بسم الله الرحمن الرحيم

Sudan University of Science & Technology

College of Graduate Studies

# Synthesis and Characterization of Sodium Carboxymethyl Cellulose from the sawdust of Pine wood

تخليق وتشخيص صوديوم كاربوكسي ميثيل السيليلوز من نشارة خشب الصنوبر

A Thesis submitted in Partial Fulfillment for the Requirement of the Degree

of

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بسم الله الرحمن الرحيم

( ......... وَقُل رَّبِّ زِدْنِي عِلْمًا )

(طه : 114)

I

# Dedication

dedicated to

Soul of my father,

My lovely mother

My husband

brothers

And

Sisters

# *Acknowledgements*

# Abstract

Sawdust or wood dust is a by-product of cutting, grinding, drilling, sanding, or otherwise pulverizing wood with a saw or other tool. It is composed of cellulose, hemicelluloses and lignin. This study aimed to utilize sawdust of wood for preparing sodium- carboxymethylcellulose (Na-CMC). Cellulose was isolated from sawdust of pine wood, then the cellulose powder was converted to carboxymethylcellulose (CMC) by etherification process using sodium monochloroacetic acid (Na-MCA) as etherfying agents in presence of sodium hydroxide. The amount of cellulose (2.5 g), reaction temperature (55 °C) and amount of monochloroacetic acid, MCA (2.5 g) were kept constant. The effect of various amounts of either sodium acetate or sodium nitrate was studied in this reaction for the production of Na-CMC of maximum Degree of Substitution (DS) value. The optimum amounts of these salts were found to 5g $CH_3COONa$ or 5g $NaNO_3.$ In the presence of this amount of salt, the produced CMC materials were found to have high DS values of 0.963 with $CH_3COONa$, and 1.18 with $NaNO_3$. The produced CMC was characterized using XRD diffractometer and Fourier Transform Infrared spectra (FT-IR). The two techniques together indicated the successful production of Na-CMC material.

# الخلاصة

تعتبر النشارة أو نفاية الخشب هي الناتج الثانوي من قطع أو سحن أو ثقب أو صنفرة أو حتى سحن الخشب بمنشار أو أي أداة أخرى ، وتحتوي على السليلوز والهيمي سليلوزات واللجنين. تهدف هذه الدراسة إلى استخدام نشارة الخشب في تحضير الكاربوكسي ميثيل سليلوز الصوديوم (Na-CMC) . تم فصل السليلوز من نشارة خشب الصنوبر ، ثم حول مسحون السليلوز إلى كاربوكسي ميثيل السليلوز عن طريق الأثيرة باستخدام حمض الخل احادي الكلور للصوديوم (Na-MCA) كعامل للأثيرة في وجود هيدروكسيد الصوديوم .الكمية من السليلوز (2.5g) وحرارة التفاعل (55°C) وكمية حمض الخل أحادي الكلور MCA (2.5g) كل هذه العوامل ظلت ثابتة .

تمت دراسة تأثير الاختلاف سواءً كان في كميات خلات الصوديوم أو نترات الصوديوم المستخدمة في هذا التفاعل لإنتاج (Na-CMC) بأعلى درجة من الاستبدال . الكميات المثالية لهذه الأملاح وجدت أنها 5g لخلات الصوديوم أو 5g لنترات الصوديوم . وفي وجود هذه الكميات من الملح وجدت كميات الـ CMC الناتجة بأعلى درجة من الاستبدال هي 0.963 مع خلات الصوديوم و 1.18 مع نترات الصوديوم . الكاربوكسي ميثيل سليلوز الناتج تم تشخيصه باستخدام تقنيتي XRD diffractometer و (FT-IR) Fourier Transform Infrared Spectra . كلا التقنيتين أكدت بنجاح إنتاج مادة الكاربوكسي ميثيل سليلوز الصوديوم .

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**List of abbreviations**

| | |
|---|---|
| CMC | Carboxymethylcellulose |
| DP | Degree of polymerization |
| DS | Degree of substitution |
| FTIR | Fourier transforms infrared |
| H-CMC | Acid Carboxymethylcellulose |
| Na-CMC | Sodium- Carboxymethylcellulose |
| Na-MCA | Sodium-monochloroaciticacid |

# Chapter one

# Introduction

**Introduction**

Carboxymethylcellulose (CMC) is the most important commercial cellulose ether. It is an anionic polyelectrolyte prepared by reaction of sodium chloroacetate with alkali cellulose. The sodium form of carboxymethylcellulose is commonly known as CMC, but food-grade is also known as cellulose gum. CMC is sold as a white to off-white powder, and is available in several grades and in a variety of types depending on the degree of substitution (DS), viscosity and particle size (Mark et al. 1985). There is a wide array of commercial uses for CMC due to its particular properties. CMC is soluble in water when the degree of substitution is higher than 0.5, giving high viscosity in dilute solutions. It has a thickening effect, film-forming ability, and excellent behavior as protecting colloid and adhesive (Rinaudo and Reguant 2000). CMC is non-toxic and it is currently finding an increasing number of applications in the pharmaceutical, medical and food industries. It is a key component in controlled drug-release pills and in the manufacture of personal care products (Melia 1991). It is also used in gels applied as protecting agents during heart, thorax and cornea surgery (Nomori and Horio 1997).

**1.1 Natural woods**

Natural woods are taken from different types of trees and based on these types of trees are classified into two main groups, softwoods and hardwoods. Trees are either coniferous (bears cones and have needle shaped leaves that stay green all year round) or deciduous (has flat leaves that fall in autumn). The timber that comes from the coniferous tree is known as softwood and the timber that comes from deciduous trees is known as hardwood. Although these terms suggest that softwoods are soft and easy to cut and shape

whereas, hardwoods are hard and more difficult to shape this is not the case. For example, balsa wood which is noted for its lightness and softness is actually classified as a hardwood. (www.technologystudent.com/ )

Classifying wood as either a hardwood or softwood comes down to its physical structure and makeup, and so it is overly simple to think of hardwoods as being hard and durable compared to soft and workable softwoods. This happens to be generally true, but there are exceptions, such as in the cases of wood from yew trees, softwood that is relatively hard. And also wood from balsa trees, a hardwood that is softer than softwoods (Table 1.1).

**Table 1.1: Comparison between hardwood and softwood, (http://www.diffen.com)**

|  | **Hardwood** | **Softwood** |
|---|---|---|
| Definition | Comes from angiosperm trees that are not monocots; trees are usually broad-leaved. Has vessel elements that transport water throughout the wood; under a microscope, these elements appear as pores. | Comes from gymnosperm trees which usually have needles and cones. Medullary rays and tracheids transport water and produce sap. When viewed under a microscope, softwoods have no visible pores because of tracheids. |
| Uses | Hardwoods are more likely to be found in high-quality furniture, decks, flooring, and construction that needs to last. | About 80% of all timber comes from softwood. Softwoods have a wide range of applications and are found in building components (e.g., windows, doors), furniture, medium-density fiberboard (MDF), paper, Christmas trees, and much more. |
| Examples | Examples of hardwood trees include alder, balsa, beech, hickory, mahogany, maple, oak, teak, and walnut | Examples of softwood trees are cedar, Douglas fir, juniper, pine, redwood, spruce, and yew |
| Density | Most hardwoods have a higher density than most softwoods. | Most softwoods have a lower density than most hardwoods |
| Cost | Hardwood is typically more expensive than softwood | Softwood is typically less expensive compared to hardwood. |
| Growth | Hardwood has a slower growth rate. | Softwood has a faster rate of growth. |
| Shedding of leaves | Hardwoods shed their leaves over a period of time in autumn and winter. | Softwoods tend to keep their needles throughout the year. |
| Fire Resistance | More | Poor |

### 1.1.1 Soft wood

Softwood comes from gymnosperm trees, usually evergreen conifers, like pine or spruce. Pine, is a relatively cheap wood used in the building trade and for furniture. It is pale in colour, quite easy to cut and shape, and machines relatively well fig1.1



Fig 1.1: A photographic picture of Pine wood

### 1.1.2 Hardwood

Hardwood comes from angiosperm or flowering plants such as oak, maple, or walnut, that are not monocots. Mahogany is quite expensive and is used for good quality furniture and hardwood windows. It is light brown in colour and more difficult to use compared to pine (Fig 1.2).



Fig1.2: A photographic picture of mahogany wood

### 1.1.3 Chemical Composition of Wood

Wood is essentially composed of cellulose, hemicelluloses, lignin, and extractives. Table 1 presents major chemical compositions of some wood species. Each of these components contributes to fiber properties, which ultimately impact product properties.

**Table (1.2): Chemical Composition of Some Wood Species (Sjostrom, 1993).**

| Constituent | Scots Pine | Spruce | Eucalyptus | Silver Birch |
|---|---|---|---|---|
| Cellulose (%) | 40 | 39.5 | 45.0 | 41.0 |
| Hemicellulose | | | | |
| Glucomannan (%) | 16.0 | 17.2 | 3.1 | 2.3 |
| Glucuronoxylan (%) | 8.9 | 10.4 | 14.1 | 27.5 |
| Otherpolysaccharides (%) | 3.6 | 3.0 | 2.0 | 2.6 |
| Lignin (%) | 27.7 | 27.5 | 31.3 | 22.0 |
| Totalextractives (%) | 3.5 | 2.1 | 2.8 | 3.0 |

**1.2 Sawdust**

Sawdust or wood dust is a by-product of cutting, grinding, drilling, sanding, or otherwise pulverizing wood with a saw or other tool; it is composed of fine particles of wood. It is also the byproduct of certain animals, birds and insects which live in wood, such as the woodpecker and carpenter ant. It can present a hazard in manufacturing industries, especially in terms of its flammability. Sawdust is the main component of particleboard.



**Fig 1.3: A photographic picture of sawdust of wood**

### 1.2.1 Practical uses

A major use of sawdust is for particleboard; coarse sawdust may be used for wood pulp. Sawdust has a variety of other practical uses, including serving as mulch, as an alternative to clay cat litter, or as a fuel. Until the advent of refrigeration, it was often used in icehouses to keep ice frozen during the summer. It has been used in artistic displays, and as scatter. It is also sometimes used to soak up liquid spills, allowing the spill to be easily collected or swept aside. As such, it was formerly common on barroom floors (Felman and David, 2005).

Sawdust is used in the manufacture of charcoal briquettes. The claim for invention of the first commercial charcoal briquettes goes to Henry Ford who created them from the wood scraps and sawdust produced by his automobile factory (Green and Harvey 2006).

### 1.3 Pine tree

Pines are conifer trees in the genus *Pinus,* in the family Pinaceae. They are the only genus in the subfamily Pinoideae. Counting varieties and subspecies, the plant list of the Royal Botanic Gardens, Kew and Missouri Botanical Garden accepts 175 names of pines as current, together with some thirty or forty unresolved and many more synonyms or misapplied (Farjon, 1984).



**Fig. 1.3: Japanese red pine (*Pinus densiflora*), North Korea**, (https://en.wikipedia.org)

**1.4 Cellulose**

**1.4.1 Definition and chemical structure of cellulose**

Cellulose is the major chemical component of fiber wall and contributes 40-45% of the wood's dry weight. It is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units (Crawford, 1981). Cellulose is an important structural component of the primary cell wall of green plants. Cellulose is the most abundant organic polymer on Earth (Klemm et al, 2005). The cellulose content of cotton fiber is 90%, that of wood is 40–50% and that of dried hemp is approximately 45% (Piotrowski et al, 2011).
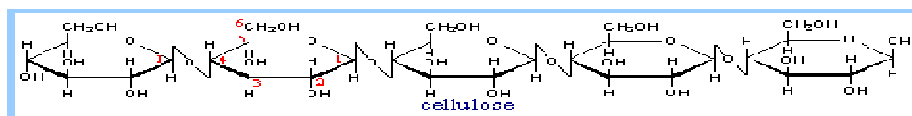


**Scheme (1.1): Schematic representation of cellulose structure,**

(https://www.rpi.edu/dept/bcbp/molbiochem/MBWeb/mb1/part2/sugar.htm)

**1.4.2 Properties of cellulose**

Cellulose has a strong tendency to form intra- and inter-molecular hydrogen bonds by the hydroxyl groups on these linear cellulose chains, which stiffen the straight chain and promote aggregation into a crystalline structure and give cellulose a multitude of partially crystalline fiber structures and morphologies (Klemm et al, 2005).

Cellulose is mainly used to produce paperboard and paper. Smaller quantities are converted into a wide variety of derivative products such as cellophane and rayon. Conversion of cellulose from energy crops into bio-fuels such as cellulosic ethanol is under investigation as an alternative fuel source. Cellulose for industrial use is mainly obtained from wood pulp and cotton (Klemm et al, 2005).

Cellulose has no taste, is odorless, is hydrophilic with the contact angle of 20–30 (Bishop and Charles, 2007), is insoluble in water and most organic solvents, is chiral and

is biodegradable. It can be broken down chemically into its glucose units by treating it with concentrated acids at high temperature. Cellulose is derived from D-glucose units, which condense through β (1→4)-glycosidic bonds. This linkage motif contrasts with that for α (1→4)-glycosidic bonds present in starch, glycogen, and other carbohydrates. Cellulose is a straight chain polymer: unlike starch, no coiling or branching occurs, and the molecule adopts an extended and rather stiff rod-like conformation, aided by the equatorial conformation of the glucose residues. The multiple hydroxyl groups on the glucose from one chain form hydrogen bonds with oxygen atoms on the same or on a neighbor chain, holding the chains firmly together side-by-side and forming microfibrils with high tensile strength. This confers tensile strength in cell walls, where cellulose microfibrils are meshed into a polysaccharide matrix.

Compared to starch, cellulose is also much more crystalline. Whereas starch undergoes a crystalline to amorphous transition when heated beyond 60–70 °C in water (as in cooking), cellulose requires a temperature of 320 °C and pressure of 25 MPa to become amorphous in water (Serge Pérez and William Mackie, 2001).

Many properties of cellulose depend on its chain length or degree of polymerization, the number of glucose units that make up one polymer molecule. Cellulose from wood pulp has typical chain lengths between 300 and 1700 units; cotton and other plant fibers as well as bacterial cellulose have chain lengths ranging from 800 to 10,000 units (Klemm et al, 2005). Molecules with very small chain length resulting from the breakdown of cellulose are known as cellodextrins; in contrast to long-chain cellulose, cellodextrins are typically soluble in water and organic solvents.

Plant-derived cellulose is usually found in a mixture with hemicellulose, lignin, pectin and other substances, while microbial cellulose is quite pure, has a much higher water content, and consists of long chains.

Cellulose consists of crystalline and amorphous regions. By treating it with strong acid, the amorphous regions can be broken-up, thereby producing nano-crystalline cellulose, a novel material with many desirable properties (Peng et al, 2011). Recently, nano-crystalline cellulose was used as the filler phase in bio-based polymer matrices to produce nano-composites with superior thermal and mechanical properties (Pranger and Tannenbaum, 2008).

## 1.4.3 Sources of cellulose

Cellulose in its native form is distributed throughout the plant kingdom, in trees, shrubs, and grass. It contains about 40% of the carbon in plant. The cell walls of green algae and some flagellates and the membranes of most fungi also contain cellulose. Cellulose never occurs in a pure form; in softwood and hardwood; it constitutes about 40-50% of the weight. In flax 70-85%, where as cotton seed hairs, which are the purest source, contain more than 90% (Table 1.3).

**Table 1.3: Natural sources of cellulose, (David N.-S. Hon, 1996)**

| Source | Cellulose content% |
|--------|--------------------|
| Bagasse | 35-45 |
| Bamboo | 40-55 |
| Cotton | 90-99 |
| Flax | 70-75 |
| Hemp | 75-80 |
| Jute | 60-65 |
| Kapok | 70-75 |
| Ramie | 70-75 |
| Straw | 40-50 |
| Wood | 40-50 |

## 1.5 Cellulose derivatives

Cellulose and cellulose derivatives are important commercial products for plastics, textiles, packaging, films, lacquers, and explosives. More recently, water and diluted

alkali soluble cellulose derivatives have been developed. Researchers are finding ways to use these derivatives as finishing and sizing agents for textiles, as absorbable surgical gauze, protective colloids, adhesives, thickening agents for foods, creams, ointments and pastes, and in pharmaceutical, printing, paper, and other industries.

Wood cellulose is the principal raw material for cellulose derivative products, and several million tons are produced each year. The second source of cellulose derivatives is cotton linters (chemical cotton). Cotton linters find preferred use in certain products such as in cellulose acetate for plastics or high-tenacity rayon. For other applications cellulose acetate is more often made from wood cellulose.

The hydroxyl groups (-OH) of cellulose can be partially or fully reacted with various reagents to afford derivatives with useful properties like mainly cellulose esters and cellulose ethers (-OR). In principle, though not always in current industrial practice, cellulosic polymers are renewable resources (Jason et al, 1997).

**1.5.1 Cellulose Esters**

Cellulose esters are generally water insoluble polymers with good film forming characteristics. Cellulose esters and organic cellulose esters are important and widely used in pharmaceutical controlled release preparations such as osmotic and enteric coated drug delivery systems. These polymers are often used with cellulose ethers concurrently for preparation of micro-porous delivery membranes. Cellulose esters categorized in organic and inorganic groups. Various types of organic cellulosic esters have been used in commercial products or in pharmaceutical investigations such as cellulose acetate (CA), cellulose acetate phthalate (CAP), cellulose acetate butyrate (CAB), cellulose acetate trimelitate (CAT), hydroxyl-propylmethyl cellulose phthalate (HPMCP) and so on. The most available formulations in market which made by these polymers are enteric coated dosage forms which are usually produced applying acid resistant polymeric coats

containing phthalate derivatives of cellulose esters especially cellulose acetate phthalate. Inorganic cellulose esters such as cellulose nitrate and cellulose sulphate are less important than organic cellulose esters in pharmaceutical industries. Cellulose nitrate or pyroxylin is a transparent compound with good film forming ability but rarely applied alone in pharmaceutical formulations due to its very low solubility in currently used pharmaceutical solvents as well as their very high flammability. The use of pure cellulose nitrate in drug formulations only limited to one topical anti-wart solution named collodion that made with 4% (w/v) concentration in diethyl ether/ethanol mixture as solvent. Cellulose nitrate/cellulose acetate mixture is also exploited to prepare micro-porous membrane filters used in pharmaceutical industries (Shokri and Adibkia, 2013).

The properties of a cellulose derivative depend on the degree of polymerization (DP) and the degree of substitution (DS). As DP decreases solubility in polar solvents increases, moisture resistance increases. For cellulose acetate, as DS increases melting point increases, vapor permeability decreases.

## 1.5.2 Cellulose Ethers

Cellulose ethers are high molecular weight compounds produced by replacing the hydrogen atoms of hydroxyl groups in the anhydroglucose units of cellulose with alkyl or substituted alkyl groups. The commercially important properties of cellulose ethers are determined by their molecular weights, chemical structure and distribution of the substituent groups, degree of substitution and molar substitution (where applicable). These properties generally include solubility, viscosity in solution, surface activity, thermoplastic film characteristics and stability against biodegradation, heat, hydrolysis and oxidation. Viscosity of cellulose ether solutions is directly related with their molecular weights. The properties of cellulose ethers are controlled by DP and DS. Examples of mostly used cellulose ethers are: Methylcellulose (MC), Ethylcellulose (EC), Hydroxyethylcellulose (HEC), Hydroxypropylcellulose (HPC),

hydroxypropylmethylcellulose (HPMC), carboxymethylcellulose (CMC) and sodium carboxymethylcellulose (Na-CMC) (Shokri and Adibkia, 2013).

Sodium-carboxymethylcellulose (CMC) is the most widely used ether, prepared by the reaction of chloroacetic acid and cellulose, water soluble, large DS range (usually 0.7-1.2), water solubility increases with DS, Used in milk products, dressings, jellies, syrups (termed cellulose gum).

### 1.5.2.1 Carboxymethylcellulose (CMC) Sodium Salt

Carboxymethylcellulose (CMC) is a chemical derivative of cellulose that can be formed by its reaction with alkali and chloroacetic acid, where some of the hydroxyl groups (-OH) are substituted with carboxymethyl groups (-CH$_2$COOH). Synonyms: CMC; Carboxymethyl ether cellulose sodium salt; Sodium carboxymethylcellulose; Sodium cellulose glycolate; Cellulose glycolic acid sodium salt.

### 1.5.2.2 Chemical Structure of CMC

The CMC structure is based on the β-(1→4)-D-glucopyranose polymer of cellulose as shown in Scheme 1.2.
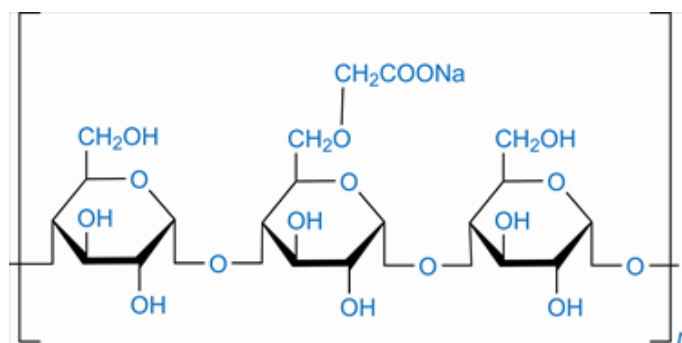


**Scheme 1.2: Schematic representation of Na-CMC structure,**

https://www.google.com/search?q=Na-CMC+structure

### 1.5.2.3 Properties of CMC

The properties of CMC depend on the degree of substitution and the length of the cellulose chains. The degree of substitution (DS) is the number of carboxymethyl groups per glucose unit and may vary in commercial products from 0.4 to 1.5. CMC is non-toxic and becomes very viscous when combined with water. It is used as a thickener for foods and as an emulsion stabilizer in products like ice cream. CMC is also used in personal lubricants, diet pills, water-based paints, detergents and paper coatings.

CMC is white to off white powder, soluble in aqueous solution, high viscosity, it is soluble at up to 50 mg/ml concentration but heat may be required. It is typically used at concentrations less than 20 mg/ml.

Under normal conditions, the effect of temperature on solutions of CMC is reversible. Slight temperature variation has no permanent effect on viscosity. However, long periods of heating CMC solutions at high temperatures, such as autoclaving, will degrade CMC and permanently reduce viscosity. This makes CMC very difficult to sterilize. Gamma-irradiation, like heating, will degrade CMC.

The viscosity of CMC solutions are both concentration and temperature dependent. As the temperature increases, the viscosity decreases. As the concentration increases, the viscosity increases (Muroi, N., et al, 1997)

### 1.5.2.4 Synthesis of CMC

CMC is produced in a Williamson ether synthesis from alkali cellulose with monochloroacetic acid (MCA) or its sodium salt (Na-MCA) in an aqueous or aqueous alcoholic medium (slurry). Hader et al (1952), as depicted in equation 1.1,1.2   illustrated the reaction for the manufacture of CMC. It is essentially a two step process. In the first step, cellulose is suspended in alkali to open the bound cellulose chains, allowing water to enter. Once this happens, the cellulose is then reacted with sodium monochloroacetate to yield sodium carboxymethyl cellulose. Latif et al (2006) also schematically showed the

carboxymethylation of cellulose using sodium monochloroacetate as carboxymethylating agent.

Step one

R-OH +NaOH--------→RONa+H$_2$O …………………………………………1.1

Step two:

R-ONa+ Cl-CH$_2$-COONa------→R-O-CH$_2$-COONa ………………………1.2
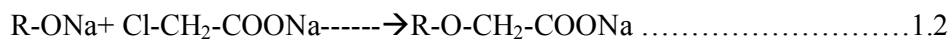
Scheme 1.3: Schematic illustration for the manufacturing of CMC, (Andrew et al 1998)

Hader et al (1952) studied the carboxymethylation of cellulose with MCA. They observed that during this reaction, hydrolysis of MCA occurs forming glycolate and sodium chloride and hydrochloric acid, respectively (Eq. 1.3).

NaOH + ClCH$_2$COONa → HO-CH$_2$COONa + NaCl …………………….. 1.3
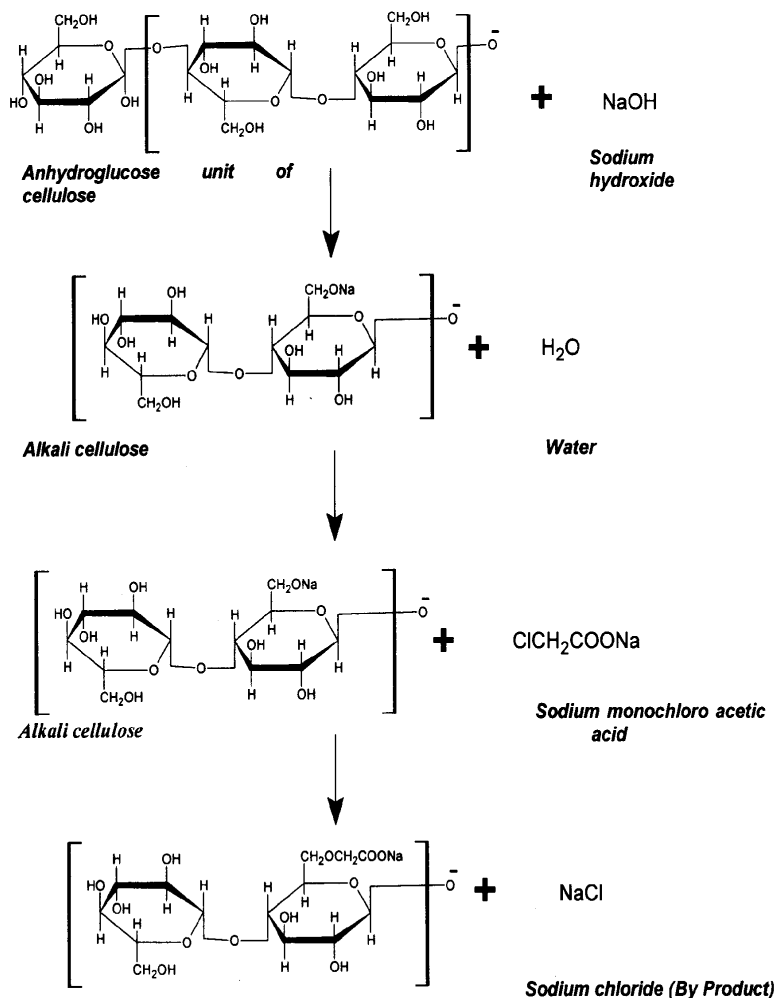


**Scheme 1.3: The reaction for the synthesis of carboxymethylcellulose (Latif et al, 2006)**

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**1.6 Applications of CMC**

There is a wide array of commercial uses for CMC due to its particular properties. CMC is soluble in water when the degree of substitution is higher than 0.5, giving high viscosity aqueous solutions. It has a thickening effect, film-forming ability, and excellent behavior as protecting colloid and adhesive. Most of the CMC applications are based on its rheological properties. The ability of CMC to function as a thickener or flow-control agent depends largely on its degree of substitution and on the molecular weight, but also on the relative stiffness of the cellulosic backbone (Rinaudo and Reguant, 2000).

CMC is non-toxic and it is currently finding an increasing number of applications in the pharmaceutical, medical and food industries. It is a key component in controlled drug-release pills and in the manufacture of personal care products (Melia, 1991). It is also used in gels applied as protecting agents during heart, thorax and cornea surgery (Nomori and Horio, 1997).

CMC materials have various industrial applications; many of these applications are dependent on their levels of purity. Unpurified CMC materials are used for many technical applications, whereas, highly purified CMC materials are applied for pharmaceutical and food industries (Table 1.4).

**Table (1.4): CMC grades and their typical applications, (Stigsson et al, 2001)**

| Quality | Examples of application areas | Content of CMC [%] | Content of salts [%] |
|---|---|---|---|
| Technical | detergents, mining floating | < 75 | > 25 |
| semi-purified | oil and gas drilling muds | 75 – 85 | 15 – 25 |
| Purified | paper coating, textile sizing and printing, ceramic glazing | > 98 | < 2 |
| extra purified (cellulose gum) | food, toothpaste, pharmaceuticals | > 99.5 | < 0.5 |

CMC has found application in building construction because its high water retention stabilizes aqueous solutions of clay, which in turns helps to control the adhesion by providing bonding strength and improves workability.

In cosmetics and pharmaceutical industries extra purified grades are used for instance as fat-free ointment base or as tablet filling matrix. Mixed esters of CMC like CMC acetate butyrate (CMCAB) showed zero-order release of the active component when used as filling matrix for drug-delivery agents (Posey-Dowty et al, 2007).

In food-grade purity, NaCMC is commonly known as "cellulose gum" or as food additive E 466. Though no maximum permissible quantities are named ("quantum satis"), its use is restricted to certain applications. An addition of CMC is forbidden e.g. for honey, butter or minced meat. In food applications, CMC improves consistency, and emulsion stability and controls and provides e.g. freeze-thaw stability of deep-frozen products. CMC is neither digested nor resorbed in the human intestinal tract (Scherz, H. 1996). In veterinary medicine, CMC is used in abdominal surgeries in large animals, particularly horses, to prevent the formation of bowel adhesions.

CMC materials also are used as dirt absorbent in the synthetic detergent and in the daily chemical industry, such as toothpaste. The glycerin solution of Carboxymethyl cellulose can used in toothpaste for gum base. For the ceramic industry Carboxymethyl cellulose uses as adhesives, plasticizers, suspending agent and fixing agent. For the textile, textile printing and dyeing industry as sizing agent to CMC for cotton, silky, chemical fiber, blended and other strong materials. For the Mining flotation Industry Carboxymethyl cellulose can be used in mining flotation to separate the metals and impurities as a high-purity, high-efficiency suspending agent. In the oil-drilling industry as an ingredient of drilling mud, where it acts as a viscosity modifier and water retention agent.

In its initial application, CMC is used as soil carrier and re-deposition inhibitor in detergents as anionic dirt particles are repelled by the anionic charges of the dissociated CM-group. It is used in deep-well drilling as flotation aid in drilling mud. Purified products are used in surface coatings and e.g. in paper industry due to the affinity of CMC

to cellulose for coatings and pulp sizing to improve fiber retention, filler/pigment/dye yield as well as paper strength. CMC also improves the printability and smoothness of paper. Together with gelatin CMC is used as a coacervate to encapsulate ink in the production of non-carbon copy papers (http://www.sino-cmc.com/)

## 1.7 Previous studies

Carboxymethyl cellulose (CMC) was prepared from bleached cellulose pulps obtained from different wood species. The pulps were carboxymethylated by successive reaction steps using monochloroacetic acid as an etherifying agent and isopropyl alcohol as a solvent. The best results of etherification were obtained in case of cotton linter pulp. The degree of substitution (DS) of CMC was found to be dependent upon the source of cellulose, but generally it was high in case of cotton linter pulp. The second etherification reaction step increases the degree of substitution (DS) up to 1.9, which in turn improved the CMC solubility in water. Qualitative and quantitative analysis of CMC were carried out to determine the moisture, sodium chloride, degree of substitution, purity and viscosity of methyl cellulose (Latif et al, 2006).

CMC was produced from several bleached cellulose pulps of non-wood species. The pulps were carboxymethylated by two successive reaction steps in aqueous medium under identical conditions. The degree of substitution (DS) of CMC was found to be dependent upon the source of the cellulose pulp. The purity of the CMCs was found to be more than 99% for all produced CMC (Barba et al, 2002).

Saputra et al (2014) reported the production of CMC which involves four main processes, the isolation of α-cellulose from the water hyacinth, the formation of alkali-catalyzed reaction (alkalization) of cellulose, the reaction with chloroacetic acid (carboxymethylation) and finally the purification of the CMC itself to remove undesirable compounds. In their research, the studied factors were the concentration of NaOH in the alkalization and the ratio of the solvent between isobutanol and ethanol. The produced

CMC materials were characterized by FT-IR spectroscopy and values of DS. The formation of CMC material was indicated by the appearance of absorption bands at 1400 – 1600 cm-1 in the FT-IR spectra. The highest DS value was found to be 1.76 and the purity of CMC was discovered to be 93.24%.

Adinugraha et al (2005) studied the carboxymethylation reaction of cellulose extracted from banana pseudo stem. The pseudo stem was dried, ground to pass 20 mesh screens. The powder was extracted using 8% NaOH at 100 °C for 3.5 h, and then bleached using 5% NaOCl at 30 8C for 3 h. Sodium Monochloracetate (ClCH$_2$COONa, NaMCA) was used as carboxymethylating agent and the reaction was conducted at a temperature of 55 °C for 3 h in the presence of isopropanol. At optimum conditions, the degree of substitution (DS), viscosity, purity and crystallinity were reported to be 0.75, 4033 cps, 98.23 and 38.33%, respectively.

Carboxymethylcellulose (CMC) samples with different degrees of substitution were also reported by Dapia et al (2005) from Eucalyptus globulus pulps made in formic acid-peroxyformic acid medium (Milox delignification) and subjected to a chlorine free bleaching. The properties of the synthesized materials i.e. rheological behaviour, solubility and molar mass were determined and examined in relation to their total degree of substitution.

The conversion of Sago waste pulp, which contains around 57% (w/w) cellulose, to CMC was also studied by Pushpamalar et al (2006). Sodium monochloroacetate was used as an etherification reaction. The reaction was optimized against temperature, concentration and reaction time. The optimized product has a large degree of substitution (DS) of 0.821. The purity of the CMC was investigated by Fourier Transform Infrared spectra (FT-IR).

**1.8 Objectives**

The main objectives of this study were:

- To extract cellulose from sawdust of pine wood.

- To convert the extracted cellulose to carboxymethylcellulose (CMC).

- To study the carboxymethylation conditions for the production of CMC with high degree of substitution (DS).

- To characterize the as-synthesized CMC materials using various spectroscopic techniques.

# Chapter two

# Experimental

# Chapter two

## Experimental

### 2.1 Materials

The materials used in this research are:

Sawdust of pine wood powdered 40-60 mesh; Sodium hydroxide (Assay 98%, Mwt 40, Oxford Lab Chem., India). Sodium hypochlorite; Ethanol (Assay 95%, LR, Loba Chemie, India); Monochloroacetic acid (Assay , LR, FSA Laboratory, 1751, England); Hydrochloric acid (35-38%, Mwt 36.46 Alpha Chemika, India); Acetic acid (Assay 99.5, Mwt 60.05, LR, Scharlau Chemie, 64, Spain); Nitric acid (Assay 69.72, Mwt 63.01, LR, Loba Chemie, 7697, India); Methanol (Assay 99.9%, Mwt 32.04, Darmstadt, Germany); Sodium acetate (Assay 99%, Mwt 82.03, Alpha Chemika, India); Sodium nitrate (Assay 99%, Mwt 84.99, Superfit Labware); Potassium bromide (Assay 99% , Mwt 119.01, CDH laboratory reagent).

All chemicals were used as purchased without any further purification.

### 2.2 Methods

#### 2.2.1 Preparation of the sample

The saw dust of pine wood, which was collected from Furniture Factory, was washed, air-dried, ground, and sieved to less than 60 meshes, dried at 80 °C.

#### 2.2.2 Extraction of cellulose

The extraction of cellulose was conducted according to the method reported by Adinugraha et al, (2005). The sample was cooked in an aqueous solution of 8 % NaOH at sample to solvent ratio of 1:20 (w/v) for 3.5 h at 100 °C. The mixture was then filtered and washed with distilled water. The color of the cellulosic material was bleached using 5 % alkaline NaOCl for 3 h at 30 °C. The material was then washed with copious amount of

distilled water until the odor of hypochlorite could no longer been detected, and then dried at 60 °C in the oven.

### 2.2.3 Synthesis of sodium carboxymethyl cellulose:

The extracted cellulose from sawdust was then converted to CMC in two steps, alkalization and etherification of cellulose under heterogeneous conditions according to the method reported by Adinugraha et al, (2005). Minor changes were made to examine the effect of different electrolytes on the value of Degree of Substitution (DS). Typically, 2.5 g of extracted cellulose powder were weighed and alkalized at 25 °C for 1 h in a shaking water bath with 10 mL of 15 % concentration of NaOH in Ethanol (solvent). After the alkalization process was over, 2.5 g of monochloroacetic acid (MCAA) and various amounts of either sodium acetate or sodium nitrate were added and the temperature was raised to 55 °C and the reaction was continued for 3 h. The slurry was neutralized with  90 % of acetic acid and filtered .The obtained CMC was washed  by 70% ethanol four times to remove undesirable byproducts, then dried at   60 °C in an oven.

### 2.2.4 Determination of Degree of Substitution

The degree of substitution (DS) of the CMC material was determined by the standard method (ASTM, 2005). 2 gm of CMC material and 37.5 mL of 95% ethyl alcohol were agitated in 250 mL beaker for 5 min. Then 5 mL of nitric acid were added and the mixture was agitated for 2 min, and then heated in a hotplate to boiling for 5 min. The solution was then removed from hotplate and further stirred for 15 minutes. After the solution had settled, the supernatant liquid was filtered and discarded, whereas, the precipitate was washed with 80 mL of 95 % ethanol which has been heated to 60 °C until the acid and salt were removed. Then the precipitate was washed with a small quantity of

anhydrous methanol and transferred to a clean beaker and heated to remove the alcohol and dried at 105 °C for 3 hours.

A quantity of 0.25 g of acid-carboxymethylcellulose form (H-CMC) was weighed in 250 mL Erlenmeyer flask and 50 mL of distilled water were added and stirred. An amount of 12.5 mL 0.5 N NaOH was added and boiled for about 15 min. The hot solution was titrated with 0.3N hydrochloric acid using phenolphthalein as indicator to observe the color change from Mexican pink (dark pink) to colorless. The carboxymethyl content and the degree of substitution were calculated according to equations 2.1 and 2.2 (Pushpamalar et al, 2006).

Carboxymethyl content (CM%) = $[(V_0-V_n)*N*0.058*100]/M$ ……………………2.1

DS = $(162*CM\%)/[5800-(57*CM\%)]$ ……………………………………………2.2

Where:

$V_0$ = Volume of HCl (in ml) used to titrate the blank.

$V_n$ = Volume of HCl (in ml) used to titrate the sample.

N = Normality of HCL used.

M = Quantity of a sample (g).

162 = Molecular weight of the anhydrous glucose unit.

58 = Molecular weight of carboxymethyl group.

**2.2.5 Characterization of Carboxymethylcellulose**

**2.2.5.1 X- Rays Diffraction (XRD) analysis**

The XRD patterns of the powder CMC materials were obtained using XRD diffractometer. The samples were ground down to particle sizes of about 0.005 mm and pressed into a sample holder. The instrument used to do this is an X-ray powder diffractometer  it consists of an X-ray tube  capable of producing a beam of monochromatic X-rays that can be rotated to produce angles from $0 - 70°$ dependant on sample and send the information to a computer.

**2.2.5.2 Fourier transforms Infra Red (FT-IR) spectroscopy**

The Fourier Transforms Infra Red (FT-IR) spectra of extracted cellulose and carboxymethyl cellulose products were obtained using Infra Red (IR) spectrometer to get the spectra. The samples were dried in the oven at 60 °C. About 0.2 mg of sample and 2 mg of KBr were mixed and ground finely and the mixture was compressed to a form a transparent disk. Transmission was measured at the wave number range of $4000–400 \text{ cm}^{-1}$.

# Chapter Three

# Results and discussion

<p style="text-align:center"><strong>Chapter Three</strong></p>

<p style="text-align:center"><strong>Results and discussion</strong></p>

## 3.1 Yield of cellulose and Caroxymethylcellulose (CMC)

The product yield was measured based on dry weight. The percentage of cellulose (Cellulose %) in sawdust sample was calculated from equation 3.1. The yield of cellulose extracted from sawdust of pine wood in this study was found to be about 50 %.

Cellulose % = (weight of extracted cellulose/weight of sawdust samples)*100   ……3.1

Whereas, the net dry weight of carboxymethyl cellulose was calculated from Equation 3.2. The yield of CMC was found to be.

Product Yield (%) = (weight of dried CMC/dry weight of cellulose)*100 ……………3.2

## 3.2 Degree of substitution for CMC materials

The Degree of Substitution was calculated for CMC materials produced in the presence of sodium acetate salt (CMC-A) or sodium nitrate salt (CMC-B) as well as in the absence of any salt (CMC-C). The estimation of DS was obtained according to method () and Eq. The results are listed in Table 3.1.

The effect of amount of sodium acetate ($CH_3COONa$) was investigated by running the carboxymethylation reaction at different weight of $CH_3COONa$ i.e. 1.25, 2.5, 5 or 7.5 g. The cellulose (2.5 g), reaction temperature (55 °C) and amount of monochloroacetic acid, MCA (2.5 g) were kept constant. The results are illustrated in Fig. 3.1. A maximum DS value of 0.963 was obtained with 5 g of $CH_3COONa$. The DS increases as the amount of $CH_3COONa$ increases up to 5 g and then decreases. The increment in DS is probably due to greater availability of the $CH_3COONa$, which facilitates the carboxymethylation of

<p style="text-align:center">23</p>

the cellulose. However, at higher concentrations of $CH_3COONa$ in the proximity of cellulose molecules the DS decreases again, because in $SN_2$ reaction become slower due to steric effects.
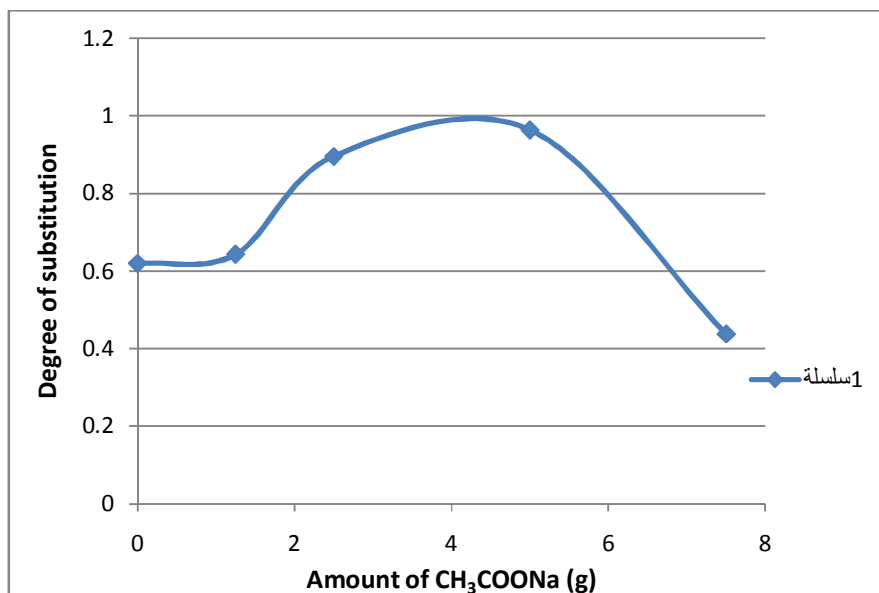


**Fig 3.1: Effect of amount of CH₃COONa on the DS of CMC produced from sawdust of pine wood**

Sodium nitrate exhibited similar trend in DS values as in the case of sodium acetate, the results are depicted in Fig. 3.2. As can be seen obviously, a maximum DS of 1.18 was obtained with 5 g of $NaNO_3$. The DS increases as the amount of $NaNO_3$ increases up to 5 g and then decreases. This could be explained in a way similar to that specified in the case of sodium acetate.
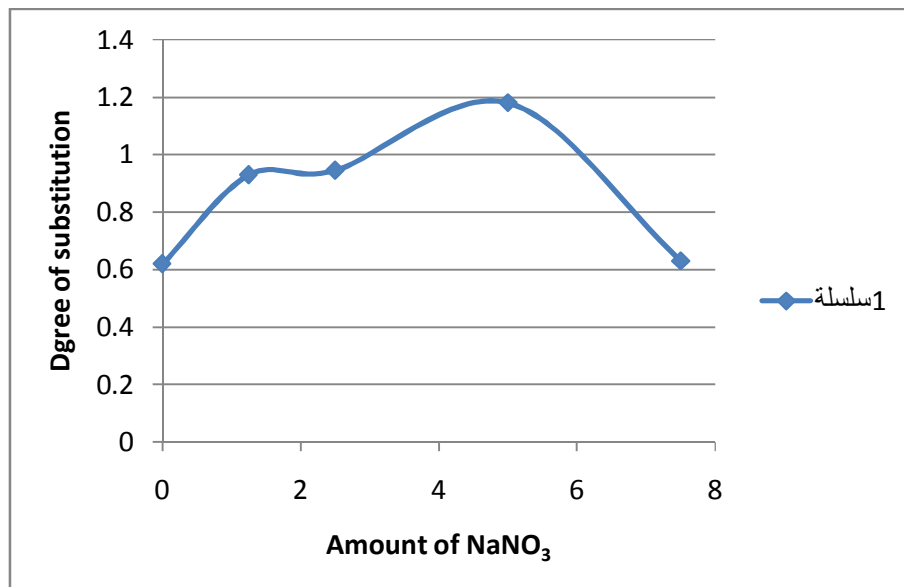
**Fig 3.2 Effect of amount of NaNO$_3$ on the DS produced from sawdust of pine wood**

**Table 3.1: The degree of substitution for CMC materials produced from sawdust of pine wood**

| Weight of CH$_3$COONa | Weight of NaNO$_3$ | %CMC | DS |
|---|---|---|---|
| 1.25 | 0.0 | 18.79 | 0.643 |
| 2.5 | 0.0 | 24.36 | 0.895 |
| 5.0 | 0.0 | 25.75 | 0.963 |
| 7.5 | 0.0 | 13.57 | 0.437 |
| 0.0 | 1.25 | 25.06 | 0.929 |
| 0.0 | 2.5 | 25.40 | 0.945 |
| 0.0 | 5.0 | 29.93 | 1.18 |
| 0.0 | 7.5 | 18.44 | 0.629 |
| 0.0 | 0.0 | 22.27 | 0.619 |

A comparison between DS value of CMC for different sources of cellulose is shown in Table (3.2). Significant differences were observed in the DS values. Different experimental conditions and chemicals used are the causes of the difference.

**Table 3.2: DS value of CMC from different sources of cellulose.**

| Sources of Cellulose | Reference | Degree of Substitution (DS) |
|---|---|---|
| Water hyacinth | Barai *et al*., 1996 | 0.24-0.73 |
| Sago waste | Pushpamalar *et al*., 2006 | 0.33-0.82 |
| Sugar beet pulp cellulose | Togrul and Arslan, 2003 | 0.11- 0.67 |
| Lantana camara | Varshney *et al*., 2006 | 0.20-1.22 |
| Palm Kernel Cake | Bono et al.,  2009 | 0.67 |

## 3.3 XRD result for CMC isolated from sawdust of pine wood

The XRD diffraction patterns of carboxymethylcellulose samples which were fabricated from sawdust are shown in Fig. 3.3. It is very clear that these patterns are quite similar to commercial CMC used for detergent industries. The XRD diffraction patterns of all CMC samples i.e. (CMC-A), $NaNO_3$ (CMC-B), exhibited abroad diffraction line of $2\theta$ angle of about 22°. However, the fabricated CMC-A and CMC-B exhibited sharp lines of NaCl and $NaNO_3$, respectively, which indicates the presence of of NaCl and $NaNO_3$ residues in the respective samples. A more efficient washing is likely required for the complete removal of these residues.
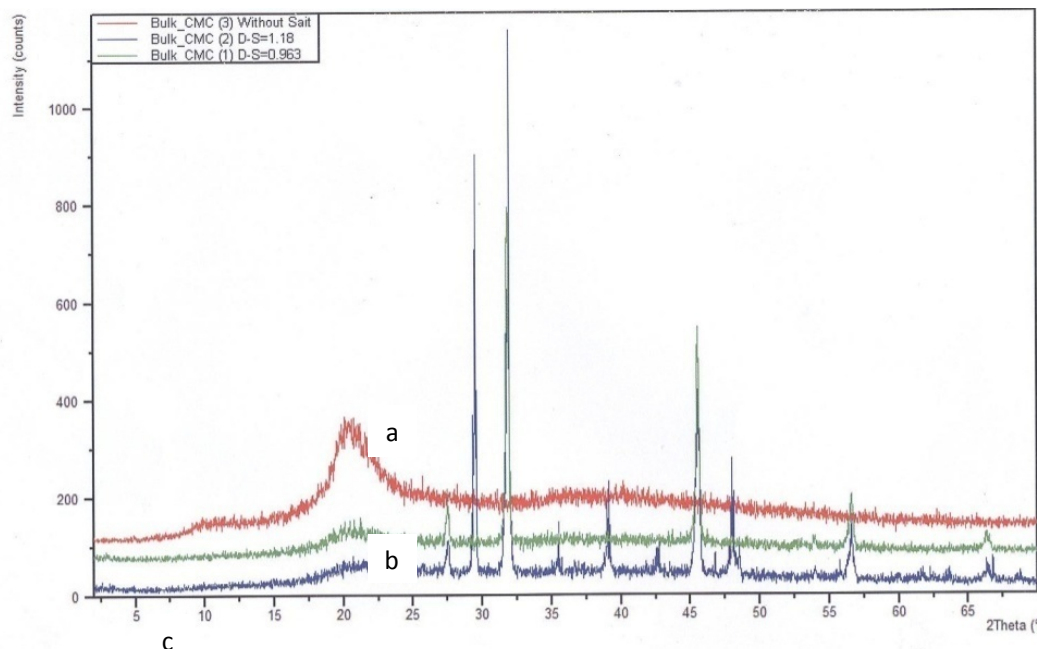
**Fig. 3.3: The XRD patterns of CMC fabricated from sawdust pine wood: a- In the absence of salts, b- In the presence of NaNO$_3$ salt, and c- In the prensence of sodiumacetate salt**

## 3.4 FT- IR result of Cellulose isolated from sawdust of pine wood

The Cellulose isolated from sawdust of pine wood was characterized by FT-IR spectroscopy, its spectrum is depicted in Fig3.4. The FT-IR spectrum of the sample shows a broad absorption band of approximately 3416 cm$^{-1}$, which could be assigned to the stretching frequency of the hydroxyl group (-OH). The band at 2903 cm$^{-1}$ is due to C–H stretching vibration. The bands at 1371, 1319 cm$^{-1}$ are assigned to –CH$_2$ bending and –OH bending vibrations, respectively. The band at 1058 cm$^{-1}$ is due to C–O–C stretching. The absence of absorption bands at wave numbers in the regions of C-H aromatics (1500-1600 cm$^{-1}$) or C=O carbonyls (1750 cm$^{-1}$) indicates complete removal of lignins or hemicellulose, respectively.
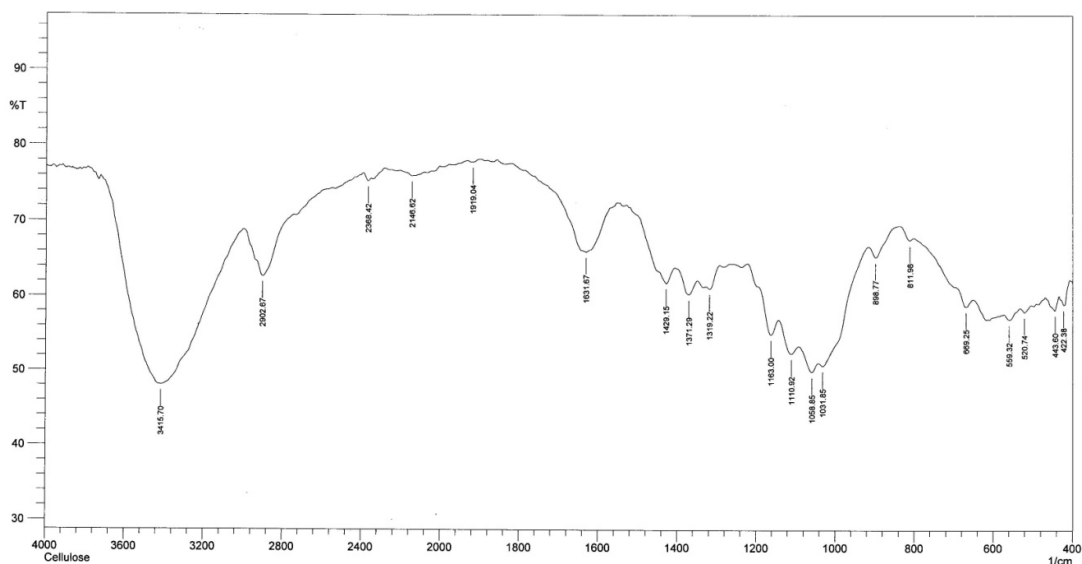
**Fig. 3.4: The FT-IR spectrum of cellulose isolated from sawdust of pine wood**

## 3.5 The FT-IR result of CMC materials fabricated from sawdust of pine wood

Figures 3.5 - 3.7show the FT-IR spectra of carboxymethylcellulose (CMC) synthesized from the carboxymethylation of cellulosic materials of pine wood sawdust at optimum condition in the presence ($CH_3COONa$ and $NaNO_3$) or absence of salt. The presence of a new and strong absorption bands at 1620 and 1614.31 $cm^{-1}$ are due to the -$COO^-$ group, which could be used as an evidence to indicate the replacement of hydroxyl groups with carboxyl group when the carboxymethylation reaction occurred. Consequently, for all CMC samples, the FT-IR spectra indicate the typical absorptions of the cellulose backbone as well as the presence of the carboxymethyl ether group at about 1059 and 1057 $cm^{-1}$.
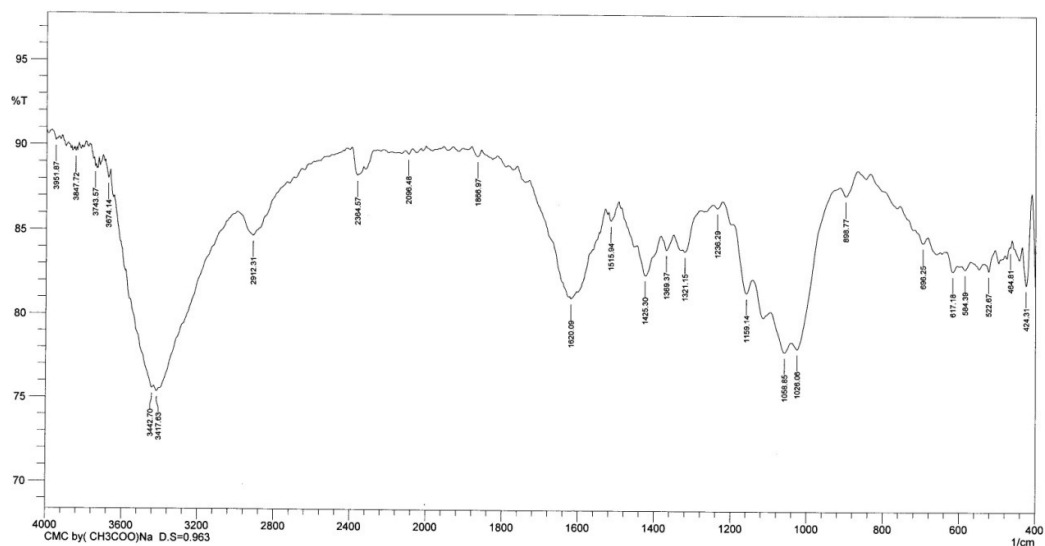
28

**Fig 3.5: The FT-IR spectrum of CMC (DS 0.963) synthesized from cellulosic pine wood sawdust at optimum conditions using CH₃COONa electrolyte salt**.
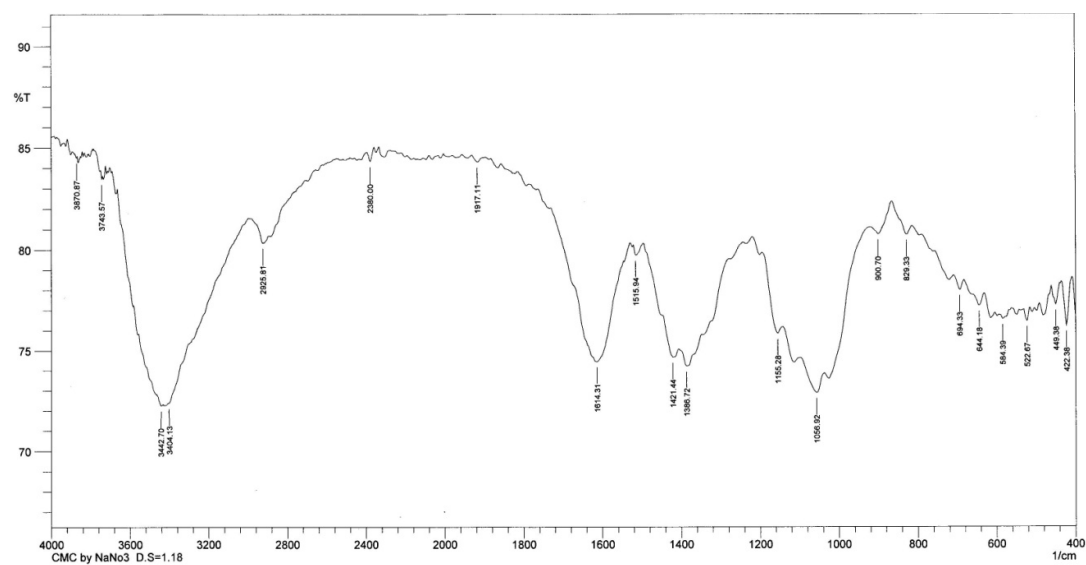


**Fig. 3.6: The FT-IR spectrum of CMC (DS 1.18) synthesized from cellulosic pine wood sawdust at optimum conditions using NaNO₃ electrolyte salt.**
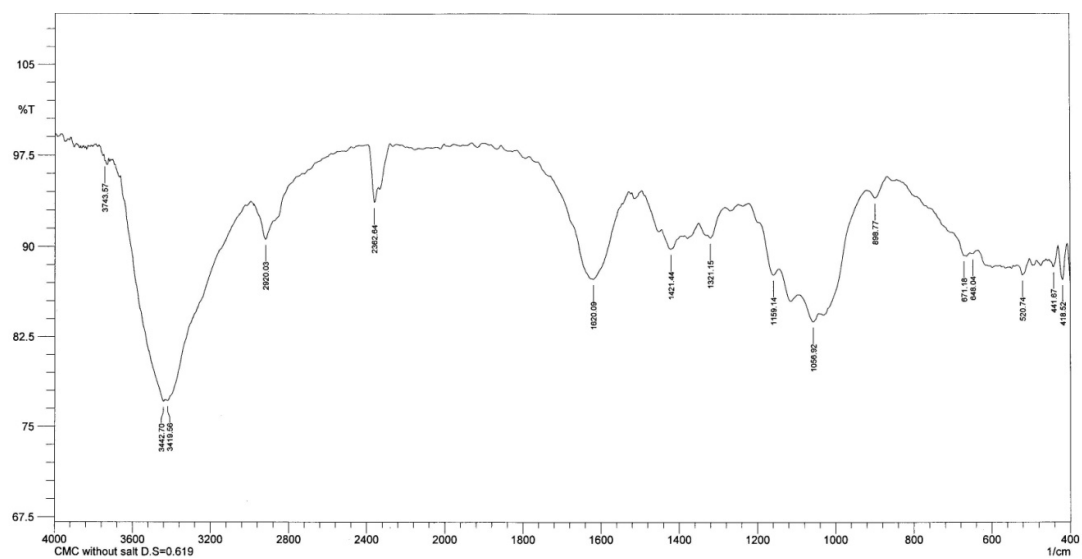
**Fig. 3.7: The FT-IR spectrum of CMC (DS 0.619) synthesized from cellulosic pine wood sawdust at optimum conditions in absence of electrolyte salt.**

**3.6 Concolusion**

In this work, CMC is successfully extracted from sawdust of pin wood by carboxymethylation. The optimizated product has a DS values of 0.963 with $CH_3COONa$, and 1.18 with $NaNO_3$ and the optimum condition were 50 ml ethanol as the solvent medium, cellulose (2.5 g), reaction temperature (55 °C) and amount of monochloroacetic acid, MCA (2.5 g).

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