

Sudan University of Science and Technology

College of Graduate Studies

**Synthesis and Characterization of Carboxymethyl
Cellulose from (Date palm) *Phoenix dactylifera L.* Leaves**

تحضير وتشخيص كربوكسى ميثيل السليلوز من الياف شجرة نخيل البلح

A Dissertation Submitted in Partial Fulfillment for the Requirements of
Master Degree in Chemistry

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Declaration

We the undersigned below declare that the dissertation entitled "Synthesis and Characterization of Carboxymethyl Cellulose from (Date palm) Phoenix dactylifera L. leaves submitted by Khadija Hassan Ahmed Albasheer to the college of graduate studies at Sudan University of Science and Technology in partial fulfillment of the requirement for the award of the degree of MSc., in chemistry is a part of a project entitled "Preparation, Characterization and Applications of Cellulose Derivatives" that is carried out under the guidance of the following supervisors:

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We further declare that the work reported in this project has not been submitted and will not be submitted, either in part or in full, for the award of any other degree in this university or any other university or institute.

Dedication

This dissertation is dedicated to my parents for their continuous support and endless love.

Acknowledgment

First and foremost I would like to praise Almighty Allah who gave me the strength and patient to complete this research. Special thanks to my supervisor Dr. Essa Esmail Mohammad who have helped me with his valuable suggestions and guidance. My thanks extend to the members of the research group and to all academic staff and technicians in the department of Chemistry (SUST) for their technical support.

Abstract

The aim of this study was to synthesize and characterize carboxymethyl cellulose (CMC) from *Phoenix dactylifera L.* (date palm) leaves by etherification reaction using sodium mono chloroacetic acid (MCAA) and sodium hydroxide. The optimum reaction parameters were found to be 55 °C, 30% sodium concentration, 3g MCAA/1g cellulose and 4 hours reaction time to give 0.77 as the highest degree of substitution (DS). FTIR shows that successful isolation of cellulose and the synthesized CMC has shown the characteristic peaks at 1726, 1602 and 1419 cm^{-1} that are attributed to carboxymethyl substituent. The CMC product is water soluble.

مستخلص البحث

هدفت هذه الدراسة لتحضير وتشخيص كربوكسى ميثيل السليلوز من سعف الياف النخيل عن طريق تفاعل الأثيرة بأستخدام أحادي كلورو حمض الخليك فى وجود هيدروكسيد الصوديوم. وقد وجد أن معاملات التفاعل المثلى هى عند درجة 55°C وتركيز هيدروكسيد الصوديوم 30% و1 جرام من السليلوز مقابل 3 جرام من أحادي كلورو حمض وزمن تفاعل 4 ساعات ليعطى 0.77 كأعلى قيمة لدرجة الأستبدال. طيف الأشعة تحت الحمراء أوضح نجاح عملية عزل السليلوز ومنتج كربوكسى ميثيل السليلوز المحضر أظهر إمتصاصات مميزة عند 1726 و1602 و 1419 cm^{-1} والتي تعزى لمستبدل الكربوكسى ميثيل. وأخيرا فقد وجد أن ناتج CMC ذائب فى الماء.

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CHAPTER ONE

Introduction and literature review

1.1 Introduction

Natural fibers in simple definition are fibers that are not synthetic or manmade. They can be sourced from plants or animals (Ticoalu *et al.*, 2010). The plants, which produce cellulose fibers can be classified into bast fibers (jute, flax, ramie, hemp, and kenaf), seed fibers (cotton, coir, and kapok), leaf fibers (sisal, pineapple, and abaca), grass and reed fibers (rice, corn, and wheat), and core fibers (hemp, kenaf, and jute) as well as all other kinds (wood and roots) (Faruk *et al.*, 2012).

Lignocellulosic fibers, also called “plant” fibers, “natural” fibers or “vegetable” fibers, are materials rich in lignin, hemicellulose and cellulose and are used for various applications, depending on their composition and physical properties. In the last two decades, the world fiber production increased 0.8 million ton. However, the last few years have shown signals of a possible stabilization in world production (FAO, 2008).

Basically, a natural fiber is composed of rigid crystalline cellulose micro fibrils which embedded in an amorphous matrix of lignin and hemicelluloses. In most plant fibers, the cellulose micro fibrils are at an angle to the cell axis called the micro fibrillar angle (MFA). MFA is considered as a key factor to explain the mechanical properties of fibers, especially their stiffness. A lower MFA means the cellulose microfibrils are well oriented along the fiber axis and therefore these fibers will have relatively lower elongations (Reddy and Yang 2007). The chemical composition (in terms of cellulose, lignin, and

hemicelluloses), MFA, as well as the crystallinity index (CrI) of the cellulose are structural parameters that vary from a plant fiber to another and are important variables that determine the overall properties of the fibers. As a result, natural fibers exhibit a very large variation as a function of the species. Moreover, the procedures used for the extraction of the fine fibers from the bast (retting) greatly impact the properties of the fibers (Tahri, 2011).

Synthetic fibers have high stiffness and strength, which make them widely used in textile, industry, as well as in composites. However these fibers show some disadvantages in terms of biodegradability energy consumption, processing, costs and machine abrasion, so there has been an increased interest in production of natural fibers for textiles and composites (Bismarck, *et al.*, 2005; Tahri *et al.*, 2016).

The applications of natural fibers are growing in many sectors such as automobiles, furniture, packing and construction. In addition, they are used as human food, animal feed, in cosmetics and medicine as well as for other biopolymers and fine chemicals. This is mainly due to their advantages compared to synthetic fibers, i.e., low cost, low weight, less damage to processing equipment, improved surface finish of moulded parts composite, good relative mechanical properties, abundant and renewable resources (Reddy and Yang, 2005; Yousif, *et al.*, 2012).

1.2 Lignin: Source and structure

Lignin is one of the most predominant biopolymers present in plants. Together with cellulose and hemicelluloses, lignin builds up the cell wall in an arrangement which is regulated on the nano-scale and results in lignin-carbohydrate network structures. Lignin is present in all vascular plants making it second to cellulose in abundance among polymers in nature.

Since lignin, like many other biomass components, is formed via the photosynthesis reaction, it is renewable and it has been estimated that the annual production of lignin on earth is in the range of $5\text{--}36 \times 10^8$ tons. In woody plants from the gymnosperm and angiosperm phylum, the lignin content is in the order of 15–40 per cent whereas in herbs, lignin content is less than 15 per cent. Low lignin content is usually encountered in annual plants. In growing plants, on the other hand, lignin constitutes an integral part of the cell walls with chemical linkages to all types of polysaccharide constituents present. For spruce wood, it has been shown that the major portion of lignin is covalently linked to the hemicelluloses, with a minor amount being linked to cellulose (Belgacem and Gandini, 2011).

The quantification of lignin present in wood and other plants is usually done indirectly by weighing the solid residue that remains after complete hydrolysis of all polysaccharides present in the material (Dence, 1992). The insoluble material, denoted Klason lignin, is thought to be formed by comprehensive condensation of the original lignin structure by the strong acidic conditions used in the hydrolysis.

1.3 Hemicelluloses: Source and structure

Hemicelluloses are the second most abundant polysaccharides in nature after cellulose. They occur in close association with cellulose and lignin and contribute to the rigidity of plant cell walls in lignified tissues. Hemicelluloses constitute about 20–30 per cent of the total mass of annual and perennial plants and have a heterogeneous composition of various sugar units, depending on the type of plant and extraction process, being classified as xylans (1,4-linked d-xylose units), mannans (1,4-linked d-mannose units), arabinans (1,5-linked l-arabinose units) and galactans (1,3-linked d-galactose units).

Xylan is one of the major constituents (25–35 per cent) of lignocellulosic materials. It has a linear backbone structure consisting of 1,4-linked d-xylopyranose residues. These may be substituted with branches containing acetyl, arabinosyl and glucuronosyl residues, depending on the botanic source and method of extraction. Xylans are the main hemicelluloses in hardwood and they also predominate in annual plants and cereals making up to 30 per cent of the cell wall material.

1.4 Cellulose: Source and structure

Cellulose is the most abundant polymer on earth, which makes it most common organic compound. Annual cellulose synthesis by plants is close to 10^{12} tons. Plants contain approximately 33% cellulose, whereas wood contains around 50% and cotton 90%. Most of cellulose is utilized as a raw material in paper production this equates annually. From this only 4 million tons are used for further chemical processing annually (Mari, 2009).

Among the polysaccharides the structure of cellulose is unique and simple however, this influences its chemical significantly. Cellulose being rigid, highly crystalline and insoluble in common organic solvents is an ideal structure engineering material (Hon, 1996; Marthur and Marthur, 2001).

Cellulose is a polydispersity linear homo polymer, consisting of regio- and enantioselectively β -1, 4- glycosidic linked D-glucoopyranose units (so-called anhydroglucose units [AGU]), it has been shown by ^1H NMR spectroscopy that the β -D-glucoopyranose adopts the $^4\text{C}_1$ chair conformation, the lowest free energy conformation of the molecule (Kester and Fennema, 1986). As a consequence, the hydroxyl groups are positioned in the ring plane (equatorial), while the hydrogen atoms are in the vertical position (axial). The polymer contains free hydroxyl groups at the C2, C3, and C6 atoms. Based on the -OH groups and the oxygen atoms of both the pyranose ring

and the glycosidic bond, ordered hydrogen bond systems from various types of supramolecular semi-crystalline structures.

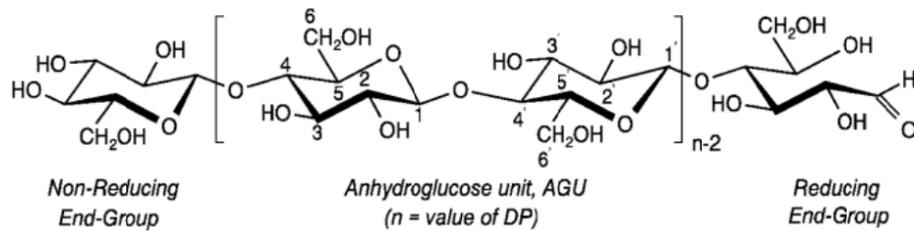


Figure 1.1: Molecular structure of cellulose (Michell and Higgins, 1965)

Three hydroxyl groups are available for reaction in each repeating unit of cellulose, the structure of cellulose being largely affected by hydrogen bonds and van der Waals forces. Hydrogen bonding within neighboring cellulose chains may act to determine the straightness of the chain (O'sullivan, 1997), and impart improved mechanical properties and thermal stability of cellulose fibers. Inter-chain hydrogen bonds may introduce order or disorder into the system depending on their regularity (O'sullivan, 1997). So, understanding hydrogen bonding within the I α and I β structures is important as it governs the stability and properties of these polymorphs (Moon *et al.*, 2011) and of cellulose itself. With the hydroxyl groups being equatorial to the cellulose ring plane, intra- and inter chain hydrogen bonding is most prevalent within the (110) plane in the triclinic structure and within the (200) plane in the monoclinic structure, hence the name “hydrogen-bonded” plane (Moon *et al.*, 2011). On the other hand, intra-chain hydrogen bonding is dominated by strong O3- H·O5 bonds (O'sullivan, 1997, Moon *et al.*, 2011).

Inter-chain hydrogen bonding within the other planes (010), (100) in the triclinic structure and the planes (110) and (110) in the monoclinic structure is substantially lower and attractive van der Waals forces are believed to dominate the cohesion forces between cellulose chains (Moon *et al.*, 2011). Within these planes, the number of weak inter-chain hydrogen bonds in the

I β structure is believed to be larger than in the I α polymorph and it has been suggested that it would contribute to the higher stability of the I β form, as compared to the I α form (Hult *et al.*, 2003; Moon *et al.*, 2011). The I α hydrogen bonds thermally degrade at lower temperatures, contributing to the lower I α thermal stability (Moon *et al.*, 2011).

The basic requirement for cellulose dissolution is that the solvent is capable of interacting with the hydroxyl groups of the AGU, so as to eliminate, at least partially, the strong intermolecular hydrogen bonding between the polymer chains. There are two basic schemes for cellulose dissolution (Belgacem and Gandini, 2011):

- (1) Where it results from physical interactions between cellulose and the solvent;
- (2) Where it is achieved via chemical reaction leading to covalent bond formation, these solvents usually being called "derivatizing solvents".

1.5 Isolation of cellulose

In the lignocellulosic materials, cellulose is embedded in a gel matrix composed of hemicelluloses, lignin, and other carbohydrate polymers (Hanley *et al.*, 1997, Yu *et al.*, 2005). The isolation of highly pure cellulose has been the subject of extensive studies for many years because of the complexity of cell wall structure (Sun and Hughes, 1998; Brendel *et al.*, 2000).

Extraction to dissolve hemicelluloses before or after delignification is the common method (Sun *et al.*, 2004). It is well known that treatment of the lignocellulosic materials with chlorite can remove almost all of the lignin, and the following isolation of cellulose with alkali extraction can be performed at room temperature, which has been applied to isolate cellulose from woody materials for analysis for more than a century.

Many effects have been made to isolate cellulose from various biomass sources, in which delignification and alkali extraction is considered as the most efficient method for separating cellulose from straws by releasing large amounts of lignin and hemicellulosic polysaccharides, respectively (Sun *et al.*, 2004). In particular, most of lignin can be removed in a delignification step using chlorite. Delignification can significantly facilitate the extraction of the hemicelluloses during alkali treatment and therefore result in the residues of cellulosic polymers having a high purity. On the basis of the investigation of polysaccharides obtained from the delignified OAT (Organic Anion Transporters) tissues (Buchala *et al.*, 1972).

Sun *et al.*, (1998) extracted cellulose from wheat straw holocellulose (using 24% KOH and 2% boric acid at 20°C for 2 h and obtained 41.8–43.0% of cellulose.

Liu *et al.*, (2006) used delignification and alkali extraction to isolate cellulose from ryegrass. They found treatment at 22°C with 18% NaOH and 18% KOH for 2 h and 10% NaOH and 10% KOH for 16 h yielded 28.2, 28.8, 22.7, and 23.4%, respectively, of cellulose residue from untreated ryegrass leaves and 35.7, 36.8, 32.8, and 34.6%, respectively, from the dejuiced ryegrass leaves. For each cellulosic fraction, the glucose content was 71.6, 69.6, 67.8, 66.7, 69.7, 68.6, 63.9, and 61.7%, respectively.

Sun *et al.*, (1998) isolated cellulose from dewaxed wheat straw after alkali extraction, followed by delignification and alkali extraction. Dewaxed wheat straw was first treated with 3% NaOH at 45 °C for 2–15 h with a low extractant/sample ratio. The treatments resulted in the release of 32.7–41.5% hemicellulose-lignin complexes, which contained 9.3– 14.2% associated lignin. The residues of the treated straw were sequentially delignified with NaClO₂ and then extracted with 10% KOH at 25 °C for 16 h. The yields of cellulose ranged 38.0–39.9%. This procedure could be used to obtain cellulosic and hemicellulose polymers from straws.

Adinugraha and Marseno, (2005) reported a method to isolate cellulose from Cavendish banana pseudo stem for further utilization. Cellulose preparations were obtained from the banana pseudo stem powder ground to pass 20 mesh after extraction with 8% NaOH at 100 °C for 3.5 h, followed by bleaching with 5% NaClO₂ at 30 °C for 3 h.

Reddy and Yang, (2007) obtained single cells of cellulose fiber from wheat straw after dewaxing, alkali extracting with 2% NaOH solution at 95 °C for 45 min, and maceration with 10% (w/w) nitric acid and 10% (w/w) chromic acid solution.

Alemdar and Sain, (2008) extracted cellulose nanofibres from wheat straw by chemi-mechanical technique of alkali and acid treatment, followed by mechanical treatments of dry crushing, disintegration and defibrillation.

1.5.1 Isolation of cellulose by organic solvent extraction

Organic acid pulping such as acetic acid pulping has been proved to be an effective method to delignify and fractionate straws (Pan *et al.*, 1999).

Lam *et al.*, (2001) Studied rice straw pulping using formic acid. Approximately 85% of delignification with a cellulose pulp yield of 44.4% was obtained under relatively mild cooking conditions (temperature, 100 °C; cooking time, 60 min; and formic acid concentration, 90%). They thought the advantage of this technique compared with cooking in basic environments was that most of the silicon derivatives remain in the pulp. One of the developments in acetic acid pulping is the FORMACELL process, based on the addition of 5–10% formic acid to aqueous acetic acid, resulting in improved selectivity of delignification

Sun *et al.*, (2004) found that wheat straw lignin and hemicelluloses were degraded in the medium containing 80% acetic acid and 0.92–13.5% nitric acid. The treatment with 80% acetic acid and 0.92% nitric acid as a catalyst at 120 °C for 20 min resulted in more than 81% original hemicelluloses and 92% original lignin degradation. As the nitric acid concentration increased to

8.5%, more than 96% original hemicelluloses and approximately 98% original lignin were degraded and yielded the cellulose approaching 96% purity.

1.6 Date palm (*Phoenix dactylifera* L.)

1.6.1 Classification of palm tree

Family: *Areceaceae*

Genus: *Phoenix*

Kingdom: *Plantae*

Order: *Arecales*

Species: *P. dactylifera*.

Date palm (*Phoenix dactylifera* L.) is one of the most important tree crops in desert areas of Northern Africa, Southern Asia and the Middle East (Hodel *et al.*, 2003). It is a multipurpose tree that provides food, materials for shelter, fuel and timber products in a harsh environment, where only few plants can grow (Zaid *et al.*, 1999). Date palm fruit is a good source of carbohydrates, fiber, minerals and vitamins, as well as having anti-mutagenic and anti-carcinogenic properties (Al-Farsi *et al.*, 2005).

Dates are rich in certain nutrients and provide a good source of rapid energy, due to their high carbohydrate content (70–80%). Moreover, date fruits contain fat (0.20–0.50%), protein (2.30– 5.60%), dietary fiber (6.40–11.50%), minerals (0.10– 916 mg/100 g dry weight), and vitamins (C, B1, B2, B3, and A) with very little or no starch (Al-Shahib and Marshal 2003). Date fruit is also a good source of important phytochemical, including carotenoids, phenolics, and flavonoids. Date fruit can not only provide antioxidant, antimutagenic, and immunomodulatory benefits to health but also has diverse medicinal values, including antihyperlipidemic, anticancer,

gastroprotective, hepatoprotective, and nephroprotective properties (Tang *et al.*, 2013).

Today, date palm is found in both old and new world where dates are grown commercially in large quantities (Zabar and Borowy, 2012). The total world number of date palms is about 120 million trees, distributed in 30 countries and producing nearly 7.5 million tons of fruit per year (FAO, 2013). Arab countries account for 70% of the world's date palms number and are responsible for 67% of the global production of date palm (El-Juhany, 2010). Date palm has a major socio-economic importance not only for its fruit but also as an ornamental plant (Morton, 1987). Dates are the main income source and staple food for local populations in many countries in which they are cultivated, and have played significant roles in the economy, social, and environment of those countries (Chao and Krueger, 2007; Saafi *et al.*, 2008). The date palm tree has a minimum water demand and tolerates harsh weather and high levels of salinity; in fact, it is more salt tolerant than any other fruit crop (FAO 1982; Alhammadi and Kurup, 2012).

Date palm tree (*Phoenix dactylifera L.*) plays a central role in the economy of North Africa and Middle East countries (Botes and zaid, 2002; Janick *et al.* 2008; El-Deek *et al.*, 2010). Palm-based lignocelluloses are the most abundant renewable biomass yielded from photosynthesis. Generally palm biomass can divide into three main categories: Oil palm frond (OPF), oil palm trunk (OPT) and empty fruit Bunches (EFB). This biomass composed of primarily of plant cell wall materials that consist of three main biopolymers- cellulose (~30-50% by weight), hemicelluloses (~19-45% by weight), lignin (~15- 35% by weight) (Sauian, *et al.*, 2013).

Multi-purpose surveys regarding date palm were carried out in different countries worldwide. Special focus was paid to the importance of date palm uses, cultivation, pests, diseases, genotyping in addition to its cultivars identification. Chao and Krueger (2007) highlighted the biology, uses and cultivation of date palm in the U.S.A. Studies on date palms in developing countries seemed to be extensive and intensive. Many researchers evaluated date palm by products, while others focused on the effect of certain physical conditions on the growth and yield of the date palm (Alrasbi *et al.*, 2010; Alhammadi and Kurup, 2012; El-Hadrami and Al-Khayri, 2012; Mahmoud and El-Bana, 2013).

In Sudan, date palm is the most important fruit tree in the northern part of the country, where it has been cultivated for more than 3000 years (Osman, 2001). Dates culture in Sudan is intensified in the Northern and River Nile States in about 900 km along the banks of the Nile. Beside Southern Egypt, this area is thought to be a land of origin for dry date's cultivars. Other production areas include Darfur where the 1.5 million palms there are thought to be of seedling origin. Khartoum, Red Sea and North Kordofan States are currently involved in date's culture activity. The major dry cultivars are Barakawi which constitutes about 55% of Sudan's dates, Gondaila, Bit-tamoda, Kulma, and Gargoda beside other minor Nubian cultivars such as Nawwa, Kajnosa, Garjicola and Sherwa. The semi-dry cultivars include Mishrig Wadlaggai and Mishrig Wadkhatib, while Madina is the sole soft cultivar. Dates population in Sudan is around 8 million palms.

1.7 Cellulose derivatives: Carboxymethyl cellulose

Carboxy methyl cellulose (CMC) is one of the most important cellulose derivatives which is obtained by chemical modification of natural cellulose. It's a linear long chain water soluble ionic polysaccharide derived from cellulose (Bono, *et al.*, 2009). CMC is generally prepared by the reaction of alkali cellulose with mono chloroacetic acid. By reacting the free hydroxyl group in the anhydroglucose units (AGU) with various chemical substitution groups, the introduction of substituent disturbs the intermolecular and intramolecular hydrogen bonds in cellulose, which leads to liberation of hydrophilic character of numerous hydroxyl groups and restriction of the chains to close associate (Toğrul and Arslan, 2003). However substitution with alkyl groups reduces the three OH-6 in the anhydroglucose unit can be substituted and the maximum degree of substitution (DS) is being 3 (Salami *et al.*, 1994). Carboxymethylation of polysaccharide is a widely studied conversation, since it's simple and leads to products with a variety of promising properties. In general, the polysaccharide is activated with aqueous alkali hydroxide mostly sodium hydroxide and converted with monochloroacetic acid or its sodium salt. CMC was first prepared in 1918 and was produced commercially in the early 1920 in Germany (Balsler *et al.*, 1986).

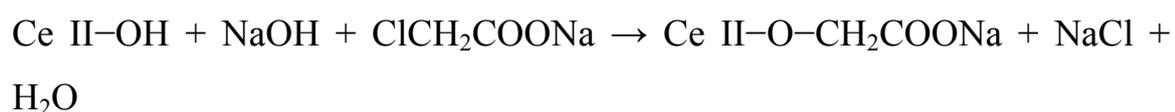
It's important to note that, carboxy methyl cellulose has an acid function, meaning that CMC is an anionic polyelectrolyte, CMC has many interesting properties when dissolved in aqueous solution, but this depends on the CMC grade and the solution condition.

1.7.1 Synthesis of Carboxymethylcellulose (CMC)

Sodium carboxymethylcellulose (Na-CMC) was produced by conversion of alkali cellulose swollen in aqueous NaOH and a surplus of organic solvent (e.g. isopropanol, ethanol) with monochloro acetic acid (MCAA) or its

sodium salt (Na-MCA). The hydroxyl groups in cellulose are usually replaced by the carboxymethyl groups in the order of C2>C6> C3 (Kutsenko *et al.*, 2005).

In practice, the manufacturing of CMC involves two step, In the first step, the cellulose is treated with NaOH, often in the presence of inert solvent, which act as both swelling agent and a dilatant and thus facilitate good penetration of NaOH into the cellulose structure (Latif *et al.*, 2007). The alkali cellulose is accessible and reactive toward MCA, which is added to reaction in the second step. The reaction between alkali cellulose and the etherification agent carried out in aqueous system. According to the following reaction:



A considerable amount of the etherifying agent, up to 30%, is consumed in side reaction with the aqueous NaOH forming predominantly sodium glycolate by hydrolysis of chloroacetate. The CMC can be neutralized and dried immediately to give a technical grade or neutralized and washes to give a purified grade (Adinugraha and Marseno, 2005).

1.7.2 Application of CMC

Despite the large variety of cellulose derivatives that have been made, there is continuous expansion on the worldwide market of cellulose ethers because of their availability, economic 'efficiency and easy handing.

CMC is non-toxic component, therefore increasing the number of application in pharmaceutical, medical and food industries. It has also interesting application such as film formation agent, gives a mechanical and chemical resistant film, binding agent; to bind large amount of water, stabilizing agent to keep suspended particles or dissolved molecules stable

through chemical interaction, water retention agent to prevent water from escaping, protective colloid to keep suspended particles stable.

A polymer commonly used by drilling fluid industry is carboxymethylcellulose (CMC) with a wide range of uses in paper industry, in food products, in pharmaceuticals and in drilling fluids (Benchabane and Bekkour, 2006; Amorim *et al.*, 2007) due to hydrogen bonds that associated with structure of molecular cellulose, it neither melts nor dissolves readily in common solvents (Hattor, *et al.*, 2004, Adinugraha and Marseno, 2005). But its water-soluble derivatives have found various applications (Kirk and Othmer, 1997) in food, pharmaceutical, detergents and increased the accessibility of fibers to chemicals by cosmetics industries. It is used as a preservative for swelling. Cellulose fibers are swollen in concentrated coating of fresh fruit and thickener for pharmaceutical NaOH.

1.8 Previous studies

Many studies were handled for converting cellulose extracted from different natural resources to carboxymethylcellulose (CMC). Many parameters were considered to optimize the yields, Degree of substitution (DS) value and rheological behavior of the synthesized CMC material.

Aruna *et al.*, (2017) studied the synthesis of CMC from palm kernel cake (PKC) being abundant agricultural by product consists of 20%-30% cellulose, hence considered as one of the alternative secondary resource of cellulose. Therefore efforts are made in which cellulose is extracted from PKC and CMC is synthesized which is used as anti-caking agent, emulsion, stabilizer and thickener agent.

Pushpamalar *et al.*, (2006) isolated cellulose from sago waste and converted it to CMC by etherification using sodium monochloroacetate in the presence of sodium hydroxide. The reaction was optimized against temperature, concentration of NaOH and reaction time. The optimized product has a large

value of DS of 0.821. The optimized DS value was obtained using pure isopropyl alcohol as the solvent medium, reaction period of 180 min, 6.0 g of sodium monochloroacetate, 10 mL of 25% NaOH aqueous solution and a reaction temperature of 45°C. Fourier Transform Infrared (FT-IR) spectra were used to characterize the CMC product.

Adinugraha and Marseno, (2005) studied the synthesis and characterization of Na-CMC from Cavendish banana pseudo stem. The cellulose powder was extracted using an aqueous solution of 8% NaOH at 100°C for 3.5 h, and then bleached with an aqueous solution of 5% NaOCl at 30 °C for 3 h. The cellulose was then alkalinized with 5–30% NaOH at 25°C for 1 h then variable quantities of 3-7 g of ClCH₂COONa were added per 5 g cellulose. The results showed that the cellulose alkalinized by 15% NaOH gave CMC of the optimum properties, i.e. DS of 0.75, viscosity of 4033 cps, purity of 98.63 % and crystallinity of 38.33 %.

Aguir and M'henni, (2006) studied the production of CMC from bleached cellulose pulps obtained from *Posidonia oceanica*. The carboxymethylation reaction was carried out with NaOH and monochloro acetic acid (MCA) as the reagent. The highest DS (2.75) was obtained with *n*-butanol at an optimum temperature of 80°C. The best molar ratios of cellulose/NaOH and cellulose/MCA were 1/3.

Hutomo *et al.*, (2012) studied the synthesis and characterization of Na-CMC from pod husk of Cacao. The optimum conditions used to produce CMC of higher DS value of 0.75 were 15% NaOH, temperature 55.93°C, 4g NaMCA and 3h reaction period. The aqueous solution of CMC of the highest DS value (0.75) exhibited viscosity of 206.10 cps.

Varshney *et al.*, (2006) synthesized CMC from cellulose isolated from *Lantana camara*, using optimized set of conditions include 20% NaOH aqueous solution, an amount of MCA of 2.05 mol/AGU, carboxymethylation time of 3.5 h, temperature of 55 °C and isopropyl

alcohol as a solvent medium. The resulting CMC had a viscosity of 600 cps (1% solution) and 7500 cps (2% solution) and DS value of 1.22.

Haleem *et al.*, (2014) studied the synthesis of CMC from the waste of cotton ginning (CGW) industry. The isolated cellulose was converted to CMC by etherification reaction using Na-MCA and different concentrations of sodium hydroxide (NaOH) (5 – 40 g/100 mL). The optimum NaOH concentration for the carboxymethylation reaction was found to be 20 g/100 mL NaOH which provided the highest DS value (0.874). The aqueous solution of optimized CMC exhibited the highest viscosity.

Mat Som, (2004) reported the preparation and characterization of CMC from oil palm empty fruit bunch fibers. The work involved manipulation of three variable parameters namely, reaction temperature (55, 60 and 70 °C), time of reaction (4, 6, 8, 16, 18 and 20 h) and concentration of sodium hydroxide (2.6 moles and 3.4 moles per mole of monochloro acetic acid). Thirty-six grades of CMC material were produced and characterized. The findings showed that the percent yield of CMC, moisture content, DS, purity, viscosity and ash content were in the range of 49.76 – 58.62%, 7.3 – 8.8%, 0.74 – 0.95, 85.5 – 99.5%, 116 – 2217 cps and 15.2 – 20.2%, respectively. Overall judgment on the selection of the best processing conditions was preferably of 55 °C, 2.6 moles NaOH and 4 h reaction time. The conversion of cellulose to CMC material was indicated by the FT-IR spectra of as-synthesized and commercial CMC materials. Both materials exhibited similar patterns with the presence of peaks at the fingerprint regions between 1300 and 1580 cm^{-1} due to the presence of carboxymethyl group.

Latif *et al.*, (2007) reported the synthesis and characterization of CMC from rayon grade wood pulp and cotton linter. The dried cellulose was alkalized using 40% NaOH solution at 25 °C for 1.5 hour. The carboxymethylation reactions were conducted using various amounts of Na-MCA (5-7g) per 5 g of cellulose, a temperature of 55 °C, reaction time of 3.5 h and isopropyl

alcohol solvent. The optimum DS value of the synthesized CMC was found to be 1.9.

Heydarzadeh *et al.*, (2009) studied the catalyst-free conversion of alkalized cellulose to fine CMC at mild conditions. The preparation of CMC was conducted using sodium hydroxide solution in sequential reactions involve MCA species at desired conditions. CMC has been successfully synthesized in a batch reactor with DS value of 0.15 to 0.7 and excellent purity of 99.3% at pH 7. The maximum DS of 0.7 was obtained using 40% monochloroacetate (MCA) and 30% NaOH. CMC samples were characterized by SEM and FT-IR techniques. The synthesized CMC was easily dissolved in water and was found to be of pharmaceutical and food grade.

Joshi *et al.*, (2015) studied the synthesis and characterization of CMC from mixed office waste papers (MOW). After deinking, the cellulosic pulps of MOW papers were functionalized with carboxymethyl group to give CMC of high value of DS. The carboxymethylation process was completed using NaOH and $\text{ClCH}_2\text{COONa}$ in an alcoholic medium. Maximum DS value of 1.07 was obtained by conducting the reaction process at 50°C for 3 hours using solutions of 0.094 M NaOH and 0.108 M $\text{ClCH}_2\text{COONa}$.

1.9 Objective of the study

The main objective of the present study was to optimize the conditions of carboxymethylation of cellulose from date palm leaves (*Phoenix dactylifera* L. originated from Khartoum, Sudan.

The specific objectives of the study were:

- 1)** To purify and characterize cellulose from date palm leaves.
- 2)** To study the effect of different reaction parameters (namely, concentrations of sodium hydroxide and monochloroacetic acid as well as the temperature) on the carboxymethylation process.
- 3)** To characterize the produced CMC samples.

CHAPTER TWO

Materials and methods

2.1 Sample collection and pretreatments

Raw-dry date palm leaves (*Phoenix dactylifera L.*, (Barakawi cultivar)) were collected from Khartoum State (Sudan), washed, air-dried and ground using an electrical grinder. The sample was authenticated by Medicinal and Aromatic Plants and Traditional Medicine Research Institute (National Center for Research, Khartoum-Sudan).

2.2 Chemicals

Sodium hydroxide pellets (Minimum assay: 98%, LOBA Chemie, India). Acetic acid (Minimum assay: 99.9%, ALPHA CHEMIKA, India). Clorox (Aqueous solution of 5.25% Sodium hypochlorite). Iso-propanol (Minimum assay: 99.0%, ALPHA CHEMIKA, India). n-Butanol (Minimum assay: 99.0%, LOBA Chemie, India). Ethanol (Minimum assay: 94.8~ 95.8%, DUKSAN PURE CHEMICAL, Korea). Methanol (Minimum assay: 99.5%, LOBA Chemie, India). Monochloro acetic acid (Minimum assay: 95.5%, S D Fine Chem Limited (SDFCL), India). Nitric acid (Minimum assay: pure

69~72%, S D Fine Chem Limited (SDFCL), India). Hydrochloric acid (Minimum assay: 35-38%, LOBA Chemie, India). Phenolphthalein. Potassium bromide (FT-IR grade, LOBA Chemie, India).

2.3 Purification of cellulose from date palm (*Phoenix dactylifera L.*) leaves

100 grams of the leaves were soaked in a 500ml solution of 1M (4% NaOH), at 80 °C for 4 hours with constant stirring. Sodium hydroxide solution was removed by decantation and the content were washed several times with distilled water. This step was repeated four times until the color of the supernatant turned pale yellow. The resulting product was bleached using a mixture of Clorox solution (1 liter of 1.7% NaOCl) with a buffer solution (1 liter of a mixture of 27 grams of sodium hydroxide and 75 ml of concentrated acetic acid) at 80 °C for 4 hours. The bleaching step was repeated four times and finally the product was washed thoroughly with distilled water. The product was left to dry first at room temperature and then at 100 °C in an oven.

2.4 Optimization of the carboxymethylation of cellulose

2 grams of purified cellulose was suspended in 40 ml of iso-propanol and stirred continuously. 10 mL of 20% (w/v) NaOH solution were added drop wise over a period of 30 min. The mixture was stirred for one hour at room temperature. 6 grams of monochloro acetic acid were dissolved in 10 mL of isopropanol were added to the alkalinized cellulose and the temperature was raised to 55 °C. The reaction was allowed to continue for 2 hours then neutralized with 90% acetic acid and filtered. The obtained CMC was washed with 70% ethanol five times to remove undesirable materials and dried at 60 °C in an oven. The above experiment was repeated using the same 20% concentration of sodium hydroxide but varying reaction times of 3 and 4 hours (Table 2.1). The whole process was typically repeated with 30% concentration of NaOH (Table 2.1).

Table 2.1: Preparation of carboxymethyl cellulose

Sample	Cellulose (gram)	MCAA (gram)	NaOH (%)	Heating temperature (°C)	Reaction time (Hours)
S1	2	6	30	55	2
S2	2	6	30	55	3
S3	2	6	30	55	4
S4	2	6	40	55	2
S5	2	6	40	55	3
S6	2	6	40	55	4

The dried CMC was dispersed on 60 mL of 95% ethanol, stirred for 5 minutes. then 10 mL of 2M nitric acid were added and the mixture was agitated for 2 min. The mixture was then heated to boiling for 5 min and 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 and with hot 80% ethanol at 60 °C, until the acid and salts were removed. Finally, the precipitate was washed with methanol and transferred to a beaker and heated until alcohol was removed. The beaker with the precipitate was dried in an oven at 105 °C.

2.5 Determination of the degree of substitution (DS)

The degree of substitution (DS) of all samples was determined by a back titration method. In a typical experiment, an amount of 0.25 g of as-synthesized CMC was weighed in 250 mL conical flask then 50 mL distilled water were added and stirred well. 12.5 mL of 0.5 N NaOH solution were added and boiled for about 15 min, and the hot solution was titrated against a solution of 0.3 N hydrochloric acid using phenolphthalein as an indicator. The carboxy methyl content and the degree of substitution were calculated based on equations 2.1 and 2.2.

Carboxy methyl content (% CM) = $[(V_o - V_n) \times N \times 0.058 \times 100] / M$

(2.1)

DS = $162 \times \% \text{ CM} / [5800 - (57 \times \% \text{ CM})]$

(2.2)

Where V_o = the volume (in mL) of HCl used to titrate the blank.

V_n = the volume (in mL) of HCl used to titrate the sample material.

N = normality of HCl used, M = the amount (g) of sample taken for analysis.

58 = the molecular weight of carboxymethyl group.

2.6 Synthesis of sodium carboxymethylcellulose at optimum conditions

From the DS values of the samples, the sample with the highest DS (**S6**) was chosen and synthesized for further analysis. For fabrication of CMC at optimum reaction conditions exactly typical conditions were followed but the amount of cellulose was 60 grams and the ratios of the other chemicals were kept constant as shown in Table 2.1.

2.7 Infrared spectroscopy

The infrared spectroscopic analysis was carried out for purified cellulose, commercial CMC and as-synthesized CMC using Fourier Transform Infrared spectrometer, FT-IR, Shimadzu (model 8400S - Japan). Few milligrams of sample mixed with sufficient amount of KBr and pressed to a form a transparent disk. The infrared spectra of samples were recorded between 400 and 4000 cm^{-1} using a resolution of 4 cm^{-1} and 8 numbers of scans.

2.8 X-ray diffraction (XRD) analysis

XRD patterns were obtained to investigate the variation in crystallinity of purified cellulose and carboxymethyl cellulose (CMC) with DS of 0.77. The samples were scanned at 2 Θ /min with a 2 Θ angle range from 2 Θ to 80 Θ using an X-ray diffractometer (Philips/X'Pert Pro Panalytical-PW 3040/60 MPD, Almelo, The Netherlands).

CHAPTER THREE

Results and discussion

3.1 Effects of different parameters on carboxymethylation reaction

The carboxymethylation reaction was optimized using different concentrations of sodium hydroxide and different reaction time while the amounts of cellulose, monochloroacetic acid and the reaction temperature were kept constant.

3.2 Effect of sodium hydroxide concentration on carboxymethylation reaction

The effect of the concentration of NaOH solution (30% and 40% concentrations of sodium hydroxide) on the value of DS was studied while the other parameters were kept constant. Figure 3.1 shows that 30% concentration of NaOH aqueous solution has given the highest DS (0.77) when compared with 40% concentration (0.45). This could be explained by the fact that carboxymethylation involves two competitive reactions taking place simultaneously.

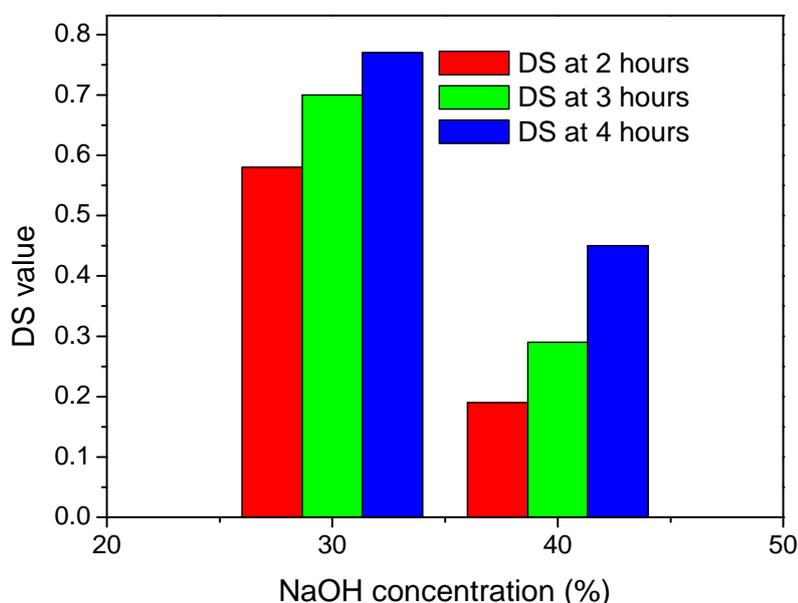


Figure 3.1: Effect of sodium hydroxide concentration on the carboxymethylation reaction

At optimum concentrations of NaOH the first reaction involves the reaction between cellulose hydroxyl groups and sodium monochloroacetic acid to give CMC while the second one involves reaction between sodium hydroxide and sodium monochloroacetic acid to give sodium glycolate. Similar results were reported by Pushpamalar *et al.*, (2006).

3.3 Effect of reaction time on carboxymethylation reaction

The influence of the reaction time (2, 3 and 4 hours) on carboxymethylation reaction was considered at 30 and 40% concentrations of sodium hydroxide and the value of DS was plotted against the reaction time in Figure 3.2. It was found that when the time of reaction increases the value of DS increases as well. The maximum value of DS (0.77) was obtained at reaction period 4 hours when the concentration of sodium hydroxide was 30%. This could be due to better reactivity conditions on prolonging the duration up to 4 hours resulted from more diffusion and adsorption of the reactants on cellulose fibers. This leads to better contact between MCA and cellulose fibers and more hydroxy groups become accessible to MCA (Singh and Singh, 2013).

On the other hand, when the concentration of sodium hydroxide was 40% at reaction period of 4 hours, the value of DS was 0.45 which is lower than the value of DS (0.77) at 30% NaOH concentration at similar duration of time. It is worth noting that all the values of DS at 30% concentration of sodium hydroxide were found to be higher than the corresponding values of DS at 40% and even the DS value at 2 hours (30%) is higher than the DS value at 4 hours (40%). This could be explained by the fact that at 40% NaOH concentration the reaction between sodium hydroxide and sodium monochloroacetic acid to give sodium glycolate is favoured compared to the reaction between cellulose hydroxy groups and sodium monochloroacetic acid to give CMC.

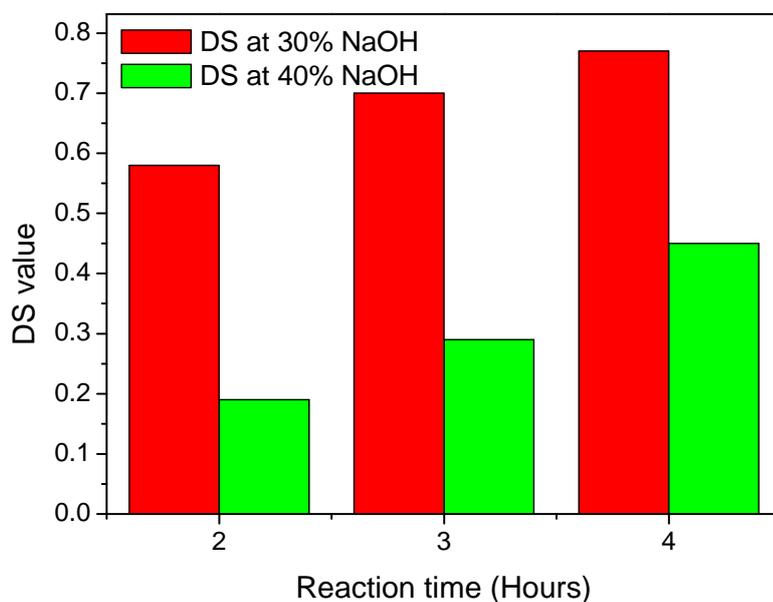


Figure 3.2: Effect of reaction period on the carboxymethylation reaction

3.4 FT-IR analysis of cellulose, date palm leaves, synthesized and commercial carboxy methyl cellulose

FT-IR spectroscopy was used to verify the successful purification of cellulose from date palm leaves (*Phoenix dactylifera L.*, (Barakawi cultivar)) and to identify the main functional groups of date palm leaves. It was also used to examine the changes in the structure of the cellulose fibers as a result of carboxymethylation reaction, as well as the for commercial CMC sample. Figure 3.3 shows the FT-IR spectrum of cellulose purified from date palm leaves. It is evident that, the broad absorption band at 3426 cm^{-1} is due to the stretching vibration of intra- and intermolecular hydrogen bonding of O-H group. The band at 2913 cm^{-1} is due to C-H asymmetric stretching vibration of a saturated sp^3 hybridized system while C-H symmetric stretching vibration appeared as a weak and not well defined shoulder. The adsorption band at 1629 cm^{-1} is attributed to bending vibration of -OH group.

The absorption bands appeared between 1405 and 1059 cm^{-1} could be attributed to bending vibrations of $-\text{CH}$, stretching vibrations of C-O and stretching vibrations of C-C .

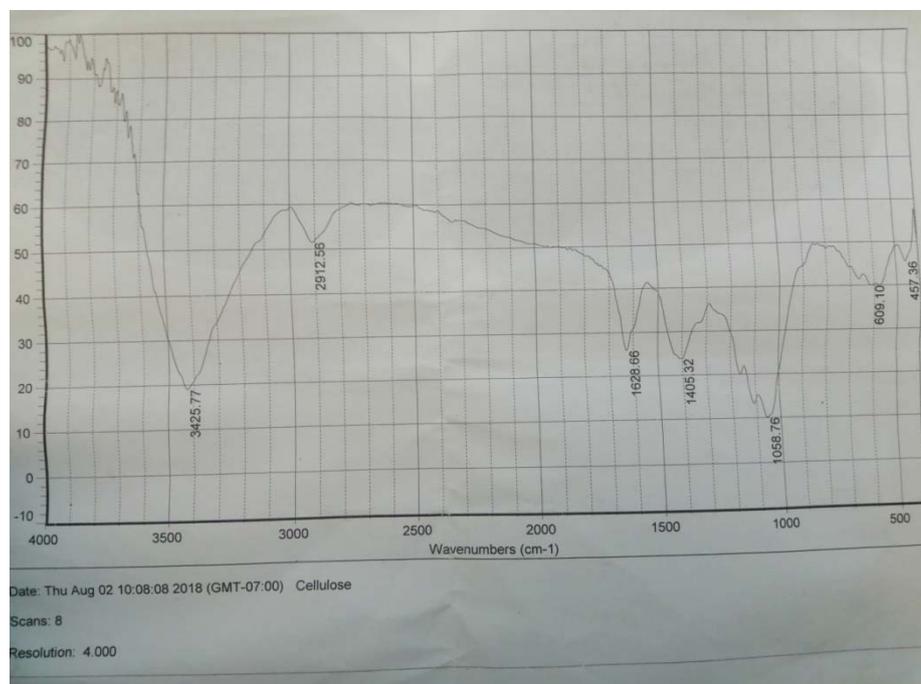


Figure 3.3: FT-IR spectrum of purified cellulose

Figure 3.3 also shows the absence of the stretching vibration of the carbonyl group (C=O) of hemicellulose at 1700-1800 cm^{-1} and also the stretching vibration of the aromatic double bond ($-\text{C}=\text{C}-$) of lignin at 1500-1600 cm^{-1} indicating the successful purification of cellulose from date palm leaves.

Figure 3.4 shows the FT-IR spectrum of date palm leaves. As can be seen from Figure 3.4, the main absorption bands of date palm leaves were appeared at 3428, 2920, 2852, 1737, 1631, 1510, 1456, 1250, 1100 and 1047 cm^{-1} . Except the peaks at 1737 and 1510 cm^{-1} all other absorption bands were also detected and identified in purified cellulose. The peak at 1737 cm^{-1} is attributed to carbonyl absorption band of hemicelluloses while the peak at 1510 is due to the aromatic carbon double bond ($\text{C}=\text{C}$) which is characteristics of lignin containing compounds specifically in natural fibers.

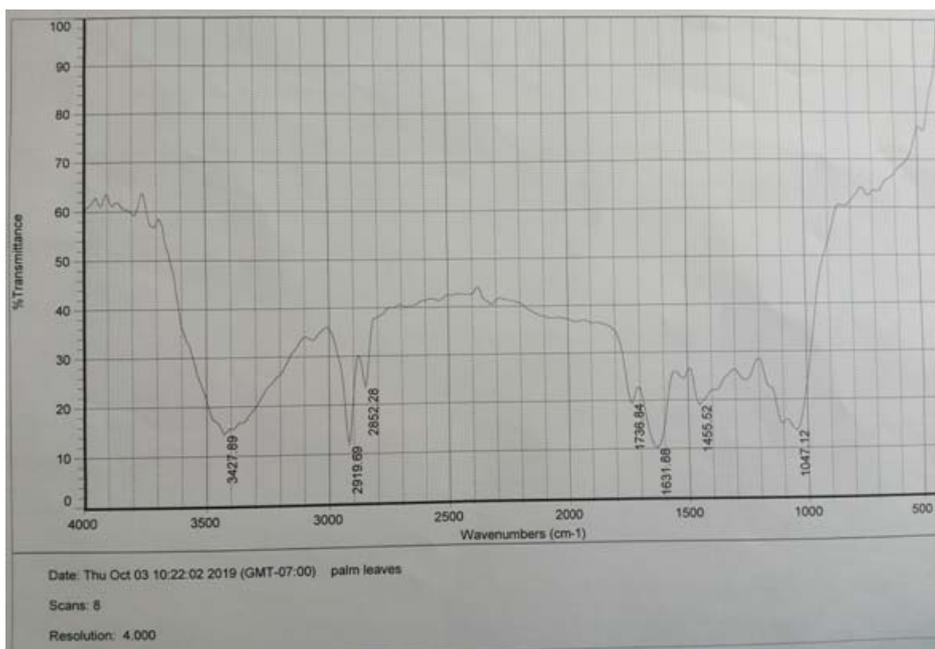


Figure 3.4: FT-IR spectrum of date palm leaves

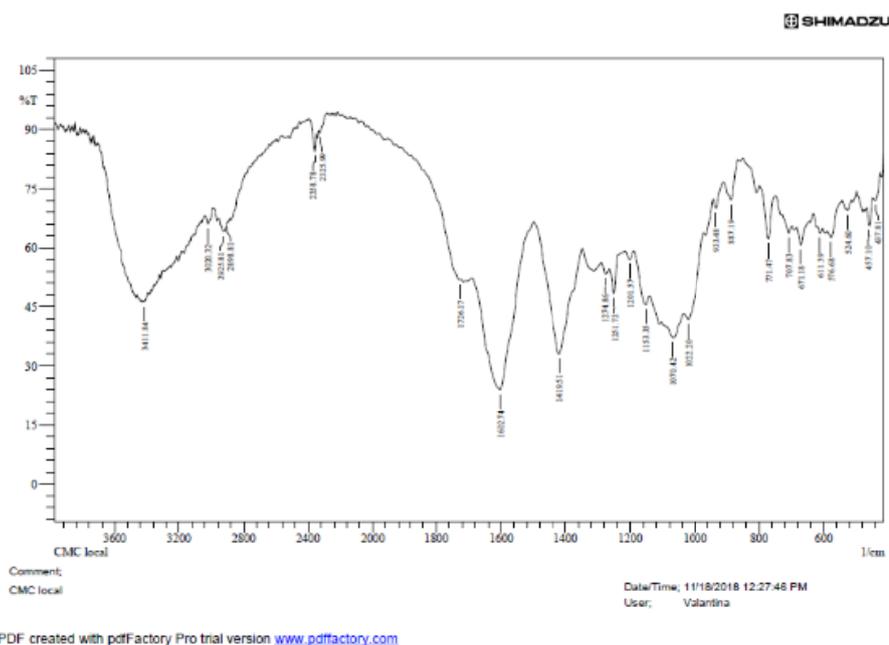


Figure 3.5: FT-IR spectrum of synthesized CMC (DS 0.77)

Figures 3.5 and 3.6 show the FT-IR spectra of the synthesized CMC products with DS values of 0.77 and 0.58. Comparing Figure 3.5 to FT-IR spectrum of cellulose (Figure 3.3), it is clearly evident that the two spectra have some dissimilarity resulted from the presence of a number of peaks at 1726, 1602 and 1419 cm^{-1} which indicate the presence of carboxymethyl

substituent. Similarly Figure 3.6 also showed these characteristics absorption bands of the carboxymethyl substituent but with lower intensity somewhat.

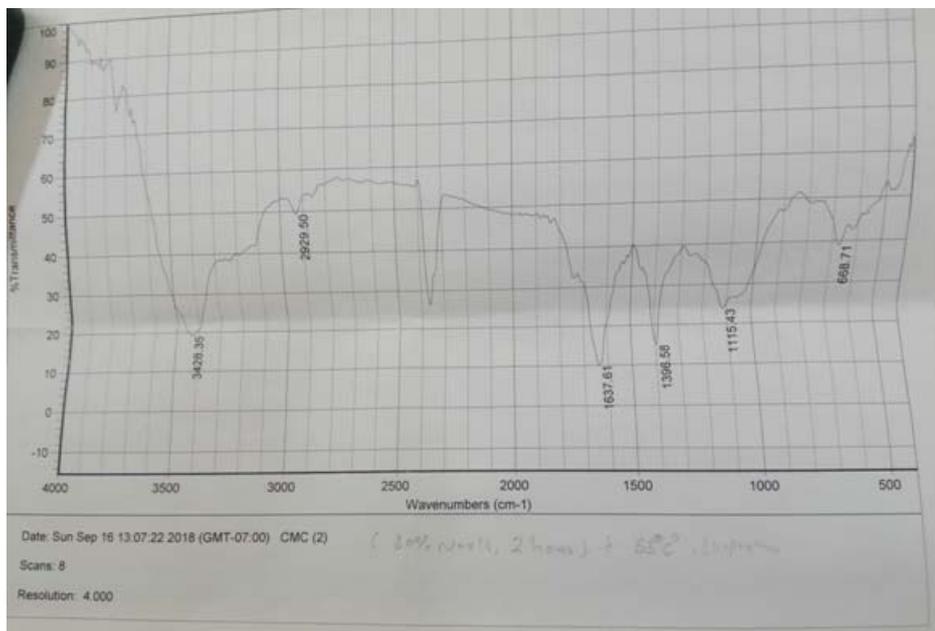


Figure 3.6: FT-IR spectrum of synthesized CMC (DS 0.58)

Figure 3.7 shows the FT-IR spectrum of commercial CMC. This spectrum is similar to that in Figures 3.5 and 3.6, with minor differences such as the presence of well-defined peak at 1726 cm⁻¹ for the synthesized products which is not appeared or not well defined for the commercial CMC.

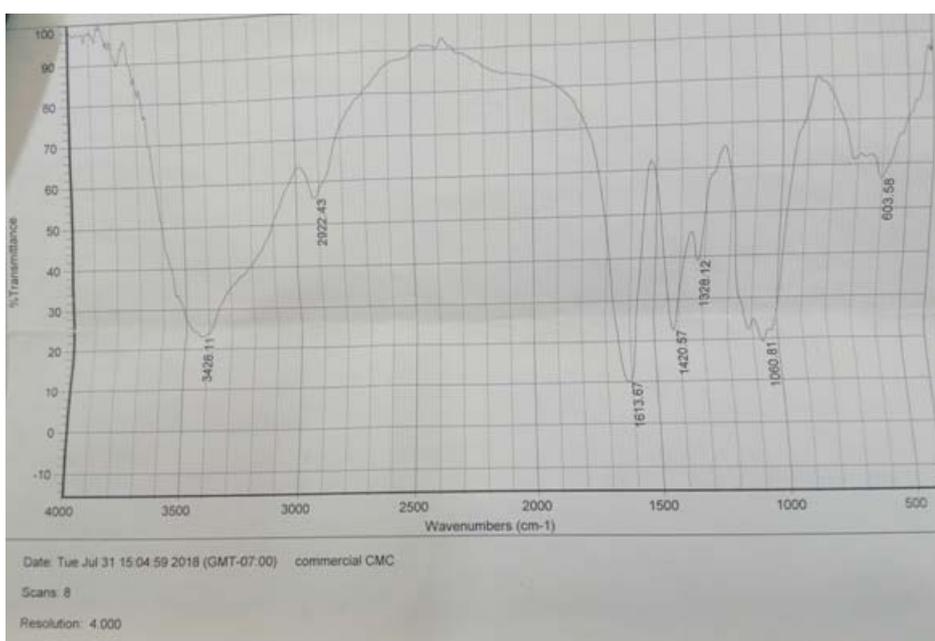


Figure 3.7: FT-IR spectrum of commercial CMC

3.5 X-ray diffraction (XRD) analysis

Figures 3.8 and 3.9 display the X-ray diffractograms of the purified cellulose from date palm leaves and the synthesized CMC (DS 0.77). As can be seen from

Figure 3.8, an intense sharp peak appears at a 2Θ value of 20° - 25° which is related to the crystalline structure of cellulose I. In addition, another characteristics peak emerges at a 2Θ value of 15° - 17° which is relevant to the amorphous phase of cellulose (Poletto *et al.*, 2014; Chieng *et al.*, 2017). The XRD curve of CMC (DS 0.77) in Figure 3.9 shows clear differences in comparison to Figure 3.8 which involve almost disappearance of the two peaks at 2Θ values between 15° - 17° and 20° - 25° . This probably due to diminishing of the hydrogen bonding as a result of carboxymethylation reaction and hence the crystalline structure converts to amorphous one.

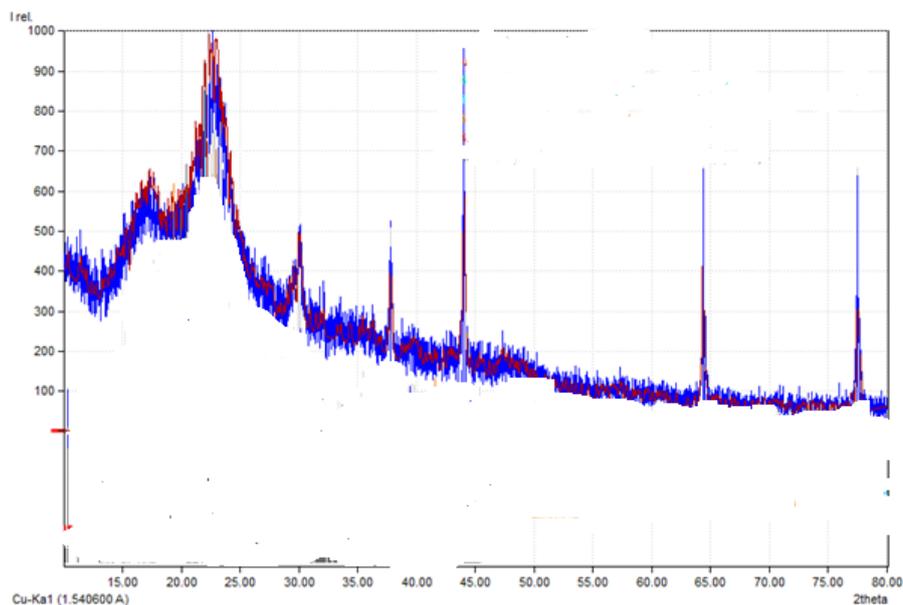


Figure 3.8: XRD curve of the purified cellulose

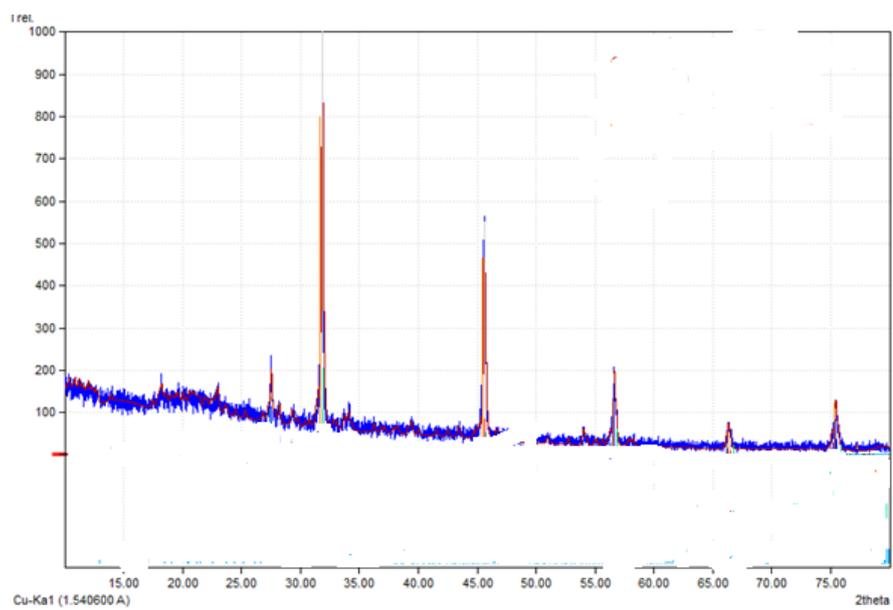


Figure 3.9: XRD curve of synthesized CMC (DS 0.77)

Conclusion and recommendation

The cellulose purified from date palm leaves (*Phoenix dactylifera L.*, (Barakawi cultivar)) leaves was successfully converted to CMC by alkalization using NaOH followed by etherification using monochloroacetic acid (MCA). A number of carboxymethylated products with DS ranging between 0.19-0.77 were obtained. The reaction conditions for the product with the highest DS (0.77) were: reaction time 4 hours, reaction temperature 55°C, concentration of sodium hydroxide 30%, amount of MCCA, 6g and amount of cellulose, 2g. The product with DS 0.77 is highly water soluble and viscous solution.

The author recommends further studies regarding the optimization of the reaction parameters by varying all the parameters and investigates their effects on carboxymethylation process. Furthermore, characterization of the produced CMC samples using ¹HNMR, ¹³CNMR, SEM and rheology is of a great importance. Application of the products in different field such as food, pharmaceuticals, petroleum sector, etc., is highly recommended.

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