CHEMICAL AND PHYSICAL PROPERTIES OF NATURAL AND MODIFIED GROUND PEANUT HULLS

A thesis presented to the faculty of the Graduate School of Western Carolina University in partial fulfillment of the requirements for the degree of Masters of Science in Chemistry.

By

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Deepest gratitude and praise for the Father whose love is so personal and unconditional.

"Dont be afraid, because I am with you. Dont be intimidated; I am your God. I will strengthen you. I will help you. I will support you with my victorious right hand." Isaiah 41:10 GW
"I will give you thanks, O LORD, with all my heart. I will tell about all the miracles you have done." Psalm 9:1 GW

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ATR	Attenuated total reflectance
b	Langmuir Equilibrium constant (ppm^{-1})
C_e	Concentration of MB in solution in equilibrium with hulls (ppm)
C_f	Concentration of MB solution after mixing with hulls (ppm)
C_i	Concentration of MB solution before mixing with hulls (ppm)
d	Density of 2-propanol (0.789 g/mL)
E^o_{red}	Standard reduction potential (V)
FT-IR	Fourier Transform Infrared
HD	High density
LD	Low density
MB	Methylene blue
M	Molar mass of MB (319.85 g/mol)
m_2	weight of dry hulls
m_1	weight of hulls filled with 2-propanol
m_h	Mass of hulls added to MB solution (g)
m_s	Mass of the MB solution added to the hulls (g)
n	Number of moles of MB adsorbed in the sample
q_e	Surface coverage at equilibrium (mmol MB/g of hull)
Q_o	Adsorption capacity (mmol MB/g of hull)
V	Total pore volume per gram of hull

ABSTRACT

CHEMICAL AND PHYSICAL PROPERTIES OF NATURAL AND MODIFIED GROUND PEANUT HULLS

Holly D. Truluck, Masters of Science in Chemistry
Western Carolina University (July 2017)
Advisor: Dr. Carmen L. Huffman

The chemical and physical characteristics of peanut hulls was assessed using methylene blue (MB) adsorptivity, physical analysis to assess surface area, and FT-IR spectroscopy to analyze chemical composition of the hulls. Peanut hulls are an agriculture waste that show promise for cation adsorption due their lignocellulosic makeup. Adsorption is a process in which a thin layer of molecules adheres to a surface with which they come in contact. The ground peanut hulls are separated by density into two categories, high density (HD) and low density (LD). These two types of hulls react differently to an alkaline peroxide modification process, and therefore have different MB adsorption capacities. Unmodified HD hulls adsorb 0.08 ± 0.05 mmol of MB per gram of hull and unmodified LD hulls adsorb 0.2 ± 0.05 mmol of MB per gram of hull. Once modified, the adsorption capability increases depending on the modification procedure used. The chemical and physical characteristics of unmodified and modified ground peanut hulls were assessed to explain these differences. A 2-propanol displacement test showed that LD hulls have more empty space than HD hulls, which provides greater accessibility to adsorbates. Infrared spectroscopy showed the modifying alkaline solution dissolves lignin and other alkaline soluble hull components, which further increases the surface area of the hulls. The modification may also result in an increase of C=O functional groups, which would be strong binding sites for cations. It was determined that ground peanut hulls may be an appropriate biosorbent for cationic contaminants in low concentration, but a modification involving minimum concentrations of 0.45 M NaOH and 15% hydrogen peroxide is needed to raise the adsorption capacity of the hulls.

CHAPTER ONE: INTRODUCTION

1.1 Motivation

The US Environmental Protection Agency has many guidelines and regulations for waste water discharge, which helps to minimize pollution.[1] However, pollution can still occur if the remediation processes are not followed or are not adequate for the waste. The development of waste remediation techniques is still advancing as new products are produced each year. A common pollutant in our fluvial systems is ionic dyes.[2,3]

Dyes like methylene blue (MB, Figure 1) are used in the medical field because they are helpful to observe transparent cells due to their staining of the tissue.[4]

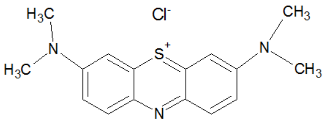

Figure 1. Molecular structure of methylene blue.

The membranes of most cells are selectively permeable and will allow MB to enter the cell, making the interior of the cell blue.[4] In the medical field, the dye is used in a test for breast cancer patients to assess axillary (underarm) node status.[4] Methylene blue is also known to improve hypotension by inhibiting nitric oxide synthase and guanylate cyclase.[5] MB improves hypoxia and hyper dynamic circulation in cirrhosis of the liver, severe hepatopulmonary syndrome, and results in temporary and reproducible enhancement in blood pressure and cardiac function in septic shock.[5] The use of MB as both a diagnostic tool and a drug means pathways exist for MB to be a contaminant in the medical wastewater stream.

Dyes are also used in the textile industry. Due to the low levels of dye-textile retention, the textile industry generates a great amount of polluted water with high contents of different kinds of dyes.[3] MB is a well-known cationic dye that has wide applications that include coloring papers, dyeing cottons, wools, silk, leather, and coating for paper stock.[6] The use of MB in these industries may lead to the production of contaminated waste water.[7]

If released into water, MB is expected to adsorb to suspended solids and sediment due to laboratory studies that indicate a strong adsorption to soil.[7] Although MB is not strongly hazardous, it can have some harmful effects.[4] MB is used to treat methemoglobinemia and urinary tract infections.[8] A common side effect of MB is abnormal urine or stool color.[8] Some less frequent side effects of MB treatment include mild bladder irritation, dizziness, headache, increased sweating, nausea, abdominal pain, diarrhea, upset stomach, frequent urination, or stomach cramps.[8] Some more harmful effects can include such as heartrate increase, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis.[6] Large doses of MB can cause chest pain and confusion.[8] MB may interact with acetazolamide, antacids, sodium bicarbonate, or diuretics.[8]

The environmental challenge of the removal of dyes from wastewater has led to governmental legislation that requires textile wastewater to be treated.[6] Therefore, there is a great need to have an effective procedure to effciently remove these dyes.[6] The percentage of dye that enters the wastewater is 50% of the dye used in the dyeing processes due to the low levels of dye-fiber fixation in dye-using textile industries.[3] Even when the concentration of dye in drinking water is just 1.0 mg/L, it could have a significant color, making it unfit for human consumption.[3] Dyes in water can also affect the life of aquatic plants as they can make the water less transparent and reduce sunlight transmission through the water.[3] Even a small quantity of dye in water could be toxic and highly visible, thus the removal of color from waste effluents becomes environmentally important.[3]

Some conventional methods to remove ionic contaminants from aqueous waste include ion exchange resins, membrane processing, reverse osmosis, and adsorption onto activated carbon.[9] Activated carbons are versatile adsorbents that can be used to remove contaminants by adsorption.[10] The use of ion exchange resins is one of the most common ways for removing ionic contaminants from aqueous solution. An ion exchange reaction removes cations or anions that are dissolved in solution and substitutes them with innocuous cations or anions from the surface of the resin.[11] The type of functional group within a resin and its charge dictate the efficiency and application of the specific resin.[11] Ion exchange resins are very efficient at the removal of many different ions from wastewater. However, use of resins requires a large capital investment and on-going operational costs.[9] They also are associated with the generation of secondary wastes, which presents treatment problems. The wastes from ion exchange can include a large quantity of sludge, which makes them less environmentally friendly to use than other methods.[9]

1.2 Background

1.2.1 Adsorption

Adsorption is a process in which molecules adhere to a surface with which they come in contact.[12] The Langmuir model is a common model applied to adsorption studies due to its ability to predict a wide range of experimental data.[13] The Langmuir model assumes the surface of the adsorbent is homogeneous, all binding sites are equivalent, and that there is no interaction between adjacent adsorbate molecules on the surface.[13] The Langmuir equation provides the surface coverage (q_e) for an adsorbate on an adsorbent when the two components are at equilibrium:

$$q_e = \frac{Q_o b C_e}{1 + b C_e} \tag{1}$$

where Q_o is the adsorption capacity, or maximum amount of adsorbate than can adhere to a surface; C_e is the concentration of the adsorbate in solution at equilibrium; and b is the equilibrium constant for the adsorption process.[14]

To remove ions from aqueous waste using a biomaterial is called biosorption. Several biomaterials that show high adsorption capabilities of metals and dyes include bark, rice husk, sawdust, nut shell, peat and much more.[15–17] Often, these materials contain cellulose, hemicellulose, pectin, lignin, and protein.[15] These compounds have a high affinity for ions due to the presence of hydroxyl groups and/or carbonyls, which are good ligands for cations.[18]

1.2.2 Peanut Hulls

Peanut hulls have a similar make up to the biomaterials listed above and are a very porous material that consists of mostly fiber which is 45% cellulose (Figure 2) and 33% lignin (Figure 3), as well as 1% fat, 7% protein, 4% ash and 10% moisture.[16] Figure 2 shows the two glucose units in the cellulose monomer. Lignin is a more complicated structure than cellulose as it is made up of the three monomers shown in Figure 3. The monomers bind together in an irregular pattern that varies from substance to substance.

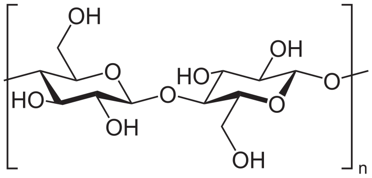

Figure 2. Molecular structure of cellulose.

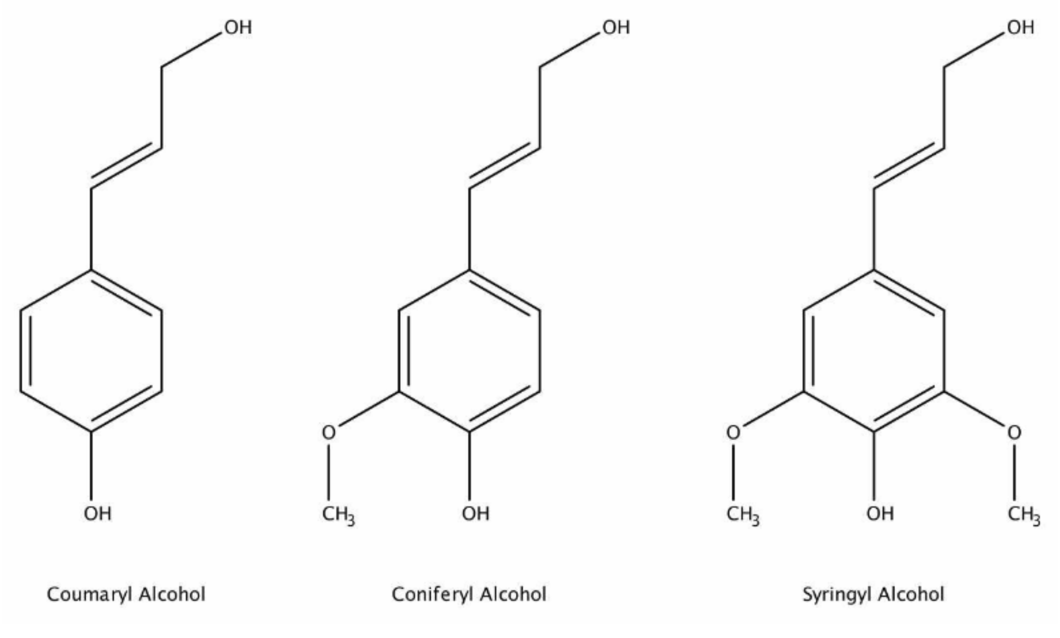

Figure 3. The three phenyl propane monomers of lignin.

Peanut hulls are used in the production of soap, cosmetics, wallboard, plastics, linoleum, and as a replacement for synthetic food ingredients.[19] The hulls also have a few health benefits, as antioxidants are found naturally in the shell, and they contain vanillin which has potential benefits on human cancer cells.[19] However, peanut hulls have practically no nutritional value and the composition differs based on peanut varieties and manufacturing environment.[19] The high content of cellulose and lignin should make peanut hulls a good candidate for cation adsorption.[16,20] Peanut hulls are also an agricultural industry waste product and therefore the hulls may be a cost efficient alternative to ion exchange materials or common sorbents, costing \$0.0015/dm^3 (unmodified) compared to \$1-2/dm^3 for activated carbon, the most effective product used for metal and dye removal at this time.[21,22]

In studies of the use of jute fibers to remove copper from water, an oxidative bleaching modification of the fibers greatly enhanced the copper uptake,[14] and a similar result was observed when modifying peanut hulls.[20] In the jute fiber study, this increase in adsorption was attributed to the increase in the number of acidic groups in the sorbent by measuring MB adsorption.[14] Ion binding enhancement from oxidative bleaching is likely due to two factors: (1) The basic solution dissolves lignin or other alkaline soluble material, opening the fibrous structure to create a greater surface area, and (2) the peroxide oxidizes cellulose alcohol groups into carbonyls, increasing the strength of chemical binding sites.

1.2.3 Methylene Blue Adsorption

Methylene blue (Figure 1) has a variety of uses that are applied in the medical field, dye industries, and research for adsorption due to its cationic properties. A methylene blue adsorption method has been used to estimate acidic groups in adsorbents.[23] This same technique is also use to estimate the oxidative degradation of cellulosic materials like cotton during chemical processing.[24] When such a sample is treated with a standard solution of methylene blue, the colored cationic dye is adsorbed quantitatively and retained by anions present in the material, forming a strong ionic linkage, unable to break under normal washing conditions.[3] An example of a test using methylene blue adsorption is determining the scouring efficiency of cotton.[24] The scouring treatment cuts the cellulosic chains and allows for more polymerization of cotton than that of natural cellulose.[24]

1.3 Research Goals and Methodology

Based on their high lignin and cellulose content,[16] peanut hulls may be a good biosorbent for the removal of cations from contaminated wastewater. Previous studies have shown that peanut hulls are a moderately effective biosorbent for both Cu and MB.[20,25] In these studies, it was shown that ground peanut hulls can be physically separated into a low density type and a high density type, and the low density hulls have a greater affinity for these sorbates than the high density type. In all cases, adsorptivity was enhanced by a chemical modification of the hulls that involved adding hulls to a mixture of sodium hydroxide and hydrogen peroxide. The goals of this project are (1) to characterize the chemical composition of unmodified and modified ground peanut hulls and (2) to characterize the physical properties, such as surface area, and adsorptivity of both types of hulls. Ultimately, the research will address the usefulness of peanut hulls as a biosorbent for methylene blue and the role of chemical modification in the adsorption process.

Characterization methods include FT-IR microscope spectroscopy to assess chemical composition, a porosity test to assess surface area,[26] and a MB adsorption test[14] to assess cation adsorptivity. In addition to the characterization of unmodified and modified hulls, hulls modified by either sodium hydroxide or hydrogen peroxide alone will help to determine what role each component plays in the modification process. The same modifications will be repeated on pure, crystalline cellulose to clarify the significance of the cellulose in the adsorption process. The results will direct how the modification method could be optimized to ensure a more efficient adsorption.

CHAPTER TWO: EXPERIMENTAL

2.1 Materials

Roasted, unsalted peanuts in the shell were purchased from Ingles in Sylva, North Carolina, USA. Laboratory grade sodium hydroxide pellets (Fisher Scientific), potassium dihydrogen phosphate (Fisher Scientific), methylene blue (Aldrich Chemical Company), 30% hydrogen peroxide (Fisher Science) and anhydrous 2-propanol (Alfa Aesar) were used without further purification or modification. Ultrapure water from a Milli-Q water filtration system purchased from Millipore was used throughout the experiments.

2.2 Methods

2.2.1 Hull Preparation

Hulls were removed from the peanuts and seed coats by hand, then ground using a Hamilton Beach coffee grinder (model 80370). The ground peanut hulls were then sieved using USA test standard stainless steel sieves with various sizes of mesh to retrieve hulls in the 0.5 mm to 1 mm size range. Ground hulls were washed with near boiling ultra-pure water, filtered and rinsed with ice cold, ultrapure water. The unmodified peanut hulls were then left to dry completely before separating according to their density.

To separate the hulls by density, the hulls were added to a beaker with ultrapure water with slight stirring to allow for separation of floating and sinking hulls to occur. The hulls that float (low density, LD) were decanted twice fairly quickly, filtered and placed to dry on a watch glass. The rest of the hulls that sank (high density, HD) were filtered and placed on a separate watch glass to dry as well. Testing was completed separately on each type of hull.

2.2.2 Modification of Hulls

A known mass of sodium hydroxide pellets was placed in a 100 mL volumetric flask and diluted to 100 mL with 30% hydrogen peroxide and water depending on the desired concentration of hydrogen peroxide. This solution was then added to a temperature-controlled, water-jacketed beaker set to 20 °C. Roughly 2 g of either the low density (LD) or high density (HD) unmodified ground hulls were added to the alkaline peroxide solution once the alkaline peroxide solution reached the set 20 °C. The external temperature bath was turned off after two hours, and the temperature of the mixture was allowed to rise freely within the beaker. The reaction was left overnight to ensure the reaction was complete. The modified hulls were filtered and rinsed with ultrapure water until the pH of the rinse was neutral and left to dry. Several modification procedures were used in which the concentration of the base and concentration of hydrogen peroxide were varied. These concentrations are listed in Table 1.

Table 1. Concentrations of reagents used in different modification procedures.

	[NaOH]	% H_2O_2
Modification 1	0.95	30
Modification 4	0.45	15
Modification NaOH	0.95	–
Modification H_2O_2	–	30

2.2.3 Fourier Transform Infrared Microscope Spectroscopy

A Fourier transform infrared (FT-IR) microscope spectrometer was used to determine chemical composition of the peanut hulls. The measurements were recorded using a Thermo Nicolet Centaurus FT-IR Microscope (Thermo Fisher Scientific Co.) spectrometer equipped with a mercury cadmium telluride (MCT) detector. Specifically, a MCT-A detector was used as it offers the highest mid-IR sensitivity and is ideal for low throughput analysis when high sampling rates are required.[27] This higher sensitivity provides significantly greater IR response for small amounts of energy reaching the detector.[27] The detector was cooled with liquid nitrogen before use.

The FT-IR measurements were acquired in the range of 4000-650 cm^{-1} with a resolution of 4 cm^{-1}. A background spectrum was collected at 64 scans in transmittance mode to ensure accurate representation of the surrounding environment of the laboratory. Each sample spectrum was collected at 32 scans in the reflectance mode and with Norton-Beer strong apodization. This helps improve the signal to noise ratio with minimum effect on the linewidth.[28] The data spacing used was 0.5cm^{-1}. Several spectra were taken of several particles within each type of hull.

2.2.4 Empty Space Analysis

The method to determine the volume of empty space within the hulls is based on the displacement of water with 2-propanol solvent that is retained by the material without swelling.[14,26] About 0.5 g of hulls were soaked with ultrapure water in an 100 mL round bottom flask under vacuum to saturate empty space within the hulls with water. These hulls were stirred under vacuum for 2 to 3 hours to ensure no water from the air is interfering with the saturation before filtering with vacuum. Once filtered, about 10 mL of 2-propanol was used to rinse the hulls three times before placing the hulls in a 100 mL beaker with about 20 mL of 2-propanol (enough to cover the hulls completely) for 15 min. This process displaces the water by dilution of the water within the hulls with 2-propanol to ensure no further swelling of the hulls.[3] The hulls were then filtered, divided equally and placed into two weighed glass centrifuge tubes. The hulls were centrifuged for 30 min using a Clay Adams Compact II Centrifuge at 3200 rpm to remove excess 2-propanol from the surface of the hulls. After centrifuging, the hulls were weighed (m_1) and placed in a vacuum oven (National Appliance Company, Model 5831) for 15 min set between 80 °C and 100 °C to remove all 2-propanol from the pores. The hulls were placed in a desiccator to cool before weighing again (m_2). The difference between the two masses is the mass of 2-propanol in the empty space of the hulls. This can be converted to a volume using the density of 2-propanol assuming that the density of 2-propanol is constant ($d = 0.789\,\mathrm{g/mL}$). The total pore volume per gram of hull (V) is

$$V = \frac{m_1 - m_2}{d \times m_2} \tag{2}$$

2.2.5 Methylene Blue Adsorption

An adsorption isotherm was made to determine the concentration of methylene blue (MB) to be used in the adsorption studies. A concentrated MB solution (0.02 M) containing 15.625 mM potassium dihydrogen phosphate and 10 mM sodium hydroxide as a buffer. The use of the two bases as a buffer ensures that the MB (pKa=3.8)[29] is kept in a positively charged state in order to be adsorbed. The stock solution was diluted serially to contain eight different concentrations between 0.0002 M to 0.02 M. Each MB solution was then added to hulls and put on a tube revolver (Fisher Scientific) on mode 00 for a minimum of 18 hours. Mode 00 consists of rotation at 40 rpm with periodic shaking. After mixing, the solutions were diluted in order to reach an absorbance within the calibration range. All visible spectra were acquired using an Agilent 8453 UV-Vis spectrophotometer recording the absorbance at 664 nm. Sample concentrations were determined using a calibration curve that followed Beer's Law. The calibration standards consisted of eight solutions in the range of 0.2 ppm to 20 ppm so that the visible absorbance at 664 nm was close to 1 or lower. Absorbance at 664 nm was recorded three times, and the average was used as the peak maximum.

Surface coverage (q_e) is defined as the number of moles of MB adsorbed per gram of hull. The number of moles of MB adsorbed in the sample (n) is calculated from the decrease in MB concentration:

$$n = \frac{(C_i - C_f)m_s}{M \times 1000} \tag{3}$$

where C_i and C_f are the concentrations of MB before and after mixing with hulls (in ppm), respectively, m_s is the mass of the MB solution added to the hulls, M is the molar mass of MB and the 1000 is a conversion factor to obtain a result in mmol MB. The surface coverage is obtained by dividing the number of moles of adsorbed MB by the mass of the hulls used (m_h):

$$q_e = \frac{n}{m_h} \tag{4}$$

A plot of q_e vs. C_e was fit with the Langmuir isotherm (Equation 1). A MB concentration within the saturation zone (the flat part of the curve) was used for remaining adsorption studies.

A MB stock solution was then prepared consisting of 5 mM MB, 15.625 mM potassium dihydrogen phosphate, and 10 mM sodium hydroxide. Modified and unmodified hulls were placed in separate vials, and the MB stock solution was added at a ratio of 0.01 g of hull per 1 mL of MB solution. These samples were put on the tube revolver as before. A mechanical pipet was used to extract the methylene blue solution from the hulls, and the solution was diluted in order to reach an absorbance within the calibration range. The eqilibrium surface coverage (q_e) was then calculated as described above. New MB standards and calibration curves were made for each experiment.

CHAPTER THREE: RESULTS AND DISCUSSION

3.1 Chemical Analysis

FT-IR spectroscopy was used to investigate the chemical composition of ground peanut hulls. Each spectrum was divided into two regions, the 3800-2800 cm^{-1} range and the 1800-700 cm^{-1} range. Spectra were then smoothed using a moving average, which was calculated by averaging the absorbance of surrounding data points for a given wavenumber. In the 3800 cm^{-1} to 2800 cm^{-1} range, seven values were used to calculate the moving average. In the 1800 cm^{-1} to 700 cm^{-1} region, five values were averaged. The spectra were then normalized by dividing each absorbance value by another specific absorbance at a particular peak maximum.

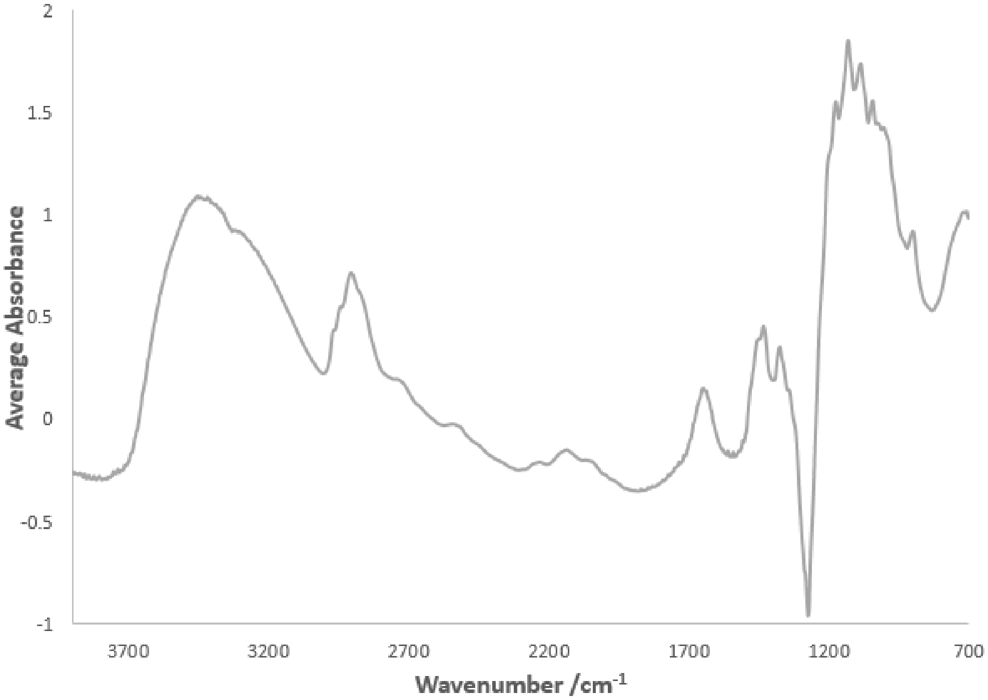

Figure 4. Full FT-IR spectrum of unmodified crystalline cellulose.

For the 3800-2800 cm^{-1} range, the reference band was at about 2900 cm^{-1}, and in the 1800-700 cm^{-1} range, the reference band was at about 1130 cm^{-1}. Finally, multiple spectra for a particular sample type were averaged together. Each final spectrum is an average of 3-12 spectra.

Figure 4 shows the IR spectrum of crystalline cellulose. A full analysis of the cellulose structure has been provided in the literature and gives insight to the features of the spectrum.[30] Band assignments are listed in Table 2.[30]

Table 2. Assignments for notable bands in the cellulose spectra.

Wavenumber (cm^{-1})	**Assignment**
1430	CH_2 bending
1375	C-H bending
1170	C-O stretching
1130	C-O stretching
1080	C-O stretching
1040	C-O stretching
895	CH_2 stretching

Figure 5 shows a comparison of the IR spectra of crystalline cellulose and both high density (HD) and low density (LD) hulls in the high wavenumber region. The broad band at 3447 cm^{-1} is present in the spectra for all three substances, although it is more broad for the hulls. This band is attributed to the bound OH stretch in water within the hull or cellulose. A band around 2900 cm^{-1} is also present in all three spectra, but it is more resolved for the cellulose spectrum. Since this region is attributed to the alkyl CH stretching region, there are likely some unique alkyl components in the hulls, which will be addressed later.

Figure 6 is the low wavenumber region of the spectra for cellulose and both HD and LD hulls. A notable band difference from cellulose to the hulls occurs at the 1180 cm^{-1} band which shifts to 1170 cm^{-1} and is more intense than the band at 1130 cm^{-1} in the hulls spectra. This 1180 cm^{-1} band is assigned to the C-O ester bonds within the hull indicating that there are more ester bonds in the hulls than crystalline cellulose. Significant bands observed in the spectra for all three substances are consistent with the bands assigned in Table 2.

Figures 7 and 8 show the high and low wavenumber regions of the IR spectra of unmodified cellulose and cellulose that was treated by the various modification processes. When cellulose was modified, no significant changes could be seen in the FT-IR spectra. The minor bands that occur

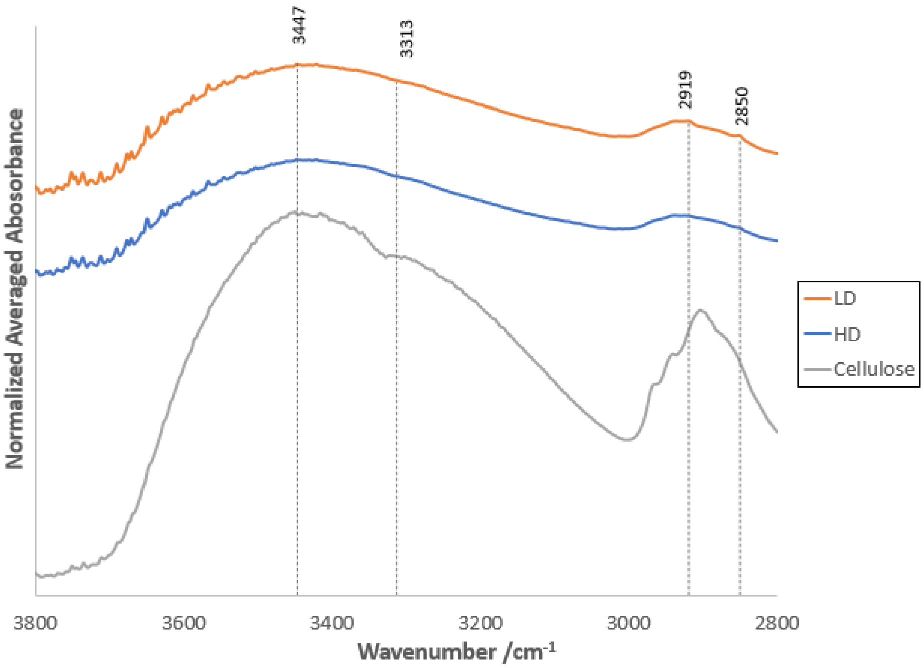

Figure 5. FT-IR spectra of unmodified cellulose, HD and LD hulls from 3800-2800 cm^{-1}.

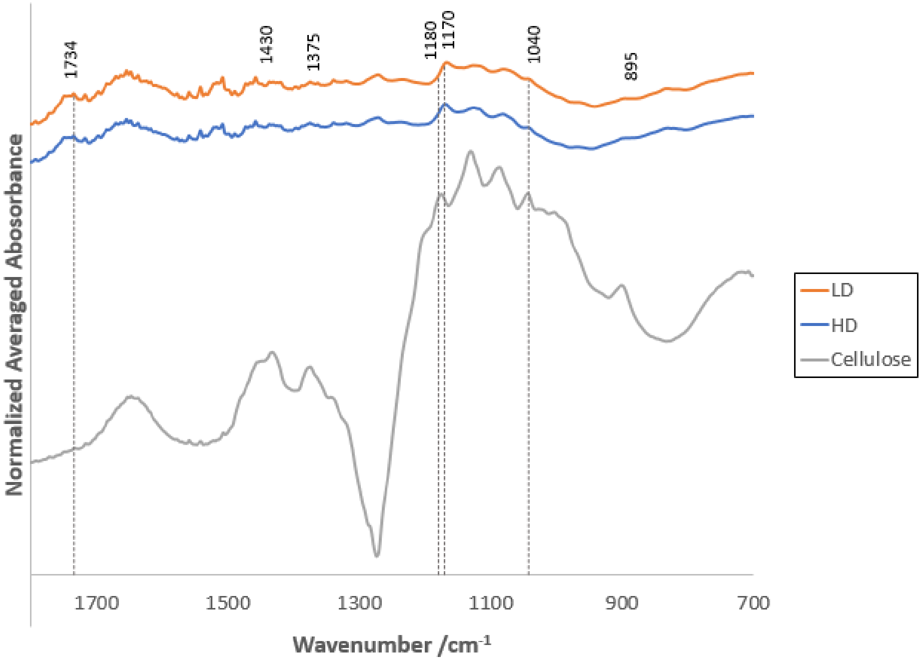

Figure 6. FT-IR spectra of unmodified cellulose, HD and LD hulls from 1800-700 cm^{-1}.

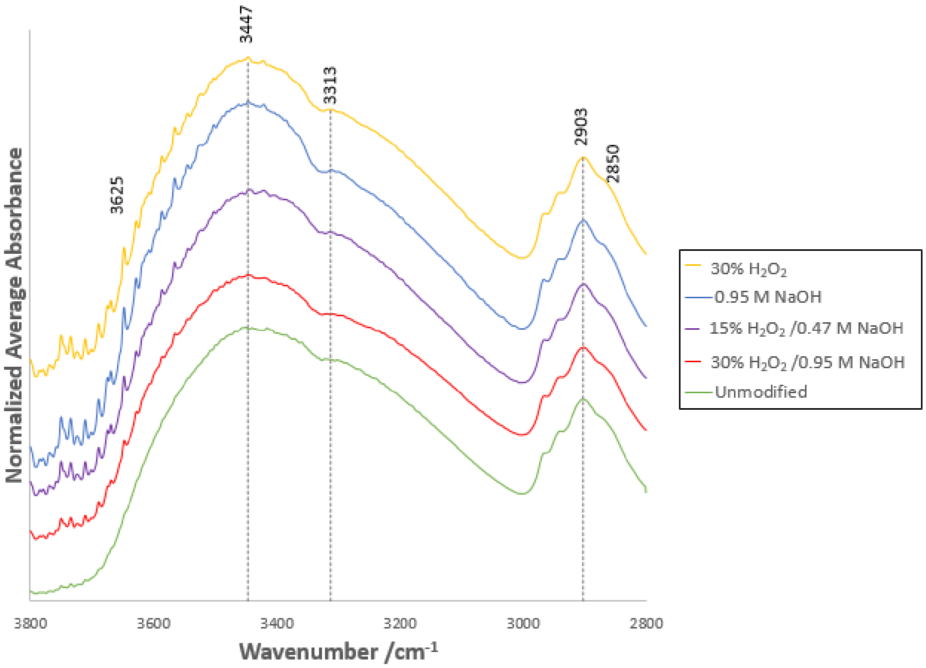

Figure 7. FT-IR spectra of unmodified and modified cellulose from 3800-2800 cm^{-1}.

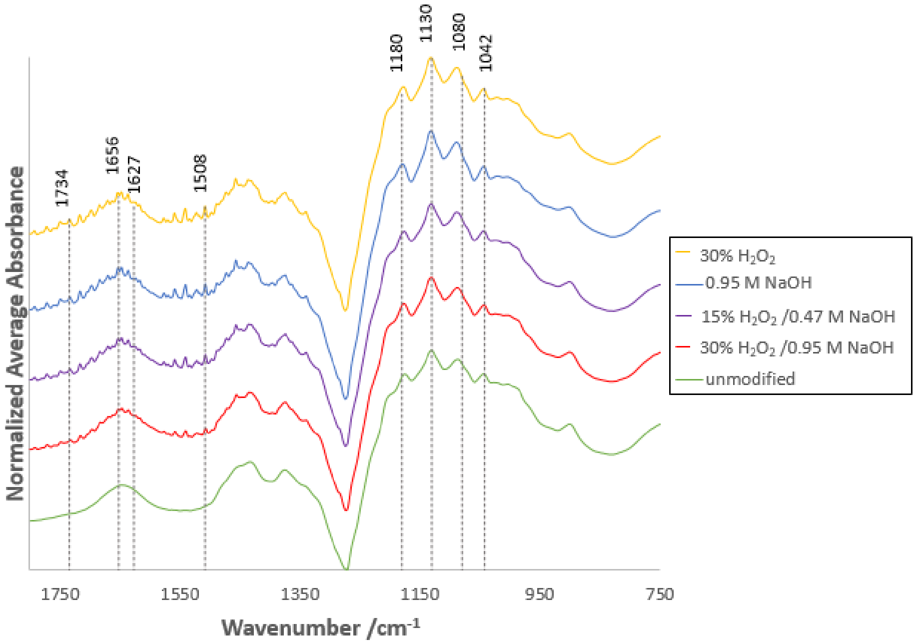

Figure 8. FT-IR spectra of unmodified and modified cellulose from 1800-700 cm^{-1}.

between 3800-3400 cm^{-1} and 1800-1400 cm^{-1} in the modified cellulose spectra are attributed to water vapor.

Figures 9 and 10 show the high energy range of the spectra of HD and LD hulls, respectively. In both sets of spectra, the very broad spectral band with a maximum at approximately 3400 cm^{-1} was assigned to the OH vibration of hydrogen-bonded hydroxyl groups.[31] A shoulder at around 3625 cm^{-1} is observed in the spectra of modified hulls as the concentration of NaOH increased in the modification process and is assigned to free hydroxy group of water.[32] This shoulder at 3625 cm^{-1} is not present in the cellulose spectra (Figure 7) or unmodified hulls which suggests this ordering is induced by the NaOH deprotonation of alcohol groups on cellulose which can order neighboring H_2O molecules.

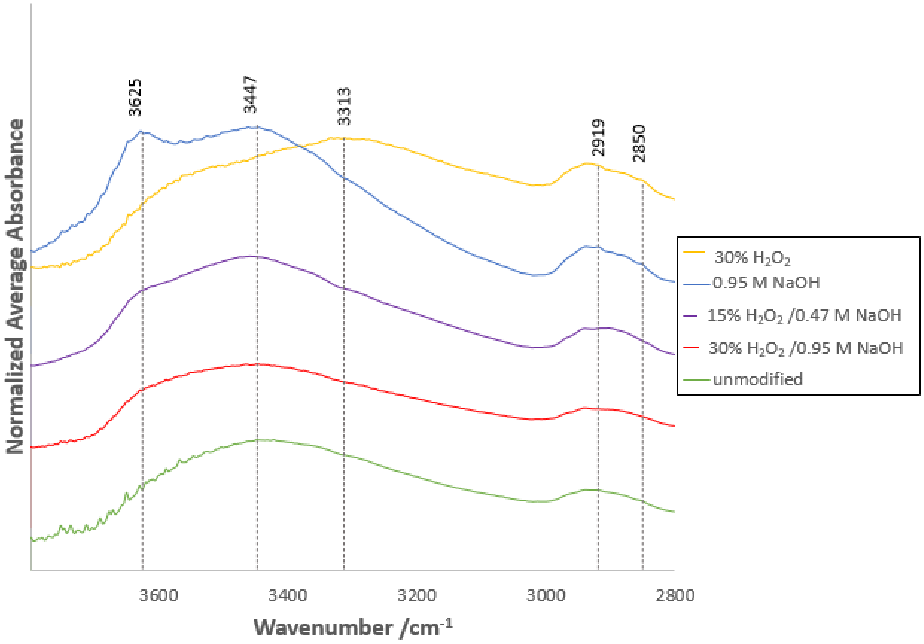

Figure 9. FT-IR spectra of unmodified and modified HD hulls from 3800-2800 cm^{-1}.

The broad band around 3300 cm^{-1} in the spectrum for H_2O_2 modified hulls may be due to H_2O_2 itself trapped within the hulls. Figure 11 shows the FT-IR ATR spectra of the combination of 0.95 M NaOH and 30% H_2O_2 as well as just 30% H_2O_2. There is a band around 3355 cm^{-1} attributed to the hydroxy groups within H_2O_2. Interestingly, this band is not significant in the

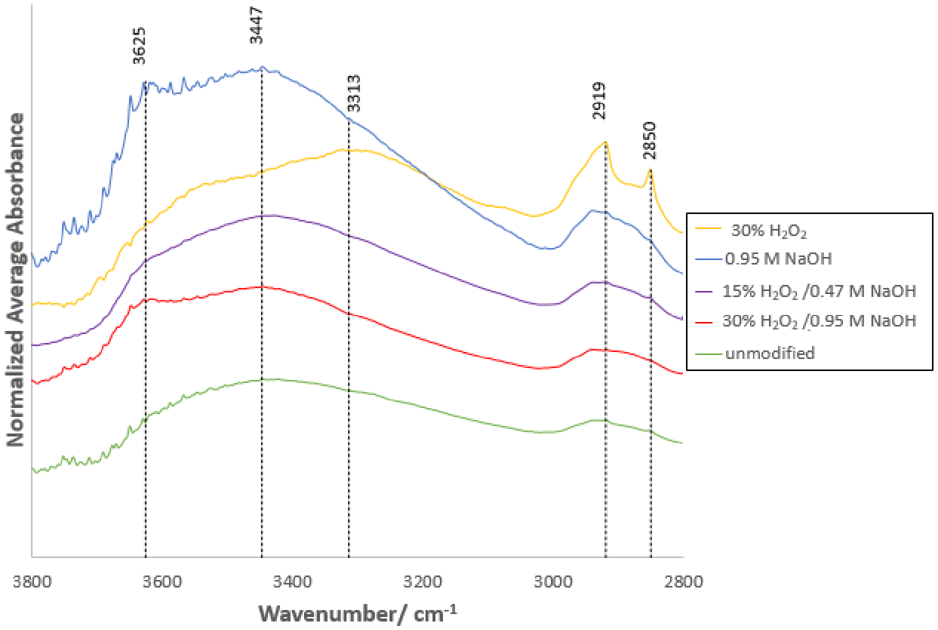

Figure 10. FT-IR spectra of unmodified and modified LD hulls from 3800-2800 cm^{-1}.

spectra of hulls in which the NaOH/H_2O_2 combination was used in the modification process.

The other broad band shown in the 3800-2800 cm^{-1} range of the hulls spectra (Figures 9 and 10) at approximately 2900 cm^{-1} is attributed to the asymmetric and symmetric CH stretching vibrations of the methyl and methylene groups of aliphatic components. The band at 2900 cm^{-1} becomes two resolved bands at 2919 and 2850 cm^{-1} only in specific LD hull pieces, and since these spectra were averaged, the two resolved bands look like small features on the 2900 cm^{-1} band and as a small shoulder in NaOH modified HD hulls. However, these two resolved bands always occur in the spectra of H_2O_2 modificatied LD hulls as seen in Figure 10. The band at 2919 cm^{-1} is assigned to CH_2 anti-symmetric stretching, and the band at 2850 cm^{-1} is assigned to CH_2 symmetric stretching.[33] Resolved methylene bands suggest the presence of long alkyl chains, such as those found in fatty acids and lipids. The bands are broadened for short chains or when many types of CH_2 groups are present. The fact that resolution is observed for the LD hulls suggests they contain some fatty components, which is consistent with their lower density. These components may be dissolved by the alkaline modification but appear to remain with a solely

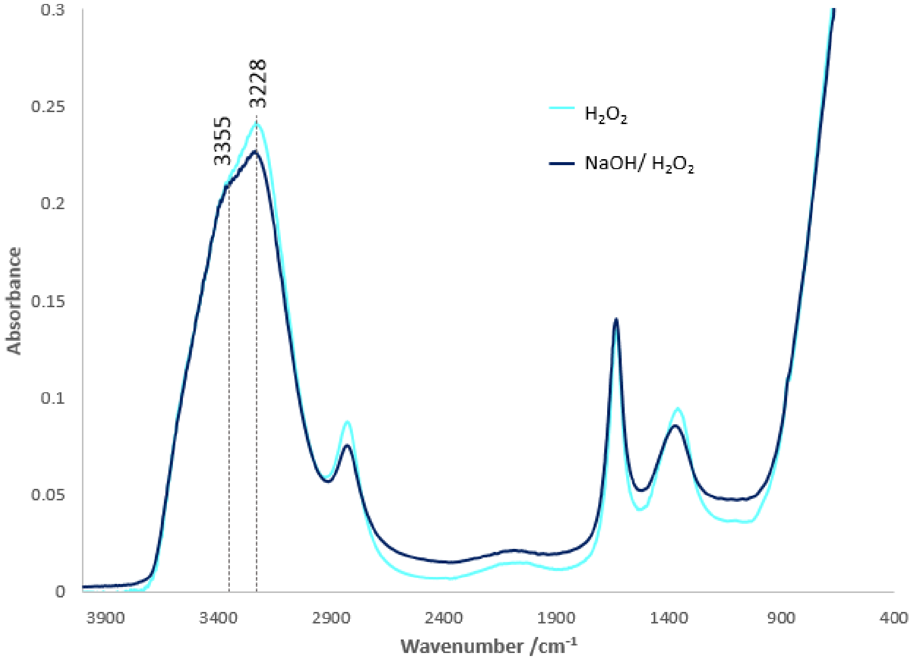

Figure 11. FT-IR ATR spectrum of the combination of NaOH and H_2O_2 compared to a spectrum of H_2O_2.

H_2O_2 treatment. Yang et al. presented a FT-IR spectra of hemicellulose that shows these two specific resolved bands which is consistent with the bands sometimes seen in the LD hulls (Figure 10).[34]

Figures 12 and 13 show the low energy range of the LD and HD hull spectra. A small band at 1734 cm^{-1} was assigned to a C=O stretching vibration. This band does not appear in the cellulose spectrum, suggesting it is due to another component of the hulls, such as the C=O bond in fatty acid methyl esters.[33] The band is most prominent in the spectra of unmodified hulls and the H_2O_2 modified hulls. This is consistent with the analysis of the band resolution around 2900 cm^{-1} in Figures 9 and 10. Since this band is not present in the spectra of hulls modified with NaOH, the component responsible for this band is likely removed with the use of NaOH.

A new band corresponding to carbonyl groups was expected when the hulls were modified, since alcohol groups in cellulose can be oxidized in alkaline peroxide solutions.[14] In a study of jute fibers modified by a similar alkaline peroxide method, a band at 1733 cm^{-1} was attributed

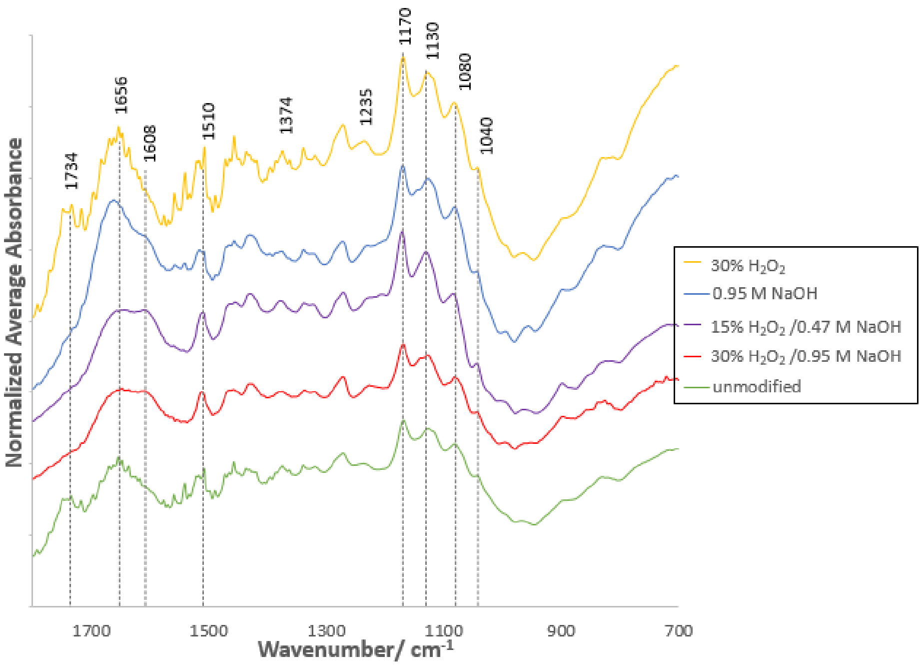

Figure 12. FT-IR spectra of unmodified and modified HD hulls from 1800-700 cm^{-1}.

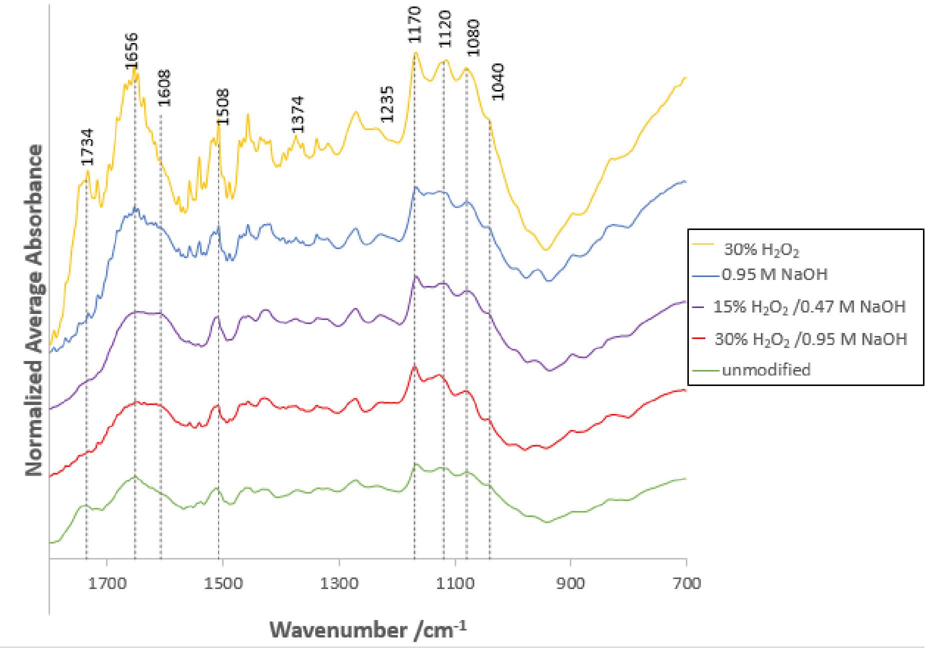

Figure 13. FT-IR spectra of unmodified and modified LD hulls from 1800-700 cm^{-1}.

to the formation of carboxylic acid groups,[14] but this was not observed for peanut hulls. Instead, the growth of a band at 1608 cm^{-1} was observed. (See Figures 12 and 13.) The cellulose spectrum does not show the shoulder at 1608 cm^{-1}. However, it is observed in the spectrum of modified hulls. This band is most prominent in the hulls for which NaOH and H_2O_2 are combined in modifications 1 and 4. Historically, in mercerized cellulose (cellulose treated with NaOH), this band has been attributed to bound water,[30] but it could also be a due to C=O stretching of a ketone or other carbynl group.[32] Studies of alkaline peroxide oxidation of cellulose results in the formation of ketones at 1608 cm^{-1} from the secondary alcohols and aldehydes from the breaking of cellulose chains.[14]

3.2 Physical Analysis

The volume of empty space within the hulls is directly related to the accessibility of an adsorbate because a greater volume of empty space results in a greater surface area per mass of material. Surface area is proportional to adsorption capacity. Figure 14 shows the volume of the empty space per gram of ground peanut hulls for both the HD and LD hulls as a function of the modification procedure. The numerical values are provided in Table 3.

Table 3. Volume of the empty space within HD and LD hulls. Standard deviation between measurements taken in triplicate is reported.

Modification	**HD (mL/g)**	**LD (mL/g)**
unmod	0.4 ± 0.1	1.1 ± 0.2
mod 1	0.7 ± 0.1	2.9 ± 0.8
mod 4	0.5 ± 0.2	1.6 ± 0.5
NaOH	0.37 ± 0.08	1.9 ± 0.5
H_2O_2	0.3 ± 0.2	1.2 ± 0.2

For unmodified hulls, the LD hulls have nearly three times the volume of empty space than the HD hulls. This was expected given the LD hulls have a lower density than the HD hulls. This trend is consistent for all of the modified hulls, as well. In modification 1, the increase in volume for LD is large, again nearly a factor of three. This is attributed to the dissolution of lignin or other alkaline soluble components,[35] which frees up space within th hulls. In modifi-

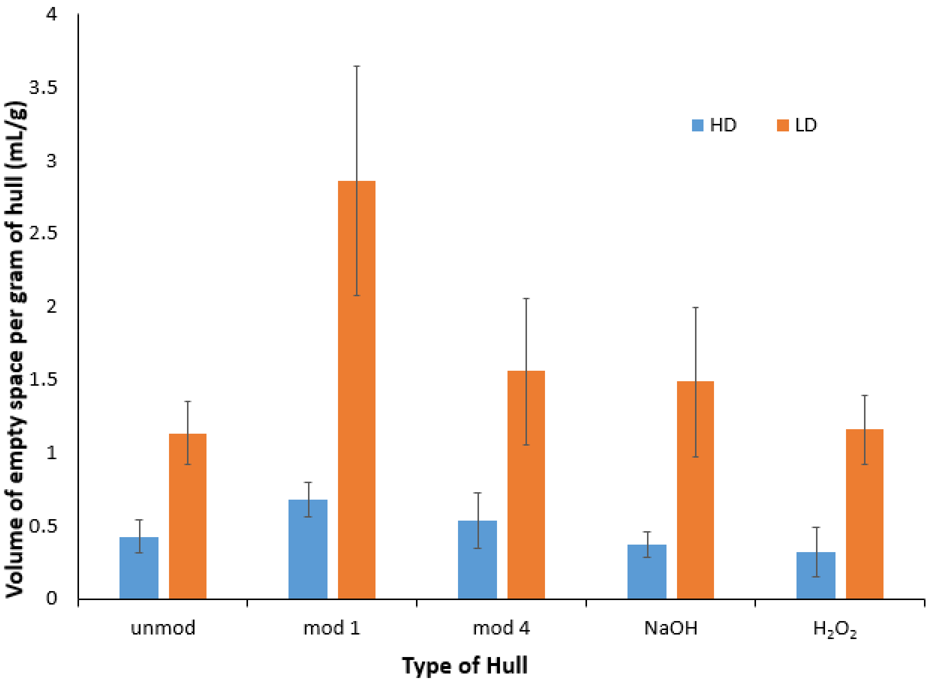

Figure 14. The volume of empty space per gram of hull for each type of hull. Error bars represent the standard deviation between measurements taken in triplicate.

cation 4, the concentrations of NaOH and H_2O_2 are cut in half and therefore less of an increase in volume is seen. However, the improvement of accessibility is more effective when NaOH and H_2O_2 are combined than either of the reagents on their own. When NaOH and H_2O_2 are combined, decomposition of hydrogen peroxide occurs in the sodium hydroxide solution. It is an auto-accelerating reaction that generates significant amounts of heat and oxygen.[36] The decomposition reaction is complex with intermediates such as HO_2^-.[37]

The HD hulls show little to no change in the volume of empty space within the hull when modified. This constant accessibility is attributed to HD hulls having less lignin or other alkaline soluble components in its composition. Since there is less to be dissolved and removed during modification, the volume of empty space does not increase. This is consistent with the analysis of the IR band at 1734 cm^{-1} (ester) in spectra for modified hulls. (See Figures 12 and 13.) The band at 1734 cm^{-1} disappears when the hulls are modified using NaOH, suggesting that there are alkaline soluble components removed during modifications using NaOH.

3.3 Adsorptivity

Methylene blue (MB) adsorption was used to test the feasibility of using peanut hulls as a biosorbent. By comparing adsorptivity of hulls to that of cellulose, an understanding of the role of cellulose in adsorption can be developed along with its role in the biosorptivity of the hulls. A concentration of 5 mM is normally used for the estimate of oxidative degradation as seen in literature.[14] A methylene blue isotherm was completed in order to confirm that 5 mM is beneficial for adsorption studies. This can be seen in Figure 15, confirming that 5 mM or roughly 1600 ppm is within the saturation zone.

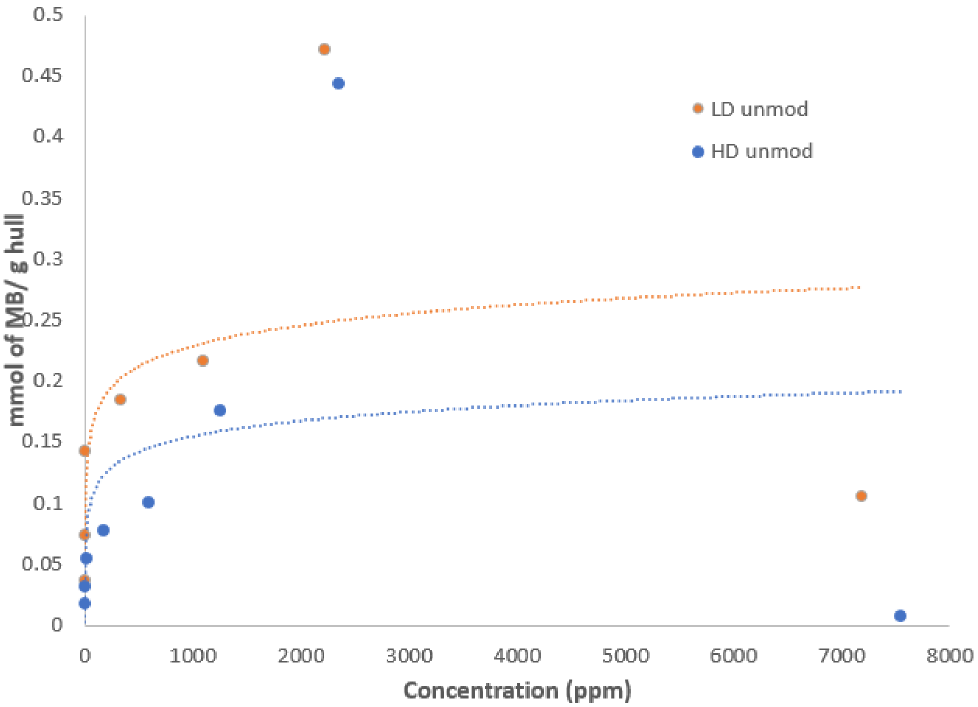

Figure 15. An adsorption isotherm for methylene blue binding to peanut hulls. Data was fit using the Langmuir model (Equation 1).

Figure 16 shows the amount (mmol) of MB adsorbed per gram of hull for cellulose, LD hulls and HD hulls as a function of the modification process. Values are provided in Table 4. In calculation of the average MB adsorptivity for unmodified HD hulls, one value of the six trials was removed as an outlier using the Iglewicz and Hoaglin's robust test for multiple outliers.[38] The data gives a modified Z score of five indicating the value of 0.29 mmol MB/g hull is an outlier.

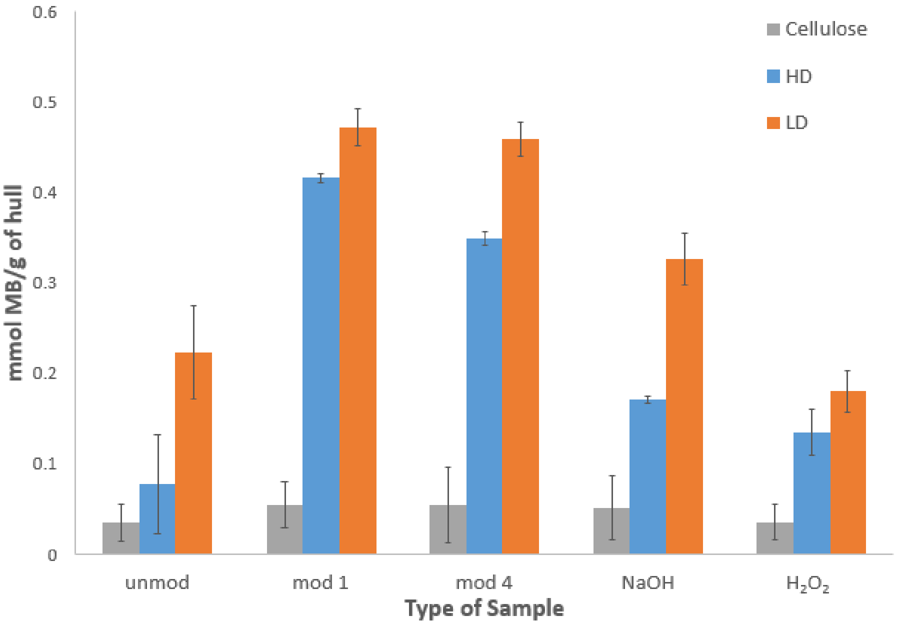

Figure 16. The surface coverage of methylene blue for cellulose, HD hulls, and LD hulls. Error bars represent the standard deviation between the multiple measurements taken.

Table 4. MB adsorption data for cellulose, HD, and LD hulls.

	Cellulose (mmol/g)	**HD (mmol/g)**	**LD (mmol/g)**
unmod	0.03 ± 0.02	0.1 ± 0.1	0.22 ± 0.05
mod 1	0.05 ± 0.03	0.416 ± 0.005	0.47 ± 0.02
mod 4	0.05 ± 0.04	0.349 ± 0.007	0.46 ± 0.02
NaOH	0.05 ± 0.03	0.171 ± 0.004	0.33 ± 0.03
H_2O_2	0.04 ± 0.02	0.13 ± 0.02	0.18 ± 0.02

The cellulose used in the MB adsorption was crystalline and was not expected to adsorb much due to the lack of accessibility within the tightly packed structure. In Figure 16, the amount of MB adsorbed per gram of cellulose does not change upon modification. Natural cellulose, like what is found in peanut hulls, is not as tightly packed and could behave differently when adsorbing MB. In all cases, LD hulls have a greater adsorptivity than HD hulls. This is expected based on the greater volume of empty space found in LD hulls, which results in greater accessibility for

MB molecules. Unlike cellulose, the hulls do show an increase in adsorptivity when modified.

For unmodified hulls, LD hulls always have a greater adsorptivity than HD hulls, which is attributed to the greater volume of empty space within LD hulls. Both HD and LD hulls that have been modified by modification 1 show a large increase in surface covreage. The increase is by a factor of four for HD hulls and by a factor of two for LD hulls. This is expected for LD hulls because the amount of empty space also increases when these hulls are modified. However, the large increase is unexpected for HD hulls since previous results showed HD hulls do not have as much of an increase in empty space upon modification. This suggests the increase in adsorptivity may be due to something other than dissolution of alkaline soluble material, such as a chemical change, even though no unique chemical signatures were found in the IR spectra. A similar but smaller increase in surface coverage was observed with modification 4, presumably because the reagent concentrations were half of that used in modification 1. When using just NaOH, a small increase in adsorption is observed but much less than what is observed for modifications involving both NaOH and H_2O_2. The increase in adsorption is likely due to dissolution of alkaline soluble components and in this case, LD hulls have a slightly greater increase. This is presumably because of a greater content of alkaline soluble components as is suggested by the increase in empty space, see Figure 14. The modification using just H_2O_2 shows a slight increase in surface coverage for HD hulls and a slight decrease in coverage for LD hulls, but the level of uncertainty suggest that these changes may not be significant. Although H_2O_2 is a strong oxidizer ($E^o_{red} = 1.78\,\text{V}$),[39] the chemical changes induced by using H_2O_2 alone (without NaOH) do not appear to have an affect on adsorption. The effect is much more pronounced in an alkaline environment, perhaps because of the combination of the H_2O_2/NaOH mixture used.

If modified, the ground peanut hulls show promise for removal of low concentration contaminants. Modification should involve both NaOH and H_2O_2 to ensure enhanced effectiveness, but lower concentrations of each (0.45 M NaOH and 15% H_2O_2 as in modification 4) are sufficient to achieve moderate adsorption.

CHAPTER FOUR: CONCLUSIONS AND FUTURE DIRECTIONS

A series of studies were completed to characterize natural and modified ground peanut hulls. The hulls were separated by density and both high density (HD) and low density (LD) hulls were studied separately then compared. The research found that peanut hulls would be useful as a biosorbent for methylene blue (MB), especially if the modification technique is used. The role of chemical modification in the adsorption process is significant to increase adsorption of natural peanut hulls. When modified, the HD and LD hulls have some differences in accessibility and adsorption of MB. The use of modification 1, which contains the highest concentrations of NaOH and H_2O_2 (0.95 M NaOH and 30% H_2O_2), produces the highest surface coverage with 0.416 ± 0.005 mmol of MB per gram of HD hulls and 0.47 ± 0.02 mmol of MB per LD hulls. The accessibility of the hulls modified by modification 1 is also the highest when compared to other modifications studied. The volume of empty space in these hulls is 0.7 ± 0.1 mL/g for HD hulls and 2.9 ± 0.8 mL/g for LD hulls. Decreasing the concentration of H_2O_2 and NaOH when using modification 4 still resulted in an increase in both the volume of empty space and the MB surface coverage for HD hulls, but it did not increase as much as was observed for modification 1. For LD hulls, the increase in adsorption was about the same for both methods, but the volume of empty space increased more with the high concentration modification than the low concentration modification. This suggests that LD hulls have more content being removed in the modification processes than HD hulls. The FT-IR spectra verify that the combination of NaOH and H_2O_2 removes lignin or other alkaline soluble components of the hulls which creates more accessibility for an adsorbate.

These results directed how the modification method could be optimized to ensure a more efficient adsorption. It is evident that the modification that is most efficient at increasing adsorption is modification 1. However, modification 4 could be used for LD hulls to obtain similar results with a lower cost. Future studies could determine if a minimum concentration of NaOH and H_2O_2 could be used to enhance adsorption.

In past studies, it was assumed the adsorption of aqueous copper using peanut hulls is a chemisorption, homogenous, and ion exchanging process involving the conversion of cellulose-based alcohol groups to carboxylate groups. However, a significant increase in carboxylate groups is not observed in the IR spectra for either HD or LD hulls. The band assignment for the carboxylate region is also attributed to a broad bound water band and therefore, an increase in the number of carboxylates is not certain. Raman spectroscopy paired with the IR results could shed more light on any carbonyl functional groups present due to oxidation. Also, a more in-depth chemometrics treatment of infrared and/or Raman data could help to more clearly distinguish features of LD and HD hulls and attribute subtle spectroscopic features to chemical changes within the hulls upon modification.

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