An- Najah National University

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Extraction of Cellulose Powder from Argania Spinosa (Stems and Seeds) Trees

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Dedication

With all proud I dedicate my thesis first to my precious country Palestine. Second to my dearest people to my heart my father and mother, to my brothers Abdullah and Ahmed, to my sisters Reem and Amnah, then I dedicate my success to my university and to every one who supports me and last and not least to myself.

Acknowledgement

Before any one I would thank God who makes it easy for me to complete my work in this thesis. I would like to thank my family for their endless support, encouragement, guidance and care.

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Alson I would like to thank my colloquies and my head mistress. Finally thank all of those who supported me throughout my study.

الإقرار

انا الموقع ادناه مقدم رسالة تحت عنوان :-

Extraction of Cellulose Poweder from Argania Spinosa (Stems and Seeds) Trees

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Declaration

The work provided in this thesis, unless otherwise referenced, is my own research and has not been submitted else where for any other degree or qualification.

Student's Name: **اسم الطالب: رهام نضال حطاب**

Signature **التوقيع:**

Date **التاريخ: 2016/4/7**

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List of abbreviations

APC	Argan Press Cake
APC-SB	Bleached Argan Press Cake
AO	Argan Oil
APC-Cell	Argan Press Cake Cellulose
APC-WE	Argan Press Cake Water/Ethanol Purification
APC-AC	Argan Press Cake Acid Pulping Cellulose
SEM	Scanning Electron Microscopy
WAXS	Wide Angle X-Ray Scattering
FTIR	Fourier Transform Infrared Spectroscopy
MWD	Molecular Weight Distribution
MCC	Microcrystalline Cellulose
TGA	Thermogravity Analysis
K-number	Kappa Number
NMR	nuclear Magnetic Resonance
DP	Degree Of Polymerization
DS	Degree Of Substitution
CA	Cellulose Acetate
CAP	Cellulose Acetate Phthalate
CAB	Cellulose Acetate Butyrate
CAT	Cellulose Acetate Trimelitate
HPMCP	Hyroxy Propyl Methyl Cellulose Phthalate
CS	Cellulose Sulfate
CN	Cellulose Nitrate
GPC	Gel Permeation Chromatography
HPLC	High – Performance Liquid Chromatography
OD	Over Dry

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Abstract

Argan press cake (APC) is an agricultural waste material generated from the oil production of *Argan* nuts. It is a dark-brown powder containing cellulose and other components such as hemicelluloses, proteins, and lipids. In this study, an alkaline processing approach consisting of applying a mild cooking treatment at 80^{o}C in a solution containing sodium hydroxide (12%) and sodium sulfate (8%) was developed to extract cellulose form APC. Yellowish cellulose pulp was thereof obtained and was further subjected to an HPHEp bleaching operation to enhance the purity of cellulose to a large extent. Sugar analysis, molecular weight analysis and other spectroscopic techniques demonstrated that the extracted cellulose could be classified as a cellulose powder that would be qualified for pharmaceutical and

food applications. Other pulping methods were investigated such as acid pulping and pulping with ethanol–water solution. Cellulose obtained by these methods showed low quality and low yield. For these reasons they were briefly investigated.

Chapter One

Introduction

1.1 Background

The binomial name ***Argania Spinosa*** (L.) skeels. Local names for argan:- **Arabic**: Argan, Alouz-elbarbary (fruit) mean; Berber almond. **Berber;** Argan, Ardjan, Tizment or Feyyacha (Fruits) [1].

In English: Argan tree (the tree of iron) and also known as the olive tree of Morocco. In **French** it is known as Aganier [1]. The other name is green gold for its avails.

The Argan tree is a unique tree that grows in Morocco country and considered to be the native of this tree, it also grows in Tindouf ,a western Mediterranean Algerian region [1- 3].

Other countries such as Israel and Mexico tried to plant it [2]. Some sources say that they failed and didn't reach the recommended results.

Until now it is unknown, why it only grows in morocco and Algerian with such high quality. However other countries tried to provide the necessary condition for its growth but with no acceptable results [4].

Argan is almost unknown outside Morocco or Algeria, it only in the western part between Essaouira and Agader in Morroco. It is estimated that there are over 20 million Argan trees which play a vital role in the food chain and environment [5].

The argan forest now cover less than one million hectares, unfortunately in less than a decade, more than a third of the argan forest was removed.

Researchers agree that without aggressive invention, the argan tree will be lost over the next 20 years. The tree is thorny, evergreen with about 8-10 meter high [5], it lives longer than olive and requires no cultivation, the tree starts to bear fruit when reaches 5-6 years old. At age 60 year , it reaches its maximum production

It is life span is about 200to 250 years and tree coppice readily when cut. The tree leaves are tough, lanceolate, evergreen, paled on the lower side. The trunk of tree is twisted which make of easier for goats to climb and eat its leaves and fruits [4].

The fruits color is green to bright yellow, oval shape, fleshy exterior like olive, but larger, its peel thick, bitter, gummy, containing unpleasant milky latex. The average production of fruit per tree is about 8 kg annum [4].

There are 1-3 nuts per fruit [1], which are brown, about 2 cm long with tough shell, taking almonds- kernels shape. The nuts are collected and squeezed to produce oil.

Some benefits of tree are listed below:-

Human, can benefit from the Argan tree since its oil is considerable to be good for cooking and is rich in vitamin E.

Also the locals mix argan oil with honey and almonds to make almond butter [2], and can mix it with white germ and honey to make porridge (Oatmeal). The residue of oil extraction is a thick paste with a chocolate color its flavor similar to peanut butter, when sweetened it can be served in breakfast [2].

The exterior pulp of the seed is used to feed goats and sheep [5].

The wood of this tree is tough and heavy so it may be a good source for charcoal and, hence the shell nut is used in firewood for cooking [1].

Because of its hardness the tree timber is indestructible and resists insects and hence the argan wood is used in carpentry [2].

Argan oil itself can be used in medication. It is an anti-oxidative material, rich in flavonoids and tocophercols[6-9]. These anti-oxidants are essential for many activities such as, controlling the free radicals, stimulates circulation of blood, enhancing activity of vitamin C, acting as natural anti-inflammatory, and strengthening the immune system.

Moreover the argan oil can be used for medication against acne, skin allergies, chicken box, burns and in hair treatment which give it strength and shine [10-15]. Beside , the argan oil facilitated digestion, and may lower the cholesterol and this is due to its high content of poly unsaturated fatty acids (80%) in which 30% of it is linoleic acid [16-19] .

The oil is also potentially important to those who are susceptible to, infections, kidney and liver degeneration, eczema, sterility in males and miscarriage in females [9].

A method of extracting cellulose polymer from the argan cake (the residue of pressed seed pulp after extraction argan oil) [20] which is (Kraft pulping) as indication in this work.

1.2 Cellulose.

Cellulose is a long chain complex carbohydrate polymer, or polysaccharide consisting of 3,000 or more glucose units depends on the source, the molecular formula is $(C_6H_{10}O_5)_n$.

Cellulose is the most abundant and renewable organic compound on earth, the basic structural component of plant cell wall that surround plant cell [21] , and making plant stem, leaves, and branches so strong. The percent of its existence: 33% vegetables, 90% cotton, and 50% wood [22].

1.2.1 Cellulose structure.

The cellulose is composed of D-glucose unit linked by beta-1,4 glycosidic bond [23], cellulose could be named as (1,4 B-D- glucopyranside).

Cellulose structure, with its repeat unit, is shown in the following

Figure 1.1

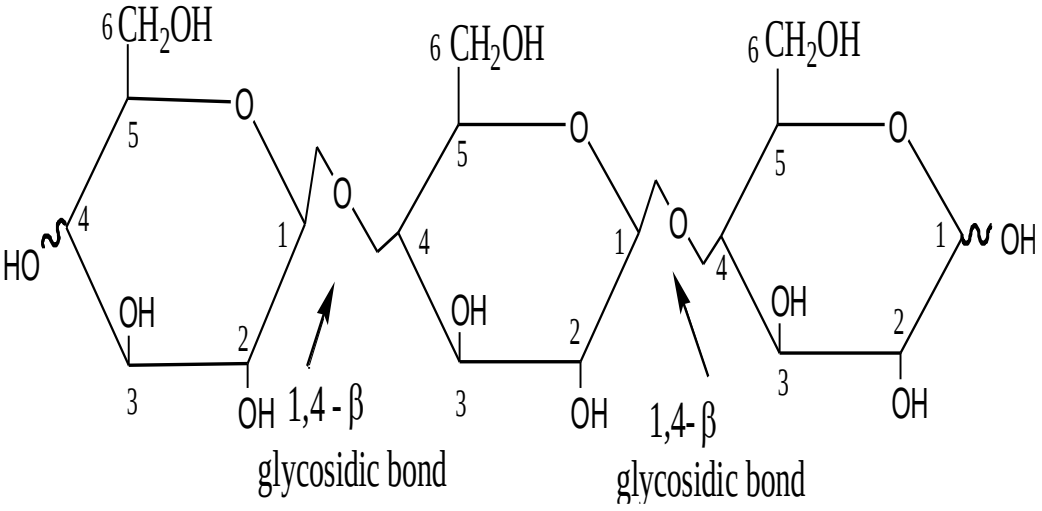


Figure 1.1: The structure of cellulose repeat unit

The cellulose molecule containing three different types of hydro glucose units, the reducing end with a free hemi-acetal (aldehyde) group at C-1, the non-reducing end with a free hydroxyl at C- 4, and the internal rings joined at C-1 and C-4[22].

The following figure will illustrate the types of anhydro glucose units.

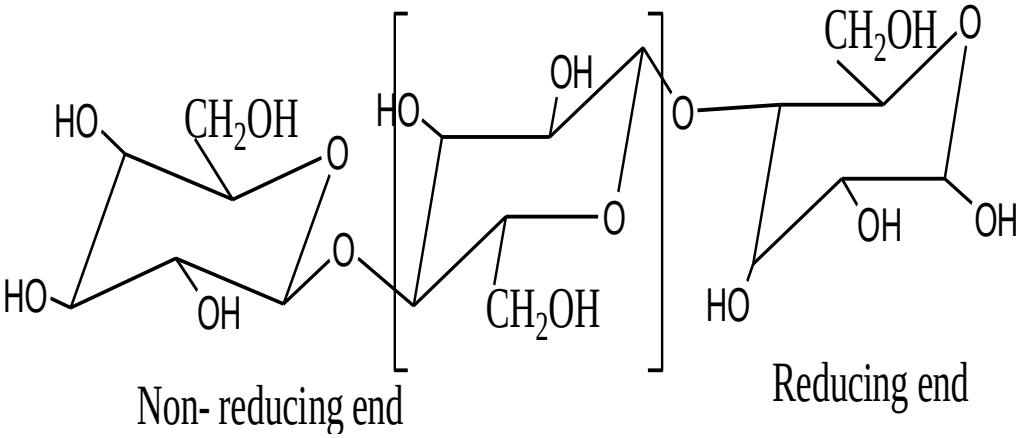


Figure 1.2: The structure of cellulose with the types of hydro glucose repeated units

The hydroxyl groups in cellulose polymer are positioned in ring plane (equatorial), while, the hydrogen atoms are in the vertical position (axial).

The polymer contains free hydroxyl groups at C-2, C-3 and C-6 atoms as shown in Figure 1.2 [24]. Both intra- and inter molecular hydrogen bonding in cellulose and van der Waals forces result in the formation of microfibriles , which in turn form fiber [22].

The following figure will illustrate the hydrogen bond in cellulose

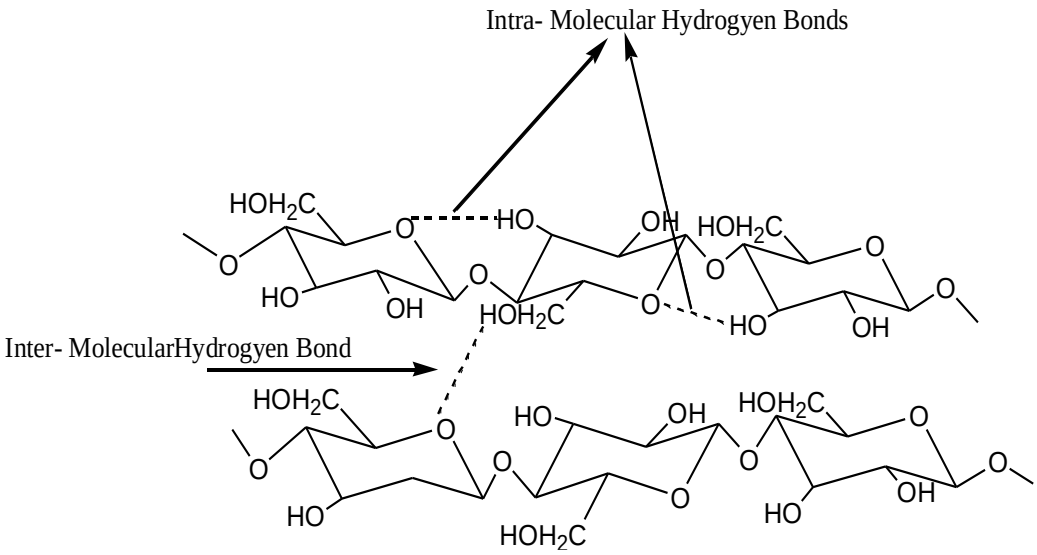


Figure 1.3: The hydrogen bond in cellulose

The intermolecular hydrogen bonding in cellulose is responsible for sheet-like nature of the native polymer.

The presence of molecular hydrogen bonds is the main reason that leads to high relation with single-chain conformation and stiffness. The presence of intra- and inter molecular hydrogen bonds in solid cellulose lead in some cases to heterogeneous distribution of consistent when deterivatives to be produced. The order of macromolecules in a cellulose fiber is not uniform throughout the whole structure. Cellulose has a crystalline region (very high order) and amorphous region of low order [22]. The degree of crystalinity of cellulose usually in the range 40%-60%, depends on the origin and method of cellulose extraction and treatment [25] . Crystallinty of cellulose can be measured by different X-ray techniques and NMR (nuclear magnetic resonance) method. Six different types of crystalline polymorphs for cellulose are known: I, II, III, III_I , III_{II} , IV_I and IV_{II} that

differ in their unit cell dimension. Cellulose I and II are found in nature which others are manufacture through chemical or heat treatments [26- 27]. Cellulose morphology represents a well-organized architecture of fibrillar elements. Recent electron microscope and WAXS (wide- angle X-ray scattering) data indicate that the diameter of cellulose fiber may differ in the range 3 to 35 nm depending on the cellulose source [26, 28].

The microfibril can reach micrometers which in turn form the macrofibriles. Micro-and macro fibrils represent the construction units of the cellulose fiber.

The following table illustrates some examples a bout micro fibril diameter of various cellulose samples [26].

Table 1.1: Micro fibril diameter for some of cellulose samples

Sample	Micro fibril diameter (nm)
Bacteria cellulose	4-7
Cotton linter	7- 9
Ramie	10-15
Dissolving pulp	10-30
Valonia cellulose	10-35

The molecular weight of cellulose depends on the number of monomers that form the cellulose and represented by DP (degree of polymerization). DP can be calculated by dividing the molecular weight of cellulose sample on the molecular weight of glucose.

The DP of cellulose depends on the source and method of cellulose extraction. The DP greatly affects the chemical and physical properties for

cellulose. The following table illustrated some examples for DP of cellulose according to their sources [22].

Table 1.2: The DP for cellulose sources

Source	DP
Bacteria	5000
Rayon	305
Kraft pulp	975
Sulfite pulp , bleached	1255
Cotton	15300

1.2.2 Natural source for cellulose.

The main sources of natural cellulose are what produced from: wood, agriculture residues, water plant, grasses, other plant substances and some kind of bacteria and algae [26].

Commercial cellulose production depends highly on pure nature source such as wood and cotton [29, 30].

1.2.3 Properties of cellulose.

According to various literature sources, I present here the cellulose physical and chemical properties.

Cellulose is a white material with different types classified according to their molecular length and degree of chemical stability. Alpha cellulose is the longest and most stable one [31]. Cellulose is insoluble in cold or hot water, because of the strong hydrogen bond that are found among the chains. As mentioned earlier, there are three hydroxyl groups available on each anhyroglucose ring, the replacement of at least one group or all groups of hydroxyls with other functional groups disrupts the crystalline region

and reduces inter-chain hydrogen bonding. This result is a cellulose derivative that is soluble in common solvents like, THF, DMF, DMSO, aqueous bases, cuam, cuen and N, N Dimethylacetamide [32].

Humans can't metabolize cellulose because the human body lacks the necessary enzymes to break down beta acetal linkage.

These enzymes are synthesized by some anaerobic bacteria like Cellulomonas living in harmony in the gut of herbivores [33].

Cellulose loses its stature and strength and chars at temperatures above 160 ^{o}C [28]. Dry cellulose tends to strongly absorb water moisture hence it is considered as a dry agent.

Carbon-carbon bonds in the chain stiffness and cohesion forces [28].

1.2.4 Cellulose derivatives and applications.

As was mentioned earlier in this chapter replacing the hydroxyl groups in part or in full with other functional groups provides derivatives with useful and commercial properties.

Wood cellulose is the principal raw material for cellulose derivative products. The second source of cellulose for cellulose derivatives is cotton linters (chemical cotton). Cotton linters have been used in certain products such as in cellulose acetate for plastics or high-tenacity rayon. For other applications cellulose acetate is more often made from wood cellulose [34].

1.2.4.1 Cellulose esters

It is a water insoluble cellulose based polymer with good film forming characteristic [34]. The most important and major cellulose ester is cellulose acetate (CA). It is usually prepared by reacting cellulose with acetic anhydride in the presence of sulfuric acid as a catalyst or acetic chloride in presence of a base such as triethyl amine [35]. The acetate groups may replace one or more of the cellulose hydroxyl groups, depending the molar ratios of acetic anhydride to cellulose. Fully substitution would put three acetate groups on the monomer and the material would be said to have a **degree of substitution** of 3 [36].

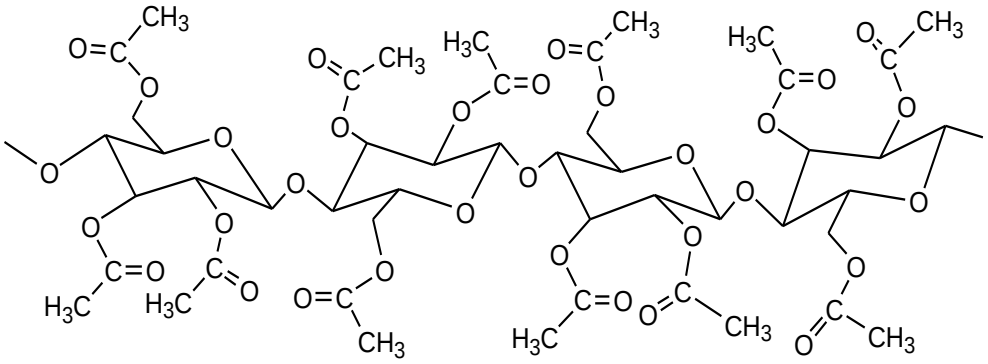


Figure1. 4: The Structure of cellulose triacetate

There are unlimited number of applications for cellulose acetate which include textiles, frames and eyeglasses, plastics, osmosis membranes, cigarette filters, medical tapes, decorative ribbons, upholstery, films in production of liquid crystal display screen (LCD), wound dressing, electrical insulation, sea water desalination, drinking water purification, waste water treatment, concentration of fruit juices and artificial kidney [36-38].

Some of the trade names for cellulose acetate are tenite, zyl and zylonite, cellon and rhodoide. The idealistic properties of cellulose acetate involve: good toughness, deep gloss, high transparency and described as natural material [39, 40].

In general the typical properties for cellulose acetate depend on the DP and the DS. As the DP decreases, the solubility of cellulose acetate in polar solvents and moisture resistance increases. For cellulose acetate as the DS increases, the melting point increases and vapor permeability decreases [41].

Cellulose acetate phthalate (CAP), cellulose acetate butyrate (CAB), cellulose acetate trimelitate (CAT) and hyroxupropylmethyl cellulose phthalate (HPMCP) are examples of organic cellulose ester that are used in the medical industry [36].

Inorganic cellulose esters are also known and have several important industrial applications. The following is some of the most important inorganic cellulose :

Cellulose sulfate (CS): used manufacturing flame- retardant fiber [35].

Cellulose phosphate (cellphos): used in protein chromatography ion exchange chromatography, cation exchange media, collector for analytical pre concentration of traces and treatment of kidney stones [35].

Cellulose nitrate (CN): mainly used in all categories of explosives such as , blasting agents, propellants and shooting agents , igniting agents , pyrotechnical agents, detonating agents and primarily used as gun powders [35,42].

1.2.4.2 Cellulose ethers

Cellulose ethers are water soluble polymers produced by alkaylation of cellulose. In this etherification process the hydrogen atoms of hydroxyls groups in the anhydroglucose units of cellulose is replaced with an alkyl or substituted alkyl groups [43, 44].

The properties of cellulose ethers as was mentioned before depend on the DP and the DS.

Since cellulose ether is water soluble , that makes it useful in some application such as viscosity control, flow behavior, rheology of solutions, cosmetics, food applications (milk products, dressing, jellies and syrups) , pharmaceuticals and personals care products [43,45].

Other applications for cellulose ethers are stabilizer, construction (cement), paper, textiles, oil field chemical, adhesives, inks, lacquers and polishing [45,46].

Beside water solubility, there are other commercial properties for cellulose ether such as solution viscosity (because of its high molecular weight), surface activity, thermoplastic film characteristics and stability against biodegradation, heat, hydrolysis and oxidation [43].

The most important cellulose derivatives which have several industrial applications are carboxyl methyl cellulose (CMC), methyl cellulose (CM), hydroxyl ethyl cellulose (HEC), hydroxyl propyl cellulose (HPC), ethyl cellulose (EC) and hydroxyl propyl methyl cellulose (HPMC) [44,45] .

1.2.5 Microcrystalline cellulose (MCC)

MCC is water insoluble microcrystalline polymer prepared by partial hydrolysis of the wood pulp (cellulose) in acidic media [47].

The degree of polymerization is less than 400 and the size of the particle is between 2.5 – 500 nm [48]. Its most important property is that it is moisture resistance. MCC is particularly used in the field of medicines in general it is used as bulking agent in food, emulsifier, anti- caking and dispersing agent and stabilizer [49].

1.2.6 Microbial cellulose

Microbial cellulose is a source of pure cellulose without hemicelluloses and lignin. It is much longer and stronger than plant cellulose. This kind of cellulose has a good role in medical industries like, scaffold for tissue engineering, synthetic Dura mater and artificial blood vessels [50].

Other applications of microbial cellulose are in diet food, OLED substrate, and paper and as gloss on a finished cover magazine.

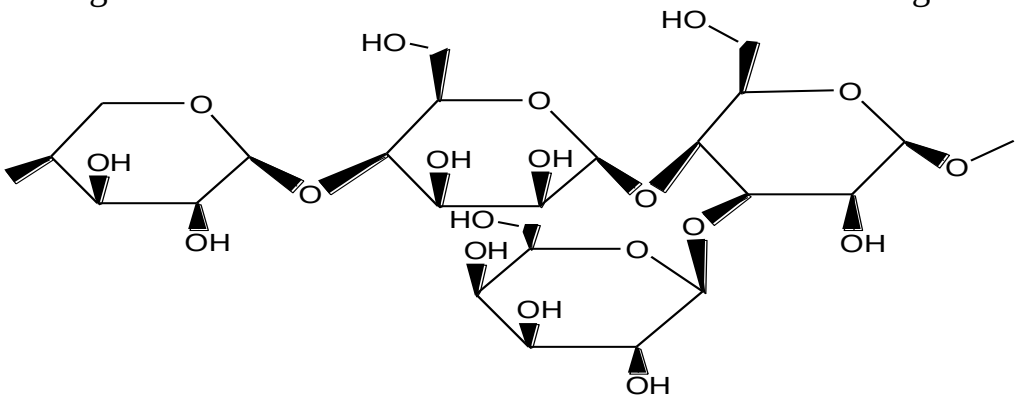
1.3 Methods of extracting cellulose plants and Agricultural waste.

There are several processes for extracting pure cellulose form its sources. A cellulose plant is usually linked with other complex compounds such as lignin, hemicelluloses and other materials (extractives).

Brief definitions of these materials are listed below.

1.3.1 Hemicelluloses.

A polymer that belong to group of heterogeneous polysaccharide which is composed of several carbohydrates monomer. The structural unit of this mixed polymer consists of hexose and pentose sugars like mannose, xylose, glucose, galactose and arabinose. Hemicellulose plays an important role in linking the cellulose fibers to lignin [51,



-Xylose- β–(1,4)-Mannose- β–(1,4), Glucose - α - (1,3)- Galactose

Figure 1.5: A representative structure of Hemicelluloses.

1.3.2 Lignin

A 3D non carbohydrate macromolecule, lignin is the second most abundant natural polymer in the world. It has an important role in hardening the cell wall [28].

In addition it binds to cellulose and forms an effective barrier against attacks by insect and fungi. Lignin structure is random and unorganized, so its structure is yet to specified . It is composed of three monomers that make up almost lignin in nature which are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol [53].

During the pulping process, the cross- linked network of lignin oxidizes causes the breaking of the polymer [54] and hence, giving more of the aromatic acids, its color light yellow and insoluble in water. The following figure is an illustration for lignin structure and monomers.

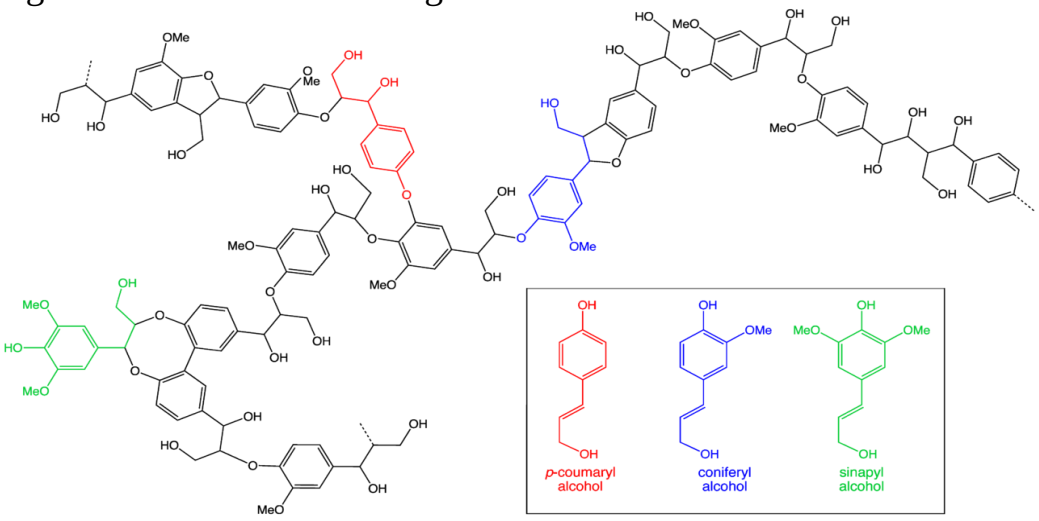


Figure 1.6: The chemical structure for lignin

1.3.3 Extractives.

It is a mixture of compounds that present in raw samples of cellulose sources; type and quantity of compounds vary according to the source. In general most extractives can be (solubilized) extracted by non polar or medium polar organic solvents [55].

The types of extractives are volatile oils, fats and waxes, wood resin, tannins and lignans.

1.4 Stages of cellulose extraction from APC

1.4.1 Sample preparation.

The process of sample preparation depends on the source. For example wood required debarking and chipping then storing the sample at specific temperature or out of humidity. Organic solvent might be used to remove extractives before the second stage.

1.4.2 Pulping.

The pulping process aimed to get rid of lignin and hemicelluloses, and extract cellulosic pulp with high quality for industrial applications.

There are two types of pulping processes: mechanical and chemical pulping.

1.4.2.1 Mechanical pulping.

The mechanical pulping involves forcing the sample against revolving stone which grinds the sample into pulp by abrasive action. The stone is sprayed with water to remove fiber from the pulp stone and to prevent fiber damage due to friction generated heat. The heat generated by grinding softens the lignin binding the fibers and the mechanized forces separate the fibers to form ground samples [56].

The advantages of this kind of pulping that produce high pulp yield and low cost. The disadvantages of this process that removes a little lignin content and this lead to produce samples that is not as high quality as

other pulping methods, also the samples would be in low strength, low permanence and a tendency to pale with time (primarily caused by high levels of lignin).

The types on mechanical pulping include pressurized ground wood (PGW), refiner mechanical pulp (RMP) and thermo mechanical pulp (TMP) [56].

1.4.2.2 Chemical pulping

In chemical pulping the wood samples are cooked in a chemical that oxidize lignin, hydrolyses hemicellulose and separate them from cellulose. This type of pulping results in high quality pulp , however of low yield comparing with mechanical pulping.

During the pulping process, almost one half of the sample turned into dark liquor as waste. The cooked pulp is then washed and screened to achieve a more uniform quality. The black liquor is separated out from the pulp before the bleaching process.

The three types of chemical pulping are Sulfite, Kraft and Semi chemical pulping (Uncommon).

1.4.2.3 Sulfite pulping

In this process calcium as the sulfite base is used. Recently the base has been changed to magnesium, ammonia or sodium. The main solution is sulfurous acid with pH less than 1.7 as the base is added the pH increases. According to pH , the sulfite pulping is classified into three types which are acid sulfite, neutral sulfite and alkaline sulfite [57]. The purpose of sulfite pulping is not heavy lignin fragmentation. The advantages of this type are

in its high yield, the pulp produced is easy to bleach and the pulp is flexible and has good swelling properties.

The disadvantages includes long cooking time approximately 6-8 hours, pulp is week, poor chemical recovery and it is considered a pollutant factor due to the emission SO_2 gas [58].

1.4.2.4 Kraft (sulfate) pulping

In this method sodium hydroxide (NaOH) and sodium sulfide (Na_2S) are used to pulp the wood. Kraft pulping is used mostly in the paper industry [58]. Sodium hydroxide and sodium hydrosulfide are the reagents that delignify wood. A solution of pH >12 and cooking duration ranges from 0.5-3 hours at temperatures between 160-180 ^oC are the pulping conditions. There are two setbacks in using Kraft pulping; one is that a dark pulp accompanies this process which means more bleaching is required, and hence, more work need to be done to recover the materials in the process [59]. The pulp produced by the Kraft process is stronger and has better dimensional stability and resistance for aging.

1.4.3 Bleaching.

It is the process of removal of lignin left after pulping to enhance the physical and optical qualities (whiteness and brightness) of the pulp [60].

The bleaching processes is used to brighten the pulp without removing the residual lignin , for this hydrogen peroxide is used to break down the chromatographic groups however , it does not remove lignin completely .

The approach gives a temporary brightness that discolors from exposure to sun rays and oxygen. The other approach is the true bleaching used in totally is removing all the residual lignin by adding oxidizing agents to the pulp in varying combination of sequences [61] , depending on the end use of the product.

This type creates a longer lasting and maybe permanent whiteness, but it weakens fibers strength and reduces its DP. The most common bleaching agents are chlorine **C**, chlorine dioxide **D**, hydrogen peroxide **P**, sodium hydroxide **E** and hypochlorite **H.**

1.5 Scope

The *Argan* tree is a tropical plant that grows only in the semi desert region of the south-western region of Morocco.

It belongs to the *Sapotaceae* family and represents the only endemic species of the genus *Argania*.

In spite of its 'forest' status, the *Argan* tree is indeed a multipurpose tree, mainly used for fodder and as an oil-yielding resource. The fruit of the *Argan* tree is (similar to walnut tree or almond tree) a stone-fruit with pulp covering a lignified endocarp (the nut) containing one to three kernels (the seeds) from which an edible oil can be extracted by various methods, such as hand compression, mechanical press technique, and solvent extraction. The most effective process for collecting *Argan* oil is the mechanical press method where the ripe-fruit pulp and peel are removed, and then *Argan* nuts go through consecutive drying and grinding stages to produce a

brownish dough. The dough is pressed directly to produce the oil in approximately 43% yield. The extraction residues known as *Argan* press-cake (APC) is a dark-brown powder and generally still contains approximately 10% of oily components.

APC is considered as a waste agricultural material and is currently used for cattle feed. Previous studies documented its composition of 26.3% moisture, 3.6% ash, 24.6% nitrogen-containing derivatives, 18.9% lipids, and 26.6% of carbohydrates with 17.6% cellulosic products.

Cellulose is one of the main components of APC, which makes it potentially attractive and a low-cost source of cellulose. It has been well known that cellulose carries various interesting properties which can lead to diverse applications in paints, personal products, tableting aid for pharmaceuticals, and stabilizers or fat replacement for foods. In addition, cellulose can also produce considerable derivatives by means of chemical and physical modifications. One of the most valuable cellulosic derivatives is microcrystalline cellulose (MCC) which is generated by acid or enzymatic hydrolysis of cellulose with high cellulose I content. Acid penetrates the amorphous region and cleaves the β-1,4-linkage between cellulose repeating units to produce cellulosic products of low molecular weight containing most oligosaccharides and a small amount of water-soluble glucose.

As the original source of MCC production, the cost of cellulose production associated with the production of MCC and other value-added derivatives needs to be considered. In this study, our aim is to develop a facile and

effective extraction to obtain relatively low-cost cellulose with high purity from agricultural waste APC. The physicochemical properties of the extracted cellulosic product were thoroughly investigated.

Chapter Two

Expermenal

2.1 General Experimental

2.1.1 Materials

All reagents were purchased from Aldrich Chemical Company and used as received unless otherwise specified. Kraft pulping was performed using a high Parr Reactor model: Buchiglasuster, BMD 300 (Switzerland). *Argan* press cake was obtained from Morocco (Tugaza *Argan*, Morocco). A picture of argan press cake (APC) is shown in figure 2.1

Figure 2.1: Argan press cake

2.1.2 Material characterization of extracted cellulose from argan press cake (APC-cell)

The Infrared (IR) spectra of APC-cell were recorded using Fourier Transform IR Spectrum (FTIR) 400 (PerkinElmer, USA) equipped with a

Universal Attenuated Total Reflectance (UATR). The following parameters were used: resolution 4 cm^{-1}, spectral range 650-4000 cm^{-1}, number of co-added scans 32.

Scanning Electron Microscopy (SEM) was performed using TM-1000 (Hitachi, Pleasanton, CA). A small amount of APC-cell powder was mounted on the SEM sample stage with a conductive carbon tape attached and the surface morphology of APC-cell was observed.

Thermal analysis of APC-cell was performed using Pyris1TGA (PerkinElmer, USA). Thermograms of samples were recorded between 37 and 600ºC at heating rate of 10 ºC/min in a flow of N_2 at 20 mL/min.

The Pyris Analysis software was used to calculate the first derivative of thermograms (DTG), as well as, estimate the percent weight loss and the decomposition temperature for each sample.

Wide angle x-rays diffraction (XRD) patterns were acquired using SmartLab X-Ray Diffractometer (Rigaku HD 2711N, Japan). SmartLab uses a Cu target (λ=1.541867 Å), voltage of 40 KV, and current of 44 mA. The x-ray scans over the two theta scanning range of 5°- 50° were performed to determine the crystalline morphology of the samples.

2.2.1 Removal of lipids from Argan press cake

Lipids present in APC were removed using a Soxhlet extraction method. A sample of 100 g of APC was placed in a 1000 mL round bottom flask, and then 500mL of toluene was added. The extraction of lipids from APC was performed for 3 h. Toluene solvent containing lipids was filtered under the

reduced pressure to remove insoluble residuals. Toluene was then removed under reduced pressure using rotary evaporator. The weight of the residue was about 3.8 g (lipids). The APC (crude) free of lipids was saved and used for extraction of cellulose.

2.2.2 Extraction of cellulose from Argan press cake (Kraft pulping)

Kraft pulping was conducted in a high Parr Reactor of one liter capacity. In all experiments, amount of argan press cake and the liquor ratio was 9:1, respectively. Several experiments were performed to study the effect of cooking temperature, holding time on product yield and quality amount of sodium hydroxide and sodium sulfide used in the cooking process varies from 13 gm to 26 gm and 4.5 gm to 9 gm, respectively per 100g argan press cake. At the end of pulping, the produced pulp was collected by suction filtration, washed several times with tap water, air dried at room temperature, and stored in plastic bags for further use. Various pulp properties were determined according to standard methods mentioned earlier. Results obtained from pulping experiments are summarized in Table 2.1

Table 2.1: Effect of Kraft pulping conditions on pulp quality and yield using 100g of APC

Sampi No.	Temperature (°C)	Time hours	Wt .of N NaOH (g)	Wt. of Na_2 (g)ŏ	Wt. of Pulp (g)	Pulp Yield%
1	Room temp.	12	26	13	145	16.29
2	50	2	26	13	132	16.3
3	60	2	26	13	88	12.85
4	90	1.5-2	26	13	65	12.4
5	90	1.5-2	13	5	102	18.33
6	100	1.5-2	26	13	55.02	12.36
7	100	1.5-2	13	5	67.54	15.9
8	110	1.5-2	26	13	58.78	15.19
9	110	1.5-2	13	5	66.88	17.28
10	160	2	25	…..	30.5	8.567
11	160	1	25	…..	38.2	10.73

In all reaction: the total weight of the reaction mixture was about 500 g. This weight produce a consistency of 10% (APC/total weight)

2.2.3 Another method of pulp extractions

In the second extraction approach, an acid pulping was used, which consists of using 0.75% H_2SO_4 to soak APC sample in 5% concentration (w:v) at 75°C for 1 h. The sample in this case was labeled as APC-AC. The process was conducted in a round bottom flask (1.0 L) fitted with a magnet stir bar and a condenser. APC was suspended in a solution of acetic acid containing 0.75% sulfuric acid as a catalyst at a consistency of 10%. The

flask contents were heated at 75 ^{o}C for about 1.0 hr then the reaction mixture was allowed to cool to room temperature. The product was collected by suction filtration, washed thoroughly with water to a neutral pH and labeled as APC-AC. The procedure was performed on several samples at various concentration of sulfuric acid to study the effect of H_2SO_4 concentration and reaction time on cellulose yield and quality**.** In All experiments products were either turned to black with low yield of cellulose or product has a similar looking to the crude APC.

2.4 Purification of crude cellulose (cellulose bleaching) The purification of crude cellulose obtained from APC Kraft pulping (APC-Cel) was performed using a bleaching sequence (HPHEp) operation as described below.

2.4.1 H-stage

Crude cellulose (AOC-Cel) of 100 g was added to a plastic bag containing 900 mL of 1 wt% NaOCl (w:w of crude cellulose weight). The plastic bag was placed in a water bath of 45°C for 1 h. At the end of the reaction, the sample in the plastic bag was washed with fresh water until NaOCl was completely removed and the sample was ready for use in the next step.

Table 2.2: Yields of APC-Cel of various samples obtained from H-stage results.

Sample No.	Temperature (°C)	Wt .of N NaOH (g)	Wt. of Na_2S(g)	Pulp Weight (g)	Yield%
1	Room temp.	26	13	138	95
2	50	26	13	129.5	94
3	60	26	13	81.65	97
4	90	26	13	57.02	95
5	90	13	5	94.33	97
6	100	26	13	48.62	97
7	100	13	5	60.14	98
8	110	26	13	50.88	93
9	110	13	5	59.08	97
10	160	25	…..	28	98
11	160	25	…..	33.48	97

2.4.2 P-stage

A solution mixture of 900 mL consisting of 2 wt% H_2O_2 (w:w of crude cellulose weight), 0.5 wt% $MgSO_4.7H_2O$ (w:w of crude cellulose weight), and 3 wt% NaOH (w:w of crude cellulose weight) was added to the plastic bag which already contained the cellulose pulp obtained from the first H-stage.

The plastic bag was then placed in the water bath and the reaction was performed at 60°C for 1 h. Subsequently, the cellulose pulp in the plastic bag was washed to remove chemicals and ready for use in the next step.

Table 2.3: Yields of APC-Cel of various samples obtained from P-stage.

Sample No.	Temperature (°C)	Wt .of N NaOH (g)	Wt. of Na_2S (g)ŝ	Weight of pulp (g)	% Yield
1	Room temp.	26	13	133	89
2	50	26	13	124.2	87
3	60	26	13	78.1	92
4	90	26	13	55.88	94
5	90	13	5	89.07	97
6	100	26	13	44.67	89
7	100	13	5	57	90
8	110	26	13	46.24	92
9	110	13	5	53	95
10	160	25	…..	24.05	97
11	160	25	…..	29.06	97

2.4.3 Second H stage

The H stage was repeated to make sure the complete oxidation and removals of residual lignin, results are summarized in Table 2.5.

Table 2.4: Yields of APC-Cel of various samples obtained from the 2nd H-stage.

Sample No.	Temperature (°C)	Wt .of NaOH (g)	Wt. of Na_2S (g)	Pulp weight (g)	% Yield
1	Room temp.	26	13	126	90
2	50	26	13	121.1	96
3	60	26	13	77.02	89
4	90	26	13	53.61	93
5	90	13	5	85.22	97
6	100	26	13	41.9	96
7	100	13	5	53.45	96
8	110	26	13	43.18	97
9	110	13	5	50.1	91
10	160	25	…..	21.77	98
11	160	25	…..	26.93	97

2.4.4 Ep stage

The last bleaching step was performed in the same plastic bag containing the cellulose pulp obtained from the second H-stage, where a 900 mL fresh solution consisting of 1 wt% NaOH (w: w of crude cellulose weight) and 0.5 wt% H_2O_2 (w:w of crude cellulose weight) was added to the plastic bag. The reaction was conducted in a water bath at 70°C for 90 min. At the end, the cellulose pulp was washed thoroughly to remove chemicals and then dried in the oven at 60°C. The resulting cellulose was weighed and the yield of the purified cellulose was determined. The sample in this case was labeled as APC-cell.

Table 2.5: Yields of APC-Cel of various samples obtained from the Ep-stage.

Sample No.	Temperature (°C)	NaOH (g)	Wt. of Na_2S (g)	Pulp weight (g)	% Yield
1	Room temp.	26	13	119	92
2	50	26	13	108.01	92
3	60	26	13	70.06	97
4	90	26	13	47.13	97
5	90	13	5	80.11	98
6	100	26	13	40.37	96
7	100	13	5	50.93	93
8	110	26	13	39.89	96
9	110	13	5	48.13	96
10	160	25	…..	18.03	96
11	160	25	…..	22.57	98

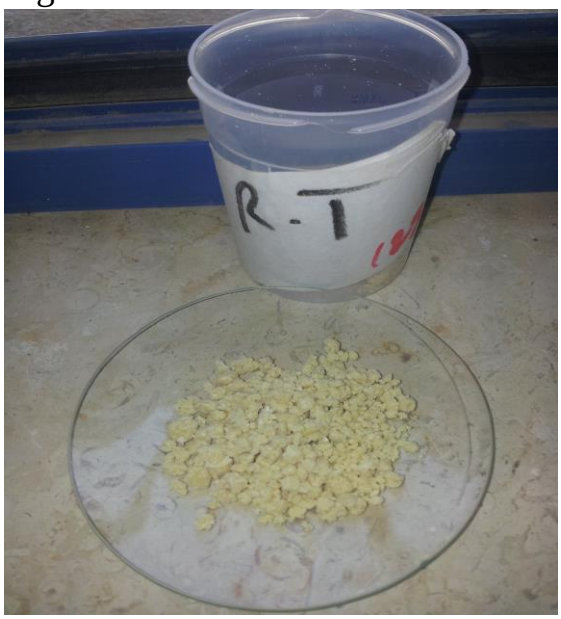
2.4.5 Calculation of final yield

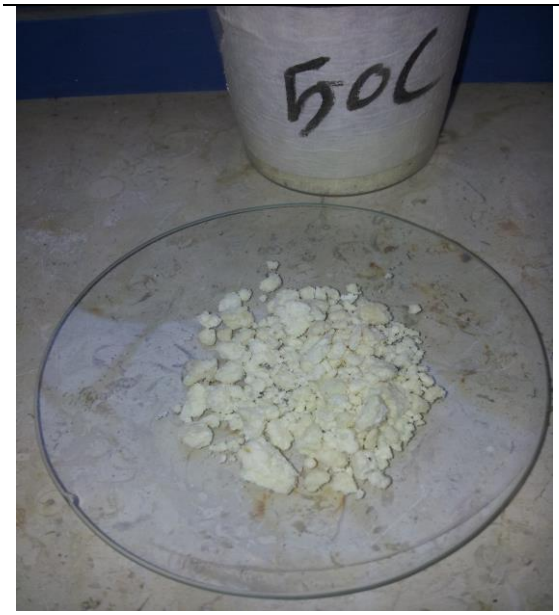
The yield of the product was calculated based on the OD weight of the final product. The product after the last bleaching stage was dried in an oven at about 105 °C then weighed. Percent yield was calculated by dividing the dry weight of the product over the weight of the crude-APC. Results are summarized in Table 2.7.

Table 2.6: Percent yield of the cellulose obtained using the Kraft pulping followed with the HPHEp bleaching sequence

Sample No.	Temperature (°C)	NaOH (g)	Wt. of Na_2S (g)	Yield (%)
1	25	26	13	11.4
2	50	26	13	11.8
3	60	26	13	11.4
4	90	26	13	10.0
5	90	13	5	16.6
6	100	26	13	10.0
7	100	13	5	12.6
8	110	26	13	10.21
9	110	13	5	14
10	160	25	…..	7.66
11	160	25	…..	8.453

Images of the color of the bleached samples are shown in the following Figure 2.2.





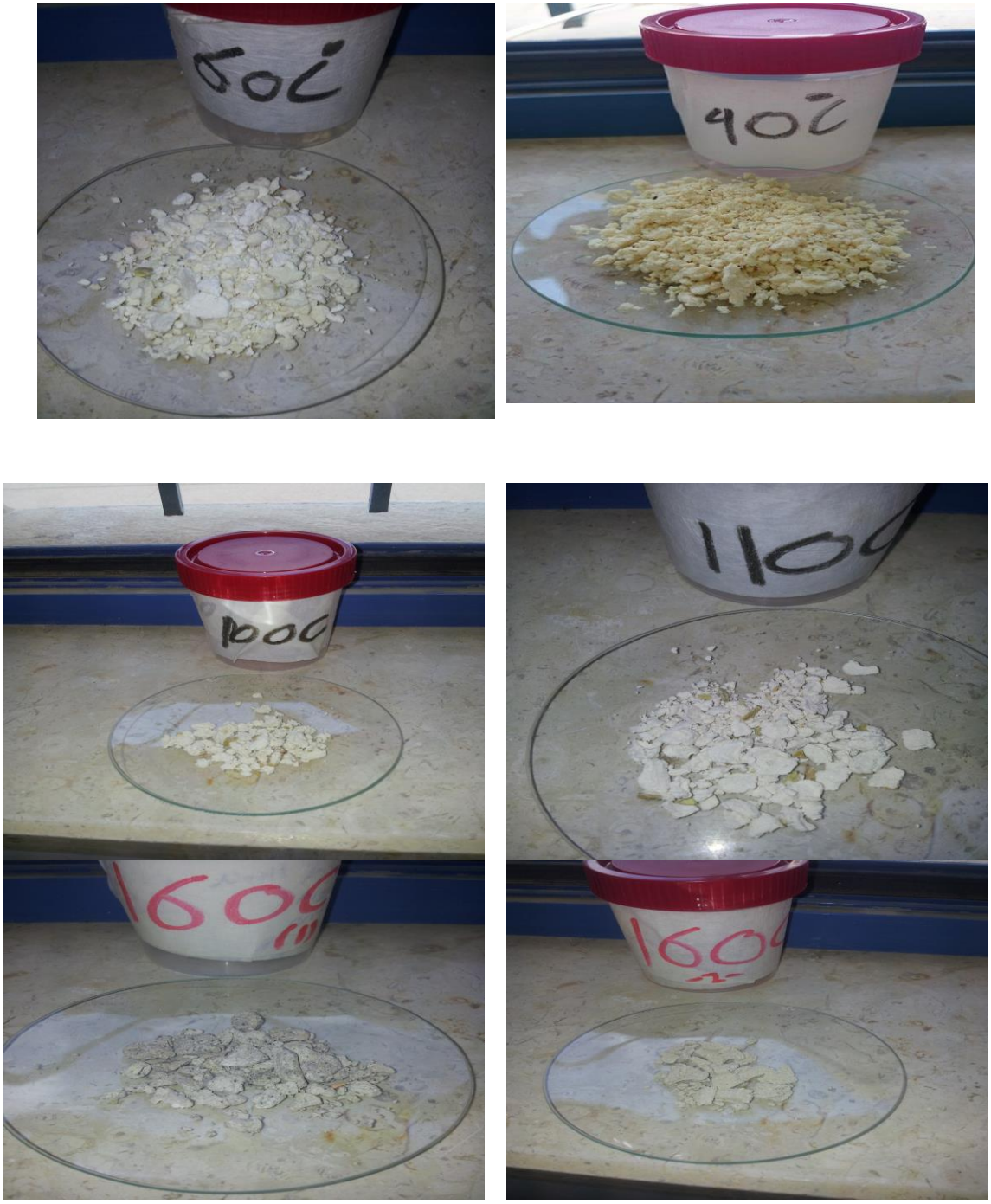


Figure 2.2: Images of the product labeled with the Kraft cooking temperature

2.5 Analysis of the bleaching pulp.

Samples of the bleached pulp (APC-Cel) were subjected to evaluation for: K-number (Kappa number), Density, FT-IR, SEM, x-ray, sugar test and GPC.

2.5.1 K-number.

The kappa number is used to provide feedback that gives and supports optimum pulping conditions, and it's an indication of lignin content.

2.5.1.1 Preparation of reagents. [62, 63]

A- Potassium permanganate ($KMnO_4$) with (0.02± 0.001) mol/L.

This reagent was prepared in a 1 L volumetric flask by dissolving 3.161 g of $KMnO_4$ in 1 L of distilled water.

B- Sodium thiosulfite ($Na_2S_2O_3$) standard solution with (0.02±0.001 M).

This reagent was prepared by dissolving 24.84 g $Na_2S_2O_3.5H_2O$ in 1 liter of distilled water.

C- Potassium iodide (KI) solution with concentration 1.0 M.

The reagent was prepared by dissolving 166.0 g in 1 liter of distilled water.

D- Sulfuric acid (H_2SO_4) solution with concentration 2M.

The solution was prepared by dissolving 112.0 ml of conc.H_2SO_4 in 1liter of distilled water in a volumetric flask.

E- Sulfuric acid (H_2SO_4) solution with concentration 1M.

The solution was prepared by dissolving 56.0 ml from conc. H_2SO_4 in 1liter of distilled water.

F- Starch indicator solution with concentration 5 g/L.

The previous solution was prepared by dissolving 0.5 g of starch in a 100 ml of boiling distilled water. After complete dissolution of the starch, the solution was saved in a plastic bottle.

2.5.1.2 General procedure for determining the K-number.

1. Oven dried pulp (1.00 g) was weighted and placed in a blender.

2. To it was added a 400 mL of distilled water, and the blender machine was run for 3 min.

3. The contents of the blender was transferred to an Erlenmeyer flask, and then was added 50.0 mL of potassium permanganate using a pipette. The pulp was left in connect with $KMnO_4$ for 10 min at room temperature with stirring.

4. After10 min potassium iodide (10 mL) was added to the mixture followed with a 50 mL of 2M H_2SO_4 solution.

5. The produced mixture was titrated instantly with standard solution of $Na_2S_2O_3$, the titration was continued until pale-yellow color appeared, and then 2-3 mL of starch as indicator was added to the mixtures till a blue color appeared. Then a titration process was continued until the blue color disappeared.

6. The above steps from (1 to 5) were applied on a blank solution exactly, except no pulp was used in the blank solution.

The results of kappa number calculations were shown in the following table.

Table 2.7: The kappa number results.

Sample Number	Temperature (°C)	NaOH (g)	Wt. of Na_2S (g)	Kappa number	Lignin Contents
Raw Argan cake	25	……	……..	25.99	3.8985
1	25	26	13	17.4	2.61
2	50	26	13	14.9	2.235
3	60	26	13	9.026	1.3539
4	90	26	13	2.477	0.3715
5	90	13	5	6.43	0.9645
6	100	26	13	0.824	0.1236
7	100	13	5	2.37	0.3555
8	110	26	13	Nearly zero	…….
9	110	13	5	0.449	0.06735
10	160	25	…..	0.743	0.11145
11	160	25	…..	0.431	0.06465

2.5.2 Density of APC-Cell

1. A known amount of dry pulp was grinded by mortar until it became fully soft like flour.

2. A dry empty graduated cylinder was weight and in it was placed a known weight of the ground pulp. The pulp in the cylinder was pressed by glass container for 20 min.

3. The graduated cylinder with pulp was weight and the volume of pulp was taken.

The density will be calculated using the following equation.

Density= Mass/ Volume

The result of the density will be shown in the following table.

Table 2.8: The density of selective samples APC-Cel.

Sample number	Temperature (°C)	Wt. of NaOH (g)	Wt. of Na_2S (g)	Density g/ml
2	50	26	13	0.921
3	60	26	13	0.806
5	90	13	5	0.859

2.5.3 Sugar Analysis

The purity of APC-cell was determined based on the monomer content measured after an acid hydrolysis.

APC-cell of 300 mg obtained from HPHEp bleaching sequence (Sample No. 6) was added to 3 mL of 72% H_2SO_4. The mixture was heated at 37°C for 60 min and then was diluted to 4% H_2SO_4 with deionized (DI) water followed by an autoclave operation at 121°C for 1 h. Next, the resulting solution was filtered (Grade 4 filter paper, Whatman, USA) and the filtrate was analyzed by normal phase High Performance Liquid Chromatrography (HPLC , Merck Hitachi) equipped with refractive index detector and an Aminex HPX-87H column (Bio-Rad Labs, Hercules, CA). The HPLC running parameters were set at 45°C with an aqueous solution of 5 mol/L H_2SO_4 as a mobile phase at a flow rate of 0.6 mL/min.

2.5.4 Dissolution of APC-cell for molecular weight (MW) analysis of APC-cell

APC-cell (sample No 6) was dissolved in lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) solvent system to determine the molecular weight of APC-cell. APC-cell sample (64 mg) was suspended in 10 mL DI water at room temperature followed by two consecutive exchanges with 10 mL methanol in a time interval of 1 h each, and the sample solvent was then replaced by another two consecutive exchanges with 10 mL anhydrous DMAc. The first DMAc exchange lasted for 1 h and the second remained overnight. At the end of each exchange, the solvent was removed from the sample suspension by vacuum filtration. After the last DMAc exchange, the activated APC-cell sample was transferred to a vial filled with 4.0 mL of 8% LiCl/DMAc (w:v) solvent. The mixture was stirred until a clear solution was achieved in about 2 h. The clear solution was diluted with 60 mL anhydrous DMAc to produce a solution concentration of APC-cell with1.0 mg/mL for MW analysis. Next, Gel Permeation Chromatography (GPC, DAWN® HELEOS® II and the Refractive Index detector Optilab® T-REX, Wyatt Technology, USA) combined with High-Performance Liquid Chromatography (HPLC, 1260 Infinityl, Agilent, USA) was used to determine the MW of APC-cell. The data acquisition was carried out in 0.5 s intervals with the ASTRA 6.1 software (Wyatt Technologies, USA). The mobile phase of 0.5% LiCl/DMAc (w:v) and APC-cell sample solution were filtered through 0.25 µm filters (Millex LCR, Millipore, USA) prior to use. The system equipped with three separate columns (MIXED-B, 300 x 7.5 mm, Agilent, USA) was

operated at 25°C with a flow rate of 1 mL/min and the running time was 40 min. The calibration was done with polystyrene 30,000 g/mol at 0.5016 g/mL in 0.5% LiCl/DMAc.

Chapter Three

Results and Discussion

3.1 Extraction and Characterization of Cellulose from Argan Press Cake.

Three different extraction methods were compared in this study:

- Pulping with aqueous organic extraction
- Pulping with acid extraction
- Kraft pulping

3.1.1 Aqueous organic extraction

3.1.1.1 Pulping with water/ethanol mixture:

Water/ethanol purification of Argan cake was performed in a successive treatment of water and ethanol immersion. Argan press cake was first immersed in deionized water at 1% (w:v) and stirred at 90^{o}C for 6 h. The precipitation of Argan press cake after removal of water was treated with absolute ethanol again at 1% (w:v) and stirred at 45^{o}C for 2 h. The purified Argan press cake collected from water/ethanol purification was dried at 50^{o}C and it was denoted as APC-WE.

The FT-IR spectra of argan press cake and APC after water/ethanol purification (APC-WE) are shown in Figure 3.1, The figure shows similarity to the pure APC spectrum except for three peaks at 2916, 2850,

and 1744 cm^{-1}. These three peaks could be attributed to the CH_2 stretching and C=O stretching, suggesting that APC-WE still contains residues of organic acids [64]. In the meantime, the peak intensities at 1031 and 1628 cm^{-1} significantly increase, suggesting that the cellulosic and protein components have been concentrated after the water/ethanol purification.

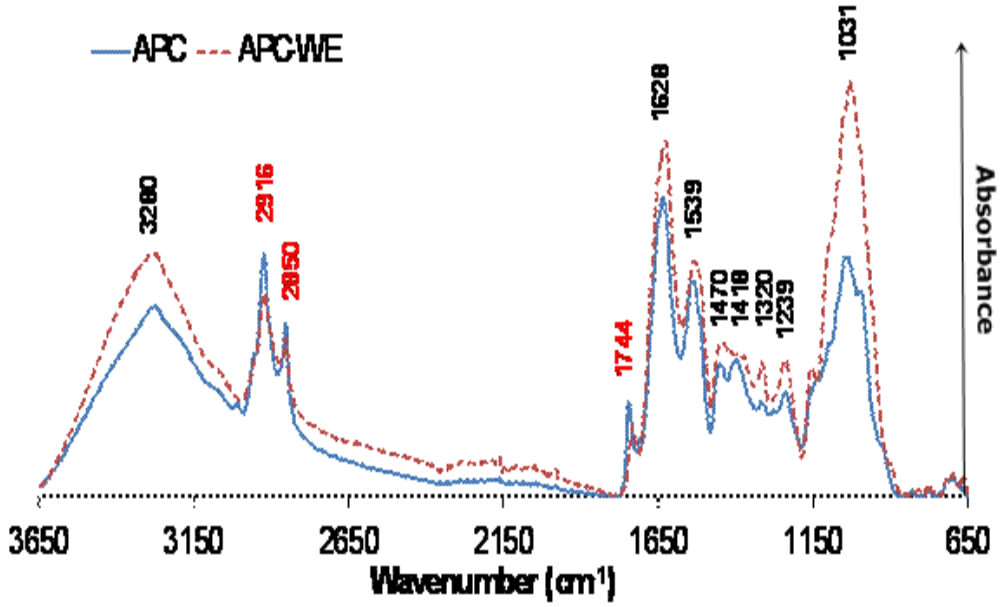


Figure 3.1: FTIR spectra of APC and cellulose extracted from APC by water/ethanol treatment (APC-WE).

3.1.1.2 Bleaching of APC extracted with water-Ethanol (APC-WE)

APC-WE was subjected to bleaching in order to purify the cellulosic component and remove the impurity from cellulose probably consisting of proteins, aliphatics, sugars and pigments, scouring and bleaching treatments were used. In this process APC-WE was added to a 1.0 L of solution consists of 1 g Triton X-100 and 4 g sodium hydroxide in water.

The filtration was used to collect the Argan press cake precipitated on the filter paper and it was rinsed by DI water till free of chemicals.

Next, the collected Argan press cake was subjected to a bleaching treatment in a 1.0 L solution 0.25 g Triton X-100, 0.35 g sodium hydroxide, 0.7 g sodium carbonate, 3 g sodium silicate and 6 g commercial bleach. The mixture was heated at 90^{o}C for 1.5 h. The filtration was used again to separate Argan press cake from the bleaching solution. The bleached Argan press cake was rinsed and dried at 50^{o}C and denoted as APC-SB.

The FTIR spectra of APC and APC-WE after bleaching (APC-BC) are shown in Figure 3.2. analyzed the product of centrifuged precipitation from the separate scouring mixture just after the APC scouring and filtration (APC-BC).

The spectra shows the typical peaks at 1033, 1056, 1161, 899 and 688 cm^{-1} [65] indicating that a great amount of cellulosic components has been extracted from the pure APC. The proteins, sugars, and organic alcohols/acids associated with peaks between 1200 and 1800 cm^{-1} have been further removed. The above analyses based on FTIR spectra have demonstrated that the bleaching treatment is efficient to a certain degree. The impurities are minimized during the pulping and completely removed during the bleaching process.

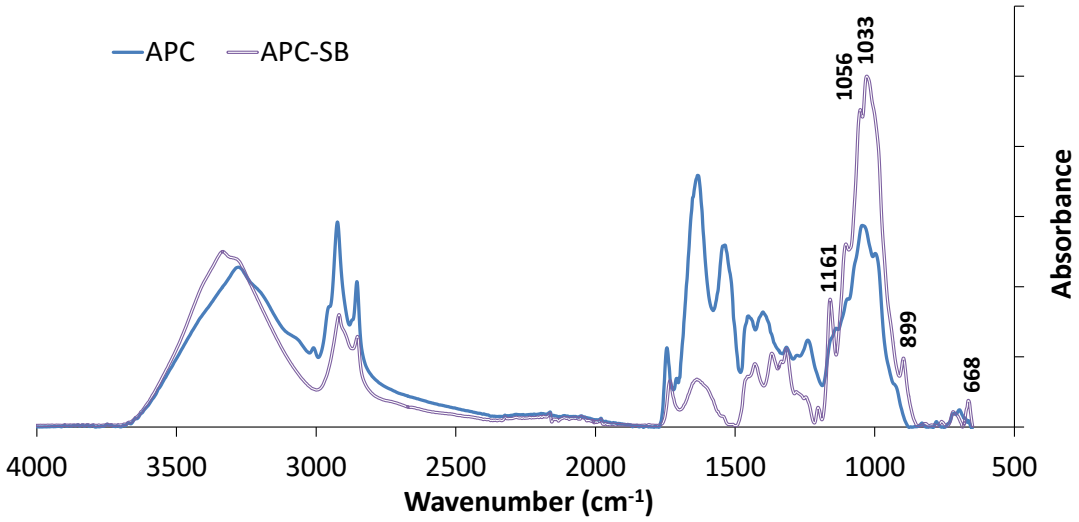


Fig. 3.2: FTIR spectra of raw Argan press cake (APC) and the product from scouring and bleaching treatments of Argan press cake (APC-SB)

3.1.2 Pulping with acid extraction

The highest yield of cellulose obtained from APC using the acid pulping process was 5.2%, it was obtained using an aqueous solution of 0.5% H_2SO_4 and a cooking time of 1 hr at about 70 ^oC. The product was designated as APC-AC. Increasing the cooking time from 1 hr to 3 hr decreased the yield from 5.2% to 1.2 %. The results indicate that, cellulose is undergoing fast hydrolysis in an acid solution. Raising the concentration of H_2SO_4 (V/V) from 0.5% to 2.0% result in no cellulose was obtained on a suspension which when subjected to suction filtration produces traces of solid. Reducing the concentration H_2SO_4 solution to 0.3%, increase the yields but with high content of impurities.

Figure 3.3 shows the FTIR spectra of the APC and APC-AC obtained by acid pulping. The spectrum of APC-AC shows a vibration at 1744 cm^{-1}

associated with the presence of lipids, suggesting that the acid pulping removed certain amount of oily chemicals from APC exhibiting similar effect to the water/ethanol treatment. However, a significant decrease in the intensity of the vibration 1628 cm^{-1} (due to the presence of proteins) in the spectrum of APC-AC. This indicates that acid pulping is a relatively efficient approach to remove protein components from APC.

When comparing APC and APC-WE, a small amount of impurities such as lipids and proteins is still present. In addition the yield was low, due to these reasons the acid pulping may not be efficient to facilitate the extraction of cellulose from APC.

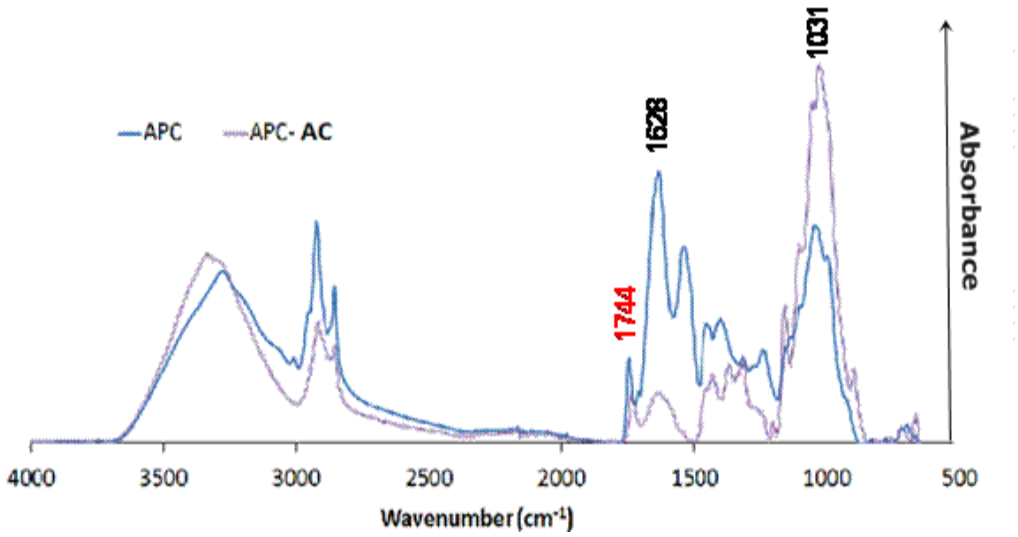


Figure 3.3: FTIR spectra of APC and cellulose extracted from APC by acid pulping (APC-AC).

3.1.3 Kraft pulping

3.1.3.1 Removal of Extractable Materials from APC

Prior to kraft pulping lipids present in APC were removed using a Soxhlet extraction method. The removal of lipids from APC was carried out using toluene. After evaporation of toluene under reduced pressure , a pale yellow residual liquid was produced which represented about 3.8% of the APC content.

3.1.3.2 Pulping

Kraft pulping was conducted to extract crude cellulose from APC. It was carried in a high pressure reactor. It could be also carried out in a round bottom flask of 1 L volume. Using round bottom flask didn't affect extracted cellulose quality or yield. In this work, all the kraft pulping was carried out in a high pressure reactor because it is more convenient and safer. The kraft pulping was performed on samples of 50.0 g weight and 100.0 g weight. Several reaction conditions (temperature, quantity of NaOH, quantity of Na_2S, consistency and time) were evaluated. All results are summarized in Chapter II. Best obtained results are summarized in Table 3.1. Best results regarding yield and cellulose purity were obtained using pulping solution containing 13% NaOH and 5% Na_2S as shown in sample 5 table 3.1. The pulping temperature was a 110 °C and reaction time was about 90 min.

Table 3.1: The results of the best %yield in Kraft pulping.

Sample No.	Temperature (ºC)	Wt. Of Na_2S (g)	Wt. Of NaOH(g)	% Yield of pulp
5	90	5	13	18.33
7	100	5	13	15.9
8	110	13	26	15.19
9	110	5	13	17.28

3.1.3.3 Bleaching

After pulping, the color of produced cellulose color was dark brown; the dark brown is due to the residual lignin, which remained in the pulp because of its high molecular weight and the nature of chemical bonds it has [60,66].

Bleaching is the treatment of cellulosic fiber with chemicals to increase cleanliness and brightness. Pulping alone will not remove lignin completely, severe and longer pulping might be applied to remove more lignin, but this will affected cellulose properties such as, decreasing the pulp strength and molecular weight. Bleaching usually removes residual lignin with minimal effect on cellulose [67].

Bleaching chemicals are oxidizing agents that oxidize certain lignin bonds, thus degrading lignin and make it water extractable [67].

A bleaching process usually performed in several stages, all stages form together a bleaching sequence. The efficiency of bleaching cycle depends on the controlling of the operating environment within each stage [67].

Bleaching is achieved through chemical reactions. Operating conditions include temperature, time, chemical concentrations and the degree of

alkalinity and acidity (pH). These conditions must be kept in balance in order to get the desired degree of bleaching in the same time minimizes the destruction of cellulose fiber. Consistency (an amount of fiber being bleached in relation to the volume of liquid) is a factor that should be considered [67].

The main factor in choosing a bleaching chemical is the selectivity of the bleaching agent. Selectivity is the ability of the chemical agent to attack lignin without damaging the cellulose chain [67].

The amount of bleaching needed in the bleaching sequence to obtain the brightness desired in the finished pulp is determined by the kappa number which represents the lignin content of unbleached pulp [67].

Kappa number was determined as shown in the experimental part.

In determination of kappa number, three chemical reactions occured between the lignin and the permanganate in an acidic medium.

First, the lignin is oxidized and solubilized by ($KMnO_4$). The following equation illustrated the first reaction.

$$\text{lignin} + MnO_4^- \longrightarrow \text{Oxidized lignin} + H^+ + MnO_4^- (\text{excess}) \qquad \textbf{Eq. 3.1}$$

In the second reaction, the excess permanganate reacts with potassium iodide producing iodine. As shown in Eq. 3.2.

$$10\,I^- + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{+2} + 5I_2 + 8H_2O \qquad \textbf{Eq. 3.2}$$

In the last reaction iodine reacts with thiosulphate to produce iodide and sulphate anions as shown in Eq. 3.2.

$$I_2 + 2\,S_2O_3^{-2} \longrightarrow 2I^- + 2\,S_4O_6^{-2} \qquad \textbf{Eq. 3.3}$$

The extracted cellulose samples were subjected to bleaching sequence consists of multistage HPHEp.

During the bleaching stages all non-cellulosic materials such as residual lignin and hemicellulose are oxidized and solubilized in water, and removed from cellulose. Selected samples were subjected to bleaching, these samples are shown in Table 3.2.

The final best yield obtained after pulping and bleaching under the aforementioned conditions was about 14% with lignin content of about 0.06% as shown in the experimental part.

This high purity cellulose powder could be valuable precursor for pharmaceutical products and food applications. The sample 9 (Table 3.2) that was produced under these condition was subjected to analysis by various spectroscopic and analytical method.

Kappa number calculated using the following equations.

$$K = \frac{p \times f}{w} \qquad \textbf{Eq. 3.4}$$

$$p = \frac{(b - a)\,N}{0.1} \qquad \textbf{Eq. 3.5}$$

Where:

K= kappa number

F= factor for correction to 50% permenganate , depend on value of P.

W= weight of moisture- free pulp in the specimen, g.

P= amount of 0.1N permanganate consumed by the test specimen, mL.

b= amount of the thiosulfate consumed in blank determination, mL.

a= amount of thiosulfate consumed by the test specimen, mL.

N= normality of thiosulfate

The following table define and illustrates the function of bleaching chemical used in this study.

Table 3.2: Bleaching chemicals

Chemicals		**Function**
H	Hypochlorite	Oxidize, brighten and solubilize lignin.
P	Hydrogen Peroxide	Oxidize, brighten and high-yield pulps.
Ep	Sodium Hydroxide in presence of low concentration of hydrogen peroxide	Hydrolyzed chloro lignin and solubilize lignin.

Table 3.3: Results of selected samples bleached with HPHEp sequence.

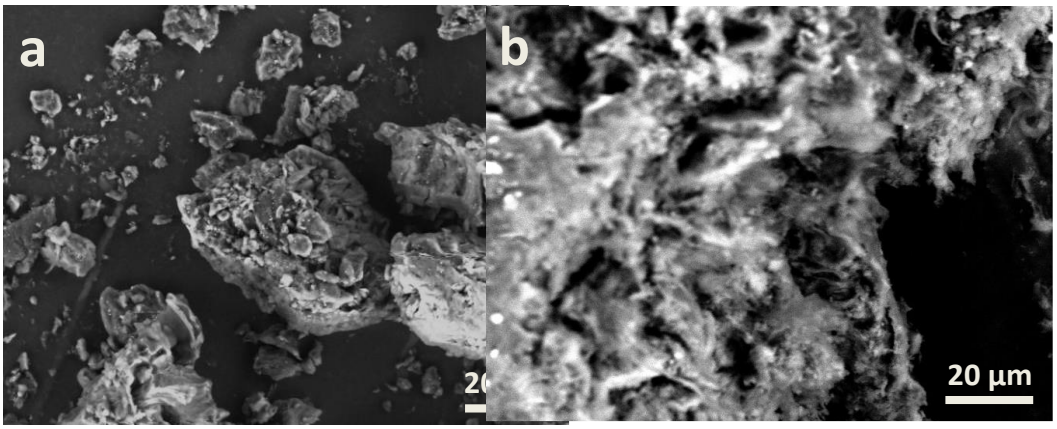
Sample No.	**Kappa No.**	**Lignin content**	**% Final yield**
6	0.824	0.1236	79.5
7	2.37	0.3555	78.7
8	Nearly zero	.....	79.07
9	0.449	0.06735	80.6
10	0.743	0.11145	89.6
11	0.431	0.06465	88.5

3.1.4 Analysis of extracted cellulose

Cellulose sample extracted from APC using the Kraft pulping and the bleaching sequence HPHEp was labeled as APC-Cell. The texture of the extracted cellulose was in the powder form.

3.1.4.1 SEM analysis of APC-Cell

SEM images of APC and cellulose powder APC-cell are shown in Figure 3.4. At low magnification as shown in Fig. 3.4c-d, the surface of APC appears to be smoother than APC-cell probably due to the presence of lipids in APC. Some small and white particulates aggregate easily as observed in APC image. This is not the case in APC-cell, which may provide evidence that the removal of impurities from APC has been successfully achieved. Fiber-like objects can be clearly identified in Fig. 4d and 4f, suggesting that cellulosic products have been well purified from APC. These SEM images further demonstrated the effectiveness of the removal of the impurities and to obtain pure cellulose from APC via Kraft pulping and HPHEp bleaching operations.



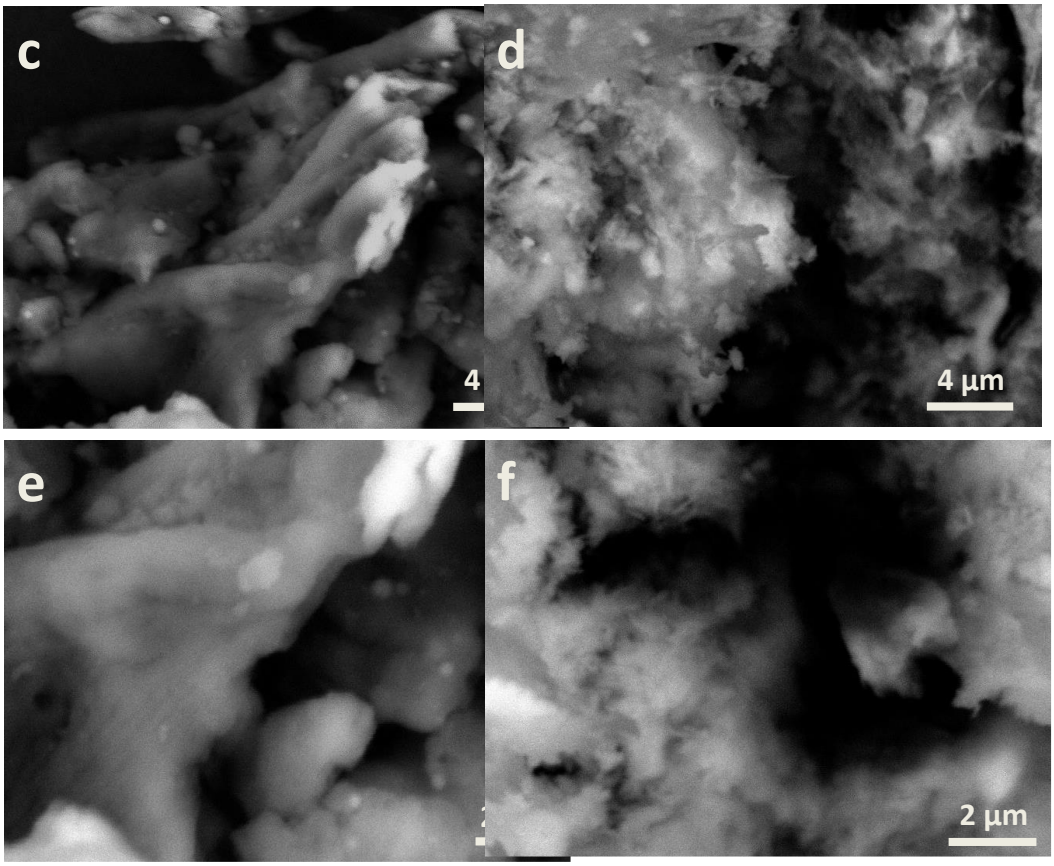


Figure 3.4: SEM images of APC (a, c, e) and cellulose extracted from HPHEp bleaching sequence (APC-cell) (b, d, f) under different magnifications.

3.1.4.2 Thermal gravimetric analysis of APC-Cell

Thermogram curves of APC and APC-cell are shown in Figure 3.5a-b and the maximum decomposition temperatures are shown in Table 3.4. The first derivative curve of weight loss of APC indicates that there are four decomposition stages in the APC corresponding to the presence of four major components. According to FTIR analyses and the reference [65**]** the first stage occurs at maximum decomposition temperature at 54.5°C in the range of 40-150°C and is associated with absorbed water that accounts for approximately 9.3%. The second stage in the range of 150-300°C shows

the maximum decomposition temperature at 238.2°C, suggesting that protein and lipid components may have been decomposed in this range. Protein and lipids may account for about 18% of the APC weight. The third stage in the range of 300-380°C shows the maximum decomposition temperature at 333.1°C that is related to the cellulosic component accounting for about 29% of the APC weight. The maximum decomposition temperature in the fourth stage in the range of 380-550°C slightly shifts to 379.3°C, perhaps due to the presence of impurities in APC. The component decomposed in the fourth stage could be lignin which account for about 21.7% of the APC weight [68] Given that the impurities have been removed in the case of APC-cell, the maximum decomposition temperature at 319.2°C for APC-cell is similar to the decomposition temperature of pure cellulose. The decomposition rate of APC-cell in the range of 250-380°C has greatly increased as compared to APC, suggesting that cellulosic component has been well purified.

Table 3.4 Decomposition temperatures (T*m*) of different components of APC and APC-cell

Sample IDs	Tm_1 (°C)	Tm_2 (°C)	Tm_3 (°C)	Tm_4 (°C)	Tm_5 (°C)
APC	54.5	238.2	333.1	379.3	N/A
APC-cell	N/A	N/A	330.8	378.4	449.2

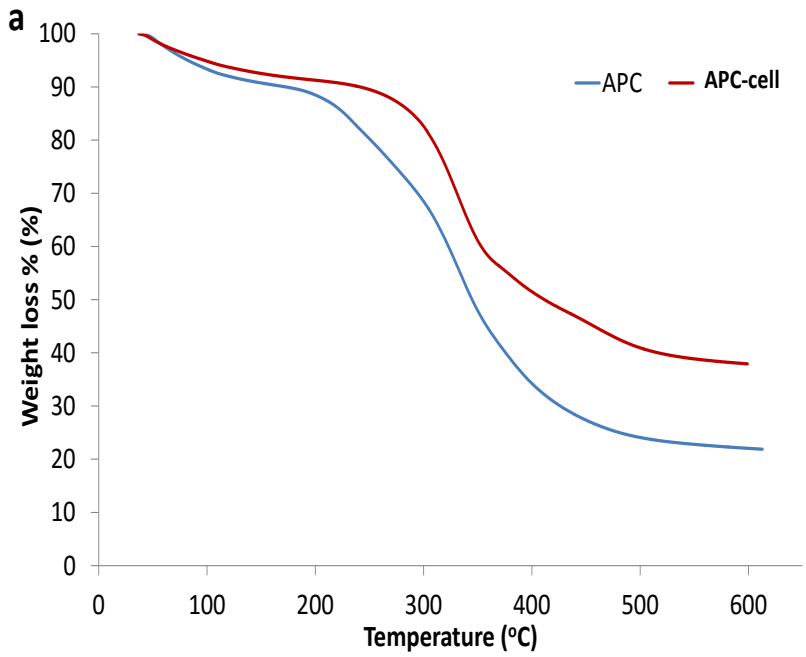


Figure 3.5a TGA thermograms for APC and APC- cell

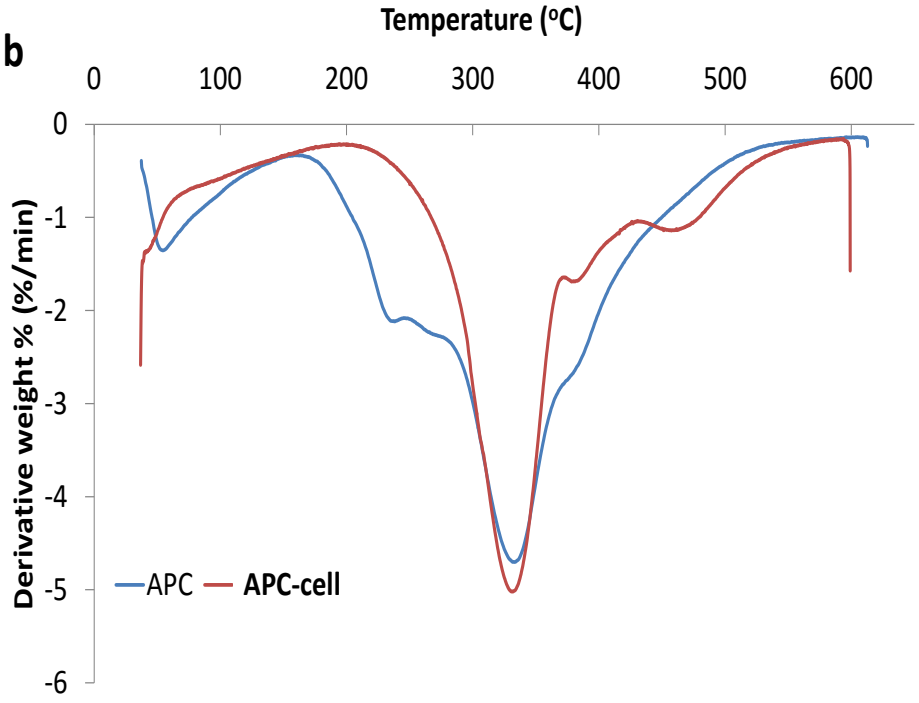


Figure 3.5b DTG curves of weight loss of APC and cellulose extracted from APC by HPHEp bleaching (APC-cell).

3.1.4.3 X-ray diffraction of APC-Cell

The X-ray diffraction patterns of APC and APC-cell are shown in figure 3.6 where APC-cell clearly shows three peaks at approximately 15°, 18.5° and 22.8° corresponding to planes associated with Miller indices $1\bar{1}0$, 110, and 200, respectively. XRD results suggest that the cellulose extracted from APC via Kraft pulping and HPHEp bleaching operations (APC-cell) exhibits a crystalline morphology of cellulose I**.**

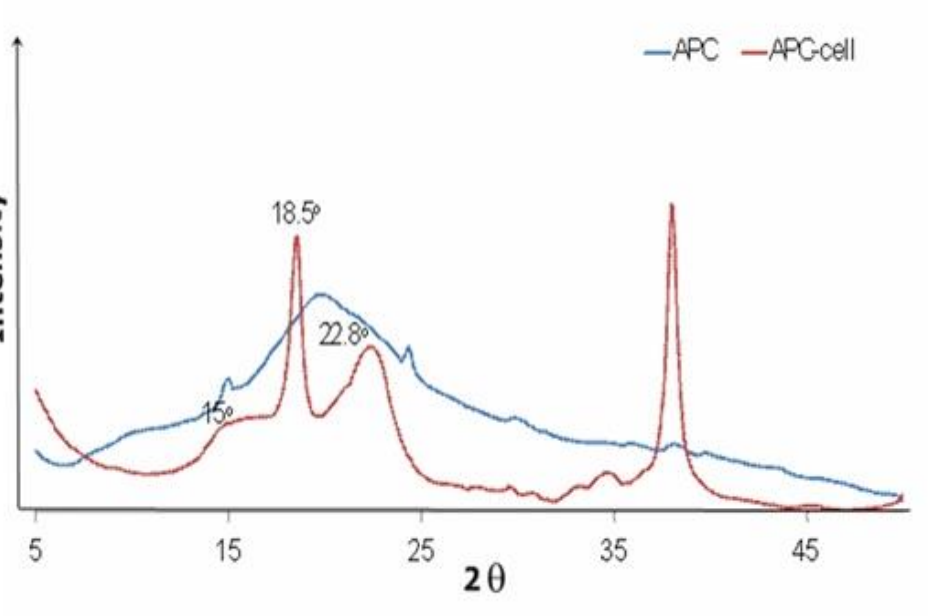


Figure 3.6 XRD patterns of APC and cellulose extracted from APC by HPHEp bleaching (APC-cell).

3.1.4.4 Sugar analysis of APC-cell

Crude APC and cellulose extracted from APC using the HPHEp bleaching sequence (APC-cell) were subjected to sugar analysis to compare the purity of cellulose. Figure 3.7a shows the chromatogram of APC, exhibiting high content of hemicelluloses (glucose, fructose, arabinose, galactose, xylose, and mannose). The chromatogram of APC-cell reveals that the hydrolysis products were composed of almost pure glucose

monomer (glucose) although other sugars such as D-xylose and D-fructose exist in a fairly small amount less than 3% of the total sugars.

(Figure 3.7b). The sugar analysis suggests that the 95% purity of cellulose extracted from APC via HPHEp bleaching has been achieved.

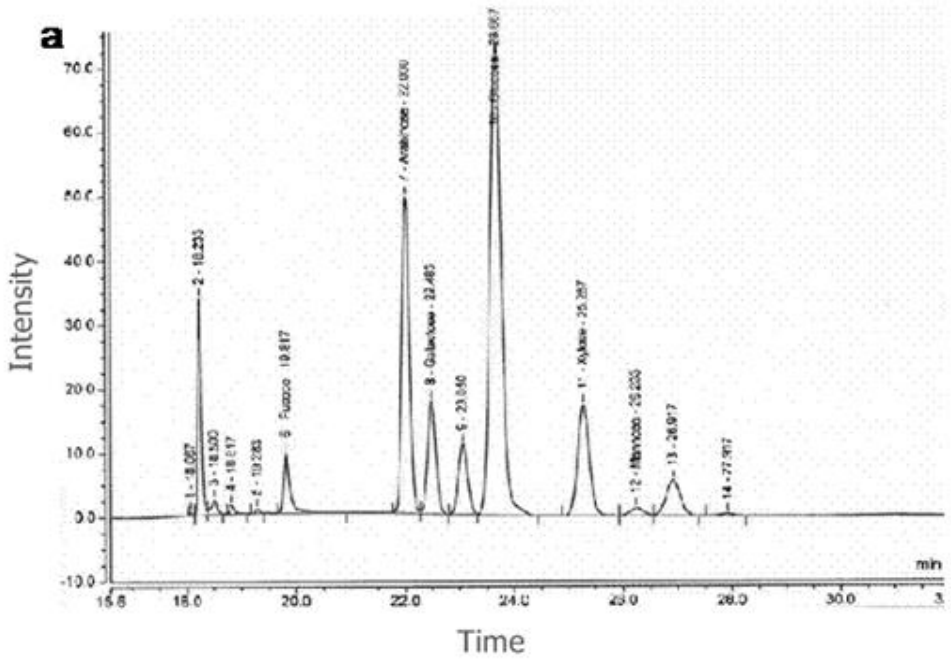


Figure 3.7a Sugar analysis from HPLC chromatogram of APC

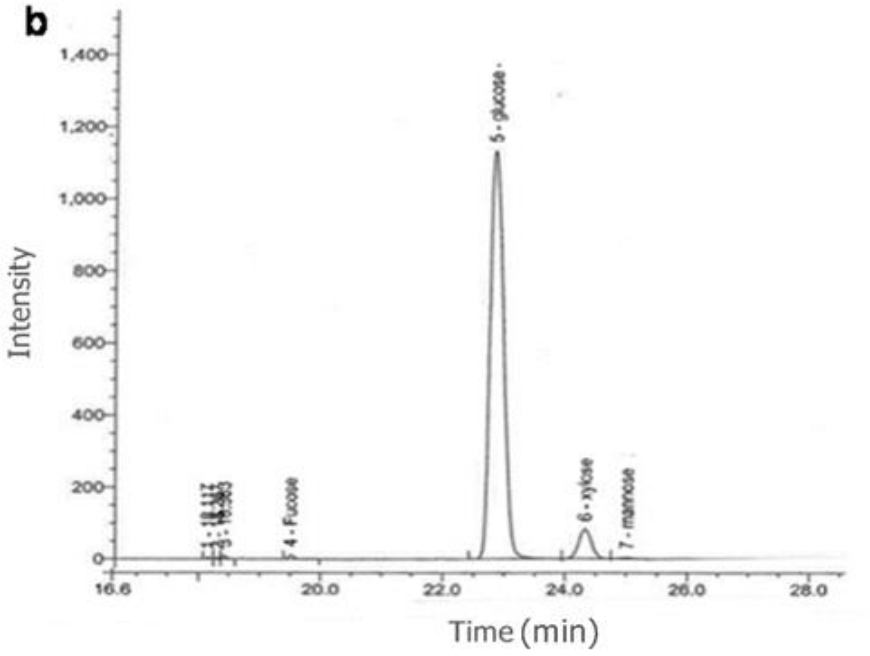


Figure 3.7b Sugar analysis from HPLC chromatogram of cellulose extracted from APC by HPHEp bleaching (APC-cell).

3.1.4.5 Molecular weight analysis of APC-Cell

GPC analysis was performed to investigate the molecular weight of cellulose extracted from APC via HPHEp bleaching sequence. GPC analysis results are shown in Figure 3.8. Two molecular weight data, number average molecular weight (Mn) and weight average molecular weight (Mw) were calculated according to the reference [69**]**. The molar mass distribution is represented by the blue dotted line and the UV chromatogram is the black dotted line.

The Mn and Mw of APC-cell were determined to be 80.2 kDa and 219.9 kDa with degree of polymerization (DP) of about 500.

The DP is consistent with that shown in the literature for cellulose powder [70, 71]. The polydispersity index (2.7) and the shape of the molar mass curve show a large fraction of APC-cell with low molecular weight.

The Mn , Mw , DP and Polydispersity index were calculated using the following equation.

$$Mn = \frac{\Sigma\, Ni\, Mi}{\Sigma\, Ni} \qquad \textbf{Eq. 3.6}$$

$$Mw = \frac{\Sigma\, Ni\, Mi^{2}}{\Sigma\, Ni\, Mi} \qquad \textbf{Eq. 3.8}$$

$$\text{Polydispersity} = \frac{Mw}{Mn}$$

$$DP = \frac{Mw}{M} \qquad \textbf{Eq. 3.9}$$

Where:

Mn= average number of molecular weight.

Mw=average weight of molecular weight.

M_i = the molecular weight of the chain.

N_i= the number of chains of that molecular weight.

DP = degree of polymerization.

M = molecular weight of monomer

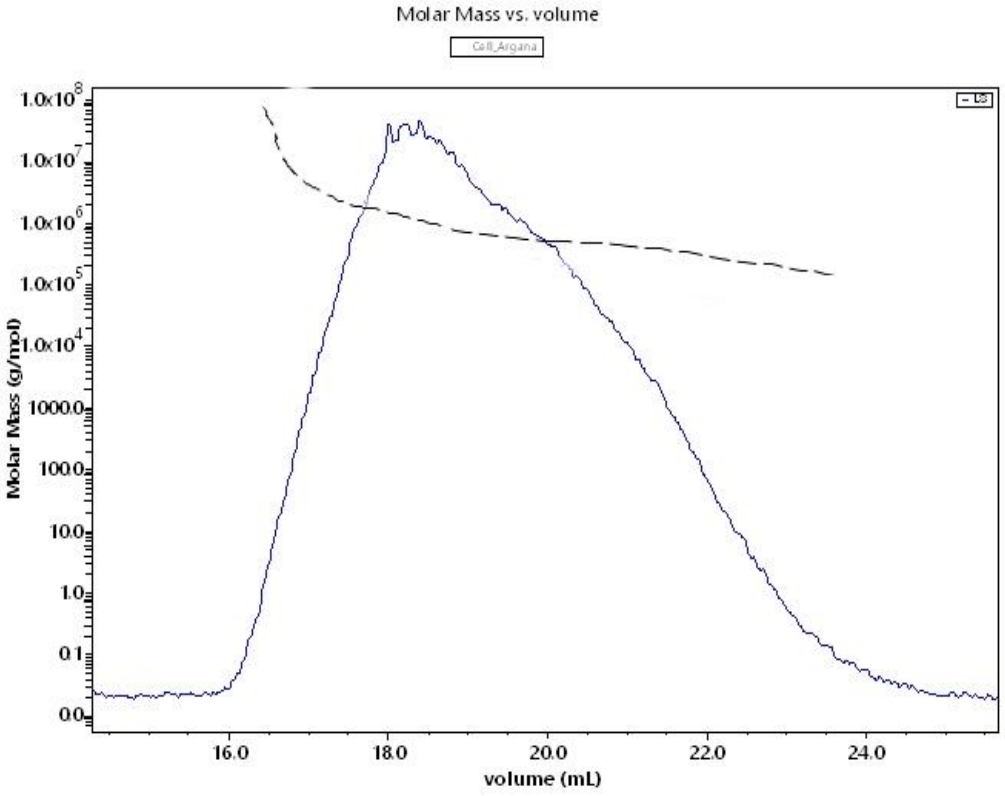


Figure 3.8 Molar mass distribution versus elution time for cellulose extracted from APC by HPHEp bleaching (APC-cell).

3.1.4.6 FT-IR of APC-Cell

The FTIR spectra of APC and APC-cell after HPHEp bleaching are shown in Figure 3.9. The spectrum of APC-cell shows that impurities such as proteins and lipids were removed because the peaks at 1744 and 1628 cm^{-1} are greatly decreased or completely disappear.

The typical peaks at 1033 and 1056 cm^{-1} associated with cellulosic macromolecule indicating the enhanced presence of sugar components. The results from the comparison amongst the FTIR spectra of the APC, APC-WE, APC-AC and APC-SC reveal that HPHEp combined with Kraft pulping is an effective extraction approach to not only enhance the purify of cellulose but also to remove most impurities completely as compared to water/ethanol treatment and acid pulping. The HPHEp bleaching sequences containing a series of bleaching operations with hypochlorite (NaOCl), hydrogen peroxide (H_2O_2) in basic medium followed by extraction with sodium hydroxide (NaOH) in the presence of low concentration of hydrogen peroxide [72,73**]** demonstrates the merit of producing cellulose from APC.

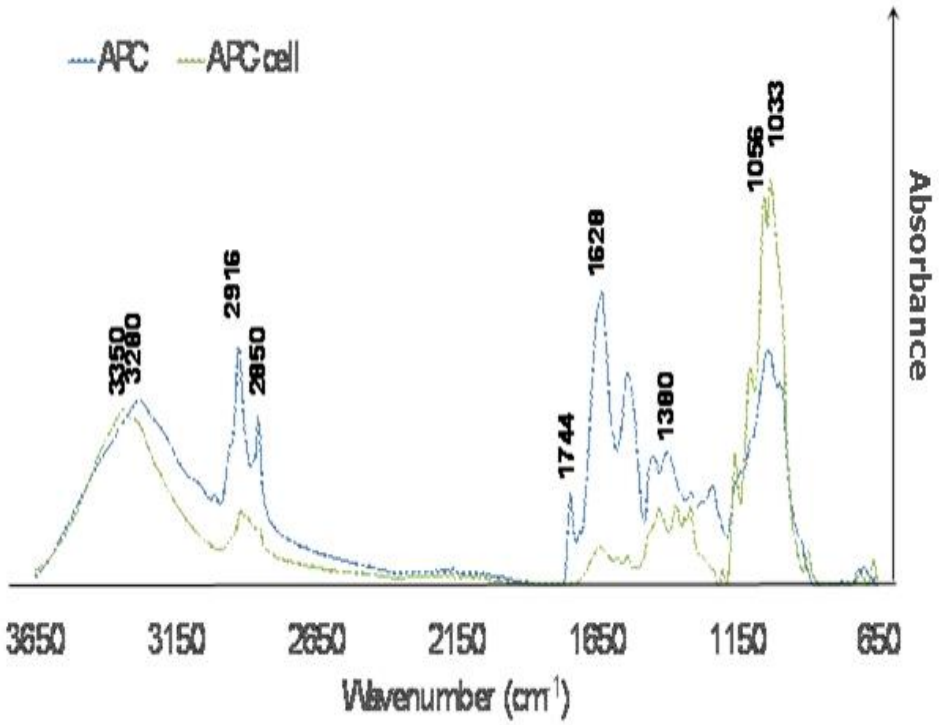


Figure 3.9 FTIR spectra of APC and cellulose extracted from APC by HPHEp bleaching sequence (APC-cell).

Conclusions

An alkaline pulping (Kraft pulping) combining with the bleaching sequence HPHEp was used in this study to extract and purify cellulose from *Argan* press cake, a biomass resource known as agricultural wastes.

As compared to other extraction approaches, the Kraft pulping followed by HPHEp bleaching operation lead to the extraction of cellulose with high purity as shown in several analytical analyses.

Material characterization, sugar analysis, and molecular weight measurements of the extracted cellulose confirmed the quality and the purity of cellulose obtained from APC. In the light of low-cost of APC, the extracted cellulose may be a potential value-added product for food and pharmaceutical applications.

Future work

1- Develop a method for increasing the percentage yield of extracted cellulose from APC.

2- Scale up the amounts from lab process into multi-kilos process.

3- Develop method for converting extracted cellulose into commercial derivative like cellulose ester or ether.

4- Using anthrone method for testing carbohydrates.

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جامعة النجاح الوطنية

كلية الدراسات العليا

استخلاص مشتقات السيليلوز من شجرة الاركان بذور و سيقان

اعداد

رهام نضال عبدالله حطاب

اشراف

أ.د شحده جودة

د. عثمان حامد

قدمت هذه الاطروحة استكمالا لمتطلبات الحصول على الماجستير في الكيمياء بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس , فلسطين .

2016

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اشراف

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الملخص

الارجان كيك هو من المخلفات الزراعية , يتكون من انتاج الزيت من جوزالارجان , لونه بني غامق , يحتوي على السليلوز , ومركبات اخرى كالهميسليلوز والبروتينيات و الليبيدات.

في هذه الدراسة تم استخلاص السليلوز من الارجان كيك , لذا تم تطوير نهج المعالجة القلوية , التي تتالف من تطبيق المعالجة تحت ظروف معتدلة , درجة حرارة 80 مئوي , ومحلول يحتوي على هيدروكسيدالصوديوم (12%) , و كبريتيد الصوديوم (8%) .

تم الحصول على لب سليلوزي مصفر , لذا تم تعريضه لعملية التبيض بسلسلةHPHEp لتعزيز نقاء السليلوز الى حد كبير . أظهر تحليل السكر وتحليل الوزن الجزيئي والتقنيات الطيفية الأخرى , ان السليلوز المستخرج يمكن تصنيفه على شكل مسحوق السليلوز التي من شأنها تكون مؤهلة لتطبيقات الدوائية والغذائية.

تم استخدام طرق اخرى ل Pulping , وهي acid pulping , pulping مع محلول الماء و الايثانول . السليلوز الذي تم الحصول عليه من الطرق السابقة , منخفض الجودة و منخفض العائد ,لهذا لم تدرس دراسة وافرة .