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Biomass Derived Lignin Polymer Modification for Sustainable Chemical Engineering Applications

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Honors Thesis

Biomass Derived Lignin Polymer Modification for Sustainable Chemical Engineering Applications

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1. Abstract

Lignin is an abundant naturally occurring plant-based polymer that is branched, highly unsaturated, and rich in aliphatic and aromatic hydroxyl groups. Lignin is a significant byproduct of the wood pulp and paper industries; however, it has yet to be widely utilized in commercial applications due to its non-linear structure, broad range of molecular weights, hydrophobicity, high rigidity, and brittleness. Recent investigations into modifying lignin to broaden its potential uses have shown promising results. This thesis explores different modification techniques of the naturally occurring hardwood lignin polymer for specific applications in areas of water treatment and polyurethane (PU) production. The first project utilized lignin phenolation and subsequent amination for the removal of toxic anionic azo dyes from solution. Each reaction step characterized by Fourier transform infrared (FTIR) spectroscopy to confirm chemical reaction, and ultraviolet-visible light spectroscopy (UV-vis) to monitor dye removal over time throughout multiple dye removal tests. The second project aimed to modify lignin to act as the foundational polyol and isocyanate precursors of PU synthesis, for ultimate use in a completely lignin-based PU product. Building upon the successful results in the synthesis of two modified lignin-based polyols, these polyols were employed to develop three partially lignin-based PUs. Each of the lignin-based PU products were characterized by FTIR spectroscopy, and both water contact angle goniometry and thermogravimetric analysis (TGA) to assess wettability and thermal stability of the final PU products respectively.

2. Background

Lignin is the second most abundant naturally occurring polymer in the world, next to cellulose [1]. Initiated by monolignol oxidation for radical formation, lignin is formed by an in-situ free radical polymerization of three monolignols that are passed from the plant cell cytoplasm to the plant cell wall [2]. These alcohols can then be identified within the final lignin structure as the *p*-hydroxylphenyl, gauiacyl, and syringyl repeat units, as shown in Figure 1. The distribution of these residues is dependent on the plant matter in which they appear. Softwood lignin exhibits approximately 90% gauiacyl units, while hardwood lignin exhibits between 50-75% gauiacyl units with the remainder due to syringyl units [3]. However, herbaceous plant matter exhibits a wide variety of ratios between all the three repeat units that is further dependent on plant type under investigation (i.e. grasses, palms, leaves, or flowers) [3].

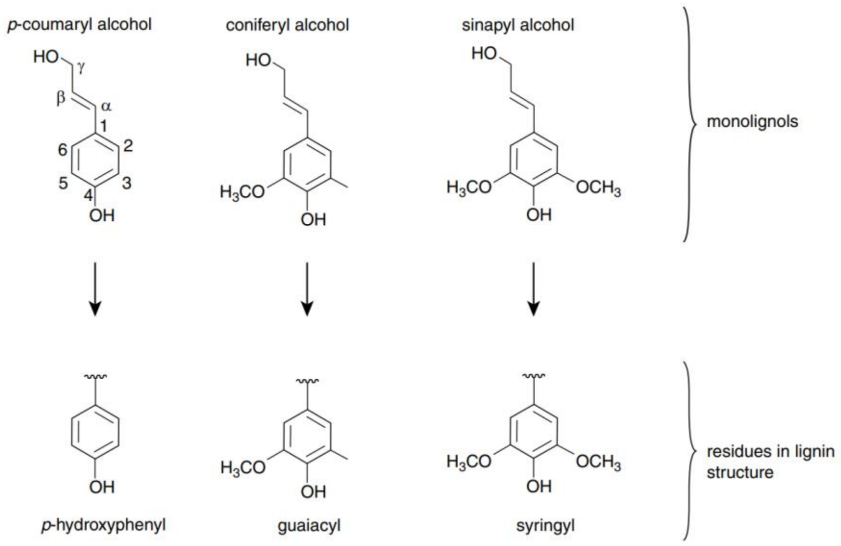


Figure 1. Monolignol to lignin primary residue structures [3]

Lignin is already being harvested commercially as a byproduct of the delignification process in the wood pulp and paper making industries. However, the biopolymer has yet to be widely utilized due to its unique and intrinsically difficult properties to work with, including but not limited to having a non-linear structure, a broad range of molecular weights, high hydrophobicity, high rigidity, and brittleness [4]. In the process of delignification, lignin is separated from the usable paper pulp in a solution of black liquor from which the polymer may then be precipitated out in one of four pulping processes shown in Figure 2 [3]. Currently, black liquor is burned as a low efficiency energy source in many papermills. However, due to the shear rate of black liquor production, millions of tons of lignin are underutilized every year [5]. Because paper production industries target hard- and softwoods for pulp production, this thesis divulges the valorization of hardwood lignin that has been harvested via the alkaline kraft pulping process.

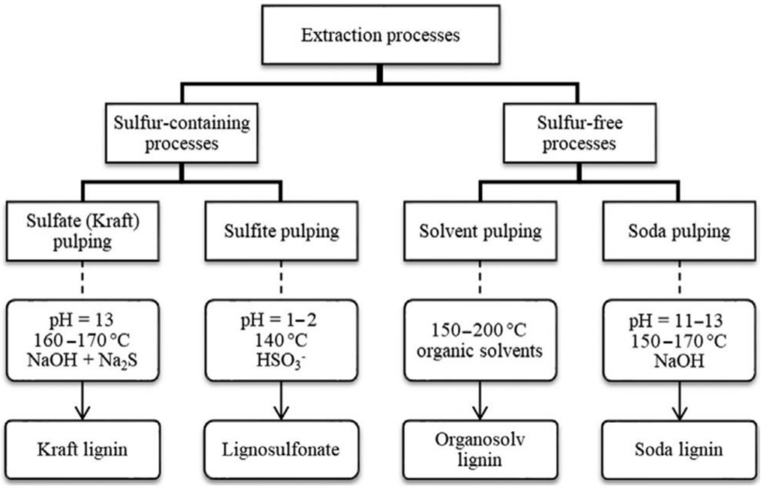


Figure 2. Lignin extraction processes [3]

This thesis aims to modify hardwood kraft lignin for amplified engineering properties. The utilization of lignin in this way not only helps create a more circular economy by repurposing one of the largest waste streams of an inherently necessary industry, but also promotes the end-of-life product degradation given the naturally sourced basis of the bio-mass derived lignin products. The two applications to be examined are: lignin amination for anionic dye removal water treatment and lignin modification for sustainable alternatives in polyurethane production.

3. Lignin modification for dye removal water treatment

A 2022 study reported that on an annual basis approximately 108 tons of synthetic dyes are produced globally, with azo dyes accounting for 60-70% of synthetic dye production [6]. Concern arises because azo dyes exhibit carcinogenic, mutagenic, and teratogenic properties that severely threaten human and environmental health and safety when improperly disposed of [6]. To mitigate these threats, lignin amination shows promising results for anionic azo dye removal. By utilizing the ionic interaction between the partial positive charge associated with the newly added amine groups in the biopolymer, the partial negative charges in the anionic dyes can be targeted and drawn out of solution. For this purpose, the following project aims to assess the ability of lignin to be aminated by Mannich reaction, and further to evaluate the dye removal properties of aminated lignin, specifically for Congo red (CR) and methyl orange (MO) dye removal. These dyes are classified as synthetic anionic azo dyes and are mass produced for use in the textile industry [6]. When made into an aqueous solution, the sodium ions dissociate from each of the dyes leaving a partial negative charge on each of the sulfonate functional groups, as shown in Figures 3.

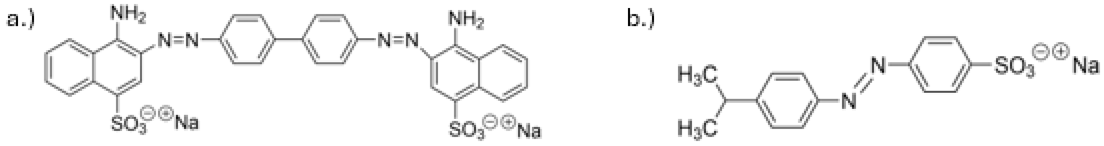


Figure 3. Chemical structures for the dyes studied: a) Congo red; b) methyl orange

To increase the success of the amination modification, the lignin was first phenolated to introduce more readily available aromatic hydroxyl groups into the lignin structure, which proved to be an excellent precursor in the preparation of aminated lignin. Both the phenolated and aminated lignin products were characterized by FTIR spectroscopy, then the aminated lignin was used to carry out CR and MO dye removal tests. Various pH values and concentrations of aminated lignin were used for dye removal treatment. UV–vis was used to monitor dye removal over time, and pH changes were also recorded over the 96 hour time frame.

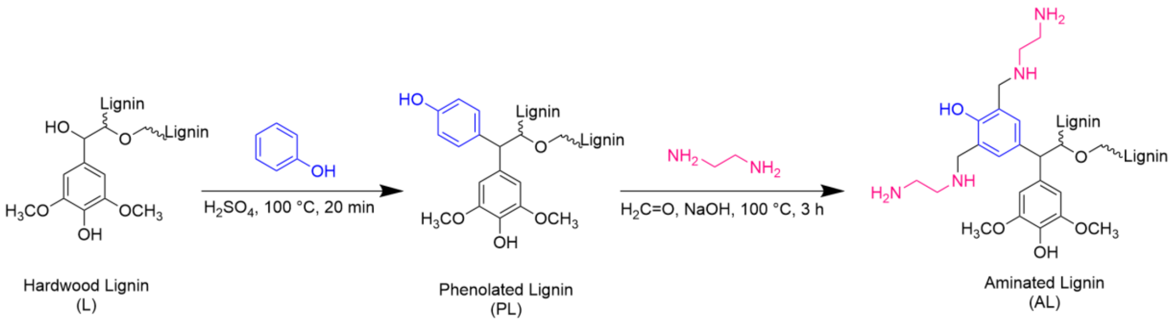
3.1 Materials and methods

3.1.1 Materials

Kraft lignin (CAS 9005-53-2) was purchased from TCI America. A 89% purity phenol solution (CAS 108-95-2) was purchased from Amresco. A 98% purity sulfuric acid (CAS 7664-93-9), 37% formaldehyde solution (CAS: 50-00-0), and sodium hydroxide (CAS 1310-73-2) were all purchased from MilliporeSigma. Hydrochloric acid (CAS 7647-01-0) was purchased from ThermoFisher Scientific. Congo red dye (CAS 573-58-0) was purchased from VWR Chemical. A 99% purity ethylenediamine solution (CAS 107-15-3) was purchased from Alfar Aesar Chemical. Methyl orange dye (CAS 547-58-0) was purchased from LabChem, Inc.

3.1.2 Synthesis

With a final goal of introducing amine groups to the lignin structure, the biopolymer was first phenolated to introduce more readily available aromatic hydroxyl reaction sites for the amination reaction. This created less sterically hindered reaction sites relative to the aromatic hydroxyl groups native to the lignin structure, thus promoting the ortho- para-addition of the ethylene diamine (EDA) amine source. This reaction schematic is displayed in Scheme 1.



Scheme 1. Hardwood lignin phenolation and subsequent amination

Lignin phenolation: In the phenolation process, a 1:2 by mass ratio of lignin to phenol was used. In a 25 mL round bottom flask, 1 g of kraft lignin was slowly dissolved in 1.87 mL of phenol while stirring vigorously. The solution was placed in a silicone oil bath at 100 °C, where 0.033 mL of 72% sulfuric acid catalyst was added. The solution was allowed to react with continuous stirring for 20 minutes, at which point it was removed from the oil bath and allowed to cool to room temperature. The phenolated lignin was then precipitated out of solution with a 2 M solution of hydrochloric acid (HCl). Approximately 28 mL of HCl were added until the solution reached a 4.45 pH value. The purification of the final phenolated lignin (PL) product utilized an acidified aqueous solution (0.01 M HCl) and two subsequent deionized-water centrifuge washes at 10 °C, and a relative centrifuge force (rcf) of 7000, for 15 minutes. Post centrifuging, the solid product was plated on a petri dish for drying. The recovered product was oven dried at 50 °C, and the final product was recovered as a fine black powder.

Lignin amination: The amination reaction is conducted in a sodium hydroxide (NaOH) solvent. In a 25 mL round bottom flask, 0.5 g of PL was slowly added to 4 mL of a 1 M NaOH solution, while stirring continuously. Once fully dissolved, the flask was transferred into a silicone oil bath at 100 °C, where 1.22 mL of formaldehyde and 0.83 mL of EDA were added to solution. The solution was allowed to react for 3 hours with continuous stirring. After reaction, the sample was allowed to cool to room temperature. The product was dialyzed using snakeskin dialysis tubing with a molecular weight exclusion of 3500 Da. The sample was dialyzed over a period of 2 days with 5 water changes. The dialysis was stopped after the water remained clear for at least 5 hours. The remaining contents of the dialysis tubing were then plated on a petri dish and allowed to fully dry in the fume hood at room temperature. The recovered product was a fine dark powder.

3.1.3 Water dye removal methods

Upon completion of the aminated lignin (AL) synthesis, multiple dye removal tests were conducted for CR and MO dyes. Across two sets of trials, the dye solution pH and the AL concentration used for treatment were varied. Across all trials, 10 mL of dye solution was used at a concentration of 0.0125 mg/mL and 0.0128mg /mL of CR and MO dyes respectively. These tests were carried out over a period of 96 hours, with centrifuge separation after both 48 hours and 96 hours of AL treatment. UV-vis was used to monitor the dye removal progress over time. The UV-vis results for all the dye removal tests can be found in Appendix A.5-15.

Varied pH trials: The varied pH trials assessed the dye removal properties of AL in dye solutions at a basic (pH circa 10), native, and acidic (pH circa 4) case. Both native dye cases were slightly alkaline, around 8.8-9 on the pH scale. The basic and acidic case solutions were adjusted with the addition, on the order of microliters, of either 1 M NaOH or 1 M HCl. Each of these trials were treated with approximately 1 mg AL per 10 mL of dye solution. The actual values used in these trials are outlined in Table 1.

Table 1. Initial solution conditions for varied pH dye removal tests

Solution Components (mg/mL)	**CR Basic pH = 9.98**	**CR Native pH = 8.87**	**CR Acidic pH = 3.84**	**MO Basic pH = 10.09**	**MO Native pH = 9.16**	**MO Acidic pH = 3.88**
HCl	---	---	0.0073	---	---	0.0073
NaOH	0.060	---	---	0.088	---	---
[AL]	0.111	0.119	0.118	0.118	0.107	0.112
CR	0.0125	0.0125	0.0125	---	---	---
MO	---	---	---	0.0128	0.0128	0.0128

Varied AL concentration trials: The varied AL concentration trials used the native pH cases of each of the dyes and were treated with either a low concentration, approximately 0.5 mg, or high concentration, approximately 2 mg of AL per 10 mL of dye solution. Exact quantities of starting materials used for each of these tests can be found in Table 2.

Table 2. CR and MO dye solutions used to assess the impact of AL concentration

Solution Components (mg/mL)	**CR, high [AL]**	**CR, low [AL]**	**MO, high [AL]**	**MO, low [AL]**
CR	0.0125	0.0125	---	---
MO	---	---	0.0128	0.0128
[AL]	0.058	0.205	0.054	0.206

3.2 Results and Discussion

FTIR: FTIR spectroscopy was used to determine the chemical structure of unmodified lignin, PL, and AL, these spectra are shown below in Figure 4. FTIR was used to quantify the increase in aromatic hydroxyl groups in PL as well as to identify the EDA complexes in the AL structure. For each of these reactions, a peak ratio between the absorbance of the peak of interest and a reference peak was used to quantify the increases in functional groups of interest. A reference peak at 1032 cm^{-1}, corresponding to the carbon-oxygen (C-O) stretch in ether groups, was used in both cases [7]. This is a regularly occurring functional group in the unmodified lignin starting material and is not expected to change throughout these reactions, thus making the ether group a reliable reference peak to monitor increases in peaks associated with newly added functional groups.

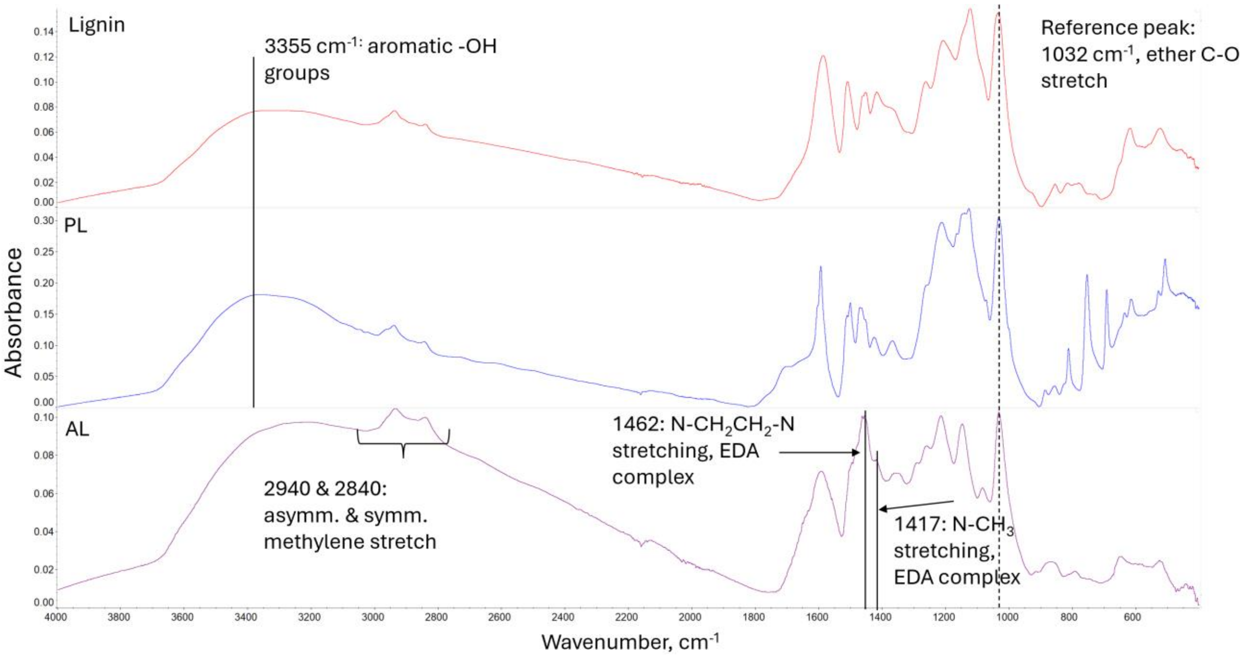


Figure 4. FTIR spectra of unmodified lignin, PL, and AL products.

The peak of interest following the phenolation reaction was at 3355 cm^{-1} that is associated with aromatic hydroxyl groups [8]. When compared to the reference peak, the unmodified lignin exhibited a peak ratio of 0.441 for aromatic hydroxyl absorbance to ether stretching absorbance. This peak ratio increased by 34.5% after the lignin phenolation reaction, confirming the addition of aromatic hydroxyl groups due to the modification reaction. As for the AL, peaks at 1417 cm^{-1} and 1462 cm^{-1} both associated with EDA complexes became prominent post Mannich reaction, indicating successful addition of amine functional groups [7]. The peak at 1417 cm^{-1} is characteristic of stretching across the entire EDA structure, while the peak at 1462 cm^{-1} is associated with stretching specifically between the nitrogen and methyl group of EDA [7]. These peaks increased by a 34.2% and 71.0% respectively. Additionally, a 128% and 105% increase in peaks at 2840 cm^{-1} and 2940 cm^{-1} respectively was observed which suggests a large increase in the number of methylene groups present in the final AL structure [8]. This is consistent with the Mannich reaction predictions, as there are two additional methylene groups in the final structure due to each EDA addition and one additional methylene group due to the linkage formed by the formaldehyde between the secondary amine and lignin phenolic ring. This further confirms Mannich reaction success.

Dye removal test results: The initial colors for the dye removal tests are shown in Appendix A.1. Because both CR and MO dyes are also used as pH indicators, the acidic trials for both dyes exhibit significantly different colors than the basic and native cases. A UV-vis scan was taken for each of these samples at the zero hour to establish an initial color peak for each trial. The true red color of the basic and native CR trials exhibited an initial color peak at 498 nm, while the deep purple color in the acidic case exhibited an initial color peak at 562 nm. The MO trials exhibited color peaks at 465 nm and 478nm for the yellow and orange colors respectively.

The initial color peaks decreased significantly within the first 16 hours of treatment with AL. However, after 23 hours of treatment it was clear that although the dye was being removed from solution, the dye aggregates remained suspended which led to a considerable bias in the UV-vis readings. The suspended dye particulates gave the samples a hazy appearance, pictured in Appendix A.2. Most notable in the acidic trials, the solution is hazy and dull in color, contrary to the very transparent and richly colored initial photos (Appendix A.1). This increase in solution opacity due to the suspension of AL-dye aggregates in each of the samples led to an overall increase in UV-vis absorption. This trend was particularly notable in the acidic trials and high concentration AL treatment trials. The UV-vis scans in Appendix A.10 clearly illustrates a decrease in color peak despite an overall increase in UV absorption. To mitigate this bias, each of the samples was centrifuged to force the settling of the AL-dye aggregates out of solution. After 48 and 96 hours of AL treatment, the samples were centrifuged with a rcf of 7000 for 10 minutes at room temperature. The final dye solution colors are shown in Appendix A.3.

To quantify the amount of dye removed from each of the trials over time, the percent dye removal was calculated for each set of UV-vis scans using equation (1). In the acidic trials, each of the dyes underwent a color change as the solution pH surpassed the indicator dye equivalence points. For these calculations, the maximum amplitude of each color peak was used, as opposed to the amplitude at one specific wavelength. For example in Appendix A.7, for the acidic CR trial, the absorbance associated with the zero hour initial color peak amplitude at 562 nm was compared to that of the final color peak amplitude was at 498 nm.

These results are plotted in Figures 5 & 6 for the varied pH and varied concentrations of AL used for treatment respectively.

$$\left(\frac{initial\ absorbance-measured\ absorbance}{initial\ absorbance}\right) * 100 = \%\ removal \tag{1}$$

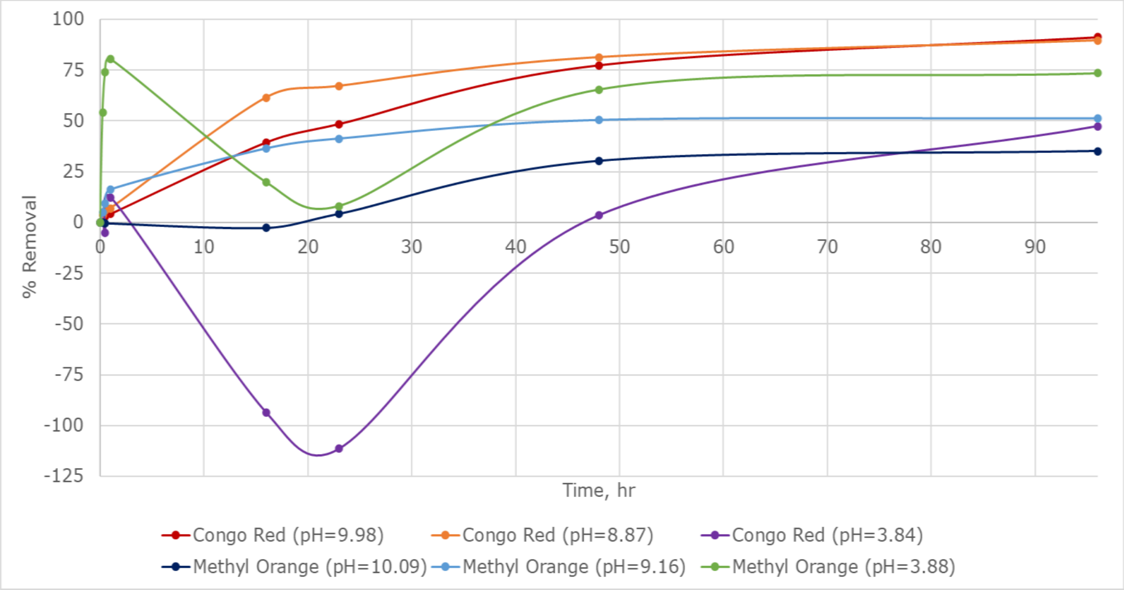


Figure 5. Percentage dye removal over time of varied pH dye removal tests

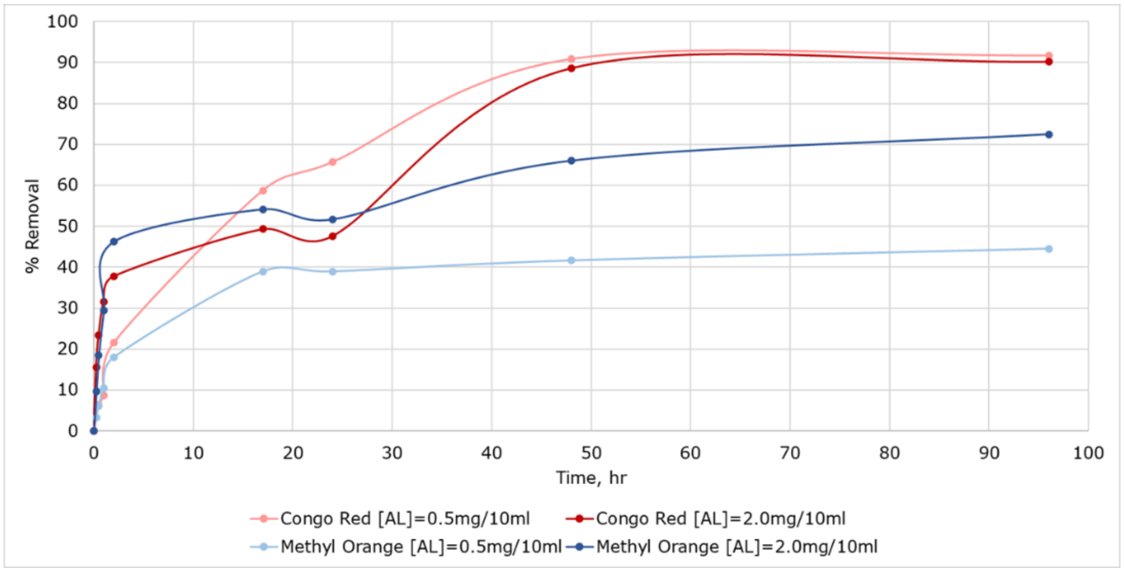


Figure 6. Percentage dye removal as a function of time for various AL concentrations

The CR trials achieved an 89-91% dye removal across all trials, while the MO trials achieved only a 35-73% dye removal across all trials. Each of the acidic tests exhibited extreme declines in percent dye removal after 23h hours, this is attributed to the dye particulates suspended in solution causing the solution to have an opaque appearance and further causing the UV-vis absorption readings to be higher than anticipated. A similar result was observed for the high concentration AL trials, with slight declines in percentage dye removal after 23 hours of treatment. However, post centrifuging, the percentage dye removal increased drastically and is a much more accurate reflection of the amount of dye removed from solution in each case.

Moreover, pH neutrality was restored over time for all AL treatment trials. This result was visible in the acidic trials as the colors changed for each of the indicator dyes when surpassing the equivalence point. This color change is documented between Appendices A.1 & 2 which picture the dye removal samples at the zero hour and after 23 hours of AL treatment. The changes in pH over time for this set of trials was monitored and is plotted in Figure 7. The best results were seen in the MO trials which deviated by 2-3 pH values towards neutrality from initial values.

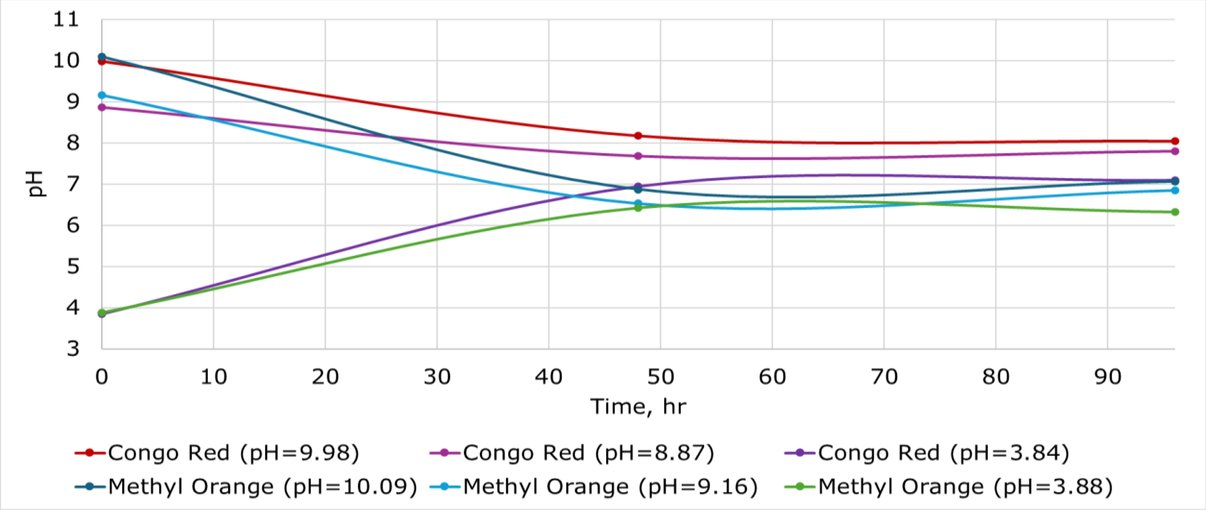


Figure 6. pH changes over time for the varied pH dye removal trials

The more significant results for restored neutrality seen in MO as opposed to CR is attributed to the number of sodium cations left in solution after dye removal. Because MO only has one ionic site, as opposed to CR which has two, it releases half as many sodium ions into solution and further has half as much influence on the activity of the hydronium ion concentration in solution. The excess sodium cations decrease hydronium activity and further increase pH. In the case of MO there is less influence due to low sodium ion concentration, which allows these trials to be more responsive to pH neutrality restoration.

3.3 Project Conclusions

The reaction schematic for lignin amination by Mannich reaction allows for a biomass derived and potentially biodegradable dye removal agent. Additionally, while AL has the potential to remove any anionic dyes from solution, the best results were seen with CR. This is attributed to CR having two anionic sites that are targeted by the AL for dye removal, as opposed to MO which only has one. As a result, CR consistently achieved 89-91% dye removal, as opposed to MO which achieved between 35-73% dye removal across all trials. The trails varying the concentration of AL used for treatment exhibited very consistent dye removal over time for both dyes and both concentration levels. This suggests that given the appropriate treatment time, similar results can be achieved for each dye while using less AL. Further, centrifuging was deemed a necessary step to truly remove the dye from solution. While the AL can precipitate the anionic dyes out of solution, a more rigorous physical treatment process is necessary to remove the suspended particulates from the samples.

4. Lignin modification for sustainable alternative in polyurethane production

Polyurethanes (PU) are a versatile plastic that require polyol and isocyanate precursors which are typically petrochemically derived. Typical PU synthesis exhibits poor degradability, requires extreme reaction conditions, and produces toxic byproducts that threaten human health and safety [9]. Using lignin-based polyol and isocyanate alternatives as feedstock materials shows promise for more sustainable PU production but requires the appropriate lignin modification. Implementation of modified lignin-based PU production would not only minimize toxicity risks associated with the synthesis of PU precursors, including the use of cyanide and the production of phosgene gas, but it would also promote the biodegradability of the final PU products. Modified by phenolation and hydroxypropylation, lignin was first used as a polyol in the synthesis of a partially lignin-based PU. These modification methods were evaluated with the intent of increasing the number of available aromatic and aliphatic hydroxyl groups, respectively. The polyol products were then reacted with methylene diphenyl isocyanate (MDI), a commonly used diisocyanate for industrial-scale PU production, to form a partially lignin-based PU. For each reaction step, the products were characterized by FTIR spectroscopy, water contact angle goniometry, and TGA to confirm chemical composition, assess surface wettability, and analyze thermal stability, respectively. The resultant lignin-based PUs offer a lower toxicity and more environmentally friendly alternative to current petrochemically based PU foams, coatings, and elastomers.

4.1 Materials and methods

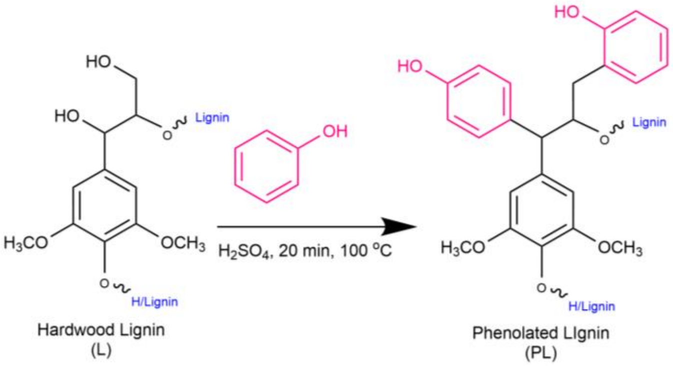
4.1.1 Materials

Kraft lignin (CAS 9005-53-2) was purchased from TCI America. A 89% purity phenol solution (CAS 108-95-2) was purchased from Amresco. A 98% purity sulfuric acid (CAS 7664-93-9), and 37% formaldehyde solution (CAS: 50-00-0), propylene oxide (CAS 75-56-9) and potassium hydroxide (CAS 1310-58-3) were all purchased from MilliporeSigma. 4,4'-Methylenebis(phenyl isocyanate) 98% purity (CAS 101-68-8) was purchased from ThermoFisher Scientific. Dimethyl sulfoxide, 99.9% purity (CAS 67-68-5) was purchased from Sgima-Aldrich.

4.1.2 Synthesis

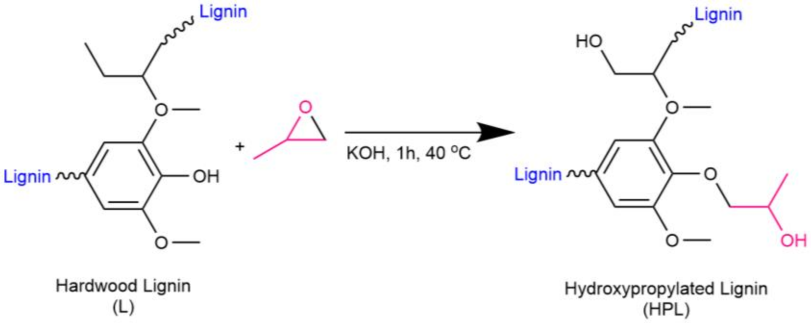
Unmodified lignin has an ample number of naturally occurring aliphatic and aromatic hydroxyl groups already present in the biopolymer. However, the shear complexity of the naturally occurring lignin polymer makes these hydroxyl groups extremely sterically hindered and unlikely to react. The following syntheses are used with the intent of creating an enhanced lignin-based polyol by increasing the number of aromatic and aliphatic hydroxyl groups available for reaction via lignin phenolation and lignin hydroxypropylation.

Lignin phenolation: This means of lignin modification was used as previously described in section 3.1.1, and displayed in Scheme 2 below. Briefly, phenol was used as the aromatic hydroxyl source, reacted in a 1:2 by mass ratio of unmodified lignin: liquid phenol, with a sulfuric acid catalyst. The product was centrifuge washed, and oven dried, yielding a dark fine powder as the final product.



Scheme 2. Hardwood lignin phenolation

Lignin hydroxypropylation: This means of lignin modification was used to increase the number of aliphatic hydroxyl groups readily available for reaction, as outlined in Scheme 3. Propylene oxide was used as the aliphatic hydroxyl source, carried out in a 2.5 M potassium hydroxide (KOH) solution. In a 25 mL round bottom flask, 0.5 g of kraft lignin was slowly dissolved in 5 mL of the 2.5 M KOH solution while stirring continuously. Once fully dissolved, the flask was transferred into a water bath at 40 °C. Then 5mL of propylene oxide was added dropwise to solution and allowed to react for one hour. The solution was then allowed to rest at room temperature for 24 hours. A 2.0 M HCl solution was then added dropwise until the solution reached a pH circa 2.5 and a precipitate was formed. The solution with precipitate was then centrifuge washed with deionized water three times at a rcf of 7000, for 15 minutes, at 11°C. Finally, the solid product was placed in the oven at 50 °C until completely dried. The final product was recovered as a fine black powder.

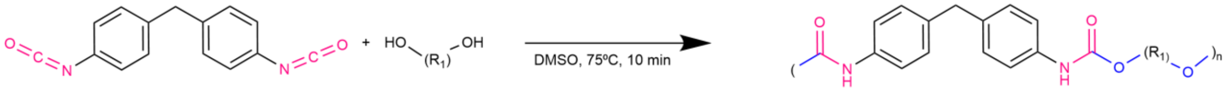


Scheme 3. Hardwood lignin hydroxypropylation

Lignin-based PUs: These reactions aimed to synthesize a partially lignin-based PU in its simplest form, using only a polyol and isocyanate in dimethyl sulfoxide (DMSO) solvent without any additives. Three lignin-based PUs were synthesized using unmodified lignin, PL, and HPL as polyol sources in conjunction with MDI. As outlined in Scheme 4, this reaction forms the imperative and complex urethane linkage, which is a convoluted functional group with amine, amide, carbonyl, ester, and ether-like constituents. Prior to PU synthesis, a solution of each lignin polyol in DMSO solvent was prepared using approximately 0.1 g of lignin polyol per 1 mL of DMSO solvent. Actual values for these stock solutions are listed in Table 3. Each of these solutions was sonicated for 25 minutes immediately after mixing and allowed to rest for at least 24 hours before use.

Table 3. Lignin polyol-DMSO stock solutions used for lignin-based PU syntheses

Lignin type	**Lignin amount, g**	**DMSO amount, mL**
Unmodified Lignin	0.15670	15
PL	0.10836	10
HPL	0.10836	10



Scheme 4. Partially lignin-based PU synthesis utilizing lignin-based polyols in conjunction with MDI

In a silicone oil bath at 75 °C, 5 mL of lignin polyol solution was added to a 25 mL round bottom flask. While stirring vigorously, approximately 800 rpm, 0.5 g of MDI was added to solution. Immediately upon isocyanate addition, the flask was covered with a rubber septum situated with a needle vent. After 10 minutes reaction time, the flask was removed from the oil bath and allowed to cool to room temperature. The final product was then plated on a petri dish and allowed to dry in the fume hood at room temperature. If after 24 hours the product was not fully dried, the petri dish was moved to the oven at 50 °C until completely dry. Photos of the recovered lignin-based PU products can be found in Appendix B.1. The same products were used for contact angle analysis. To perform this analysis, each of the lignin-based PU products were hot-pressed into thin films. The hot press was operated at 150 °C for 300 seconds for all PU samples. After hot pressing each of the lignin-based PU samples, three small thin films were obtained. The water droplet contact angle photos were recorded using Kruss drop shape analyzer – DSA25.

4.2 Results and discussion

4.2.1 FTIR spectroscopy

FTIR spectroscopy was employed to determine the chemical composition of each of the polyol and respective PU products. A reference peak at 1032 cm^{-1}, corresponding to the C-O stretching in ether functional groups, was used as this group is not expected to change throughout the modified polyol syntheses, nor during the PU synthesis [7]. The lignin-based polyol FTIR spectra are shown in Figure 8. The unmodified lignin exhibited a peak ratio of

0.494 for the absorbance due to hydroxyl groups to the ether functional groups. Upon comparison of this peak ratio, it was determined that the PL exhibited a hydroxyl peak that increased by 8.2%, while the HPL hydroxyl peak increased by 16%, relative to the unmodified lignin ratio.

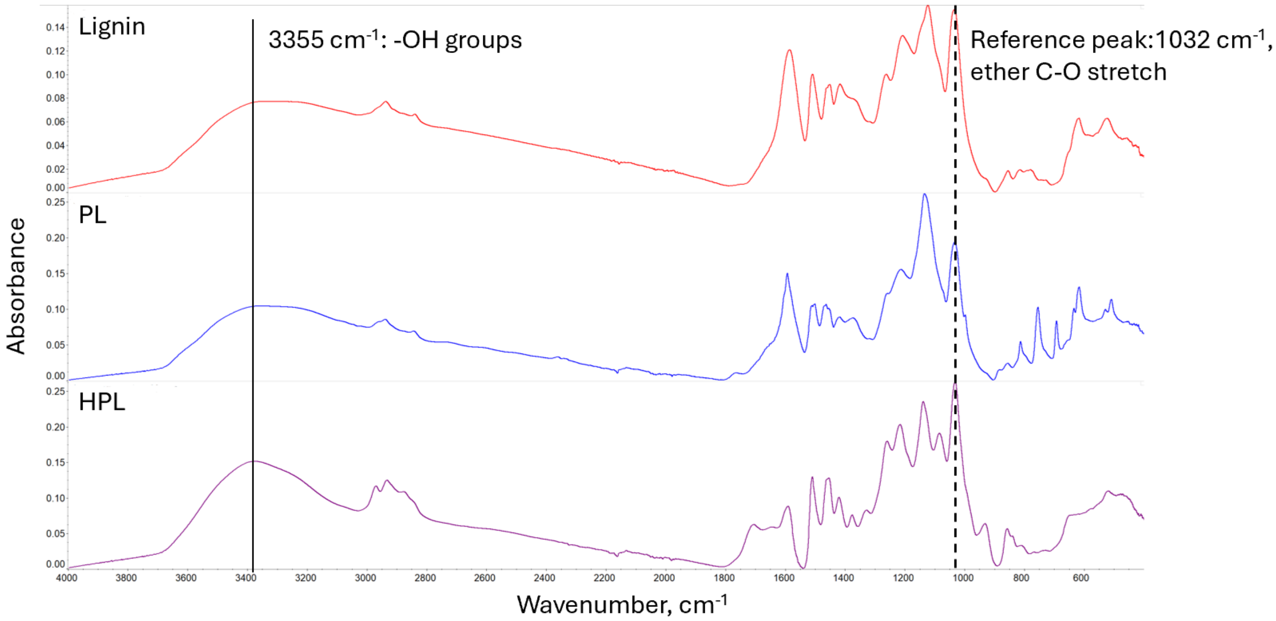


Figure 7. FTIR spectra of lignin-based polyols

In the synthesis of the lignin-based PUs, many new peaks, characteristic of the urethane linkage, appeared in the FTIR spectra. These peaks are outlined in Figure 9 and include peaks at: 3305 cm^{-1} and 1643 cm^{-1}, associated with secondary amines; 1190 cm^{-1} and 1015 cm^{-1}, associated with ether groups; and at 1705 cm^{-1} that is characteristic of carbonyl compounds [7], [8]. Each of these peaks were observed across all three lignin-based PU samples, and thus confirmed the PU synthesis reaction between the lignin polyols and MDI. Additionally, the absence of peaks associated with the isocyanate functional group, at 2275 cm^{-1}, and hydroxyl groups, at 3355 cm^{-1}, indicates that the starting materials were fully reacted [7]. An FTIR spectra of the MDI starting material may also be found in Appendix B.3.

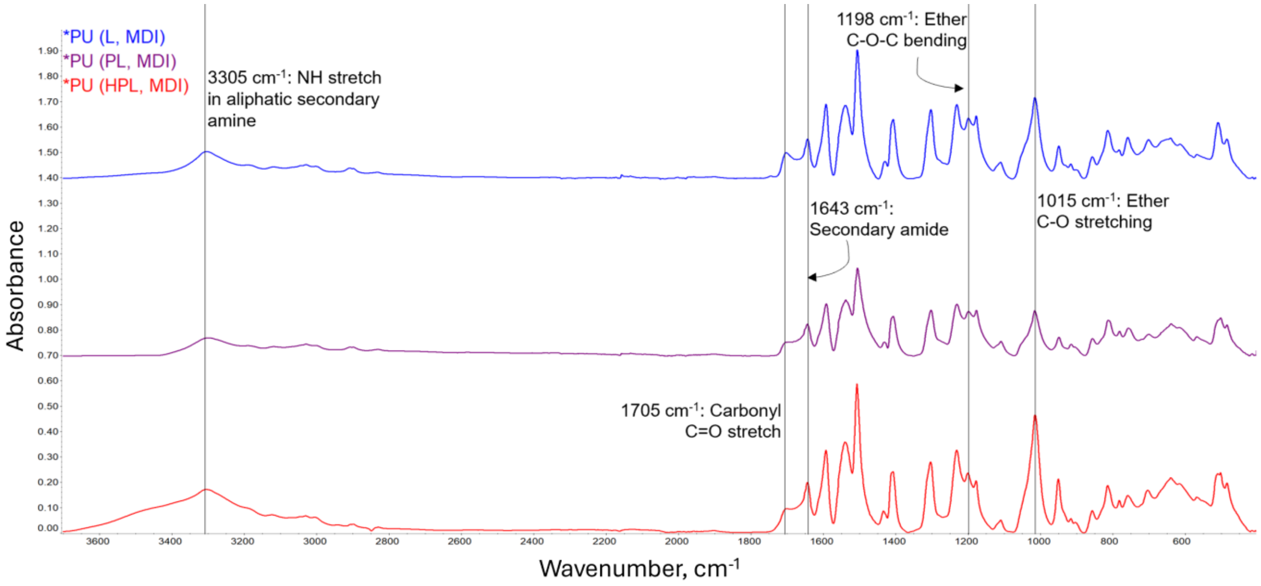


Figure 8. FTIR spectra of lignin-based PUs

The PU sample synthesized with the unmodified lignin yielded a dark gel. After approximately 7 minutes reaction time and while stirring at approximately 600 rpm, a thick gel was formed that stopped the stir bar from rotating entirely, even when raised above 900 rpm. After the total 10 minutes reaction time and cooling, the gel was easily sliced and scraped out of the round bottom flask and placed on a petri dish. The gel product was shiny, and bouncy, with some resistance to deformation, however very low elongation and compression properties. After approximately 10 minutes of drying in the petri dish, the gel was noticeably leaching out the DMSO solvent. The solvent was pipetted out of the dish, so that the sample could dry out completely. When completely dry, the sample was recovered as black crystal-like grains, pictured in Appendix B.4. Moreover, upon re-submerging the dried crystals in DMSO solvent for approximately an hour, the grains had become swollen with solvent and reformed the initial gelatinous structure.

The PU samples synthesized with the modified lignin polyols yielded very similar products. Both products dried as light brown thin flakes, pictured in Appendix B.2. The PL-based PU was very brittle and very easily ground into a fine powder, showing very little mechanical rigidity. The HPL-based PU was recovered in slightly larger, but much thinner flakes. Although brittle, the flakes held the initial shape of the drying dish until moderate pressure was applied at which point the flakes quickly crumbled into many smaller flakes.

4.2.2 Water contact angle analysis

Water contact angle goniometry was used to analyze the hydrophobicity of the lignin-based PU products. Despite using a completely flat hot press, some warpage in the films was observed, particularly for the HPL-based PU sample. However, due to extreme brittleness across all the PU samples, before and after hot pressing, it was not possible to flatten the samples any further without compromising the size of the thin film. Regardless of warpage, the thin films were used to carry out nine, 3 µL, water droplet trials each. The results of these trials are pictured in Figure 10, and the average and standard deviations of these trials are listed in Table 4 for each of the lignin-based PU samples.

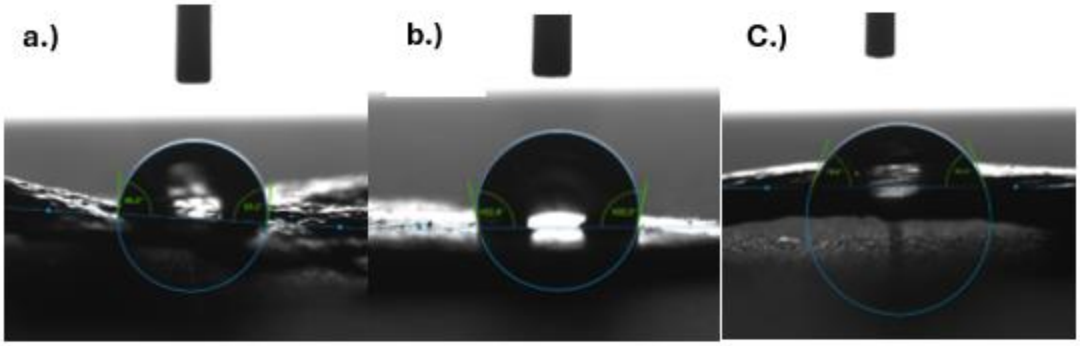


Figure 9. Water contact angle images for a) Lignin-based PU, b) PL-based PU, and c) HPL-based PU products

Table 4. Water contact angle averages and standard deviations for lignin-based PU film samples

Unmodified lignin-based PU	**PL-based PU**	**HPL-based PU**
92.65° ± 2.43	102.73° ± 3.94	68.71° ± 12.68

The water contact angle data demonstrate that the unmodified and phenolated lignin PU films are hydrophobic. In contrast, the HPL-PU film was hydrophilic demonstrating significant chemical modification of the lignin was achieved through hydroxyphenolation. It was observed that the HPL-based PU samples had a much higher standard deviation than the other two samples. This is attributed to the significant warpage observed in only the HPL-based PU. In addition to controlling wettability through the chemical modification of the lignin polyol, the hydrophobicity of the PU samples could also be further tailored through the inclusion of additives into the PU formulation.

4.2.3 Thermogravimetric analysis

TGA was used to assess the thermal stability of both the modified lignin-based polyols, as well as all three lignin-based PU products. Samples of approximately 15 mg were used for each TGA run (with exact values listed in Appendix B.2). The TGA experiment was run over a temperature range of 20-800 °C, these results are plotted for the polyol and PU products in Figure 11.

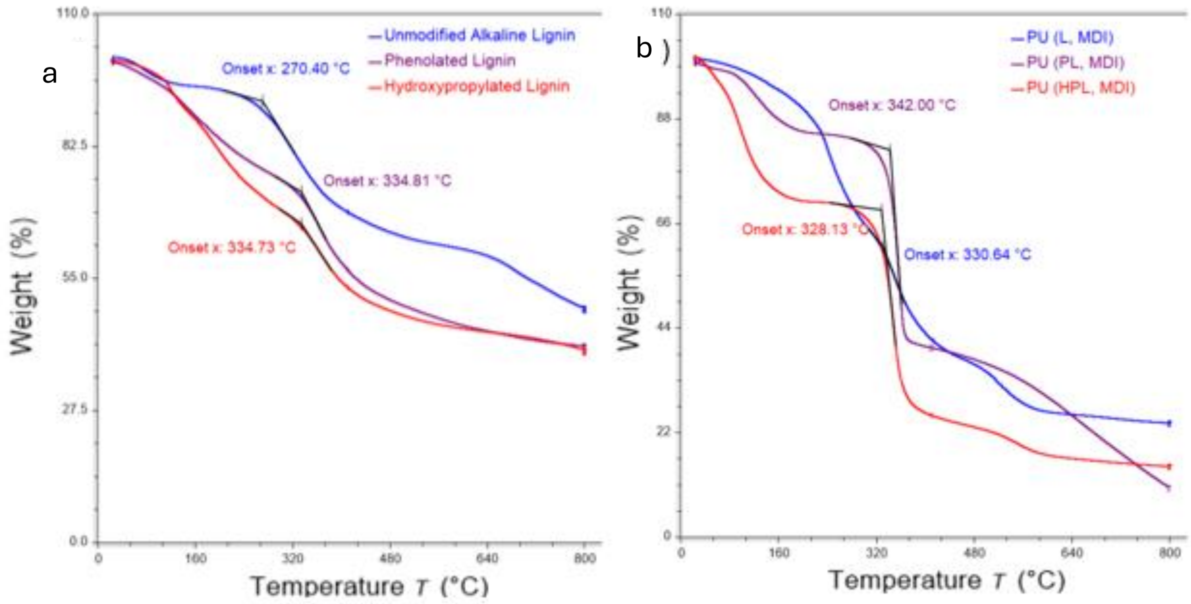


Figure 10 TGA traces for a) lignin-based polyols and b) lignin-based PU products

The TGA of the lignin-based polyols shows very similar behavior between the two modified lignin (PL and HPL) samples. These two samples exhibit nearly identical onset temperatures, that are higher than that of the unmodified lignin, suggesting a higher thermal stability. Additionally, the onset temperature for the modified trials was easily identifiable as opposed to the unmodified lignin sample which appears to have two separate onset temperatures. The modified samples exhibiting only one onset temperature aids in determining where the true thermal stability of a sample lies. This same trend was carried forward into the lignin-based PU products. The two modified lignin-based PU samples, despite means of modification, behaved very similarly. These two trials exhibited distinct and similar onset temperatures, and further thermal stability, relative to the unmodified lignin-based PU sample.

4.3 Project Conclusions

The goal of the project was to utilize lignin as the foundational polyol precursor of polyurethane synthesis. The successful synthesis of two modified lignin-based polyols and further the successful synthesis of three lignin-based PUs, establishes lignin as a reasonable basis for PU synthesis. With high thermal stability and a trend of hydrophobic properties, lignin-based PUs shows promising results for applications as thermoplastic or elastomeric seals. At this point, PU additives can begin to be assessed for tailored final properties targeted for specific applications, i.e. elastomeric seals, or foams.

5. Overall Conclusions

Lignin makes up a highly abundant waste stream in the paper industry and is profoundly underutilized when burned as a low-efficiency fuel source. The described projects outline just a few of the plethora of different applications lignin can be valorized for. These projects, among many, act as evidence for the successful modification and application of kraft lignin, specifically regarding the water treatment and polyurethane production industries. This form of valorization research promotes a circular economy by utilizing another industry's waste stream and promotes sustainability by offering alternatives to current petrochemically sourced materials, as well as promoting the biodegradability of lignin-based products given the natural sourcing of the material.

6. Future Efforts

With the successful synthesis of multiple lignin-based polyols and partially lignin-based PU, the ability for lignin to be used as the isocyanate precursor to PU production can begin to be assessed. Isocyanate synthesis is notorious for using and producing toxic starting materials and byproducts. I plan to focus my future research on the synthesis of a lignin-based isocyanate for use in an entirely lignin-based PU. Conjointly, I will begin assessing the lignin-based PU behavior and responses to different PU additives, as well as monitoring property changes in the tailoring of applied lignin-based PUs.

7. Acknowledgements

I would like to thank my thesis advisor, Dr. Keisha Bishop Walters, for all of the time and energy she has invested in me over the past few semesters. She has shown me so much patience and support throughout my projects and beyond. She motivates and inspires me to become a better engineer, researcher, and person every day. I would also like to thank Ph.D. candidate David Chem who welcomed me onto the lignin modification projects. David has shown me so much patience and understanding even in my most trying times, he has helped create such a safe and comfortable lab environment for me as a new researcher, and always encourages and supports my lab endeavors. Lastly, I would like to thank the honors college for funding throughout my first year of research.

8. References

[1] Wang, B.; Wen, J.-L.; Sun, S.-L.; Wang, H.-M.; Wang, S.-F.; Liu, Q.-Y.; Charlton, A.; Sun, R.-C. Chemosynthesis and Structural Characterization of a Novel Lignin-Based Bio-Sorbent and Its Strong Adsorption for Pb (II). *Industrial Crops and Products* **2017**, *108*, 72–80. https://doi.org/10.1016/j.indcrop.2017.06.013.

[2] Tobimatsu, Y.; Schuetz, M. Lignin Polymerization: How Do Plants Manage the Chemistry so Well? *Current Opinion in Biotechnology* **2019**, *56*, 75–81. https://doi.org/10.1016/j.copbio.2018.10.001.

[3] Rumpf, J.; Do, X. T.; Burger, R.; Monakhova, Y.; Schulze, M. *Lignin-Based Materials for Biomedical Applications*; 2021; pp. 105–158. https://doi.org/10.1016/c2019-0-01345-3.

[4] del Río, J. C.; Rencoret, J.; Gutiérrez, A.; Elder, T.; Kim, H.; Ralph, J. Lignin Monomers from beyond the Canonical Monolignol Biosynthetic Pathway: Another Brick in the Wall. *ACS Sustainable Chemistry & Engineering* **2020**, *8* (13), 4997–5012. https://doi.org/10.1021/acssuschemeng.0c01109.

[5] Bajwa, D. S.; Pourhashem, G.; Ullah, A. H.; Bajwa, S. G. A Concise Review of Current Lignin Production, Applications, Products and Their Environmental Impact. *Industrial Crops and Products* **2019**, *139*, 111526. https://doi.org/10.1016/j.indcrop.2019.111526.

[6] Oladoye, P. O.; Bamigboye, M. O.; Ogunbiyi, O. D.; Akano, M. T. Toxicity and Decontamination Strategies of Congo Red Dye. *Groundwater for Sustainable Development* **2022**, *19*, 100844. https://doi.org/10.1016/j.gsd.2022.100844.

[7] Silverstein, R. M.; Webster, F. X.; Kiemle, D. J. *Spectrometric Identification of Organic Compounds, 8th Edition | Wiley*. Wiley.com. https://www.wiley.com/en-sg/Spectrometric+Identification+of+Organic+Compounds%2C+8th+Edition-p-9780470616376 (accessed 2024-04-26).

[8] Dean, J. A. *Lange's Handbook of Chemistry*, 14th ed.; Elsevier Science Publishers: Amsterdam, The Netherlands, 1992; Vol. 45.

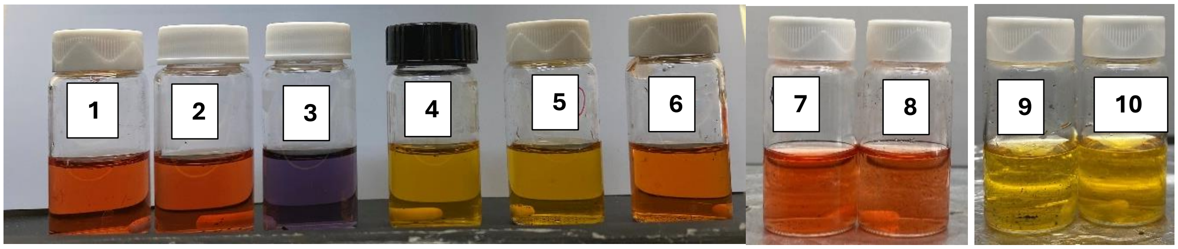
[9] Knolker, H.-J.; Braxmeier, T.; Schlechtingen, G. A Novel Method for the Synthesis of Isocyanates under Mild Conditions. *Angewandte Chemie International Edition* **1995**, *34* (22), 2497–2500.

9. Appendices

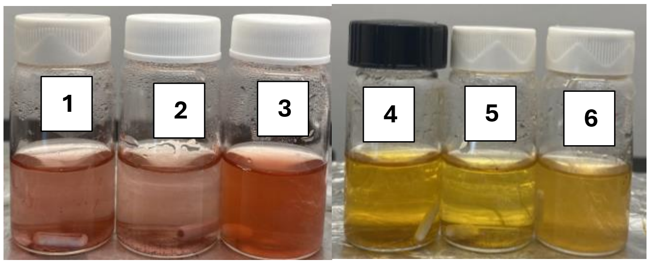
The following sections include data to support the findings and conclusions for each of the projects included in this thesis. All figures and tables in the appendices include details on the samples and experimental conditions in the captions.

9.1 Appendix A

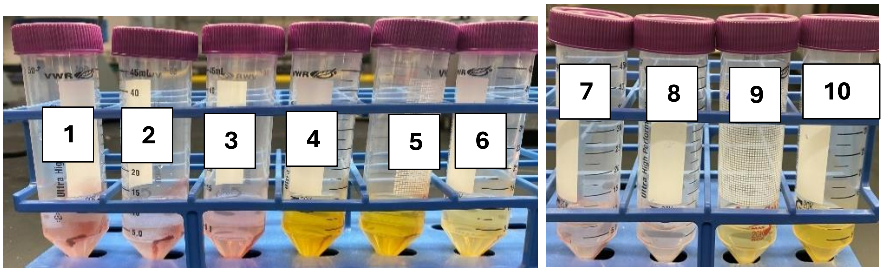
Supporting material for lignin modification project with applications in dye removal water treatment.



A.1 Initial colors of dye removal tests 1) CR basic, 2) CR native, 3) CR acidic, 4) MO basic, 5) MO native, 6) MO acidic, 7) CR high [AL], 8) CR low [AL], 9) MO low [AL], 10) MO high [AL]



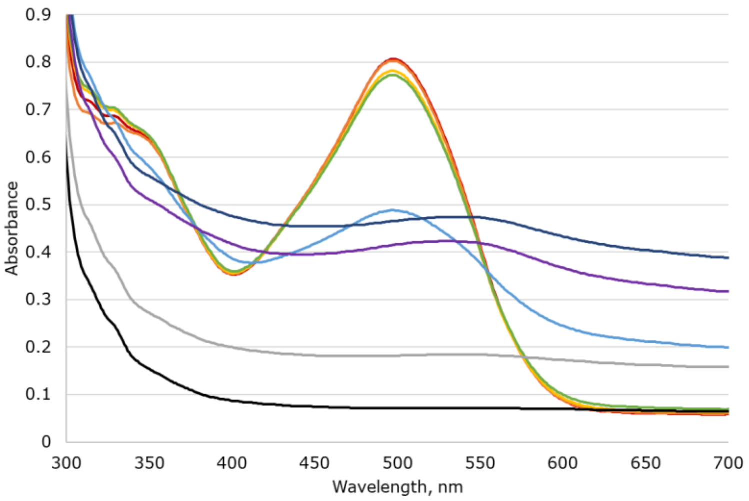
A.2. Varied pH dye removal trials after 23 hours of AL treatment, 1) CR basic, 2) CR native, 3) CR acidic, 4) MO basic, 5) MO native, 6) MO acidic



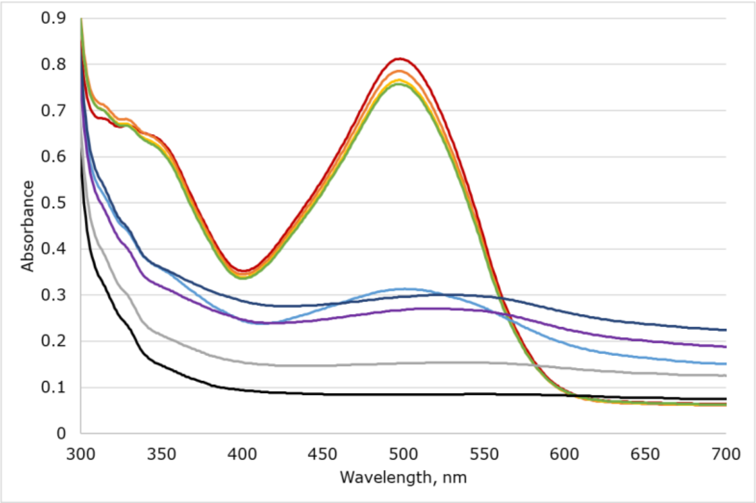
A.3. Final colors of dye removal tests 1) CR basic, 2) CR native, 3) CR acidic, 4) MO basic, 5) MO native, 6) MO acidic, 7) CR high [AL], 8) CR low [AL], 9) MO low [AL], 10) MO high [AL]

— 0h	— 0h15	— 0h30
— 1h	— 16h	— 23h
— 48h	— Post Centrifuge 48h	— Post Centrifuge 96h

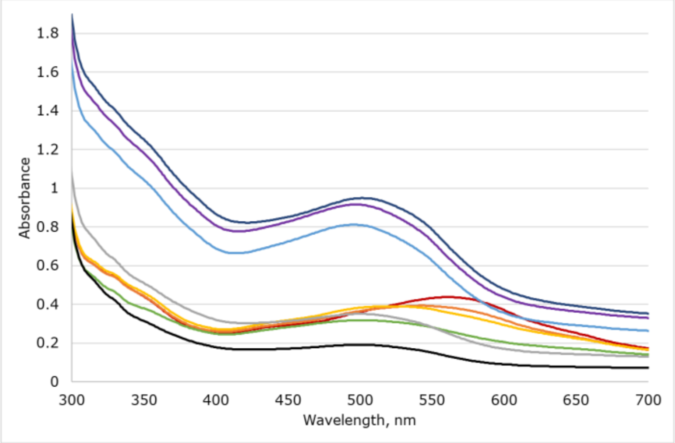
A.4 UV-vis time study legend for varied pH trials



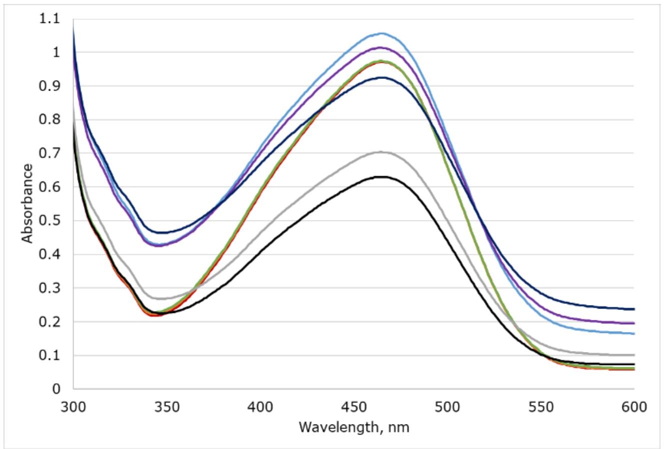
A.5. UV-vis time study of CR dye removal from aqueous solution using 1 mg AL at pH = 9.98



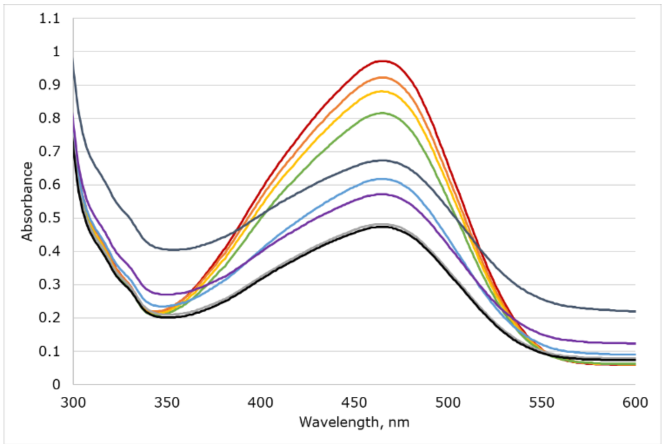
A.6. UV-vis time study of CR dye removal from aqueous solution using 1 mg AL at pH = 8.87 (native)



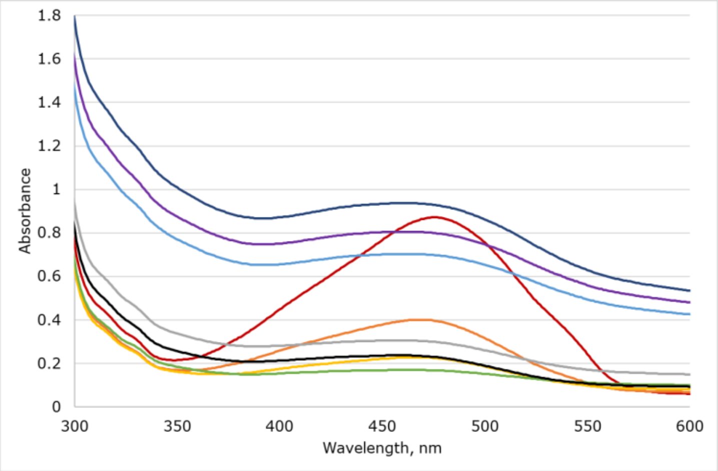
A.7 UV-vis time study of CR dye removal from aqueous solution using 1 mg AL at pH = 3.84



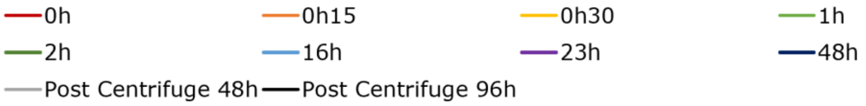
A.8 UV-vis time study of MO dye removal from aqueous solution using 1 mg AL at pH =10.09



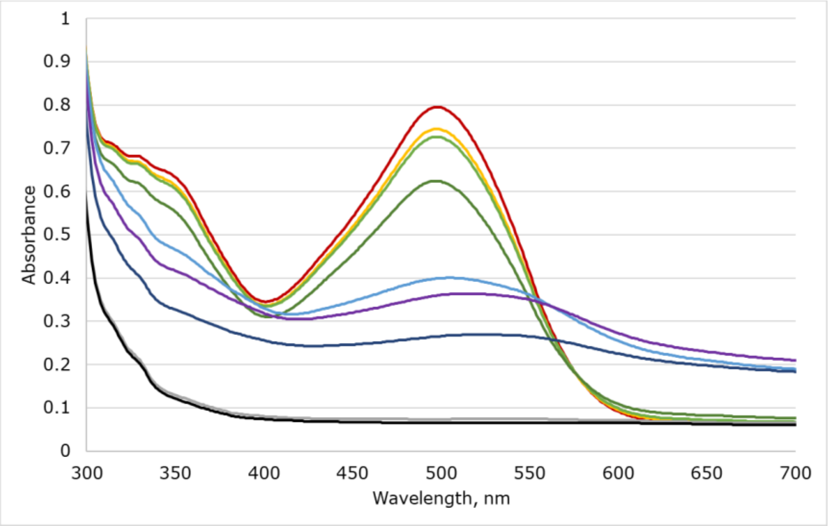
A.9. UV-vis time study of MO dye removal from aqueous solution using 1 mg AL at pH = 9.16



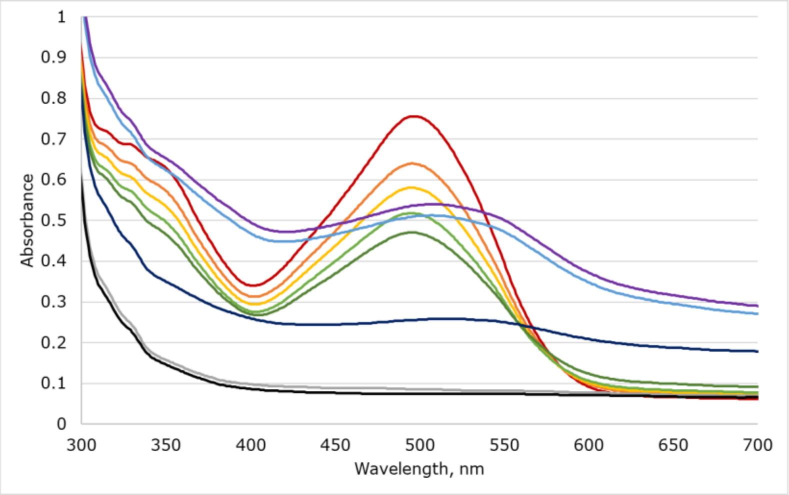
A.10. UV-vis time study of MO dye removal from aqueous solution using 1 mg AL at pH = 3.88



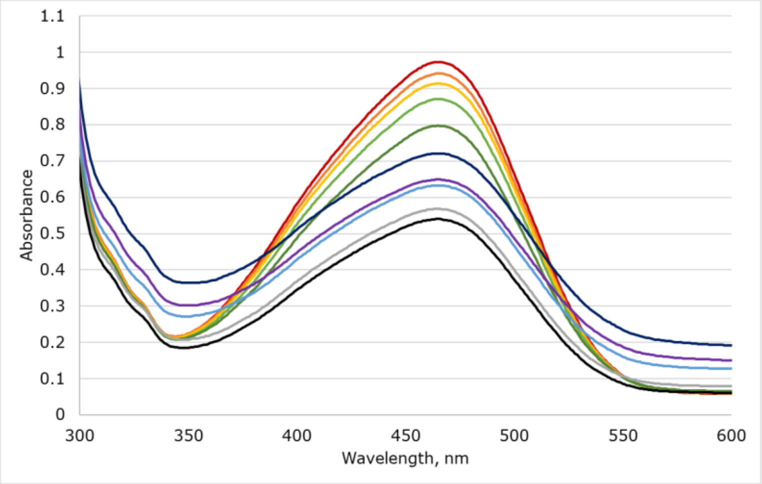
A.11. UV-vis time study legend for varied concentrations of AL used for treatment



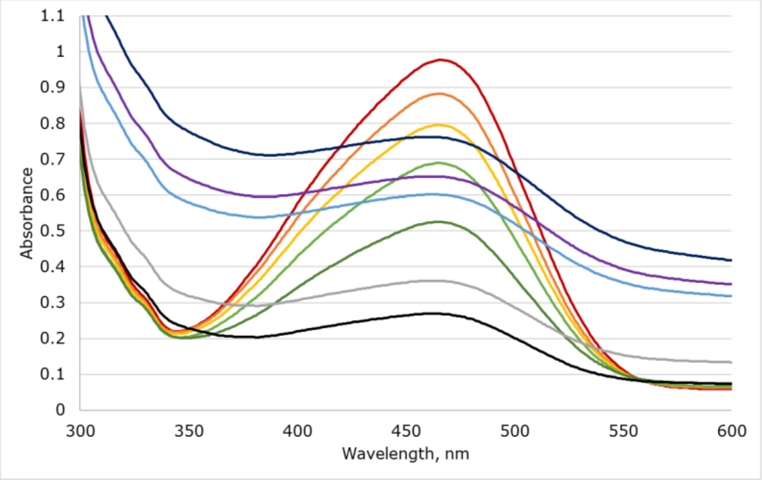
A.12 UV-vis time study of CR dye removal from aqueous solution using 0.5 mg AL



A.13. UV-vis time study of CR dye removal from aqueous solution using 2.0 mg AL



A. 14. UV-vis time study of MO dye removal from aqueous solution using 0.5 mg AL



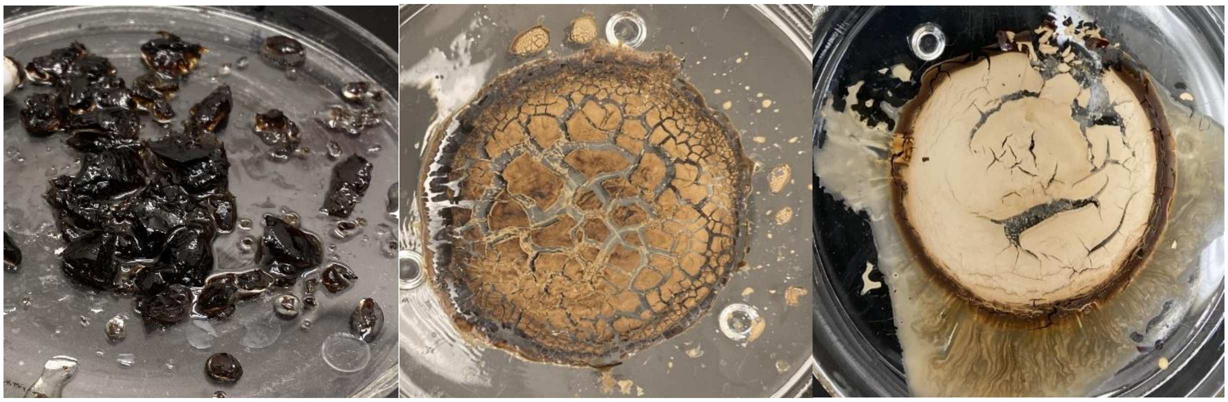
A.15. UV-vis time study of MO dye removal from aqueous solution using 2.0 mg AL

A.16 Tabulated values of pH changes for dye removal tests

Time	CR basic	CR native	CR acidic	MO basic	MO native	MO acidic
0 hour	9.98	8.87	3.84	10.09	9.16	3.88
48 hour	8.17	7.68	6.95	6.87	6.53	6.42
96 hour	8.04	7.8	7.1	7.06	6.85	6.32
pH Δ	1.94	1.07	3.26	3.03	2.31	2.44

9.2 Appendix B

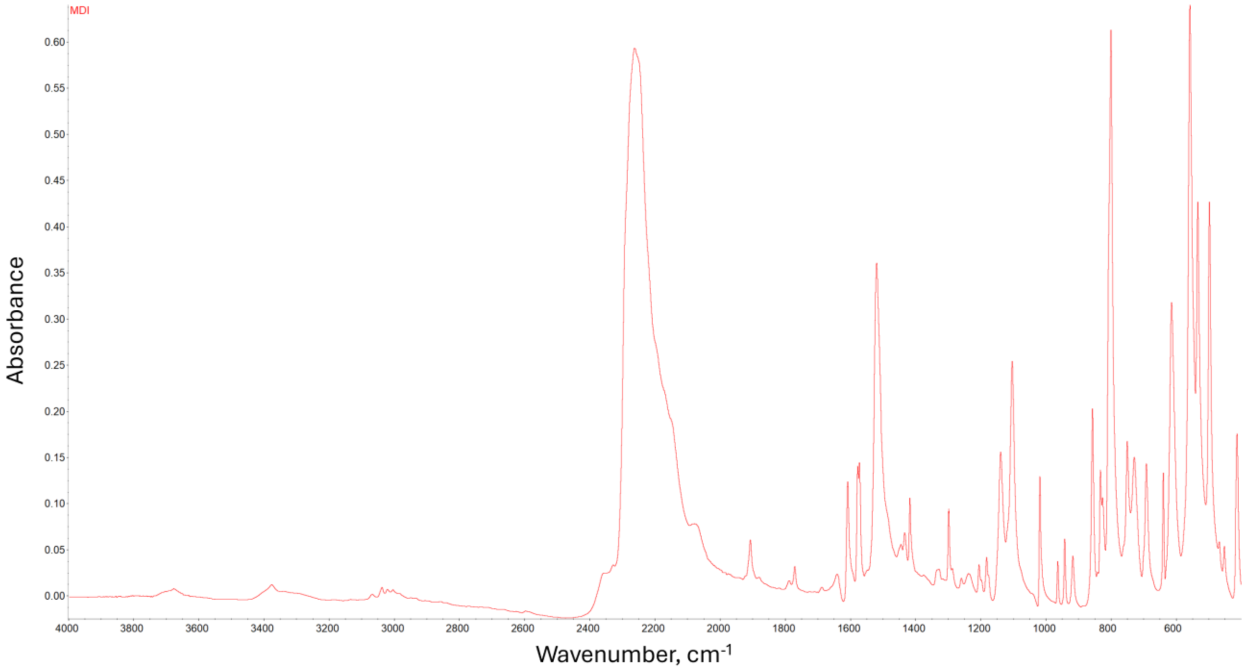
Supporting materials for lignin modification project for sustainable alternative in polyurethane production.



B.1. Lignin-based PU products: unmodified lignin (left), PL (center), HPL (right)

B.2. Sample masses used for TGA analysis

Sample	Lignin	PL	HPL	L-PU	PL-PU	HPL-PU
Amount, mg	17.94	17.82	14.38	15.28	14.72	16.02



B.3 FTIR spectra of MDI starting material

B.4 Dried unmodified lignin-based PU crystals