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Sudan University of Science and Technology  
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**Isolation, Modification, and Characterization of Cellulose  
from Wood Pulp of *Acacia nilotica***

عزل وتعديل وتشخيص السيليلوز من نشارة خشب شجرة السنط

A dissertation Submitted in Partial Fulfillment of the Requirements of a  
Bachelor (honors) Degree in Chemistry

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## **Dedication**

This research work is dedicated to our respective parents. They have given us the drive and encouragement, and without their love and support this project would not have been made possible.

To our families and friends whom supported us all the time.

## **Acknowledgment**

First of all we would like to thank Allah (God) for giving us inspiration, courage, energy and patience to complete this study.

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## Abstract

The aim of this study was to isolate, modify, and characterize cellulose from wood pulp of *Acacia Nilotica*. The isolation of cellulose was done using alkaline hydrolysis of wood fibers in aqueous solution of sodium hydroxide (4% w/v) and bleaching steps. Citric acid was used to modify the isolated cellulose. The results have shown that the percentage of cellulose is 30.81%.

FTIR spectra of the isolated cellulose and the modified cellulose were displayed their characteristic absorption bands. FTIR spectrum of cellulose has displayed the characteristic stretching and bending absorption bands of  $\text{-OH}$  ( $3330\text{ cm}^{-1}$ ),  $\text{-CH}$  ( $1058\text{ cm}^{-1}$ ),  $\text{-C-O}$  ( $1110\text{ cm}^{-1}$ ). On the other hand the FTIR spectrum of the modified cellulose has shown in addition to cellulose characteristics bands the stretching vibration of a carbonyl group  $\text{-C=O}$  at  $1733\text{ cm}^{-1}$ .

## مستخلص البحث

هدفت هذه الدراسة لعزل وتعديل و تشخيص بوليمر السيليلوز من نشارة خشب شجرة السنط. تمت عملية العزل باستخدام التحلل القاعدي لألياف الخشب باستخدام محلول هيدروكسيد الصوديوم (٤%) وخطوات لقصر اللون. أستخدم حمض الستريك لمعالجة السيليلوز وأوضحت النتائج أن نسبة السيليلوز تصل الى (٣٠,٨١%) وأطياف الأشعة تحت الحمراء للسيليلوز المعزول والمعدل أعطت إمتصاصات مميزة.

OH- $3330\text{cm}^{-1}$ ، وظهر امتصاص CH- عند  $1058\text{cm}^{-1}$ ، وظهر أمتصاص CO- عند  $1110\text{cm}^{-1}$  طيف الأشعة تحت الحمراء للسيليلوز أظهر ترددات الاستطالة والانحناء لمجموعات، في الجانب الآخر فقد اظهر طيف الأشعة تحت الحمراء للسيليلوز المعدل كل الامتصاصات المميزة للسيليلوز مع ظهور إمتصاص لمجموعة الكربونيل C=O عند  $1733\text{cm}^{-1}$

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## Chapter one

### Introduction and literature review

#### 1.1 Definition of natural fibers

Natural fibers can be defined as bio-based fibers or fibers from vegetable and animal origin. This definition includes all natural cellulosic fibers (cotton, jute, sisal, coir, flax, hemp, abaca, ramie, etc.) and protein based fibers such as wool and silk. Excluded here are mineral fibers such as asbestos that occur naturally but are not bio-based. Asbestos containing products are not considered sustainable due to the well-known health risk that resulted in prohibition of its use in many countries. On the other hand there are manmade cellulose fibers (e.g. viscose-rayon and cellulose acetate) that are produced with chemical procedures from pulped wood or other sources (cotton, bamboo). Similarly, regenerated (soybean) protein, polymer fiber (bio-polyester, PHA, PLA) and chitosan fiber are examples of semi-synthetic products that are based on renewable resources [1]. Vegetable fiber structure is formed by a central channel called as lumen, responsible for water and nutrients transportation, and by the cell wall. The cell wall of each fiber is composed by several layers as followed middle lamella, the thin primary wall, and the secondary wall, which is subdivided into external secondary wall (S1), middle secondary wall (S2) and internal secondary wall (S3). These layers are composed of micro fibrils oriented into space in defined (angles) form [2].

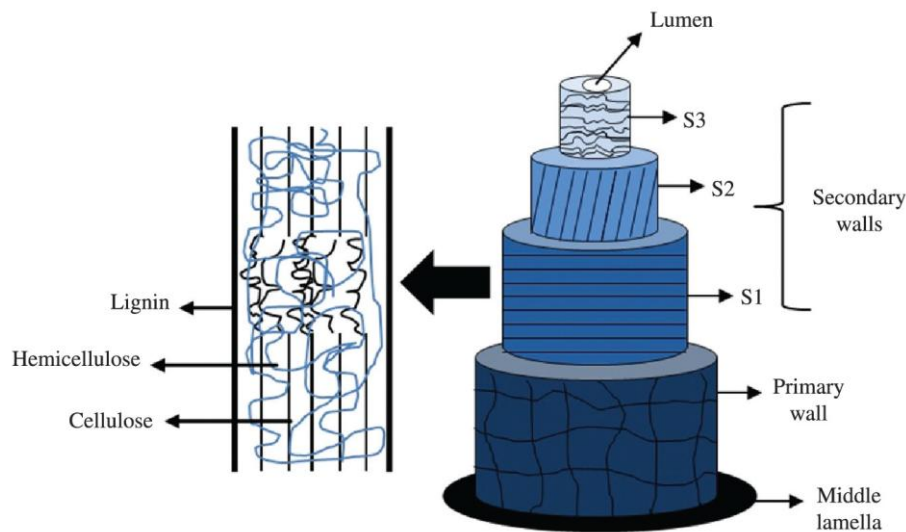
#### 1.2 Objective

The objective of this study is to isolate and modified cellulose from *Acacia nilotica* wood pulp.

#### 1.3 Holocellulose

The carbohydrate portions of the vast majority of plants are composed of cellulose and hemicellulose polymers with minor amounts of other sugar

polymers such as starch and pectin. The combination of cellulose and the hemicelluloses are called holocellulose and usually accounts for 65-70 percent of the plant dry weight. These polymers are made up of simple sugars, mainly, D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose, D-glucuronic acid, and lesser amounts of other sugars such as L-rhamnose and D-fructose [3].

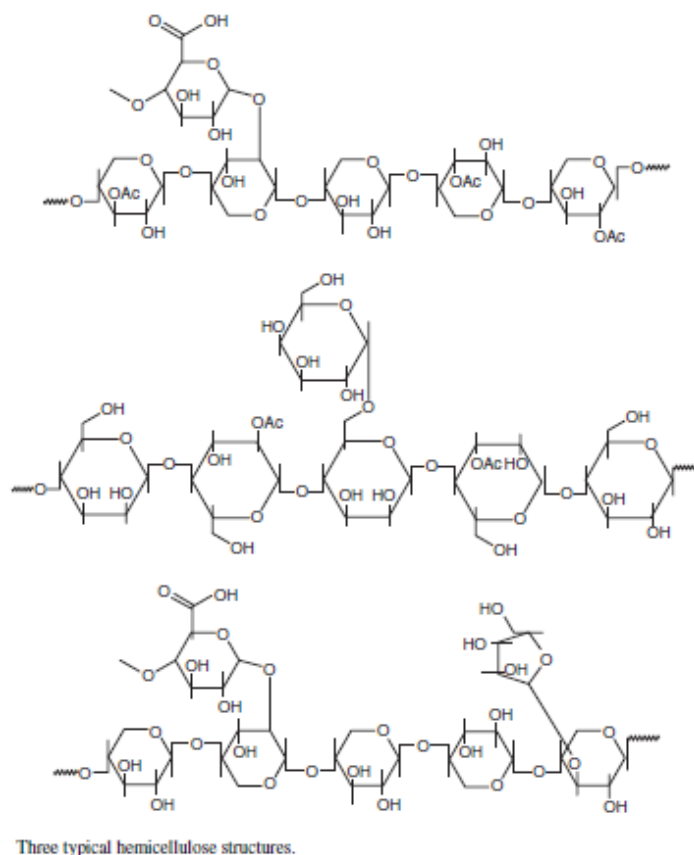


**Figure 1.1:** Schematic representation of plant fiber structure: primary wall, middle lamella, lumen, S1 - external secondary wall, S2 – middle secondary wall and S3 -internal secondary wall [2].

#### 1.4 Hemicelluloses

In general, the hemicellulose fraction of plants consists of a collection of polysaccharide polymers with a lower DP than cellulose and containing mainly the sugars D-xylopyranose, D-glucopyranose, D-galactopyranose, L-arabinofuranose, D-mannopyranose, and D-glucopyranosyluronic acid with minor amounts of it consisting of one repeating sugar unit linked  $\beta$ -(1-4) with branch points (1-2), (1-3), and/or (1-6). Hemicelluloses usually consist of more than one type of sugar unit and are sometimes referred to by the sugars they contain. For example, galactoglucoman, arabinoglucuronoxylan,

arabinogalactan, glucuronoxytan, glucomannan, etc. The hemicelluloses also contain acetyl and methyl substituted groups [3].



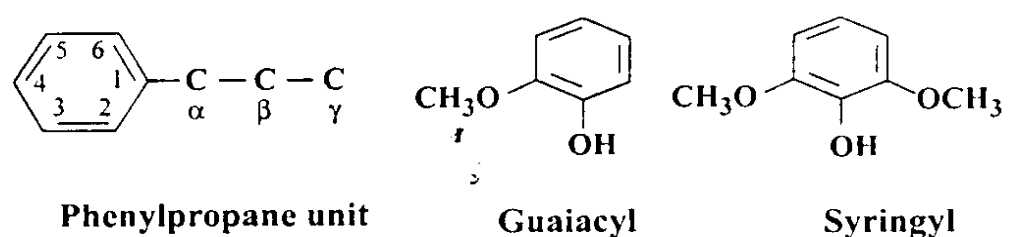
**Figure 1.2:** Three typical hemicellulose structure [6].

### 1.5 Lignin

Lignins are amorphous, highly complex, mainly aromatic, polymers of phenyl propane units. Lignin can be classified in several ways but they are usually divided according to their structural elements 16. All plant lignin consist mainly of three basic building blocks of guaiacyl, syringyl and *p*-hydroxyphenyl moieties, although other aromatic type units also exist in many different types of plants. There is a wide variation of structures within different plant species. The phenyl propane can be substituted at the  $\alpha$ ,  $\beta$ , and  $\gamma$  positions into various combinations linked together both by ether and carbon to carbon linkages.

Lignin is distributed throughout the secondary cell wall with the highest concentration in the middle lamella. Because of the difference in the volume of middle lamella to secondary cell wall, about 70% of the lignin is located in the secondary wall [3].

The function of lignin in plants is as an encrusting agent in the cellulose/hemicellulose matrix. It is often referred to as the plant cell wall adhesive. Both lignin and extractives in plants reduce the digestibility of grasses to animals. Lignin are also associated with the hemicelluloses forming, in some cases, lignin-carbohydrate complexes that are resistant to hydrolysis even under pulping condition.



**Figure 1.3: Building blocks of lignin [3].**

## 1.6 Cellulose

Cellulose is the most abundant natural polymer in the world. It is estimated that 830 million tons of cellulose are produced each year through photosynthesis". If the average plant (on a dry weight basis) contains 40% cellulose, the annual agro-based resource would be approximately 2000 million dry tons. This compares to 225 x 10<sup>9</sup> tons which is the estimated world reserve of petroleum and natural gas[3]. Cellulose is a linear and fairly rigid homopolymer consisting of D-anhydroglucopyranose units (AGU). These units are linked together by β-(1→4) glycosidic bonds formed between C-1 and C-4 of adjacent glucose moieties. In the solid state, AGU units are rotated by 180° with respect to each other due to the constraints of β-linkage. Each of the AGU units has three

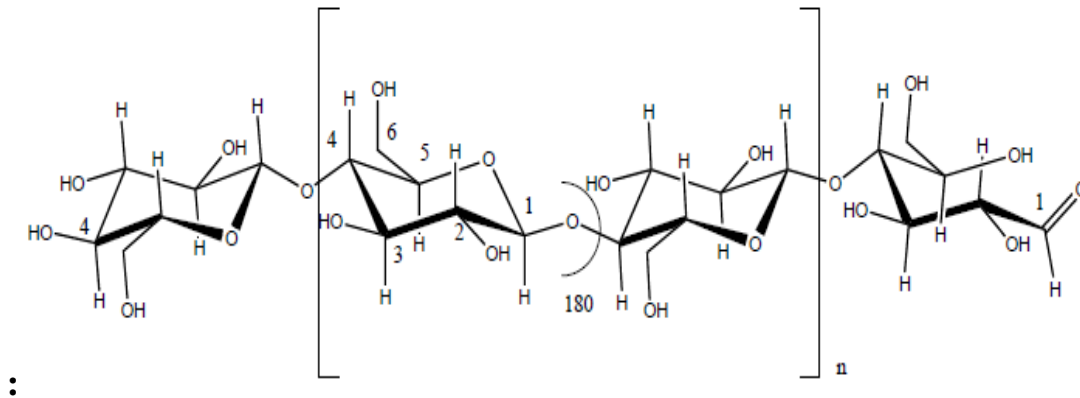
hydroxyl (OH) groups at C-2, C-3 and C-6 positions. Terminal groups at the either end of the cellulose molecule are quite different in nature from each other. The C-1 OH at one end of the molecule is an aldehyde group with reducing activity. Aldehyde groups form a pyranose ring through an intramolecular hemiacetal form. In contrast, the C-4 OH on the other end of the chain is an alcohol borne OH constituent and thus is called the non-reducing end. It has been known from the infrared spectroscopy (IR), X-ray crystallography and nuclear magnetic resonance (NMR) investigations, that the AGU ring exists in the pyranose ring form and that this adopts the  $4C_1$ -chair formation which constitutes the lowest energy conformation for D-glucopyranose [4].

The chemical character and reactivity of cellulose is determined by the presence of three equatorially positioned OH groups in the AGU, one primary and two secondary groups. In addition, the  $\beta$ -glycosidic linkages of cellulose are susceptible to hydrolytic attack. hydroxyl groups do not only play a role in the typical reactions of primary and secondary alcohols that are carried out on cellulose, but also play an important role in the solubility of cellulose. Cellulose is insoluble in common organic solvents and in water this is due to the fact that the hydroxyl groups are responsible for the extensive hydrogen bonding network forming both, intra- and intermolecular hydrogen bonding as shown in. In order to dissolve cellulose, the prevailing hydrogen bonding network must be broken. There are two possible mechanisms by which the OH groups in the cellulose molecule form hydrogen bonds. One is by the interaction between suitably positioned OH groups in the same molecule (intra-molecular). These are located between C2-OH and C6-OH groups and C3-OH with end cyclic oxygen. The other mechanism occurs when neighboring cellulose chains (intermolecular) interact via their C3-OH and C6-OH groups. Intra-molecular hydrogen bonds between the hydroxyl group at the C-3 and oxygen of the pyranose ring were first described in the 1960s by Liang who claimed the existence of a second

‘pair’ of intramolecular hydrogen bonds between the C-6 and C-2 of the neighboring AGUs [4].

Actually the building block for cellulose is cellobiose since the repeating unit in cellulose is a two sugar unit. The number of glucose units in a cellulose molecule is referred to as the degree of polymerization (DP) and the average DP for plant cellulose ranges from a low of about 50 for a sulfite pulp to approximately 600. This would mean an approximate molecular weight for cellulose ranging from about 10,000 to 150,000. Cellulose molecules are randomly oriented and have a tendency to form intra- and intermolecular hydrogen bonds. As the packing density of cellulose increases, crystalline regions are formed. Most plant derived cellulose is highly crystalline and may contain as much as 80 percent crystalline regions. The remaining portion has a lower packing density and is referred to as amorphous cellulose [3].

Cellulose can be regarded as a very important raw material for several purposes. Recently, cellulose has been in the public eye due to its possible use in the production of biofuels. Cellulose is extensively used as a raw material in the paper industry in the production of paper and cardboard products. However, this is not its only use: cellulose has shown its versatility in numerous applications. Moreover, it can be chemically modified to yield cellulose derivatives. These are widely used in various industrial sectors in addition to being used as a source for commodity goods. Efficient utilization of cellulose as a material source has been challenging, especially in chemical industry, due to poor solubility low density, nonabrasive, combustible, nontoxic, low cost, and biodegradable properties. A lot of research works have been performed all over the world on the use of cellulose fibers as a reinforcing material for the preparation of various types of composites. However, lack of good interfacial adhesion, low melting point, and water sensitivity make the use of cellulose-fiber reinforced composites less attractive[4].



**Figure 1.2:** Molecular structure of cellulose representing the cellobiose unit as a repeating unit showing reducing (right) and non-reducing (left) end-groups. When considering only one of these glucopyranose structures, repeated anhydroglucopyranose units (AGU) are rotated 180° with respect to each other [4].

## 1.7 *Acacia nilotica*

### 1.7.1 Distribution of Acacia

Is a tree species of great importance in the economy of Sudan. It yields gum Arabic of which the country exports over 80% of the world's demand. A Senegal has a wide distribution from the 200mm. Isohyet on the sandy soils of western Sudan over 800mm of annual rainfall in central Sudan on the Clay soils of Eastern Sudan the species is found in areas with mean annual rainfall of 400mm or more [7].

### 1.7.2 Botanical description

*Acacia nilotica ssp. nilotica* is an evergreen, usually moderate-sized (2.5-25 m) tree with a short, thick and cylindrical trunk; bark is grey, reddish-brown or black, rough, furrowed. Leaves are alternate, bipinately compound, 5-15 cm

long; axis fairly hairy, with 3-8 pairs of side axes (pinnae) 1-4 cm long; leaflets 10-30 pairs on each side axis, small, narrowly oblong, 3-6 mm long, blunt at the ends with tiny hairs along edges, grey-green [5].

### **1.7.3 Local names**

Afrikaans (lekkerruikpeul,ruikpeul); Amharic (cheba); Arabic (garad,sunut,sunt); English (prickly acacia, Egyptian thorn, babul acacia, Arabic gum tree, scented thorn, scented-pod acacia); French (gommier rouge,Acacia de Cayenne, Acacia d'Arabie,acacia agomme); German (Gummi-AkazieArabischeAkazie); Hindi (dauria,babla,kauria,godi,babul,telia,kikar,godi babul); Italian (Acacia d'Egitto); Ndebele (isanqawe, umtshanga); Somali (tuger); Swahili (mgunga); Tamil (karuvelum); Tigrigna (chea, geredchea, ghered); Tongan(nombe,mungnombie,mukoka); Trade name (babul); Tswana(motlabokgosi); Urdu (babar) [5].



## **Chapter two**

### **Materials and methods**

#### **2.1 Sample collection**

Wood fibers were collected from Alabasia-Industrial area, Omdurman-Sudan and were used as-received.

#### **2.2 Chemicals**

Sodium hydroxide (97%, CDH, India), Acetic Acid, Sodium hypochlorite solution (Clorox 5%), Citric Acid, Distill Water.

#### **2.3 Isolation of cellulose**

50 grams of wood fiber were immersed in a 4% sodium hydroxide solution and the content was heated in water bath at 80C for four 4 hours with continuous steering. This step was repeated many times until the dark brown color was changed to pale yellow color and finally the content was washed with distilled water several times. The fiber was then subjected to a bleaching step using a mixture of acetate buffer (prepared by adding 27g of sodium hydroxide to 75 mL of acetic acid and diluted with distilled water to 1 liter) by adding 100 mL of a solution of a buffer composed of acetic acid and sodium hydroxide 100 ml of Clorox solution in water bath to about two 2 hours until change of color to white it was washed with distill water to neutralize the solution by using methyl red. (it take about 6 hours). The pure cellulose was filter by using weighted piece of muslin ,the collected cellulose was dried by oven at 50 C, to about four 4 hours (higher temperature will damage it) the collected cellulose was weighted.

#### **2.4 Characterization methods**

##### **2.4.1 Infrared spectroscopy**

The pure cellulose was examined by FT-IR-8400S (Shimadzu, Japan) Infrared spectrometer to determine its functional groups. Few grams of sample were thoroughly mixed with potassium bromide and ground into fine powder in a Mortar. The fine powder was compressed into a transparent disk. The sample

was scanned in the range 400 to 4000 with a number of scan 10 and a resolution of  $4\text{cm}^{-1}$

## **2.5 Modification of cellulose**

2 grams of cellulose were suspended in an aqueous solution of a 1% citric acid which followed by a homogenization step using I.K.A., Trux stirrer. The solution was casted and left to dry. The dried film was heated in an oven at  $165\text{C}$  for ten minutes. The unreacted citric acid was removed by washing with distilled water several times in a centrifuge. The fiber was characterized using FT-IR as detailed above (2.4.1).

## Chapter three

### Results and discussion

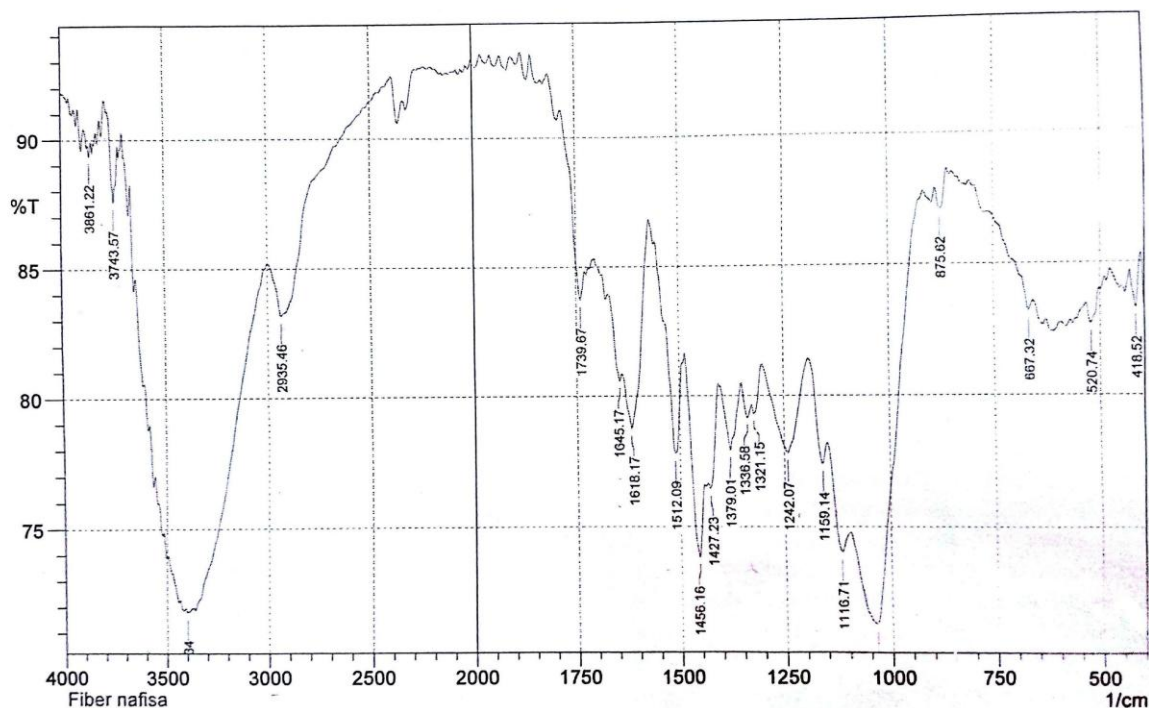
**Table3.1: Percentage of cellulose.**

Component	Percentage %
Cellulose	30.81

The percentage of cellulose in the wood is about (50%) this percent (30.81) may be appropriate, because it varies from wood to other.

### 3.2. FTIR measurements

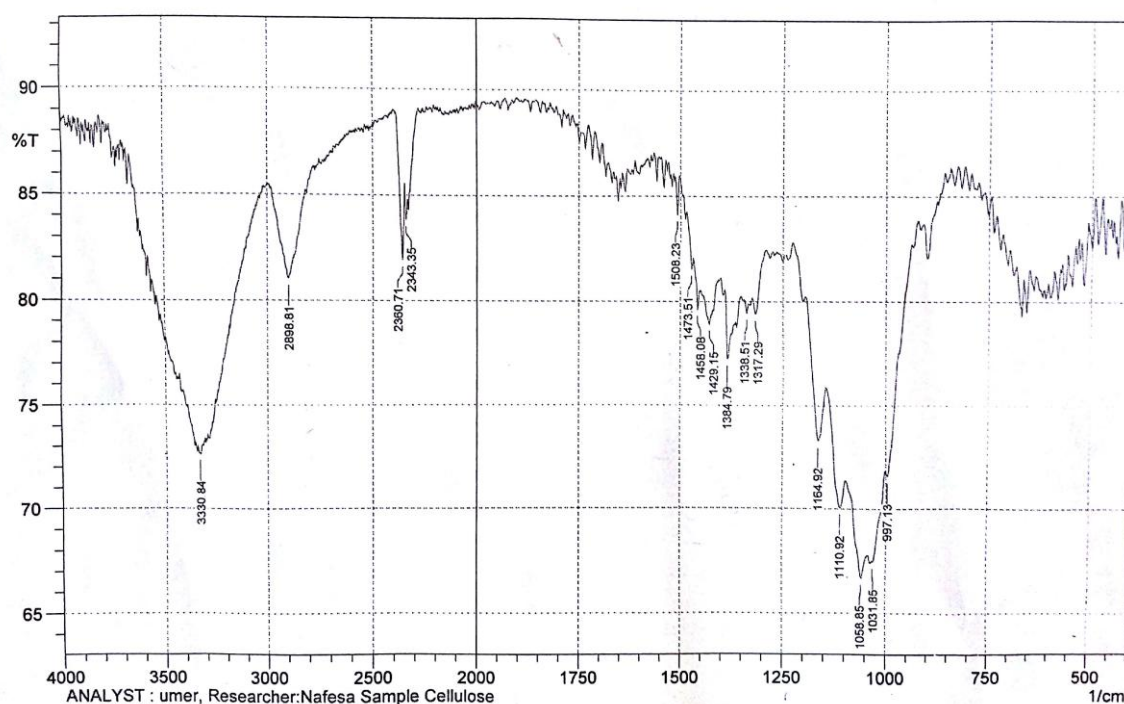
FTIR analyses were carried out to examine the functional groups present in the wood pulp.



**Figure 3.2.1: The FTIR spectrum of *Acacia nilotica* wood pulp.**

As can be seen from the spectrum (Figure 3.2.1), the peak at  $3382\text{ cm}^{-1}$  is due to OH stretching vibration, whereas the peak at  $2935\text{ cm}^{-1}$  is attributed to stretching

vibration of  $-CH$  ( $sp^3$  hybridized) of alkane. The peak at  $1733$  is due to carbonyl group stretching vibration and the peaks around  $1427$ ,  $1456$ ,  $1379$ ,  $1338$   $cm^{-1}$  are characteristic bands of  $CH$  bending vibrations. The peak around  $1512$   $cm^{-1}$  is attributed to  $-C=C$  aromatic stretching vibration. The peak at  $1645$   $cm^{-1}$  is characteristic to adsorbed water and the peak at  $1116$   $cm^{-1}$  is due to  $-CO$  stretching vibration and the peak at  $875$   $cm^{-1}$  is due to  $-CH$  rocking vibration. It could be concluded from above that all the characteristics absorption bands of wood fiber.

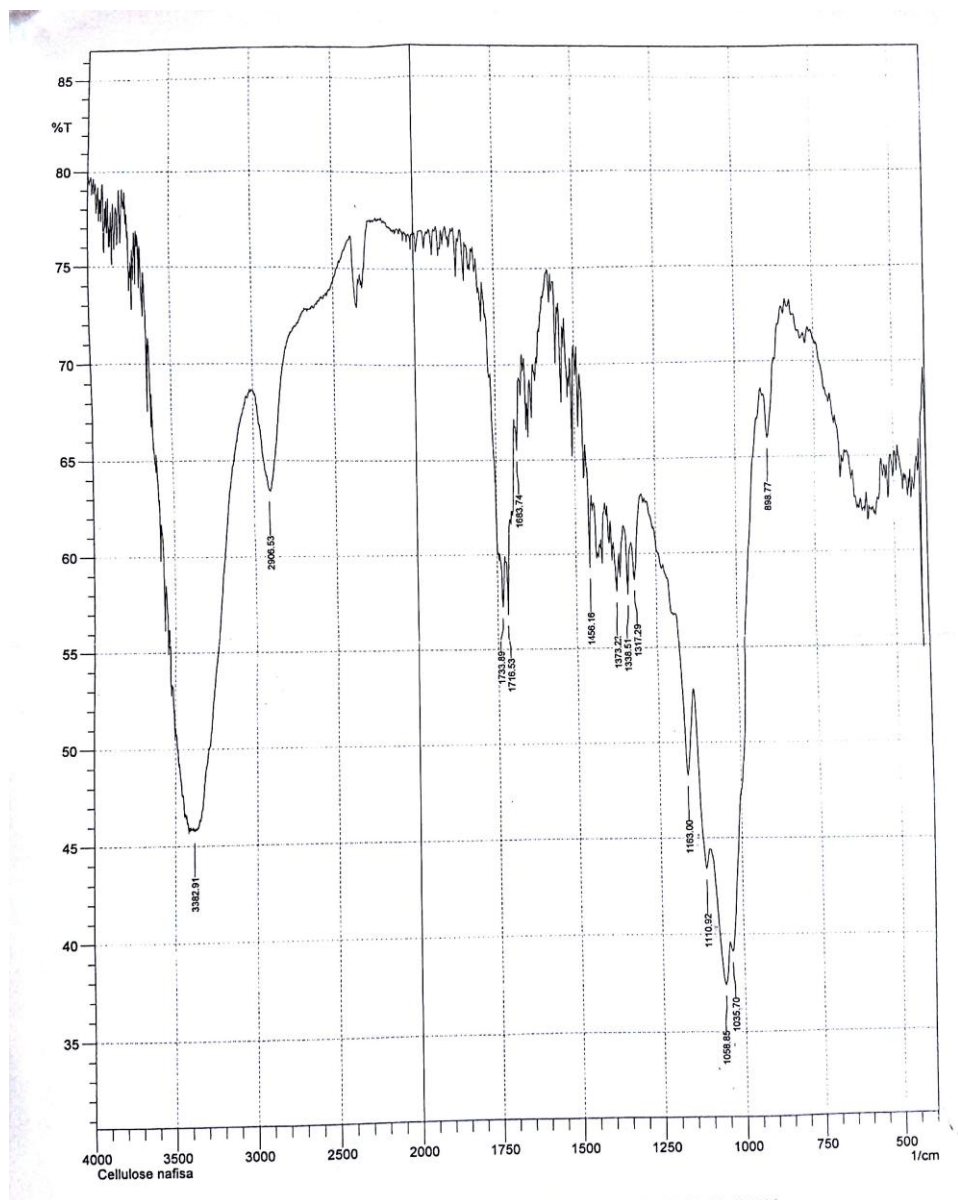


**Figure 3.2.2: The FTIR spectrum of the isolated cellulose.**

As can be seen from the spectrum Figure 3.2.2, the peak at  $3330$   $cm^{-1}$  is due to  $-OH$  stretching vibration, whereas the peak at  $2898$   $cm^{-1}$  is attributed to absorption band of  $-CH$  ( $sp^3$  hybridized) stretching vibration of alkane, and the peaks between  $1456$  to  $1373$   $cm^{-1}$  are due to bending vibrations of  $-CH$ .  $1058$  to  $1110$   $cm^{-1}$  is due to  $-CO$  stretching vibration.

As can be seen from the spectrum Figure 3.2.3, the peak at  $3882$   $cm^{-1}$  is due to  $-OH$  stretching vibration, whereas the peak at  $2906$   $cm^{-1}$  is attributed to

absorption band of -CH ( $sp^3$  hybridized) stretching vibration of alkane. We can notice that the intensity decrease is correlated with appearance of band around  $1733\text{ cm}^{-1}$  allotted to the vibration of carbonyl group -C=O, stretching vibration. The peaks around  $1110$  to  $1133\text{ cm}^{-1}$  are due to -CO stretching vibration.



**Figure 3.2.3: The FTIR spectrum of the modified cellulose.**

## **Conclusion**

The isolation, modification and Characterization of cellulose from Acacia nilotica wood pulp were investigated in this study. Cellulose was successfully isolated and modified.

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