Chapter One

Introduction

1.1 General Introduction

Carboxymethylcellulose (CMC) or Cellulose gum is a cellulose derivative with carboxymethyl groups ($-CH_2-COOH$) bound to some of the hydroxyl groups of the glycopyranose monomers that make up the cellulose backbone. It is often used as its sodium salt i.e. sodium carboxymethylcellulose (Adinugraha et al 2005).

The newest member of the cellulose derivatives family to be introduced commercially, carboxymethylcellulose, is finding acceptance in industry. It's the reaction product of monochloroacetic acid (MCAA) on alkali cellulose, and is, generally, supplied to the trade as the sodium salt which is a white, granular, odorless, and tasteless powder. This salt is, readily, soluble or dispersible in water or alkaline solutions to form, highly, viscous solutions useful for their thickening, suspending, and stabilizing properties. Furthermore, these solutions can be evaporated to form tough films (Adinugraha et al 2005).

The sodium salt of carboxymethylcellulose is known, in the trade, by several different names including cellulose gum, sodium cellulose glycolate, Carboxymethocel, Collocel and CMC. The first two are used as, general, trade designations; the last three are trade names for specific types sold by individual producers (Alvarez et al, 2008).

Carboxymethylcellulose is, usually, used in the form of its sodium salt (cellulose gum) which, so far, is its most important, industrial, derivative. Low substituted types, soluble in alkali but not in water. A highly substituted form, insoluble in alkali or water but soluble in organic solvents, has also been produced. The potassium salt resembles the sodium salt in many of its properties and gives a similar solution in water. The ammonium salt also is water soluble, and is, particularly, interesting because it is unstable and loses ammonia on heating to 50 – 60°C. The chief insoluble salts of carboxymethylcellulose so far investigated are those of lead, silver, mercury, and aluminum, all of which are colorless. The copper and nickel salts which are blue, and the ferric salt is red (Anna et al, 1945).

Carboxymethylcellulose is a cellulose derivative which is most, widely, used food, personal care, detergent, mining flotation, paper making, oil drilling and textile in the world because of its important properties, such as are high viscosity, water preservation, good acid resistance and salt resistance (Anna et al, 1945).

1.2 Biomass

To many people, the most familiar forms of renewable energy are the wind and the sun. But biomass (plant material and animal waste) is the oldest source of renewable energy, used since our ancestors learned the secret of fire (Tillman, 2000).

Until recently, biomass supplied for more renewable electricity or “bio-power”than wind and solar power combined (EIA, 2008).If developed properly, biomass can and should supply increasing amounts of bio-power. In fact, numerous reports were published of utilizing biomass as a renewable source of energy in America for future clean energy.

Sustainable, low-carbon biomass can provide a significant fraction of the, new; renewable energy we need to reduce our emissions of heat-trapping gases, like carbon dioxide, to levels that scientists claim will avoid the worst impacts of global warming.

Without sustainable, low-carbon bio-power, it will likely be more expensive and take longer to transform to a clean energy economy (Tillman, 2000).

But, like all energy sources, bio-power has environmental risks that need to be mitigated. If not carefully, managed for energy, biomass can be harvested at unsustainable rates, damage ecosystems, produce harmful air pollution, consume large amounts of water, and produce net greenhouse emissions (Tillman, 2000).

However, most scientists believe there is a wide range of biomass resources that can be produced sustainably and with minimal harm, while reducing the overall impacts and risks of our current energy system. Implementing proper policy is essential to secure biomass benefits and avoid its risks (Bohn et al, 2005)

Based on the bioenergy principles, UCS' work on bio-power is dedicated to distinguish between beneficial biomass resources and those that are questionable or harmful, in a practical and efficient manner, so that beneficial resources can make a significant contribution to our clean energy future (Bohn et al, 2005).

Biomass is a renewable energy source not only, because the energy that comes from the sun, but also because biomass can re-grow over a relatively short period of time. Through the process of photosynthesis, chlorophyll in plants captures the sun's energy by converting carbon dioxide from the air and water from the ground into carbohydrate compounds composed of carbon, hydrogen, and oxygen (Bohn et al, 2005).

When these carbohydrates are burnt, they turn back into carbon dioxide and water and release the energy they captured from the sun. In this way, biomass functions as a sort of natural battery for storing solar energy. As long as biomass is produced sustainably—meeting current needs without diminishing resources or the land's capacity to re-grow biomass and recapture carbon—the battery will last indefinitely and provide sources of low-carbon energy (Andreas et al, 2005).

1.2.1 Types Biomass

Most scientists believe that a wide range of biomass resources are “beneficial” because their use will, clearly reduce overall carbon emissions and provide other benefits. Among other resources, beneficial biomass includes:

- Energy crops that don’t compete with food crops for land,
- Portions of crop residues such as wheat straw or corn Stover,
- Sustainably-harvested wood and forest residues, and
- Municipal and industrial wastes.

Beneficial biomass use can be considered part of the terrestrial carbon cycle, the balanced cycling of carbon from the atmosphere into plants and then into soils and the atmosphere during plant decay. When bio-power is developed properly, emissions of biomass carbon are taken up or recycled by subsequent plant growth within a relatively short time, resulting in low net carbon emissions.

Beneficial biomass sources generally maintain or even increase the stocks of carbon stored in soil or plants. Beneficial biomass also displaces carbon emissions from fossil fuels, such as coal, oil or natural gas, the burning of which adds new and additional carbon to the atmosphere and causes global warming.

Among beneficial resources, the most effective and sustainable biomass resources will vary from region to region and also depend on the efficiency of converting biomass to its final application, be it for bio-power, biofuels, bio-products, or heat (Foley et al, 2009).

1.3 Lignin

Lignin is the third most abundant polymer in nature. It is present in plant cell walls and confers a rigid, impermeable resistance to microbial attack and oxidative stress. Lignin is a complex polymer of phenyl propane units, which are cross-linked to each other with a variety of, different, chemical bonds. It constitutes the most abundant non-polysaccharide fraction in lignocelluloses (De-la-Rubia et al, 2002). The three monomers in lignin are p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol; they are joined through alkyl–aryl, alkyl–alkyl and aryl–aryl ether bonds Fig 1.1. Lignin embeds the cellulose thereby offering protection against microbial and enzymatic degradation. Furthermore, lignin is able to form covalent bonds to some 11 hemicelluloses, e.g. benzyl ester bonds with the carboxyl group of 4-O-methyl-D-glucuronic acid in xylan (Lousada and Telmo, 2010).

1.4 Cotton fuzz

Cotton is a soft, fluffy staple fiber that grows in a boll, or protective case, around the seeds of cotton plants of the genus Gossypiumin the family of Malvaceae. The fiber is almost pure cellulose. Under natural conditions, the cotton bolls will tend to increase the dispersal of the seeds.

The plant is a shrub native to tropical and subtropical regions around the world, including America, Africa and India. The greatest diversity of wild cotton species is found in Mexico, followed by Australia and Africa.

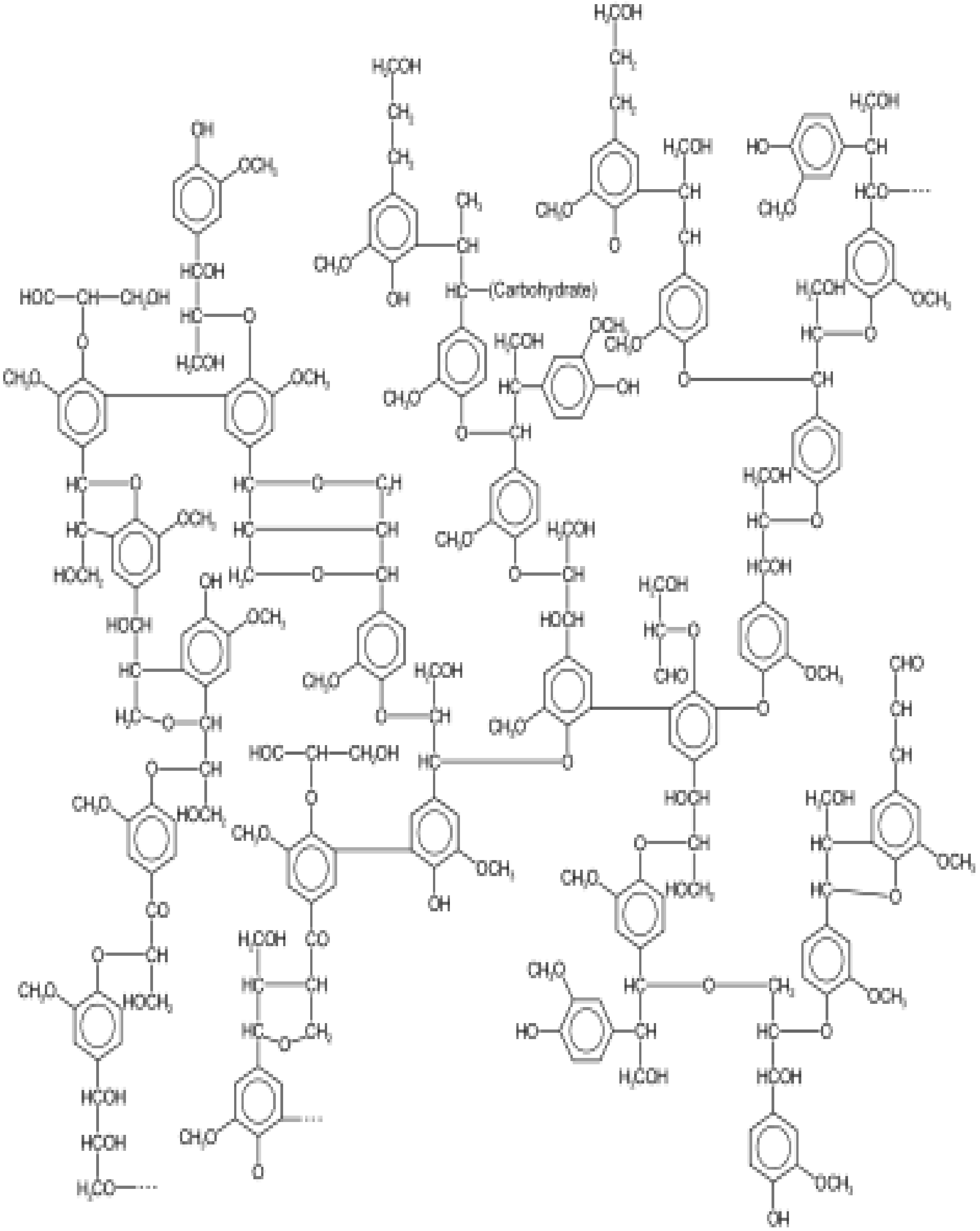


Fig. 1.1: **The lignin structure, (Wells, 1984)**

1.4.1 Types of cotton

There are four commercially grown species of cotton, all domesticated in antiquity:

- Gossypiumhirsutum, is upland cotton, native to Central America, Mexico, the Caribbean and southern Florida (90% of world production).
- Gossypiumbarbadenseis known as extra-long staple cotton, native to tropical South America (8% of world production).
- Gossypiumarboreum is tree cotton, native to India and Pakistan (less than 2%).
- Gossypiumherbaceumis Levant cotton, native to southern Africa and the Arabian Peninsula (less than 2%).

The two new cotton species account for the vast majority of modern cotton production, but the two Old World species were, widely, used before the 1900s. While cotton fibers occur naturally in colors of white, brown, pink and green, fears of contaminating the genetics of white cotton have led many cotton-growing locations to ban the growing of colored cotton varieties, which remain a specialty product (Haquet et al, 2002).

Cotton is used to make number of textile products. These include, terrycloth for absorbent bath towels and robes, denim for blue jeans and cambric popularly used in the manufacture of blue work shirts (from which we get the term "blue-collar"); and corduroy, seersucker, and cotton twill. Socks, underwear, and most T-shirts are made from cotton. Bed sheets often are made from cotton. Cotton also is used to make yarn used in crochet and knitting. Fabric also can be made from recycled or recovered cotton that otherwise would be thrown away during the spinning, weaving, or cutting process. While many fabrics are made completely of cotton, some materials blend cotton with other fibers, including rayon and synthetic fibers such as polyester. It can either be used in knitted or woven fabrics, as it can be blended with elastine to make a stretcher thread for knitted fabrics, and apparel such as stretch jeans. (Lieseand Perrin, 2001).

1.4.2 Cotton seeds

Mature seeds are brown ovoid, weighing about a tenth of a gram. By weight, they are 60% cotyledon, 32% coat and 8% embryonic root and shoot Fig 1.2. These are 20% protein, 20% oil and 3.5% starch. Fibers grow from the seed coat to form a boll of cotton lint. The boll is a protective fruit and when the plant is grown commercially, it is stripped from the seed by ginning and the lint is then processed into cotton fiber. For every hundred weight of fiber, about one hundred and sixty weights of seeds are produced. The seeds are about 15% of the value of the crop and are pressed to make oil and used as animal feed. About 5% of the seeds are used for sowing the next crop (Smith,2006).

Figure 1.2: **Cotton seeds, (http://scottonexport.com)**

1.5 Hemicellulose

Hemicelluloses are the second most abundant polymers and differ from cellulose in that they are not chemically homogeneous. Hemicelluloses are branched, with 5-carbon monosaccharides (pentoses), including D-xylose and D-arabinose, 6-carbon monosaccharides (hexoses) including D-mannose, D-galactose and D-glucose and sugar acids mainly acetyl- and methyl- substituted groups. These polymers, usually, present themselves together in the hemicellulose structure, hence there, noted names such as galactomannan, arabinoglucuronoxylan or glucuronoxylan. The average molecular formula for hemicellulose is $(C_5H_8O_4)_n$. Because the degree of polymerization n is 50 to 200, hemicelluloses have a lower molecular weight compared to cellulose and branches with short lateral chains that are easily hydrolyzed into monosaccharides(Saha, 2003; Schellerand Ulvskov, 2010). Many hemicelluloses are soluble in alkaline solutions. Hemicelluloses in green biomass like straws and grasses are composed mainly of xylan, while softwood hemicelluloses contain, mainly, glucomannan. In many plants, xylans are heteropolysaccharides with backbone chains of 1, 4-linked β-D-xylopyranose units. In addition to xylose, xylan, may, contain arabinose, glucuronic acid, or its 4-O-methyl ether, acetic acid, ferulic and p-coumaric acids. The most important biological role of hemicelluloses is their contribution to strengthening the cell wall by interaction with cellulose and, in some walls, with lignin. Hemicelluloses are bound via hydrogen bonds to the cellulose microfibrils in the plant cell wall, crosslinking them into a robust network. Hemicelluloses are also covalently attached to lignin, forming together a highly complex structure with cellulose.

1.6 Cellulose

Cellulose is the main constituent of the plant cell wall; it is the most abundant organic polymer on Earth (Klemmet al, 2005). Cellulose can be defined as a linear polymer contains β-(1- 4)-D glucopyranose units as shown in Figure 1.3. There are many types of cellulose named as cellulose (I, II, III, IV and V) and the mechanical properties depend on these types of cellulose. Type I exhibits better mechanical properties (Alvarezet al, 2008). The cellulose content of cotton fiber is 90%, that of wood is 40-50% and that of dried hemp is, approximately, 45%. Cellulose is a polysaccharide composed of linear glucan chains linked together by β-1,4-glycosidic bonds with cellobiose residues as the repeating unit at different degrees of polymerization, depending on resources. Its molecular formula is $(C_6H_{12}O_6)_n$, where n represents the degree of polymerization. Cellulose chains are grouped together to form microfibrils, which are bundled together to form cellulose fibers. The cellulose microfibrils are, mostly, independent but the ultrastructure of cellulose is, largely, due to the presence of covalent bonds, hydrogen bonds and Van der Waals forces. Hydrogen bonding within a cellulose micro fibril determines 'straightness' of the chain but inter-chain hydrogen bonds might introduce order (crystalline) or disorder (amorphous) into the structure of the cellulose. The crystalline structure makes cellulose resistant to acids and alkalis, but in the amorphous structure, cellulose is more susceptible to enzymatic degradation (De-la-Rubia et al, 2002). In nature, cellulose appears to be associated with other plant compounds and this association may affect its biodegradation. Total hydrolysis of cellulose will break the chemical bond and yields D-glucose (monosaccharide), but partial hydrolysis yields a disaccharide (cellobiose) and polysaccharides in which n is in the order of 3 to 10.

1.6.1 Structural Unit of Cellulose

Cellulose consists of a linear chain of several hundred to many thousands of β (1→4) linked D-glucose units (13-14). The multiple hydroxyl groups on the glucose from one chain form hydrogen bonds with oxygen atoms on the same or on a neighbor chain, derived from D-glucose units, which condense through β(1→4) glycosidic bonds (Deguchi et al, 2006).

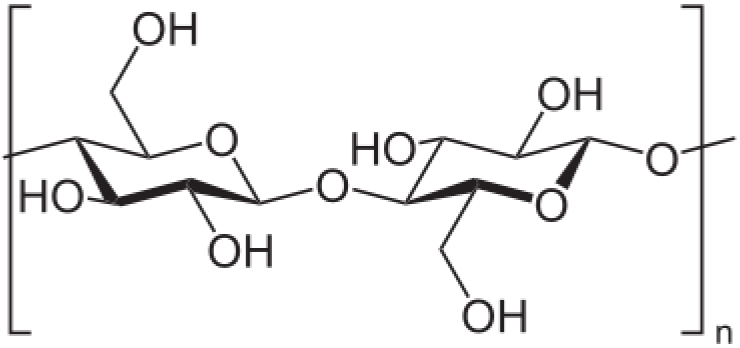


Figure 1.3: Cellulose, a linear polymer of D-glucose units (two are shown) linked by β (1→4)-glycosidic bonds, (Nishiyama et al, 2002)

1.6.2 Properties of Cellulose

Cellulose has no taste; it is odorless and hydrophilic with the contact angle of 20–30°. It is chiral, biodegradable and insoluble in water and most organic solvents. It can be broken down chemically into its glucose units by concentrated acids at high temperatures (CharlesBishop, 2011).

Many properties of cellulose depend on its chain length or degree of polymerization, i.e. the number of glucose units, that make-up one polymeric molecule.

Cellulose from wood pulp has typical chain lengths between 300 and 1700 units. Whereas, cotton and other plant fibers as well as bacterial cellulose have chain lengths ranging from 800 to 10,000 units.

1.6.3 Derivatives of Cellulose

Cellulose and cellulose derivatives are important commercial products for plastics, textiles, packaging, films, lacquers and explosives. Many cellulose derivatives, which are soluble in water or dilute alkali, 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, pharmaceuticals, printing papers and other industries derivatives like 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 many cellulose esters and cellulose ethers (Table 1.1). In principle, though not always incurrent industrial practice, cellulosic polymers are considered renewable resources.

Table 1.1: cellulose derivatives and their application sectors, (Granstrom, 2009)

Product	Production (t/a)	FG	DS	Solubility	Applications
Cellulose acetate	900000	-Oac	0.6-0.9 1.2-1.8 2.2-2.7 2.8-3.0	Water, 2-methoxy ethanol, Acetone, Ethanol	Coating and membrane
Cellulose nitrate	200000	$-NO_2$	1.8-2.0 2.0-2.3 2.2-2.8	Ethanol, methanol, acetone	Membranes and explosive
Cellulose xanthate	32000000	-C(S)Sna	0.5-0.6	NaOH/water	Textiles
Carboxymethyl cellulose	300000	$-CH_2COONa$	0.5-2.9	Water	coatings, paints, adhesives, and pharmaceuticals
Methylcellulose	150000	$-CH_3$	0.4-0.6 1.3-2.6 2.5-3.0	4% aq. NaOH Cold water Organic solvent	Films, textiles, food & tobacco industry
Ethyl cellulose	4000	$-CH_2CH_3$	0.5-0.7 0.8-1.7 2.3-2.6	4% aq. NaOH Cold water Organic solvent	Pharmaceutical industry
Hydroxyethyl cellulose	50000	$-CH_2CH_2OH$	0.1-0.5 0.6-1.5	4% aq. NaOH Water	Paints, coating, films & cosmetics

1.6.4 Products of Cellulose

Cellulose is considered the most complex form of carbohydrates and it is present in the cell walls of all plants. Because of their strength, cells with thick walls have been used in various industries. Besides the natural product being used in the textile industry, artificial fibers are derived directly from cellulose as well as countless other products. Cellulose chemistry is an important phase of organic chemistry (Chattopadhyay et al, 1946).

Cotton, a very pure form of cellulose, has been used for a very long time in the production of artificial fibers and other cellulose products. Wood is another, very available, source. When certain woods are treated with concentrated acids or alkalis, the bond between wood fibers and lignin is broken, and the pure cellulosic fibers can be removed. These fibers may then be reorganized as paper, or they may be further chemically treated. If the chemical treatment merely causes the dissolution of the fiber into its component molecules, these molecules may be synthesized into artificial fibers or converted into cellulose plastics. But if the molecules themselves are broken down, their component elements, carbon, hydrogen and oxygen, may be recombined to form wood sugar. Thereafter, wood sugar may be transformed into yeast or alcohol and thus become available for food or as the raw material for, numerous, industrial products (http://www.wikipedia.or.ke/index.php/Cellulose).

1.7 Dissolution of cellulose

The dissolution of cellulose is explored by various solvent systems that lead to a homogeneous solution. The reactions that are carried out under homogeneous conditions are only considered in this part. Two main classes of solvents are introduced, namely, derivatising and non-derivatising solvent systems.

In order to dissolve cellulose, one has to find a suitable solvent to break down the prevailing hydrogen bond network, i.e. the initial supra-molecular structure of cellulose should be destroyed in order to obtain a homogeneous (one-phase) solution. The accessibility of the C_6-OH groups in the cellulose structure is the limiting factor for the solubility of cellulose, as it is the main site for the formation of intermolecular hydrogen bonds (Kondo, 1996).

Furthermore, cellulose derivatives with unsubstituted C_6-OH groups have a tendency to form gels upon dissolving (Itagaki et al, 1997). The solubility of cellulose can be analyzed even though it is not that straight forward and the results have to be interpreted with caution. In general, the analysis is based on monitoring changes in chemical structures and physical properties. This can be done by light scattering or by rheological measurements on the molecular level. The possible derivatisation by the solvent can be investigated by NMR or other spectroscopic techniques (Nehlset al, 1994; Heinzeet al, 1998).

1.7.1 Derivatising solvent systems

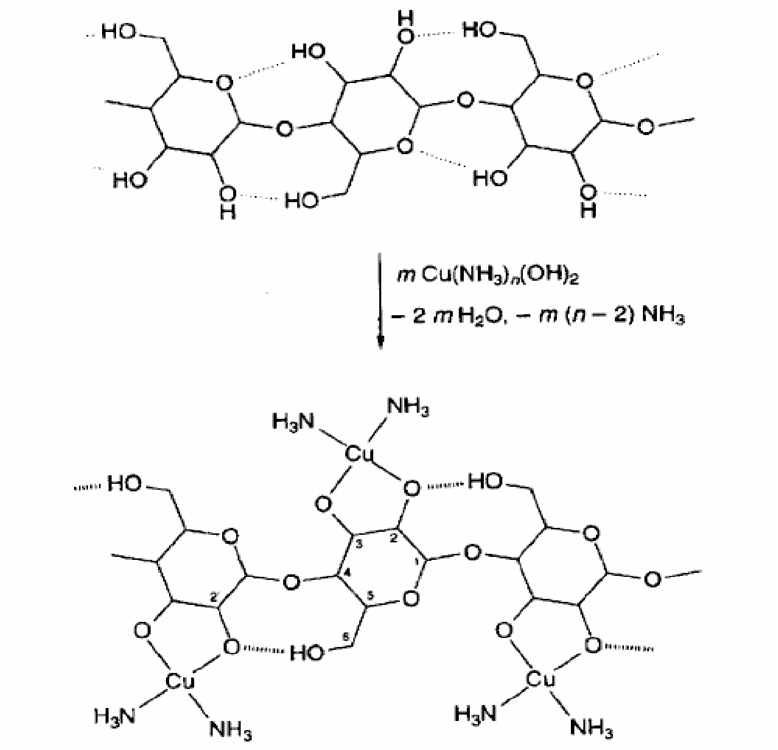
Derivatising solvent systems dissolve cellulose via covalent modification to yield unstable ethers, esters and acetals (Heinzeet al, 1998). Chemical interactions between cellulose and the solvent, on the molecular level, are fairly well defined and understood. However, the interference of the hydrogen bond system along and between the cellulose chains during the, simultaneous, dissolution and derivatisation is not, completely, understood. Moreover, the differences in solubility of unsubstituted and substituted sites on the AGU into surrounded solvent are yet a matter to be explored. The functional groups introduced during the dissolution should be, readily, removed prior to the regeneration step. For example, they can be removed by hydrolysis after further derivatisation. Dissolution with derivatising solvents systems lacks reproducibility due to the side reactions and unidentified structures few of these solvents work very efficiently. For example, the N_2O_4–DMF system has been used to produce cellulose sulphates (Granstrom, 2009).

1.7.2 Non-derivatising solvent systems

In contrast to the derivatising solvent systems, the non-derivatising solvent systems dissolve cellulose without any, chemical, and modification to form a homogeneous phase. These systems consist of one or more components there has been a great deal of research focusing on the non-derivatising solvent systems. However, only few solvent systems are suitable for controllable and homogeneous media requirement for the chemical modification of cellulose. In some cases, restrictions of use include the high reactivity of solvents, which may lead to side reactions and, also, toxicity. In addition, the solution may lose its homogeneity during the reaction was, in some cases, the partially reacted cellulose aggregates. Such aggregates, may, precipitate out of solution or form gels. This hinders the reaction from running to completion. It can also result in practical problems such as the stirring of the solution becomes difficult due excessive viscosity (Granstrom, 2009).

1.7.3 Conventional aqueous solvent systems

Cellulose can be dissolved in aqueous solvent systems containing metals such as copper in copper (II) ammonium hydroxide (CAH) and Copper (II) ethylene diamine (CEDA) solution (Klemmet al, 2005). The dissolution mechanism involves de-protonation of C_2-OH and C_3-OH during the metal complex formation as shown in Scheme 1.1.



Scheme 1.1: **The formation of CAH-cellulose complex, (Heinzeet al, 1998).**

1.8 Extraction of plant fibres' components

Cellulose, hemicelluloses and lignin are well known as major components of plant fibers, Such as flax, cotton, jute, hemp, and sisal. Cellulose exists enclosed by others two components as microfibrils (Heux et al, 2004; Lui et al, 2001). It is reported to be responsible for the mechanical, natural, property of these fibers. Depending on the source, it can be obtained as intertwined microfibrils with 2–20 μm diameter and 100–40,000 nm length in the cell wall (Brown and Itoh, 1984; Benziman et al, 1980). The existence of nanofibers having a diameter of 5-50 nm and several millimeters length was confirmed by amorphous region as well as nano-crystalline domain. These regions can be separated using controlled acid hydrolysis (Alloin et al, 2004).

A great deal of attention has been devoted to cellulose production due to its numerous, diversity of, uses in the industry. The extraction of cellulose from natural fibers is Fig 1.4 considered as one of the, most, important ways to produce cellulose. First of all, hemicelluloses extraction and lignin separation from fibers is performed by the treatment of the fibers with alkali or bisulphates. Therefore, Extraction of cellulose could be performed using different extraction procedures and each method has its advantages and drawbacks to the quality and quantity of cellulose (Alvarezet al, 2008).

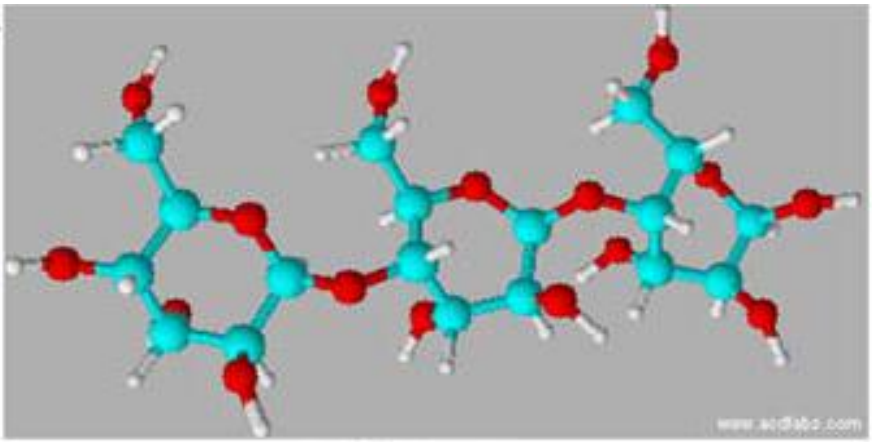


Figure 1.4: **A schematic representation for the structure of cellulose, (Alvarez et al, 2008)**

Cellulose was extracted from sisal (Alvarez et al, 2008) and it was converted to nano-cellulose. Sisal fibers were pre-treated prior to extraction by washing, several times, using distilled water and then dried for 24h at 80**C**. De-waxing step was conducted by boiling, copped, preconditioned fibers in soxhlet for 6h in a mixture of ethanol/toluene (1:2 V/V) as a solvent, rinsed with ethanol for 30 min and dried. Whereas, extraction of cellulose was carried out through two different procedures. One procedure was adopted from Sun and Sun (2002) and Su et al, (2004). Another procedure was reported by Chattopadhavay and Sarkar(1946) and Mazumdar et al (1948). Nano-fibers were prepared by acid hydrolysis of collected celluloses adopting the two procedures, using sulphuric acid (H_2SO_4) solution 60 wt. % at 45 **C**, for 30 min under continuous agitation. The celluloses materials produced by any of the two procedures were characterized using different physical techniques such as X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Scanning Electronic Microscopy (SEM) and Differential Scanning Calorimetry (DSC). The results showed that both two procedures led to purified cellulose. Nano-fibers were characterized by Atomic Force Microscopy (AFM).

1.9 Carboxymethyl cellulose (CMC)

Carboxymethyl cellulose (CMC) or cellulose gum is a cellulose derivative with carboxymethyl groups ($-CH_2-COOH$) bound to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone. CMC is an important water-soluble material which is, often; used as in its sodium, salt i.e. sodium carboxymethyl cellulose. It is obtained from the reaction of the hydroxyl groups of the anhydroglucose unit (AGUs) of cellulose with monochloroacetic acid (MCAA). CMC is considered one of the, most, important cellulose derivatives, and is used in the fields of food, cosmetics and paints as a viscosity modifier, thickener, emulsion stabilizer, water-retention agent. CMC also has a tremendous, potential for use in pharmaceutical products including site-specific or controlled-release drug delivery system, carrier matrices due to its high bio-compatibility, bio-degradability and low immunogenicity. CMC is nonpoisonous and tasteless white or light yellow free-flowing powder with stable properties and is soluble in water. Its water solution is neutral or alkaline, transparent, viscous liquid. In petroleum exploration and drilling process, it is, mainly, used as the filtrate reducer of drilling fluid, to increase the viscosity and yield of mud. With favorable carrying performance, it improves the rheological property of drilling fluid. CMC is used as binding, thickening, suspending, emulsifying, dispersing, stabilizing and, sizing agent. CMC is the most, commonly, used anti-redeposition agent (Adinugraha et al, 2005)

1.9.1 Synthesis of carboxymethyl cellulose

Sodium carboxymethyl cellulose (Na-CMC) was produced by the conversion of the cellulose, which was steeped in aqueous NaOH and a surplus of organic solvent such as ethanol. The alkaline cellulose is etherified by MCAA or its sodium salt. In this reaction, the hydroxyl groups in cellulose are, usually, replaced by carboxymethyl groups in the order of $C_2 > C_6 > C_3$ (Adinugrahaet al, 2005).

In practice, the manufacturing of CMC involves two steps (Scheme 1.2). In the first step, the cellulose is alkalized with NaOH in the presence of an inert solvent, which act both as swilling agent and as a diluting agent and thus facilitate good penetration of NaOH into the cellulose structure. The cellulose-NaOH activation reaction is often refers to alkalization reaction (Scheme 1.2). The reaction of producing CMC is, generally, performed at room temperature. The temperature used during mercerization has a significant impact on the properties of the end product i.e. on the CMC quality (Anwar et al, 2007).

The second step, involves the reaction of alkali-cellulose with MCAA in aqueous system in the presence of the inert solvent (Eq 1.1).

$$\text{Cell-OH} + \text{NaOH} + \text{ClCH}_2\text{COONa} \rightarrow \text{Cell-O-CH}_2\text{COONa} + \text{NaCl} + \text{H}_2\text{O} \quad \ldots\ldots\ldots.\ 1.1$$

In this reaction, a considerable amount of the etherifying agent, up to 30%, is consumed in side reaction with aqueous NaOH forming predominantly sodium glycolate by the hydrolysis of the chloroacetate (Heinzeet al, 1998). The CMC can be neutralized and dried immediately to give a technical grade or neutralized and wash to give a purified grade.

Rustamovet al, (2001) used different cellulose containing materials in the synthesis of CMC as sodium salt. They used waste cotton-gin as cellulose source in this study. Preparation of high homogeneity product with high value of degree of substitution (DS) and molecular mass has been confirmed experimentally. The increase of mass-diffusion of raw materials by addition of micro-accelerator has been predicted and, experimentally, proved. Moreover, a suitable mathematic model to investigate the relationship between chemical reaction and cellulose mass diffusion considering coefficient of non-globular particles has been suggested and tested and the obtained results confirmed theoretical assumptions. The rate of mass-diffusion of solid phase can be considered fundamental criteria, providing approximately that the same concentration of alkali exists in all points of cellulose raw materials during its treatment with aqueous solution of sodium alkali.

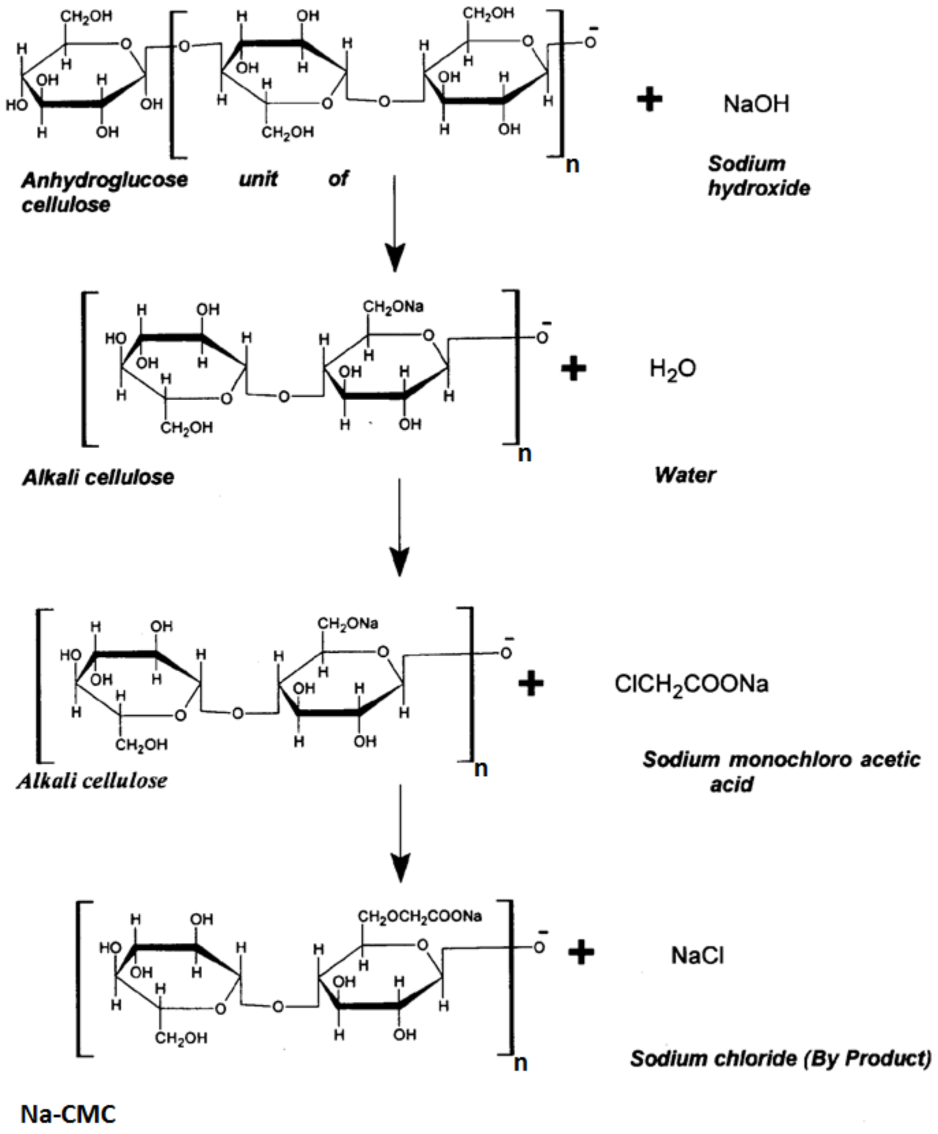
Another study in preparation of CMC was presented by Anwar et al,(2007). CMC material was prepared from bleached cellulose pulps, collected from various natural cellulosic sources including Piceasmithiana (Picp), Eucalyptus globules (Eup) and Cotton linter pulp (CLP). Alkalization of dried cellulose was performed by adding a solution of NaOH (40%) at ambient temperature for 1.5 hours. Amounts of 5-7 g of sodium monochloroacetate per 5 g of cellulose were added then the temperature was raised to 55 ºC and kept for 3.5 hours. The obtained pulps, which were carboxymethylated from one reaction step, were etherified again using isopropyl alcohol as a solvent while monochloroacetic acid (MCAA) was used as an etherifying agent. Cotton linter pulp gave the best etherification product and high DS as well, with dependency on cellulose source. The DS increased to 1.9 upon the second etherification step. This study showed that preparation of CMC with high quality can be done through two consecutive etherification steps from linter cotton pulps.

Conversion of cellulose fibers to its valuable derivative, CMC was carried out and CMC was obtained with high purity (> 90%) which allows this product to be used in pharmaceutical applications. Alpha cellulose which is obtained from short cotton fiber was used as raw material to produce CMC. Sequential concentrations of sodium hydroxide were used with monochloroacetic acid (MCAA) at optimum reaction conditions to prepare desired CMC. Batch reactor was employed to synthesize alkali cellulose with DS values of 0.15- 0.7.The maximum DS value was observed under concentration of 40% MCA and 30% solution of NaOH at pH of 7. CMC, product, purity was investigated using techniques such as scanning electron microscope (SEM) and FTIR (Heydarzadeh et al, 2009).The synthesis and characterization of CMC from water hyacinth was presented by (Saputra et al, 2014).The first step was the preparation of water hyacinth cellulose from plant. This was followed by de-waxing step (the second step), which was conducted in order to remove pectin and waxes. An aqueous solution of 1% sodium chlorite ($NaClO2$) was added to the plant powder after de-waxing step for delignification. Furthermore, alkalization by 17.5% NaOH aqueous solution was conducted for removal of lignin and hemicelluloses and the resulting cellulose was washed and neutralized in warm water using acetic acid. The conversion of cellulose into

CMC was performed through three main processes. Ethanol and isobutanol mixture was utilized as solvent for alkalization of cellulose in different ratios. Whereas, NaOH with concentration of 5M to 35M was added drop wise. The carboxylation of cellulose was performed at 60 ºC using sodium chloroacetic acid. The products were then purified and neutralized using 96% ethanol and were characterized by FT-IR. Their impurities and values of DS were evaluated.

Adinugrahaet al (2005) reported the extraction of cellulose from banana pseudo stem using 8% NaOH at 100 C for 3.5 h. The extracted cellulose was then bleached using 5% NaOCl at 30 C for 3 h. The cellulose was alkalized at 25 C for 1 h using aqueous solutions of 5–30% NaOH. Amounts of 3- 7 g of sodium monochloroacetate (Na-MCA) were added (per 5 g cellulose) to the slurry and the temperature was adjusted to 55 ºC for 3 h. Alkalization was followed using 15% NaOH, whereas, etherification was conducted using 1.2 g (w/w) of Na- MCA. The produced CMC exhibited high DS value, viscosity 0.75, 4033 cps, purity 98.23 and 38.33%, respectively.

The synthesis of CMC has been reported by manyre searchers from various sources. For instance, Ahmad, et al,(2006), converted sago pulps to CMC by etherification using sodium monochloroacetate and sodium hydroxide. The reaction was carried out at optimum temperature of 45 C for 3 hours using an aqueous solution of 25% NaOH and. The optimized product has a large value of DS of 0.821, which was found comparable to commercial CMC materials. FTIR spectra were used to indicate the conversion of sago pulps to CMC material.



Scheme 1.2: The carboxymethylation reaction for production of CMC, (Anwar et al 2005)

1.9.2 Applications of Carboxymethyl cellulose (CMC)

Sodium carboxymethylcellulose (CMC) is water soluble salt produced in large crude commercial grade quantities without any refinement for use in detergents, drilling fluids and paper industry. At high degrees of purity, CMC is used as a food additive. Given its hydrophilic character, good film forming properties, high viscosity, and adhesive performance, among other features, CMC has a wide variety of applications, which are listed below:

1.9.2.1 Industrial Technical Uses

CMC is used in most of the compositions of cement and building materials because it acts as a stabilizer and hydrophilic agent. It improves the dispersion of sand in cement, and intensifies its adhesive action. It is also used as glue in upholstery (Anna et al, 1945).

The detergent industry is the largest consumer of CMC. Technical grade CMC compositions are, most often, used for soaps and detergents. CMC acts as an inhibitor of the re-deposition of grease in fabrics after it has been removed by the detergent (Anna et al, 1945).

CMC coating reduces the consumption of wax in waxed paper and paper board, ensuring less penetration of the wax into paper. Similarly, the consumption of printing ink is reduced as a result of the surface shining. In addition, because it makes the surface smooth, CMC makes paper more resistant to grease and improves the union between fibers, thereby improving the color of the paper. It is also used as a dispersant aid in the extrusion of fibers from the pulp and prevents their flocculation (Granstrom, 2009).

In pesticides and water-based sprays, CMC acts as a suspending agent. It also functions as glue to attach the insecticide to the leaves of plants after application.

Sometimes, CMC is used as an aid in the deterioration of certain fertilizers that are highly polluting (Saputra et al, 2014).

CMC is added to various compositions of glues and adhesives that are used for almost any material. It is widely used in the leather industry. Adhesives that join wood to other wood have been, effectively, made by combining CMC with starch and phenol formaldehyde.

Crude or purified CMC is used in drilling sludge as a colloid thickener and is applied when removing the drill from the hole to avoid sediments (Granstrom, 2009).

The main use of CMC in the plastics industry is to help increase the viscosity of plastics such as latex. Moreover, CMC is used in oil paints and varnishes. It acts as a thickener and suspends the pigment in the fluid. The majority of water-soluble ethers are used to join pieces of porcelain. They have good baking properties and CMC solutions create very little ash (Saputra et al, 2014).

Crude CMC is used as sizing agent for fabrics. CMC is also used in combination with starch in laundry operations. To give a better finish to fabrics in the manufacturing process, the fabric is impregnated with CMC and is then treated with acid and heat. It is also a very effective agent in fabric printing and as a thickening agent in paints and textile varnishes (Saputra et al, 2014).

1.9.2.2 Food Technical Uses

CMC is used in food as an auxiliary agent in the churning of ice cream, creams and dairy products, as an auxiliary to form gels in gelatins and puddings, and as a thickener in salad dressings and fillings. It is also used as suspending agent in fruit juices, as a protective colloid in emulsions and mayonnaise, as a protective agent to cover the surface of fruits and as a stabilizer in ready- to- bake products. Because CMC is not metabolized by the human body, it has been approved for use in foods that are low in calories (Anna et al, 1945).

1.9.2.3 Medical Technical Uses

The most innovative applications of CMC are in the area of medicine. CMC solutions are used to form gels that are used in heart, thoracic and cornea surgery. In thorax operations, the lungs are stapled and then covered with a solution of CMC to prevent air leaks and fluid ingress. In the field of orthopedics, CMC solutions are used in lubricating the joints of the bones, most often in the wrists, knees and hips. The fluid is injected into these joints to prevent erosion, swelling and possible destruction of the cartilage attached to bones (Anna et al, 1945).

CMC is also used in dental impression materials, and in toothpastes and gels. This water soluble ether serves as a thickener, stabilizer, suspending agent and former of films in creams, lotions, or shampoos, and is widely used in hair care products (Granstrom, 2009).

CMC is also used in the manufacture of diapers and sanitary products of this type. Because it is hydrophilic, CMC helps gelatinize liquid and promotes retention (Anna et al, 1945).

1.9.2.4 Pharmaceutical Technical Uses

CMC is used to coat tablets with high degrees of purity and low viscosity. CMC is insoluble in the acidic environment of the stomach but soluble in the basic medium of the intestine. It is also used for form gels, to transport the drug, to disintegrate tablets and as a stabilizer for suspensions, emulsions, sprays and bio-adhesive tablets which attach internally to the mucus of a body part (Anna et al, 1945).

1.10 Objectives

The main objectives of this study were:

- To extracted cellulose from cotton fuzz.
- To convert the extracted cellulose to carboxymethylcellulose (CMC).
- To study the effect of addition of sodium chloride salt (NaCl) in the production of CMC with high degree of substitution.

Chapter Two

Materials and Methods

2.1 Materials

Cotton fuzz samples were collected from Elbagair, Aljazeera State, Sudan. Chemicals were used as they are without any further purification.

Sodium hydroxide (Ex pure, Oxford lab chem,India), Sodium chloride (Extra pure, Central Drug House, India), Potassium bromide (FT-IR grade, CDH, India), Hydrochloric acid (35-38%, Alpha chemika, India), Nitric acid (50-52%, Qualikems fine chemicals, India), Ethanol (99.9%, SDFCL (SD fine-chem limited), India), Methanol (99.9%, SDFCL (SD fine-chem limited, India) andMonochloroaceticacid (Min assay: 99.0%, BDH,England).

2.1.1 Preparation of Sample

Raw cotton fuzz materials was extracted from the seed, cleaned by washing and air-dried.

2.2 Methods

2.2.1 Extraction of Cellulose

An appropriate quantity of cotton fuzz was soaked in a suitable quantity of water in a beaker for about 20 minutes, and then cooked in 8% NaOH at a ratio of cellulose: solvent of 1:20 (w/v) for 3.5 h at 100 **C**. The obtained, cellulosic pulp was filtered then washed using distilled water and bleached with a solution of Clorox (5% sodium hypochlorite) for 3 h at 30 **C**. The bleached cellulose was washed again distilled water until the odor of hypochlorite can no longer, be detected, and then washed with ethanol and oven dried at 60 **C**.

2.2.2 Synthesis of sodium carboxymethylcellulose (CMC)

Five grams of extracted cellulose were transferred into a, round bottom, flask and suspended in a 100 mL of ethanol (95%) and stirred continuously in a water bath at 25 C. A volume of 12 mL of 50% NaOH aqueous solution was added drop wise over a period of 30 min. then stirred for 1 h at the same temperature (alkalization). After alkalization, 5 grams of monochloro acetic acid (MCAA) and NaCl (2,4,6,8,10 and 12 g) were added and the temperature was raised to 55**C**. The reaction was allowed to proceed for 1 h then the mixtures were neutralized with 90% acetic acid and filtered. The prepared carboxymethylcellulose (CMC) solid was washed with 70% ethanol four times to remove undesirable byproducts then dried at 60 °C in the oven.

2.2.3Determination of the degree of substitution (DS)

2.2.3.1 Conversion of Na-CMC to H-CMC carboxymethylcellulose

Absolute values of degrees of substitution (DS) were determined following the method reported by Pushpamalar et al (2006). According to this method, 4 g of CMC product and 60 mL ethanol were agitated in a 250 mL beaker for 5 min, then 10mL of 2M nitric acid were added and the mixture was agitated for extra 2 min. The mixture was heated to boiling for 5 min then agitated further for 15 min and left to settle. The supernatant liquid was filtered and discarded. The precipitate was washed with 80 mL of 95% ethanol. Further washing was done using a portion of 80% of hot ethanol (heated at 60 **C**) until the acid and salt were, completely, removed. The precipitate was, subsequently, washed with methanol then transferred to a beaker and heated until the alcoholic odor was completely, diminished. The precipitates were dried in the oven at 105 **C** for four hours.

About 0.5 g of washed dried CMC was weighed in a 250 mL; Erlenmeyer, flask and 100 mL of distilled water were added. Followed by the addition of 25 mL of 0.5 N sodium hydroxide aqueous solution and the mixture were boiled for about 15 min. The hot solution was titrated against standard 0.3N Hydrochloric acid using Phenolphthalein as indicator. The Carboxymethyl(CM) content and the degree of substitution (DS) were calculated from equations 2.1 and 2.2, respectively.

Carboxymethylcontent (CM%) = [(V_0-V_n)xNx0.058x100]/M ……..…………… 2.1

Degree of substitution (DS) = (162x(CM%)/[5800-(57x(CM%)] ……………...… 2.2

Where (V_0) is the volume of HCl(in mL) used to titrate the blank (aqueous solution of 0.5 N NaOH); (V_n) is the volume of HCl (in mL) used to titrate the sample (CMC); (N)is the normality of HClsolution; (M)is the quantity (in g) of CMC sample taken; 58 is the molecular weight of carboxymethyl group(Pushpamalar et al, 2006).

2.2.4 Characterization Methods

2.2.4.1 Fourier Transform Infra-Red analysis (FT-IR)

The Fourier transform infrared (FT-IR) spectra of extracted cellulose and produced CMC samples were recorded by Shimadzu FT-IR-8400 S. The pellets were made by grinding the sample powder with FT-IR grade KBr then pressing the mixture. The transmission was measured at wave number range of 400-4000cm^{-1}.

2.2.4.2 Determination of Viscosity

One and two grams of the as-synthesized CMC and poly anionic cellulose (PAC-LV) were weighed and dissolved separately in 100 mL of distilled water and agitated for 24 hours (Scott stirrer). Then Thermo-electron rotational viscometer, (model Haake Viscotester Plus), was used to measure the viscosity of, dissolved, cellulosic materials. The conditions are listed in Table: 2.1.

Table 2.1: The conditions for viscosity measurement of as-synthesized CMC and commercial PAC-LV materials

Conditions	Value
Percentage of CMC	1and 2 %
Percentage of PAC-LV (Commercial)	1 and 2 %
RPM	200
Spindle	01
Temperature	25 °C

Chapter Three

Results and discussion

3.1Conversion of Cotton Fuzz to CMC material

This project studies the carboxymethylation of cellulose isolated from cotton fuzz wastes, which were collected from cotton seed oil factory. The effect of sodium chloride (NaCl) salt on the carboxymethylation reaction in the presence of ethanol will only be considered. Different amounts of NaCl salt ca. 2, 4, 6, 8, 10 and 12 g were added and the produced materials were labeled accordingly i.e. CMC-2, CMC-4, CMC-6, CMC-8, CMC-10 and CMC-12 (Table 3.1). The value of DS as well as FT-IR spectra of the produced CMC materials will be taken as a key to investigate this effect.

As it had been established in literature, the degree of substitution (DS) of carboxymethyl group in CMC can be determined using conventional volumetric titration method. The value obtained corresponds to the absolute value of DS (Gapor et al, 2004).Table 3.1 and Figure 3.1present the variation of DS values, of as-synthesized CMC materials, is the increased amount of NaCl.

The increment in DS is probably due to greater availability of the NaCl which facilitates carboxymethylation of cellulose. The presence of NaCl interrupts the arrangement of cellulose molecular structure, and hence assisted the attachment of extra carboxymethyl to the cellulose backbone. However, at extremely high concentrations of NaCl in the proximity of cellulose molecules the DS drastically decreases to lower value. This could be assigned to crowding hindrance associated with copious NaCl molecules. It could also be attributed to the cellulosic backbone degradation caused by increased concentration.

Table 3.1: Variation of the Degree of substitutions of CMC with different weights of NaCl

Sample	Weight of NaCl(g)	DS
CMC-2	2	0.399
CMC-4	4	0.464
CMC-6	6	0.558
CMC-8	8	0.749
CMC-10	10	0.845
CMC-12	12	0.490

However, table 3.1 and fig 3.1 show an increase in DS up to CMC 10 and then a drastic (= 50 %) was deserved

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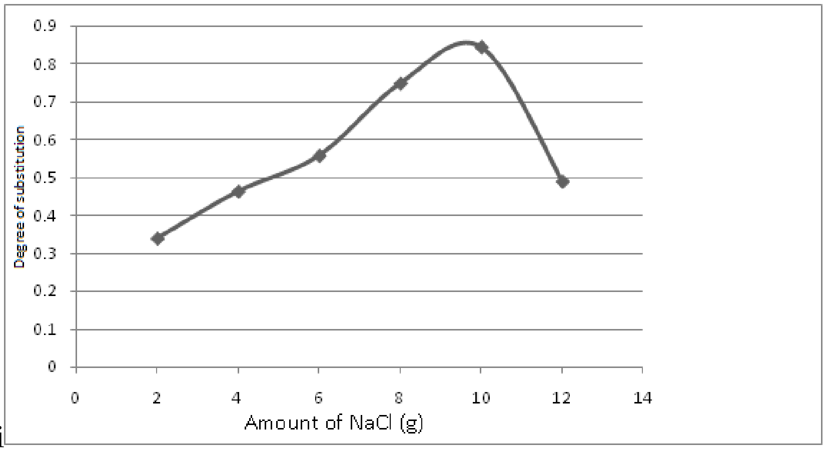

Fig 3.1: Variation of DS with NaCl added amounts (grams)

3.2 Fourier Transform Infra-Red (FT-IR) analysis

Fourier transform infrared (FT-IR) spectroscopy is widely used to characterize cellulose derivatives as it provides a simple method of obtaining direct information on chemical changes that occur during various chemical treatments (Alen et al,2002).

Figure 3.2 shows the FT-IR spectrum of untreated cotton fuzz. The broad absorption band at 3284 $cm^{-1}$is attributable to the stretching frequency of the –OH group as well as intra-molecular and intermolecular hydrogen bonds. Whereas, the band at 2898 cm^{-1} is assigned to $\mathrm{C-H}$ stretching vibration.The absorption bands of frequencies centered at 1427 and 1317 cm^{-1}values are assigned to $–CH_2$ scissoring and –OH bending vibration, respectively. The band at 1058 cm^{-1} is due to $\mathrm{OCH-O-CH_2}$ stretching (Kondo, 1997).

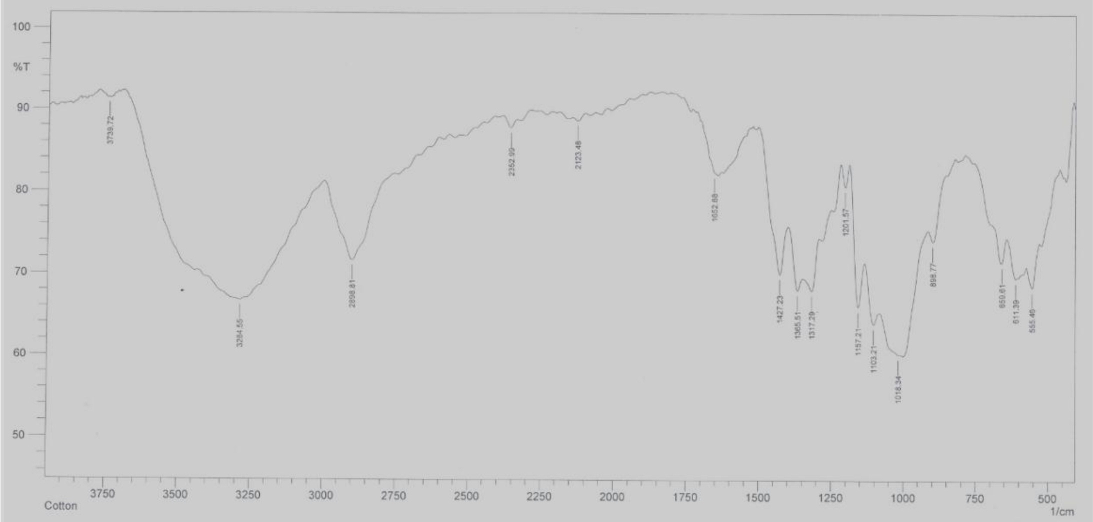

Fig 3.2: The FT-IR spectrum of untreated cotton fuzz

The FT-IR spectrum of as-synthesized CMC-2 is depicted in Figure 3.3. It shows typical absorption bands of the cellulose backbone as well as the presence of the carboxyl groups (peaks at 1645cm^{-1} and 1740 cm^{-1}).It is clearly evident that a broad absorption band at 3419cm^{-1} is due to the stretching frequency of the –OH group, whereas bands at 2896 $cm^{-1}$are attributable to C-H stretching vibration. The bands around 1429 cm^{-1} are assigned to $\mathrm{-CH_2}$ scissoring. The band at wave number 1060 cm^{-1} is due to $\mathrm{OCH-O-CH_2}$ stretching (Ahmed et al, 2006).

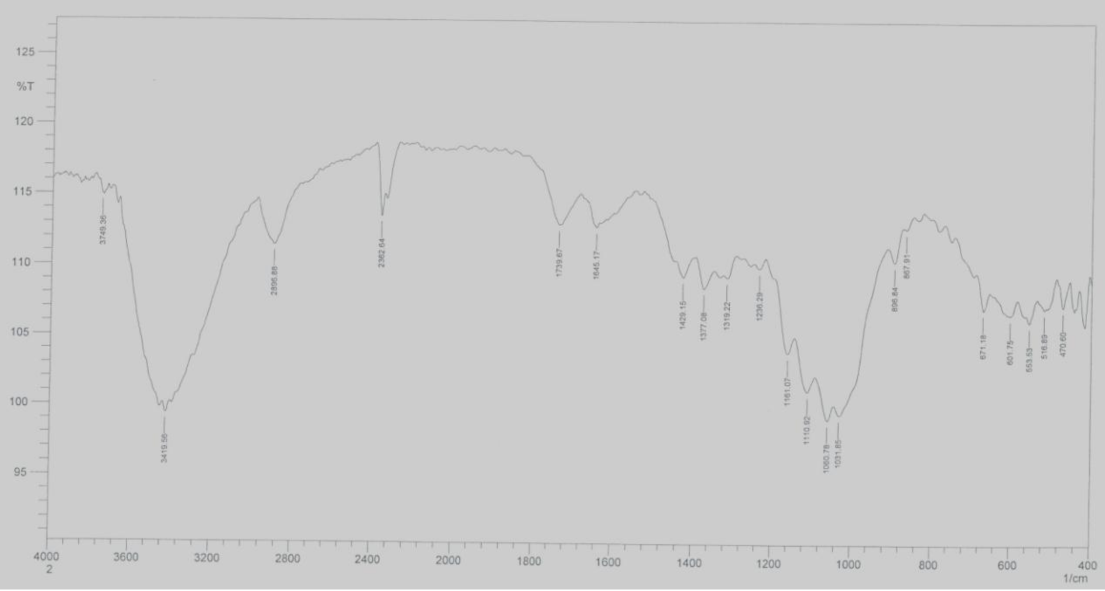

Fig. 3.3: The FT-IR spectrum of as-synthesized CMC-2(D.S 0.399)

The FT-IR spectrum of as-synthesized CMC-4 in Figure 3.4 is almost similar to that of CMC-2 material. It shows typical absorption bands of the cellulose backbone as well as the carboxyl species stretching frequencies at 1636 cm^{-1} and 1734 cm^{-1}. However the intensity of the former peak decreased, while that of later peak increased when compared to the spectrum of CMC-2 sample. It is also clearly evident that a broad absorption band at 3421cm^{-1} is due to the stretching frequency of the –OH group, whereas the peak at a frequency of 2900$cm^{-1}$is attributable to C-H stretching vibration. The band around 1434$cm^{-1}$is assigned to $-\mathrm{CH_2}$ scissoring. The band at wave number of 1056 cm^{-1} is due to $\mathrm{OCH}-\mathrm{O}-\mathrm{CH_2}$ stretching (Ahmedet al, 2006).

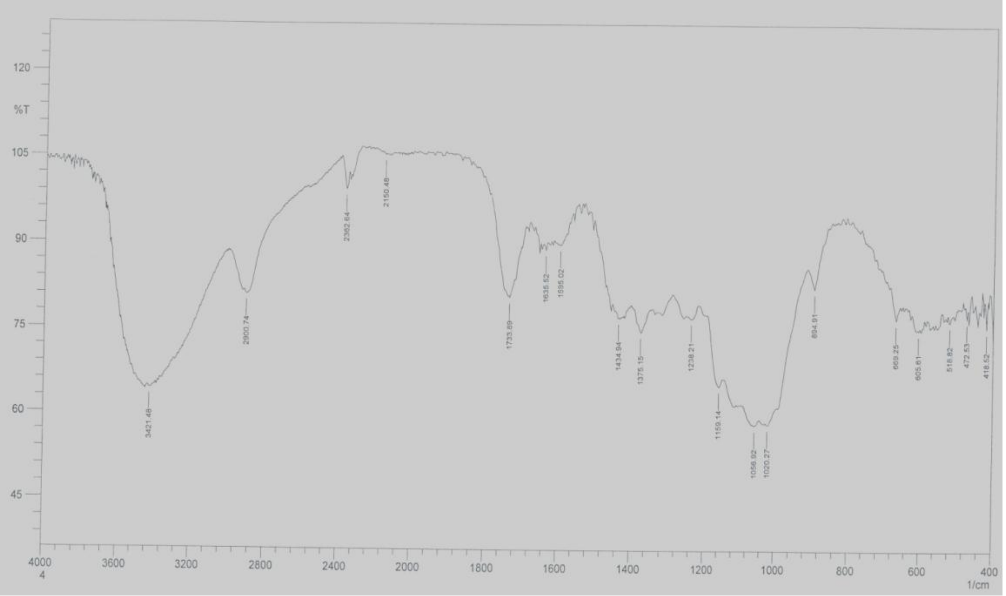

Figure 3.4: FT-IR spectrum of as-synthesized CMC-4(D.S 0.464)

The FT-IR spectrum of as-synthesized CMC-6 material is presented in Figure 3.5. Although it has a greater DS value compared to CMC-2 and CMC-4 materials, it almost shows all the absorption bands. However, the intensity of the carboxyl group bands clearly modified. The intensity of the peak at 1738 cm^{-1}increased whereas that at 1646 cm^{-1} decreased. This could be due to the attachment of more carboxymethyl groups. The other bands did not show any obvious change. The broad absorption band at 3386cm^{-1} is due to the stretching frequency of the –OH group and an intense peak at 2908cm^{-1}attributable to C-H stretching vibration. The band around 1431$cm^{-1}$is assigned to $-\mathrm{CH_2}$ scissoring. The band at wave number 1056 cm^{-1} is due to $\mathrm{OCH-O-CH_2}$ stretching (Ahmedet al, 2006).

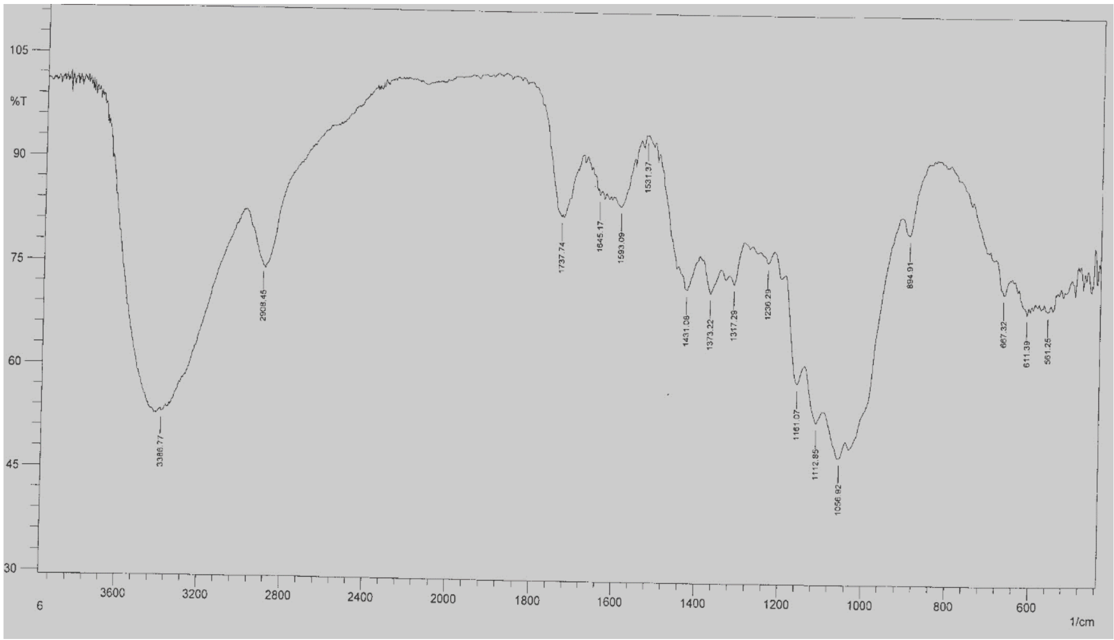

Fig. 3.5: The FT-IR spectrum of as-synthesized CMC-6(D.S 0.558)

The FT-IR spectrum of as-synthesized CMC-8 material is depicted in Figure 3.6. It shows the typical absorption bands of the cellulose backbone as well as the peaks of carboxylic group. Interestingly, the later peaks exhibited the same features of samples CMC-4 and CMC-6, i.e. the intensity of the band at 1734 cm^{-1} increased on proximity of that at 1636 cm^{-1}. Whereas, the cellulose backbone peaks did not show any drastic change.A broad absorption band at 3419cm^{-1} is due to the stretching frequency of the –OH group and the bandat 2894cm^{-1} is attributable to C-H stretching vibration. The peak around 1436cm^{-1}is assigned to $-\mathrm{CH_2}$ scissoring, whereas, that at wave number of 1060 cm^{-1} is due to $\mathrm{OCH - O - CH_2}$ stretching (Ahmed, M., et al, 2006).

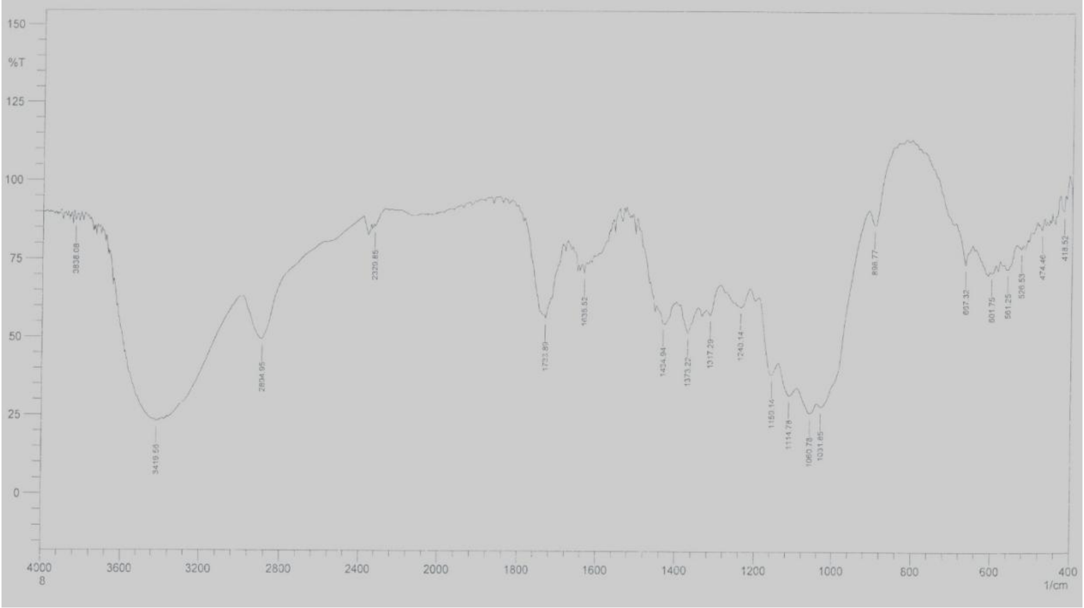

Fig. 3.6: The FT-IR spectrum of as-synthesized CMC-8(D.S 0.749)

The FT-IR spectrum of as-synthesized CMC-10, which is illustrated in Figure 3.7, shows all the absorption bands of the previously discussed CMC materials. The increment in intensity of the carboxyl group at 1732 cm-1 band is quite obvious here, while the intensity depression of the other band at 1636cm^{-1} is also observed. This trend was found consistent with the highest value of DS (0.845) registered from this sample. The other absorption bands of cellulose backbone were also observed and could be discussed in a way similar to that of previously discussed CMC materials.

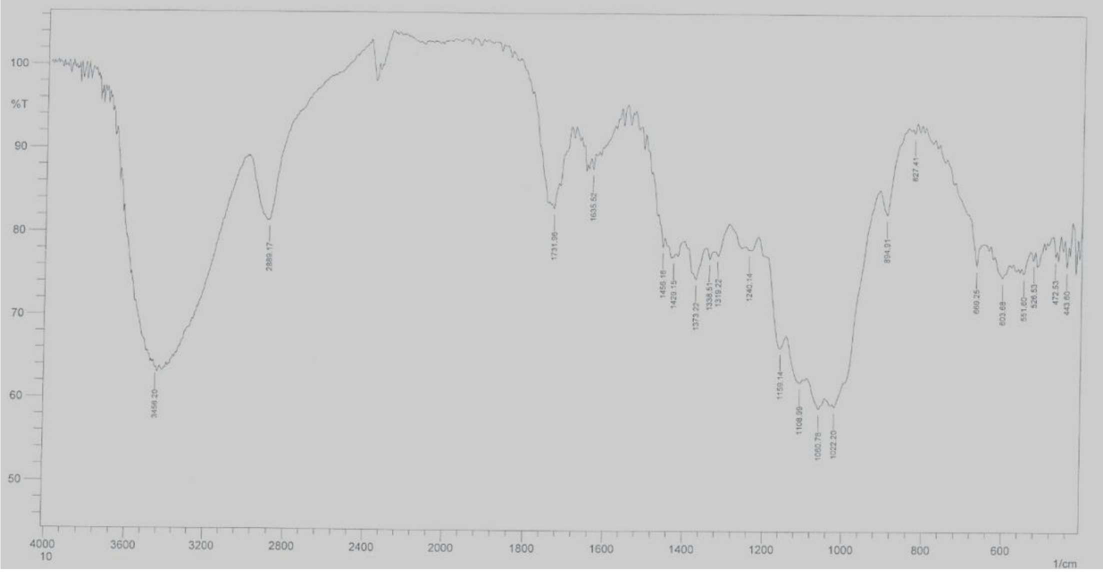

Figure 3.7: The FT-IR spectrum of as-synthesized CMC-10(D.S 0.845)

The FT-IR spectrum of as-synthesized CMC-12material is depicted in Figure 3.8.Interestingly, the spectrum of this sample is closer to that of CMC-2 sample but with a clear enhancement in the peak at 1740 cm^{-1}. The other absorption frequency of carboxyl group at 1645 cm^{-1} showed an increment in intensity compared to sample CMC-12. This situation is quite consistent with the low value of DS computed for this sample. All other bands of cellulose backbone are observed and could be discussed as illustrated earlier for other CMC samples.

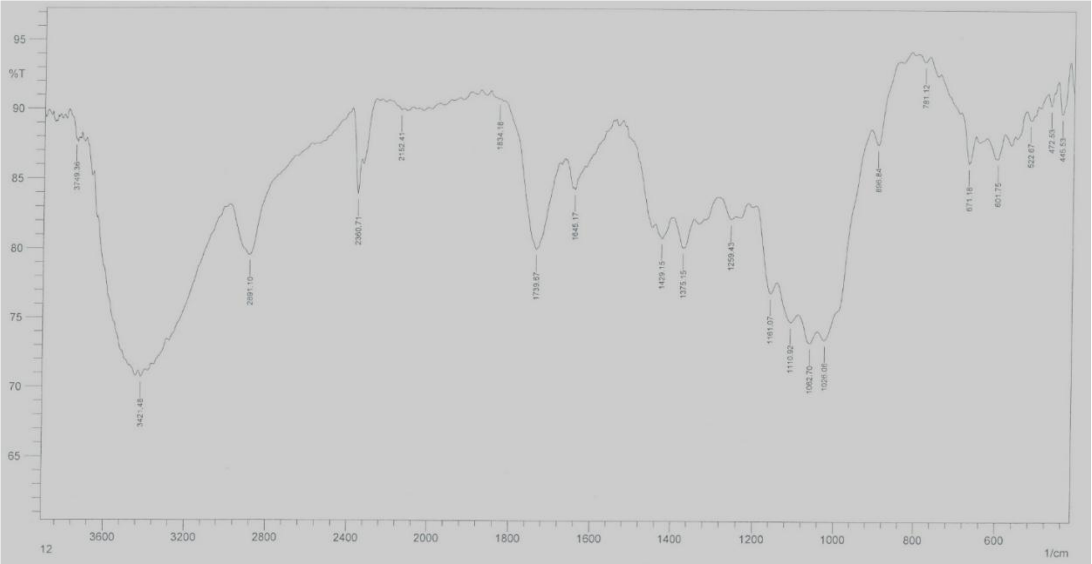

Fig. 3.8: The FT-IR spectrum of as-synthesized CMC-12(D.S 0.490)

The absorption frequencies of FT-IR spectra of as-synthesized CMC materials from cellulose isolated from cotton fuzz are summarized in Table 3.1.It is clearly evident that all CMC materials exhibited the characteristic peaks of carboxymethyl functionalized cellulosic materials beside the bands of the cellulose backbone. The presence of strong absorption bands at frequencies of 1635 - 1645 cm^{-1}as well as 1730 – 1740 cm^{-1}confirm the presence of COO^{-} group. It is quite interesting to note that the intensity of the later peaks was observed to be, directly, proportional to the DS value of the produced CMC material. While the intensity of former peaks were found to be inversely proportional to DS value of the synthesized material.

Table 3.2: **The functional groups frequencies of as-synthesized CMC materials**

CMC	O—H st.vib	C—O st.vib	COO- st.vib	COO- st.vib	CH_2 scissoring
CMC-2	3419	1161	1645	1740	1429
CMC-4	3421	1159	1636	1734	1434
CMC-6	3386	1161	1646	1738	1431
CMC-8	3419	1159	1636	1734	1436
CMC-10	3458	1159	1636	1732	1455-1429
CMC-12	3421	1161	1645	1740	1420

Conclusions

- Cellulose was successfully extracted from cotton fuzz by an aqueous solution of sodium hydroxide and purified with an alkaline aqueous solution of sodium hypochlorite. The cellulose was then converted to carboxymethylcellulose (CMC) through alkalization with ethanol sodium hydroxide solution then, subsequently, etherified with monochloroacetic acid at 55 **C**.
- Various quantities of sodium chloride salt were added to the reaction mixture to enhance the value of the degree of substitution (DS) of the produced CMC material.
- The DS value was observed to increase with increasing the amount of NaCl to certain level. The optimum quantity was investigated to be 10 g.
- The DS value of the optimized CMC material was detected to be 0.845.
- The Fourier transform infrared (FT-IR) spectroscopy confirmed the successful conversion of extracted cellulose to CMC material and reveal a reasonable relationship between the intensity of carboxylic group bands and the value of DS of the synthesized material.

Recommendations

This project aims to introduce NaCl salt to enhance the DS value of the CM prepared from cotton fuzz wastes using isopropanol. FT-IR spectroscopy was used to confirm the conversion of cellulose to CMC. It also provided a reasonable indication of the relative values of DS of the produced materials. Interesting findings were obtained, however, many points need to be considered for more useful data:

- Study the effect of other salts such as sodium acetate, sodium nitrate, etc., on the DS value of CM material.

- Applying further studies on the relationship between the area of carboxylic acid peak and DS value.

- A comparative FT-IR study of commercial CMC materials of various DS values.

- Conducting alternative validated spectroscopic technique to test the reliability of the FT-IR technique.

Reference

Adinugraha, M.P., Haryadi, Marseno, D.W., (2005). Synthesis and characterization of sodium carboxymethyl cellulose from cavendish banana pseudo stem, Carbohydrate Polymers, **62**(2), 164-169.

Ahmad, M., Lim, Y.Y., Langford, S.J., Pushpamalar, V., (2006). Optimization of reaction conditions for preparing carboxymethylcellulose from sago waste, Carbohydrate Polymers, **64**, 312-318.

Alen, R., Malkavaara, P., Pere, J., Ristolainen, M., (2002). Reflectance FTIR microspectroscopy for studying effect of xylan removal on unbleached and bleached birch Kraft pulps. Holzforschung, **56**(5), 513–521.

Alloin, F., Dufresne, A., Paillet, M., Samir, M., (2004). Tangling effect in fibrillated cellulose reinforced nanocomposites.Macromolecules, **37**, 4313–4316.

Alvarez, V.A., Morán, J.I., Vazquez, C. A., Vera, A., Viviana, P., (2008). Extraction of cellulose and preparation of nanocellulose from sisal fibers. Cellulose, **15**, 149.

Andreas, B., Brigitte, H., Dieter, K., Hans-Peter, F., (2005). Cellulose: Fascinating Biopolymer and Sustainable Raw Material. Angew. Chem. Int, **44**(22).

Anna P. W., C.B. Hollabaugh., Leland H. Burt, (1945). Carboxymethylcellulose. Uses and Applications, Ind. Eng. Chem, **37**(10), 943–947.

Anwar, T., Latif, A., Noor, S., (2007). Two-step synthesis and characterization of carboxymethylcellulose from Rayongrade wood pulp and cotton linter; Chem. Soc.Pak, **29**(2), 143-150.

ASTM (1994). Standard test method for sodium carboxymethylcellulose , Philadelphia ASTM committee on standards, 291-298. (ASTM: D 1493-94).

Benziman, M., Brown, R.M.J., Cooper, K.M., Haigler, C.H., White, A.R., (1980). Cellulose biogenesis: polymerization and crystallization are coupled processes in Acetobacterxylinum. National Academy of Science, USA, 4

Bohn, A., Fink, HP., Heublein, B., Klemm, D., (2005). Cellulose: Fascinating Biopolymer and Sustainable Raw Material, Anqew Chem Int Ed Engl, **44**(22), 3358-93.

Boudet, A.M., Chabannes, M.1., Chabbert, B., Jauneau, A., Joseleau, J.P., Ruel, K., Yoshinaga, A., (2001). In situ analysis of lignins in transgenic tobacco reveals a differential impact of individual transformations on the spatial patterns of lignin deposition at the cellular and subcellular levels, Plant J, **28**(3), 271-282

Brown, R.M.J., Itoh,T., (1984). The assembly of cellulose microfibrils in Valoniamacrophysa. Planta, **160**, 372–381.

Charles Bishop. (2011). Vacuum deposition onto webs, films, and foils. ISBN 1437778682, 9781437778687.

Chattopadhyay, H., Sarkar, P.B., (1946). A New Method for the Estimation of Cellulose. Proc Nalt Inst Sci India, **12**(1), 23–46.

Crawford, R. L., (1981). Lignin biodegradation and transformation. New York: John Wiley and Sons.

Deguchi, Kaoru, H., Koki,Shigeru,T., (2006). Cooking cellulose in hot and compressed water. Chemical Communications, (31), 3293-5.

De-la-Rubia, T., Martínez, J., Muñoz-Dorado, J., Pérez, J., (2002). Biodegradation and Biological Treatments of Cellulose, Hemicellulose and Lignin: an Overview." International Microbiology, **5**(2), 53-63.

Denny. M.w., Estevez, J.m., Lu, F.,Martone, P.t., Ralph, J., Ruel, K., Somerville, C., (2009). Discovery of Lignin in Seaweed Reveals Convergent Evolution of Cell-Wall Architecture. Current biology: CB., **19** (2), 169–75.

Energy Information Administration (EIA), (2008). Renewable energy trends. Washington, **37**(1), 181–189

Foley, A, J., Hill, J., Larson, E., Lynd, L., Pacala, S., Reilly, J., Searchinger, T., Socolow, R., Somerville, C., Tilman, D., Williams, R., (2009). Beneficial biofuels—The food, energy and environment trilemma, **325** (5938), 270-271.

Gapor, A.B., Hassan, W.H.W., Rosnah, M.S., Top, M.D., 2004. production of carboxymethylcellulose (CMC) from oil palm Empty Fruit Bunch (EFB). MPOB Information Series. http://palmoilis.mpob.gov.my/publications/TOT/TT-228.pdf.

Gargulak, Jerry, D., Lebo, McNally, Stuart E. Jr., Timothy, J., (2001). Lignin".Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc.

Granstrom, M, (2009). Cellulose derivatives: synthesis, properties and applications, Faculty of Science University of Helsiniki Finland.

Haquet, J. R. M. F., Mille, B.˜T., Moulherat, C., Tengberg, M., (2002). First Evidence of Cotton at Neolithic Mehrgarh, Pakistan: Analysis of Mineralized Fibres from a Copper Bead, Archaeological Science, **29** (12), 1393.

Heinze, T., Heinze, U., Klemm, D., Philipp, B., Wagenknecht, W., (1998). Comprehensive Cellulose Chemistry, Fundamentals and Analytical Methods, Wiley-VCH, Weinheim, 1.

Henri, C., Paul, L., Yoshiharu, N., (2002). "Crystal structure and hydrogen-bonding system in cellulose Iβ from synchrotron x-ray and neutron fiber diffraction. Journal of American Chemical Society, **124**, 9074–9082.

Heux, L., Mahrouz, M., Malainine, M.E., Vignon, M.R., (2004). Arabinan-cellulose composite in Opuntiaficus-indica prickly pear spines Carbohyd Res., **339**(1), 123–131.

Heydarzadeh, H.D., Najafpour, G.D., Nazari-Moghaddam, A.A., (2009). Catalyst-Free Conversion of Alkali Cellulose to Fine Carboxymethyl Cellulose at Mild Conditions, World Applied Sciences, **6**(4),564-569.

Itagaki, H., Kondo, T., and Tokai, M., (1997). Physical gelation process for cellulose whose hydroxyl groups are regioselectively substituted by fluorescent groups, Polymer, **38** (16), 4201-4205.

Klemm, D. B., Fink, H.P., Heublein, B., (2005) “Cellulose: Fascinating Biopolymer and Sustainable Raw Material.” AngewandteChemie International., **44**(22):3358-93.

Kondo, T. J. (1996). A Fourier transform infra-red spectroscopic analysis of the character of hydrogen bonds in amorphous cellulose, Polymer, **37**(3), 393-399.

Liese M. Perrin., (2001). Resisting Reproduction: Reconsidering Slave Contraception in the Old South, American Studies, **35** (2), 255–274.

Lousada, J., Telmo, C., (2010). The explained variation by lignin and extractive contents on higher heating value of wood, University of Tra´s-os-Montes and Alto Douro (UTAD), Forestry Department, 1013-5001-801 Vila Real, Portugal.

Ludwig, C.H., Sarkanen, K.V.(eds) (1971). Lignins: Occurrence, Formation, Structure, and Reactions, Polymer Science Part C: Polymer Letters, **10** (3), 228–230

Lui,Y., Rong, M.Z., Yang, G.C., Zeng, H.M., Zhang, M.Q. (2001). The effect of fiber treatment on the mechanical properties of unidirectional sisal-reinforced epoxy composites, Compos Sci Technol, **61**,1437–1447.

Mazumdar, A.K., Pal, K.B., Sarkar, P.B., (1948). The hemicelluloses of jute fibre. J Tex Inst, **39**(T44): 44–58.

Nehls, I., Philipp, B., Stscherbina, D., and Wagenknecht W., 1994.Characterization of cellulose and cellulose derivatives in solution by high resolution carbon-13 C-NMR spectroscopy. Progr. Polymer Sci.,**19**, 29–78.

Nishiyama, Y., Chanzy, H. J., Langan, P., (2002). Crystal structure and hydrogen-bonding system in cellulose Iβ from synchrotron x-ray and neutron fiber diffraction. Journal of American Chemical Society, **124**, 9074–9082.

Rustamov, Y. I.O., Karamamedov, G.A.O., Samedov, T. A.G., Shakhbazov, G. T. G., (2001). Theoretical Aspects of the Technology in Synthesis of Sodium Carboxymethyl Cellulose from Various Raw Materials Iranian Polymer Journal, **10**(2), 91-98

Saha, B.C., (2003). Hemicellulose Bioconversion, Journal of Industrial Microbiology and Biotechnology,**30**, 279-291.

Saputra, A.H, Qadhayna L., Pitaloka, A.B., (2014). Synthesis and Characterization of Carboxymethyl Cellulose (CMC) from Water Hyacinth Using Ethanol-Isobutyl Alcohol Mixture as the Solvents, International Journal of Chemical Engineering and Applications, **5**(1),36-40.

Scheller, H. V., Ulvskov, P., (2010). Hemicelluloses, Plant Biology,**61**(1), 263. 91.

Smith, C. W., (2006). The Encyclopedia of Seeds, CABI, 105–109.

Su, Y., Sun, J.X., Sun, R. C., Sun, X.F. (2004). Comparative study of crude and purified cellulose from wheat straw. J Agric Food Chem, **52**, 839–847.

Sun, R.C., Sun, X.F., (2002). Fractional and structural characterization of hemicelluloses isolated by alkali and alkaline peroxide from barley straw, CarbohydPolym, **49**, 415–423

Tillman, D. A., (2000). Biomass cofiring: the technology, the experience, the combustion consequences". Biomass & Bioenergy, **19**(6), 365-384.

Transformations on the spatial patterns of lignin deposition at the cellular and subcellular levels, Plant J, **28** (3), 271–282.

Updegraff, D.M., (1969). Semimicro determination of cellulose in biological materials".Analytical Biochemistry, **32** (3), 420–424.

Wells, A. F., (1984). Structural Inorganic Chemistry, 5th Edition. Oxford University Press, Oxford, UK.