An-Najah National University

Faculty of Graduate Studies

Optimization and Scale up of Cellulose Extraction Process From Olive Industry Solid Waste

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Dedication

I, with all modesty, dedicate this thesis to:

1- My father God bless and rest his soul.
2- My dear, kind mother for her love, encouragement and support, god protect her.
3- My elder brother Diaa for his support and bearing all the costs and to my brother Shadi; God bless them all.
4- My sisters: Dima, Roaa, Hadeel and their children: Donia, Ahmed, Leen, Lana and all the family; God bless them.

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Thank God who helped me to complete this thesis.

Special thanks to my dear brother and sweetheart Diaa, without him after God

I couldn’t reach this goal, so I thank him for his continuous support, encouragement and guidance me. Special thanks to my family for their encouraging and helping me till I finished my research.

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحت عنوان:

Optimization and Scale up of Cellulose Extraction Process From Olive Industry Solid Waste

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي من نتاج جهدي الخاص باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل، أو أي جزء منها لم يقدم من قبل لنيل أية درجة علمية أو بحثية لدى أية مؤسسة تعليمية أو بحثية أخرى.

Declaration

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

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Date: **التاريخ:** ٢٠١٥/١٠/٢٩

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OILW	Olive Industry Liquid Waste
OISW	Olive Industry Solid Waste
DP	Degree of Polymerization
DS	The Degree of Substitution
MC	Methyl Cellulose
HEC	Hydroxy Ethyl Cellulose
HPMC	Hydroxy Propyl Methyl Cellulose
CMC	Carboxy Methyl Cellulose
CA	Cellulose Acetate
CAP	Cellulose Acetate Propionate
CAB	Cellulose Acetate Butyrate
IR	Infrared
FTIR	Fourier Transform Infrared Spectroscopy
EMS	Electron Microscopy Sciences
SEM	Scanning Electron Microscope
OD weight	On Dry weight
GC/MS	Gas Chromatography/ Mass Spectrometry
RPM	Rotation Per Minute
TCF	Totally Chlorine Free
K-Number	Kappa Number
Cuene	Cupriethylenediammine
IV	Intrinsic viscosity

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Abstract

Olive Industry Solid Waste is the remaining part of the grain of the olive industry after squeezing it, it consists of wood seeds and pulp. The OISW consists of cellulose, hemicelluloses, lignin and extractives.

In this work, cellulose the most valuable ingredient of OISW, was extracted in a multistep process. The process begins with pre-hydrolysis stage which opens the OISW structure and makes it more accessible for chemicals. Also in this stage, most of the hemicelluloses materials present in OISW are degraded and dissolve in water. In the prehydrolysis stage, different materials were evaluated and satisfactory results were obtained using water alone. Then OISW was subjected to the pulping process using an aqueous solution of sodium sulfide and sodium hydroxide. In the pulping stage most of the lignin is degraded and removed. The produced pulp was then subjected to a bleaching process to remove residual colored materials. Excellent results were obtained using the bleaching sequence H_tPH_tEp . The amount obtained form OISW was about 30%. The process was then

scaled up to 5 kilograms of OISW using a 20 kilograms reactor. The amount of cellulose obtained was 1.2 kg (24%).The obtained cellulose was evaluated using various analytical and spectroscopic techniques: K-number, Intrinsic Viscosity, Soxhlet Extraction, SEM and FT-IR.

The extracted cellulose, was successfully converted into carboxylmethyl cellulose (CMC) by reacting it with sodium hydroxide and chloroacetic acid. CMC is an important cellulose ether, which have wide industrial application particularly in cosmetics, food, detergents, paints and other consumer products. The derivative was analyzed by FT-IR and the degree of substitution was determined.

The most important results of this work are:

1- The process of extracting cellulose from the OISW was scaled up to multikilograms.
2- The extracted cellulose was successfully converted into cellulose ether (CMC).

Chapter One

Introduction

1.1 Background

The olive oil industry represents one of the most economically important agro-food sectors in the Mediterranean and Middle Eastern regions including Palestine. According to the Palestinian Ministry of Agriculture, the West Bank of produces approximately 33000-35000 metric tons of oilin good year [1].

The number of olive trees in Palestine is more than ten million they are planted in an area of more than 900 thousand dunamswhich constitutes about 45-50% of the cultivated area [2]. This means, that the olive oil industryis the backbone of the Palestinian agricultural economy. Oil produced at olive mills from crushed olive which is pressed and centrifuged to separate water from oil produces environmental wastes causing a serious disposal problem of this waste in two aspects: the first is liquid waste(OILW) 56% of olive industry waste and is known in Palestine as "Zubarr"; the second is solid waste (OISW = pomace, also locally known as Jeft) 44% of olive industry waste[3].

In many countries, OISW is usually burned or left to rot, thus releasing more CO_2 into the atmosphere that contribute to the global warming. On the other hand, the OILW tends to be disposed of via the sewage system or unguided release above ground, which has negative implications on wild life as well as on surface and underground water quality, as a result olive industry loses economic value.

The challenge is to utilize and convert these waste materials into useful and low-cost value added materials.Jeft components are similar to wood components, consisting of cellulose (40-50%), lignin (18-35%) , Extractives (4-10%), and hemicelluloses (25-35%) [4].

1.2 Cellulose

Cellulose; is an organic polymer, the repeating unit of the cellulose polymer is anhydroglucose with the formula $(C_6H_{10}O_5)n$ [5] ، n is average value which could be over 1000 or 10000 (depending on source) [6]. Cellulose can be obtained from unlimited number of sources among these are algae, fungi, invertebrates, bacteria, marine animals (tunicate), and plant (flax, hemp, cotton, fiber) [7]. The primary occurrence of cellulose is the forest wood [8].The proportion of cellulose in various sources is shown in Table 1.1 [9]. As shown in table 1.1, cotton has the highest contents of cellulose followed by wood.

Table 1.1: The Proportion of Cellulose in Many Sources

Source	Cellulose(%)
Cotton	90-99
Hemp	75-80
Wheat	49-54
Flax	70-75
Jute	60-65
Leaf fiber	40-50
Corn cobs	45
Kenaf	47-57

Cellulose is white powder is a water insoluble polymer, it is hydrophilic, chiral, rigid, and biodegradable, has no taste, odorless. Thedensity of powered cellulose is 0.2-0.5 g/cm^3, the melting point is 260-270 °C [10].

Cellulose is a linear chain polymer of ß-1,4-linked D-glucose (anhydroglucose) units links through an oxygen covalently bonded to C1 and C4 of adjacent units to form a long chain 1,4 glucans as shown in Figure 1.1. This figure shows that.cellulose has three hydroxyl groups: secondary on C2 and C3 and primary on C6 [11]. These hydroxyl groups show reactivity if treated with sodium hydroxid to form alkoxide as shown in Figure 1.1.

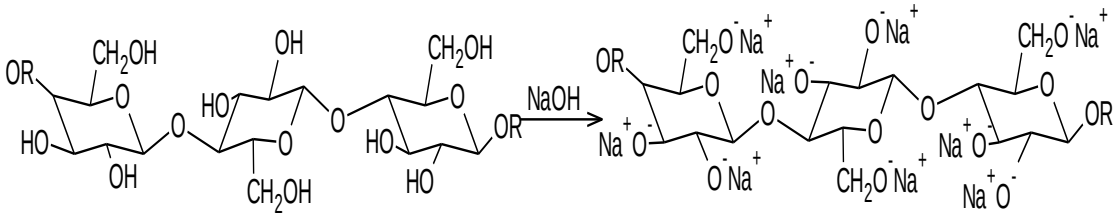


Figure 1.1: Reaction of Cellulose with Sodium Hydroxide

The presence of the intra- and inter-chain hydrogen bonding network in cellulose structure gives it special properties such as: stability even at high temperature, and stiffness.It also contains two region which distinguish it from other natural polymers such as starch; crystalline and amorphous regions as shown in figure 1.2 [12].

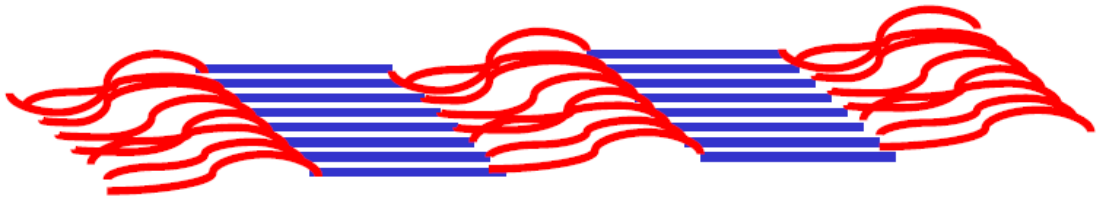


Figure 1.2: The Crystalline Region (blue) and Amorphous region (red)

The size of the cellulose chain depends on the source of the cellulose. Table 1.2 shows the average degree of polymerization (DP) of the cellulose from various source [9].

Table (1.2): Average Degree of Polymerization of Cellulose from Various Sources

Source	Average Degree of polymerization
Cotton fibers	8000-14000
Cotton linters	1000-6500
Bagasse	700-900
Bacterial cellulose	2700
Wood fibers	8000-9000
Flax fibers	7000-8000

1.3 Cellulose Derivatives and Applications

Cellulose derivatives are important commercial products for plastics, textiles, packaging, films, explosives, and as additives in food, pharmaceuticals, and cosmetic industries [13,14].

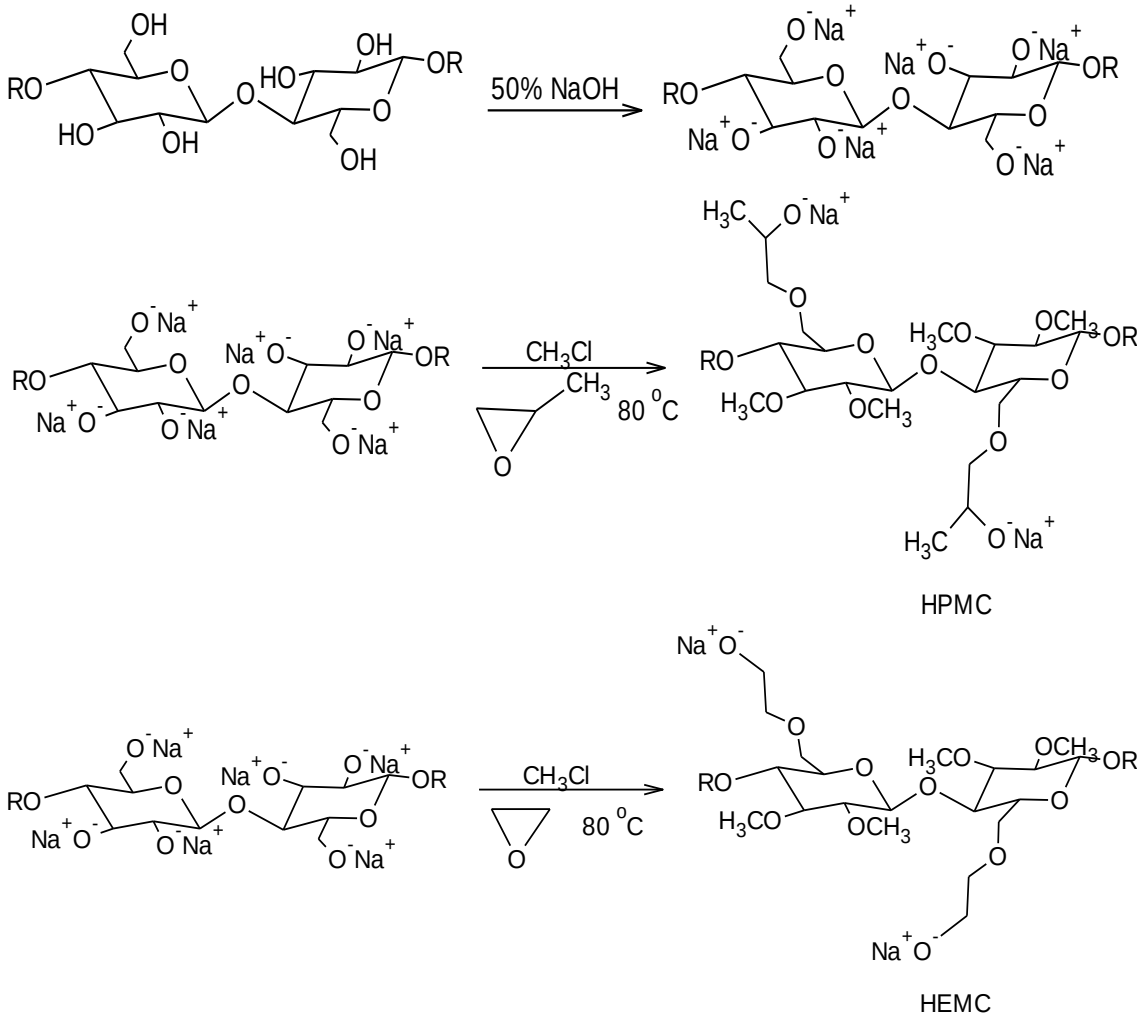
The D-anhydroglucopyranose units has three hydroxyl groups, these groups can be partially or fully reacted with various reagents to afford derivatives with useful properties [15], these properties depend heavily on the type, distribution, and uniformity of the substitution group [9].

The average number of hydroxyl groups replaced by the substituent is known by the degree of substitution (DS); the maximum is three. And derivatives of high DS are often less sensitive to water.

1.4 Cellulose Ether

The most common cellulose derivatives are cellulose ethers and cellulose esters. Cellulose ethers are an important class of polymers with unlimited number of applications [16]. For instance, methylcellulose (MC), hydroxyethyl cellulose (HEC), hyroxypropyl methylcellulose (HPMC) which are prepared as in the scheme 1.1 below by replacing the hydrogen

atoms of hydroxyl groups in the anhydroglucose units of cellulose with alkyl or substituted alkyl groups [17,18] are widely used in food, films, textiles, foodand tobacco industry [19]. These compounds act as thickeners in paints and in construction.



Scheme 1.1: Synthetic of Some Cellulose Ethers.

1.4.1CarboxymethylCellulose

Carboxymethyl cellulose (CMC) is the most important commercial water soluble cellulose ether. It is usually prepared in a degree of substitution that ranges from 0.4–1.5. It is widely used in cosmetics, food,

paints,pharmaceutical, coatings, and adhesives. The structure of this compound is shown in figure 1.3.

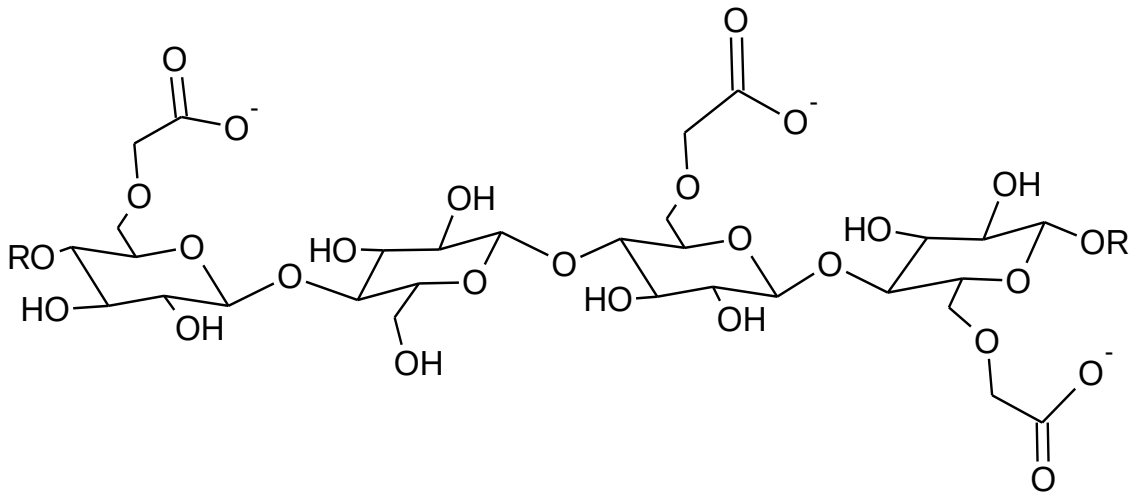


Figure 1.3: Chemical Structure of Carboxymethyl Cellulose

1.5 Cellulose Ester

Cellulose esters are derivatives of cellulose in which the proton of the hydroxyl groups are replaced with an acyl group (acetyl, propionyl) or nitro [20], so it is functionalized in organic and inorganic group. Organic ester include cellulose acetate (CA), cellulose acetate propionate (CAP), and cellulose acetate butyrate (CAB). Inorganic esters include cellulose nitrate, cellulose sulfate, cellulose phosphate.

Cellulose acetate is one of the most commercially important cellulose esters [21], it is extensively used in the textile and polymer industries [22].It is produced by the reaction of cellulose with an excess amount of acetic anhydride in acetic acid in the presence of sulfuric acid as the catalyst. The average molecular weight of cellulose acetate ranges from 30000 to 60000.It is a white powder that is odorless, tasteless, and is soluble in organic solvents[23].

It has diverse applications such as fibers, films, laminates, adhesives, coatings, plastic products, food packaging, and used in cigarette tow [24,25].Because of its low-cost, toughness, gloss, high transparency, and natural feel, it is widely used in textiles [26].

1.5.1 Nitrocellulose

Cellulose nitrate, an inorganic cellulose ester, is produced under heterogeneous reaction conditions, by the reaction of cellulose with nitric acid. During this reaction some protons of the hydroxyl (-OH) groups of each glucose unit in the cellulose are replaced by nitro ($-NO_2$) groups as shown in figure 1.4 [27,28].

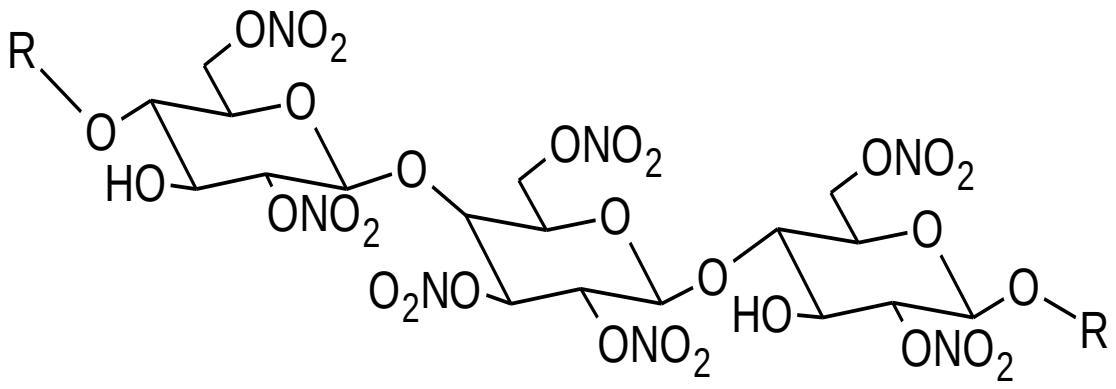


Figure 1.4: Chemical Structure of Nitrocellulose.

Cellulose nitrate is a white, odorless, tasteless substance. It is used in wood finish, ink bases, filter membranes, explosives and in paints [29,30].

1.6 Lignin

Lignin is a phenolic macromolecule that imparts strength and decay resistance to the plant secondary cell wall and is thought to have been

essential to the evolution of terrestrial plants[31].A representative structure of lignin is shown in Figure 1.5 [32]. As shown in Figure 1.5 lignin has no definite repeating unitsand for this reason, it is considered as macromolecule and not a polymer.

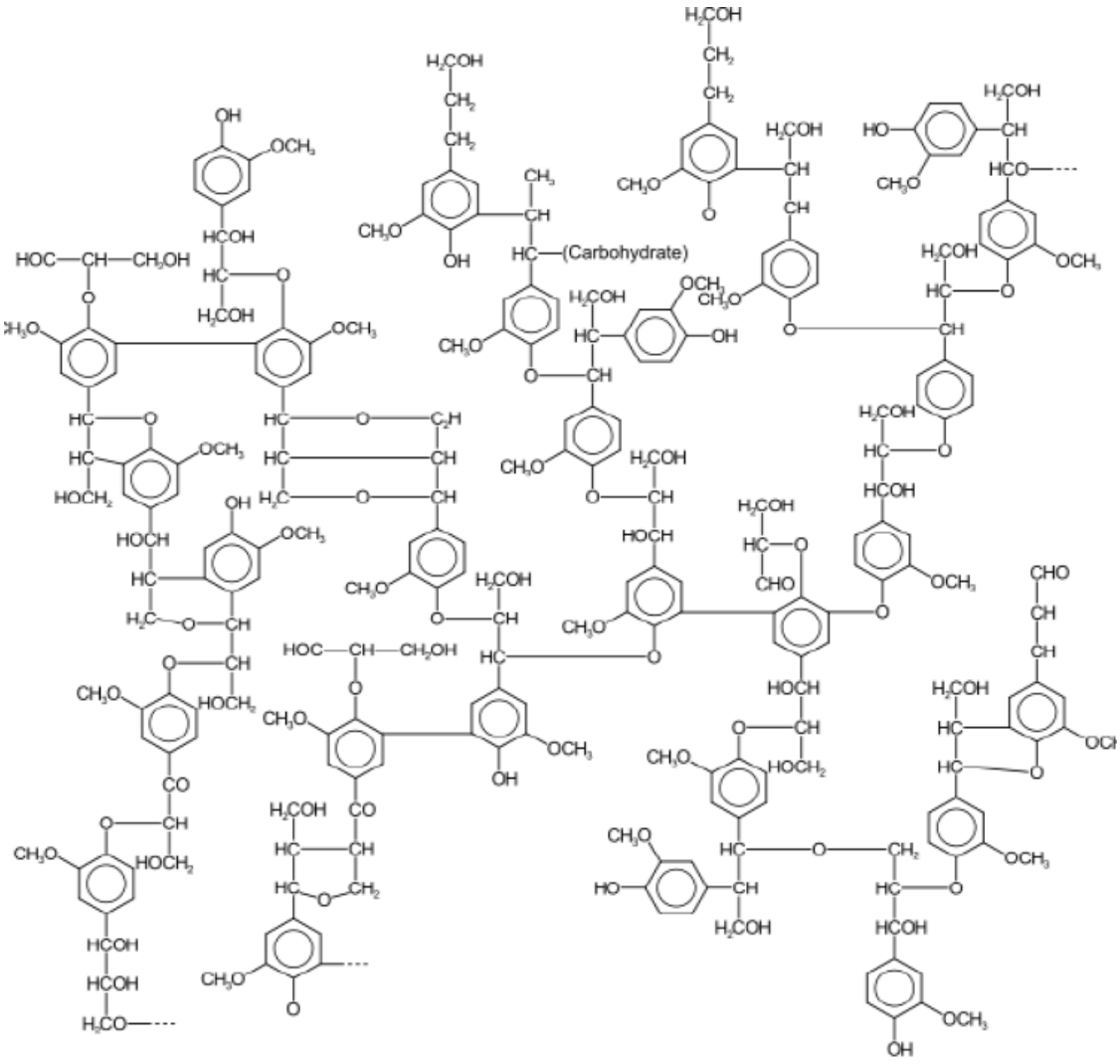


Figure 1.5: Representative Chemical Structure of Lignin

It consistof an irregular array of variously bonded hydroxy- and methoxy-substituted phenylpropane units. The precursors of lignin biosynthesis are p-coumaryl alcohol (I), coniferyl alcohol (II), and sinapyl alcohol (III) [4] shown in figure 1.6.

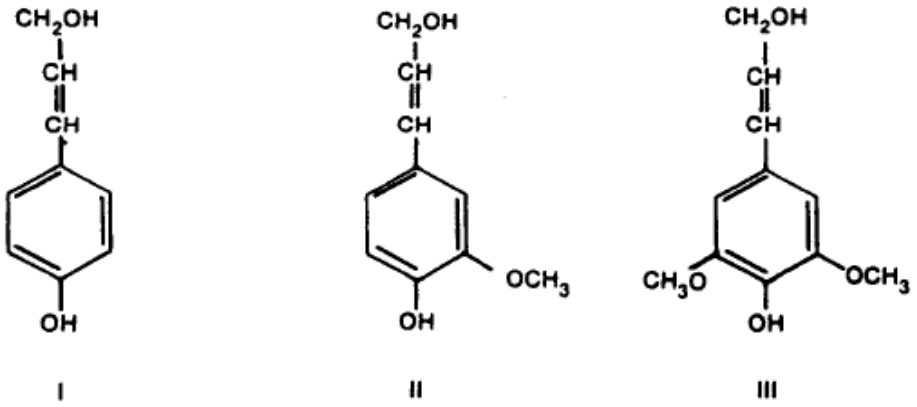
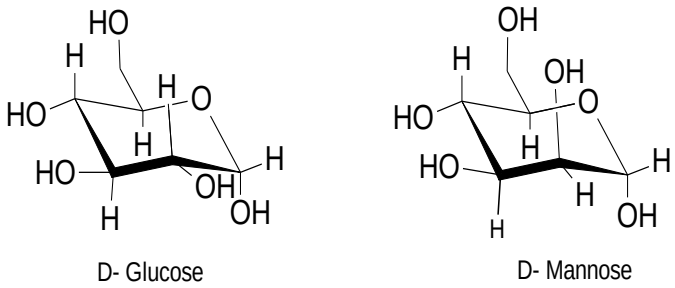


Figure 1.6: Precursors of Lignin

1.7 Hemicelluloses

Hemicelluloses are heterogeneous polymers with various sugar repeat units arranged in different proportions and with different substituents. Hemicellulosesis branched polymer and are composed of about 500-3000 sugar units, and thus have shorter chains than cellulose [33].

Their general formulas are $(C_5H_8O_4)n$ and $(C_6H_{10}O_5)n$ [34]. They are soluble in alkali solution and easily hydrolyzed by acids [4]. The principal building sugars of hemicellulose are thepentoses: D-xylose and L-arabinose and the hexoses: D-glucose, D-mannose, D-galactose and their corresponding uronic acids, the structure of these monosugars are shown in Figure 1.7.



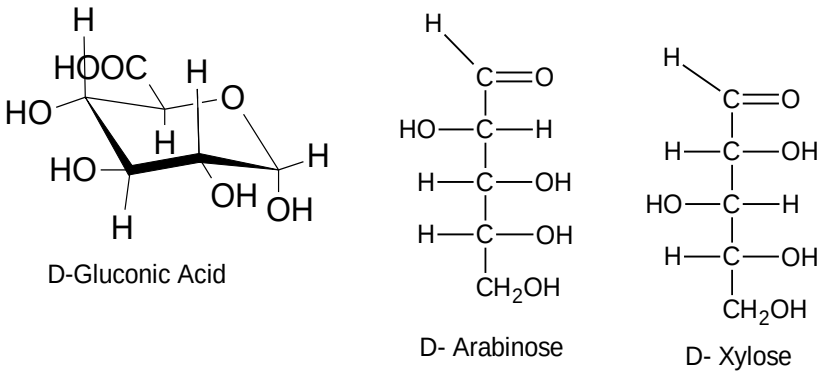


Figure 1.7: structure of monosugars of hemicellulose

Hemicelluloses form hydrogen bonds with cellulose, covalent bonds(mainly α-benzyl ether linkages) with lignin, and ester linkages with acetyl units and hydroxycinnamic acids.

1.8 Extractives

Extractives are the minor component of wood [35]. The extractives are usually non-polar and soluble in non-polar solvents. They include fats, waxes, alkaloids, proteins, simple and complex phenolics, simple sugars, pectins, mucilages, gums, resins, terpenes, starches, glycosides, saponins, and essential oils. The main function of these materials are as intermediates in tree metabolism, energy reserves, and part of the tree's defense mechanism against microbial attack. They contribute to wood properties such as color, odor, and decay resistance. Wood also contains small amount of inorganic material that form ash after wood burning. They are usually less than 1% of wood composition[4].

1.9 Method of Extraction of Cellulose from Plants:

Cellulose is the main component of various plants such as hemp, kapok, sisal, bagasse, wheat straw, sugar beet pulp, cobs, soybean hulls, oat hulls,

rice hulls, bamboo. The commercial sources of cellulose are: Cotton, that contains about 90-99% cellulose, and wood that contains about 40-50% cellulose [36,37].

The method of extracting cellulose from its sources includes several steps: pre-hydrolysis, pulping, and bleaching with different reagent.

1.9.1 Pre-hydrolysis

In this stage wood is heated under pressure of steam in acidic conditions. During this stage, the majority of the hemicelluloses are fragmented into low molecular weight sugars and other chemicals such as acetic acid and methanol. In this stage, the wood becomes more accessible for chemicals used in the pulping stage.

1.9.2 Pulping

The pulping stage can be performed in two different ways, chemical pulping and mechanical pulping [38]. Chemical pulping could be Kraft or acid sulfite process. In the chemical pulping, usually heat and chemicals are used to fragment lignin and convert it from water-insoluble to water-soluble materials[39].

1.9.2.1 Kraft Process

Kraft process is the most popular chemical pulping process, in this process white liquor which is a mixture (of NaOH and Na_2S) is used to release the cellulose by breaking the bonding between cellulose and lignin, and then breaking lignin into small molecules [40]. White liquor and wood are

cooked in the reactor at about 160°C to produce pulp and black liquor.Then the pulp is washed with water [41].

1.9.2.2Sulfite Process

In this process, a bisulfate solution of $Mg(HSO_4)_2$ is used as a delignifying medium.The bisulfate is brought to a digester with wood where the actual cooking takes place at elevated temperature and pressure. Sulfite pulping process has many advantages like high initial brightness and easy bleachability of sulfite pulps [42].

1.9.2.3Mechanical Pulping

In the mechanical pulping methods a certain percentage of water soluble extractives and other components are dissolved during pulping. It can be done in two different ways, the grinding process and the refining process [43].

1.10 Bleaching

Bleaching is the removal of color pigments in the structure of wood using various oxidizing chemicals in a multistage process. During this process the brightness of pulp is increased by lignin removal or lignin decolorization [44]. During the bleaching process, the conjugated double bonds are oxidized and break into water-soluble less-colored materials. The bleaching process is important because it converts pulp from dark color into lighter colors. Also it improve stability and cleanliness [45].

Examples of the oxidants used in the bleaching process are chlorine, chlorine dioxide, oxygen, ozone and hydrogen peroxide in alkali (NaOH). The most important bleaching agent isthe best one[46].

1.11 Aims of the Study

The aims of this project are:

1. Optimize the developed bench process of extracting cellulose powder from OISW to increase product yields and to ensure consistent product quality.
2. Scale up the developed bench process of extracting cellulose powder from OISW to multi kilograms.
3. Characterize the extracted cellulose powder polymers by various spectroscopic and analytical techniques.
4. Investigate the possibility of converting the extracted cellulose powder into the commercially valuable cellulose ether carboxymethylcelluloseand evaluate the properties of the produced carboxymethylcellulose and compare it to the commercially available one.

Chapter Two

Experimental

2.1 Materials

All reagents were purchased from Aldrich Chemical Company, and used without any further purification unless otherwise specified. Kraft pulping was performed in a high Parr Reactor (model: büchiglasuster, bmd 300). Fresh jeft was obtained from an olive factory from kufur-rai town in Palestine and stored in a freezer at about 0 to -5 ^{o}C .

Infrared (IR) spectra were recorded using a Nicolet 6700 Fourier transform infrared (FTIR) spectrometer equipped with the Smart Split Pea micro-ATR accessory. The smart Split Pea is a horizontal attenuated total reflectance micro sampling accessory for Thermo Electrons Nicolet FT-IR spectrometers. The Split Pea is designed for analysis of very small samples of bulk solids, powders, and liquids using the ATR technique. The accessory has a diamond ATR crystal. The following parameters were used: resolution 4 cm^{-1}, spectral range 225-4000 cm^{-1}, number of scans 128. Moisture content was determined according to Tappi standard T 210 cm-03 [47]. Cellulose powder viscosity was determined according to standard process ISO 5351-1 [48], which involves the dissolution of the pulp in an aqueous solution of copper ethylene diamine using a Cannon-Fenske viscometer. Kappa number was determined using the TAPPI standard method T236 cm-85 [49]. Electron microscopy scanning (EMS) analysis

was performed using Hitachi S-3400N variable pressure SEM system coupled with the Oxford EDS system.

2.2 Extraction of Cellulose from Jeft

Cellulose was extracted from OISW (jeft)samples by a 3-stage process consisting of:

1. Pre-hydrolysis
2. Pulping
3. Bleaching

2.3 Pre-hydrolysis

2.3.1Pre-hydrolysis in Acetic Acid

OISW (100 gOD weight) was placed in a high Parr Reactor (model: büchiglasuster, bmd 300) and to it was added an aqueous solution of acetic acid (5%) to produce a suspension with a 5% consistency. The reactor was pressurized to 50 psi and heated to 160 ^{o}Cin 30 min. Then it was maintained at this temperature for about 2.0 hr. At the end of the pre-hydrolysis stage, the jeft was washed with tap water, and stored in plastic bags for further use.

2.3.2 Pre-hydrolysis in Distilled Water

OISW (100g OD weight) was placed in a high Parr Reactor (model: büchiglasuster, bmd 300) and to it was added enough water to produce a suspension with a 5% consistency. The reactor was pressurized to 50 psi and heated to 160 ^{o}C in 30 min. Then it was maintained at this temperature

for about 2.0 hr. At the end of the pre-hydrolysis stage, the jeft was washed with tap water, and stored in plastic bags for further use.

2.4 kraftPulping

General Procedure for Kraft Pulping:

The kraft pulping was conducted as in the pre-hydrolysis stage in a high parr reactor of 1.0 L capacity. PrehydrolyzedOISW (with water) was placed in the reactor and to it was added the white liquor. The produced suspension was heated to 160^{o}C in about 30 min and maintained at this temperature for 2 hr.

The white liquor is an aqueous solution of sodium sulfide (Na_2S) and sodium hydroxide (NaOH). White liquor with various sulfidity and active alkaline were evaluated to determine the best cooking conditions. Sulfidity is equal to [Na_2S/(NaOH+Na_2S), and active alkali is defined as [NaOH+Na_2S], where the concentrations are expressed as g/L Na_2O. The sulfidityis 25% and active alkali used in this work is13% and15% OISW oven dry weight (OD). At the end of the cooking time, the produced pulp was collected by suction filtration or centrifugation, washed several times with tap water, air dried at room temperature, and stored in plastic bags for further use. Yield was calculated by dividing the oven dried weight (OD weight) of the produced pulp by the original weight of the starting jeft (OD weight). The results are summarized in Table 2.1.

Table 2.1: Pulping Results

Run No	Weight of Jeft (g)	Active Alkali(%)	Sulfidity (%)	Percentage Yield(%)
1	100	13	25	28
2	100	15	25	18
3	100	15	25	46
4	200	15	25	37
5	200	15	25	44
6	200	15	25	36

2.5 Bleaching

Bleaching was performed in a multistep sequences process using various oxidants as shown below:

Oxidants labeling

H: Sodium hypochlorite.

E_p: Extraction with NaOH and H_2O_2.

P: Hydrogen peroxide.

Ht: Sodium hypochlorite/triethyl amine.

2.5.1 Sodium Hypochlorite Stage (H-stage)

Olive pulp was treated with 0.5 % of sodium hypochlorite, the experiment was conducted in a plastic bag at 10% consistency (The consistency was calculated according to equation 2.1) on a 100 g or 200 g samples as shown in Table 2.2. The bleaching temperature and time are 60^{o}C and 1 hr, respectively for sample 1. The pH of the bleaching solution was adjusted to 10. The bleaching of samples number 2 was carried out at 10% consistency for 30 min at 55°C. After the bleaching timewasover, the pulp was removed by suction filtration, washed with plenty of water and its OD

weight was determined to be used for yield calculation. The produced samples were never dried and used in the next step.Results are summarized in Table 2.2.

$$\text{Consistency}=\frac{Weightofpulp}{Weightofbleachingsolutio} \qquad \text{Eq.2.1}$$

Table 2.2: Results of Bleaching with H-stage

sample	Temperature (C)°	Pulp weight before bleaching (g)	Percentage Yield (%)
1	60	25	90
2	55	79	96

2.5.2 Extraction with Sodium Hydroxide and Hydrogen Peroxide (E_p-stage)

Pulp produced at H stage was used as a starting pulp in this stage. The bleaching was performed in a plastic bag. To the pulp was added enough solution of sodium hydroxide (1%) and hydrogen peroxide (0.5%) to produce a suspension with a 10% consistency. The plastic bag was sealed and placed in a water bath for 90min at temperature of 70^{o}C.After thebleaching time was over, the pulp was collected by suction filtration and washed with plenty of water. The pulp OD weight was determined and used in yield% calculation.

Pulp was never dried and used in the next stage of bleaching.

The percentage yield was calculated by dividing the dry weight of the bleached product by the starting bleaching pulp (OD weight). Results are summarized in Table 2.3.

Table 2.3: Results of Bleaching with E_p-stage

sample	Pulp Weight (g)	Percentage Yield (%)
1	23	95
2	13	81
3	35	96
4	52	97
5	69	84
6	38	90

2.5.3 Bleaching with Hydrogen Peroxide (P-stage).

In this experiment, pulp produced from the Ep stage was treated with an aqueous solution of H_2O_2(2%) containing a 0.5% $MgSO_4.7H_2O$, and 3.0% NaOH (based on pulp weight). The experiment was conducted in a sealed plastic bag at 10% consistency for 1 hr, at 60 ^oC.After the bleaching time was over, the pulp was collected by suction filtration, washed with plenty of water and its OD weight was determined. Pulp was never dried and used as a starting material in the next stage.

The percentage yield was calculated by dividing the dry weight of the bleaching produced by the starting bleaching pulp (OD weight). Results are summarized in Table 2.4

Table 2.4: Results of Bleaching with P-stage

sample	Pulp Weight (g)	Percentage Yield (%)
1	21	90
2	15	94
3	41	86
4	63	86
5	76	95
6	49	78

2.5.4 Bleaching with Sodium Hypochlorite/Triethylamine (H_t-stage)

Pulp was treated with an aqueous solution of sodium of hypochlorite (1%) and triethylamine (0.15%). As usual, the bleaching was conducted in a sealed plastic bag at 10% consistency, for 1 hr, and at 60 ^{o}C.After the bleaching time was over, the pulp was removed by suction filtration, washed with a plenty of water, and its OD weight determined.. The percentage yield was calculated by dividing the dry weight of the bleaching produced by the starting bleaching pulp (OD weight).

This stage was ran in duplicate to confirm results. Results are summarized in Table 2.5.

Table 2.5: Results of Bleaching with H_t-stage

sample	Pulp Weight (g)	Percentage Yield (%)
1	16	95
2	42	99
3	67	94
4	65	75

A summary of all results obtained using various bleaching sequences are summarized in Table 2.6. Kappa Number and Lignin Content and final yield(%) was calculated according to equation 2.2, 2.3and 2.4 respectively.

Table 2.6: Result of Various Bleaching Sequence

Sample	Bleaching Sequence	Kappa Number	Lignin Content	Final Yield of sequence (%)
1	HE_pP	4.21	0.63	77
2	$H_tPH_tE_p$	3.03	0.45	64
3	$H_tPH_tE_p$	5.54	0.83	80
4	$H_tPH_tE_p$	4.83	0.72	75
5	$HPHE_p$	2.98	0.45	74
6	$H_tPH_tE_p$	5.59	0.84	52

Calculation:-

Kappa Number=$\frac{P*f}{W}$Eq.2.2

P=$\frac{(b-a)N}{0.1}$

where:

K = kappa number

f = factor for correction to a 50% permanganate consumption, dependent on the value of *p* (see Table 1)

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

p = amount of 0.1*N* permanganate actually consumed by the test specimen, mL

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

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

N = normality of the thiosulfate

wt.% of lignin = 0.15 x Kappa Number Eq. 2.3

- How to calculate final yield of bleachingsequence(%):

Final Yield(%)= wt of pulp after pulping process(OD weight)*% yield of bleaching stages(1^{st} stage * 2^{nd} stage *3^{rd} stage…)/weight of pulp after pulping process(OD weight)* 100% Eq.2.4

For example sample No 1:

Final Yield(%)=$\frac{25*(90\%*95\%*90\%)}{25}$* 100%

= 77%

2.6 Pulp Analysis

Produced pulp samples were evaluated after bleaching by subjecting them to K-Number and density test analysis.

2.6.1 K-Number

2.6.2 Reagents Preparation

- Potassium iodide (KI) solution:

  A solution of KI (1.0 mol/L) was prepared by dissolving potassium iodide (166.0 g) in a 1.0 L distilled water.

- Sodium thiosulfite ($Na_2S_2O_3$)standard solution:

  A solution of ($Na_2S_2O_3$) (0.1±0.001 mol /L) was prepared by dissolving 24.82 g $Na_2S_2O_3$. $5H_2O$ in 1.0 Liter distilled water.

- Potassium permanganate ($KMnO_4$)standard solution:

  A solution of $KMnO_4$ (0.02±0.001 mol /L) was prepared by dissolving 3.161g $KMnO_4$ in 1 Liter water.

- Sulfuric acid (H_2SO_4) solution

  Sulfuric acid solutions with two different concentrations were prepared, one with 1M and the other solution with 2M.

- Starch solution:

  The starch solution was prepared by dissolving 0.5 g of starch in a 100 mL of cold distilled water and then heated up to boiling.

2.6.3General Procedure for Determining K-number:

An oven dried pulp (1.00 g) was weighed and placed in a blender. To the pulp was added 400 mL distilled water blended for 3 min to disintegrate the pulp and increase its accessibility for chemicals. The pulp was then transferred into an Erlenmeyer flask and to it was added 50.0 mL of 0.02 M potassium permanganate and left to stand at room temperature for 10 min. Then 10.0 mL of potassium iodide and 50.0 mL of sulfuric acid (2M) were added to the flask. The resulting mixture was titrated with a standard solution of sodium thiosulfate (0.02 M). The titration was continued until a light purple –yellow color appeared. Then 2-3 mL starch solution was added to the flask at this point a blue color appeared, the titration was continued until the blue color disappeared.

The above procedure was also performed on a blank solution and no pulp was used.

2.6.4 Density

A sample of cellulose powder ground using a blender was introduced into a 100 mL graduate cylinder (50 mL height). The cylinder and content was taped on a soft surface for about 20 min. The volume and the weight of the cellulose present in the cylinder were determined and used to calculate the density of the cellulose. Results are summarized in Table 2.7.

Table 2.7: Density and Intrinsic Viscosity of Selected Samples of Extracted Cellulose Powder.

Sample	Density (g/mL)	Cuene (IV) (Centipoise)
1	0.362	2240
2	0.323	2210
5	0.315	2190

2.7Pulp Extraction at Multi Kilograms Scale

2.7.1 Scale-up the Pulping Process

The pulping process was carried out in a large reactor (20.0 kg capacity). To the reactor was added 5 kg of pre-hydrolyzed OISW in water. To the OISW in the reactor was added a solution of the white liquor enough to produce a mixture with 5% consistency. The white liquor has a suflidity of 25% and effective alkaline of liquor is 20%.The temperature of reactor was increased gradually over 30 min to 160 ^{o}C. The pressure at this temperature was about 50 psi. The mixture was maintained under these conditions for about 2h. Then it was cooled to room temperature andthe produced pulp was collected and washed with plenty of water. The pulp was kept in plastic bags for further use. Yield was calculated by dividing the oven dried weight (OD weight) of the produced pulp by the original weight of the starting jeft(OD weight) and the percentage yield (after kraft pulping) was 39 %.

2.7.2 Large Scale Bleaching.

2.7.2.1 Sodium Hypochlorite Stage (H-stage):

The H-stage was performed in large reactor at 10% consistency. All the pulp collected from the experiment described in 2.3.1 section was placed in the large reactor and to it was added a solution sodium hypochlorite (5%). The suspension was heated at 45 ^{o}Cfor 2 hr. After the reaction time was over is finished, the pulp was washed with a plenty of water, and saved for the next stage.

2.7.2.2 Sodium Hydroxide with Hydrogen Peroxide Stage (E_p-Stage):

The E-stage was conducted in the large reactor at 10% consistency for 90 min at 70°C using an aqueous solution of sodium hydroxide (1%) and hydrogen peroxide (0.5%). After the reaction time was over, the produced pulp was washed with plenty of waterand the yield was calculated by dividing the treated bleaching pulp produced (OD weight) by the starting bleaching pulp (OD weight) and the pulp was saved for the next stage.

2.7.2.3 Hydrogen Peroxide Stage (P-Stage)

Olive pulp obtained from P-stage was placed in the large reactor and to it was added a solution of 2% H_2O_2 containing 0.5% $MgSO_4.7H_2O$, and 0.5% NaOH, at a 10% consistency at60°C for 120 min. After the reaction time was over, the pulp was washed with plenty of water. The yield was calculated by dividing the pulp produced (OD weight) by the weight of starting pulp

The results of bleaching are shown in Table 2.8, and analysis results are found in Table 2.9.

Table 2.8: Results of Large Scale Bleaching

Bleaching stage	Weight of pulp(g)	Percentage Yield (%)
H-stage	1755	92
Ep-stage	1614	94
P-stage	1517	97
H-stage	1472	82
P-stage	1207	89

Table 2.9: Result of Bleaching Sequence

Bleaching Sequence	Kappa Number	lignin Contents	Final Yield (%)	Density (g/mL)
HE_PPHP	3.46	0.519	61	0.514

2.8Extraction of Residual Materials from Cellulose

Bleached pulp was subjected to soxhlet extraction to determine type and amount of residual extractives. Cellulose (20 g dry) was loaded in a soxhlet extractor and subjected to extraction with chloroform (300 mL). The extraction was continued for about 4 hr. Then chloroform was evaporated, and the produced yellow residual material was weighed. Results are summarized in Table 2.10.

Table 2.10: Results of Soxhlet Extraction

Sample	Extracts (%)
5	0.252
6	0.51
Large scale pulp	0.302

2.9 Preparation of Carboxymethylcellulose (CMC)

The preparation of carboxymethylcellulose was carried out according to the procedure reported in the literature [50]. The reaction was carried out in a 1 L Pyrex reaction kettle. The reaction kettle was outfitted as follows: with a thermocouple inserted through a rubber septum, a Teflon bladed agitator on a glass shaft attached to a mechanical mixer, a gas inlet polyethylene tubing inserted through an adapter fitted with a rubber septum, and a gas outlet adapter connected to a gas trap partially filled with oil.A sample of the produced powder cellulose(10.0 g)was added to the reaction kettle and suspended in isopropyl alcohol (250 mL). The produced suspension was

mechanically agitated. To the suspension was added 30 ml of NaOH (15%) dropwise. The produced mixture was agitated at room temperature for one hour under N_2. Then 10.0 g of sodium chloroacetate suspended in an aqueous solution of isopropyl alcohol (85 wt%wt) was added in three portions to the reaction kettle contents. The mixture was heated at 70 ^oC for 2 hr under N_2.

Produced CMC was then filtered and washed three times with a solution of 80% isopropyl alcohol in water, and finally with pure methanol, then it was dried in an oven at 65 $^oC$to produce about 11.2 g of CMC in the NaCMC (95.5% yield, DS 0.50). Dried CMC was ground using Wiley mill by passing through a 20 mesh screen [11].

A sample of high purity was prepared by dissolving 2.0 g of the product in 75 mL water at room temperature. The resulting solution was centrifuged for 10 min at 6000 rpm and decanted to a beaker. CMC was then precipitated by addition of acetone (250 mL). The precipitated fraction was washed with water several time, dried and found to weigh 0.055 g (2.75 %). The CMC sample and the insoluble fraction were analyzed by FT-IR.

2.10 Degree of Substitution of Prepared Sodium Carboxymethyl Cellulose (Na-CMC):

Degree of substitution was determined according to ASTM D1439 standard method[51]. A sample of Na-CMC (2.0 g) was suspended in a 20 ml of 95 % ethanol for 15 min. Then to it was added 10% HCl (5.0 mL) to convert it into the acid form, the mixture was stirred at room temperature for about 30

minutes to ensure complete acidification. After that, it was centrifuged to remove liquid. The solid was washed with an aqueous methanol solution (80%) at least three times and finally with anhydrous methanol, each time the liquid was removed by centrifuge and decantation. The solid was dried in an oven at 105 ºC for 2 hours and kept in desiccators for about 30 min. About 0.5 g of dry acid CMC was weighed in an Erlenmeyer flask (250 ml), to it was added to 100 mL of distilled water and stirred. Then 0.3 M NaOH (25 ml) was added and the mixture was stirred at room temperature until a clear solution was obtained. The solution was then titrated with 0.3 M HCl. Phenolphthalein was used as an indicator. The titration was carried out in triplicate. The consumed volume of HCl used was recorded and used to determine DS of CMC.

2.11 Fourier Transform Infrared Spectroscopy (FTIR)

A small sample of the purified CMC shown in section 2.4.1 was placed in an oven at 80 ºC to remove residual moisture. About 0.2 mg of the sample was placed directly on the window of the Split Pea and its IR spectrum was generated.

2.12 Determination of CMC Viscosity.

A 2.0 % solution CMC was prepared in distilled water and its viscosity was determined using Brookfield viscometer using spindle No. 6 at 20rotation per min (RPM), the viscosity is 2500 centipoise.

Chapter Three

Results and Discussion

Jeft composition is similar to that of wood, it consists of four main components: extractives, cellulose, lignin and hemicellulose. The goal of this study is to extract cellulose from olive industry solid waste, this means optimization of the developed small scale process of extracting cellulose powder from OISW to increase product yields and to ensure consistent product quality then scale up the process into multi kilograms. The work shown in this thesis is a continuation of work carried out previously at our laboratories[3]. Another objective of this work is to develop a process for converting the extracted cellulose into the value added material carboxymethylcellulose (CMC).

3. Extraction of Cellulose from OISW

3.1 Analysis of OISW by SEM and X-ray

An image of OISW obtained by SEM at various magnifications are shown in Figure 3.1(A,B and C). The image reveals the presence of two morphology structures in OISW the major one which is porous and related to the olive pulp and minor one which is the hard part and related to the seeds. For this reason the pulping and bleaching stages used in this works are a milder version to those used in wood industry.

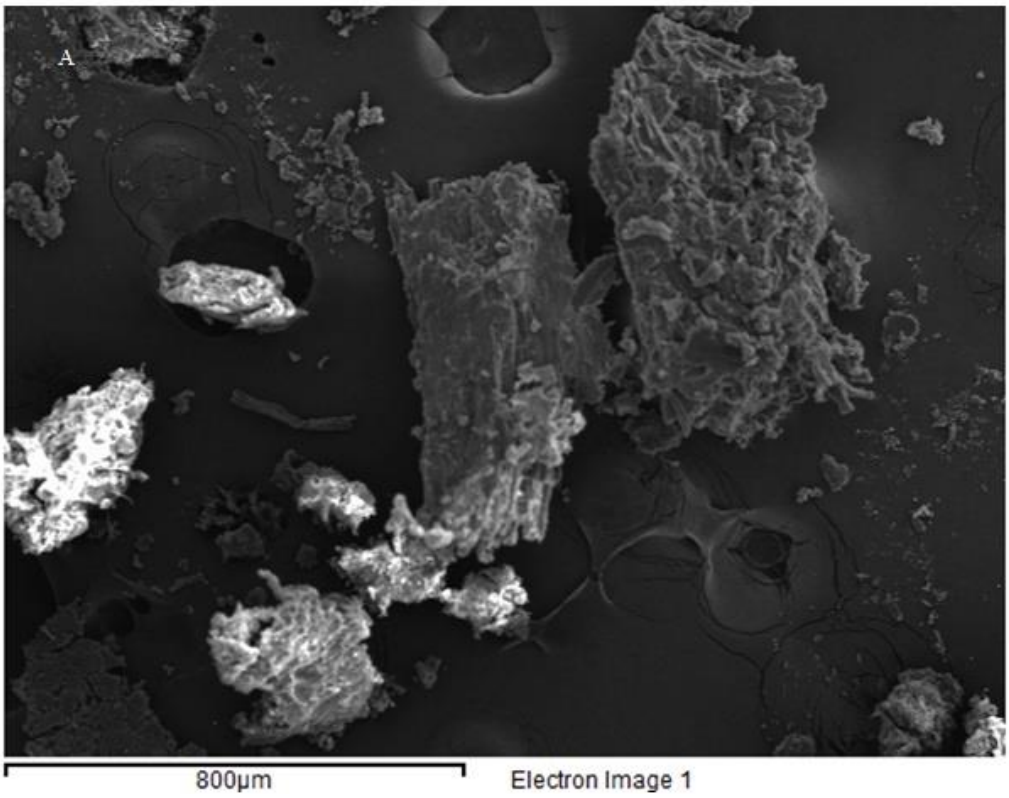


Figure 3.1(A): SEM Image of OISW at 250x.

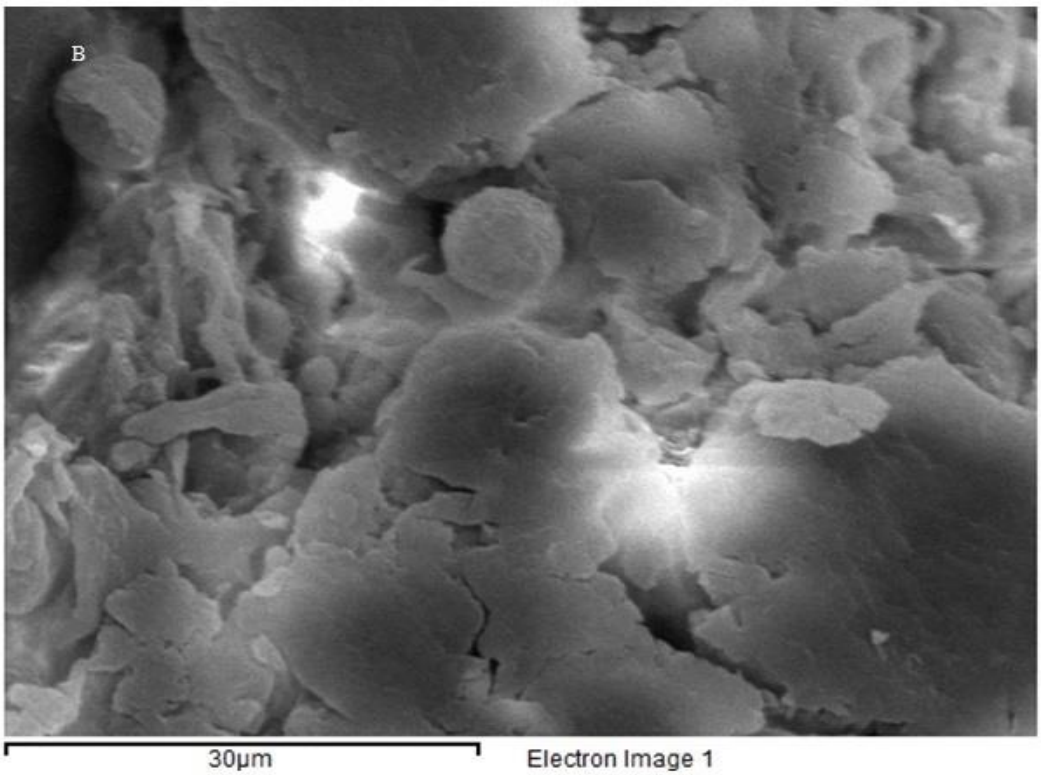


Figure 3.1(B): SEM Image of OISW at 5000x.

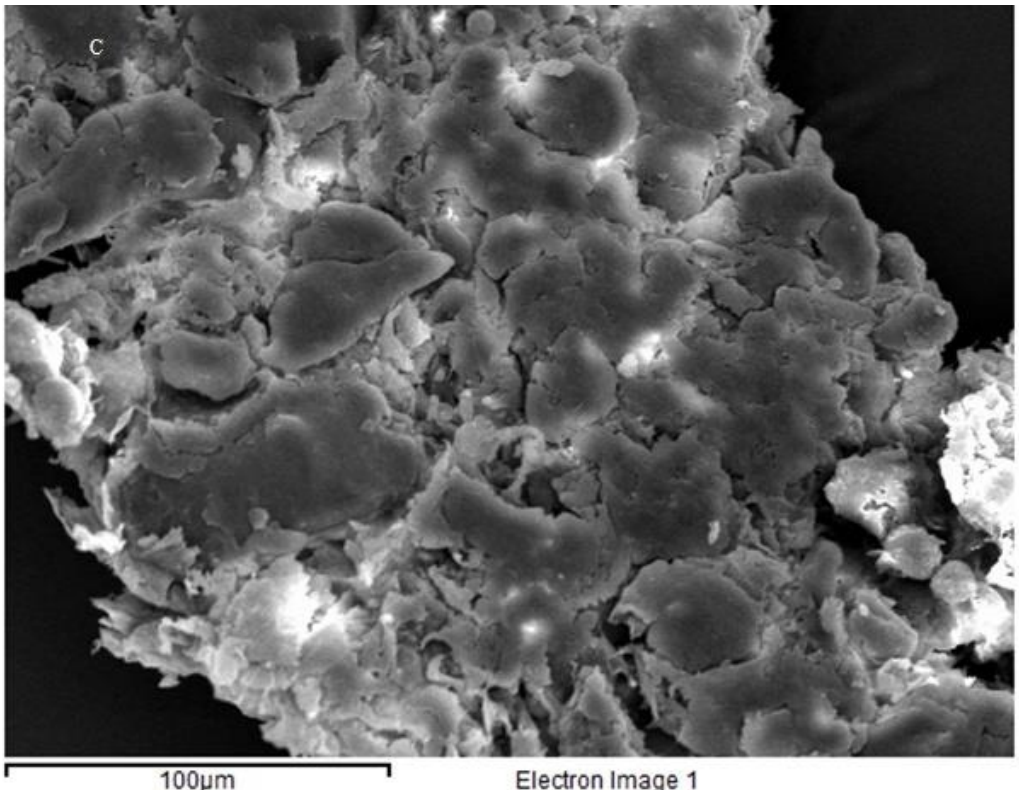


Figure 3.1(C): SEM Image of OISW at 1000x.

The x-ray analysis of OISW reveals the presence of several metals as shown in Figure 3.2(A and B). The metals are: Ca, K, Cu. Au is present due to sample coating which is performed in sample preparation for SEM.

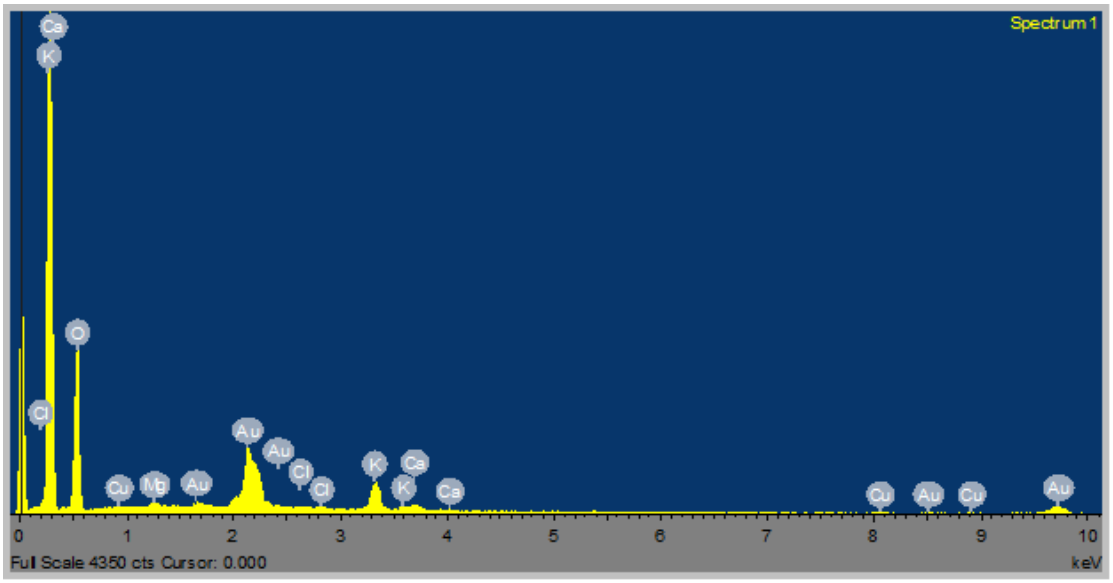


Figure 3.2(A): X-Ray Spectra of OISW

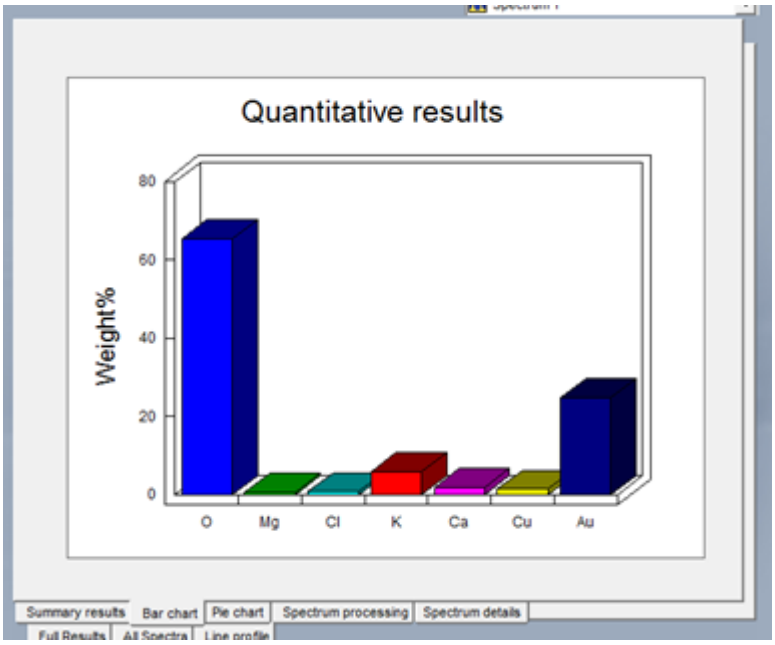


Figure 3.2(B): Metals Present in OISW

3.2 OISW Pre-Hydrolysis

A Pre-hydrolysis stage was first performed on OISW. The prehydrolysis was carried out in water with reflux under pressure. The purpose of this stage is to remove some of the hemicelluloses and lignin present in OISW. This treatment opens the cellulose structure and make it more accessible to pulping and bleaching reagents. This way less chemicals will be consumed on the later stages of extracting cellulose form OISW and more pure cellulose will be obtained. Several conditions and reagents were tested in this stage such as water, an aqueous diluted solution of acetic acid and an aqueous diluted solution of sodium hydroxide. Water was found to be good enough to obtain reasonable results. During the pre-hydrolysis acetic acid is generated through acetyl cleavage from the hemicellulose polymers [52]. Presence of acetic acid enhance the removal of lignin and hemicelluloses.

3.3 Pulping of Olive Industry Solid Waste

Pre-hydrolyzed Jeft was subjected to pulping process (Kraft pulping). In this step OISW was suspended in a solution of sodium hydroxide and sodium sulfide with various ratio and at 160°C and 50Psi in order to determine the best condition of the reaction which produce highest yield of cellulose with lowest k-number (low content of lignin) due to removal of large amount of lignin that become soluble in water.

The yield was calculated according to equation 3.1.

$$\%\ \text{yield} = \frac{\text{oven dry weight of produced pulp}}{\text{oven dry weight of raw material}} * 100\ \% \qquad \text{eq. 3.1}$$

In Table 3.1, shows the results of pulping OISW at various alkalinity and sulfidity conditions. The active alkaline term equals to the weight of Na_2S and NaOH in gram per liter of liquid and sulfidity term equal to[Na_2S/(NaOH+Na_2S)] in gram per liter of liquid. In this process, the white liquor was mixed with the jeft and heated at 155-160 ^oC for 2 hr under a pressure (50 psi).

Table 3.1: Results from Pulping of OISW at Various Conditions

Run	Weight of OISW (g)	Active Alkali(%)	Sulfidity (%)	Percentage Yield (%)
1	100	15	25	46
2	200	15	25	37
3	200	15	25	44
4	200	15	25	36

As shown in Table 3.1 the pulping experiment was repeated 4 times to confirm the reproducibility. Almost similar results were obtained from all experiment.

During the pulping process, lignin undergoes fragmentation into low molecular weight polymers which dissolve in the white liquor. At the end of the pulping stage the color of the white liquor turned to black, for this reason it is known as a black liquor. Cellulose produced from the pulping process usually has a light brown color due to the left over lignin. Some of the lignin is attached to the cellulose chain through covalent bond as shown in Figure 3.3. The pulp goes through a bleaching sequence to remove the residual lignin [5].

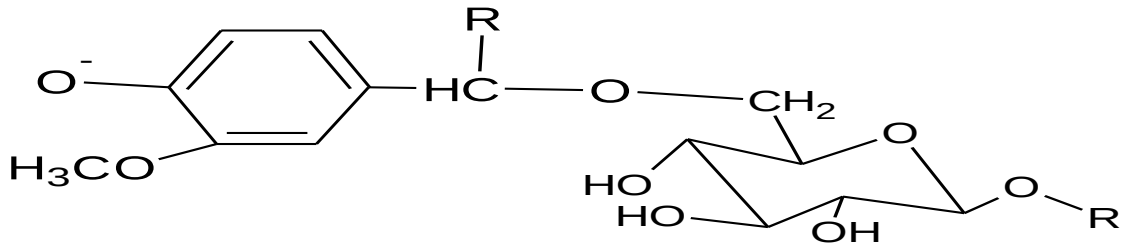


Figure 3.3: Residual Lignin attaching with Cellulose

3.4 Bleaching

As was mentioned earlier, after the completion of the Kraft pulping process the pulp color was brown due to residual lignin that is linked to pulp through covalent bond. In the bleaching process various types of oxidizing agents are used as bleaching agents in separate steps under suitable reaction conditions. The bleaching agents oxidize left over lignin that is attached to cellulose chain to produce white cellulose that is suitable for food and pharmaceutical applications.

In the bleaching process, the pulp were subjected to various bleaching sequences: HEpP, HPHEp, and H_tPH_tEp and these are summarized in Table 3.2.

Table 3.2: Bleaching Steps

Process Used	**Letter Designation**
Sodium hypochlorite	H
Sodium hydroxide and Hydrogen peroxide	Ep
Hydrogen peroxide	P
Sodium hypochlorite and triethyl amine	H_t

All bleaching stages were successively performed in sealed plastic bags in water bath with controlled heating and shaking. At the end of the bleaching stage, the pulp was collected by suction filtration, washed with thoroughly with water, andair dried. Yield and Kappa number were then determined, which is related to a mount of lignin remaining in the pulp after bleaching. A brief summary of individual stages is shown below:

In the H-stage, sodium hypochlorite solution (NaClO) was used asan oxidizing agent. It is broadly used in both potable water and waste treatment, and it is one of the most popular oxidizing agents.It has been widely used from the early history of fiber bleaching because this reagent is easy to prepare, handle and transport than gaseous chlorine.

Bleaching with sodium hypochlorite was usually is carried out at pH higher than nine, since at pH lower than 9,NaOCl turns to the acidic form (HOCl) which is not stable and causes de-polymerization of the cellulose chain [53]. The goal of this treatment is to produce pulp with high brightness and oxidize aromatic and alcohols of lignin to acid functional groups making lignin more soluble in bleaching solution as shown in figure 3.4.

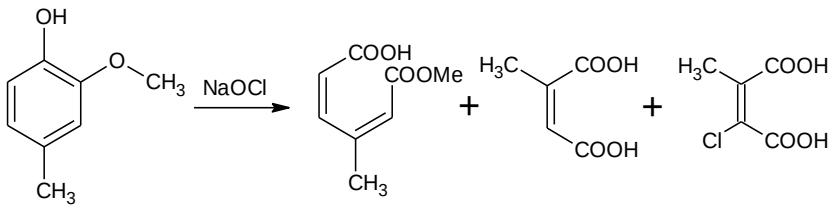


Figure 3.4: Oxidation of Lignin to Acid Functional Group

After the sodium hypochlorite stage pulp is treated with caustic soda containing low concentration of hydrogen peroxide,sodium hydroxide breaks the lignin-carbohydrate bond and converts oxidized lignin intoit's salt so it becomes soluble in water [54].

Hydrogen peroxide is commonly used in the mechanical pulping but in recent years it became an integral part of all totally chlorine free (TCF) chemical pulp bleaching sequences.

Hydrogen peroxide is highly selective, reacts rapidly with lignin and improves the brightness of pulp. In alkaline medium,it is hydrolyzed into hydrogen (H^+) and perhydroxyl ions (HOO^-) as shown in Equation3.2.

$$H_2O_2 + H_2O \rightarrow HOO^- + H_3O^+ \quad (Ka = 2 * 10^{-12}) \text{Eq} \qquad 3.2$$

The acid ionization constant of hydrogen peroxide is very low but it is a good bleaching material due to its strong oxidizing properties in a basic medium. At the same time, pH should not exceed 11 because at high pH perhydroxyl anion is unstable and decomposes. So hydrogen peroxide alone is relatively ineffective so it should be combined with NaOH at a pH below 11 [55].

A summary of Kappa number, bleaching sequence and lignin contents of cellulose samples treated with various bleaching sequences are presented in Table 3.3.

Table 3.3: Summary of the Analysis Results on Bleached Samples of Cellulose Extracted from OISW

Sample	Bleaching Sequence	Kappa Number	Lignin Content	Final Yield (%)
1	HEpP	4.21	0.63	77
2	H_tPH_tEp	3.03	0.45	64
3	H_tPH_tEp	5.54	0.83	80
4	H_tPH_tEp	4.83	0.72	75
5	HPHEp	2.98	0.45	74
6	H_tPH_tEp	5.59	0.84	52

As shown in Table 3.3, sample 5 was chosen for the analysis by various techniques, it was chosen because it has the lowest lignin content shown by its lowest K-number. The Kappa number is an indication of the residual lignin content or bleachability of wood pulp by a standardized analysis method. Low Kappa number means lower lignin content. It is determined using a T236 cm-85 standard method.

The bleaching sequence used to produce sample 5 was chosen for scaling up the process to about 5.0 kg of OISW. In the large scale process a 20 kg high pressure reactor shown in Figure 3.5was used. The result is shown in table 3.4.

Fig 3.5: The Large Scale Reactor Used to Pulp and Bleach 5.0 Kg of OISW

Table 3.4: Result of bleaching sequence

Bleaching Sequence	Kappa Number	lignin Contents	Final Yield (%)
HE_pPHP	3.46	0.519	61

From Table 3.4 as shown, the percent of lignin content is 0.519 which indicate that the produced pulp is almost free of lignin.

3.5 FT-IR of Cellulose Extracted from OISW Using Large Scale

FTIR of cellulose is shown in Fig 3.6. The spectrum shows a peak at 3293.09 cm^{-1} which corresponds to the OH-stretching vibration. The bands at 2895.17 cm^{-1}correspondsto the C–H stretching vibration, the band at 1427.05 cm^{-1}corresponds to the CH_2 bending vibration, the band at 1314.38 cm^{-1}correspondsto the C-O,C-H stretching, the band at 1159.62 cm^{-1}corresponds to the O-C-O,C-O stretching.

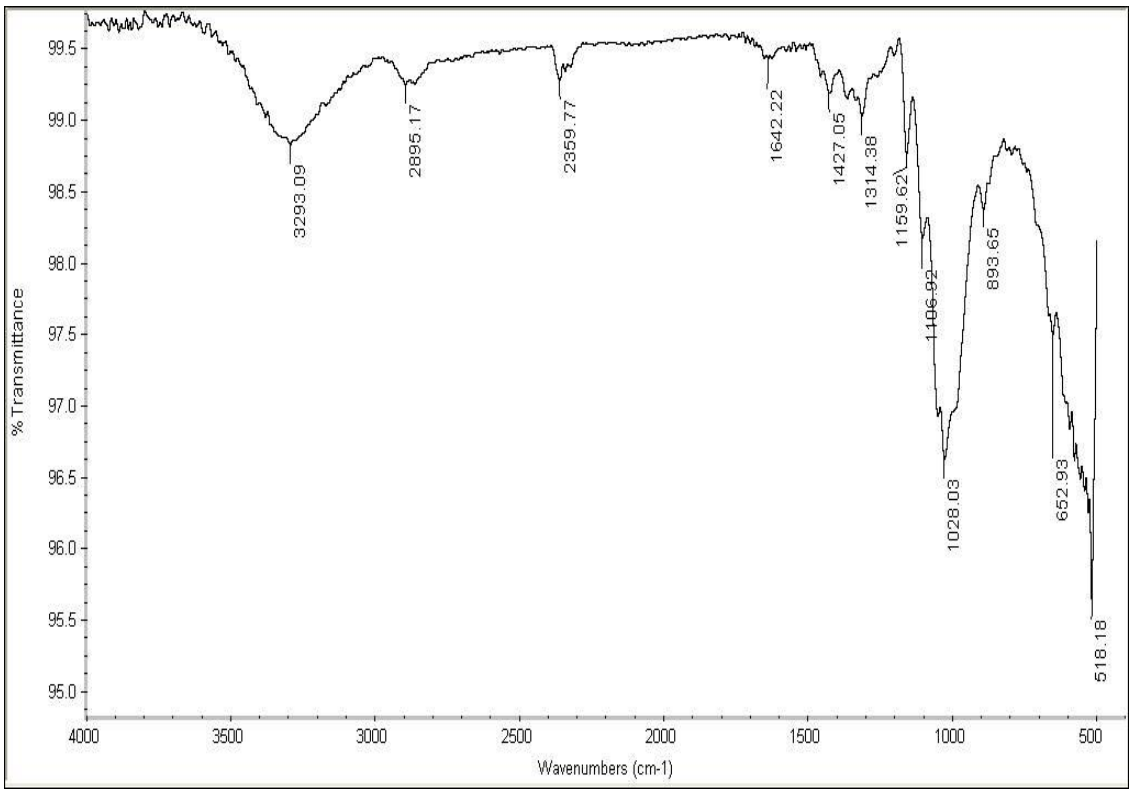


Figure 3.6: FT-IR of Cellulose Extracted from OISW

3.6 Soxhlet Extraction of Cellulose Obtained Using Large Scale from OISW

Soxhlet extraction was performed on raw cellulose obtained from OISW using chloroform solvent. Weight of obtained extractives was about 10 mg, so the percentage of extractives in the extracted cellulose is about 0.3 to 0.5%. This value is normal for bleached pulp.

3.7 Preparation of CMC

Carboxymethylcellulose is an important cellulose ether, it has large number of industrial applications. A sample of pulp produced from OISW was converted into CMC. The synthesis diagram of CMC is shown in Figure 3.7. A shown in Figure 3.7, synthesis of CMC is a one pot process that involves two steps, in the first step, cellulose is converted into alkaline cellulose by reacting it with NaOH in isopropyl alcohol. Then in the second step alkaline cellulose is converted into CMC by reacting it with sodium chloroacetate followed bya neutralization to pH of about 6.0.

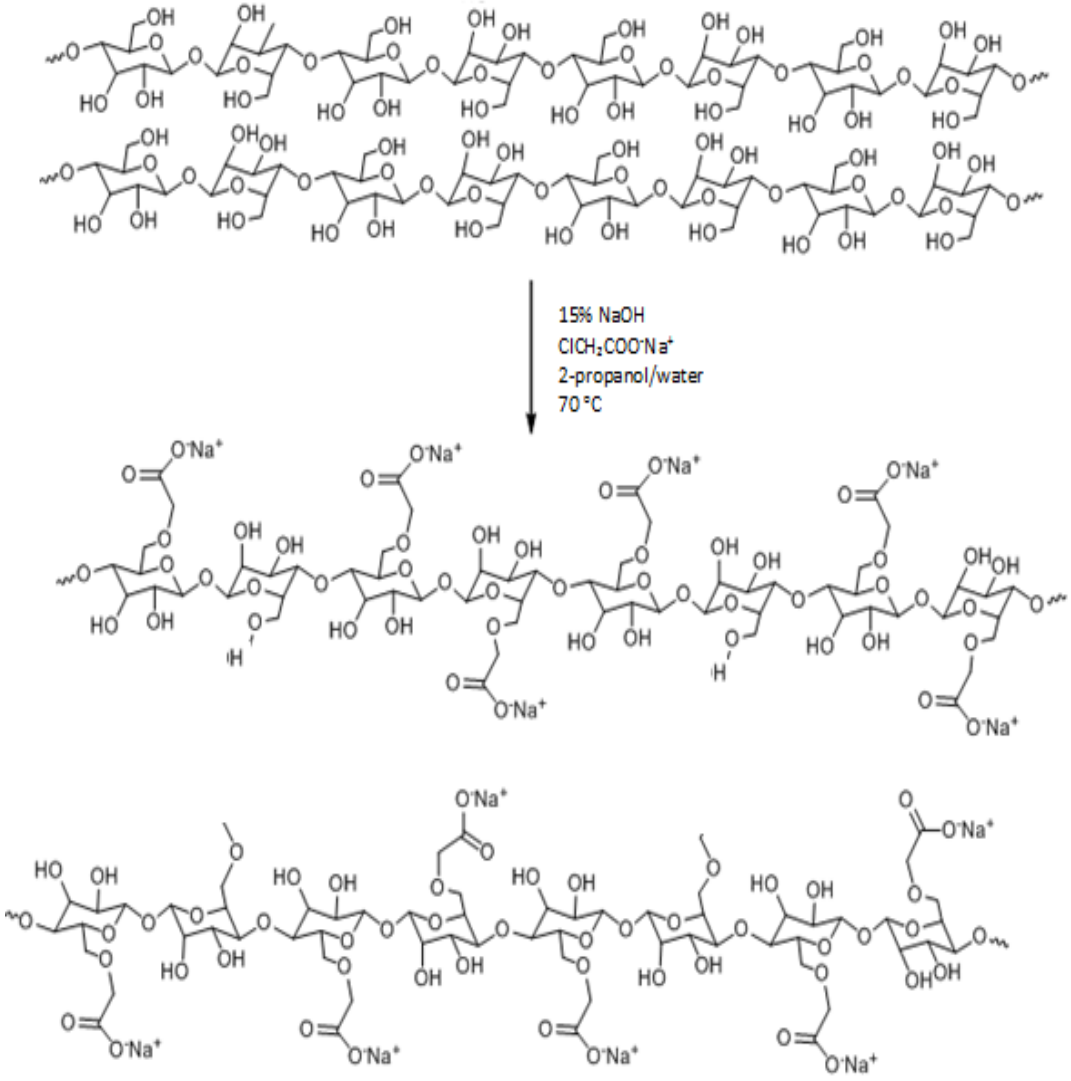


Figure 3.7: Synthetic Diagram for CMC from OISW

3.7.1 Reaction Mechanism for the Preparation of CMC

The reaction mechanism for the formation of CMC is shown in Fig 3.8

As shown in Fig 3.8, sodium hydroxide abstracts protons from the hydroxyl groups of the anhydroglucose repeating units to form alkali cellulose, which then undergoes S_N2 reaction with the sodium monochloroacetate (NaMCA) to form, after protonation, CMC [56].

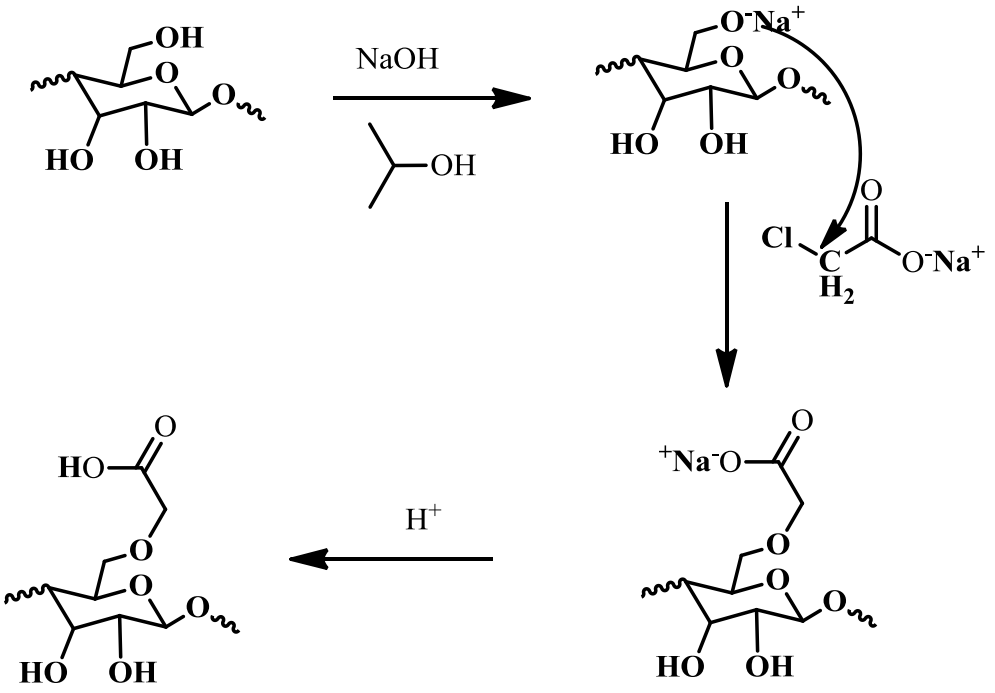


Fig 3.8: Reaction Mechanism for Forming CMC from Cellulose

3.7.2 FT-IR of CMC

FTIR of prepared CMC is shown in Fig 3.9. Also in Figure 3.9.The FT-IR of CMC control from Aldrich in shown. The spectrum shows a peak at 3400 cm^{-1}which is corresponds to O-H stretching. The bands at 1610–1650 cm^{-1} which is corresponds to the carbonyl (C=O) stretching vibration of the carboxyl, C=O group. The bands at about 1430 – 1440 cm^{-1} and 1327 cm^{-1} could be attributed to CH_2 and OH bending vibration, The band at 1152 – 1173 cm^{-1} corresponding to C-O ring band and C-O-C glycosidic ether band showed at 1072 – 1130 cm^{-1} arises from the polysaccharide components was observed in all the spectra (Garside and Wyeth, 2003). In addition, the peak at 996 – 1050 cm^{-1} corresponding to the C-O-C of the

pyranose ring stretching vibration. The 892 – 936 cm^{-1} peak is related to the β-(1,4)-glycosidic linkages between the glucose units in cellulose [57].

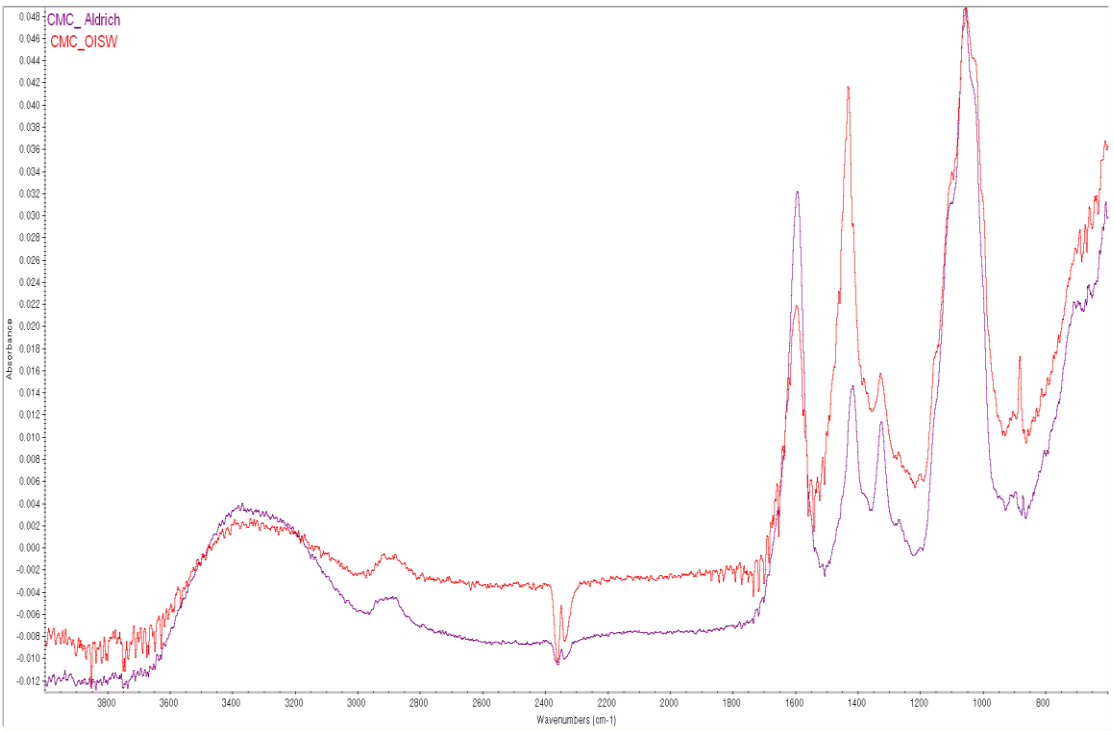


Figure 3.9: FT-IR of CMC from OISW and Control CMC from Aldrich

3.7.3 Degree of substitution of CMC

The degree of substitution of carboxyl group in CMC was determined by titration of known concentration of CMC with sodium hydroxide as shown in the experimental part. Degree of substitution was calculated according to equations 3.3 and 3.4

Carboxyl content (meq/kg) = [meq of NaOH ($V_{NaOH}XN_{NaOH}$) – meq of HCl ($V_{HCl}XN_{HCl}$)] x 1000 (g/kg)/ wt. of CMC (g). Eq. 3.3

Degree of Substitution DS = [Carboxyl content (meq/kg) X 162 (MW of anhydroglucose repeat unit)]/ 1 X 10^6 Eq. 3.4

Degree of substitution was shown to be proportional to amount of sodium chloroacetate and amount of sodium hydroxide used. The results are shown in Table 3.5.

Table 3.5: Degree of Substitution of Prepared CMC as a Function of Amount of Sodium Hydroxide Used.

Sample No.	NaOH* (%)	Weight of NaOH (g)/g gram of cellulose extracted from cellulose	DS/ anhydroglucose unit
1	13	3.0	0.45
2	18	3.0	0.52
3	25	3.0	0.57
4	28	3.0	0.54

*During the process of making CMC, for every gram of cellulose 3.0 g of 13% NaOH or 18% or 25% or 28%NaOH were used to study the effect of NaOH concentration on degree of substitution.

Conclusions

1. Jeft is an important source of cellulose.
2. Cellulose extracted from jeft proved to be identical with commercial cellulose.
3. 3-The pulping lab scale process developed from small scale to large scale (5 kilograms).
4. The percentage of extractives in the extracted cellulose is less than 0.5% and this value is normal for bleached pulp.
5. Extracted cellulose was successfully converted to carboxymethylcellulose with a degree of substitution ranging from DS=0.45-0.57. Degree of substitution could be controlled by varying the amount of sodium hydroxide used.

References

1- **Verbal information from Palestinian Ministry of Agriculture**, October 2010.

2- Salman, M.; Hawamda1, A. ; Amarnii, A.A.; Rahil1, M. ; Hajjeh1, H.; Natsheh1, B. ; Abuamsha R. ***Evaluation of the Incidence and Severity of Olive Leaf Spot Caused by Spilocaeaoleaginaon Olive Trees in Palestine***.**American Journal of Plant Sciences**, 2, 457-460, 2011.

3- Hamed, O. A.;Fouad,Y.; Hamed, E. M.; Al-Hajj, N. ***Cellulose Powder from Olive Industry Solid Waste***. **Bioresources**, 7, 4190-4201, 2012**.**

4- Pettersen, R.C. ***The Chemical Composition of Wood. The Chemistry of Solid Wood. Rowell Rager M. Advances in Chemistry Series 207***. Washington, DC: **American Chemical Society**, 57–126, 1984.

5- Vitz.J.;Erdmenger.T.;Haensch.C.;Schubert,U.S. ***Extendeddissolution studies of cellulose in imidazolium based ionic liquids***. **Green Chemistry**,11, 417-424, 2009.

6- Moon, R.J.; Martini, A.;Nairn, J.;Simonsen, J.; Youngblood, J.Cellulose nanomaterials review: ***structure, properties andnanocomposites.*** **Royal Society of Chemistry Journal**, 40, 3941-3994, 2011.

7- Poletto, M.;Pistor, v.;Zattera, A. J. ***Structural Characteristics and Thermal Properties of Native Cellulose.Cellulose-Fundamental Aspects***.**Theo van de Ven and Louis Godbout.InTech,** 45-68, 2013.

8- Alhaj, N.R.A. Synthesis of Specialty Polymer from Cellulose Extracted from Olive Industry Solid Waste. An-Najah National University, Palestine, 2013.

9- Varshney, V. K.; Naithani, S. Chemical Functionalization of Cellulose Derived from Nonconventional Sources. Cellulose Fibers: Bio- and Nano-Polymer Composites.SusheelKalia, B. S. Kaith, InderjeetKaur. Springer Berlin Heidelberg, 43-60, 2011.

10- Sharada, R.; Venkateswarlu, G.; Venkateswar, S.; AnandRao, M. Applications of Cellulases-Review. International Journal of Pharmaceutical, Chemical and Biological Sciences. 4, 424-437, 2014.

11- Ambjornsson, H.a.; Schenzel,K.; Germgard,U. Carboxymethyl Cellulose Produced at Different Mercerization Conditions and Characterized by NIR FT Raman Spectroscopy in Combination With Multivariate Analytical Methods.Bioresources, 8, 1918-1932, 2013.

12- Davis, M; Baker, J; Rignall, T; Himmel, M. Changes In Cellulose Morphology of Pretreated Yellow Poplar During Enzymatic Hydrolysis, NationalBioenergy Center, National Renewable Energy Laboratory.

13- Shokri, J.; Adibkia, K. Application of Cellulose and Cellulose Derivatives in Pharmaceutical Industries. Cellulose-Medical, Pharmaceutical and Electronic Applications.Theo Van de Ven and Louis Godbout.InTech, 47-66, 2013.

14- Baumgartner, S.; Kristl, J.; Peppas, N.A. Network Structure of Cellulose Ethers Used in Pharmaceutical Applications during Swelling

and at Equilibrium. Plenum Publishing Corporation, 19, 1084-1090, 2002.

15- Pérez,S.;Mackie,W.Cellulose. https://en.wikipedia.org/wiki/Cellulose.

16- Bodvik, R. Bulk and interfacial properties of cellulose ethers. Royal Institute of Technology, Sweden, 2012.

17- Marques-Marinho, F.D.; Vianna-Soares, C.D. Cellulose and It's Derivatives Use in the Pharmaceutical Compounding Practice. Cellulose-Medical, Pharmaceutical and Electronic Applications.Theo Van de Ven and Louis Godbout.InTech, 141-162, 2013.

18- Elidrissi, A.; El barkany, S.; Amhamdi,H.; Maaroufi, A. Elaboration of the new cellulose derivative films (HECA) based on "Stipa Tenacissima" cellulose of Eastern Morocco.Journal of Materials and Environmental Science.Morocco, 1, 197-204, 2010.

19- Nacheva, I.; Georgieva, L.; Tsvetkov, Ts. Possibilities for Application of Cellulose Derivatives under Cryoconservation of Probiotics. Bulgarian Journal of Agricultural Science, 13,153-159, 2007.

20- AbdManaf, M.E,; Tsuji, M.; Nobukawa, Sh.; Yamaguchi, M. Effect of Moisture on the Orientation Birefringence of Cellulose Esters. Polymers, 3, 955-966, 2011.

21- Djuned, F.M.; Asad, M.; Ibrahim, M.N.M.; Dand, W.R.W. Synthesis and Characterization of Cellulose Acetate from TCF Oil Palm Empty Fruit Bunch Pulp. Bioresources, 9, 4710-4721, 2014.

22- Barkalow, D. G.; Rowell, R. M.;. Young, A.A. New Approach for the Production of Cellulose Acetate: Acetylation of Mechanical Pulp with

Subsequent Isolation of Cellulose Acetate by Differential Solubility. Journal of Applied Polymer Science, 37, 1009-1018, 1989.

23- Koschella, A.; Dorn, S.; Heinze, T.; Togola, A.; Paulsen, B.S. Synthesis and characterization of branched polysaccharides by reaction of cellulose with 2,3,4,6-tetraacetyl-1-bromo-α Dglucopyranoside. Arkivoc USA, 76-89, 2012.

24- Gopiraman, M.; Fujimori, K.; Zeeshan, K.; Kim, B. S.; Kim, I. S. Structural and Mechanical properties of Cellulose Acetate/Graphene Hybrid Nanofibers: Spectroscopic Investigations. EXPRESS Polymer Letters Journal, 7, 554–563, 2013.

25- Li Loo, M.M.; Hashim, R.; Leh, C.P. Recycling Of Valueless Paper Dust To A Low Grade Cellulose Acetate: Effect Of Pretreatments On Acytylation. Bioresources, 7, 1068-1083, 2012.

26- Biswas, A.; Saha, B.C.; Lawton , J.W.; Shogren , R.L.; Willett, J.L. Process for obtaining Cellulose Acetate from Agricultural by-products.Carbohydrate Polymers Journal, 64, 134–137, 2006.

27- Springate, M.E. Cellulose Nitrate Plastic (Celluloid) in Archaeological Assemblages: Identification and Care. Northeast Historical Archaeology,26, 63-72, 1997.

28- Fowler, Andrew H. K. Some aspects of the Surface and Bulk Chemistry of Cellulose Nitrates as studied by ESCA and other Spectroscopic TechniquesThesis. Durham University, England, 1984.

29- Liang Su, T.; Christodoulatos, C.Destruction Of Nitrocellulose Using Alkaline Hydrolysis. Defense Technical Information Center Compilation Part Notice, 73, 337-343,1996.

30- Adekunle, I.M. Production of Cellulose Nitrate Polymer from Sawdust.E-Journal of Chemistry, 7, 709-716, 2010.

31- Meyer, K.; Shirley, A.M.; Cusumano, J.C.; Bell-Lelong, D.A.; Chapple,C. Lignin monomer composition is determined by the expression of a cytochrome P450-dependent monooxygenase in Arabidopsis. Proceedings of the National Academy of Sciences, 95, 6619–6623, 1998.

32- Salameh, Y.F.A. Methods Of Extracting Cellulosic Material From Olive Pulp. An-Najah National University, Palestine, 2009.

33- Nascimento, M.S.; Santana, A.L.B.D.; Maranhao, C.A.; Oliveira, L.S.; Bieber, L. Phenolic Extractives and Natural Resistance of Wood. Biodegradation-Life of Science.Chamy, R.; Rosenkranz, F, 349-370, 2013.

34- Sun, R.C. Detoxification And Separation Of Lignocellulosic Biomass Prior To Fermentation For Bioethanol Production By Removal Of Lignin And Hemicellulose. Bioresources,4, 452-455, 2008.

35- Kirker, G.T.; Blodgett, A.B.; Arango, R.A; Lebow, P.K.; Clausen, C.A. The role of extractives in naturally durable wood species.International Biodeterioration& Biodegradation, 82, 53-58, 2013.

36- Chauhan, Y.P.; Sapkal, R. S.; Sapkal, V. S.; Zamre, G. S. Microcrystalline Cellulose From Cotton Rags (Waste From Garment And Hosiery Industries). International Journal OfChemical Sciences, 7, 681-688, 2009.

37- Kopania, E.; Wietecha, J.; Ciechańska, D. Studies on Isolation of Cellulose Fibres from Waste Plant Biomass.InstituteBiopolymers and Chemical Fibres, 20, 167-172, 2012.

38- Zhang,H. Process Modeling in Pulping Process. Saimaa University of Applied SciencesThesis.Eastern Finland,Imatra, 2010

39- Jahan, M.S.; Ahsan, L.; Noori, A.; Quaiyyum, M. A. Process For The Production of Dissolving Pulp From TremaOrientalis (Nalita) By Prehydrolysis Kraft And Soda-Ethylenediamine (Eda) Process. Bioresources, 3, 816-828, 2008.

40- Hubbard, C. R.; Peascoe, R. A.; Keiser, J. R.Pulp And Paper Plant Materials Issues Addressed By X-Ray And Neutron Diffraction Methods. JCPDS-International Centre for Diffraction Data, 46, 278-284, 2003.

41- Jahan, M.S.;Rawsan, S.;Chowdhury, D.A.N.; Al-Maruf, A. Alternative Pulping Process For Producing Dissolving Pulp From Jute. Bioresources, 3, 1359-1370, 2008.

42- Shahzad, M.A. Effect of Temperature and Time on Acid Sulfite Cooking for Dissolving PulpThesis. Karlstad Universit, Sweden, 2012.

43- Reme, P.H. Some Effects Of Wood Characteristics And The Pulping Process On Mechanical Pulp Fibres Thesis. Norwegian University of Science and Technology.Trondheim, Norway, 2000.

44- Taylor, J.H.; Akida, K.M. Indirect Adaptive Model Predictive Control Of AMechanical Pulp Bleaching Process. 9th IASTED International Conference on Control and Applications, 3, 163-168, 2015.

45- UYSAL, B.; AyhanOzifci, M.A. The Effects of Wood Bleaching Chemicals on the Bending Strength of Wood.Turkish Journal Of Agriculture And Forestry, 23, 615-619, 1999.

46- Kristiansson, L. Chemical Bleaching Of Wood And Its Aging. Linköping University, Sweden, 2012.

47- TappiTest Method, T 210 cm-03, Tappi Press.Sampling and testing woodpulp shipments for moisture, 2003.

48- ISO Standards Handbook: Paper, board and Pulps.ISO 5351 1:1981, 1, (2003).

49- Tappi Test Method, T 236 cm-85, Tappi Press.Pulp Properties Committee of the Process and Product Quality, 1996.

50- Bhattacharyya, D.; Singhal, R.S.; Kulkarni, P.R. A Comparative Account of Conditions for Synthesis of Sodium CarboxymethylStarch from Corn and Amaranth Starc.Carbohydrate Polymer, 27, 247–253, 1995.

51- Analytical method for determining degree of substitution in the product (A.S.T. M. Method).Document CK-G06, D-1439-03, 2005.

52- Tappi. Atlanta. 1994. Glasenapp.A..O. Kordsachia. J. Odermatt.and R. Patt. Das Papier (50(6):300). 1996.Glasner. A. Proc. Tappi Pulping Conf. Book 2.p. 681.

53- Koda, K. Effect of Oxidative Reactions on the Lignin Degradation and Delignification during Chlorine Bleaching of Kraft Pulp Thesis. Hokkaido University, JAPAN, 2000.

54- Andelin, J. Pulp Bleaching Technology. Technologies for reducing dioxin in the manufacture of bleached wood pulp. Congress of the U.S., Office of Technology Assessment, 41-52, 1989.

55- Jae Lee, W. Oxidation Of Sugarcane Bagasse Using ACombination Of Hypochlorite And Peroxide Thesis.LouisianaState University and Agricultural and Mechanical College, United States,2005.

56- Stigsson, V.; Kloow, G.; Germgard, U. An Historical Overview Of Carboxymethyl Cellulose (CMC) production on an industrial scale.Paper Asia, 17, 16-21, 2001.

57- Viera, R.G.P.; Filho, G.R.;Assuncao, R.M.N.; Meireles, C.S.; Vieira, J.G. and Oliveira, G.S. Synthesis and characterization of Methylcellulose from Sugar cane Bagasse Cellulose. Carbohydrate Polymer, 67, 182-189, 2007 .

جامعة النجاح الوطنية
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تحسين ورفع مستوى عملية اخراج السيليولوز من مخلفات الزيتون الصلبة(الجفت)

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شذى فايز رضا ذياب

إشراف
أ.د.شحدة جودة
د.عثمان حامد

قدمت هذه الأطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في الكيمياء بكلية الدراسات العليا في جامعة النجاح الوطنية، نابلس- فلسطين.

2015

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الملخص

الجفت هو الجزء المتبقي من حبات الزيتون بعد عصرها، حيث يتكون من بذور الخشب وألياف اللب. الجفت يتكون من السيليولوز وشبه السيليولوز والليجنين ومركباتأخرى.

تم في هذه الدراسة إستخلاص السيليولوز من الجفت في عملية تتكون من عدة خطوات ومراحل.تبدأ العملية بمرحلة غسل السيليولوز التي تعمل على فتح هيكل الجفت وتجعلها أكثر قابلية للمواد الكيميائية، أيضا في هذه المرحلة معظم مواد شبه السيليولوز الموجودة في الجفت تتحلل وتذوب في الماء. في مرحلة غسيل السيليولوز تمت تجربة عدة مواد لكن معاملة الجفت مع الماء لوحده كانت أكثر جدوى. ومن ثم جرى تعريض الجفت لعملية Pulpin باستخدام محلول من كبريتيد الصوديوم وهيدروكسيد الصوديوم. في مرحلة Pulping معظم الليجنين يتحلل ويختفي. و اللب الناتج يتم تعريضه لعملية التبييض لإزالة المواد الملونة المتبقية. أفضل وأحسن سلسلة تبييض كانت H_tPH_tEp. نسبة السيليولوز المستخلصة كانت 30%. ومن ثم تم رفع كمية الجفت إلى 5 كغم باستخدام مفاعل له قدرة على حمل 20 كغم. كمية السيليولوز التي تم الحصول عليها 1,2 كغم أي ما تعادل نسبة 24%. و تم تحليل السيليولوز باستخدام تقنيات تحليلية وطيفية مختلفة: K-number، IV، Extraction، SEM،FT-IR.

تم بنجاح تحويل السيليولوز إلى كربوكسي ميثيل سيليولوز وذلك عن طريق تفاعل هيدروكسيد الصوديوم مع حمض الكلورواسيتيك. ويعد كربوكسي ميثيل سيليولوز أهم سيليولوز إيثري، له مجال واسع في التطبيقات الصناعية التي تشمل مواد التجميل، الغذاء، المنظفات، دهانات وصناعات أخرى.تم تحليل هذا المشتق باستخدام FT-IR وإيجاد درجة الاستبدال.

وأهم نتائج هذا العمل:

1- العمل على رفع عملية الإستخلاص إلى كيلوغرامات.

2- تم تحويل السيليولوز المستخلص بنجاح إلى السيليولوز الإيثري(كربوكسي ميثيل سيليولوز).