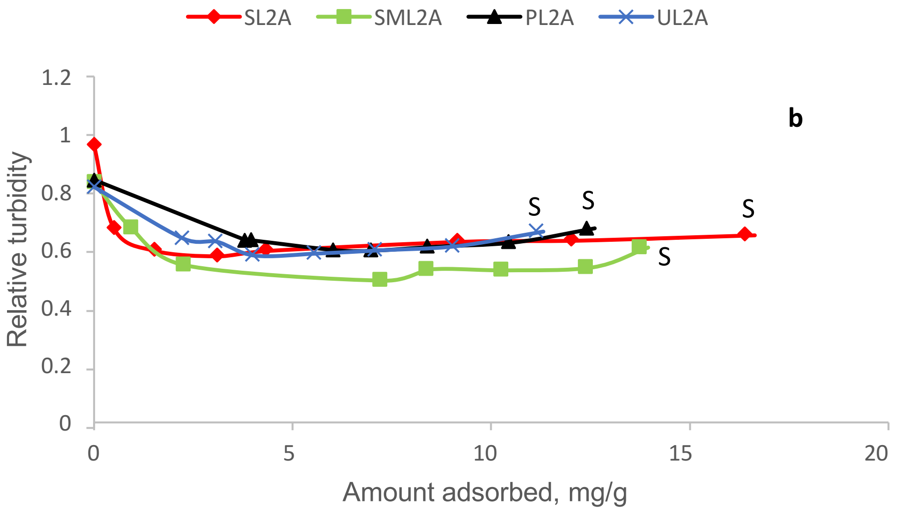
Figure 5.6. The relative turbidity of aluminum oxide suspension as a function of the dosage of (a) purified PUL1A, PSL1A, purified PSML1A, and PPL1A (b) purified PUL2A, PSL2A, and

PSML2A. The experiments were conducted under the conditions of 25 °C for 30 minutes at pH 6 with stirring at 300 rpm.

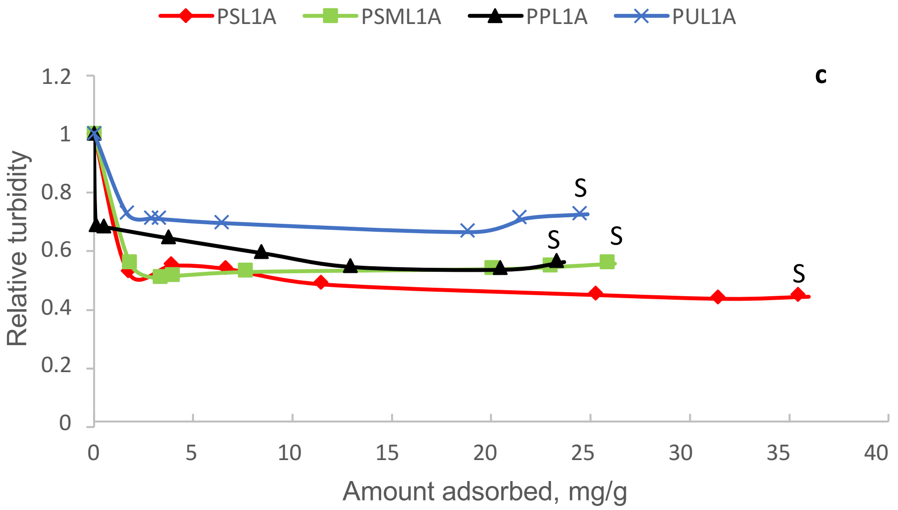
5.3.8. Correlation between relative turbidity, adsorbed polymers and zeta potential

To better understand the mechanism underlying the ability of lignin copolymers to decrease the relative turbidity of alumina suspensions (Figures 5.5 and 5.6), the relative turbidity of the suspension was plotted as a function of adsorbed copolymers (Figures 5.1 and 5.2) in Figure 5.7. It is seen that the initial adsorption of the copolymers from 0.3 mg/g to 5.0 mg/g played an important role (specially for purified samples), but the increase in the adsorption did not impact the relative turbidity. The last points on each curve (point S) show the relative turbidity of alumina suspensions at the maximum adsorption amount that was reached in Figure 5.1 and 5.2. Figure 5.7 (a) and (b) showed that SMLA copolymer was more effective than other samples, while the PSLA copolymer was more effective than PSMLA and PULA copolymers in reducing the relative turbidity of the suspensions.





SL2A
SML2A
PL2A
UL2A
b
Relative turbidity
1.2
1
0.8
0.6
0.4
0.2
0
S
S
S
S
0
5
10
15
20
Amount adsorbed, mg/g



PSL1A
PSML1A
PPL1A
PUL1A
c
Relative turbidity
1.2
1
0.8
0.6
0.4
0.2
0
S
S
S
S
0
5
10
15
20
25
30
35
40
Amount adsorbed, mg/g

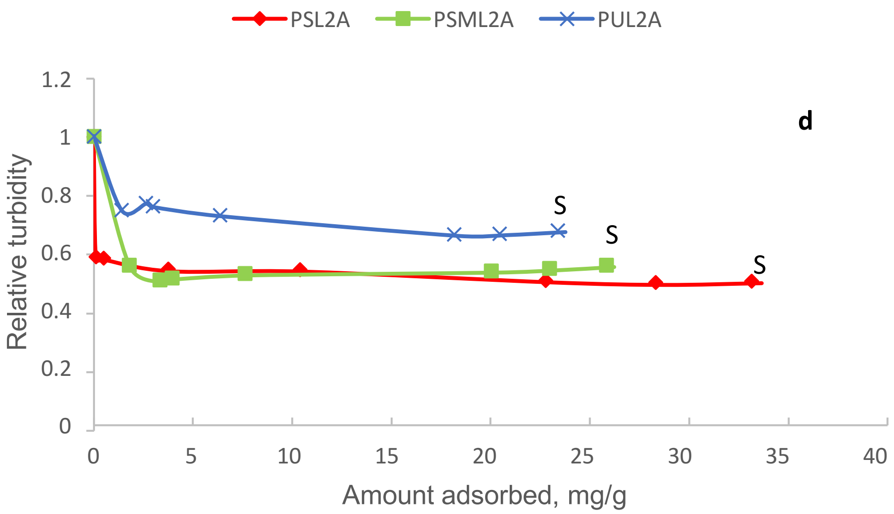
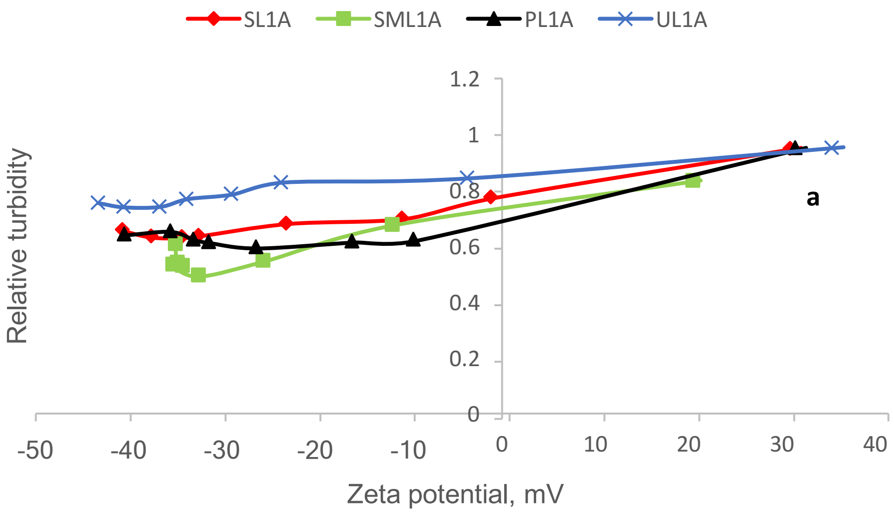
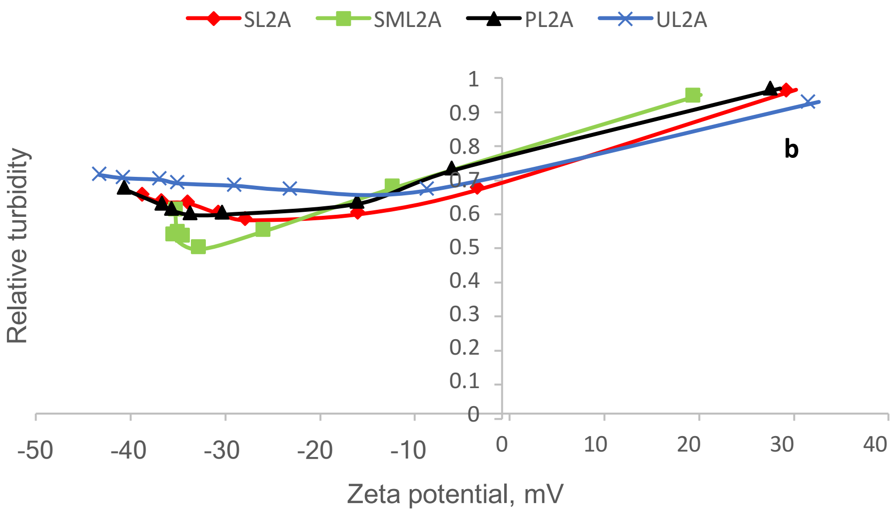


Figure 5.7. Relationship between the relative turbidity and the amount of adsorbed copolymer derived from lignin 1 (a and c), or lignin 2 (b and d), unpurified (a and b) and purified (c and d).

The relationship between the relative turbidity and zeta potential of the suspensions is illustrated in Figure 5.8. The data suggests that by reducing the zeta potential, the relative turbidity dropped, but the minimum relative turbidity was not achieved at approximately zero zeta potential value except for sample of the unmodified lignin copolymer. These results suggest that patching or bridging mechanics were the main reason for the relative turbidity drop for these samples. Interestingly, the minimum relative turbidity was achieved at neutral zeta potential for SLA copolymer, which shows that charge neutralization was the main mechanism for the removal of the particles for this sample. In one study, the relative turbidity of clay suspensions increased to 1.27 with the decrease in the zeta potential of clay particles to -40 mV via using carboxymethylated xylan (Konduri and Fatehi, 2017). In another work, the relative turbidity of the kaolin suspension was decreased to 0.3 when the zeta potential of kaolin suspension was positive (50 mV) (Wang et al., 2011).


SL1A
SML1A
PL1A
UL1A
Relative turbidity
1.2
1
0.8
0.6
0.4
0.2
0
-50
-40
-30
-20
-10
0
10
20
30
40
Zeta potential, mV
a


SL2A
SML2A
PL2A
UL2A
Relative turbidity
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-50
-40
-30
-20
-10
0
10
20
30
40
Zeta potential, mV
b

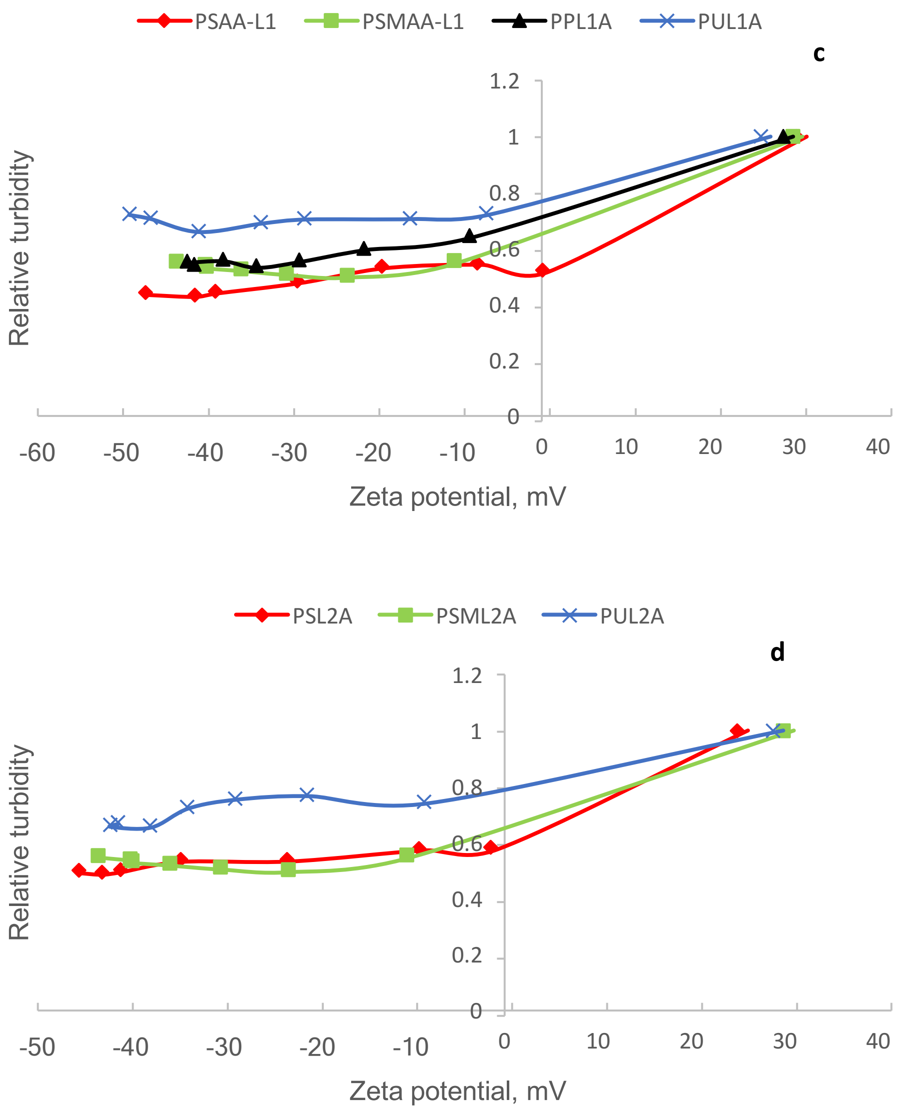
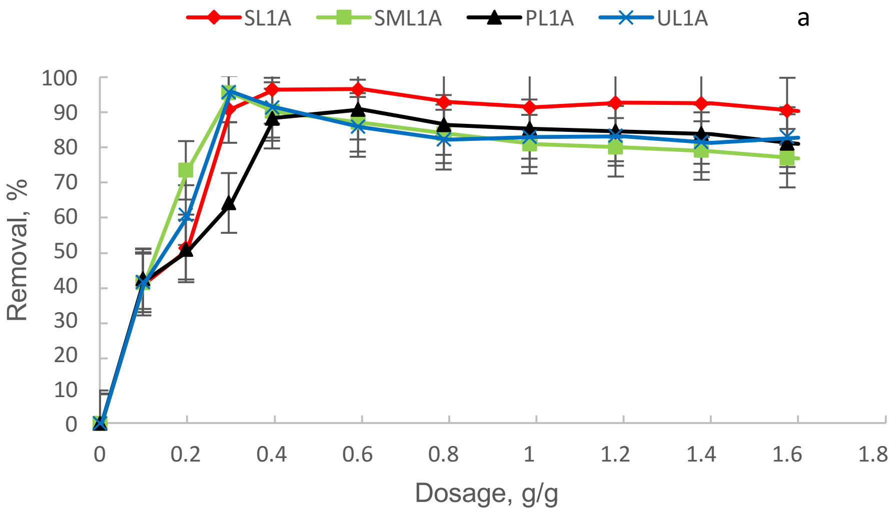


Figure 5.8. The relationship between relative turbidity and zeta potential of the alumina suspensions for copolymers derived from lignin 1 (a and c), or lignin 2 (b and d), unpurified (a and b) and purified (c and d).

5.3.9. Dye removal

To further investigate if the copolymers can act as flocculants for solution systems, the removal of dyes as a function of the copolymer dosage was investigated and the results are shown in Figure 5.9. Interestingly, the unpurified copolymers behaved very similarly and a dosage of less than 0.2 mg/g was sufficient for removing more than 90% of dye from the solutions. In a previously reported study the addition of the copolymer from 10 mg/L to 100 mg/L enhanced the removal of azo-dyes to 70% at pH 6.7 from a simulated solution (Fang et al, 2010; Dahri et al., 2013). In one study, copolymerized lignin (cationic polyelectrolyte) was used as a flocculant for removing 95%, 94%, 95% of three anionic dyes (acid black 1, reactive red 2, and direct red 23) with the concentrations of the three dyes of 50 mg/L and 250 mg/L at 6.5 pH (Fang et al., 2010). Moreover, oxidized lignin can remove 70% of ethyl violet and 85% of basic blue dyes, with the concentration of both dyes solutions of 100 mg/L (Couch et al., 2016). When the copolymer concentration exceeded the optimal dosage, the dye removal declined slightly (Figure 5.9). This may be due to an excess of the copolymer leading to charge reversal and thus redispersion of dye particles in the solution (Rojas and Hubbe, 2005; López-Maldonado et al., 2014).



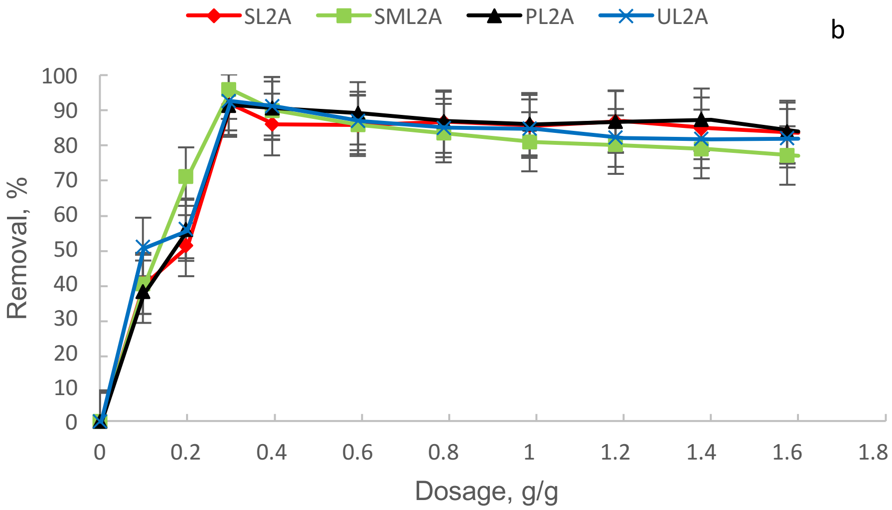
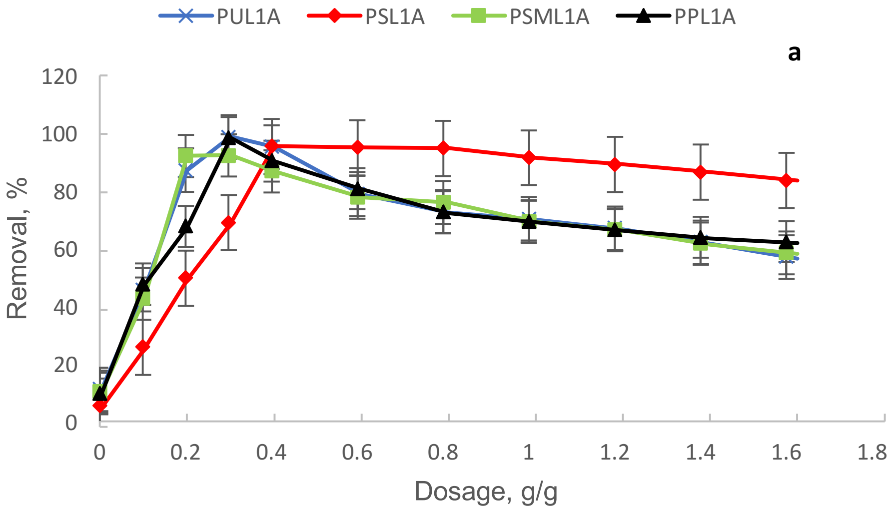


Figure 5.9. Removal of ethyl violet from dye solutions (concentration) as a function of the dosage of (a) unpurified SL1A, SML1A, PL1A and UL1A polymer, and (b) purified SL2A, SML2A, PL2A and UL2A polymer. The experiments were conducted under the conditions of 25 °C for 2h at pH 6.

5.3.10. Dye removal using purified copolymers

Figure 5.10 shows the removal of dyes as a function of the dosage of purified lignin copolymers. It is seen that PSLA copolymer functioned more effectively than PSMLA and PULA copolymer. This behaviour is attributed to the higher charge density of sulfated lignin copolymer as stated in a previous chapter (Li et al., 2008). In other cited work, copolymerized lignin (cationic polyelectrolyte) with a charge density of 2.55 meq/g was more effective as flocculant than unmodified sample (Fang et al., 2010).



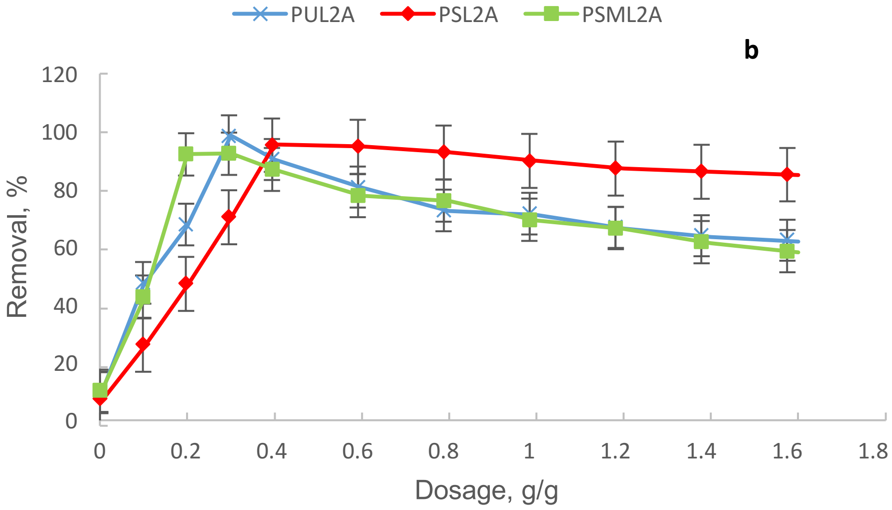


Figure 5.10. Removal of ethyl violet from dye solution as a function of the dosage of (a) PSL1A, PSML1A, PPL1A, and PUL1A polymer, and (b) PSL2A, PSML2A, and PUL2A polymer. The experiments were conducted under the conditions of 25 °C for 2h at pH 6.

It is noted that the copolymers behaved very similarly in aluminum oxide suspension and dye solution. The charge densities and the concentrations of the dye play important roles in obtaining the maximum dye removals in the past (Fang et al., 2010).

5.4. Conclusions

In this chapter, the adsorption of lignin copolymers on aluminum oxide particles was discussed. It was observed that the unpurified SMLA was more effective than other products. It is also seen that the purified PSLA was more effective than other purified products. The zeta potential analysis confirmed that the zeta potential of the suspension was independent of the copolymer type and purification. The relative turbidity analysis confirmed that the unpurified PL1A and SL2A affected the zeta potential more than other samples. Interestingly, the purified samples affected the relative turbidity very differently and they had different flocculation mechanisms for removing the particles. The dye removal analysis confirmed that the unpurified copolymers behaved very similarly. However, purified lignin copolymers had different flocculation efficiencies. The SLA copolymer acted more effectively, and these results were due to a higher molecular weight and charge density of SLA copolymers than others.

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Chapter 6: Conclusions and recommendations

6.1. Summary of conclusions

The present work mainly focussed on preparation of sulfated (SL), sulfomethylated (SML), phenolated (PL) and acrylic acid grafted kraft lignin polymers and their flocculation performance in alumina suspensions and as well as in dye solutions. The adsorption behaviour of modified lignin polymers on alumina suspensions was studied successfully. The effect of polymer concentration, charge density and molecular weight on the flocculation of alumina suspensions was systematically investigated. The application of modified lignin polymers in the removal of dyes from model solutions was successfully employed.

In the process of synthesizing sulfated lignin, the process conditions were optimized and sulfated lignin with a high charge density of 1.90 meq/g was obtained under the conditions of 160 °C, 3 h, and 6.5 molar ratio of H_2SO_4/lignin. The synthesis of sulfated lignin was further confirmed by using molecular weight, FTIR and elemental analysis.

In synthesis of sulfomethylated lignin, formaldehyde and sodium sulfite were used in grafting of sulfomethyl groups to kraft lignin. The process conditions were optimized to obtain sulfomethylated lignin (SML) with desired properties. SML with maximum charge density of 1.50 meq/g and solubility of 99% was obtained under the conditions of 50 °C, time of 1 h and 20 g/L lignin concentration, 0.5 moles NaOH concentration, and 0.1 mol/mol lignin/sodium hydroxymethylsulfonate. The attachment of sulfomethylate group to lignin was further confirmed using molecular weight, FTIR and elemental analysis.

In the process of synthesising phenolated lignin (PL), a phenolate group was grafted on to kraft lignin using liquefied phenol under acidic conditions. PL with maximum solubility of 85 wt.% was obtained under the conditions of phenol/lignin molar ratio of 7.3, the temperature of 80°C, the reaction time of 4 h. Furthermore, the grafting of phenolate group on lignin was confirmed by FTIR, molecular weight and elemental analysis.

In preparation of lignin acrylic acid copolymer, purified or unpurified modified lignin (SL or SML or PL) was copolymerized with acrylic acid with potassium persulfate and sodium thiosulfate as intiators. Purified sulfated lignin copolymer with maximum charge density of 3.40 meq/g was obtained under the conditions of AA/lignin molar ratio 8, 3 h at 70 °C, 0.35 mol/L of lignin at pH 2 and 1.5 w.t.% initiator dosage. Similar process conditions were considered for copolymerizing sulfomethylated and phenolated lignins with acrylic acid. The structure, physical and chemical properties of modified lignin copolymer was further confirmed via studying the properties of unmodified and modified lignin copolymer using charge density, molecular weight, FTIR, ^{1}HNMR, elemental and thermogravimetric analysis

The adsorption and zeta potential studies confirm that, modified polymers adsorbed on alumina surface via electrostatic interactions. By increasing the concentration of polymer, adsorption of polymers on the surface of alumina also increased. Purified SL-acrylic acid copolymer exhibited maximum adsorption of 43.3 mg/g under the conditions of 110 mg/L polymer concentration, 30 °C pH 7 and 0.5 h. Relative turbidity studies indicates that, flocculation behaviour of alumina suspensions depends on polymer concentration, adsorbed amount of polymer on alumina surface and zeta potential of alumina particles. Purified SL-acrylic acid lignin copolymer caused a maximum reduction in relative turbidity up to 0.4. Furthermore, all the modified lignin copolymers exhibited effective removal of ethyl violet dye from model solutions, with purified SL copolymer showing high performance.

6.2. Recommendations for future work

As investigated in the thesis, synthetic suspensions or solutions were used as models for flocculation studies. However, the industrially produced samples may have different compositions and conditions. Thus, it is good to investigate further on industrial samples to generate more industrially attractive results.