

Sudan University of Science and Technology



College of Science



Department of Scientific Laboratories – Chemistry

Isolation of Cellulose from Different Sources

عزل السيليلوز من مصادر مختلفة

**Thesis submitted in Partial Fulfillment of the Requirements for
The award of the Degree of honour B.Sc in Chemistry**

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

قال تعالى:

{وَهُوَ الَّذِي أَنْزَلَ مِنَ السَّمَاءِ مَاءً فَأَخْرَجْنَا بِهِ نَبَاتَ كُلِّ شَيْءٍ
فَأَخْرَجْنَا مِنْهُ خَضِرًا نُخْرِجُ مِنْهُ حَبًّا مُتَرَاكِبًا وَمِنَ النَّخْلِ مِنَ طَلْعِهَا
قِنَوَانٌ دَانِيَةٌ وَجَنَّاتٍ مِنْ أَعْنَابٍ وَالزَّيْتُونَ وَالرُّمَّانَ مُشْتَبِهًا وَغَيْرَ
مُتَشَابِهٍ انظُرُوا إِلَى ثَمَرِهِ إِذَا أَثْمَرَ وَيَنْعِهِ إِنَّ فِي ذَلِكَ لَآيَاتٍ لِقَوْمٍ
يُؤْمِنُونَ }

صدق الله العظيم

سوره الانعام الايه (99)

Dedication

To our mother ..

To our father ..

To our colleagues and every one who helped us on this research .

ACKNOWLEDGEMENT

First and foremost, We wholeheartedly acknowledged GOD ALMIGHTY for making it possible for us to complete this project and for showering upon us HIS boundless grace, mercy and wisdom during our studies at Sudan University of Science and Technology .We would like to express our sincere appreciation to our research supervisor, Dr Dalia Mohammed Osman , for her consistent encouragement, guidance and support to carry out and complete this project, and for giving us an opportunity to work on this project. We consider it a great privilege to have been her students, and We would like to take this opportunity to offer our deepest gratitude for everything she has done for us and We wish her all the best in the coming years. We would like to thank all who help or guide us to complete this research

Abstract

This study is about isolating Cellulose from different sources and converting the isolated cellulose to its derivatives and analyze it. Cellulose was isolated from residue of tea fibers, palm leaf and newspaper by using sodium hydroxide solution (1M). And the isolation percentage was (9%, 16.16% and 33% respectively). Then the isolated cellulose was identified qualitatively by simple chemical test that used to identify carbohydrates as Tollen's test and Fehling's test, results was positive for the two tests. The isolated cellulose was converted to cellulose derivatives (Cellulose acetate – Cellulose nitrate). The isolated cellulose and its derivatives were analyzed by using infra-red spectroscopy the spectrum of the extracted cellulose from the three sources showed the same results: the presence of (O-H), (C-O) , (CH Aliphatic) and (C-C) .

The spectrum of Cellulose acetate show the presence of (O-H), (C-O), (C-H Aliphatic) and (C-C).

The spectrum of Cellulose nitrate show the presence of (O-H), (C-O), (CH Aliphatic) in two different area, and (R-O-NO₂)

The importance of the research is in isolating Cellulose from sources that considered useless and convert the isolated cellulose to its derivatives and synthesis of bio-plastics which is bio-degradable without effecting the environment

مستخلص البحث

هذا البحث يختص بعزل السليلوز من عدة مصادر ثم تحليله كيميائياً و طيفياً باستخدام الأشعة تحت الحمراء و تكوين وتحليل مشتقاته.

حيث تم عزل السليلوز من متبقي ألياف الشاي ، سعف النخيل وورق الصحف باستخدام محلول هيدروكسيد الصوديوم بتركيز (1M) . و كانت نسب الاستخلاص 9%، 16.16%، 33% على التوالي . ثم تم التعرف عليه وتشخيصه بالتحاليل النوعية المستخدمة في تشخيص الكربوهيدرات مثل اختبار تولن و اختبار فهلنج حيث كانت النتائج ايجابية للاختبارين و تم تحضير مشتقات من السليلوز المعزول (خلات سليلوز و نترات سليلوز) حُلل السليلوز المعزول و مشتقاته باستخدام التحاليل الطيفية بالأشعة تحت الحمراء حيث أوضح طيف السليلوز المعزول من الثلاث مصادر نفس النتائج و هي وجود زمرة الكحول ، (C-H) الاليفاتيه، (C-C) و (C-O) .

أما بالنسبة لطيف خلات السليلوز أظهر زمرة الكحول ، (C-H) الاليفاتيه ، (C-O) و (C-C) . و طيف نترات السليلوز أظهر زمرة الكحول ، (C-H) الاليفاتيه في مديين مختلفين، (C-O) و (R-O-NO₂) .

و تكمن أهمية البحث في عزل السليلوز من مصادر مهدرة و ذلك بغرض تخليق بلاستيك حيوي يتحلل طبيعياً دون أن يؤثر على البيئة .

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Chapter One

1- Introduction

1-Intorduction

1.1-Natural products:

A chemical substance produced by a living organism; a term used commonly in reference to chemical substances found in nature that sometimes have distinctive pharmacological effects. The term natural product has also been extended for commercial purposes to refer to cosmetics , dietary supplements , and foods produced from natural sources without added artificial ingredients . Natural products may be extracted from the cells , tissues and secretions of microorganisms , plants and animals^[1].

Three major categories can be used to divide natural compounds. In the first category there are those compounds which are present in all cells of the organisms and play a central role in the metabolism and reproduction in them. They are called primary metabolites. Nucleic acids, common amino acids and sugars are included in them. In the second category there are polymeric materials with high molecular weights such as lignins, cellulose and proteins made up of cellular structures. In the third category there are those compounds which may be present in smaller amounts. They are called secondary metabolites^[2].

Main Classes of Natural Products:

- Carbohydrates.
- Lipids.
- Proteins.
- Nucleic Acids^[1].

The choice of isolation procedure to isolate natural products depends on the nature of the source material and the compounds to be isolated. Prior to choosing a method, it is necessary to establish the target of the extraction. Some of the used extraction method : Maceration, Boiling,

Soxhlet, Supercritical fluid extraction, Sublimation and Steam distillation^[3].

1.2-Carbohydrates:

Carbohydrates are a major class of naturally occurring organic compounds, which come by their name because they usually have, or approximate, the general formula $C_n(H_2O)_m$ with n equal to or greater than three. Among the well-known carbohydrates are various sugars, starches, and cellulose, all of which are important for the maintenance of life in both plants and animals. Carbohydrates are defined as aldehydic or ketonic compounds with some number of hydroxyl groups^[4,5].

1.2.1-Classification of Carbohydrates :

On the basis of the number of forming units three major classes of carbohydrates can be defined :

- Mono saccharides are formed by only one polyhydroxyaldehydic or ketonic unit (glucose - fructose)^[5].
- Di saccharide or oligosaccharide are formed by short chain of mono saccharidic units (from 2 to 20 units) linked one to the next by glycosidic bonds (lactose - sucrose)^[5].
- Polysaccharide are polymers consisting of (20 to 10^7) monosaccharidic units ; they differ each other for the monosaccharides recurring in the structure, for the length and the degree of branching of chain or for the type of links between units (starch - cellulose)^[5].

1.2.2-Physical properties of Carbohydrates:

The physical properties of carbohydrates depend primarily on their micro-saccharide composition, glycosidic linkage, functional groups present, molecular size and branching. In addition chemical modification of the carbohydrate structure, such as functional group protection, can result in marked changes in the physical properties of these molecules^[6].

High crystalline polysaccharides like cellulose and highly branched or cross linked polymers such as starch are often insoluble in aqueous solvents . There are few organic solvents that can dissolve these unmodified carbohydrates^[6].

1.2.3-Chemical properties of Carbohydrates:

The chemical properties of carbohydrates depend on the monosaccharide residues present, the linkage positions and configurations . The most common reactions of carbohydrates are: hydrolysis , oxidation/reduction and complexation^[6].

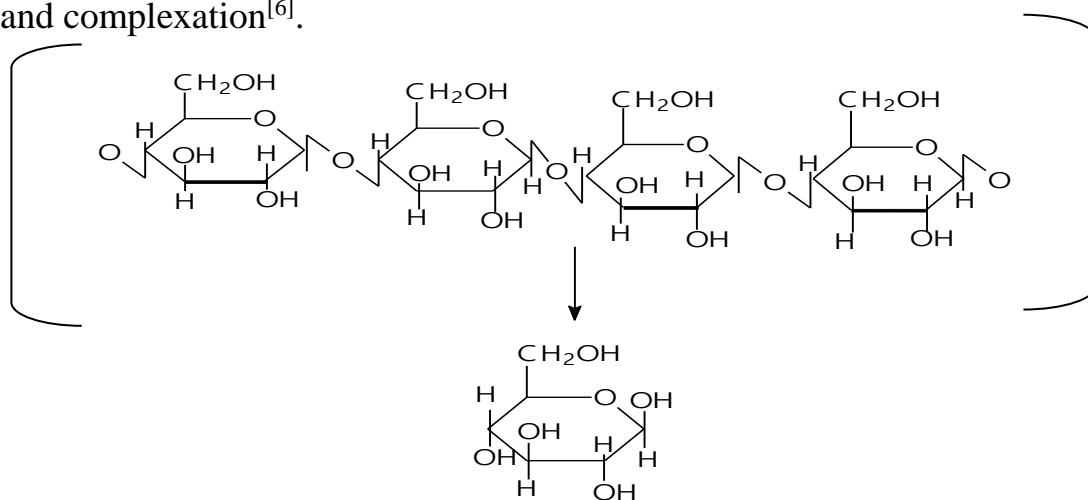
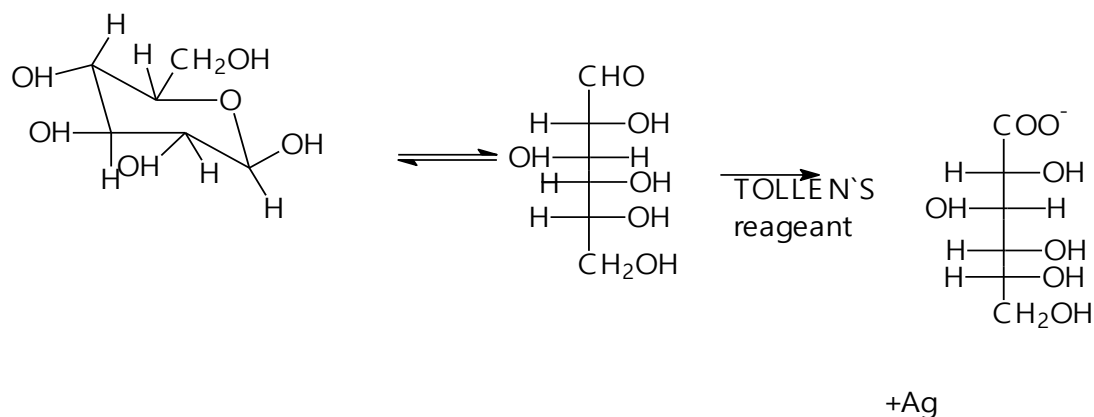


Fig (1.1): Hydrolysis of cellulose to glucose



Fig(1.2) Oxidation of Carbohydrates (Tollen`s reagent)

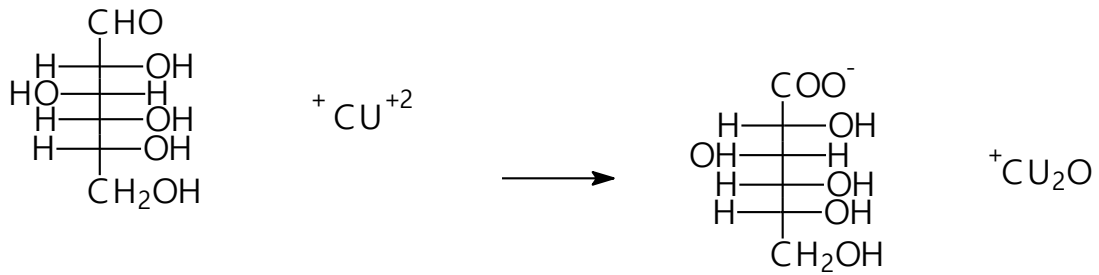
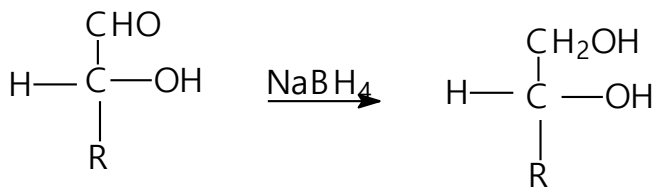


Fig (1.3) : oxidation of carbohydrates (Fehling`s Test)



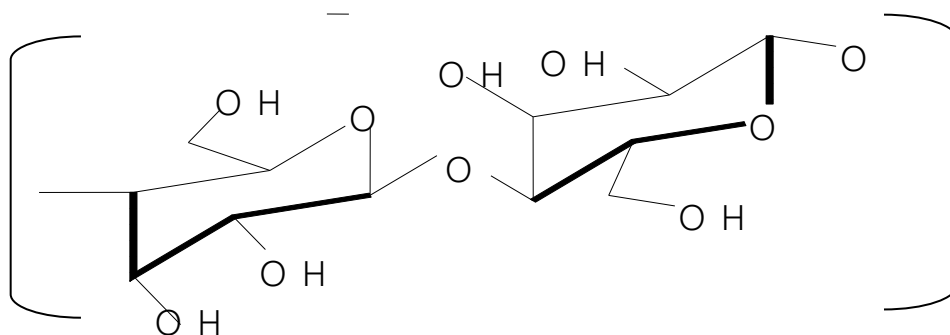
Fig(1.4): Reduction of carbohydrates

1.3-Cellulose:

Cellulose was discovered in 1838 by the French chemist Ansel me payen , who isolated it from plant matter and determined it`s chemical formula. Cellulose is an organic polysaccharide with the formula (C₆H₁₂O₆). Consisting of a linear chain of several hundred to over ten thousand β (1-4) linked D-glucose units. cellulose is essential structural component of cell walls in higher plants and is the most abundant organic polymer on earth^[7].

Cellulose is one of the most widespread biopolymer found globally , existing in a variety of living species such as plant, animals, bacteria and some amoebas. Natural fibers mainly consist of cellulose, lignin, and hemicellulose but also include low quantities of pectin , pigments and extracts. Cellulose chains are biosynthesid by enzymes, deposited in a continuous fashion and aggregate to form microfibrils. The microfibrills further aggregate on the macroscale to form fibers. The natural fibers

themselves act as a composite materials, assembling in a mainly lignin matrix^[8].



Fig(1.5): structure of cellulose

Cellulose is a polysaccharide consisting of E-1,4 glycosidic linkages of anhydroglucoseunits . Hydrogen bonds (H-bonds) can be easily formed within and between cellulosic chains. Cellulose is insoluble in water and in most of organic solvents, but it is soluble in certain ionic liquids . The insolubility in water is often referred to as strong intermolecular hydrogen bonding between cellulose molecules. Because of its insolubility cellulose itself is difficult to be used in industry, but its derivatives are much easier to handle^[9].

1.3.1-Physical Properties of Cellulose:

Cellulose has no taste, is odorless, hydrophilic with the contact angle of 20-30° and it can be broken down chemically into its glucose units by treating it with concentrated acid at high temperature. Cellulose is soluble in schweizer'sreagent ,cupriethylenediamine , cadmiumethylenediamine (cadoxen) , N-methylmorpholine N-oxide and lithium chloride / dimethylacetamide^[10].

1.3.2- Chemical properties of cellulose:

Cellulose chemistry did not arise until established the basic chemical formula of cellulose . In 1926, the macromolecular nature of cellulose was finally recognized and accepted . Following those studies published that cellulose was a linear homopolymer of anhydro-D-glucose units linked together by β -1,4-linkage. Generally, 20 \approx 30 repeating units give all cellulose properties. Each cellulose chain has two ends, one with an original C4-OH group is called the non reducing end and the other with an original C1-OH is called the reducing end. Additional carbonyl and carboxyl groups can be introduced into cellulose by chemical treatments, such as by bleaching chemicals . Many characteristic properties are determined by the molecular structure, including hydrophilicity and degradability. The multiple OH groups on cellulose molecule and its linear structure enable the formation of crystalline fiber bonded by extensive hydrogen bonds^[8].

1.3.3-Structure and reactivity of cellulose :

The chemical and physical properties of cellulose can only be properly understood by acquiring knowledge of the chemical nature of the cellulose molecule in addition to its structure in the solid state^[11].

A profound understanding of the structural properties of native cellulose is a requirement to understand the effects of different substituents on the chemical and physical properties of cellulose and its derivatives. When considering macromolecules of any kind, three structural levels must be distinguished:

1) The molecular level: on this level the cellulose is treated as a single macromolecular. At the molecular level the following concepts are considered: chemical constitution, molecular mass, molecular mass

distribution, the presence of reactive sites and potential intramolecular interactions^[11].

2) The supramolecular level :This is one step further up from the molecular level and considers cellulose molecules as interacting with other cellulose chains in the form of packing and mutual ordering of the macromolecules to form larger structures. At the supramolecular level the following concepts are of importance: aggregation of the molecular chains to form elementary crystals and fibrils, the degree of order within and around the fibrils and fibrillar orientation with respect to the fiber axis^[11].

3) The morphological level: This level covers structural entities formed by cellulose molecules. As the structures get larger, they may become very complex. On the morphological level, the existence of distinct cell wall layers in native cellulose fibers or in skin-core structures in man-made cellulosic fibres are investigated. Presence of voids or interfibrillar interstices is also studied.^[11]

1.3.4 -Cellulose molecule at the molecular level :

Payen was the first to determine the elemental composition of cellulose as early as in 1838.5 He found that cellulose contains 44 to 45% carbon, 6 to 6.5% hydrogen and the rest consisting of oxygen. Based on these data, the empirical formula was deduced to be (C₆H₁₀O₅). However, the actual macromolecular structure of cellulose was still unclear. Haworth proposed a chain-like macromolecular structure in the late 1920s, whereas Staudinger delivered the final proof of the highly polymer nature of the cellulose molecule^[11].

Cellulose is a linear and fairly rigid homopolymer consisting of D-anhydroglucopyranose units (AGU). These units are linked together by β

-(1→4) glycosidic bonds formed between C-1 and C-4 of adjacent glucose moieties. In the solid state, AGU units are rotated by 180° with respect to each other due to the constraints of β-linkage. Each of the AGU units has three hydroxyl (OH) groups at C-2, C-3 and C-6 positions. Terminal groups at the either end of the cellulose molecule are quite different in nature from each other. The C-1 OH at one end of the molecule is an aldehyde group with reducing activity. Aldehyde groups form a pyranose ring through an intramolecular hemiacetal form. In contrast, the C-4 OH on the other end of the chain is an alcoholborne OH constituent and thus is called the non-reducing end. It has been known from the infrared spectroscopy (IR), X-ray crystallography and nuclear magnetic resonance (NMR) investigations, that the AGU ring exists in the pyranose ring form and that this adopts the 4C1-chair formation which constitutes the lowest energy conformation for D-glucopyranose^[11].

The chemical character and reactivity of cellulose is determined by the presence of three equatorially positioned OH groups in the AGU, one primary and two secondary groups. In addition, the β-glycosidic linkages of cellulose are susceptible to hydrolytic attack. The hydroxyl groups do not only play a role in the typical reactions of primary and secondary alcohols that are carried out on cellulose, but also play an important role in the solubility of cellulose. Cellulose is insoluble in common organic solvents and in water. This is due to the fact that the hydroxyl groups are responsible for the extensive hydrogen bonding network forming both, intra- and intermolecular hydrogen bonding. In order to dissolve cellulose, the prevailing hydrogen bonding network must be broken^[11].

1.3.5 Isolation of Cellulose:

The isolation of highly pure cellulose has been the subject of extensive studies for many years because of the complexity of plants' cell wall structure. The combination of the chemical and the mechanical treatments is necessary for the dissolution of lignins, hemicelluloses, and other noncellulosic substances. A protocol based on acidified sodium chlorite is frequently applied to delignify woody materials as an initial step in the extraction of cellulose. Alkali extraction to dissolve hemicelluloses before or after delignification is the common method. In the paper industry, pulping and bleaching is used to remove lignins, hemicelluloses, and other noncellulosic substances and obtain pulp fiber with high cellulose purity and brightness via chemical and mechanical processes. Chemical pulping including either soda, sulfate, or sulfite are the main methods to isolate cellulose fibers from lignocellulosic materials. In these procedures, NaOH, Na₂S, H₂SO₄, Na₂SO₃, NaHSO₃ and/or SO₂ are present as the major active chemicals for impregnation and delignification. Alkali treatment could extract hemicellulose-lignin complexes that are soluble in alkaline solution. Thereafter, the obtained samples undergo delignification and/or alkali extraction to extract cellulose with relatively high purity^[8].

1.3.6-Hydrolysis of Cellulose :

Many researchers have focused on the hydrolysis of cellulose with dilute acids and concentrated acids, enzymes and other types of catalysts . Hydrolysis of cellulose is a key technology for effective use of lignocelluloses because glucose can be efficiently converted into various chemicals, biofuels, foods and medicines. Hydrolysis of cellulose includes the processing steps that convert the cellulose and hemicellulose

into monomeric sugars. The factors that have been identified to affect the hydrolysis of cellulosic biomass include porosity or accessible surface area, cellulose fiber crystallinity, and the content of lignin and hemicellulose. Hydrolysis method should fulfill the following requisites: increase sugar yield, avoid degradation or loss of sugars, minimize the formation of inhibitory by-products, and be cost-effective^[8].

The first technology for the acid hydrolysis of cellulose was developed by Faith in 1923. In the process, sulfuric acid solution was used to treat wood waste in brick lined percolators, a dilute sugar solution was obtained. Many processes were reported to be effective in the hydrolysis of cellulose using acids such as Hydrochloric acid, Hydrofluoric acid, Sulfuric acid and organic acids (Oxalic, Maleic, Fumaric)^[12].

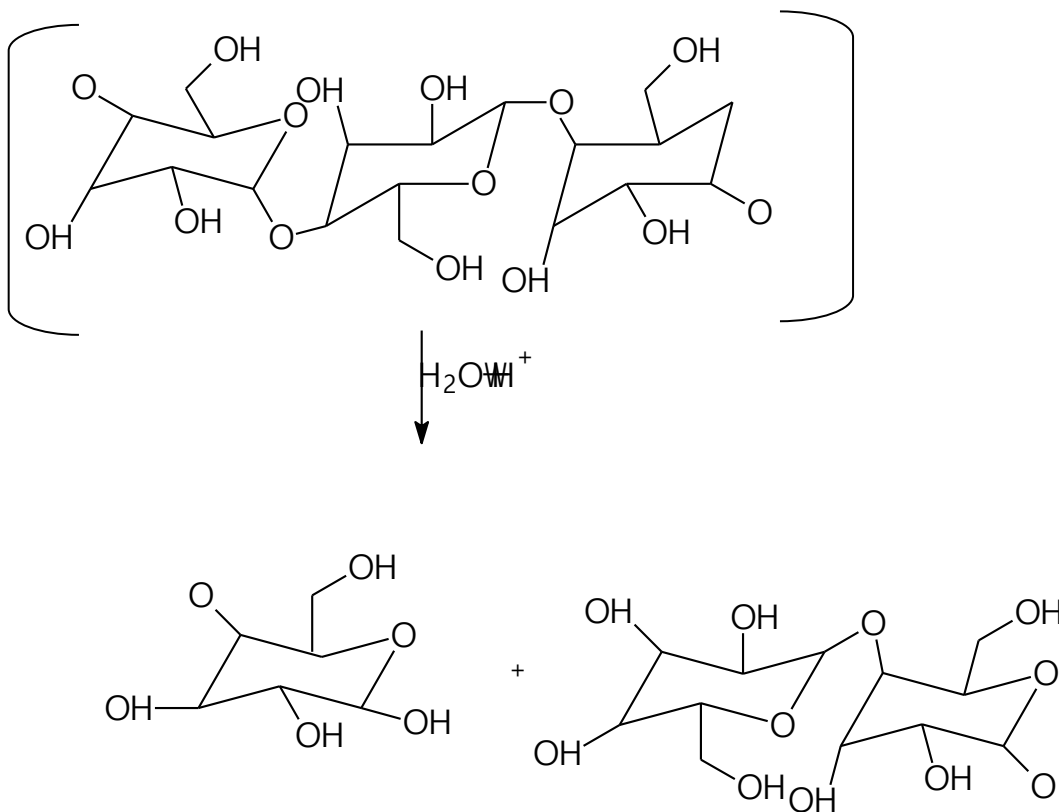


Fig (1.6): Hydrolysis of Cellulose by acid

1.4-Cellulose derivatives:

All cellulose derivatives are based on the substitution of hydroxyl groups of cellulose by other functional groups. Thus, a definition term Degree of substitution needs to be introduced here: The degree of substitution (DS) of a polymer is the (average) number of substituent groups attached per base unit (in the case of condensation polymers) or per monomeric unit (in the case of addition polymers). The term has been used mainly in cellulose chemistry where each anhydroglucose (E-glucopyranose) unit has three reactive (hydroxyl) groups; degrees of substitution may therefore range from zero (cellulose itself) to three (fully substituted cellulose). In the case of cellulose acetate, DS is the average number of acetyl groups attached per anhydroglucose unit ^[9].

Table (1.1) :Commercially important cellulose esters and ethers

Product	Solubility	Application
Cellulose acetate	Water, 2-methoxy ethanol, Acetone Chloroform	Coatings and membranes
Cellulose xanthate	NaOH/water	Textiles
Cellulose nitrate	Methanol, Acetone Ethanol	Membranes and explosives
Carboxymethyl cellulose	Water	Coatings, paints, adhesives and pharmaceuticals
Methyl cellulose	aq. NaOH4% Cold water Organic	Films, textiles, food- and tobacco industry

	solvents	
Hydroxyethyl cellulose	4 %aq. NaOH Water	Paints, coatings, films and cosmetics
Ethyl cellulose	aq. NaOH4% Cold water Organic solvents	Pharmaceutical industry

1.4-Cellulose acetate:

Cellulose acetate was historically discovered by Paul Schützenberger in 1865, by reacting cellulose with acetic anhydride. Cellulose triacetate was industrialized much earlier than acetone-soluble cellulose diacetate . Cellulose Triacetate could be applied as photographic film, artificial silk or hornlike plastic materials. But the major commercial breakthrough was the application of cellulose diacetate as a textile fiber. The success of cellulose acetate fiber lasted until 1960's when cheaper petroleum-based synthetic fibers (such as nylon and polyester) entered textile market. World consumption of cellulose acetate is mainly in four different markets: filter tow for cigarettes, textile fibers, polarizer protection film in liquid crystal displays (LCD) and coatings, plastics and membranes^[9].

Commercial cellulose esters and ethers are produced under heterogeneous reaction conditions by using acids and acid anhydrides as reagents. On the other hand, the main synthetic route for ethers is Williamson ether synthesis. Major drawbacks of heterogeneous phase reactions are the limited reaction rates and lack of regioselectivity in certain reactions. The ramification of these drawbacks are that the accessibility of free hydroxyl groups of cellulose is the determining factor for selectivity and for the DS. In contrast, when carrying out reactions in homogeneous solutions,

the regioselectivity of the reaction is determined by the reactivity differences among the free hydroxyl groups on the cellulose molecules, not by their accessibility. In addition to controllable selectivity of the reaction, the DS values can be tuned varying from low DS derivatives to highly substituted compounds. Therefore, the material properties of the obtained cellulose derivative may also be adjusted in the desired way^[11].

1.4.2-Cellulose nitrate :

Among the most important inorganic cellulose esters cellulose nitrate is customized mainly as coating, propellant and brilliant ink. Historic applications such as billiard balls or celluloid films are no longer of importance, but the manufacture of table tennis balls (imported from China) using cellulose nitrate continues as there are no alternatives with the same properties. Other cellulose esters used as polymers or bioplastics are cellulose propionate and cellulose acetobutyrate^[13].

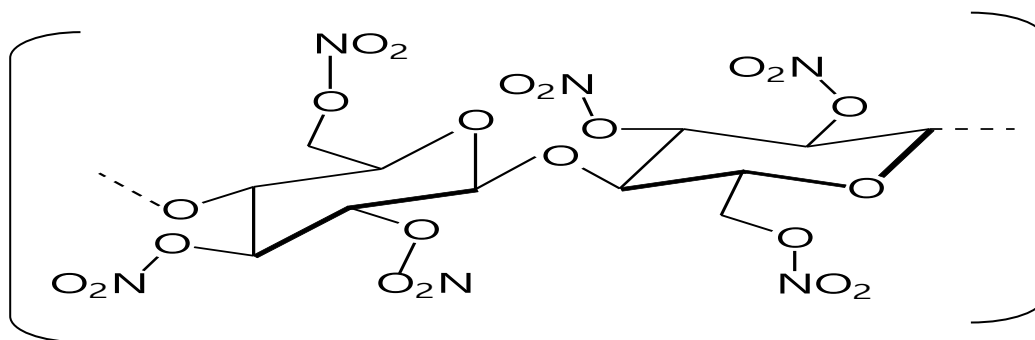


Fig (1.7): structure of cellulose nitrate .

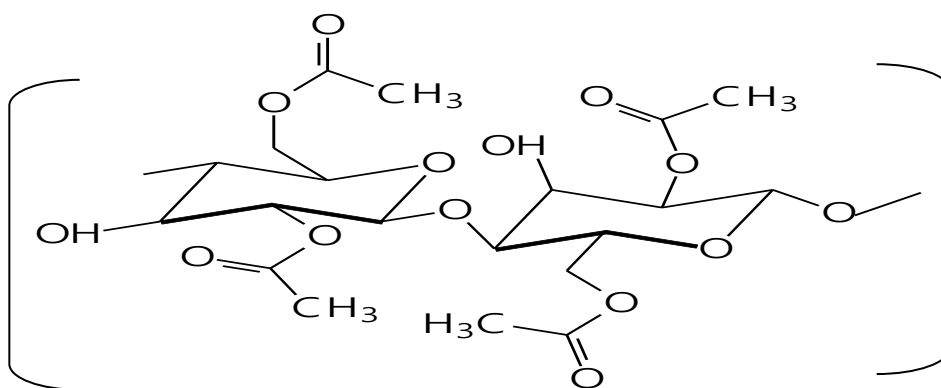
1.4.3-Cellulose ethers:

Cellulose ethers are mainly used for function polymers in the construction industry and in the pharmaceutical and cosmetics industry. They are applied as binders and thickeners, stabilizer and other additives. Among these, there is the carboxymethylcellulose (CMC), used in detergents, as

thickeners in food, coatings and thickeners in pharmaceuticals and cosmetics and as additive in the paper industry^[13].

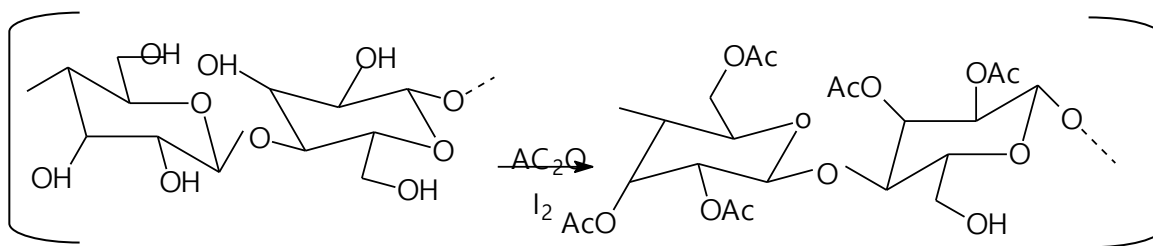
1.5-Acetylation of cellulose:

Acetylation of cellulose has been comprehensively studied in different Ionic Liquids. Reactions have been carried out either in the presence of a base or without and using acetic anhydride or acetic chloride as reagents. Ionic liquids have been found to function not just as solvents but also as active base catalysts for the acetylation reactions^[11].



Fig(1.8): structure of cellulose acetate.

Commercially, cellulose acetates are produced by the reaction of cellulose with an excess of acetic anhydride in the presence of sulphuric acid or perchloric acid as the catalyst. Due to the heterogeneous nature of the reaction, it is impossible to produce partially acetylated cellulose directly. In contrast, acetylation of cellulose in IL can be controlled to yield derivatives with various DS values. Furthermore, when ILs are used as the reaction media, the amounts of reagents can be reduced as catalyst is not needed for the reaction. This also makes the recyclability of the solvent easier and achievable^[11].



Fig(1.9):Acetylation of cellulose

Acetylation of polysaccharides has been known for many decades . For example, acetylation of cellulose in the presence of acetic acid and acetic anhydride is well known. In the case of cellulose acetate, it is customary to produce cellulose triacetate (CTA) first, and then hydrolyze it to produce cellulose acetate (CA) with the desired degree of substitution . Conventional acetylation processes typically involve solvents such as methylene chloride or high temperatures with sulfuric or perchloric acid as a catalyst. There has been some recent studies in polysaccharide esterification , particularly the use of ionic liquids to dissolve cellulose and prepare cellulose acetates . Other paths for esterification include dialkylcarbodiimide, N,N-carbonyldiimidazole, iminiumchlorides, transesterification, and ring-opening esterification . An alternative approach reported is to use iodine as a catalyst for the esterification of cellulose and starch in the presence of acetic anhydride . The reactions are generally conducted at 100°C without the use of additional solvents^[14].

What is the role of iodine? First of all, it is known that iodine can form a complex with amylose and other glucose polymers . The complexation may help the solubility of cellulose in the acetic anhydride. The cellulose-Ac₂O-iodine reaction mixture appears to be heterogeneous at 100°C below 5 %mole iodine but becomes homogeneous as iodine approaches 5% mole. Secondly, iodine may serve as a catalyst^[14].

1.6-Analysis of Cellulose:

1.6.1-Identification of Cellulose by Chemical tests:

To identify Cellulose by Chemical tests it must be Hydrolyzed or treat mechanically (steam, explosion, wet and dry milling) or swelling treatment(Dimethyl sulfoxide , Dimethylformamide)^[15].

All carbohydrates have unique chemical properties that allow them to be identified. Some react similarly to the same test; however, by using number of tests, each of the sugars may be identified by set of reactions. Ketoses, sugars that contain a ketone group, often differ in their chemical properties from the aldoses, sugars which contain an aldehyde group. The following tests is used to identify carbohydrates in general : Fehling`s , Brady`s, Tollen`s, Benedict`s, Seliwanoff and Iodine Test^[16].

1.6.2-Infrared(IR) Spectroscopy:

Infrared spectroscopy is certainly one of the most important analytical techniques available to today's scientists. One of the great advantages of infrared spectroscopy is that virtually any sample in virtually any state may be studied. Liquids, solutions, pastes, powders, films, fibers, gases and surfaces can all be examined with a judicious choice of sampling technique. As a consequence of the improved instrumentation, a variety of new sensitive techniques have now been developed in order to examine formerly intractable samples. Infrared spectroscopy technique is based on the vibrations of the atoms of a molecule. An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. The energy at which any peak in an absorption

spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule^[17].

1.7 Aims of this Study :

This research was aimed to :

- Isolation of Cellulose from Black Tea, Newspaper and Leaf Palm .
- Conversion Cellulose to their derivatives .
- Analysis of Cellulose and Cellulose derivatives by using chemical tests and IR spectroscopy .

Chapter Two

2- Materials ,Instruments and Methods

2-Materials ,Instruments and Methods

2.1-Materials:

2.1.1-Sample:

-Black Tea.

-Newspaper.

-Leaf Palm.

2.1.2-Materials:

-Sodium hydroxide.

-Chloroform(99.8%).

-Acetic anhydride(1.082 g/cm^3).

-Iodine.

-Sodium thiosulphate.

- Absolute ethanol(99.9%).

-Acetic acid glacial (1.05 g/cm^3).

-Acetic acid (1.049 g /cm^3).

-Clorox.

-Concentrated Sulfuric acid(98%).

- Concentrated Nitric acid(69%).

- Silver Nitrate.

- Ammonia solution(25%).

-Fehling`s Reagent.

-Brady`s Reagent.

-Sodium hydroxide solution (10%).

2.2-Instruments:

-IR spectrometer (Shimadzu).

-IR spectroscopy (Thermo Nicolet 300).

2.3-Methods:-

2.3.1-Method of sampling:

-Newspaper was cut into small pieces.

-Black Tea leaves were collected after boiling and dried at room temperature.

-Leaf palm was dried at room temperature for week then cut to small pieces.

2.3.2-Method of isolation:

2.3.2.1-Isolation of cellulose from News paper:

20 g of sample was weight , and mixed with sodium hydroxide solution (1M) in a beaker equipped with stirrer. The mixture was stirred for 6 hours then filtered. The filtrate was bleached by Clorox (50ml in 250ml of distilled water) and buffer solution (35ml of Sodium hydroxide and 75ml Acetic acid) at 80°C in water bath for 3 hours then filtered. The filtrate was washed with distilled water and dried at room temperature.

2.3.2.2-Isolation of cellulose from Black Tea :

20 g of sample was weight then Sodium hydroxide(1M) was added to and stirred for 2 hours .The process was repeated until the color of the solution was nearly colorless then filtered. The filtrate was bleached by Clorox (50ml in 250ml of distilled water) and buffer solution (35ml of Sodium hydroxide and 75ml Acetic acid) at 80°C in water bath for 3 hours then filtered. The filtrate was washed with distilled water and dried at room temperature.

2.3.2.3-Isolation of cellulose from Palm leaf:

50 g of sample was weight and stirred with Sodium hydroxide (1M) for 2 hours . The process was repeated until the solution turn to almost colorless then filtered . The filtrate was bleached by Clorox (50ml in 250ml of distilled water) and buffer solution (35ml of Sodium hydroxide and 75ml Acetic acid) at 80° C water bath for 3 hours then filtered. The filtrate was washed with distilled water and dried at room temperature.

2.3.3-Acetylation of cellulose in the presence of iodine :

Excess of Acetic anhydride was added to 4 g of cellulose (isolated from leaf palm) and 1.28 g of iodine then heated at 80-100°C for 8 hours . The reaction mixture cooled at room temperature then treated with saturated solution of sodium thiosulphate and stirred for 30 min . Absolute ethanol was added to the mixture then it was filtrated , washed with ethanol and dried at room temperature.

2.3.4 -Acetylation of cellulose and forming Cellulose acetate film:

2ml of acetic acid , 0.6 ml of acetic acid anhydride and 4 drops of sulfuric acid was added to 0.5 g of cellulose(isolated from Palm Leaf) in flask and stirred , the flask was closed and left over a night . The solution was

pour with stirring into 50 ml of water then it was filtrate , after it dried , 0.2 g of the dry product was placed in small beaker contained 5 ml of chloroform and stirred then the solution was poured in Petri dish and left to evaporate slowly.

2.3.5-Nitration of Cellulose :

1ml of concentrated sulfuric acid and 1 ml of concentrated nitric acid was added to 1 g of cellulose(isolated from Palm Leaf) , the solution was stirred then cold water was added , filtrated and washed with cold water.

2.3.6-Identification of Cellulose :

2.3.6.1-Hydrolysis of Cellulose:

The cellulose was grind then few drops of concentrated sulfuric acid and water was added to it , the solution was boiled for 15 minutes in water bath . Finally it was neutralized by sodium hydroxide, the solution was identified using the following tests .

2.3.6.2 -Fehling`s test:

1 ml of both fehling's (A,B) reagent was added to the sample then heated.

2.3.6.3- Tollen`s test:

Aqueous silver nitrate was mixed with sodium hydroxide solution , drops of ammonia was added drop wise until the precipitated silver oxide completely dissolve . The sample was added to the solution and heated.

2.3.7-Analysis of Cellulose and Cellulose derivatives using IR Spectroscopy :

A quantity of the sample was grinded with potassium bromide until it became powder, this powder mixture was then pressed by using

mechanical press to form a disc though which the beam of the spectrometer can pass.

Chapter Three

3- Results and Discussion

3.Results and Discussion

3.1 Results:

3.1.1 Isolation of Cellulose :

The Cellulose was isolated from Black Tea, Newspaper and Leaf Palm by alkali treatment.

Table (3.1): Shows the percentage ,shape and color of the isolated cellulose.

Sample	Shape and color of cellulose	Percentage of cellulose % (w/w)
Black Tea	Pale Yellow powder	9
Newspaper	White fiber	33
Leaf palm	White and yellowish fiber	16.16



Fig (3.1): Isolated Cellulose from Newspaper.

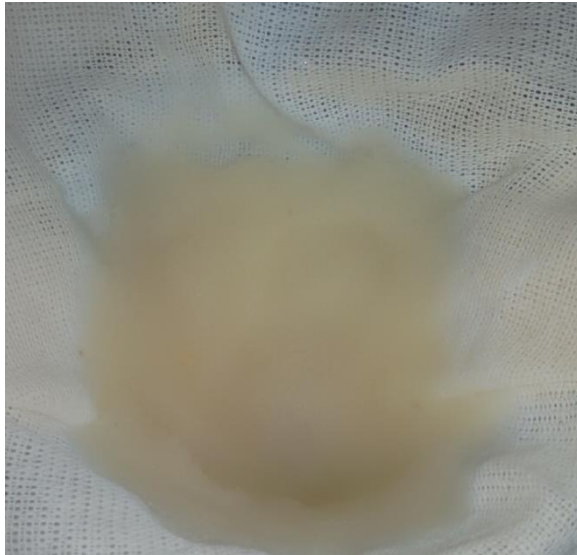


Fig (3.2): Isolated Cellulose from Black Tea.

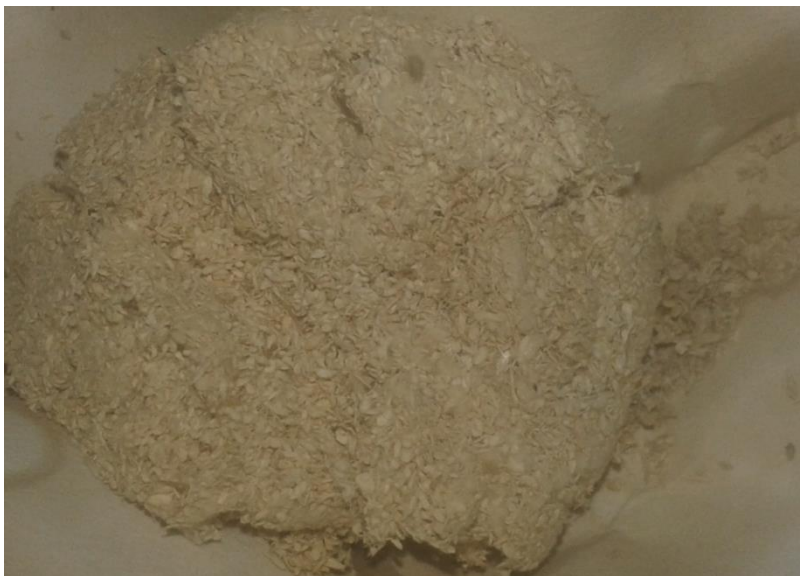


Fig (3.3): Isolated Cellulose from Leaf palm.

3.1.2 Acetylation of Cellulose in the presence of Iodine :

Acetylation of Cellulose in the presence of Iodine gave a light brown product.

3.1.3 Acetylation of Cellulose and forming Cellulose acetate film:

Acetylation of Cellulose gave a white yellowish fiber then it was converted to cellulose acetate film.

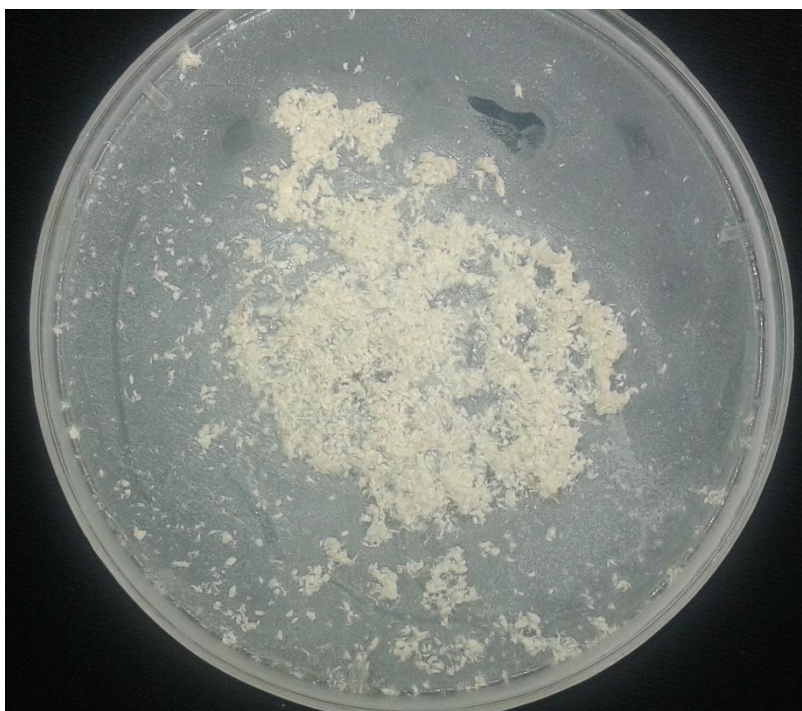


Fig (3.4): Cellulose acetate Film.

3.1.4 Nitration of Cellulose:

The Nitration of cellulose gave a yellow product.

3.1.5 Identification of Cellulose:

3.1.4.1 Identification of Cellulose from News paper:

The product of the hydrolysis was identified using fehling`s test , and Tollen`s test and the following table show the result.

Table (3.2) The results of identification tests(newspaper cellulose).

Test	Result
Fehling`s test	Brown precipitate was formed
Tollen`s test	Silver mirror was shown

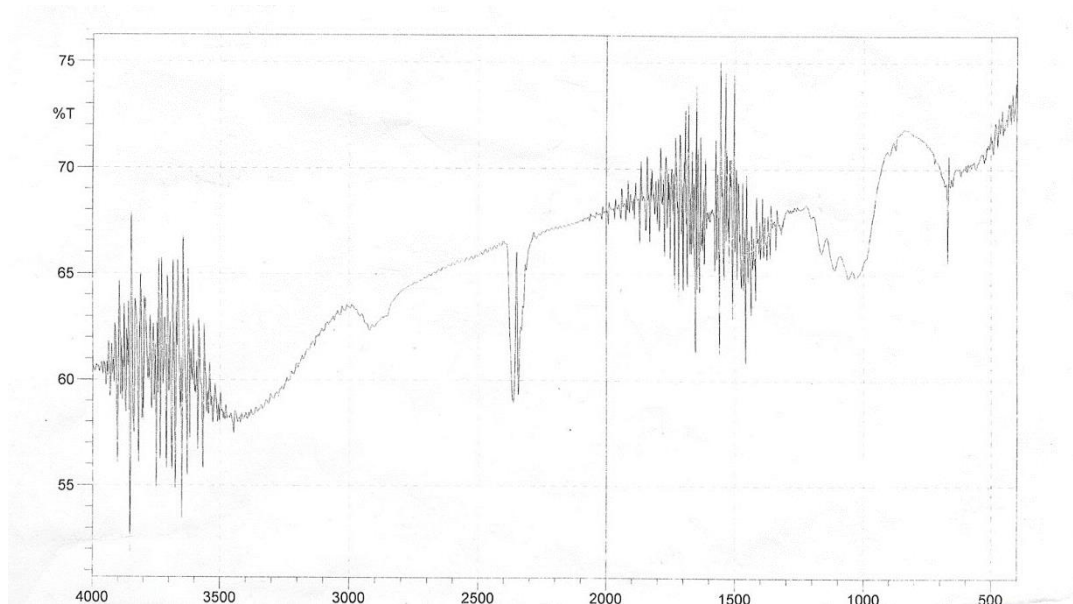
3.1.4.2 Identification of isolated cellulose from leaf palm :

The product of the hydrolysis was identified using fehling`s , Brady`s and Tollen`s test and the following table show the result.

Table(3.3) The results of identification tests(leaf palm cellulose).

Test	Result
Fehling`s test	Brown precipitate was formed
Tollen`s test	Silver mirror was shown

3.1.5 Analysis of Cellulose and Cellulose derivatives using IR Spectroscopy :



IR spectrum(Fig 3.1) showed $\nu(\text{KBr})$ (isolated Cellulose from Leaf Palm)

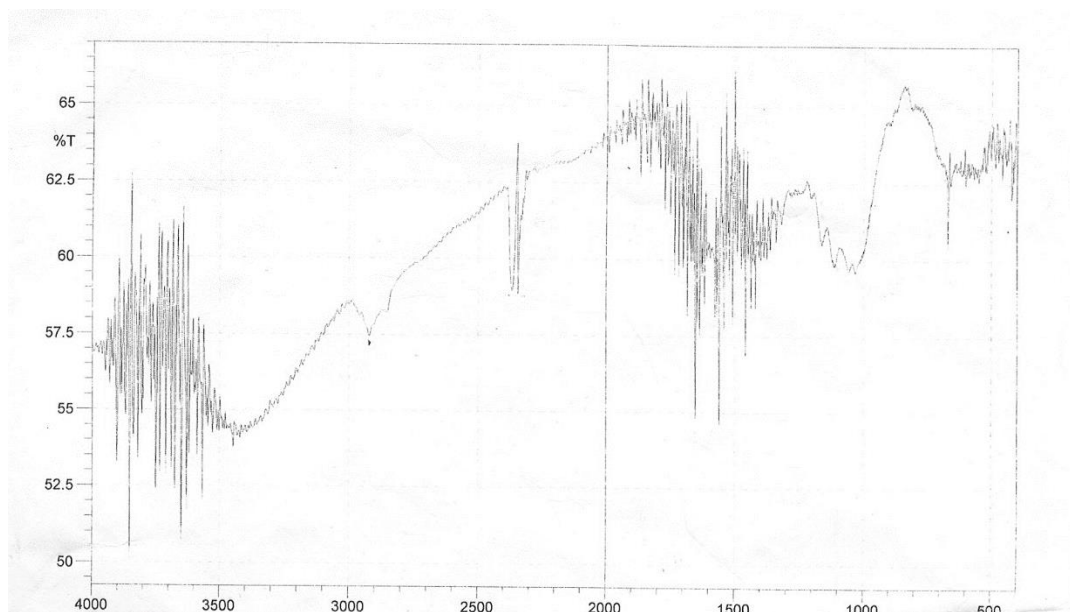
The spectrum show the following peaks:

3450 (OH bond)

2980 (CH Aliphatic)

1050 (C-O)

680 (C-C long chain)



IR spectrum (Fig3.2) showed $\nu(\text{KBr})$ (isolated Cellulose from Newspaper)

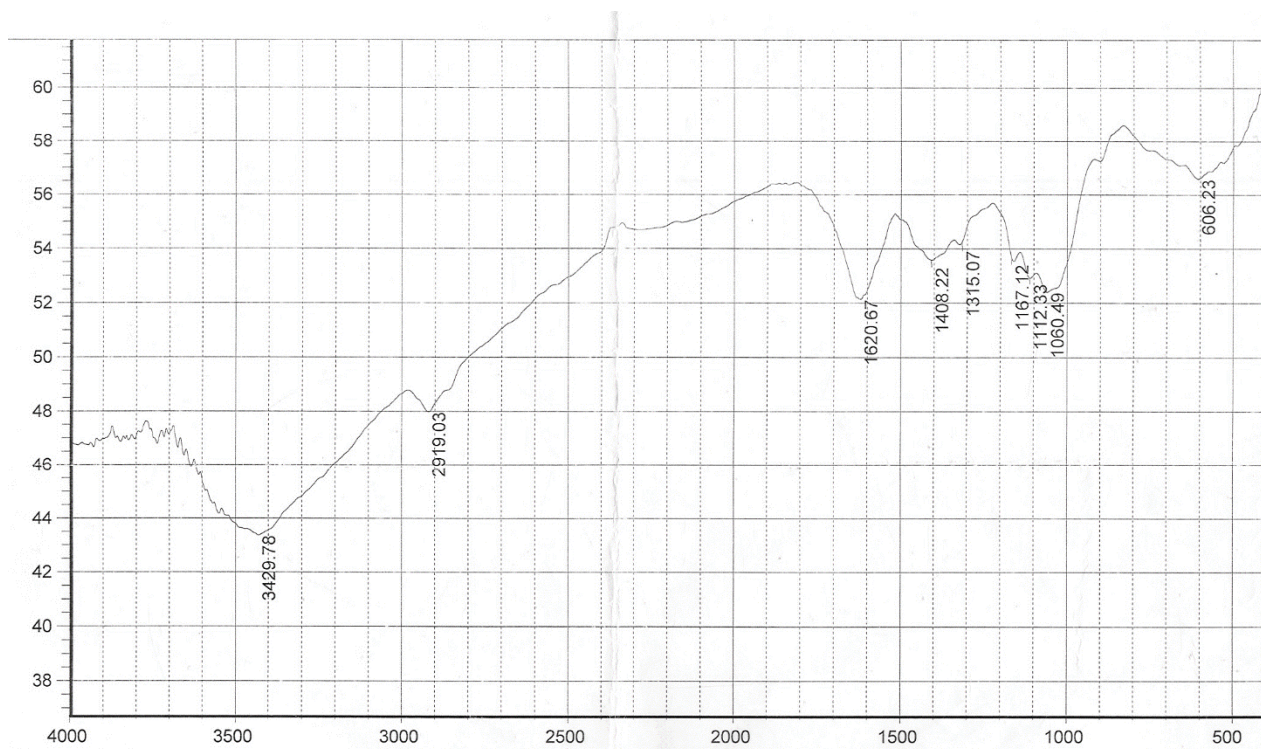
The spectrum show the following peaks:

3450 (OH broad)

2980 (CH Aliphatic)

1050 (C-O)

670 (C-C long chain)



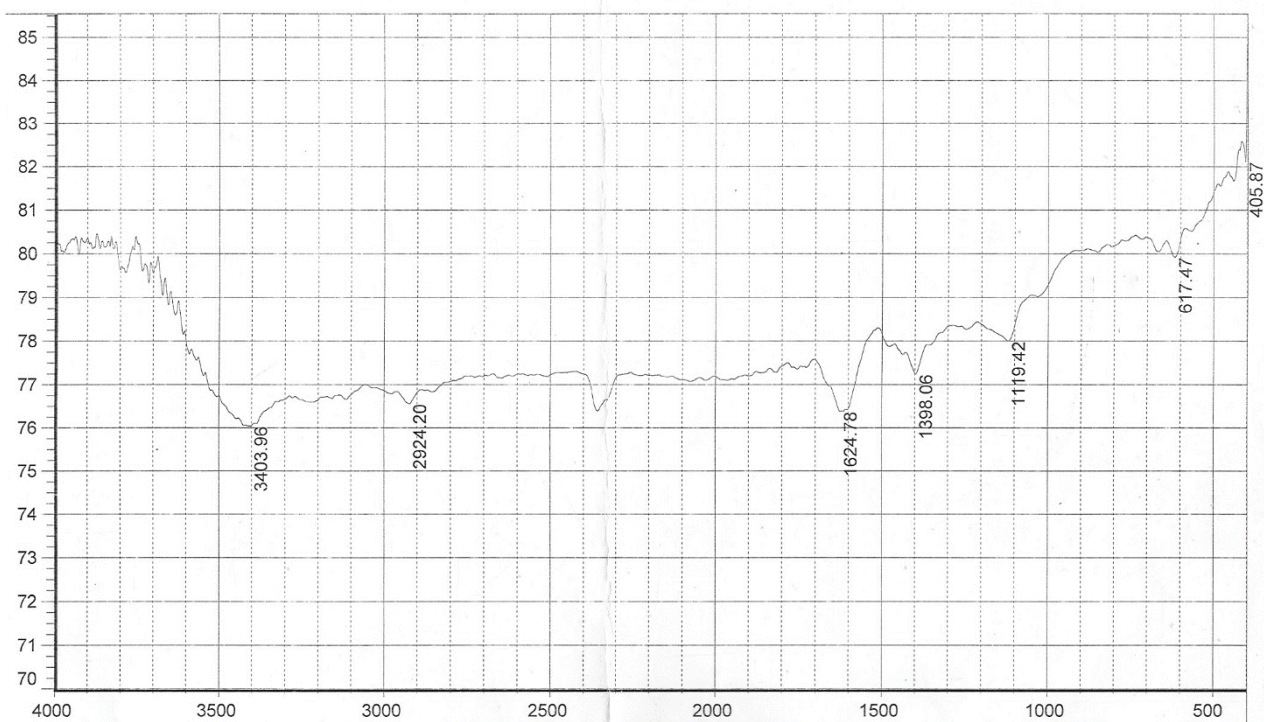
IR spectrum(Fig 3.3) showed $\nu(\text{KBr})$ (isolated Cellulose from Black Tea)

3429.78 (OH)

2919.03 (CH Aliphatic)

1060.49 (C-O)

606.23 (C-C long chain)



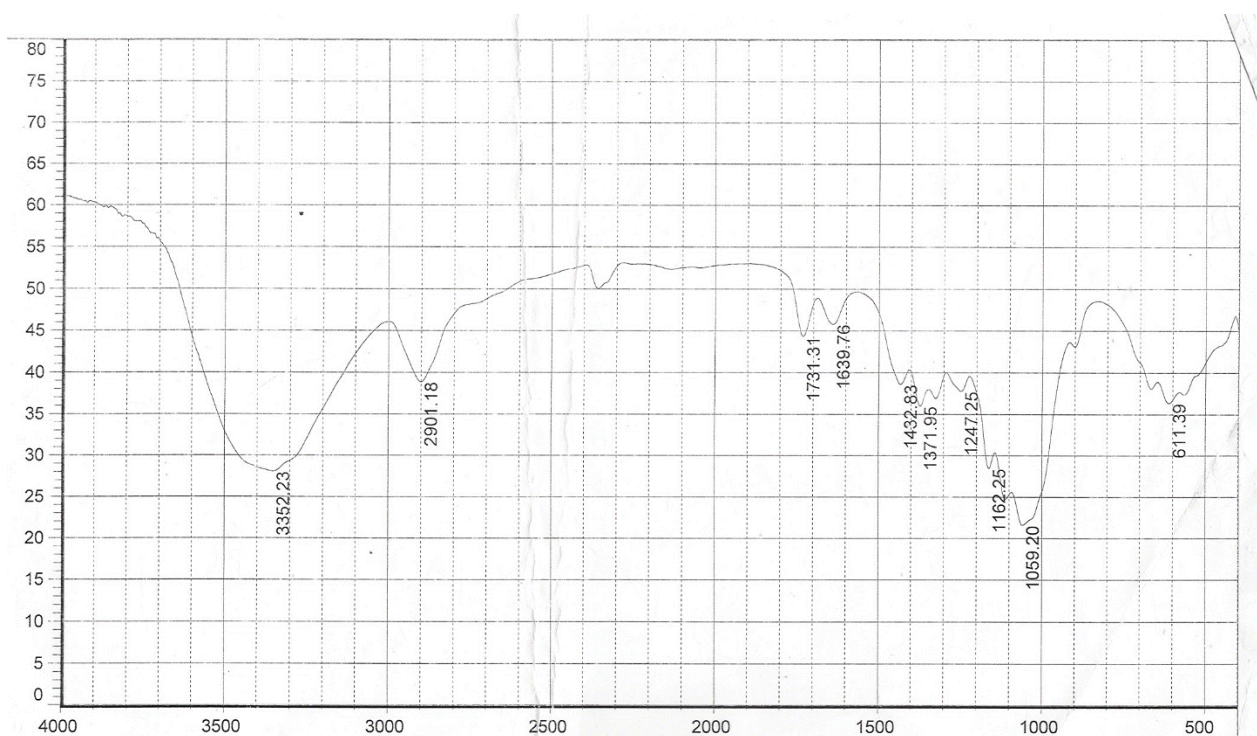
IR spectrum(Fig 3.4) showed $\nu(\text{KBr})$ (Cellulose Acetate in the presence of Iodine)

3403.96 (OH)

2924.20 (CH Aliphatic)

1119.42 (C-O)

617.47 (C-C long chain)



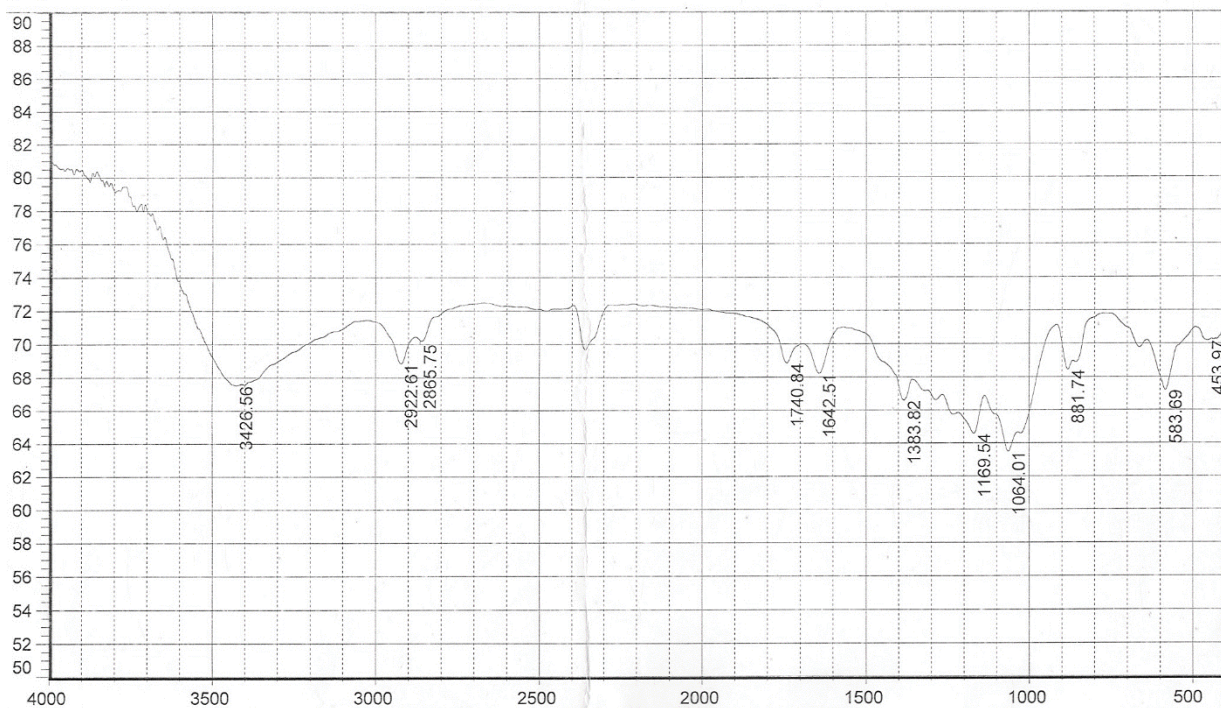
IR spectrum(Fig 3.5) showed $\nu(\text{KBr})$ (Cellulose Acetate)

3352.23 (OH)

2901.18 (CH Aliphatic)

1059.20 (C-O)

611.39 (C-C long chain)



IR spectrum(Fig 3.6) showed $\nu(\text{KBr})$ (Cellulose Nitrate)

3426.56 (OH)

2922.61(CH Aliphatic)

2865.75(CH Aliphatic)

1642.51 (R-O-NO₂)

1064.01 (C-O)

3.2-Discussion:

Cellulose was isolated from different sources by sodium hydroxide (1M) and stirring, percentage of Cellulose in Black Tea 9%, in Newspaper 33% and in Leaf Palm 16.16%.

The isolated Cellulose from Palm tree leaves was pure, but if organic solvent or carbon disulfide was used it would become more pure as in previous study [Preparation and study of Bio-Plastic from leaf palm Powder and its Cellulose Extraction with low density Poly Ethylene, By Tariq A. Mandel Yusra M. Al-Obaidy, University of Anbar] show that the extracted cellulose using carbon disulfide is pure.

The isolated Cellulose from Newspaper when compared it to a previous study [Extraction of Cellulose from some Industrial and Plant's Waste and its hydrolysis using new heterogeneous catalyst By Muna Hasson Aboody September 2013] the percentage of the extracted cellulose was 20% and the concentration of the sodium hydroxide was (7.5%). The difference in the concentration of Sodium hydroxide effect on the percentage of the isolation.

Cellulose acetate film didn't show clearly maybe due to the presence of cellulose (partial acetylation).

IR spectrum of Cellulose from the three sources are similar and show the (OH), (C-O) also the (C-C long chain) which indicate the structure of Cellulose.

IR spectrum of Cellulose Acetate in the presence of iodine and the absence of Iodine show the same peaks in the spectrum of Cellulose which may indicate that it needs a recrystallization, and Cellulose Acetate in the presence of iodine spectrum wasn't obvious may be due to the

long time between the acetylation and the analysis using IR spectroscopy and this may refer that the acetylation happened but it was hydrolyzed in the time between the acetylation and the analysis .

IR spectrum of Cellulose Nitrate show two peaks of (CH Aliphatic) mean that they are in different environment one of them is near the nitro group , the nitro peak indicate that the nitro is connected to the oxygen which confirm the structure of Cellulose Nitrate , the presence of (OH) mean the nitration wasn't completed and it needed recrystallization .

In the identification of Cellulose , first the Cellulose was hydrolyzed to break it down to the monosacharide sugar then test it by:

Fehling`s reagents: gave brown participtate which mean the presence of reducing sugars .

Tollen`s test: silver mirror was formed that mean the presence of aldehyde or alpha-hydroxy ketone and that confirm the structure of Cellulose.

Conclusion:

Cellulose was isolated by alkali treatment from three sources : Black Tea, Newspaper and Palm Leaf (9%, 33%, 16.16% respectively) cellulose Acetate and Cellulose Nitrate were formed .Then the Cellulose and it`s drevitaves were analyzed using IR spectroscopy and the cellulose was identified by using some chemical test.

Recommendations:

- 1- Isolate Cellulose from other sources that considered waste or not usefull .
- 2-Try other method to isolate high purity Cellulose like organic solvents.
- 3- Use the isolated cellulose to form other derivatives , polymers or bio-plastics.

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